FERROCENE

ANNUAL SURVEY COVERING THE YEAR 1973

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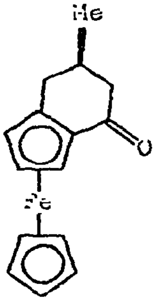
CONTENTS

1. Reviews

Peet and Rockett have surveyed the synthesis, properties and reactions of 1,2-disubstituted ferrocenes[1]. Yamakawa has briefly reviewed the chemistry of ferrocene[2].

2. Structural Determinations

The crystal and molecular structure of tetra-tert-butylferrocene was determined by X-ray analysis. The crystals had orthorhombic symmetry, space group Pbnb, with cell dimensions, $a = 11.79$, $b = 33.42$, $c = 12.21$ Å and $Z = 8$. The ferrocene nucleus was found to have a conformation that was intermediate between the staggered and eclipsed conformations[3]. The crystal structure and absolute configuration of [2Rp, 5Sc(sic)]-ferroceno[2,3]cyclohex-2-en-1-one (2.1) was determined by X-ray diffraction. The compound had space group P2,2,2, with unit cell dimensions $a = 9.97$, $b = 19.05$, $c = 6.54$ Å with four molecules in the unit cell[4]. The crystal structure of the product (2.2) obtained from the reaction of cyclopentadiene with the 2-ferrocenyl-2-propyl cation has been determined by X-ray diffraction methods. The compound crystallized in the monoclinic system, space group $P2_1/c$ with unit cell dimensions $a = 10.733$, $b = 8.122$, $c = 16.873$ Å; $\beta = 110.95^{\circ}$; $Z = 4$. The X-ray data confirmed structure (2.2) which had previously been postulated from ^{1}H NMR evidence. The compound was thought to be formed by addition of cyclopentadiene to the 2-ferrocenyl-2-propyl cation to give an intermediate (2.3) followed by proton elimination[5].



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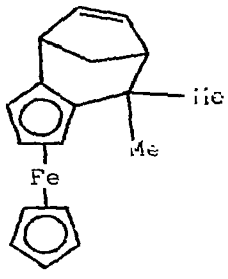

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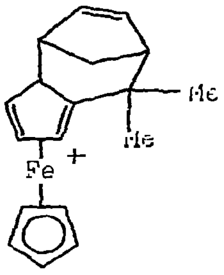

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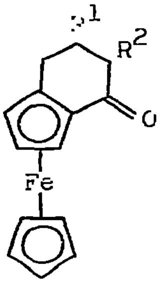
The crystal and molecular structure of 1,2-diiodoferrocene was determined by X-ray crystallography. In this molecule the cyclopentadienyl rings were flat and coplanar with the substituents[6]. The X-ray diffraction method has been used to determine the structure and absolute configuration of (-)-2,3-ferroceno-5-exo-methylcyclohex-2-en-1-one (2.4; R^1 = Me, R^2 = H)[7].

The crystal and molecular structure of the ferricinium gold cation (2.5) as the tetrafluoroborate salt, has been determined by X-ray crystallography. The structure presents several interesting features, one of the cyclopentadienyl ring carbon atoms acts as a bridge between the two gold atoms, C-Au distances 2.13 and 2.27 Å. The differences between these two bond distances were ascribed to steric and electronic factors. The Au-Au distance (2.768 Å) falls within the range observed previously for cluster systems and one gold atom is bound to the iron atom (Au-Fe, 2.818 Å) providing the first example of a ferrocene with a direct Fe-M bond and the first determination of the Au-Fe bond distance. The two cyclopentadienyl rings are almost eclipsed and form a dihedral angle of 16°[8]. The single crystal X-ray structure analysis of bis(pentalenyl)iron has confirmed it as a [2]ferrocenophane (2.6) with a strained bridge. The two planar cyclopentadienyl rings are tilted to give a dihedral angle of 23.6° and the molecule is near the eclipsed conformation with a mean rotation angle of 10° [9].



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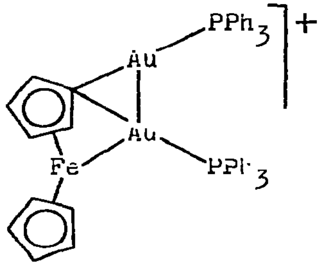

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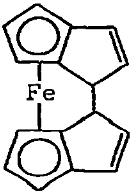

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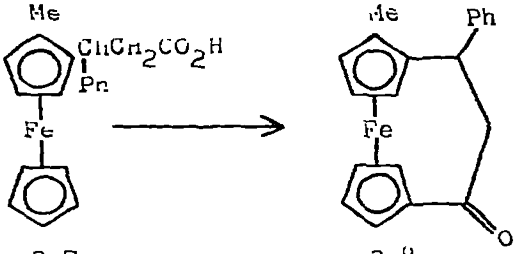
The crystal structure of 2,1'-trimethylene-1-[α-phenyl-α-hydroxy-propyl]ferrocene was determined by X-ray crystallography. The compound crystallized in the monoclinic system, space group $P2_1/n$ with unit cell dimensions a = 11.42, b = 13.25, c = 11.48 Å; β = 97.75°, with four molecules in the unit cell. The structure was in agreement with that proposed earlier by Moise *et al*[10] from infrared and NMR data[11]. The ketone (2.8) was obtained by cyclization of the ferrocenylpropionic acid (2.7). The crystal structure and relative conformation of the racemic diastereoisomer of the ketone have been determined by X-ray crystallography. The cyclopentadienyl rings were almost planar and parallel, they occupied an eclipsed conformation. The relative conformation of the racemate (2.8) was R_pS_c or S_pR_c. The PMR spectra of the ketones supported the proposed conformations[12]. The crystal and molecular structure of 1,12-dimethyl-[1,1]ferrocenophane was determined by X-ray diffraction. The compound crystallized in the monoclinic system, space group $P2/c$ with unit cell dimensions a = 18.14, b = 6.10, c = 18.67 Å, β = 119° 40'. The molecules existed in the eclipsed form with an *exo*-methyl configuration (2.9)[13].



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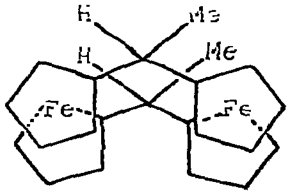

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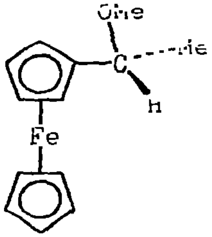
3. Stereochemistry of Ferrocenes

The metallation of 1-ferrocenyl-1-methoxyethane with n-butyllithium in ether, hexane and THF proceeded slowly to give a random mixture of 2-, 3- and 1'-lithioferrocenes. The products were characterized as the benzophenone adducts and the ratios obtained were both time and solvent dependent. Experiments with the optically pure ether (3.1) indicated the net asymmetric induction obtained in the formation of the derivative (3.2) was only about 10% of that observed for the corresponding nitrogen compound[14].



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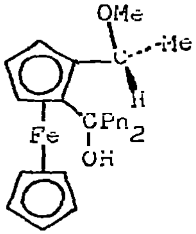

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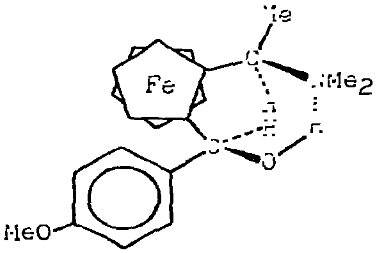

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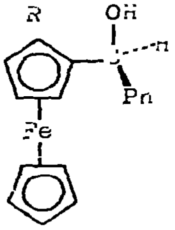
Ugi and co-workers have further investigated the stereoselective metallation of optically active α-ferrocenyl tertiary amines. The lithiation of (R)-N,N-dimethyl-1-ferrocenylethylamine followed by treatment with anisaldehyde gave (S,R,S)-2-(*p*-methoxyphenyl)hydroxymethyl-N,N-dimethyl-1-ferrocenylethylamine in good yield (3.3). The absolute configuration of this compound was confirmed by a single-crystal X-ray determination. This is the first absolute configurational determination of a 1,2-ferrocene derivative with chiral substituents and it will enable unequivocal assignments to be made for a large number of optically active ferrocene derivatives[15].

The preparation of (R,S)-N,N-dimethyl-1-ferrocenylethylamine was achieved by treatment of 1-ferrocenylethanol with $MeSO_2Cl$ in trimethylamine followed by dimethylamine[16]. Substitution by malonate of the hydroxyl group in the diastereoisomeric alcohols (3.4 and 3.5; R = Me, CH_2NMe_2) has been investigated. The mechanism and stereochemistry of the reaction were studied by intramolecular cyclization of the substitution products and by the relative reactivities of the alcohols. The form of the intermediate carbonium ions with high fulvene character was discussed[17]. Dabard and Patin have described the



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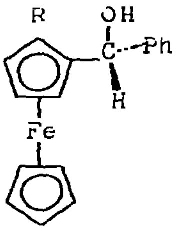

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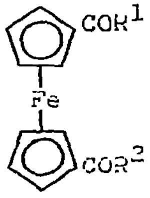

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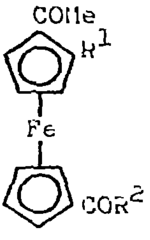
selective reduction of unsymmetrical 1,1'-diacylferrocenes (3.6; R^1 = alkyl, Ph, 2-thienyl; R^2 = alkyl, Ph, 2-thienyl) by triphenyltin hydride to give the corresponding 1-acyl-1'-alkylferrocenes. On treatment with acetyl chloride under Friedel Crafts conditions the trisubstituted ferrocenes (3.7 and 3.8; R^1 = Et, $PhCH_2$; R^2 = alkyl, Ph, 2-thienyl) were obtained. The diacylferrocenes (3.6; R^1 = Me; R^2 = Me, Et, Ph) were converted to the [5]ferrocenophanes (3.9; R = Me, Et, Ph) with benzaldehyde[18]. In a related study, the same authors report the Clemmensen reduction of the diacylferrocenes



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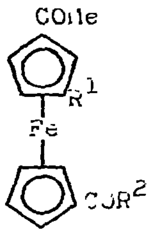

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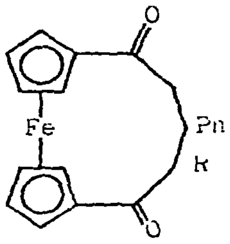

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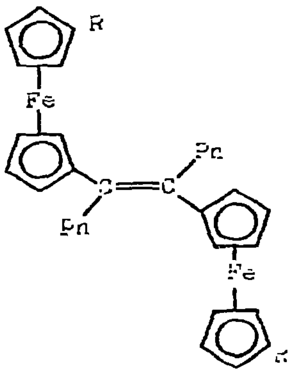
(3.6; R^1 = Me, Et, Pr; R^2 = Et, Pr, CH_2Ph) to the corresponding dialkylferrocenes. Under the same conditions, 1-acyl-1'-benzoylferrocenes gave the *trans*-olefins (3.10; R = H, Et, Pr, Bu, $PhCH_2CH_2$) in addition to the simple reduction products. A pinacol intermediate was suggested for the dimerization step[19].

Stereoselective syntheses were used to prepare the *endo*- (3.11; R^1 = H, R^2 = NH_2) and *exo* (3.11; R^1 = NH_2, R^2 = H) aminoferrocenophanes. Electrochemical or sodium reduction of the appropriate hydroxyimine gave the *endo*-isomer while conversion of the *endo*- or *exo*-alcohol to the azide with hydrazoic acid followed by catalytic hydrogenation gave the *exo*-isomer. The same routes were used in the synthesis of the ferrocenophane (3.12). The observed stereoselectivity was ascribed to sterically preferred *exo*-attack by the reagent in the product forming step in each synthetic route. The racemic *endo*- and *exo*-amines (3.11; R^1 = H, R^2 = NH_2 and R^1 = NH_2, R^2 = H respectively) were resolved into the corresponding enantiomers[20]. The diastereoisomeric pair of ferrocenecyclohexenones (3.13 and 3.14) was prepared from (S)(+)-2-methyl-2-phenylsuccinic acid by Friedel Crafts acylation of ferrocene



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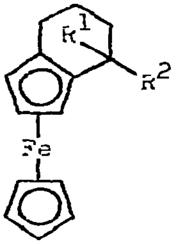

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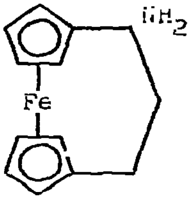

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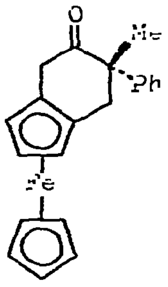
with the monomethyl ester (3.15) followed by cyclization. The corresponding β-substituted ferrocenecyclohexenones were prepared in the same way from the other monomethyl ester of the succinic acid. The absolute configuration of each compound was determined by chemical correlation methods and the optical purities were estimated by isotopic dilution[21]. The reaction of 1,2-ferrocenedicarboxaldehyde with methylmagnesium iodide and the reduction of 1,2-diacetylferrocene with potassium borohydride



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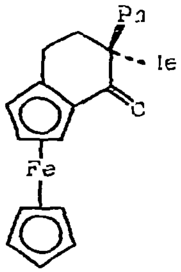

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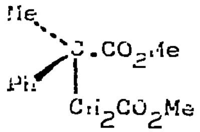

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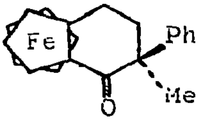
gave asymmetrical and pseudoasymmetrical 1,2-bis(α-hydroxyethyl)ferrocenes. The stereochemistry of these compounds was investigated[22]. The aluminium chloride epimerization of the diastereoisomeric α-phenyl-α-methylferrocenylcyclohexenones (3.16) and (3.17) and the diastereoisomeric β-phenyl-β-methylcyclohexenones (3.18) and (3.19) was studied. The epimerization was shown to proceed by intramolecular inversion of the metallocenic chiral plane and by inversion of the quaternary asymmetric carbon[23].



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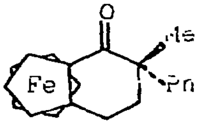

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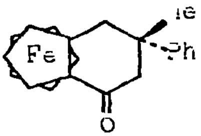

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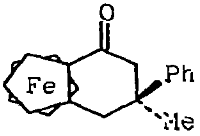
Equilibration between axial and equatorial conformations in ferrocenylcyclohexanes with substituents on the 4-position (3.20) was used to determine the average conformational free enthalpy for the ferrocenyl group. The value obtained, 2.9 kcal mol^{-1}, confirmed that the spatial requirement of the ferrocenyl group was nearly equivalent to that of the phenyl group (3.0 kcal mol^{-1}) at the equilibrium axial ⇌ equatorial[24].



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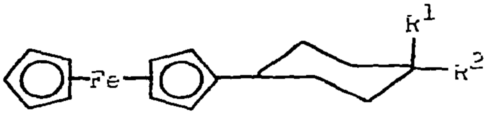

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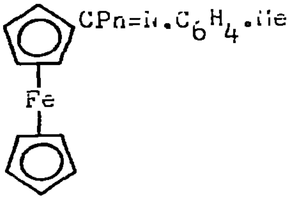
4. Spectroscopic and physico-chemical studies

The temperature dependence of the PMR spectrum of the ferrocenylimine (4.1) was examined. Line shape analysis permitted the free energy of activation for the syn-anti isomerization to be determined, $\Delta G^{\ddagger} = 19$ kcal mol^{-1} [25]. Kamezawa has recorded and analyzed the PMR spectra for a range of ferrocene derivatives. The magnitude of the coupling between the protons on the substituted cyclopentadienyl ring has been used to provide a new procedure for the assignment of the spectra of monosubstituted ferrocenes[26]. Re-orientation processes in substituted ferrocenes have been investigated by PMR spectroscopy. The PMR spectra of alkyl- and acetyl--ferrocene, 1,1'-di-tert-butyl- and 1,1'-diacetyl-ferrocene in the solid state were recorded over the temperature range 4.2-300°K at 27.5 MHz. The temperature dependence of the second moment of the resonances was used to determine the activation energies for re-orientation of the methyl and cyclopentadienyl protons. Experimental values for the second moment were compared with calculated contributions of different groups to the second moment in order to identify these groups. Introduction of a single substituent was effective in altering the magnitude of the re-orientation energy for both the substituted and the unsubstituted rings. The role of steric and electronic factors in the activation energy changes was discussed[27]. The ^{13}C NMR spectra of forty monosubstituted ferrocenes were measured at 30-40° and at room temperature. The ^{13}C chemical shifts in the substituted ferrocenes were compared with those of the corresponding benzene derivatives and a possible mechanism of electro screening was discussed[28]. The ^{13}C NMR spectra of methyl-, ethyl-, iso-propyl- and tert-butyl-ferrocene and the corresponding heteroannular disubstituted ferrocenes have been recorded and interpreted. The carbon atom adjacent to the substituents was increasingly deshielded as electron release from the substituent increased. Heteroannular interaction was shown only by the methyl group[29].



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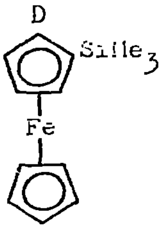

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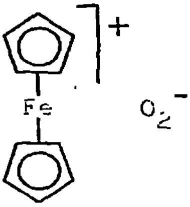

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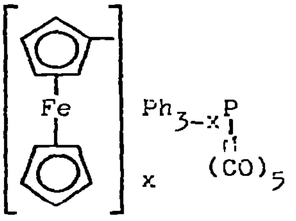
Slocum and Ernst showed that in the PMR spectrum of methoxyferrocene the protons in the 3 and 4 positions resonated at a higher field than those in the 2 and 5 positions. These assignments were based on the comparative PMR spectra of methoxyferrocene and 2-deutero-methoxy-ferrocene. These assignments were the reverse of those suggested by Kursanov <u>et al</u>[30] who proposed that the protons in the 2 and 5 positions resonated at higher field[31]. The same authors have reported the preparation and PMR spectrum of 2-deuteriotrimethylsilylferrocene (4.2). This confirmed that in trimethylsilylferrocene the upfield two-proton apparent triplet at δ4.07 ppm could be assigned to the 2,5-position protons in the substituted cyclopentadienyl ring and the downfield two proton apparent triplets at δ4.30 ppm could be assigned to 3,4-position protons. The electron withdrawal from the 3,4-positions was interpreted in terms of a resonance effect between the trimethylsilyl group and the cyclopentadienyl ring[32]. Proton multiple pulse spectra of powdered samples of ferrocene were recorded at 90 MHz and negative shielding anisotropies were obtained for the protons[33].

Several ferrocenylalkyl- and ferrocenylaryl-ketyls were generated from the corresponding ketones and deuterioketones and their ESR spectra were recorded. The hyperfine splitting constants of benzoylferrocene ketyl were determined and electron densities were assigned to various sites in the molecule.

Comparisons of the g-values for benzophenone ketyl (2.0034), benzoylferrocene (2.0062), and 2,2-dimethylpropanoylferrocene (2.0126), combined with the proton hyperfine splittings permitted a discussion of the interaction between the free electron and the ferrocenyl group[34]. Electron delocalization in the ferrocene and ruthenocene systems was investigated by the substitution of spin label systems such as the semidione, semiquinone, ketyl and naphthyl radical anions into the metallocene. Delocalization of spin density was shown to be confined to the positions on the substituted cyclopentadienyl ring adjacent to the spin label. Ferrocene and ruthenocene were both inefficient in spin delocalization[35]. Hydrogen atoms were generated in porous Vycor glass (PVG) on gamma irradiation and they were detected by ESR. When a partial monolayer of ferrocene was present essentially the same ESR signal was obtained. However UV irradiation of ferrocene on PVG at 77° K gave spectra corresponding to the cyclopentadienyl radical, the cyclobutadienyl radical ion and hydrogen atoms. Exposure of ferrocene on PVG to oxygen at 25° C in the dark gave an ESR signal from ferricinium superoxide (4.3)[36]. A theoretical study was made of the magnetic resonance properties of the lowest excited triplet state of ferrocene on the basis of the splitting of this orbitally degenerate state by the action of low symmetry perturbation and of spin-orbit coupling. It was concluded that the lifetime of this state was $>10^{-6}$ and that an ESR signal should be observable[37].

The low-temperature IR spectra of ferrocene and ferrocene-$\underline{d}_{10}$ were obtained as mulls with Nujol at 88°K. Room temperature and low temperature spectra were compared and some changes in the assignments of bands were made. The frequency of the

e_{1u} ring-metal-ring deformation mode was corrected to 179 cm^{-1} and the spectroscopic entropy was recalculated[38]. The Raman spectra of ferrocene-$\underline{h}_{10}$ and -$\underline{d}_{10}$ were reinvestigated and the librational modes of these molecules were observed near 62 cm^{-1} (-$\underline{h}_{10}$) and 40, 52 and 60 cm^{-1} (-$\underline{d}_{10}$). No important differences were reported in this work[39] from the earlier assignments[40,41]. Kotz and Nivert have measured the IR carbonyl stretching frequencies for the coordination compounds (4.4; x = 0-3 and M = Mo, W). The decrease in frequency of the A_1^1 and E modes which occurred as the number of ferrocenyl substituents increased was attributed to an increase in σ-donation by the ferrocenylphosphines. This was confirmed by the observation of similar trends in the PMR spectra of the complexes (4.5; x = 0-3) and methylbis(dimethylglyoximato)-(ferrocenylphosphine)cobalt (III). An increase in ferrocenyl substitution also increased the steric requirements of the phosphine ligand. Thus no ligand exchange was observed between triferrocenylphosphine and methylbis(dimethylglyoximato)-(pyridine)cobalt (III) while diferrocenylphenylphosphine and ferrocenyldiphenylphosphine were actively exchanged. PMR contact shifts were measured for the last two phosphines and bis(acetylacetonato)nickel (II). These results demonstrated that spin density was not delocalized from the substituted cyclopentadienyl ring to the unsubstituted ring through the



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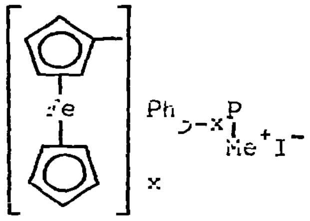

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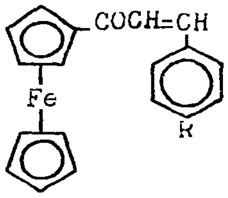

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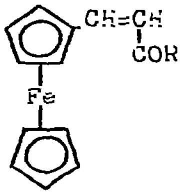
iron atom. More spin density was delocalized into the phenyl groups than into the ferrocenyl groups and this was interpreted in terms of the lower electron releasing power of the phenyl than of the ferrocenyl group. Cyclic voltammetry of the ligand $FcPh_2P$ and the complex (4.4; x = 1, M = Mo) demonstrated a reversible, one-electron oxidation of the ferrocenyl group at +0.48 and +0.62V respectively[42]. The IR and UV spectra for several vinyl ketones (4.6 and 4.7) have been recorded, the compounds were prepared by standard methods[43].

The IR spectra of ferrocene in the solid state have been recorded in the temperature range 15-300°K; a phase change at 160°K was indicated by large changes in the spectrum. The low temperature spectra were interpreted in terms of a staggered molecule with symmetry D_{5d}. The spectrum obtained in an argon matrix at 15°K showed a number of additional bands corresponding to inactive modes in the isolated molecule. At 60°K the internal rotation frequency of the cyclopentadienyl rings was observed at 44 cm^{-1} and gave a potential energy barrier to rotation of 0.9 kcal $mole^{-1}$ [44]. The phase transition in crystalline ferrocene was investigated by following the intensity change with temperature of the two infrared absorption bands, $\nu_{16}(E_{1g})$ and $\nu_4(A_{1g})$, associated with inactive molecular modes. The results suggested that at low temperatures there was an ordered lattice with noncentrosymmetric sites. There was no abrupt change in intensity at the phase transition and this indicated the persistence of the low temperature, short range, order into the high temperature phase. The results were consistent with a structure for the high temperature phase in which there was a centrosymmetric lattice containing a large number of staggered molecules[45]. The vibrational modes of bis(π-cyclopentadienyl)metal complexes were reviewed and the selection rules for ferrocene and ruthenocene crystals were given. Raman spectra at 80°K for these molecules were reported together with the ferrocene low frequency spectrum measured at 80, 135 and 180°K. A comparative assignment of the molecular vibrations was made and for both ferrocene and ruthenocene the frequency of the ring tilt mode ν_{21} was higher than that of the metal-ring stretching modes[46].

The electronic spectra of ferricinium salts in the region of the band system $\underline{I}(^2E_{1u} \leftarrow {}^2E_{2g})$ at about 16,200 cm^{-1} have been studied under high resolution at low temperature (4.2°K). Analysis of the vibrational fine structure in the spectra of the salts [4.8; $X^- = PF_6^-$, BF_4^- and $(CCl_3CO_2H)_2\text{-}(CCl_3CO_2^-)$] indicated that the excited state ($^2E_{1u}$) was split into two Kramers doublets and the magnitude of the splitting was a function of the anion. Comparisons of several ferricinium $^2E_{1u}$ vibrational frequencies with the corresponding values for ground state ferrocene suggested that the iron $4p_x$ and $4p_y$ orbitals were minimally involved in the metal-ligand bonding[47]. The Mössbauer spectra of ferrocene, ferricinium fluoroborate, 1,1'-dibenzoylferrocene and the salt (4.9) were recorded. The isomeric shifts and quadrupole splittings were determined and it was shown that both the iron atoms in the fluoroborate (4.9) were equivalent[48]. The dynamic and structural characteristics of the smectic phase of the diacetylferrocene + 4,4'-di-n-heptyloxyazoxybenzene system were investigated using Mössbauer spectroscopy[49]. Ferrocene, enriched with ^{57}Fe, has been investigated by Mössbauer spectroscopy as a solution in cholesteryl myristate liquid crystal. Changes in the orientation of the external magnetic field demonstrated anisotropy in the magnetic susceptibility of the liquid crystal solution[50].

Schildcrout found that ferrocene was amenable to study in the ion source of a mass spectrometer at high pressures (up to 1.5 x 10^{-2} Torr) and 400°K. Rapid charge transfer between the two fragment ions Fe^+ and $(C_5H_5)Fe^+$ and neutral ferrocene was observed with rate constants of 2.6 x 10^{-9} and 2.4 x 10^{-9} cm^3 $molecule^{-1}$ sec^{-1} respectively. The reactions were exothermic for the ground-state reactants. Formation of a stable binuclear adduct $(C_5H_5)_3Fe_2^+$ from ferrocene and $(C_5H_5)Fe^+$ was also observed. The charge transfer reaction with $(C_5H_5)Fe^+$ was six times faster than adduct formation. The rate constants for charge transfer were about twice those predicted by polarization theory. The good agreement obtained suggested that steric and energetic barriers to the reactions were minimal[51]. The ESCA (electron spectroscpy for chemical analysis) method was used to measure the ionization energy of the Fe-$2p_{3/2}$ level of ferrocene, 1,1'-dibenzoylferrocene, diferrocenylmethylium tetrafluoroborate (4.9) and ferricinium tetrafluoroborate. From the results obtained it appeared that the two iron atoms in (4.9) had approximately the same charge and that it did not differ appreciably from that in ferrocene. The compounds studied all exhibited a positive charge on the iron[52].



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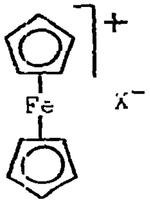

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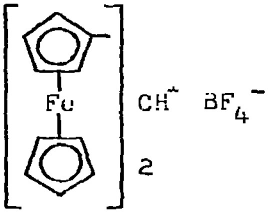

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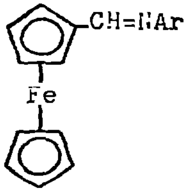
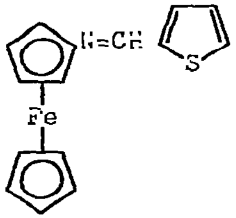


4.10

The kinetics of hydrolysis for a series of Schiff bases, (4.10; Ar = Ph, α-naphthyl) and (4.11) was investigated.

The rate determining step in hydrolysis of the thienyl complex (4.11) at pH4 was thought to be attack of water on the cation (4.12). At pH<4 the rate determining step involved the decomposition of the zwitterion (4.13) to give ferrocenylamine and 2-thiophenecarboxaldehyde[53]. Rate constants were measured



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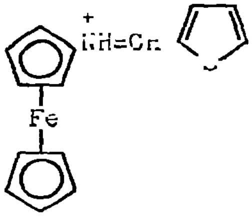

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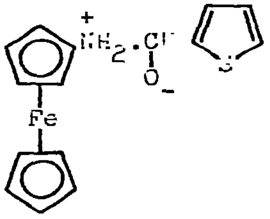


4.13

for hydrogen-deuterium and hydrogen-tritium exchange of metallocenes and organic aromatic compounds in $Me_3COH-Me_3COK-Me_2SO$ The rates of exchange increased in the order ferrocene<cymantrene< diphenylmethane<triphenylmethane<nickelocene with nickelocene exchanging 5 x 10^6 times faster than ferrocene[54]. A thermal conductivity manometer was used to determine the enthalpy of sublimation for ferrocene; a value of 17.7 ± 0.4 kcal $mole^{-1}$ was obtained. This figure is in good agreement with other literature values which were obtained using alternative techniques[55].

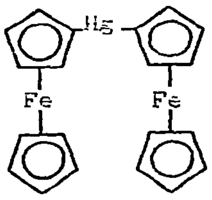
5. Reactions of ferrocene

Temperature dependence of products and product proportions was found in the alkylation of ferrocene with ethyl bromide and aluminium chloride with heptane as solvent and in the presence of lithium aluminium hydride. At 70°, mono-, di- and tri-ethylferrocenes were formed in the ratio 9:4:3. Below 40° only mono- and di-alkyl derivatives were obtained; at 30-40° the ratio of mono- and di-ethylferrocene was 7:5 with an overall conversion of 70-80%. The yield of alkylated ferrocenes was increased by using higher concentrations of aluminium chloride and by higher temperatures. Under the same conditions and at 40° ethylferrocene underwent partial disproportionation to ferrocene (10%) and diethylferrocene (10%)[56]. The Friedel Crafts acylation of ferrocene with chlorides or anhydrides of the perfluorocarboxylic acids $C_nF_{2n+1}CO_2H$ (where $n \leqslant 7$) in the presence of aluminium chloride and in dichloromethane as solvent, gave the corresponding perfluoroacylferrocenes. These ketones were reduced with lithium aluminium hydride to the respective alcohols and characterised as such, they were much less reactive than the nonfluorinated analogues[57]. Ferrocene carboxylic acid was prepared in high yield (>88%) by acylation of ferrocene with o-chlorobenzoylchloride in the presence of aluminium chloride and hydrolysis of the product with potassium-tert--butoxide in monoglyme[58]. The treatment of ferrocene with an equimolar mixture of lithium aluminium hydride and aluminium chloride followed by methyl chloride gave decamethylferrocene and nonamethylferrocene in 22% and 50% yields respectively[59]. Ferrocene and hydrochloric acid in an organic solvent were found to be useful for the reduction of the enedione structure RCOCH=CHCOR' (e.g. R = R' = Fc; R = R' = Ph) to give $RCOCH_2CH_2COR'$. When the reduction was complete the ferrocene was recovered quantitatively by the addition of ascorbic acid and sodium bisulphite to the aqueous layer[59].

6. Ferricinium salts

Denisovich and Gubin have studied the reduction of ferrocenylmercury chloride, diferrocenylmercury and other organometallic compounds. Ferrocenylmercury chloride in

90% dioxan was reduced by a two electron process to ferrocene ($E_{\frac{1}{2}}$ values -0.27 and -1.84V). Electron-releasing and electron-withdrawing substituents in the second cyclopentadienyl ring had little effect on the half-wave potentials. Diferrocenylmercury was reduced only with difficulty by a two electron process to give ferrocene[60]. In a related study, the half-wave potentials for the second wave in the polarographic reduction of a series of organomercury chlorides, including ferrocenylmercury chloride, were correlated with the $p\underline{K}_a$ values for the parent organometallic compounds. Similar correlations were made for a set of symmetrical organomercury compounds and a set of σ-derivatives of (π-cyclopentadienyl)iron dicarbonyl. The appropriate ferrocene compound (6.1 and 6.2) was included in each set. The results suggested that polarographic reduction of symmetrical organomercury compounds and organomercury salts under controlled conditions should enable the $p\underline{K}_a$ values for the respective parent compounds to be determined to an accuracy of ±3 $p\underline{K}_a$ units[61]. In an investigation of the adsorption of the ferrocene-ferricinium couple at an electrode, oscillopolarograms were recorded for $[(\pi\text{-}C_5H_5)_2Fe]^+BF_4^-$ in 0.1M sulphuric acid over a range of potentials. Increasing peak height and width was observed with increasing potential and this effect was ascribed to autoinhibition. Measurements of peak area demonstrated that inhibition of the reduction began



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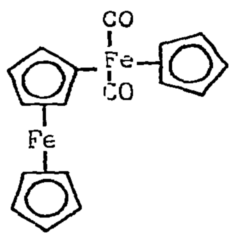

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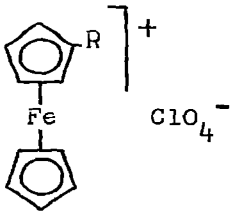
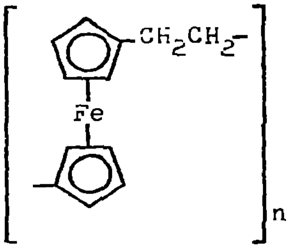


6.3

with the formation of 1.7×10^{-9} mole of ferrocene per sq. cm. of electrode surface. This corresponded to only a few monolayers of ferrocene on the electrode surface[62]. Results have also been obtained with the rapid and Tast polarographs; the latter was found to be more accurate than the former. Tast-polarograms were obtained over a range of drop times from 0.1 to 4.0 sec. As the time was increased so the adsorption prewave increased as well as the current at the beginning of a basic wave, the current decreased at potentials between -0.3 and 1.0V. The adsorption of ferrocene on the electrode caused the adsorption prewaves and inhibited the current that was dependent on the drop time. Good agreement was obtained between the experimental results and the theoretical model[63]. The reversibility of the oxidation of ferrocene to the ferricinium ion in aqueous ethanol solutions has been examined by the same group using alternating current polarography. Both active and reactive components of the a.c. were recorded by using a vector-polarograph CLA. The peak heights of the current-potential curves were proportional to the concentration of ferrocene and were highest in 96% ethanol[64]. The effects of concentration, temperature, surfactant and gelatin additives and the height of the mercury column on the ferricinium-ferrocene redox system were examined by classical polarography at a dropping mercury electrode in an aqueous medium. The electrode process was confirmed as a one-electron step which was complicated by adsorption of the reduction products on the surface of the electrode[65].

Electrodes were prepared that consisted of the alkyl derivatives of ferrocene and the corresponding alkylferricinium perchlorates (6.3). These electrodes were useful because of the very high rate of electron exchange between ferrocene and its oxidized form[66]. Polarography and electron transfer equilibria of some ferrocene containing polymers were studied. The oxidation half-wave potentials of polyvinylferrocene (6.4) and almost completely cyclized polydivinylferrocene (6.5) were similar to those of ferrocene and [3] ferrocenophane respectively. In the polarograms of triferrocenylbenzene (6.6) and polyethynylferrocene only one oxidation step was observed which suggested that the electronic interactions between the ferrocene units was small in these compounds[67]. Difficulties were encountered in the polarographic



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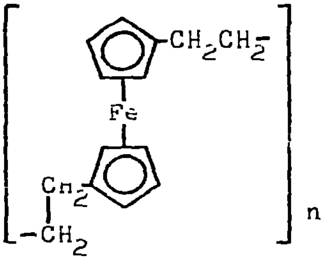

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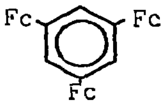
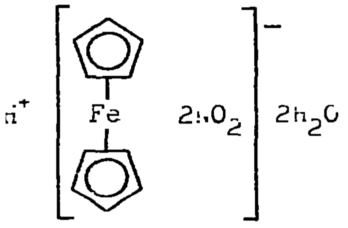


6.6

study of the ferrocene-ferricinium system in a wholly aqueous medium because of the low solubility of the product ferrocene and its consequent adsorption on the mercury surface. Aqueous ethanol was preferred as the solvent. The dependence of the limiting current on the concentration of ferrocene was determined and the change in the half-wave potential with the proportion of ethanol in the solvent was measured[68]. Ferrocene and bis(π-biphenyl)chromium have been proposed as reference electrode systems in non-aqueous solvents. The difference between their half-wave potentials (1.2-1.3V), remains constant for a range of solvents[69].

Aly has investigated some reactions of ferricinium trichloroacetate. When treated with nitrite ion, an acid nitrito complex (6.7) was produced. The ferricinium ion was reduced by hydroxide or iodide ion in the absence of oxygen. When the cation was treated with 8-hydroxyquinoline both the cyclopentadienyl to iron bonds were cleaved and the iron (III) complex was isolated[70]. The electrolytic reduction of ferricinium trichloroacetate in acid was investigated. The reduction potential of the cation was more negative than that of hydrogen evolution under the same conditions. Polarization data suggested that the efficiency of reduction of the ferricinium cation decreased at the limiting current. The energy of activation for the reduction varied between 13.7 and 5.7 kcal mole^{-1} depending on the applied potential. The results indicated that the reduction of the ferricinium ion passed from a kinetically-controlled to a diffusion-controlled process as the cathodic potential was increased[71]. Liquid electron ion exchangers (redoxites) were prepared in the reduced form by dissolving alkylferrocenes in $(BuO)_3PO$ and in octanol, nonanol and decanol. The oxidized form was obtained by treatment with potassium dichromate or by dissolution of the corresponding ferricinium perchlorates in an organic solvent. The oxidizing potentials of the redoxites were dependent on the composition of the aqueous phase[72]. Yates and McClelland have compared two independent methods for the estimation of hydronium ion activity ($\underline{a}^*_{H+}$) in aqueous sulphuric acid. Previous methods based on five different acidity scales and which referred to the standard tetraethylammonium ion were compared with a recent method which used a combined polarographic-glass electrode approach, with no liquid junction, and employed the ferrocene--ferricinium ion couple as reference electrode. Good agreement was obtained between the two approaches over a concentration range of 10-70% sulphuric acid where log $\underline{a}^*_{H+}$ varied over about ten logarithmic units. It was concluded that useful approximate values of hydronium ion activities can be either measured directly or estimated and these will be valuable in the study of acid catalyzed reactions[73].



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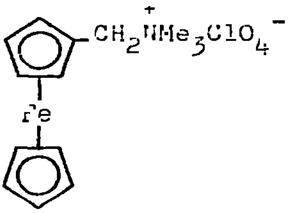


6.8

The redox potential of ferrocene was measured in sulphuric acid and it was found to be independent of acid concentration[74]. Kinetic studies have been carried out on the ferrocene-ferricinium ion oxidation-reduction system. Two groups of electron transfer reactions were investigated; (1) the electron transfer between the oxidized and reduced forms of different ferrocene derivatives, and (2) the oxidation of ferrocene derivatives by iron (III). The Marcus relation for outer-sphere electron transfer was used to correlate the kinetic results and this enabled the rate constants to be calculated for the self-exchange reaction between each ferrocene compound and its oxidized form. The rates for the iron (III) oxidations were lower than the theoretical values but a good fit was obtained for the measured cross-reaction rate constants for the ferrocene-ferricinium ion system based on the Marcus relation[75]. The electrical conductivity isotherms for ferricinium perchlorate, sodium ferrocenylcarboxylate and the salt (6.8) were determined between 15° and 45°. These ions obeyed the Walden-Pisarzherskii rule in this temperature range[76]. Mayeda and Bard have examined the annihilation reaction between the ferricinium radical cation and the superoxide radical anion. These two ion radicals were produced alternately in the same electrochemical cell by pulsing the electrode potential between the oxidation potential of ferrocene and the reduction potential of oxygen. Homogeneous electron transfer between these radical ions gave ferrocene and singlet oxygen[77].

The electrochemical oxidation of ferrocene was studied in dimethoxyethane and tetrahydrofuran. Standard potentials were obtained as functions of supporting electrolyte concentrations and of the dissociation constants of the dissolved species. The standard potential of the ferrocene-ferricinium couple was calculated[78]. The kinetics of homogeneous oxidation of ferrocene by p-benzoquinone in the presence of nitric acid and hydrogen peroxide in water-methanol mixtures were investigated. The oxidation by hydrogen peroxide in the presence of sulphuric acid was found to be slow and autocatalytic[79]. During cathodic reduction or anodic oxidation the differences in density of the reduced and oxidized species in the ferrocene--ferricinium system caused a convective flow near the electrodes in mixed solvents. This resulted in asymmetry of the polarization curves[80]. The blue solutions obtained from the oxidation of ferrocene were investigated. The colour was attributed to the formation of a complex ferrocene-ferricinium ion FcH_2^+ in aqueous solution. Yellow ferricinium ion solutions were prepared electrochemically in aqueous dimethylsulphoxide and the addition of ferrocene to these solutions gave the blue dimeric species FcH_2^+[81].

Ferrocene has been used in conjunction with a bright platinum electrode as an oxidation-reduction system in pentamethylphosphoric diamide as the solvent. This medium was similar in its electrochemical applications to hexamethylphosphoric triamide[82]. Lubach and Drenth have used a kinetic method to investigate the oxidation of ferrocene by molecular oxygen and hydrogen peroxide in aqueous acidic ethanol. The rate was found to be first order in oxygen and second order in ferrocene and in acid. The reaction product was the ferricinium ion and hydrogen peroxide was suggested as a reaction intermediate The ferricinium ion was slowly decomposed to iron cations under the conditions used[83]. Aly has suggested that reduction of ferricinium ion to ferrocene in the presence of iodide or hydroxide takes place by electron transfer from the anion to the ferricinium ion. Reduction was accompanied by ring-metal bond cleavage when it was carried out in the presence of air[84].

The ability of cobaltocene to form salts with trichloroacetic acid and picric acid was compared to that of ferrocene. With trichloroacetic acid cobaltocene underwent an almost instantaneous reaction which took place in the absence of oxygen to give the cobalticinium ion whilst the corresponding reaction with ferrocene was relatively slow and catalysed by oxygen. A similar effect was obtained with picric acid, the reaction with cobaltocene was fast whilst that with ferrocene was relatively slow[85]. The ferrocene catalyzed autoxidation of 3-hydroxybutan-2-one was studied in 50 vol.% aqueous ethanol-perchloric acid. The rate determining step equation (6a) was the acid catalyzed enolization of the substrate. Subsequently, both the enol form of the substrate and ferrocene were oxidized by oxygen equations (6b and 6c) [86].

$$\mathrm{MeCOCHOHMe} \xrightarrow{H^+} \mathrm{MeC(OH){=}C(OH)Me} \qquad (6a)$$

$$\mathrm{MeC(OH){=}C(OH)Me} + \mathrm{Fe(C_5H_5)_2}^+ \longrightarrow$$

$$[\mathrm{MeCOC(OH)Me}]^{\cdot} + \mathrm{Fe(C_5H_5)_2} + \mathrm{H}^+ \qquad (6b)$$

$$\mathrm{MeC(OH){=}C(OH)Me} + \mathrm{Fe(C_5H_5)_2} + \mathrm{O_2} + \mathrm{H}^+ \longrightarrow$$

$$[\mathrm{MeCOC(OH)Me}]^{\cdot} + \mathrm{Fe(C_5H_5)_2}^+ + \mathrm{H_2O_2} \qquad (6c)$$

Ferrocene was oxidized to ferricinium tetrachloroferrate by sulphuryl and trichloromethanesulphonyl chloride in benzene at reflux temperature. A free-radical mechanism was proposed with attack by chlorine radicals on ferrocene[87].

An ab initio self consistent field-linear combination of atomic orbitals-molecular orbital calculation has been used to obtain the first ionization potentials of ferrocene as the difference of the total energy for the neutral molecule and the positive ion. The computed sequence of ionization potentials was:

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

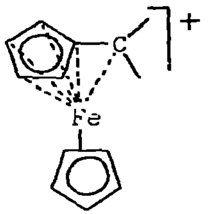
which was in good agreement with experimental evidence. This was different from the sequence of orbital energies for the ground state of the neutral molecule which was found to be:

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

It was concluded that Koopman's theorem was not valid for ferrocene[83].

7. Ferrocenyl carbenium ions

Previous evidence on the structure of α-ferrocenylcarbenium ions has been reassessed and further PMR and Mössbauer studies have been reported. The PMR results were for 2-substituted ferrocenylcarbenium ions and suggested that rotation of the methylene carbon relative to the ring was restricted. The ferrocenylcarbenium ion showed a Mössbauer isomer shift of 0.57 mm/sec and quadrupole splitting of 2.29 mm/sec. These observations and the NMR results favoured the carbon participation model (7.1) rather than the resonance or diene-iron π-complex models for the carbenium ion[89]. The two optically active forms (7.2) and (7.3) of the 1-ferrocenylethylcarbenium ion were formed in acidic solvents. These chiral cations interconverted slowly by rotation around the exocyclic bond. The first-order rate constant for racemisation was 6.32 × 10^{-5} s^{-1} in CF_3CO_2H at 40°. The derived thermodynamic parameters (ΔH = 81.5 kJ mol^{-1}, $T\Delta S$ = -22.2 kJ mol^{-1}), which constitute the free-energy barrier to rotation around the Fc—$\overset{+}{C}$HMe bond agreed well with results that had been obtained previously using PMR spectroscopy[90].



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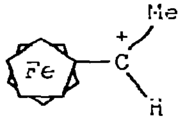

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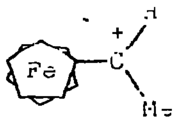
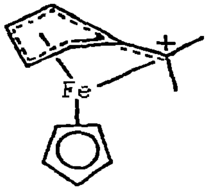


7.3

The PMR spectra of a series of α-ferrocenylcarbenium ions which were constrained by three and four membered carbon bridges, were compared with the spectra of cations derived from 1,1'-diethylferrocene where similar steric and electronic effects were present. The results[91] appeared to support the bent cyclopentadienyl structure (7.4) for the α-ferrocenylcarbenium ion which was proposed by Cais[92].

The PMR spectrum of the cation (7.5) was recorded and the ring protons α- and β- to the methyl substituent in the C_5H_4Me ligand appeared as two equally intense multiplets. It was concluded that the rotational freedom of the cyclopentadienyl ring was restricted as a result of steric repulsion between the methyl substituent and the bulky t-butyl group[93]. This was explained easily if it was assumed that the fulvene ligand was distorted in the manner suggested by Cais[92] or

Gleiter (7.6)[94]. The reaction of triferrocenylmethyl salts



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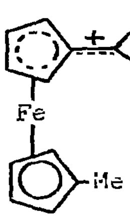

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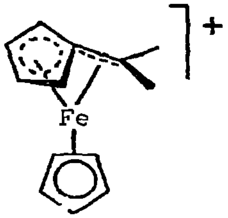
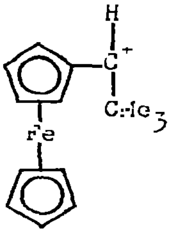


7.6

(anion = HCl_2^- or ClO_4^-) with Grignard reagents, n-butyllithium. or sodium ethoxide resulted in addition of the nucleophile to the carbenium carbon atom. For example n-butyllithium gave $BuC(Fc)_3$[95]. Secondary ferrocenylcarbenium ions in CF_3CO_2H, were shown to undergo quantitative double-shift rearrangements to generate isomeric tertiary carbenium ions. For example, the carbenium ion (7.7) gave the tertiary carbenium ion (7.8)[96].



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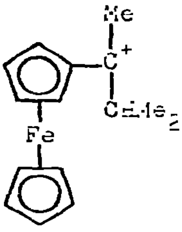
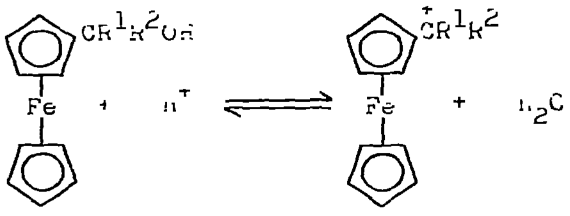


7.8

The ^{13}C NMR spectra were studied for $Fc\overset{+}{C}HR$ (R = H, Me and Ph). The chemical shifts and the coupling constants suggested that the high stability of the carbenium ions had its origin in the extensive delocalization of charge throughout the whole carbon skeleton, with some sharing of the charge by the iron atom. Also a fulvene-like structure for the substituted cyclopentadienyl ring was inferred[97]. Feinberg has compared the PMR spectra of interannularly bridged ferrocenylcarbenium ions with the corresponding non-bridged ferrocenylcarbenium ions. The similarity of the spectra suggested that iron-ring shifts were not involved in the stabilization of the carbenium ions. This suggestion was supported by the relative thermodynamic stabilities of the bridged and non-bridged species as measured by the pK_{R+} values in sulphuric acid. The properties of the carbenium ions were best interpreted in terms of classical resonance stabilization[93]. In acid solution, ferrocenylcarbinols (7.9) are in equilibrium with the corresponding ferrocenylcarbenium ions and the pK_R^+ of the ions (7.10; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = H$, $R^2 = Ph$;



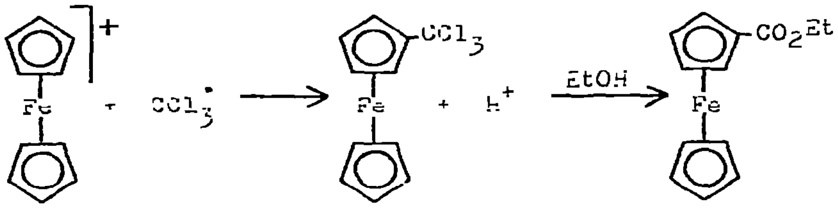
7.9 7.10

$R^1 = H$, $R^2 = Fc$; $R^1 = R^2 = Fc$) were determined spectrophotometrically. These ions were reduced on the dropping mercury electrode and the mechanism of the electrode process was established by electrolysis with a controlled potential. A free radical was generated in a one electron process and this dimerized. For example the radical $Fc\dot{C}HPh$ dimerized to give two isomeric 1,2-diferrocenyl-diphenylethanes[99].

8. Ferrocene chemistry

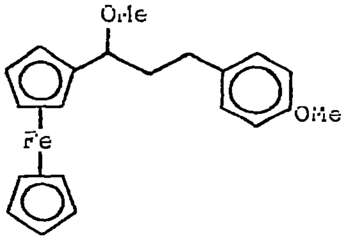
(i) Photochemistry

The photochemical substitution of ferrocene in carbon tetrachloride-ethanol solution has been examined by flash photolysis. The initial reaction proceeds by charge transfer excitation to give a radical pair (8.1) and these combine with the elimination of a proton to the trichloride (8.2). Ethanol solvolysed this compound to form ethyl ferrocenecarboxylate. (8.3) In the absence of ethanol the trichloromethylferrocene (8.2) decomposed to iron (III) chloride by a first order process[100]. The groups -OCOEt, -OCOMe, -CHO, $-CH_2Ph$ and $-CH_2CH=CH_2$ were introduced into ferrocene in yields of 25-53% by the UV irradiation of ferrocene in carbon tetrachloride, dichloromethane, chloroform, benzyl chloride or allylbromide mixed with ethanol. The reactions proceeded through intermediates formed by excitation of ferrocene-halogenated hydrocarbon charge transfer complexes[101]. The Stern-Volmer constants for several aromatic hydrocarbons, including ferrocene, were determined for the photolysis of poly(vinylphenylketone) in benzene solution[102].



8.1 8.2 8.3

Solutions of formyl-, acetyl- and benzoylferrocene were irradiated with ultraviolet light in the presence of the hydrogen donors, 2-propanol, triphenylmethane, triphenylsilane, triphenyltin (IV) hydride and tri-n-butyltin (IV) hydride Photoreduction to the corresponding alcohols was observed only in the presence of the tin (IV) hydrides and the quantum yields were low. When the ferrocenyl ketones were irradiated in methanol in the absence of a reducing agent rapid decomposition of the ferrocenyl molecule occurred[103]. Bozak and Javaheripour have observed the photochemical cleavage of acylferrocenes in isopropanol-aqueous hydrochloric acid. The product obtained by irradiation of benzoylferrocene, was benzoylcyclopentadiene; it was isolated in 70% yield. The reaction probably proceeded through cleavage of the protonated acylferrocene[104]. Photolysis of 3-ferrocenyl-1-(4'-methoxyphenyl)prop-1-ene in methanol gave the ethers (8.4) and (8.5). Irradiation of the deuterated propene $\underline{p}$-MeOC$_6$H$_4$CH=CHCD$_2$Fc showed that the ether (8.4) was formed by a 1,3-hydride transfer[105]. Ali, Cox and Kemp have reported further details of the photochemistry of ferrocenyl ketones and ferrocenylcarboxylic acid in polar solvents[107]. Formylferrocene, acetylferrocene, benzoylferrocene and other ketones were irradiated in DMSO, DMF, HMPT and tetrahydrothiophen oxide; an intense purple solution was obtained (at short wavelengths) and the metallocene group was decomposed. The primary reaction product from benzoylferrocene was the salt (8.6) formed by aquation of the carbonyl group and loss of the substituted cyclopentadienyl ring. Cyclopentadiene and ferrocene were also formed. Free radical scavengers had no effect on the reaction and confirmed its polar character. The polar solvent was effective in the promotion of charge separation in the formation of the salt (8.6). A similar photodegradation mechanism was proposed for ferrocenecarboxylic acid[106].



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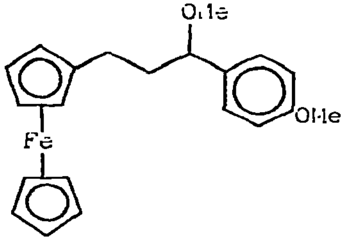
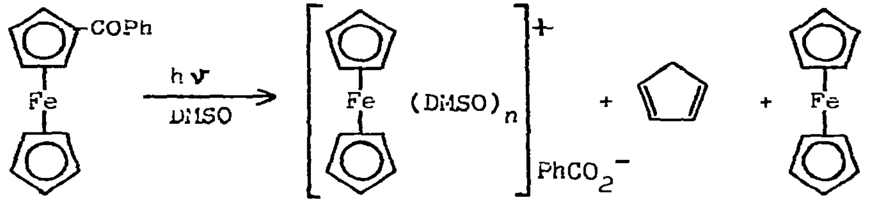


8.5

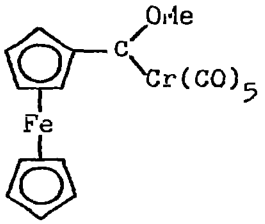
Ferrocene derivatives have been used as additives in the formulation of decomposable plastic materials for use in packaging. The decomposition under UV irradiation of polyethylene containing 1,1'-bis(4-chlorocinnamoyl)ferrocene was controlled by the addition of benzophenone or 4-(octyloxy)-benzophenone. Plastic film containing the ferrocene and benzophenone derivatives tore after exposure to sunlight for 23 days while the control sample required 35 days[108].



3.6

(ii) Derivatives containing other metals (metalloids)

Ferrocenyllithium, 1,1'-dilithioferrocene 2TMEDA, ferrocenyllithium TMEDA, and 2-lithio[(dimethylamino)methyl]-ferrocene were isolated as solids and characterized. They were all air-sensitive except ferrocenyllithium which was a relatively air-stable solid. Ferrocenyllithium was allowed to react with chromium hexacarbonyl and then with trimethyl-oxonium tetrafluoroborate to give the ferrocenylcarbene complex (3.7)[109]. Lithioferrocene and 1-lithio-2-chloroferrocene were treated with $(\pi\text{-}C_5H_5)Ni(PPh_3)Cl$ to form the binuclear complexes (8.8; R = H and 8.8; R = Cl) respectively. The monosubstituted ferrocene product was unstable and was attacked by mercury (II) chloride in situ. The product (8.8; R = Cl) was cleaved rapidly by hydrochloric acid and mercury (II) chloride to form the initial reagent $(\pi\text{-}C_5H_5)Ni(PPh_3)Cl$[110].



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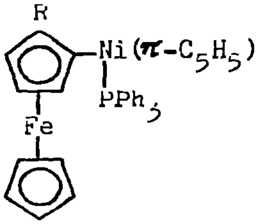

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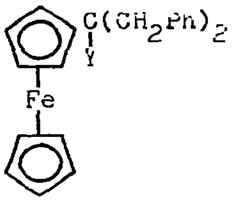
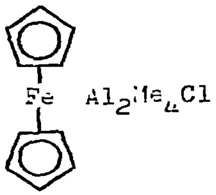


8.9

Ferrocenylmethylcyanide was lithiated with n-butyllithium and condensation of the lithiated intermediate with benzyl chloride gave α,α-dibenzylferrocenylmethyl cyanide (8.9; Y = CN). The lithiated intermediate was also condensed with methyl iodide, butyl bromide and 1,2-dichloroethane to give the corresponding α-disubstituted ferrocenylmethyl cyanides. When the ferrocenyl-cyanide (8.9; Y = CN) was treated with butyllithium the cyanide group was displaced and on hydrolysis the corresponding ferrocenylpropane (8.9; Y = H) was isolated[111]. The ferrocene-aluminium compound (8.10) has been obtained by treatment of ferrocenemercurichloride with trimethylaluminium, it was characterized by X-ray, mass spectrometric and NMR methods[112].

Lithiated ferrocenylacetylene, FcC≡CLi was condensed with triethylchlorosilane and diethyldichlorosilane to give the products $FcC{\equiv}CSiEt_3$ and $(FcC{\equiv}C)_2SiEt_2$ respectively in yields of 68-97%[113]. 1-*exo*-(Trimethylsilyl)-2,3-ferrocenoindene (8.11) was prepared selectively from 2,3-ferrocenoindenyllithium and trimethylchlorosilane. When the indene (8.11) was treated with excess n-butyllithium followed by hydrolysis it isomerized to give 1-*endo*-(trimethylsilyl)-2,3-ferrocenoindene (8.12). The ferrocenyl-indenes (8.11 and 8.12) both underwent carbon-silicon bond cleavage when treated with two equivalents of iron (III) chloride in methanol to give the same product,



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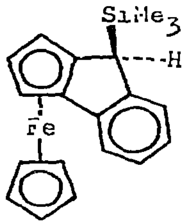

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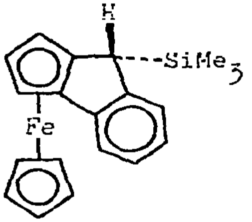


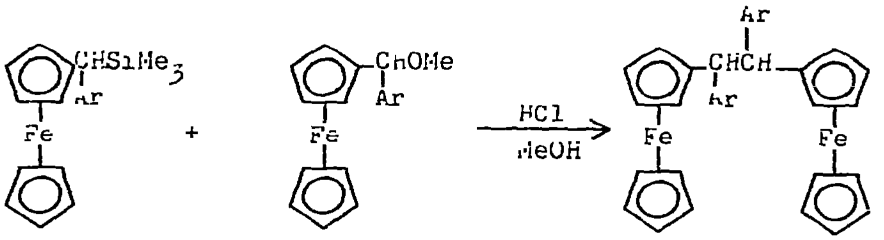
8.12

1-*exo*-methoxy-2,3-ferrocenoindene[114]. A series of ferrocenylmethyl derivatives of silicon and germanium was prepared and these compounds underwent methanolysis in the presence of ferric ions to give ferrocenylmethyl methyl ether (equation 8a).

$$FcCH_2MRMe_2 + 2FeCl_3 + 2MeOH \longrightarrow FcCH_2OMe + RMe_2MOMe + 2FeCl_2 + 2HCl \qquad (8a)$$

M = Si,Ge

The results suggested that a ferricinium intermediate was formed, by oxidation with the iron (III), and this underwent nucleophilic attack by methanol at the silicon or germanium atom[115]. The methanolysis of [α-(trimethylsilyl)benzyl]ferrocene (8.13; Ar = Ph) and [*p*-methyl-α-(trimethylsilyl)benzyl]ferrocene (8.13; Ar = *p*-MeC_6H_4) in the presence of iron (III) gave the corresponding methyl ethers (8.14; Ar = Ph and 8.14; Ar = *p*-MeC_6H_4). However the acid catalysed methanolysis of these α-trimethylsilyl derivatives in the presence of the corresponding ethers afforded 1,2-diferrocenyl-1,2-diaryl-



(8b)

8.13 8.14 8.15

ethanes (8.15) (equation 8b)[116]. The mechanism suggested for this reaction was as follows:

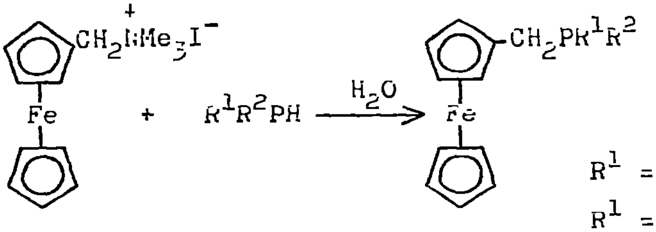
$$FcCH(Ar^1)OMe + H^+ \rightleftharpoons FcCH^+Ar^1 + MeOH$$

$$FcCH(Ar^2)SiMe_3 + FcCH^+Ar^1 \rightleftharpoons Fc^+CH(Ar^2)SiMe_3 + Fc\dot{C}HAr^1$$

$$Fc^+CH(Ar^2)SiMe_3 + MeOH \longrightarrow Fc\dot{C}HAr^2 + Me_3SiOMe + H^+$$

$$Fc\dot{C}HAr^1 + Fc\dot{C}HAr^2 \longrightarrow (FcCHAr^1)_2 + (FcCHAr^2)_2 + FcCH(Ar^1)CH(Ar^2)Fc.$$

Diferrocenyltin dichloride was formed from diferrocenylmercury and tin (II) chloride, the reaction was facilitated by the use of strongly coordinating solvents such as THF. The compound was stable in air but was cleaved to ferrocene on heating to just above the melting point and protolysis was observed in concentrated hydrochloric acid. The corresponding tin derivative of cymantrene was reported in the same paper[117]. Marr and White have prepared several ferrocenylmethylphosphines (8.16) by the reactions of phenylphosphine, diphenylphosphine and diphenylphosphine oxide with dimethylaminomethylferrocene methiodide (equation 8c). When α-substituted ferrocenylmethyl



(8c)

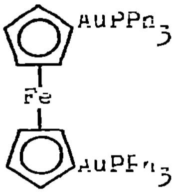
$R^1 = R^2 = Ph;$

$R^1 = H, R^2 = Ph.$

8.16

alcohols were treated with phenylphosphine and diphenylphosphine, the phosphine behaved both as a nucleophile, displacing the hydroxy group to give a (ferrocenylmethyl)phosphine, and as a reducing agent to give the corresponding ferrocenylalkane[118].

The treatment of 1,1'-dilithioferrocene with Ph_3PAuCl in tetrahydrofuran gave the ferrocenyl-gold derivative (8.17) which was unstable in solution but stable for several days as a solid[119]. Ferrocenyl(triphenylphosphine)gold was treated with acetyl chloride or CCl_3COCl to give ferrocene, biferrocenyl and Ph_3PAuCl. Treatment with electrophiles such as $(CH_3CO)^+BF_4^-$ and $O_2N^+BF_4^-$ also gave ferrocene, biferrocenyl and $[FcAu(PPh_3)AuPPh_3]BF_4$. Replacement of the gold by the electrophile did not occur[120]. Buerger and Kluess have



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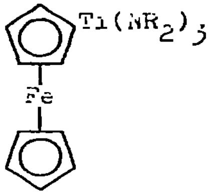
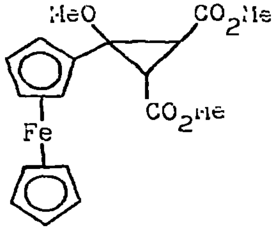


8.18

prepared dialkylamidotitanium (8.18; R = Me, Et) and 1,1'-bis(dialkylamidotitanium) derivatives of ferrocene by treatment of lithio- and 1,1'dilithio-ferrocene with dialkylamidotitanium bromides. The link between the cyclopentadienyl ring and titanium was shown to be a σ-bond by ^1H and ^{13}C NMR and IR spectroscopy. The bond was stable at 60° for short periods[121].

A comparative study was carried out of the reactions of two ferrocenyl carbene complexes $[(CO)_5CrC(Fc)OMe]$ and $[(CO)_5CrC(Fc)NC_4H_8]$ with each of the olefins dimethyl fumarate and 1,1-diphenylethylene. The methoxy compound gave the cyclopropane (8.19) when heated with the ester but with the phenyl-olefin only starting material was recovered. When the pyrrolidinyl complex was heated in excess of the ester the pentene derivative (8.20) was obtained. Treatment of the same complex with the phenyl-olefin also gave a pentene derivative, $Ph_2C{=}CHC(NC_4H_8)(Fc)CH_2CHPh_2$ (8.21) as the major product. It was suggested that these results were not consistent with the participation of a free carbene species Fc(X)C: where X = OMe, NC_4H_8[122]. The reaction of 1,1'dibromoferrocene with cymantrenyl copper or silver in the presence of copper (I) bromide gave the cymantrenyl ferrocene derivative (8.22 and 8.23; R = Br). The treatment of (8.23; R = Br) with copper (II) acetate gave (8.23; R = $OCOCH_3$) and treatment with copper phthalimide followed by hydrazine gave the ferrocenylamine (8.23; R = NH_2)[123].



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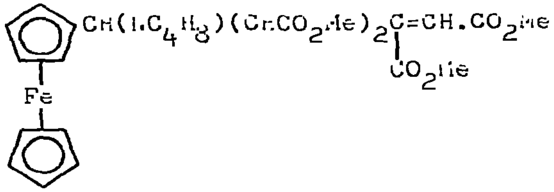

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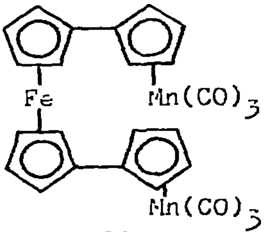

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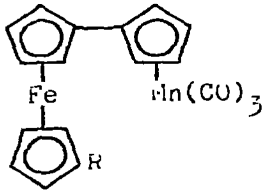
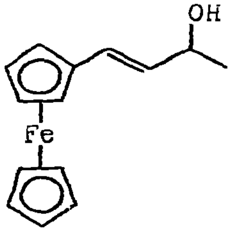


8.23

The ferrocenylalcohol (8.24) eliminated water on heating with diiron nonacarbonyl in benzene in the presence of copper (II) sulphate. The ferrocenylbutadiene formed was isolated as the iron tricarbonyl complex (8.25). Isomerization of the alcohol (8.24) was also observed to give the ketone (8.26)[124].



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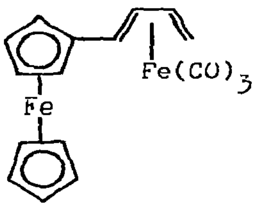

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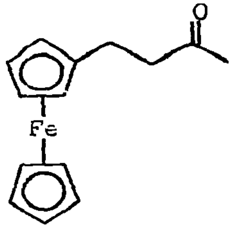
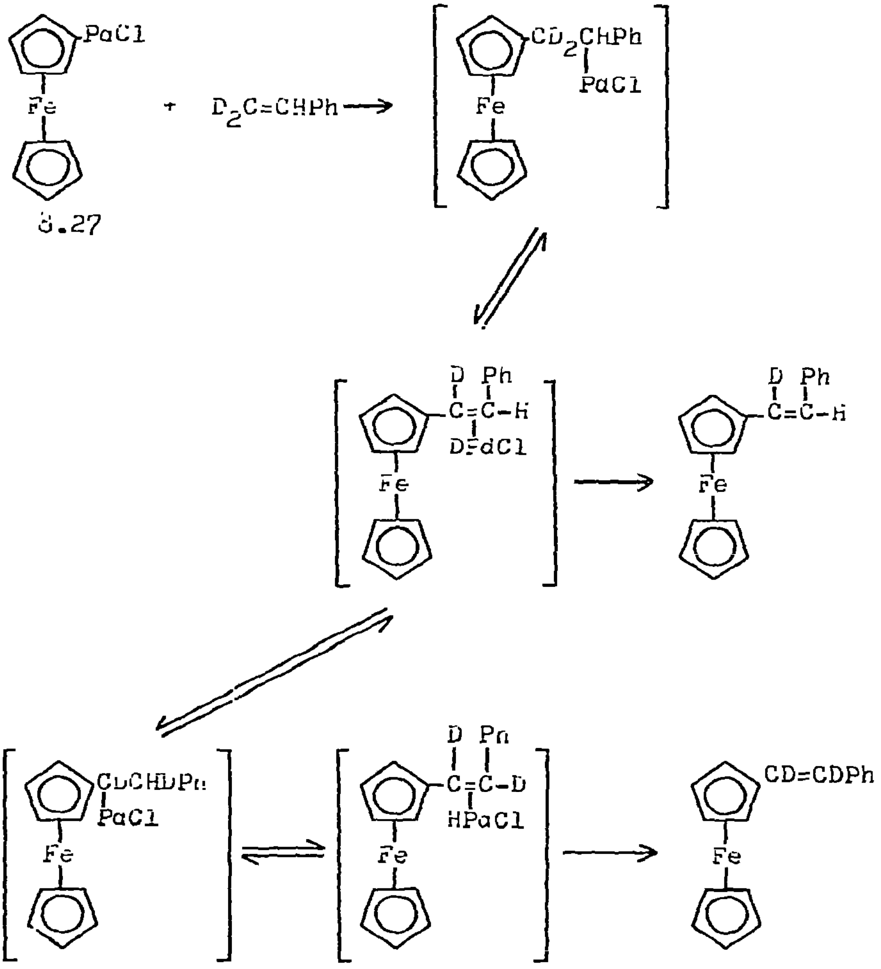


8.26

The reaction of styrene-β,β-d_2, *p*-methylstyrene-β,β-d_2 and *p*-methoxystyrene-β,β-d_2 with ferrocenylpalladium chloride (8.27) formed *in situ* from ferrocenylmercurichloride and lithiu tetrachloropalladate, was studied by Kasahara and Izumi. Hydride shift occurred and the proposed mechanism of addition is shown in Scheme (8.1)[125]. Diferrocenylmercury and

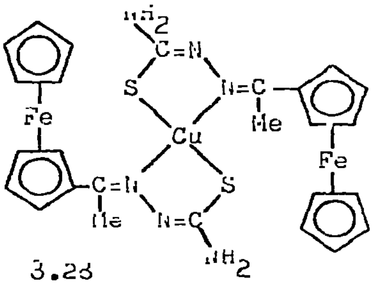


Scheme 8.1

cymantrene were pyrolysed in the presence of silver powder to give cymantrenylferrocene together with the symmetrical coupling products biferrocene and bi(cymantrene)[126]. Rausch, Klemann and Kovar have given full experimental details for the preparation of (chloromercurio)ferrocene and 1,1'-bis-(chloromercurio)ferrocene. Ferrocene and mercury (II) acetate were heated in methanol and the intermediate acetate was treated with lithium chloride. Alternatively ferrocene was heated with sodium acetate in methanol and then a solution of mercury (II) chloride in methanol was added[127].

(iii) <u>Complexes of ferrocene containing ligands</u>

The treatment of acetyl- and 1,1'-diacetyl-ferrocene with thiosemicarbazide gave the corresponding thiosemicarbazones



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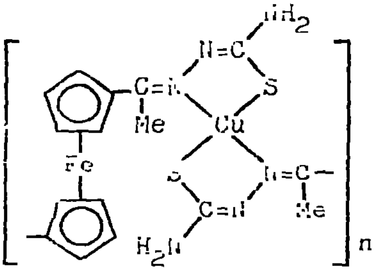
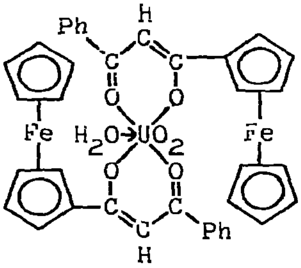


8.29

which with copper (II) acetate formed the copper complexes (8.28 and 8.29) respectively[128]. The ligands 1- and 1,1'-di-(1-phenyl-propan-1,3-dione)ferrocene were treated with ethanolic or acetone solutions of $UO_2(NO_3)_2 6H_2O$ to give the uranium complexes (8.30 and 8.31) respectively[129].



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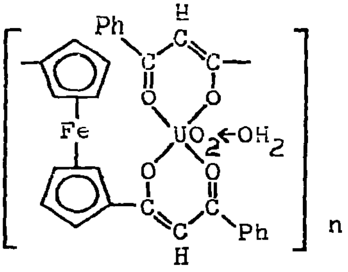
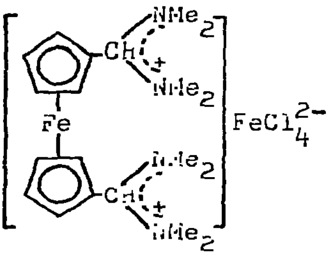


8.31

(iv) General chemistry

Cyclopentadiene was treated with sodium and iron (II) chloride in the presence of acrylonitrile to give (2-cyanoethyl)ferrocene in low yield together with some bis(2--cyanoethyl)ferrocenes[130]. The direct conversion of fulvenes to substituted ferrocenes was reported by Mueller-Westerhoff. 6,6-bis-dimethylaminofulvene was treated with iron (II) chloride in tetrahydrofuran to give the salt (8.32). Alkaline hydrolysis of this intermediate (8.32) gave 1,1'-bis(N,N-dimethyl carboxamide)ferrocene in high yield[131]. When benzenecyclopentadienyliron was heated to 40° in tetrahydrofuran it gave ferrocene (51%): $2C_6H_6FeC_5H_5 \longrightarrow (C_5H_5)_2Fe + 2C_6H_6 + Fe$. In a similar manner naphthalenecyclopentadienyliron was converted to ferrocene[132]. The glycidylferrocene (8.33)



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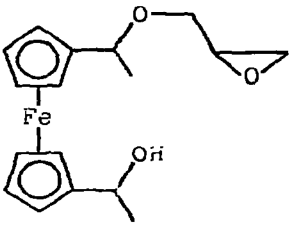
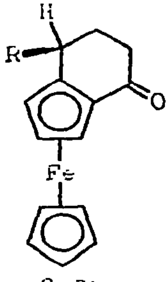


8.33

was formed by treatment of 1,1'bis(α-hydroxyethyl)ferrocene with sodium and then condensation of the sodio derivative with epichlorohydrin. Diglycidyl derivatives were not formed in the reaction. The epoxide (8.33) has been homopolymerized to give a product with a low heat resistance (40% loss in weight at 300° in air). Improved thermal properties were obtained when the polymer was crosslinked with either p-phenylenediamine or phthalic anhydride. Phenol-formaldehyde resins have been hardened with the epoxide (8.33) to give insoluble resins with high heat resistance (8% loss in weight at 300° in air)[133].

The cyclization of acids $FcCH_2CHRCH_2CO_2H$ (R = Me, Ph) gave the isomeric ketones (8.34 and 8.35) and these ketones were reduced to the corresponding cyclic alcohols and hydrocarbons[134]. The synthesis in high yield of five 1,1'-dichloro-2-ferrocenylcyclopropanes was achieved by the addition of dichlorocarbene, generated by the phase transfer method, to the corresponding vinylferrocenes. Dichlorocarbene was generated from chloroform and aqueous sodium hydroxide and benzyltriethylammonium chloride was the phase transfer catalyst. The mass spectra of the five ferrocenylcyclopropanes were reported; the spectra were relatively uncomplicated and similar to those of the corresponding phenyl-cyclopropanes[135]. Horspool,



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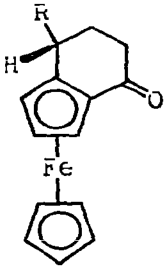

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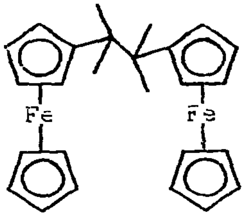
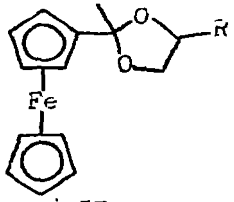


8.36

Thomson and Sutherland have reported the preparation of 2,3-diferrocenyl-2,3-dimethylbutane (9.7%) (8.36) by the treatment of 2-ferrocenylpropene with hydrobromic acid and acetic acid followed by zinc dust and quenching with water. A mixture of ferrocene containing products was obtained and the required compound was separated by fractional crystallization[136]. β-Methyl-γ-ferrocenyl-β-hydroxybutyronitrile $FcCH{=}CHCMe(OH)CH_2CN$ was treated with $Fe_3(CO)_{12}$ in benzene in the presence of copper (II) sulphate pentahydrate to give $FcCH{=}CHCOMe$, $FcCH{=}CHCMe{=}CHCN$, $FcCH{=}CHCMe{=}CHCNFe(CO)_3$ and methyl cyanide[137].

Ethyl- and 1,1'-diethyl-ferrocene were treated with bromine and gave pentabromocyclopentane and tetrabromoethylcyclopentane. The treatment of 1,1',3,3'-tetra-*tert*-butylferrocene with bromine afforded the corresponding ferricinium tribromide in good yield. The same ferrocenes when treated with an excess of iodine formed adducts which resembled ferricinium salts[138]. A by-product from the polyrecombination reaction of ferrocene which was regarded previously as a terferrocenyl has now been identified postively as *trans*-1,2-diferrocenylethylene[139]. Paushkin and Shevchik have reported the preparation of the dioxolane (8.37; R = H) by treatment of acetylferrocene with ethylene glycol in the presence of *p*-toluenesulphonic acid. The substituted dioxolane (8.37; R = CH_2Cl) was obtained by the same route with epichlorohydrin as the reagent. The same reagent was used with 1,1'-diacetylferrocene to give the corresponding bis(dioxonalyl)ferrocene[140]. A mixture of the acids (8.38; R = Me) and (8.39; R = Me) was cyclized by polyphosphoric acid to give the products (8.40 and 8.41). Only the ester (8.40; R = Me) was obtained in the presence of trifluoroacetic acid anhydride. The diacids (8.38; R = H) and (8.39; R = H) were cyclized by trifluoroacetic acid anhydride to give the anhydride (8.42) which underwent rearrangement in the presence of aluminium chloride to give the acid (8.40; R = H)[141].



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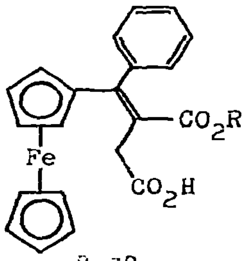

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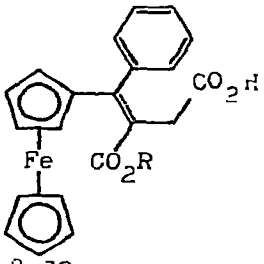

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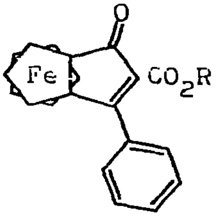

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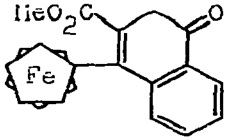

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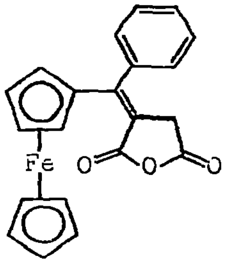
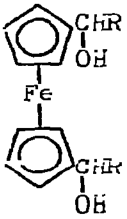


8.42

Yamakawa and Hisatome have prepared several 1,1'-bis-(α-hydroxyalkyl)ferrocenes (8.43; R = H, Me, Pr^i, Ph) and separated them by crystallization and chromatography into the corresponding *meso* and racemic isomers. *Cis* and *trans* isomers of the 7-oxa[3]ferrocenophanes (8.44; R = H, Me, Pr^i, Ph) have also been prepared and characterized. Ring closure of the diols (8.43) to the ferrocenophanes (8.44) was achieved by shaking a benzene solution of the diol with 2N aqueous hydrochloric acid. The ferrocenophanes were cleaved to the corresponding diols by stirring for five days in benzene solution with acidic alumina. Both ring-closure and ring-opening reactions proceeded with marked, but not complete, stereospecificity; *meso*- or *erythro*-diol (8.43)$\rightleftharpoons$*trans*-ether (8.44) and racemic or *threo*-diol (8.43)$\rightleftharpoons$*cis*-ether (8.44). A mechanism involving an intermediate α- 1'-(α-hydroxyalkyl)-ferrocenyl carbenium ion was proposed and was supported by the PMR spectra of the diols (8.43) and the ethers (8.44) in trifluoroacetic acid[142]. The preparation of the benzoquinoline (8.45) from 1-ferrocenyl-1-buten-3-ol and 2-naphthylamine in methylenechloride containing aluminium chloride has been reported[143].



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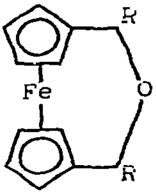

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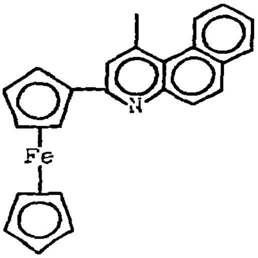

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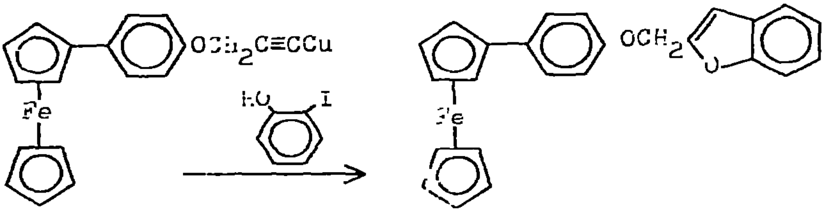
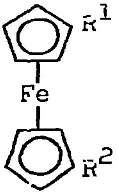
A Russian patent has described the preparation of the arylferrocene (8.47) from the copper acetylide (8.46) and *o*-iodophenol in pyridine[144]. Astruc reported that the



8.46 8.47

ferrocenylketones (8.48; R^1 = H, R^2 = COMe or Ph; R^1 = R^2 = COMe or Ph) underwent double ligand exchange with mesitylene in the presence of aluminium chloride to give the dication (8.49) in good yields[145]. The treatment of



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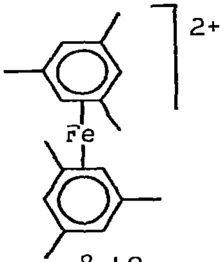

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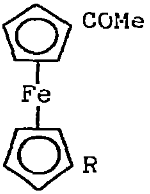


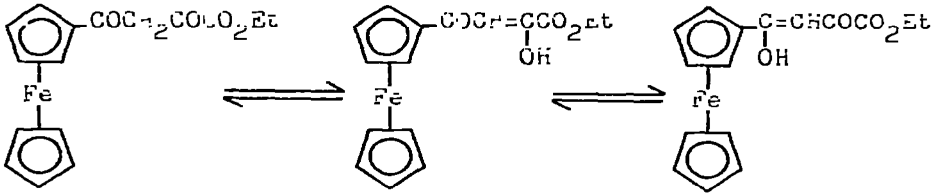
8.50

formylferrocene with $Me_2C(OH)CN$ in methanol, in the presence of potassium carbonate as the catalyst, gave FcCH(OH)CN[146].

The treatment of acetylferrocene with tri(ethoxy)methane in the presence of perchloric acid gave 2,6-diferrocenylpyrylium perchlorate in high yield. This pyrylium salt was transformed to 2,6-diferrocenylpyridine by heating with ammonium acetate in acetic acid. The condensation of ferrocenyllithium with 2,6-dimethyl-γ-pyrone gave 2,6-dimethyl-4-ferrocenylpyrylium perchlorate after treatment with perchloric acid. This salt was converted to 2,6-dimethyl-4-ferrocenylpyridine on treatment with aqueous ammonia[147]. The thermal decompositions of acetyl- and 1,1'-diacetyl-ferrocene were studied at 480-540°. The activation energies of decomposition were 41.8 and 48.3 kcal $mole^{-1}$ respectively and cyclopentadiene was found to inhibit the decomposition of the disubstituted derivative[148].

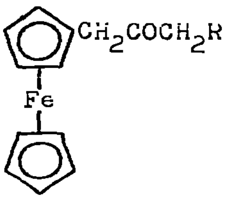
The heteroannularly substituted ferrocenes 1,1'-diformyl- and 1,1'-diacetyl-ferrocene and one homoannularly substituted derivative, 1,2-diformylferrocene, were condensed successfully with both aliphatic and aromatic diamines. The structures of the polymerization products were investigated and cyclic dimers were shown to be present in most of the product mixtures[149] 1,1'-Diacetylferrocene and ethylenediamine were copolymerized in the presence of acid. The copolymer was heated to 250-350° when it thermally degraded[150]. The cyclohexenones (2.4; $R^1 = H$, $R^2 = Pr^i$; $R^1 = Pr^i$, $R^2 = H$) were obtained from the corresponding ferrocenylbutyric acids by cyclization under Friedel-Crafts conditions. Each of the cyclohexenones (2.4) was obtained as the racemate which on reduction gave the respective epimeric alcohols. The stereochemistry of each alcohol was assigned on the basis of its absorption spectra[151]. Benzoylferrocene was treated with a preformed mixture of $Me_2C(OH)C{\equiv}CH$ + n-BuLi to give 2-methyl-5-phenyl-5-ferrocenyl-2,5-dihydroxy-3-pentyne. It was noted that benzoylferrocene was unaffected by di-Grignard reagents formed from acetylenic carbinols but it did condense with the corresponding di-lithium derivatives[152].

Acetylferrocenes (8.50; R = H, Cl, CO_2Me, CN) were reduced with triethylsilane in trifluoroacetic acid to give the corresponding ethylferrocenes in good yields. The rate of the reaction increased in the order $H < Cl < CO_2Me$ and there was no evidence for intermediate alcohol formation[153]. Ethyl-α-amino-β-ferrocenoylacrylate and N-substituted ethyl-α-amino-β-ferrocenoylacrylates were prepared by the reaction of ethyl-α-hydroxy-β-ferrocenoylacrylate (8.51) with ammonia and alkyl- and aryl-amines respectively. Tautomerism in these molecules was investigated. The electron withdrawing carbethoxyl group and electron donating ferrocene nucleus caused enolisation of the keto group in the α-position to give structure (8.51) rather than (8.52)[154]. Toma and Salisova



8.51 8.52

have reported their attempts to prepare ferrocenylacetone. Ferrocenylmethyl-diazomethyl ketone (8.53; RH = N_2), prepared by treatment of ferrocenylacetyl chloride with diazomethane in ether, was shaken with hydriodic acid. The product (8.53; R = H) obtained in low yield (<10%), was an air and light sensitive yellow oil. It was oxidized readily to ferrocenylpropanedione. The Claisen condensation of ferrocenylacetonitrile with ethyl acetate gave the keteneimine (8.54) and not the expected nitrile of 2-ferrocenylacetoacetic acid[155].



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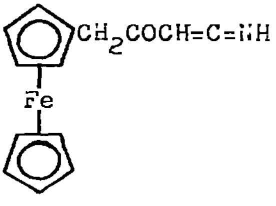

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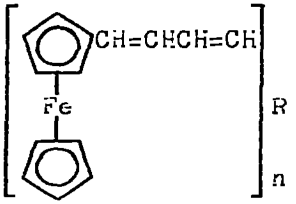

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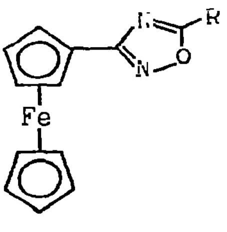
Vittal and Domorovskii have described the base-catalysed (1% aqueous sodium hydroxide) condensation of ferrocenecarbaldehyde with acetaldehyde to give β-ferrocenylacrylaldehyde. Treatment of this product with the sodium reagent Na$[(EtO)_2P(O)CHCO_2Et]$ gave the butadiene (8.55; n = 1; R = CO_2Et) in 80% yield which was hydrolysed to the free acid. The same reaction with Na$[(EtO)_2P(O)CHCOPh]$ gave the benzoyl derivative (8.55; n = 1; R = COPh) while treatment with $[(EtO)_2P(O)CH_2]_2$*p*-C_6H_4 and sodium methoxide in DMF gave the binuclear product (8.55; n = 2; R = *p*-C_6H_4) in 46% yield[156].

The treatment of dimethylaminomethylferrocene methiodide with sodium nitrite in acetonitrile gave 3-ferrocenyl-5-methyl-1,2,4-oxadiazole (8.56; R = Me) and the same reaction in propionitrile gave 3-ferrocenyl-5-ethyl-1,2,4-oxadiazole (8.56; R = Et)[157]. Dimethylaminomethylferrocene methiodide was heated with benzimidazole in dimethylformamide to give 1-(ferrocenylmethyl)benzimidazole. The corresponding 2-alkylbenzimidazoles were prepared similarly[158]. Good yields



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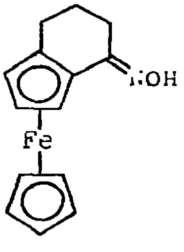

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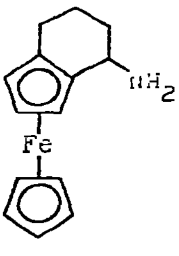
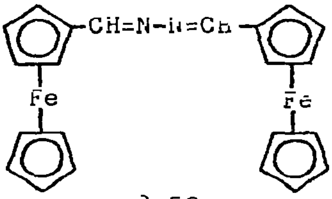


8.58

of the exo and endo isomers of the amine (8.58) were obtained by electrochemical reduction of the oxime (8.57) at a mercury pool cathode. The endo isomer was the dominant product as in the chemical reduction of the oxime[159].

The relative reactivities of hydrazine and substituted hydrazines with ferrocenyl-aldehydes and -ketones have been determined. With formylferrocene, unsymmetrical dimethyl- and diethyl-hydrazine each gave the corresponding hydrazone whilst with hydrazine the azine (8.59) was formed. Acetylferrocene was inert to substituted hydrazines and gave the corresponding azine with hydrazine[160]. A series of ferrocenylhydroxamic acids was prepared by treating esters, chlorides or anhydrides



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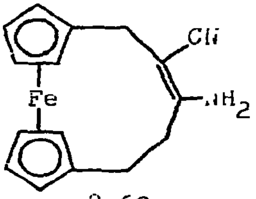
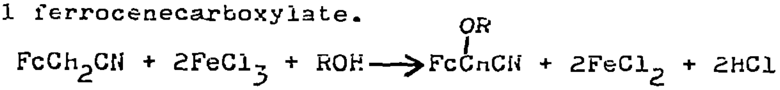


8.60

of ferrocenylaliphatic acids with hydroxylamine[161]. When ferrocenylacetonitrile was treated with two equivalents of iron (III) chloride in alcohol at room temperature α-methoxy-ferrocenylacetonitrile was obtained together with a trace of methyl ferrocenecarboxylate.

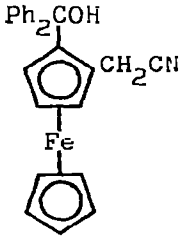


$$\mathrm{FcCH_2CN + 2FeCl_3 + ROH \longrightarrow Fc\overset{OR}{\overset{|}{C}}HCN + 2FeCl_2 + 2HCl}$$

R = Me, Et, H

A mechanism was proposed for this reaction in terms of electron transfer processes that involved substituted ferricinium ion intermediates[162]. Cyclization of 1,1'-bis-(2-cyanoethyl)ferrocene with ethylaniline in ether gave the [5] ferrocenophane (8.60) in 50% yield[163].

Rockett and Peet reported that substituted 1-cyanomethyl-2-hydroxymethylferrocenes, in the presence of cyanide ion, were converted into the corresponding amide while at the same time the hydroxy-group was displaced by cyanide. For example, in non-aqueous media the nitrile (8.61) was converted into the amide (8.62). It was suggested that the hydrolysis of the nitrile was assisted by intramolecular addition of the hydroxy-group to the carbon-nitrogen bond followed by attack of the cyanide ion on the diaryl-substituted carbon atom in the intermediate oxonium species (8.63)[164]. 1,1'-Bis(cyanoacetyl)-ferrocene was reduced by sodium borohydride to the corresponding diol which was dehydrated with phosphorus oxychloride to give *cis*, *cis*-, *trans*, *trans*- and *cis*, *trans*-1,1'-bis(β-cyanovinyl)-ferrocene[165]. A series of ferrocenyl-isothiocyanates (8.64; $X = CH_2, CH_2CH_2$, *p*-C_6H_4, *m*-C_6H_4, *p*-$C_6H_4CH{=}CHCO$) were prepared by treating the corresponding ferrocenyl-amines with thiophosgene[166]. The kinetics and orientation of acid D-H exchange of ferrocenylcarboxylic acid methyl ester and ferrocenylphenylsulphone were determined. For the methyl ester, exchange in the unsubstituted cyclopentadienyl ring occurred three times as fast as exchange in the substituted ring whilst in the sulphone this exchange was ten times as fast[167].



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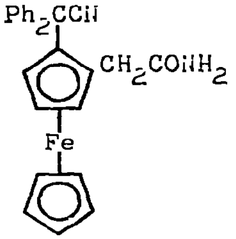

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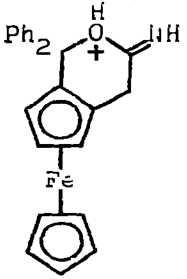
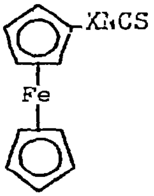


8.63

N-Ethylferrocenecarboxamide (8.65) was metallated with 1.5 equivalents of n-butyllithium and condensed with electrophiles to give the corresponding 2-substituted N-ethyl-N-methylferrocenecarboxamides. For example condensation with dimethylsulphate gave 2-methyl-N-ethyl-N-methylferrocenecarboxamide (8.66)[168]. The rate of abstraction of iodine by phenyl radicals from iodoferrocene was investigated. Iodoferrocene was shown to be slightly more reactive to the phenyl radical than iodobenzene. It was thought that the iron atom was involved in the homolytic abstraction process[169]. The first perhalo and oxidatively stable metallocene, decachloroferrocene (8.67; M = Fe), was prepared from 1,1'-dichloroferrocene by repeated metallation with n-butyllithium and condensation with hexachloroethane. When no attempt was made to purify the intermediates from each reaction, five lithiation-chlorination reactions gave a 42% overall yield of (8.67; M = Fe). When ruthenocene was lithiated and chlorinated seven times a 14% yield of the perhalo-derivative (8.67; M = Ru) was obtained. The perhalo metallocenes (8.67; M = Fe, Ru) underwent heteroannular dilithiation on reaction with



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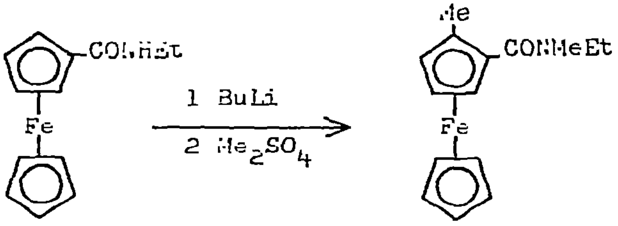

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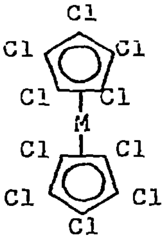


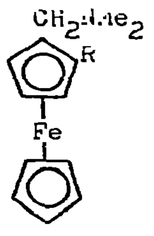
8.67

n-butyllithium and direct nucleophilic substitution on reaction with sodium methoxide[170].

9. Biferrocenes ferrocenophanes and annelated ferrocenes

Biferrocene, diferrocenylmethane, diferrocenylethane and [1,1]ferrocenophane were each diprotonated in BF_3-H_2O. The ferrocenophane rapidly eliminated hydrogen to give the diferricinium ion, the three singly bridged ferrocenes were oxidized slowly, even in the absence of air[171]. Treatment of the ferrocenylgold complex (9.1; R = $AuPPh_3$) with bromine in dichloromethane gave a mixture of the meso form of the biferrocenyl (9.2) and the bromoferrocene (9.1; R = Br). A similar reaction was observed when the reagent was chlorine[172].

The Mossbauer spectrum of biferrocenylene (II, III) picrate (9.3; X = picrate) showed only one, quadrupole split, absorption and suggested that only a single type of iron atom was present in the molecule; ESCA results supported this suggestion. The room-temperature magnetic moment (1.88 BM) was close to the spin-only value of 1.73 BM and contrasted with the values for ferricinium complexes and biferrocene (II, III) picrate (2.3-2.6 BM). A fractional oxidation state for each of the iron atoms was therefore indicated[173]. 1,1'-Biferrocenylene was prepared in improved yield by coupling 1,1'-dibromoferrocene in biphenyl with a copper bronze catalyst. Oxidation of 1,1'-biferrocenylene with benzoquinone in the presence of picric acid gave the ferricinium salt (9.3; X = picrate) while the salt [9.3; X = $(TCNQ)_2$] was obtained by oxidation with tetracyano-p-quinodimethane (TCNQ). For the mixed valence salts a near IR transition was observed at 1500 nm. which was assigned to an intramolecular intervalence exchange. Comparison of biferrocenylene with biferrocene suggested that there was a



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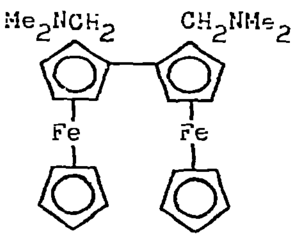
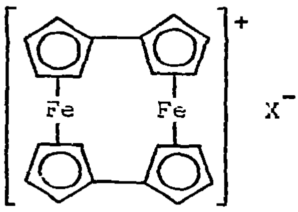


9.2

greater geometrical change on partial oxidation of the former compound than the latter[174]. A new route to 1,1'-biferrocenylene was reported from dilithium fulvalene. The lithium salt was condensed with iron (II) chloride to give biferrocenylene together with polyferrocenylenes (9.4; n = 0, 1, 2 ....). The salts [9.3; X = picrate, $(TCNQ)_2^-$, BF_4^-] were prepared and investigated in a similar manner to that described above[175]. It was also found that the room temperature bulk conductivity of [9.3; X = $(TCNQ)_2^-$] was greater than $10\Omega^{-1}cm^{-1}$ [175].



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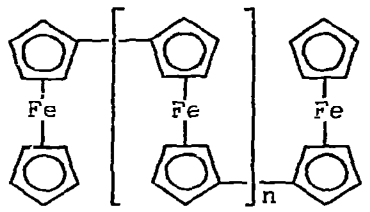

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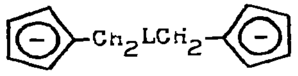

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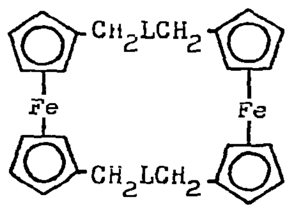
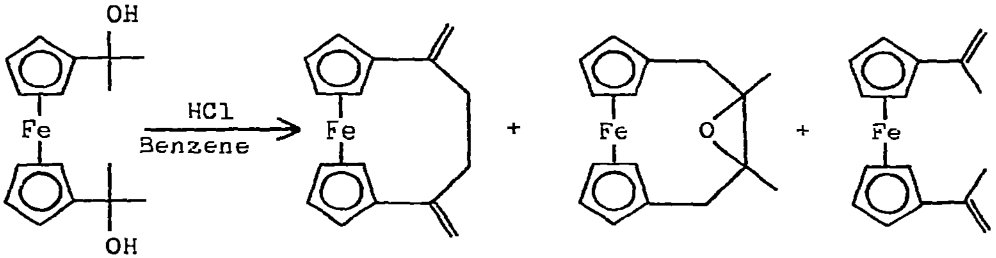


9.6

Katz, Acton and Martin have reported their attempts to prepare metallocene polymers by treatment of ligands having two linked cyclopentadienyl groups with transition metal halides. The dianions (9.5; L = $C\equiv C$ and $CH=CH$) were stirred with iron (II) chloride or hexammineiron (II) thiosulphate in diethyl ether. Dimeric products (9.6; L = $C\equiv C$ and $CH=CH$) were obtained in each case, no polymers were formed. Further details of the synthesis of the cyclic oligomers, $[1^n]$ ferrocenophanes, were given[176]. The mass spectra of ten ferrocenophanes and ten ferrocenophanones were recorded and for all the compounds the molecular ion was the base peak. The spectra indicated that the bonds joining bridges to the ferrocene nucleus resisted cleavage[177]. A mass spectrometric study of a series of ferrocenophanes was made by Carroll, Pflug and Winstead. The ferrocenophanes were 2,3'-, 2,4'-, 2,5'-, 3,4'- and 3,4-diacetyl[3]ferrocenophane and the molecular ion was the base peak in these five compounds. Fragment ions with relative intensities greater than 10 percent only occurred in the ferrocenophanes that had an acetyl group in the position alpha to the methylene bridge[178].

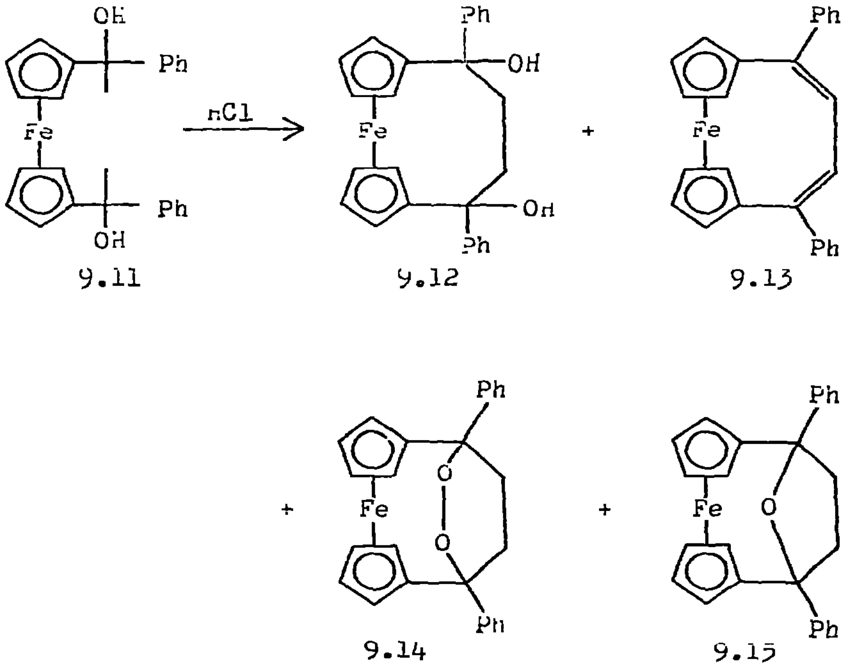


9.7 9.8 9.9 9.10

The reaction of acryloyl chloride with ferrocene in methylene chloride at -78° in the presence of aluminium chloride gave [3]ferrocenophan-1-one in good yield. When

]

the same reaction was carried out at higher temperatures some propanoylferrocene was also formed[179]. Hisatome and Yamakawa have observed the intramolecular cyclization of 1,1'-bis-(α-hydroxyisopropyl)ferrocene (9.7) under acid conditions to give a mixture of [4]ferrocenophanes (9.8 and 9.9). At low acid strength, 3M hydrochloric acid in benzene, only the ferrocenophane (9.9) was obtained together with the vinylferrocene (9.10) while with 6M hydrochloric acid both cyclic products (9.8 and 9.9) were formed. Under reducing conditions, 3M hydrochloric acid and ascorbic acid, the sole product was the vinylferrocene (9.10). When oxygen was bubbled through the acid solution of the diol (9.7) then the [4]ferrocenophanes (9.8 and 9.9) were formed in low yields (3% each) and no other products were isolated. Stable α-ferrocenylcarbenium ions were invoked as intermediates in these transformations[180].

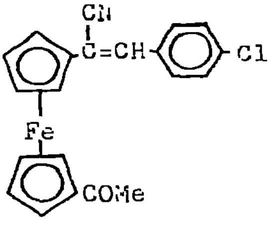


9.11 9.12 9.13

9.14 9.15

When a benzene solution of the diol (9.11) was stirred with 7M hydrochloric acid, a mixture of the [4] ferrocenophanes (9.12-9.15) was obtained. The diol (9.12) was dehydrated with *p*-toluenesulphonic acid to the butadiene (9.13) and the peroxide (9.14) rearranged on alumina to the phenoxy-ether (9.15). Reduction of the peroxide (9.14) with lithium aluminium hydride gave the diol (9.12). From these reactions the authors concluded that the first-formed product in the acid catalyzed cyclization was the peroxide and this was subsequently converted to the other ferrocenophanes (9.12, 9.13 and 9.15)[181].

Toma and Salisova have described routes to a number of [3]-, [4]- and [7]-ferrocenophanes using internal Michael addition. The [4] ferrocenophane (9.17) was prepared by condensation of ferroceneacetonitrile with *p*-chlorobenzaldehyde to form 2-ferrocenyl-3-(*p*-chlorophenyl)acrylonitrile. Friedel



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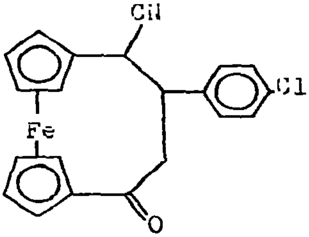

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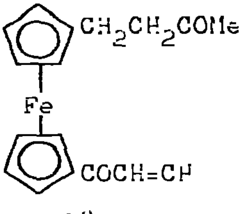

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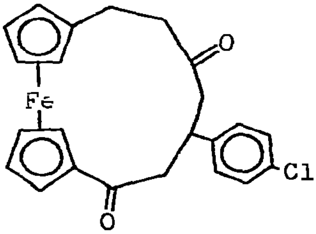

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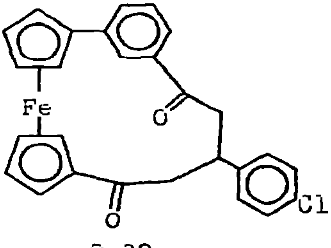

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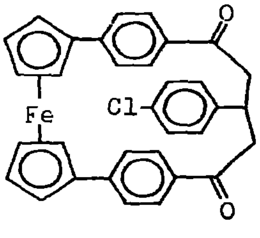


9.21

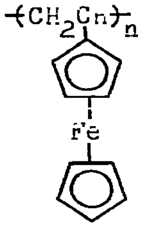
Crafts acylation of this nitrile gave the acetylferrocene (9.16) which cyclized smoothly and in high yield to the product (9.17). Treatment of the diketone (9.18) with sodium hydroxide in ethanol gave the [7]ferrocenophane (9.19) in good yield; the diketone was formed by condensation of *p*-chlorocinnamoyl chloride with 3-oxobutylferrocene[182]. The same authors report the introduction of one *m*-phenylene group and two *m*- or *p*-phenylene groups between the ferrocene group and a five--membered bridge in ferrocenophanes. The [8]ferrocenophane (9.20) was formed by internal Michael addition of a precursor similar to those used to form the bridged ketones (9.17 and 9.19) Condensation of *p*-chlorobenzaldehyde with 1,1'-bis(*p*-acetylphenyl)ferrocene in the presence of base gave the ferrocenophane (9.21)[183].

10. Ferrocene containing polymers

Lorkowski has discussed the synthesis of ferrocene containing polymers and the mechanisms of polymer formation. Possible applications of ferrocene polymers were suggested, these were as electron exchange resins, as polymers with special magnetic and electrical properties and as components in systems for the cold curing of unsaturated polyester resins[184]. The polymerization of vinyl- and ethynyl-ferrocene was studied in the presence of a variety of initiators and catalysts. Ethynylferrocene was polymerized with lauroyl peroxide and triisopropylboron as radical initiators and with substituted phosphine-transition metal complexes as catalysts. Vinylferrocene was polymerized in the presence of soluble Ziegler catalysts. The thermal and electrical properties of the polymers were investigated[185]. Polymerization of vinylferrocene in benzene with azobisisobutyronitrile (AIBN) as the initiator gave small yields of low-dispersity low molecular weight (5000) polyvinylferrocene (10.1). Higher yields were obtained by continuous or multiple addition of AIBN while high molecular weight polymers and binodal polymers were formed when higher concentrations of monomer were used. Bulk polymerization allowed yields of 80% to be realized, the molecular weight and the proportion of insoluble polymer increased with a decrease in temperature from 80° to 60°. The soluble polymer was often binodal with branching in the high molecular weight node. The low molecular weight polymer was fractionated readily from benzene-methanol mixtures[186].

The kinetics of the free radical polymerization of vinylferrocene were investigated. The results suggested that the termination reaction was monomolecular and intramolecular. It was proposed that in the termination reaction an electron was transferred from the iron atom to the polymer chain radical and this deactivated the radical and left an unpaired electron in the ferrocene nucleus. This proposal was supported by the Mössbauer and ESR spectra of the polymer which confirmed the presence of unpaired electrons[187]. The homopolymerization of 1-ferrocenyl-1,3-butadiene and the copolymerization of this monomer with styrene have been examined. The polymerizations were carried out in the presence of azodiisobutyronitrile and for the styrene-ferrocenylbutadiene system the average molecular weight ranged from 1500 to 1950[188]. Ponder and Barnhill have described the application of ferrocenylbutadiene as a monomer for the preparation of homo- and co--polymers which were used as binders in solid propellants. The butadiene was synthesised from ferrocenecarbaldehyde and allyllithium in THF which gave 1-ferrocenyl-3-buten-1-ol and this was dehydrated to the product on alumina at 155° [189].

The bulk polymerization of ferrocenylacetylene in the presence of 10% by weight of dispersed sodium at temperatures above 130° gave a polymer (10%) of molecular weight 1700 which was 90-93% soluble. An anionic mechanism for the polymerization was proposed. Other methods for the polymerization of ferrocenylacetylene, the structures of the products obtained and the mechanisms of polymerization were reviewed briefly[190]. Ferrocenylacetylene was copolymerized with isobutylene in the presence of boron trifluoride at -20 to -100° to give a copolymer of molecular weight 29000-39000 The yield of the polymer increased as the temperature was lowered from -20 to -70° but decreased if the temperature was lowered further[191]. Sasaki and Pittman have reinvestigated the reaction of acetylferrocene with triethylorthoformate under acid conditions. In contrast to the earlier report by Schlögl and Soukup[193] the dimeric ketone (10.2) was found to be the dominant product and the cyclic trimer (10.3) was formed in only low yield. Catalysis of the reaction with *p*-toluenesulphonic acid rather than dry hydrogen chloride led to a complex mixture of products including ethyl ferrocenoate and low molecular weight polyvinylferrocene. Mechanistic schemes involving α-ferrocenylcarbenium ions were discussed[193]. Polymers were prepared in high yield by the reaction of ferrocene with aldehydes or ketones in the presence of a



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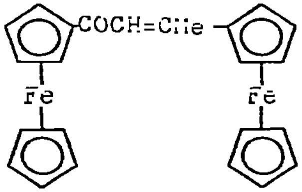

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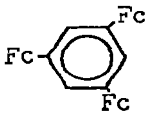
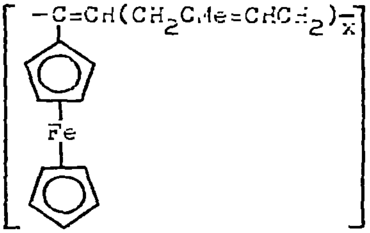


10.3

Lewis acid using an aprotic, polar solvent with a dipole moment $\geqslant$0.5D. For example, ferrocene was treated with benzaldehyde in dimethylformamide in the presence of iron (III) chloride to give a benzaldehyde-ferrocene copolymer[194].

The effects of reaction conditions on the products and yields in the copolymerization of ethynylferrocene with isoprene have been studied in the presence of $Bu^i_3Al-TiCl_4$ as catalyst. At a catalyst concentration of 2% polyisoprene was formed while a concentration of $\geqslant$30% catalyst was required to form the copolymer (10.4). Polymers (10.5 and 10.6) from ethynylferrocene were also obtained. The physical properties of the polymeric products were discussed[195]. Ayers, McManus and Pittman have



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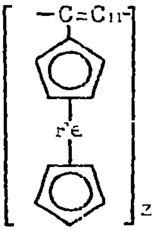

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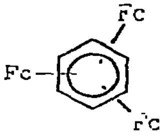
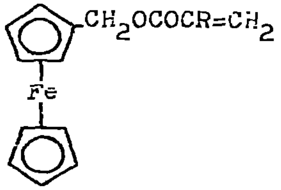


10.6

polymerized ferrocenylmethyl methacrylate (10.7; R = H) with maleic anhydride, acrylonitrile and *N*-vinyl-2-pyrrolidine in benzene or benzene-ethyl acetate solution with AIBN as the initiator to give high yields of copolymers. Ferrocenylmethyl acrylate (10.7; R = Me) was copolymerized with maleic anhydride under the same conditions. With a range of six comonomers, the acrylates (10.7) exhibited lower relative reactivity ratios (r_1) and higher values of r_2 than the corresponding copolymerizations with methyl acrylate or methyl methacrylate. In addition, the low Q values obtained for the monomers (10.7; R = H), 0.03-0.11 and (10.7; R = Me), 0.08-0.15, compared with the values for methyl acrylate (0.46) and methyl methacrylate

(0.74), confirmed that the ferrocenyl-acrylates (10.7) were less reactive than expected[196]. Vinylferrocene was copolymerized with butadiene in the presence of azobis(2-methyl-5- hydroxyvaleronitrile). The copolymer was used as a binder to improve the burning rate of solid propellants[197]. Vinylferrocene and butadiene were copolymerized in toluene using azobis(2-methyl-5--hydroxyvaleronitrile) as the initiator. The copolymers were useful as binders for propellants and they also increased the burning rate[198].

The preparation and utility of thiazole-containing ferrocene condensation polymers were investigated. The thermal stability of the polymers was rather low and some of them decomposed at 300° [199]. The synthesis of poly[oxy(biscyclopentadienylzirconium)-oxycarbonylferrocenylcarbonyl] from biscyclopentadienylzirconium dichloride and the sodium salt of 1,1'-ferrocenedicarboxylic acid was studied as a function of several reaction variables. The yield of polymer varied with pH and it reached a maximum at approximately pH = 7.5. Yields were better in systems that empolyed a saturated aqueous solution of disodium 1,1'-ferrocene dicarboxylate[200]. Glycidyl methacrylate-alkyl methacrylate copolymers were heated with excess N-(ferrocenylmethyl)aniline for several hours when the nucleophile cleaved more than 95% of the epoxy groups to give a polymer with useful paramagnetic and redox properties[201].



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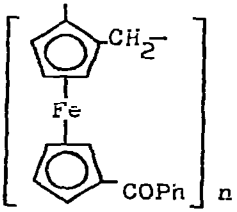


10.8

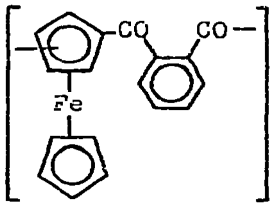
1,1'-bis(α-hydroxyethyl)ferrocene was investigated as a curing agent for phenol-formaldehyde resin at 120° to give a cross-linked structure. The cured product showed greater resistance to oxidative thermal degradation than phenolic resins cured with urotropine[202]. Friedel-Crafts acylation of poly(methyleneferrocenylene) with benzoyl chloride and aluminium chloride in dichloromethane at 25° gave 42% of a soluble benzoylated polymer (10.8). Under the same conditions at 40° an insoluble polymer (72.5%) was obtained with PhC- and methylene crosslinking groups. At 80° the predominant product was a second insoluble polymer (90%) with only PhC- as the crosslinking group. The benzoylated polymer (10.8) was stable at 400° while the methylene crosslinked polymer showed a 3% weight loss at 300°. The poor thermal stability of the latter was attributed to the presence of ferricinium groups which were active as centres for the initiation of degradation. Ferricinium groups were detected in both of the crosslinked polymers by EPR methods[203]. When acetylferrocene-furfural polymers were heated to 400° in vacuo decomposition occurred. The distribution of the iron released by the destruction of the ferrocenyl part of the molecule in the glassy carbon residue was investigated[204].

11. Applications of ferrocene

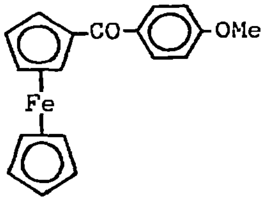
(i) Ferrocene catalysts

A number of ferrocene polymers, including the ketone (11.1) were active as catalysts in the dehydration of alcohols. Dimethylvinylcarbinol was dehydrated to isoprene in yields of up to 95% in the temperature range 180-300° and iso-propanol was dehydrated to propene (92.5%) at 400°. The catalytic activity of the polymers was ascribed to magnetically ordered metallocene residues in the matrix. Slow degradation of the polymers to iron oxides was observed under the reaction conditions used[205]. Catalysts for the reaction between alkyl isocyanates and alcohols have been compared. The reaction was used as a model system on which to evaluate the effect of additives on propellant binders containing polybutadiene terminated with hydroxyl groups. Ferrocene and ferrocene derivatives were the most effective catalysts both in the presence and absence of light. The catalyst was degraded by ammonium perchlorate and by light in the presence of air[206].

The *cis*-*trans* photochemical isomerization of butenes was sensitized by ferrocene at temperatures above 90° and in the absence of oxygen. When oxygen was present then photochemical oxidation occurred with the formation of acetaldehyde, propionaldehyde and formic acid. The yields and proportions of the products were dependent on the proportions of the reactants, the concentration of ferrocene, the temperature and the UV wavelength used[207]. Ferrocene derivatives were found to be effective photostabilizers of polyethylene film. Film that contained benzoylferrocene or *p*-methoxybenzoylferrocene (11.2) had 30-35% higher tensile strength and 25-30% ultimate elongation than nonstabilized film after ultra-violet irradiation for one hundred hours at 25°[208]. The photopolymerization of vinyl



11.1



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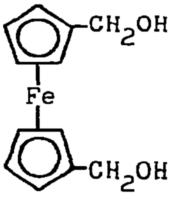


11.3

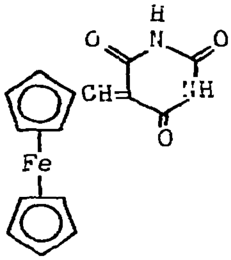
compounds was catalysed by ferrocene derivatives containing active halides. A mixture of 98 parts acrylic acid and 2 parts

0.2:10, ferrocene:benzenesulphonyl chloride was irradiated with UV light to give solid poly(acrylic acid) in five minutes. No polymerization occurred in thirty minutes in the absence of the catalyst[209].

Ferrocene mixed with organic halides was effective in initiating the polymerization of vinyl monomers such as acrylonitrile and acrylamide; thus ferrocene in carbon tetrachloride initiated the radical polymerization of methyl methacrylate and the cationic polymerization of isobutyl vinyl ether[210]. Unsaturated polyesters were polymerized in the presence of 0.1% ferrocene derivatives. For example the copolymerization of monomers such as styrene, triethylene glycol dimethylacrylate or divinyl adipate was carried out in the presence of 1,1'-bis(hydroxymethyl)ferrocene (11.3) at 0° using benzoyl peroxide as the catalyst[211]. The ferrocenyl-barbiturate (11.4) was successfully used as a catalyst for the combustion of composite explosives[212].

(ii) <u>Biochemical applications</u>

Ferrocenylisopropylamine (11.5) has been shown to have a higher binding affinity to cytochrome P-450 than isopropylamphetamine. This was related to the inhibition by the amine (11.5) of the oxidative N-dealkylation of isopropylamphetamine in liver microsomal suspension and the inhibition of elimination of N-alkylamphetamines in the rat. The half-lives of N-alkylamphetamines such as (+)- and (-)-benzylamphetamine, (+)-isopropylamphetamine and (++)-biamphetamine in the isolated perfused rat liver, were increased from 5-20 min. to 200 min. by the addition of equimolar amounts of the ferrocenylamine (11.5)[213]. Acetylferrocene nitroguanylhydrazone was prepared and screened for antineoplastic activity against Walker carcinosarcoma 256. It was found to be inactive[214]. The reaction of ferrocenylacetyl chloride and S-ferrocenylvaleric acid with cholesterol gave cholesteryl ferrocenylacetate (38%) and cholesteryl S-ferrocenylvalerate (43%) respectively[215].



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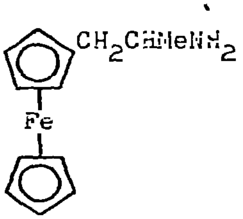
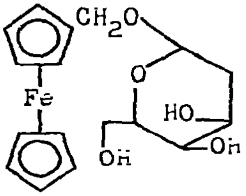


11.5



11.6

Overend and coworkers reinvestigated the acid-catalysed hydrolysis of ferrocenylmethyl β-D-glucopyranoside (11.6) in $H_2{}^{18}O$. The glucose formed contained no ^{18}O enrichment and this showed that cleavage of the bond between the oxygen and aglycon-carbon occurred during the hydrolysis. This result was contrary to an earlier report[217] that the ^{18}O enriched glucose was formed. The mode of bond cleavage suggested was supported by the isolation of glucose and methoxymethylferrocene from the acid catalysed methanolysis of the glucopyranoside (11.6)[217]. Ferricinium ion salts were treated with human γ-globulins in buffer solution at pH9 when the ferricinium group was broken down and the Fe (III) was taken up by the protein[218]. The preparation of ferrocene in a single stage reaction from an iron salt, cyclopentadiene and sodium as a reducing agent at 60° has been reported[219]. Rosenberg and Bilow have described the use of polyferrocenylene cross-linked with aryl di- and tri-sulphonyl chlorides as laminating resins for glass fabrics. Since polyferrocenylene formed insoluble polar complexes with the sulphonyl chlorides it was convenient to prepare separate solutions of the two components and mix them immediately before use[220]. The drying rates of thin films (0.08-0.35mm) of linseed oil were reduced when vinylferrocene was incorporated in the proportion of 5% by weight. The drying rates of very thin films (0.08mm) were independent of added vinylferrocene[221]. A method was reported for the simultaneous determination of iron and silicon in organometallic derivatives. A sample (10mg) of a ferrocenyl-silane was fused with sodium peroxide in a bomb and the melt was dissolved in water and acidified with sulphuric acid. The silicon and iron were then determined by differential photometry[222]. Gilbert and Monti have reported the details of an undergraduate exercise on the dry chromatographic separation of ferrocene, acetylferrocene and 1,1'-(diacetyl)-ferrocene with dichloromethane as the solvent[223]. Ferrocene derivatives such as methylferrocene, chloroferrocene and acetylferrocene were found to be more effective as antiknock additives in gasoline than ferrocene, they also formed less deposit. On the other hand they were less soluble than ferrocene[224]

Light sensitive copying materials were prepared and these contained aromatic hydroxy compounds and either ammonium ferrocenedisulphonate or ammonium ferrocenesulphonate. These compounds were found to be light sensitive, easy to handle, inexpensive and heat-fixable[225]. A series of metallocenes were used as photoconductors in electrophotography. For example, a photoconductive coating was prepared using ferrocenylbis(2-methyl-4-diethylaminophenyl)methane as the photoconductor[226]. A solid propellant that consisted of an oxidizing agent (mainly NH_4ClO_4) and a polybutadiene or polyurethane resin had its burning rate increased by the addition of 0.01-5% ferrocene. For example the addition of 0.5% ferrocene more than doubles the burning rate[227]. Ferrocenylbutadiene, prepared from formylferrocene and allyl Grignard reagent followed by dehydration with copper (II) sulphate, was useful as a binder for solid propellants[228]. 2-Ferrocenyltetrahydrofuran, prepared by reduction of methyl-β-ferrocenyltetrahydrofuran, increased the burning rate and improved the performance of solid propellants[229]. Triphenylsilyferrocene, diferrocenylsilane diol and other silanols have been used as high-temperature lubricants and hydraulic fluids. The compounds were prepared by Friedel-Crafts alkylation of ferrocene with the appropriate chlorosilane[230].

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