FERROCENE

ANNUAL SURVEY COVERING THE YEAR 1974.

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CONTENTS

Ferrocene; Annual Survey covering the year 1973 see J. Organometal. Chem., 79(1974)223-304.

1. REVIEWS

Cais has reviewed the problem of aromaticity in the metallocenes and the role of the metal atom in their reactions. The following aspects of ferrocene chemistry were summarized: (1) electrophilic substitution, (2) intra- and inter-annular effect (3) oxidation and reduction, (4) substituent effects of the ferrocenyl group[1].

Chemical bonding in organometallic sandwich compounds has been discussed briefly by Prins[2]. The literature for 1972 covering substitution reactions of ferrocene and other hydrocarbon-metal π-complexes was surveyed by Knox[3]. The general chemistry of these compounds was also surveyed[4].

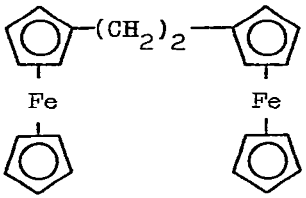
Slocum and Sugarman have reviewed the directed metallation reaction, that is lithiation with n-butyllithium at a position ortho to a substituent on an aromatic ring. The use of this reacti for the preparation of 1,2-disubstituted ferrocenes was included in the review[5]. Zeppezauer briefly reviewed the development of organometallic chemistry including the structure and chemistry of ferrocene[6].

The mass spectrometry of transition metal π-complexes has been discussed by Gaivoronskii and Larin[7]. Rosenblum has reported results in several fields of organo-iron chemistry including the formation of organic semiconductors incorporating ferrocene[8]. The effect of structure on the thermal stability of siloxanes containing ferrocene and cymantrene groups has been surveyed by Skorokhodov[9]. Shul'pin and Rybinskaya have discussed the chemistry of the ferrocenophanes[10]. Nesmeyanov and Kochetkova have reviewed the current trends in the practical uses of ferrocene and its derivatives[11].

2. STRUCTURAL DETERMINATIONS

X-ray diffraction studies showed that ferrocene which is monoclinic at room temperature, becomes triclinic below the phase transition temperature of 165°K. The lattice parameters for monoclinic ferrocene (295°K) were a = 10.59, b = 7.64, c = 5.96 Å, β= 121.1° and for triclinic ferrocene (80°K) they were a = 10.53, b = 7.52, c = 5.71 Å, α= 90.5, β= 119.9, γ= 89.4° [12].

The crystal and molecular structure of 1,2-bis(ferrocenyl)-ethane (2.1) was determined by X-ray crystallography. The compound crystallized in the orthorhombic space group *Pbca* with four molecules in a cell of dimensions a = 10.06, b = 10.43, c = 16.23 Å. The two ferrocene moieties were symmetrically equivalent and *trans* to one another in the solid state[13].



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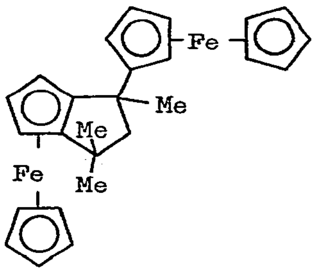

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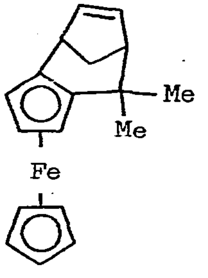
The crystal and molecular structure of α,α,γ-trimethyl -γ-ferrocenyl-1,2-trimethyleneferrocene (2.2) was determined from X-ray diffractometer data by direct methods, and refined to *R* 0.117 for the 4075 observed structure factors. The unit cell of the crystals was orthorhombic with a = 14.72, b = 24.63, c = 11.35 Å, space group *Pbca*, Z = 8. The second ferrocenyl group was *exo* as previously postulated from ^{1}H NMR data [14, 15]. The structure of the adduct (2.3) formed between the 2-ferrocenyl-2-propyl cation and cyclopentadiene has been confirmed by X-ray crystallography. The two η-cyclopentadienyl rings are tilted out of coplanarity by an angle of 7° [16].



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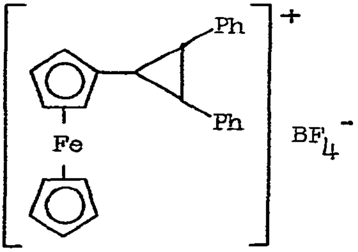


2.4

The crystal and molecular structure of ferrocenyldiphenylcyclopropenium tetrafluoroborate (2.4) was determined by a single crystal X-ray diffraction study. The compound crystallized in the monoclinic system, space group $P2_1/c$, with a = 8.219, b = 14.70 c = 17.857 Å; β = 103.6°. The cyclopentadienyl rings were eclipsed and offset from the parallel by 2.7°. Three details of the structu supported metal participation in stabilization of the cation: (1) the cyclopropene ring was bent up towards the ferrocenyl group and this facilitated interaction of the filled nonbonding $3dz^2$ of the iron with the empty orbital of the cyclopropenium moiety, (2) the carbon-carbon bond distance between the ferrocenyl group and the cyclopropene ring was slightly elongated and this was consistent with the mixing of metal orbitals with empty orbitals on carbon, (3) the cyclopentadienyl carbon atom attached to the cyclopropene ring was slightly tilted towards the iron and this shift would tend to facilitate orbital overlap[17].

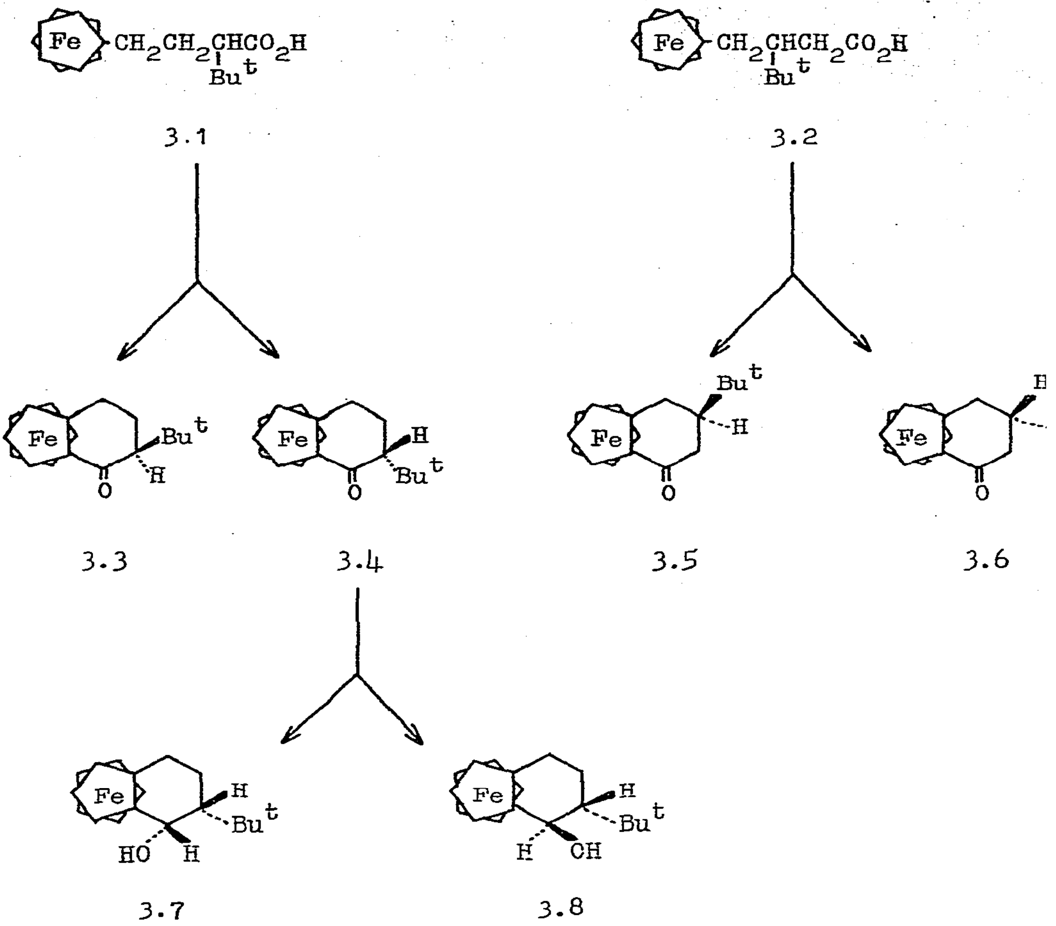
The crystal and molecular structure of ferrocenylbis-

(triphenylphosphine)digold tetrafluoroborate was determined by X-ray crystallography. It had space group $P2_1/\underline{a}$ with a = 14.46, b = 30.54, c = 9.51 Å, β = 92.6°; Z = 4. The metal atoms formed a Au-Au-Fe chain with a cyclopentadienyl bridge between one gold atom and the iron atom. The crystals consisted of discrete $[C_5H_5FeC_5H_4Au_2(PPh_3)_2]^+$ and BF_4^- ions[18].

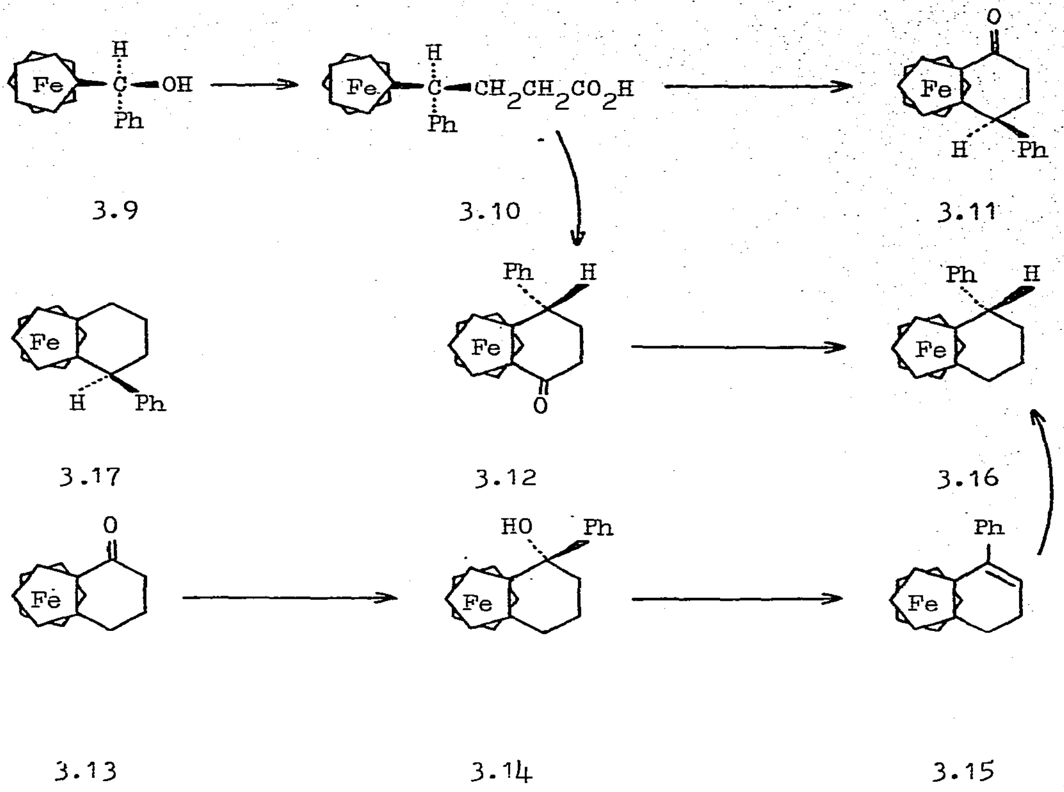
3. STEREOCHEMISTRY OF FERROCENES

Ferrocene was acylated with t-butylsuccinic anhydride to give a mixture of two isomeric ketones which were reduced under Clemmensen conditions to the substituted ferrocenylbutyric acids (3.1 and 3.2). Cyclization of the acids with trifluoroacetic anhydride gave the two pairs of cyclohexenones (3.3, 3.4, 3.5 and 3.6). The ratio of the exo (3.3) to endo (3.4) isomers in the product mixture obtained by cyclization of the butyric acid (3.1) was 4:1 and the endo-ketone (3.4) was obtained by treating the exo-ketone (3.3) with sodium methoxide. Each of the four ferrocenocyclohexenones (3.3 - 3.6) was reduced to a pair of ferrocenocyclohexenols in which the endo-alcohol was usually in excess over the exo-alcohol. Thus the ketone (3.4) gave the alcohols (3.7 and 3.8) in the ratio 9:1. The relative configurations of all the stereoisomers were determined by their chemical and spectroscopic properties[19].

Kimny, Moise and Tainturier have determined the absolute configurations of γ-phenylferrocenocyclohexenone. The ferrocenylphenylcarbinol (3.9) was converted in two stages to the γ-ferrocenyl-γ-phenylbutyric acid (3.10) and then cyclized to

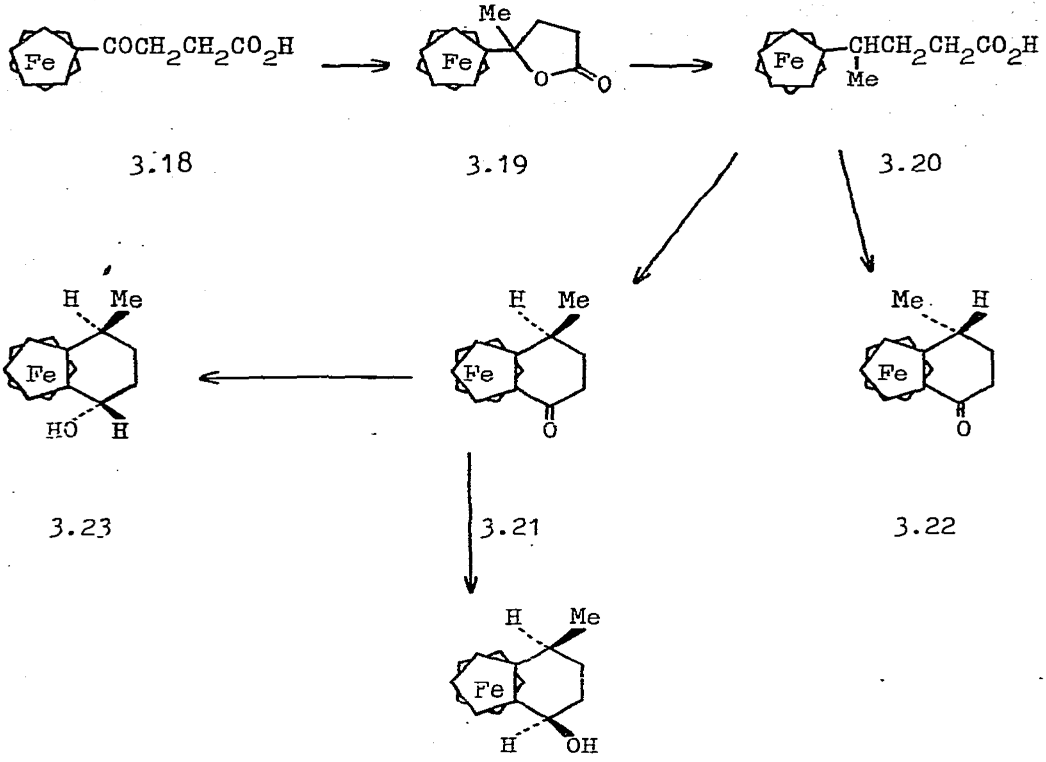


a mixture of the ferrocenecyclohexenones ·(3.11 and 3.12). These products were distinguished by relating them to the optically active ketone (3.13). This ketone was treated with phenylmagnesiu bromide to give the cyclohexenol (3.14) which was dehydrated to the cyclohexadiene (3.15). Stereoselective reduction of the cyclo hexadiene gave the cyclohexene (3.16) which was obtained also by Clemmensen reduction of the cyclohexenone (3.12). The cyclohexeno



(3.11) was related in the same way to the cyclohexene (3.17)^{20}.

Uysal and Gautheron have investigated also the stereochemistry of γ-substituted ferrocenecyclohexenones. The ferrocenoylpropionic acid (3.18) was treated with methylmagnesium iodide to form the lactone (3.19) and this was reduced with hydrogen over a catalyst to give the carboxylic acid (3.20). This acid was cyclized with trifluoroacetic anhydride to the isomeric cyclohexenones (3.21 and 3.22) which were obtained in the ratio 9:1. Reduction of the cyclohexenone (3.21) with lithium aluminium hydride gave the epimeric alcohols (3.23 and 3.24) with the endo:exo ratio of 9:1. By contrast, reduction of the ketone (3.22) gave epimeric alcohols in the endo:exo ratio of 9:11. The relative configurations of the cyclohexenones (3.21 and 3.22) were determined by relating one of them (3.22) to the cyclohexenone (3.13)[21].

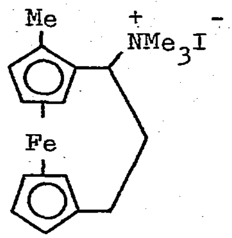


3.18 3.19 3.20

3.23 3.21 3.22

3.24

Nucleophilic substitution of the chiral [3]ferrocenophanes (3.25 and 3.26) with NH_3, NaN_3 and Me_2NH afforded the corresponding [3]ferrocenophanes in which the quaternary ammonium or hydroxyl group was replaced by NH_2, N_3 or Me_2N respectively with retention of configuration[22].



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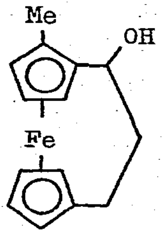
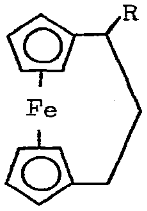


3.26

The racemic ferrocenophane (3.27; R = NMe_2) was prepared by treating the corresponding alcohol (3.27; R = OH) with $Me_2NH-AlCl_3$. The amine (3.27; R = NMe_2) was partially resolved, quaternised and hydrolysed to give the chiral alcohol (3.27; R = OH) with the same sign of rotation. The amine (3.27; R = NMe_2) was treated with n-butyllithium and the lithiated intermediate was condensed with PhCN, dimethylformamide or PhCHO to give (3.28; R = PhCO, CHO and PhCHOH) respectively[23].



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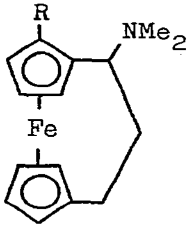
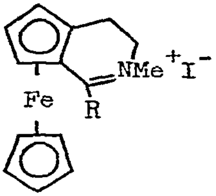


3.28

The stereochemistry of the reduction of the methiodides (3.29) was dependent on both the substituent on the carbon atom α to the cyclopentadienyl ring and on the reagent used. Reduction of the methiodide (3.29; R = Me) with sodium borohydride gave the endo-methyl derivative (3.30; R^1 = H, R^2 = Me) as the dominant product while reduction of the methiodide (3.29: R = H) with the methyl Grignard reagent gave the exo-methyl product (3.30; R^1 = Me,

R^2 = H). The physical properties of the products (3.30) were interpreted by conformational analysis[24].



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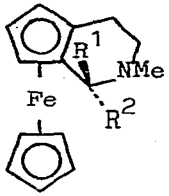

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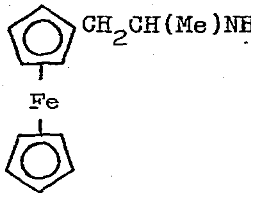


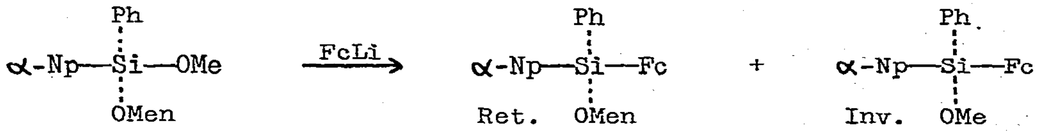
3.31

The racemic amine (3.31) obtained by the lithium aluminiu hydride reduction of 1-ferrocenyl-2-nitro-1-propene was resolv into the enantiomers by crystallization of the tartrate or dib tartrate salts[25]. Bifunctional optically active organosilicon compounds of known absolute configuration were treated with fer cenyllithium to give optically active α-ferrocenylsilanes. The stereospecificity of the reactions was high although either ret or inversion of configuration was observed depending on the rea Thus the silane (3.32) was converted to the ferrocenylsilane (with retention of configuration while the chlorosilane (3.34) g the inverted product (3.35). The methoxysilane (3.36) underwen inversion when attacked at the o-menthyl group to give (3.38) but the methoxy group was displaced by ferrocenyl with retenti of configuration to form the silane (3.37)[26].

(3.32)

(3.33)

(3.34) (3.35)



(3.36) (3.37) (3.38)

Goldberg and Bailey have reported further details[27] of the stereochemical situations which arise when two constitutionally identical substituents are bound to adjacent ring carbon atoms in ferrocene[28].

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

Hartree-Fock-Slater (HFS) calculations, employing the Xα exchange but no muffin-tin approximations, were carried out for ferrocene. The calculated ionization potentials and charge distribution were compared with Hartree-Fock and experimental results. It was concluded that the HFS calculations gave a realistic picture over a wide range of the photoelectron spectrum and the relative positions found for the metal d and ligand valence levels agreed with experimental results. A transition state calculation was found to be necessary to give the qualitatively correct ionization potentials[29].

A molecular-orbital calculation for ferrocene using the SCF Xα scattered-wave method was carried out for ferrocene. Good agreement was obtained between the theoretical and the observed optical spectrum for d-d transitions and charge-transfer excitations.

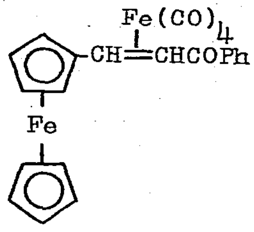
The calculated ionization spectrum agreed well with experimental measurements but it led to a different interpretation for the two lowest ionization potentials. The order of energy levels for the highest occupied orbitals in ferrocene and the lowest unoccupied orbital was found to be $e_{1g}(\pi\text{-Cp}) < e_{1u}(\pi\text{-Cp}) < e_{2g}(3d) < A_{1g}(3d) < e^{*}_{1g}(3d)$[30].

A new semiquantitative SCF LCAO molecular orbital calculatio scheme which involved an intermediate neglect of differential over has been applied to ferrocene and several other molecules. The results compared favourably with those obtained by <u>ab initio</u> calculations[31]. The ^{13}C NMR spectra of acyl-; 1,1'-diacyl- and vinylferrocenes in CF_3CO_2H and H_2SO_4 were recorded and compared with the spectra obtained in aprotic organic solvents[32].

^{13}C NMR spectra were recorded for a series of substituted ferrocenes and from the results it was concluded that electron-donating substituents increased the electron density in the β-position and decreased it in the α-position. Electron-accepting substituents exhibited the opposite effect[33].

The ^{13}C-^{1}H and ^{1}H NMR spectra of β-benzoylvinylferrocene and cinnamoylferrocene and their iron carbonyl complexes (4.1, 4.2 and 4.3) were recorded and interpreted. The resonances of both the α- and β- substituted cyclopentadienyl ring atoms were split in the ^{13}C-^{1}H NMR spectra of all the complexes. In the iron carbonyl complexes (4.1, 4.2 and 4.3) there was a reduction in the degree of conjugation of the α,β- unsaturated ketone system and this phenomenon was discussed on the basis of the ^{13}C-^{1}H and ^{1}H NMR data[34].

The ^{13}C pulse Fourier transform NMR spectra of the ferriciniu salts, $[(RC_5H_4)_2Fe]^{+}PF_6^{-}$ (R = H, Me, Et, CMe_3), were recorded as



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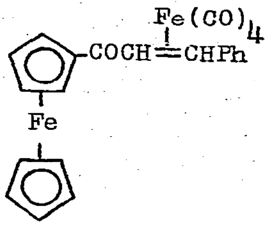

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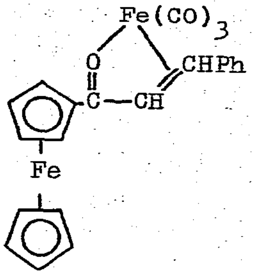

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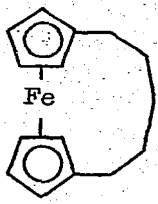


4.4

solutions in acetone. The ring carbons gave a single signal for R = H; two signals for R = Me or Et [the C-2(5) and C-3(4) signals overlapped] and three signals for R = CMe$_3$[35]. ^{1}H-^{13}C NMR cross-polarization studies of a ferrocene single crystal revealed strong transient oscillations instead of the more usual exponential behaviour of cross-polarization. The oscillations arose from coherence effects caused by the dipolar coupling between the ^{1}H and ^{13}C atoms and were rationalised in terms of a simple model[36]. The interchange between the two conformers of [5]ferrocenophane (4.4) brought about by inversion of the methylene bridge has been investigated by ^{13}C and ^{1}H NMR spectroscopy. The temperature dependence of the chemical shifts of the bridge methylene groups was determined, the resonance of the central methylene group was shifted to lower field by 3ppm over the temperature increase studied[37].

The wideline ^{1}H NMR spectra of a number of bis(cyclopentadienyl (including ferrocene), dibenzene and bis(cyclooctatetraene) metal complexes were examined in the temperature range 178-381^{o}K and the second moments of the line widths were calculated. These experimental values were compared with theoretical values based on the Van Vleck model. The results indicated that there was no substantial difference in metal-ring bonding between metallocene and dibenzene compounds[38].

The protonation of a series of acylferrocenes in FSO_3H-$SO_2ClF(SO_2)$ solution was studied by ^1H NMR spectroscopy. The sit of protonation was found to be the carbonyl oxygen atom and there was no evidence for the protonation of the iron atom. Although it was thought that the proton attached to the carbonyl oxygen could, at the same time, be associated (<u>via</u> hydrogen bonding) wit the iron atom. Temperature dependent ^1H NMR spectra of protonate acylferrocenes $FcCROH^+$ (R = Me, Et, Ph, OMe) were observed which indicated intermolecular hydrogen exchange with the acid solvent system[39]. Isotropic nuclear magnetic resonance shifts for $[Fe(\eta-C_5H_5)_2]PF_6$ and $[Fe(\eta-C_5H_4Me)_2]PF_6$ were measured at a series of temperatures between 202 and 324°K. The room temperature solution magnetic moments of these ferricinium salts were measured Theoretical expressions for magnetic susceptibilities and ESR <u>g</u> values were deduced, and these expressions were used to interpret known ESR <u>g</u> values and the ^1H NMR data and the magnetic moments obtained in this investigation. It was found that the dipolar term contributed approximately 55% to the observed resonance shift for the methyl protons and approximately 25% to the ring proton shifts. It was concluded that for $[Fe(\eta-C_5H_5)_2]^+$ the $^2A_{1g}$ level was below the $^2E_{2g}$ level by about 200 cm^{-1}. It was suggested that the former was not a pure electronic level but a vibronic one of symmetry A_{1g} which resulted from Jahn-Teller induced vibrational coupling with $^2E_{2g}$[40].

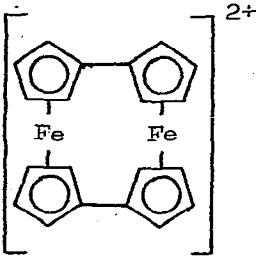
The effects of light, gamma radiation, oxygen and nitrogen on ferrocene adsorbed on porous silica have been investigated by

ESR techniques. After ultraviolet irradiation ferrocene dissociated primarily into C_5H_5 radicals together with $C_4H_4^-$ or the $C_5H_4^-$ radical anion; atomic hydrogen was also produced. Gamma irradiation apparently had no effect on the ferrocene. No evidence was obtained for the adsorption of nitrogen by ferrocene but oxygen adsorption at room temperature produced an O_2^- spectrum with a hyperfine structure due to the five hydrogens of a cyclopentadienyl ring of the ferrocene[41].

The infrared spectra (3200-400 cm^{-1}) of monocrystal films of $M(\eta\text{-}C_5H_5)_2$ (M = Fe, Ru, Os) using polarized radiation and the laser-Raman spectra of solid samples of these compounds at +20° to -190° were recorded. The fundamental vibrational frequencies were assigned. Symmetry forbidden vibrations appeared in the solid state[42]. The rate of cyclopentadienyl ring exchange between first transition series metallocenes, $(\eta\text{-}C_5H_5)M$ and LiC_5D_5 has been studied by an IR technique. The rate of exchange decreased in the order M = Cr, $Mn > Ni > V \gg Fe$, Co. The relative reactivity towards ring exchange paralleled the reactivity towards nucleophilic substitution and was explained in terms of the donor or acceptor properties of the metallocene[43].

The infrared spectra of Fc_2CO, $Fc_2C{=}NH$, $Fc_2C{=}CH_2$, $FcC{=}NHCy$ (Cy = cymantrenyl), FcCOCy and $Fc_2C{=}NN{=}CFc_2$ were recorded and correlated with the structures of these molecules[44]. Rate constants have been measured for the quenching by ferrocene of triplet states in a number of organic compounds in ethanol. In most cases the triplets were quenched and did not show transient absorptions. Over the range 8,000-17,000 cm^{-1} the rate constants increased with an increase in the triplet energy. The quenching mechanism was considered and the lowest triplet level of ferrocene was determined as 15,000±1,000 cm^{-1} [45].

Ferrocene and ferrocene derivatives were active in quenching the photoreduction of fluorenone by triethylamine. A mechanism involving triplet-triplet energy transfer was proposed[46]. The Moessbauer chemical shift and quadrupole splitting parameters wer determined for a number of ferrocene derivatives. While the chem shift was independent of the nature of the substituent, the quadrupole splitting was sensitive to the electronic effects of the substituents. The results were in better agreement with the Shustorovich and Dyatkina MO description of ferrocene than with alternative calculations made by Dahl and Ballhausen[47]. The ^{57}Fe Moessbauer spectra (300 and 4.2°K) have been determined for dioxidized biferrocenylene (4.5) and two mono-oxidized [1.1]ferroce ophanes (4.6). A large quadrupole splitting (2.89 mm/sec at 300°K) was obtained for the biferrocenylene (4.5) and this was interpreted in terms of extensive delocalization of e_{2g} electrons resulting from an Fe-Fe bonding interaction. For the ferrocenophanes (4.6) temperature dependence of the spectra was noted and this was thoug to be associated with a phase transition wherein the Fe-Fe distanc was changed to permit greater Fe-Fe exchange interaction[48].



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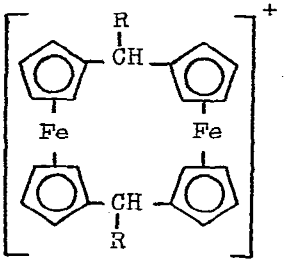


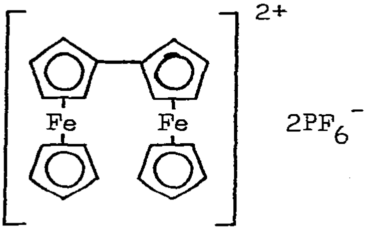
R = H, Me

4.6

Morrison and Hendrickson have recorded the Moessbauer spectrum of dioxidized biferrocenylene (4.6) as the hexafluorophosphate. The chemical isomer shift $\delta = 0.573$ mm sec^{-1} (vs. metallic iron) and the quadrupole splitting $\Delta = 2.951$ mm sec^{-1}. The spectrum of the magnetically perturbed sample confirmed that the electric field gradient at the Fe(III) centres was negative[49].

Moessbauer spectra were recorded for the systems 3-5 wt.% diacetylferrocene (containing 90% ^{57}Fe) with 4,4'-diheptyloxyazoxybenzene and 4,4'-dioctyloxyazoxybenzene and ferrocene with chloesteryl myristate. The results were used for elucidating the structures of the liquid crystals[50]. Moessbauer spectroscopy has been used to determine the displacement anisotropy and the angle of inclination of layers of diacetylferrocene in the liquid crystal matrix provided by 4,4'-di(heptyloxy)azoxybenzene[51].

Fleischmann and Fritz have reported the spectroscopic and polarographic investigation of the complexes formed between two molecules of the thiosemicarbazone (4.8) and cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) ions. The results indicated that the ligand formed complexes in its imine form and that strong electron delocalization in the complex occurred but without significant participation by the electrons on the central iron atom[52].



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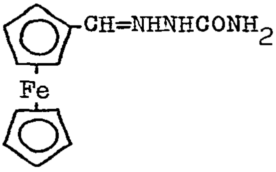

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The protonation of substituted ferrocenyl ketones in aqueous sulphuric acid has been investigated, pK_a values were determined for the conjugate acids of eleven ketones. Substituent effects and charge delocalization were discussed, several of the compounds were useful as indicators in the measurement of acidity using H_o scales[53]. A study was made of the use of methyl isobutyl ketone as a solvent for polarography. For ferrocene in this solvent the half-wave potential was +0.44V, the diffusion current constant was 2.32V and the product of the diffusion current constant and the square root of the solution viscosity was 1.83V[54]. A polarographic study of acylbenchrotrenes and their oximes showed the $Cr(CO)_3$ to be electron withdrawing, $\sigma = 0.74$. The following order of electron withdrawing groups was determined, benchrotrenyl > 2-thienyl > cymantrenyl > phenyl > 2-pyrrolyl > ferrocenyl[55].

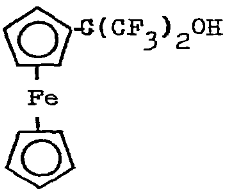
The chromatographic separation of several substituted ferrocen was achieved on columns of polystyrene beads crosslinked with 2% divinylbenzene using cyclohexane as the solvent. The separation appeared to be achieved through weak interaction between the solute and gel matrix rather than by molecular sieving as was demonstrated by the different distribution coefficients for ferrocene, ruthenocene and osmocene[56].

Isomeric vinylferrocenes and diastereomeric N-phenylethylferrocenecarboxamides were separated by high pressure liquid-liquid chromatography[57].

5. REACTIONS OF FERROCENE

Ferrocene was attacked by hexafluoroacetone in the presence of aluminium chloride in methylene dichloride to give the propanol (5.1). Similar reactions took place when pentafluoroferrocene was the reagent and when ferrocene was replaced by acetyl- or benzoylferrocene. In the absence of the Friedel Crafts catalyst the reactions required forcing conditions (15 days at 180°C in a Carius tube)[58].

Ferrocene was heated to 150° with tetracyanoethylene in sulpholane to form cyanoferrocene (40%) and (tricyanovinyl)ferrocene (16%) (5.2). Chloromercuriferrocene was treated with the same reagent to give the same vinylferrocene (5.2). Ethylferrocene gave a random mixture of disubstitution products and suggested a radical substitution mechanism[59].



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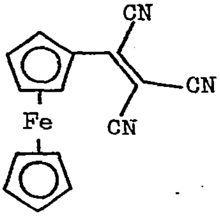

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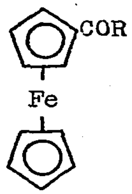
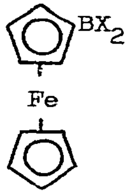


5.3

1,1'-Dimethylferrocene was prepared in high yield by treating a methanol-sodium methoxide slurry with iron(II) chloride, iron powder and methylcyclopentadiene[60]. The treatment of ferrocene with o-(RO_2C)C_6H_4COCl (R = alkyl) in the presence of aluminium chloride gave o-carboxybenzoylferrocene in good yield[11].

Acylferrocenes (5.3; R = Me, $CHMe_2$, cyclohexyl, 1-adamantyl, Ph) were obtained in yields of 41-76% by treatment of ferrocene with the corresponding acid chlorides in hexane and using molybdenum hexacarbonyl as the Friedel-Crafts catalyst. The products were free from diacylated ferrocenes[62]. Ferrocenylboron halides (5.4; X = Br, I) were prepared directly in good yield by the reaction of ferrocene with BX_3 (X = Br, I) in carbon disulphide. Halogen exchange gave the ferrocenyl-boranes (5.4; X = F, Cl)[63].

An excess of ferrocene was allowed to react in the presence of aluminium chloride and aluminium with the following polyaromatic molecules: biphenyl; diphenylmethane; fluorene;



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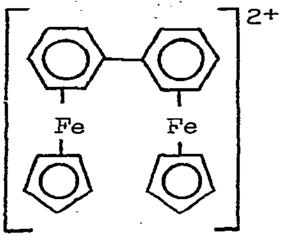


5.5

9,10-dihydroanthracene; 1,2:4,5-dibenzo-1,4-cycloheptadiene; 3,3'4,4'-tetramethylbiphenyl; *p*-terphenyl, anthracene, phenanthr pyrene, chrysene, *p*-phenylnaphthalene and 1,2:5,6-dibenzanthrace Two η-cyclopentadienyliron (II) moieties π-bonded to each of the arenes to give dications which were isolated as the PF_6^- salts. For example ferrocene and biphenyl gave the dication (5.5)[64].

Ferrocene was decomposed thermally at 570^{o} and 150-520 mm pressure to give hydrogen, methane, ethane and ethylene. Under similar conditions acetylferrocene gave hydrogen, methane, ethan ethylene and carbon monoxide[65]. The iodination of ferrocene in 1,2-dichloroethane gave $(\eta\text{-}C_5H_5)_2FeI_4$, which was thought to be iodoferricinium triiodide. When this was dissolved or sublimed it gave $[(\eta\text{-}C_5H_5)_2Fe]^+I_3^-$ [66].

When ferrocene was heated with thiourea at 140^{o} in a sealed, evacuated tube a 1:3 ferrocene:thiourea clathrate was formed. Th clathrate exhibited a reversible phase transition at 162^{o}K which compares with the phase transition of ferrocene at 163.9^{o}K. Ferrocene and nickelocene together gave a mixed clathrate althoug nickelocene itself was not taken up by thiourea[67].

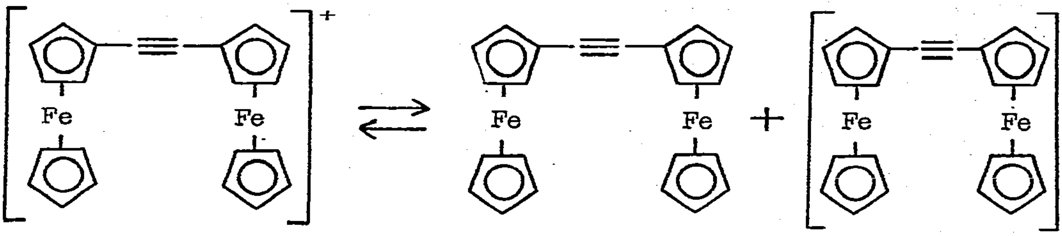
The solubility of ferrocene in cyclohexane, heptane, isoocta carbon tetrachloride and other perhaloalkanes, carbon disulphide and dioxan was determined at 25° and in some cases at two other temperatures. The results were discussed and interpreted in terms of the Scatchard-Hildebrand theory[68].

6. FERRICINIUM SALTS

The ferricinium ion was shown to exhibit a molecular electronic Raman effect. The transitions occurred at 213 cm^{-1} and 1,580 cm^{-1} to spin-orbit levels of the ground electronic configuration $(a_{1g})^2(e_{2g})^3$. The positions of the spin-orbit states obtained from the Raman spectrum of $[(\eta\text{-}C_5H_5)_2Fe]BF_4$ agreed with EPR data[69].

The rotating ring-disc electrode method was used for identification of the products of the alkaline reduction of nitroferrocene. It was shown that the cathodic reduction of this compound involved formation of anion-radicals of nitroferrocene, unstable ferrocenylhydroxylamine and aminoferrocene[70]. The ferrocene-ferricinium electrode was investigated in water, acetonitrile, ethanol, dimethylsulphoxide and dimethylformamide using single scan cyclic voltammetry and phase sensitive ac polarography. In all five solvents the oxidation-reduction was pseudo-reversible with an electron transfer rate constant of approximately 10^{-2} cm/sec. In each solvent a slow irreversible step involving the ferricinium cation followed the electron transfer. Therefore slow cyclic voltammetry or polarography are the preferred methods rather than potentiometry if ferrocene is used as a reference electrode in non-aqueous solvents[71].

One electron oxidation of diferrocenylacetylene (6.1) gave the purple mixed-valence diferrocenylacetylene cation (6.2) and further oxidation gave the stable pale green dication (6.3). The mono- and di-cations (6.2 and 6.3) were characterized by cyclic voltammetry and absorption spectroscopy. The cation (6.2) exhibited an intervalence transfer transition in the IR and underwent disproportionation as indicated in Scheme 1. Approximately 90% of the species in the equilibrium mixture at 25° are the

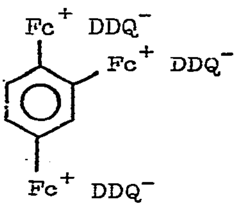


6.2 6.1 6.3

SCHEME 1

monocations (6.2)[72]. The oxidation of both 1,2,4- and 1,3,5-triferrocenylbenzene with 2,3-dichloro-5,6-dicyanoquinone (DDQ) gave only the trioxidized salts (6.4 and 6.5). Unsuccessful attempts were made to prepare mixed valence state ferrocene salts by changing the ratio DDQ to the cyclic trimer in the reaction mixture. Even when a large excess of the cyclic trimers were used only the trisalts (6.4 and 6.5) were isolated[73].

Ferricinium complexes were obtained by the oxidation of ferrocene with o-chloranil. The first formed products were the mono- and tri-ferricinium ions (6.6 and 6.7). Further hydrolysis of the simple ferricinium salt (6.6) gave the product (6.7)



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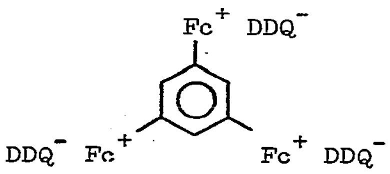

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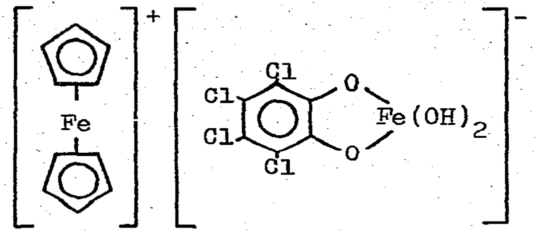

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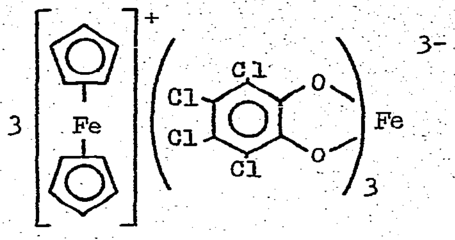

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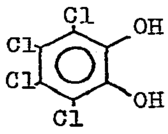

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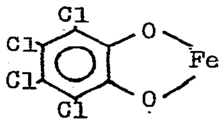

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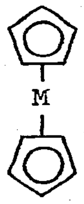


6.10

together with the diol (6.8) and its iron (II) salt (6.9)[74]. The addition of ferrocene, at room temperature, to a benzene solution of trichloroacetic acid gave almost quantitative yields of ferricinium trichloroacetate and trichloroacetaldehyde.

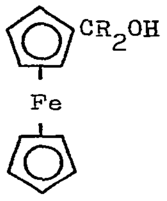
$$2FcH + 3CCl_3CO_2H \longrightarrow 2(FcH^+CCl_3CO_2^-) + CCl_3CHO + H_2O$$

The kinetics of this reaction were studied by spectroscopic methods and they were found to be dependent on the strengths of the acids used. With permethylferrocene the rates of oxidation were much higher than with ferrocene. The results indicated that the electron donor properties of the ferrocenes and the acid strength of the oxidizing agent were both important factors in the reaction[75].

Ferrocene was oxidized by the complex $(PhCN)_2PdCl_2$ in benzene to the ferricinium salt $FcH^+PdCl_3^-$ while vinylferrocene gave a binuclear olefin complex, $(FcCH{=}CH_2.PdCl_2)_2$ under the same conditions[76]. The chemical and electrochemical oxidation of the iron group metallocenes (6.10; M = Fe, Ru, Os) has been reinvestigated. Ferrocene gave only the ferricinium ion at platinum and mercury anodes while ruthenocene and osmocene did not give isolable metallicinium salts. The reactivity of the three metallocenes (6.10; M = Fe, Ru, Os) towards mercury (II) chloride has also been studied. Unstable complexes with the stoichiometries $(\eta\text{-}C_5H_5)_2Fe.6HgCl_2$ and $(\eta\text{-}C_5H_5)_2Fe.7HgCl_2$ were obtained from ferrocene while stable 1:1 complexes were formed by ruthenocene and osmocene. The osmocene complex was the most stable and least soluble of the three[77].

7. FERROCENYLCARBENIUM IONS

Ferrocenylcarbinols (7.1; R = alkyl) were dehydrated with sodium tetraphenylborate to give the corresponding α-ferrocenyl-carbenium ions (7.2; R = alkyl) in yields of 59-82%[78]. The spec scopic properties of 1-acetyl-1'-α-hydroxyethylferrocene,



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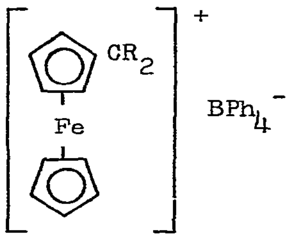

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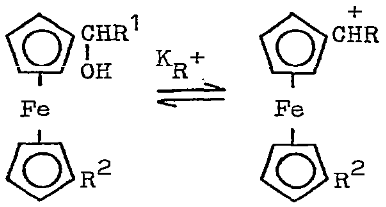

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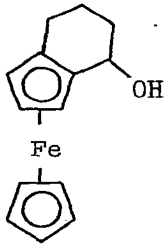
7.4

1,1'-bis(α-hydroxyethyl)ferrocene and their corresponding α-ferrocenylcarbenium ions have been interpreted in terms of intramolecular hydrogen bonding between the interannular substit uents. The restricted rotation required by the hydrogen bond ga rise to distinct conformers and one or more pairs of enantiomers[79].

The equilibrium between ferrocenyl alcohols (7.3; R^1 = H, Me, Ph, R^2 = H; R^1 = Me, R^2 = Et, Br, CHOHMe) and the α-ferrocenyl carbenium ions (7.4; R^1 = H, Me, Ph, R^2 = H; R^1 = Me, R^2 = Et, Br, CHOHMe) in aqueous sulphuric acid has been studied. The ferrocenophane alcohols (7.5 and 7.6) were investigated in the same way. The equilibrium constants K_{R^+} and the pK_{R^+} values were determined and the latter were correlated with the pK_a values of the corresponding ketones. The pK_{R^+} values were compared with the solvolysis rates for the appropriate ferrocenylalkylacetates and a good correlation was obtained. The ferrocenylalcohols (7.3, 7.5 and 7.6) were not good acid-base indicators by comparison with the corresponding ketones[80]. The vinylferrocene (7.7) was converted to the binuclear α-ferrocenylcarbenium ion (7.8) on treatment with sodium tetraphenylborate in acetic acid. The carbenium ion



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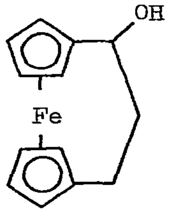

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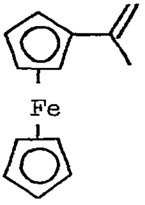

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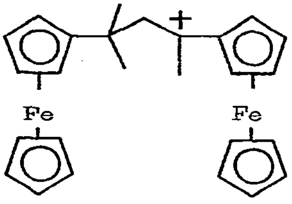

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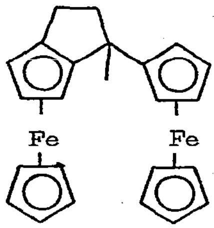

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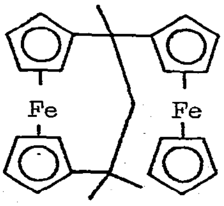
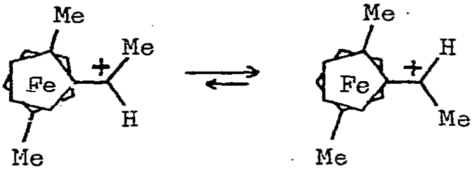


7.10

decomposed in acetone and nitromethane at room temperature to th ferrocenophanes (7.9 and 7.10) in 90% yield[81].

Watts and Turbitt have investigated the structure and bondi in a series of ferrocenylcarbenium ions. The carbenium ions (7.1 and 7.12) were generated in CF_3CO_2H and the rate of isomerism [(7.11) ⇌ (7.12)] was measured using ^1H NMR spectroscopy. The thermodynamic quantities related to the free energy barrier to rotation around the exocyclic bond were calculated. The rate of racemization of the ferrocenylcarbenium ions (7.13 and 7.14) in CF_3CO_2H was determined by measuring the loss of optical activity at 546 and 578 nm (Hg source) and the free-energy barrier to rota around the $Fc-(\overset{+}{C}HMe)$ bond was calculated. ^1H NMR spectroscopy wa used to investigate the behaviour of the ferrocenylcyclohexyl



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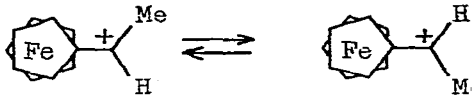

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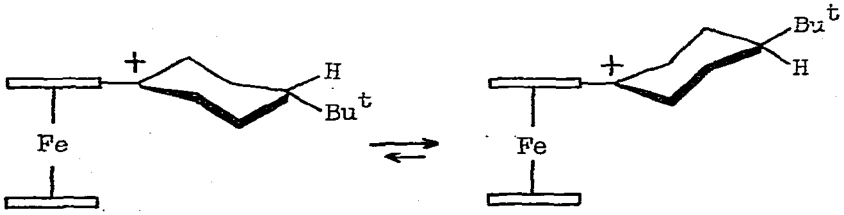

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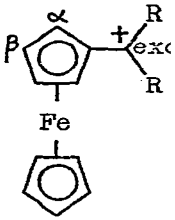


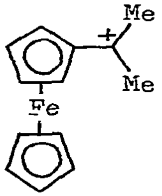
7.17

carbenium ion [(7.15) ⇌ (7.16)][82]. From $p\underline{K}_R{}^+$ measurements eviden was obtained relating to the distribution of positive charge in ferrocenylalkylium ions. The ferrocenyl-cation (7.17) is more stabilized by methyl substitution at the β-than at the 1'- position and substitution at the α-position exerts a destabilizing effect. It was shown also that cation stability was sensitive to structural deformation of the system caused by interannular bridging. A series of 1-(acetylferrocenyl)-3-phenylallylium cations were treated with sodium methoxide and from the analysis of the products obtained it was concluded that an acetyl substituent reduces the capacity of the ferrocenyl group to delocalize positive charge. The ability of the ferrocenyl group to stabilize a cation was compared with that of the ruthenocenyl group by measuring the $p\underline{K}_{R^+}$ values of two 1-metallocenylethylium cations. The ruthenocenyl group was more effective than the ferrocenyl group in stabilizing a carbenium ion[83].

From the results described in the last two papers, the following conclusions concerning the structure in solution of ferrocenylcarbenium ions were made: (a) there was no evidence for stabilization of the system by ring slip displacement of the fulvene ligand as was suggested by Richards[84, 85], (b) the 16-electron formulation proposed by Pettit[86] was discounted, (c) there was no evidence to support a strong bond between the iron atom and C_{exo} of the fulvene ligand, (d) the detection of restricted ligand rotation supported a structure containing a folded fulvene ligand, as proposed by Cais[87] and Gleiter[88], (e) the preferred geometry of the carbenium ion in the ground state could be a ring tilted structure with C_{exo} on the open side of the sandwich.

α-Substituted 1-ferrocenylethylium and 1-ferrocenyl-1-methylethylium cations were generated in CF_3CO_2H. These cations rearranged to give a mixture of the isomeric β- and 1'- substituted cations in the presence of ferrocene or an alkylferrocene. The rearrangement occurred by means of an equilibrium controlled transfer of the ($\mathrm{Me\overset{+}{C}H}$) or ($\mathrm{Me_2\overset{+}{C}}$) group between cations with ferrocene or an alky ferrocene functioning as the transport agent. Thermodynamically more stable ferrocenylalkylium ions (e.g. $\mathrm{Fc\overset{+}{C}HPh}$, $\mathrm{Fc_2\overset{+}{C}H}$) and rut cenylalkylium ions did not undergo rearrangement[89].

The ferrocenylalkylium ion (7.18) generated by treating 2-ferrocenylpropan-2-ol with trityl tetrafluoroborate in dichlor methane, was treated with a large excess of cyclopentadiene. On of the products isolated (7.19) was that formed by a 1:1 additio



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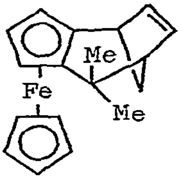

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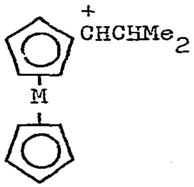


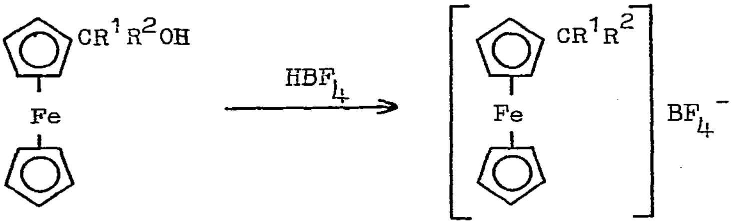
7.20

of the cation (7.18) and cyclopentadiene followed by deprotonatio The structure of the addition product (7.19) was determined by X-ray methods[90].

The relative stabilities of α-ferrocenyl- and α-phenyl-vinyl carbenium ions have been compared by measuring the rates of acid-catalysed hydration of ferrocenyl- and phenyl-acetylene, the relative rates obtained were 1.0 and 10^{-5} respectively. The corresponding reactions of vinylferrocene and styrene were also included in the comparison and the relative rates were 0.11 and 0. The faster hydration of the acetylenes was ascribed to retent of the extended conjugation of the ground state in the carbenium ion intermediates[91].

The ^1H and ^{13}C NMR spectra of the cations (7.20; M = Fe, Ru, Os) have been compared. The results confirmed that all three ⍺-metallocenylcarbenium ions (7.20) were chiral. The alkyl group in the ferrocene cation (7.20; M = Fe) showed major involvement in charge stabilization while the metallocene group was relatively more important in the cations (85; M = Ru, Os). In each case the positive charge was extensively delocalized over the whole metallocenyl group[92].

Allenmark has described a convenient synthetic route to ferrocenylacetonitriles and N,N-dialkylferrocenylmethylamines. The ⍺-ferrocenylcarbenium fluoroborate (7.22; R^1 = Me, Ph; R^2 = H, Ph) was precipitated quantitatively by stirring an ethereal solution of the carbinol (7.21; R^1 = Me, Ph; R^2 = H, Ph) with fluoroboric acid. The salt (7.22), dissolved in dichloromethane, was stirred with aqueous sodium cyanide to form the nitrile (7.23; R^1 = Me, Ph; R^2 = H, Ph). The amine (7.24; R^1 = Me, Ph; R^2 = H, Ph) was obtained



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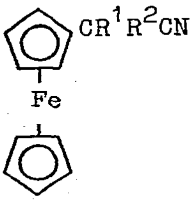

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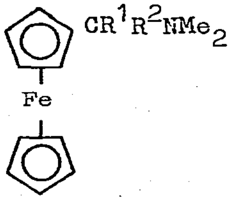


7.24

by the addition of the solid salt (7.22) to a solution of dimethyl amine in dichloromethane[93].

8. FERROCENE CHEMISTRY

(i) Photochemistry

The photochemistry of benzoylferrocene in hydroxylic solvents was investigated. Benzoylferrocene absorbed light in methanol, anhydrous ethanol and 1-propanol between 313 and 472 nm which resulted in the formation of excited states and the subsequent oxidation of the complex to the benzoylferricinium cation. Eviden was presented for hydrogen-bonding between the keto group of benzoylferrocene and the hydroxylic solvents. It was assumed that the primary step in the photoreaction was an electron-transfer from benzolylferrocene to the solvent[94].

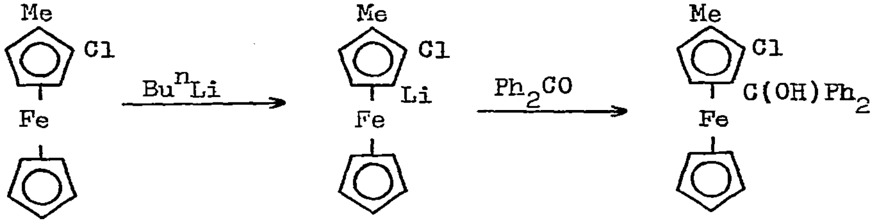
$$\mathrm{FcCOPh} + \mathrm{ROH} \xrightarrow{h\nu} (\mathrm{FcCOPh})^{+} + e^{-}(\mathrm{ROH})$$

The irradiation of ferrocene in the presence of N_2O in ethanol or cyclohexane at 253.7 nm gave a yield of nitrogen which was a continually increasing function of N_2O concentration. At wavelengths greater than 313 nm no nitrogen was formed. Alkyl substituents on the ferrocene gave an increased yield of nitrogen and this effect appeared to run in parallel with the influence on the half-wave potentials. The mechanism was thought to involve an electron transfer to N_2O from a photoexcited ferrocene in competition with its spontaneous deactivation. The quantum yield of this photoexcited species was found to be less than unity so it was deduced that it was not the primary photoexcited state[95].

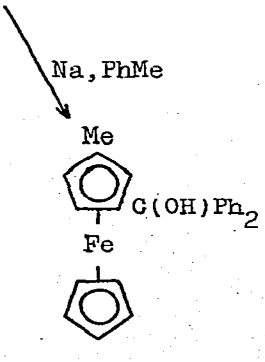
The irradiation (365 or 313 nm) of a solution of ferrocene, azulene and sodium acetate in carbon tetrachloride-ethanol gave ethyl 1-azulenecarboxylate. This product was not formed in the absence of ferrocene. When the reaction was carried out in a mixture of chloroform and ethanol, 1-formylazulene was formed. Ethyl- and acetyl-ferrocene were less efficient as catalysts in this reaction[96].

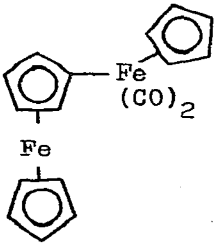
(ii) Derivatives containing other metals (metalloids)

A specific route to 1,2,3-trisubstituted and 1,3-disubstituted ferrocenes has been reported. 2-Chloro-1-methylferrocene (8.1) was metallated with n-butyllithium to form the 3-lithio intermediate (8.2) and this was treated with benzophenone to give the 1,2,3-trisubstituted ferrocene (8.3). This compound was dechlorinated with sodium in toluene to give the 1,3-disubstituted product (8.4) in 34% yield overall. 1,3-Dimethylferrocene was obtained from the same starting material by treating the lithio intermediate with methyl iodide rather than benzophenone[97].



8.1 8.2 8.3





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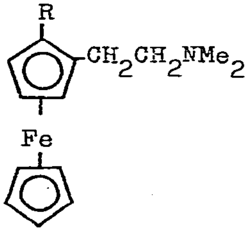
8.4

Ferrocenyllithium and 1,1'-dilithioferrocenetetramethylethylenediamine were treated with $(\eta\text{-}C_5H_5)_3UCl$ to give mono- and bis-[tris(η-cyclopentadienyl)uranium]ferrocene respectively. These π-bonded organouranium compounds were very sensitive to oxygen and moisture[98]. The treatment of ferrocenyllithium with bromodicarbonylcyclopentadienyliron gave the complex (8.5). The reaction of ferrocenoic acid chloride with $(\eta\text{-}C_5H_5)Fe(CO)_2Na$ gave $FcCOFe(CO)_2(\eta\text{-}C_5H_5)$; the corresponding tungsten derivative was prepared by a similar route[99].

1-Lithio-2-[(dimethylamino)ethyl]ferrocene (8.6; R = Li) was treated with tri-n-butylborate to give the boronic acid [8.6; R = $B(OH)_2$]. The boronic acid was converted to the corresponding chloro, bromo and iodo derivatives (8.6; R = Cl, Br and I).



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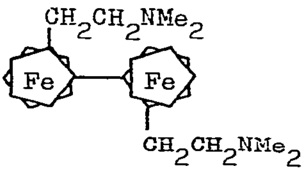

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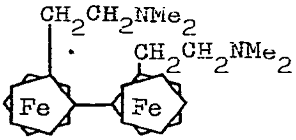
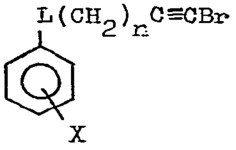


8.8

Treatment of the lithio-ferrocene (8.6; R = Li) with paraformaldehyde gave the alcohol (8.6; R = CH_2OH) and treatment with cobalt (II) chloride gave the isomeric biferrocenes (8.7 and 8.8)[100]

Peet and Rockett have called attention to the explosion hazard inherent in the use of perchloryl fluoride, a reagent suggested previously for the conversion of lithioferrocene to fluoroferrocene[1] The trisubstituted ferrocenes (8.10; R^1,R^2 = Me,Et; X = halogen; L = O, Se, Te; n = 1-3) were formed from the bromoacetylenes (8.9; X = halogen; L = O, Se, Te; n = 1-3) and the appropriate 1,1'-dialkyl ferrocene in the presence of n-butylamine, hydroxylamine hydrochloride as reducing agent and copper chloride as a catalyst[102].

Reuter and Damrauer have described the formation and physical properties of ferrocenyltrimethylsilylketone (8.12). Formylferrocene



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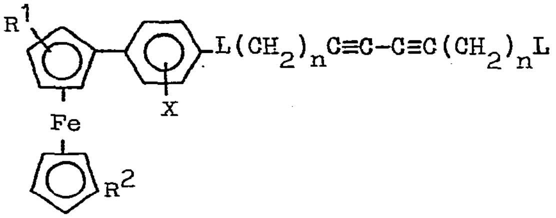
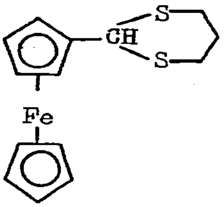


8.10

was treated with 1,3-propanedithiol in the presence of hydrogen-chloride to give the dithiane (8.11). Metallation of this intermediate with n-butyllithium gave the α-lithio derivative and the α-trimethylsilyl compound was formed from it with trimethylchlorosilane. Careful hydrolysis afforded the required ketone (8.12) in good overall yield. The IR carbonyl stretching frequency of the trimethylsilyl ketone (8.12) was 1589 cm^{-1}, a lowering of 83 cm^{-1} from acetylferrocene. This difference was interpreted in terms of extreme steric crowding of the ketone group. The pKa value for the compound (8.12) was measured as -2.8(± 0.3) and was close to the value for acetylferrocene suggesting that the ferrocenyl group dominates its basicity[103].

The acid catalysed protodeboronation of ferroceneboronic acid and protodesilylation of ferrocenyltrimethylsilane have been studied under first order conditions. Protodeboronation occurred 7.0×10^6 and protodesilylation occurred 2.7×10^4 times as fast as in the corresponding benzene derivatives, phenylboronic acid and phenyltrimethylsilane respectively[104]. The alkylsilanes R_3SiH (R_3 = Me_2 Et_3) added to vinyl-ferrocenes (8.13; R^1 = Me, Et, Ph) to give ferrocenyl-disilanes (8.14). Competitive reactions were carried



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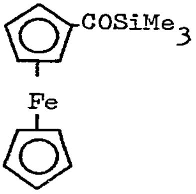

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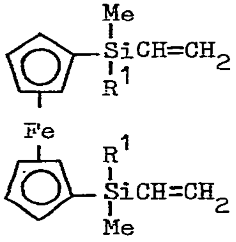

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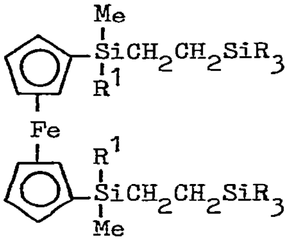
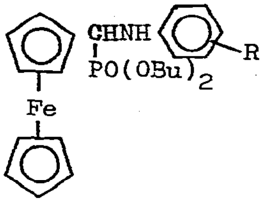


8.14

out also between vinyl- and propenyl-ferrocenes[105]. The phosphorus compounds (8.15; R = H, m-Cl, p-Cl, p-Br, o-OH, m-OH, m-NO_2, p-CO_2H and 8.16) were formed by addition of dibutyl phosphite to the carbon-nitrogen bond of the corresponding anils[106].

Ferrocenemethanol was heated with the alkyl arsines $MeAs(NMe_2)_2$ and Me_2AsNMe_2 to give the ferrocene arsenic derivatives (8.17 and 8.18) respectively[107]. The condensation of ferrocenethiol with haloalkanecarboxylic acids gave a series of ferrocenylthioalkanecarboxylic acids (8.19)[108]. Ferrocenyl-gold complexes (8.21; R = H, Cl, OMe, CH_2NMe_2) have been prepared by the reaction of gold complexes (8.20; R = H, Cl, OMe, CH_2NMe_2) with tetrafluorobori acid. An X-ray study of the complex (8.21; R = H) verified the existence of a gold-gold bond with the ferrocenyl group behaving as a bridge between the two gold atoms. The plane of the triangle C-Au-Au was approximately perpendicular to the cyclopentadienyl ring. The Au-Fe distance (2.82 Å) was short and it was thought that Au-Fe interaction might constitute a chemical bond but it did not distort the ferrocenyl group.



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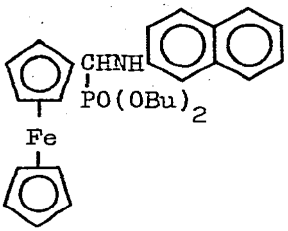

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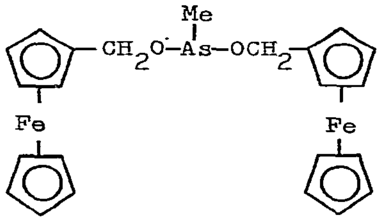

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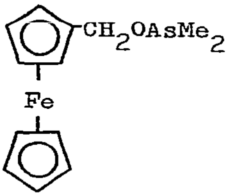

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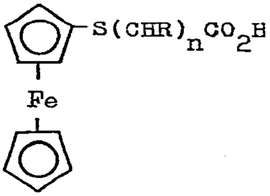
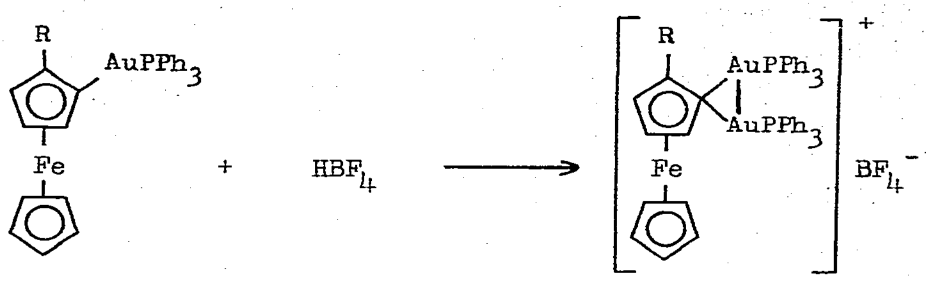
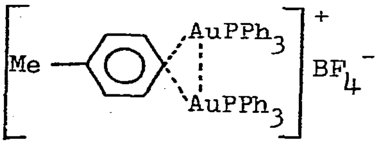


8.19

Treatment of the complexes (8.21; R = H, Cl, OMe, CH_2NMe_2) with nucleophiles such as phosphines, amines and halides gave $^+AuPPh_3$ transfer reactions with regeneration of the initial gold complexes (8.20; R = H, Cl, OMe, CH_2NMe_2). The treatment of diferrocenylmercury with the tolyl complex (8.22) also gave the ferrocenyl complex (8.21; R = H)[109,110].



8.20 8.21



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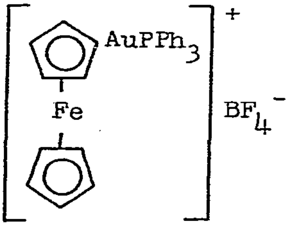

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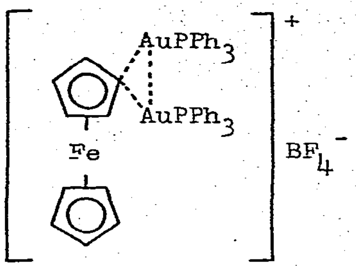
Diferrocenylmercury was treated with $MeAuPPh_3$ in the presence of fluoroboric acid to give the red crystalline ferrocenylgold salt (8.23). Similar reactions were carried out with bis(1'-bromoferrocenyl)mercury and bis(1'-carboxymethylferrocenyl)mercury[1]

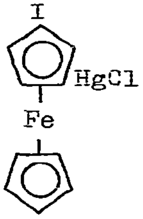
The reaction of HBF_4 with vinyl(triphenylphosphine)gold gave $[CH_2 = CH(AuPPh_3)_2]^+BF_4^-$. Treatment of this salt with ferrocenyl(triphenylphosphine)gold gave the ferrocenyl-gold compound (8.24) and vinyl(triphenylphosphine) gold[112]. The reaction of ferrocenylmercurichloride with $HCCO_3(CO)_9$ gave $FcCCo_3(CO)_9$[113].

Iodoferrocene was treated with mercury (II) acetate to give a mixture of the 3-chloromercuri- and 1'-chloromercuri-iodoferrocenes (8.25 and 8.26) together with bis(2-iodoferrocenyl)mercury (8.27). This compound (8.27) appeared to be formed from 2-chloromercuri-iodoferrocene during chromatography and although two isomers were anticipated[114] only a single product with a sharp melting point



8.24

was eluted. Metallation of the binuclear complex (8.27) with n-butyllithium gave 1,2-dilithioferrocene which was carbonated to the corresponding diacid and then dehydrated to the intramolecular anhydride. Iodination of the symmetrical compound (8.27) gave 1,2-diiodoferrocene[115].



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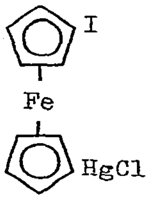

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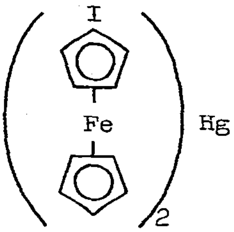
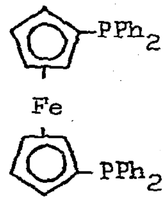


8.27

(iii) Complexes of ferrocene containing ligands

The reaction of 1,1'-bis(diphenylphosphino)ferrocene (8.28) with mercury (II) halides and mercury (II) thiocyanate gave complexes of the type (8.29 and 8.30; X = Cl, Br, I, SCN). In all these complexes the phosphino-ferrocene (8.28) behaved as a bidentate ligand with the phosphorus atoms bonded to the mercury. On reaction of the ligand (8.28) with mercury (II) cyanide the cation (8.31) was formed and it was isolated as either the BF_4^- or PF_6^- salt. Treatment of the phosphino-ferrocene (8.28) with SnX_4 (X = Cl, Br) gave complexes in which the phosphorus was bound to tin[116].



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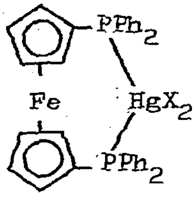

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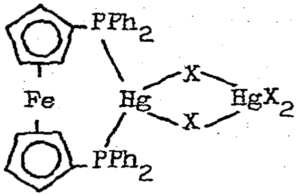

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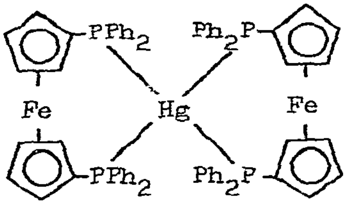

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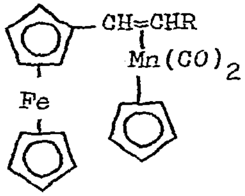
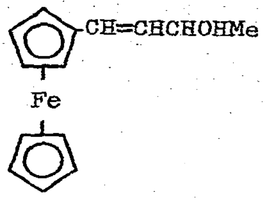


8.32

The treatment of tricarbonylcyclopentadienylmanganese with vinyl- and β-benzoyl-vinylferrocene gave the complexes (8.32; R = H) and (8.32; R = COPh) respectively[117]. The ferrocene secon ary alcohols (8.33 and 8.34) were dehydrated with copper sulphate in the presence of diiron nonacarbonyl to form the π-diene iron-tricarbonyl complexes (8.35 and 8.36) respectively[118].

Alper has described the formation of thiopivaloylferrocene (8.38) from pivaloylferrocene (8.37) P_4S_{10} and the *ortho*-metallat of this sulphur compound (8.37) with sodium tetrachloropalladate in methanol to form the complex (8.39)[119]. Ferrocene carboxylic acid (L_1) and ferrocene 1,1-dicarboxylic acid (L_2) were treated with uranyl nitrate to give the complexes $[UO_2(L_1)_2(H_2O)_2]$ and $[UO_2(L_2)(H_2O)_2]_n$. The latter complex was thought to have a polyme structure (8.40). The ligands (1-phenylpropan-1,3-dione)ferrocene (L_3) and 1,1'-di(phenylpropan-1,3-dione)ferrocene (L_4) when treated



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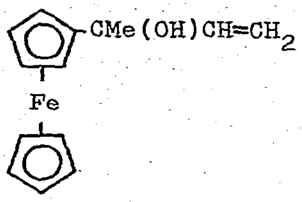

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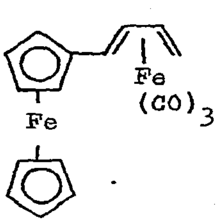

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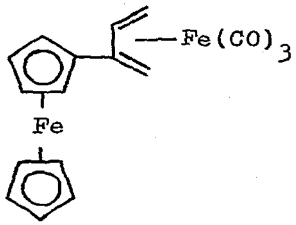
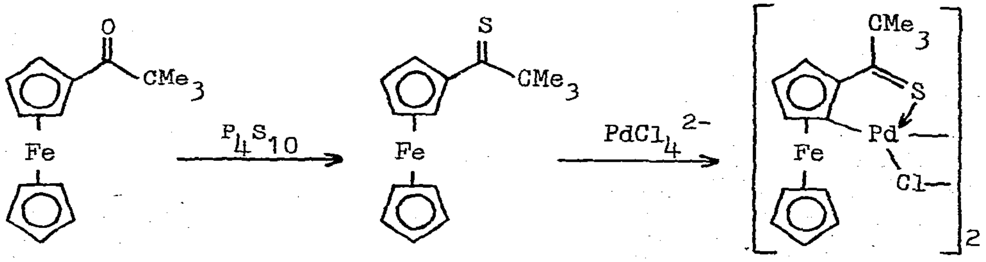


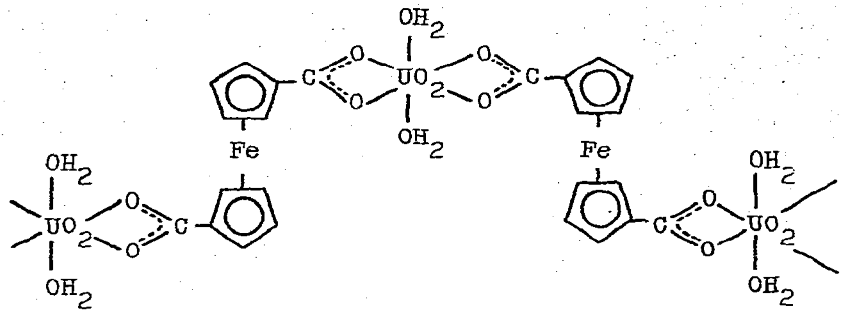
8.36

with uranyl nitrate gave the complexes $[UO_2(L_3)_2(H_2O)]$ (8.41) and $[UO_2(L_4)(H_2O)]_n$ (8.42)^{120}.

Imai and Ota have compared the properties of several acetoacetylferrocene complexes of first-row transition metals. The manganese (II) complex (8.43; M = Mn) was tetrahedral while the copper (II) complex (8.43; M = Cu) was square planar. The chelate



8.37 8.38 8.39



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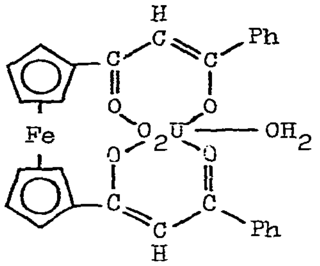

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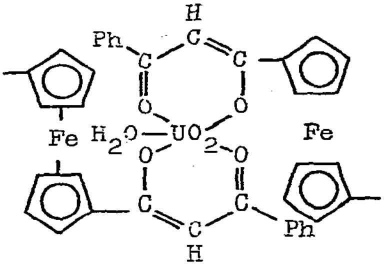


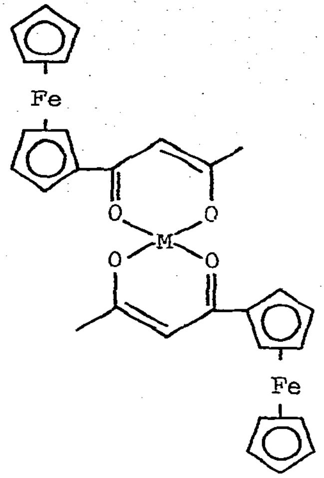
8.42

complexes readily formed adducts with pyridine, the adducts (8.44; M = Mn, Co, Cu) were octahedral as was the mixed adduct (8.45). The electronic spectra of the complexes were analyzed in terms of O_h symmetry for the cobalt (II) and nickel (II) chelates and by C_{2h} symmetry for the copper (II) chelate[121].

(iv) General chemistry

The diamide (8.46) was formed from formylferrocene, t-butylcyanide, benzaldehyde and phenylacetic acid and was cleaved selectively to give benzylphenylacetamide (8.47)[122].

Trans-1,2-diferrocenoylethylene (18%) (8.48) was formed as the principal product from the acetylation of ferrocene with the diacid chloride of fumaric acid in the presence of a large excess



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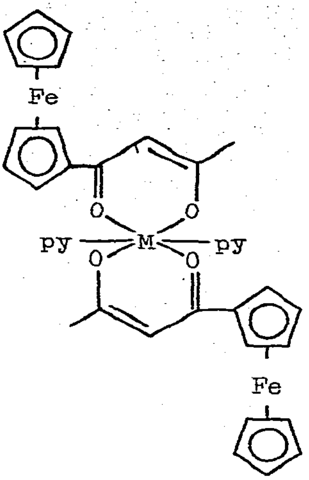

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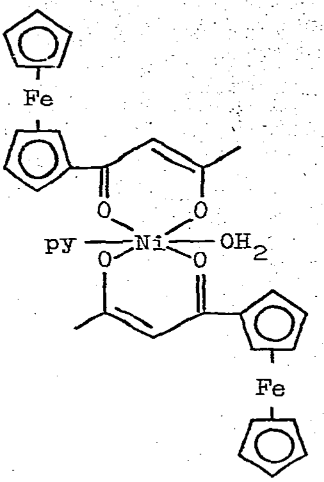
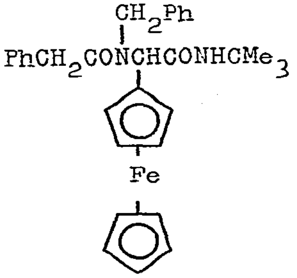


8.45

of sodium chloride. 1,2-Diferrocenylethane and trans-β-ferrocenoylacrylic acid were also formed in low yield[123].

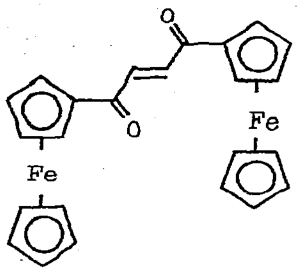
Mono- and 1,1'-di-haloacylferrocenes have been prepared by Friedel Crafts acylation of ferrocene and cinnamoylferrocene with haloacyl halides. Typical products were the ketones (8.49;



8.46

$PhCH_2CONHCH_2Ph$

8.47



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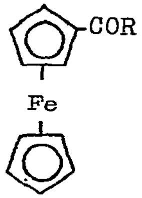
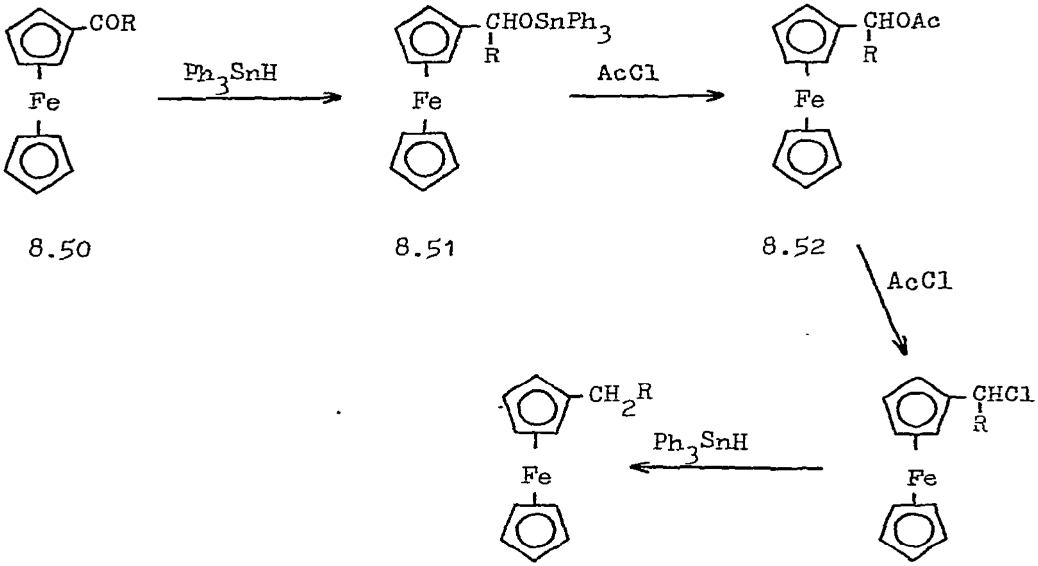


8.49

R = CH_2CH_2Cl, CH_2CH_2Br, CHClMe) and they were effective in inhibiting the growth of bacteria[124]. Patin and Dabard have examined the mechanism of reduction of ferrocene aldehydes and ketones to ferrocene alkanes by triphenyltin hydride and acetyl chloride. The carbonyl compounds (8.50; R = H, Me) gave the tin complexes (8.51; R = H, Me) on treatment with triphenyltin hydri

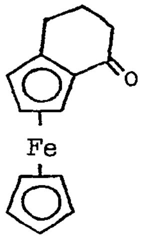


8.54 8.53

and these intermediates formed the acetates (8.52; R = H, Me) with acetyl chloride. Further reaction with acetyl chloride converted the acetates (8.52) to the chlorides (8.53; R = H, Me) which were reduced with triphenyltin hydride to the alkanes (8.54; R = H, Me). The importance of stable α-ferrocenyl carbenium ions in the reduction was emphasised[125].

Acylferrocenes FcCOR (R = Me, Ph) were reduced with Ph_3SnH to give the corresponding alcohols, but in the presence of a radical initiator, mixtures of FcCHOHR, $FcCH_2R$ and FcCHROCHRFc were obtained. When the ferrocenylcyclohexenone (8.55) was treated with Ph_3SnH only the <u>endo</u> isomer (8.56) was obtained. In the presence of a radical initiator a 73/27 mixture of <u>endo-exo</u> (8.56) was formed. The mechanisms of the reductions were discussed in terms of ionic and radical reactions[126].

Reduction of the ferrocenyl-ketones FcCOR (R = Me, Et, Pr, Ph, $PhCH_2$, 2-thienyl) by $Ph_3SnCl\text{-}AlCl_3$ gave $FcCH_2R$, the product yield decreased with increasing size of R[127]. The substituted acetylferrocene (8.57) was treated with dimethylformamide and phosphorus oxychloride followed by sodium hydroxide at 100° to form the ferrocenylacetylene (8.58). This acetylene was converted to the trimer (8.59) by heating with sodium in toluene[128].



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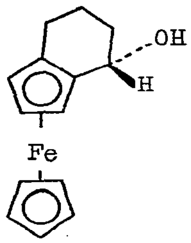
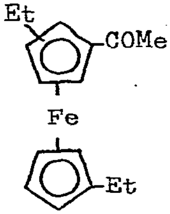


8.56

The reaction of acylferrocenes (8.60) with methylmagnesium



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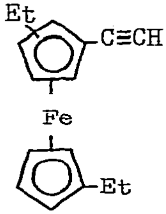
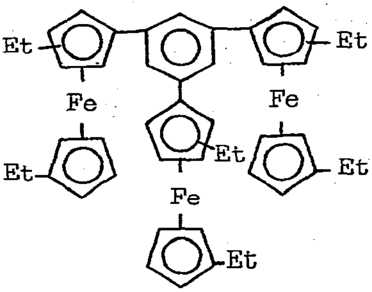
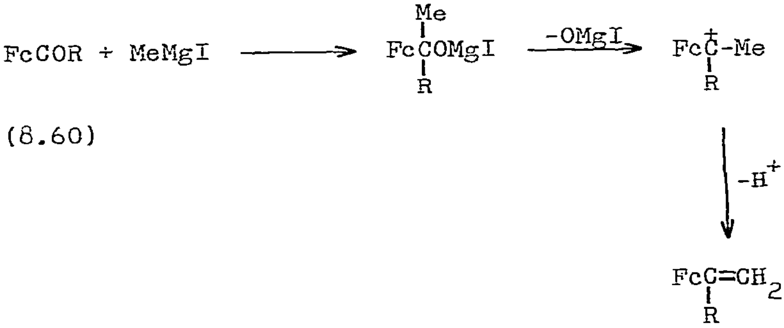


8.58



8.59

halides was investigated. Products other than the expected alcohol were obtained only when methylmagnesium iodide was used; the corresponding bromide gave the alcohol. The reaction with the iodide was thought to proceed via a carbenium ion (8.61).



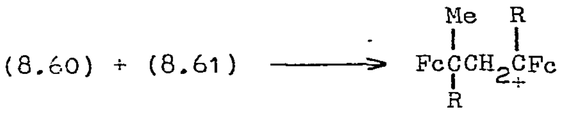
$$\mathrm{FcCOR + MeMgI \longrightarrow Fc\overset{Me}{\underset{R}{C}}OMgI \xrightarrow{-OMgI} Fc\overset{+}{\underset{R}{C}}{-}Me}$$

(8.60)

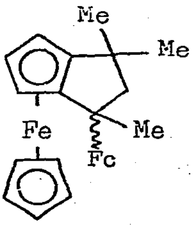
(8.61)

$$\xrightarrow{-H^+} \mathrm{Fc\underset{R}{C}{=}CH_2}$$

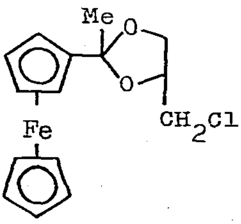
(8.62)



$$\mathrm{(8.60) + (8.61) \longrightarrow Fc\overset{Me}{\underset{R}{C}}CH_2\overset{R}{\underset{+}{C}}Fc}$$



8.63

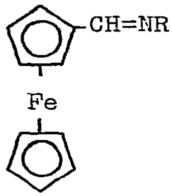


8.64

For benzoyl-ferrocene (8.60 R = Ph) the major product was the olefin (8.62; R = Ph) and with acetylferrocene homoannular ring closure occurred to give compound (8.63)[129].

1,1-Diferrocenylethylene was prepared by Grignard addition of methylmagnesium iodide to diferrocenylketone and pyrolysis of the resulting carbinol[130]. Acetylferrocene was condensed with epichlorohydrin in carbon tetrachloride in the presence of tin (IV) chloride to give the dioxolanylferrocene (8.64)[131].

The Schiff bases (8.65, R = m-$O_2NC_6H_4$, p-ClC_6H_4, p-$MeOC_6H_4$, $C_{10}H_7$, m-$H_2NC_6H_4$) were prepared by the condensation of formylferrocene with the corresponding amine. Reduction of the Schiff bases with lithium aluminium hydride gave the corresponding amines (8.66)[132].



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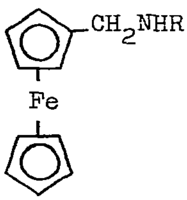

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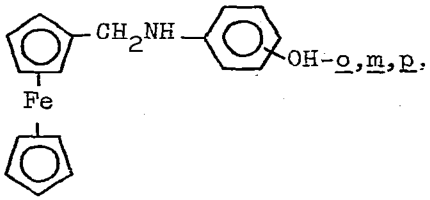

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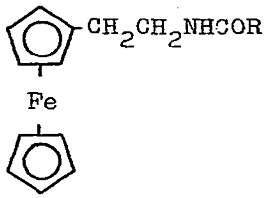

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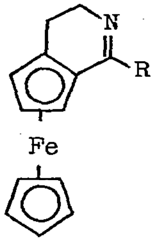

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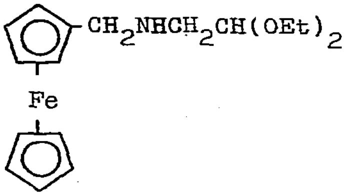
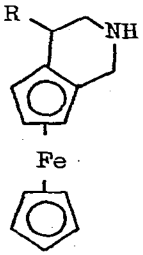


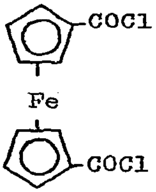
8.70



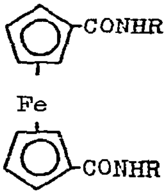
8.71

The secondary amines (8.67) were obtained by reduction of the corresponding imines with lithium aluminium hydride in ether-THF mixtures[133]. Popp and Moynahan have cyclized the amides [8. R = Me, $CH_2C_6H_3(OMe)_2$-3,4] with polyphosphoric acid to give the dihydropyridines [8.69; R = Me, $CH_2C_6H_3(OMe)_2$-3,4] while cyclizat of the hydrochloride of the aminomethylferrocene (8.70) with HCl gave the tetrahydropyridine (8.71; R = OH) as the hydrochloride. Cyclization of the amine (8.70) under reducing conditions (pallad on charcoal) gave the tetrahydropyridine (8.71; R = H)[134].

The ferrocenyl-carboxamides (8.73; R = Me, Et, Bu, Ph, $\underline{m}$-$MeOC_6H_4$, $\underline{m}$-ClC_6H_4) were prepared by treating the acid chloride (8.72) with the appropriate amine[135].



8.72



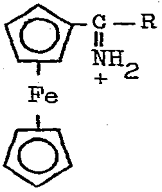
8.73

The addition of $PhSO_2Cl$ to the oximes (8.74 and 8.76) in the presence of base gave the corresponding ketone and either the amide (8.75) or the sulphonic acid derivative (8.77).

$$\underset{(8.74)}{\mathrm{FcC(Ph){=}NOH}} \longrightarrow \mathrm{FcCOPh} + \underset{(8.75)}{\mathrm{FcCONHPh}}$$

$$\underset{(8.76)}{\mathrm{FcC(R){=}NOH}} \longrightarrow \mathrm{FcCOR} + \underset{(8.77)}{\mathrm{FcC(R){=}NOSO_2Ph}}$$

R = Me, Et, Pr, CH_2Ph



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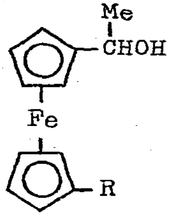
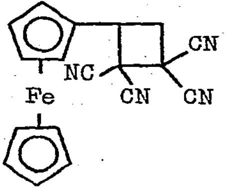


8.79



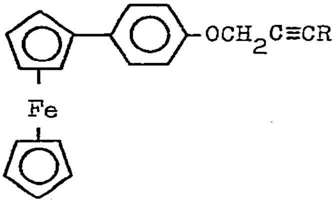
8.80

In the absence of base the cation (8.78) was formed[136]. The ferrocenylcarbinols (8.79; R = H, Cl, CO_2Me, CN) were reduced with triethylsilane to give the corresponding 1,1'-substituted ethylferrocenes. When the reaction was run in acetic acid-trifluoroacetic acid mixtures the rate was reduced as the electron withdrawing capacity of the ring substituent increased[137].

Vinylferrocene was treated with tetracyanoethylene to give the ferrocenylcyclobutane (8.80)[138]. A similar reaction was reported by Berger et al who treated substituted vinylferrocenes with tetracyanoethylene. It was proposed that the reaction was a two step process which involved a charged centre and this was stabilized by the ferrocenyl group[139].

Solvolyses of 2-(p-ferrocenylphenyl)ethyl-1,1-d_2-tosylate in acetone-water, glacial acetic acid and formic acid showed enhancements in the extent of label scrambling from C-1 to C-2 relative to labelled 2-phenyl tosylate. This enhancement was consistent with the ferrocenyl group being an electron donor[140].

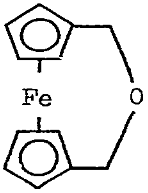
A series of N-(2-substituted ferrocenylmethyl)-N,N,N-trimethylammonium iodides was reduced with sodium in liquid ammonia or with sodium amalgam to give the corresponding 2-substituted methylferrocenes. The effectiveness of these two methods of reduction in this system was compared. Reduction of a series of N-(p-substituted benzyl)-N-ferrocenylmethyl-N,N-dimethylammonium halides occurred with cleavage of either the ferrocenylmethyl-nitrogen bond or the benzyl-nitrogen bond to give methylferrocene or dimethylaminomethylferrocene respectively[141]. Treatment of the phenylferrocene (8.81; R = H) with $PhOCH_2C{\equiv}CBr$ in butylamine in the presence of copper (I) chloride gave the diacetylene derivative (8.81; R = $C{\equiv}CCH_2OPh$) in good yield[142].



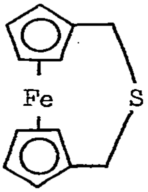
8.81

9. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

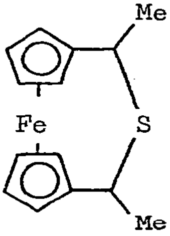
The reaction of 1,1'-di(hydroxymethyl)ferrocene with hydrogen sulphide gave a mixture of 2-oxa[3]ferrocenophane (9.1) and 2-thia[3]ferrocenophane (9.2). When the diol was treated with hydrogen sulphide in the presence of catalytic amounts of sulphuric acid only the ferrocenophane (9.2) was isolated. Under similar conditions 1,1'-di(α-hydroxyethyl)ferrocene gave 2-thia-1,3-dimethyl[3]ferrocenophane (9.3)[143].



9.1

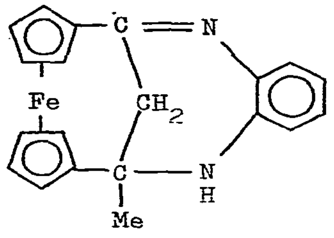


9.2

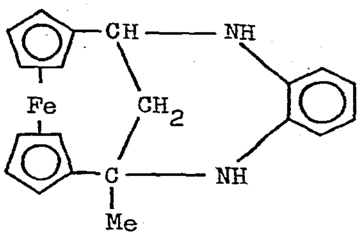


9.3

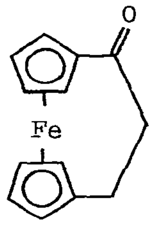
1,1'-Diacetylferrocene-aluminium chloride complexes and o-phenylenediamine were heated together in the molten state to give the bridged ferrocene (9.4). Reduction of this compound (9.4) with sodium borohydride gave the bridged ferrocene (9.5)[144].



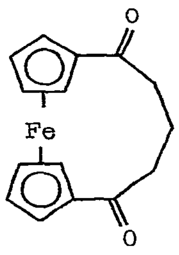
9.4



9.5

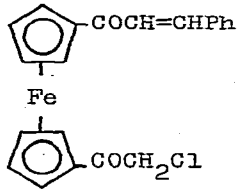


9.6

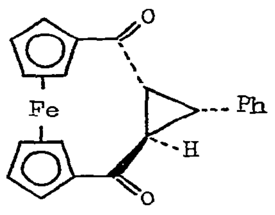


9.7

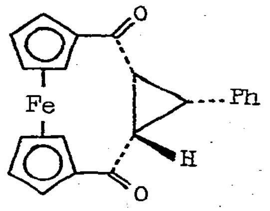
The ^{13}C and ^{1}H NMR spectra were recorded for a series of ferrocenophanes of the types (9.6 and 9.7)[145]. Treatment of the diketone (9.8) with alcoholic potassium hydroxide gave the [4] ferrocenophane (9.9) with formation of a cyclopropane ring in the bridge. The product was isolated as a mixture of two isomers



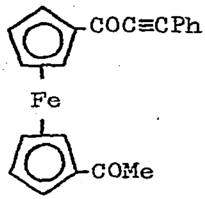
9.8



9.9



9.10



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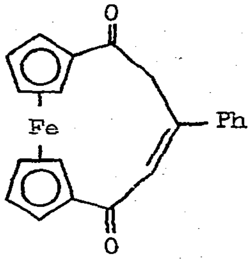
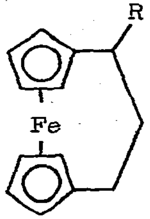


9.12

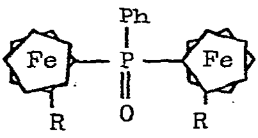


9.13

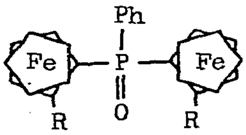
(9.9 and 9.10). Cyclization of the acetylferrocene (9.11) under the same conditions gave the [5]ferrocenophane (9.12)[146].

Nucleophilic substitution of the ferrocenophane (9.13; R = NMe_3I) was investigated. Treatment of this quaternary sal with dimethylamine, ammonia and sodium azide gave the products (9.13; R = NMe_2, NH_2, and N_3) respectively with retention of configuration. It was thought that the iron atom played an im role in the reaction mechanism[147].

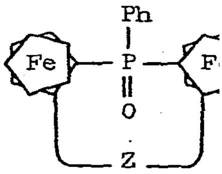
Metallation of phenyldiferrocenylphosphine oxide gave two isomeric dianions (9.14 and 9.15; R = Li), treatment of the mi with trimethylchlorosilane, bromine, carbon dioxide benzaldehyd and PhCH=NPh gave bifunctional products [9.14 and 9.15; R = SiM



9.14



9.15



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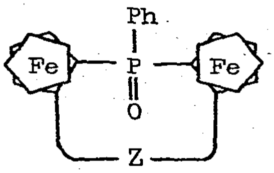

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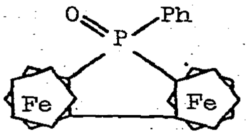
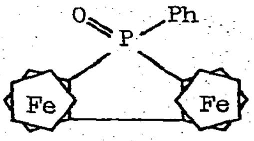


9.18



9.19

Br, CO_2H, CHOHPh and CH(Ph)NHPh] respectively. Cyclic products [9.16 and 9.17, Z = $SiMe_2$, $SiPh_2$, $SnBu_2$, C(OH)Ph] were obtained with dimethyldichlorosilane, diphenyldichlorosilane, di(n-butyl)tin dichloride and ethyl benzoate. The biferrocenes (9.18 and 9.19) were formed when cobalt chloride was the reagent. The isomeric products were separated by chromatography and characterized by ^1H NMR spectroscopy[148].

FERROCENE CONTAINING POLYMERS

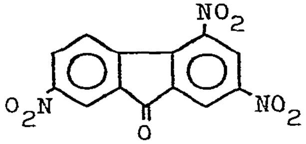
Ferrocene was polymerized in ketones and other polar solvents with a Lewis acid catalyst such as ferric chloride to give a brown flexible polymer with semiconductor properties[149]. Ferrocene was polymerized with crotonaldehyde in the presence of iron (III) chloride to give a crotonaldehyde-ferrocene copolymer in good yield. This copolymer was elastic, flexible, vulcanizable and it had a high electrical conductivity[150].

George and Hayes have investigated the polymerization of vinylferrocene in chloroform. Low molecular weight products were obtained by using initial monomer concentrations of 4.0 and 1.0 mole l^{-1}.. The spectroscopic properties of these polymers were similar to the properties of polymers prepared in benzene solution with a radical initiator. A small proportion of chlorine($<1\%$) was incorporated into the polymer and a radical initiation mechani was suggested with transfer of a hydrogen atom from solvent to monomer as the initiation step[151].

The radical polymerization of divinylferrocene has been examined at several temperatures and at various concentrations of monomer. The polymerization rate constants followed the Arrhenius relationship and gave an activation energy of 22.3 kcal mole $^{-1}$. The rates of reaction were five times faster than theoretically predicted and this was attributed to the formation of crosslinked structures which trapped macroradicals. Linear polymers containing cyclic units were shown to be present in the product by IR and ^{1}H NMR spectroscopy[152].

The reactivity ratios for vinylferrocene (r_1) and isoprene (r_2 determined during the formation of an isoprene-vinylferrocene copolymer at 150° in the presence of t-butylperoxide were $r_1 = 0.54$ and $r_2 = 1.56$[153]. Vinylferrocene was copolymerized with N-vinylcarbazole in the presence of azobisisobutyronitrile. The copolymer were treated with trinitrofluorenone (TNF) (10.1) to give copolymer (10.2) with carbazole-trinitrofluorenone charge-transfer complex sites. The copolymers were oxidized with dichlorodicyanoquinone to give copolymers (10.3) with both ferricinium and ferrocene sites in them. The copolymers (10.3) were treated with TNF to give polymers having ferrocene, ferricinium and carbazole-TNF charge-transfer sites[154].

1-Ferrocenyl-1,3-butadiene and other ferrocene derivatives that contained conjugated side chains were prepared <u>via</u> a Wittig type reaction. The ferrocenyl carbonyl compounds used were very similar to the benzene analogues in their reactivity towards Wittig reagents. <u>Cis</u> and <u>trans</u> isomers were formed in most of the Wittig reactions and the cis isomer of the ferrocenyl diene was converted usually to the trans isomer on purification. The homopolymerization of 1-ferrocenyl-1,3-butadiene, 4-ferrocenyl-1,3-pentadiene, 1-phenyl-1,3-butadiene and 4-phenyl-1,3-pentadiene gave very low molecular weight polymers. Copolymerization of these monomers with styrene gave low molecular weight polymers[155]. Ethynylferrocene was heated with azobisisobutyronitrile under nitrogen at 180-240° to give poly(ethynylferrocene) (10.4) in competition with the cyclic trimer. The polymer was completely conjugated and had an electrical conductivity of $2 \times 10^{-14}\Omega^{-1}\ cm^{-1}$. Attempts to form the same polymer from acetylferrocene with zinc chloride were unsuccessful and led to polymers containing hydroxyl and carbonyl groups[156].



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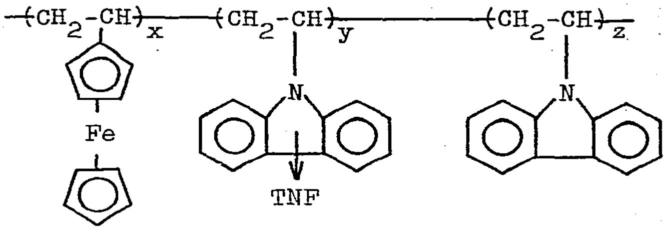

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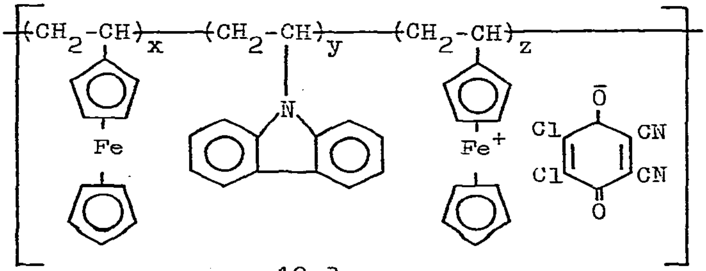
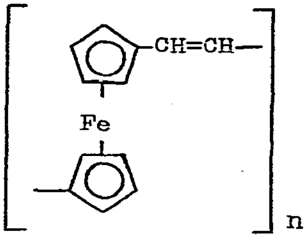


10.3

The polymerization of ferrocenylacetylene with di-t-butyl-peroxide at 160° or with sodium at temperatures above 130° gave soluble polymers with molecular weights of 1400 and 2500 respectively

The polymers contained free radical centres and gave an ESR signal. Conjugated, unsaturated bonds were also detected in the products[15]



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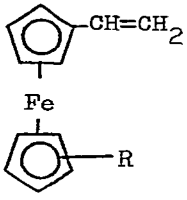


10.5

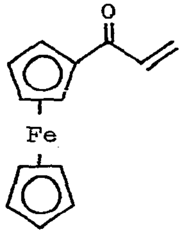
Poly(ferrocenylacetylene) was obtained by the polymerization of ferrocenylacetylene with di-t-butyl peroxide or powdered sodium. A ladder structure with conjugated double bonds was proposed for the polymer and molecular weights up to 1700 were obtained[158].

A ferrocenylacetylene-phenylacetylene copolymer of molecular weight 800-1800 was formed from ferrocenylacetylene and phenylacetylene in heptane solution at 50-70°C with an aluminium chloride catalyst. The copolymer was formed in greatest yield at 70° and the yield was almost independent of the monomer proportions[159].

Ferrocenylacetylene was polymerized with dibenzoyl peroxide to give poly(ferrocenylacetylene) with semiconductor properties[160]. Ethylene was polymerized with alkylvinylferrocenes (10.5; R = Me, Et, Pr, Bu, C_5H_{11}) at temperatures up to 300°C and pressures of 700-3000 atmospheres to yield heat-resistant copolymers[161].

Heteroorganic polymers produced by aqueous emulsion polymerization of alkenylferrocene with diene monomers in the presence of an emulsifying agent and an activator had increased thermal stability if an alkenylcarborane was added to the monomer mixture[162]. The preparation of poly(vinyl alcohol) fibres containing ferrocene has been reported[163]. Dimethylferrocene-1,1'-dicarboxylic acid (0.05-1 mole per cent) has been incorporated into dimethyl terephthalate-ethylene glycol polymers by polycondensation to give light stable polymers[164]. p-Ferrocenylacetophenone has been polymerized to poly-p-ferrocenylphenylacetylene in the presence of ten metal chlorides. Mercury (II) chloride was the most efficient and gave 89% conversion while cadmium (II) chloride was the least effective with 39% conversion. The brown black polymers were insoluble in common solvents and showed good thermal stability up to 220-240°. The electrical conductivities and unpaired electron densities confirmed that these polymers were semiconductors comparable with other p-substituted polyphenylacetylenes[165].

Ferrocene derivatives and furans were copolymerized in the presence of an acidic or basic catalyst and heated in vacuo to give ferrocene-furan resins. Mono- and 1,1'-di-substituted ferrocenes with acyl and α-hydroxyalkyl groups were used with furfural or furfuryl alcohol[166]. Lewis and Ponder have described the homopolymerization of ferrocenylvinyl ketone (10.6) by a free radical route to give low molecular weight polymers. The rate of polymerization was similar to that found for styrene and vinylferrocene. Styrene and methyl vinyl ketone were copolymerised with ferrocenylvinyl ketone to yield benzene-soluble products[167].



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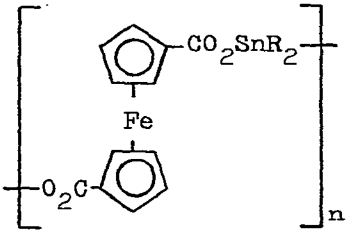
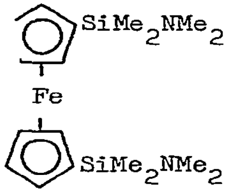


10.7

Carraher and Lessek have synthesised polymeric organotin esters of ferrocenecarboxylates by an interfacial method. A diorganotin dihalide was treated with disodium ferrocenedicarboxylate to give the oligomers (10.7; R = Me, Bu^t, octyl, Ph, $PhCH_2$) by interfacial polymerization. The yield of oligomer decreased in the order of alkyl substituents on tin: Me > Et > Bu^t > octyl and in the order of halogen atoms on tin: I > Br > Cl. The yield was increased when either the organotin halide or the ferrocenecarboxylate was in excess[168].

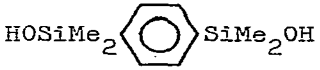
The disilyldiamine (10.8) was synthesized from 1,1'-dilithioferrocene and (dimethylamino)dimethylchlorosilane and was polymerized with three aryl disilanols (10.9, 10.10 and 10.11). Melt polymerizations gave the highest molecular weight polymers with



10.8

$Ph_2Si(OH)_2$

10.9



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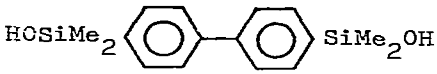

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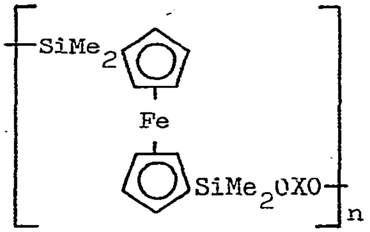

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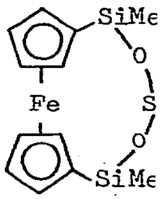


10.13

the idealized structures (10.12; X = $SiPh_2$, $SiMe_2C_6H_4SiMe_2$, $SiMe_2C_6H_4C_6H_4SiMe_2$). In one case, where the silanol was dihydroxydiphenylsilane, intramolecular cyclization was found to compete with polymerization and this resulted in the isolation of the [5]ferrocenophane (10.13). The polymers were cast as tough, flexible films and fibres were drawn from the melt. TGA and DSC measurements on the ferrocene polymer formed from the silanol (10.10) confirmed that it had comparable thermal stability to the corresponding benzene polymer[169].

11. APPLICATIONS OF FERROCENE

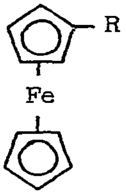
(i) Ferrocene catalysts and photosensitizers

The bulk polymerization of methyl methacrylate and acrylonitrile in the presence of ferrocene, carbon tetrachloride and benzene has been investigated. The yield of polymer increased with increasing concentration of ferrocene while with increasing concentration of carbon tetrachloride the yield reached a maximum[170]. The quantitative conversion of methyl methacrylate to polymer in the presence of ferrocene, carbon tetrachloride, copper (II) chloride and cellulose has been reported[171].

Maggioni has described the formation of pyrocatechol and hydroquinone in a total overall yield of 95% and a ratio of 2.3:1 by the hydroxylation of phenol with hydrogen peroxide in the presence of ferrocene or 1,1'-diacetylferrocene[172]. Ferrocene, acetylferrocene and phenylferrocene were used as catalysts in the oxidation of cycloalkanes by oxygen to give hydroperoxides[173]. Mono-, di- and tri-substituted ferrocenes bearing acyl, alkyl, alkoxy, and hydroxylalkyl groups were used as catalysts in the aerial oxidation of isobutyraldehyde to isobutyric acid[174].

Photosensitive copying papers have been produced containing 1,1'-disubstituted ferrocenes (11.1; R = H, alkyl, aryl, SO_3L, halo, CO_2H) together with a chelating ligand for iron such as phenanthroline. Exposure of the paper to mercury lamp radiation decomposed the ferrocene with release of iron which was then complexed to give an orange-red positive image[175]. A photosensitive composition has been developed for copying paper that contains a ferrocenesulphonic acid, an aromatic hydroxy compound and a bindi agent. The iron produced by photodecomposition of the ferrocene derivative combines with the hydroxy compounds, for example γ-resorcinic acid, 1,2-dihydroxynaphthalene, 1,8-dihydroxy-3,6-naphthalene disulphonic acid and o-aminophenol, to give blue, vio green and reddish brown images respectively[176].

A substituted ferrocene (11.2; R^1 = H, C_{1-4}alkyl, $PhCH_2$, Ph; R^2 = H, CN, COMe, valeryl, p-MeC_6H_4CO, p-MeC_6H_4) and a diazonium salt were mixed and coated on a support to give a photosensitive copying material[177]. A photosensitive copying material, for elec static photography, that contained a ferrocene derivative and a chelating agent (e.g. o-phenanthroline) was reported by Goto, Kojima and Kusakada[178]. Poly(vinyl chloride) films that containe 0.1% ferrocene became brittle after four to five weeks in sun lig whereas in the absence of ferrocene this process took more than eleven weeks[179].



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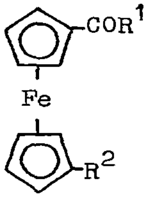


11.2

(ii) Ferrocene stabilizers and improvers

The addition of 0.1-0.5% ferrocene to chloroprene prevented the spontaneous polymerization of this monomer[180]. The incorporation of poly(methyleneferrocenylene) into staple fibres prepared from viryon, vinal and rayon by moulding or by chemical methods gave fibres with increased resistance to UV and γ-irradiation. The highest resistance to UV degradation was displayed by vinyon fibres which contained 6% of the acetylated ferrocene polymer included by moulding[181].

Isotactic polypropylene was stabilized to UV degradation in air by the incorporation of oxo-derivatives of ferrocene. Four ferrocene derivatives were studied each at a concentration of 0.8%[182]. Improved thermal and hydrolytic stability was claimed for a refrigerator lubricant based on the siloxane polymer $RO[(RO)SiRO]_nR$ which contained aminosilylferrocene, or other organometallic additives, as antioxidants[183].

Unsaturated polyesters were formed by the condensation of glycols and dicarboxylic acids in the presence of modifiers such as 1,1'-diaminoferrocene and ferrocene-1,1'-dicarboxylic acid. The polyesters were hardenable at low temperatures and were claimed to have improved physicomechanical properties[184]. Ferrocenylmethyl carboxyhydrazide was condensed with aldehyde groups produced on glycogen and cat gut mucopolysaccharide by periodate oxidation and on DNA by Feulgen hydrolysis. The reaction gave an electron-opaque deposit suitable for ultrastructural localization of these tissue components. The reaction product was also rendered visible in an optical microscope by treatment with aqueous silver nitrate. Thiol groups produced in wool were visualized by reaction with chloromercuriferrocene followed by treatment with silver nitrate to deposit metallic silver at the sites of the thiol groups. The use of chloromercuriferrocene overcame the problem of the mercury derivative being unstable to the conditions present in an electr microscope[185].

The addition of ferrocene to a polystyrene resin used as met casting resin prevented smoke formation and gave a good surface finish to the cast metal. The resin contained between 0.3 and 1 of iron[186]. Low concentrations (0.1-0.8%) of ferrocene behaved a smoke inhibitor for poly(vinyl chloride) or polyurethane moul ings[187].

(iii) Ferrocene in analysis

The potential application of stable iminoxyl radicals as analytical reagents for ferrocene derivatives has been investigat electrochemically. The iminoxyl radicals were oxidized with the loss of one unpaired electron at a platinum microdisc electrode and in an acid or neutral aqueous-organic medium. The radicals were useful both as reducing and oxidizing agents in amperometric titration of ferrocenes[188].

The parameters in the construction and operation of a hydrog atmosphere flame ionization detector, capable of detecting small concentrations of ferrocene, were investigated. The following factors were found to be important for the efficient operation of this gas chromatographic detector: high electrode heights, large gas flow rates, diffuse hydrogen gas flow and the correct detector geometry[189].

A method has been developed for the direct estimation of iron (III) in silicate rocks. The iron (III) was released into solution by treatment of the rock sample with hydrofluoric acid and it was determined by titration with ferrocene in 2-methoxyethanol[190].

Rhenium in alloys has been determined by amperometric titration of rhenium (VII) with ferrocene in aqueous acetic and hydrochloric acid[191]. Ferrocene was used as a reagent for the direct amperometric oxidation-reduction titration of molybdenum (VI) in aqueous-organic solvents. The electrode potentials for the Mo(VI)/Mo(V) system were measured as a function of the concentration and nature of the acid (HCl, H_2SO_4, $HClO_4$ and H_3PO_4) and the organic solvent used. At the equivalence point the ratio of ferrocene to Mo(VI) was 1:1[192].

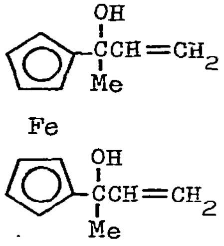
Ferrocene has been used as a reagent for the determination of phosphorus in steels. The phosphorus was extracted as molybdophosphate, the molybdenum (VI) in the complex was determined by amperometirc titration with ferrocene in iso-butanol-acetone-aqueous hydrochloric acid and the amount of phosphorus was calculated from the stoichiometric composition of the molybdophosphate[193].

(iv) Combustion studies

Reed has used a butadiene-vinylferrocene copolymer containing 0.5-15% iron to increase the burning rate of a propellant which consisted of ammonium perchlorate, aluminium powder, the copolymer and an isodecyl perlargonate plasticizer[194]. In a related patent the same author described an alternative combustion promoting copolymer which was a copolymer of butadiene, isoprene or chloroprene with ferrocenylmethyl methacrylate, isopropylferrocene or 1-ferrocenylbutadiene[195].

Ferrocenyl hydroxybutenes, prepared from 1,1'-diacetylferrocene and vinylmagnesium chloride, were found to be good combustion catalysts in ammonium perchlorate based propellants[196]. A ferrocene containing combustion promoting composition has been developed for the destruction of woody growth. The composition contained 80-90 parts by weight of ferrocene, or its alkyl derivatives, absorbed onto 5-10 parts of activated carbon. This was coated with ammonium perchlorate, finely divided aluminium and finally with calcium phosphate or a silicon derivative to give a free-flowing dispersible product. The activated carbon provided a large surface area for the absorption of atmospheric oxygen, and when the product was in contact with carbonaceous material it soon initiated smouldering which often resulted in complete destruction[197].

Epoxyethylferrocene was found to behave both as a burning rate catalyst and a curing agent in solid propellants that containe ammonium perchlorate and a polybutadiene binder[198]. The vinylferrocene (11.3), prepared from 1,1'-diacetylferrocene and vinylmagnesium chloride, was cocured with hydroxy-terminated polybutadie polymer using a diisocyanate curing agent. The polymer, together with ammonium perchlorate and a metal fuel, produced a good rocket propellant in which the ferrocene derivative behaved as a ballistic modifier to increase the propellant burning rate[199]. 1-Isopropenyl 2-ferrocenoyl carborane was successfully used as a burning rate catalyst[200]. When ferrocene was incorporated into unsaturated polyesters, polyurethane and polyethylene the polymers burnt with reduced soot and carbon monoxide formation[201].



11.3

Granular combustion compositions were prepared that contained a ferrocene derivative. For example butylferrocene was absorbed onto activated charcoal mixed with ammonium perchlorate and aluminium powder and then coated with calcium phosphate or silicon compounds to give a free flowing dispersible material. When this material was applied to a piece of wood, the wood smouldered until it was completely burnt[202].

N-ferrocenylmethylpyrrolidine behaved as a processing aid, a bonding agent and a ballistic modifier and it also improved the mechanical properties of solid propellants when it was used as a coating for ammonium perchlorate[203]. Easily combustible polystyrene resin foams were prepared by mixing ferrocene with the monomer before foaming. The foam was useful as a packaging material[204].

A vinylferrocene-butadiene copolymer was incorporated into the binder of propellant systems to provide a high concentration of the burning-rate catalyst (vinylferrocene) in a form which was not subject to degradation by evaporation, migration or crystallization. Improved burning rates were achieved by using the copolymer to replace butylferrocene in propellants based on polybutadiene, ammonium perchlorate and aluminium powder[205].

A vinylferrocene-butadiene copolymer was found to be a good burning rate catalyst in ammonium perchlorate based propellants[206].

(v) General applications and miscellaneous reports

Wenzel and Langheim have claimed the formation of methyl ruthenocene carboxylate-$^{103}\underline{Ru}$, with a radioactive yield of 15% from the initial inorganic ruthenium activity, by the treatment of methyl ferrocene carboxylate with $^{103}RuCl_3$[207].

The toxicological properties of alkylferrocenes have been evaluated by Shugaev and Bitkina. These compounds were non-toxic towards small mammals by inhalation or acute intragastric administration. Topical application to the eye caused surface conjunctivitis and to the skin caused surface dermatitis. Chronic oral administration produced anaemia and degenerative kidney and liver lesions. The authors conclude that alkylferrocenes are sa for industrial handling if contact with skin and mucous membrane is avoided[208].

Primer coatings on steel with good corrosion resistance and adhesion properties were formed by dipping steel sheet into a butanol or decalin solution of a film-forming compound such as ferrocene and then burning off the solvent[209].

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