FERROCENE

ANNUAL SURVEY COVERING THE YEAR 1975

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CONTENTS

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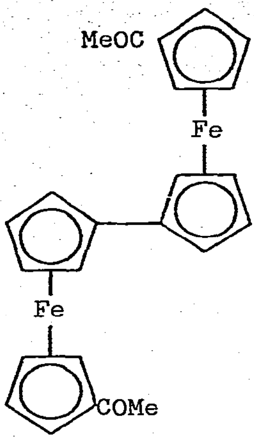
1. REVIEWS

A brief review of some aspects of ferrocene chemistry has been included in a more general survey of η-cyclopentadienyl and η-arene transition metal compounds[1]. Perevalova and Nikitina reviewed the chemistry of bis(η-cyclopentadienyl) compounds of transition metals[2]. Moessbauer spectroscopy of metal sandwich compounds, mainly ferrocenes, was reviewed by Good and co-workers[3]. As part of Gmelin's Handbook of Inorganic Chemistry a supplementary work, dealing with ferrocene and mono-substituted ferrocenes, was published. This was of the usual high standard that is expected of this series[4].

2. STRUCTURAL DETERMINATIONS

The previously proposed molecular structure of bis[tris-(diethylamido)titano]ferrocene has been confirmed by X-ray crystallography[5]. The crystal and molecular structure of bis[1'-(1-acetylferrocenyl)] (2.1) was investigated by X-ray diffraction studies. The molecule had a trans configuration with the acetyl groups situated in the plane of the η-cyclopentadienyl rings[6]. X-ray diffraction has been used to confirm the crystal and molecular structure of phenylacetylferrocene[7]. The crystal and molecular structure of diferrocenyltin dichloride (2.2) has been determined by X-ray crystallography. The tin-cyclopentadienyl bond was bent out of the plane of the ring and towards the iron atom by 6.8° [8].



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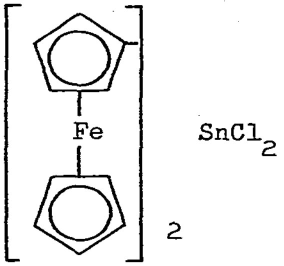

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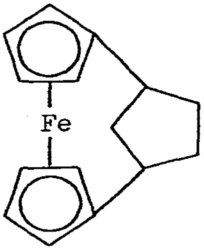

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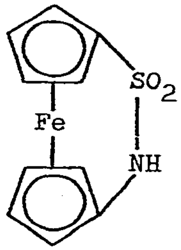
The crystal and molecular structure of 1,1-(1",3"-cyclopentylene)ferrocene (2.3) prepared by cleavage of ferrocene with aluminium chloride, has been determined by X-ray crystallography. The two cyclopentadienyl rings are eclipsed and have a dihedral angle of 11°. The cyclopentylene bridge is distorted and asymmetrical[9]. The crystal and molecular structure of [2]ferrocenophanethiazine-1,1-dioxide (2.4) has been determined by X-ray crystallography, the cyclopentadienyl rings were tilted out of coplanarity by 23°. The iron-carbon bond lengths ranged from 1.962 to 2.096 Å. Comparisons of the Moessbauer spectrum of this compound with those of ferrocene derivatives with less tilted or parallel cyclopentadienyl rings confirmed that the ring-metal bond energy was not reduced by ring tilting[10]. Changes in the crystal structure of ferrocene with temperature have been studied by X-ray powder diffraction at carefully controlled temperatures in the range 15-295°K. The calculated cell parameters and volume showed a discontinuity at 164°K from triclinic below, to monoclinic above, this temperature. The mechanism of the transition was discussed[11].

It has been proposed that the component of the Gibbs free energy arising from short-range interactions for transfer of a single ferrocene molecule and a single ferricinium ion from water to a non-aqueous solvent will not be similar. The previous assumption that these two components were similar neglectedthe relatively small size of the ferricinium ion and the fact that ferrocene has a quadrupole moment while the ferricinium ion was not quadrupolar[12]. Ferrocene, chloroferrocene and 1,1'-dichloroferrocene have been studied by an Extended Hueckel Theory programme, with an s, p and d orbital basis. The variation in total energy, including an interatomic Madelung factor, was calculated as a function of the angle of rotation of the cyclopentadienyl rings and a number of stable conformations were indicated. Calculated dipole moments were in close agreement with the experimental values[13]. DeKock has discussed the utility of the frontier orbital concept to the problem of proton attack on several molecules. However in the case of ferrocene the order of one-electron orbital energies is different from the order of ionic states given by photoelectron spectroscopy and predictions of the site of proton attack on ferrocene cannot be made by the frontier orbital concept[14]. The ground state of the ferricinium ion was shown to be low spin $^2E_{2g}$ from INDO SCF molecular orbital calculations[15].

3. STEREOCHEMISTRY OF FERROCENES

The effect of the ferrocenyl substituent on the *cis*-proton signal in the ^{1}H NMR spectra of stereoisomeric 2-ferrocenyl-2-methylcyclopropanecarboxylic-1 acids and their ester derivatives was investigated. The ferrocenyl group exerted a deshielding effect on the cis-protons. It was concluded that the stereoisomers assumed the mean conformation (3.1) with the proton H_1 present in the ferrocene deshielding zone[16]. The isomer distributions in the alcohol products obtained on hydroboration of vinylferrocenes has been determined. Vinylferrocene and 2-ferrocenylpropene (3.2) gave predominant addition at the β-carbon atom (98-99%) and this was attributed to the steric effect of the metallocene. Substitution on the β-carbon by alkyl or aryl groups led to an increased proportion of α-addition. Alkyl groups were more effective in promoting α-attack (63-95%) than were phenyl or substituted phenyl groups (10-28%). These results were discussed in terms of the electronic effect of the substituents[17]. Ferrocene, methylferrocene, phenylferrocene, 1,1'-dimethyl- and 1,1'-diphenyl-ferrocene have been monoacylated and heteroannularly diacylated with o-chlorobenzoyl chloride and aluminium chloride to give isomeric mixtures of the corresponding o-chlorobenzoylferrocenes. The mixtures were separated by chromatography allowing the isomer



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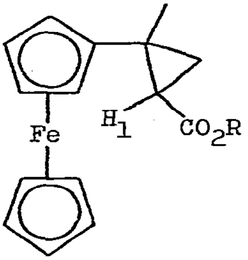

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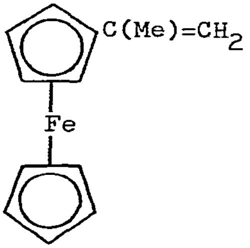

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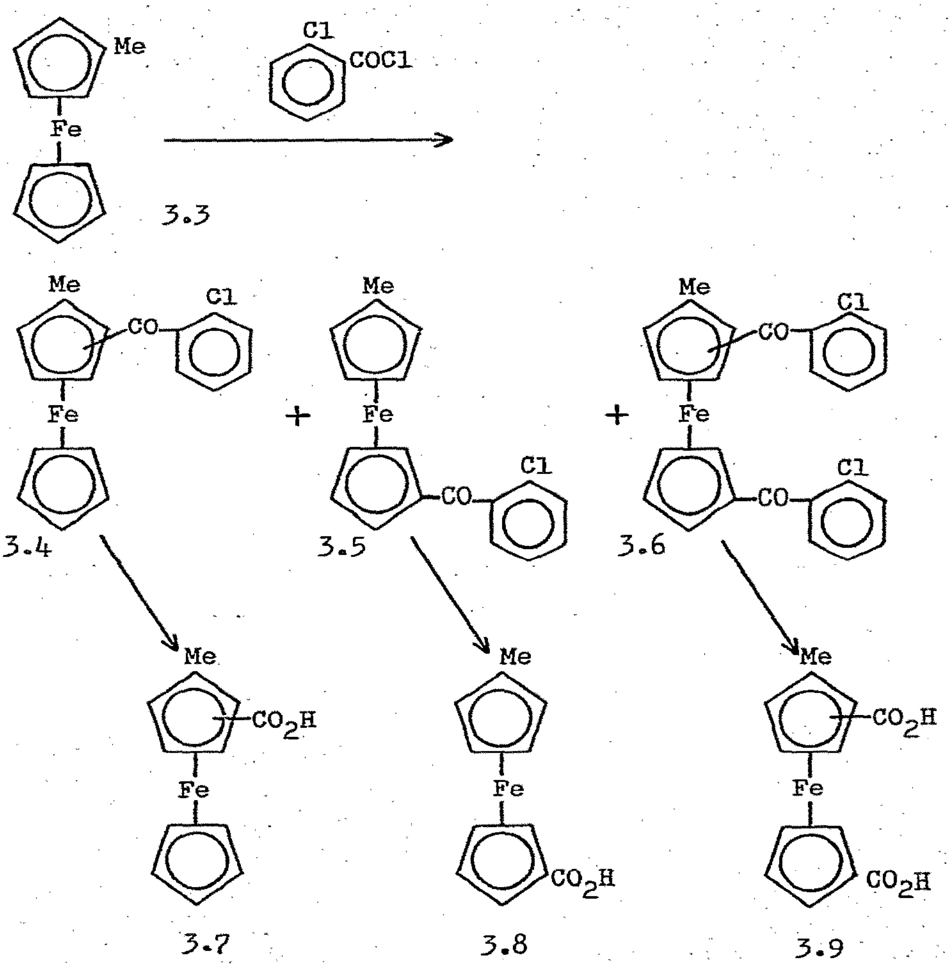
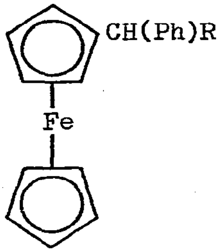
distributions and relative site reactivities to be determined. The o-chlorobenzoyl group was cleaved with potassium t-butoxide to give the corresponding ferrocene carboxylic acids. Thus methylferrocene (3.3) was acylated to form the benzoylferrocenes (3.4, 3.5 and 3.6) and these were converted to the ferrocenecarboxylic acids (3.7, 3.8 and 3.9)[18].



(+)-1-Ferrocenyl-2-aminopropane was converted into diastereoisomeric R-O-methyl mandelic amides and its optical purity was estimated by ^1H NMR spectroscopy[19]. Direct conversion of optically active (+)-α-ferrocenylbenzylamine (3.10; R = NH_2) to the dimethylamine (3.10; R = NMe_2) with formaldehyde and borohydride and then to (-)-α-ferrocenylbenzylalcohol (3.10; R = OH) with perchloric acid and benzene has been described. The reaction proceeded with high retention of optical purity[20]. (±)-S-(1-Ferrocenylethyl)thioglycolic acid (3.11) was prepared from (±)-1-ferrocenylethanol and thioglycolic acid in the presence of trifluoroacetic acid. The acid (3.11) was resolved into enantiomers by fractional crystallization of the diastereomeric salts with ephedrine. Treatment of the (+)(3.11) acid with mercury (II) chloride gave (R)-(—)-1-ferrocenylethanol[21]. α-Ferrocenylisobutylamine was used in a four component condensation to give N-benzoyl-N-[(R)-α-ferrocenylisobutyl]-(S)- and -(R)- valine tert-butylamide. The reaction was found to be highly stereoselective[22].



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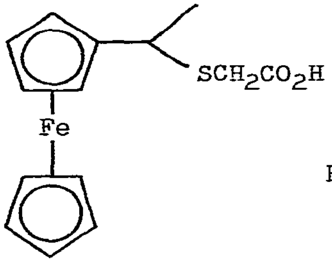

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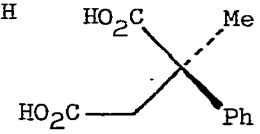

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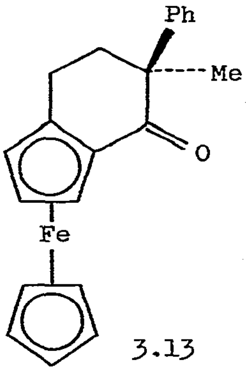
Des Abbayes and Dabard have prepared the two diastereoisomeric pairs of methylphenylferrocenylcyclohexenones (3.13-3.16) from the optically active reagent (+)-(5)-phenyl-2-methyl-

-2-succinic acid (3.12). The four cyclohexenones (3.13-3.16) were shown to be optically pure by isotopic dilution with tritium labelled racemates. Reduction of the cyclohexenones (3.13 and 3.16) gave the cyclohexene (3.18) while (3.14 and 3.15) gave (3.17) in the same way. The authors proposed that the diastereogenic cyclization of γ-ferrocenylbutyric acids to ferrocenylcyclohexenones was kinetically controlled and led preferentially to the isomer with the largest endo group[23].



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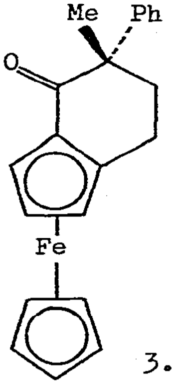

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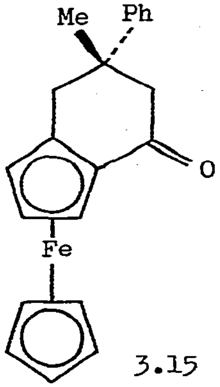

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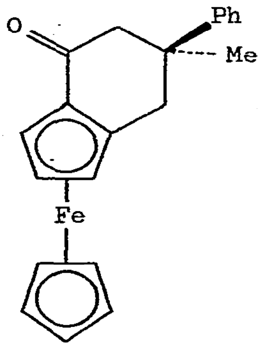

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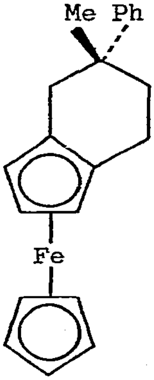

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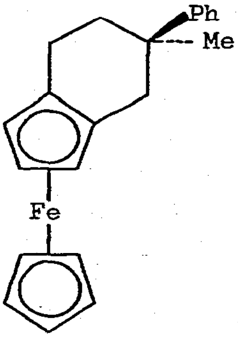
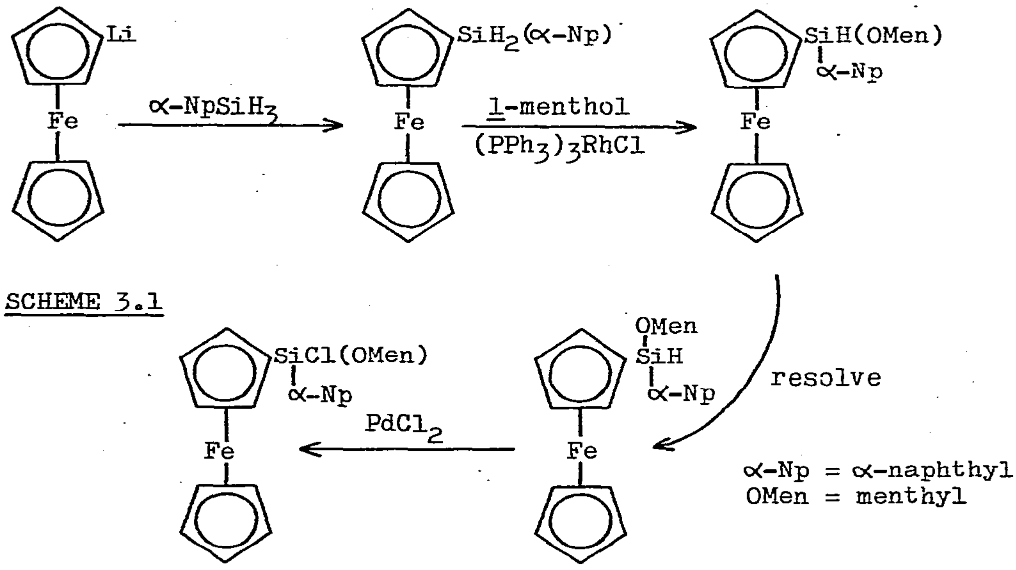


3.18

The preparation of two bifunctional and optically active α-ferrocenylsilanes (3.19 and 3.20) was described (Scheme 3.1) by Corriu and co-workers. The absolute configuration of these ferrocenylsilanes was determined by chemical correlation[24].

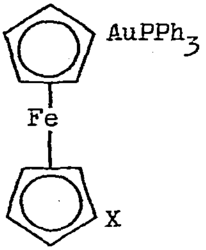


SCHEME 3.1

3.20 $[\alpha]_D = +10.9^\circ$ 3.19 $[\alpha]_D = +27^\circ$

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

^{1}H NMR spectra have been reported for homoannular isomeric diethyl- and diacetyl-ferrocenes and for 1,3-di-t-butylferrocene. The ring proton chemical shifts were discussed in terms of the inductive, conjugative and hyperconjugative effects of the substituents[25]. The ^{1}H NMR spectra of a series of mono- and di-acetyl [3] ferrocenophanes were investigated by computer matching and NMR shift reagents such as Eu(fod)$_3$. A systematic investigation was made of the effect of acetylation on the NMR chemical shift of protons on both the substituted and unsubstituted rings of the [3] ferrocenophane systems. These changes in chemical shift were interpreted in terms of the anisotropy of the non-bonding hybridized d orbitals of the iron atom and the perturbations of these orbitals caused by the introduction of an acetyl group[26]. The protonation of ferrocene and ruthenocene has been examined at several acid strengths by ^1H NMR spectroscopy and the metal atoms were shown to be weakly basic, ferrocene pK = -7.8. Extensive π-hydrogen-bonding with the cyclopentadienyl rings was indicated in weakly protonating systems[27]. The ^1H NMR spectra of the ferrocenyl-gold complexes (4.1 and 4.2; X = H, Cl, Br, OMe, CO_2Me) were recorded and assigned. The effects of the $AuPPh_3$ groups on the proton chemical shifts were discussed[28].



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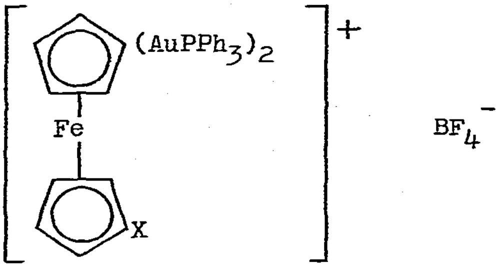

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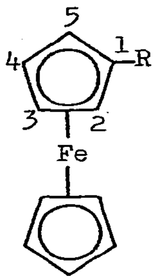
Electron exchange between ferrocene and the ferricinium ion has been investigated quantitatively by ^1H NMR line width measurements in the temperature range 0-30°. The rate was dependant on the first power of the concentration of each reactant in acetonitrile and the rate constant for an ionic strength $< 0.1M = 5.7 \times 10^6\ M^{-1}sec^{-1}$ at 25° and the activation energy $E_a = 5$ kcal mol^{-1} [29].

The ^1H and ^{13}C NMR spectra for several ferrocenes and ferrocenophanes with chiral substituents have been analysed in order to measure the influence of such groups. The difference in screening which arose from diastereotopy of the cyclopentadienyl carbon atoms was usually larger than the non--equivalence of the corresponding proton chemical shifts[30]. Transient oscillations observed in ^1H-^{13}C NMR cross-polarization studies of ferrocene were subjected to quantitative analysis. The oscillations were discussed in terms of a strong dipolar interaction of the ^{13}C with a directly bonded proton. Damping was determined by further interactions of these two spins with other protons[31]. Kohler and Matsubayashi have recorded the ^{13}C NMR spectra of selected 1,1'-, 1,2-, and 1,3-disubstituted ferrocenes. The chemical shifts and the ^{13}C- ^1H coupling constants have been used to devise methods for peak assignment based on: (a) analysis of the fine structure generated by coupling with protons on the α-carbon atom of the substituent, (b) evaluation of the numerical value of $^1J(CH)$, and (c) comparison of the chemical shift values for η-cyclopentadienyl rings with one and two substituent groups[32].

^{13}C NMR spectra of some <u>para</u> and <u>meta</u> substituted phenylferrocenes were recorded and interpreted[33]. The substituent caused shifts were compared with those obtained from similarly substituted biphenyls. The substituent caused shifts were correlated with Hammett parameters and with the reactivity parameters of Swain and Lupton[34]. The ^{13}C NMR spectra for a series of ferrocenylalkylium ions were obtained from CF_3CO_2D solutions of the corresponding alcohols. From the results it was concluded that (i) the α-carbon atom was probably sp^2 hybridized, (ii) the positive charge was delocalized throughout the ferrocene system, (iii) progressive alkyl substitution of the α-carbon atom allows it to sustain a higher proportion of the positive charge, (iv) distribution of charge to nine ring carbon atoms (C_2-C_{10}) was relatively insensitive to alkyl substitution whilst one carbon atom (C_1) was relatively sensitive, (v) two carbon atoms (C_2 and C_3) carry a higher positive charge than the other carbon atoms[35]. Selective deuteration coupled with ^{13}C NMR spectroscopy has been used to investigate the electronic effects of alkyl groups on ferrocene. In the series of alkyl substituents on ferrocene (4.3; R = Me, Et, $CHMe_2$, CMe_3, CH_2CMe_3) it was observed that the shielding of the β-carbon atoms in the substituted ring, C-3, C-4 was almost independent of the substituent while the α-carbon atoms C-2, C-5, were more shielded than the β-carbons when R = Me, Et and CH_2CMe_3 and less shielded when R = $CHMe_2$ and CMe_3. It was considered that hyperconjugation in these compounds was insignificant[36].

The ^{13}C NMR spectra for ferrocene, ethylferrocene, acetylferrocene, 1-ferrocenylethanol and the 1-ferrocenylethyl carbenium ion, each enriched with ^{57}Fe, have been measured and analyzed. Splitting of the C_{exo} resonance by coupling with ^{57}Fe was demonstrated. The coupling constants $^1J_{^{57}Fe-^{13}C}$ were determined and shown to depend on the position of the carbon atom and the nature of the substituent. Chemical shifts for ^{57}Fe were measured for ferrocene, protonated ferrocene and acetylferrocene[37]. NMR examination of ^{57}Fe enriched ferrocene and ferrocene derivatives has enabled $^1J(^{57}Fe-^{13}C)$ coupling constants and ^{57}Fe chemical shifts to be obtained. Measurements on the cation (4.4) enabled the absence of coupling between iron and the exocyclic carbon atoms to be confirmed and argued for a structure (4.4) without essential change of the symmetry of the ferrocene nucleus. Thus α-ferrocenylcarbenium ions are stabilized principally by delocalization over the whole ferrocenyl group[38].



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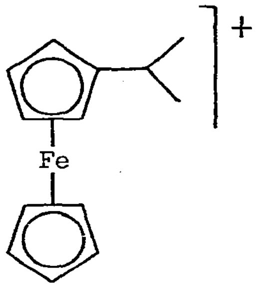

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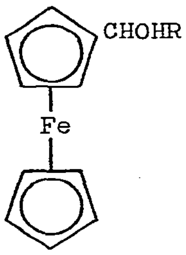

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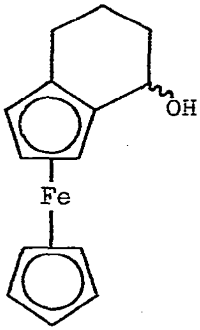
The ESR spectra of some orbitally degenerate sandwich compounds, including the ferricinium ion, were obtained at liquid helium temperatures. Analysis of the spectra and the anisotropic Zeeman effects in the compounds indicated that the Jahn-Teller distortions observed were dynamic. The distortions were correlated with covalent delocalization of the singly occupied degenerate metal 3*d* orbital over the cyclopentadienyl rings and gave the following order: $(\eta\text{-}C_5H_5)_2Fe^+ < (\eta\text{-}C_5H_5)_2Mn < (\eta\text{-}C_5H_5)_2Co < (\eta\text{-}C_5H_5)_2Ni^+$ [39].

The OH frequencies in the infrared spectra of several α-hydroxyalkylferrocenes (4.5; R = Me, Et; 4.6) have been measured and assigned. The relationship between the OH frequency and its conformation and intramolecular hydrogen bonding were discussed[40]. The solution Raman spectra of ferrocene, ruthenocene and osmocene were reinvestigated and the results generally supported previous assignments. For ferrocene the weak line at 1186cm^{-1} was found to be polarized and this was reassigned as an overtone of an out-of-plane cyclopentadienyl mode at about 600cm^{-1} [41].

The UV absorption spectrum of ferrocene was reinvestigated in the region 500-700nm. Four levels were indicated in the 1.8 eV region with separations greater than 0.5 eV. A weak absorption band, $\varepsilon \sim 0.3$ l mol^{-1} cm^{-1}, was observed near to 630nm [42]. Electronic excitation of ferrocene was observed by tunnel spectroscopy using $Al-Al_2O_3-Al$ junctions alloyed with ferrocene. Electron levels were observed at 620, 660 and 705mV[43]. The electronic absorption spectrum of ferrocene was



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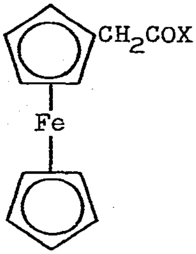

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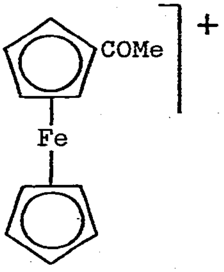


4.8

recorded in twelve different solvents at 77°K and maxima occurred at 420 and 320nm. In cyclohexane and benzene the long wavelength maxima occurred at 405 and 407nm respectively whilst in carbon tetrachloride and chloroform the short wavelength band was not observed. It was thought that molecular orbitals situated on the cyclopentadienyl rings were involved in the production of the long wavelength band[44]. The electronic absorption spectrum was examined in detail and the excited states of ferrocene were calculated using the singly excited configuration interaction method[45]. The introduction of ethyl substituents into ferrocene and cobalticinium chloroplatinate resulted in similar changes in their electronic absorption spectra[46].

The cation $(\eta\text{-}C_5H_5)_2Fe^+$ was formed in the mass spectrometric fragmentation of $(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_7)Fe$ and its derivatives[47]. The mass spectra of the haloacetylferrocenes (4.7; X = Cl, Br, I, H) have been measured. A major ion (4.8) was formed by attack of residual water on the haloacetylferrocene, halogen migration to iron was also important[48]. The negative ion mass spectra of ferrocene and a mixture of ferrocene with sulphur were recorded. In the latter spectrum most of the fragments contained some sulphur atoms of which $[S_nC_5H_5]^-$ (n = 1, 2) were more abundant and comparable to $[C_5H_5]^-$. The structures of the ions were discussed[49].

Foster and Beauchamp have used ion cyclotron resonance spectroscopy to investigate the gas-phase ion chemistry of ferrocene. The ions observed were Fe^+, $(\eta\text{-}C_5H_5)Fe^+$, $(\eta\text{-}C_5H_5)_2Fe^+$ and $(\eta\text{-}C_5H_5)_3Fe_2^+$. The last mentioned ion, presumably a triple-decker sandwich, was observed at higher pressures while Fe^+ and $(\eta\text{-}C_5H_5)Fe^+$ disappeared at these pressures. Product distributions and rate constants for the charge exchange reactions of the principal primary ions were measured by trapped ion methods. The proton affinity of ferrocene was determined as 213 ± 4 kcal mol^{-1}, a value slightly lower than that for methylamine, by proton transfer reactions between ferrocene and other molecules[50].

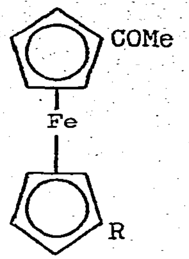
Moessbauer spectra of ferricinium trichloroferrate containing the natural mixture of iron isotopes or ^{57}Fe were recorded at 80 and 300°K. The asymmetry of the spectrum was due to the orientation effect and to the Gol'danskii-Karyagin effect. The structure of the molecule was thought to be polymeric with a planar configuration of the anion[51]. Solutions of diacetylferrocene in 4,4'-di-n-heptyl-oxyazoxybenzene and 4,4'-di-n-octyloxyazoxybenzene possessing the nematic and smectic mesophases were investigated by Moessbauer spectroscopy. Gamma resonance was observed in both phases[52].

1,1'-Diacetylferrocene was incorporated into liquid crystals which had both smectic and nematic phases. A 4-9kg magnetic field was used to order the samples in the nematic phase and these were then cooled to the smectic phase for the Moessbauer measurements. It was confirmed that a non-zero effect was observed only when the ferrocene derivative was present as a solid component[53]. In the temperature range 43.5-123.5° formylferrocene was found to exist in a viscous nonbirefringent phase with enthalpy of transition 3.0 kcal mol^{-1} and entropy of transition 9.5 cal deg^{-1} mol^{-1} at 43.5°. Imines formed between formylferrocene and p-substituted anilines exhibited normal crystal melting behaviour[54].

The combustion enthalpies of $(C_5H_5)_2M$ (M = Cr, Mn, Fe, Co and Ni) were measured calorimetrically. The dissociation energies and standard formation enthalpies of these compounds were calculated[55]. The relative heats of formation of a series α-ferrocenyl carbenium ions, generated from the corresponding alcohols in 96.1% sulphuric acid, and the relative heats of protonation of some ferrocenyl ketones were measured. The ferrocene substituent stabilized a cation by 9 kcal/mol more than a pair of phenyl substituents which confirms the high stability of α-ferrocenyl cations. When one or two hydrogen atoms in the α-ferrocenyl carbenium ion were replaced by phenyl or methyl groups the stability of the cation was not enhanced. It was proposed that most of the charge on α-ferrocenyl cations was delocalized into the ferrocene group and the substituent effects observed were those for substitution β to a cationic carbon, not directly on it[56].

The rate of hydrogen-deuterium exchange between ferrocene or cymantrenylferrocene and trifluoroacetic acid was determined. All nine positions of the ferrocenyl group took part in the exchange and the exchange was faster by an order of magnitude for ferrocene than for cymantrenylferrocene[57]. Equilibrium constants have been determined for the protonation of ferrocenyl ketones and the dissociation of ferrocenyl alcohols in a mixture of trichloroacetic acid and benzene. In each case, extensive conversion to ferrocenylcarbenium ions was indicated. The change in equilibrium constant with solvent was correlated with the Taft solvent polarity factor[58].

Livar, Salisova and Toma have carried out a kinetic investigation of the internal Michael addition of several heteroannularly disubstituted ferrocenes in sodium methoxide and methanol to give the [m]ferrocenophanes. The acetylferrocenes [4.9; R = $COCH{=}CHPh$, $COC{\equiv}CPh$, $COCH{=}CH.C_6H_4.4\text{-}Cl$, $C(CN){=}CH.C_6H_4.4\text{-}Cl$] and the benzoylferrocenes (4.10; R^1 = 3-Me, R^2 = $COCH{=}CHPh$, $COCH{=}CH.C_6H_4.4\text{-}Cl$; R^1 = 4-Me, R^2 = $COCH{=}CH\text{-}C_6H_4.4\text{-}Cl$) were studied in order to determine the effect of bridge structure and size on the cyclization[59]. The



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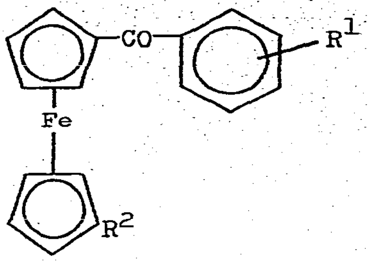


4.10

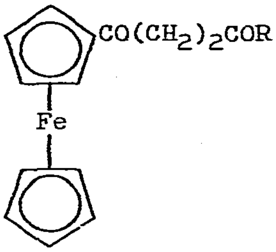
solvolysis of 2-ferrocenylethyl-1,1-$\underline{d}_2$ tosylate in aqueous ethanol, formic acid or CF_3CH_2OH and the treatment of 2-ferrocenylethyl-1,1-$\underline{d}_2$ chloride with aluminium chloride in methylene dichloride did not result in scrambling of the deuterium from carbon-1 to carbon-2. This suggested that 1,2-ferrocenyl shifts did not take place in these reactions. The mass spectral fragmentations of 2-ferrocenylethyl-1,1-$\underline{d}_2$ derivatives and their unlabelled counterparts were analysed[60].

The dependence of the redox acidity function $R_0(H)$ on solvent composition over a range of ethylene glycol-water and diethylene glycol-water mixtures has been determined. The $R_0(H)$ function, based on a ferricinium ion/ferrocene couple, was compared with the H_0 function in these solvent mixtures[61]. The acidity function, $\underline{H}_{GF}$, based on the measured difference $\underline{E}$ between the ferrocene half-wave potential $\underline{E}_{1/2}$ and the glass electrode potential $\underline{E}_g$ was established for aqueous solutions of H_3PO_4, H_3PO_3, and methanesulphonic and p-toluenesulphonic acids. The variation of the acivity coefficients of ferrocene and ferricinium ion with acid concentration was determined and this data together with the $\underline{H}_{GF}$ values was used to calculate proton activities, log $\underline{a}_{H+}$, relative to the tetraethylammonium ion. The acidity scale obtained was considered to be a better operational measure of acidity in concentrated acids than spectrophotometrically determined acidity functions[62]. A kinetic study of the polarographic hydrolysis of (2-thenylideneamino)ferrocene was carried out. The hydrolysis followed two concurrent mechanisms with different temperature coefficients[63].

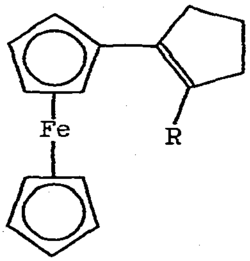
Cyclic voltammetry was used to examine the electrochemistry of the ferrocenylphosphines $FcPh_2P$, Fc_2PhP and Fc_3P and their complexes of the type LBH_3, LMe^+I^-, $LM(CO)_5$ and $L_2M(CO)_4$, (M=Mo and W). Well-defined, one electron, reversible redox waves were observed for the oxidation of each ferrocenyl group except for Fc_3P when the redox waves overlapped. In the complexes of $FcPh_2P$ the oxidation potential for the ferrocenyl group increased whilst for the complexes of Fc_2PhP and Fc_3P no change was observed. Infrared spectra of the complexes $LM(CO)_5$ at various stages of ferrocenyl group oxidation showed that the intense E/A_1^1 mode shifted to higher frequencies for each ferrocenyl group oxidized. It was concluded that the coordinating ability of the ferrocenylphosphines was not appreciably altered upon oxidation[64]. Formal oxidation potentials, relative to the standard hydrogen electrode at 25^o, were determined for a number of substituted ferrocenes by potentiometric titration in an aqueous-organic solution. These potentials were correlated with the ability of the ferrocenes to act as stabilizers for polymers subject to irradiation. It was proposed that the ferrocenes were active as stabilizers by undergoing reversible oxidation[65]. The change in the electroactivity range of ferrocene with the change in composition of a water-sulphuric acid solvent has been investigated. A convenient reference potential was provided by ferrocene at low sulphuric acid levels[66].

5. REACTIONS OF FERROCENE

The ferrocenylketones (5.1) were formed by treatment of ferrocene with the appropriate acylalkanoyl chloride. Thus the ketone (5.1; R = Ph, n = 4) was obtained from $PhCO(CH_2)_4COCl$ and ferrocene. These ferrocenylketones were effective in the treatment of iron-deficiency anaemia[67]. Pentanoyl chlorides were treated with ferrocene in the presence of aluminium chloride to give ferrocenylcyclopentenes (5.2; R = Ph, PhCO, $PhCH_2$, $X.C_6H_4.CO$, 2-furoyl, 2-thenoyl, Cl). Thus $Ph(CH_2)_4CO_2H$ was heated with thionyl chloride to give the acid chloride and this was converted to the ferrocenylphenylcyclopentene (5.2; R = Ph) with ferrocene and aluminium chloride. These compounds were used in the treatment of iron deficiency anaemia[68]. The Friedel-Crafts acetylation of ferrocene with acetyl chloride has been reinvestigated. It was found that the proportions of the products, acetylferrocene and two diacetyl derivatives (5.3 and 5.4), were changed by altering the proportions of the reactants. The



5.1



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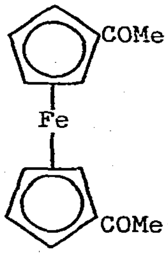
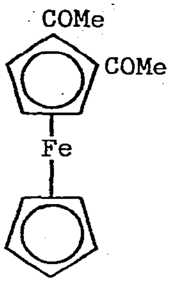


5.3

1,1'diacetyl compound (5.3) was the dominant product in almost every case but the yield of 1,2-diacetyl ferrocene



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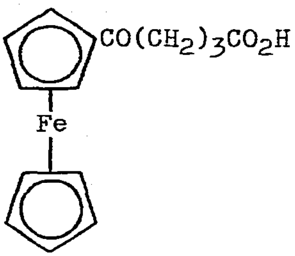
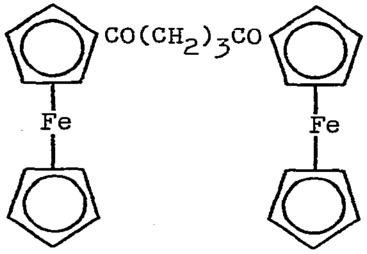


5.5

(5.4) was raised to 8.9% by using a ferrocene: aluminium chloride: acetyl chloride ratio of 1 : 10 : 10 and slow addition of the ferrocene in methylene chloride to the acetylation mixture[69].

The Friedel-Crafts reaction of ferrocene with glutaryl chloride $ClCO(CH_2)_3COCl$ was investigated. Depending upon the reaction conditions and the molar ratios of the reactants three products (5.5, 5.6 and 5.7) were isolated[70].



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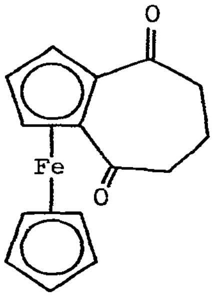
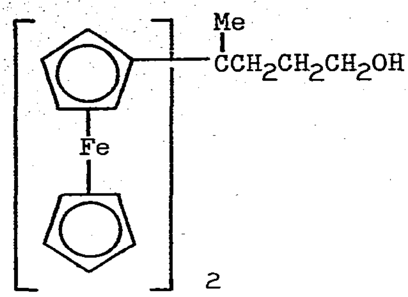


5.7

A convenient student laboratory experiment, involving the preparation and Friedel-Crafts acetylation of ferrocene, has been described[71]. Ligand exchange of ferrocene with benzene and mesitylene was catalyzed by $AlCl_3$, $GaCl_3$, $AlBr_3$, $ZrCl_4$ and $HfCl_4$ whilst BF_3, $SnCl_4$, $TiCl_4$, $ZnCl_2$ and $(Me_2CHCH_2)_3Al$ had no catalytic activity[72].

The clathrate compounds formed between ferrocene, nickelocene or cymantrene and thiourea have been used as the basis of a separation method for removing ferrocene from 1,1'-diethylferrocene and cymantrene from acetylcymantrene[73]. Ferrocene was incorporated into a thiourea host as a clathrate inclusion compound. Tricarbonylcyclopentadienylmanganese does not form a thiourea clathrate in the absence of ferrocene but in the presence of ferrocene the manganese complex was incorporated. Attempts to incorporate substituted ferrocenes were unsuccessful[73].

The solvation of ferrocene in mixtures of water and an organic solvent has been investigated. Ferrocene was preferentially solvated by the organic solvent, propylene carbonate, and addition of the organic cosolvent to a water-rich solvent mixture considerably increased its solvation. However, addition of water to a solvent mixture rich in the organic solvent produced little change in solvation[74]. Ferrocene was combined with methyl levulinate to give methyl 4,4-diferrocenylpentanoate, this product was reduced to 4,4-diferrocenyl-1--pentanol (5.8) and was also converted to 3,3-diferrocenylbutyl isocyanate (5.9). The isocyanate was formed by hydrolysis of the ester to the pentanoic acid, conversion to the acid chloride and then to the azide which was decomposed to the product (5.9). The pentanol (5.8) and the butyl isocyanate (5.9) were used as burning rate catalysts in solid propellants for rockets[75]. Ferrocene was metallated with $Hg(OAc)_2$



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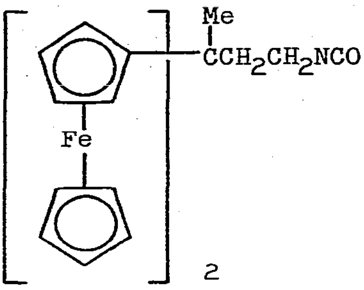


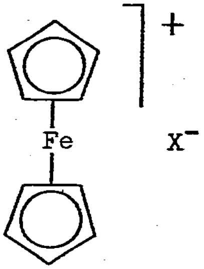
5.9

six times faster than with $Tl(OAc)_3$ and mercuration occurred thirty times faster in acetic acid than in methanol. The effect of introducing successive ethyl substituents into ferrocene was not additive and was taken as evidence against primary interaction between the iron atom and mercury. Vinylferrocene underwent addition of $Hg(OAc)_2$ to the double bond rather than ring metallation[76].

Complete hydrogenation of ferrocene was achieved with palladium (10% on carbon) as the catalyst in an acidic medium under mild conditions (20-50° and one atmosphere hydrogen pressure). The overall reaction was: $Fe(\eta\text{-}C_5H_5)_2 + 4H_2 + 2H^+ \longrightarrow Fe^{2+} + 2\ \text{cyclo-}C_5H_{10}$ which was first order in catalyst and zero order in ferrocene. Autoretardation occurred due to adsorption of the reaction products onto the palladium surface[77]. Ferrocene was added to a quinoline soluble coal-tar pitch and its effect on the size of the mesophase spherules formed in the pitch on heating was observed. At a low concentration of ferrocene the size of the spherules and the amount of quinoline insoluble material formed on heat treating at 430° for 90 min increased[78].

6. FERRICINIUM SALTS

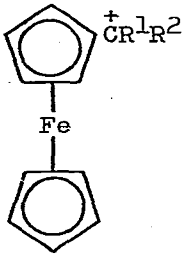
Laser Raman spectra have been recorded for the ferricinium salts (6.1; $X^- = I_3^-$, BF_4^-, $FeCl_4^-$ and picrate$^-$). The vibrational modes involving the iron atom were resonance enhanced and slightly modified in frequency by comparison with the corresponding bands in ferrocene. The observation of the electronic Raman allowed transition $E_{(1/2)g}(^2A_{1g}) \longleftarrow E_{(3/2)g}(^2E_{2g})$ has been described, together with its interpretation. Evidence for a Jahn-Teller effect was not obtained and the electronic Raman results were in agreement with previously reported EPR results[79]. The electrode reaction of the ferrocene-ferricinium ion couple has been examined at high pressure, 1000 kg cm^{-2}, as a function of pressure by a cyclic current step method. Contraction of the solvated molecule in the transition state occurred with a monotonic increase in rate as the pressure increased[80]. Thermal decomposition of the ferricinium salts (6.1; $X = FeCl_4$, $FeCl_4$.o-phenanthroline, picrate) gave ferrocene together with iron (II) and iron (III) salts while decomposition of the tetraphenylborate (6.1; $X = BPh_4$) gave only ferrocene. The mechanistic implications of these reactions were considered[81].



6.1

7. FERROCENYL CARBENIUM IONS

The α-ferrocenylcarbenium ions (7.1; R^1 = H, Me; R^2 = H, Me, Et) were formed in sulphuric acid and investigated by ^{13}C NMR spectroscopy. Carbon shifts and C-H coupling constants suggested that charge was delocalized into the ferrocenyl group[82]. In the α-ferrocenylcarbenium ions (7.2; R = H, Me, Et), the protons on the methylene group adjacent to the positive centre were magnetically nonequivalent and a similar nonequivalence was observed for the hydrogen atoms bonded to C-2 and C-5 and for C-3 and C-4. The results were explained in terms of conformational effects[83]. The ^{13}C NMR spectra of several ferrocenyl alkanes, ketones and alcohols (7.3; R = H, Me, CH_2OH, CHMeOH, $CHOHCHMe_2$, $CHOHCMe_3$, CMe_2OH, $CMeOH.CHMe_2$, $CMeOH.CMe_3$, COMe, $COCMe_3$; 7.4; R = Me, COMe) have been recorded. The ^{13}C chemical shifts and the associated CH coupling constants have been assigned. The spectra of the α-ferrocenylcarbenium ions (7.5; R^1 = H, Me; R^2 = H, Me, $CHMe_2$, CMe_3) were measured in CF_3CO_2D and some previous chemical shift assignments were corrected. The



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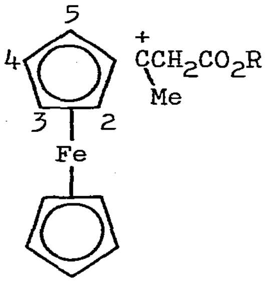

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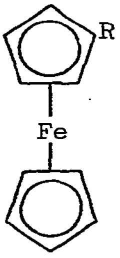
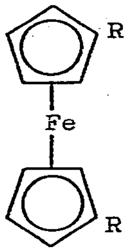


7.3

effect of alkyl substitution at the α-carbon was discussed in detail and the results were interpreted in terms of a fulvene structure (7.6) for the cation with half the positive charge residing on the iron atom and the other half distributed uniformly over the eleven carbon atoms of the ligands[84].



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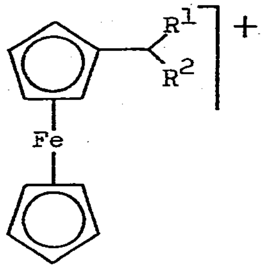

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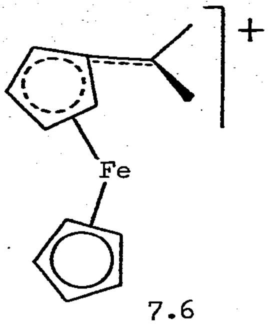
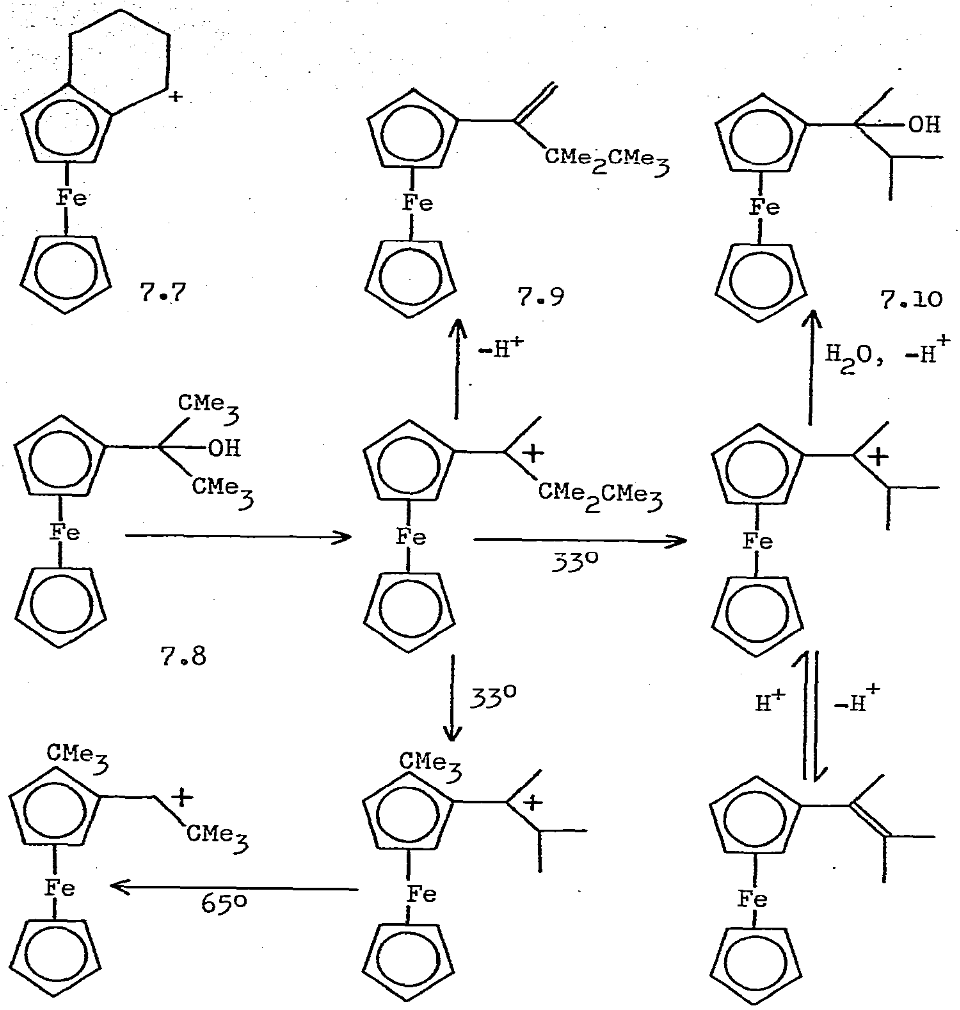


7.6

The formation of the α-ferrocenylcarbenium ions (7.5; R^1 = H, Me, R^2 = H, Ph, $C_{10}H_9Fe$) and (7.7) has been reported. The stabilities of the cations were determined by measuring pK_{R+} values in aqueous perchloric acid-dioxan mixtures and the diferrocenylphenylcarbenium ion was found to be more stable than the diphenylferrocenylcarbenium ion by a factor of $3pK_{R+}$ units. The reactions of the carbenium ions with nucleophilic reagents such as water, amines and cyanide ions were studied. Yields were measured and the stereochemistry of the reactions determined[85]. Watts and Abram[86] have reinvestigated the work of Hon and Tidwell[87], on the behaviour of highly substituted (1-hydroxyalkyl)ferrocenes in acidic media, and obtained results similar to those reported earlier. An ^1H NMR investigation of the behaviour of the alcohol (7.8) was carried out in trifluoroacetic acid when the alkene (7.9) and the alcohol (7.10) were obtained as the main products.

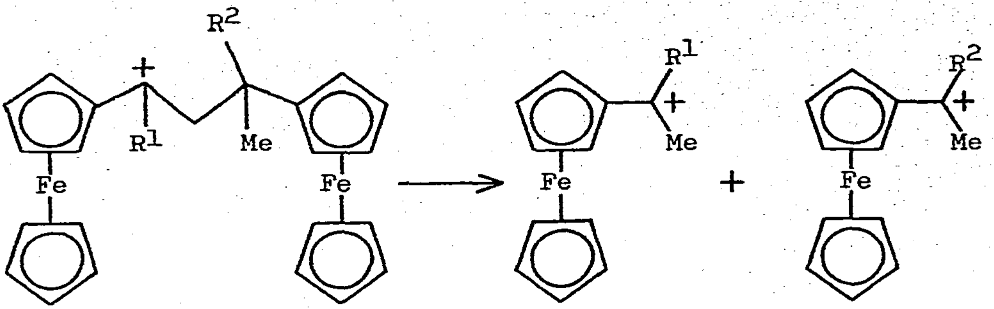
7.7



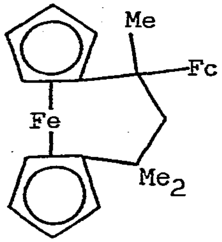
SCHEME 7.1

The reaction pathways suggested are shown in Scheme 7.1.

Ferrocenylcarbenium ions (7.11; $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = R^2 = Me$) fragment immediately and quantitatively in trifluoroacetic acid to give the corresponding cations (7.12 and 7.13). The bridged ferrocenes (7.14 and 7.15) dissolved in trifluoroacetic acid to give FcC^+Me_2 as the only observable species. These reactions were conveniently monitored by ^1H NMR spectroscopy[88]. The protonation of



7.11 7.12 7.13



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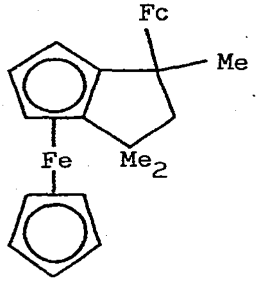

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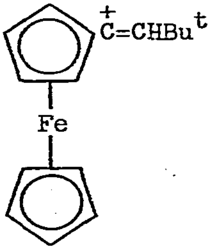
t-butylethynylferrocene generated the vinyl cation (7.16) and this was converted relatively slowly in CF_3CO_2H to the addition product (7.17). Steric rather than electronic



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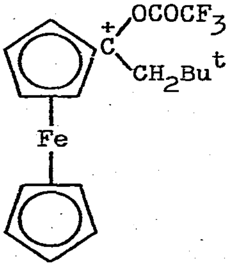

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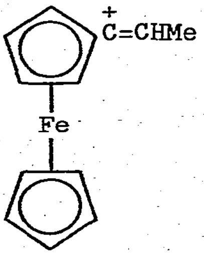
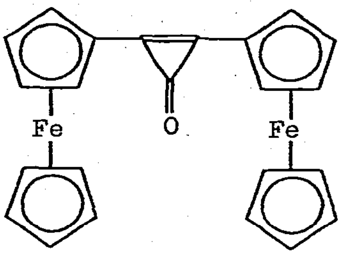


7.18

effects were shown to be important in determining the rate of collapse of ferrocenylvinyl cations as the cation (7.18) had a much shorter lifetime[89]. Treatment of $C_3Cl_3^+AlCl_4^-$ with two moles of ferrocene in methylene dichloride at -70° gave diferrocenylcyclopropenone (7.19) while three moles of ferrocene gave the triferrocenylcyclopropenium cation as the



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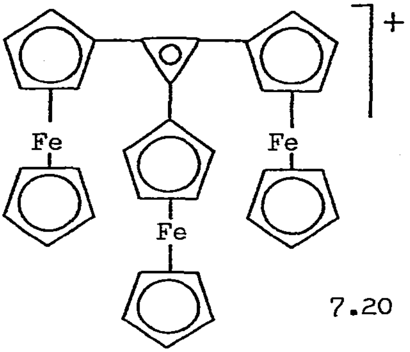


7.20

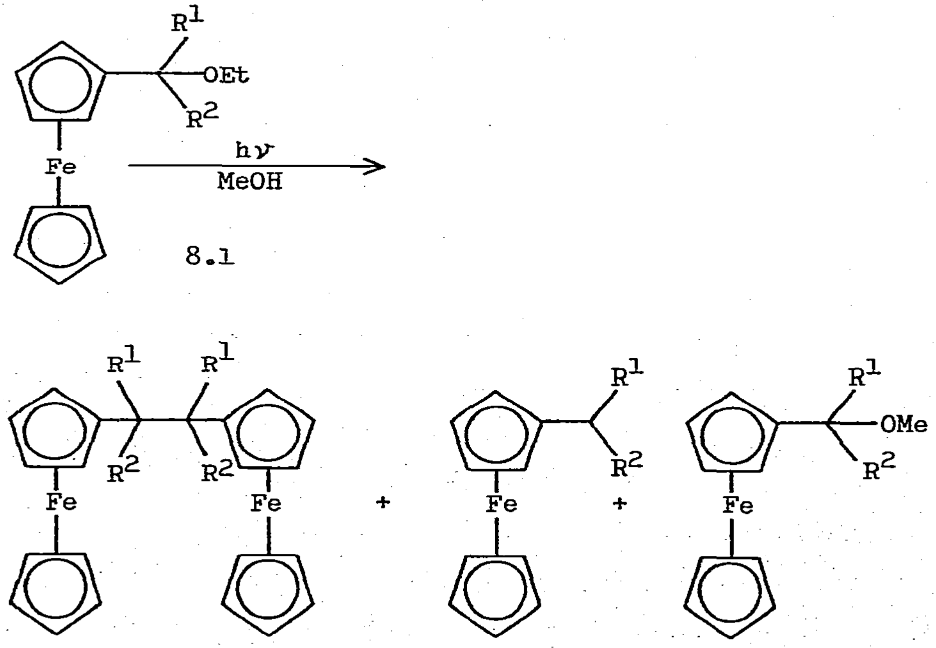
perchlorate (7.20). The high pK_{R+}, >10 indicated effective aromatic stabilization of the cyclopropenium ring by the ferrocenyl groups[90].

8. FERROCENE CHEMISTRY

(i) Photochemistry

The photolysis of ferrocene in carbon tetrachloride was examined in the presence and absence of a free radical scavenger. Ferricinium chloride and ferricinium tetrachloroferrate were isolated[91,92]. The photochemistry of ferrocene carboxylic acid and ferrocene-1,1'-dicarboxylic acid was examined in deoxygenated hydroxylic solvents. Photooxidation only occurred on irradiation within the intramolecular charge--transfer bands at 265nm[93]. The quantum yields of decomposition were measured for the photolysis of ferrocene, the ferricinium cation and several other organometallic molecules. It was found that the '18 electron' species were photostable whilst those that contained unpaired electrons were not[94]. The photochemical reactions of the ferrocenyl-ethers (8.1; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$, $R^1 = R^2 = Me$; $R^1 = Ph$, $R^2 = H$; $R^1 = Ph$, $R^2 = Me$; $R^1 = R^2 = Ph$) were investigated. The optimum conditions for the formation of the products (8.2 and 8.3) were found to require vanadium (II) sulphate, purified nitrogen and sodium carbonate as the acid scavenger. There was a decrease in the amount of radical dimerization as the bulk of the substituent increased[95].

A series of ferrocene-aldimines and -ketimines was irradiated in the presence of benzophenone as the sensitizer.



8.1

8.2

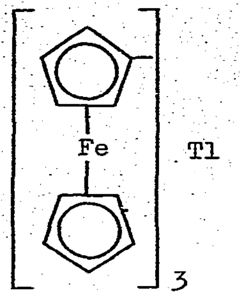
8.3

Photochemical hydrolysis occurred to give the corresponding ferrocene-carbaldehydes or -ketones. The possible mechanisms of aldehyde or ketone formation were discussed[96]. The treatment of ferrocene with lithium chloride in acetone gave a photosensitive adduct $(\eta\text{-}C_5H_5)_2Fe.LiCl$ which was characterized by infrared spectroscopy. Ultraviolet irradiation of the adduct in acetone gave chlorocomplexes of Fe (III) together with some ferricinium ion[97]. A photosensitive complex was formed between ferrocene and lithium chloride in acetone and it gave iron (II) salts on photolysis. Iron (III) complexes were formed by subsequent thermal reactions[98]. Laser photolysis was used to investigate the quenching by ferrocene of triplet states of various energies in organic compounds. Those triplet states with energies in the range 15000-24000 cm^{-1} were quenched efficiently, $k_Q = (6 \pm 1) \times 10^9$ $mole^{-1}$ sec^{-1}, while those with energies less than 14000 cm^{-1} were quenched less effectively[99]. Herkstroeter has used a series of seventeen sensitizers, with triplet energies in the range 23 to 43 kcal mol^{-1}, to measure the rate of energy transfer to ferrocene using flash kinetic spectrophotometry. The triplet energy of ferrocene fell between 38 and 41 kcal mol^{-1}. However, reasonably efficient energy transfer to ferrocene occurred from sensitizers with energies appreciably less than 38 kcal mol^{-1} indicating that the geometry of the ferrocene triplet state changed during energy transfer[100].

Flash photolysis has been used to examine the quenching of the methylene blue triplet state by ferrocene in ethanol. The rate of quenching was diffusion controlled and involved electron transfer from ferrocene to the lower lying triplet of methylene blue[101]. The quenching of biacetyl phosphorescence by ferrocene was studied. The Stern-Volmer constants were 2.8×10^6, 3.1×10^6 and 5.8×10^6 l mol^{-1} in cyclohexane, chloroform and carbon tetrachloride respectively. The relative bimolecular rate constants for the energy transfer were not affected by the solvent and they were independent of the diffusion rate constants in these solvents. The phosphorescence quenching involved an energy transfer from the lower energy triplet of biacetyl to the lowest energy triplet of ferrocene[102]. Ferrocene, ruthenocene, osmocene and cobalticinium perchlorate were used as quenchers of electronically excited benzil and ruthenium-$(2,2'\text{-bipyridine})_3^{2+}$. For all the quenchers studied the quenching obeyed Stern-Volmer kinetics and it was found that the best quenchers had the lowest absorption maxima[103]. Wilkinson has observed a correlation between the energy levels in quenchers and plots of the quenching rate constants against the energies of organic triplet states. Ferrocene and octahedral iron (III) complexes were used as the quenching agents for the triplet states in a range of organic compounds. Quenching took place by electronic energy transfer. This process, as well as the production of ligand field excited states was discussed[104].

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

Ferrocenyllithium was treated with thallium (I) chloride and then iodoferrocene to give tri(ferrocenyl)thallium (8.4) which on hydrolysis gave the thallium oxide (8.5) and ferrocene. Di(ferrocenyl)butylthallium (8.6) was prepared in the same way and was hydrolysed to the thallium oxide (8.7)[105]. The



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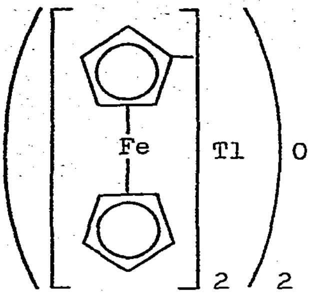

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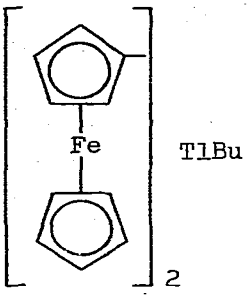
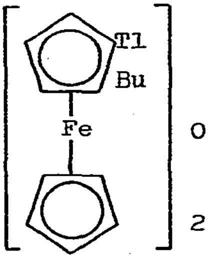


8.6

ferrocenylsilicenium ion (8.9) has been generated by treatment of ferrocenyldiphenylsilane (8.8; R = H) with triphenylcarbenium perchlorate in methylene chloride at -60°. The silicenium ion was trapped as the deuterio derivative (8.8; R = D) by the addition of $NaBD_4$[106]. Lithium ferrocenylacetylide was treated with trialkylchlorosilanes and dialkyldichlorosilanes to give the silylethynylferrocenes (8.10 and 8.11; R = Me, Ph) respectively. Hydrogenation of these compounds gave the corresponding silylethylferrocenes[107].



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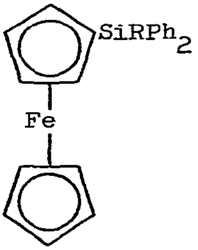

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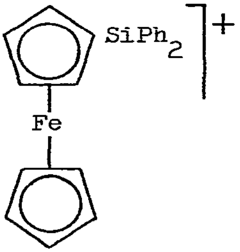
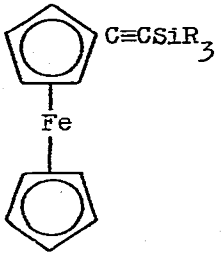


8.9

The treatment of FcC≡CLi with R_3GeCl and R_2GeCl_2 gave the ferrocenylgermylacetylenes (8.12; R = Me, Et, Ph) and (8.13; R = Me, Et, Ph) respectively. These acetylenes were hydrogenated in the presence of Raney nickel to give $FcCH_2CH_2GeR_3$

and $(FcCH_2CH_2)_2GeR_2$[109]. The hydrosilylation of ferrocenylacetylene was investigated. The order of reactivity of the silanes was $FcSiHMePh > Et_3SiH > Ph_3SiH$ and with Ph_3SiH only the trans isomer $FcCH{=}CHSiPh_3$ was isolated whilst Et_3SiH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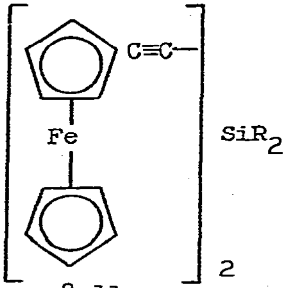
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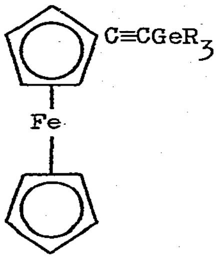
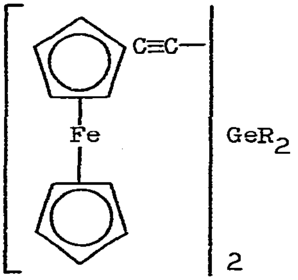

8.12

gave both $FcCH{=}CHSiEt_3$ and $FcC(SiEt_3){=}CH_2$. Hydrogenation of the latter reaction mixture over $Pd/CaCO_3$ gave $FcCH_2CH_2SiEt_3$ and $FcCHMeSiEt_3$[108]. Diferrocenyldicymantrenyltin (8.14)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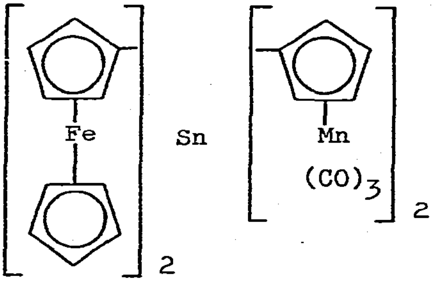
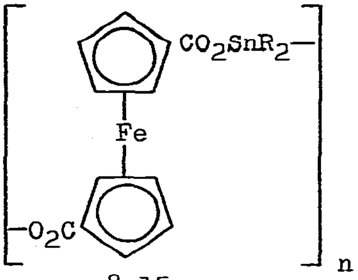

8.14

was obtained by treating cymantrenyllithium with diferrocenyltin dichloride, diferrocenyldiphenyltin was prepared in the same way. These compounds were cleaved by mercury (II) chloride to ferrocenylmercurichloride and cymantrenylmercurichloride[110]. Polymeric organotin esters of ferrocenecarboxylates with the idealized structure (8.15) were obtained by interfacial condensation of disodium 1,1'-ferrocenedicarboxylate with organotin dihalides R_2SnCl_2. The yield of polymer decreased in the order of alkyl substituents on tin: R = Me > Et > Bu ~ Octyl. Higher yields were obtained with phenyl- rather than benzyl-tin chlorides. The yield also decreased with decreasing size of halogen in the tin compound R_2SnX_2 in the order: X = I > Br > Cl[111].

The conversion of diferrocenylphenylphosphine oxide to the di(hydroxymethylferrocene) compound (8.16) has been described. The synthesis involved acetylation to the diacetyl derivative, oxidation to the dicarboxylic acid, esterification and then reduction to the product (8.16)[112].



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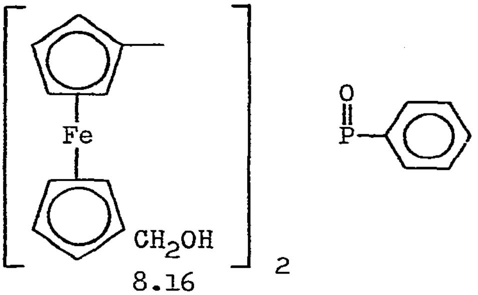
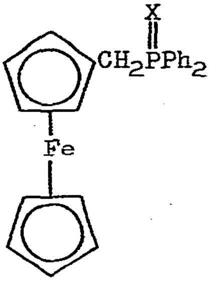


8.16

Triferrocenylphosphine oxide has been formed by the direct oxidation of triferrocenylphosphine with manganese dioxide or potassium permanganate. Oxidation with oxygen over alumina was much less effective. Triferrocenylphosphine oxide gave a 1 : 1 adduct with mercury (II) chloride[113]. The oxidation of diferrocenylphosphine oxide with potassium permanganate or oxygen in the presence of alumina gave $Fc_2P(O)OH$, and treatment with sulphur in benzene gave $Fc_2P(S)OH$. Treatment of $Fc_2P(O)H$

and $Fc_2P(S)OH$ with phosphorus (V) chloride gave $Fc_2P(O)Cl$ and $Fc_2P(S)Cl$ respectively[114]. The treatment of (ferrocenylmethyl)diphenylphosphine with hydrogen peroxide or sulphur gave the corresponding oxide (8.17; X = O) and sulphide (8.17; X = S). When the oxide (8.17; X = O) was treated with two mole equivalents of n-butyllithium lithiation occurred on the α-carbon atom and condensation of the lithiated intermediate with electrophiles gave both mono- and di-α-substituted derivatives. Similar treatment of the sulphide (8.17; X = S) with n-butyllithium followed by an electrophile gave only mono-α-substituted ferrocenes[115]. Water soluble, alkali metal salts of thiophospinates containing ferrocene were obtained by treating the appropriate diferrocenylphosphine oxide with an excess of sulphur in boiling benzene and then neutralizing the resultant diferrocenylthiophosphinic acid to the salt[116].



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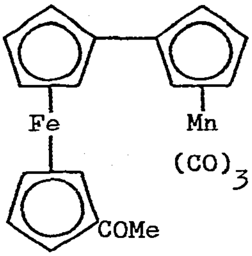
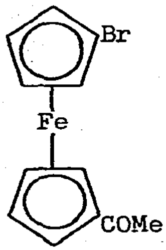


8.18

The acetylation of cymantrenylferrocene with acetic anhydride in the presence of phosphoric acid gave 1'-acetyl-1-cymantrenylferrocene (8.18). The treatment of the bromo-ferrocene (8.19) with cymantrenylsilver also gave the acetyl-ferrocene (8.18). The lithiation of cymantrenylferrocene with n-BuLi followed by tri(n-butyl)borate gave the boronic acid (8.20)^{117}. The reaction of acetylferrocene with methyl-



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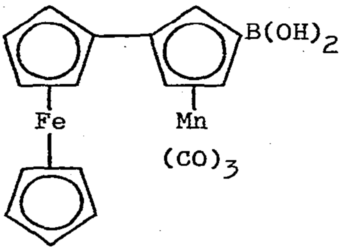

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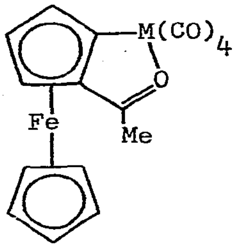
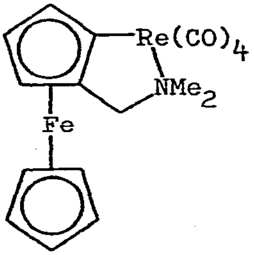


8.21

pentacarbonyl-rhenium and -manganese gave the homoannular metallation products (8.21; M = Re) and (8.21; M = Mn) respectively. Methylpentacarbonyl-rhenium with dimethylaminomethylferrocene gave the homoannular metallation product (8.22). With methylpentacarbonylmanganese a methyl group on the nitrogen was metallated to give the complex (8.23)^{118}. The treatment



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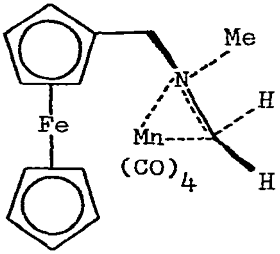
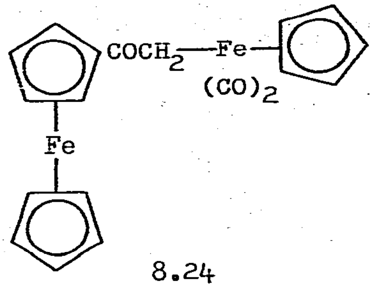


8.23

of sodium (η-cyclopentadienyl)-dicarbonyliron with ferrocenoylmethylchloride gave the σ-bonded complex (8.24). The σ-bond was cleaved by iodine to give the complex (8.25; R = I) and ferrocenoylmethyliodide in good yields. The bond was also cleaved by $LiAlH_4$, phenyllithium and (η-lithiocyclopentadienyl)-

tricarbonylmanganese to give bis(η-cyclopentadienyldicarbonyliron), the complex (8.25; R = Ph) and the manganese tricarbonyl derivative [8.25; R = (η-C_5H_4)Mn$(CO)_3$] respectively[119].



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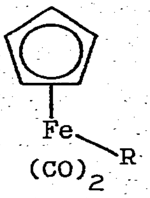
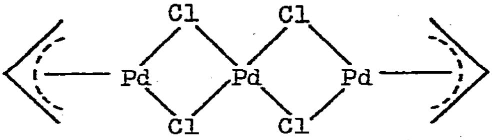


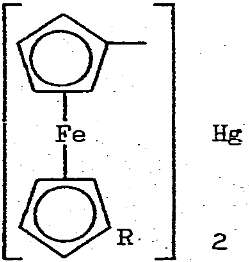
8.25

The reaction of ferricinium trichloropalladate with allyl chloride or bis(η-allylpalladium chloride) gave the palladium complex (8.26)[120]. The diferrocenylmercury compounds (8.27;



8.26

R = Cl, Br, OMe, CO_2Me) were treated with $MeAuPPh_3$ and fluoroboric acid to form the ferrocenylgold salts (8.28; R = Cl, Br, OMe, CO_2Me) and these were converted by sodium



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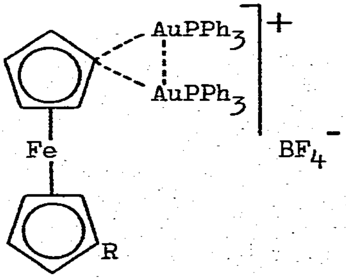

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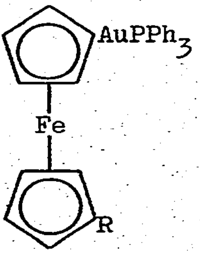
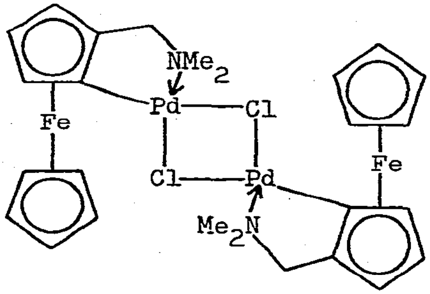


8.29

chloride to the neutral ferrocenylgold compounds (8.29; R = Cl, Br, OMe, CO_2Me)[121].

8. (iii) Complexes of ferrocene-containing ligands

Gaunt and Shaw have examined the internal metallation of [(dimethylamino)methyl]ferrocene with sodium chloropalladate (II) to give the binuclear complex (8.30) which was converted to the mononuclear complex (8.31) with thallium (I) acetylacetonate[122]. [(N,N-Dimethylamino)methyl]ferrocene (DAMF) combined with cobalt salts in methylene dichloride to give the complexes $CoX_2.(DAMF)_2$, where X = Cl, Br, I, NCS. The salts $DAMFH^+X^-$, where X = Br, I, ClO_4, NO_3 HSO_4, were formed by carrying out the same reaction in ethanol[123]. 1-[(Dimethylamino)methyl]-2-(diphenylphosphino)ferrocene was shown to behave as a bidentate ligand with the Group VIB metal carbonyls. However with pentacarbonyliron and cobalt carbonyl it behaved as a monodentate ligand with the phosphorus acting as the electron donor. The electrochemistry of the Group VIB metal carbonyl complexes was investigated and for the chromium complex (8.32) the cyclic voltammogram consisted of two reversible one electron redox waves and a third irreversible



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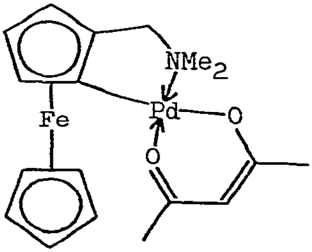
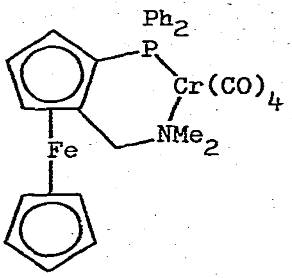


8.31

wave. It was concluded that the first redox wave represented the process $Cr^{0} \longrightarrow Cr^{+}$, the second $Fe^{2+} \longrightarrow Fe^{3+}$ and the third to further chromium oxidation $Cr^{+} \longrightarrow Cr^{n+}$ with concomitant destruction of the complex[124]. The reaction of β-benzoylvinylferrocene with $Fe_2(CO)_9$ gave $(FcCH{=}CHCOPh)Fe(CO)_4$, similarly cinnamoylferrocene gave $(FcCOCH{=}CHPh)Fe(CO)_4$.



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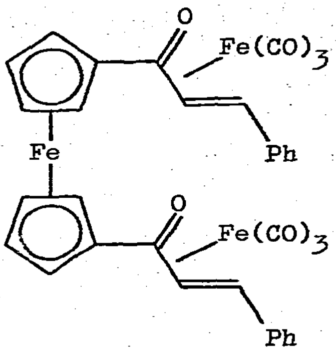
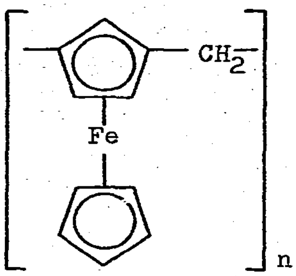


8.33

The treatment of 1,1'-dicinnamoylferrocene with $Fe_3(CO)_{12}$ gave the iron tricarbonyl complex (8.33)[125].

8. (iv) General chemistry

Poly(methyleneferrocenylene) (8.34) was treated with diazotised p-nitroaniline and arylation occurred in both the substituted and unsubstituted cyclopentadienyl rings. The nitro group was reduced to $-NH_2$ by tin (II) chloride[126]. Methylferrocene was oxidized to ferrocenecarboxylic acid by treatment with potassium t-butyloxide in $(Me_2N)_3PO$ followed by hydrochloric acid. Similar treatment of 1,1'-dimethylferrocene gave 1'-methylferrocenecarboxylic acid[127]. t-Butylferrocene has been prepared in good yield by the treatment of acetylferrocene with methylmagnesium in toluene[128].



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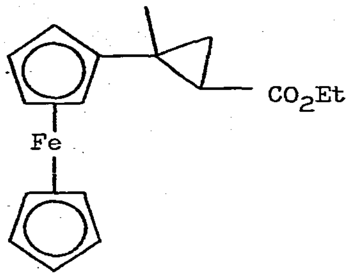
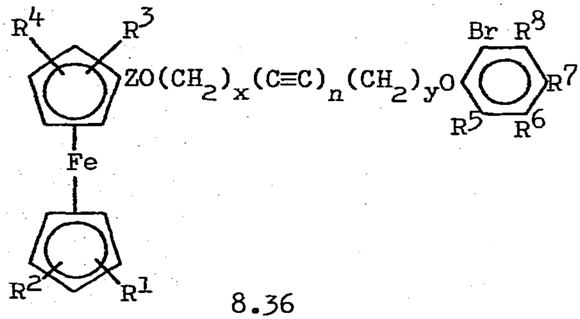


8.35

2-Ferrocenylpropene was treated with ethyl diazoic ester to give stereoisomeric esters of the trisubstituted cyclopropane (8.35). The esters were separated by chromatography and were converted into the corresponding carboxylic acids, methyl esters and alcohols[129]. Diazonium salts from o-, m-, and p-nitroanilines were stirred with 1,1'-diethylferrocene to give the corresponding heteroannular di(nitrophenyl)-1,1'-diethylferrocene derivatives. The nitro groups were subsequently reduced to form the amines[130].

The preparation of the ferrocene derivatives (8.36; Z =



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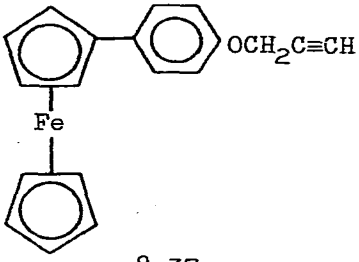
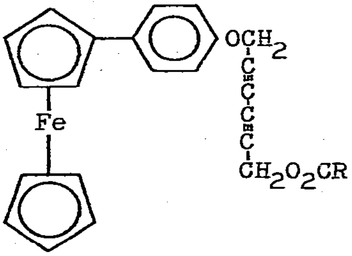


8.37

arylene; R^1 = H, alkyl, R^2 = H, aryl, aryloxy; R^3 = H, dialkylaminomethyl; R^4 = H, halo, substituted alkyl, x = 1-4, n =y=1,2; R^5 = H, Br, I; R^6, R^7 = H, iodo; R^8 = I, Br) has been reported[131]. The p-ferrocenylphenylacetylene (8.37) was condensed with $RCO_2CH_2C{\equiv}CH$ in the presence of copper (II) acetate to give the diacetylenes (8.38) which were cyclized with sodium hydrogen sulphide to the ferrocene containing fatty acid derivatives (8.39; R = $C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$)[132]. The diacetylenes (8.40; n = 1, X = 2-Cl;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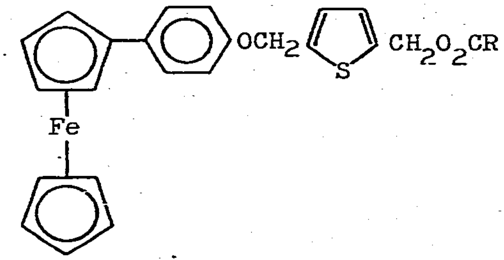
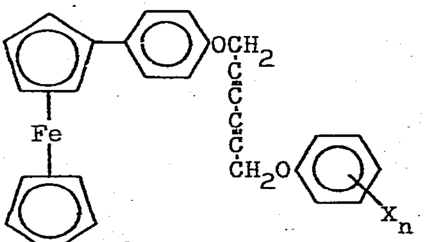

8.39

n = 2, X = 2,4-Cl_2; n = 3, X = 2,4,5-Cl_3, 2,4,6-Cl_3) were cyclized with hydrogen sulphide or sodium hydrogen sulphide in base to give the thiophens (8.41)[133].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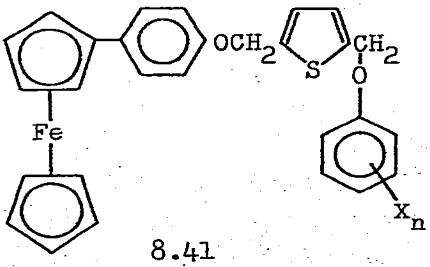
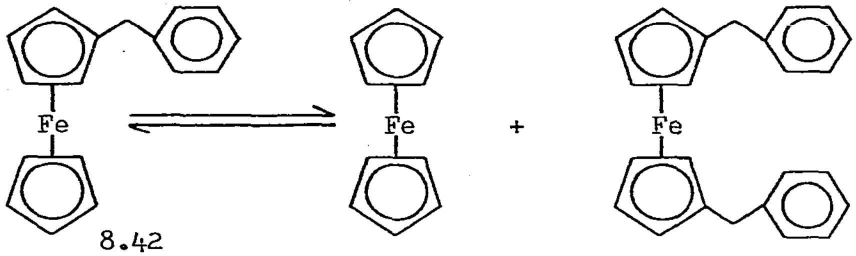

8.41

Astruc and Dabard have observed three types of ligand exchange on heating benzylferrocene (8.42) with aluminium powder and aluminium chloride in benzene. Disproportionation by exchange of cyclopentadienyl groups gave ferrocene and 1,1'-dibenzylferrocene (8.43), replacement of cyclopentadienyl by benzene gave the cations (8.44 and 8.45) while auto-condensation produced the binuclear cations (8.46 and 8.47). Alkylation of ferrocenes with protonated cyclopentadienyl groups to give cyclopentylene ferrocenes was also observed[134].



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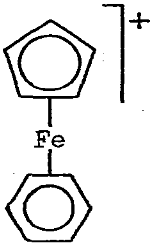

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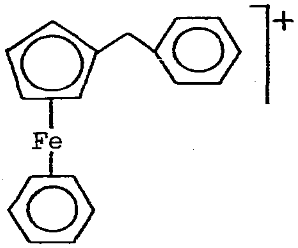

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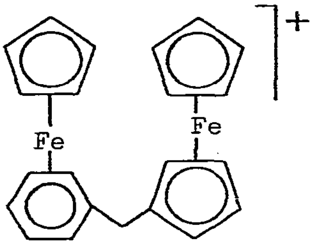

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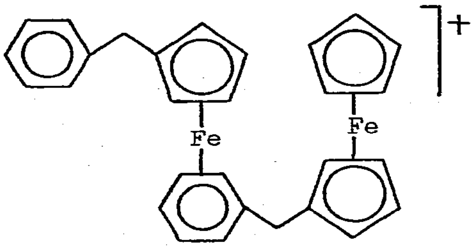

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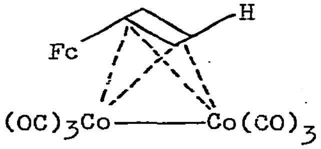
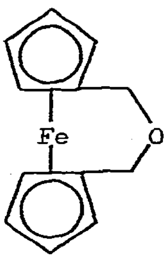
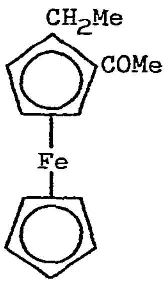


8.43

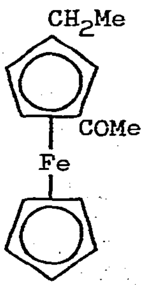
Ethynylferrocene oligomerized in the presence of $(PPh_3)_2Ni(CO)_2$ and its polymer-anchored analogue to give the linear dimer FcCH=CHC≡CFc, the linear trimer FcCH=CHC(=CHFc)C≡CFc and 1,2,4-triferrocenylbenzene. As the crosslink density of the anchored catalyst increased the rate of oligomerization decreased but product distribution was unaltered. The treatment of ethynylferrocene with one equivalent of $Co_2(CO)_8$ at 25° gave the complex (8.48). Reaction of ethynylferrocene with trans-$(PPh_3)_2IrCl(CO)$ gave the two linear oligomers together with the six coordinate complex $CO(Cl)(FcC{\equiv}C)H(PPh_3)_2Ir$. This complex underwent facile elimination to give the starting materials[135]. The ether linkage of the ferrocenylmethyl-ether (8.49) was cleaved by lithium in tetrahydrofuran[136]. The treatment of benzoylferrocene with $(CH_2CO_2)Li_2$ (prepared from lithium naphthylide and acetic acid) gave $FcC(OH)PhCH_2CO_2H$ which was dehydrated and decarboxylated by sulphuric acid to give $FcCPh{=}CH_2$. Similarly acetylferrocene gave $FcCMe{=}CH_2$ at pH∼6 and $FcCMe{=}CHCO_2H$ at pH∼1[137]. The acetylation of ethylferrocene has been reexamined in order to optimise homoannular substitution. When the



8.49



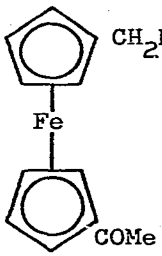
8.50



8.51

reaction was carried out at -5° over seven hours using an equimolar mixture of ethylferrocene, acetyl chloride and aluminium chloride and adding the ethylferrocene to the acetylation mixture, the 2-acetylferrocene (8.50) was obtained in 20% yield and the 3-acetylferrocene (8.51) in 56% yield, together with 23.5% of the heteroannular isomer (8.52). The 1,2-isomer (8.50) was removed by thin layer chromatography and the mixture of isomers (8.51 and 8.52) oxidized to the respective diacetyl compounds with manganese dioxide. 1,3-Diacetylferrocene was isolated from the product mixture by thin-layer chromatography[138].

The thermal decomposition of 1,1'-diacetylferrocene at 520° gave hydrogen, methane, ethane and ethylene together with minor products. When the surface area of the furnace was increased by packing, the yields of the principal pyrolysis products were reduced. The addition of cyclopentadiene was effective in reducing the yield of methane. Parallel results were obtained by the pyrolysis of ethylferrocene although ethane was the main product in this case[139]. Acetylferrocene was reduced almost quantitatively to 2,3-diferrocenyl-2,3-butanediol (8.53) by constant current electrolysis in aqueous-



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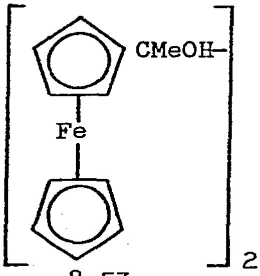

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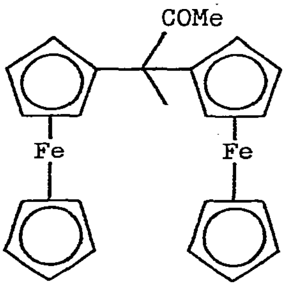
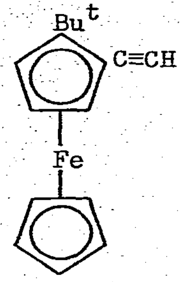


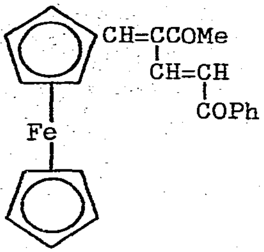
8.54

-ethanolic sodium hydroxide at the decomposition potential of sodium amalgam. The diol (8.53) was oxidized easily to acetylferrocene and in the presence of acid it quantitatively rearranged to give 2,2-diferrocenylbutane-3-one (8.54). When heated with acetic anhydride it dehydrated to give 2,3-diferrocenyl-1,3-butadiene[140]. The reaction of carboxy-, methoxycarbonyl-, carbamoyl- and 1,1'-diacetyl-ferrocene with $^{103}RuCl_3$ gave the corresponding ruthenocene-^{103}Ru derivatives. The ferrocene derivatives were also treated with $^{59}FeCl_3$ and $^{191}OsCl_4$ to give the corresponding ferrocene-^{59}Fe and osmocene-^{191}Os compounds[141]. Acetylferrocene was converted to vinylferrocene by heating with alumina in isopropanol[142]. The reaction of acetylferrocenes, containing a bulky 2-alkyl substituent, with isopropylmagnesium bromide gave enolate salts which were converted into ethynylferrocenes by a thermally induced elimination. For example, 2-acetyl-t-butylferrocene gave the alkyne (8.54a)[143].

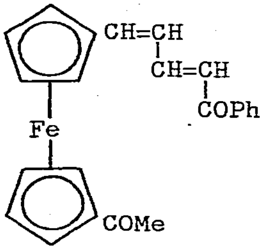
1,1'-Diacetylferrocene was converted to a mixture of the mono- and di-hydrazones by heating with 2,4-dinitrophenylhydrazine[144]. The reaction between diazonium salts and acetyl-, 1,1'-diacetylferrocene, formylferrocene and 1-ferrocenyl-2-phenylethylene was examined. The major products were arylferrocenes and coupled fulvenes with the proportions of these products dependent on the nature of the diazonium salt[145]. The Friedel-Crafts acetylation of 5-ferrocenyl-1-phenyl-2,4-pentadien-1-one and 5-ferrocenyl-1-phenyl-1,4-pentadien-3-one was investigated. Acetylation took place on the unsubstituted cyclopentadienyl ring as well as the double bond of the chalcones to give the compounds (8.55 and



8.54a

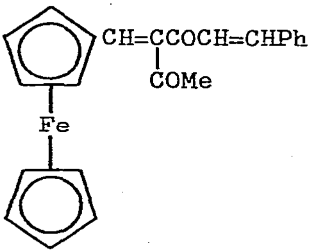


8.55



8.56

8.56) and (8.57 and 8.58) respectively together with some diacetylated product. In the light of these results the Friedel-Crafts acetylation of the chalcone (8.59) was



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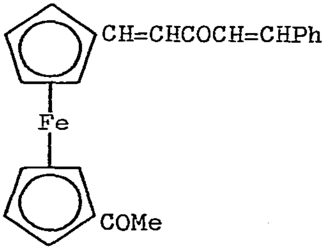
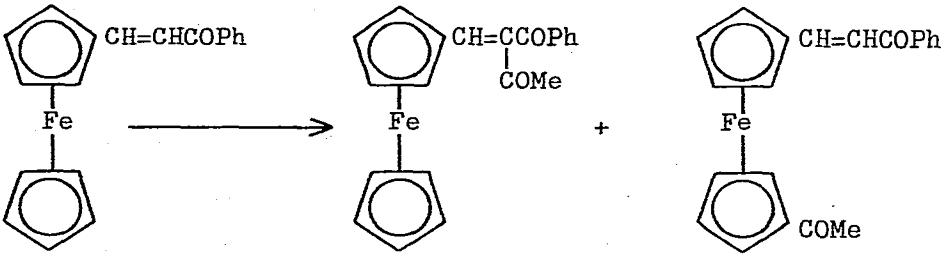


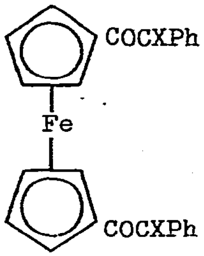
8.58

reinvestigated and two monoacetylated products (8.60 and 8.61) were isolated[145] and not the 2-substituted product previously reported[146].



8.59 8.60 8.61

The bis(phenylacetyl)ferrocene (8.62; X = H_2) was oxidized to the ketone (8.62; X = O) by heating it to reflux with *p*-nitroso-N,N-diethylaniline[147]. The α,β-unsaturated acylferrocenes (8.63; R = H, *m*-, *p*-NH_2, *p*-NMe_2, *p*-OMe, *p*-, *o*-F, *p*-Cl, *p*-Br) were reduced to the corresponding secondary alcohols (8.64; R = H, *m*-, *p*-NH_2, *p*-NMe_2, *p*-OMe, *p*-, *o*-F, *p*-Cl, *p*-Br) with lithium aluminium hydride[148]. Formylferrocene was condensed with secondary amines and $Me_2C(OH)CN$ to give the nitriles [8.65; R = NH_2, NMe_2, NEt_2, $N(OEt)_2$, piperidino, morpholino]. The vinylferrocenes (8.66; R = piperidino, morpholino) were prepared in the same way[149]. The reaction of thiols RSH with $FcCO(CH_2)_nCl$ gave a series of ferrocenyl-thiols $FcCO(CH_2)_nSR$(R = Ph, Me_2CH, 2-thienyl, Et, *p*-ClC_6H_4) which were oxidized with a per-acid to give the corresponding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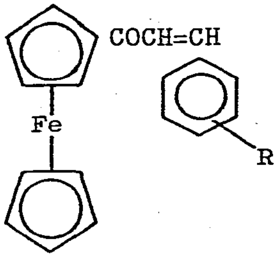
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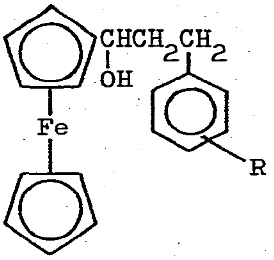
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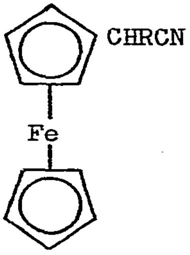
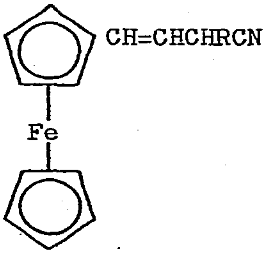

8.65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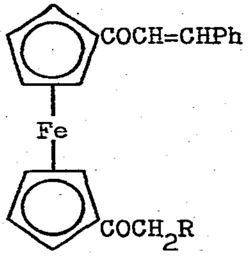
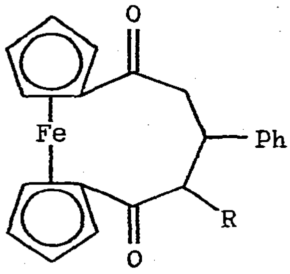

8.67

sulphoxides[150]. In sulphuric-acetic acid mixtures the cinnamoylferrocenes (8.67; R = Me, Ph, 3-FC_6H_4, 4-FC_6H_4, 3-MeC_6H_4 and 3-$MeOC_6H_4$) were converted to a mixture of erythro- and threo-2-substituted 3-phenyl[5]ferrocenophane-1,5-diones (8.68)[151].



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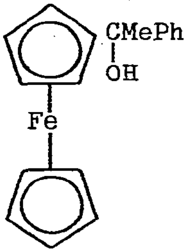

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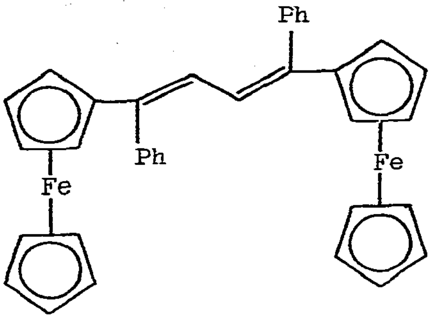
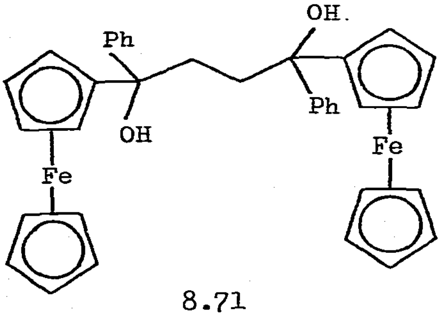
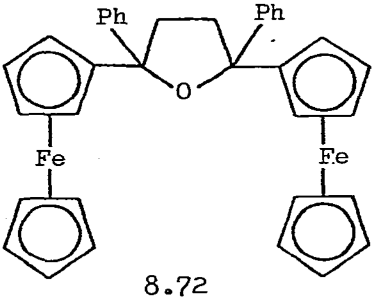


8.70

The hydroxyalkylferrocene (8.69) was oxidatively dimerized with oxygen in hexane containing SiO_2 or Al_2O_3 to give initially a peroxide which led to the diferrocenylbutadiene (8.70), the diferrocenyldiol (8.71) and the tetrahydrofuran derivative (8.72)[152]. The ferrocenyl-alcohol (8.73; R^1 = Me, R^2 = H) was dehydrated to give the olefin (8.74) by chromatography on silica gel. The reaction was thought to proceed via an intermediate α-ferrocenyl carbenium ion.

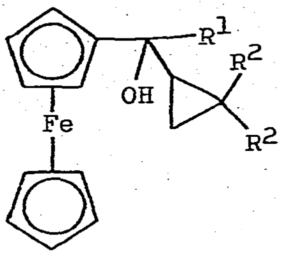


8.71

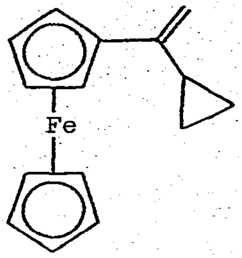


8.72

On chromatography of the alcohol (8.73; $R^1 = R^2 = Me$) ring



8.73



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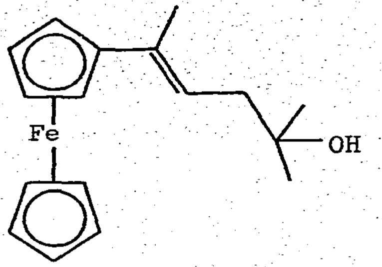
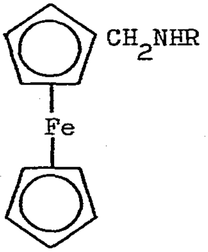


8.75

opening of the cyclopropyl moiety occurred to give the olefinic alcohol (8.75). The ring opening reaction was shown to be highly stereospecific[153].

N-substituted aminomethylferrocenes (8.76; R = Me, Et, Pr, Ph, β-naphthyl) were formed by condensation of the appropriate primary amine with formylferrocene and reduction of the resulting imine with hydrogen over palladium in ethanol[154].



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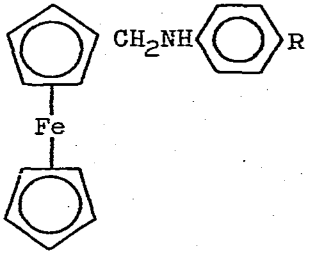

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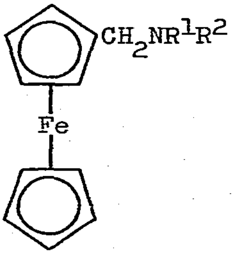
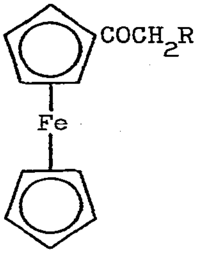


8.78

The displacement of the hydroxy-group from ferrocenylmethanol by amines has been reinvestigated. The formation of anilines (8.77) was confirmed and the reaction was extended to the preparation of the aliphatic amines [8.78; $R^1 = H$, $R^2 = Bu^t$, CH_2Ph, $CONH_2$, cyclohexyl; $R^1, R^2 = (CH_2)_5$] by the addition of acetic acid to the reaction mixture[155]. Ketones with active methylene groups (8.79; R = H, Me, Ph) were condensed with aminal esters $Me_2NCH{=}CHCH(OEt)_2$ or amidinium salts $Me_2NCR^1{=}CR^2CH{=}\overset{+}{N}Me_2\ ClO_4^-$ (R^1, R^2 = H, Me, Ph) in the presence of sodium methoxide to form the 5-(dimethylamino)pentadienones (8.80; R^1, R^2, R^3 = H, Me, Ph). The cyclization of these products to pyridines and phenylketones and their conversion to polymethinium salts was described[156]. Imines have been



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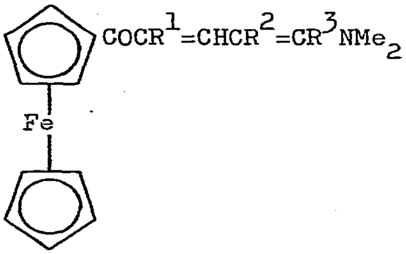
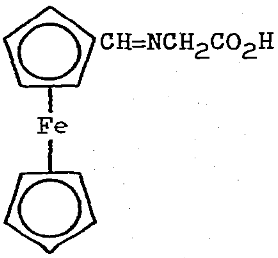


8.80

formed by the condensation of formylferrocene with α-amino acids and their esters. Seventeen imines were obtained in yields varying between 87 and 95%, a typical product was the glycine derivative (8.81)[157].

The reaction of the ferrocenyl-azomethines, FcCH=NR [R = Ph, 2, 3, 4-$C_6H_2(OH)_3$, 3-$NO_2C_6H_4$], with nitromethane in alcohol gave the olefin $FcCH{=}CHNO_2$ in good yield[158].



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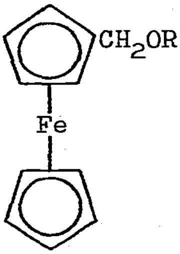

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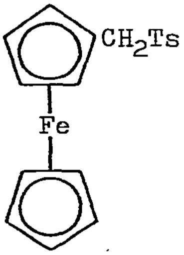
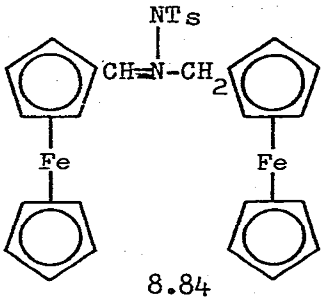


8.83

The thermal decomposition of alkali metal salts of the tosylhydrazone of ferrocenecarbaldehyde in protic solvents gave the ether (8.82) and the tosylates (8.83 and 8.84). The addition of thermally generated carboethoxycarbene to vinylferrocene gave cis- and trans-isomers of the cyclopropane (8.85)[159]. The reaction of the ferrocenyl-azomethine (8.86) with acetone in ethanol gave the ferrocenylbenzoquinoline (8.87) which readily formed a methiodide[160]. The pyrrole-ferrocene (8.89), formed by treatment of the azapentalene (8.88) with lithium in THF and then iron (II) chloride, was less stable than the isoelectronic di(η-indenyl)iron. While it was stable at low temperatures under nitrogen it decomposed in solution[161].



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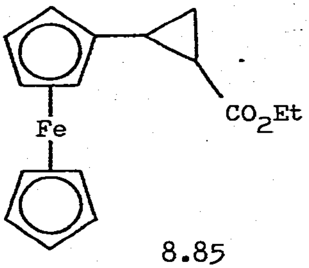

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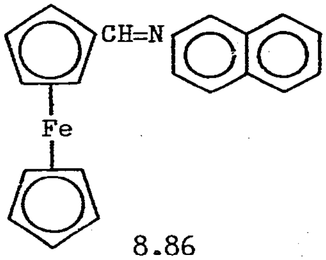

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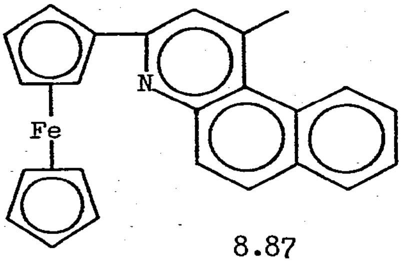
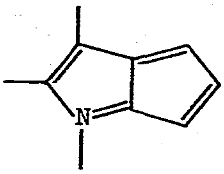


8.87

The pyrrolemethylene derivative (8.90) was prepared by condensing formylferrocene with 3,4-dimethyl-3-pyrrolin-2-one[162].



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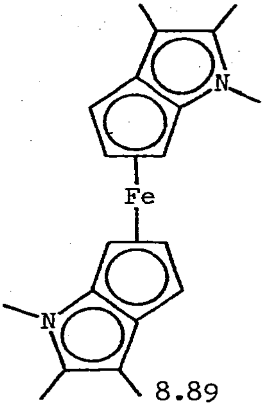

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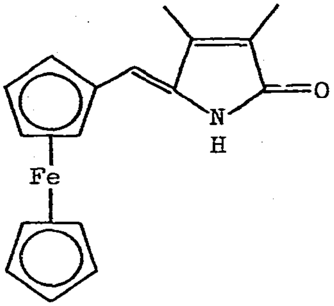
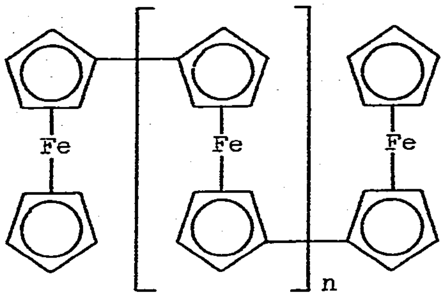


8.90

Some ferrocene derivatives of thiophene have been prepared and characterised[163]. The thermal and oxidative stability of polychlorinated ferrocenes was investigated. As the chlorine content increased the thermal stability decreased and the oxidative stability increased. This increase in oxidative stability was explained on the basis of inductive electron withdrawal from the central iron atom by the chlorine atoms. This electron withdrawal was also thought to weaken the metal to ring bond hence explaining the decrease in thermal stability. It was also thought that the metal to ring bond could be weakened by steric crowding due to an eclipsed conformation of the chlorine atoms[164].

9. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

Biferrocene and dicymantrene were formed by metallation of the parent compound with an alkali metal and treatment of the intermediate salt with copper (I) bromide in ether in the temperature range -10 to 100^{o}[165]. Chloromercuriferrocene and 1,1'-bis(chloromercuri)ferrocene were converted to a mixture of the oligomers (9.1; n = 0-4) and (9.2) by treatment with Li_2PdCl_4[166]. Acylation of biferrocene with benzoyl chloride under Friedel-Crafts conditions gave the mono- and di-benzoyl compounds (9.3 and 9.4). Reduction of these ketones with lithium aluminium hydride gave the expected secondary alcohols while the diketone (9.4) gave in addition the benzyl derivatives (9.5; R = CH_2Ph, CHOHPh)[167].



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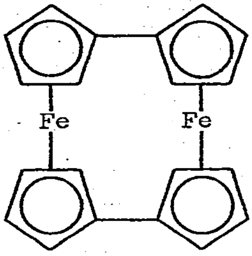

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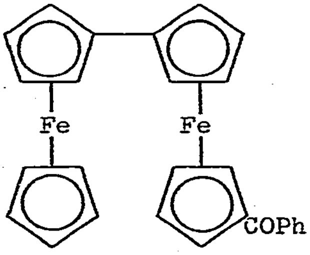

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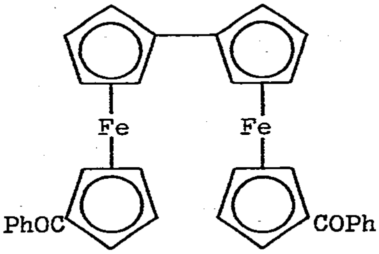
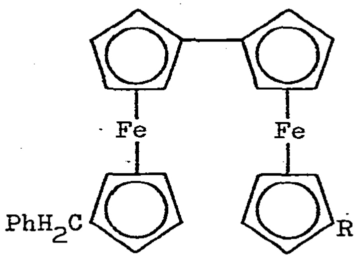


9.4

The intervalence transfer transition in the mixed-valence cations of three disubstituted biferrocenes (9.6; $R^1 = R^2 =$

Me, R^1 = Me, R^2 = CH_2OH) and (9.7; $R^1 = R^2$ = Me) was examined. The mono- and dications of the biferrocenes were generated electrochemically and their spectra were recorded in the visible



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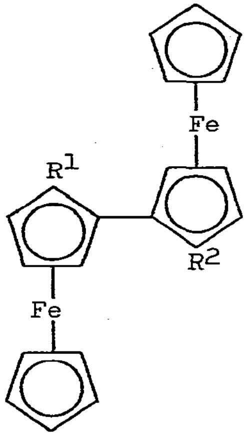
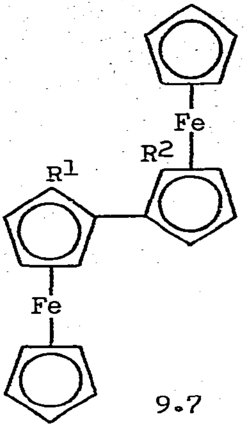


9.6

and near infrared regions. The spectral results obtained for the monocations[168] supported the predictions of a simple model for intervalence transfer transitions proposed by Hush[169]. Two distinct bands were observed in the visible spectra of the biferrocene dications. It was proposed that these bands arose from separate ligand to metal transitions from the cyclopentadienyl ligands (at lower energy) and the fulvalene ligand.

Morrison and Hendrickson have investigated intervalence electron transfer in partially oxidized biferrocene (9.8), biferrocenylene (9.9), the [1.1]ferrocenophane (9.10) and 1',1'''-diiodobiferrocene (9.11). Mixed valence and average valence species were detected in the cation (9.8) while the relatively isotropic $\underset{\sim}{g}$ tensor ($g_1 \sim 2.3$, $g_2 \sim 2.0$, $g_3 \sim 1.9$) obtained from the Moessbauer study of the biferrocenylene



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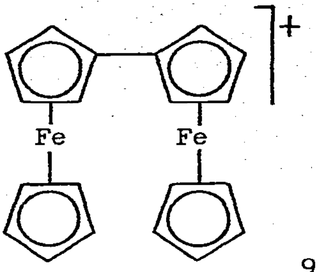

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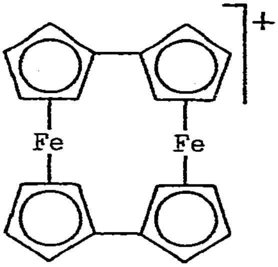
cation (9.9) was interpreted in terms of delocalization of the single unpaired electron over two iron centres (average valence). A similar interpretation was applicable to the diiodo cation (9.11). The unusual temperature dependence



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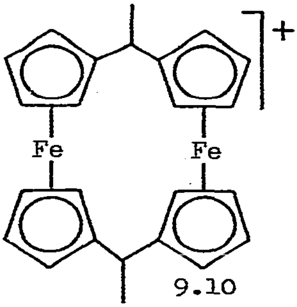

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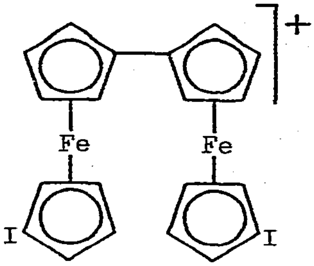
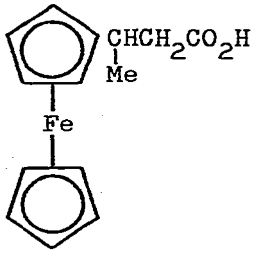


9.11

of the Moessbauer spectrum of the [1.1]ferrocenophane cation (9.10) was rationalized by invoking conversion of the inner doublet for the Fe (III) site to a magnetic spectrum at the lowest temperatures. The observed diamagnetism of the dioxidized ($Fe^{III}Fe^{III}$) form of the [1.1]ferrocenophane (9.10) was offered as evidence for direct iron-iron interaction in these complexes[170]. The oxidation state properties of biferrocene, 1,1'-terferrocene (9.1; n = 1) and 1,1'-quaterferrocene (9.1; n = 2) were investigated via electrochemical techniques. In these compounds all of the ferrocene groups were oxidizable to the ferricinium ion at distinct potentials. Partial oxidation of the polymeric compounds gave a series of discrete mixed-valence ions. The mixed-valence ions were found to exist as oxidation state isomers, for example Fc-Fc$^+$-Fc and Fc$^+$-Fc-Fc, which differed with regard to the site of oxidation. The visible and near infrared absorption spectra of the partially oxidized species were recorded and discussed[171].

The redox properties of 1,1'-polyferrocenes were studied. Electron transfer isomerism and weak metal-metal interactions in the mixed valence compounds were observed[172]. The ferrocenyl-acid (9.12) was cyclized to (α-oxo-γ-methyltrimethylene)-1,1'-ferrocene which when treated with methyllithium gave syn-and anti-(α-methyl-α-hydroxy-γ-methyltrimethylene-1,1'-ferrocenes which were reduced to give the ferrocenophanes (9.13 and 9.14). Similarly lithium aluminium hydride reduction of (α-oxo-γ-methyltrimethylene)-1,1'-ferrocene followed by treatment of the resultant alcohols with aluminium chloride and methyllithium gave the ferrocenophanes (9.13 and 9.14)[173]. A series of



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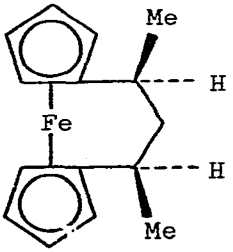

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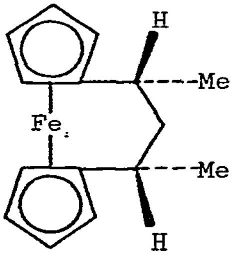
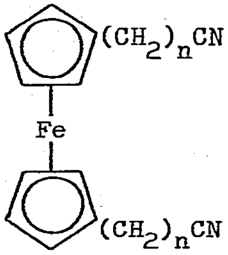


9.14

[*m*]ferrocenophanes (9.16; *m* = 3, 5, 11, 15) was prepared *via* cyclization of 1,1'-bis(ω-cyanoalkyl)ferrocenes (9.15; n = 1, 2, 5, 7) using methylmagnesium iodide and sodium *N*-methylanilide. The possible conformations of the macrocylic ferrocenophanes were discussed[174]. The cyclization of the acetylferrocenes (9.17; R = H, Me, Et, Cl) with benzaldehyde in an acetic acid to sulphuric acid mixture gave the ferrocenophanes



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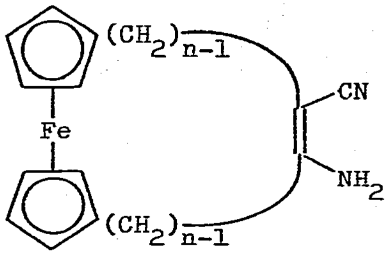
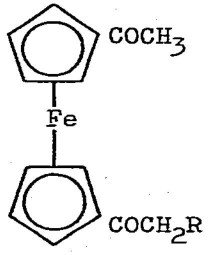


9.16

(9.18; R = H, Me) and (9.19; R = Me, Et, Cl). Cyclization of (1-chloroacetyl)-1 cinnamoylferrocene gave *threo*-2-chloro-3-phenyl[5] ferrocenophane-1,5-dione together with some 1,1'-(3-phenyl-1,2-cyclopropanedicarbonyl)ferrocene[175].



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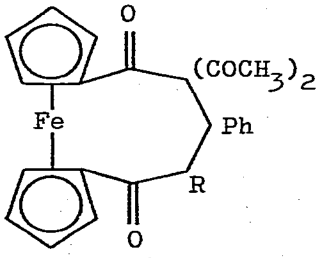

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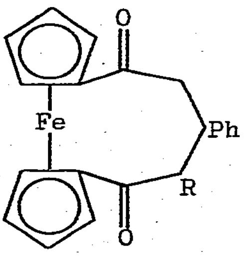
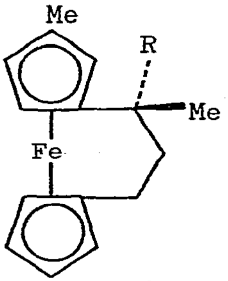


9.19

The hydroxy group in the [3]ferrocenophane (9.20; R = OH) was converted to the amino group with ammonia and aluminium chloride to give the amine (9.20; R = NH_2) with retention of configuration at the reaction site. The reaction proceeded through a configurationally stable α-ferrocenylcarbenium ion. The dimethylamino group was introduced under the same conditions^{176}.



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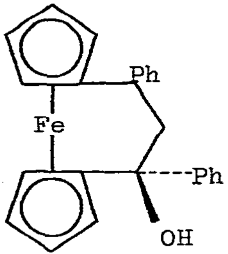

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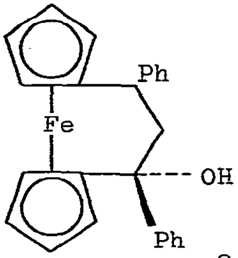
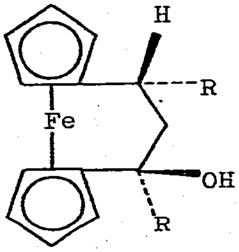


9.22

Dodey and Gautheron have examined the stereochemistry of reduction of α-hydroxyferrocenophanes with aluminium chloride and lithium aluminium hydride. In each case reduction was accompanied by retention of configuration at the functional carbon, thus the tertiary alcohols (9.21 and 9.22) were reduced to the corresponding hydrocarbons with retention of configuration^{177}. The [3]ferrocenophanols (9.23; R = Me, Ph) were treated with aluminium chloride and then either water or lithium aluminium



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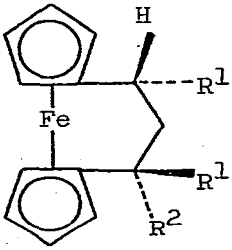

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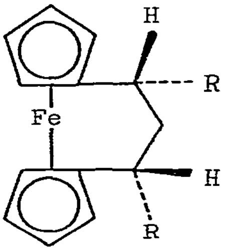
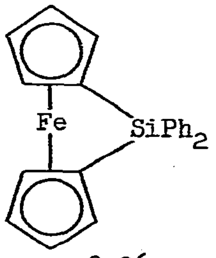


9.25

hydride to give inversion of configuration at the γ-carbon atom with the formation of the alcohol (9.24; R^1 = Me, Ph, R^2 = OH) or the hydrocarbon (9.24; R^1 = Me, Ph, R^2 = H). It was proposed that the α-ferrocenylcarbenium ion formed first was inverted to the thermodynamically stable configuration and then underwent nucleophilic addition to give the observed products. When the [3] ferrocenophanols (9.23; R = Me, Ph) were treated with an equimolar mixture of $LiAlH_4.AlCl_3$ the hydrocarbons (9.25; R = Me, Ph) were obtained with retention of configuration. A concerted mechanism was proposed involving Al------OH interaction[178].

Szilard-Chalmers reactions in ferrocenophanes have been studied. The (n,γ) reactions of ferrocene and four trimethylene bridged ferrocenes were compared and retentions were measured in the solid state and in solution. The observed retentions decreased as the number of methylene bridges increased and as the polarity of the solvent increased. The results were interpreted in terms of the ease with which the recoiling iron atom was able to recombine with organic groups in the molecule and on competition for the iron atom between the solvent and the organic groups in the molecule[179]. The [1]ferrocenophane



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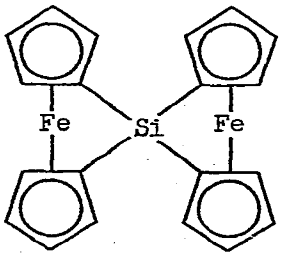

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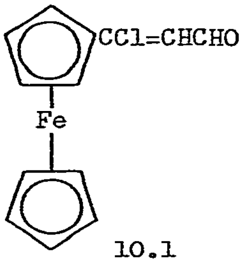
(9.26) has been prepared by treatment of the TMEDA complex of 1,1'-dilithioferrocene with diphenyldichlorosilane, the corresponding binuclear [1]ferrocenophane (9.27) was formed with tetrachlorosilane as the reagent, yields were 23% and 7% respectively. Spectroscopic properties of the two compounds indicated severe ring-tilt distortion[180].

10. FERROCENE CONTAINING POLYMERS

The rate of the AIBN initiated polymerization of vinylferrocene has been investigated in the presence of several anionic and nonionic emulsifying agents. Rates decreased sharply after 10-30% conversion[181]. The copolymer obtained by heating chloroprene and vinylferrocene with 4,4'-azobis(4--cyanovaleric acid) in dioxane was used as a binder for propellants based on ammonium perchlorate, high burning rates were achieved[182]. Vinylferrocene and a series of ferrocene containing acrylates were incorporated into a wide variety of organic copolymers and linseed oil films[183]. The heat treatment of copolymers formed from furfuryl alcohol and either ferrocenedicarboxylic acid or vinylferrocene was carried out under purified nitrogen to give glassy carbons containing iron. The effects of various functional groups bound to the ferrocene precursor on the structure and electrical properties of the glassy carbons were discussed[184]. 1-Ferrocenyl-1,3-butadiene was polymerized and copolymerized to give polymers which were useful in coatings for exposed surfaces of space vehicles, for protecting rubber against sunlight and for protecting against ultra-violet and γ radiation in other applications[185].

The treatment of ferrocenoyl chloride with pentaerythritol arsenite methacrylate and pentaerythritol arsenite acrylate gave pentaerythritol methacrylate tris(ferrocenoate) and pentaerythritol acrylate tris(ferrocenoate) respectively. These ferrocene compounds were copolymerized with butadiene to give polymers which were useful as binders and catalysts for propellant compositions[186]. The vinyl monomers (10.1 and 10.2) were polymerized and each was copolymerized with styrene under thermal conditions. Cross-linked insoluble polymers were obtained which were characterized by spectroscopy and elemental analysis. Copolymerization constants were determined and the reactivity of the p-ferrocenylstyrene monomer (10.2) was discussed by application of the Huckel LCAO-MO method to obtain its molecular characteristics[187]. Pittman and Lai



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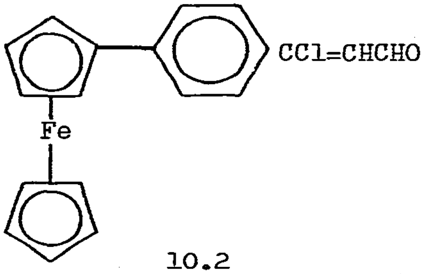


10.2

have carried out the free radical polymerization of ferrocenylmethyl acrylate in benzene with azobisisobutyronitrile at 120° for 120 h to give 47-62% of poly(ferrocenylmethyl acrylate) with number-average molecular weight 17,300[188]. Salts of polyferrocenylene, poly(vinylferrocene) and poly(ethynylferrocene) with dichlorodicyanoquinone and iodide were semiconductors with a maximum conductivity in the range 35-65% iron (III). Increases in conductivity of the order 10^6-10^8 were realised and were almost independent of the anion used[189].

Ferrocenylmethyl acrylate, ferrocenylmethyl methacrylate and vinylferrocene were homopolymerized and oxidized to the ferricinium polymer salts with dichlorodicyanoquinone, o-chloranil and tetracyanoethylene. The physical and spectroscopic properties of these salts were discussed[190]. Pittman has oxidized ferrocene polymers with chloranil, picrate, tetracyanoquinodimethan and other salts to give semiconductor materials. The conductivities were compared with the ferrocene-ferricinium ratio and the nature of the anion[191]. Butyl rubber was vulcanized in the presence of ferrocene or a ferrocene polymer and a metal salt to form a resin with good fire resistance[192]. Bicomponent resin compositions were prepared which incorporated ferrocene. For example, a solution was prepared by mixing tetraethylene glycol dimethacrylate with small quantities of ferrocene and hydroquinone. A second solution was prepared by mixing tetraethylene glycol dimethacrylate with small quantities of cumene hydroperoxide and p-benzoquinone. When the solutions were mixed they gelled in 50-60 seconds to give a 5 mm thick polymer sheet when cast between teflon plates[193]. Unsaturated polyester resins were prepared by treating an unsaturated polyester with styrene in the presence of ferrocene and di-t--butylperoxide[194].

Butadiene and ferrocenylmethyl acrylate were copolymerized in dioxane in the presence of azobis(2-methyl-5-hydroxyvaleronitrile) to give a hydroxy terminated polymer. This polymer was used as a binder-catalyst for propellants containing isodecyl perlargonate, aluminium powder and ammonium perchlorate[195]. (Ferrocenylmethylthio)succinic acid was copolymerized with 2-butene and 1,4-diol and with 1,5-pentanediol and ethylene glycol. These copolymers were used in the formulation of solid propellants which had good physical properties[196]. A series of thermally stable organometallic polymers was prepared containing various combinations of carboranes, ferrocenes and siloxane groups[197]. Ferrocene containing polyquinoxalines were prepared by polymerizing ferrocenyl-1,2-diketones with aromatic bis(*o*-diamines) at 20-200°[198].

11. APPLICATIONS OF FERROCENE

(i) Ferrocene catalysts and photosensitizers

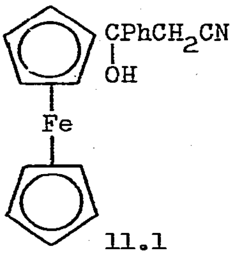
Styrene was polymerized thermally in the absence of an initiator and in the presence of ferrocene. In the presence of ferrocene an increase in the rate of polymerization was observed but the degree of polymerization remained constant. The ultraviolet and visible spectra of ferrocene and some substituted ferrocenes were recorded in styrene, benzene, *n*-heptane and ethanol. The values of the extinction coefficients obtained in styrene and benzene were higher than those in *n*-heptane and ethanol. It was proposed that there was a ferrocene-styrene interaction and a kinetic scheme involving propagation with styrene in such an interaction state was proposed to account for the enhanced rate of polymerization[199]. Styrene was polymerized thermally in the presence of low concentrations of vinylferrocene and in the presence and absence of 2,2'azobisisobutyronitrile (AIBN). These polymerizations were studied in bulk and also in benzene solution. The bulk polymerizations exhibited high initial rates followed by a decrease in the rate of polymerization. It was thought that this decline in rate in the presence of vinylferrocene was due to the progressive formation of a retarder. The thermal polymerization of styrene in the presence of ethylferrocene but in the absence of AIBN and solvent was also examined. The effect of ethylferrocene on the rate of polymerization of styrene was similar to that of vinylferrocene[200].

A dispersion containing silica, styrene-butadiene resin, water and iso-propanol was coated on the aluminium surface of a laminated paper and overcoated with a solution of ferrocene and ceric sulphate in methyl cellulose. This surface was scanned with a recording needle using 60 V D.C. to give a green image on a yellow background[201]. Vinylferrocene and methylmethacrylate were copolymerized in the presence of azobisisobutyronitrile. This copolymer was mixed with styrene-butadiene copolymer, trinitrofluorenone and o-phenanthroline in dichloroethane. The mixture was coated on a paper support. This paper was useful for direct printout photocopying, a sepia colour developed on exposure to ultraviolet radiation and no development was required[202]. In a series of related patents Kojima, Goto and Tsuiki have described the use of photosensitive compositions based on vinylferrocene copolymers, organic halides and either aromatic amines such as diphenylamine or leuco compounds such as leucomalachite green. The compositions were coated on paper supports and formed presensitized printing plates or copying sheets. They showed good storage stability[203,204,205].

Ferrocene (0.05-0.5%) behaved as a sensitizer to degradation by light when incorporated in polyethylene without effecting the mechanical and physical properties of the polymer when it was used as a packaging material[206]. Ferrocene and ferrocene derivatives were effective in sensitizing the photodegradation of disposable polyethylene articles[207]. Ferrocene mixed with benzoyl peroxide has been used as a curing accelerator for polyester resins in the temperature range -10 to 0° C. Moulds of increased hardness were obtained by comparison with conventional curing agents[208]. Silicon carbide whiskers were formed at 1000° by a vapour phase catalytic reaction of silicon and carbon compounds. The reaction was carried out by passing a gaseous mixture of the compounds through a heated vertical tube furnace in the presence of a volatile catalyst such as ferrocene or pentacarbonyliron[209].

11. (ii) Ferrocene stabilizers and improvers

β-Ferrocenyl-β-hydroxyphenylpropionitrile (11.1) β-ferrocenyl-β-hydroxypropionitrile (11.2) and p-ferrocenylaniline (11.3) in the presence of oxaphenamide inhibited the degradation by light of polyethylene[210]. Ferrocene polymers



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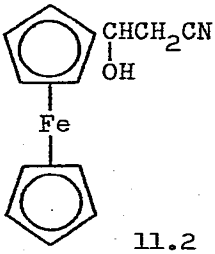

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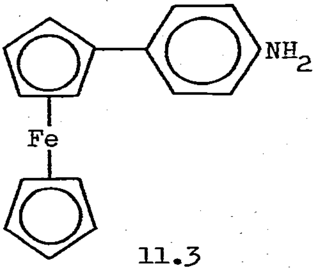
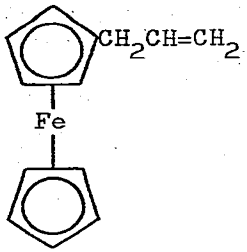


11.3

were mixed with organic electron donors and electron acceptors to give photoelectroconductive compositions[211]. Vinylferrocene and the ferrocenyl olefins (11.4, 11.5, 11.6) were used in unsaturated polyester resins containing a crosslinking agent and peroxide initiator to accelerate the crosslinking and



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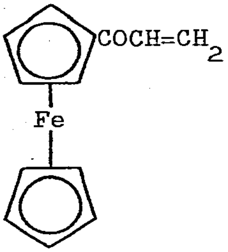

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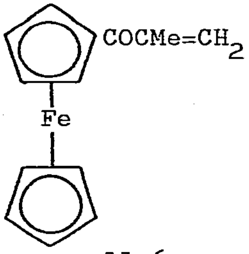


11.6

hardening of the resins[212]. Ferrocene in the presence of $EtO(SiMe_2O)_{15}Et$ improved the breakdown resistance of electric insulator resin compositions[213].

Ferrocene and ferrocene derivatives have been used as activators in the free radical crosslinking of polyethylene. A polymer with improved thermal, dielectric and mechanical properties was obtained[214]. The efficient absorption of UV irradiation by ferrocene compounds was utilised to protect polyethylene from UV degradation. The polymer was sprayed with a 10% solution of a benzaldehyde-ferrocene polymer in methylene dichloride[215]. A polyethylene film which had been coated twice with a 10% solution of ferrocene in dichloromethane, had greatly increased stability to ultraviolet irradiation. Similarly films of polypropylene, polystyrene, ethylene-vinyl acetate copolymer and polycarbonate were stabilized by coating with ferrocene[216]. Polyethylene was stabilized to thermal degradation by the addition of ferrocene and p-ferrocenylaniline (11.3). It was proposed that ferrocene decomposed to give cyclopentadiene and the cyclopentadienyl radical which combined with macroradicals from the polymer[217]. Ferrocene and acetylferrocenes have been used as stabilizers for low-pressure polyethylene against degradation by heat, UV and γ irradiation[218].

A polystyrene resin containing ferrocene was used to make metal casting patterns. The presence of ferrocene or one of its derivatives prevented smoke formation and produced a cast product with an attractive surface[219]. Mixtures of styrene with diethylene glycol-1,1'-ferrocene-diacetic acid-fumeric acid copolymer, diethylene glycol-1,1'-ferrocenedicarboxylic acid-fumaric acid copolymer or diethylene glycol-1,1'-bis(α-hydroxyethyl)ferrocene-fumaric acid copolymer harden at room temperature in the presence of methylethyl ketone peroxide or bibenzyl peroxide to give hard and strong polymers. The ferrocene derivatives behaved as accelerators of hardening and their optimum concentrations were 0.002-0.003%[220,221]. Rubbers and plastics, such as polyethylene, were stabilized towards thermal degradation by the inclusion of ferrocene or a ferrocene polymer and an anti-aging compound, such as phenyl-β-naphthylamine[222]. The fire resistance of poly(vinyl chloride) was enhanced by the inclusion of ferrocene and salts of lead (II)[223]. The further addition of finely powdered calcium carbonate gave a polymer which on combustion produced very low yields of hydrogen chloride[224]. Kato and Maekawa have prepared polymers with good dielectric breakdown strength by blending polyethylene with a small proportion of ferrocene[225] or a ferrocene-aldehyde polymer[226]. Polyethylene was blended with a small proportion of ferrocene and a liquid rubber to give a polymer composition with good electrical insulation properties which was used for coating wires[227].

Conducting and semi-conducting polymer compositions with good resistance to degradation were obtained by vulcanizing a mixture of carbon black, chloroprene rubber and ferrocene or a ferrocene polymer[228]. Synthetic rubbers, such as ethylene--propylene-diene rubbers, were vulcanized with a mixture of ferrocene, sulphur, a peroxide and a metal halide or carboxylate, such as nickel (II) acetate to give a rubber with good thermal stability[229]. Hydrocarbon polymers such as polyethylene were rendered fire-resistant by the incorporation of ferrocene and metal carbonates[230]. The addition of polymeric ferrocene derivatives to epoxy resins considerably increased their pot life[231]. Ferrocene polymers were incorporated into polyethylene and ethylene-5-ethylidene-2--norbornene-propylene rubber when they were used for electrical insulation. The electrical breakdown strength of the insulation was improved considerably[232,233]. Polyethylene was moulded with 8-hydroxyquinoline and ferrocene, a ferrocene derivative or benzaldehyde-ferrocene polymer to give an electrical insulator with a high breakdown voltage[234].

Polyethylene, a benzaldehyde-ferrocene copolymer and 8-hydroxyquinoline were incorporated into a mixture which showed good electrical insulation properties[235]. In related patents, a liquid rubber[236] or a siloxane oligomer[237] were included in the mixture to give the required insulating properties, or the ferrocene polymer was replaced by ferrocene[238]. Di- and tri-acetate fibres were modified by the addition of formylferrocene. The modified fibres showed increased tensile strength and they were resistant to thermal oxidative degradation[239]. When acrylates were compounded with organic peroxides and ferrocene derivatives, anaerobic polymerizable compounds were obtained which were useful in the manufacture of adhesives[240]. Ferrocene was incorporated in impact resistant polymer blends[241]. Ferrocene was used as an electrochemically active stabilizer in liquid crystals[242].

11.(iii) Ferrocene in analysis

Molybdenum was determined in molybdenum-tungsten alloys by titration with ferrocene. In a mixture of hydrochloric and acetic acids Mo (VI) oxinate is reduced with ferrocene whereas the oxinates of W (VI), Fe (III) Ti (IV), Cr (III) and Al (III) are unaffected and only V (V) can interfere. The acid solution of molybdenum was titrated potentiometrically with 0.01 M ferrocene in ethanol[243]. This method was extended for the estimation of molybdenum in steel and other alloys. The errors ranged from -4.8 to +o.6% for 2.03-97.5% Mo in different alloys[244]. A spectrophotometric method was devised to estimate molybdenum in niobium based alloys. The method depended upon the oxidation of ferrocene to the ferricinium ion by Mo (VI) in hydrochloric to acetic acid mixtures[245]. Ferrocene was used as a reducing agent for molybdenum (VI) in the colourimetric determination of molybdenum with thiocyanate. The procedure developed enabled molybdenum to be determined in the presence of large amounts of niobium, tungsten, rhenium, tantalum and zirconium[246]. Ferrocene has been used as a reagent in the potentiometric determination of molybdenum in steels and other alloys[247].

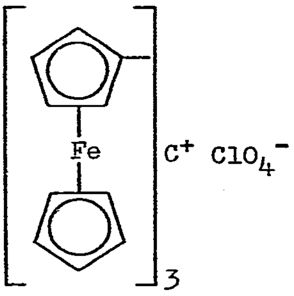
Ferrocene was used in the determination of vanadium in steels by an amperometric method. Vanadium as vanadium (IV) was determined in an acid aqueous-ethanolic medium containing

0.01 M ferrocene by following the oxidation current of ferrocene at +0.72 V against the permanganate reference electrode[248]. Platinum micro-disc electrodes were used in the amperometric titration of ferrocene solutions (0.1-0.001 M) with iron (III) in alcohol without applying an external emf. This method was used to analyse alloys containing 0.5-25% iron. The conditions were chosen such that Ni (II), Cu (II), Cr (II), Co (II), Mn (II), Sn (IV), Re (VII) did not interfere and interfering W (VI), Nb (V) and Ti (IV) were masked with citric or tartaric acid[249]. Antimony in alloys was determined by amperometric titration of Sb (V) with ferrocene in hydrochloric acid-acetone mixtures. Large amounts of Bi (III), Tl (III), Ga and Pb (II) did not interfere with the titration but Cu (II) and Fe (II) did interfere[250]. The ferrocene-ferricinium couple has been investigated as an electrode in aqueous-organic solvents[251]. Ferrocene was used during the photometric determination of rhenium (VII)[252]. The ferricinium ion was used as an oxidizing agent in the reversible titration of cytochrome C and cytochrome C oxidase[253].

11. (iv) Combustion studies

Pentaerythritol triferrocenoate methacrylate was formed by hydrolysis of pentaerythritol arsenite methacrylate, evaporation and stirring the residue with ferrocenoyl chloride in chlorobenzene. The corresponding acrylate was made in the same way. The products were each copolymerized with butadiene to give polymers useful as combustion catalysts and binders for solid propellants[254]. A related patent has described a similar application for ferrocenylmethyl acrylate copolymers of butadiene[255]. Pentaerythritol methacrylate triferrocenoate was copolymerized with butadiene and the resulting polymer was used as a combustion modifier. A high combustion rate was achieved and the processing and storage problems associated with butylferrocene catalysts were eliminated[256]. The copolymer formed between (acrylyloxyacetyl)ferrocene and butadiene was used to formulate propellant binders with high burning rates[257]. Triferrocenylmethyl perchlorate (11.7) was used as the burning rate catalyst in propellants based on ammonium perchlorate. The mechanical properties and processing characteristics of the propellant were improved as compared with a similar propellant containing butylferrocene[258].

Combustion catalysts for composite solid propellants were formulated by treating an alkylferrocene such as butylferrocene with methylal. The catalysts were involatile noncrystallizable liquids which did not migrate or evaporate from within the propellant on storage[259]. Poly(ferrocenylbutadiene) (11.8) was incorporated into conventional propellants as a nonvolatile nonmigrating burning rate modifier in ammonium perchlorate based propellants[260]. Liquid polynuclear ferrocene derivatives



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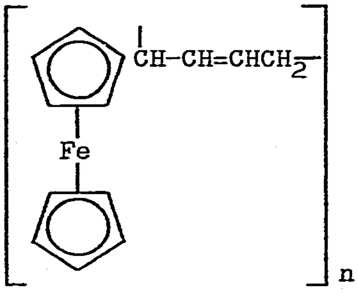
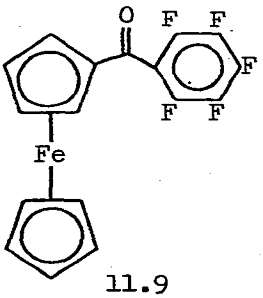


11.8

were found to be useful as combustion catalysts in solid propellants[261]. 1,1'-Bis(1-glycidoxyalkyl)ferrocenes have been claimed as curing agents for binders in solid rocket-propellants, as coatings for oxidizer crystals such as ammonium perchlorate, as plasticizers for solid propellants and as combustion catalysts. The compounds were formed by treating 1,1'-bis(1-hydroxyalkyl)ferrocenes with alkali metal alkyls to give the alkali metal salts and combining the salts with epihalohydrins to give the products[262]. Soot formation in the combustion of fuel in diesel engines was considerably reduced by the addition of a small proportion (0.05-0.5%) of ferrocene or 1,1'-diethylferrocene to the fuel[263].

11. (v) General applications and miscellaneous reports

Lubricant-coolant fluids based on petroleum oils and used for the cold pressure shaping of metals showed improved lubricating properties at higher temperatures when pentafluorobenzoylferrocene (11.9), (0.3%) was added[264]. Ferrocene, p-anisaldehyde-ferrocene copolymer and cinnamaldehyde-ferrocene copolymer were used as antistatic agents in polyethylene[265].



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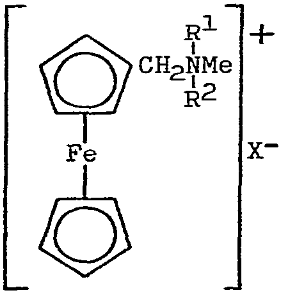

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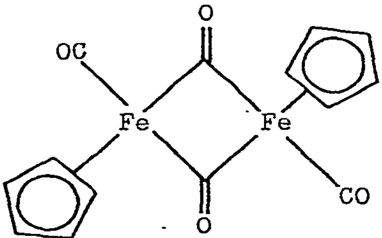


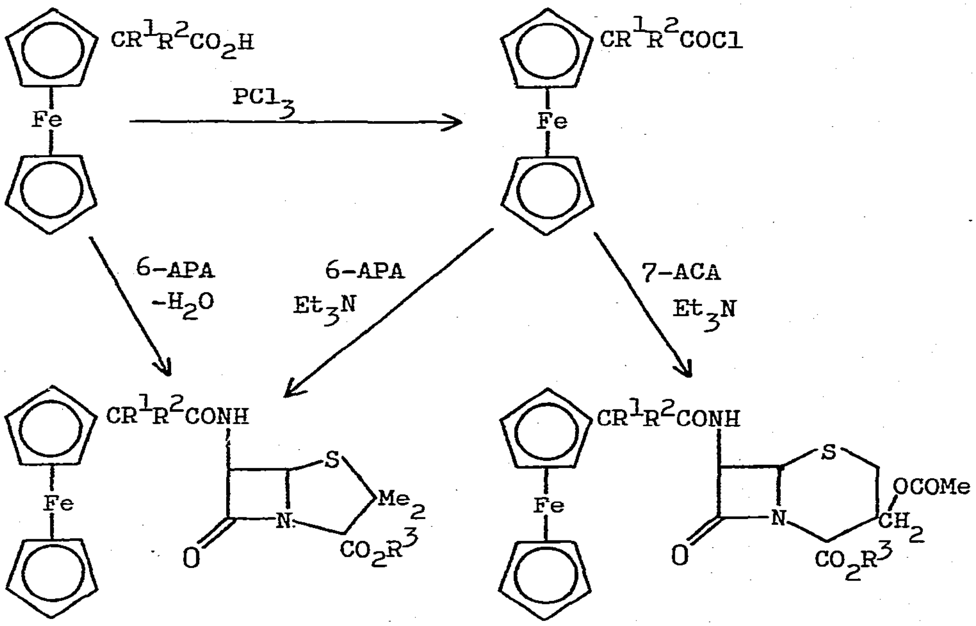
11.11

The addition of ferrocene-based ammonium salts (11.10; R^1 =

C_{1-5} alkyl or CH_2CH_2OH; $R^2 = C_{1-18}$ alkyl; $X = Cl^-$, Br^-, I^-, NO_3^-, SO_4^{2-}, $MeSO_4^-$, $Me_2PO_4^-$, ClO_4^-) to a polymer surface gave improved antistatic properties[266]. A mixture of poly(vinylchloride), ferrocene, dioctyl sebacate, lead sulphate, lead stearate, calcium carbonate and zinc borate was milled at 150° and pressed at 160° into a sheet. When the sheet was burnt very little hydrochloric acid gas was evolved[267]. Another patent gave further details for the preparation of fire resistant poly(vinyl chloride) compositions[268]. A high resolution electron microscope was used to study carbon layers formed by catalytic graphitization of acetylferrocene-furfural resins heated at 400-1500°. Free α-Fe particles were formed at all temperatures and graphite was observed only above 800°. At higher temperatures the iron particles increased in size and carbon layers were formed on them[269].

Films of poly(vinylferrocene), deposited on quartz discs, were converted to iron oxide films in either a 200 Watt oxygen plasma at room temperature or thermally in oxygen at 380° C. The iron oxide films were suitable for use as semitransparent masks in the manufacture of integrated circuits[270]. Coatings containing iron (III) oxide which were useful for transparent masking with improved resolution in the preparation of printed circuits were prepared by oxidation of poly(vinylferrocene)[271]. Graphite fibres were passed through a 2% solution of ferrocene in benzene, the solvent was allowed to evaporate and the coated fibres were heated to 800° to decompose the ferrocene and leave a film of metallic iron. Graphite-resin composites prepared from such coated fibres showed increased shear strength when compared with composites made from uncoated fibres[272]. Ferrocene polymers, such as the ferrocene p-anisaldehyde copolymer, were subjected to controlled heating to 70-300° and cooling to give new ferromagnetic materials. These were fabricated into thin sheets, moulded shapes and powders, they were used as magnetic shielding materials, magnetic memory cores and in magnetic tapes[273]. Ferrocenes and ferrocene polymers were used as primary layers in the direct generation of conductor patterns on substrates by subsequent electroless deposition. Ferrocene polymers based on vinyl-, allyl- or diphenyl-ferrocene were deposited from solution and ferrocene compounds were deposited from the vapour phase as a thin film on the substrate. The film was subjected to electron bombardment to give a pattern of cross-linked ferrocene polymer. After removal of the uncross-linked material, the organic residue in the polymer was removed under oxidising conditions and the remaining iron oxides were reduced under hydrogen to leave a film of free iron. This film was effective in the nucleation of subsequent electroless deposits[274]. The thermal decomposition of bis(η-cyclopentadienyldicarbonyliron) (11.11) in an inert atmosphere at 165° gave $(\eta\text{-}C_5H_5)_4Fe_4(CO)_4$ which decomposed at 210° to give ferrocene[275]. Ferrocene has been proposed as a convenient vehicle on which to demonstrate to undergraduates the use of instrumental methods in chemistry[276].

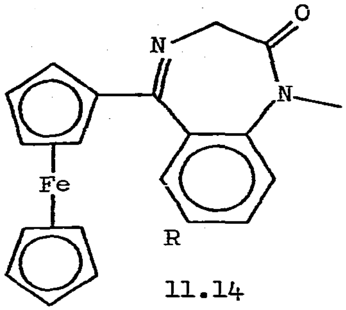
Ferrocene derivatives of penicillin (11.12) and cephalosporin (11.13) were prepared by the condensation of ferrocenylacetic acid chlorides with 6-aminopenicillanic (6-APA) and 7-aminocephalosporanic acids (7-ACA). The ferrocenyl-penicillins (11.12; R^1, R^2 = H, Me; R^3 = H) were characterised as the benzylamine salts (11.12; R^1, R^2 = H, Me; $R^3 = PhCH_2NH_3$) and the corresponding cephalosporins were characterised as the adamantanamine salts (11.13; R^1, R^2 = H, Me; $R^3 = C_{10}H_{15}NH_3$). The ferrocene derivatives (11.12; R^1, R^2 = H, Me, R^3 = Na and 11.13; R^1, R^2 = H, Me; R^3 = Na) exhibited antibiotic activity against various strains of <u>staphylococcus</u> <u>aureus</u> and they also behaved as β-lactamase inhibitors[277]. Intragastric treatment of anaemic mice with 1,1'-diethyl-α,α'-thiaferrocene achieved a complete cure. The ferrocene compound was efficiently absorbed from the intestine and stored principally in the liver[278]. 5-Ferrocenyl-1,4-benzodiazepin-2-ones (11.14; R = H, I) were prepared and tested. They were relatively nontoxic and they were inactive



11.12

11.13

in screening for muscle relaxant, anticonvulsant and taming activity in mice[279]. The ferrocene nucleus has been incorporated into a steroid skeleton at ring-A and with two conjugated double bonds in ring-C and ring-D. Several compounds were synthesised and the two conjugated double bonds were reduced to give saturated ferrocenylsteroids. Some of these derivatives showed antibacterial activity[280]. The synthesis of the



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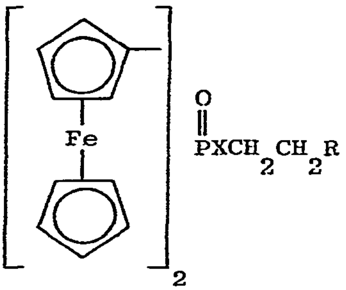

11.15

diferrocenylphosphinic esters (11.15 X = O S; R = NMePh, SEt) in yields of 41-65% has been reported. The esters were formed by condensation of sodium diferrocenylphosphinate and -thiophosphinate with $ClCH_2CH_2NMePh$ and $ClCH_2CH_2SEt$, they exhibited anti-cholineesterase activity[281].

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