FERROCENE
ANNUAL SURVEY COVERING THE YEAR 1981*

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CONTENTS

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1. REVIEWS

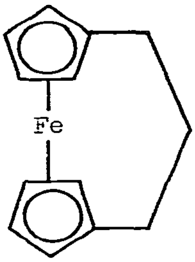
The recent chemistry of π-organometallic complexes in general has been reviewed [1]. Sosin has reviewed the preparation and properties of polymers derived from unsaturated ferrocene derivatives [2]. Metallocene containing polymers, coordination polymers and related polymers have been reviewed briefly [3]. Mixed valence complexes, including biferrocenes have been the subject of an introductory review [4]. The chemistry of π-cyclopentadienyl, π-arene and related organometallic complexes reported during 1979 has been the subject of a general review [5]. Three paradoxes reported in the chemistry of ferrocene have been the subject of a brief review [6]. Nesmeyanov has presented a survey of the chemistry of sigma and pi complexes of iron, manganese and rhenium for the years 1969-1979 [7]. The antitumour activity of metallocenes has been the subject of a brief review [8].

2. STRUCTURAL DETERMINATIONS

The crystal and molecular structure of the ordered low-temperature phase of ferrocenecarbaldehyde has been determined by X-ray crystallography. The cyclopentadienyl rings were almost eclipsed and the carbaldehyde side chain was almost coplanar with the substituted ring. The structure has been used as the basis for a model for local structural correlations in the high temperature disordered phase [9]. The disordered and metastable ordered structures of nickelocene have been investigated by X-ray diffraction and comparisons made with ferrocene. Nickelocene was isostructural with ferrocene at room temperature. The two metallocenes were characterized at 295°K by the same model of disorder with four possible molecular states. It was shown that the evolution of the disordered phase of nickelocene and ferrocene in the temperature range 5-295°K was different [10].

The charge-transfer reaction between the ferrocenophane (2.1) and 7,7,8,8,-tetracyano-p-quinodimethane (TCNQ) gave a 1:2 salt $[Fe(\eta-C_5H_4)_2(CH_2)_3]^{\ddagger}[(TCNQ)_2]^{\overline{\cdot}}$. The crystal and molecular structures of this salt have been determined by

X-ray analysis. The structure consisted of segregated stacks of $[(\mathrm{TCNQ})_2]^{\overline{\cdot}}$ dimers and trimethyleneferrocenium ions [11]. The cyclopentadienyl rings in each of the ferrocenyl groups of 1,1-dicyano-2,2-diferrocenylethylene were shown to be parallel and eclipsed by X-ray crystallography [12]. The eclipsed configuration of 3,4-dimethylphosphaferrocene (2.2) has been



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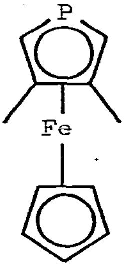

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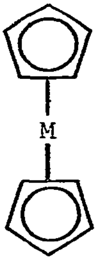
confirmed by X-ray crystallographic measurements at 74^{o}K. Comparisons have been made with results obtained at room temperature. A qualitative study of the charge density distribution shows a strong peak in the phosphorus region suggesting a localised lone pair of electrons and this was at variance with the electrophilic character of phosphorus [13]. The crystal structure and molecular geometry of the ferrocenium salt, $[(\eta\text{-}C_5H_5)_2Fe]_2As_4Cl_{10}O_2$, have been determined by X-ray analysis. The η-cyclopentadienyl rings were eclipsed and the $As_4Cl_{10}O_2^{2-}$ anion contained two $Cl_2As\text{-}O\text{-}AsCl_2$ moieties held together by two chloride ions, each of which bridged three As(III) atoms [14].

3. THEORETICAL STUDIES

Rotation of the cyclopentadienyl rings in the monoclinic, triclinic and orthorhombic phases of ferrocene has been studied by ^1H NMR spectroscopy. Determination of the spin-lattice relaxation time and the second moment of NMR absorption at several temperatures demonstrated that the barrier to rotational reorientation of the rings was greatest in the orthorhombic phase [15]. INDO SCF molecular orbital calculations have been carried out for the metallocenes (3.1) and $M(\eta\text{-}C_5H_5BH)_2$ ($M=Cr^-, Mn, Fe^+$) and the bonding characteristics of the η-cyclopentadienyl and η-borabenzene ligands were compared. The calculations suggested that differences in ground states might



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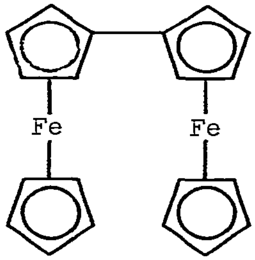
be found both within and between the two series of compounds. The results were discussed in terms of the simple ligand field model [16]. The structures and properties of (η-pentafulvene)--iron and -chromium complexes, including those derived from substituted ferrocenes, have been discussed and comparisons made with the uncomplexed ligands. Some conclusions were drawn on the folding of the ligand and electron distribution in the exocyclic double bond [17]. The frequencies and shapes of normal vibrations in symmetry coordinates were calculated for bis(η-cyclopentadienyl)metal compounds (3.1; M = Fe, Mg, Ca, V, Cr, Mn, Ni, Ru, Os). The normal shape of the vibrations was only slightly dependent on the metal. The force constants were also determined [18].

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

The absorption spectra of transient species produced on X-ray irradiation of ferrocene and biferrocene (4.1) in frozen glass matrixes were recorded. Ferrocene and biferrocene anions were produced and for the biferrocene anion the intervalence transfer band was observed at approximately 2050nm [19].



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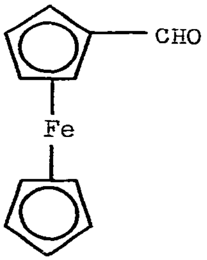

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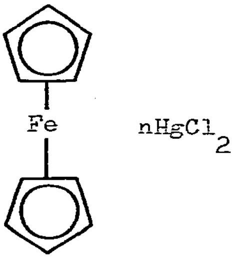
Multiphoton dissociation and ionization of ferrocene and nickelocene in effusive and in supersonic molecular beams has been investigated. Detection by mass spectrometry revealed that bare metal ions were generated almost exclusively [20]. Several mono- and bi-nuclear ferrocene compounds and ferrocenium cations have been examined by XPS in order to compare the iron $2p_{3/2}$ core binding energies of the neutral and charged species. The binding energy of the ferrocenium iron atom was 709.8 eV and was only 1.8 eV greater than the value for ferrocene. This difference was in contrast with previous reports but was in accordance with the small increase in the calculated total charge on iron as ferrocene was oxidized to ferrocenium [21].

The kinetic energy distribution has been measured for electrons ejected from ferrocene by impact of thermal Ne($^3\underline{P}_2$) atoms. The intensities of the iron 3d bands were very weak compared to those of the cyclopentadienyl ring π-bands. It was suggested that the iron orbitals were shielded by the cyclopentadienyl rings against the impact of metastable atoms [22]. The intramolecular and intermolecular dynamics of ferrocenecarbaldehyde (4.2) in both the ordered, $T < 317^\circ K$, and disordered, $T = 317\text{-}396^\circ K$, phases have been investigated by incoherent quasielastic and inelastic neutron scattering. The unsubstituted cyclopentadienyl ring underwent five-fold jump reorientations between indistinguishable positions over the temperature range examined. The disordered phase showed complex molecular motions which involved internal rotation together with whole-molecule rotational and translational components [23]. The reorientational motions of the cyclopentadienyl rings in ferrocene, nickelocene and ruthenocene have been investigated by incoherent quasi-elastic neutron scattering. The activation energy for ring rotation in ferrocene varied with temperature and above the 164°K phase transition, fell by half to 4.4±0.5 kJ mol^{-1}. The rings were observed to jump between only five orientations on the observable time scale [24].

Moessbauer spectra of the mercury (II) chloride adducts (4.3; n = 2,7) have been recorded. Anomalously high quadrupole splittings were observed and these were interpreted in terms of Fe-Hg bonding [25]. Periodic variations with time of the optical density in the electronic absorption spectra of ferrocene, octamethylferrocene (4.4) and the ferrocenium ion in ethanol under irradiation with visible light have been studied. The period of optical density oscillation was dependant on the ferrocene and oxygen concentrations. It was concluded that the variations arose through the formation and decomposition of the complexes containing ferrocene, ferrocenium, ethanol and oxygen [26]. Electronic spectra have been measured and formation constants determined for the charge transfer complexes formed by ferrocene and 1,1'-dimethylferrocene with $C(NO_2)_4$ in methanol and cyclohexane [28]. The UV-visible absorption spectra of methylated ferrocenes have been recorded and it was found that the addition of a methyl group caused a hypsochromic shift of 1.5nm in the



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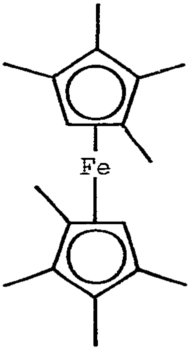

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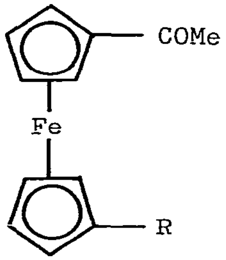
440nm band. The total shifts observed gave a linear correlation with the changes in energy of the antibonding molecular orbital of the cyclopentadienyl ring [29].

Dynamic disorder in ferrocene has been studied by Raman and IR spectroscopy in the temperature range 30-300°K. Spectra of perdeuteroferrocene were also obtained. The temperature dependence of the low-frequency spectra were interpreted in terms of dynamical disorder arising from fluctuations in molecular conformation. These fluctuations accounted for only 15% of the enthalpy variations in the phase transition of ferrocene [30]. The laser Raman spectra of ferrocene were obtained for the stable (orthorhombic) and metastable (triclinic) low-temperature phases and the stable (monoclinic) high-temperature phases. The skeletal vibrational modes, the CH bending mode and the lattice modes below 100cm^{-1} showed characteristic changes for the different phases [31]. The infrared spectrum of ferrocene has been recorded at very high pressures. The results confirmed the presence of a phase transition of approximately 11.5 kbar which was slow except under shear stress [32]. The infrared and Raman spectra of gaseous acetylferrocene and 1,1'-bis(acetyl)ferrocene (4.5; R = H, COMe) respectively have been recorded in the range 20-4000cm^{-1}. The spectra were interpreted and the thermodynamic functions at 298-450°K were reported for these gaseous ferrocenes [33].



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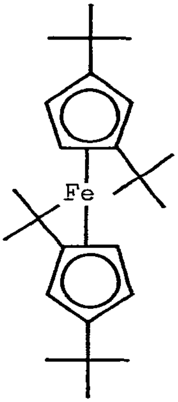

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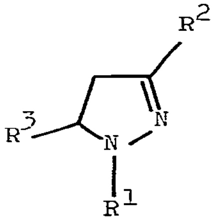

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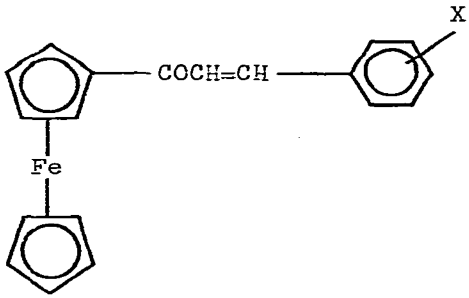
The high resolution ^1H NMR spectrum of ferrocene has been recorded in the nematic phase. From the results it was concluded that the η-cyclopentadienyl rings were undergoing independent free rotation [34]. ^1H NMR spectroscopy has been used to determine the barrier to ring rotation in 1,1',3,3'-tetra-tert-butylferrocene (4.6). The coalescence temperature from the spectra was -27.5°C and $\Delta G^{\ddagger}$ for ring rotation was calculated as 13.1 kcal mol^{-1} [35]. The ^1H NMR spectra of the ferrocenylpyrazolines (4.7; R^1 = COMe, Ph; R^2, R^3 = ferrocenyl, Ph, p-BrC_6H_4, p-$MeOC_6H_4$) were recorded and interpreted. The chemical shifts and coupling constants were affected by the position of the ferrocenyl substituent [36]. Substituent and conformational effects in the chalcone analogues (4.8 and 4.9; X = H, 4-F, 4-Cl, 4-Br, 4-CN, 4-OMe, 4-NMe_2, 3-Cl, 3-NO_2, 3-OMe) have been investigated by ^1H and ^{13}C NMR spectroscopy. The ketone (4.8) was non-planar and the chemical shifts of the α-H and α-C atoms were more sensitive to the resonance effects of substituents then to inductive effects. The corresponding shifts in the isomer (4.9) were more sensitive to inductive effects [37].



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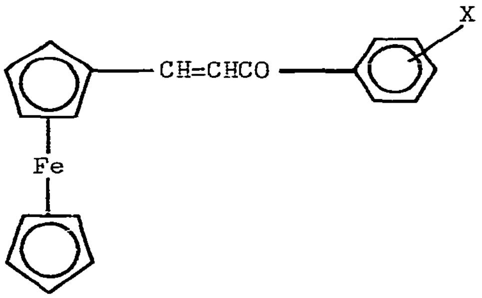

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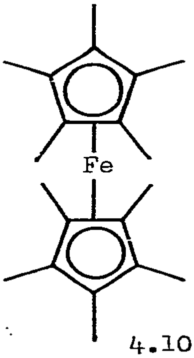
High-resolution solid-state ^{13}C NMR spectroscopy has been used to study ring reorientation in permethylferrocene (4.10). It was concluded that the reorientation occurred as jumps between symmetry related orientations, with jumps of $2\pi/5$ highly favoured over $4\pi/5$. The activation energy determined for the jump process was 13.5 $kJmol^{-1}$ [38].

^{13}C NMR chemical shifts in solid ferrocene, permethylferrocene (4.10) and several other metallocenes were determined. The ^{13}C shielding tensor anisotropy seemed to reflect the character of bonding in these molecules [39]. The ^{13}C NMR spectra of



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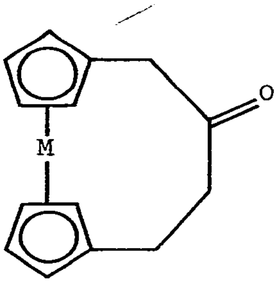

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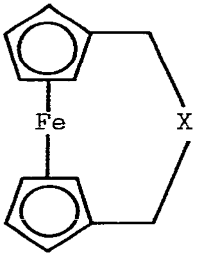

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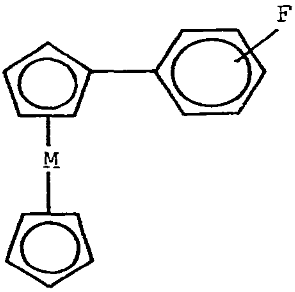
[4]ferrocenophan-2-one and [4]ruthenocenophan-2-one (4.11; M = Fe, Ru) respectively were recorded and interpreted. The carbonyl ^{13}C signal of [3]ruthenocenophan-1-one was shifted to higher field than that of the corresponding ferrocene derivative and this difference was attributed to electron delocalization caused by conjugation of the carbonyl group with the η-cyclopentadienyl ring [40]. The ^{13}C NMR spectra of the ferrocenophanes (4.12; X = CH_2, NPh, O, S, Se) have been recorded and interpreted. The electronegativity of the X species in the bridge affected both the chemical shifts and the coupling constants but no simple relationship was found [41].

Site reactivities to electrophilic substitution in monosubstituted ferrocenes have been correlated with ^{13}C NMR chemical shifts, however steric effects were significant in some cases [42]. The ^{13}C NMR spectrum of poly(vinylferrocene) has been recorded and interpreted. The syndiotactic form was the most thermodynamically stable configuration that allowed minimum steric and polar repulsions [43]. The ^{19}F NMR spectra of 3- and 4-fluorophenylferrocene, ruthenocene and osmocene have been recorded and analysed by the Taft equation to give inductive substituent constants for the metallocenyl groups of -0.032 and -0.042 and -0.062 respectively and resonance substituent constants of -0.107, -0.097 and -0.095 respectively [44]. The ^{57}Fe NMR spectra of 20 ferrocene derivatives with natural abundance of ^{57}Fe have been recorded using ferrocene as internal standard. The chemical shift contributions of the substituents have been discussed qualitatively [45].

The heat capacities of large crystals and powdered crystals of ferrocene have been determined in the temperature range 13-300°K. The effect of crystal size was shown by the shape of the heat capacity curve for the λ-type transition from the metastable low temperature to the high temperature phase. The heat and entropy of the transition were unaffected [46]. Suga and Sorai have discussed the metastable phases of ferrocene that are shown to be present by thermal analysis [47]. The heat capacities of ferrocene, acetyl-, (4.5; R = H), 1,1'-diacetyl-, (4.5; R = COMe) benzoyl- and 1,1'-dibenzoyl-ferrocene have been determined by differential scanning calorimetry in the temperature range 20-100°C. The results were in agreement with those reported previously and some correlations were discussed [48]. The vapour pressures and the heats of sublimation have been determined for ferrocene, acetylferrocene (4.5; R = H) and 1,1'-diacetylferrocene (4.5; R = COMe). Enthalpies and free energy functions were calculated for the last two compounds [49]. The thermal decomposition of ferrocenium picrate involved a two step process. The first step



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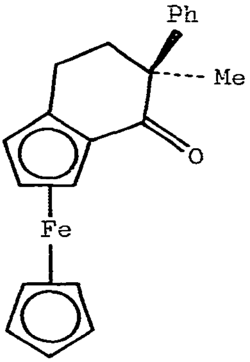

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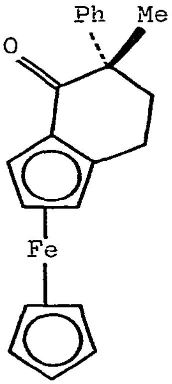
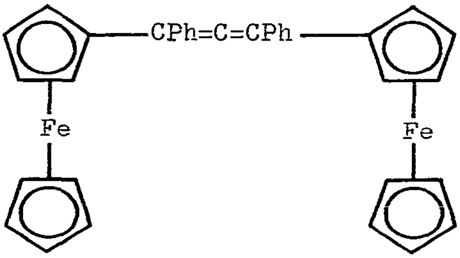


4.15

was sensitive to the method of sample preparation and ferrocene was identified as a primary decomposition product [50].

Epimerization of the metallocene chiral centre in the ferrocenylcyclohexenones (4.14 and 4.15) took place in nitromethane in the presence of aluminium chloride by an intramolecular mechanism. It was considered that the inversion occurred either by rotation of the ions $[(\eta\text{-}C_5H_5)Fe]^+$ and $[AlCl_3$, acylcyclopentadiene$]^-$ in a caged ion pair or by $\sigma-\pi$ rearrangement proceeding through $\eta^1-\eta^5$ interconversion of the $AlCl_3$, acylcyclopentadiene ligand. When benzene was used to replace nitromethane, exchange of cyclopentadienyl for benzene took place with retention of configuration [51]. 1,3-Diferrocenyl-1,3-diphenylallene (4.16) has been synthesized and subjected to partial optical resolution by chromatogrphy on triacetyl cellulose in ethanol. Both enantiomers were obtained but in different optical purities. A number of 1,3-diferrocenylpropenones and related compounds were also characterized [52].



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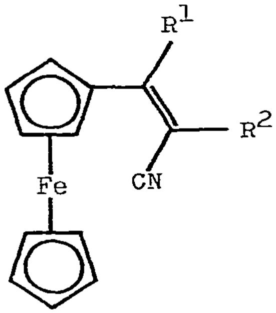
A wide range of ferrocene derivatives was separated by thin layer chromatography on silica gel with toluene-petroleum ether--acetone mixtures as the eluants. The relationship between the structures of the ferrocene derivatives and the R_f values was investigated. The R_f values decreased with an increase in polarity of the substituents and an increase in the number of substituents of the same type. The R_f values increased with an increase in polarity of the eluant [53]. A series of ferrocenyl alcohols was separated by thin layer chromatography on silica gel precoated glass plates. The alcohols were detected by spraying with 3.5% molybdophosphoric acid solution or by irradiation with ultraviolet light at 254nm [54].

5. ELECTROCHEMISTRY AND PHOTOSENSITIVE ELECTRODES

The electrochemical oxidation of ferrocene in aqueous micellar solutions has been studied by cyclic voltammetry and voltamperometry on rotating-disc electrodes. Ferrocene, in neutral solutions, was oxidized <u>via</u> a reversible one-electron process with a rate limited by the diffusion of the micelle particles [55]. The synthesis and properties of a series of decamethylmetallocenes have been described. Decamethylferrocene was one of the compounds included in a cyclic voltammetric study. The results confirmed the electron donating character of the ten methyl groups. The ^{13}C and ^{1}H NMR and ultraviolet-visible spectra were also recorded [56]. Formation of the anion radicals of the ferrocenylcyanoethylenes (5.1; $R^1 = R^2 = H$, Me; $R^1 = H, R^2 = Me$), either electrochemically or by electron transfer from cyclooctatetraene dianion, caused <u>cis</u> to <u>trans</u> isomerization [57]. The ferrocene-ferrocenium electrode has been used to evaluate the sign and magnitude of the ideal part of the diffusion potential in heterogeneous water-salt media [58].



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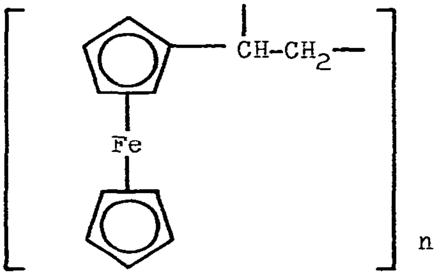

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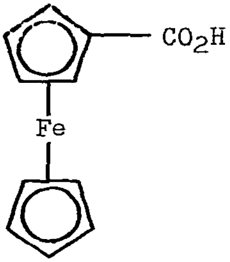
A ferrocenium electrode has been prepared which functioned over a large concentration range. The cell was designed as follows: Pt/$(\eta\text{-}C_5H_5)_2Fe$, $[(\eta\text{-}C_5H_5)_2Fe]BF_4$, 1M KCl + 0.01M HCl/ saturated KCl., AgCl/Ag; and experimental data was obtained for this system [59]. The absolute electromotive force of the standard ferrocene-ferrocenium electrode in aqueous and non-aqueous media has been measured against the standard hydrogen electrode in the same solutions. The values varied from 4.82V in water to 4.58V in methanol and the differences were attributed to the difference in the surface potentials of the solvents [60]. Platinum electrodes coated with electrochemically active poly-(vinylferrocene) (5.2) have been obtained by allowing the polymer to adsorb spontaneously from methylene chloride solution. The process was faster when the solution was subjected to UV irradiation. X-ray photoelectron spectroscopy was used to confirm that the adsorbed polymer was exclusively in the reduced, ferrocene, state while polymer in solution was extensively photooxidized to the ferrocenium ion. The characteristics of the films were investigated electrochemically [61].

Poly(vinylferrocene) (5.2) films have been deposited on platinum electrodes by electrochemical and r.f. plasma initiated polymerization, by spontaneous adsorption and also by photochemical deposition. The polymer film thicknesses were estimated by photoelectron spectroscopy and by cyclic voltammetry. Good agreement was obtained between results obtained by the two techniques [62]. The electrochemistry of radiofrequency plasma polymerized films of vinylferrocene on platinum electrodes has been examined. When the electrochemical reaction was conducted under near-equilibrium conditions the cyclic voltammetric and chronopotentiometric waveshapes were affected by solvent swelling of the polymer film. When the oxidation or reduction was driven by a large potential step, the rate of the film reaction was controlled by Fickian diffusion of electrochemical charge through the film [63]. Electrodes coated with polyphenylene oxide films containing amino groups were prepared by selective electrochemical oxidation of phenol derivatives substituted with amino groups, for example, tyramine and N-(o-hydroxybenzyl)aniline. In the case of tyramine the amino groups were condensed with formylferrocene to give an electroactive film. This film was characterised by multiple reflection infrared spectroscopy and by X-ray photoelectron spectroscopy and it was studied by cyclic voltammetry [64]. The electrochemistry of poly(vinylferrocene) (5.2) and poly(vinylferrocene acrylonitrile) films on platinum electrodes has been investigated by cyclic voltammetry. A model was proposed to account for the electrochemical behaviour of the films and good agreement was obtained with the experimental results [65].

Voltammetric measurements have been made for an oxidized platinum electrode, chemically modified with 3-aminopropyltriethoxysilane and ferrocenecarboxaldehyde and immersed in sulpholane containing Et_4NClO_4. Comparisons were made with results obtained in acetonitrile and it was concluded that the contribution made by solvent repolarization to the activation energy of the electron transfer process between platinum and ferrocene was independent of whether ferrocene was in solution or bound to the platinum electrode [66]. Chromium (III) chloride hexahydrate was heated in aqueous sodium hydroxide and a complex was formed when a methanolic solution of ferrocenecarboxylic acid (5.3) was added. A tin (IV) oxide coated glass electrode was coated with the ferrocenecarboxylic acid-chromium complex and the electrochemistry of this system was investigated. Cyclic voltammograms were obtained for the chromium-ferrocene modified SnO_2 glass electrodes. The modified electrodes were stable between potentials of -1.0V and +1.0V against a standard calomel electrode [67]. Ferrocene derivatives have been attached to electrodes by a variety of methods and the modified electrodes were examined by X-ray photoelectron spectroscopy. In many cases the ferrocene was present as the ferrocenium ion [68].

The mechanism of charge transfer at the interface of n-gallium arsenide electrodes and the molten salt electrolyte of aluminium chloride and n-butylpyridinium chloride has been studied using the ferrocene-ferrocenium ion couple as the redox system [69, 70, 71]. Current-voltage measurements at varying light intensities on a photoelectrochemical (PEC) cell have been used to determine series resistance losses and ideal fill factors. The PEC cell used the system n-GaAs/$AlCl_3$-n-butylpyridinium chloride, ferrocene/ferrocenium ion couple [72]. Textured (100) and polished (111), (100) single-crystal n-Si surfaces have been compared as photoanode materials. The surfaces have been functionalized with (1,1'-ferrocenediyl)-



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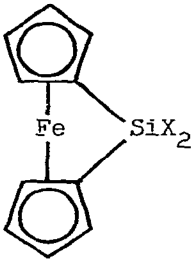

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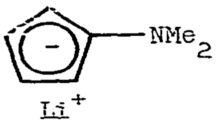
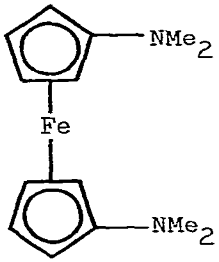
dimethylsilane (5.4; X = Me) and (1,1'-ferrocendiyl)dichlorosilane (5.4; X = Cl) and textured surfaces were found to bind twice the number of organometallic residues as polished surfaces. The chemically derivatized surfaces were characterized by electron microscopy, Auger spectroscopy and electroanalysis [73]. Germanium and silicon single crystals have been cleaved in an electrolyte containing ferrocene, ferrocenium hexafluorophosphate and tetrabutylammonium perchlorate in ethanol. The stable surface barrier heights were measured from photocurrent-potential plots. The addition of hydroxymethylferrocene to this system reduced the germanium barrier height from 0.19 to 0.14eV but silicon was unchanged at 0.68eV. The results were explained in terms of the inability of hydroxymethylferrocene to dislodge ferrocene from silicon surfaces and an ability to replace it on germanium surfaces [74]. Ferrocene was effective in stabilizing n-type silicon electrodes temporarily against photocorrosion after a thin oxide layer had been formed. The electrodes were useful in solar cells [75].

6. PREPARATIONS OF FERROCENE

Ferrocene has been prepared in almost quantitative yield by electrolysis of cyclopentadiene in dimethylsulphoxide with lithium chloride as electrolyte and an iron anode [76]. Ferrocene has been prepared in yields of up to 75% by treatment of iron (II) chloride with cyclopentadiene in diethylamine [77].

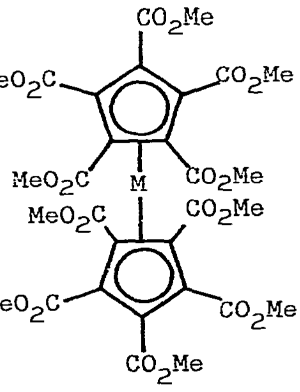


6.1



6.2

Reaction of cyclopentadienyllithium with N,N-dimethyl-O-(methylsulphonyl)hydroxylamine afforded N,N-dimethyl-1,3-cyclopentadienylamine which gave the corresponding lithium salt (6.1) on treatment with n-butyllithium. Reaction of this lithium salt with iron (II) chloride produced 1,1'-bis(dimethylamino)ferrocene (6.2) [78].



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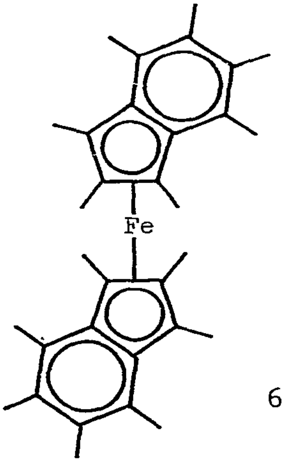
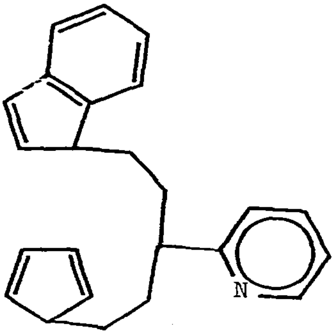


6.4

Reaction of potassium or thallium pentakis(methoxycarbonyl)cyclopentadienide with transition metal halides gave the corresponding η^5-pentakis(methoxycarbonyl)cyclopentadienyl derivatives (6.3; M = Mn, Fe, Co, Ni) which were water soluble [79]. Heptamethylindene has been converted to the corresponding ferrocene complex (6.4) with iron (II) chloride [80].



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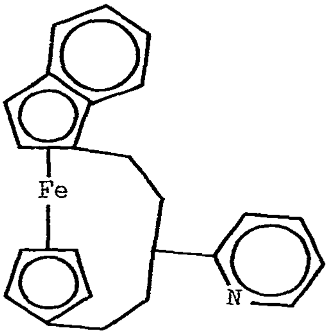
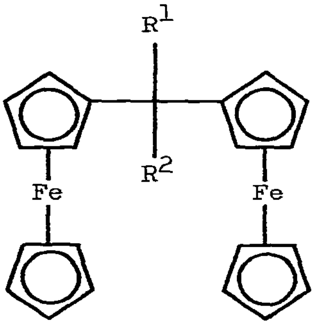


6.6

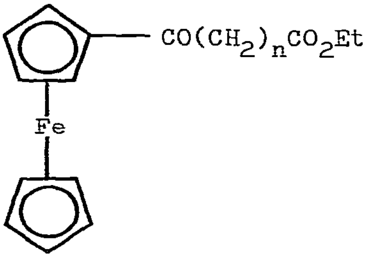
The substituted indene (6.5) has been used to prepare the stable iron complex (6.6) [81].

7. REACTIONS OF FERROCENE

Treatment of ferrocene with bromine and iodine in benzene gave 1:1 and 1:2 ionic complexes respectively with enthalpies of formation of -136.0 and -106.7 kJ mol^{-1} [82]. The reaction of ferrocene with the acetals and ketals $R^1R^2C(OEt)_2$, where $R^1 = H$, $R^2 = H$, Me, $CH{=}CH_2$, CH=CHMe, Ph; $R^1 = R^2 = Me$, gave the corres-



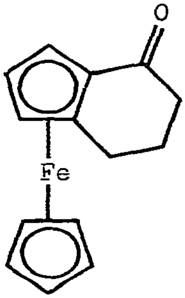
7.1



7.2

ponding bis(ferrocenyl)derivatives (7.1) [83]. Ferrocene has been acylated with ester chlorides of dicarboxylic acids to give the corresponding ferrocenoyl derivatives (7.2; n = 2-8). Clemmensen reduction of these esters (7.2; n = 2-8) followed by base hydrolysis gave ω-ferrocenylalkanoic acids. A series of 1-(ω-anisoylalkyl)-1'-cinnamoylferrocenes was prepared and an unsuccessful attempt was made to cyclize these molecules [84, 85].

Friedel-Crafts reaction of ferrocene with butyrolactone gave 1,2-(α-oxotetramethylene)ferrocene (7.3) which was oxidized with bromine and sodium hydroxide to give 1,2-ferrocenedicarboxylic acid (7.4) in 56% yield. Esterification of the diacid (7.4) with methanol gave predominantly the monomethyl ester [86, 87]. Ligand exchange reactions between ferrocene and o-, m- and p--toluidine gave the corresponding (η^5-cyclopentadienyl)(η^6-toluidine)iron cations (7.5) which were isolated as the hexafluorophosphates [88]. The reaction of ferrocene with [2.2]paracyclophane in the presence of aluminium chloride and aluminium powder



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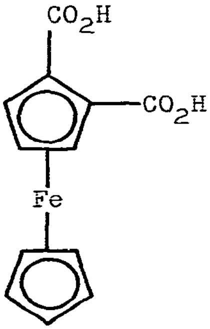

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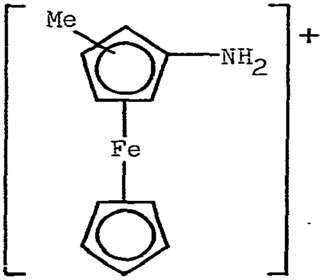
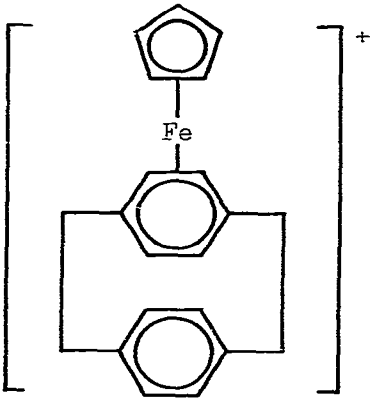


7.5

gave the products of ligand replacement (7.6 and 7.7) [89]. The quenching rate constants and radical yields for the electron transfer reactions between triplet methylene blue and ferrocene in acetonitrile were determined by an emission-absorption flash technique. The rate constants were diffusion-controlled and the radical yields increased rapidly with the free enthalpy gained in the electron-transfer process [90].



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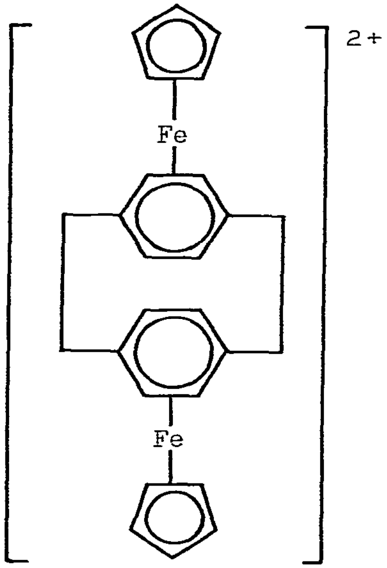


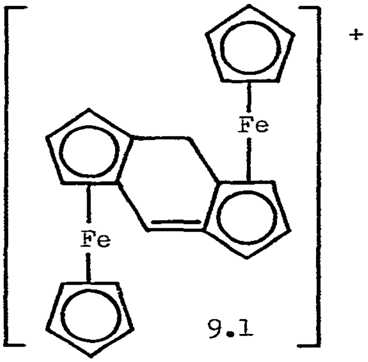
7.7

8. INTERCALATION COMPOUNDS CONTAINING FERROCENE

The intercalation of ferrocene in lamellar FeOCl was carried out by using a solution of ferrocene in benzene or in the vapour phase. The expansion of the Van der Waals gap and the shift of the FeOCl layers was confirmed by X-ray crystallography. Moessbauer spectroscopy at $<100^{o}$K indicated that oxidation of ferrocene molecules to ferrocenium ions was balanced by reduction of equal number of Fe^{3+} ions to Fe^{2+}. "Electron hopping" between Fe^{2+} and Fe^{3+} was observed at temperatures $>245^{o}$K and ferrocenium ions were no longer detected [91]. The heat capacity of a 3:1 thiourea-ferrocene channel inclusion compound has been measured in the temperature range 13^{o}-280^{o}K. Five phase transitions were found, the two lowest temperature transitions were associated with an order-disorder-type of reorientation of the molecular axis of ferrocene in the thiourea host lattice [92]. Solvent and steric effects were found to be more important than ionization potential effects in the formation of intercalation compounds between ferrocene, substituted ferrocenes, nickelocene and FeOCl [93].

9. FERROCENIUM SALTS AND MIXED VALENCE SALTS

The formal potential of the ferrocene-ferrocenium redox couple was found not to be independent of the nature of the solvent. Possible structural reasons for this have been investigated by determination of the difference between the partial molal entropies of ferrocene and the ferrocenium ion in nine solvents. Small positive values and negative values were obtained in hydrogen-bonded solvents while large positive values were obtained in dipolar aprotic solvents. These results were in constrast to the small positive values predicted by the Born model. The differences were explained in terms of additional solvent ordering around the ferrocenium ion by comparison with the ferrocene molecule [94]. The effects of anionic and cationic surfactants on the oxidation of ferrocene and butylferrocene by iron (III) salts (nitrate or bromide) and hexacyanoferrate (III) ion have been investigated by stopped-flow techniques. The second order rate constants for these reactions were estimated [95]. The effect of acid (H_2SO_4,HCl,$HClO_4$,HBF_4) concentration and solvent composition on the redox potential of the ferrocene-ferrocenium ion couple has been investigated. A relationship was found between the potential and the composition of the organic-aqueous solution used [96].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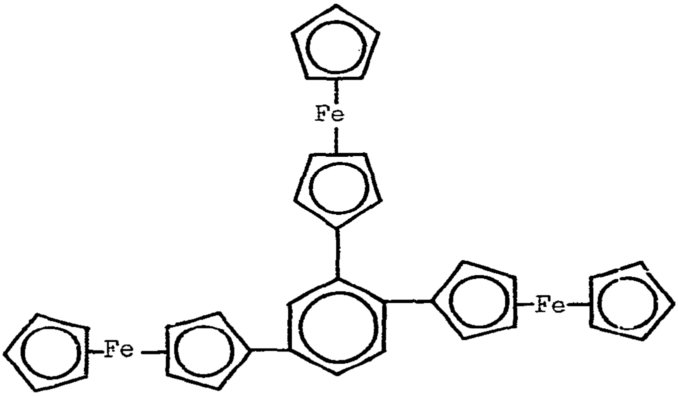
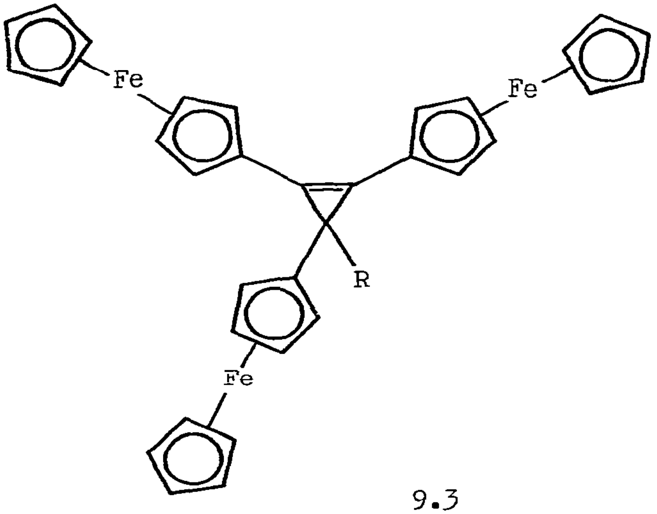

9.2

The reaction of sodium azolides (pyrazolide, dimethylpyrazolide, imidazolide and benzotriazolide) with ferrocenium salts gave the corresponding azoylferrocenes. The azole anion

(Az^-) reduced the ferrocenium ion to ferrocene according to the following equation and formed a short lived radical which was identified using spin traps.

$$[(\eta\text{-}C_5H_5)_2Fe]^+ + Az^- \longrightarrow (\eta\text{-}C_5H_5)_2Fe + Az^\bullet$$

A further reaction then took place between the radical and ferrocene or ferrocenium ion to give the corresponding azolylferrocene [97]. The Moessbauer spectra of mixed-valence salts

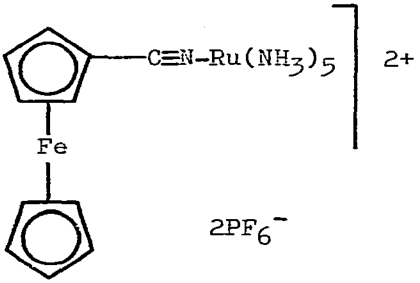


9.3

of 1',1'''-dialkylbiferrocene cations have been obtained in the temperature range 4.2°K to 300°K. The temperature dependence of the spectra was interpreted in terms of conformational changes in the cations [98]. The temperature dependence observed in the Moessbauer spectrum of the cation (9.1) has been explained in terms of an increase in the rate of intervalence-electron transfer between the two iron atoms as the temperature increased. A cyclic voltammetric study of the cation (9.1) indicated that the iron-iron interaction was greater than that in the monocation of biferrocene at room temperature [99].

Diferrocenylketone and triferrocenylketone have been oxidized and studied by Moessbauer spectroscopy as part of an investigation of mixed-valence compounds. Anomolous Moessbauer behaviour was observed, with the recoil-free fraction differing between Fe^{2+} and Fe^{3+}. The oxidation products of 1,3,5- and 1,2,4-triferrocenylbenzene (9.2) were examined and the latter (9.2) exhibited mixed-valence behaviour in solution [100]. Photooxidation of ferrocene to the ferrocenium ion by carbon tetrachloride, sodium anthraquinone-1-sulphonate or 9,10-dicyanoanthracene was brought about by visible light in solutions of aqueous cetyltrimethylammonium chloride or bromide and sodium dodecyl sulphate [101]. The 3-substituted triferrocenylcyclopropenes (9.3; R = H, Me, OMe, p-Me.C_6H_4, CN) have been synthesized by nucleophilic addition to the corresponding cyclopropenium ions. Oxidation of the cyclopropenes (9.3) has been investigated by cyclic voltammetry. Reversible waves corresponding to the stepwise oxidation of the three iron sites were observed with weak interaction between the ferrocene groups in the corresponding mixed valence species. The thermal rearrangement of the cyclopropene (9.3; R = p-Me.C_6H_4) proceeded much faster than that of the phenyl analogue, tetraphenylcyclopropene [102].

Oxidation of the heteronuclear complexes (9.4 and 9.5) has been studied by cyclic voltammetry. The two reversible waves observed in each case corresponded to sequential oxidation of the ruthenium ion and then the iron. Weak heteronuclear



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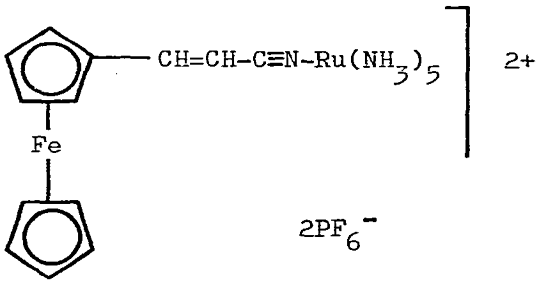
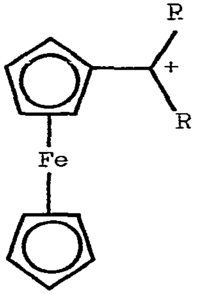


9.5

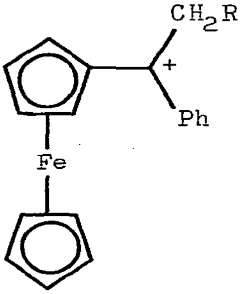
coupling in the mixed-valence ions was indicated by the results [103]. Ferrocene and [3]ferrocenophane have been protonated and the electronic absorption spectra measured in EtOH and in HBF$_3$OH where the intensity was much higher. The increased intensity was ascribed to ring tilting [104]. Moessbauer spectroscopy has been used to examine the structure of iron-protonated ferrocene in trifluoromethanesulphonic acid. The high quadrupole splittings observed were explained in terms of ring-tilting and distribution of charge [105].

10. FERROCENYL CARBENIUM IONS

The structures of the carbenium ions (10.1; R = H, Me) have been investigated spectroscopically in frozen acid media. ^{1}H NMR spectra did not show evidence for Fe-H bonded species while the Moessbauer spectra for the primary carbenium ion (10.1; R = H) were interpreted in terms of stabilization of the positive charge by orbital overlap with the iron atom [106]. Rate constants for the addition of water and for deprotonation in aqueous methyl cyanide have been determined for a series of ferrocenyl-stabilized carbocation salts. Both alcohol and alkene were formed from the cations (10.2; R = Ph, t-Bu and 10.3; R = Ph) but the cation (10.2; R = CPh$_3$) reacted exclusively by deprotonation and the cations (10.3; R = H, Me) mainly by addition. The bulky β-substituents (t-Bu and CPh$_3$) retarded both reactions by steric and conformational effects.



10.1



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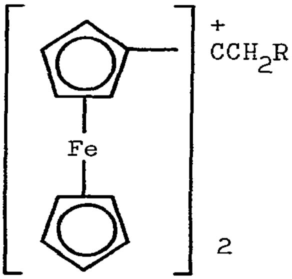

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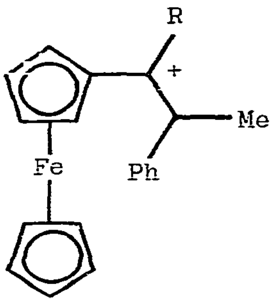

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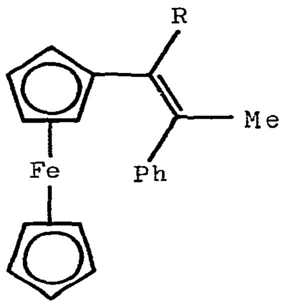
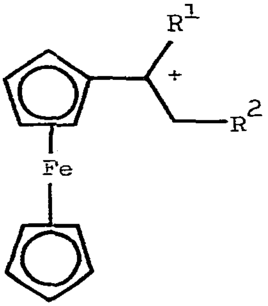


10.5

The effects of added chloride or perchlorate ions were investigated [107]. Ferrocenylalkylium ions (10.4; R = H, Me, Ph) have been shown to undergo preferential exo-deprotonation in base and a similar exo-stereoselectivity was associated with protonation of the resultant alkenes (10.5) in trifluoroacetic acid [108].



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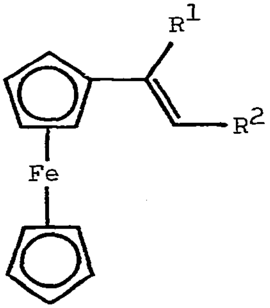

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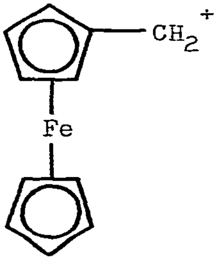
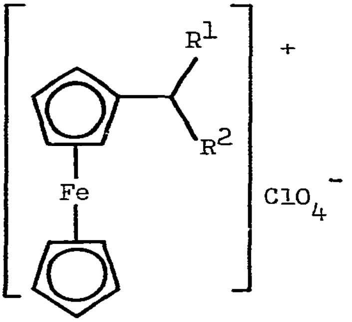


10.8

The base-catalyzed deprotonation of the ferrocenylcarbenium ions (10.6; R^1 = Ph, R^2 = Bu^t; R^1 = ferrocenyl, R^2 = H) to the corresponding ferrocenylethylenes (10.7) has been the subject of a kinetic study. Initial state conformation and ion pair formation were considered to be important factors in the mechanism [109]. Rate constants for the formation of the ferrocenylmethyl carbenium ion (10.8) and for the nucleophilic addition of water and pyridine were determined. Secondary α-hydrogen isotope effects on carbenium ion (10.8) formation were found and the results were discussed in terms of the possible structural models of the cation [110]. Treatment of ferrocene with the ketones R^1COR^2 where R^1 = Ph, 3-indolyl, ferrocenyl, R^2 = H; R^1 = ferrocenyl, R^2 = Me, in thepresence of phosphorus oxychloride and perchloric acid gave the perchlorates of the corresponding ferrocenylmethyl carbenium ions (10.9) [111]. Ferrocene has been attacked by aldehydes and ketones under strongly acid conditions to form α-ferrocenylalkyl carbenium ions which were trapped by amines and mercaptans to give α-ferrocenylalkyl-amines and -sulphones respectively. Thus ferrocene combined with Me_3CCHO to form a carbenium ion which was trapped with $HSCH_2CO_2Me$ to form the thiolate (10.10) [112].



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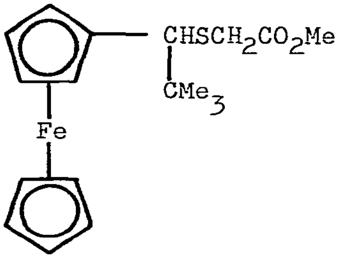
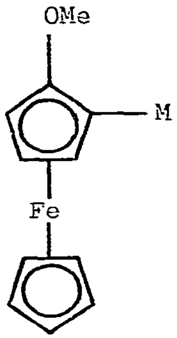


10.10

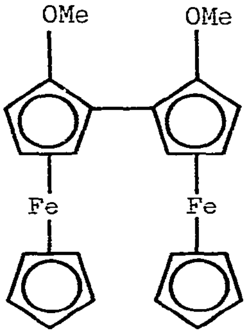
11. FERROCENE CHEMISTRY

(i) Derivatives containing other metals (metalloids)

Diferrocenylketimine has been prepared by the reaction of lithioferrocene with cyanoferrocene [113]. The reaction of 1-lithio-2-methoxyferrocene with $(CuBr.PPh_3)_4$ or $AgNO_3.3PPh_3$ gave the corresponding metal derivatives (11.1; M = Cu, Ag). These metal derivatives were coupled in the presence of copper (II) chloride to produce the biferrocenes (11.2 and 11.3) [114]. (1,1'-Ferrocenediyl)dichlorosilane has been used to derivatize n-type silicon photoanodes and the rate of reduction of the surface-confined ferrocenium ion was studied. The reducing



11.1



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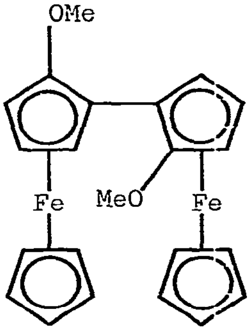
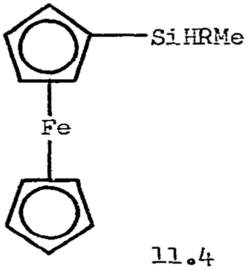


11.3

agents used included iodide ion, tris(2,2'-bipyridine)cobalt (II) ion, ferrocene, 1,1'-dimethylferrocene, phenylferrocene, bis-(η^5-indenyl)iron, hexaammineruthenium (II) ion, hexacyanoferrate (II) ion and dimethyldithiocarbamate [115]. Hydrosilylation of



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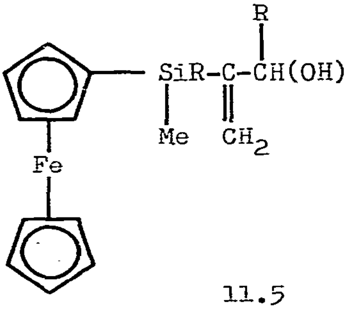
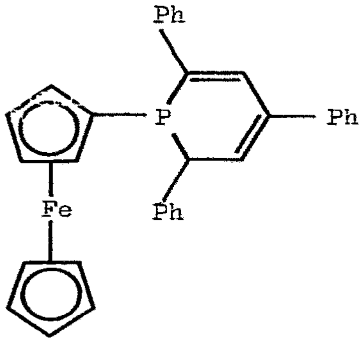


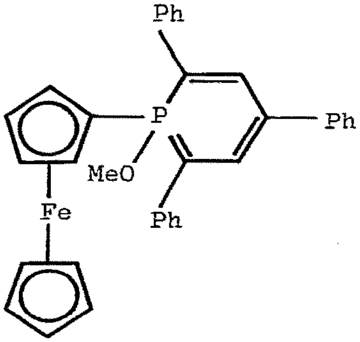
11.5

the acetylenes $RCH(OH)C\equiv CH$, where R = Pr, Ph, with the ferrocenyl-silanes (11.4; R = Me, Ph) gave preferentially the α-isomers (11.5) together with some of the corresponding β-isomers [116].

The reaction of (dimethylamino)methylferrocene (L) with organotin halides gave the adducts Ph_2SnX_2L, where X = Cl, Br, I, Me_2SnCl_2L and Ph_3SnClL [117]. The ferrocenyldihydrophosphorine (11.6), obtained by addition of ferrocenyllithium to the appropriate phosphorine, has been oxidized with mercury (II)

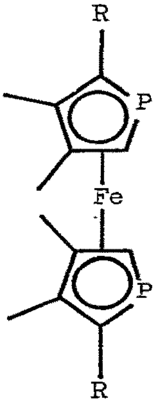


11.6



11.7

acetate in methanol to the λ^5-phosphorine (11.7) [118]. The diphosphaferrocene (11.8; R = H) underwent Friedel-Crafts acylation with $ClCO_2Et$ to form the ester (11.8; R = CO_2Et) which was hydrolyzed subsequently to the carboxylic acid (11.8; R = CO_2H). The phosphorus atoms in the complex (11.8; R = H) were attacked by $Fe(CO)_4$.THF in boiling benzene to form the product (11.9; R = H) and this was converted by Friedel-Crafts



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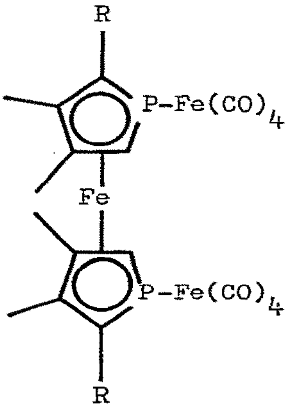
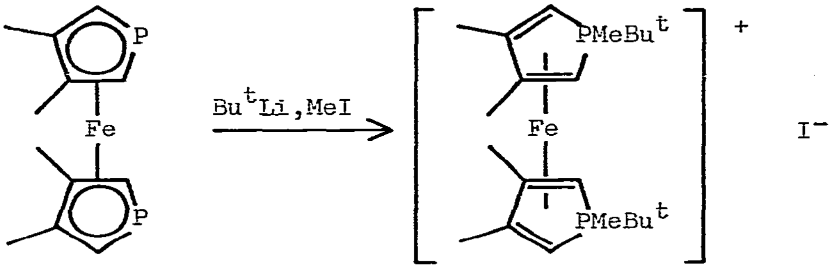


11.9

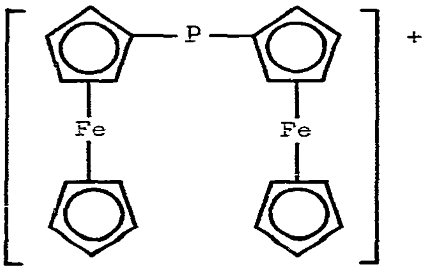
acetylation to the derivative (11.9; R = COMe) [119]. The phosphaferrocene (11.10) has been treated with t-butyllithium and then methyliodide to form the stable green paramagnetic (η^4-phospholium)iron halide (11.11) which is a 17-electron species. The structure of this product (11.11) has been confirmed



11.10 11.11

by X-ray crystallography and the mechanism of formation was discussed [120].

Treatment of chlorodiferrocenylphosphine or tetracarbonyl(chlorodiferrocenylphosphine)iron with a stoichiometric quantity of aluminium chloride at -78°C gave the corresponding ferrocenyl stabilized phosphenium ions (11.12 and 11.13). ^{31}P NMR and Moessbauer spectra were consistent with the phosphenium ion structure rather than a ferrocenium ion substituted species [121].



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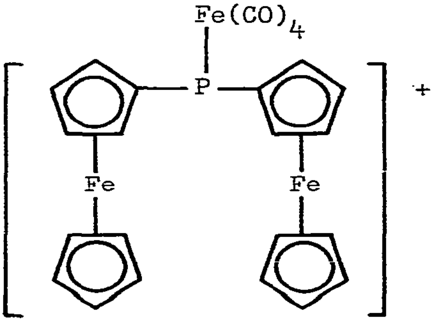
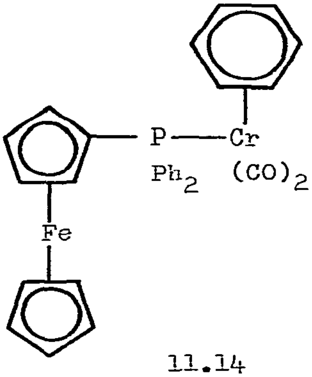


11.13

ate constants have been determined for hydrogen-deuterium xchange in this chromium complex (11.14). The effect of the errocenyl-phosphine ligand was compared with triphenylphosphine nd carbonyl. Ferrocenyldiphenylphosphine was a stronger lectron donor than triphenylphosphine in basic solution whilst



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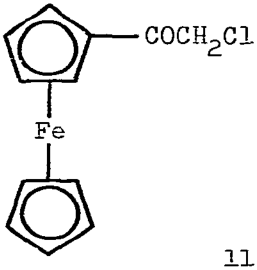
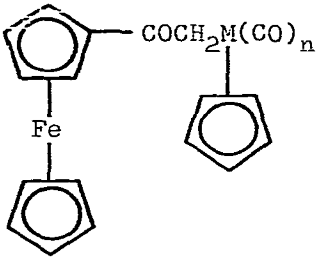


11.15

n acidic solution there was only a small difference in the xchange rate [122].

Treatment of the ferrocenyl-ketone (11.15) with NaM(CO)$_n$-η-C_5H_5), where M = Fe, W, Mo; n = 2, 3; gave the corresponding α-metallated ketones (11.16). The reactions of the ketones 11.16) were investigated [123]. Cocondensation of chromium toms with phenyl- or p-tolyl-ferrocene at liquid nitrogen emperatures gave the diferrocenyl (η-arene)chromium complexes 11.17; R = H, Me). Oxidation of the neutral complexes (11.17) ave the corresponding cationic species which were isolated as he iodides or tetraphenylborates [124]. The kinetics of ercuration of ferrocene with mercury (II) acetate have been einvestigated spectrophotometrically. The results were nterpreted in terms of rapid complex formation followed by ate determining conversion of the complex to products. The ormation of similar complexes with mercury (II) chloride was nvestigated by ^{1}H NMR spectroscopy and evidence was obtained or the formation of 1:1 iron-bound mercury species. Improved yntheses of acetatomercuriferrocenes from the corresponding hloromercuriferrocenes were also reported [125]. The omplexing of metallocenes with inorganic electron acceptor



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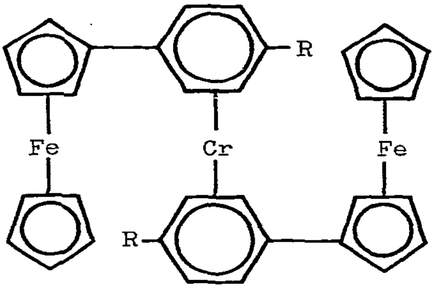
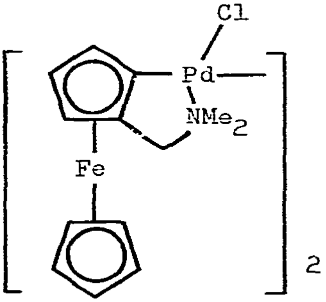


11.17

compounds has been investigated [126].

(ii) Complexes of ferrocene containing ligands

The (dimethylamino)methylferrocene-palladium complex (11.18) has been résolved into optically pure enantiomers via the (S)-proline derivatives [127]. The chiral ferrocenyl-



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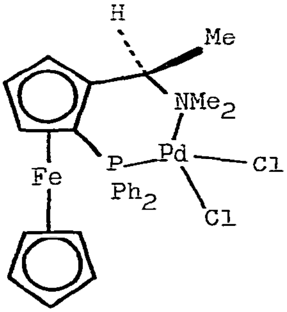
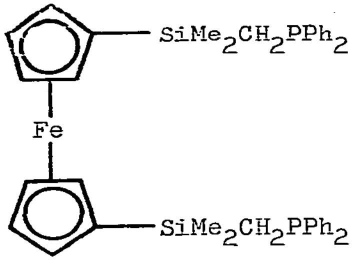


11.19

phosphine-palladium complex (11.19) has been used as a catalyst for the asymmetric hydrosilylation of olefins in the preparation of optically active norbornyl and 1-phenylethyl alcohols and bromides [128]. The diphosphinoferrocene (11.20) has been prepared from the corresponding cyclopentadienide ion and behaved as a bidentate ligand towards molybdenum, manganese,



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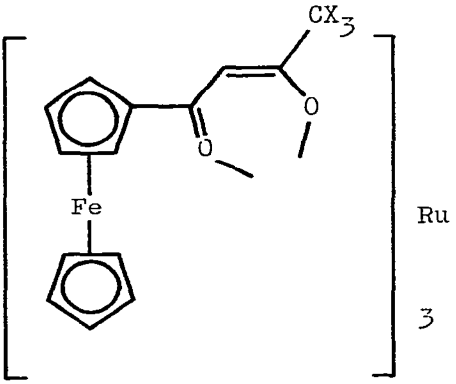
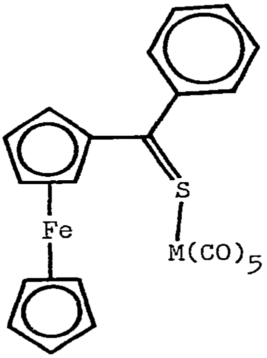


11.21

cobalt and nickel compounds. Both 1:1 and 2:2 complexes were obtained [129].

Several transition metal complexes of 1-ferrocenyl-1, 3-pentanedione (FPDH) have been prepared and characterized. Manganese, cobalt and nickel gave octahedral species of the type $M(FPD)_2(H_2O)_2$ while manganese and cobalt also gave the tetrahedral complexes $M(FPD)_2$. Square planar complexes, $M(FPD)_2$, were obtained with nickel and copper [130]. The ferrocenyl-β-diketonate complexes (11.21; X = H, F), prepared from the free diketones and ruthenium (III) chloride, have been studied by thermal analysis. Decomposition began at 227°C



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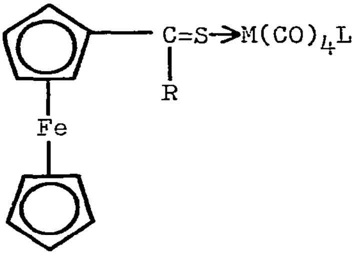
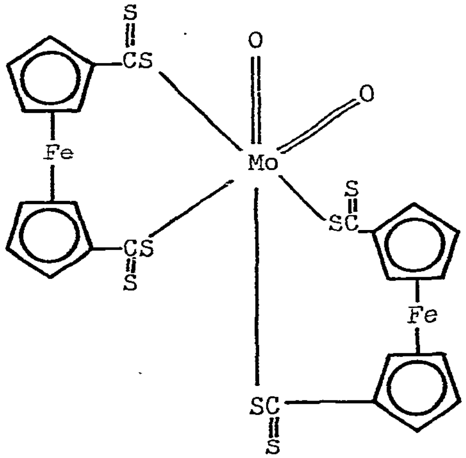


11.23

and was followed by loss of methyl or trifluoromethyl and then cleavage of the chelate ring [131]. The complexes formed between ferrocenylphenylthioketone and group VI metal carbonyls (11.22; M = Cr, Mo, W) have been studied by ^{13}C NMR spectroscopy. The carbon nuclei in the cyclopentadienyl groups were dishielded by comparison with the free ligand. The deshielding decreased in the series $W \gg Mo > Cr$ [132].

The ferrocenylthioketone-metal carbonyl complexes (11.23; R = Me, Ph, L = CO, M = Cr, Mo, W; R = Ph, L = PPh_3, M = W) have been prepared by reaction of the thioketone with the appropriate metal carbonyl [133]. The reaction of diethylammonium ferrocenedithiocarboxylate with MoO_2Cl_2 in methanol gave the cis-complex (11.24). A similar reaction of the same ligand with $Na_2MoO_4 2H_2O$ in aqueous solution gave the oxygen bridged complex (11.25). The infrared spectra of the molybdenum complexes (11.24 and 11.25) were discussed [134]. Piperidinium ferrocenedithiocarboxylate underwent metathesis with metal halides to form the binuclear complexes (11.26; M = Cu, Zn, Pd). The copper complex (11.26; M = Cu) was compared with copper bis(ferrocenecarboxylate) [135].



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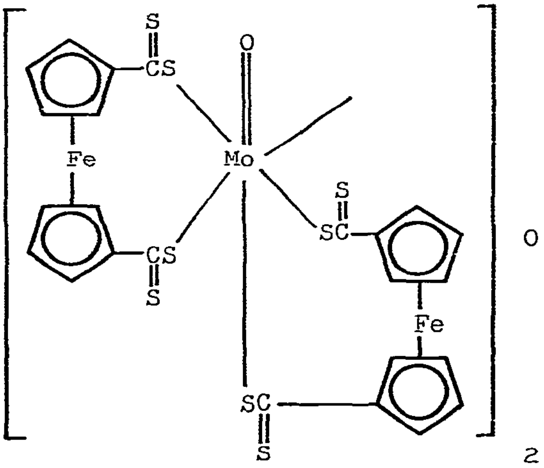

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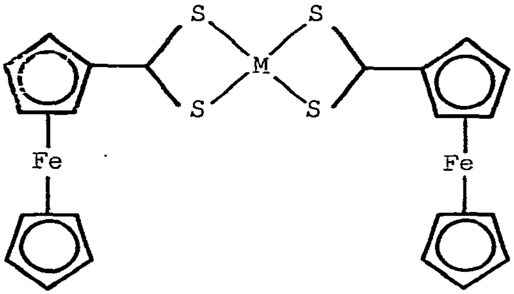
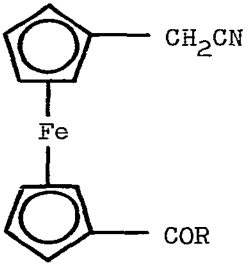


11.26

(iii) General chemistry

Friedel-Crafts acylation of ferrocenylacetonitrile with 4-methylbenzoyl chloride or acetic anhydride gave the corresponding heteroannularly disubstituted ferrocenes (11.27; R = p-MeC$_6$H$_4$, Me) [136]. Unsaturated ferrocenylketones have been treated with hydrazines to form the corresponding ferro-



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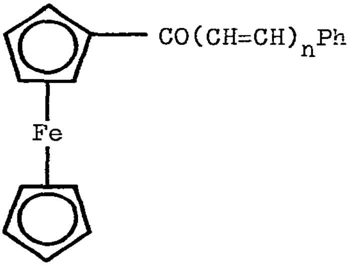
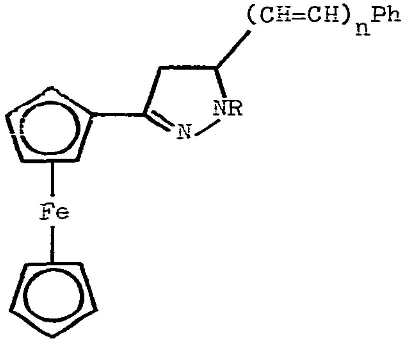


11.28

cenylpyrazolines. Thus the ketones (11.28; n = 2, 3) were treated with phenylhydrazine and acetylhydrazine to form the pyrazolines (11.29; R = Ph, Ac, n = 1, 2) [137]. Ferrocenylketones, such as 1,1'-diacetylferrocene, have been converted selectively to the corresponding acyloins, such as the hydroxyketone (11.30), by treatment with iodosobenzene, PhI=O or its



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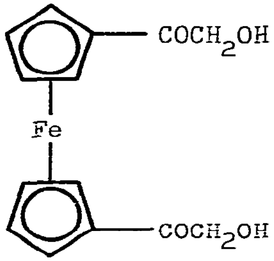
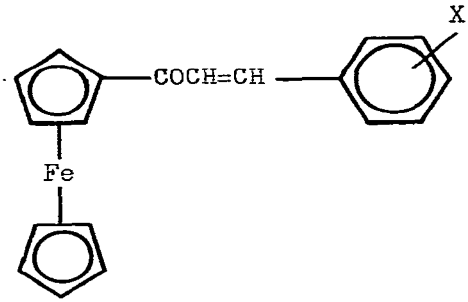


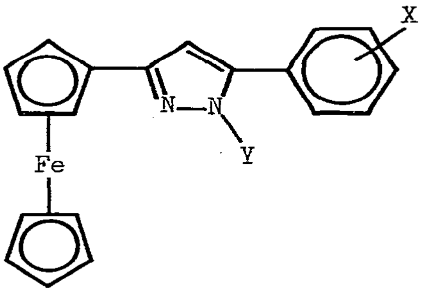
11.30

diacetate PhI(OAc)$_2$ in methanolic sodium hydroxide [138].

Ferrocenylchalcones (11.31; X = H, *p*-Cl, *p*-Me, *m*-, *p*-NO$_2$), prepared from acetylferrocene and the appropriate substituted benzaldehyde, underwent cyclic condensation with hydrazine in acetic acid and phenylhydrazine to give the corresponding pyrazoles (11.32; X = H, *p*-Cl, *p*-Me, *m*-, *p*-NO$_2$; Y = Ac, Ph). The chalcones (11.31) gave the dibromides by addition of bromine across the olefinic double bond and these dibromides were attacked by 2-naphthol and 1-naphthylamine to form the corresponding benzofurans and indoles [139]. Treatment

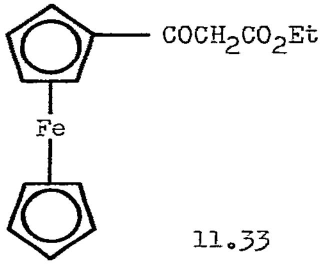


11.31



11.32

of the ferrocenyl-ester (11.33) with amines R^1R^2 NH gave the corresponding ferrocenoylacetanilides (11.34; $R^1 = R^2 = H$; $R^1 = H$, R^2 = p-ClC_6H_4, 2,3-, 2,6-$Me_2C_6H_3$; R^1 = Et, R^2 = o-ClC_6H_4). When the acetanilide (11.34; R^1 = H, R^2 = 2,3-$Me_2H_6H_3$) was heated with orthophosphoric acid the cyclic derivative (11.35) was formed and treatment of the same acetanilide with sulphuryl chloride gave the dichloro derivative (11.36) [140]. Trifluoroacetylferrocene has been reduced by



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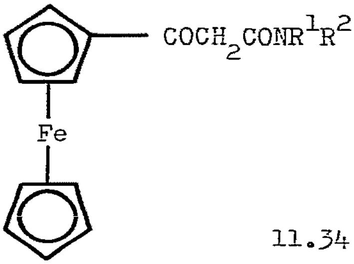
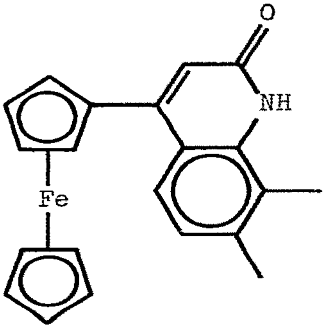


11.34



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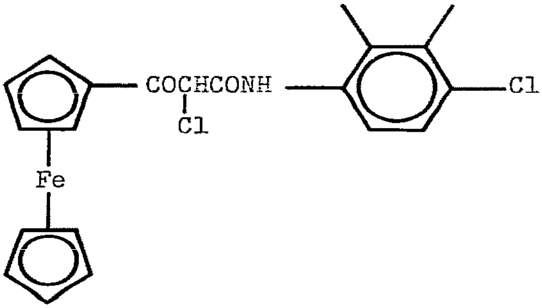
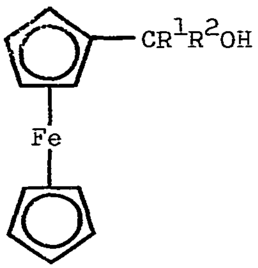


11.36

fermenting baker's yeast to give 1-ferrocenyl-2,2,2-trifluoroethanol in good yield [141].

The reduction of acyl- and 1,1'-diacyl-ferrocenes to the corresponding alkylferrocenes with sodium borohydride in dioxan or dimethoxyethane was catalysed by $AlCl_3$, $BF_3.OEt_2$, BF_3 and H_2SO_4 [142]. Ferrocenylmethanols (11.37) have been converted to the corresponding 1-ferrocenylalkylphenylsulphides (11.38;



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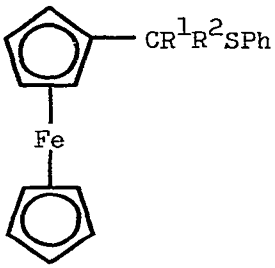

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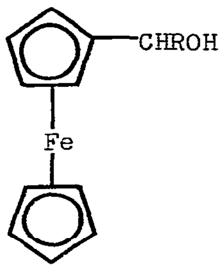
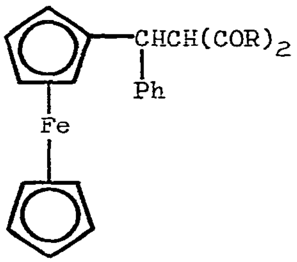


11.39

R^1 = H, Me; R^2 = H, Me, Et, $CHMe_2$, Ph) by treatment with thiophenol in dichloromethane containing trifluoroacetic acid [143]. The oxidation of ferrocenylmethanols (11.39; R = Me, Ph, substituted-Ph) with bis(triphenylsilyl)chromate, $(Ph_3SiO)_2CrO_2$, to the corresponding ketones has been the subject of a kinetic investigation. The reaction involved an initial slow transesterification followed by a fast oxidation [144].



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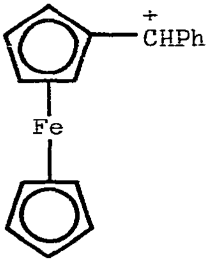

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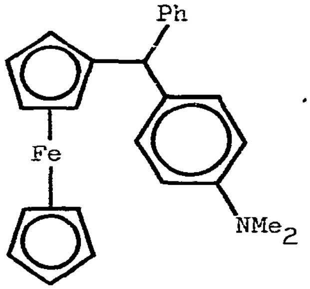
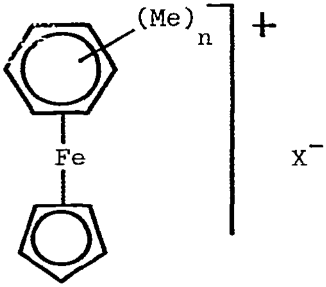


11.42

The β-diketones (11.40; R = Ph, Me) were cleaved heterolytically by Lewis acids, for example, magnesium bromide, zinc chloride and tin (IV) bromide, to give the carbenium ion (11.41) which formed the amine (11.42) on treatment with N,N-dimethylaniline. The carbenium ion (11.41) was also formed by reaction of ferrocenyl(phenyl)methanol with magnesium bromide



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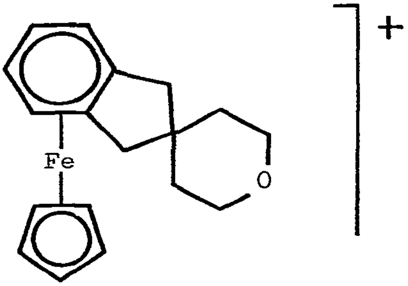
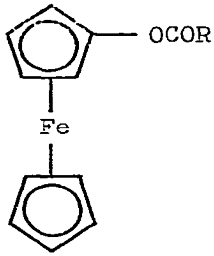


11.44

[145]. The cationic complexes (11.43; X^- = BF_4^- or PF_6^-, n = 0-6) have been synthesised in quantitative yields by ligand exchange between ferrocene and the corresponding arene. The complex $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6Et_6)]^+PF_6^-$ was prepared by a similar route in lower yield. When the arene was hexasubstituted, sodium amalgam reduction gave the corresponding 19-electron neutral species which were thermally stable. The properties of these 19-electron species have been investigated [146]. Ferrocene has been treated with substituted arenes in the presence of aluminium chloride and aluminium to form (η-arene)-(η-cyclopentadienyl)iron cations such as the spirane (11.44) [147].

The ferrocenyl esters (11.45; R = Me, CH_2Cl, CH_2OMe, CH_2NHAc, C_6H_5, 2-Cl.C_6H_4, 4-Me.C_6H_4, $CH{=}CHC_6H_5$) have been obtained by acylation of iodoferrocene with the appropriate carboxylic acid, RCO_2H. The acetate (11.45; R = Me) combined with bromoethane and $MeOCH_2CH_2Cl$ to give the ethers (11.46; R = Et, CH_2CH_2OMe) respectively [148]. Bromo- and iodo-ferrocene combined with phthalimide in the presence of copper (I) oxide to form N-ferrocenylphthalimide in 37-92% yield, 1,1'-dibromo- and 1,1'-diiodo-ferrocene underwent the same reaction [149]. As part of an investigation of polystyrene-bound (η-cyclopentadienyl)metal catalysts, 7-chloro-7-phenylnorbornene was treated with n-butyllithium to form the phenylcyclopentadienide ion which was in turn coupled with $FeCl_3$/Fe to form 1,1'-diphenylferrocene [150].



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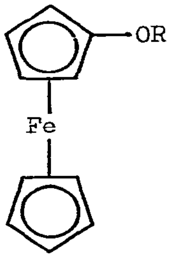

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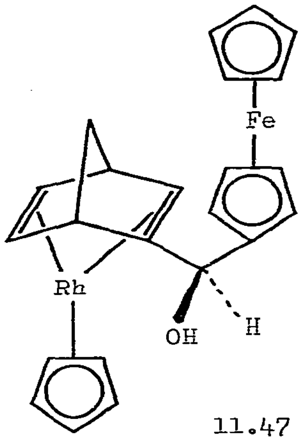

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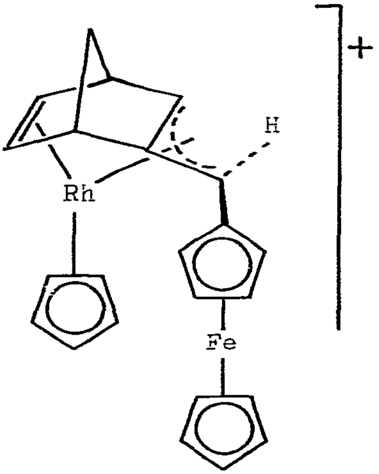

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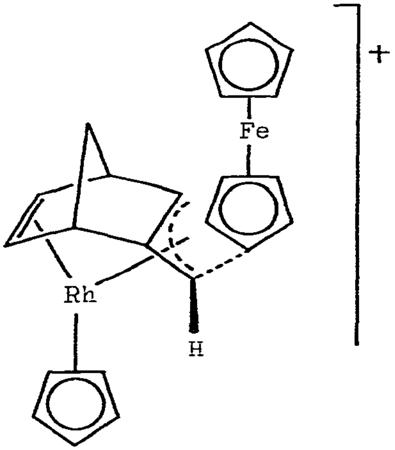
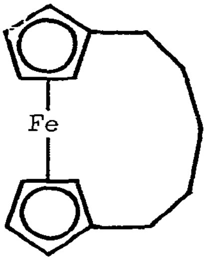


11.49

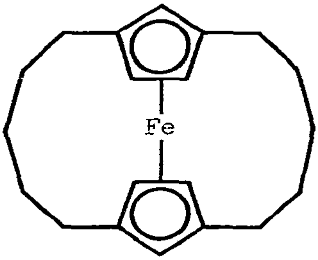
Treatment of the rhodium complex (11.47) with sulphuric acid gave a mixture of two isomeric complexes (11.48 and 11.49) in a ratio of 4:1. The formation of this product mixture was discussed [151].

12. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

The pentamethylene-ferrocenes (12.1, 12.2 and 12.3) were prepared by bridge-enlargement reactions of the appropriate α-ketones followed by reduction. The ^{1}H NMR spectra of the polybridged ferrocenes were briefly discussed [152]. Diethyl



12.1



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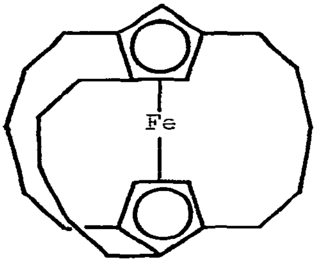

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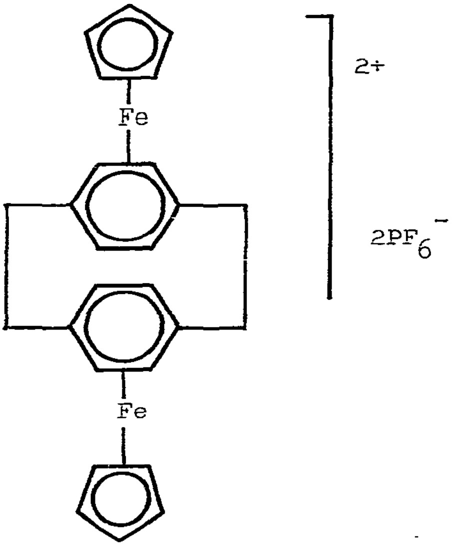
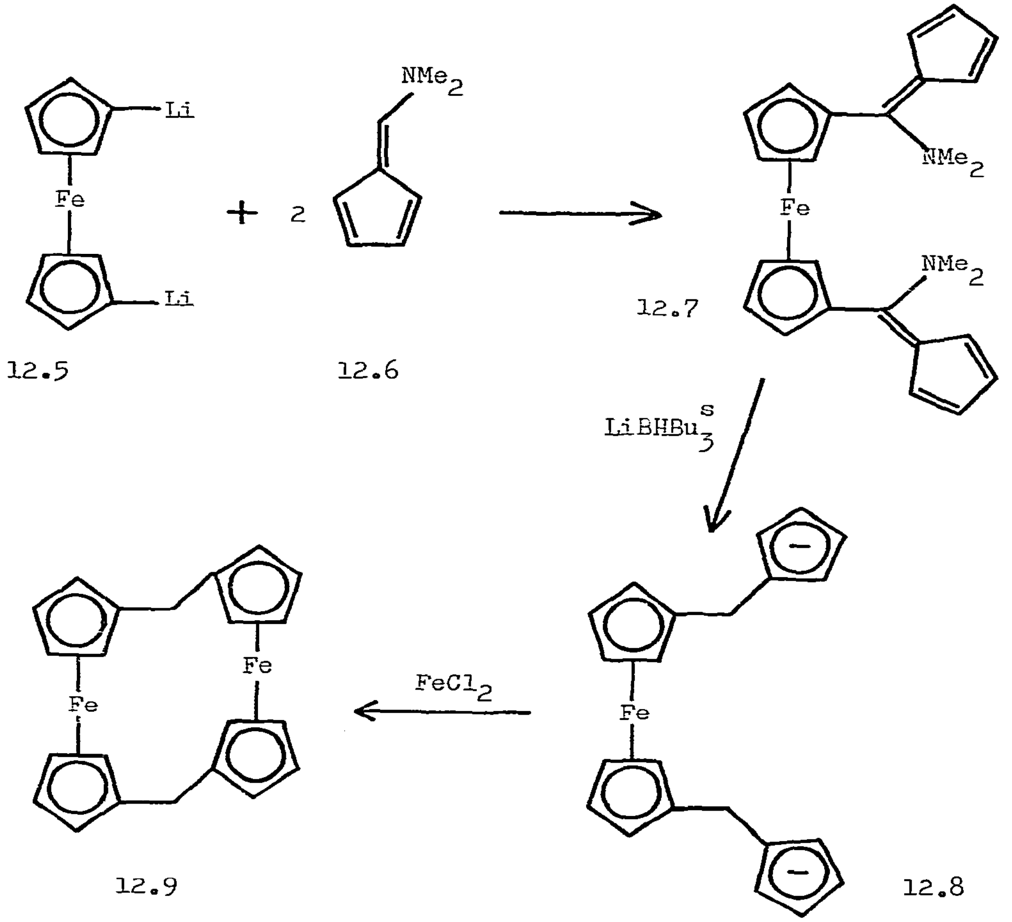


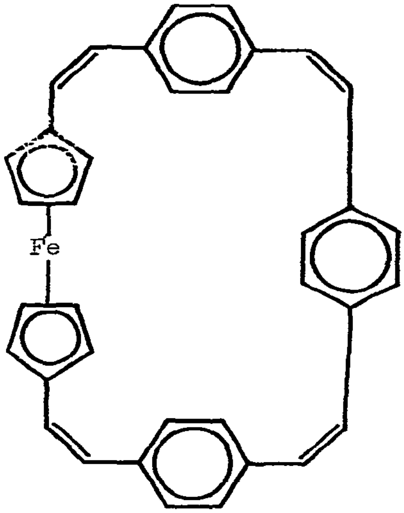
12.4

malonate, ethyl acetoacetate and ethyl cyanoacetate underwent Michael addition with 1,1'-dicinnamoylferrocene to give the corresponding [7]ferrocenophanes [153]. Ferrocene has been heated with [2.2]paracyclophane in the presence of aluminium powder and aluminium chloride to form the paracyclophane complex (12.4) [154].

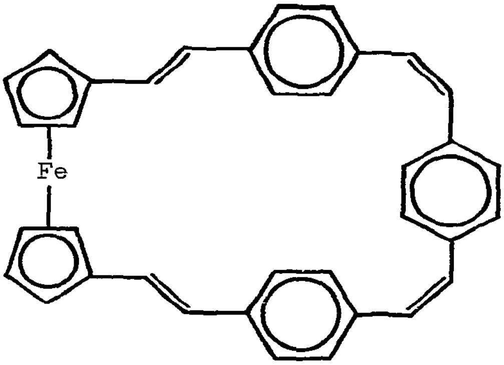
The synthesis of [1.1]ferrocenophane (12.9) by an efficient route has been reported. 1,1'-Dilithioferrocene (12.5) underwent addition to 6-dimethylaminofulvene (12.6) to form the intermediate 1,1'-bis(6-fulvenyl)ferrocene (12.7). This fulvene (12.7)



was then reduced with $LiBHBu^s_3$ in THF to the 1,1'-bis(cyclopentadienylmethyl)ferrocene dianion (12.8) followed by coupling with iron (II) chloride to give [1.1]ferrocenophane (12.9) in 45% yield. Substituted ferrocenophanes were obtained in the same way [155]. A series of ferrocenophanetetraenes, including (12.10, 12.11 and 12.12) has been prepared by multiple Wittig reactions and the extent of planarity and conjugation in these molecules was investigated [156].



12.10



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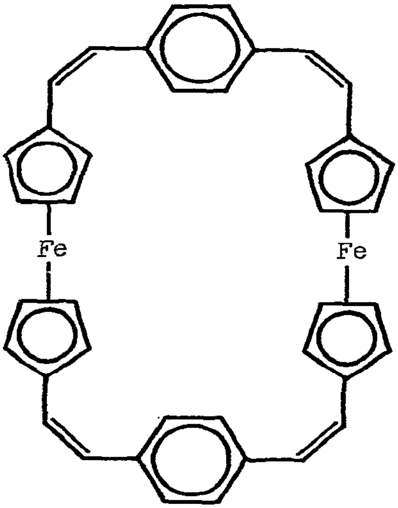

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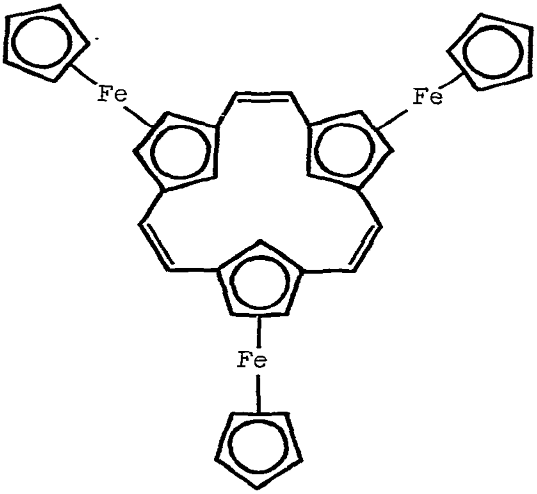
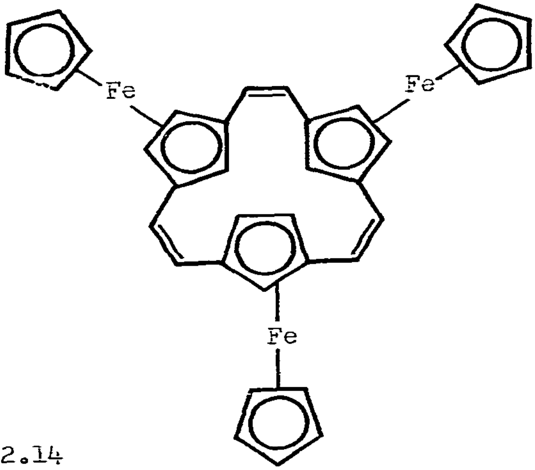


12.13

Reductive coupling of 1,3-diformylferrocene with TiCl$_3$-LiAlH$_4$ in diglyme gave a mixture of the *syn*- (12.13) and *anti*-isomers (12.14) of [2.2.2](1,3)ferrocenophane-6,8,10-triene. 1,3-Dihydroxymethylferrocene combined with the dimercaptan (12.15) to form the ferrocenophane (12.16) and with *p*-bis(mercaptomethyl)benzene



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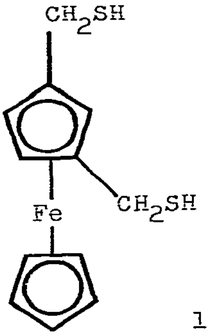

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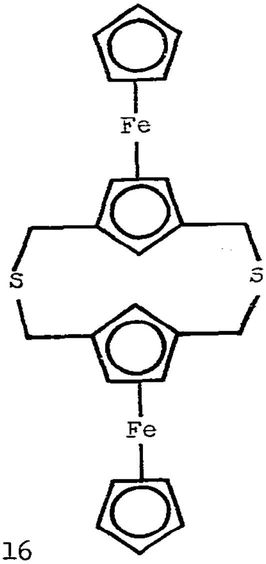

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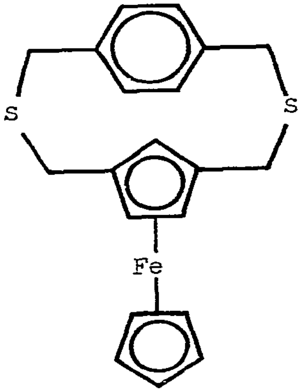
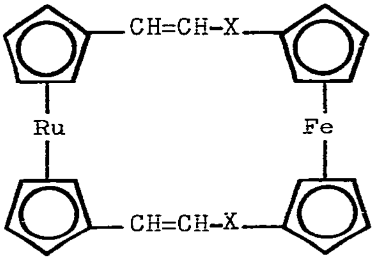


12.17

to give the analogous ferrocenophane (12.17) [157]. Several ferrocenoruthenocenophanes and ruthenocenophanes have been synthesised by condensation of the appropriate metallocene-1,1'-dicarbaldehydes with 1,1'-diacylmetallocenes in base. Among the compounds prepared were the mixed metallocenophanes (12.18;

X = CO, COCH=CH) [158]. The electronic and NMR spectra of the ferrocenophanes [12.19; -Y- = CH=CHCO, CH=CHCH=C(CN), CH=CHCOCH=CH,



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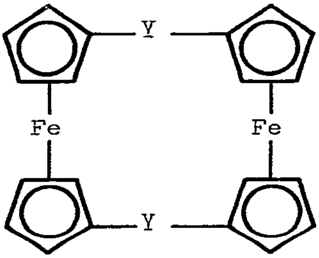
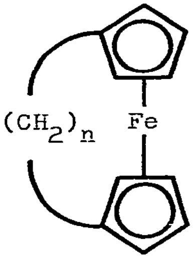


12.19

CH=CHCH=CHCO, CH=C(CN)CH=CHC(CN)=CH] have been recorded and transannular electronic interactions evaluated. The ferrocenophanes (12.19) were prepared by intermolecular base catalyzed condensation [159].

Treatment of the ferrocenophanes (12.20; n = 4, 5) with acryloyl chloride in the presence of aluminium chloride gave the corresponding [3][4]- and [3][5]- ferrocenophanes (12.21 and 12.22; n = 4, 5). The structure of the dibridged product (12.22; n = 4) was determined by X-ray analysis [160]. The



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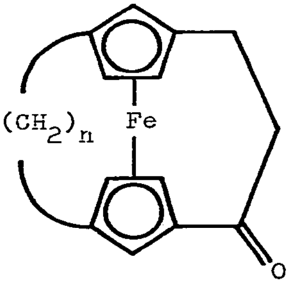

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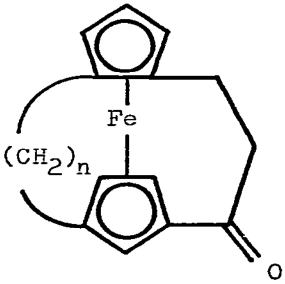
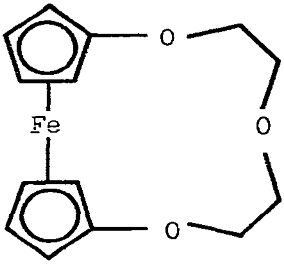


12.22

reaction of 1,1'-dihydroxyferrocene with the chloro-ethers $Cl[(CH_2)_2O]_n(CH_2)_2Cl$, where n = 1-4, and 2,2'-bis(2-chloroethoxy)-1,1'-binaphthyl gave the corresponding polyoxaferrocenophanes. For example, condensation with $Cl(CH_2)_2O(CH_2)_2Cl$ gave the trioxaferrocenophane (12.23) [161]. The acetylation of [5]ferrocenophane gave a mixture of the isomeric diacetyl[5]ferrocenophanes. One of these isomers, 3,4'-diacetyl[5]ferrocenophane (12.24) underwent a base catalyzed condensation with benzaldehyde or 4-chlorobenzaldehyde to give among other products the [5][5]ferrocenophanedione (12.25; X = H, Cl) [162].



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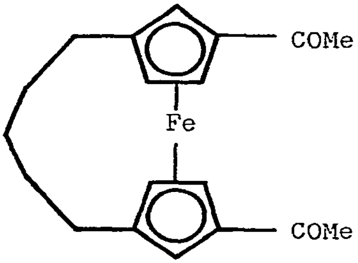
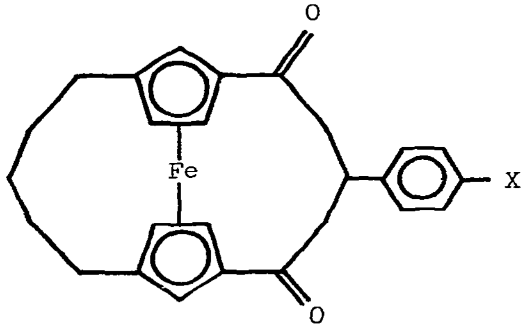


12.24

The ferrocenyl crown ether (12.26) has been prepared and used to form complexes with the Li^+, K^+ and Ca^{2+} ions. The ^1H, ^{13}C and ^{15}N NMR spectra of the ligand (12.26) and the complexes derived from it have been recorded and interpreted [163]. Reaction of the 1-ferrocenylalkyl ethers $FcCH_2OR$, where R = Me, $PhCH_2$, Ph, $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CH_2)$, with hydrogen sulphide in acetic acid gave a mixture of (ferrocenylmethyl)hydrogensulphide, bis(ferrocenylmethyl)disulphide and bis(ferrocenylmethyl)sulphide. The 2-oxa[3]ferrocenophanes (12.27; $R^1 = R^3 = Me$, $R^2 = R^4 = H$, X = O) underwent stereospecific transformations with the same reagent to give the corresponding 2-thia[3]ferrocenophanes (12.27; $R^1 = R^3 = Me$, $R^2 = R^4 = H$, X = S) [164].

Ferrocene paracyclophanes have been obtained by stirring 1,1'-di(hydroxymethyl)ferrocene with dithiols in methylene chloride containing a trace of trifluoroacetic acid. Thus the mononuclear paracyclophane (12.28) was obtained when di(4,4'-



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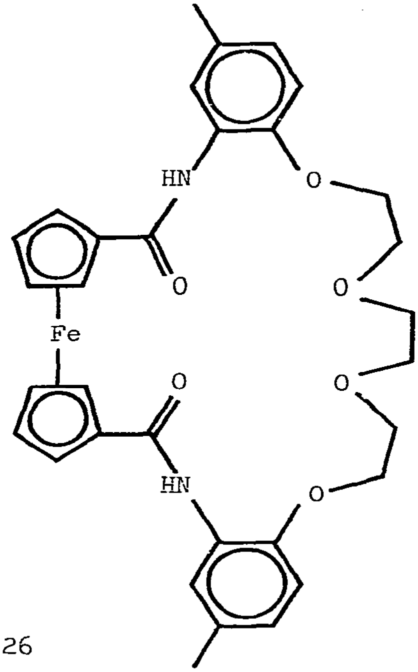
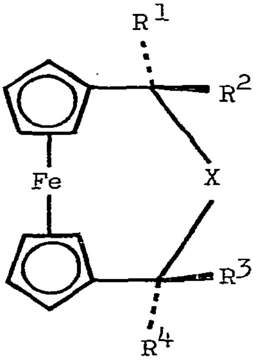


12.26

-dimercaptomethylphenyl)methane was the reagent while the dithiophenols di(4,4'-dimercaptophenyl)methane and di(4,4'-dimercaptophenyl)ether gave the binuclear cyclophanes (12.29;



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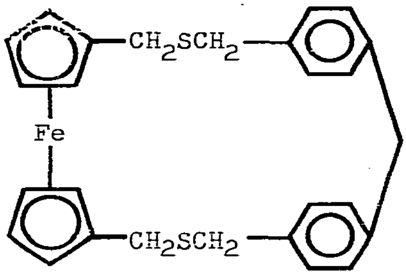

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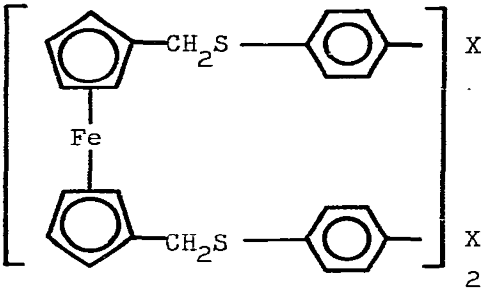
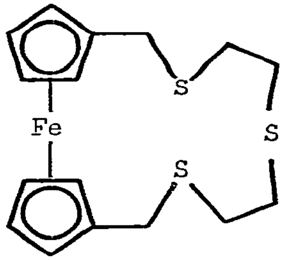


12.29

X = CH$_2$, O) respectively [165]. A series of polyoxathia and polythia ethers was prepared in the same way by the cyclization of 1,1'-bis-(hydroxyalkyl)ferrocenes with the thiols $(HSCH_2CH_2)_2X$ (X = O, S). For example, the treatment of 1,1'-bis(hydroxymethyl)ferrocene with $(HSCH_2CH_2)_2S$ in the presence of trifluoroacetic acid gave the polythia ethers (12.30 and 12.31) [166].



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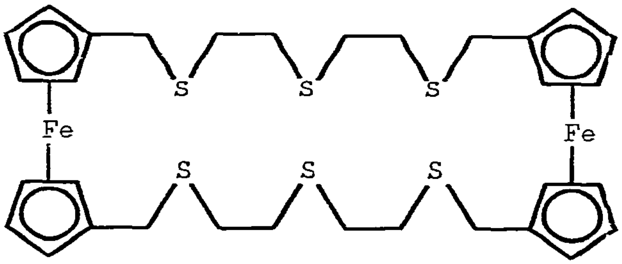
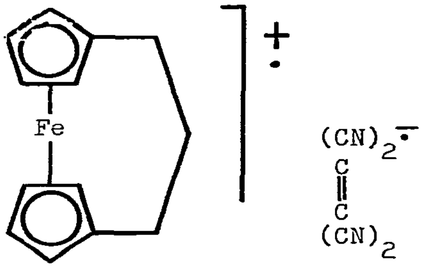


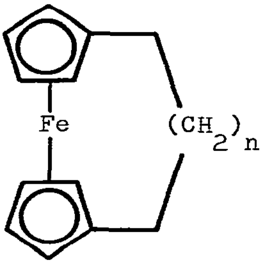
12.31

The ion-radical salt (12.32) has been obtained in high yield from the free ferrocenophane and tetracyanoethylene. The crystal and molecular structure has been confirmed by X-ray crystallography [167].

The Moessbauer spectra have been obtained and X-ray crystallographic measurements made for several [4]- and [5]-ferrocenophanes. Correlations were obtained between the iron-

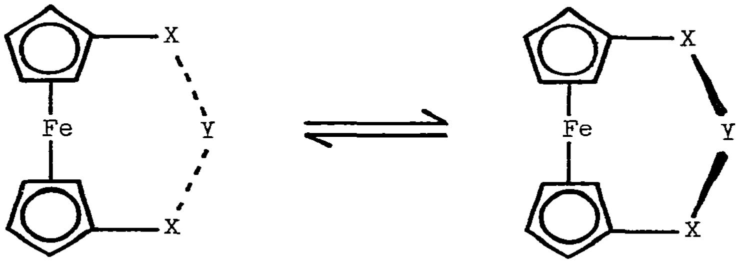


12.32



12.33

cyclopentadienyl ring distance and the electronic charge and electric field gradient at the iron nucleus [168]. The protonation of [3]-. [4]- and [5]-ferrocenophanes (12.33; n = 1, 2, 3) has been examined in HBF$_3$OH. The results obtained were consistent with the earlier findings of long-lived metal protonated species. ^{1}H NMR spectra of [3]- and [4]-ferrocenophanes in trifluoroacetic acid have been interpreted in terms of rapid exchange between solvent and ferrocene [169]. Variable temperature NMR spectroscopy has been used to determine the bridge reversal barriers (12.34 ⇌ 12.35) in the ferrocenophanes (12.34;

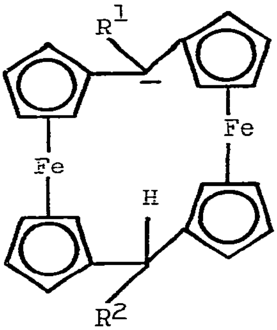


12.34

12.35

X = CH_2, Y = CH_2, O, S; X = S, Y = CH_2 or CMe_2). The energy barrier for [3]ferrocenophane (12.35; X = Y = CH_2) was 40.4 kJ mol^{-1} which is a lower value than that for ring reversal in cyclohexane [170]. Accurate energy data for the bridge reversal fluxion of the [3]ferrocenophanes (12.34, 12.35; X = X = Y = S; X = X = S, Y = Se or Te; X = X = Se, Y = S, Se or Te) has been obtained in the same way. The bridge reversal in the [3]ferrocenophanes was closely analogous to six-membered heterocyclic ring reversal but it was a much higher energy process. The probable mechanism of the bridge reversal process (12.34$\rightleftharpoons$12.35) was discussed [171].

Evidence for an intramolecular C-H-C hydrogen bond in the carbanion (12.36; R^1 = R^2 = H, Me) has been obtained by ^{1}H and



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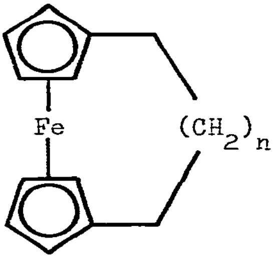

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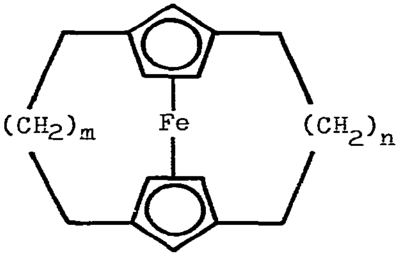

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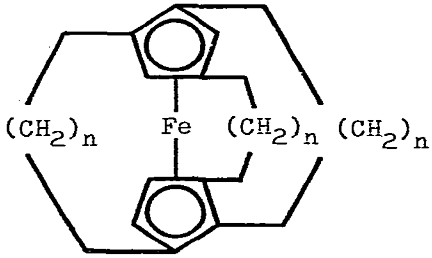


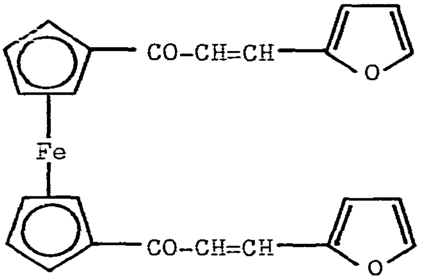
12.39

^{13}C NMR spectroscopy. The carbanion (12.36) was obtained as the deep red lithium salt on the addition of butyllithium to [1.1]ferrocenophane in THF [172]. The oxidation potentials for 34 ferrocenophanes with hydrocarbon bridges and bridges containing ketone groups have been measured by cyclic voltammetry and interpreted. Among the compounds examined were the singly-, doubly- and triply bridged ferrocenophanes (12.37; n = 1, 2, 3; 12.38: m = n = 1, 2, m = 1, n = 2; 12.39; n = 1, 2). For the hydrocarbon bridged compounds the measured potentials correlated with the iron to cyclopentadienyl ring distances while the alignment of the carbonyl group with the cyclopentadienyl rings was important in the ferrocenophanones [173]. The Hartree-Fock (HF) instabilities in a series of bimetallocenes and bimetallocenylenes containing Fe, Co, Ni or Cr as the central metal atom have been investigated via a semiempirical INDO Hamiltonian. The HF picture was only valid for iron and strong correlation effects were found for the Co, Ni and Cr complexes [174]. Ferrocenylruthenocene has been prepared by Ullmann coupling of iodoruthenocene with a large excess of iodoferrocene in the melt phase. In the mass spectrum, preferential loss of a cyclopentadienyl radical occurred from the ferrocene unit rather than the ruthenocene unit [175].

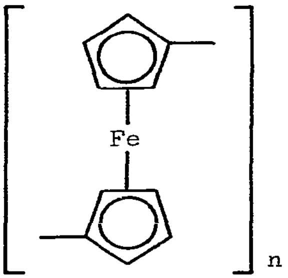
13. FERROCENE-CONTAINING POLYMERS

1,1'-Diacetylferrocene and 1,1'-bis[β-2-furyl)-acryloyl]-ferrocene (13.1) have been polycondensed with biuret [$(H_2NCO)_2NH$] to give polyferrocenyleniminoimides. The polymers were stable up to 225°C and showed semiconducting properties [176]. Intermediate species formed in the polymerization of acetylferrocene and 1,1'-diacetylferrocene with zinc chloride have been examined. A zinc chloride complex of the enol form of acetylferrocene was the initial species isolated and this combined with a further molecule of acetylferrocene to give a dimer as two isomeric forms. Heating this dimer with zinc chloride gave polymers containing conjugated double bonds together with free iron [177]. The condensation of p-ferrocenylaniline, acetylferrocene oxime and p-ferrocenylphenol with $P(S)Cl_3$ gave insoluble dark brown polymeric products which were thermally stable in air at $\leqslant$ 200°C [178].

The radical copolymerization of α-cyclopentadienylidene ethylferrocene with butadiene or isoprene gave brown rubbery



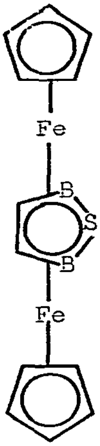
13.1



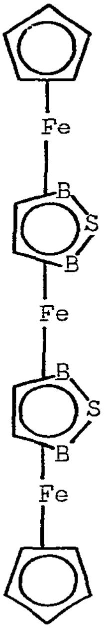
13.2

polymers containing up to 3.02% iron and with molecular weights up to 28,840 [179]. Several styrene-vinylferrocene copolymer samples have been prepared and characterized. Adsorption of the polymers from chloroform solution on to pyrogenic Al_2O_3, SiO_2 and TiO_2 has been examined. Adsorption was found to depend on the solvent, the adsorbent and the copolymer composition. The presence of only a small number of vinylferrocene groups in the copolymer caused a sharp increase in adsorption over that observed for polystyrene [180]. The copolymerization of isopropenylferrocene, 1-ferrocenyl-1,3-butadiene and vinylferrocene with butadiene, chloroprene or isoprene gave low molecular weight liquid prepolymers containing carboxyl end groups. These prepolymers underwent subsequent chain extension to give products suitable for use as polymeric binders. Analysis for iron indicated that ferrocene monomers were efficiently incorporated into the polymers [181]. 1,1'-Dibromoferrocene and 1,1'-diiodoferrocene underwent dehalogenation and polymerization with magnesium to form poly(1,1'-ferrocenylene)(13.2) in yields of up to 77%. Fractions of the polymer showed number-average molecular weights up to 4600 and spectroscopic analysis indicated regular 1,1'-ferrocenylene units. The polymer had high thermal stability and was converted to a semiconductor by doping with acceptors such as TCNQ and iodine [182].

Chemical oxidation, irradiation or electrochemical oxidation of polymers with pendant ferrocenyl groups, or other low ionization potential groups, gave cationic polymers. These were potentially useful as polymer-modified electrodes, as semiconducting polymers



13.3



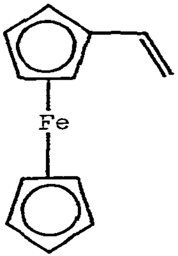
13.4

and as resists for high resolution electron beams [183]. Thouless instability conditions in several polydecker sandwich complexes, including the iron complexes (13.3 and 13.4), have been studied by semiempirical INDO calculations. Hartree-Fock fluctuations were observed of the singlet, triplet and non-real type and the origins of the instability conditions were examined. The Hartree-Fock instabilities for closed shell complexes, such as the metallocenes (13.3 and 13.4) have been compared with doublet fluctuations in open shell species and were extrapolated to infinite polymer chains [184].

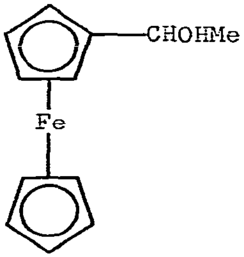
14. APPLICATIONS OF FERROCENE

(i) Ferrocene catalysts and photosensitizers

Crosslinking of potassium thiocyanate treated 4-acetylstyrene-4-(bromoacetyl)styrene copolymer took place on UV irradiation. The addition of ferrocene increased the extent of crosslinking [185]. Vinylferrocene (14.1) vinyl-1,1'-diethylferrocene and α-hydroxyethylferrocene (14.2), 0.025-0.5% have been added to polyethylene in order to produce a photodegradable material [186, 187]. The photodegradation of high density



14.1



14.2

polyethylene film was sensitized by the incorporation of a ferrocene derivative, 0.01 mol/kg. Degradation was complete over a period of 2-3 months in daylight. The polymer was useful in agriculture and forestry [188].

Elastomers based on mercaptoalkyl siloxanes and unsaturated siloxanes were oxygen curable in the presence of ferrocene accelerators [189]. A reduction in the IR curing time by a factor of 7.5 has been achieved for oligoester acrylate by using azobisisobutyronitrile and ferrocene as the curing agents [190]. The effect of solvents on the ferrocene catalysed oxidation of butyraldehyde to butyric acid has been investigated. The rate was dependent on the polarity of the reaction medium and it increased with increasing solvent polarity [191]. A catalyst containing ferrocene, has been developed for the removal of nitrogen oxides from exhaust gases [192].

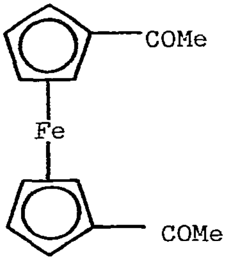
A ferrocene-activated carbon-potassium catalyst was effective for ammonia synthesis under mild conditions. The catalytic activity increased as the concentration of ferrocene increased [193]. A Moessbauer spectroscopic study of the catalyst indicated that it contained Fe_3C as small particles. A correlation was proposed between the Moessbauer characteristics and the activity of the catalyst in ammonia synthesis [194].

Abandoned powdered sulphide ores, for example galena, have been treated with ferrocene and hydrogen at 400°C to enhance the magnetic susceptibility of the mixture. Considerable concentration of the lead sulphide was achieved on magnetic separation [195].

Ferrocene has been incorporated in a protective layer for the photoconductive layer of an electrophotographic element [196]. Image intensifiers, such as ammonium thiocyanate, were effective in achieving a 5X increase in the optical density of photoimaging materials based on ferrocene and tetrabromomethane [197].

(ii) Ferrocene Stabilizers and Improvers

Ferrocene has been used as an inhibitor in polymer compositions based on a butylmethacrylate-methacrylamide copolymer and which were used in sealing gastight threaded joints [198]. The utility of poly(ethylene) in electrostatic coating was improved by treatment with ferrocene [199]. A small proportion of 1,1'-diacetylferrocene (14.3) 0.05-0.7 mol %, has been added to poly(ethylene terephthalate) during polymerization to increase the photostability and improve the quality of aluminium-coated films. Gold and bronze shades in the films were obtained by changing the proportion of the ferrocene additive [200].



14.3

Liquid crystal display devices with good response characteristics and service life have been prepared using cyclohexanecarboxylic acid esters containing dibutylferrocene and either tetracyanoethylene or 2,3-dichloro-5,6-dicyanoquinone [201, 202]. Ethyl p-anisalaminocinnamate liquid crystals with smectic-A and monotropic smectic-B phases have been investigated by Moessbauer spectroscopy using ferrocene containing ^{57}Fe as a label. Evidence was obtained for complex formation between liquid crystal molecules and the label [203]. Cyclohexanecarboxylic acid ester based liquid crystal compositions containing dibutylferrocene (0.5%) and tetracyanoquinodimethane (0.5%) have been prepared. The liquid crystal display devices exhibited a good service life and good response characteristics [204].

(iii) Ferrocene in Analysis

Ferrocene has been used successfully as the reagent for the spectrophotometric determination of iridium in the presence of palladium [205]. The redox potentials for the system $AuCl_4^-/Au$ in aqueous-organic solvents containing hydrochloric or sulphuric acid have been determined. The equilibrium constant and free energy charge were calculated for the following reaction:

$$AuCl_4^- + 3(\eta\text{-}C_5H_5)_2Fe \rightleftharpoons Au + 3[(\eta\text{-}C_5H_5)_2Fe]^+Cl^- + Cl^-$$

In this reaction the gold was precipitated quantitatively and it was suitable for the estimation of gold [206].

The aromatic compounds in crude oil and petroleum products were converted to the corresponding (η-arene)(η-cyclopentadienyl)-iron hexafluorophosphates by ligand exchange with ferrocene. The hexafluorophosphate salts were identified by thin-layer chromatography and it was shown that toluene, _p_-xylene, naphthalene and benzene were present in nearly all the samples [207, 208]. Coulometrically generated copper (II) in acetonitrile has been used as an analytical oxidant for the determination of ferrocene. Micromole quantities of ferrocene, n-butyl-, amyl-, t-butyl- and di-n-butyl-ferrocene were determined accurately [209]. The simultaneous microdetermination of carbon, hydrogen and iron in ferrocene derivatives has been achieved by combustion in oxygen using an electric furnace and $AgMnO_4$ as catalyst [210].

(iv) Combustion Control

An investigation has been carried out on the combustion of poly(vinyl chloride). The presence of ferrocene, zinc pyromellitate and iron (III) pyromellitate suppressed smoked formation and promoted extinction [211]. The addition of ferrocene polymers and antimony (III) oxide to flexible poly(vinyl chloride) improved flame retardation and suppressed smoke formation. Using 0.025% ferrocenylpropene-formic acid polymer and 1% Sb_2O_3 a smoke reduction of 2.5% was obtained together with a char increase of 2.5% [212]. The use of ferrocene in the prevention of smoke during the combustion of hydrocarbons has been studied. The addition of 0.1 wt% of ferrocene to diesel fuel greatly reduced smoke formation. As part of this investigation ferrocene was prepared by the reaction of cyclopentadiene with iron (II) chloride tetrahydrate or iron (III) chloride in strongly basic solution [213].

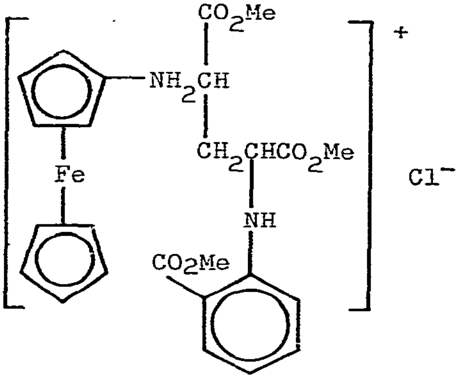
Ferrocene, iron naphthenate and manganese naphthanate have been added (0.1% by weight) to gasoline. Carbon monoxide and formaldehyde in the exhaust gas were reduced by 88% and 19% respectively [214]. Ethyl-, diethyl- and t-butyl-ferrocene have been pyrolysed at 450-560°C in glass or steel tubes. Rate constants were obtained and the optimum conditions for precipitation of solid products and for the evenness of distribution within the reactor tube were determined [215].

The effect of iron compounds on the decomposition of ammonium perchlorate-hydroxyl-terminated polybutadiene composite propellants has been investigated by differential thermal analysis. The catalytic activity of butylferrocene, dimethylferrocene and dibutylferrocene was compared with the catalytic activity of iron (III) oxide. All the ferrocenes were catalytically as active as the iron (III) oxide but the mechanism was different. The iron oxide lowered the decomposition temperature whereas the ferrocenes reduced the activation energy for the decomposition [216].

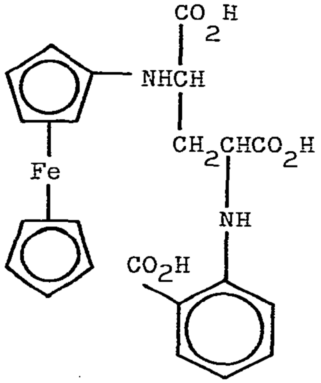
(v) Biochemical and Biological Applications

Ferrocenylamine has been used to prepare the diester (14.5) which was converted to the triacid (14.6). The latter compound (14.6) at 40 mg kg^{-1} gave 30% inhibition of sarcoma 37 in mice [217]. Ferrocenyl ketones (14.7; R = $CH{=}CHCl$, $C{\equiv}CH$, CH_2CH_2Cl, $CH{=}CHPh$) and related compounds were found to show antimicrobial activity against bacteria, yeasts and fungi [218].

The biological fate of ferrocene, labelled with ^{59}Fe and tritium, deposited by inhalation in the respiratory tract of rats has been investigated. Most of the tritium label was excreted in the first day but the ^{59}Fe label was retained in the

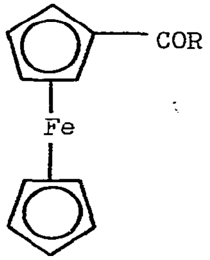


14.5

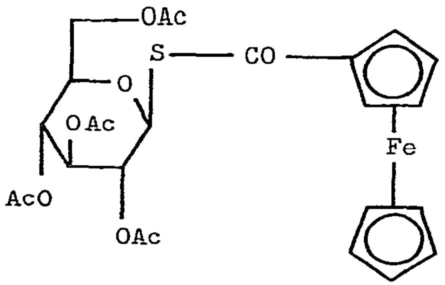


14.6

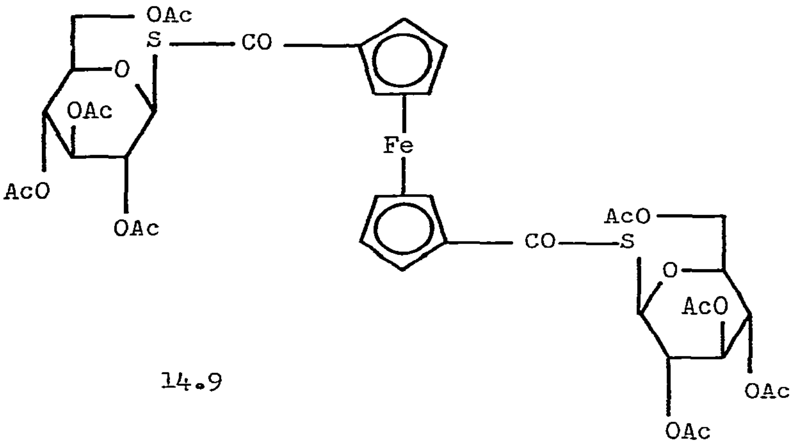
bronchopulmonary and nasopharyngeal regions during the experiment [219]. A series of ferrocenyl-sugar derivatives has been prepared. For example, the reaction of ferrocenoyl chlorides with 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranose produced the thioesters (14.8 and 14.9) [220]. Ferrocenes labelled with ^{14}C have been prepared by condensation of ferrocenecarbaldehyde



14.7

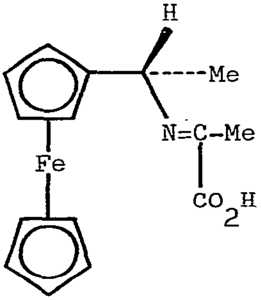


14.8

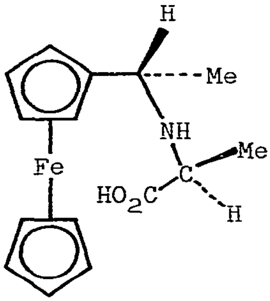


14.9

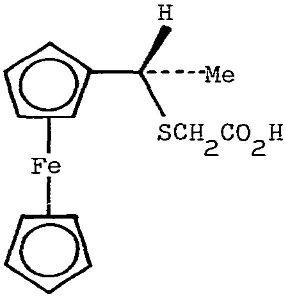
with a labelled amino sugar such as glycosamine, galactosamine and mannosamine [221].



14.10



14.11



14.12

(S)-1-Ferrocenylethylamine has been condensed with pyruvic acid to produce the Schiff base (14.10) which was hydrogenated over Pd/C to give a diastereoisomeric mixture which contained an excess of the L-alanine derivative (14.11). Treatment of the isomer (14.11) with trifluoroacetic acid-ethane-1,2-dithiol produced L-alanine and the thioglycolate (14.12) which was readily converted back to the original starting amine. D-Alanine was obtained in a similar manner from (R)-1-ferrocenylethylamine and pyruvic acid [222].

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