FERROCENE

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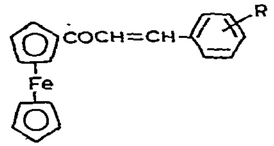
CONTENTS

Reviews. Slocum and Ernst have reviewed homoannular electronic effects in substituted ferrocenes[1], while the photochemistry of metallocenes including ferrocene has been discussed by Bozak[2]. The mass spectrometry of ferrocenes has been surveyed[3] and the electrophilic substitution and related reactions of ferrocene have been reviewed briefly[4]. Neuse and Rosenberg[5] have described the synthesis and properties of all types of metallocenes, and in particular ferrocene, polymers. A review in Japanese has been published[6] on the applications of ferrocene as a combustion additive when it behaves as an anti-knock and as a smoke reducing agent.

Theoretical studies. A total coordinate analysis of ferrocene has been carried out and kinematic couplings between some ligand and framework normal modes of the metallocene were observed. These couplings accounted for some frequency shifts from free (ionic) to complexed cyclopentadienide without any change in the harmonic force field of the ligand. The calculated mean amplitudes of vibration for ferrocene were compared with the values obtained by electron diffraction. Good agreement was achieved between the observed and calculated values[7].

The indexes of reactivity of the ferrocenyl chalcones (1) and (2) were calculated by the LCAO Hückel molecular orbital method. In each compound the lowest value of cation localization energy was determined in order to indicate the position that was the most susceptible to electrophilic attack[8]. Modified Extended Hückel (SCC) calculations on the ferrocenylcarbonium ion (3) indicated that the cyclopentadienyl rings were tilted and that the α-methylene group was bent towards the iron atom[9]. All of the iron–carbon bonds had similar overlap populations and about half the positive charge was located on the iron atom while the other half was distributed uniformly over both rings.



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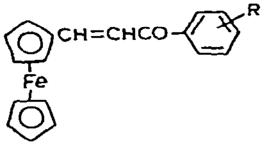

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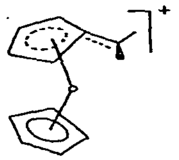
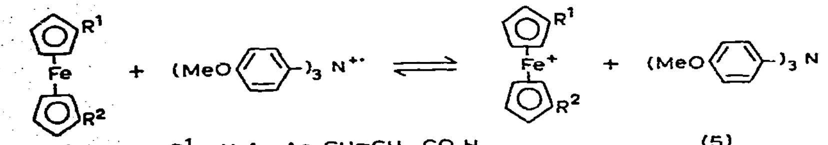


(3)

The rates of hydrogen–deuterium exchange on the methyl groups of several acetyl substituted π-cyclopentadienyl and π-benzene metal carbonyls and ferrocene were measured in the presence of base and found to correlate with the pK_a values of the corresponding carboxylic acids. Acetylferrocene showed the lowest rates of exchange[10]. Rate constants have been measured also for the H–D exchange between ferrocene or substituted ferrocenes and CF_3CO_2H–CH_3CO_2D. Only small differences in rate were found between different ferrocene ring protons; thus the unsubstituted ring in methoxyferrocene was more reactive than the substituted ring[11] by a factor of 3.5. Molecular core binding energies have been determined for several transition metal carbonyls and π-cyclopentadienyl compounds[12]. The results for ferrocene suggest that a small positive charge resides on the ring and the iron atom has a small negative charge. Solvent–solute interactions for solutions of ferrocene in hydrocarbons were investigated by comparing the experimentally observed and additive values for the dielectric constant. Over the temperature range $-80°$ to $20°$ and at concentrations of 10^{-4} to 10^{-1} $\text{mole} \cdot l^{-1}$ the strongest interactions were observed in benzene[13]. Determinations of the molar Cotton–Mouton constant ($2.0 \cdot 10^{-15}$) and of the molar Kerr constant of ferrocene in CCl_4 solutions have been used to give the principal molecular polarizibilities of ferrocene[14], $b_1 = b_2 = 20.90$ and $b_3 = 15.1$ Å^3. A low temperature differential thermal analysis study of ferrocene has detected a phase transition at 164 K and disintegration[15] of the crystalline material at < 130 K. The disintegration temperature was dependent on the rate of cooling. The Raman spectrum of the solid was unaffected by disintegration. When the sample was in the form of a polycrystalline powder or when a pressure of 10 bar was applied, then no disintegration was observed.

Ferricinium salts. Ruff and coworkers[16] have used a photographic technique to measure directly the diffusion coefficients of ferrocene and the ferricinium ion in the presence of ferrocene and thus determined the rate of electron exchange between the cation and ferrocene. The measured second order rate constants confirmed that the rate was close to the diffusion limit. The results also suggest that electron transfer takes place through an activated complex in which the reactants are as close together as possible. In a polarographic and potentiometric study of the oxidation of metallocenes and dimetallocenylmethanes it was observed that a reversible one-electron process occurred[17]. The ease of oxidation was in the order OcH > RcH > FcH[*] at the dropping mercury electrode. Irreversible oxidation of OcH in two consecutive one-electron steps and irreversible oxidation of RcH by a one step two-electron process was observed at the rotating platinium disc electrode. However, the potentiometric oxidation of OcH was a reversible two-electron process. Transmission of the electronic effects of substituents to the metal atom in RcH was considered to take place by an inductive mechanism as demonstrated by the linear relationship between the half wave potentials and the substituent constants σ_p^0. The electron transfer between ferrocene and ferricinium ions at low concentrations under reversible second order conditions has also been studied[18] by a stopped flow technique. A total of 22 reactions was examined using ferrocene and seven substituted ferrocenes. The electrode potential for each compound was determined and the equilibrium constants for the exchange reactions were calculated. The experimentally determined rate constants were then compared with values calculated using the Marcus relationship for adiabatic outer-sphere electron transfer reactions. The oxidation of ferrocene to ferricinium ion by iron(III) has been studied in acidic acetone–water solvents at 25° [19]. The rate of oxidation was sensitive to the ligands on the iron(III), the pH, the substituents on ferrocene and the proportion of acetone in the solvent. It was suggested that the mechanism involved transfer of an electron from the molecular orbitals of ferrocene with lobes of maximum electron density in the plane midway between, and parallel to, the cyclopentadienyl rings to d_π orbitals on iron(III) with the ligands on iron(III) acting as bridging groups. The effect of solvent on the reduction potential of the ferrocene–ferricinium couple was investigated by polarographic measurement of the half-wave potentials[20]. Increasing the proportion of dimethyl sulphoxide in an aqueous mixture increased the reduction potential while the potential for the Fe^{2+}–Fe^{3+} couple decreased under the same conditions. Reduction of the ferricinium ion in aqueous ethanol by the same technique has shown that both the half wave potential and the limiting current depend on the proportions of the components of the solvent[21].

The homogeneous electron transfer between ferrocene or substituted ferrocenes (4) and tri-*p*-anisylamine(5) has been investigated by internal reflection spectroelectrochemistry[22]. The experimentally determined exchange rates varied over a range of six orders of magnitude and were compared with the rates predicted by Marcus theory. Agreement was within an order of magnitude in each case and the relative rates were correctly predicted. The standard free energy of the reactant pair was predominant in determining the rates.



(4)

R^1 = H, Ac, Ac, $CH{=}CH_2.CO_2H$
R^2 = H, H, Ac, H, H

(5)

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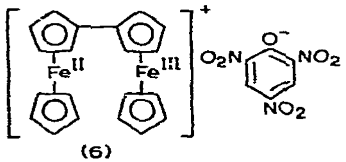
[*] Oc = osmocene; Rc = ruthenocene; Fc = ferrocene

Dove and Carty found that acylferrocenes were oxidized to the ferricinium cations by silver tetrafluoroborate as in the equation:

$$\mathrm{FcCOR + AgBF_4 \xrightarrow{Et_2O} (FcCOR)^+BF_4^- + Ag}$$

1,1′- and 1,3-diacetylferrocene initially formed complexes with $AgBF_4$ without oxidation. When these complexes were exposed to liquid SO_2 the ferricinium salts were formed[23].

Intramolecular electron exchange in the diferrocene $[Fe^{II}Fe^{III}]$ picrate (6) [AS70; p.77] has been studied by spectroscopic methods and by comparison with the diferrocene $[Fe^{III}Fe^{III}]$ fluoroborate (7)[24]. The mixed valence band observed for the picrate (6) at 1850 nm has been assigned to electron transfer between the Fe^{II} and Fe^{III} atoms. The NMR results suggested a very rapid electron transfer and the temperature dependance of the Mössbauer spectrum was consistent with an exchange process taking place at a rate $< 10^7$ sec^{-1} in the solid state. Polarographic half wave potentials were measured for a range of ferrocenophanes (8) and their olefin, alkyl and ketone derivatives. Comparisons with ferrocene and substituted ferrocenes suggest that structural, conformational and electronic effects were important in determining the observed oxidation potentials[25]. Polarography has been used also to show that the reduction of nitroferrocene to ferrocenylhydroxylamine occurred in two stages, the first, a one-electron step affords an intermediate anion-radical and this was reduced to the product in a three-electron step[26]. In a subsequent investigation[27] the cathodic reduction of nitroferrocene at an amalgamated gold electrode gave ferrocenylhydroxylamine (9) that was unstable and disproportionated to aminoferrocene (10) and the anion (11). Evidence for the proposed formation of the cyclopentadienide ion (12) was presented.



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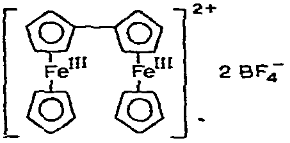

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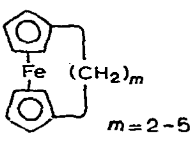
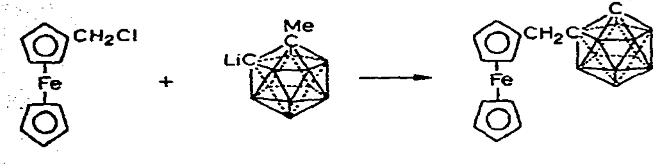


(8)

$$\mathrm{FcNHOH + (FcNH_2OH)^+ \longrightarrow FcNH_2 + (C_5H_5NO)^- + (C_5H_5)^- + Fe^{2+} + H_3O^+}$$

(9) (10) (11) (12)

The reduction potentials of four *o*- and *m*-carboranylferrocenes have been measured potentiometrically and the substituent constants calculated[28]. The ferrocenyl group was introduced by direct reaction between chloromethylferrocene (13) and a lithio-carborane such as 1-methyl-2-lithio-*o*-carborane (14) to give the ferrocenylcarborane (15) or by treatment of ferrocenylacetylene with decaborane and methyl cyanide in toluene to give the carborane (16). The formation and reactions of ferrocene zwitterions (internal ferri-



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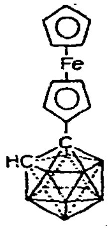
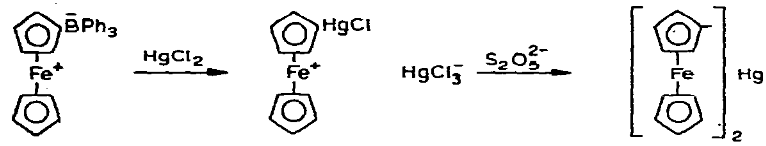


(16)

cinium salts) has been examined[29]. For example, treatment of ferrocenylboronic acid with the phenyl Grignard reagent gave the green triphenylferricinium borate (17) and this was converted to the blue chloromercuriferricinium salt (18) with mercuric chloride. Subsequent reduction of the salt (18) with bisulphite gave diferrocenylmercury (19). Cowan

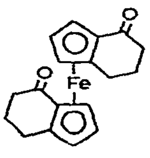


(17) (18) (19)

and coworkers[30] have investigated symmetry distortions in ferricinium compounds (see above) in the solid state by magnetic susceptibility and electron spin resonance measurements over the temperature range 2 to 300 K. The biferrocenes (6 and 7) showed larger distortions from axial symmetry than those observed previously when the experimentally determined values for effective magnetic moment were compared with theoretical curves. The ESR results were in good agreement with the distortions determined by the susceptibility measurements. A large reduction in the distortion factor for the dication (7) was indicated at low temperatures. When ferrocene, acetylferrocene and acetoacetylferrocene were treated with 1/1 stoichiometric amounts of Cu^{II} or Fe^{III} in acetonitrile they were oxidized to the corresponding ferricinium ions[31]. The kinetics of this oxidation by Cu^{II} and the effects of transition metals on the redox potentials of the ferrocenes were examined polarographically at a rotating Pt electrode.

Spectroscopic studies. Iogansen[32] has used his model based on collective electronic movements to calculate the excitation energies for the electronic levels in ferrocene. Good agreement with the experimentally determined values was obtained when participation by 6 π-electrons was assumed. The ultraviolet spectra of ferrocene and ferrocenyl groups directly bound together (diferrocene and terferrocene) have been compared with ferrocenyl groups linked through one or two methylene bridges (1,1- and 1,2-diferrocenylethane)[33]. Di- and terferrocene showed bathochromic shifts that increased with the size of the molecule and stronger absorption in the visible than the ferrocenylalkanes. The components of the bands at 27 765–31 600 and 19 870–22 470 cm^{-1} in the electronic absorption spectrum of ferrocene at 4.2 K have been observed and the vibrational spacings within each band have been determined[34]. Falk and Lehner[35] have used the relationship between rotatory and dipole strength of the "ferrocene band" near 440 nm in the optically active ketone (20) and the corresponding diol to show that the transition was forbidden on both electrical and magnetic grounds. These results were used in a discussion of the origin of optical activity in some ferrocene derivatives and the relationship of this property to molecular configuration.

Slocum and Stonemark[36] have studied the temperature dependence of the PMR spectrum of 1-isopropyl-2-dimethylaminomethylferrocene (21) in aromatic solvents. The amine (21) contains two groups that exhibit geminal magnetic nonequivalence, the protons of the *N*-methylene group show a smooth decrease in chemical shift difference with decreasing temperature while the isopropyl methyl groups show an initial decrease followed by an increase in chemical shift difference with decreasing temperature. The *syn–anti* isomerization of imines derived from benzoylmetallocenes (22) has been studied by examination of the temperature dependence of the PMR spectra[37]. The effect of a ferrocenyl group bound to nitrogen on the configurational stability of tertiary amines (23) has been investigated by the same technique. It was concluded that the ferrocenyl group does not exert any unusual electronic effect[38]. The dibenzyl mercaptal (24), prepared by lithiation of dimethylaminomethylferrocene, conversion to the formylferrocene and treatment of the product with benzylmercaptide showed magnetically nonequivalent *N*-methylene protons[39] (see also AS68; p.381). The reaction between ferrocenylmercury chloride and halogens has been studied by nuclear quadrupole and electron paramagnetic resonance[40]. At -20°C in CH_2Cl_2 the mercury chloride formed insoluble, blue 1/1 adducts with chlorine and bromine that appeared to contain the ferricinium cation associated with a radical anion through the mercury (25; X = Cl, Br).



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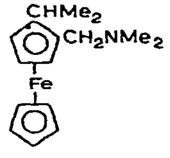

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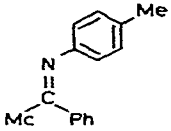

Mc = Fc, Rc
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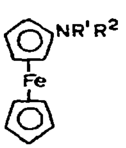

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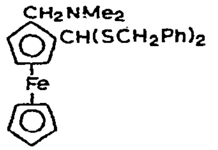

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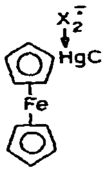
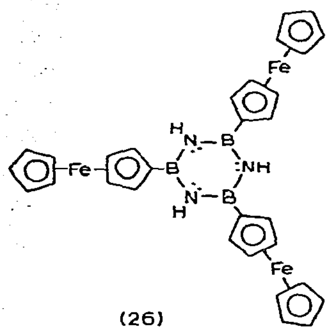


(25)

Treatment of the complex (25; *X* = Br) with thiosulphate gave diferrocenyl mercury which was converted to bromoferrocene by successive reaction with bromine in CH_2Cl_2 and $Na_2S_2O_3$. Iodoferrocene was obtained directly by treatment of the complex (25) with iodine. Kotz and Painter have described the preparation of the interesting *B*-triferrocenylborazine (26) from ferrocenyldichloroborane and ammonia[41]. Cyclic voltammetry of the borazine gave a reversible oxidation at +0.37 V, compared with ferrocene at +0.48 V. This oxidation involved the removal of three electrons. Controlled potential coulometry showed that this was a simultaneous process. The mass spectrum at 70 eV showed only the parent molecule ion and the doubly charged molecule ion with no fragmentation. Ferrocene–borazine π-interaction has been advanced as an explanation for these properties. The laser–Raman spectrum of ferrocene-d_{10} was measured for the crystal and in solution[42]. The results obtained supported the previous assignments made for ferrocene[43].

Structural determinations. The crystal structure of the hydrated salt (27) has confirmed its formulation as the tetrachlorozincate[44]. The cyclopentadienyl rings deviate by only 7° from the eclipsed position and the bond distances and angles in the ferrocenyl group are normal. X-ray crystallography[45] has been used also to confirm the structure of 1-acetyl-1′-benzoylferrocene. The phenyl ring was rotated out of the plane of the cyclopentadienyl ring by 43°37′. The crystal and molecular structure of [1,1,1]ferrocenophane was determined by X-ray crystallography[46]. The compound crystallizes in the monoclinic system, space group $P2_1/c$, the unit cell dimensions are, $a = 6.008(3)$, $b = 18.906(9)$, $c = 22.53(1)$ Å; $\beta = 108.52(1)°$; with four trimers per unit cell. There are three ferrocene units joined by methylene groups to form a single large ring (28). The iron atoms almost form an equilateral triangle with an average Fe–Fe distance of 6.09 ± 0.09 Å. From the data obtained it was concluded that the non-bonded hydrogen–hydrogen repulsions are the predominant factor in determining the conformation of molecules of this type. The crystal structure of FcCH=CHCN was investigated by Weissenberg X-ray techniques. The alignment of the acrylonitrile group is flat and almost coplanar with respect to the cyclopentadienyl ring. The crystals of the nitrile which is asymmetric were composed of one optical isomer[47] either *d* or *l*. The structure of *N*-formylaminomethylferrocene ($FcCH_2NHCHO$) was determined by the same technique[48]. It has space group $P2_1/c$ with $a = 8.9161$, $b = 14.3329$, $c = 16.6763$ Å, $\beta = 90.758°$; $Z = 8$. It was found that the molecule had two possible configurations (29) and (30). A structural analysis of 2-(triferrocenylmethyl)-tetrahydrofuran (31) showed it to have a triclinic space group $P\bar{1}$ with $a = 10.943$, $b = 14.434$, $c = 17.237$ Å, $\alpha = 98.7°$, $\beta = 95.0°$ and $\gamma = 96.3°$, $d = 1.60$[49]. The



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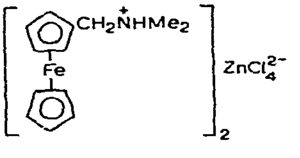

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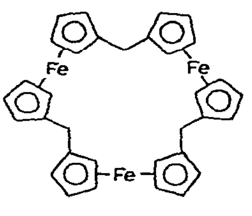

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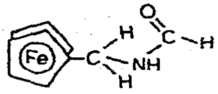

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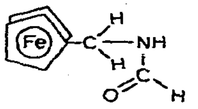

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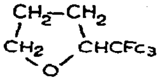
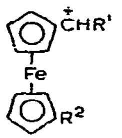


(31)

asymmetric part of the unit cell contains two molecules and the cyclopentadienyl rings are effectively planar.

Ferrocenylcarbonium ions. Determinations of pK_{R^+} for the α-ferrocenyl carbonium ion (32) have been made by a spectroscopic method in the presence of heteroannular electron releasing and electron-withdrawing substituents (R_2)[50]. The latter substituents reduced the stability of the carbonium ion. The rates of solvolysis for ferrocenylcarbinol acetates were correlated with the pK_{R^+} values of the corresponding carbonium ions [see AS 70; p.81). The α-ferrocenylcarbonium ions (33 and 34) were formed by dissolving the corresponding α-ferrocenylcarbinols in 100% trifluoracetic acid at -10°[51]. Analysis of the PMR spectra of the carbonium ions by spin decoupling confirmed the long range coupling between the carbinyl hydrogen (H_6 in 35) and the ring hydrogen atoms H_2 and H_3. These results, and the high field chemical shifts observed for H_2 and H_5 lead the authors to propose a model for the carbonium ion where the trigonal carbinyl carbon atom was co-planar with the cyclopentadienyl ring. The ring carbon atoms were not bound equally to the iron atom and steric effects brought H_5 near to iron (35). A low temperature PMR study was carried out on ferrocenylketones in $CDCl_3SO_2FSO_3H$ solutions. It was found that the protonated ketones (36) showed spectra similar to those of the corresponding ferrocenylcarbinyl cations (37). The authors suggested that the same type of electron donation from the ferrocenyl group was important in both cases[52]. They also point out that these proposals support Traylor's hypothesis that electron release from the ferrocenyl group in ferrocenylcarbinyl cations occurs by a conjugative mechanism, such as iron–carbon conjugation (38)[53].



R'=H,Me

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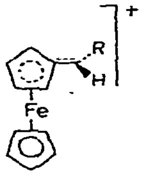

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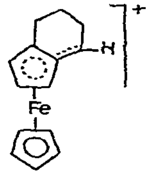

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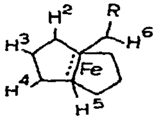

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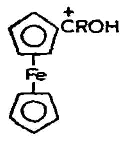

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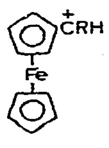

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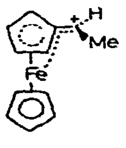

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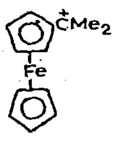
Ferrocenylethylenes dissolved in 90% formic acid to give solutions of α-ferrocenyl carbonium ions in equilibrium with the unprotonated species[54]. These combined by an ionic addition mechanism to give dimeric carbonium ions which can cyclize by both homo- and hetero-annular pathways. For example, 2-ferrocenylpropene in formic acid gave the α-ferrocenylcarbonium ion (39) which attacked the unprotonated olefin to give the dimeric carbonium ion (40). This carbonium ion cyclized to give the homo-annular (41) and hetero-annular (42) products. Stable [3]- and [4] ferrocenophane carbonium



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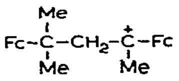
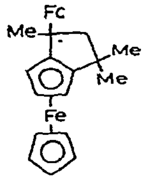


$\mathrm{Fc{-}\overset{Me}{\underset{Me}{C}}{-}CH_2{-}\overset{+}{\underset{Me}{C}}{-}Fc}$

(40)



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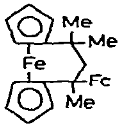
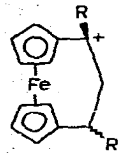


(42)

ions (43 and 44) respectively were obtained from the corresponding alcohols which were formed by Grignard reaction or reduction of the corresponding ketones[55]. The PMR spectra revealed larger coupling constants between cyclopentadienyl ring *ortho* protons in the ring that was adjacent to the cationic centre [top ring in (43)] than those observed in the rings remote from it [bottom ring in (43) and both rings in (44)]. These differences were interpreted in terms of interaction between the cationic charge and the cyclopentadienyl π-electrons or the iron atom. Sonda and Moritani[56] used the ferrocene diester (45), prepared from 1,1′-diacetylferrocene (see scheme) in the synthesis of the ferrocenophane (46). The tosylhydrazone of this ketone was prepared and its sodium salt thermally



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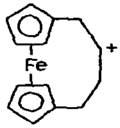

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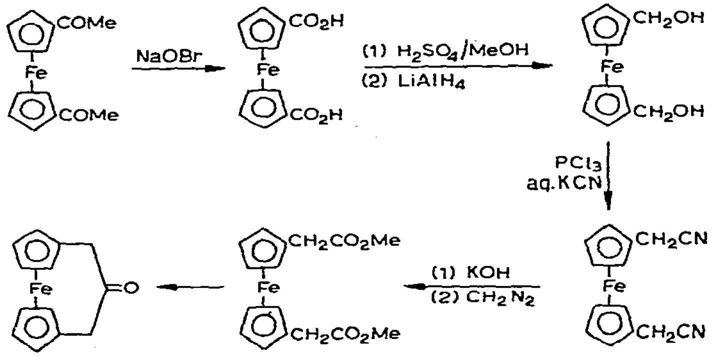

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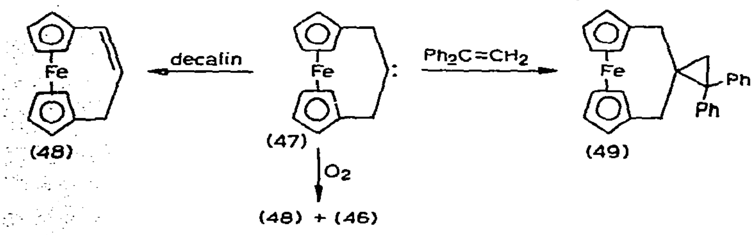
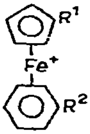


decomposed to give the carbene (47). This intermediate (47) in decalin gave the olefin (48), with oxygen it formed (46 and 48) and with diphenylethylene the cyclopropane (49) was obtained.

Reactions of ferrocene. The electrochemical behaviour of cyclopentadienyl complexes has been studied in aqueous solution. A new method for the preparation of ferrocene by the electrolysis of cyclopentadienylthallium(I) in $HCONMe_2$ with an iron anode was described[57]. In the preparation of the π-cyclopentadienyl-π-benzeneiron cations (50) from substituted ferrocenes (51) and benzenes by ligand exchange, it was found that small alkyl substituents (51; R = Et) facilitated the ligand exchange whilst larger alkyl and aralkyl groups (51; R = n-Pr, $CHMe_2$, CH_2Ph) inhibited the exchange because the steric retardation was greater than the accelerating effect of the electron-releasing substituent[58]. PMR spectroscopy was used to measure the relative nucleophilicities of ligands as follows; π-C_6H_6 in (50; $R_1 = R_2 = H$) < π-C_5H_5 in (50; $R_1 = R_2 = H$) < C_6H_6 < π-C_5H_5 in ferrocene, and a mechanism of ligand exchange was proposed. The [2] ferrocenophanes

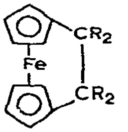


R^1 = H, Me, Et, n-Pr, $CHMe_2$, CH_2Ph;
R^2 = Me, Et, n-Pr, $CHMe_2$, CMe_3, Ph

(50)

FcR

(51)



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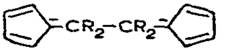
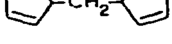


(53)

(52; R = H, R = Me) have been prepared by coupling of the dianions (53; R = H, R = Me) with $FeCl_2$[59]. The failure of the compounds to undergo Friedel–Crafts acetylation or metallation with n-butyllithium, and their spectroscopic properties, were discussed in terms of the ring-tilted structures. Treatment of dicyclopentadienylmethane with n-butyllithium gave the dianion (54) which was coupled with iron(II) chloride in THF to afford di-, tri- and tetranuclear cyclic ferrocenes (55, 56, 57) respectively, together with higher oligoferrocenes[60]. The dimer, [1,1] ferrocenophane (55) was air labile and gave a mixture of partially oxidized products including the dione (58).



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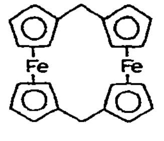

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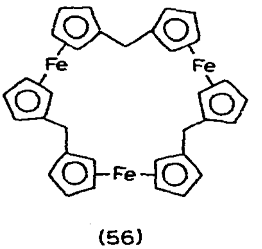

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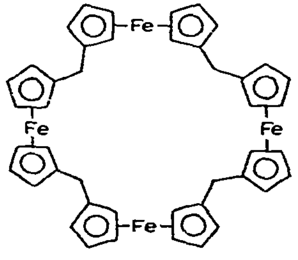

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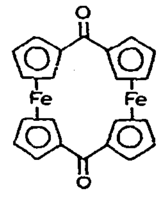
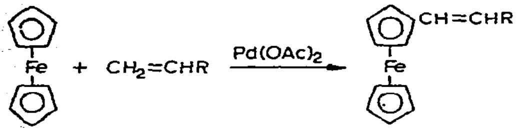


(58)

An improved route to diferrocenylphenylphosphine and diphenylferrocenylphosphine, using the phenylchlorophosphine, aluminium chloride and ferrocene, was reported by Sullivan and McEwen[61]. Ferrocenyl olefins (59) were prepared by the direct reaction of ferrocene with an olefin in the presence of palladium(II) acetate. The reactivity of the olefin towards ferrocene was increased when it was substituted with an electron-withdrawing group[62]. A one-step synthesis of 1,2-(α-ketotetramethylene)ferrocene (60) was achieved by heating together ferrocene and γ-butyrolactone in the presence of $AlCl_3$[63]. Ferrocene was condensed with PhNCO in the presence of Lewis acids to give FcCONHPh; under similar conditions ferrocene was condensed also with $2,4\text{-}Me_2C_6H_3OCN$ and 1,2-naphthoquinone to give (61) and (62) respectively[64]. When the ethoxycyclopentadienyl-iron carbonyl (63) was heated 1,1′-diethoxyferrocene was formed. Ethoxyferrocene was produced by treating the ethoxycyclopentadienyl derivatives (64) and (65) with sodium cyclopentadienide[65]. Irradiation of cyclopentadienyl iron carbonyls (66 and 67) in the presence of Hg gave ferrocene together with some mercury containing iron carbonyls[66].



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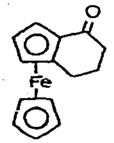

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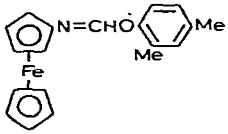

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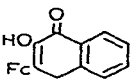

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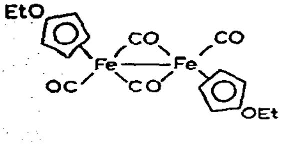

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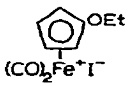

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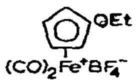

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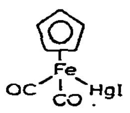

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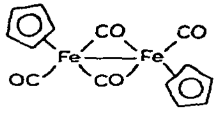
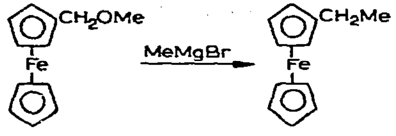


(67)

Decacyanoferrocene was prepared from silver pentacyanocyclopentadienyl and $FeCl_3$ in MeCN[67].

Ferrocene chemistry. Stephens and co-workers have reported a convenient route to alkylferrocenes through cleavage of the ethers of hydroxymethylferrocene by Grignard reagents in benzene. Thus the alkylferrocene (69) was obtained in 90% yield from the ether (68) and methylmagnesium bromide[68]. The reaction of acetylferrocene with methylmagnesium iodide has been reinvestigated. Under forcing conditions the principal products were t-butylferrocene, 2-ferrocenylpropene and the olefins (70 and 71)[69]. Using similar conditions, 2-ferrocenyl-2-propanol gave the same range of products, reaction mechanisms



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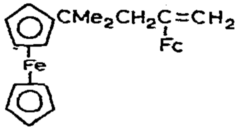

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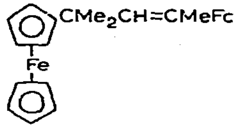
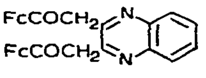


(71)

were discussed. The novel methylation at the α-ferrocenyl carbon was shown to be general by the efficient alkylation of ferrocenylphenylmethanol with a range of Grignard reagents.

Acetylferrocene was treated with sodium in ethanol and then diethyloxalate to give 1,6-diferrocenyl-1,3,4,6-hexanetetrone or 2,4-dioxo-4-ferrocenylbutyric acid depending on the reaction conditions[70]. Condensation of the tetrone with *o*-phenylenediamine and phenylhydrazine gave (72) and (73) respectively, and treatment of the ferrocenylbutyric acid with phenylhydrazine and 1,2-diaminoethane gave (74) and (75). The condensation of acetylferrocenes with tosylhydrazine gave the corresponding tosylhydrazones[71].



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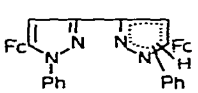

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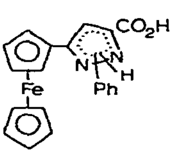

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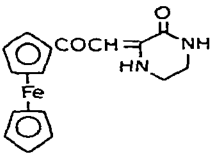
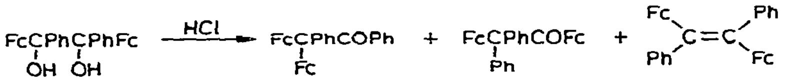


(75)

Triphenyltin hydride in acetyl chloride has been used to reduce acylferrocenes FcCOR, to the corresponding alkylferrocenes $FcCH_2R$[72]. This reaction was shown to proceed via the acetate $FcCRHOCOCH_3$ which gave FcCRHCl with the acetyl chloride and the chloride was reduced by the triphenyltin hydride. In the absence of the tin hydride no reduction occurred. α-Ferrocenyl-β-benzoxazolylethylene was prepared by the reaction of formylferrocene with 2-methylbenzoxazole in the presence of sodium amide or by treatment of the imino ester $FcCH{=}CH({=}NH_2Cl)OMe$ with *o*-aminophenol[73].

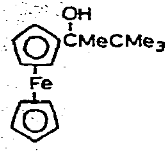
Rausch and Pryde have repeated the work of Weliky and Gould[75] on the reduction of benzoyl ferrocene to the pinacol (76) and the rearrangement of this compound. They found that the pinacol rearranged to the pinacolone (77) which was in agreement with the earlier conclusion but two other products (78) and (79), were isolated. When pivaloylferrocene ($FcCOMe_3$) was treated with MeMgBr and $CoCl_2$ both ferrocene and the



$$\underset{\text{OH}\ \ \text{OH}}{\text{FcCPhCPhFc}} \xrightarrow{\text{HCl}} \underset{\text{Fc}}{\text{FcCPhCOPh}} + \underset{\text{Ph}}{\text{FcCPhCOFc}} + (\text{Fc})(\text{Ph})\text{C}{=}\text{C}(\text{Ph})(\text{Fc})$$

(76) (77) (78) (79)

Grignard addition product (80) were isolated[74]. When benzoylferrocene was reduced under Clemmensen conditions, benzylferrocene and nine bimolecular reduction products were isolated[76]. The product obtained from the reaction between ferrocenylacetonitrile and methylmagnesium chloride was the amino nitrile (81)[77] and not the ketenimine (82) as previously reported.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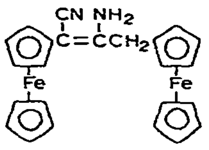
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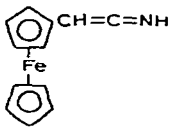
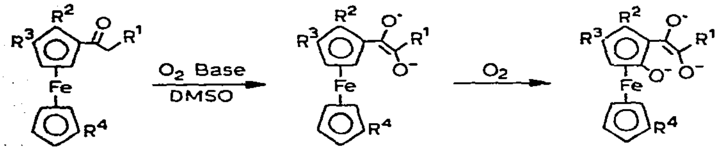
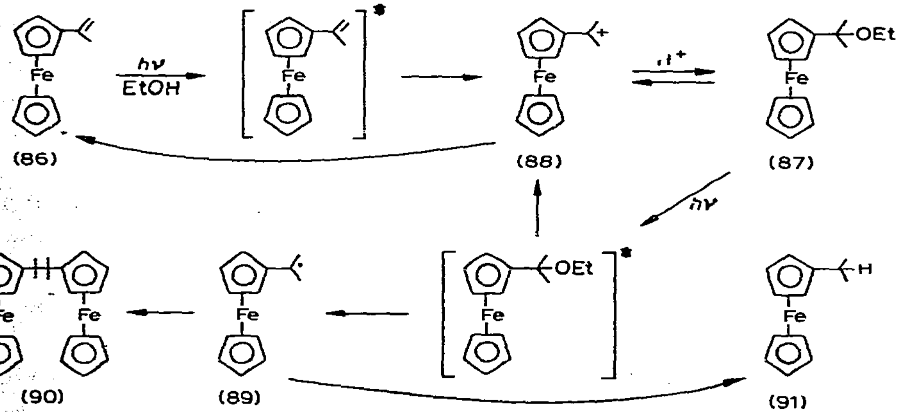

(82)

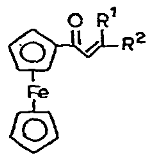
McDonnell and Pochopien have reported the full details of the oxidation of metallocenyl ketones to stable paramagnetic semidiones [AS 69; p.669]. The oxidations of 23 ferrocenyl ketones (83) and a ruthenocenyl ketone by oxygen in dimethyl sulphoxide to the semidiones (84) were studied by EPR spectroscopy[78]. The results showed little electron-spin delocalisation into the cyclopentadienyl rings and enabled the relative rates of semidione formation to be correlated with the substituents. The interannular electronic effects of substituents were considered to be mainly inductive in nature. The slow rate of hydrogen–deuterium exchange at the alkyl groups α to the semidione implicated a dianion intermediate in the exchange process. An excess of oxygen in the oxidation of (83) caused the product (84) to suffer oxygenation in the 2-position of the metallocene ring (85).



Baker and Horspool[79] have studied the photolysis of ferrocenyl olefins (86) and ethers (87). To explain the range of products obtained a reaction scheme involving both carbonium ion (88) and radical intermediates (89) was proposed. In a typical experiment the olefin (86) afforded the ether (87) and the corresponding alcohol together with the alkene (91) and the coupled product (90).



Cyclopropylferrocenylketones (93) were prepared by the addition of dimethylsulphoxonium methylide to the corresponding unsaturated ketone (92). The ketones (93) were transformed into the olefins (94) via the Wittig reaction[80].



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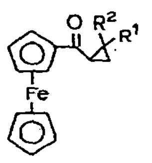

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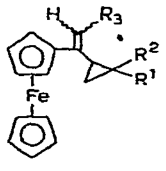
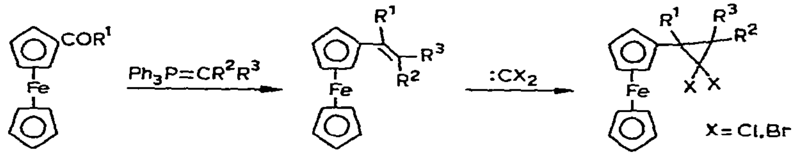


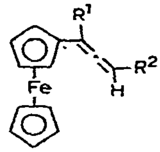
(94)

A series of substituted ferrocenyl olefins (96) were obtained by treatment of ferrocenyl ketones (95) with Wittig reagents. These olefins were converted to cyclopropane derivatives (97) by reaction with dichloro- and dibromo-carbenes[81]. The reaction of the dibromo-



(95) (96) (97)

(ferrocenyl)cyclopropanes (97, R^3 = H) with n-BuLi gave the corresponding ferrocenyl allenes (98) as the initial products but after a short time isomerization gave the ferrocenylmethylacetylenes (99). The ferrocenylcyclopropanes (100) were converted into ferrocenylbutadienes by heating with sodium carbonate in acetonitrile or ethanol. It was suggested that the butadienes were formed by deprotonation of the intermediate ferrocenylallyl cation (101) from the ring opening of the cyclopropane with elimination of bromide[82,83]. 2-Ferrocenylbutadiene has been shown to participate in the Diels–Alder reaction with typical dienophiles such as maleic anhydride and *p*-benzoquinone to give 1/1 adducts[84].



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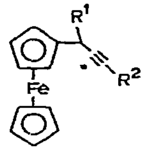

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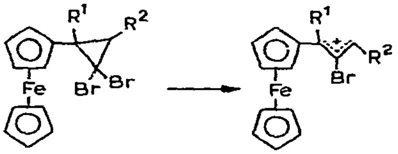
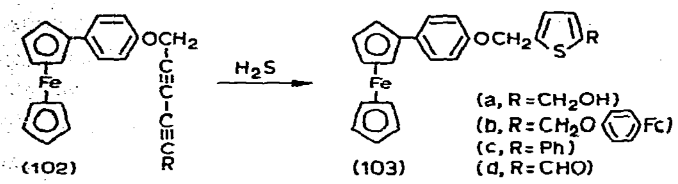


(100) (101)

The diene was prepared by treatment of acetylferrocene with vinylmagnesium bromide and dehydration of the resulting 2-hydroxy-2-ferrocenylbutene with methyl chloroformate in pyridine. An improved method for the synthesis of 1-ferrocenyl-1,3-butadiene from formylferrocene, n-butyllithium and allyltriphenylphosphonium bromide has been described[85].

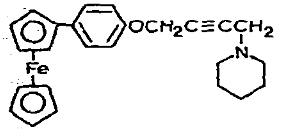
The hexadiynes (102a, b) were cyclized by H_2S or NaSH in organic solvents to form the corresponding thiophenes (103a, b), the pentadiyne (102c) cyclized in the same way to give (103c)[86]. The formylthiophene (103d) was obtained on oxidation of (103a) by



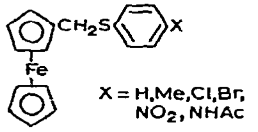
(102) (103)

manganese dioxide in $CHCl_3$. The conjugated acetylenes (102a, b, c) were formed by condensation of the appropriate monosubstituted acetylenes in the presence of pyridine[87]. The same group of workers has prepared the heterocyclic derivatives of some *p*-ferrocenylphenol-substituted acetylenes by condensation of the acetylene with paraformaldehyde or formalin and the heterocycle. With piperidine the derivative (104) was obtained[88].

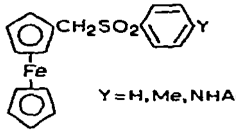
Nine ferrocenylmethyl sulphides (105) and sulphones (106) have been prepared by treating the methiodide of dimethylaminomethylferrocene with alkaline *p*-substituted thiophenols or the sodium salts of *p*-substituted phenylsulphinic acids[89]. The thermolysis



(104)

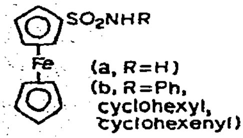


(105)

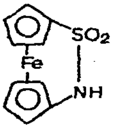


(106)

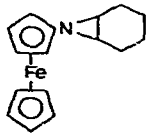
of ferrocenylsulphonyl azide gave the sulphonamide (107a) and the corresponding solvent adduct (107b), together with ferrocene. Photolysis of the azide gave the same sulphonamide (107a) and the intramolecular insertion product (108) with small proportions of ferrocene[90]. Competition between $FcSO_2N{-}N_2$ and $FcSO_2{-}N_3$ cleavage is discussed and mechanisms for the thermal and photochemical decompositions are proposed. The thermolysis and photolysis of ferrocenyl azide in benzene gave the expected triplet nitrene products, azoferrocene (FcN=NFc) and aminoferrocene ($FcNH_2$). Products of $Fc{-}N_3$ bond cleavage were also isolated, that is ferrocene and phenylferrocene, which suggested that the ferrocenyl radical was an intermediate. In the presence of oxygen nitroferrocene was isolated in good yield. When the reaction was carried out in cyclohexene C–H insertion products were obtained as well as the aziridine (109). This was claimed as the first example of the addition of an arylnitrene to an olefin to give an aziridine[91,92].



(107)

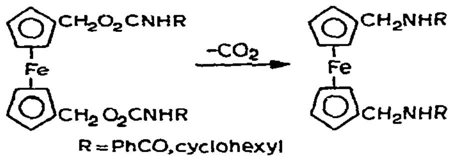


(108)



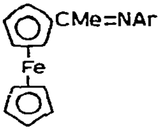
(109)

The carbamoylferrocene (110) was prepared from 1,1′-bis(hydroxymethyl)ferrocene and benzoyl or cyclohexyl isocyanate in toluene[93]. In the absence of solvent CO_2 was eliminated to give a product (111) containing secondary amine groups. Hydroxymethylferrocene underwent similar addition with adipoyl and sebacoyl isocyanates, to form, after elimination of CO_2, the diamide (112). Aromatic amines have been condensed with acetylferrocene in toluene containing alumina to give the α-ketimines (113)[94]. Vishnyakova and coworkers have described similar condensations between substituted acetylferrocenes (114) and diamines to form di-imines (115)[95].

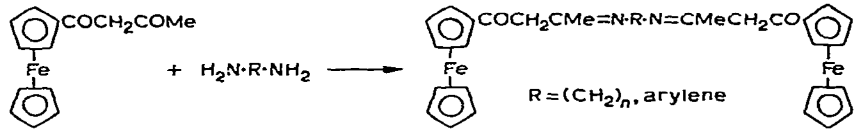


(110) (111)

(112)

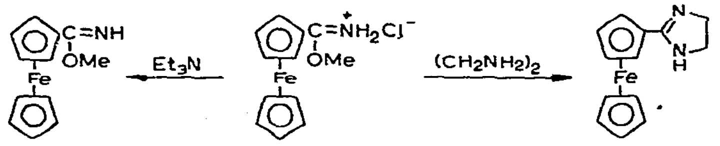


(113)



(114) (115)

The preparation and reactions of ferrocenylimino ester salts (116) have been reported by Nametkin and coworkers[96]. Treatment of cyanoferrocene with hydrogen chloride in ether–methanol gave the imino-ester (116) in 89% yield. The ethyl homologue was obtained in the same way. Pyrolysis at 145°C gave ferrocenecarboxamide whilst hydrolysis afforded the corresponding ferrocenecarboxylic esters. The free imino ester (117) was liberated from the salt (116) with Et_3N in Et_2O in good yield. Ferrocenyl heterocycles were obtained by condensation of the imino ester salt (116) with the appropriate diamine, thus ethylenediamine gave the derivative (118) in 99% yield.

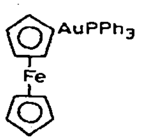


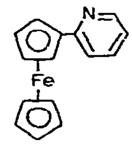
(117) (116) (118)

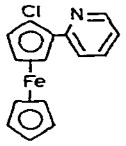
Esters were formed between two unsaturated alcohols ($CH{\equiv}CCH_2OH$ and $N_3CH_2CH_2OH$) and the acid chlorides of ferrocenecarboxylic acid and ferrocene-1,1′-dicarboxylic acid[97]. The acetylenic protons on the two esters with acetylene groups were replaced by copper. Sato and coworkers[98] have studied the condensation of haloferrocenes with carboxylic acids in the presence of copper(I) oxide to afford the corresponding ferrocenyl carboxylates. The mechanism and the synthetic utility of the reaction were examined. In a related investigation[99], these workers have investigated the catalytic activity of tetrakis(acetonitrilo)copper(I) perchlorate in $MeNO_2$ in the conversion of haloferrocenes to biferrocene. When triphenylphosphine was present the product was ferrocenyltriphenylphosphonium perchlorate. This reaction was markedly solvent dependent and a mechanism was proposed. The synthesis of fluoroferrocene has been achieved by the treatment of lithioferrocene with ClO_3F[100]

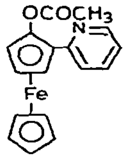
The gold complex (119) was brominated in CCl_4 at -20° to give, after evaporation, bromoferrocene as the major metallocene product (55%) together with biferrocene (18%) and bromotriphenylphosphinegold(I) (70%)[101]. Chlorination under similar conditions gave chloroferrocene (26%) and biferrocene (70%) with chlorotriphenylphosphinegold(I) while iodination gave only iodoferrocene (82%) and iodotriphenylphosphinegold(I) (98%).

The mass spectrometric study of two series of chloroferrocenes $(C_5H_{5-n}Cl_n)Fe(C_5H_5)$ and $(C_5H_{5-n}Cl_n)_2Fe$ has been described, and the effect of incremental addition of chlorine was examined[102]. The molecular ion was the most intense peak in each case and primary fragmentation processes were described.


(119)


(120)


(121)

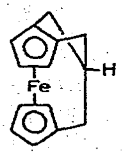

(122)

Competition between metallation of the ferrocenyl group and addition across the carbon–nitrogen double bond in 2-ferrocenylpyridine (120) has been studied in light petroleum, THF and TMEDA[103]. A different range of products was obtained in each case, products with light petroleum were similar to those obtained previously in ether. Heteroannular dimetallation was observed in petroleum and TMEDA but not in THF. t-Butyllithium in ether was effective as a metallating agent and underwent addition to the carbon–nitrogen double bond while methyllithium behaved only as a monometallating agent.

The methiodide of the pyridylferrocene (121) was prepared and irradiated in dilute sulphuric acid to give 1-methylpyridinium-2-(2-chlorocyclopentadienylide). Treatment of pyridylferrocene (121) with copper acetate gave the acetate (122)[104].

Nitroferrocene was studied polarographically and in anhydrous acetonitrile it showed two diffusion controlled polarographic waves[105]. The first corresponded to a reversible one electron reduction and the second to an irreversible three electron reduction.

An unsuccessful attempt was made to prepare the bridgehead bridged ferrocene (123)[106]. The cyclic ketone (124) was prepared but this only underwent partial reduction to give the alcohol and (123) was not obtained.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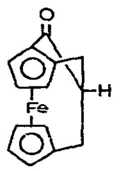
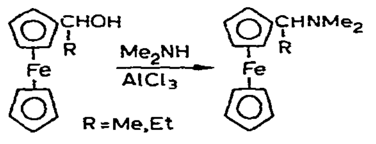
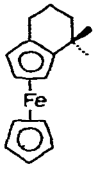

(124)

A convenient route to *N,N*-dimethylaminomethylferrocenes has been described by Dixneuf[107]. The 1-ferrocenyl alcohols (125) were treated with dimethylamine and aluminium chloride in 1,2-dichloroethane to give the corresponding amines (126) in 80% yields. Both the *endo* (127a) and *exo* (127b) cyclohexenols gave the *exo*-amine (127c) in 80% yield indicating *exo* attack by the reagent on the intermediate carbonium ion. Hydrolysis of the *exo*-methiodide (127d) to the alcohol (127b) was complete in 5 min, under the same conditions the *endo*-methiodide (127c) required 6 days for complete hydrolysis. The optically active amine (128) was converted successively to the methiodide, the alcohol and the starting amine by the same reactions with retention of configuration.

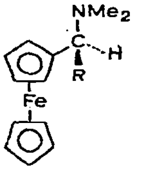


(125) (126)



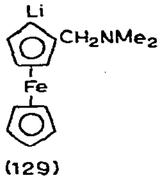
(127)

a, R^1=H, R^2=OH
b, R^1=OH, R^2=H
c, R^1=H, R^2=NMe_2
d, R^1=NMe_3I, R^2=H
e, R^1=H, R^2=NMe_3I

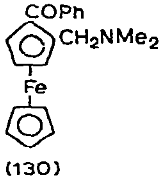


(128)

N,N-Dimethylaminomethylferrocene was lithiated and the 2-lithio intermediate (129) was condensed with benzaldehyde to give the ketone (130) and with ethylene oxide to give 2-(β-hydroxyethyl)-*N,N*-dimethylaminomethylferrocene[108, 109].

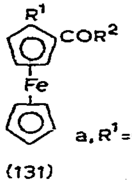


(129)



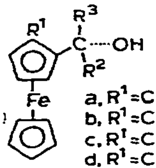
(130)

Stereochemistry of ferrocenes. Grignard addition to the aldehyde or ketone (131) was found to afford only alcohols with the relative configuration (132) rather than (133)[110]. This result was rationalised in terms of the preferred stereochemistry of the transition state. Reduction of (131a) with potassium borohydride was less selective and gave mixtures of the alcohols (132f, 90% and 133f, 10%). The stereoselectivity was lost when a chiral rather than an achiral reagent was used. Thus 1-dimethylaminomethyl-2-lithioferrocene on treatment with ketones gave the two diastereoisomeric products (132 and 133) in equal amounts. The selective preparation of alcohol (132 or 133) was achieved by inverting the order in which the substituents R^2 and R^3 were introduced.



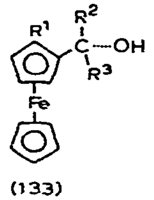
a, R^1=CH_2NMe_2, R^2=Me

(131)



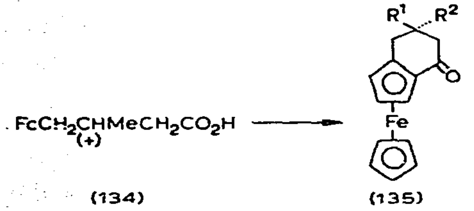
(132)

a, R^1=CH_2OH, R^2=Me, R^3=H
b, R^1=CH_2NMe_2, R^2=Et, R^3=Me
c, R^1=CH_2NMe_2, R^2=Me, R^3=Et
d, R^1=CH_2NMe_2, R^2=Ph, R^3=Et
e, R^1=CH_2NMe_2, R^2=Et, R^3=Ph
f, R^1=CH_2NMe_2, R^2=H, R^3=Me



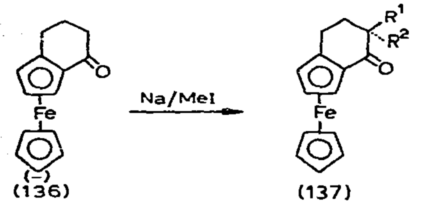
(133)

The cyclization of the (+)-butyric acid (134) under Friedel–Crafts conditions gave a mixture of the ketones (135a and b)[111]. The methylation of the (–)-cyclohexenone (136) also failed to show stereoselectivity and gave a mixture of (137a and b). The ketones (137a and b) and the corresponding enantiomers were reduced with $LiAlH_4$ to give eight alcohols, four (–)-ferrocenecyclohexenols with an *Rp* chirality and four (+)-alcohols with an *Sp* chirality. The conformations of the alcohols were discussed.



(134) (135)

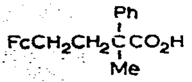
a, R^1 = Me, R^2 = H
b, R^1 = H, R^2 = Me
c, R^1 = Ph, R^2 = Me
d, R^1 = Me, R^2 = Ph



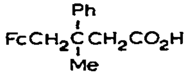
(136) (137)

a, R^1 = H, R^2 = Me
b, R^1 = Me, R^2 = H
c, R^1 = Ph, R^2 = Me
d, R^1 = Me, R^2 = Ph

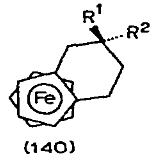
In a related investigation ferrocene was acylated with the acid chlorides $MeO_2CCMePhCH_2COCl$ and $MeO_2CCH_2CMePhCOCl$. After saponification and reduction the acids (138 and 139) were obtained[112]. The acids were cyclized with trifluoroacetic anhydride to give two pairs of ketones (137c and d, and 135c and d) which were reduced to give two cyclohexenes (140a and b).


$\mathrm{FcCH_2CH_2\overset{Ph}{\underset{Me}{C}}CO_2H}$

(138)


$\mathrm{FcCH_2\overset{Ph}{\underset{Me}{C}}CH_2CO_2H}$

(139)

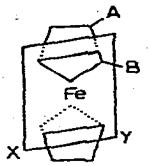


(140)

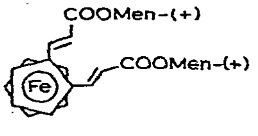
a, R^1 = Ph, R^2 = Me
b, R^1 = Me, R^2 = Ph

1,2-Disubstituted ferrocenes possess a chirality plane XY (141) and Goldberg synthesized molecules where the different achiral substituents (A and B) were replaced by two constitutionally identical but chiral groups. Two identical groups of the same chirality replaced A and B to give two enantiomers (142 and 143) and two groups of the opposite chirality gave two achiral diastereoisomers (144 and 145). In these last two molecules the XY plane is a plane of pseudochirality or pseudoasymmetry. Each of these isomers was prepared from 1,2-diformylferrocene and the appropriate carbomenthoxyacetic acid[113] The absolute configuration of these pseudoasymmetric compounds was also determined by Goldberg[114].

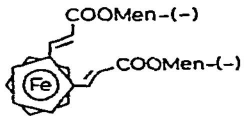
The nucleophilic substitution of dimethylamine for the acetate group in (*R*)-α-ferrocenylethylacetate (146) proceeded with retention of configuration[115]. The amine product



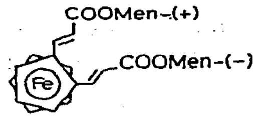
(141)



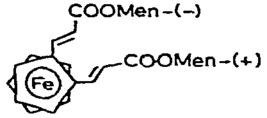
(142)



(143)



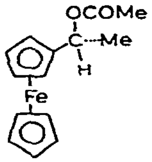
(144)



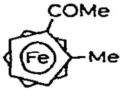
(145)

was reconverted to the starting material (146) with configurational retention by reaction of the methiodide with base and esterification of the resulting alcohol.

It has been shown that the acid catalyzed racemization of optically active acyl ferrocenes e.g. (136 and 147) proceeds intramolecularly but optically active alkylferrocenes do not undergo racemization under acid conditions[116].



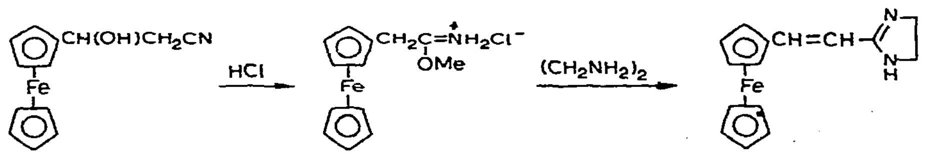
(146)



(147)

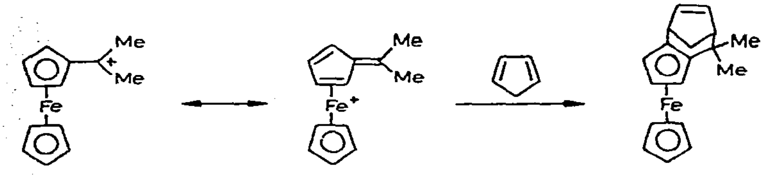
The importance of conformational preference and intrinsic diastereomerism in contributing to geminal group magnetic nonequivalence has been discussed for some 1-dimethylaminomethyl-2-haloferrocenes[117]. The racemization of optically active (+)-1,2-(α-keto-tetramethylene)ferrocene has been achieved in nitromethane with aluminium chloride as catalyst. A ligand exchange mechanism has been proposed for the racemization.

A mixture of the *cis-* and *trans*-ferrocenylethylene (150) was prepared from the nitrile (148) by treatment with dry HCl in ether–methanol to form the imine (149) and subsequent reaction with ethylenediamine in dry methanol[118]. The *trans* form only of (150) was isolated from the condensation of formylferrocene with 2-methyl-2-imidazoline in the presence of sodium methoxide.



(148) (149) (150)

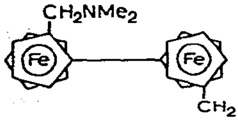
Turbitt and Watts have reported the stereospecific cycloaddition of cyclopentadiene to α-ferrocenylcarbonium ions (151) to give 1/1 adducts such as the olefin (152). It is convenient to draw the canonical form in which the carbonium ion is represented as a metal complexed fulvene (151b) for this reaction^{119}.



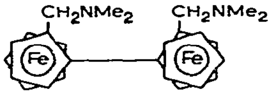
(151 a) (151 b) (152)

The relative stereochemical sizes of ferrocene and benzene were established and it was found that ferrocene > benzene^{120}.

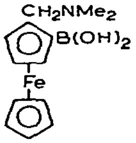
Biferrocenyls, ferrocenophanes and annelated ferrocene derivatives. The direct synthesis of 2,2''- and 2,5''-disubstituted biferrocenes by the coupling of 2-substituted lithioferrocenes in the presence of cobalt chloride has been described^{121}. The isomeric biferrocenes (153 and154) were obtained in 86% yield, compared with 46% by the previously described boronic acid route. Biferrocenes with large substituents, e.g., 2-quinolyl and with two different substituents were also formed in good yield.



(153)



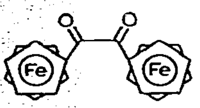
(154)



(155)

The optically active boronic acid (155) was converted to a mixture of the biferrocenes (153 and 154) with cupric acetate^{122}. The isomer (154) was optically active while isomer (153) was inactive thus substantiating the previous assignments of configurations [AS 69; p.696].

The second of the three isomeric terferrocenyls has now been synthesised unambiguously by Goldberg and Breland^{123}. Ferrocil (156) was condensed with acetone in DMSO under basic conditions and the hydroxyketone product (157) reduced to 1,2-diferrocenylcyclopentadiene through three stages. The diene was treated with n-butyllithium, ferric chloride and the cyclopentadienide ion to give the product (158) in 10% yield.



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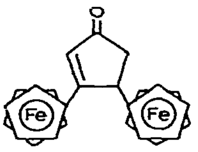

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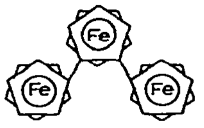

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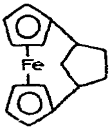
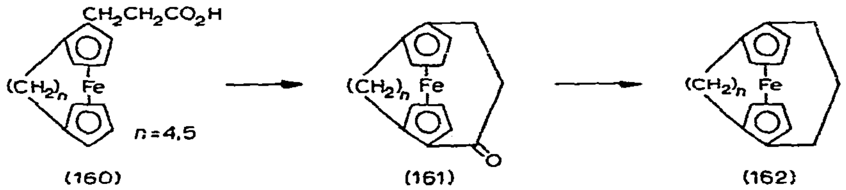
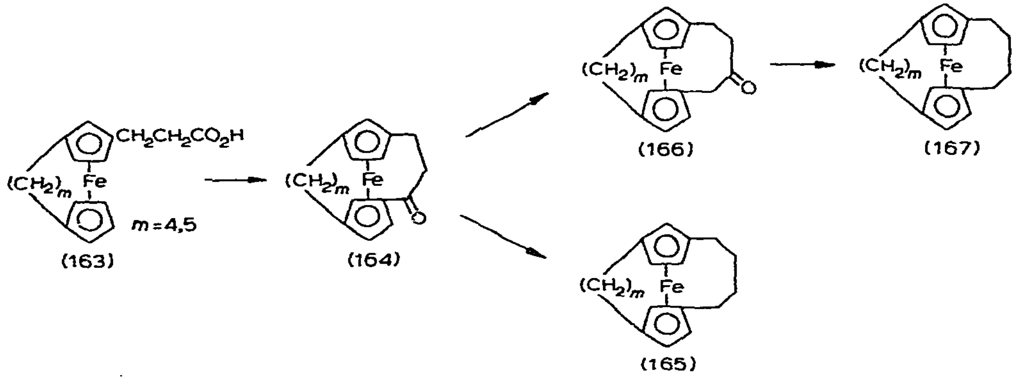


(159)

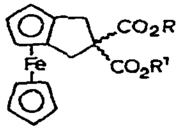
Physical methods and Friedel–Crafts acetylation have been used to confirm the structure of the controversial ferrocenophane (159) that was formed in the preparation of π-benzene-π-cyclopentadienyliron complexes[124].



Brown and Winstead have reported the synthesis of a series of [3] [4] - and [3] [5] ferrocenophanes (161 and 164) by intramolecular cyclization of the appropriate [4] - and [5] ferrocenophanes (160 and 163) with trifluoroacetic anhydride[125]. The propionic acids (160 and 163) were obtained from the corresponding acetylferrocenophanes by NaH-catalysed condensation with ethyl carbonate. The trimethylene bridge in each of the ketones (164) was extended by reaction with diazomethane to give the ketones (166). The carbonyl groups in the ketones (161, 164 and 166) were reduced with $LiAlH_4/AlCl_3$ mixtures to give the ferrocenophanes (162, 165 and 167) respectively.



The cyclization of bis(ferrocenylmethyl)maleate half esters (R^1 = Fc) gave a mixture of the homoannular and heteroannular products (168 and 169)[126]. An unsuccessful attempt was made to prepare 7,7′-spirobi[3]ferrocenophane-6,6′-dione (170) from (169) However the dione (170) was obtained by cyclization of bis(ferrocenylmethyl)malonic acid[127]. The dione was shown to have the absolute configuration (–)-(7*S*).



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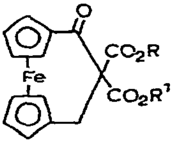

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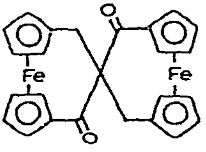
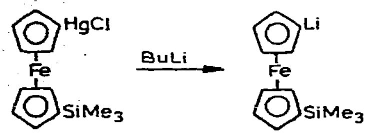


(170)

Derivatives containing other metals (metalloids). The lithioferrocene (172) was formed by treatment of the mercuri chloride (171) with two molecules of n-butyllithium[128]. It has been used to prepare a range of heteroannularly-substituted trimethylsilylferrocenes (173) by treatment with aldehydes, ketones, amines and nitriles.



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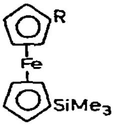


(173)

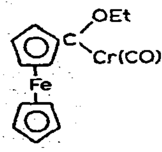
The ferrocenylchlorosilane $FcSiMe_2Cl$ was prepared by condensing lithioferrocene with dimethyldichlorosilane[129]. The chlorosilane was reduced to the silane (174a) and hydrolysis, in the presence of aniline gave the silanol (174b) and in the presence of triethylamine the siloxane (174c). Some vinylsilylferrocenes, for example (174d), were prepared by condensation of lithioferrocene with the corresponding chlorosilane at –40° [130]. The condensation

$FcSiMeR^1R^2$

a, R^1=H, R^2=Me
b, R^1=OH, R^2=Me
c, R^1=OMe_2SiFc, R^2=Me
d, R^1=Ph, R^2=CH=CH_2

(174)

of lithio- and 1,1′-dilithioferrocene with perfluoropropene ($CF_3CF=CF_2$) gave perfluoropropenyl- and 1,1′-bis(perfluoropropenyl)ferrocene respectively[131]. The reaction of ferrocenyllithium with chromium hexacarbonyl followed by treatment with triethyloxonium tetrafluoroborate gave ethoxyferrocenylcarbenepentacarbonylchromium (175)[132].



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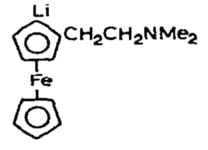

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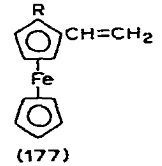
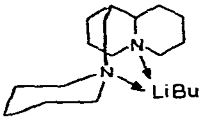


(177)

N,N-Dimethylaminoethylferrocene was lithiated in the 2-position (176). This lithio intermediate was condensed with a series of electrophiles to form the corresponding 2-substituted derivatives. The methiodides of each of the 2-substituted compounds were treated with KOH in monoglyme to give the 2-substituted olefins (177)[133].

The asymmetric lithiation of substituted ferrocenes was reported. When isopropylferrocene was treated with the n-BuLi-(–)-sparteine complex (178) and condensed with trimethylchlorosilane and carbon dioxide (+)-1,1′-bis(trimethylsilyl)-3-isopropylferrocene and (+)-3-isopropylferrocene-1,1′-dicarboxylic acid were obtained[134]. Asymmetric lithiation was achieved at the 2-position by the lithiation of the (+)-ferrocenylpiperidine (179) which afforded the (1*R*)-2-lithioamine derivative (180). Condensation of this lithio intermediate with electrophiles gave a series of chiral 2-substituted ferrocenes of known absolute configuration.



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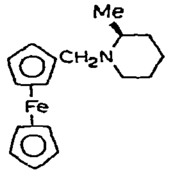

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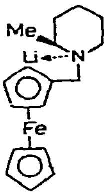
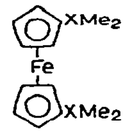


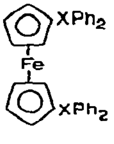
(180)

1,1′-Dilithioferrocene was condensed with a series of halophosphines and -arsines to give the corresponding 1,1′-disubstituted derivatives (181 and 182). Reaction of the dilithiated ferrocene with elemental sulphur gave the ferrocenophane (183) which was reduced with $LiAlH_4$ to give the dithiol[135].



X = As or P

(181)



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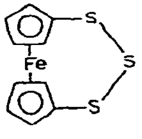

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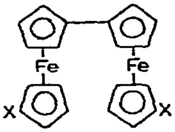


X = Cl, Br or I

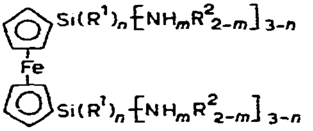
(184)

1,1′-Dihaloferrocenes were prepared in good yields by the reaction of 1,1′-dilithioferrocene with bromine, iodine, tosylhalides, dihalotetrafluoroethanes (XCF_2CF_2X) and hexachloroethane. In many of these reactions small quantities of the 1,1′-dihalobiferrocenes (184) were isolated[136].

The complex $AuCl_3PPh_3$ was treated with ferrocenyllithium to give the ferrocenylgold derivative $(Fc)_2AuClPPh_3$ [137].

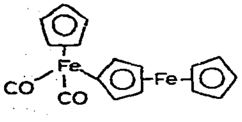
When 1-acetyl-2-chloromercuriferrocene was passed through an alumina column which had been treated with basic sodium cyanide, bis(2-acetylferrocene)mercury was formed in good yield (81%)[138].

Heteroannularly disubstituted silylferrocenes with nitrogen attached to the silicon were prepared from the silicon-substituted cyclopentadienes and iron(II) chloride[139]. The silylferrocenes were converted to the corresponding alkoxy and aryloxy silicon derivatives by treatment with an alcohol or phenol[140]. These silylferrocenes containing functional alkoxy or aryloxy groups were also prepared from the substituted cyclopentadienes and iron(II) chloride[141]. The ferrocenylsilanes (185; R^1, R^2 = alkyl or aryl; n = 0–2; m = 0–1) increased the thermo-oxidative stability of polyorganosiloxanes.



(185)

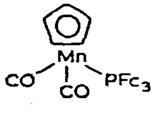
Complexes of ferrocene-containing ligands. Nesmeyanov and coworkers have described the synthesis of the σ-ferrocenyl complex (186) from diferrocenylmercury and π-cyclopentadienylirondicarbonyl iodide[142]. Some chemical reactions of (186) have been examined.



(186)

1,1′-Ferrocenebis(dimethylarsine) (FDMA) (181, X = As) and 1,1′-ferrocenebis(diphenylarsine) (FDPA) (182, X = As) act as ligands with Group VI metal carbonyls. Complexes of the type FDMA-$M(CO)_4$ and FDPA-$M(CO)_4$ (M = Cr, Mo and W) were isolated. Prolonged reaction of FDMA with $Mo(CO)_6$ gave the bridged complex μ-FDMA-[FDMA-$Mo(CO)_3$]$_2$ and $(FDMA)_2Mo(CO)_3$. It was proposed that the former complex has a bridging diarsine and a facial arrangement of donor arsenic atoms in the Mo coordination sphere while the latter complex has one unidentate and one bidentate arsine with a meridional arrangement of the donor arsenic atoms about the Mo atom[143]. FDMA and FDPA also behave as ligands with solutions of tetrahalometallates to give the simple four coordinate complexes $M(FDMA)X_2$ (M = Pd, Pt; X = Cl, Br, I) and $M(FDPA)X_2$ (M = Pd; X = Cl, Br, I and M = Pt; X = Cl). These complexes react with an excess of ligand to give five coordinate $[M(FDMA)_2X]^+$ ions and four coordinate $[M(FDMA)_2]^{2+}$ ions[144].

Triferrocenylphosphine displaced a carbonyl group from cyclopentadienylmanganese tricarbonyl in UV light, to give the complex (187). A similar complex was formed with benzenechromium tricarbonyl[145].

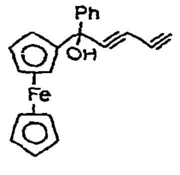


(187)

Some coordination compounds have been prepared by treatment of π-complexes of titanium, iron and palladium with ferrocenyl-β-diketones[146].

Ferrocene-containing polymers. Benzylferrocene and 1,1′-dibenzylferrocene were treated with 1,4-dichlorobutyne and $NaNH_2$ in liquid ammonia to give the acetylenes (188 and 189) respectively, presumably through the intermediate ferrocenyl carbanions[147]. When the 1,1′-dibenzylferrocene was in excess, a polymer with the repeat unit (190) was obtained.

Ferrocene–acetylene polymers with the idealized repeat unit (191) and molecular weights in the range 1600–3000 were prepared from 1,1′-dibenzoylferrocene and the disodium salt of either 2,4-butadiyne or 1,4-diethynylbenzene in liquid NH_3 and tetrahydrofuran[148]. The polymerisation of ferrocenylacetylene in the presence of benzoyl peroxide was found to obey the first order rate law with an activation energy of 9.98



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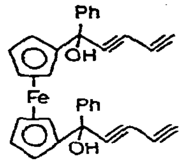

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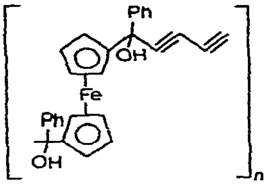

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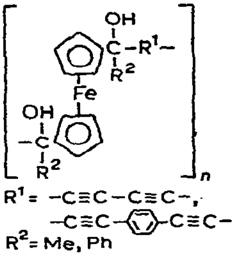


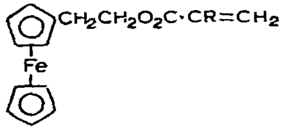
(191)

kcal·mole^{-1} [149]. Optimum conversion of monomer to polymer was obtained at 230°C.

Free radical and anionic solution homopolymerisation and copolymerisation were used to prepare poly(1-ferrocenyl-1,3-butadiene) with elastomeric properties[150, 151].

Ferrocene–xylylene copolymers were prepared by treating ferrocene with p-$(HOCH_2)_2$-C_6H_4 (or its telomers) in the presence of an acid catalyst. These thermosetting copolymers were useful as lacquers for laminates[152].

The solution polymerisation of 2-ferrocenylethyl acrylate and methacrylate (192; R = H and Me) respectively have been investigated and found to conform to the expected first order radical chain polymerisation mechanism[153]. Activation energies for the polymerisation of the monomers have been determined as 18.6 and 21.7 kcal·mole^{-1} for acrylate and methacrylate respectively. The copolymerisation of the same monomers with styrene, vinylacetate, methylacrylate, methylmethacrylate has also been examined and the reactivity ratios determined. The monomers (192; R = H and Me) were found to be more reactive in copolymerisation than ferrocenylmethyl acrylates and methacrylates.



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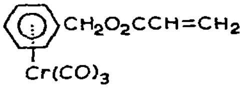
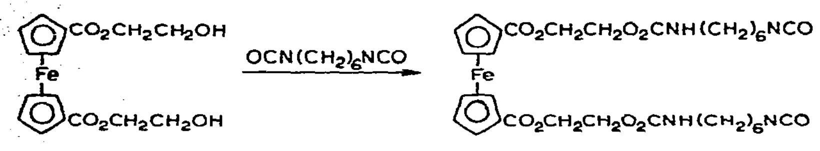


(193)

The succeeding paper described the solution copolymerisation of the acrylate (192; R = H) with the acrylate chromium tricarbonyl (193) in the presence of azobis(isobutyronitrile)[154]. Poly(ferrocenylmethylacrylate), poly(ferrocenylmethylmethacrylate) and poly(ferrocenylethylene) were prepared by polymerisation of the monomers in benzene with the same catalyst. When these polymers were treated with strongly electron-attracting compounds such as tetracyanoethylene, dichlorodicyanoquinone and o-chloroanil polymeric charge transfer derivatives were formed[155]. The ferrocene monomers were copolymerized with styrene, methylacrylate, methylmethacrylate and vinylacetate and the relative reactivity ratios of each copolymerisation were determined[156].

The dimethyl ester of ferrocene-1,1′-dicarboxylic acid was heated with ethylene glycol in the presence of KOH–$Zn(OAc)_2$ to give the diol (194)[157]. On heating the diol with two moles of a diisocyanate in chlorobenzene the ferrocene diisocyanate (195) was formed and this was converted to a polyurethane with water.



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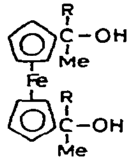
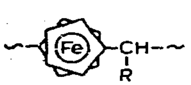


(196)

Ferrocene was polycondensed with terephthaloyl chloride and adipoyl chloride in the presence of a Friedel–Crafts catalyst to give polymers with a poly-ketone structure[158].

1,1′-Divinylferrocene was polymerized in the presence of azobisisobutyronitrile to give an insoluble polymer. Polycondensation of the ferrocenyl alcohol (196; R = Me) using boron trifluoride etherate gave a soluble polymer and the alcohol (196; R = H) under the same conditions gave a mixture of soluble and insoluble polymers[159, 160]. Radical and ionic intermediates in polymerisation were discussed and the ferricinium ion was implicated in the mechanism.

The ferrocene polymer (197) was prepared by solution polymerisation of α-ferrocenylmethylcarbonium fluoroborate as a glass-like brittle solid with a number average molecular weight up to 20000 and a softening point below 120°C[161]. On cross-linking with 1,1′-di(α-hydroxyethyl)ferrocene in the presence of BF_3Et_2O a polymer with improved thermal and mechanical properties was obtained (198). At 500°C, 75% of the cross-linked polymer remained as a char, compared with 60% for the non cross-linked one when the two were examined by thermogravimetric analysis under nitrogen.



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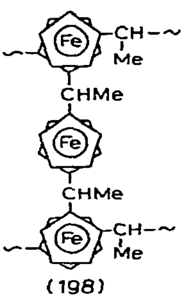

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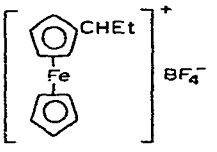

(199)

The carbonium ion (199) as the fluoroborate salt underwent self condensation on heating with nitroethane to form polymers (197) with M_n up to 20000[162]. The changes in M_n and intrinsic viscosity during the polymerisation were interpreted in terms of a rapid primary growth followed by an induction period, a second growth stage and finally cross-linking.

1,1′-Bis(α-hydroxyethyl)ferrocene was copolymerized with a dialcohol, such as 1,6-hexanediol, in the presence of BF_3OEt_2 as catalyst to give a polymer with the repeat unit (200)[163]. The polymers were claimed as propellant binders and burning-rate controllers in rocket fuels.

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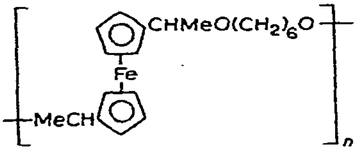

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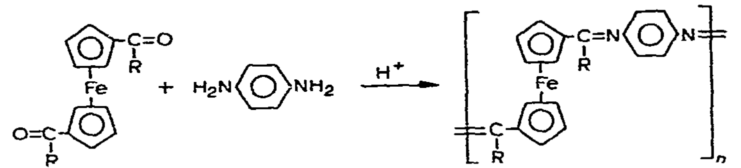


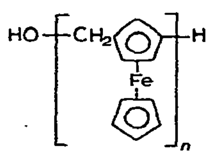
(201) (202)

Polymeric Schiff bases (202) have been prepared by acid-catalysed poly-condensation of 1,1′-diformylferrocene and 1,1′-diacetylferrocene (201; R = H and Me respectively) with aliphatic and aromatic diamines, such as *p*-phenylenediamine[164]. Thermogravimetric analysis in an inert atmosphere showed 30–50% weight loss at 700°, in air extensive decomposition was observed at 200–250°.

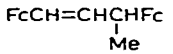
The Mössbauer spectra were recorded for ferrocenemethylethylketone copolymers pyrolysed at 500° and poly(β-ferrocenylchloroacrolein) heated to 400°. The pyrolysed polymers catalysed the dehydration of $CH_2{=}CHCMe_2OH$. This catalytic activity was caused by the finely divided oxides of iron within the polymer matrix or by the ferricinium ion[165]. Saturated ferrocene polymers were also effective dehydrating agents for the same alcohol. The reaction was studied in a continuous flow reactor at 180–300°, 42% conversion was obtained at 300°. The ferrocene–ferricinium relationship in the polymer was important in determining the catalytic activity. The polymers were prepared by the polycondensation of ferrocene with acetic acid, phthalic anhydride or methylethyl ketone in the presence of Lewis acids such as $ZnCl_2$ [166,167].

Ferrocene polymers (203) were decomposed to Fe^{III} salts with aqueous solutions of strong oxidizing agents such as Ce^{IV}, $K_2Cr_2O_7$ and H_2O_2. However mild-oxidizing agents, for example $FeCl_3$ and AgCl, gave the oxidized form of the polymer in solution, on evaporation the polymer decomposed[168].

1,1′-Oligomeric ferrocenes (from biferrocene to 1,1′-sexiferrocene) were prepared by a mixed Ullmann reaction between a haloferrocene and 1,1′-diiodoferrocene. A series of 1,2-oligomeric ferrocenes (biferrocene to 1,2-quinqueferrocene) were prepared from 1,2-diiodoferrocene[169].

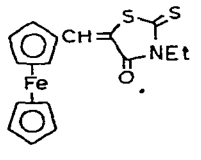


(203)



$\mathrm{FcCH{=}CH}\underset{\mathrm{Me}}{\mathrm{C}}\mathrm{HFc}$

(204)



(205)

Applications. The use of 1,3-diferrocenyl-1-butene (204) to improve the combustion of solid fuels in rocket motors has been described[170]. The olefin (204) was prepared by heating 1-ferrocenylethanol with acetic acid.

The 2-(2-n-butoxyethoxy)ethyl ester of ferrocenecarboxylic acid has found application as a combustion catalyst[171].

The addition of 0.0125% ferrocene improves the smoke point of a kerosine oil flame[172]. The use of 1,1′-dimethylferrocene as a fuel additive was claimed[173].

Ferrocene has been used as a component of the catalyst for the high pressure polymerisation of α-olefins[174]. The low molecular weight α-olefin polymers produced (C_{10}—C_{22}) were intermediates in the preparation of detergents.

An alfin catalyst containing ferrocenyltetralithium was employed in the polymerisation of butadiene to give a high molecular weight polybutadiene with up to 63% of the 1,2-structure[175]. Better processing characteristics were claimed for this polymer by comparison with material prepared using the unmodified alfin catalyst.

The initiation of methyl methacrylate polymerisation by metallocenes including ferrocene has been studied[176]. The metallocene, the nature of the solvent and the presence of added CCl_4 or a transition metal in a high oxidation state each affected the rate of conversion of monomer to polymer. The mechanism of polymerisation in the presence of CCl_4 was discussed.

Ferrocenecarboxylic acid (1–4%) has been incorporated into alkyd, polyurethane, epoxy and acrylic resins by esterification with hydroxyl groups on the polymer[177]. Films were cast from the ferrocene modified polymers and these were evaluated for UV stability.

Substituted vinylferrocenes have been used in photographic compositions to cause hardening of gelatin films on exposure to visible light and near infrared radiation[178]. The ferrocene dyes were prepared by condensation of formylferrocene with methyl-substituted benzothiazolium or pyrylium salts to give products such as the vinylferrocene (205).

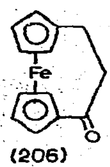
The addition of ferrocene or a monosubstituted ferrocene and *p*-benzoquinone has been claimed to improve the curing properties and pot life of epoxy resins[179].

Organosilicon derivatives of ferrocene were effective in the stabilisation of ω,ω'-hexamethyloligodimethylsiloxane against thermal oxidation[180], and similar compounds were used as antioxidants for poly(methylsiloxane) and poly(methylphenylsiloxane)[181].

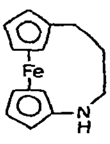
The bridged ketone (206) was converted to the bridged amine (207) through Beckmann rearrangement of the oxime to the lactam and subsequent reduction[182]. The product (207) has been used as a petroleum additive and a hematinic agent.

Similar ferrocenophanes such as (208) have been claimed as pesticides, fungicides, hematinic agents, dyes and fuel additives[183]. The diol (208) was obtained by borohydride reduction of the corresponding diketone, a product of the reaction between 1,1′-diacetylferrocene, dimethylformamide and benzene in base.

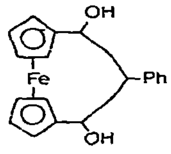
The tricyclohexyltin ester of ferrocenecarboxylic acid obtained by treating tricyclohexyltin hydride with ferrocenecarboxylic acid, has been used as a fungicidal and bactericidal agent[184]. It was claimed that ferrocenylmethylazide was useful as an insecticide[185].



(206)



(207)



(208)

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The defluorination of $(CF_3)_2CFNF_2$ to afford the fluoroimine $(CF_3)_2C{=}NF$ was achieved by heating the reactant with ferrocene and *o*-dichlorobenzene[186]. The imine was used in the formation of fluorinated copolymers.

A new method for the estimation of very small concentrations of phosphorus has been devised. The phosphorus compound was converted to 12-molybdenophosphate and this was then reduced quantitatively by ferrocene to give a blue product and ferricinium ion. The concentration of the product and ferricinium ion were determined spectrophotometrically to give the original phosphorus concentration. This method has been used to determine phosphorus in wheat leaves[187].

The treatment of 4-ferrocenylphenol with propargyl bromide in the presence of sodium ethoxide gave the corresponding 4-ferrocenylphenyl propargyl ether[188]

A later patent records the condensation of the ether with a tertiary heterocyclic amine under oxidative conditions in alcoholic copper(II) chloride as catalyst to form 1,6-bis(*p*-ferrocenylphenoxy)-2,4-hexadiyne[189].

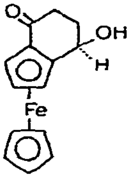
The ferrocenylethylamino protecting group has been used in the preparation of *N*-acyl-α-amino acid amides and peptides that have antibiotic applications[190].

The ferrocene–ferricinium couple has been used to determine the acidity functions of aqueous solutions of formic acid[191] and some carboxylic acids[192].

The direct preparation of ferrocene was patented; the cyclopentadienyl anion was generated from the parent hydrocarbon with KOH in $MeOCH_2CH_2OMe$ or Me_2SO and then treated with $FeCl_3 4H_2O$ [193].

Miscellaneous reports. Radioactive kryptonates of ferrocenylmethyl sulphides and sulphones have been prepared by a diffusion technique[194]. The dekryptonation of these derivatives was studied in air and in polar solvents.

The microbial hydroxylation of the ketone (136) with the mould *Sporotrichum sulfurescens* at low substrate levels gave the hydroxyketone (209) and demonstrated the oxygenation of a hydrocarbon by an enzyme system in the presence of the ferrocenyl group[195].



(209)

The separation of nineteen mono- and 1,1′-disubstituted ferrocene and biferrocenyls by thin-layer chromatography on silica has been reported. Various solvent systems and detection methods were discussed and R_f values were recorded[196].

The rate of combustion of ammonium perchlorate with a range of organic and organometallic compounds was determined calorimetrically under an argon pressure of 30–50 atm[197]. In the presence of ferrocene the rate was more than double that expected and this was attributed to the breakdown of ferrocene to give Fe and then Fe_2O_3, a combustion catalyst.

The kinetics of decomposition of ferrocene and several substituted ferrocenes was studied on several different surfaces (glass, C deposited on glass, KCl and $K_2B_4O_7$). It was found that the solid pyrolysis products catalyse the decomposition more than the surface coatings of KCl or the borate[198].

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