FERROCENE

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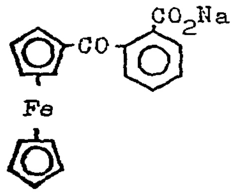
CONTENTS

1. REVIEWS

Perevalova and Nikitina have reviewed the structure and properties of the metallocenes but the methods of preparation and the physical properties of these compounds were not discussed. The article discussed the properties of the metallocenes according to the types of reaction that they underwent, the chapter headings were: hydrogen-substitution reactions of five membered metallocene rings; substituent-exchange reactions on the cyclopentadienyl ring; reactions involving the metal-ring bond and oxidation-reduction reactions of the metallocenes. The authors covered the literature on the subjects under discussion up to 1967 and there was also a summary of results published in 1968 and 1969 and partly in 1970[1]. The applications of the acylferrocene (1.1), called "ferrocerone", in the treatment of iron-deficiency anaemia have been discussed in a brief review[2]. Slocum and Ernst have surveyed electronic effects on reactivity and spectral properties in the metallocene series and they have made comparisons with aromatic hydrocarbons[3]. A well documented survey of carborane chemistry by Snaith and Wade has been published and it includes a discussion of the interesting metallocarboranes[4]. The formation and rearrangements of the carborane analogues of metallocenes have also been reviewed by Hawthorne[5].



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2. Theoretical Studies

Flesch, Junk and Svec have interpreted ionization efficiency data for the M^+, MCp^+ and $MCp_2{}^+$ ions (where M = Fe, Ni, Ru) by a deconvolution-convolution technique to obtain ionic bond dissociation energies for D(FeCp$^+$ - Cp), 7.2-7.5 eV and D(M$^+$ - Cp), 3.8-4.9 eV. Whilst the values for loss of the first Cp ring agree with those determined previously, the values for loss of the second ring are much higher than those of earlier workers and agree with theoretical predictions[6]. An LCAO-MO-SCF method has been used to calculate the first ionization potentials of ferrocene based on the difference in total energy between the neutral molecule and the positive ion. The sequence obtained was:

$$IP(e_{1g}) > IP(e_{1u}) > IP(a_{1g}) > IP(e_{2g})$$

this corresponds to the experimental determination but not to the order of energies in the neutral molecule:

$$e_{1u}(\pi - Cp) \sim e_{2g}(\pi - Cp) > e_{2g}(3d) > e_{2u}(\sigma - Cp) \sim a_{2u}(\pi - Cp) \sim e_{2g}(\sigma - Cp) > a_{1g}(3d)$$

This difference was rationalised in terms of the change in the electronic rearrangements that occurred on ionization when different types of orbits were involved in ionization. It was suggested that Koopmans theorem was invalid for the ferrocene molecule[7]. Force constant calculations for ferrocene have been made using an improved basic model, a cyclopentadienyl ring bonded to a metal atom. A symmetrised Fe-C force constant of $\sim 1.4 \times 10^5$ dyne cm^{-1} was found and good correlations between calculated and observed frequencies for the e_{1u} modes of C_5H_5Fe and C_5D_5Fe were obtained[8].

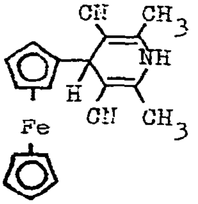
The perpendicular mean-square amplitude correction coefficients (K) of the cyclopentadienide ion, ferrocene and the corresponding perdeuterated species were calculated using harmonic force fields. The K values were larger in the complexed ligand than in the free ion except for K values greater than 0.01 Å. It was thought that this might indicate a certain loosening of the molecular framework of the complexed species but excessive deformation out of the ring plane was probably sterically hindered by the presence of the iron atom and the other ring[9].

3. Ferricinium Salts

The X-ray photoelectron spectra of the following compounds, ferrocene, biferrocene, ferrocene Fe^{III} picrate, ferrocene Fe^{III} fluoroborate, biferrocene $Fe^{II}Fe^{III}$ picrate and biferrocene $Fe^{II}Fe^{III}$ fluoroborate, were recorded using Al - K_α radiation. The first ionizations from the valence band region of ferrocene and biferrocene were almost identical which indicated there was little interaction between the two ferrocene moieties in biferrocene or in the biferrocene ions formed by the Al - K_α radiation. For the ferricinium salts the ionizations from the valence band region were complicated by the transitions due to the picrate and fluoroborate ions[10]. Direct measurement of the diffusion coefficient of ferricinium ions has been used to determine the rate of the electron exchange reaction between ferrocene and ferricinium ion in methanol, ethanol and propanol. The value obtained at room temperature was close to the diffusion limit[11]. The behaviour of ferrocene and ferricinium picrate was investigated by differential vapour pressure and conductance measurements. In pyridine, ferrocene was found to exist as stable monomers and ferricinium picrate dissociated as a simple weak electrolyte. Analysis of the potentials of half cells comprised of equimolar mixtures of ferrocene and ferricinium picrate against a silver/silver picrate electrode and the $Zn(Hg)/ZnCl_2(s)$ reference electrode gave an average value of 0.628 V versus a normal hydrogen electrode in pyridine for the standard reduction potential of the ferrocene couple. This result was combined with the standard potential of the ferrocene-ferricinium system in water to give a value of -0.227 V for the potential of a normal hydrogen electrode in pyridine versus (E°_{H})aq on the molal scale. The medium effect for the proton $(\log {}_{m}\gamma_{H})$ was found to be -3.85[12]. The standard potential (E^{0}) of the ferrocene/ferricinium ion couple in CF_3CO_2H was found to be -0.58 V[13].

The stability of the ferricinium ion in donor solvents and in the presence of mucleophiles has been studied by ESR and electronic absorption spectroscopy and by susceptibility measurements. The cation was stable in acetonitrile, acetone and nitromethane, it was decomposed by chloride and bromide ions to ferrocene and FeX_4^- while iodide reduced it to ferrocene. The weaker donor strength and high reducing power of iodide were invoked to explain this difference. In DMF, DMSO and HMPTA the ferricinium ion decomposed to ferrocene and an iron (II) octahedral complex which had solvent molecules as ligands. The addition of _o_-phenanthroline and 2,2'-bipyridyl to the ferricinium ion in acetonitrile gave similar products. The decomposition mechanism required initial exchange of ligands bound to Fe(III). The free cyclopentadienide ions formed were then effective in reducing both the Fe(III) complex and unreacted ferricinium ion[14]. Bitterwolf and Ling have reinvestigated the complexes formulated by Wassermann and co-workers as $FcH^{+}.HA^{\dot{-}}.HA$ and suggested their reformulation as $FcH^{+}.A^{-}.HA$ since no evidence for the radical anion $HA^{\dot{-}}$ was obtained (HA = trichloroacetic acid and trifluoroacetic acid)[15]. The cerium(IV) sulphate oxidation of ferrocene-1,1'-disulphonic acid in acid media $(H_o = 0$ to $-2)$ requires three equivalents of the oxidizing agent for complete breakdown of the metallocene nucleus. The mechanism proposed involved a fast initial one electron change to give the disubstituted ferricinium cation which was followed by slow cleavage of the metal-ligand bonds to yield the iron(III) cation and cyclopentadienesulphonic acid[16].

The photooxidation of ferrocene to the ferricinium ion in chloroform-ethanol was sensitized by naphthalene, it was suggested that the process involved singlet-singlet energy transfer from naphthalene to a ferrocene-chloroform complex[17]. Ferrocene has been evaluated as a charge scavenger by gamma-radiolysis in glassy hydrocarbon matrices and subsequent examination by UV and EPR spectroscopy. No evidence to demonstrate the formation of either FcH^+ or FcH^- was obtained[18]. The ferrocenyldihydropyridine (3.1) was synthesized by the condensation of formylferrocene with diacetonitrile and it was oxidized by chloranil to give (3.2). When (3.1) was treated with dichlorodicyanobenzoquinone it gave the ferricinium salt (3.3)[19]. The salt (3.5) was obtained by stirring the boronic acid (3.4) with phenylmagnesium bromide and subsequent treatment



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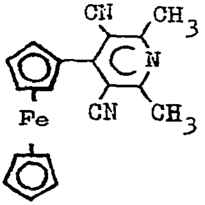

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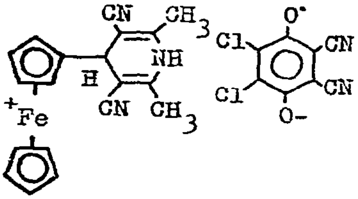
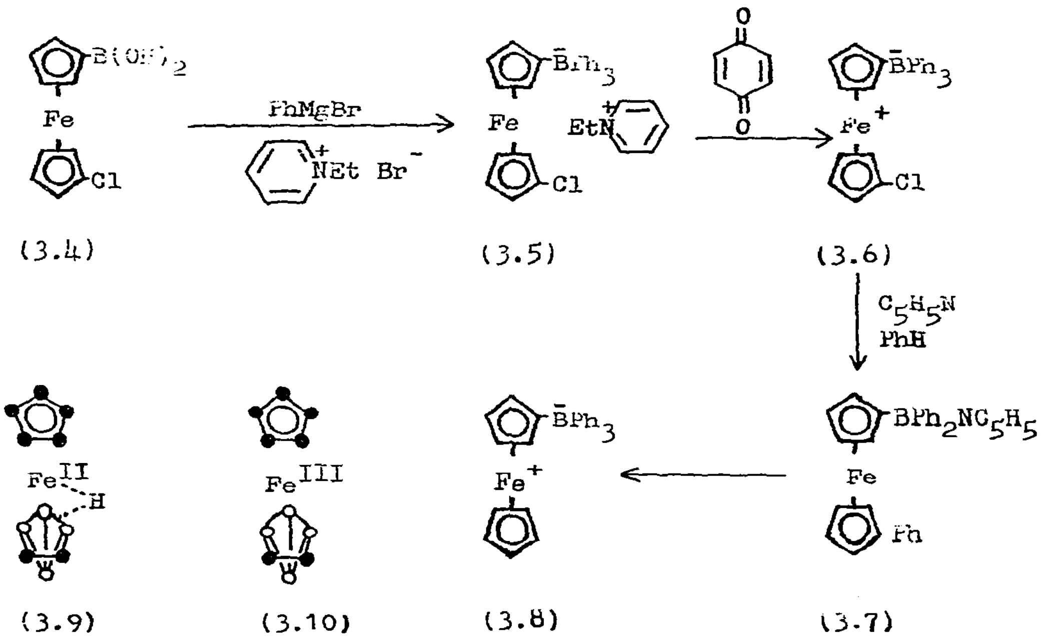


(3.3)

with N-ethylpyridinium bromide. Oxidation of the salt (3.5) with quinone gave the unstable zwitterion (3.6). A stable analogue (3.8) was formed when (3.6) was heated with pyridine in dry benzene and the product (3.7) treated with phenylmagnesium bromide[20].

A convenient preparation of ferricinium picrate was reported. A solution of ferrocene was mixed with benzoquinone in the presence of picric acid to give the picrate directly[21]. Sneddon and Grimes report the formation of the interesting ferrocene (3.9) and ferricinium (3.10) analogues that incorporate small carborane ligands. Treatment of the anion $C_2B_4H_7^-$ with π-cyclopentadienylirondicarbonyl iodide in THF at 25° gave the complex $\mu[\pi\text{-}C_5H_5Fe(CO)_2 \cdot C_2B_4H_7]$ (50%) which on subsequent UV irradiation *in vacuo* gave the compounds (3.9 and 3.10, 90%). The ^{11}B and ^{1}H NMR spectra confirmed the sandwich structures although the seventh carboranyl



(3.4) (3.5) (3.6)

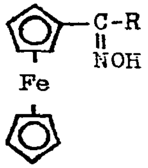
(3.9) (3.10) (3.8) (3.7)

hydrogen atom was not located with certainty[22].

4. Spectroscopic Studies

The pyrolysis of poly(β-ferrocenylchloroacrolein) gave products that contained large amounts of pure Fe_3O_4. The products of pyrolysis were investigated using Mossbauer spectroscopy[23]. The He(I) photoelectron spectra of ferrocene, 1,1'-dimethyl- and 1,1'-dichloro-ferrocene have been measured and assigned on a semi-empirical basis. A qualitative M.O. scheme for ferrocene has been proposed and compared with the predictions of ligand field theory[24]. The orbital energy sequence $d_{x^2-y^2}$, $d_{xy}(e_{2g}) > d_{z^2}(a_{1g})$ was in agreement with the predictions of Shustorovich and Dyatkina[25] and Koopmans theorem[26]. Comparisons within the series of metallocenes Cp_2Fe, Cp_2Ru, Cp_2Os were made and the ionic Cp_2Mg was also discussed. The photoelectron and electronic spectra of ferrocene and the ferricinium ion have been used to assign the relative energies of the first five molecular orbitals in ferrocene as $e_{2g} > a_{1g} > l_{1u} > e_{1g} > e_{1u}$[27]. The photoionization potentials of the filled e_{2g} and a_{1g} orbitals of ferrocene as determined by photoelectron spectroscopy show that the lowest lying 3d orbital was the a_{1g} orbital. However, the application of ligand field theory to the d-d electronic absorption spectrum of ferrocene suggested the reverse order. Hendrickson has shown that such an apparent reversal in level ordering may be expected in some cases[28]. A photoionization technique has been used to determine the ionization potentials of (trimethylsilyl)ferrocene (9.5 eV), chloroferrocene (6.83 eV) and vinylferrocene (6.75 eV)[29].

The high-resolution mass spectra of the syn- and anti- forms of the acylferrocene oximes (4.1) and (4.2) were examined at various ionizing voltages, the fragmentation patterns were presented and discussed[30]. Sheley and Fishel have established fragmentation pathways from the mass spectra of 1,1'-diacetyl- and 1,1'-dipropionylferrocene. The results suggested interaction between the substituents on the two cyclopentadienyl rings as two molecules of carbon monoxide, or carbon monoxide and ethylene, were eliminated simultaneously[31].



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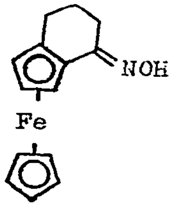

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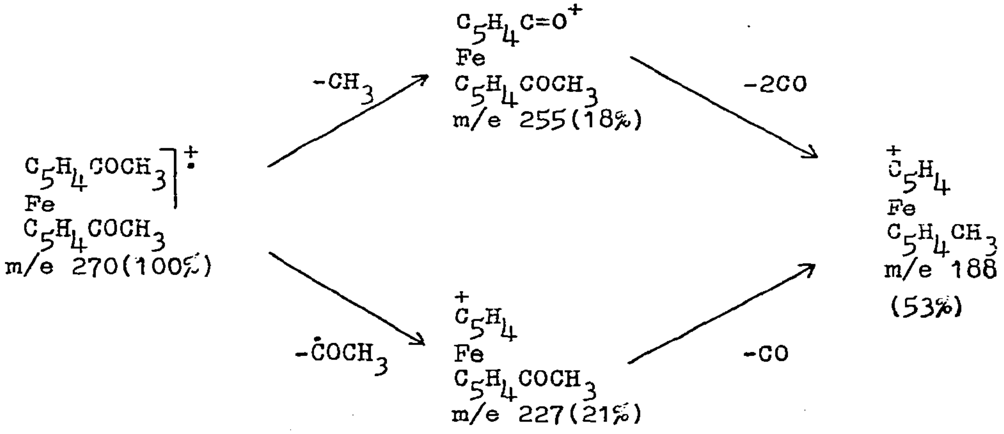
The mass spectra of several heteroannularly disubstituted ferrocenes were reported, for example the fragmentation of 1,1'-diacetylferrocene was thought to follow two paths as shown in scheme A[32].

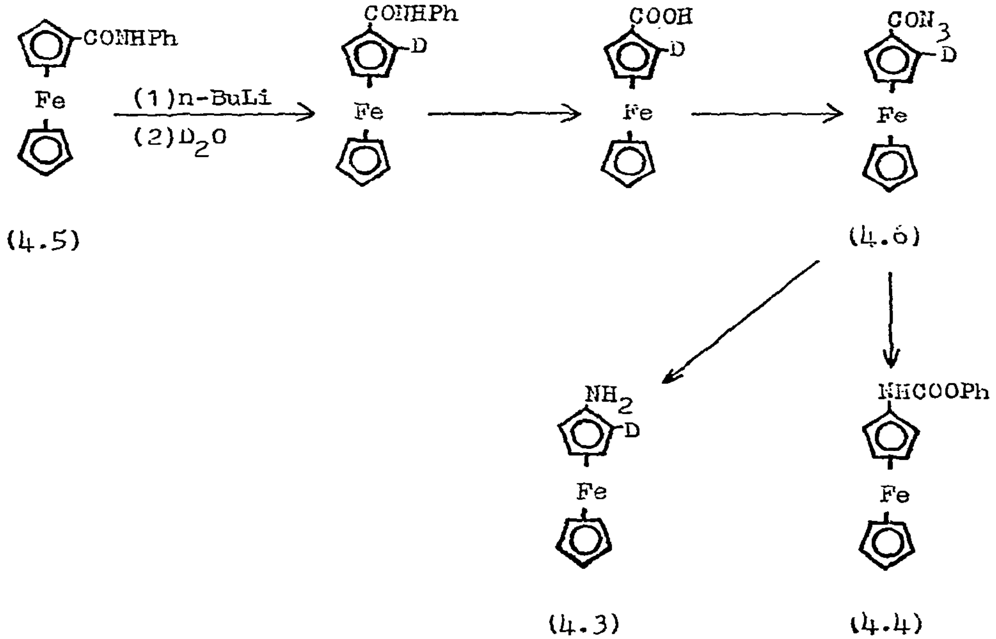


Scheme A

The enthalpy of formation of the cyclopentadienyl radical $[\Delta H_f^\circ - (C_5H_5) = 47 \pm 4$ kcal/mole$]$ was obtained from electron impact data on ferrocene[33].

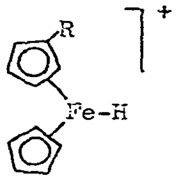
Single crystals of pure ferrocene or solid solutions of ferrocene in poly(methylmethacrylate) did not show phosphorescence at -100° or at room temperature on excitation with a N laser at 3371 Å ($\sim 10^{24}$ photons/sec). Fluorescence was observed at 4020, 4180, 5470 and 5740 Å. No evidence was found for a long-lived triplet state in ferrocene[34]. The electronic absorption spectra of several ferrocene derivatives have been studied in different environments (glasses, KBr pellets and single crystals) and as a function of temperature. The spectra of ferrocene and phenylferrocene at 4.2°K indicated that the bands at 22,700 cm^{-1} and 22,400 cm^{-1} respectively consisted of two electronic transitions. The low-energy charge transfer transition exhibited by ferricinium complexes was assigned to the ligand to metal $^2E_{2g} \rightarrow {}^2E_{1u}$ transition. Magnetic susceptibility data were obtained for several ferricinium salts and the magnetic moments were found to be independent of temperature[35]. The magnetic circular dichroism spectra of ferrocene and a series of substituted ferrocenes were measured and found to fall into two distinct categories. One group of compounds, ferrocene, n-butylferrocene, hydroxymethylferrocene and 1,1'-dihydroxymethylferrocene, gave absorption-like peaks while the others (where the cyclopentadienyl rings were substituted with a carbonyl containing group) gave S shaped curves. It was concluded that the 4400 Å band of ferrocene consists of two overlapping peaks due to d-d transitions in the metal[36]. The molecular vibrations of ferrocene were analyzed assuming that the molecule had an eclipsed structure. The harmonic force constants were presented in terms of specified symmetry coordinates and these were developed to fit the observed vibrational frequencies. Similar calculations were carried out for $Fe(C_5D_5)_2$[37].

The application of tris(dipivalomethanato)europium in the study of the NMR spectra of metallocenes was investigated by Paul, Schlögl and Silhan. In the ferrocene series the method was applied to 1,2-(α-oxotetramethylene)ferrocene and to the analysis of mixtures of isomers. It was concluded that the europium derivative was a very good paramagnetic shift reagent for the study of metallocenes[38].



2-Deuteroaminoferrocene (4.3) and the corresponding deuterated benzylurethane (4.4) were prepared by the lithiation of N-phenylferrocenecarboxamide (4.5) with n-butyllithium. The deuterated carboxamide (4.5) was then converted to the amine (4.3) and the benzylurethane (4.4) via the azide (4.6). The NMR spectra of both the amine(4.3) and the urethane (4.4) indicated that the 2-position was the least shielded position in the substituted ring of these compounds. The chemical shift assignments for the amine (4.3) were: 3,4-position protons, ~3.88 ppm; 2,5 position protons (attenuated) 4.02 ppm; 1' position 4.10 ppm and for the urethane (4.4), 3,4 position 3.98 ppm; 1' position 4.10 ppm and 2,5-position protons (attenuated) 4.47 ppm[39]. This assignment was a direct reversal of that of Gubin and co-workers[40].

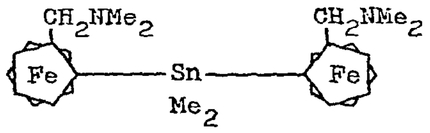
Bitterwolf and Ling have analysed the NMR spectra of methylferrocene, ethylferrocene and 1,1'-dialkylferrocenes in boron trifluoride monohydrate solution[41]. They confirmed the previous suggestion[42] that the protonated metallocene suffers restricted rotation about the ring metal bonds through ring tilting (4.7). A similar structure was proposed recently for the α-ferrocenylcarbonium ion (A.S. 71, p. 390).



(4.7)

The NMR spectra of alkyl derivatives of the isoelectronic ferrocene and cobalticinium ion have been compared. The introduction of primary or secondary alkyl groups caused a decrease in chemical shift of protons on both the substituted and unsubstituted cyclopentadienyl rings. However the t-butyl group caused a shift in only the substituted ring protons. These results were explained by invoking a resonance effect for the interannular transmission of the electronic effects of alkyl groups[43]. Weak intramolecular Fe-S bonding was proposed to explain differences in the PMR chemical shifts between some alkylthiol adducts of 1-benzoyl-2-ferrocenylethylene and the corresponding adducts of chalcone[44]. Morris and Rockett have observed the magnetic non-equivalence of tin-methyl protons in the meso-diamine (4.8), the chemical shift difference between the methyl resonances was strongly solvent dependent and an anomolous temperature dependence was found. The ferrocenophane (4.9) was less sensitive to solvent effects in accordance with the greater conformational rigidity imposed by the cyclic structure by comparison with the diamine (4.8). Substituent effects on the non-equivalence in (4.9) were investigated. The racemic forms of these complexes (4.10 and 4.11) failed to show non-equivalence under the conditions of temperature and solvent used for the meso forms, although the N-methylene protons in both diamines (4.8 and 4.10) were non-equivalent and showed temperature and solvent dependence[45].

Turbitt and Watts studied the diamagnetic anisotropy of the ferrocene molecule by examining the NMR spectra of a series of homoannularly bridged [3](1,2)-ferrocenophane (4.12) derivatives.



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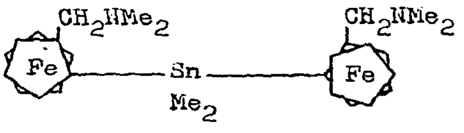

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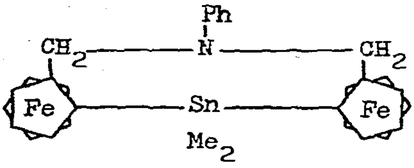

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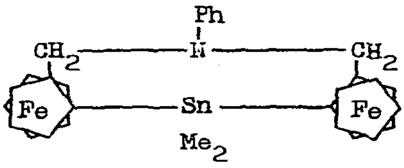
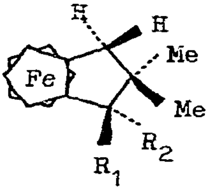


(4.11)

A comparison of the spectra of epimeric compounds in this series established that the protons located above the plane of the cyclopentadienyl ring and remote from the iron atom (exo) are shielded when compared with the protons of the same substituent which lie below the plane of the cyclopentadienyl ring (endo)[46]. These results agree with the picture (4.13) of the shielding and deshielding regions around the ferrocene molecule which is based upon the earlier work of Mulay and Fox[47]. Levy has determined the ^{13}C spin-lattice relaxation times for acetylferrocene and n-butylferrocene using an inversion-recovery pulse sequence technique. The results confirmed that the energy barrier to ring rotation was very small and demonstrated that the unsubstituted ring was



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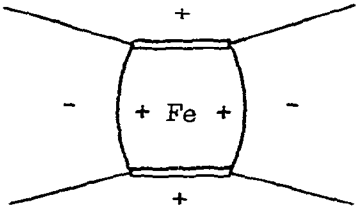
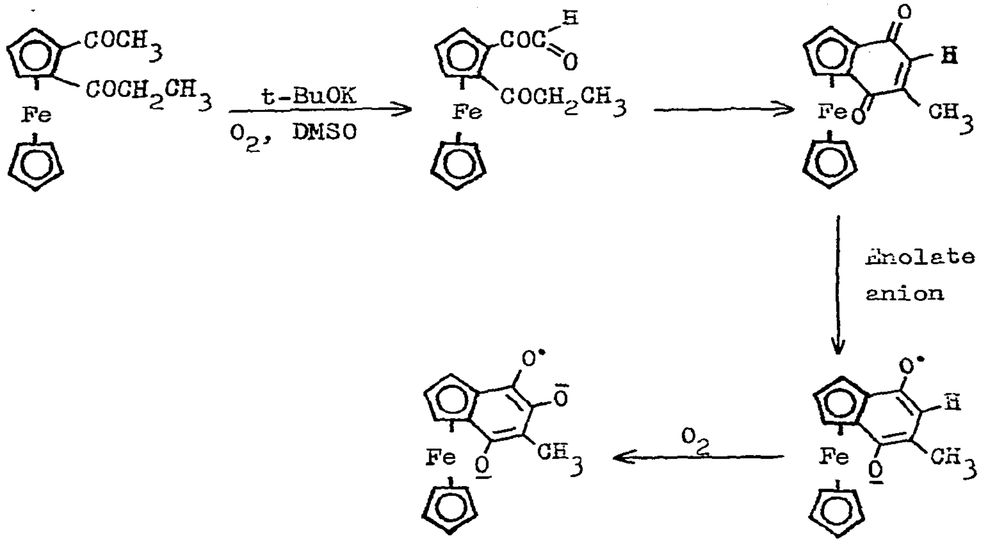


(4.13)

able to spin independently of overall molecular tumbling and revolution of the substituted ring. The spinning ratios, unsubstituted:substituted ring were ~4(acetylferrocene) and ~7(n-butylferrocene). The $^{13}C-^{1}H$ nuclear Overhauser effect was measured for ferrocene and acetylferrocene (η = 1.9 and ~1.4 respectively). The ^{13}C chemical shifts for cyclopentadienyl and side chain groups were listed[48]. The nuclear quadrupole resonance spectrum of 1,1'-dichloroferrocene showed a single resonance line at 35.48 MHz; 0.70 MHz higher than p-dichlorobenzene and this increase in frequency was ascribed to repulsion between filled 'girdle' d orbitals around the metal atom and p_z lone pair electrons on chlorine[49].

The EPR spectra and polarograms of the stable iminoxyl radicals of bis(2,2,6,6-tetramethyl-1-oxyl-4-pipiridyl azelate and the 1,1'-ferrocenedicarboxylate analogue have been reported. For the latter compound both iminoxyl groups and the ferrocene group undergo a simultaneous 3-electron decomposition at the Pt microelectrode on reduction[50]. Prins and Kortbeek found that ferricinium trichloroacetate[51] prepared by the method of Aly et al[52] had a weak ESR spectrum at 77°K which was in agreement with earlier work[53]. However on cooling to 20°K a much stronger spectrum was obtained superimposed on the former with the g-values identical with those for the $FeCp_2^+$ cation. This was taken as evidence that the spectrum at 77°K arose from an impurity which was probably the 1,1'-ditrichloroacetyl-ferricinium cation.

Wassermann and Horsfield[54] attempted to explain the differences between their results on the ESR spectra of the ferricinium ion and those of Prins and Reinders[55]. Wassermann suggested that Prins results were different because Prins had a relatively strong low field signal due to Fe^{3+} which was formed by decomposition of the ferricinium ion in acetone and dimethylformamide and Wassermann presented evidence to support his suggestions by recording the ESR spectra in the absence of solvent. A similar low field "decompositio signal was also obtained when ferricinium iodide was tested in

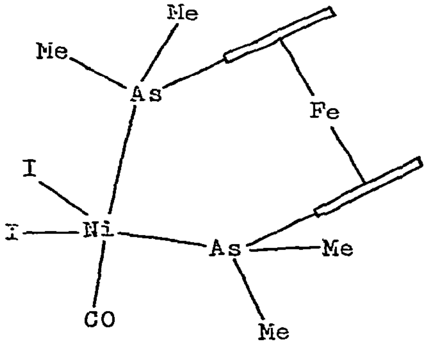


Scheme B

acetone or dimethylformamide. 1,2-Ferrocenyl diketones cyclize upon initial oxidation to form the corresponding quinones as shown in Scheme B. The EPR spectra of these molecules were recorded and it was shown that electron spin density was localised on the metal by the observation of an $Mn^{5/2}$ splitting of 5.63 gauss. The role of charge separation in electron spin delocalization was discussed briefly[56].

5. Structural Determinations

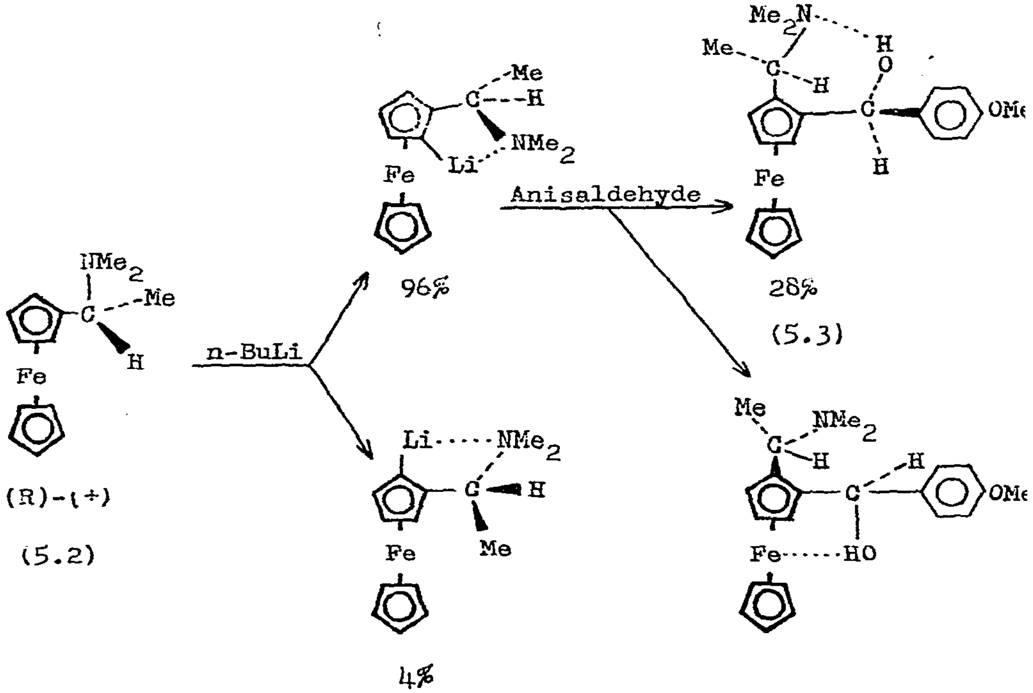
The crystal and molecular structure of the five coordinate complex diiodocarbonylferrocene-1,1'-bis(dimethylarsine)nickel(II) was determined by X-ray analysis. The complex crystallized in the space group $\underline{P}2_12_12_1$ of the orthorhombic system in a cell of dimensions a = 15.16, b = 11.51, and c = 12.01 Å. There are four molecules per unit cell and the coordination geometry about the Ni(II) ion is nearly a regular trigonal bipyramid with the ferrocene ligand occupying both an axial and equatorial position (5.1)[57].



(5.1)

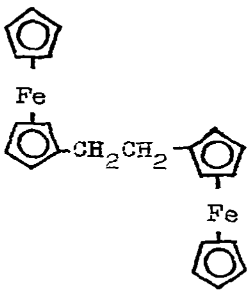
The crystal structure of 2,2-dicyanovinylferrocene $FcCH=C(CN)_2$ was investigated. It was found to crystallize in the monoclinic space group $P2_1/c$ with four molecules in the unit cell: a = 11.33, b = 7.85, c = 13.46 Å, β = 94.1°. The almost parallel cyclopentadienyl rings were found to deviate by 7° from the eclipsed conformation[58]. The absolute configuration of α-{2-[1-(dimethylamino)ethyl]ferrocenyl}anisyl alcohol (5.3) was demonstrated by X-ray crystallography. The alcohol (5.3) was prepared by the route shown from chiral N,N-dimethyl-1-ferrocenylethylamine (5.2). The crystallographic parameters of the alcohol (5.3) were: space group $P2_1$, a = 9.77, b = 11.15, c = 10.56 Å, β = 120.6°, Z = 2. The configuration about the amine substituted carbon atom was (R) and that about the hydroxy-substituted carbon atom (S). The configuration of the alcohol as a whole and with respect to the plane of chirality was (S). The conformations about the two asymmetric carbon atoms was apparently determined by the hydrogen bond formed between the hydroxyl and the amino groups[59].

The crystal structure of 1,1'-dimethylferricinium triodide was determined. The compound crystallized in a triclinic cell, space group $\underline{P}$, with the dimensions a = 14.70, b = 7.440, c = 7.97 Å, α = 70.50°, β = 81.49°, γ = 97.33°, Z = 2. The cyclopentadienyl rings in the cation were almost eclipsed with the Me groups adjacent and the rings inclined 6.6° to each other The crystal and molecular structure of 2,1'-trimethylene-1-(γ-phenyl-γ-hydroxypropyl)ferrocene was studied by X-ray methods It was found to be monoclinic with the space group $\underline{P}2_1/\underline{n}$,

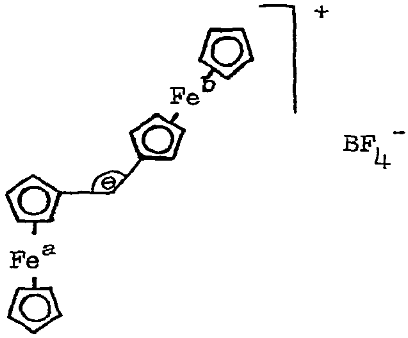


a = 11.47, b = 13.34, c = 11.50 Å, β = 97.45°, calculated d = 1.38, Z = 4. The two cyclopentadienyl rings formed an angle of 171°. The O atom of the OH group was in the endo position and the Ph group was in the exo position and perpendicular to the planes of the two rings of the ferrocene skeleton[61]. The X-ray crystal structure of 1,2-bis(ferrocenyl)ethane has confirmed the trans disposition of the ferrocenyl groups (5.4). The unsubstituted cyclopentadienyl rings were rotated by 8.5° from the eclipsed configuration[62].

The structure of the stable α-ferrocenylcarbonium salt (5.5) has been investigated by X-ray structure analysis and NMR spectroscopy. The diffraction study revealed a skewed transoid conformation with each pair of cyclopentadienyl rings planar and parallel. The mean distances between the ring planes (3.31 Å) and the mean Fe-C (ring) distances (2.05 and 2.06 Å) are close to the corresponding values for ferrocene. The exocyclic carbon atom deviated towards the iron atom (a in 5.5) from the plane of the cyclopentadienyl ring to which it was bound by an angle of 19.9°, it deviated away from iron atom (b in 5.5) by 17.7°. Thus the exocyclic carbon atom was closer to iron (a in 5.5) 2.71 Å than to iron atom (b in 5.5) 2.85 Å. The bond angle around the exocyclic carbon (θ) was 131° and appreciably greater than the value of 120° expected for symmetrical trigonal sp^2 hybridization. The NMR spectrum of the salt (5.5) at 18°C confirmed the equivalence of the two cyclopentadienyl protons α to the substituent and of those β to the substituent and demonstrated that the substituted rings flipped rapidly about the bond to the exocyclic carbon atom.



(5.4)



(5.5)

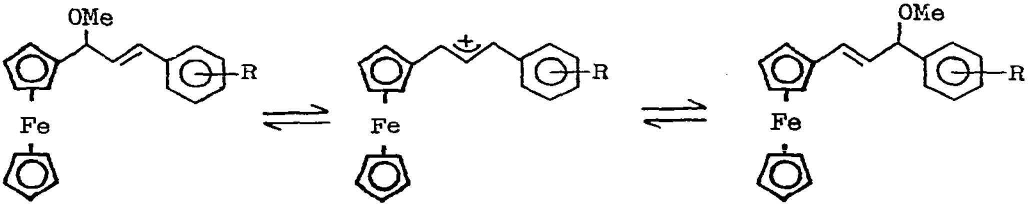
Coalescence was observed at -66°C and rotation ceased at -70°C[63]. In a related investigation, photoelectron spectroscopy was used to measure the ionization potential of the Fe-$2p_{3/2}$ level of ferrocene, the salt (5.5), ferricinium tetrafluoroborate and 1,1'-dibenzoylferrocene. The bond energies for 1,1'-dibenzoylferrocene and the carbonium ion (5.5), 709.5 and 709.6 eV respectively, suggested that the partial charges on the iron atoms were similar and these did not differ appreciably from the charge on the iron atom in ferrocene (ionization potential 709 eV). No difference was detected between the two iron atoms in the salt (5.5)[64].

The 220 MHz NMR spectra of methyl-, ethyl-, isopropyl- and t-butyl-ferrocene, together with the appropriately deuterated molecules necessary to unambiguously assign the various resonances, were recorded. The improved resolution obtained allowed differentiation of the resonances in all the molecules except isopropylferrocene. The 3,4- position protons in these molecules appeared upfield with respect to the 2,5- and 1'- position proton resonances. These relative orders of shielding were contrary to the assignments previously suggested and were thought to be indicative of a predominantly resonance mode of interaction of the alkyl groups with the ferrocene ring [65,66].

Details of the reduction of dimethylaminomethylferrocene methiodide to methylferrocene by sodium in liquid ammonia were published and this reaction was also used to prepare a series of 2-substituted alkylferrocenes. The NMR and mass spectra of these compounds were recorded[67]. The dipole moments were measured for bromo- and iodo-ferrocene (μ= 1.53, 1.46 D) respectively and for 1,1'-dibromo- and 1,1'-diiodo-ferrocene (μ= 1.83, 1.69 D) respectively. Comparison of the experimental values for the disubstituted ferrocenes, with values calculated assuming free rotation about the ring-metal bonds, indicated steric hindrance to free rotation which increased from the bromo to the iodo compounds[68].

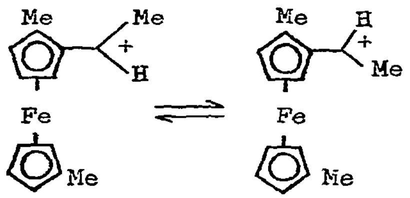
6. Ferrocenylcarbonium ions

Equilibrium constants were measured for the acid-catalysed equilibration of a series of 1-ferrocenyl-3-arylallyl cations (6.1). In each case the ferrocenylvinyl ether (6.2) was of slightly higher thermodynamic stability than its styryl isomer (6.3)[69]. The

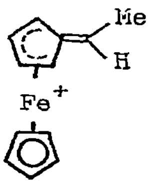


(6.3) (6.1) (6.2)

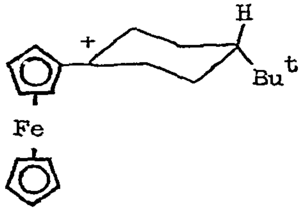
first-order rate constants for the isomerization of the secondary carbonium ion (6.4) to (6.5) were determined by PMR spectroscopy in order to estimate the free-energy barrier to rotation ($H = 86.2$ kJ mol^{-1}) about the metallocene-substituent bond. The results permitted the exclusion of the structure (6.6) for the carbonium ion but did not distinguish between the possible structures with the positive charge on the ligand rather than on the metal. The energy barrier for isomerisation of a tertiary carbonium ion (6.7) was significantly lower than for the secondary carbonium ion (6.4)[70]. The same group have observed the rearrangement of the ferrocenylcarbonium ions (6.8 and 6.11) to the isomers (6.9, 6.10 and 6.12) respectively in CF_3CO_2H. The rearrangement was catalysed by ferrocene or an alkylferrocene and the authors invoked a mechanism where the (Me_2C^+) group was transferred between cations in a series of equilibrium-controlled steps that involved binuclear intermediates (6.13) with ferrocene or alkylferrocenes acting as transport agents[71].



(6.4) (6.5)

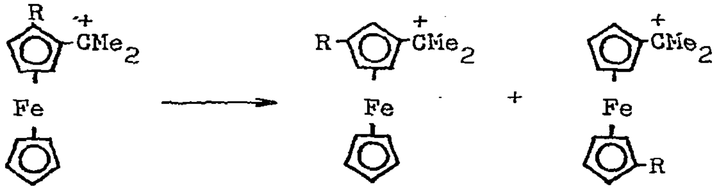


(6.6)

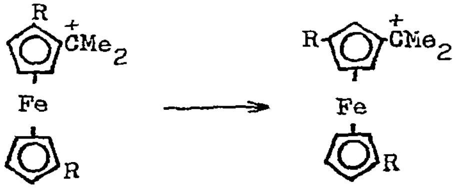


(6.7)

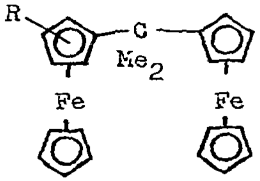
The addition product (6.15) of the α-ferrocenylphenylcarbonium ion (6.14) and nitrosobenzene contained the nitroxide radical and gave a triplet EPR spectrum thus favouring the structure 6.15b over 6.15a. This suggested that the redox tautomer 6.14b predominated over 6.14a in the carbonium ion[72]. Protonation of 2-ferrocenylpropane in concentrated sulphuric acid gave the carbonium ion (6.16) and this was quenched with water to give equimolar proportions of the two dimers (6.17 and 6.18)[73]. An NMR study was made of a series of α-ferrocenylcarbonium ions with tri- and



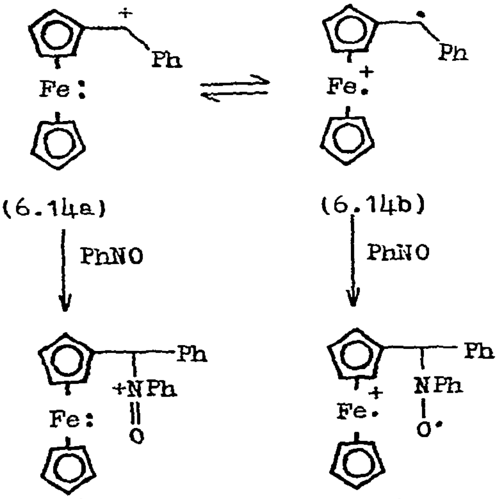
(6.8) (6.9) (6.10)



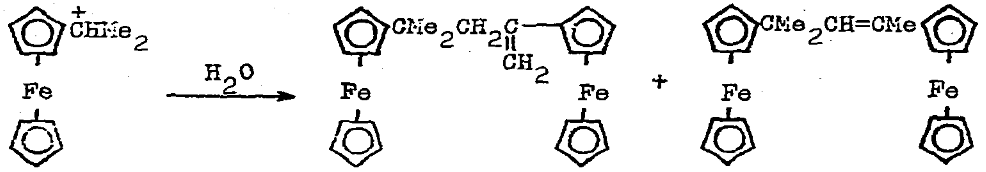
(6.11) (6.12)



(6.13)

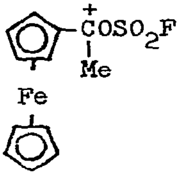


(6.15a) (6.15b)

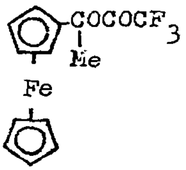


(6.16) (6.17) (6.18)

tetra-methylene bridges between the rings to reduce the susceptibility of the ions to lateral distortion. A comparison of the spectral data for these ions with those of the unbridged species suggested that the iron participation mechanism postulated by Richards and Hill was not followed. Attempts were made to observe the α-ferrocenylvinylcarbonium ions by protonation of ferrocenylacetylene in fluorosulphuric and trifluoroacetic acid. The NMR spectra suggested that the α-ferrocenylcarbonium ions (6.19) and (6.20) were present[74]. Some relevant structural investigations of carbonium ions are included in section 5, structural determinations.



(6.19)



(6.20)

7. Reactions of ferrocene

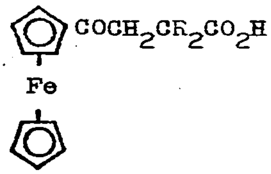
Neutron irradiation of solutions of ferrocene and iron pentacarbonyl in benzene showed that the normal ferrocene produced only about 30% more $^{59}FeCp_2$ than the ^{58}Fe depleted ferrocene. Hence it was concluded that the recoil-produced iron atoms may have come from other molecules in the solution to form radioactive ferrocene[75].

The physical properties, for example surface tension and viscosity, of liquid ferrocene were determined from 174 to 350°[76]. Kolthoff and Chantooni[77] carried out a critical study of the medium activity coefficient of ions between water (w) and methanol (m) based upon the $BPh_4^- = \gamma AsPh_4^+$ and ferrocene assumptions[78]. They concluded that it was not wise to accept a value of ion medium activity coefficient obtained on the basis of these assumptions. Equilibrium constants for the protonation of ferrocene and substituted ferrocenes in the reaction:

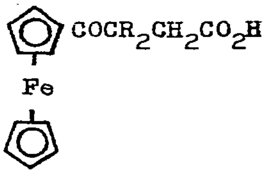
$$(\pi\text{-}C_5H_5)_2Fe + CCl_3CO_2H \rightleftharpoons (\pi\text{-}C_5H_5)_2FeH^+ + CCl_3CO_2^-$$

have been determined spectrophotometrically. The authors concluded that protonation occured at a cyclopentadienyl ring rather than at the iron atom and that electronic transmission of the polar effects of substituents through the metal atom was negligible. Work in the same laboratory has shown that the relative rate of second order metallation of ferrocene and benzene by mercuric acetate is $10^9:1$[79,80].

Dabard and Le Plouzennec have studied the electrophilic attack of 2,2-disubstituted succinic anhydrides on ferrocene. With phenyl substituents, the isomer (7.1; R = Ph) was obtained while in the presence of methyl groups a mixture of the isomers (7.1 and 7.2; R = Me) was obtained[81].



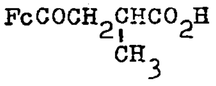
(7.1)



(7.2)

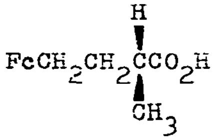
Ferrocene has been cyanoethylated with an excess of acrylonitrile or β-chloropropionitrile in the presence of aluminium chloride to form (2-cyanoethyl)ferrocene and minor amounts of 1,2-, 1,3- and 1,1'-bis(2-cyanoethyl)ferrocene[82]. The Friedel-Crafts reaction of MeCH=CHCOCl with ferrocene gave the corresponding ethylenic ketone, treatment with HCN and hydrolysis of the nitrile gave the acid (7.3) which was reduced to (±)-γ-methyl-γ-ferrocenylbutyric acid (7.4). Cyclization of (7.4) gave exo- (7.5) and endo-α-methylferrocenocyclohexanone (7.6). The reduction of (7.5) and (7.6) by $LiAlH_4$ gave a mixture of the racemic exo and endo alcohols (7.7 and 7.8), the relative stereochemistry of these ketones and alcohols was established[83].

The siloxane (7.9) was prepared by the treatment of ferrocene with $AlCl_3$ and $ClSiMe_2(CH_2)_3NCO$ and this derivative (7.9) was used as an antioxidant in polysiloxane-based liquid clutches[84]. Ferrocene and p-benzoquinone when treated with aluminium chloride gave ferricinium chloride and hydroquinone. It was found that chloranil and the enediones $RCH=CHR^1$ ($R = PhCO, MeO_2C$; $R^1 = PhCO, CO_2H, MeO_2C$) were reduced in the presence of ferrocene and aluminium chloride[85].



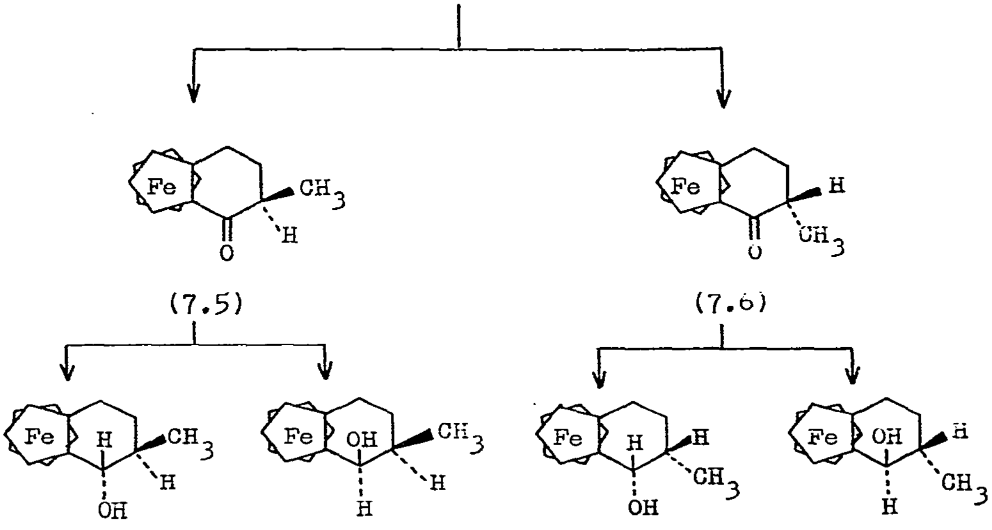
$\mathrm{FcCOCH_2\underset{CH_3}{CH}CO_2H}$

(7.3)



$\mathrm{FcCH_2CH_2\overset{H}{\underset{CH_3}{C}}CO_2H}$

(7.4)

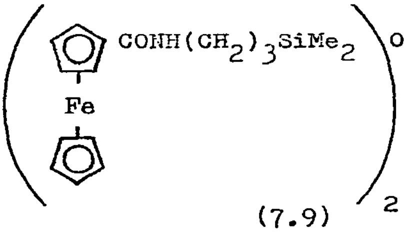


(7.5)

(7.6)

(7.7)

(7.8)



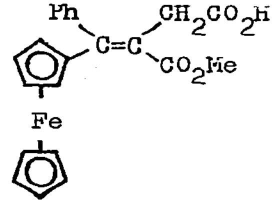
(7.9)

Mixtures of ferrocene and either mercury(II) chloride or bromide in ethanol gave a diamagnetic red precipitate which on standing changed into a blue paramagnetic solid. The empirical formula of both red and blue complexes was $\mathrm{FcH.7HgX_2}$. On the basis of IR evidence, mercury-iron interaction was proposed for the red complex while the blue species was regarded as a ferricinium salt with a complex anion. By contrast ruthenocene formed simple 1:1 adducts with mercury(II) halides[86].

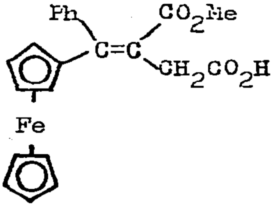
Peloso and Basato have examined the reduction by ferrocene of platinum(IV) complexes, such as trans- $Pt(PEt_3)_2Cl_4$; second order kinetics were observed in each case. Increasing solvent polarity increased the rate of reaction as was expected and the thermodynamic parameters were determined for each platinum complex-solvent system studied. An outer sphere reaction mechanism was confirmed[87]. Oxidative degradation of ferrocene and nickelocene with atmospheric oxygen gave $CH{\equiv}C.CH{=}CH_2$ as the principal volatile product while an isomeric mixture of C_4H_6 olefins was obtained with 1,3-cyclopentadiene under similar conditions[88]. Thirty two lithiated compounds including lithioferrocene were prepared by treatment of the hydrocarbon or ferrocene with butyllithium in the presence of bi- and tri-dentate polyamine ligands such as TMEDA[89].

8. Ferrocene Chemistry

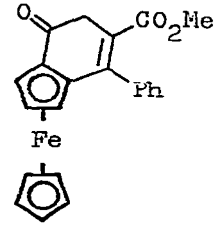
Touchard and Dabard have reported the base catalysed condensation of benzoylferrocene with methyl succinate to give a mixture of the isomers (8.1 and 8.2) which were identified as the dimethyl esters. Cyclization of the half esters (8.1 and 8.2) with polyphosphoric acid gave two isomeric products (8.3 and 8.4) while with trifluoroacetic anhydride only one of the products (8.3) was formed. The specificity of these and some related reactions was discussed[90]. The Wittig synthesis has been used



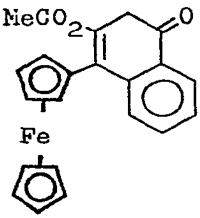
(8.1)



(8.2)

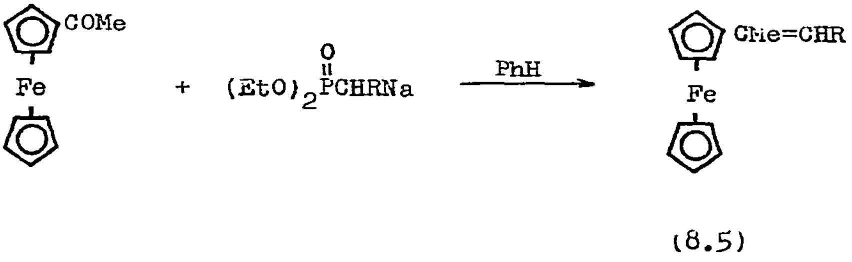


(8.3)



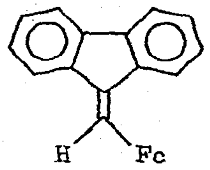
(8.4)

to prepare ferrocenylvinylketones (8.5; R = COC_6H_4.Me-**p**, COPh) and esters of ferrocenylacrylic esters (8.5; R = CO_2H, CO_2Et, CO_2Pr, CO_2Bu, CN)[91]. 9-(Ferrocenylmethylene)fluorene (8.6) was prepared by a direct Wittig condensation of tributylfluoren-9-ylidenephosphorane and ferrocenecarboxaldehyde. Compound (8.6) did not undergo topomerization and geometrical isomerization of its derivatives could not be detected even at 220° by NMR spectroscopy[92]. 1,1'-Diacetylferrocene was treated with sodium ethoxide and



(8.5)

diethyloxalate to give γ, γ'-(1,1'-ferrocenylene)-bis(α,γ-dioxobutyric acid) 8.7; R = H) and the corresponding diethyl ester (8.7; R = Et). The polyoxo compounds (8.7; R = Et) were treated with amines to give a variety of condensation products such as the pyrazole (8.7)[93].



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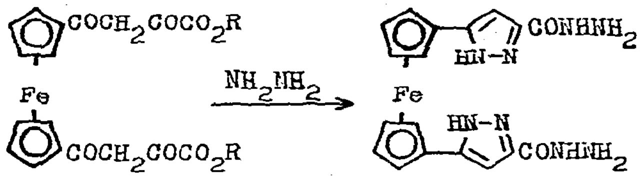
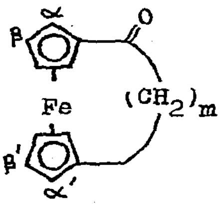


(8.7) (8.8)

A series of [m]ferrocenophan-1-ones (8.9) was acetylated under standard conditions and the relative proportions of the isomeric products were determined[94]. These results were compared with those previously obtained for the acetylation of [m]ferrocenophanes (8.10) (see Table 1)[95]. No diacetylated products were found in any of the reactions. The treatment of diphenylphosphine oxide anion (8.11) with benzoylferrocene gave the olefin (8.12)



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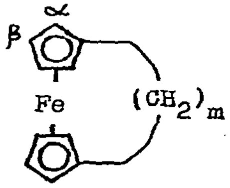


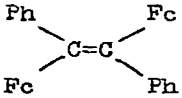
(8.10)

Table 1. Isomeric product ratios for the acetylation of [m]ferrocenophanes and [m]ferrocenophane-1-ones

Substrate	β/α	α'/α	(α+β)/α'
[3]Ferrocenophane	1.57	-	-
[3]Ferrocenophane-1-one	4.2	0.6	9.5
[4]Ferrocenophane	1.65	-	-
[4]Ferrocenophane-1-one	1.2	0.5	4.5
[5]Ferrocenophane	2.19	-	-
[5]Ferrocenophane-1-one	0.8	0.01	170

$Ph_2P\bar{O}$

(8.11)



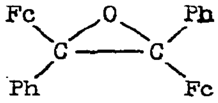
(8.12)

$PhCOCFc_2Ph$

(8.13)

$FcCOCPh_2Fc$

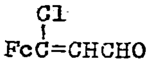
(8.14)



(8.15)

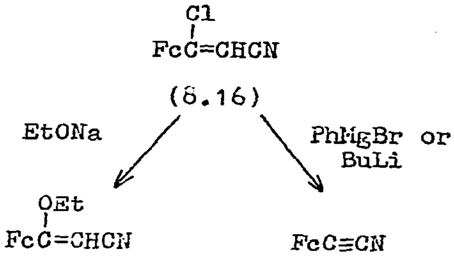
(5%) together with ferrocene (12%), benzylferrocene (4%), 1,2-diferrocenyl-1,2-diphenylethane (3%), benzoyldiferrocenylphenylmethane (8.13) (1%) and ferrocenylcarbonyl(ferrocenyl)-diphenylmethane (8.14) (4%). The formation of an olefin in this reaction was rationalized in terms of the epoxide intermediate (8.15) which decomposed to give the olefin (8.12)[96]. 1,1'-Diethylferrocene was prepared by the reduction of 1,1'-diacetylferrocene by hydrogen over a Raney nickel catalyst at 40-60°/40-80 atm.[97].

The cis- and trans-β-ferrocenyl-β-chloroacrylonitriles (8.16) were prepared by treating the aldehyde (8.17) with NH_2OH and then dehydration of the oximes with phosphorus oxychloride. The reactions of the acrylonitriles (8.16) with BuLi and sodium



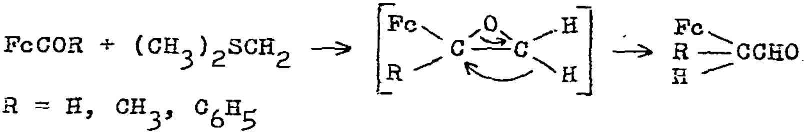
$FcC(Cl)=CHCHO$

(8.17)



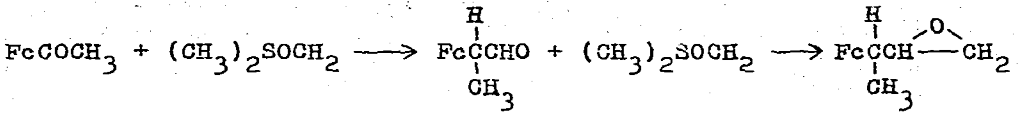
(8.16)

alkoxides were given^{98}. The treatment of 1-chloro-1'-acetylferrocene with $POCl_3$ in dimethylformamide gave 1-chloro-1'-(α-chloro-β-formylvinyl)ferrocene and this olefin gave 1-chloro-1'-ethynylferrocene when treated with aqueous sodium hydroxide^{99}. The reactions of ferrocenecarboxaldehyde, acetylferrocene and benzoylferrocene with dimethylsulphonium methylide (8.18) gave the corresponding ferrocenylacetaldehyde (8.19) and the reaction was thought to proceed through an epoxide intermediate (8.20)



(8.18) (8.20) (8.19)

which ring opened by rearrangement. The acylferrocenes with dimethyloxosulphonium methylide (8.21) were less reactive, acetylferrocene gave products (8.22) and (8.23) derived from the attack of both one and two molecules of the ylide whilst with benzoylferrocene there was no reaction^{100}.

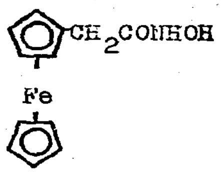


$$FcCOCH_3 + (CH_3)_2SOCH_2 \longrightarrow Fc\overset{H}{\underset{CH_3}{C}}CHO + (CH_3)_2SOCH_2 \longrightarrow Fc\overset{H}{\underset{CH_3}{C}}\overset{\quad O \quad}{CH\text{—}CH_2}$$

(8.21) (8.22) (8.23)

A series of α-carbonylferrocenes were found to undergo photoreaction with water in solvents such as dimethyl sulphoxide and pyridine, for example benzoyl ferrocene gave cyclopentadienyliron benzoate and free cyclopentadiene[101]. The electrochemical oxidation of ferrocenecarboxylic acid in acetonitrile was used as a model reaction to demonstrate the utility of a potentiostat which was able to supply large amounts of peak power to an electrochemical cell. Time improvements of more than an order of magnitude were obtained in systems with high resistance and large capacitance[102].

The hydroxamic acid (8.24) was formed in good yield from methyl ferroceneacetate and hydroxylamine in methanol, it gave salts with barium and copper(II) and it was oxidized to the ferricinium ion with silver nitrate[103]. The hydroxyl stretching frequencies of the disubstituted carbinols (8.25; R = Me, Et, Pr^i, Bu^t, Pn^{neo}) showed intramolecular O-H·····Fe hydrogen bonding (3560-3583 cm^{-1}) and in some cases free hydroxyl absorptions (3632 cm^{-1}). The carbinols (8.25; R = Me, Pn^{neo}) were dehydrated to the olefins (8.26; R = Me, Bu^t) in perchloric-acetic acid mixtures, under the same conditions the di-t-butylcarbinol (8.25; R = Bu^t) gave three products (8.27, 8.28, 8.29) within 1 min. A mechanism for the rearrangement was proposed. The rate of hydrolysis of the acetate (8.30; R = Bu^t) was 4900 times less



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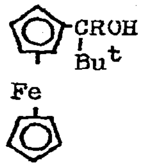
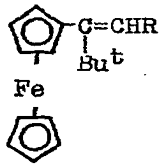
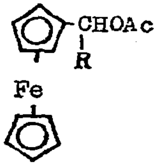


(8.25)



(8.26)



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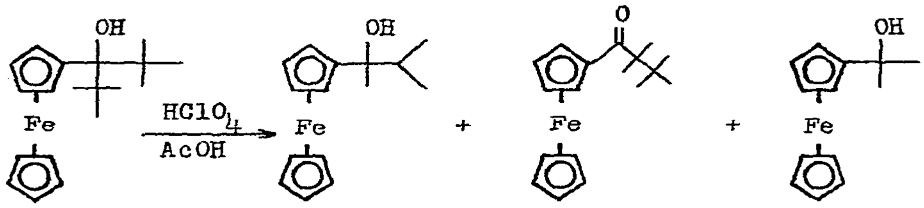
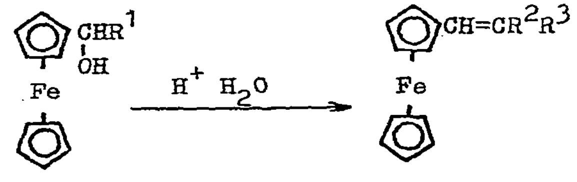


(8.27) (8.28) (8.29)

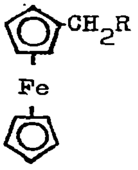
than that of the methyl homologue (8.30; R = Me) and this was attributed to steric hindrance of resonance stabilization[104]. Eisenstadt and Cais have reported an unusual elimination of HOCl from the carbinols (8.31) to form the olefins (8.32) in concentrated sulphuric acid. The acetates were pyrolysed at 160-200° at 0.1 mm Hg to give the same products. On the other hand, the acetate formed from phenyl(trichloromethyl)methanol was recovered unchanged on attempted pyrolysis[105].



$R^1 = CCl_3$; $CHCl_2$ $R^2 = R^3 = Cl$; $R^2 = H$, $R^3 = Cl$

(8.31) (8.32)

The hydroxy, dimethylamino and phenoxy (8.33; R = OH, NMe_2 or OPh) groups were displaced by aniline from the corresponding α-substituted ferrocenylmethanes to give the N-ferrocenylmethylaniline (8.33; R = NHPh). The nucleophilic character of the aniline was shown to be important in this reaction and the aniline group was displaced from (anilinomethyl)ferrocene by p-$MeOC_6H_4NH_2$. This reaction was utilized to prepare 1,2-bis(anilinomethyl)ferrocene from the hydroxymethylferrocene (8.34)[106]. N-(Ferrocenylmethyl)aniline, formed by treatment of ferrocenemethanol or the methiodide of dimethylaminomethylferrocene with aniline, underwent intermolecular rearrangement to the anilines (8.35 and 8.36) at high temperatures (186°) or in the presence of an acid catalyst such as aniline hydrochloride. Rearranged products were obtained directly with N,N-dimethylamiline while N-methylaniline resembled aniline in its behaviour towards the methiodide. The α-ferrocenylcarbonium ion was invoked as the intermediate in the rearrangement on the basis of its acid catalysis[107].



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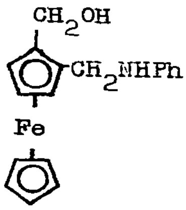

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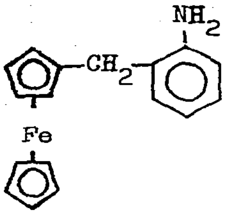

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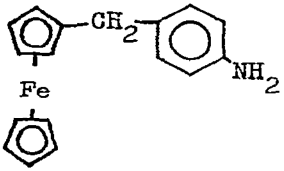

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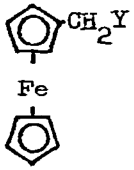
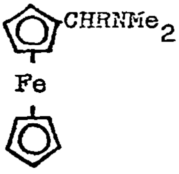


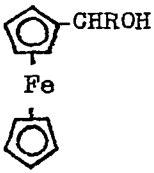
Y = OH, OAc, SCN
OCH_2Fc, NMe_3I
(8.37)

Ferrocenylcarbinols [$FcCH(R^1)OH$] were treated with an aluminium chloride-dimethylamine mixture to give the corresponding ferrocenylmethyl-amines [$FcCH(R^1)NMe_2$] in high yield. This transformation was shown to proceed with complete retention of configuration when one optically active form of the alcohol was used[108].

Dixneuf and Dabard have converted several methylferrocenes (8.37) into NN-dimethylaminomethylferrocene (60-95%) (8.38; R = H) with $(Me_2N)_2CH_2$ in acetic-phosphoric acid mixtures. Secondary alcohols (8.39) and ring substituted metallocenes such as (8.40) were converted in the same way to the amines (8.38; R = Me, Et, Ph and 8.41) respectively. The formation of the amines (8.38 and 8.41) was considered to proceed through attack of the α-ferrocenylcarbonium ion ($FcCH_2^+$) by Me_2NH. The stereochemistry of the reactions was discussed[109]. In the succeeding paper the same

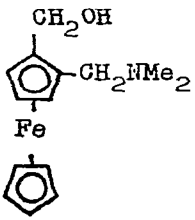


(8.38)



R = Me, Et, Ph

(8.39)



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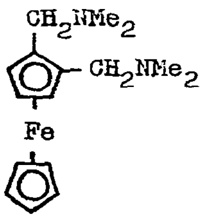
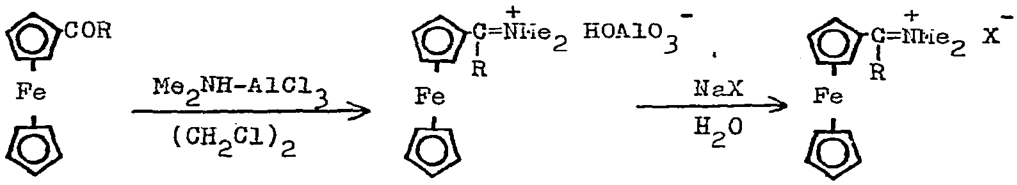


(8.41)

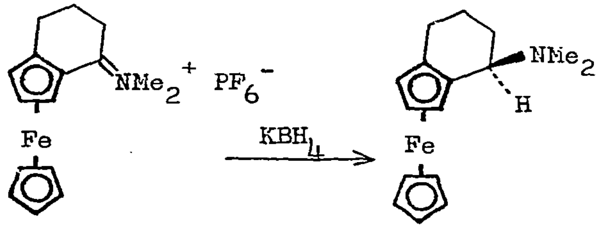
authors described the formation of the amines (8.38) from the secondary alcohols (8.39) with Me_2NH-$AlCl_3$ in ethylene dichloride. Morpholine and methylamine replaced dimethylamine in the reagent and the mechanism and stereochemistry of the reaction were discussed[110] (see AS 1971, p. 406).

Ferrocenylimmonium salts (8.42) have been prepared by stirring acylferrocenes with aluminium chloride and dimethylamine in 1,2-dichloroethane. The salts were stable in water and were reduced by borohydride to the corresponding amines, thus the salt (8.43) was reduced stereoselectively to the endo-amine (8.44)[111]. The reactions of the methyl imino ester (8.46) have been reported,



R = Ph, H
X = BF_4^-, PF_6^-

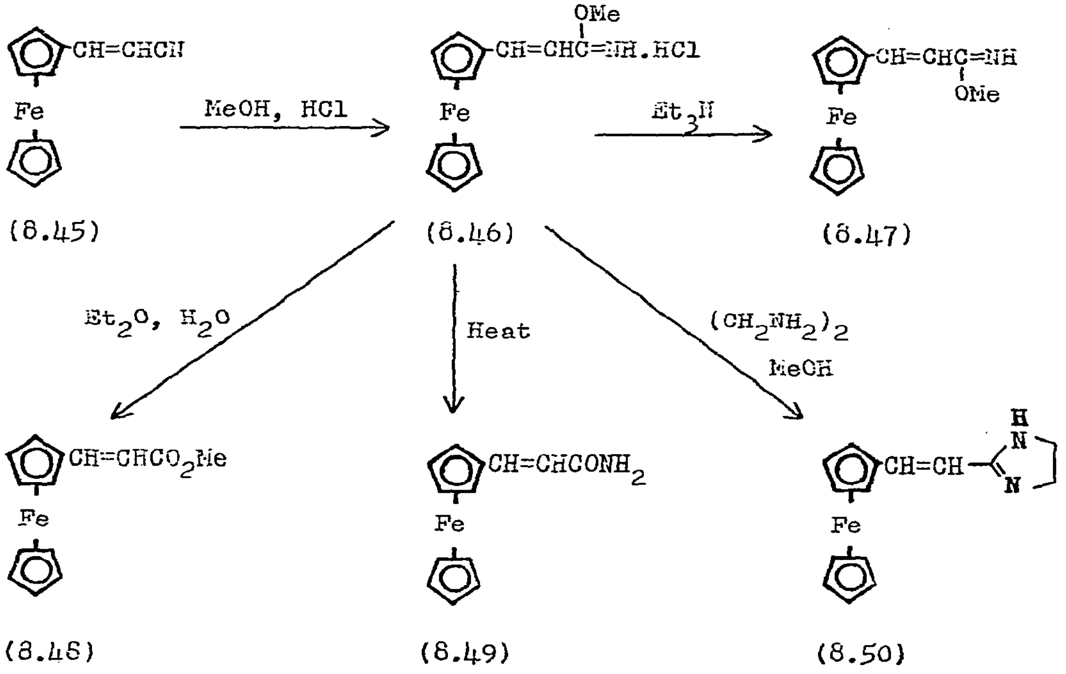
(8.42)



(8.43) (8.44)

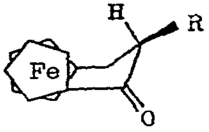
the cis and trans forms were obtained as the hydrochlorides by treatment of the acrylonitrile (8.45) with dry MeOH and HCl.

The free esters (8.47) were liberated with triethylamine, heating wi aqueous ether gave the acrylic ester (8.48) and the amides (8.49) were obtained on heating. Condensation with difunctional bases, for example ethylene diamine, gave products such as the cyclic amine (8.50)[112]. Treatment of the methylimino ester of β-ferrocenylacrylic acid with ethylene diamine in methanolic HCl gave the substituted imidazole (8.50). Similar condensations were carried out with *o*-phenylenediamine and *o*-aminophenol[113]. The use of ferrocenylimino esters in the synthesis of ferrocenyl heterocycles such as 2-ferrocenylbenzimidazole has been confirmed

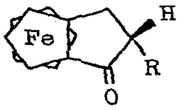


(see A.S. 1971, p. 400)[114].

Dimethylaminomethylferrocene methiodide in dimethylformamide was condensed with $RCH(CO_2Et)_2$ in the presence of sodium in toluene; hydrolysis and decarboxylation of the products gave substituted ferrocenylpropionic acids. Cyclization of the acids gave mainly heteroannular bridged ketones (8.51) and small amounts of homoannular bridged ketones (8.52; R = Me_2CH, $PhCH_2$, Bu, Et). The reduction of (8.51) and (8.52) with $LiAlH_4$ was found to be stereospecific[115]. Two new syntheses of N,N-dimethyl-1-ferrocenylethylamine were reported. The first method involved the treatment of 1-ferrocenylethanol with phosgene followed by dimethylamine.



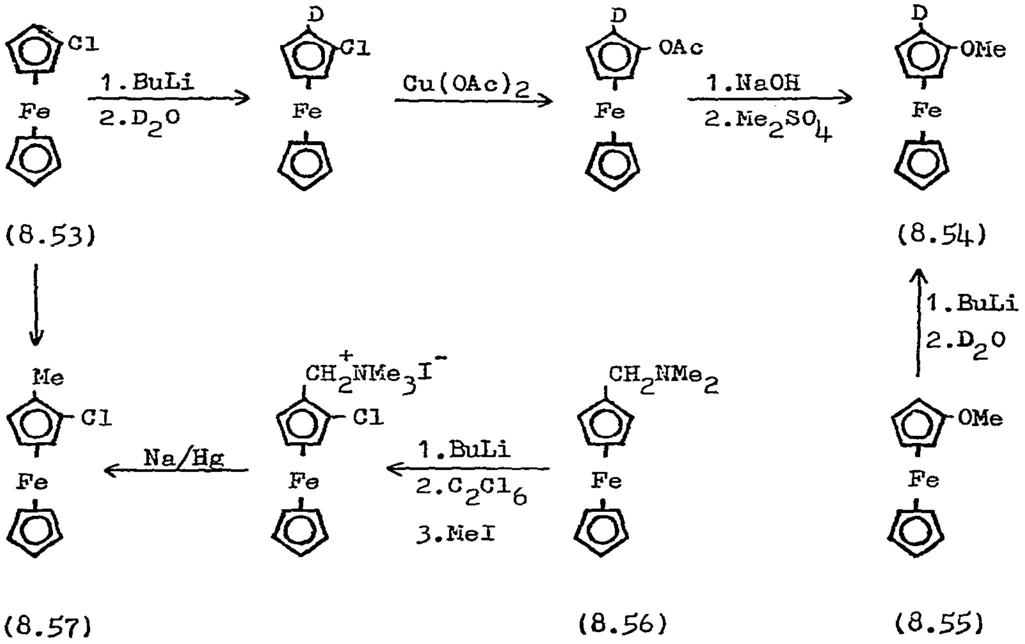
(8.51)



(8.52)

In the second method the acetoxy group was displaced from 1-ferrocenylethyl acetate by treatment with methanolic dimethylamine solution. The stereospecificity of transformations involving the α-ferrocenylethylcarbonium ion was also described. Compounds of the type Fc-CHY-Me where Y = NH_2, $\overset{+}{N}Me_3\overset{-}{I}$, N_3 and OMe were shown to interconvert stereospecifically[116]. Some salts of $FcCH_2NMe_2$ were prepared with bromomethylstilbenes for example with $RC_6H_4CR'{=}CR''C_6H_4CH_2Br$, the corresponding bromide was formed[117].

The previously reported 2-lithiation of chloroferrocene (8.53) and methoxyferrocene (8.55) has been confirmed by comparison of the products with those obtained in the 2-lithiation of [(dimethylamino)methyl]ferrocene (8.56). In a typical scheme the ferrocenes (8.53 and 8.55) were each converted through lithiation to the deuteroferrocene (8.54), while the methylferrocene (8.57) was formed from each of the ferrocenes (8.53 and 8.56)[118]. Chloroferrocene and 1,1'-dichloroferrocene were metallated with an organolithium to give 1,chloro-2-lithioferrocene and 1,1'-dichloro-2,2'-dilithioferrocene respectively. These intermediates were chlorinated to form the corresponding di- and tetra-

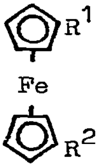


(8.53) (8.54)

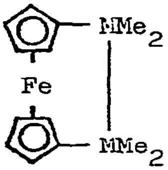
(8.57) (8.56) (8.55)

chloroferrocenes, exhaustive metallation and chlorination gave penta- and deca-chloroferrocene as the ultimate products. Similar transformations were achieved for ruthenocene derivatives[119]. The specific 2-lithiation of (dimethylamino)methylferrocene and N-ethylferrocenecarboxamide has been used to synthesise a number of 1,2-disubstituted ferrocenes including a series of 1-(dimethylamino)methyl-2-alkylferrocenes[120].

Mono- and di-lithioferrocenes were treated with chloro- or alkoxy-silanes and chlorogermanes to give twenty-one organosilyl- and organogermyl-ferrocenes and most of the compounds contained the M-M group (M = Si or Ge), typical examples are the ferrocenes (8.58; $R^1 = GeMe_3$, $R^2 = H$; $R^1 = SiMe_2GeMe_3$, $R^2 = H$; $R^1 = GeMe_2GeMe_3$, $R^2 = H$; $R^1 = R^2 = SiMe_2SiMe_3$; $R^1 = R^2 = GeMe_2GeMe_3$; 8.59; M = Si, Ge). The NMR spectra were recorded[121].



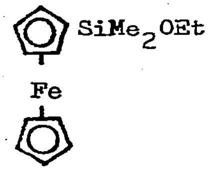
(8.58)



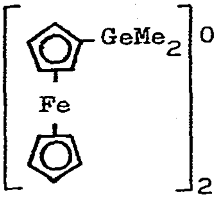
M = Si, Ge

(8.59)

In the succeeding paper, the acid-catalysed alcoholysis of the ferrocenes containing M-M bonds was described. At low concentrations of hydrogen chloride (0.053 M) protodemetallation to give ferrocene was insignificant and smooth cleavage of the M-M bonds was observed. The ferrocenylsilane (8.58; $R^1 = SiMe_2GeMe_3$, $R^2 = H$) gave the ethoxide (8.60) with ethanol, while the ferrocenylgermane (8.58; $R^1 = GeMe_2GeMe_3$, $R^2 = H$) gave the digermoxane (8.61). The disubstituted ferrocenes (8.58; $R^1 = R^2 = SiMe_2SiMe_3$) formed the bridged siloxane (8.62; M = Si) and similar products (8.62; M = Si, Ge) were formed by ring expansion in the bridged compounds (8.59; M = Si, Ge)[122].



(8.60)



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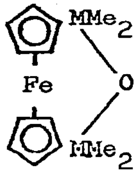
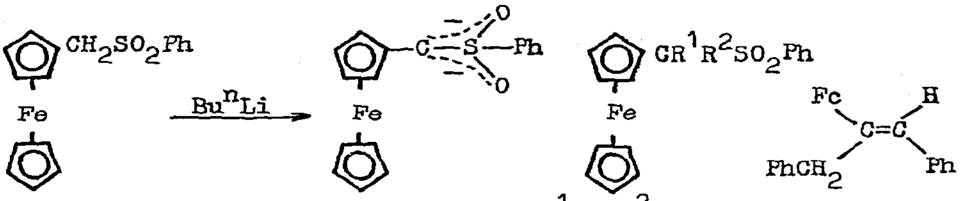


(8.62)

As a part of the same investigation Kondo, Yamamoto and Kumada have examined the alcoholysis of the same silyl- and germyl-ferrocenes (8.58) in the presence of an excess of ferric ion as either ferric chloride or ferricinium tetrachloroferrate. They suggest that oxidation of ferrocene to ferricinium is effected by the ferric ion and the highly polar M-M bond is then subject to nucleophilic attack by the alcohol. The products were similar to those obtained in the acid catalysed cleavage[123].

Evans and Marr have reported the lithiation of ferrocenylmethyl phenyl sulphone (8.63) with n-butyl-lithium to form the dianion (8.64) and this intermediate was treated with alkyl halides to give the products (8.65). Heating the dianion (8.64) with an excess of benzyl chloride gave a mixture of the cis and trans forms of the olefin (8.66). The phenyl sulphone group in the compounds (8.65) was displaced by aniline in water at the reflux temperature[124]. The fixation of molecular nitrogen on organic and organometallic compounds in the presence of di(π-cyclopentadienyl)titanium dichloride and lithium aluminium hydride has been examined. The use of ferrocenyl-lithium as



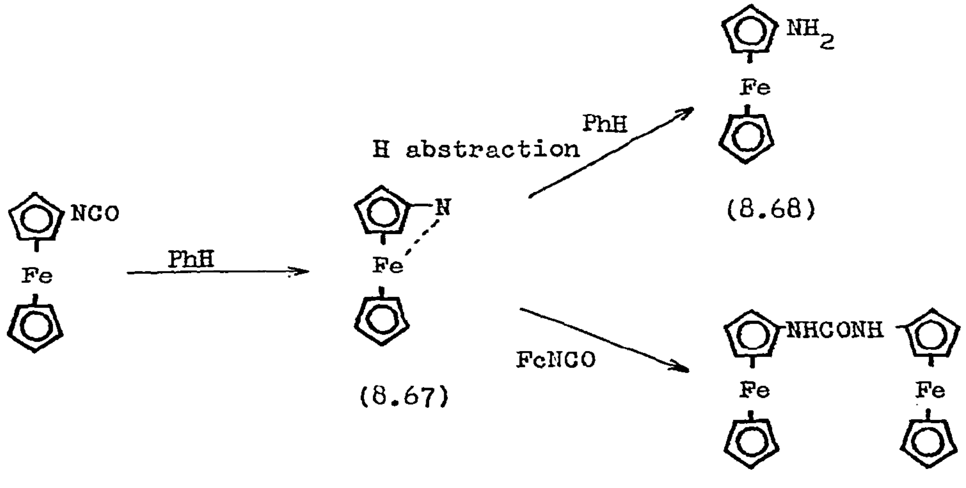
(8.63) (8.64)

$R^1 = R^2 = Me$
$R^1 = R^2 = CH_2CH_2$
$R^1 = Bu^n$, $R^2 = H$
$R^1 = PhCH_2$, $R^2 = H$
(8.65)

(8.66)

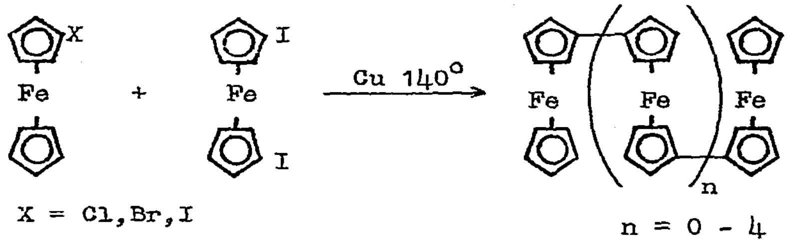
the nitrogen acceptor gave ferrocenylamine and biferrocene as the products[125].

Sutherland and co-workers have demonstrated the thermal lability of ferrocenyl isocyanate in boiling hydrocarbon solvents and dimethyl sulphoxide. To explain the formation of the products (8.68 and 8.69) the authors invoked the nitrene (8.67) as the reaction intermediate. Aromatic organic isocyanates were stable



(8.67) (8.68) (8.69)

in hydrocarbon solvents but gave the corresponding amine and symmetrical urea in dimethyl sulphoxide[126]. The mixed Ullmann reaction between a haloferrocene (8.70) and 1,1'-diiodoferrocene (8.71) gave good yields of 1,1'-oligomeric ferrocenes (8.72). The reaction conditions were varied in order to ascertain those that gave the maximum yields of each oligomer. The mass spectra of all the oligomeric ferrocenes prepared were recorded[127].



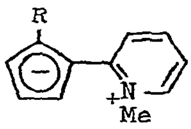
X = Cl,Br,I

n = 0 - 4

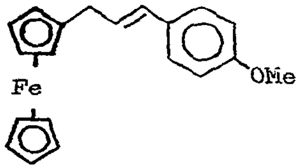
(8.70) (8.71) (8.72)

Nesmeyanov and co-workers have described the cleavage of the cyclopentadienyl-metal bond in the methiodides of 2-bromo- or 2-phenyl-α-pyridylferrocenes by UV irradiation in 0.005 M H_2SO to form the zwitterion (8.73). The UV spectrum of the ion (8.73) showed a hypsochromic shift of the principal band with increasing solvent polarity which suggested an ylide rather than a fulvene structure. The ion (8.73) was readily protonated to give cyclopentadiene derivatives and was characterised as the tetraphenylborate in this form[128]. Baker and Horspool have continued their investigation of the photolysis of ferrocenylolefins with the observation of methanol addition to the olefin (8.74) to give the ethers (8.75; R^1 = OMe, R^2 = H; R^1 = H, R^2 = OMe), the latter by a 1,3-hydride transfer mechanism. The alkane (8.75; $R^1 = R^2 = H$) was formed by secondary photolysis of the two ethers[129].

Ferrocenyltricyanoethylene (89%) was obtained by treating the gold complex (8.76) with tetracyanoethylene in boiling benzene, dicyanoacetylene gave the adduct (8.77; 76%) under similar conditions[130].


R = Br, Ph

(8.73)



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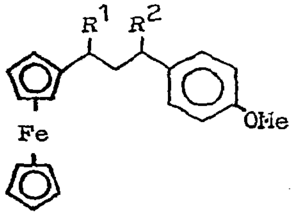
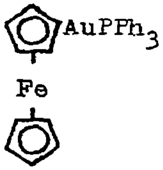


(8.75)



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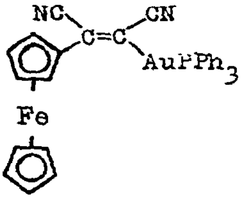
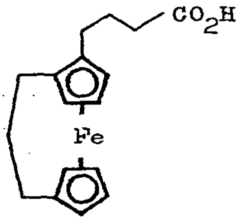


(8.77)

Further details of the effect of ferrocenyl substituents on the base hydrolysis of quaternary phosphonium iodides have been reported[131,132]. Electron release by ferrocenyl groups decreased the rate of hydrolysis, it was concluded that the inductive effect of the metallocene was small and that electron release was achieved by direct interaction between filled ha_g orbitals on ferrocene with vacant 3d orbitals on phosphorus.

The acids (8.78 and 8.79) obtained by the succinoylation of 1,1'-trimethyleneferrocene were distinguished by cyclization to the corresponding ketones and subsequent reduction to the cyclohexenes (8.80 and 8.81). Reduction of the ketones (8.82) with the Grignard reagent gave a mixture of diastereoisomeric alcohols. The proportions of the two products depended on the nature of the substituent on the ketone (8.82) and on the reagent and they were rationalized in terms of the preferred geometry of the transition state in each case[133].



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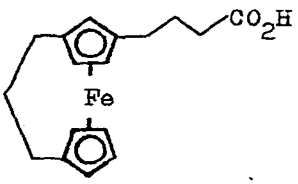

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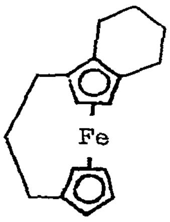

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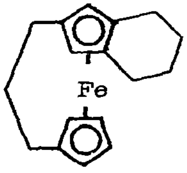
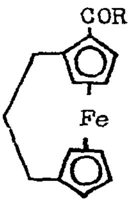


(8.81)

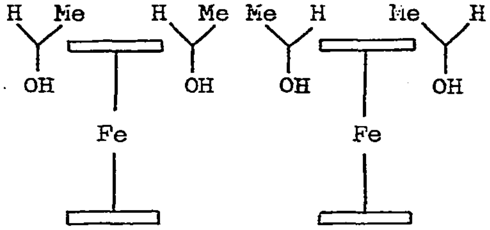


(8.82)

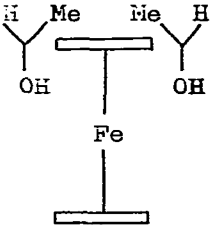
Further details of the electron transfer reactions of substituted ferrocenes (A.S. 71; 391) were reported and the results were correlated with the Marcus equation[134].

9. Stereochemistry

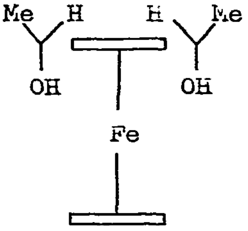
The KBH_4 reduction of 2-acyl-1-(dimethylaminomethyl)ferrocenes was stereoselective giving 90:10 mixtures of stereoisomers whilst the reduction of the corresponding 2-acyl-1-methylferrocenes gave 50:50 mixtures. The addition of Grignard reagents to the 2-acyl-1-(dimethylaminomethyl)ferrocenes was also found to be stereoselective[135]. Moise and Mugnier have obtained a mixture of four diols on treatment of ferrocene-1,2-dicarbaldehyde with methylmagnesium iodide. The same products, in different proportions, were formed on the borohydride reduction of 1,2-diacetylferrocene. The diols were separated on alumina into the racemate (9.1) and the two meso pseudoasymmetric alcohols (9.2 and 9.3), (see A.S. 1971 p. 406). The stereochemistry of the products was confirmed by successive oxidation (MnO_2) and reduction (KBH_4)[136].



(9.1)

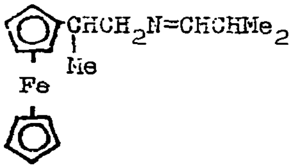


(9.2)

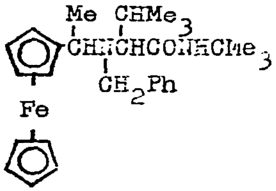


(9.3)

The preparation of racemic N,N-dimethyl-α-ferrocenylethylamine from α-ferrocenylethyl acetate and the resolution of the amine with R(+)-tartaric acid has been described in detail as an undergraduate laboratory exercise[137]. The synthesis of peptides and N-acyl-α-amino acid amines from ferrocene intermediates has been described thus the ferrocenylimine (9.4) was treated with $Me_3C.NC$ and benzyl alcohol in methanol to give the amino acid derivative (9.5) as a mixture of two diastereoisomers. The product (9.6) was obtained on cleavage of the ferrocenylethyl groups from the derivative (9.5) with trifluoroacetic acid[138]. Ugi and coworkers have reported further details of the stereospecific nucleophilic substitution at the α-carbon atom of the methiodide (9.7). This compound was converted successively to the methoxide, the secondary alcohol, the acetate, the azide, the primary amine and finally to the dimethylamine which was quaternized to give the starting material. Most of the intermediates were independently correlated with other members of the cycle and all of the transformations, with one exception, proceeded with retention of configuration. Kinetic evidence was used to demonstrate a configurationally stable carbonium-ion intermediate and the same mechanism was proposed for most of the other reactions[139].



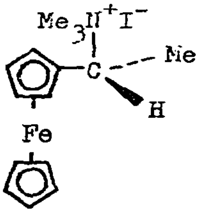
(9.4)



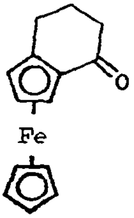
(9.5)

$\mathrm{PhCH_2NH\overset{\overset{\textstyle CHMe_2}{|}}{C}HCONHCMe_3}$

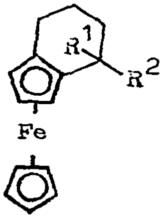
(9.6)



(9.7)



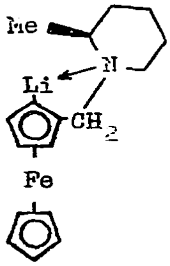
(9.8)



(9.9)

Reduction of the ketone (9.8) by triphenyltin hydride was stereoselective in the absence of a free radical initiator. The endo-alcohol product (9.9; $R^1 = H$, $R^2 = OH$), was rationalized in terms of an ionic mechanism with the bulky reagent attacking the unhindered face of the cyclohexenone ring. When a free radical initiator was present then both the endo- and exo-alcohols (9.9; $R^1 = H$, $R^2 = OH$; $R^1 = OH$, $R^2 = H$) respectively, were obtained. These results were explained by the formation of a free radical intermediate with two alternative conformations. The effect of alkyl substitution near the reaction site was examined[140].

Asymmetric lithiation of (S)(+)-(N-χ-pipecolymethyl)ferrocene to give the intermediate (9.10), has been used as the first stage in the synthesis of the optically active ketone (9.11). The absolute configuration of the (-)-ketone was established as (1S, 2R) by comparison of the ORD and CD curves of the ketone and each intermediate in the synthesis with an intermediate of known configuration[141].



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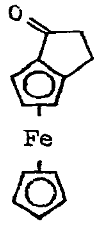


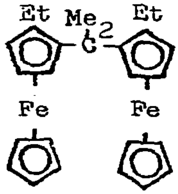
(9.11)

10. Biferrocenyls, ferrocenophanes and annelated ferrocene derivatives

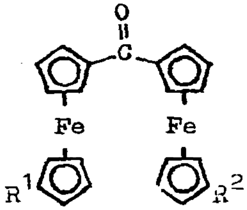
Neuse has reexamined the oligomeric by-products from the polyrecombination of ferrocene with t-butylperoxide at 200° and isolated 1,2-diferrocenylferrocene (see A.S. 1971; p. 409)[142]. Routes to di- and tri-ferrocenyl ligands have been investigated, p-diferrocenylbenzene was prepared and a convenient route to 1,1'-diphenylferrocene was described[143]. The condensation of alkylferrocenes with ketones in the presence of methanol and sulphuric acid at 65-80° gave bis(alkylferrocenyl)alkanes, thus ethylferrocene was condensed with acetone to give the binuclear compound (10.1) in 72% yield[144].

Touchard and Dabard have acetylated diferrocenylketone under Friedel Crafts conditions to form the di- and tri-ketones (10.2; R^1 = Ac, R^2 = H; R^1 = R^2 = Ac) respectively, with $ClCO(CH_2)_2CO_2Me$ the mono- and di-esters [10.2; R^1 = $CO(CH_2)_2CO_2Me$, R^2 = H; R^1 = R^2 = $CO(CH_2)_2CO_2Me$] were obtained. The products were converted to the corresponding carboxylic acids and these were cyclized, thus the ketone (10.2; R^1 = R^2 = H) gave the product (10.3). Diferrocenylmethanol was treated with malonic acid in acetic acid to give the propionic acid (10.4) and this was cyclized in the presence of trifluoroacetic anhydride to the ketone (10.5)[145].

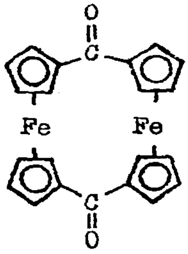
The dipole moments of a series of non-bridged and bridged ferrocenes were measured in benzene solution. The magnitudes of the moments were discussed in terms of the stereochemistry of these molecules[146]. The synthesis of the ferrocenophane (10.6) was acheived in the one-step reaction of ferrocene with acryloyl chloride in the presence of aluminium chloride at -78°. At 0° propanoylferrocene was formed in addition to the bridged ketone, while acryloylferrocene was not isolated from the reaction products at either temperature. The reaction mechanism was discussed[147]. An interesting synthesis of the ferrocenophane



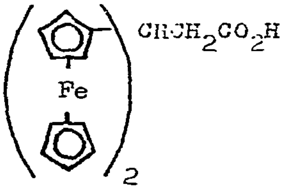
(10.1)



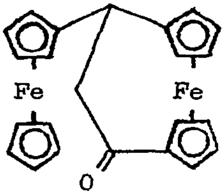
(10.2)



(10.3)

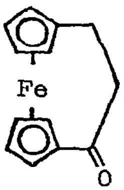


(10.4)

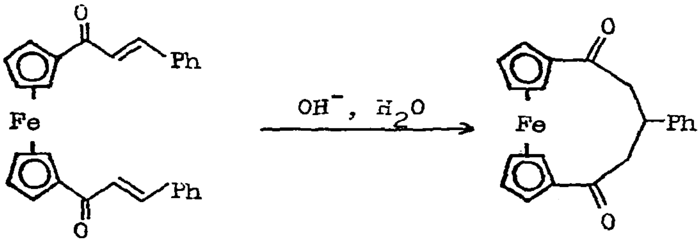


(10.5)

dione (10.8) has been acheived by Winstead. Cinnamoylation of ferrocene under Friedel-Crafts conditions gave the diketone (10.7) and in the presence of base this compound suffered a reverse aldol condensation followed by internal Michael addition to give the product (10.8) in 73% yield overall^{148}. The stepwise diacetylation of [3]ferrocenophane (10.9) under Friedel-Crafts conditions gave four heteroannular and one homoannular diacetyl



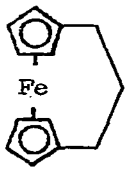
(10.6)



(10.7) (10.8)

isomers. The products and the proportions of the products were explained in terms of a complex intermediate containing acetyl[3]ferrocenophane, acetyl chloride and two moles of aluminium chloride. The NMR spectra of the mono and diacylated products were discussed[149].

The properties of mixed valence salts formed by oxidation of [0,0]ferrocenophane (10.10) have been described simultaneously and independently by two groups. Cowan and LeVanda prepared the binuclear ferrocene (10.10, 18%) by Ullmann coupling of 1,1'-dibromoferrocene, oxidation of the product with benzoquinone in the presence of picric acid gave the salt (10.11; X = picrate) and oxidation with tetracyano-p-quinodimethane (TCNQ) gave the salt [10.11; X = $(TCNQ)_2$]. The electron absorption spectra of the complexes (10.11) each showed a mixed valence transition at 1500 nm. The intensity of the transition permitted the deduction that the iron-iron interaction in the salt (10.11) was five-six times greater than in the corresponding mixed valence biferrocene Fe(II)Fe(III) picrate[150]. Mueller-Westerhoff and Eilbracht used the fulvalene dianion (10.12) as the intermediate



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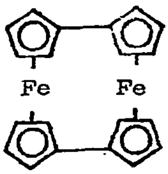
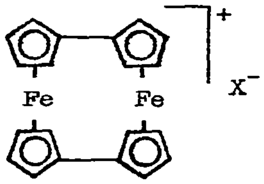
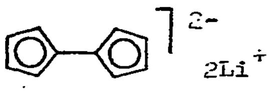


(10.10)



(10.11)

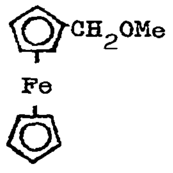


(10.12)

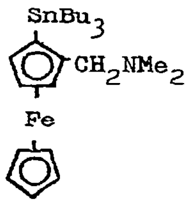
in the formation of the ferrocenophane (10.10) in 22% yield overall from sodium cyclopentadienide. The electronic spectra of the salts [10.11; X = picrate, tetrafluoroborate, $(TCNQ)_2$] showed mixed valence transitions at 1550 and 1140 nm and the room temperature bulk conductivity of compressed discs of the complex [10.11; X = $(TCNQ)_2$] was greater than $10\Omega^{-1}$ cm^{-1}, suggesting an unusually high conductivity along the main crystal axis[151].

11. Derivatives containing other metals (metalloids)

The lithiation of methoxymethylferrocene (11.1) and condensation with benzonitrile gave 1-methoxymethyl-1'-benzoylferrocene (30%) and this was presented as a possible new route to 1,1'-heteroannularly disubstituted ferrocenes[152]. Morris and Rockett have treated 1-lithio-2[(dimethylamino)methyl]ferrocene with Bu_2SnBr_2 and then butyllithium to give the ferrocenyl-tin derivatives (11.2 and 11.3). Treatment of the same lithioamine with dimethyltin dichloride and then butyllithium gave {2-[(dimethylamino)-methyl]ferrocenyl}butyldimethyltin. Thioglycollic acid was esterified with ferrocenemethanol to give the thiol (11.4) which was condensed with dibutyltin oxide to form the bis(ferrocene-



(11.1)



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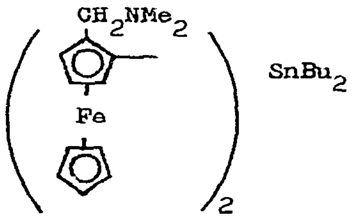
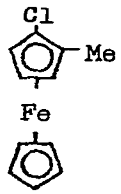


(11.3)

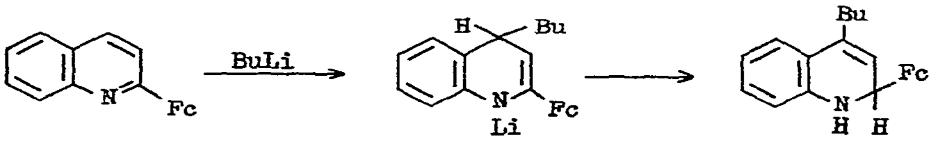
thio)tin (11.5). The dibutyltin dicarboxylate (11.6) was also prepared from ferrocene carboxylic acid and dibutyltin oxide.

$HSCH_2CO_2CH_2Fc$ (11.4) $Bu_2Sn(SCH_2CO_2CH_2Fc)_2$ (11.5) $Bu_2Sn(OCOFc)_2$ (11.6)

The ferrocene-tin compounds (11.5) and (11.6) were poor heat stabilizers for poly(vinyl chloride)[153]. 2-Chloro-methylferrocene (11.7) was lithiated with n-butyllithium α to the chlorine whilst excess butyllithium gave a mixture containing (11.7) methylferrocene and an approximately equal parts mixture of 2-methyl- and 3-methylbutylferrocene. The isolation of these butylmethylferrocenes was taken as evidence that the reaction had proceeded through an



(11.7)

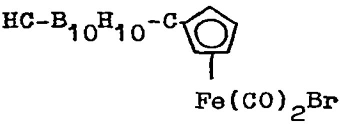


(11.8) (11.9) (11.10)

aryne intermediate[154,155].

Booth, Rockett and Ronayne have treated 2-ferrocenylquinoline (11.8) with n-butyllithium to give 1,4- addition rather than the expected 1,2- addition. The product obtained, 1,2-dihydro-2-ferrocenyl-4-n-butylquinoline (11.10) was thought to be formed from the intermediate (11.9) by a 4,2- hydrogen shift. The dihydroquinoline (11.10) was aromatised by treatment with MnO_2 whereas the product of 1,2- addition would not have undergone aromatisation[156]. Poly(vinyl chloride) was treated with lithioferrocene and the chlorine atoms were partially replaced by ferrocene during this reaction, some dehydrochlorination occurred[157]. The treatment of ferrocenylboronic acid with copper tetraphenylborate pyridinate gave ferrocene, phenylferrocene and 1,1'-diphenylferrocene[158]. Heating the carborane (11.11) with the bromide (11.12) in decahydronaphthalene gave the mono- and di-carboranylferrocenes (11.13 and 11.14) together with ferrocene. The complex (11.11) was obtained by rearrangement of σ-(3-o-carboranyl)-π-cyclopentadienylirondicarbonyl with bromine in CCl_4[159].

It was found that ferrocenylmethyl-silanes and -germanes (11.15) underwent facile cleavage in methanol in the presence of ferric chloride to give methoxymethylferrocene (11.16). The germanium derivatives (11.15; M = Ge) were cleaved faster than the corresponding silanes (11.16; M = Si)[160]. The addition of the ferrocenylamide (11.17) to poly(dimethylsiloxane) clutch fluid



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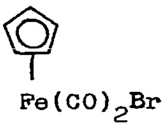

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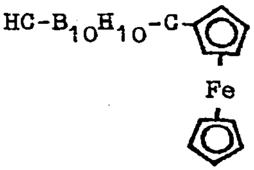

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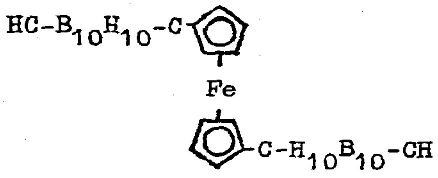
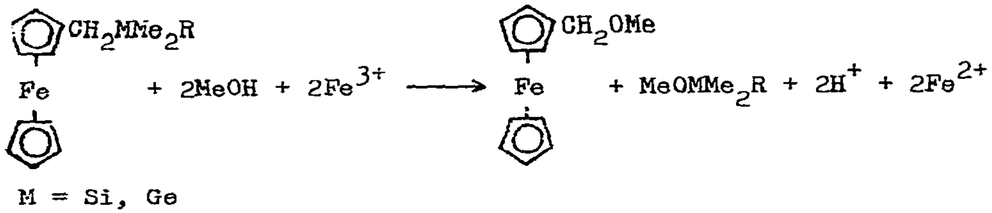
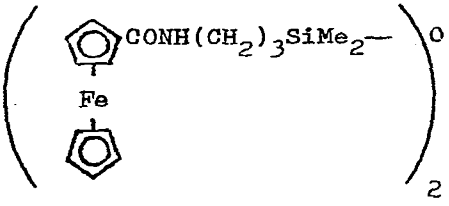


(11.14)



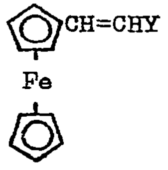
M = Si, Ge

(11.15) (11.16)



(11.17)

was claimed to improve its oxidation resistance. The additive (11.17) was formed by treating ferrocene with $ClSiMe_2(CH_2)_3NCO$[161]. Nesmeyanov and coworkers have examined the addition of tin, germanium and antimony hydrides to ethynylferrocene to give the 1,2-disubstituted ethylenes (11.18; Y = $SnPh_3$, $GePh_3$, $SbPh_2$). The carbon-tin bond in (11.18; Y = $SnPh_3$) was cleaved with mercury(II) chloride in ether to form the mercurichloride (11.19) (81%) and with bromine in chloroform to yield the vinylhalide (11.18; Y = Br) (46%). Disproportionation of (11.19) to the binuclear complex (11.20) (74%), occurred in THF-acetone containing potassium iodide. The 1,1-disubstituted ethylene (11.21) was prepared in 72% yield from $FcCCl=CH_2$ and Ph_3SnLi in THF-ether[162]. Five 1,1'-disilylferrocenes (11.22) were prepared by treatment



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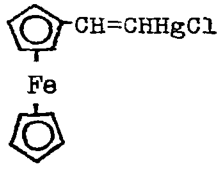

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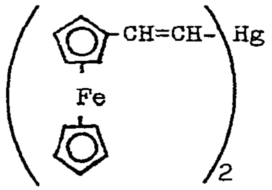

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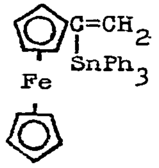

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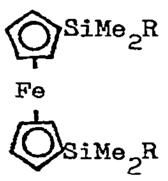
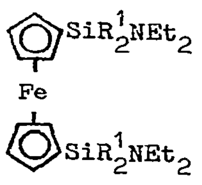


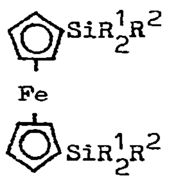
R = Me, OEt, C_8H_{17}, OPh, NEt_2

(11.22)



R^1 = Me, Et

(11.23)



R^2 = Cl, MeO, EtO, $C_8H_{17}O$, PhO, p-MeC_6H_4O, naphthyl.O, Ph_3SiO

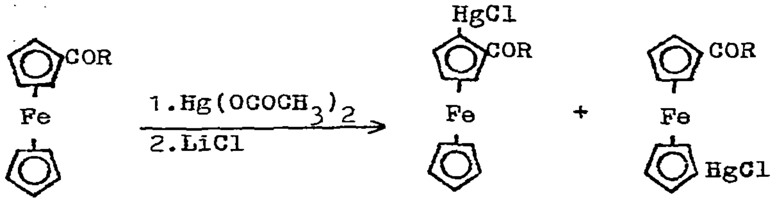
(11.24)

of the corresponding cyclopentadienyl anions with iron(II) chloride; yields of up to 70% were obtained[163].

Nucleophiles such as phenols, alcohols and silanols were effective in displacing diethylamine from the silylferrocenes (11.23) to form the derivatives (11.24) in yields of 75-95%. The ease of reaction increased in the order of the substituents (R^1) on the nucleophile: alkyl $<$ Ph_3SiO $<$ alkyl.O $<$ aryl.O $<$ Cl[164].

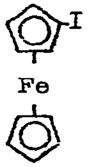
1,1'-Bis(dimethylethoxysilyl)ferrocene was prepared by adding cyclopentadienyldimethylethoxysilane and diethylamine to a suspension of sodium in toluene and then treating this mixture with iron(II) chloride. In a similar manner analogous compounds were prepared with silyl substituents containing EtO, Me, MeO, $C_8H_{17}O$, PhO, CH_2=CH and NEt_2 groups[165].

The acetoxymercuration of methoxycarbonyl-, acetyl- or formyl-ferrocene (11.25) and subsequent treatment with lithium chloride gave a mixture of 1,2- (11.26) and 1,1'-chloromercurated acylferrocenes (11.27). The chloromercuriferrocenes (11.26) and (11.27) were converted to the corresponding iodoferrocenes by treatment with iodine. Some of these iodo-ferrocenes were then used in Ullmann coupling reactions. For example iodoferrocene



R = OCH_3, CH_3, H

(11.25) (11.26) (11.27)



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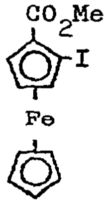
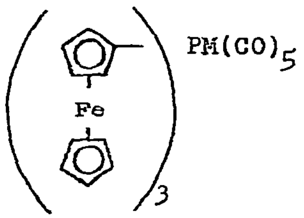
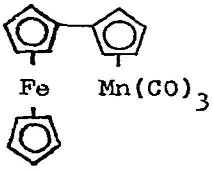


(11.29)

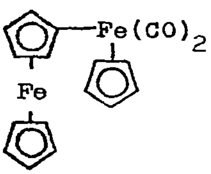


(11.30)

(11.28) was coupled with 2-iodo-1-(methoxycarbonyl)ferrocene (11.29) to give a mixture of biferrocenes[166]. Pittman and Evans have prepared triferrocenylphosphine complexes of Cr, Mo, W, Fe and Mn carbonyls for example the complexes (11.30; M = Cr, Mo, W). Force constant calculations for the CO stretching vibrations confirmed that triferrocenylphosphine was a better donor ligand than triphenylphosphine[167]. Ferrocenylcymantrene (11.31) (53%) was obtained together with biferrocenyl when chloroferrocene or bromoferrocene was heated to 120° with cymantrenylcopper in an inert atmosphere[168].

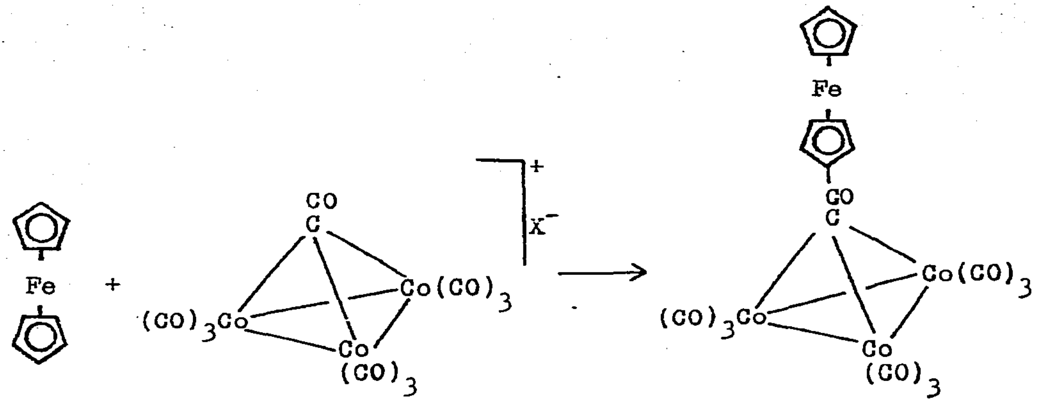


(11.31)



(11.32)

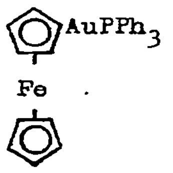
When diferrocenylmercury and π-cyclopentadienylirondicarbonyl iodide were heated in benzene to 80° or irradiated in the same solvent then the binuclear complex (11.32) was formed. The metal-ring bond was cleaved with hydrogen chloride or bromine to give the π-cyclopentadienylirondicarbonyl halide and ferrocene, with mercury(II) chloride, cleavage to ferrocenylmercurichloride was observed[169]. Ferrocene has been acylated with the novel acylium ion (11.33) to give the dinuclear complex (11.34) in 31% yield[170].



(11.33) (11.34)

The reaction of the gold complex (11.35) with HBF_4 gave the salt (11.36), the salt (11.36) was converted back to the original complex (11.35) by treatment with triphenylphosphine[171]. Perevalova and coworkers have described the formation of thioferrocenyl complexes of gold, thus treatment of the sodium salt of ferrocenylthiol with $ClAuPPh_3$ and $ClAuBu_2$ gave the complexes (11.37; R = PPh_3; Bu_2) respectively. The complex (11.37; R = PPh_3) formed a mixture of the disulphide (11.38) and the sulphonium salt (11.39) with fluoroboric acid. One of the gold ions in the salt (11.39) was coordinated with a further molecule of PPh_3 on treatment with the free ligand[172].

Ferrocenylpalladium chloride (11.40) was prepared in situ from chloromercuriferrocene and lithium tetrachloropalladate. The reaction of (11.40) with olefins, enol esters and allylic



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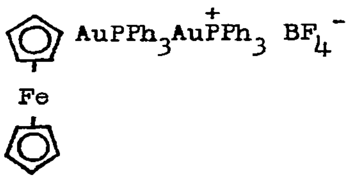

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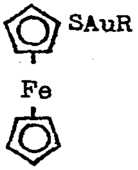

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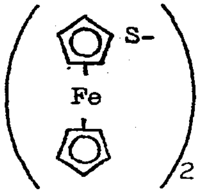

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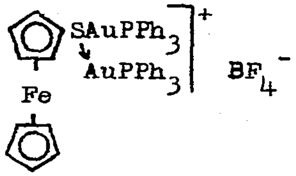
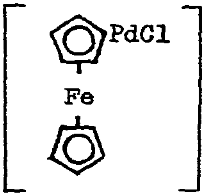


(11.39)

alcohols gave alkenyl-2-oxoalkyl- and 3-oxoalkyl-ferrocene derivatives respectively. Biferrocene was obtained as a by-product in all of the reactions[173]. The reactions of the conjugated dienes



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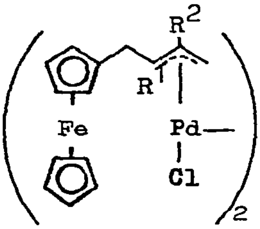

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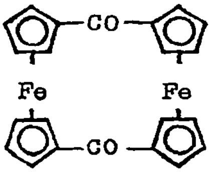
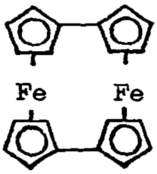
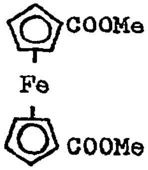


(11.42)



(11.43)



(11.44)

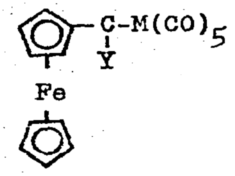
butadiene, isoprene and 2,3-dimethylbutadiene with (11.40) gave the 1-ferrocenylmethyl-π-allylpalladium chloride derivatives (11.41) which have chloro-bridged binuclear structures[174]. In a similar manner 1,1'-bis(chloromercuri)ferrocene reacts with carbon monoxide in the presence of a palladium salt to give

[1.1]ferrocenophane-1,12-dione (11.42) plus small amounts of the ferrocenylene (11.43) and the ester (11.44)[175]. The thermal decomposition of allylpalladium ferrocenyltrifluoroacetylacetonate occurred spontaneously in the solid state to give palladium and the corresponding bis(acetylacetonato)palladium[176].

12. Complexes of ferrocene-containing ligands

Connor and Lloyd have characterised a series of carbene complexes (12.1); the infrared and electronic spectra demonstrated that the ferrocenyl group was a powerful electron donor. Electron donation was confirmed as a resonance interaction with the empty p_z orbital on the carbene carbon atom by NMR spectroscopy. The mass spectra showed important differences from those previously reported for carbene complexes and this was attributed to stabilization by the metallocene group. The importance of the resonance canonical form (12.2) in the representation of bonding in the carbenes was emphasised. The similarity between this structure and those discussed previously in connection with the stabilization of α-ferrocenylcarbonium ions was noted. The carbene (12.1; M = Cr, Y = OMe) was active as a hydrogenation catalyst towards nitriles and amides[177]. Ferrocene bis-β-diketone was condensed with amines RNH_2 (R = Bu, n-C_5H_{11}, Ph, 2-naphthyl) and the condensation products gave polymeric complexes with the acetates of copper, cobalt, manganese or iron(III) chloride[178]

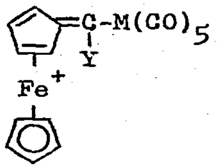
Ferrocene β-diketones and bis-β-diketones were condensed with ethylenediamine, hexamethylene-diamine, m-phenylenediamine and benzidine to give the corresponding ketimines. The ketimines were then added to transition metal salts to form metal complexes[179].



M = Cr, Y = OMe, OEt, NH_2, NMe_2, N

M = W, Y = OEt, N

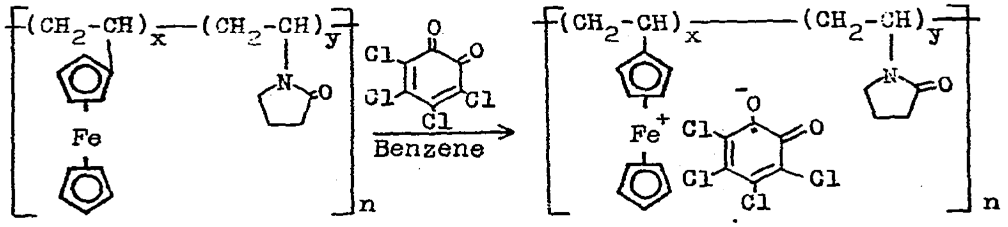
(12.1)



(12.2)

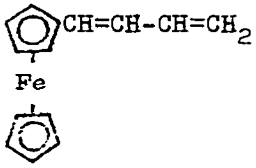
13. Ferrocene-containing polymers

Ferrocene containing polymers were prepared by the polycondensation of ferrocene with resorcinol, hydroquinone, pyrocatechol or pyrogallol in the presence of zinc chloride. The polymers were heat resistant up to 300° and they appeared to be high resistance semiconductors[180]. Vinylferrocene was copolymerized with styrene and methylacrylate in the presence of azobisisobutyronitrile and the relative reactivity ratios were determined[181]. Vinylferrocene was copolymerized with N-vinyl-2-pyrrolidone in the presence of azobisisobutyronitrile as the initiator. The copolymers (13.1) were soluble in organic solvents but when they were heated the solubility decreased markedly. Treatment of the copolymers with dichlorodicyanoquinone gave the polyferricinium salts (13.2) where the quinone was present as its radical anion[182].



(13.1) (13.2)

A series of polyazines was prepared by the condensation of 1,1'-diacetylferrocene or 1,1'-ferrocenedicarboxaldehyde with hydrazine or diamines and the thermal stability of these polymers was determined. 1,1'-Diacetylferrocene-hydrazine polymer decomposed at 235° and similar decomposition temperatures were shown by the other polyazines prepared[183]. The anionic polymerization of 1-ferrocenyl-1,3-butadiene (13.3) initiated by n-butyllithium gave a polymer with reasonable thermal stability. It was suggested that termination of the anionic polymer occurred by a proton transfer mechanism between the polydienyl anion (13.4) and the ferrocenyl nucleus (13.5), this was assuming that the lithio-ferrocene (13.5) did not promote further polymerization[184].



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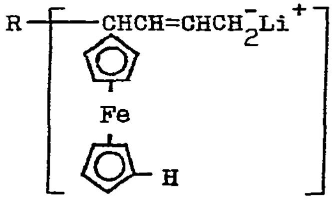

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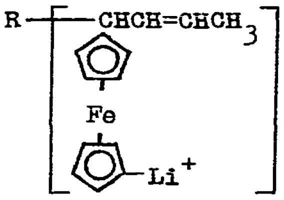
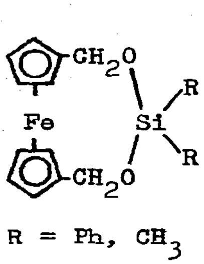


(13.5)

1,1'-Bis(hydroxymethyl)ferrocene has been polymerized with bis(dimethylamino)dimethylsilane, bis(dimethylamino)diphenylsilane and 1,4-bis(N,N-dimethylaminodimethylsilyl)benzene. The polymerizations were carried out at 0° because at higher temperatures the formation of monomeric cyclic products (13.6) competed with polymerization in some cases. The polymers (13.7) and (13.8) were low melting and were cast into films and weak fibres were drawn from the molten polymers[185]. The polycondensation of the metallocenes (13.9) and (13.10) to form the mixed metallocene



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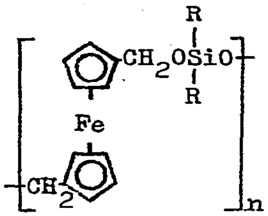

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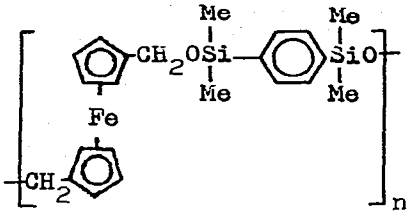
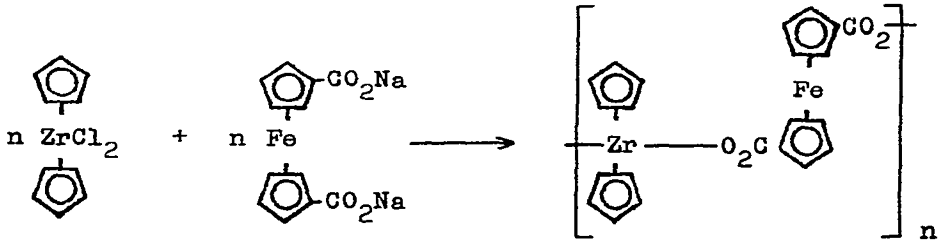


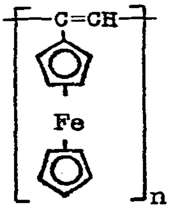
(13.8)



(13.9) (13.10) (13.11)

polymer (13.11) followed pseudo first order kinetics and a kinetic model based on the Langmuir adsorption isotherm was shown to fit the experimental results. The product was of only moderate thermal stability in air[186].

Polymerization of ferrocenylacetylene with trialkylaluminium-tetra-butyl titanate as the catalyst gave a linear polymer with pendent ferrocenyl groups (13.12). Cyclic trimers, 1,2,4- and 1,3,5-triferrocenylbenzene, were obtained when the catalyst was trialkylaluminium-titanium tetrachloride[187]. Low molecular weight polyferrocenylenes were crosslinked with 1,1'-ferrocene-



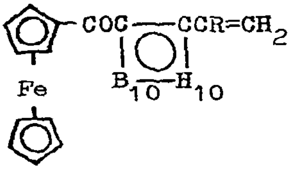
(13.12)

dicarboxaldehyde, in the presence of boron trifluoride etherate as catalyst, to give a polymer which when dissolved in dichloromethane was used as a lacquer to coat glass fibre fabric. The coated fabric was moulded to give a good quality laminate[188]. Poly(vinylalcohol) fibres were modified with a 5-18% solution of 1,1'-diacetylferrocene-formaldehyde resin and then heat treated at 140-160°. These fibres had a high radiation resistance and the introduction of the ferrocene moiety also facilitated the preservation of tensile strength and elasticity in the fibres[189].

Ion- and electron- exchange materials based on poly(vinyl alcoho were prepared by heat treating ferrocene containing compounds deposited on the surface of the polymer[190].

The half wave potentials for simple ferrocenes and ferrocene polymers were determined polarographically in dichloromethane, similar values were obtained for the structurally similar pairs-ferrocene (0.50 V) and poly(vinylferrocene) (0.54 V); [3]ferrocenophane (0.47 V) and cyclized poly(divinylferrocene) (0.43 V). Only a one-step oxidation was observed for sym-triferrocenylbenzene and the corresponding polymer polyethynylferrocene indicating that electronic interactions between metallocene groups was minimal in each case. Equilibrium constants were determined for the electron transfer reaction between ferrocenes or ferrocene polymers and iodine, higher values were obtained for the polymers than for the simple molecules while the bridged ferrocenes and the corresponding polymers gave higher values than the respective unbridged compounds[191].

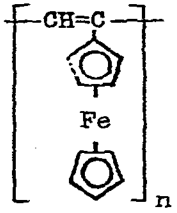
The rate of copolymerization of the ferrocenoylcarboranes (13.13; R = H, Me) with methylmethacrylate and styrene was studied at several concentrations by a dilatometric technique. The results indicated that alkenylcarboranes were reluctant to combine with vinyl monomers and that comonomer systems of large polarity difference would be most successful in copolymerization. The carboranes (13.13; R = H, Me) were prepared by metalation of the appropriate alkenylcarborane with n-butyllithium and subsequent treatment with ferrocenoyl chloride[192].



(13.13)

It was found that the acetylated, benzoylated or phthalic anhydride acylated poly(methyleneferrocenylene)s were more active than activated carbon in the catalysis of the dehydration of iso-PrOH and Me_3COH at 350-400° [193].

It has been observed that the presence of the electron donating ferrocenyl group in poly(ferrocenylacetylene) (13.14) and partially dehydrochlorinated poly(1-chloro-2-formylvinyl)-ferrocene (13.15) changed the electrical conductivity vs. temperature relationship as compared with polyacetylene for these polyconjugated polymers[194]. Thin layers of ferrocene-aldehyde condensation products containing an organic halogen compound (CBr_4) were rendered permanently electrically conducting by exposure to light so that a single exposure was sufficient for the production of many copies in an electrophotographic process[195].



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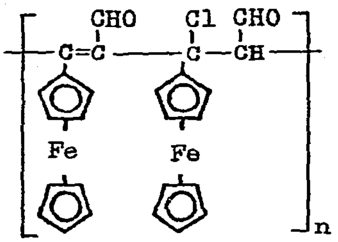


(13.15)

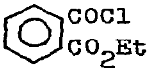
14. Biochemical Applications

When rabbits were immunized with human serum albumin labelled with 3-carboxy-4-ferrocenylphenyl isothiocyanate, specific antibodies against the carrier protein and the hapten were formed[196]. 3-Carboxy-4-ferrocenylphenylisothiocyanate was used to label antibodies and the antibody was then used for electron microscopic demonstration of the corresponding antigens. The ferrocenyl-antibody conjugates were found to be stable for several months[197].

It was found that ferrocene, ferritin and peroxidase could be used as markers for the electron-microscopical demonstration of cell surface antigens. The conjugation and purification of the ferrocene-labelled antiglobulins was the least difficult. Double marking with ferritin and ferrocene labelled antiglobulins was suitable for the differentiation of two distinct membrane antigens[198].

Treatment of ovalbumin or human immunoglobulin G with ferricinium sulphate in aqueous buffer at pH 9 gave yellow iron containing protein solutions with 14.4 moles of iron per mole of protein. Incorporation of iron was less efficient at lower pH and when $FeCl_3$ replaced the ferricinium salt[199].

Binding between the enzyme horse liver alcohol dehydrogenase and the substrate has been investigated by UV difference spectroscopy and fluorescence quenching when hydroxymethylferrocene was the substrate. One mole of the alcohol was bound per mole of active site with a dissociation constant of 1.4×10^{-4} M (measured by UV spectroscopy) and 1.8×10^{-4} M (fluorescence quenching). Secondary interaction between metallocene groups and aromatic residues in the enzyme was indicated by the same techniques[200]. The substituted benzoate (14.2), prepared by treating the acid chloride (14.1) with ferrocene under Friedel-Crafts conditions, was useful in the treatment of iron deficiency diseases[201].



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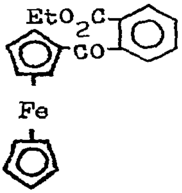


(14.2)

15. General applications and miscellaneous reports.

Ferrocene (approximately 1%) catalyses the polymerization of diisocyanates and the rate of polymerization of $OCN(CH_2)_6NCO$ was found to increase with an increase in the concentration of ferrocene[202]. Ferrocene catalysts were used to prepare polymers with isocyanurate rings in the chain[203].

A kinetic investigation of the photosensitized initiation of methyl methacrylate polymerization by ferrocene-carbon tetrachloride mixtures confirmed that the initiating species was the trichloromethyl radical formed by photochemical dissociation. Polymerization of methyl acrylate, vinyl acetate and methacrylonitrile was observed under the same conditions while acrylonitrile was photosensitized by ferrocene alone[204].

Ferrocene has been used as a curing accelerator for epoxy-resin compositions, it gave a short gelling time together with an extended pot life when compared with sodium alcolates[205].

Both ferrocene and p-ferrocenylaniline were effective in retarding the thermal degradation of high pressure polyethylene at 300-400°C and 10^{-4} mm Hg using an optimum concentration of 0.5%. Cyclopentadiene was more efficient than ferrocene thus implicating the cyclopentadienyl rings in the stabilization process[206]. The char yield of phenolic resins was increased by 17% when 1,1'-di(hydroxymethyl)ferrocene (10-20%) was incorporated, the metallocene component did not affect the mechanical properties of the resin. The inclusion of 1,1'-di(glycidyl)ferrocene and 1,2-di(hydroxymethyl)benchrotrene into epoxy and phenolic resins respectively was also investigated[207].

Treatment of cotton fibres with a benzene or toluene solution of ferrocene or nickelocene caused a large increase in the magnetic susceptibility of the fibres[208].

In an investigation of the thermal and oxidative stability of poly(phenylsiloxane) it was found that the addition of ferrocene increased the oxidation resistance of the polymer[209]. It has been claimed that higher tensile strengths of moulded polyimides were retained after heat ageing when 1% of ferrocene was added to the polymer[210].

Disilylferrocenes were evaluated as stabilisers in the thermal oxidation of poly(organosiloxanes). The efficiency of each stabilizer increased with increasing temperature and the optimum concentration was in the range 1-2%[211]. The addition of ferrocene

(0.3 weight %) to oligodimethylsiloxanes decreased the rate of degradation, reduced oxidation and caused changes in the mechanism of degradation when the siloxanes were heated at 500° in sealed ampoules[212]. Poly(vinylphenylketone) film was irradiated with a mercury arc lamp and this system was used to evaluate the quenching efficiency of some aromatic hydrocarbons. Ferrocene was the only efficient triplet quencher among the metal chelates studied[213].

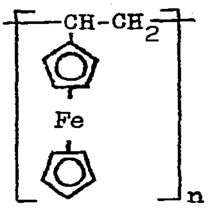
The addition of <1% p-ferrocenylaniline stabilized polyethylene compounds[214]. Polyethylene films were stabilized by β-ferrocenyl-β-(hydroxyphenyl)propionitrile, α-hydroxy-α-phenylpentadienylferrocene, 2,7-diferrocenyl-3,5-octadiene-2,7-diol and β-ferrocenyl-β-hydroxypropionitrile, and the films showed increased stability to light[215]. Polyamide fibre which had been modified with 3% ferrocenecarboxaldehyde was found to have increased radiation resistance, heat resistance and better adhesion to rubber[216].

Nitrocellulose-based propellents containing 1-2% ferrocene or a ferrocene derivative and a high plasticizer content were claimed to have enhanced low-temperature flexibility while the high-temperature properties remained unimpaired[217]. Propellent grains hyperbolically ignitable by treatment with nitric acid were prepared from 30-70% ferrocene, benzoylferrocene and/or dibenzylferrocene and 10-40% of an amine together with a binder such as an epoxy or acrylic resin. The grains were easily processable and had an ignition delay of <50 msec with concentrated nitric acid[218].

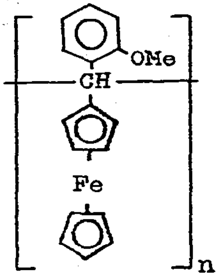
Sollott and Peterson report the formation of explosive or pyrotechnic complexes when ferrocene and ferrocene derivatives were mixed with mercury(II), mercury(I), cerium(IV) and copper(II) nitrates[219]. The addition of 0.05% ferrocene in heptane to fuel oil decreased the amount of air necessary to give soot-free combustion[220].

The effectiveness as antioxidants of 1,1'-bis(trimethylsilyl)-ferrocene, 1,1'-bis(dimethylphenoxysilyl)ferrocene, 1,1'-bis-(dimethylethoxysilyl)ferrocene and 1,1'-bis dimethyl(diethylamino)-silyl ferrocene was tested during the thermal oxidative ageing of several poly(organosiloxanes). The effectiveness of the ferrocenes increased in the order given above and the length of the induction period increased with the antioxidant concentration to approximately 2% at 280-320° [221]. Partial oxidation of the ferrocene residues to ferricinium in the polymers (15.1, 15.2 and (15.3) caused a large increase in electrical conductivity, for the vinyl polymer (15.1) the conductivity was $8 \times 10^{-12} \Omega^{-1}$ cm^{-1} and this increased to a maximum of $2 \times 10^{-8} \Omega^{-1}$ cm^{-1} at 68% conversion of ferrocene to ferricinium. Fluoroboric acid, benzoquinone and other quinones were used as oxidizing agents and the conductivity was not sensitive to the counter ion. Enhanced effects were not observed for the conjugated polymer (15.3) and the conduction mechanism was interpreted in terms of an electron hopping model[222]. The benzothiazole (15.4) and the corresponding thiacarbocyanine and dimethinemerocyanine dyes were prepared by Ushenko[223].

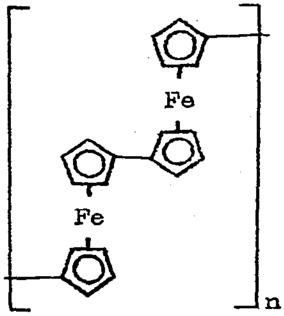
Ferrocene has been used as a substrate in an investigation of the electrochemical behaviour and surface phenomena at glassy carbon and pyrolytic graphite indicator electrodes in both aqueous and non aqueous media. Cyclic voltammetry was used to evaluate the importance of solute adsorption, acidity, presence of surfactant, scanning procedure, resurfacing methods and preparative



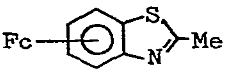
(15.1)



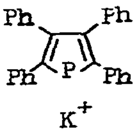
(15.2)



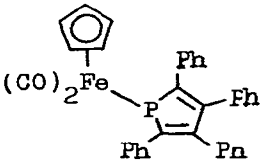
(15.3)



(15.4)



(15.5)



(15.6)

methods for the graphite[224]. Ferrocene has been used as a host system in an EPR and magnetic susceptibility investigation of bonding in cobaltocene[225].

An attempt was made to prepare a phosphaferrocene by the treatment of potassium 2,3,4,5 tetraphenylphosphol-1-ide (15.5) with $C_5H_5Fe(CO)_2I$. This gave the iron carbonyl (15.6) which when heated failed to give a phosphaferrocene[226]. Ferrocene has been detected in the mass spectrum of π-cyclohexadienyl-π-cyclopentadienyliron and was probably formed by thermal rearrangement of ligands in the source rather than by loss of CH_2 from the parent ion[227].

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