FERROCENE
ANNUAL SURVEY COVERING THE YEAR 1976

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CONTENTS

Ferrocene, Annual Survey covering the year 1975
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1. REVIEWS

Watts has surveyed the recent chemistry of η-cyclopentadienyl complexes including ferrocene [1]. The industrial uses of ferrocene and other metallocenes have been surveyed by Asai [2]. The industrial production and use of ferrocene polymers has been surveyed by Tanaka [3].

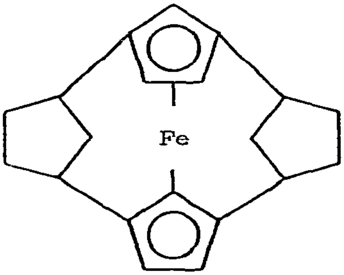
2. STRUCTURAL DETERMINATIONS

Warren has used a pseudo-axial ($C_{\infty v}$) ligand field model to calculate the second order contributions to the magnetic susceptibilities of transition metal sandwich complexes. The temperature independent paramagnetism arising from second order Zeeman interactions between the ground and excited states was evaluated for all d^x systems [4].

A CNDO-MO formalism was used to study the ground and excited state properties of unsubstituted metallocenes, these included ferrocene and the ferricinium ion. The multi-electron configuration interaction method was applied to the calculation of both photo-electron and absorption spectra. A good agreement was obtained between the calculated and observed spectra. The electronic properties of the metallocenes of the first-row transition metal ions were described and the variations in the bonding schemes within the series were rationalized [5].

The nature of the bonding in ferrocene was discussed on the basis of an ab initio LCAO MO SCF calculation and special attention was paid to the following points: (i) the relative ordering of the e_{2g}(3d) and a_{1g}(3d) orbitals; (ii) the relative ordering of the e_{1u} and e_{1g} ligand π-orbitals; and (iii) the degree of participation in the bonding of the metal 4s and 4p orbitals. It was concluded that (i) the $4e_{2g}$ was at higher energy than the $8a_{1g}$ orbital and (ii) in the ferrocene molecule the $6e_{1u}$ is at higher energy than the $4e_{1g}$ orbital [6].

The crystal and molecular structure of *syn*-bis(cyclopentyl-1",3"-ene)-(1,1'),(3,3')-ferrocenophane (2.1), prepared by the aluminium chloride cleavage of ferrocene, was determined by X-ray diffraction. The cyclopentadienyl rings were not planar and the cyclopentylene rings had a C_s conformation [7]. The crystal structure of *trans*-β-ferrocenylacrylonitrile was discussed. The arrangement of the molecules in the crystal was a compromise between charge-transfer interactions and packing requirements [8]. Bagus, Walgren and Almlof have applied Moessbauer chemical shifts, ionization potentials and



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molecular conformations to a theoretical investigation of the electronic structure of ferrocene and the ferricinium ion. SCF wavefunctions have been calculated for ferrocene and lower energy states of the ferricinium ion indicating a considerable change in electronic structure when an electron is removed from a metal d molecular orbital in ferrocene to form the cation. The difference between the ionicity of ferrocene (+1.39) and of the ferricinium ion (+1.47) was much smaller than expected. The e_{1g} ligand orbitals showed much higher covalency in the cation than in the neutral molecule and this change in structure was responsible for the small experimental differences between the Moessbauer chemical shifts of the two species. Calculated values of the six lowest ionization potentials for ferrocene were compared with the measured photoelectron spectra in order to obtain symmetry assignments of the ionic energy levels [9].

Gibb has determined changes in the electric field gradient at the iron nucleus of ferrocene by polarized Moessbauer measurements on single crystals. It was found that the molecules rotated by 20° over the temperature range 185-145°K and this change was not associated with the λ phase transition at 164°K [10].

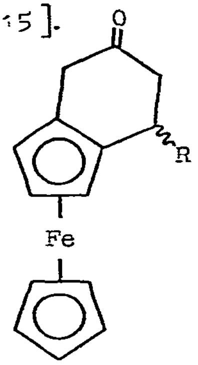
The X-ray spectra of ferrocene and a series of π-organometallic compounds were interpreted in terms of atomic orbital contributions to molecular orbitals [11]. The combustion enthalpy of ferrocene and other metallocenes have been determined in order to examine changes in the metal-cyclopentadienyl bond dissociation energy. A minimum value was obtained when the metal was manganese and maxima were given by vanadium and iron [12].

The enthalpies of formation and of combustion and the mean bond dissociation energies were determined for a series of bis(η-cyclopentadienyl) derivatives which included ferrocene [13].

3. STEREOCHEMISTRY OF FERROCENES

The relative and absolute configurations of the ferrocene-cyclohexenones (3.1; R = α- or β-Me) and the ferrocene-cyclohexenols (3.2; R^1 = H, R^2 = OH, R^3 = α- or β-Me; R^1 = OH, R^2 = H, R^3 = α- or β-Me) were determined [14].

The ferrocene-cyclohexenones (3.3; R^1 = CMe_3, R^2 = H; R^1 = H, R^2 = CMe_3), prepared by cyclization of the appropriate carboxylic acids, were reduced to form the corresponding exo- and endo-cyclohexenols. The absolute configurations and conformations of these compounds were determined. The related α-t-butyl-cyclohexenones and -cyclohexenols were also studied [15].



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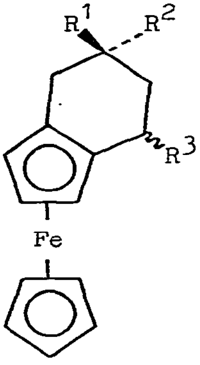

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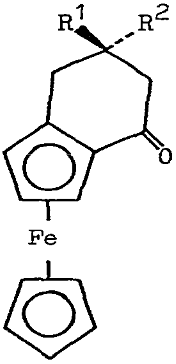

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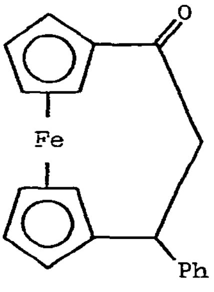
The absolute configuration of the bridged ferrocene (-)-(3.4), prepared by cyclization of (R)-(+)-β-ferrocenyl-β-phenylpropionic acid with trifluoroacetic anhydride, was determined as R. The absolute configuration was given for several other ferrocenophanes [16].

A chiral α-ferrocenylalkylamine has been used in stereoselective peptide synthesis and recovered without loss of the chiral centre. Thus α-ferrocenylethylamine (3.5) was condensed with formaldehyde, acetic acid and cyanoformaldehyde to form



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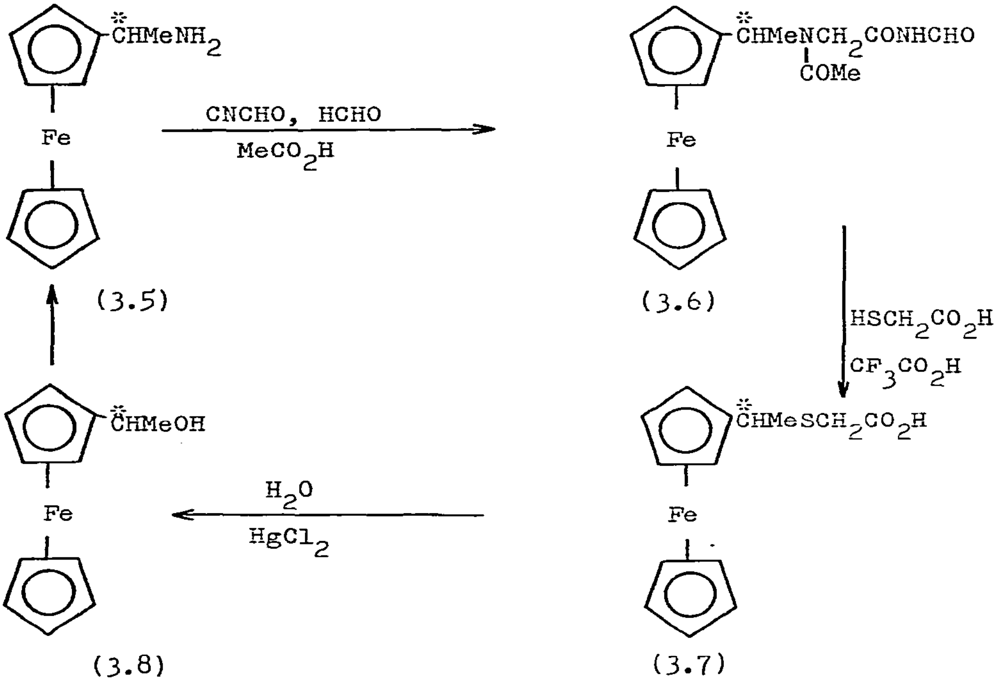
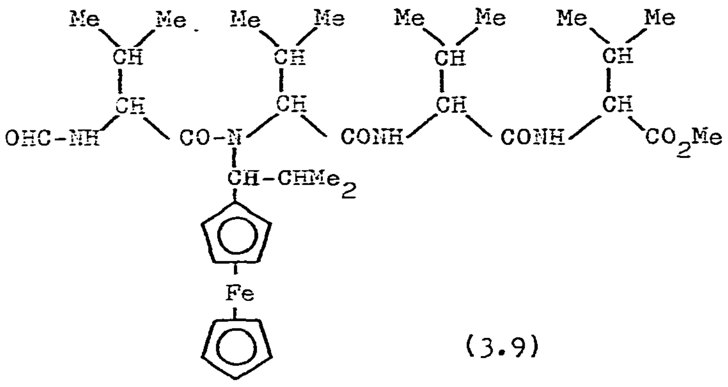
the peptide (3.6) which was treated with thioglycollic acid in the presence of trifluoroacetic acid to give the chiral carboxylic acid (3.7). This acid was converted to α-ferrocenylethanol (3.8) with aqueous mercury(II) chloride and the ethanol (3.8) was aminated to re-form the original amine (3.5). This method was used to prepare OHC-Val-Val-Val-OMe and phthalyl-Gly-Val-Gly-OCMe$_3$ [17].



A four component condensation was carried out with N-formyl-L-valine, (R)-1-ferrocenyl-2-methylpropanamine(2-R), 2-methylpropanal and N-(2-isocyano-3-methylbutanoyl)-L-valine methyl ester to give the ferrocenyl tetravaline (3.9) as a 91.2:8.8 mixture of the S,(R),S,S,S (3.9a) and S,(R),R,S,S (3.9b) diastereoisomers. The stereoselectivity was enhanced by the addition of two mole equivalents of tetraethylammonium N-formyl-L-valinate when the ratio of 3.9a:3.9b was increased to 98.5:1.5. The 98.5:1.5 mixture was converted to a 99.98:0.02 mixture after selective acidolysis with trifluoroacetic acid and thioglycollic acid [18].

(S)- and (R)-α-ferrocenylethyldimethylamine was treated with dimethyl- and diphenyl-lithiophosphine to give the corresponding phosphines in good optical yield. Typical examples were (R)-α-[(S)-2-dimethylphosphinoferrocenyl]ethyldimethylamine



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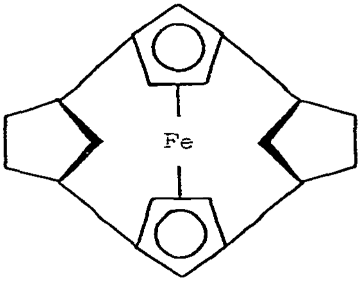
and (S)-α-[(R)-2-diphenylphosphinoferrocenyl]ethyldimethylamine [19]. Asymmetric induction in the 2-metallation of (R)-(+)-dimethyl-1-aminoethylferrocene was ten times greater than in (R)-(+)-1-methoxyethylferrocene. The latter compound also gave the 3- and 1'-lithio derivatives with random metallation being increasingly favoured by increasing solvent polarity [20].

Ferrocene was heated with aluminium chloride in heptane or aromatic solvents to give a mixture of the _syn_-, (3.10) and _anti_-biscyclopentyleneferrocene (3.11). The isomers were distinguished by ^{13}C NMR spectroscopy and the structure of the _syn_-isomer was confirmed by X-ray crystallography [21].



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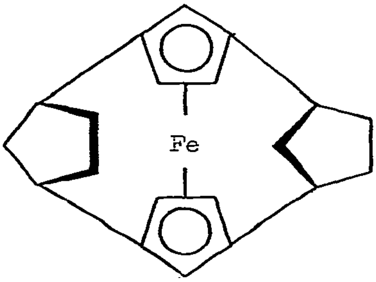

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4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

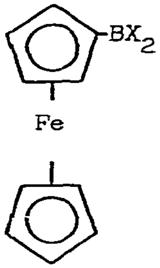
Iterative extended Hückel molecular orbital theory (IEHT) was used to calculate the ground state wave functions for ferrocene and the wave functions of several low lying states for the ferricinium ion. Photoemission spectra in terms of relative ionization potentials and the electric field gradient at the iron atom were calculated for ferrocene and _g_ values and the field gradient were calculated for the ferricinium ion. The calculated values were in good agreement with those determined experimentally. It was found that IEHT compared favourably with previous ab initio studies carried out on ferrocene and the ferricinium ion [22].

Energy changes involved in the side chain oxidation of methylferrocene have been examined for several reaction mechanisms. The energies were estimated for the transformation of the methylferricinium ion to the ferrocenylmethylcarbenium ion in acid and methylferrocene to the ferrocenylmethyl radical in neutral solution and to the ferrocenylmethylcarbanion in base by comparing the energy contents of the appropriate compounds. The energy contents were determined after structural optimisation using extended Hückel theory methods. From a consideration of the charge distribution and stability towards decomposition of the ferrocenylmethyl compounds it was clear that oxidation was favoured by basic media. The analogy between these metallocene systems and benzenoid aromatics was discussed [23].

High quality X-ray absorption spectra for solutions of ferrocene and other organometallic compounds as models for metalloproteins have been obtained by using synchrotron radiation from a positron electron accelerating ring. The extended X-ray absorption fine structure has been analyzed to obtain radial distances and atomic numbers of atoms surrounding the iron atom [24].

Gibb has investigated phase transitions of ferrocene in the thiourea-ferrocene clathrate complex by ^{57}Fe Moessbauer spectroscopy. An unusual temperature-dependent relaxation of the electric field gradient tensor was observed and arose by anisotropic reorientation of ferrocene molecules in the channels of the clathrate. A theoretical description of the anisotropic relaxation was proposed [25].

The Moessbauer spectra of 1,1'-trimethylene-, 1,1',2,2'-bis(trimethylene)-, 1,1',3,3'-bis(trimethylene)-, 1,1',2,2',3,3'-tris(trimethylene)- ferrocene and other bridged ferrocene derivatives were recorded. It was concluded that the planarity of the cyclopentadienyl rings and the ring-metal bond strength depended on the number and the position of the trimethylene bridges [26]. The Moessbauer spectra of the ferrocenylboranes (4.1; X = F, Cl, Br, I) exhibited a decrease in the quadrupole splitting as the Lewis acidity of the borane group increased while the isomer shift remained constant. It was thought that as the Lewis acidity increased the metal 3d electrons were withdrawn from the e_g orbitals to the ligand. Also, there was a corresponding electron flow from the ligand to metal which



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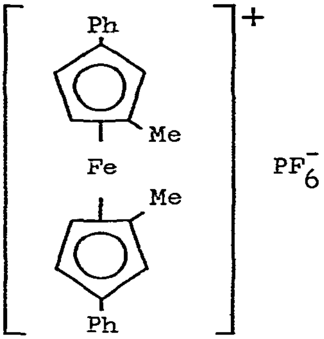

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kept the isomer shift constant [27]. The mass spectra of a series of acyl and α-hydroxyalkyl derivatives of biferrocene were recorded. For the acyl-biferrocenes the order of ease of cleavage of the Fe-ring bond depended on the substituent in the cyclopentadienyl ring and it decreased as follows: Me$>$H$\gg$ COMe$>$COPh. The fragmentation of the α-hydroxyalkyl derivatives proceeded via the ions corresponding to the $[M]^{+\cdot}$ ions of oxidation or hydrogenolysis products of the parent compound. It was suggested that the metal atom participated in the fragmentation of the biferrocenes [28].

The magnetic circular dichroism (MCD) spectrum of ferrocene in cyclohexane was measured with computer analysis of the data in the ultra-violet and visible regions. The results were compared with solution and vapour phase data for ordinary absorption in the same region. Five more transitions were found than with solution and three more transitions than with vapour phase data. The MCD spectrum of acetylferrocene was also measured [29].

Calculations of the magnetic circular dichroism (MCD) parameters for the d-d transitions of ferrocene have been reported and indicate that the transition should be dominated by MCD A terms with only weak B terms. The electronic and MCD spectra of ferrocene were measured in solution, as perspex films and in inert-gas matrices. Very strong B terms were observed with only one weak A term the sign of which was opposite to that predicted. These results suggested that considerable ligand character should be included in the d orbitals [30].

The spectroscopic and physical properties of poly(vinylferrocene) prepared by free-radical polymerization in benzene were examined. The ESR spectra showed that the polymer was paramagnetic and the presence of an ionically bound high spin complex of iron(III) was confirmed by Moessbauer spectroscopy. Infrared spectroscopy indicated the presence of vinylidene groups which were thought to have been formed by chain transfer to monomer followed by reinitiation [31].

The ^{1}H NMR spectra of twenty-nine phenylferrocenes were recorded. Hammett correlations δ_{∞}, δ_{β}, δ_{1}, against σ° constants of the substituents and $\delta = \rho_{I}\sigma_{I} + \rho_{R}\sigma_{R}$ were made with phenylferrocenes, substituted ferrocenes, (η-benzene)(η-cyclopentadienyl)-iron cations, cobalticinium salts and a series of cymantrenes. It was concluded that the resonance effect of the substituents was transmitted approximately equally to both the α- and β-positions of the substituted cyclopentadienyl ring and the inductive effect of substituents was much better transmitted into the α- than into the β-position. It was shown that the η-cyclopentadienyl ring did not possess any position analogous to the meta-position in benzene. The α-position was comparable with the ortho-position and the β-position with the para-position in benzene [32].

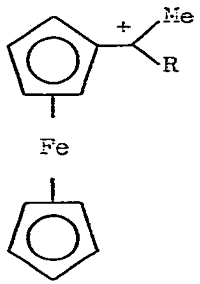
The ^{1}H NMR spectra of the ferricinium ion (4.2) and several phenylated metallocenes were recorded. The paramagnetic metal atom behaved as an internal shift reagent extending the signal range to 500 ppm which allowed a better signal assignment on the spectra as compared with the diamagnetic analogues [33]. The ^{1}H NMR spectra of single crystals of ferrocene were studied by multiple pulse techniques at room temperature. In crystals of natural shape with plane faces the angular dependence of the resonance frequency due to the anisotropy of the shielding and due to the bulk susceptibility was found to be about the same and this made analysis of the data virtually impossible. By using a single crystal sphere the shape dependent part of the susceptibility contribution was eliminated and the resolution obtained by the multiple pulse technique was improved. The data was analysed to give both the shielding tensor with $\Delta\sigma = -6.5$ ppm, $\sigma_{iso} = -4.2$ ppm from a spherical sample of tetramethylsilane and the anisotropy of the susceptibility $\Delta\chi = 30 \times 10^{-6}$ cgs units [34].

The barriers to acyl group rotation in acetylferrocene, 1,1'-diacetylferrocene, benzoylferrocene, diferrocenylketone, formylferrocene and ferrocene-[^{2}H]aldehyde (FcCDO) were determined by ^{1}H and ^{13}C NMR spectroscopy. Complete lineshape analysis over wide temperature ranges gave for ferrocene-[^{2}H]-aldehyde $\Delta G^{\neq}_{173}$ 8.79 kcal mol^{-1}, $\Delta H^{\neq}$ 7.5 kcal mol^{-1} and

$\Delta S^{\neq}$ -8 cal mol^{-1}K^{-1} and for acetylferrocene $\Delta G^{\neq}_{173}$ 8.51 kcal mol^{-1} $\Delta H^{\neq}$ 7.1 kcal mol^{-1} and $\Delta S^{\neq}$-8 cal mol^{-1} K^{-1}. Diferrocenylketone had an unexpectedly high barrier ($\Delta G^{\neq}_{143}$ 6.8 kcal mol^{-1}) and this was thought to be due to strain in the transition state. The rotational barrier of 1,1'-diacetylferrocene was lower than that of acetylferrocene by 0.7 kcal mol^{-1} and this was attributed to an interannular effect, in which one acetyl group inductively diminished the interaction of the other ring with its acetyl group [35].

^{13}C Fourier transform NMR spectroscopy has been used to determine the ^{13}C-^{13}C and ^{13}C-^{57}Fe coupling constants in ferrocene and 1,1'-dimethylferrocene. One- and two-bond ^{13}C-^{13}C(^{12}C) isotope shifts were also derived. The experimental ^{13}C-^{57}Fe coupling constant (4.70 Hz) for ferrocene was in good agreement with values calculated using the MO descriptions of Shustorovich and Dyatkina (5.24 Hz) and of Dahl and Ballhausen(2.06 Hz) [36].

The ^{13}C NMR chemical shifts were measured for a series of substituted ferrocenes. The spectra were studied in detail and the shifts of the key carbon atom were measures of the electron donor or electron acceptor properties of the substituents [37]. A series of 1-ferrocenyl-1-methylalkylium ions (4.3; R = Me, Et, i-Pr, t-Bu, CH_2Ph, Ph, m-tolyl, p-tolyl, H) was prepared by dissolving the corresponding alcohols in CF_3CO_2D. The ^{1}H NMR spectra of the freshly prepared solutions were indistinguishable from those obtained for CF_3CO_2H solutions of the same alcohols. When the solutions were kept for prolonged periods the Me-$\overset{+}{C}$ singlet slowly collapsed indicating H/D exchange of the associated protons. The rates of H/D exchange of the methyl protons of the cations varied considerably and comparison of the $t_{\frac{1}{2}}$ values showed that the exchange rate increased sharply through the series: (4.3) R = Me $<$ Ph $<$ Et $<$ CH_2Ph $<$ i-Pr $<$ t-Bu,



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and R = Ph<p-tolyl≤m-tolyl. It was thought that isotope exchange was facilitated by intramolecular proton transfer to the iron atom [38].

The ^{1}H NMR spectrum of 1,1',3,3'-tetra(t-butyl)ferrocene in 90-96% sulphuric acid showed that the iron atom was protonated. The basicity of this ferrocene derivative was lower than expected and this was attributed to steric crowding by the bulky t-butyl groups which reduced the availability of the non-bonding orbitals on the iron atom [39].

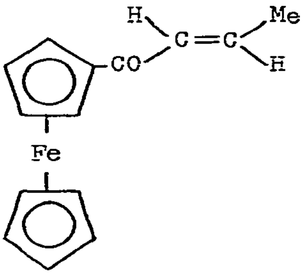
Rav and Kalidas have determined proton medium effects in ethylene glycol-water and diethylene glycol-water mixtures using the polarographic half-wave potentials of the ferrocene-ferricinium couple. It was found that the medium effect of the proton was negligible. The utility of the ferrocene-ferricinium couple in this application was compared with the extrapolation and acidity function methods [40].

Cyclic voltammetry has been used to study the oxidation of ferrocene in sulpholane. The oxidation was confirmed as a diffusion controlled one-electron process leading to a stable cation, the ferricinium ion [41]. The elution behaviour of ferrocene, a series of substituted ferrocenes and ruthenocene dissolved in either chloroform or dimethylformamide, on a gel permeation chromatography support, cross-linked poly(acryloyl morpholine) (Enzacryl^R Gel) was investigated. For most of the solutes an approximately linear relationship was obtained between logarithm molecular weight and the Wheaton Bauman absolute distribution coefficient. This indicated that the separations were effected by a molecular sieving mechanism and not by sorptive interactions [42].

The heat-capacity curves of ferrocene and nickelocene were determined, in the temperature ranges 120-200°K and 130 -300°K respectively, via differential scanning calorimetry. From the results it was suggested that nickelocene resembled ferrocene in that its structure was partially disordered at room temperature [43].

5. REACTIONS OF FERROCENE

The free energy of formation of ferrocene from gaseous iron and cyclopentadiene has been determined as -112 kcal mol^{-1}. A tris(cyclopentadiene)iron complex was implicated as the intermediate in the reaction [44]. A series of Friedel-Crafts reactions of ferrocene with substituted acryloyl chlorides was carried out. The presence of a substituent on the β-vinyl carbon of the acid chloride prevented formation of a cyclized product. For example, the reaction with but-2-enoyl chloride gave the α,β-unsaturated ketone (5.1). Annelation of ferrocene did occur when α-substituted acryloyl chlorides were used. For example the reaction with itaconoyl chloride gave the keto-ester (5.2; R = CH_2CO_2Me), the ethyl-ester (5.2; R = CH_2CO_2Et) and the diketone (5.2; R = CH_2COFc) [45].



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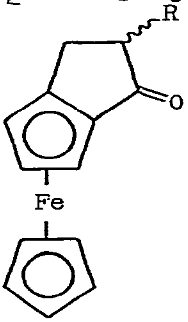

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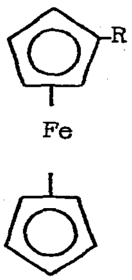
The rates of reaction of several aromatic compounds including ferrocene, with styrene in the presence of palladium(II) acetate were determined. The order of reactivity was benzene < naphthalene < ferrocene < furan. It was suggested that the reaction proceeded by electrophilic attack of Pd(II) on the aromatic ring [46].

Ferrocene has been converted directly to ferrocenecarboxylic acid by treatment with carbon dioxide and aluminium chloride at 50° The reaction involved the intermediate complex $(\eta\text{-}C_5H_5)_2Fe.(AlCl_3)_2.CO_2$ and gave product yields in the range 67-100% [47]. The preparation of some homoannularly disubstituted ferrocenes was reported [48].

Ferrocene was treated with copper(II) tetrafluoroborate in methyl cyanide to give the cation radical which on reaction with sodium cyanide gave cyanoferrocene. The cation radical was used to prepare a series of ferrocene derivatives (5.3; R = SO_2Ph, Ph, p-MeC_6H_4, CMe_2CN) [49]. Ferrocene was condensed with methyl levulinate in polyphosphoric acid to give 4,4-diferrocenylpentanoate (5.4) as the major product. Condensation of ferrocene with 5-hydroxy-2-pentanone in the presence of trifluoroacetic acid as the catalyst gave 4,4-diferrocenyl-1-pentanol (5.5). The pentanol (5.5) was also prepared by reduction of the ester (5.4) with lithium aluminium hydride [50].



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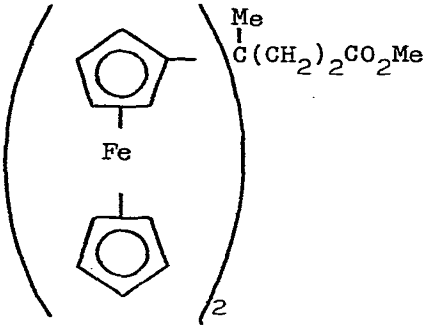

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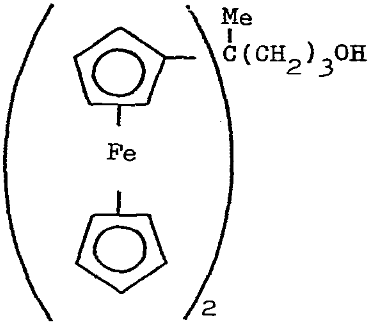

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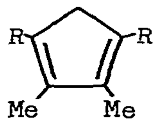
Schmitt and Ozman have described a convenient route to symmetrical polymethylferrocenes. The acetylenes $MeC\equiv CR$, where R = H, Me, were converted to the cyclopentadienes (5.6; R = H, Me) by carbonylation, esterification, cyclization and reduction. The cyclopentadienes then gave the ferrocenes (5.7; R = H, Me) [51].

Ferrocene was heated with halogeno- and methyl-naphthalene in the presence of aluminium chloride and aluminium to form the corresponding (η-cyclopentadienyl)(η-naphthalene)iron cations. When 1-bromonaphthalene was used as the reagent dehalogenated and hydrogenated complexes were obtained in addition to the expected product. The mechanism of hydrogenation was discussed [52].

Carty has described a convenient school project on the Lewis basicity of ferrocene [53]. The mechanism of ligand exchange between ferrocene and arenes in the presence of aluminium chloride was studied. It was shown that the site of attack by the aluminium chloride depended on the electronic effects of the substituents on ferrocene. In ferrocene and its alkyl derivatives two types of complexation occurred with



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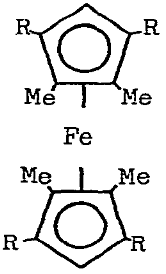

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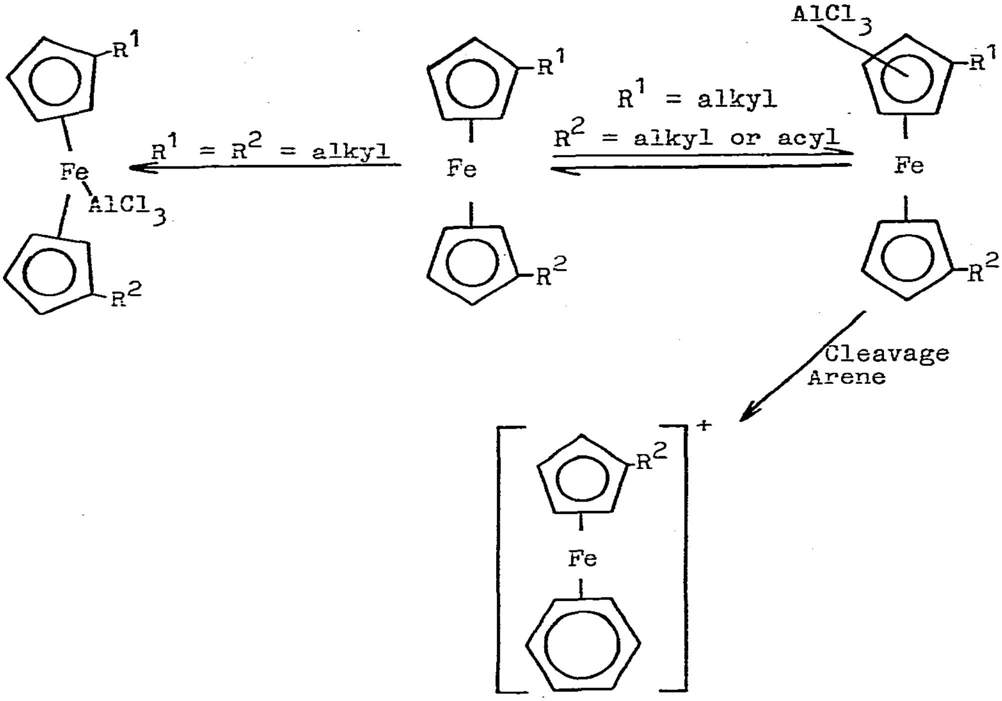
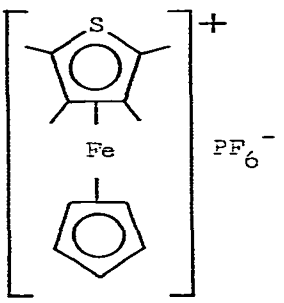


Scheme 5.1

aluminium chloride, one which enhanced ligand exchange and another which inhibited it (Scheme 5.1) [54].

6. FERRICINIUM SALTS

The (η-tetramethylthiophene)iron complex (6.1) was prepared by heating ethylferrocene with tetramethylthiophene under Friedel-Crafts conditions. The corresponding dimethylthiophene complex was prepared in the same way [55]. Ferrocenylaldehydes and ketones were diprotonated in mixtures of FSO_3H, SbF_5 and SO_2ClF to form the stable dications (6.2; R = H, Me, CH_2Cl, Ph). Energy barriers to free rotation about the iron-cyclopentadienyl



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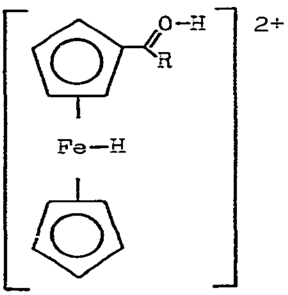

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bond were determined and discussed [56]. The addition of iodine to ferrocene in 1,2-dichloroethane gave the solid ferricinium polyiodides, $(\eta\text{-}C_5H_5)_2Fe^+I_n^-$, where n = 3, 4, 5. These complexes dissociated in the same solvent to the ferricinium cation and the triiodide anion [57].

The pyrolysis of ferricinium Reineckate *in vacuo* at 170-300° afforded a mixture of iron sulphides and chromium thiocyanate. At higher temperatures, up to 400°, hydrogen cyanide was evolved from the thiocyanate with the formation of chromium sulphides. Electron transfer from the anion to ferricinium was proposed as the first stage in the degradation, the intermediate species formed then attacked fresh ferricinium ion [58].

Anomalous results in the polarographic reduction of ferricinium acetate were rationalized in terms of adsorption of reduced neutral ferrocene on the dropping mercury cathode [59]. The effect of an (η-butadiene)tricarbonyliron group on the polarographic half-wave potential of the ferricinium ion has been determined. The results confirmed a large decrease in electron density at carbon-2 of the butadiene group on coordination to iron and a small decrease at carbon-1 [60].

A voltammetric analysis of the electron-transfer process in poly(vinylferrocene) (PVF) was made and it was found that the electrochemical behaviour of ferrocene and PVF were similar. Both systems underwent reversible oxidation and reduction. The diffusion coefficients were determined and they were quite close to those calculated from the Stokes-Einstein relationship. It was shown that the molecular weight of a polymer with electroactive sites could be determined by voltammetric studies [61].

The electrochemistry of ferrocene rendered soluble by the use of a nonionic detergent (Tween 20) in aqueous phosphate solutions at pH = 7.0 was investigated. The ferrocene-micelles readily transferred electrons with a platinum electrode and cyclic voltammetry and potentiometry indicated that the electron transfer was reversible. The ferrocene-micelle behaved as a mediator-titrant for the heme proteins of cytochrome c and cytochrome c oxidase [62].

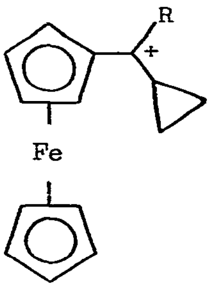
The reaction between free radicals and the ferricinium ion has been studied by pulse radiolysis. The cation was reduced to ferrocene by strong single electron reducing agents such as $H^\cdot$ and $^\cdot CH_2OH$ at rates approaching the diffusion controlled limit. Lower rates were observed with non-reducing radicals derived from acetic acid or t-butanol while oxidizing radicals including OH$^\cdot$ combined with the ferricinium ion through a more complex mechanism [63].

A kinetic investigation of the degradation of the ferricinium ion and four monosubstituted derivatives indicated that exchange of hydroxyl for cyclopentadienyl was of major importance in the reaction [64]. The mechanism of degradation of the ferricinium and t-butylferricinium cations has been investigated kinetically in aqueous hydrochloric acid at 35-100°C. The degradation was catalysed by iron(III) and was due principally to oxidation products of the chloride ion [65].

7. FERROCENYL CARBENIUM IONS

The 1-ferrocenyl-1-cyclopropylalkylium ions (7.1; R = H, Me, Ph) were stable in trifluoroacetic acid solution although on quenching with sodium carbonate varying proportions of rearranged products were obtained depending on the nature of the substituent R. Thus the cation (7.1; R = H) gave the ester (7.2; R^1 = H, R^2 = $COCF_3$), 91% and the ferrocenylolefin (7.3; R = H) 2% whilst the phenyl-substituted cation (7.1; R = Ph) gave the olefin (7.3: R = Ph) as the major product, 81%, together with a small proportion of the alcohol (7.2; R^1 = Ph, R^2 = H). A mechanistic scheme was proposed to account for these and related products [66].

The reaction between α-ferrocenylcarbenium ions and tertiary amines failed to give products from the expected ferrocenylcarbene intermediates. However the products were compatible with an electron-transfer mechanism. The tertiary amine transfers an electron to the α-ferrocenylcarbenium ion (7.4) to give the α-ferrocenylcarbinyl radical (7.5) and an aminium cation radical (7.6). The radical (7.5) then coupled with itself to form the dimer (7.9), abstracted a hydrogen atom from the



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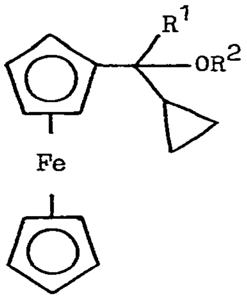

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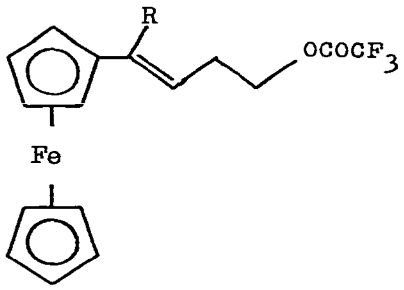

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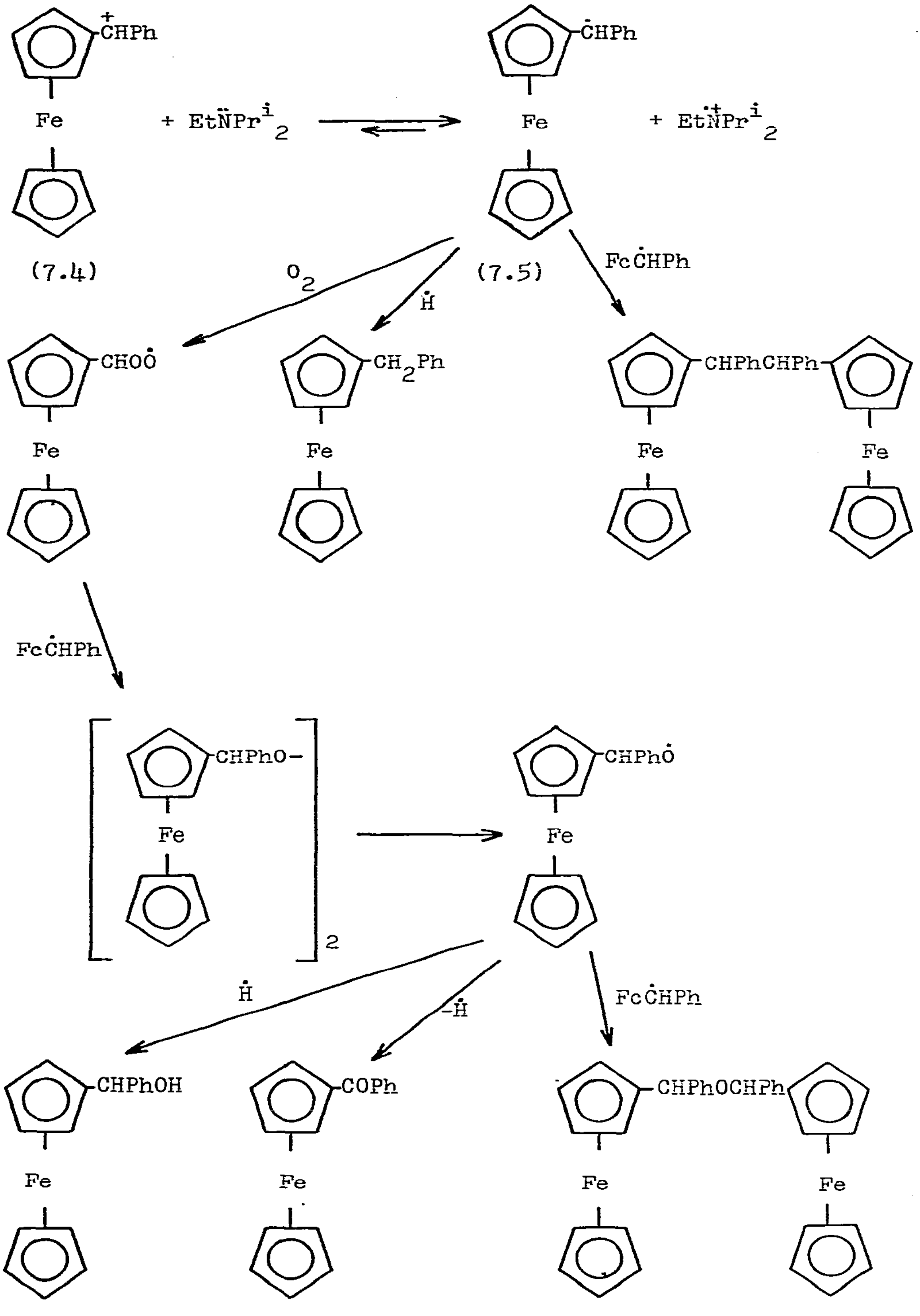
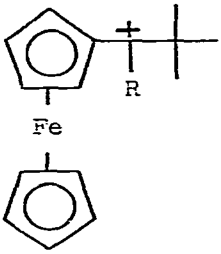


(7.4) (7.5)

(7.10) (7.11) (7.12)

initial amine to give benzylferrocene (7.8) or was attacked by molecular oxygen to form the peroxide radical (7.7) and thus the alcohol (7.10) the ketone(7.11) or the ether (7.12) [67].

The rearrangement of the t-butyl group in the carbenium ion (7.13; R = H, Me, Et, Pr^i, Bu^t, cyclopropyl, cyclobutyl) to form the carbenium ion (7.14) has been investigated by ^1H NMR spectroscopy. The rate of reaction increased with the size of the substituent R and this was attributed to increased steric hindrance between the substituent and the unsubstituted cyclopentadienyl ring. Hydrogen-deuterium exchange in the methyl group of the methylferrocenylcarbenium ion (7.15; R = H, Et, Pr^i, Bu^t) was dependent on the size of the group R in the same way [68].



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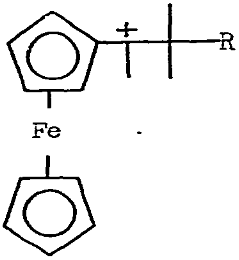

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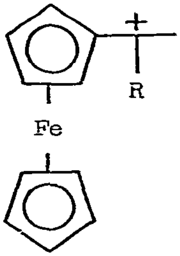
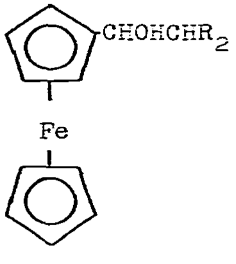


(7.15)

Treatment of the ferrocenylsecondary alcohols (7.16; R = Me, Ph) and tertiary alcohols (7.17; R = Me, Ph) with trifluoroacetic acid at 5° gave the α-ferrocenylcarbenium ions (7.18; R = Me, Ph) as the only products. The results demonstrated the occurrence of 1,2-hydride shifts to convert the tertiary carbocations to secondary α-ferrocenylcarbenium ions [69].



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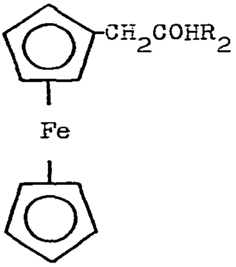

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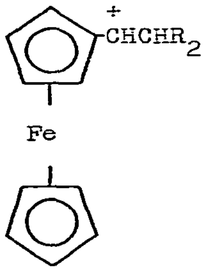

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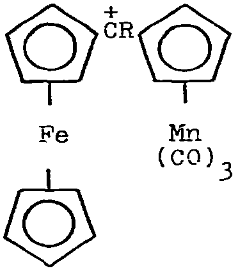
IR and ^{1}H NMR spectroscopy has been used to demonstrate that the positive charge in the mixed cymantrenyl-ferrocenyl carbenium ion (7.19; R = H, Me, Et, Ph) was delocalized into both of the organometallic groups [70]. The ferrocenylcarbenium ions (7.20; X = H, Cl, Br, CO_2Me, CN) were prepared by dissolving the corresponding carbinols in concentrated sulphuric acid and the ^{1}H NMR spectra were recorded. All the cyclopentadienyl ring protons were non-equivalent which suggested that there was hindered internal rotation around the bond between the ring and the carbenium ion centre [71].



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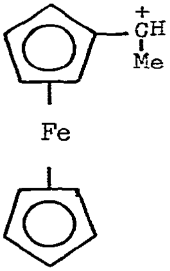


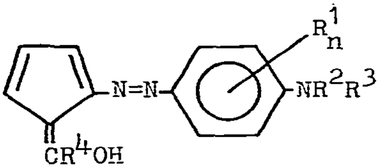
(7.20)

8. FERROCENE CHEMISTRY

(i) Photochemistry

The irradiation of the 3-ferrocenylpropanoate ion in the presence of N_2O with light of approximately 250 nm gave the 2-carboxyethylferricinium ion. The corresponding photo-oxidation of 4-ferrocenylbutanoic and 5-ferrocenylpentanoic acids also occurred. In the absence of N_2O oxidation did not take place [72].

The azofulvene derivatives (8.1; R^1 = H, OMe, OEt; R^2,R^3 = C_{1-4} alkyl, $PhCH_2$, NR^2R^3 = heterocycle; R^4 = H, Me, Ph; n = 1-2) were prepared by the photochemical coupling of ferrocenes with diazonium salts [73]. Irradiation of the complex (η-C_5H_5)Fe(CO)$_2$X, where X = Cl, Br in a range of solvents



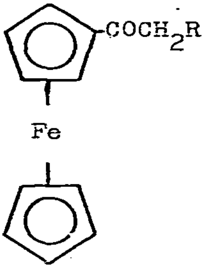
(8.1)

gave ferrocene and the corresponding iron(II) halide [74]. The possible mechanisms for the deactivation of triplet molecules by ferrocene were reviewed [75].

8. (ii) Derivatives containing other metals (metalloids)

Methoxymethylferrocene, ethoxymethylferrocene and α-methoxyethylferrocene have been metallated with n-butyllithium to give the corresponding 2-lithioferrocenes in admixture with 1'-lithioferrocenes. Some of the lithio intermediates were converted to the chloromercuri compounds which then underwent further transformations [76].

The ferrocenoylmethyliron complex [8.2; R = $Fe(CO)_2(\eta\text{-}C_5H_5)$] was treated with mercury(II) bromide and acetylchloride to give the products of σ-iron-carbon bond cleavage, the mercuriferrocene (8.2; R = HgBr), the cyclopentadienyliron halides $(\eta\text{-}C_5H_5)Fe(CO)_2X$, where X = Cl, Br and the vinylferrocene (8.3). Reactions with mineral acids were also described [77].



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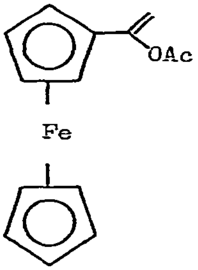

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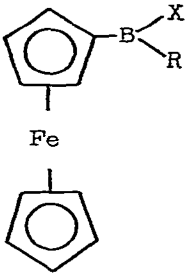

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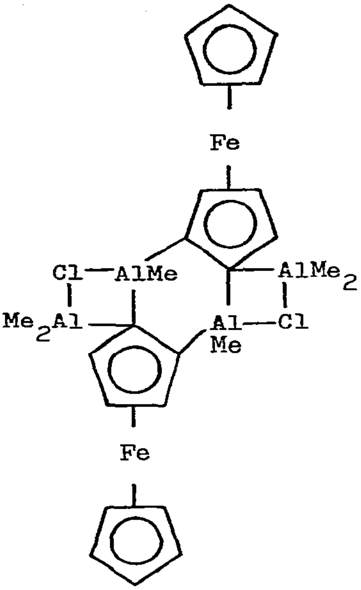
Ferrocene has been heated with boron halides including boron trichloride, boron tribromide, boron triiodide and organoboron diiodides in carbon disulphide or cyclohexane to give the corresponding ferrocenylboranes (8.4; R = X = Cl, Br, I; R = Me, Ph, X = I). The ferrocenyliodoboranes were converted to a range of derivatives by exchange of iodine for alkyl, alkoxy, thioalkyl and amino groups. The ferrocenylhaloboranes were weaker Lewis acids than phenylboranes [78].

1,1'-Bischloromercuriferrocene was heated with trimethylaluminium in toluene to form the ferrocenylalane dimer (8.5). The structure of this complex has been determined by X-ray crystallography and one carbon atom in each of the disubstituted cyclopentadienyl rings was bound to two aluminium atoms [79]. Evidence recently presented to demonstrate the formation of the ferrocenyldiphenylsilicenium ion [80] has now been shown to be



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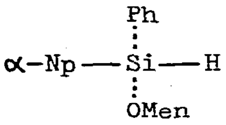
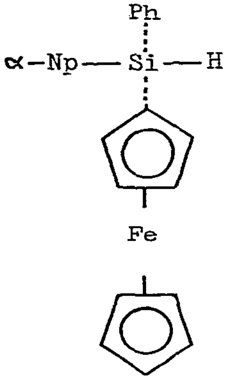


$\alpha\text{-Np}-\overset{\text{Ph}}{\underset{\text{OMen}}{\text{Si}}}-\text{H}$

(8.6)

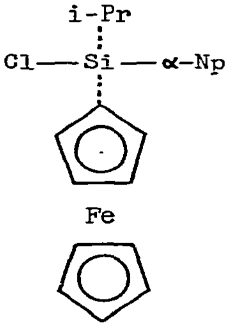


(8.7)

(α-Np = α-naphthyl,
OMen = menthoxy)

inconclusive [81]. The crystal and molecular structure of (1,1'-ferrocenediyl)diphenylsilane has been determined by X-ray crystallography. The planar cyclopentadienyl rings were bridged by the silicon atom and were tilted at an angle of 19.2° [82].

A series of optically active ferrocenyl-silanes was prepared, for example the treatment of the α-naphthylsilane (8.6) with ferrocenyllithium gave the ferrocenylsilane (8.7). The stereochemistry of the reactions and the absolute configurations of the ferrocenyl-silanes was determined [83]. The racemization of the ferrocenylsilanes (8.8, 8.9 and 8.10) was studied in hexamethylphosphortriamide. Racemization occurred via coordination of the solvent with the silicon atom



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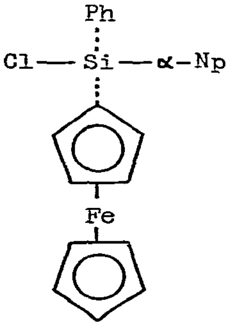

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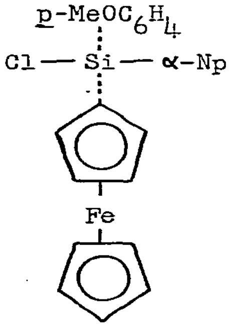
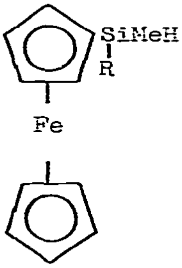


(8.10)

and the rate equation and the activation parameters were determined. The results excluded the possibility of an intermediate sp^2 siliconium ion but it was not possible to distinguish between two other potential intermediates, a hexacoordinate octahedral intermediate or a pentacoordinate siliconium ion [84].

The ferrocenylhydrosilanes (8.11; R = Me, Ph) were added to the acetylenes $CH{\equiv}CCMe(CH_2R)OH$, where R = H, Me, to give a 5:1 mixture of the olefins (8.12 and 8.13; R^1 = Me, Ph; R^2 = H, Me). The corresponding 1,1'-dihydrosilanes underwent similar reactions with the same acetylenes [85].



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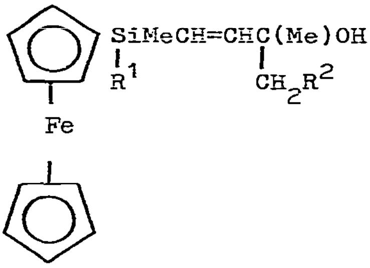

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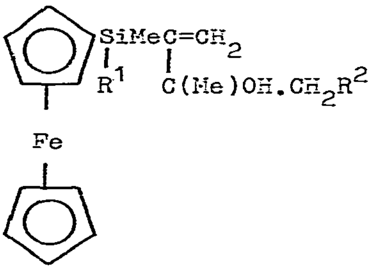

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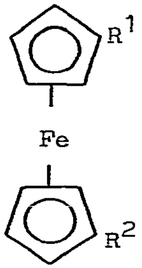
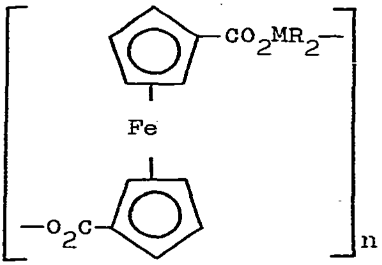


(8.14)

The ferrocenyl-silanes (8.14; R^1 = H, R^2 = $CH_2CH_2SiR^3{}_{3-n}Cl_n$, n = 1-3; R^1 = R^2 = $CH_2CH_2SiR^3{}_{3-n}Cl_n$, n = 0-3; R^3 = alkyl) were prepared by reaction of ferrocene with the corresponding vinylsilane in the presence of a Friedel-Crafts catalyst [86].

The disodium salt of ferrocene-1,1'-dicarboxylic acid has been condensed by an interfacial technique with diorgano-group IV metal halides, R_2MX_2, where R = Me, Et, Bu^t, n-octyl, Ph, $PhCH_2$; M = Si, Ge, Sn; X = Cl, Br, I to form the oligomeric polyesters (8.15). The highest yields were obtained when R was small and when the halogen and the metal were large [87]. The tetrakis(trimethylsilyl)ferrocene (8.16) was prepared by lithiation



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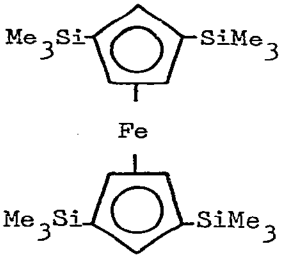


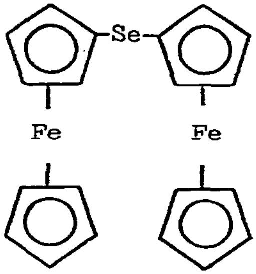
(8.16)

of 1,3-bis(trimethylsilyl)cyclopentadiene and coupling of the resultant cyclopentadienide ion with iron(III) bromide [88].

1,1,3-Tris(trimethylsilyl)cyclopentadiene was metallated with a mixture of butyllithium and TMEDA and then treated with iron(II) bromide to form 1,1',2,2',4,4'-hexakis(trimethylsilyl)-ferrocene [89]. Ferrocene has been treated with group five element halides such as phosphorus(III) chloride, arsenic(III) iodide, bismuth(III) chloride, methylarsenic dichloride and methylantimony dichloride in an organic solvent to form ferricinium halogenopentelides. These compounds were highly crystalline and one of them, $(\eta\text{-}C_5H_5)_2Fe^+BiCl_4^-$, was characterized by X-ray crystallography. The salt contained bismuth atoms in an irregular octahedral environment of chlorine atoms. The bismuth atoms were linked through halogen bridges to give an infinite chain of edge-sharing octahedra. The other products specified were $[Fe(\eta\text{-}C_5H_5)_2Fe]As_2Cl_7$ and $[(\eta\text{-}C_5H_5)_2Fe]_2As_3Cl_{10}$ [90].

Diferrocenyl selenide (8.17) was prepared quantitatively by direct coupling of chloromercuriferrocene and ferrocenyl selenocyanate. Diferrocenyldiselenide (8.18) and ferrocenyl selenocyanate were obtained from the reaction of copper(II) selenocyanate with chloromercuriferrocene. The electrochemistry and the spectroscopic properties of the selenates (8.17 and 8.18) and their mono- and dications were investigated. It was concluded that the selenium atom, like the methylene group, did not act as an effective bridge for electron transfer [91].

Enone complexes of iron (8.19; R = H, Me, Ph) were attacked by ligands such as $P(OMe)_3$ to give the adducts (8.20; R = H, Me, Ph). The reaction was sensitive to the electron-releasing power of the ligand [92]. The ferrocenylcarbenetungsten complex (8.22) has been formed by treatment of the ferrocenyltungsten



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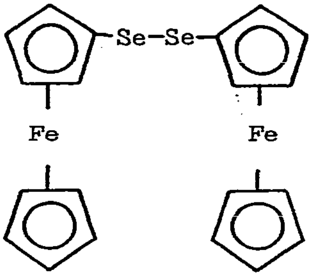

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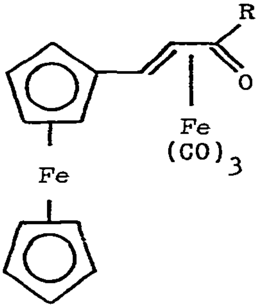

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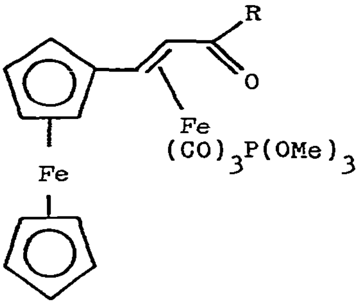
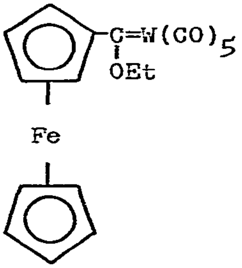


(8.20)

carbonyl (8.21) with aluminium bromide [93]. The tricarbonyl-(η-cyclopentadienyl)tungsten anion as its sodium salt was stirred with chloroacetyl ferrocene in glyme to give the tungsten complex (8.23). Several other complexes (8.24; X = CH_2, CO, CH_2CO; 8.25; M = W, Mo, X = CH_2, CO; 8.26; 8.27; M = Fe, n = 2; M = Mo, W, n = 3) were obtained in the same way. Mass spectrometric fragmentation caused ligand transfer from one transition metal to another and gave significant metal-metal bonding. Cyclic voltammetry indicated that the redox properties of the two metal centres were independent [94].



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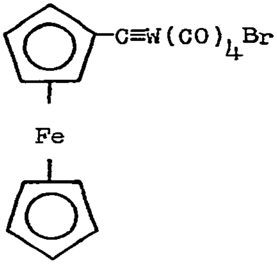

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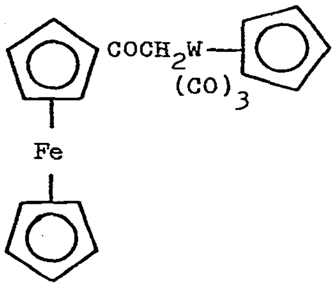

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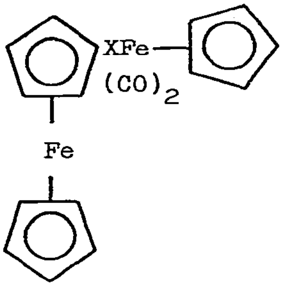

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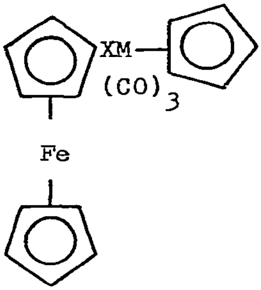

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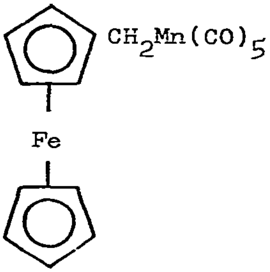

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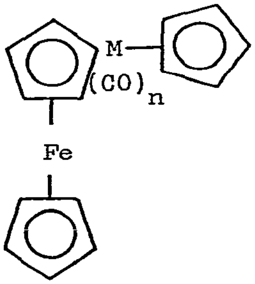
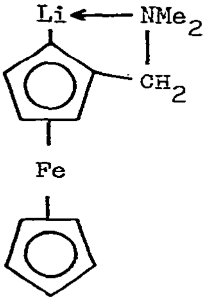


(8.27)

The lithioferrocene (8.28) was treated with a copper(I) iodide-dimethylaminomethylferrocene complex to give the copper derivative (8.29). The copper atom was replaced by the phenyl and 1-naphthyl groups when the compound was treated with iodobenzene and 1-naphthyl iodide [95].



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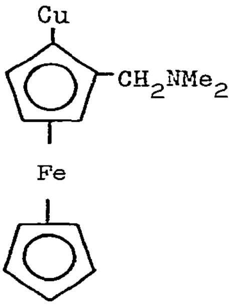
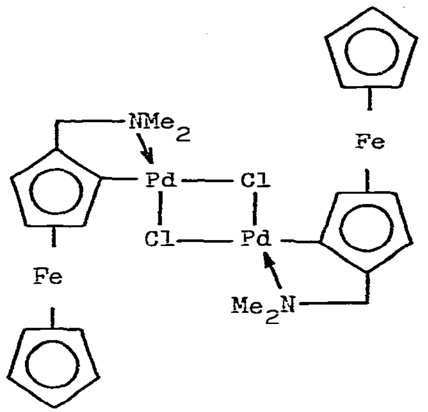


(8.29)

8. (iii) Complexes of ferrocene-containing ligands

The synthesis of the binuclear palladium complex (8.30) of dimethylaminomethylferrocene has been reported [96]. The ferrocene-rhodium complex (8.31) was found to be a good catalyst for the hydroformylation of 1-hexene [97].



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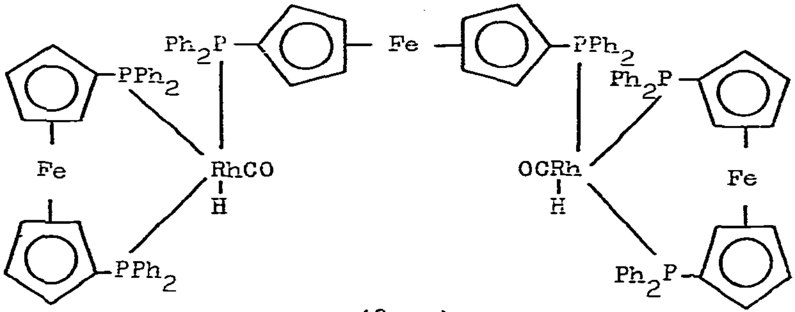
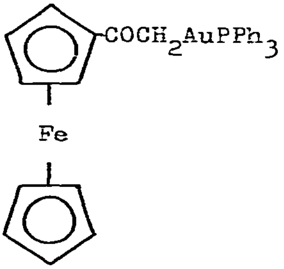


(8.31)

Treatment of acetylferrocene with the salt $(Ph_3PAu)_3O^+MnO_4^-$ gave the gold complex (8.32) [98].

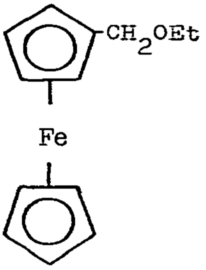


(8.32)

8. (iv) General Chemistry

Ferrocene and dicarbonyl(η-cyclopentadienyl)iron dimer were treated with imidazole and 2-substituted imidazoles (HL) to give the corresponding iron(II) compounds (FeL_2) [99]. Ferrocene formed an adduct with thiourea while substituted ferrocenes did not and this difference in behaviour has been used as the basis of a method for the separation of ferrocene from substituted ferrocenes [100].

A mixture of lithioferrocene and 1,1'-dilithioferrocene was treated with chloromethylethyl ether to give the ferrocenylmethyl ethers (8.33 and 8.34) [101].



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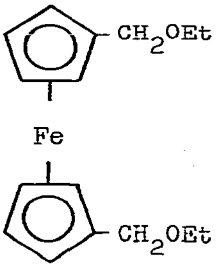

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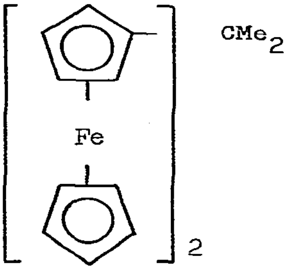
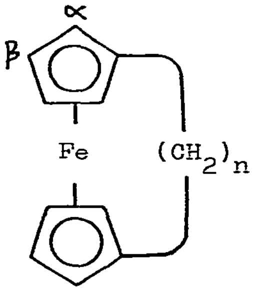


(8.35)

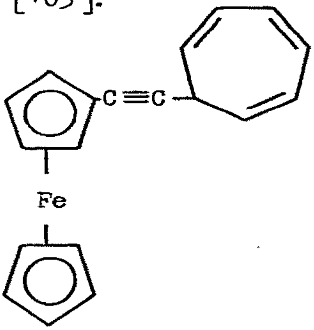
Ferrocene, t-butylferrocene and t-amylferrocene were condensed with acetone in the presence of Friedel-Crafts catalysts to form diferrocenylalkanes such as the substituted propane (8.35) [102]. The formylation of 1,1'-diethylferrocene and the ferrocenophane (8.36; n = 3,4) under Vilsmeir conditions with N,N-dimethylformamide and phosphorus oxychloride gave the β-isomer as the principal product with only a small proportion of the α-isomer. The preference for β-attack was rationalized in terms of the large steric requirement for the active reagent, $Me_2NCHOPOCl_2^+Cl^-$. The aldehyde products were reduced directly to the corresponding methyl ethers with sodium borohydride and converted to ferrocenylalkenes by the Wittig reaction [103].

Bis(1,1'-diethylferrocenyl)methane was prepared by the condensation of 1,1'-diethylferrocene with formaldehyde, dimethoxymethane or dichloromethane in the presence of aluminium chloride [104].



(8.36)

The ferrocenyl-cycloheptatriene (8.37) was prepared in good yield by the addition of tropylium tetrafluoroborate to the lithium salt of ethynylferrocene. The alkyne (8.37) was dissolved in CF_3CO_2H and when this solution was quenched with aqueous sodium carbonate the barbaralol (8.38), the trienol (8.39) and the trifluoroacetate (8.40) were isolated. A mechanism was suggested for the formation of these compounds [105].



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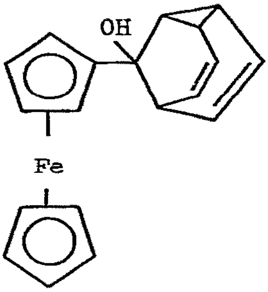

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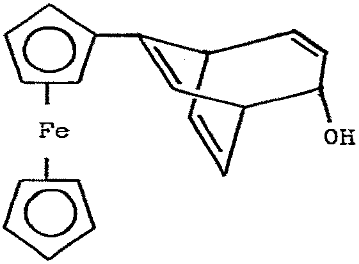

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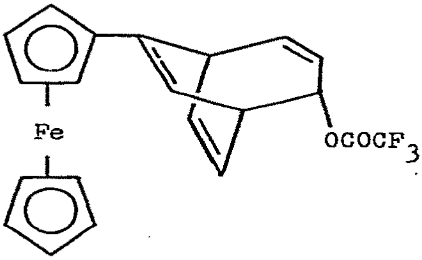
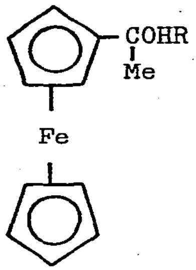


(8.40)

The acetylation of 1,1'-diethylferrocene with acetic anhydride in the presence of phosphoric acid gave a monoacetylated product. Whilst acetylation with acetyl chloride in the presence of aluminium chloride gave both mono- and di-acetylated products [106].

Floris has reported the non-Saytzeff alumina catalyzed dehydration of substituted ferrocenemethanols to give the corresponding vinylferrocenes. The alcohols (8.41; R = $CHMe_2$, Et, Pr^n) were heated to 105-180° with an excess of dry alumina to form the olefins (8.42; R = $CHMe_2$, Et, Pr^n) in yields of 78-92% [107].

Ferrocenemethanol was heated in oxygenated $(Me_2N)_2PO$ containing potassium t-butoxide to form ferrocenecarboxylic acid in high yield. Formyl-, acetyl-, and dimethylaminomethyl-ferrocenes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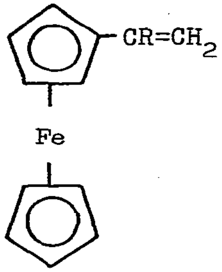
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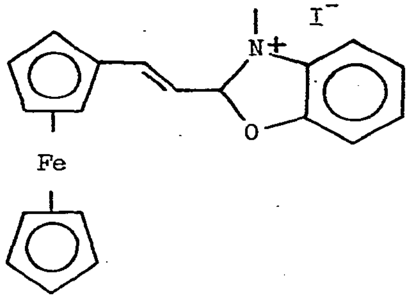
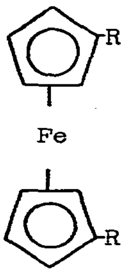

(8.43)

were oxidized in the same way. When two substituent groups were present then ferrocene-1,1'-dicarboxylic acid was obtained [108]. Formylferrocene was condensed with heterocyclic compounds containing active methyl groups to give ferrocene cyanine dyes. Nine cyanines were prepared of which the benzoxazole iodide (8.43) was typical [109].

A series of heteroannularly disubstituted ferrocenyl ketones, alcohols and alkenes were reduced with aqueous $Et_3SiH-F_3CCO_2H$. For example, the ferrocenes (8.44; R = CH_2OH, CH=CHCN, COMe) gave the reduced products (8.44; R = Me, CH_2CH_2CN, Et) respectively and the cyclic ether (8.45) gave 1,1'-dimethylferrocene [110]. Acetylferrocene was condensed with aldehydes in the presence of base to yield α,β-unsaturated ketones such as (8.46; R = CH_2=CH, p-$Cl.C_6H_4$, p-$NO_2.C_6H_4$). When the reagent was 1,3-cyclopentadiene then the ferrocenylolefin (8.47) was obtained. Condensation of formylferrocene with MeCH=CHCHO was used as the first step in the synthesis of the triene (8.48) [111].

Application of the Stobbe condensation to acetylferrocene and methyl succinate gave only the Z-form of the unsaturated acid (8.49; R = Me), however the same reaction with benzoylferrocene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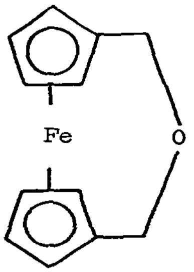
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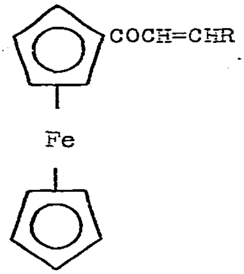

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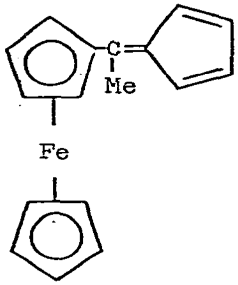

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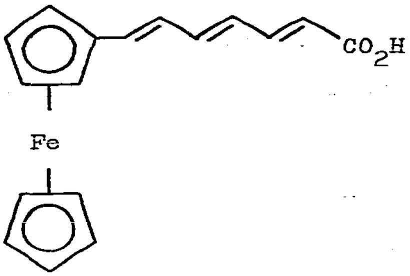
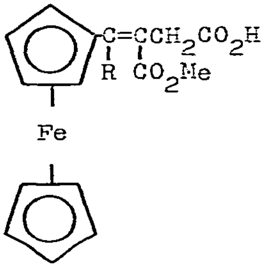


(8.48)

gave both the E- and Z-forms of the product (8.49; R = Ph) in the ratio 55:45. The three unsaturated acids were cyclized to give the corresponding cyclohexenones [112].

The treatment of the heteroannularly substituted ferrocenes (8.50; R^1 = C≡CH, COMe, R^2 = H, Et, COMe) with sulphur monochloride gave the corresponding sulphur derivatives (8.51) [113]. Ligand exchange reactions between the acyl ferrocenes [8.52; R^1 = COMe, COPh, CHO, ferrocenoyl, R^2 = H; R^1 = R^2 = COPh, CH(OH)Me, CO_2H, CO_2Me] and arenes (benzene, toluene, metsitylene, durene) in the presence of aluminium chloride were investigated.



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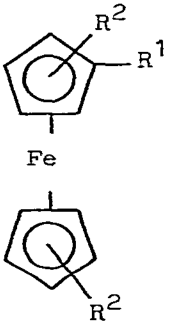

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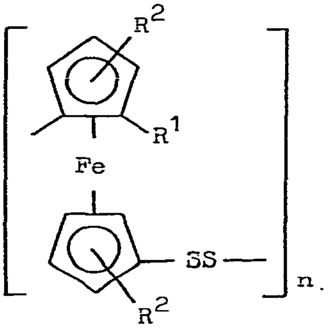

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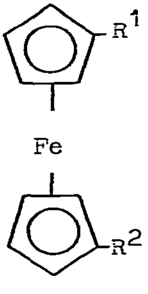
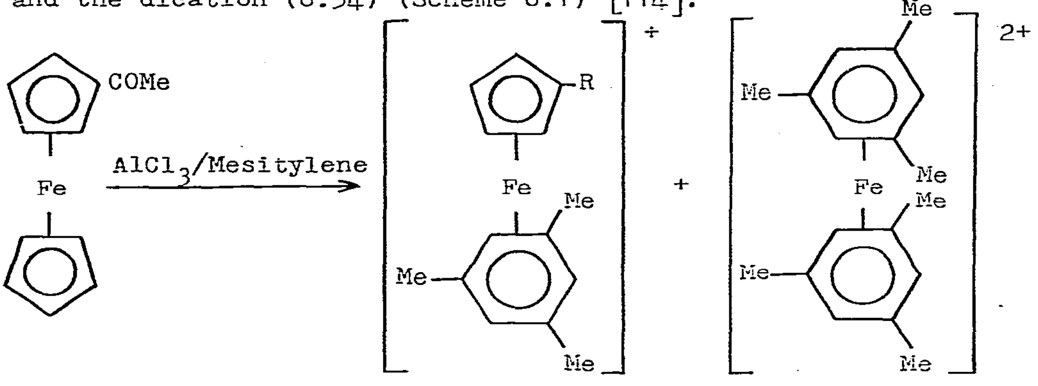


(8.52)

Single and double ligand exchange and functional group transformation occurred, for example acetylferrocene in mesitylene gave five products 8.53; R = H, COMe, C_2H_5, $C(C_6H_3Me_3)_2Me$ and the dication (8.54) (Scheme 8.1) [114].

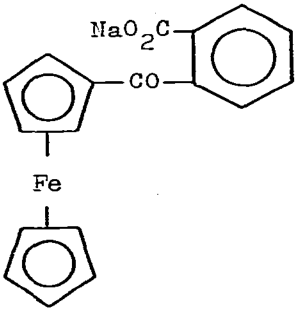


(8.53) (8.54)

Scheme 8.1

Water soluble salts of (o-carboxybenzoyl)ferrocene were prepared by treating the acid with saturated aqueous solutions of a metal carbonate or hydroxide [115]. The sodium salt of o-carboxybenzoylferrocene (8.55) was formed in 50% yield from ferrocene and the phthaloyl chloride (8.56) followed by saponification with sodium hydroxide and has been used to treat hypochromic anaemia [116].

The oxime of formylferrocene was heated with trichloromethylcyanide to give cyanoferrocene. 1,1'-Dicyanoferrocene was obtained from disodioferrocene and cyanogen bromide [117]. Mourot and Patin have used aqueous titanium(III) to reduce ferrocenylketoximes (8.57) to the corresponding ferrocenyliminium salts (8.58). Thirteen salts were prepared in excellent yield and were further reduced with lithium aluminium hydride to the primary amines (8.59) and treated with cyanoacetate to



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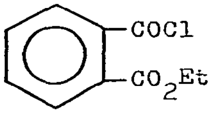

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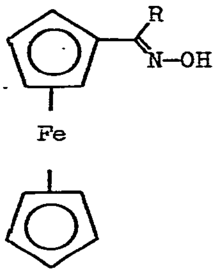
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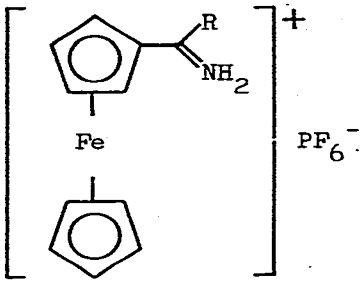
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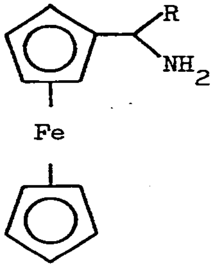
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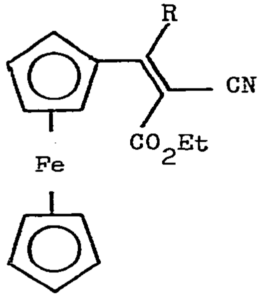
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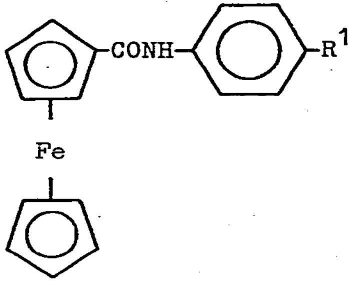
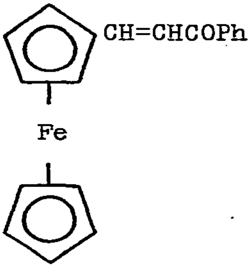

(8.61)

form the α,β-unsaturated esters (8.60). These esters were saponified and then decarboxylated with copper powder in quinoline to give the corresponding ferroceneacrylonitriles [118].

Treatment of the ferrocenyl-oximes FcCR=NOH (R = alkyl, araalkyl) with $PhSO_2Cl$ in acetone gave $FcCR{=}NH.PhSO_3H$, whereas the oximes R = p-$R^1C_6H_4$(R^1 = H, Cl, Me, OMe) with the same reagent gave the corresponding amides (8.61). The solvent was shown to play a part in the reaction. When acetone was replaced by $(CD_3)_2CO$ the iminium salt $FcCR{=}ND.PhSO_3D$ was formed [119].

Several ferrocenyl-aldimines, -ketimines and -pyrazolines have been formed by treating formylferrocene and acetylferrocene with amino acids such as alanine and glutamic acid. The α,β-unsaturated ketones (8.62 and 8.63) were condensed with hydrazine in ethanol and acetic acid to give the pyrazolines (8.64 and 8.65) respectively. Several related reactions were described [120]. The ferrocenylmethylnitramines [8.66; R = Me, CH_2CH_2CN, $CH_2CH_2N(NO_2)H$, $CH_2CH_2C(NO_2)_2Me$] were prepared by treatment of N-ferrocenylmethylpyridinium tosylate with the lithium salt $Li^+N(NO_2)R^-$. Yields were in the range 40-60% [121].



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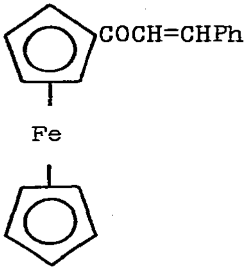

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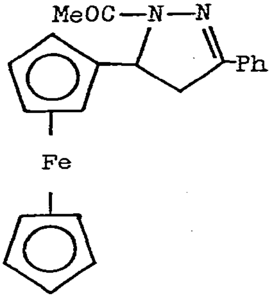

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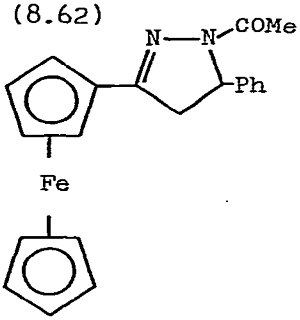

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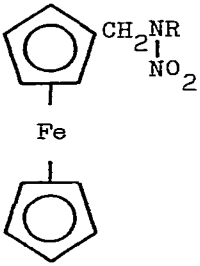


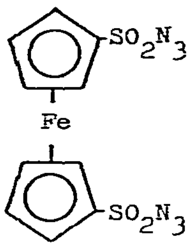
(8.66)

Dimethylaminomethylferrocene was quaternized with p-toluenesulphonyl chloride and then treated with alkali metal alkoxides to form ferrocenylmethylhydroxyalkyl ethers [122].

The photolysis of ferrocene-1,1'-disulphonyl azide (8.67) in several solvents at different wavelengths gave the azide (8.68) and the sulphonamide (8.69). Thermolysis of the azide (8.67) in cyclohexane gave the sulphonamides (8.69, 8.70 and 8.71) and the azide (8.72). Different products were formed when the azide (8.67) was irradiated in benzene or mesitylene. No intramolecular cyclization products were isolated from any of these reactions. Thermolysis of the ylide (8.73) gave ferrocenesulphonamide and sym-collidine [123].

The ferrocenylethyl-sulphonate (8.74) was prepared in good yield by the treatment of ferrocenylethanol with p-$MeC_6H_4SO_2Cl$. Reaction of the sulphonate (8.74) with sodium iodide gave ferrocenylethyl iodide which underwent reaction with the lithium salts $RC(NO_2)MeLi$ and $RN(NO_2)Li$ to give the γ-nitro- and β-(N-nitroamino)-alkylferrocenes (8.75; R = Me, CH_2CH_2CN) and (8.76; R = Me, CH_2CH_2CN) respectively [124].

The reaction of 1-(ferrocenylmethyl)pyridinium tosylate with $LiCR^1R^2NO_2$ gave β-nitroalkylferrocenes (8.77; R^1 = H, Me,



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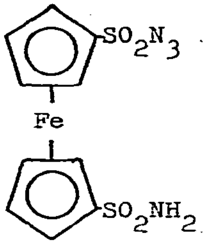

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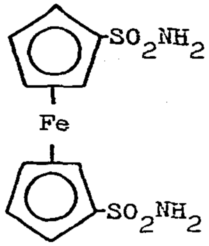

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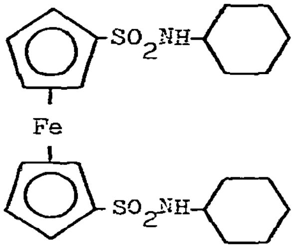

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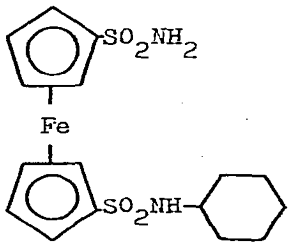

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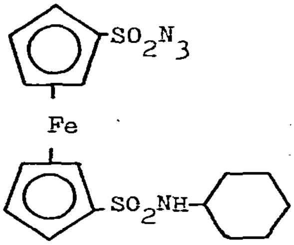

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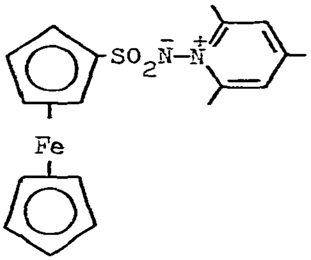

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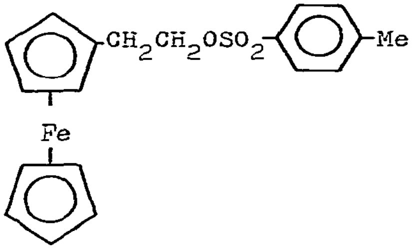

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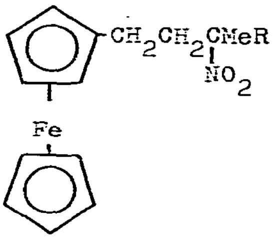

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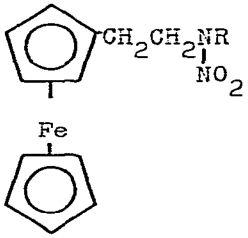

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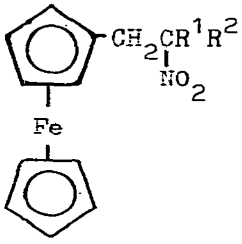

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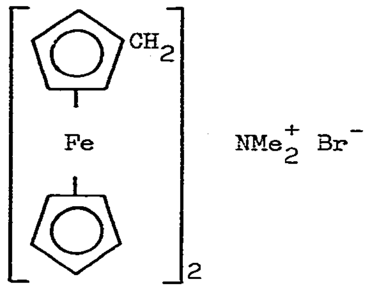

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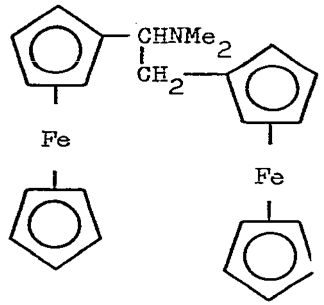
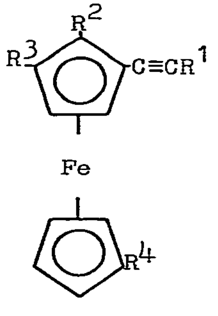


(8.79)

NO_2; R^2 = Me, Et, CO_2Me, CO_2Et, NO_2, $CH_2CH_2CO_2Me$, CH_2CH_2CN, CH_2CH_2COMe) [125]. (N,N-Dimethylamino)methylferrocene was converted to the di(ferrocenylmethyl) quaternary ammonium bromide (8.78) by cyanogen bromide at room temperature. The quaternary salt (8.78) was degraded with sodium hydroxide to ferrocenemethanol and (N,N-dimethylamino)methylferrocene and it was rearranged on heating with n-butyllithium to the tertiary amine (8.79). This product was, in turn, quaternized with methyl iodide and the resulting salt hydrolyzed to form 1,2-diferrocenylethylene [126].

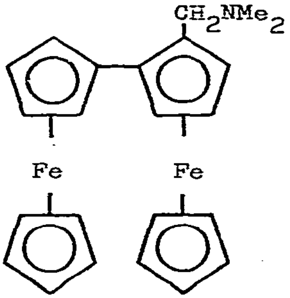
The ferrocenylacetylenes (8.80; R^1 = H, Me, Me_3C, $MeC{=}CH_2$, $PhCH_2$, FcCO, $FcC{=}CH_2$; R^2, R^3, R^4 = H, Me, Me_3C) have been synthesised. More than thirty compounds were characterized and good yields were obtained in several cases [127].



(8.80)

9. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

Biferrocenes and arylferrocenes have been formed by heating 1-copper-2-dimethylaminomethylferrocene with aryl halides. Thus the monosubstituted biferrocene (9.1) was obtained in 57% yield by using iodoferrocene as the reagent [128]. Biferrocenylene (9.2) was prepared by an Ullman coupling of 1,1'-dibromoferrocene



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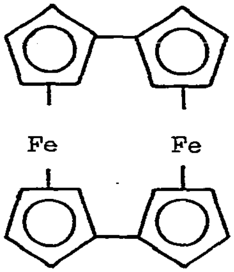
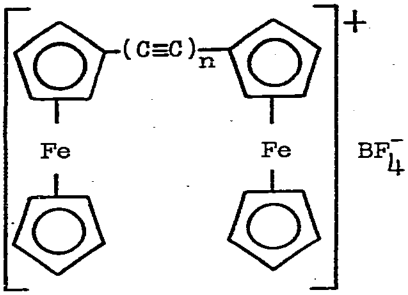


(9.2)

and by the reaction of the fulvalene dianion with iron(II) chloride. Biferrocenylene was oxidized by benzoquinone to the mixed valence monocation and to the dication. The Moessbauer spectra of the mixed valence salts indicated that both iron atoms were equivalent. The Moessbauer spectrum of the dication showed a quadrupole splitting of 3.0 mm/s which is exceptionally large for a ferricinium-type derivative. The infrared, ESR and X-ray photoelectron spectra and magnetic susceptibility of the biferrocenylene salts were recorded also and discussed [129].

The biferrocene (9.3; n = 0), diferrocenylacetylene (9.3; n = 1) and diferrocenylbutadiyne (9.3; n = 2) salts were formed by electrochemical oxidation in methylene dichloride. Bands in the near IR spectra of the acetylenes (9.3; n = 1, 2) were assigned to intervalence transfer transitions. The energy of the bands increased as the iron-iron distance increased while the intensity of the bands decreased as did the separation in half-wave potentials. The opposite effect of frequency and intensity as a function of iron-iron distance was observed in the spectra of the ferrocenophane salts (9.4; n = 0, 1). The ESR spectrum of the ferrocenophane salt (9.4; n = 1) had sharp lines and a rhombic g tensor, it strongly resembled that of the biferrocenylene salt (9.4; n = 0) and suggested that the former was a delocalized analogue of the latter [130].

The dimethylfulvene (9.5) was converted to the corresponding cyclopentadienide ion with potassium in benzene and iron(III) chloride was added to form the tetramethyl[2]ferrocenophane (9.6) in 30% yield [131]. The molecular geometry of six [3]ferrocenophanes with one, two, three or four trimethylene bridges has been investigated by Moessbauer spectroscopy. The observed changes in isomer shift and quadrupole splitting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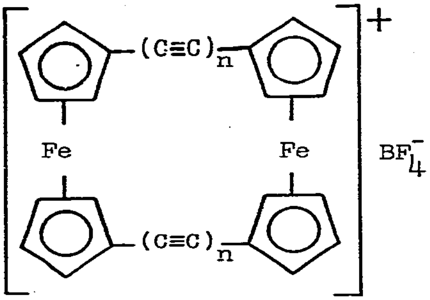
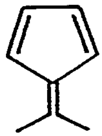

(9.4)

were rationalised in terms of ring tilting and deviations from ring planarity [132]. Cyclization of the ferrocenyl-alcohols [9.7; R^1 = CH(OH)Me, R^2 = CH(OH)Ph; $R^1 = R^2 = CMe_2OH$] in the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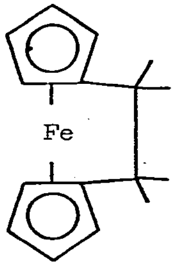
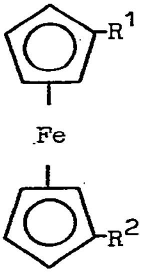

(9.6)

presence of hydrochloric acid gave the ferrocenyl-ethers (9.8 and 9.9) respectively. Lithiation of the ethers (9.8 and 9.9) followed by hydrolysis gave the ferrocenyl-alcohols [9.7; R^1 = CH(OH)Me, $R^2 = CH_2Ph$; $R^1 = CHMe_2$, $R^2 = CMe_2OH$] respectively [133]. The preparation of dibridged ferrocenophanes with four carbon chains was reported by Yamakawa and co-workers. Bridge enlargement of the dione (9.10) with diazomethane gave three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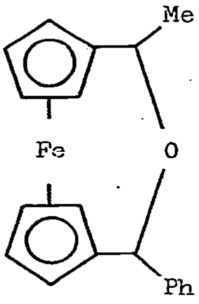
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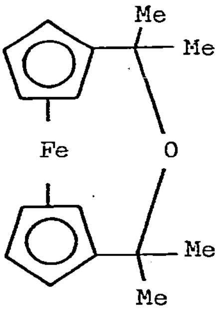
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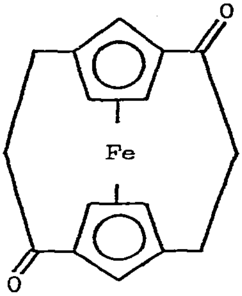

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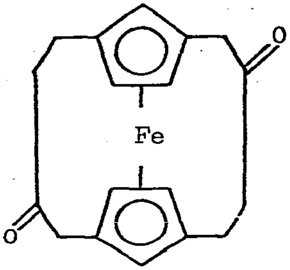

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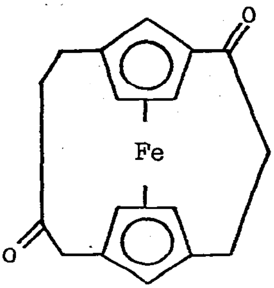

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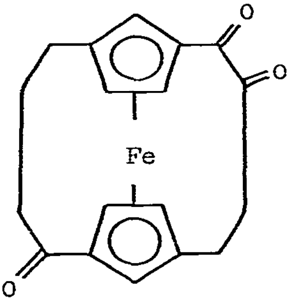

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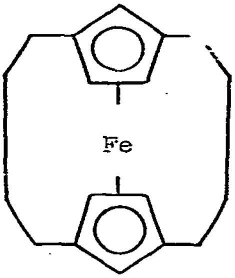

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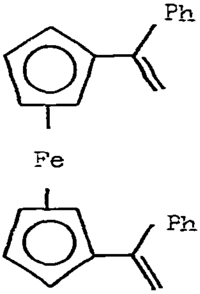

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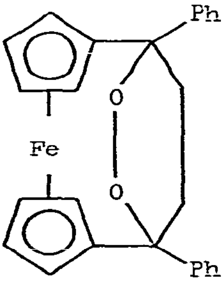

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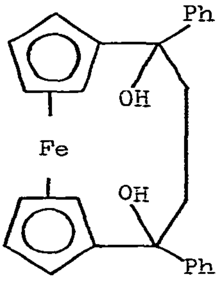

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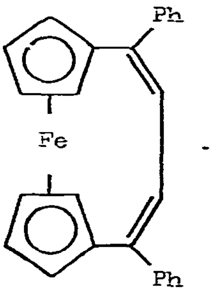

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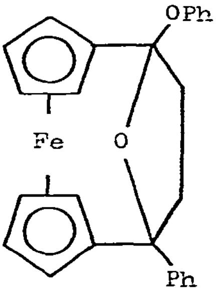

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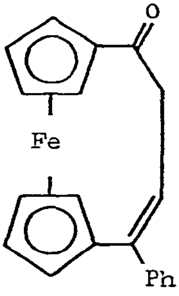
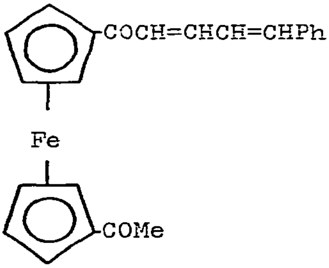


(9.20)

ferrocenophanes (9.11, 9.12 and 9.13). Treatment of the dione (9.11) with lithium aluminium hydride and aluminium chloride gave the [4](1,1')[4](3,3')-ferrocenophane (9.14). The ferrocenophane (9.14) was also prepared from [4]ferrocenophane [134].

The oxidation of 1,1'-bis(1-phenylvinyl)ferrocene (9.15) with molecular oxygen in the presence of Lewis acids such as aluminium(III) chloride, trifluoroacetic acid, and iron(III) chloride gave the ferrocenophane peroxide (9.16) together with a range of products derived from it including the diol (9.17), the diene (9.18), the ether (9.19) and the ketone (9.20). The proportions of products were dependent on the nature of the Lewis acid catalyst and mechanistic pathways were discussed [135].

The ferrocenyl-pentadienone (9.21) has been cyclized to give the ferrocenophanes (9.22 and 9.23) [136]. Acetylation of the [5]ferrocenophane (9.24; $R^1 = R^2 = R^3 = R^4 = H$) gave a mixture of products (9.24; $R^1 = R^4 = COMe$, $R^2 = R^3 = H$; $R^1 = R^3 = COMe$, $R^2 = R^4 = H$ and 9.25). Treatment of the ketone (9.25) with MeCN-NaNH$_2$-NH$_3$ followed by triethylsilane in trifluoroacetic acid gave the cyanide (9.24; $R^1 = R^3 = H$,



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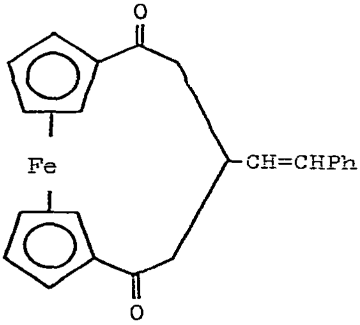

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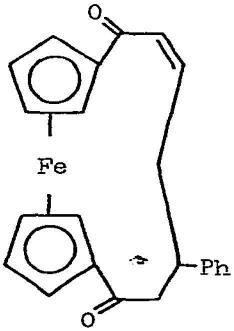

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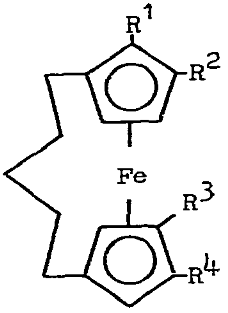

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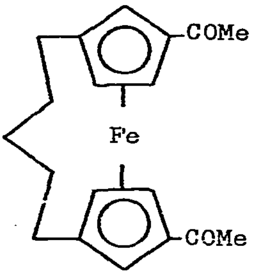

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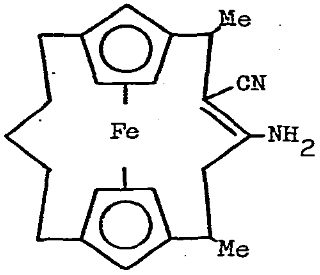
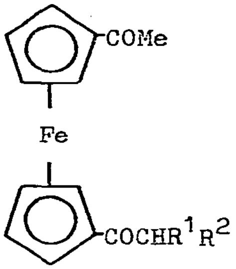


(9.26)

$R^2 = R^4 = CHMeCH_2CN$). Cyclization of this latter compound with PhNMeNa gave the doubly bridged [5]ferrocenophane (9.26) [137].

The substituted acetylferrocenes (9.27; R^1 = Me, Et, Ph; R^2 = H) were condensed with benzaldehyde to form the threo- (9.28; R^1 = Me, Et, Ph; R^2 = H) and erythro- (9.28; R^1 = H; R^2 = Me, Et, Ph) [5]ferrocenophanes whilst the acetylferrocene (9.27; $R^1 = R^2$ = Me) gave only the ferrocenylketone (9.29) [138].



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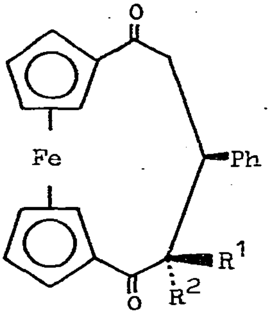

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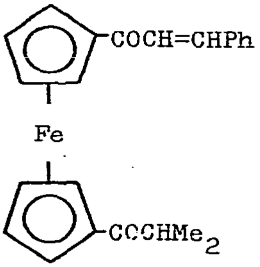
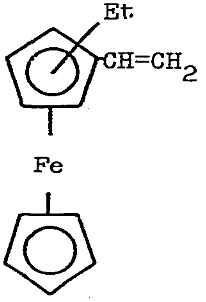


(9.29)

10. FERROCENE-CONTAINING POLYMERS

A mixture of ferrocene and polythene was pressed at 140° and 100 atmospheres and drawn six times at 100° to give co-orientated polyethylene and ferrocene [139]. Vinylferrocene was emulsion copolymerized with butyl acrylate, styrene and methylacrylic acid in presence of an organic peroxide catalyst. It was shown that no oxidation of the ferrocene moiety occurred during the polymerization [140].

The ethylvinyl-ferrocenes (10.1, 10.2 and 10.3) were prepared and their rates of polymerization were compared with that of vinylferrocene. The vinyl-ferrocenes (10.1, 10.2 and 10.3) polymerized less readily than vinylferrocene, except for the divinyl compound (10.3) which polymerized more readily in



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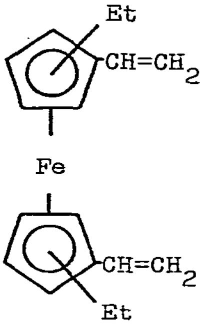

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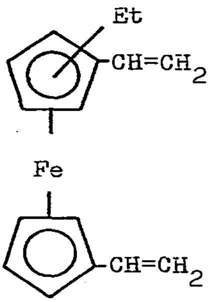


(10.3)

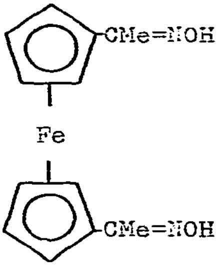
cationic polymerization [141]. Vinylferrocene and maleic anhydride were copolymerized and vinylferrocene, styrene and maleic anhydride were terpolymerized. The photochemical reactivity of these polymers with respect to photooxidation - reduction of Fast Red A and ascorbic acid was examined. In the presence of oxygen photoreaction only occurred in the presence of ferrocene or ferrocene containing polymers. It was suggested that an electron transfer took place between the photoexcited ferrocene and the Fast Red A [142].

Vinylferrocene and butadiene were copolymerized in 1,4-dioxane at 60° in the presence of 4,4'-azobis(4-cyanovaleric acid) to give low molecular weight random copolymers. The copolymers were paramagnetic which indicated that the vinylferrocene radical underwent an electron transfer termination during the copolymerization [143].

The radical copolymerization of ethylene with ferrocene and vinylferrocene has been studied. Copolymers containing ferrocene included it as part of the main chain whereas vinylferrocene copolymers contained pendant ferrocenyl groups on the polyethylene chain. Low concentrations of vinylferrocene in the mixture of monomers led to polymers enriched with metallocene. High concentrations of vinylferrocene gave decreased reactivity in copolymerization. The vinylferrocene copolymers showed better thermal stability than polyethylene [144].

The copolymerization of vinylferrocene with styrene and acrylates using a peroxide catalyst has been described. Controlled addition of the peroxide to the mixture of monomers containing sulphosuccinate and sulphoxylate as reducing agents avoided oxidation of the metallocene [145]. The reactivity of vinylferrocene and vinylcymantrene in radical initiated solution copolymerizations was investigated. Vinylferrocene was copolymerized with vinylcymantrene, N-vinylcarbazole, p-N,N-dimethylaminostyrene, 1,3-butadiene, N-vinyl-2-pyrrolidone, styrene and several electron deficient monomers. The results showed vinylferrocene to be an exceptionally electron-rich monomer in free radical polymerizations [146].

The ferrocenyldioxime (10.4) has been treated with disulphur dichloride to form a copolymer with =NOSS bridging groups. p-Ferrocenylaniline was copolymerized with the same reagent and gave an NHSS bridged polymer. The copolymers were stable in air at 200° and decomposed at 360-420° [147].



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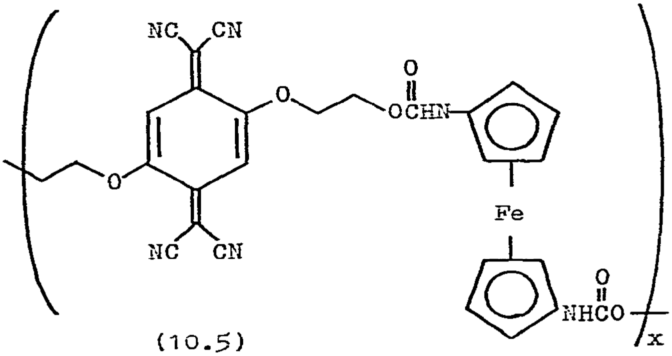
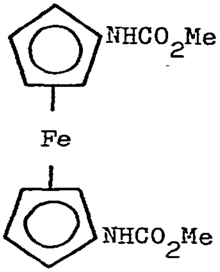


(10.5)

2-Ferrocenylbutadiene was prepared by the dehydration of methylvinylferrocenylalcohol and the butadiene was polymerized in the presence of boron(III) fluoride etherate or titanium(IV) chloride. The polymerization did not occur by an ionic or free radical mechanism. Spectroscopic evidence indicated that no double bonds were present in the poly(2-ferrocenylbutadiene) which suggested that cyclization had occurred. The polymer was thermally stable in an inert atmosphere to 270° and in air to 300° [148].

The condensation of 2,5-bis(2-hydroxyethoxy)-7,7,8,8,-tetracyanoquinodimethan with 1,1'-diisocyanatoferrocene gave a black, semiconducting charge-transfer polyurethane (10.5). Electrical conductivity measurements were performed on a compacted powder of the polyurethane, the conductivity was 3×10^{-3} ohm^{-1} cm^{-1}. A nonpolymeric model charge-transfer complex of 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethan and the amino-ferrocene (10.6) was prepared and its properties were compared with those of the polymer (10.5). The non-polymeric complex showed substantially higher electrical conductivity than the polymeric charge-transfer complex [149]. p-Ferrocenylphenylacetylene was prepared by treating the



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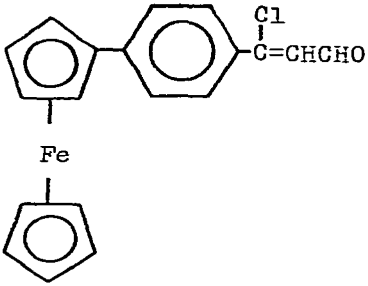


(10.7)

ferrocenyl-styrene (10.7) with alkali. The polymerization of p-ferrocenylphenylacetylene was investigated in the presence of benzoyl and lauroyl peroxides and its reactivity was compared with that of ferrocenylacetylene and phenylacetylene. The reactivities of the monomers decreased in the order: ferrocenylacetylene > phenylacetylene > p-ferrocenylphenylacetylene [150].

A metallocene polymer was formed by heating a mixture of ferrocene, benzaldehyde, dimethylformamide and iron(III) chloride to 120° in a nitrogen atmosphere. This metallocene polymer was used as the basis for preparing organic photoconductive materials. These materials were very sensitive and they were useful in electrophotographic plates and sheets, toners, optical sensors and optical tapes [151].

The reaction of 1,1'-ferrocenedicarbonyl chloride with glycidol and 1,1'-dilithioferrocene with epichlorohydrin gave diglycidyl 1,1'-ferrocenedicarboxylate and 1,1'-diglycidylferrocene respectively. The first glycidyl-ferrocene was homopolymerized by the addition of triethylamine and copolymerized with phthalic acid. The latter glycidyl-ferrocene was copolymerized with m- and p-carboranedicarboxylic acid. Both glycidylferrocenes were copolymerized with phthalic anhydride and o-dimethylolcarborane [152].

Mixed bis(η-cyclopentadienyl)titanium-ferrocene polyethers were obtained by copolymerization of bis(η-cyclopentadienyl)titanium dichloride with diols such as 1,1'-bis(hydroxymethyl)ferrocene in the presence of sodium hydroxide or triethylamine. The polyethers decomposed on heating by oxidative or non-oxidative mechanisms depending on the environment [153]. The isotropic distribution of crosslinks in divinylbenzene-styrene-vinylferrocene block copolymer has been confirmed by low angle X-ray diffraction experiments. Isotropic deformation of the network on swelling was also demonstrated. The copolymer was used as a model for crosslinked polystyrene [154].

The factors affecting the aminomethylation of poly(methyleneferrocene) with the complex $CH_2(NMe_2)_2 \cdot 2AlCl_3$ have been investigated. The functionalized polymer was cross-linked with lauroyl peroxide and quaternized with methyl iodide to give a material useful as an anion exchange resin. The original polymer was also formylated with dimethylformamide [155].

Partial oxidation of polyvinylferrocene, polyferrocenylene and polyethynylferrocene converted these compounds from electrical insulators to semiconductors. Optimal conductivities of 10^{-8} to $10^{-6}\Omega^{-1}$ cm^{-1} were achieved for 35-65% conversion of Fe(II) to Fe(III). Monooxidation of poly(3-vinylbisfulvalenediiron) also increased its conductivity to a maximum at 71% oxidation. An electron-hopping model, where each ferrocene group was surrounded by the maximum number of ferricinium groups, was used to explain the observed results [156].

11. APPLICATIONS OF FERROCENE

(i) Ferrocene catalysts and photosensitizers

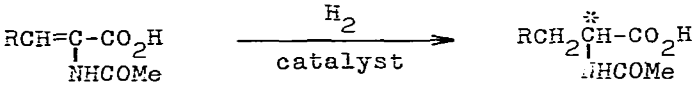
Ferrocene, an α-hydroxyalkylferrocene or a ferrocenealkoxime were added to polyethylene to prevent discoloration by light and also to ensure uniform discoloration if any occurred [157]. The addition of 0.25-1.0% of bis(p-aminophenyl)-1,1'-diethylferrocene to polyethylene increased the resistance of the polymer to degradation by UV light [158].

The addition of acetylferrocene oxime to polyethylene increased its resistance to degradation by UV light [159]. The rates of free radical polymerization of methacrylate and acrylonitrile in the dark in the presence of poly(ferrocenylmethyl methacrylate) and carbon tetrachloride were higher than those in the presence of ferrocene and carbon tetrachloride. The ferrocene-methacrylate-carbon tetrachloride system did not increase the polymerization rate of styrene [160].

The addition of ferrocene and α-phenylindole to poly(vinyl chloride) film speeded up its degradation on exposure to light [161]. The photochemical ferrocene sensitized isomerizations of cis- and trans-2-butene and trans-ClCH=CHCl were studied as functions of irradiation frequency, time and temperature. Triplet-triplet energy transfer from ferrocene to the olefins was proposed as part of the reaction mechanism [162]. The copolymerization of diethylene glycol and maleic anhydride at 200° was catalyzed by ferrocene and 1,1'-disubstituted ferrocenes. The efficiency of the catalyst decreased in the following order of the substituent groups: butyl > propyl > ethyl > methyl > hydrogen > acetyl. This order paralleled the change in redox potential of the catalysts [163].

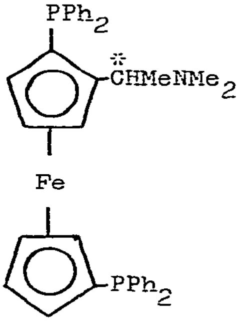
Methyl methacrylate has been polymerized in the presence of ferrocene and trichloromethanesulphonyl chloride and the order of reaction determined with respect to the chloride [164]. Ferrocene was effective in initiating the anionic polymerization of methylvinylketone [165]. Photopolymerization of epichlorohydrin was sensitized by titanium(IV) chloride and aluminium(III) chloride complexes of ferrocene, conversions of up to 45% were achieved [166].

Asymmetric hydrogenation of α-acetamidoacrylic acids (11.1) to the corresponding amino acids (11.2; R = Ph, 4-AcO.C_6H_4, 3-MeO-4-AcO.C_6H_3, 3,4-OCH_2O.C_6H_3) was catalyzed by (S)-α-[(R)-1',2-bis(diphenylphosphino)ferrocenyl]ethyldimethylamine (11.3) in the presence of $[Rh(1,5\text{-hexadiene})Cl]_2$. Yields in the range 86-94% were obtained with optical yields of 86-93% in aqueous ethanol or methanol [167].



$$\underset{\text{NHCOMe}}{\text{RCH=C-CO}_2\text{H}} \xrightarrow[\text{catalyst}]{H_2} \underset{\text{NHCOMe}}{\text{RCH}_2\overset{*}{\text{C}}\text{H-CO}_2\text{H}}$$

(11.1) (11.2)



(11.3)

Ferrocene was added to quinoline-soluble coal-tar pitch and the mixture heat-treated at 430°C in order to investigate nucleation and mesophase growth processes in the presence of the additive. Formation of mesophase spherules was accelerated and they were coated with iron, the spherules were not increased in size [168].

11. (ii) Ferrocene stabilizers and improvers

Vinylferrocene was mixed with 2,3-dichloro-5,6-dicyano-benzoquinone in acetonitrile to form a deep red charge transfer complex which absorbed strongly in the region 350-600 nm and was used as an optical filter in this region [169]. Cedar panels coated with butyl acrylate-methacrylic acid-styrene-vinylferrocene copolymer or butyl acrylate-methacrylic acid-styrene copolymer containing ferrocene were protected effectively when subjected to exterior exposure testing. However the incorporation of ferrocene as a comonomer or as an additive had no effect on salt spray corrosion resistance [170].

Ferrocene was effective in inhibiting the ω-polymerization of chloroprene [171]. The properties of polyester resins, prepared by polycondensation of glycols with unsaturated and saturated dicarboxylic acids, were improved if they were prepared in the presence of ferrocene or diethylferrocene [172]. A polyester polyacrylate containing t-butyl or cumene hydroperoxide and a polyester polyacrylate containing 0.2% ferrocene provided the two components for a two package fast-curing resin formulation. On mixing at room temperature gelation occurred in five or twenty seconds depending on the hydroperoxide [173].

The addition of dimethyltin bis(octyl thioglycolate) and either ferrocene or chromium acetylacetonate to an impact and vapour permeation resistant blend of acrylonitrile-methyl methacrylate-styrene polymer and poly(vinyl chloride) rendered the material flame resistant [174]. Alkyl-, and hydroxyalkylferrocenes such as 1,1'-dipropylferrocene and α-hydroxyethylferrocene have been used to stabilize medium-pressure polyethylene against thermal degradation. Breakdown of the polymer was followed by thermogravimetry and the addition of 0.25% of the ferrocene was effective in increasing significantly the temperature at which initial weight loss was observed [175].

Alkylferrocenes including 1,1'-diethylferrocene and 2,2-bis(1,1'-diethylferrocenyl)propane have been used to stabilize medium-pressure polyethylene towards degradation by heat and irradiation [176]. 5-(1,1'-Diethylferrocenyl)pentadiyn-1-ol (0.25-1%) has been used as a UV stabilizer in polyethylene [177]. The flame resistance of soft poly(vinyl chloride) was enhanced by the addition of a fireproofing agent such as antimony(III) oxide or zinc borate mixed with a small proportion of ferrocene [178].

11. (iii) Ferrocene in analysis

The electrochemical behaviour of 2,2,6,6-tetramethyl-4-oxopiperidinium was studied in water-acetonitrile media. The potentials of platinum electrodes were measured in the presence of this perchlorate and ferrocene when the ferrocene was reduced [179]. Rhenium(VII), dissolved in a mixture of acetic acid and concentrated hydrochloric acid, was determined by titration with ferrocene [180].

Ferrocene has been used for the amperometric titration of cerium(IV) in aqueous-organic media [181]. Ferrocene has been used in the photometric determination of arsenic [182]. The ferricinium ion has been used in the determination of rhenium by atomic absorption [183].

Ferrocene was separated conveniently from mono- and disubstituted ferrocenes by converting it to the thiourea adduct. The precipitated adduct was collected by filtration and decomposed with water to liberate ferrocene [184]. Ferrocene derivatives have been separated by thin-layer chromatography on microcrystalline cellulose. Comparisons were made with separations made on silica gel [185]. Ferrocene has been used as a reagent for the amperometric titration of molybdenum(IV) and rhenium(VII) [186].

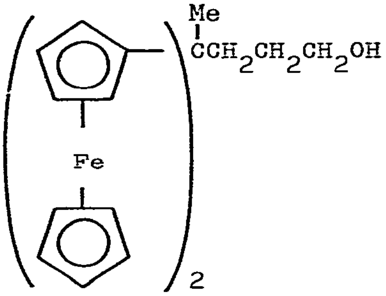
11. (iv) Combustion Studies

Ferrocenes have been heated with poly(furfuryl alcohol) at 970-2500° to form glassy carbons. The microporous structure of these carbons was investigated by small angle X-ray scattering techniques [187]. Polyesters prepared from (ferrocenylmethylthio)succinic acid and 1,5-pentanediol and ethylene glycol were investigated as binder-combustion catalysts for propellants [188].

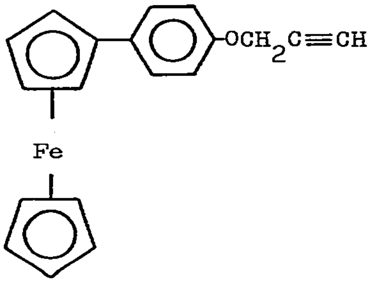
The effect of ferrocene on the burning rates of ammonia flames was investigated as part of a study on the mode of action of solid composite propellant catalysts [189]. The effect of ferrocene on the burning rates of ammonium perchlorate-polybutadiene propellant sandwiches was investigated [190].

N-(ferrocenylmethyl)pyrollidine was used as a bonding agent for oxidants and a ballistics modifier in propellants [191]. The flame resistant properties of flexible poly(vinyl chloride) were improved by adding an acetone-ferrocene copolymer [192]. 4,4-Diferrocenyl-1-pentanol and 3,3-diferrocenylbutylisocyanate were prepared and used as combustion rate accelerators in solid propellants based on ammonium perchlorate [193]. Hydroxyphenylferrocenes have been used as antiknock additives in gasoline [194].

Ferrocene was treated with 3-acetylpropan-1-ol in methylene dichloride containing trifluoroacetic acid as a catalyst to form 4,4-diferrocenylpentan-1-ol (11.4) in 62% yield. The compound was used to control the burning rate of rocket propellants [195].



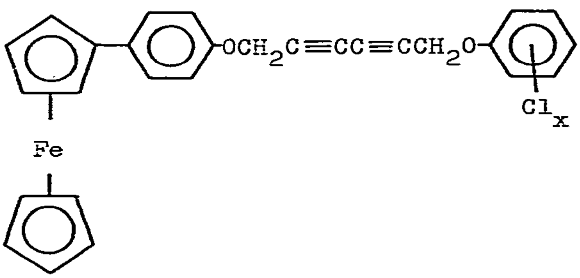
(11.4)



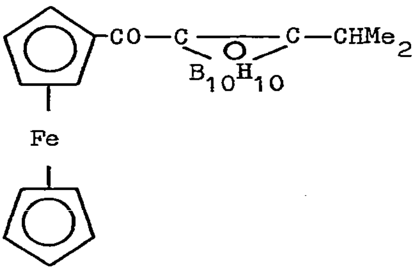
(11.5)

Hydroxyferrocenes such as 4-methyl-4-ferrocenylheptane-1,7-diol have been used as burning rate catalysts in solid propellants [196]. The ferrocenylacetylene (11.5) has been coupled with bromoacetylenes, $BrC\equiv CCH_2OR$, to give the diacetylenes (11.6; x = 1-3) which were useful as antiknock additives for gasoline [197]. Isopropenylcarborane was lithiated and treated with ferrocenoyl chloride to form the ferrocenoylcarborane (11.7) which was used to promote high burning rates in polybutadiene-ammonium perchlorate propellant compositions [198].

Lawson has investigated the effect of added ferrocene on the combustion of vinyl polymers. Early weight loss and crosslinking were observed with poly(vinyl chloride) and the ferricinium



(11.6)

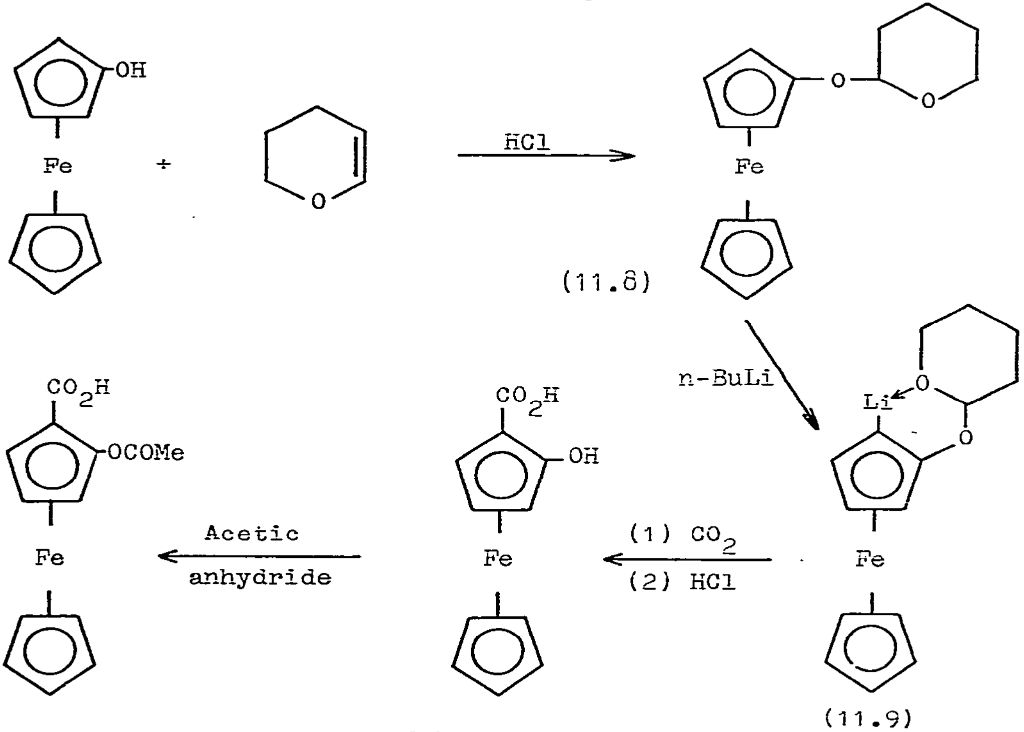


(11.7)

cation was formed. Char formation was enhanced by up to 60% and the limiting oxygen index increased by 19%. When the polymer was of low molecular weight then formation of visible smoke was suppressed and both gas-phase and condensed-phase processes were active. Smoke formation from poly(vinyl alcohol) was reduced principally through gas-phase interactions [199].

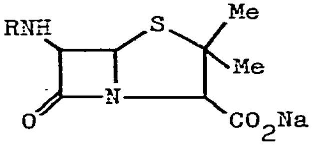
11. (v) Biochemical Applications

A convenient route was reported for the preparation of the ferrocene analogues of salicylic acid and aspirin. The reaction of hydroxyferrocene with 2,3-dihydropyran gave (ferrocenyloxy)-2-tetrahydropyran (11.8) which on lithiation gave the corresponding 2-lithiated ferrocene (11.9). The lithiated ferrocene (11.9) was used to prepare 1-carboxy-2-hydroxyferrocene and 1-carboxy-2-acetoferrocene (Scheme 11.1) [200].

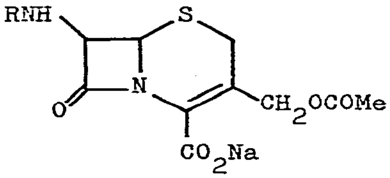


Scheme 11.1

A series of ferrocenyl carboxylic acids was prepared and condensed, via their acid chlorides or in the presence of N,N'-dicyclohexylcarbodiimide with both 6-aminopenicillanic acid and 7-aminocephalosporanic acid. The ferrocenyl-penicillins [11.10; R = $FcCH_2CO$, FeCH(Me)CO, $FcC(Me)_2CO$, FcCO] and the corresponding cephalosporins (11.11) exhibited antibiotic



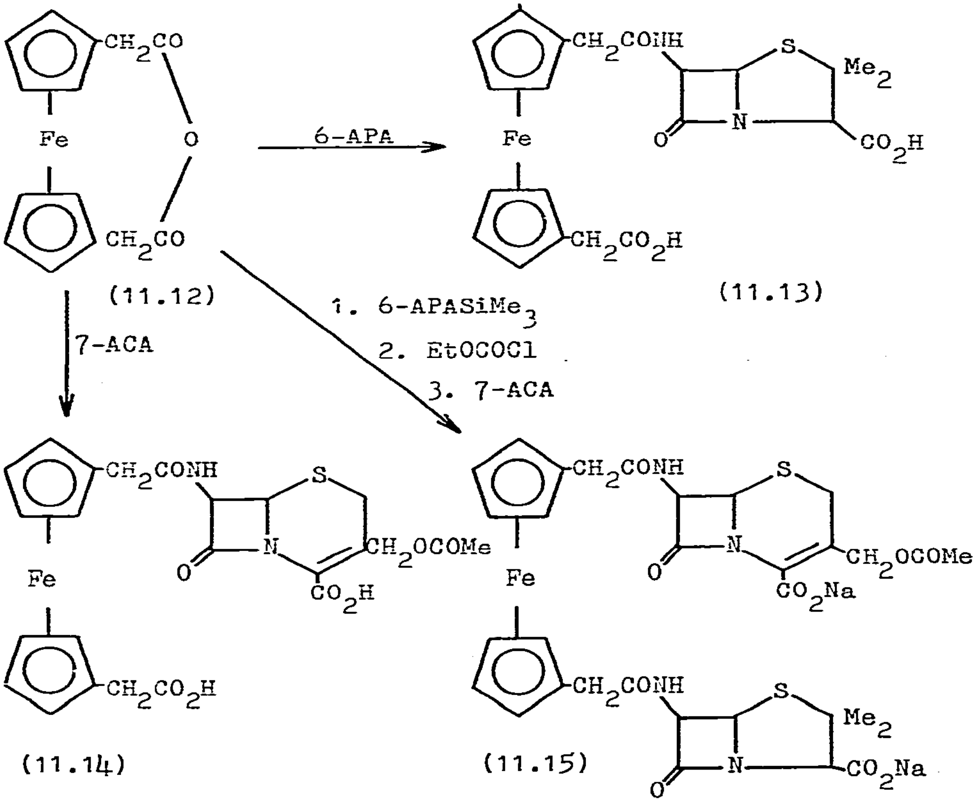
(11.10)



(11.11)

activity, some were highly active while others were potent β-lactamase inhibitors [201].

1,1'-Ferrocenediacetic acid anhydride (11.12) has been formed from the corresponding diacid with dicyclohexylcarbodiimide and converted to the 1'-substituted ferrocenylpenicillin (11.13) with 6-aminopenicillanic acid (6-APA) and to the ferrocenyl-cephalosporin (11.14) with 7-aminocephalosporanic acid (7-ACA). A mixed ferrocenyl-cephalosporin-penicillin (11.15) was also prepared. All three of these products were active antibiotics [202].



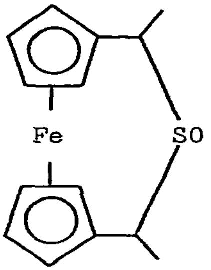
(11.12)

(11.13)

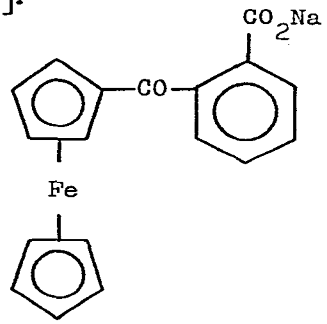
(11.14)

(11.15)

The thiadialkylideneferrocene (11.16), prepared by oxidative cyclization of 1,1'-diethyl-α,α'-thiaferrocene, has been used as a haematinic agent for the treatment of iron deficiency in animals [203].



(11.16)



(11.17)

The sodium salt of o-carboxybenzoylferrocene (11.17) has been used to treat patients with ozena at a dose rate of 0.2-0.9 g per day [204].

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