FERROCENE
ANNUAL SURVEY COVERING THE YEAR 1982*

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CONTENTS

1. REVIEWS

The chemistry of ferrocene has been discussed in a book, 'Ferrocene and Related Compounds' by A. N. Nesmeyanov [1]. The chemistry of cyclopentadienylide and pentafulvene complexes

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* Annual Survey covering the year 1981 see J. Organometal. Chem., 227 (1982) 373

formed by transition metals has been discussed [2]. A detailed review has been presented on the synthesis of transition metal complexes containing η^5-cyclopentadienyl ligands. All the methods available for the preparation of ferrocene and related compounds were reviewed [3].

Baran has prepared a brief review of the chemistry of unsaturated ferrocenylketones [4]. Watts has surveyed the chemistry of π-arene, π-cyclopentadienyl and related complexes [5].

Cullen and Woollins have reviewed the chemistry of ferrocene-containing metal complexes. The primary focus of the review was on transition metal coordination compounds [6].

Hayashi and Kumada have reviewed asymmetric syntheses catalysed by transition-metal complexes with functionalized chiral ferrocenylphosphine ligands [7].

The application of chiral ferrocenylphosphines as ligands in homogeneous catalytic asymmetric synthesis has been reviewed by Kumada, Hayashi and Tamao [8]. The chemistry of hydrocarbon-transition metal π-complexes has been reviewed by Howell [9].

Omae has reviewed the chemistry of organometallic intra-molecular-coordination compounds containing a cyclopentadienyl donor ligand. This review included a section on the preparation, properties and structure of the ferrocenophanes [10].

Solodovnikov has reviewed the use of magnetic resonance methods for the study of paramagnetic metallocenes and diarene complexes [11].

2. STRUCTURAL DETERMINATIONS

Crystallization of ferrocene at temperatures below 110°K gave single crystals of the low temperature modification which were isomorphous with ruthenocene. The crystal structure of this modification was determined at 98°K, it was orthorhombic with the cyclopentadienyl rings exactly eclipsed. On warming to 275°K the crystals underwent a transition to the monoclinic phase [12].

The crystal and molecular structures of dimethyl- and diphenyl-1,2-diferrocenylethanes have been determined by X-ray crystallography. The conformations of the compounds were discussed and compared with the corresponding alkyl- and aryl-ethanes [13].

The crystal and molecular structure of (1-ferrocenyl-1-oxoethyl)tricarbonylcyclopentadienyltungsten has been determined by X-ray crystallography. The bond distances of the carbonyl groups were not affected by the presence of electron donating ligands [14].

Formylferrocene has been condensed with $PhCH_2NO_2$ to give [E]-1-phenyl-2-ferrocenyl-1-nitroethene and the crystal structure of this product was determined by X-ray methods. The conformation of the cyclopentadienyl rings was almost staggered with a rotation angle of 32.3° [15].

The crystal and molecular structure of 5,24-dioxa-2,8,21,27-tetrathia[9,9]ferrocenophane has been determined by X-ray crystallography. The cyclopentadienyl rings were planar and had a mean twist angle of $\sim 26^\circ$ [16].

The crystal and molecular structure of octamethylferrocenium hexafluorophosphate has been determined by X-ray crystallography. Bond angles and bond lengths were measured [17].

3. THEORETICAL STUDIES

Large scale ab initio LCAO-SCF calculations carried out on ferrocene and decamethylferrocene showed that the Hartree-Fock model was unable to account for the experimentally determined metal-ring distances [18].

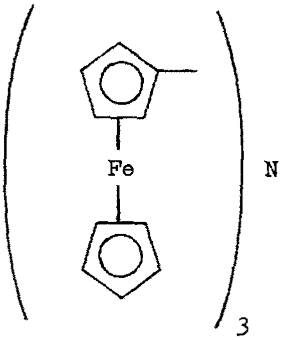
A quantum-chemical study of some homoannularly disubstituted ferrocenes has been carried out. Calculations by the EHT method were used to predict qualitatively the stability of these compounds and good agreement was obtained with experimental data [19].

A theoretical analysis has been carried out for electron transfer in molecules with interacting multiple redox centres such as dimers, oligomers and polymers, and for the application of voltammetric techniques such as rotating disc voltammetry and d.c. polarography. The analysis only considered interactions between nearest-neighbouring centres. Calculations were carried out on the interactions in biferrocene [20].

Ferrocene has been included in a theoretical study of the quantum mechanical origin for the nonvalidity of Koopmans theorem in 3d transition metal complexes. Green's function formalism was applied within the framework of a semiempirical Hamiltonian [21].

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

Triferrocenylamine (4.1) has been prepared by using acetamide as the starting material. The structure of the amine (4.1) was determined by X-ray analysis. The arrangement of the three ferrocenyl groups around the nitrogen was almost planar and the amine (4.1) was not basic [22].



4.1

An X-ray study has been carried out on the thermal oxidation and decomposition of poly(vinylferrocene) [23].

The structure of 2-ferrocenyl-3,5-diphenyl-6-oxo-6H-1,3-oxazin-3-ium-4-olate has been determined by X-ray analysis [24].

Moessbauer spectroscopy has been used to investigate phase transitions in acetyl- and carboxyl-ferrocene which occurred near the melting point. X-ray crystallography and differential thermal analysis were employed to confirm the transitions [25].

The dielectric absorption spectra of formyl- and carboxyl-ferrocene and 1,1'-dichloroferrocene have been measured in benzene at 100 MHz and 26 GHz at several temperatures. A single dielectric absorption band was found and Debye-type behaviour was shown. The dielectric relaxation appeared to take place by internal rotation about the (η-cyclopentadienyl)-iron-(η-cyclopentadienyl) axis [26 , 27].

In the mass spectrum of $CF_3SeFe(CO)_2(\eta-C_5H_5)$, an increase in temperature eased the expulsion of the $SeCF_2$ group and favoured formation of the ferrocenium ion [28].

Spectrophotometric measurements on the ferrocenium cation suggests that an isolated $^2E_{2g}$ ground level exists with the nearest excited level being approximately 2000-4000 cm^{-1} away from it. However, any explanation of magnetic resonance and susceptibility measurements require a $^2A_{1g}$ level to be the lowest and a low lying $^2E_{2g}$ level at approximately 200 cm^{-1} above the ground level. It was proposed that the electronic spectrum of the ion as suggested by the optical measurements was correct and there was a Jahn-Teller induced coupling of the ground electronic $^2E_{2g}$ level with vibrational modes of the complex. The ground spectrum consisted of two vibronic Kramers' doublets lying close together, one of which had a negligible orbital contribution to the magnetic moment similar to that expected from a Kramers' doublet of $^2A_{1g}$ origin [29].

The dissolution of ferrocene in a hexachloroplatinic acid solution was investigated spectrophotometrically at 308-318 and 318-363 K via a rotating disc method.

$$[PtCl_6]^{2-} + 2(\eta\text{-}C_5H_5)_2Fe \longrightarrow [PtCl_4]^{2-} + 2(\eta\text{-}C_5H_5)_2Fe^+ + 2Cl^-$$

At 308-318°K the reaction was diffusion controlled with an activation energy of 27-29 kJ mol^{-1}. At higher temperatures the activation energy was 64 kJ mol^{-1} when further reduction occurred and metallic platinum was produced [30].

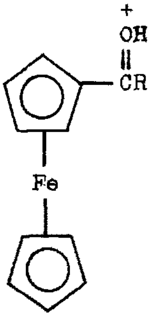
A series of decamethylmetallocenes, $M(\eta\text{-}C_5Me_5)_2$ (M = Mg, V, Cr, Fe, Co, Ni) has been prepared and characterized. The transition metal derivatives were resistant to hydrolysis and ring exchange reactions but readily underwent one-electron oxidation. The electronic spectra of these compounds were recorded and interpreted [31].

Photoacoustic spectra have been measured in the near IR region (1000-2600 nm) for several organometallic compounds including ferrocene. Bands were assigned by comparison with infrared spectra and provided fingerprints for the compounds [32].

Steric effects in ferrocene and dimethyl-, tetramethyl-, hexamethyl-, octamethyl- and decamethyl-ferrocene have been examined by ^1H and ^{13}C NMR spectroscopy [33].

Ring current effects in electron donor-acceptor complexes of ferrocene and some substituted ferrocenes have been studied by NMR spectroscopy. Equilibrium constants and Δ_o values for the complexes of ferrocene and 1,1'-dimethylferrocene with 1,3,5-trinitrobenzene were obtained. The results were consistent with the presence of a ring current in ferrocene whose magnitude was compatible with the number of π-electrons in the ring [34].

The structures of protonated ferrocenyl ketones (4.2; R = Me, Ph, p-Me.C_6H_4, p-MeO.C_6H_4, p-Cl.C_6H_4, p-CN.C_6H_4) have been investigated by ^1H NMR and Moessbauer spectroscopy. The ketones were completely protonated in CF_3CO_2H and 70% H_2SO_4. No evidence was obtained for iron protonation in these species [35].



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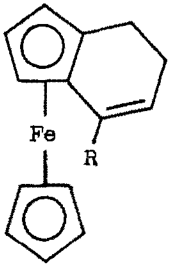

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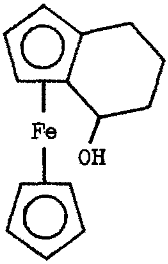
As part of an NMR investigation of isothermal and non-isothermal kinetics requiring signal averaging, the first-order isomerization of a bridged ferrocene has been examined [36].

Hydroboration of the (η-dihydroindenyl)iron complex (4.3;



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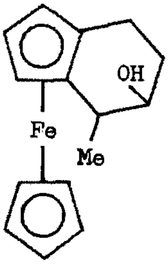


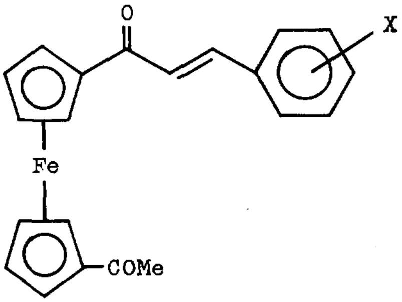
4.5

R = H) gave, after oxidation, the endo-alcohol (4.4) as the predominant product while the complex (4.3; R = Me) gave exclusively the exo-alcohol (4.5). These results showed that borane may attack the dihydroindenyl double bond from both endo and exo directions and the preference for endo attack on the dihydroindene (4.3; R = H) was used as evidence for intermediate complexation of borane with iron [37].

Secondary α-deuterium kinetic isotope effects in solvolyses of ferrocenyldideuteriomethyl acetate and benzoate have been determined in 96% ethanol as $\underline{k}_H/\underline{k}_D$ = 1.24 and 1.26 respectively. In the presence of 0.1 mol dm^{-3} $LiClO_4$ the $\underline{k}_H/\underline{k}_D$ values were 1.23 and 1.22 respectively. Plots of $\underline{k}_{observed}$ against salt concentrations revealed a combination of special and normal salt effects. The alkyl-oxygen cleavage was accompanied by 10-15% acyl-oxygen cleavage [38].

Cyclization of the cinnamoylferrocenes (4.6; X = H, 3-Cl, 3-Br, 3-CN, 3-OMe, 4-Cl, 4-Br, 4-F, 4-Me, 4-OMe) to the corresponding [5]ferrocenophanes (4.7) has been the subject of a kinetic study. The rates were correlated with the Hammett σ-constants [39].

A thermogravimetric and analytical study has been carried out on the oxidative thermal degradation of poly(vinyl chloride) in the presence of ferrocene. Ferrocene slightly destabilized the polymer, more residue was formed at the expense of carbon in the gases evolved [40].



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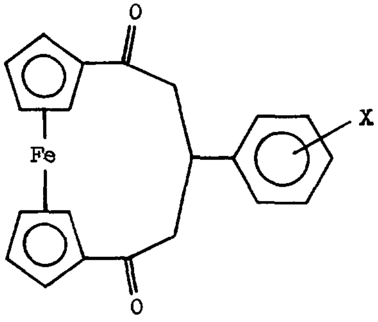


4.7

The analysis of ferrocenes by thin-layer chromatography on silica gel has been studied in several solvent systems. The effect of substituents and of solvent polarity on the Rf values relative to ferrocene was discussed [41].

Ferrocene oxathiolanes and dithiolanes have been separated by thin-layer chromatography on silica gel impregnated with triethylene glycol. The Rf values determined were compared with gas chromatographic retention times for the same compounds [42].

5. ELECTROCHEMISTRY AND PHOTOSENSITIVE ELECTRODES

Recommendations have been made by IUPAC for the measurement and reporting of electrode potentials in nonaqueous solvents vs. the ferrocene-ferrocenium ion reference redox system [43].

The electrochemical oxidation and reduction of some ferrocenophanes has been investigated. The first stage in the electrochemical reduction of ferrocenophanes and ferrocenophanediones was the formation of the anion radicals. During the reduction of [3]-ferrocenophan-6-one; 6,6-bis(cyanomethyl)-[3]-ferrocenophane and bis[(6-cyanomethyl)-[3]-ferrocenophan-6-yl] were formed. The electrochemical reduction of [3](1,1')[3]-(3,3')-ferrocenophan-6-one was investigated [44].

The electrochemical properties of [3]ferrocenophane, [4]ferrocenophane, [3][3]ferrocenophane, [4][3]ferrocenophane, [4][4]ferrocenophane, [3][3][3]ferrocenophane and [4][4][3]-ferrocenophane have been studied by d.c. polarography, pulse polarography and cyclic voltammetry. The oxidation of the ferrocenophanes proceeded via a reversible one electron process. Taft substituent constants were obtained for the trimethylene and tetramethylene groups [45].

Cyclic voltammetry has been used to investigate the electrochemical oxidation of ferrocene at a platinum electrode in ethanol, dimethylformamide and propylene carbonate and in mixtures of these solvents with water. The oxidation was quasi-reversible with slow irreversible decomposition of the ferrocenium ion. The presence of water decreased the diffusion coefficient of ferrocene but had little effect on the oxidation process [46].

Cyclic voltammetry has been used to determine the half-wave potential of the ferrocene-ferrocenium ion couple in aqueous solution. The half-wave potential was also determined in cationic micellar solutions of alkyltrimethylammonium bromide and found to be independent of the ferrocene concentration providing evidence that the pseudo-phase model or the Poisson distribution can be applied to these micellar solutions [47].

Cyclic voltammetry has been used to determine the standard potentials of the ferrocene-ferrocenium electrode in 5-40% acetone-water mixtures at 25°C. The standard potentials were used to calculate proton medium effects with reference to the normal hydrogen electrode. The results were used for comparisons with previous studies on the proton affinities of acetone-water mixtures [48].

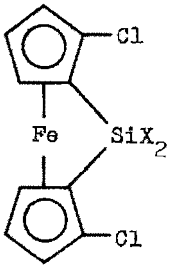
Alkyl derivatives of ferrocene have been used in the construction of electrodes [49].

Equilibrium constants for the formation of 1:1 ferrocene-tetracyanoethylene complexes at 25° have been obtained together with chronopotentiometric redox potentials. The complexes were stabilized by the presence of electron donating alkyl substituents on ferrocene which was explained by π-electron donation from cyclopentadienyl rings to the tetracyanoethylene acceptor. Electron withdrawing substituents caused a decrease in stability of the complexes [50].

The kinetics of electron transfer between ferrocene and the clathrochelate $Co(dmg)_3(BF)_2BF_4$ (dmg = the doubly deprotonated dimethylglyoxime ligand) has been investigated in methyl cyanide as a function of concentration, temperature and added $n\text{-}Bu_4NBF_4$. From the results obtained the Marcus theory was used to calculate an electron self-exchange rate constant for the cobalt complex of $1.1 \times 10^2 M^{-1} s^{-1}$. This value was similar to that obtained for $[Co(phenanthroline)_3]^{3+/2+}$ [51].

The electrical conductivity and thermoelectrical power of FeOCl and $FeOCl[Fe(\eta\text{-}C_5H_5)_2]_{1/6}$ single crystals have been investigated. The results were interpreted in terms of a hopping mechanism between Fe(II) and Fe(III). Ferrocene intercalation greatly increased the mobility of the carriers [52].

Several ferrocene derivatives including the bridged silanes (5.1; X = Ph, Cl) and the trichlorosilanes (5.2; X = Cl, CH_2NMe_2) have been used to derivatise n-type silicon electrodes. The behaviour of the derivatized electrodes was investigated by cyclic voltammetry, wide variations in response were observed but no persistence in photoresponse beyond several hundred cycles



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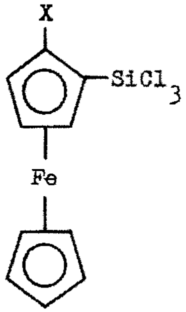

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was observed [53].

Cyclic voltammetry and open circuit potential measurements have been used to investigate the photoelectrochemical behaviour of n-type silicon in methanol with ferrocene, TMPD or tetraethylammonium iodide as the electroactive substance. The reactivity of ferrocene and TMPD with respect to holes was considerably higher than that of the iodide. Ferrocene and TMPD were effective in suppressing the photocorrosion of the n-Si electrode [54].

The electrochemistry and photoelectrochemistry of the ferrocene-ferrocenium redox couple has been studied at platinum, n-silicon and n-indiumphosphide with the ferrocene in the form of a water-soluble chromium complex of ferrocenecarboxylic acid. The stabilities of both the n-Si and the n-InP electrodes were found to be markedly dependent on the light intensity. Cyclic voltammetry using the Pt electrode indicated that the aqueous redox couple behaved in the same way as in nonaqueous solvents with a peak potential of +0.45 V vs. SCE [55].

The photoelectrochemical oxidation of decamethylferrocene, benzo[α]pyrene, 9,10-diphenylanthracene, anthracene and hexamethylbenzene was studied on $\underline{n}$-GaAs electrodes in contact with aluminium chloride-butylpyridinium chloride fused salt electrolyte via cyclic and linear sweep voltammetry. Decamethylferrocene and 9,10-diphenylanthracene exhibited quasi-reversible charge transfer behaviour. The photocurrent was increased two-three times when the electrolyte was mixed with toluene [56, 57].

The rates of permeation of electroactive solutes through ultrathin electrochemically polymerized films on electrode surfaces have been determined. Ferrocene was among the solutes examined [58].

Iridium and anodic iridium oxide electrodes combined with dichlorosilylferrocene to give strongly bonded silylferrocene monolayers. By contrast anodized platinum-platinum oxide electrodes gave thicker and variable layers of silylferrocene polymers. The electrochemical behaviour of the derivatized electrodes was explored [59].

Platinum electrodes have been coated with stable polyanionic films obtained by copolymerization of γ-methacryloyloxypropyltrimethoxysilane and used in a study of ion exchange partition of redox cations. The copolymer was used with poly(vinylferrocene) to prepare a two layer electrode with an inner polymer film containing no fixed redox sites [60].

Ruthenium oxide and superficially oxidized platinum electrodes were treated with thionyl chloride to produce activated, chlorinated surfaces. The activated surfaces were treated with aminophenylferrocene and similar reagents to give stable products. The electrochemistry of these electrodes was investigated [61].

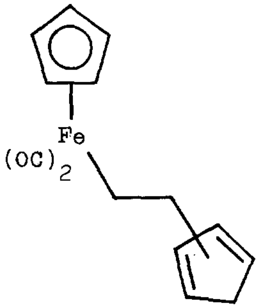
6. PREPARATIONS OF FERROCENE

Cyclic voltammetry and pulsed switching of potential have been used to study the kinetics of formation of the cyclopentadienyl anion in dimethylsulphoxide from cyclopentadiene under conditions of cathodic polarization of a platinum electrode. It was proposed that the cyclopentadienyl ions were generated as a result of an acid-base reaction of hydroxyl ions with cyclopentadiene. The hydroxyl ions were formed by the electrolytic reduction of water [62].

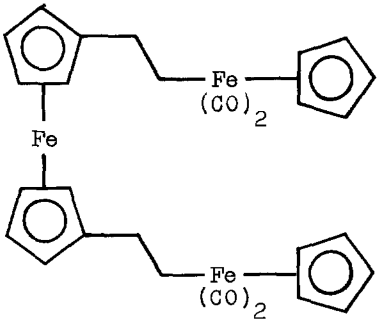
The mechanism of the electrochemical synthesis of ferrocene in solutions of cyclopentadiene in aprotic solvents on an iron anode has been studied. Cathodic generation of the cyclopentadienyl anion occurred and this interacted with iron(II) formed during dissolution of the anode [63].

Ferrocene and cobaltocene have been prepared electrochemically from the corresponding metal anode and cyclopentadiene [64].

The large-scale electrochemical synthesis of ferrocene has



6.1

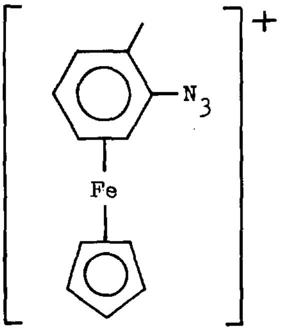


6.2

been reported. The first stage involved the formation of $Fe(OEt)_2$ and this was then converted to ferrocene in the presence of sodium ethoxide and ethanol at 30-50°C [65].

Spiro[2.4]hepta-4,6-diene underwent ring opening with sodium dicarbonyl(η-cyclopentadienyl)ferrate to form the cyclopentadiene complex (6.1) which was in turn treated with iron(II) chloride to give the 1,1'-disubstituted ferrocene (6.2). Several related reactions were reported [66].

The (η-*o*-azidotoluene)iron complex (6.3) has been subjected to photolysis in dilute solution, ring contraction took place to give 1-cyano-2-methylferrocene (6.4). Photolysis of the



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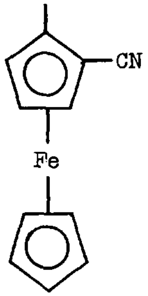

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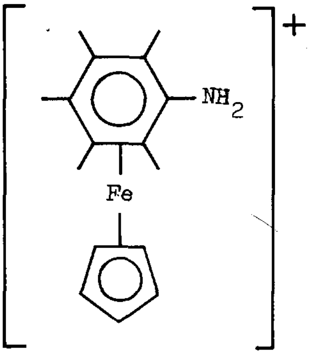
corresponding (η-*p*-azidotoluene)iron complex gave 1-cyano-3-methylferrocene as the product while under the same conditions the (η-*m*-azidotoluene)iron complex gave a mixture of the 1-cyano-2- and 1-cyano-3-methylferrocenes. The ring contraction mechanism was discussed [67].

7. REACTIONS OF FERROCENE

The ligand exchange reaction between ferrocene and pentamethylaniline in the presence of aluminium and aluminium chloride produced the complex cation (7.1). The reactions of this cation were investigated [68].



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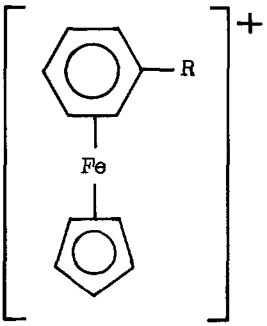

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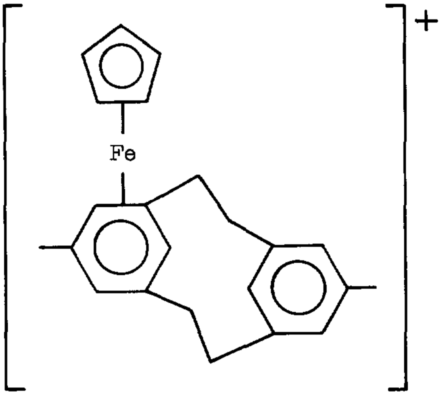
The η^6-arene complexes (7.2; R = Cl, F, $NHCOCH_3$, NH_2, $NHNH_2$) have been prepared by reaction of the arene PhR with ferrocene in the presence of aluminium powder and aluminium chloride. The complexes were isolated as the picrate salts which were explosive and light sensitive. Treatment of the picrate of the cation (7.2; R = Cl) with hydrazine hydrate produced the corresponding hydrazine derivative (7.2; R = $NHNH_2$) [69].

The reaction of ferrocene with 5,13-dimethyl[2.2]metacyclophane in the presence of aluminium chloride and aluminium powder produced the mono- and di-cations (7.3 and 7.4) which were characterized as the PF_6^- salts. The ^1H and ^{13}C NMR spectra of the cations (7.3 and 7.4) were recorded and interpreted [70].

Ferrocene has been treated with chlorosulphonic acid in ether to form ferrocenylsulphonic acid which was converted without isolation to ferrocene sulphonyl chloride (7.5) using



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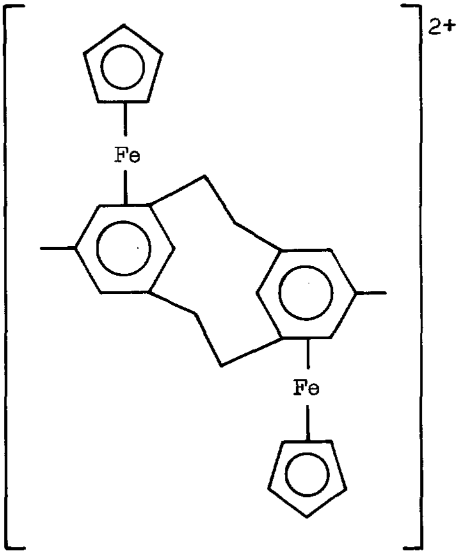

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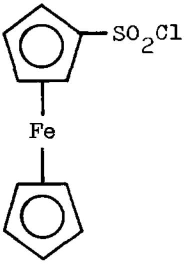
phosphorus trichloride. The sulphonyl chloride (7.5) combined with secondary amines, R^1R^2NH, to give the ferrocenylsulphonamides (7.6; R^1, R^2 = H, Me, Et, Ph, CH_2Ph) [71].

Conditions have been optimized for the alkylation of ferrocene with isobutylene in the presence of orthophosphoric acid and boron trifluoride. A yield of 97% was obtained at



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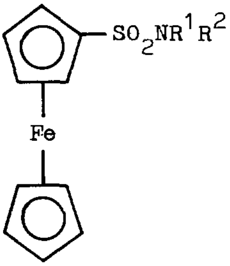
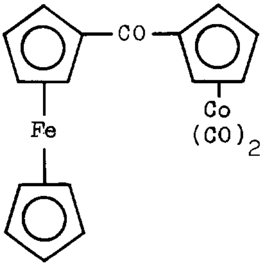


7.6

313°K using a 1:1.25 mole ratio of ferrocene:isobutylene [72].

Ferrocene has been alkylated with ethylenechlorohydrin and with dibromoethane in the presence of aluminium(III) chloride and sodium borohydride to give a mixture of ethylferrocene, 1,2-diethylferrocene, 1,2,3-triethylferrocene and (2-hydroxyethyl)ferrocene [73].

Reaction of $(\eta\text{-}C_5H_4COCl)(CO)_2Co$ under Friedel-Crafts conditions with ferrocene gave the corresponding ferrocenoyl derivative (7.7) [74].



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Titanocene and rhodocene cations have been formed in the gas phase by reaction of the metal ions (M = Ti, Rh) with either ferrocene or nickelocene (M = Fe, Ni).

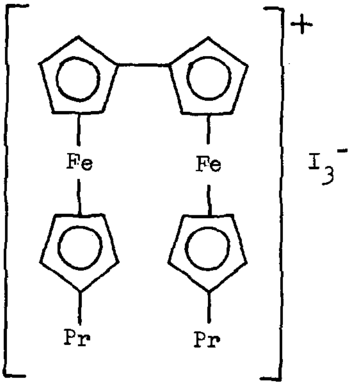
$$M^+ + M'(\eta\text{-}C_5H_5)_2 \longrightarrow [M(\eta\text{-}C_5H_5)_2]^+ + M'$$

Ion cyclotron resonance (ICR) spectrometry was used to investigate these reactions in the gas phase and the metal ions (M = Ti, Rh) were generated by a laser beam that was focused onto a pure metal plate in the ICR cell [75].

The surface of reticulated vitreous carbon (RVC) has been chemically modified by the attachment of ferrocene residues. Cyclic voltammograms have been obtained for ferrocene surface bonded to RVC by several methods and the mechanistic implications discussed [76].

8. FERROCENIUM SALTS AND MIXED-VALENCE SALTS

The crystal and molecular structure of the mixed-valence diferrocenium triodide (8.1) has been determined by X-ray crystallography. Average-valence iron was present at 298°K while ferrocene and ferrocenium groups were distinguished at 110°K. A three-dimensional network of hydrogen bonds between the cation and the anion was present at 110°K but absent at the higher temperature [77].



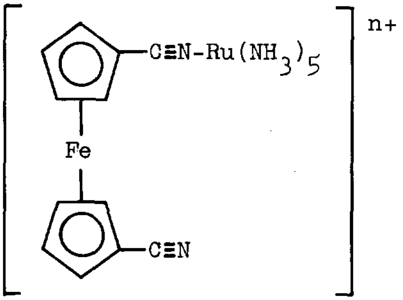
8.1

The ferrocenium ion and dimethyl-, tetramethyl-, hexamethyl-, octamethyl- and decamethyl-ferrocenium ion have been studied by ^1H and ^{13}C NMR spectroscopy and ESR spectroscopy. The results demonstrated that polymethylferrocenium ions show significant magnetic anisotropy and the isotropic shift received an appreciable contribution from pseudocontact components. The mechanism for distribution of the unpaired electron density was discussed. The ground state for the cations was $^2E_{2g}$ and the $^2A_{1g}$ state was thermally populated at room temperature in the ferrocenium ion and the dimethyl derivative [78].

The ferrocenium cation has been reduced by the ethoxide ion to ferrocene and the ethoxy radical which was identified by spin trapping. The same intermediate radical was obtained when methylferrocene in ethanol was irradiated in the presence of traces of oxygen. A mechanistic scheme was proposed to account for the results obtained [79].

The decomposition of the ferrocenium ion by hydrogen peroxide in acid has been the subject of a kinetic investigation [80].

1,1'-Dicyanoferrocene has been used to prepare the binuclear (8.2; n = 2) and the trinuclear (8.3; n = 4) mixed ferrocene-ruthenium complexes. These were then converted to the mixed valence species (8.2; n = 3 and 8.3; n = 5, 6) which were found to exhibit similar spectral, IR and UV, and electrochemical properties. Weak electronic interaction between the ferrocene group and the ruthenium nuclei was proposed but with no end-to-end interaction in the monoxidized trinuclear species (8.3; n = 5). The effect of the electrostatic contribution to the intervalence transfer transition energies was determined [81].



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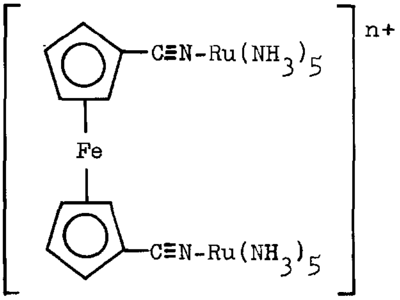
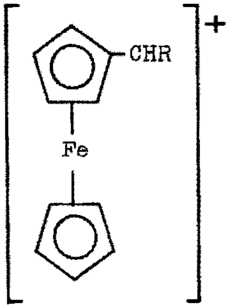


8.3

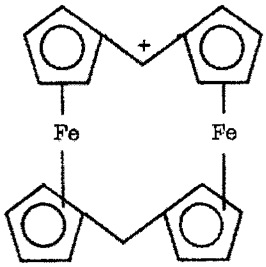
9. FERROCENYL CARBENIUM IONS

The structure of secondary ferrocenylcarbenium ions (9.1) has been investigated by ^{1}H NMR spectroscopy and ^{57}Fe Moessbauer spectroscopy. High quadrupole splittings were obtained for the ions (9.1; R = Me, Ph) which indicated iron participation using E_2 orbitals. Quadrupole splittings decreased with an increase in the electron donating power of the substituent X in the ions (9.1; R = p-C_6H_4X). High quadrupole splittings were interpreted in terms of electron withdrawal from iron-based orbitals ε_2 [82].

The effect of conformational rigidity on the stabilization of positive charge in the cis-fixed diferrocenylcarbenium ion (9.2) has been investigated. Moessbauer spectroscopy has shown that the positive charge was distributed evenly over the two ferrocenylene groups and the methinyl group. X-ray



9.1



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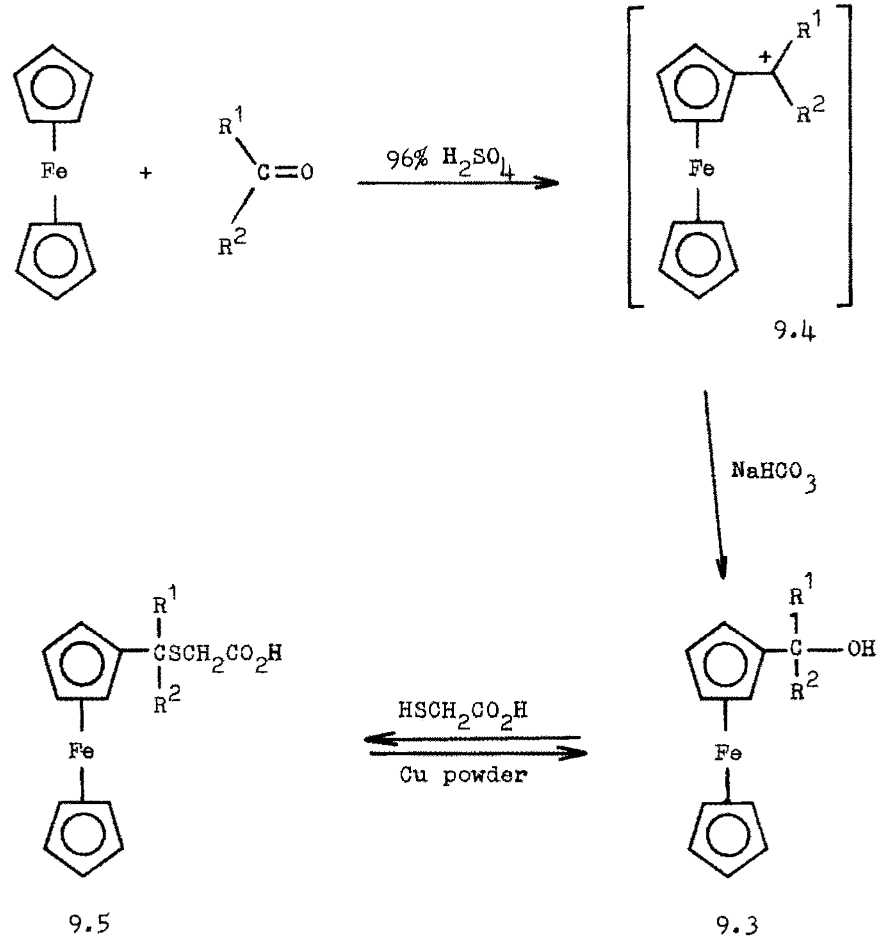

Fe
R^1
C=O
R^2
96% H_2SO_4
R^1
R^2
Fe
9.4
$NaHCO_3$
R^1
$CSCH_2CO_2H$
R^2
Fe
$HSCH_2CO_2H$
Cu powder
R^1
C
OH
R^2
Fe
9.5
9.3

crystallography was used to confirm that distortions to the structure were implicated in the stabilization of the charge [83].

A series of ferrocenyl-alcohols (9.3; $R^1 = R^2 = H$, Me; $R^1 = H$, R^2 = n-Pr, i-Pr, Ph; R^1 = Me, R^2 = Et) has been prepared by condensation of ferrocene with the appropriate carbonyl compound in concentrated sulphuric acid followed by addition of the resulting 1-ferrocenylalkylium ions (9.4) to aqueous sodium bicarbonate. The mixtures were treated with thioglycolic acid and the resultant S-(1-ferrocenylalkyl)thioglycolic (9.5) acids purified via sodium salts and hydrolysed in the presence of copper powder to produce 1-ferrocenylakyl alcohols in good yields (Scheme 9.1) [84].

10. FERROCENE CHEMISTRY

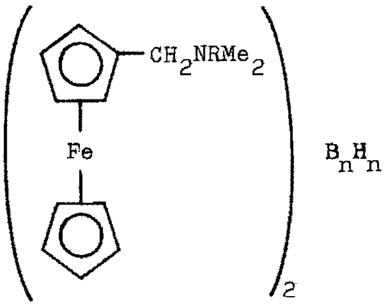
(i) Derivatives containing other metals (metalloids)

The reactions of the borane anions $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$ and $B_3H_8^-$ with ferrocenylmethyl quaternary ammonium salts have been investigated [85].

The reaction of $(Et_4N)_2B_nH_n$ (n = 10, 12) or $Et_4NB_3H_8$ with ferrocenylmethyl-N-alkyl-N,N-dimethylammonium halides gave the ferrocenylmethyl derivatives (10.1 and 10.2; R = Me, Et, Pr, allyl, $CH_2C{\equiv}CH$) respectively. Similar reactions were carried out with 1,1'-bis(alkyldimethylammonium)ferrocene dihalides to give the heteroannularly disubstituted compounds (10.3 and 10.4) [86].

A comparison has been made of the redox properties of small metallacarboranes with those of metallocenes and large metallacarborane clusters. 1,2,3-(η-C_5H_5)Fe($C_2B_4H_6$), isoelectronic with $[(\eta\text{-}C_5H_5)_2Fe]^+$, underwent reversible reduction at about 0.8 V negative of the ferrocenium reduction potential. It was concluded that a comparison of the differences in potential between successive redox processes supported the idea of an isoelectronic model for metallocenes and metallacarboranes [87].

The ferrocenyl-silane (10.5) has been used to functionalize the surfaces of smooth Au, smooth Pt, single-crystal n-type (100)Si and various other Si and Ge electrodes. Cyclic voltammetry indicated the presence of a monolayer of ferrocene on the smooth electrode surface whilst a great degree of coverage



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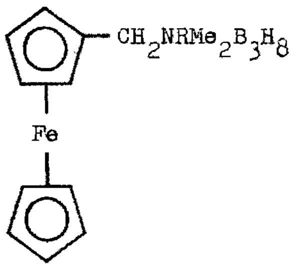

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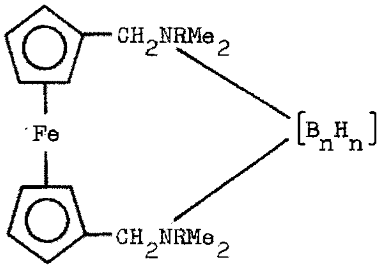

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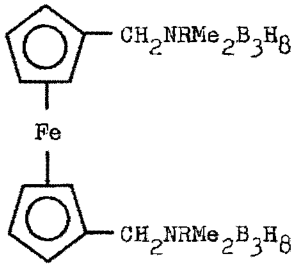
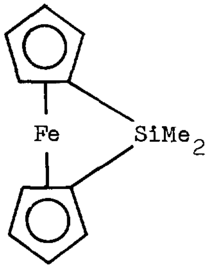


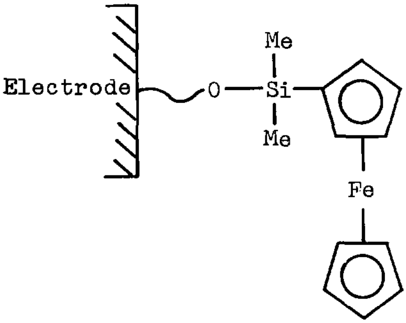
10.4

was obtained on textured and rough surfaces. ^{29}Si and ^{13}C NMR spectra indicated that the mode of attachment of the silane to the electrode was surface-O-(dimethylsilyl)ferrocene (10.6) [88].

Lithiation of ferrocene with n-butyl lithium followed by condensation with $ClSiEt_2CH{=}CH_2$ produced the ferrocenyl-silane (10.7). Treatment of ferrocene with n-amyl sodium followed by reaction with $R^1R^2_2SiCl$ produced the corresponding 1,1'-disubstituted ferrocenes (10.8; $R^1 = R^2$ = Me, Bu; R^1 = Ph, R^2 = Me). Some reactions of 1,1'-diacetylferrocene with Grignard reagents were examined also [89].

The 1,1'-dilithioferrocene-TMEDA complex has been treated with the chlorides $RMCl_2$, where R = Me, M = P and R = Ph, M = As,



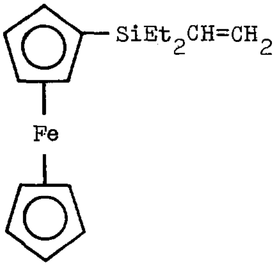


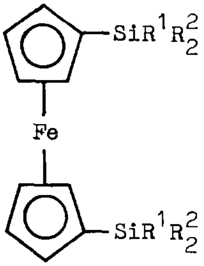
10.5

10.6

to form the [1]ferrocenophane (10.9; MR = PMe, AsPh). The phosphorus or arsenic bridge was cleaved by organolithium reagents while reactions with sulphur and metal carbonyls left the bridge intact [90].

The [1]ferrocenophane (10.9; MR = PPh) has been combined with 1-(diphenylphosphino)-1'-lithioferrocene in THF to give the oligomers (10.10; n = 1-5) after hydrolysis. Phenyldichlorophosphine was polymerized with the 1,1'-dilithioferrocene-TMEDA complex to form the polymer (10.10), molecular weight 8,900-161,000. The oligomeric and polymeric products (10.10) showed good thermal stability at ≤350°C [91].





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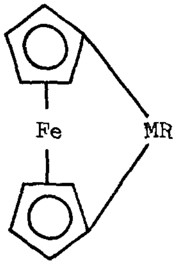

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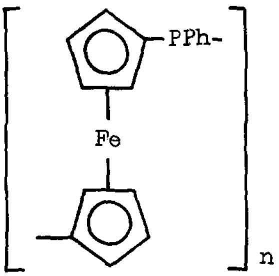
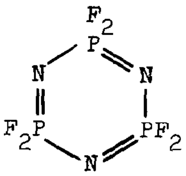


10.10

The cyclic trimeric fluorophosphazene (10.11) combined with lithioferrocene in diethyl ether at -78°C to form the ferrocenylphosphazene (10.12; X = F) which was attacked by sodium trifluoroethoxide, $NaOCH_2CF_3$, in boiling THF to give the phosphazene(10.12; $X=OCH_2CF_3$). The ferrocenylphosphazene (10.12; X = F) was characterized by X-ray crystallography. Similar reactions were carried out with cyclic tetrameric fluorophosphazene [92].

The ferrocenylaminomethylphosphonates (10.13; R^1 = 1,3,4-triazol-1-yl, 2-pyridyl, R^2 = Me, Et, Pr, Me_2CH, Bu, Me_2CHCH_2) were prepared by treating formylferrocene with an amine, R^1NH_2, and $HP(OR^2)_2$. The phosphonates (10.14; R = piperidino,



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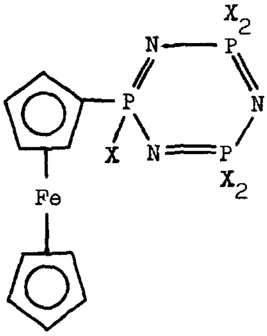

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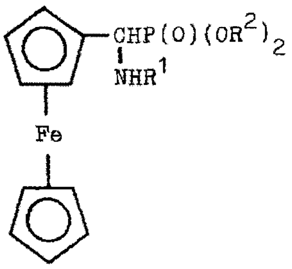

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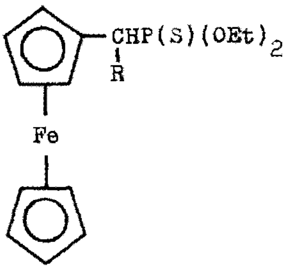

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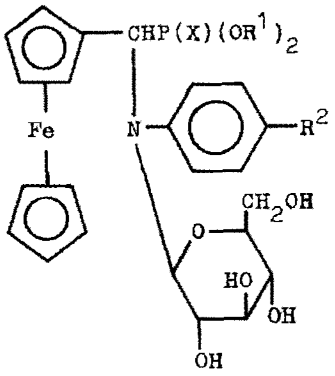
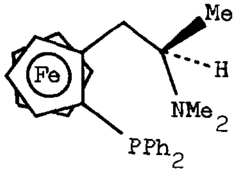


10.15

morpholino, NHPh, *p*-MeC_6H_4NH, 1,3,4-triazol-1-ylamino) and (10.15; R^1 = Et, Pr; R^2 = H, Me; X = O, S) were also prepared [93].

Several chiral ferrocenylphosphines with both planar and central elements of chirality and also a functional group on the side chain, for example 10.16 and 10.17, have been used as ligands for nickel and palladium. These complexes catalysed asymmetric Grignard cross-coupling reactions. The phosphine (10.17) was one of the most effective ligands and in the reaction of 1-phenylethylmagnesium chloride with vinyl bromide the coupling product, 3-phenyl-1-butene, was obtained in good yield and high optical purity. It was found that the ferrocene planar chirality was more important than the carbon central chirality and the presence of the dimethylamino group was important if



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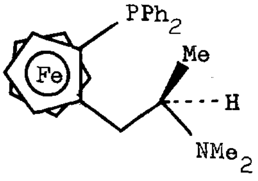
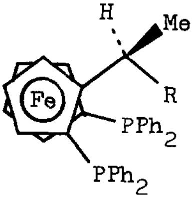
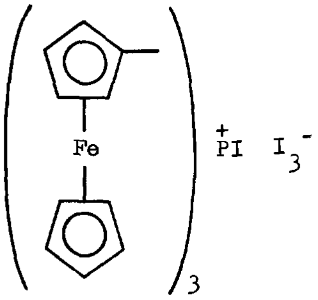


10.17

high stereoselectivity was to be achieved [94, 95].

The acetate (10.18; R = $OCOCH_3$) was produced when the amine (10.18; R = NMe_2) was heated with acetic anhydride. Treatment of the acetate(10.18; R=$OCOCH_3$) with amines gave the corresponding chiral ferrocenyl-phosphines (10.18; R = NR^1R^2, R^1R^2 = H, Me, Et, allyl, $Me_2NCH_2CH_2$, $MeNHCH_2CH_2$, $HOCH_2CH_2$ and NR^1R^2 = pyrrolidino, piperidino, 4-methyl-1-piperazinyl). Reaction of the acetate (10.18; R = $OCOCH_3$) with n-butyllithium followed by hydrolysis produced the alcohol (10.18; R = OH). The rhodium complex of this alcohol was an effective catalyst for the asymmetrical hydrogenation of acetophenone, pyruvic acid and 3,4-dihydroxyphenylmethylaminomethyl ketone hydrochloride [96].





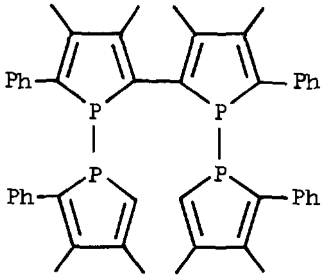
10.18

10.19

In related work nickel complexes have been used as catalysts for the asymmetric cross-coupling of <u>sec</u>-alkyl Grignard reagents with vinyl bromide. In most of the reactions the products were obtained almost quantitatively with high enantiomeric excess [97].

Triferrocenylphosphine (TFP) combined with iodine in ether-benzene to give the adducts TFP.I_2 and TFP.I_4. The latter was characterized by X-ray crystallography as triferrocenyliodide-phosphonium triodide (10.19). The positive charge was localized on phosphorus and I_3^- was present as symmetrical linear anions [98].

Thermolysis of 1-phenyl-3,4-dimethylphosphole produced the tetramer (10.20). Treatment of the tetramer with sodium naphthalenide gave the dianion (10.21) which on reaction with magnesium bromide and then iron(II) chloride gave the analogue of a bis(fulvalene)diiron (10.22). Reaction of the tetramer (10.20) with $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ afforded the phosphorus analogue



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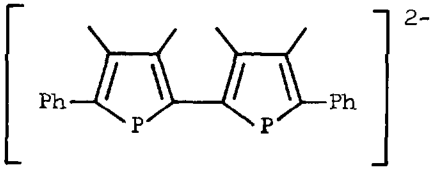

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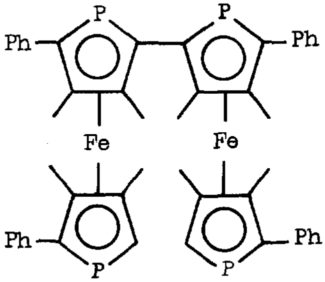

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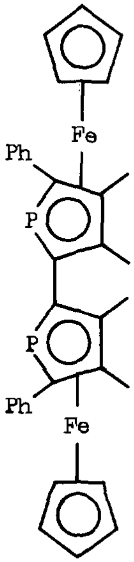
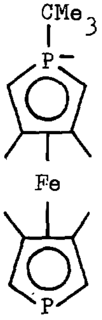


10.23

of a biferrocene (10.23) as a mixture of two diastereoisomers [99].

Treatment of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene with t-butyllithium afforded the corresponding anion (10.24). Reaction of the anion (10.24) with acyl chlorides produced the stable 1-t-butyl-1-acyl-1,1'-diphosphaferrocenes (10.25; R = COMe, COPh). X-ray analysis of these latter compounds indicated that the phosphorus atom was not bound to the iron and that they were better represented as (η^5-phospholyl)(η^4-phospholium)iron zwitterions [100].



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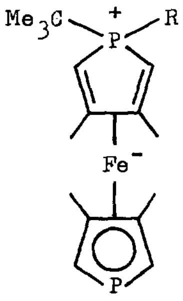
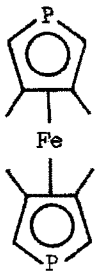


10.25

The preparation of 1,1'-diphosphaferrocenes has been the subject of a patent. For example, 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene was prepared by the lithiation of 3,4-dimethyl-1-phenylphosphole followed by treatment with iron(II) chloride in the presence of aluminium chloride [101].

Acylation of the diphosphaferrocene (10.26) with $ClCO_2Et$ gave the 2-substituted derivative (10.27; R = Et) which was hydrolyzed to the corresponding acid (10.27; R = H). Treatment of the phosphaferrocene (10.26) with benzyl bromide resulted in ligand removal to give the salt (10.28). The tetracarbonyliron complexes (10.29 and 10.30) were also prepared [102].

Ferrocene was attacked by sulphur in the presence of dodecacarbonyltriiron in benzene at 80°C to form several derivatives containing catenated sulphur (10.31; n = 3, 4, 5; 10.32; n = 1, 2, 5; 10.33) [103].



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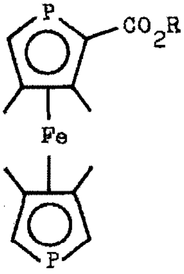

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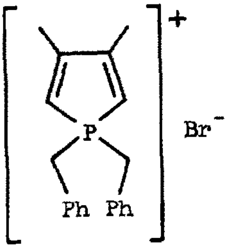

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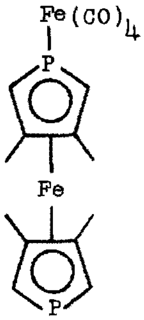

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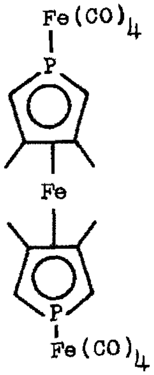

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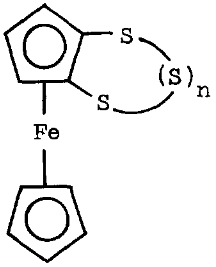
The disodium salt of ferrocene-1,1'-dithiolate combined with $BrCH_2(CH_2OCH_2)_nCH_2Br$, where n = 1-4, to form the polyoxathiaferrocenophanes (10.34; n = 1-4 and 10.35; n = 1-3). Some of the products (10.34; n = 3, 4 and 10.35; n = 1-3) were efficient complexing agents for Ag^+ [104].

A series of 1,3-diselena-[3]ferrocenophanes (10.36; Y = CH_2, CPh_2, $SiMe_2$, SiPhMe, $SnMe_2$, $SnPh_2$) have been prepared by reaction of ferrocene-1,1'-diselenol with halide complexes of the Group IV elements. In solution these compounds were fluxional by a bridge-reversal process. The spiro compound bis(ferrocene-1,1'-diselenato)tin (10.37) was also prepared and its structure was determined by X-ray analysis [105].



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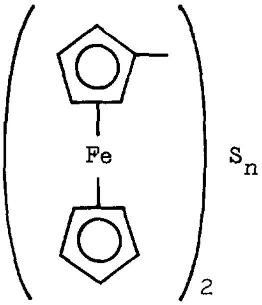

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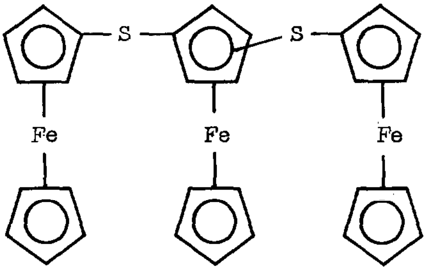

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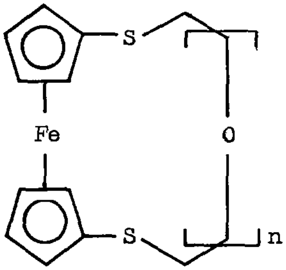

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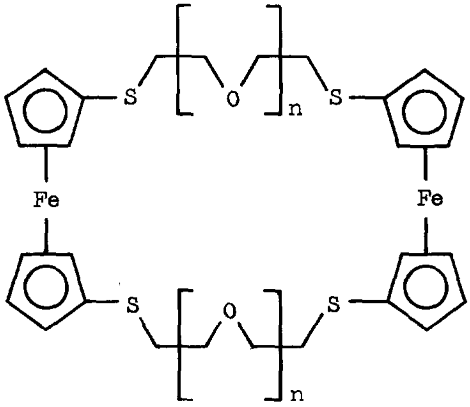

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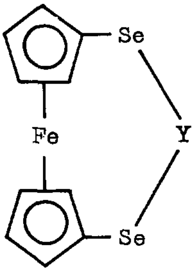

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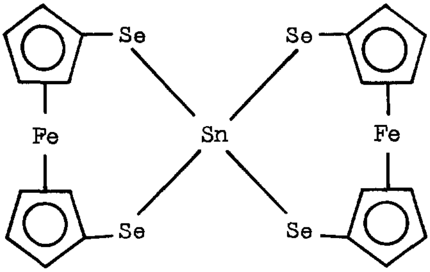
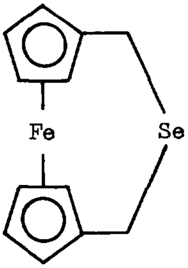


10.37

Hydrogen selenide combined with 1,1'-bis(hydroxymethyl)-ferrocene in CH_3CO_2H and CF_3CO_2H to form the 2-selena[3]-ferrocenophane (10.38) [106].



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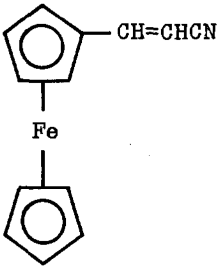

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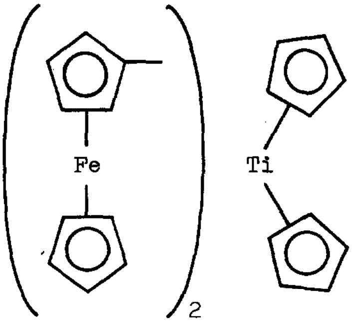
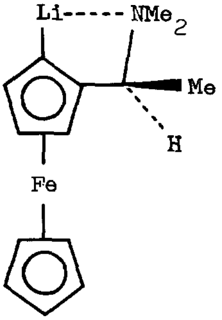
Chloromercuriferrocene underwent Pd(II)-catalyzed alkylation with acrylonitrile to form (2-cyanovinyl)ferrocene (10.39) as a mixture of <u>cis</u> and <u>trans</u> isomers which were separated by chromatography on alumina. 1,1'-Bis(chloromercuri)ferrocene gave only a low yield of 1,1'-bis(2-cyanovinyl)ferrocene [107].

Reaction-solution calorimetry has been used to determine the standard enthalpy of formation of the diferrocenyltitanium complex (10.40), ΔH_f° = 520.4 kJ mol^{-1} [108].



10.40

The chiral (R,R)-lithioferrocene (10.41) was treated with hexacarbonyltungsten to form an intermediate carbene complex which was cyclized to the binuclear carbenes (10.42; R^1 = Me, H, R^2 = H, Me) [109].



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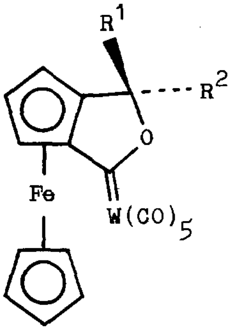

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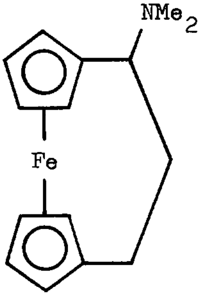
η-Allylchloro(triferrocenylphosphine)palladium, η-allylchloro(bisferrocenylphenylphosphine)palladium and η-allylchloro(ferrocenyldiphenylphosphine)palladium have been prepared from bis(η-allylpalladium) dichloride and the corresponding phosphine [110].

Asymmetric cyclopalladation of 1'-dimethylamino[3]ferrocenophane (10.43) in the presence of the sodium salt of

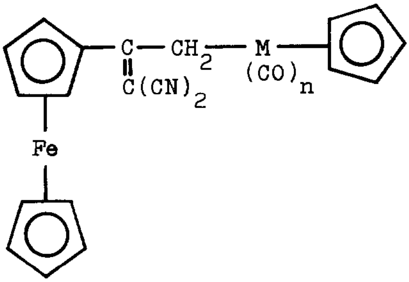


10.43

N-acetyl-D- or -L-leucine gave an optically active product in near quantitative yield. Restriction of conformational mobility of the ferrocenophane (10.43) caused the S-configuration of the chiral centre to induce preferentially Sp planar chirality [111].

The iron- and tungsten-cyclopentadienylcarbonyl complexes (10.44; M = Fe, n = 2; M = W, n = 3) have been converted by thermolysis or photolysis to the corresponding allyl complexes (10.45; M = Fe, n = 1; M = W, n = 2) [112].

Treatment of cymantrene with lithioferrocene or 1,1'-dilithioferrocene followed by reaction with triethyloxy tetrafluoroborate produced the carbene complexes (10.46 and 10.47) respectively [113].



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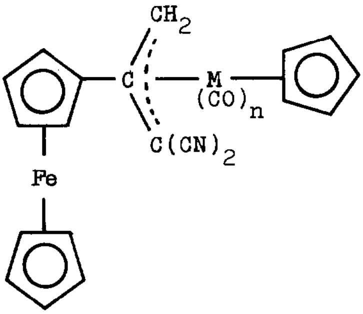

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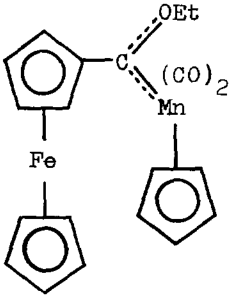

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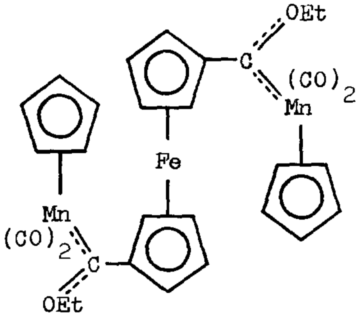

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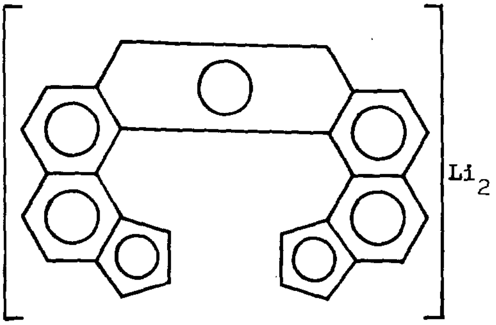
Reaction of the lithium salt (10.48) with pure iron(II) chloride gave the helical ferrocene (10.49) [114].

The ferrocenyl-ruthenium complex (10.50) has been purified by chromatography on glass beads [115].

Reaction of 1,1'-dibenzoylacetylferrocene (L) with a series of transition metal acetates produced the chelate complexes ML, where M = Fe(II), Co(II), Ni(II) and Cu(II) [116].

1,1'-Dicuproferrocene (10.51) has been prepared by the reaction of 1,1'-dilithioferrocene with $[CuBr.PPh_3]_4$. The copper derivative (10.51) decomposed at 136°C to give ferrocene, diferrocene and 1,1'-terferrocene and on reaction with copper(II)



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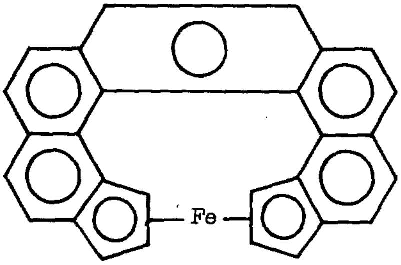

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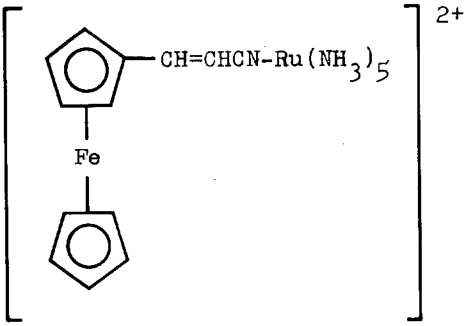
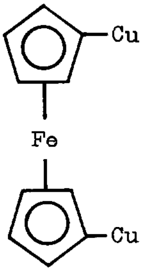


10.50

chloride, 1,1'-dichloroferrocene, 1,1'-terferrocene and polyferrocene were isolated as the major products [117].



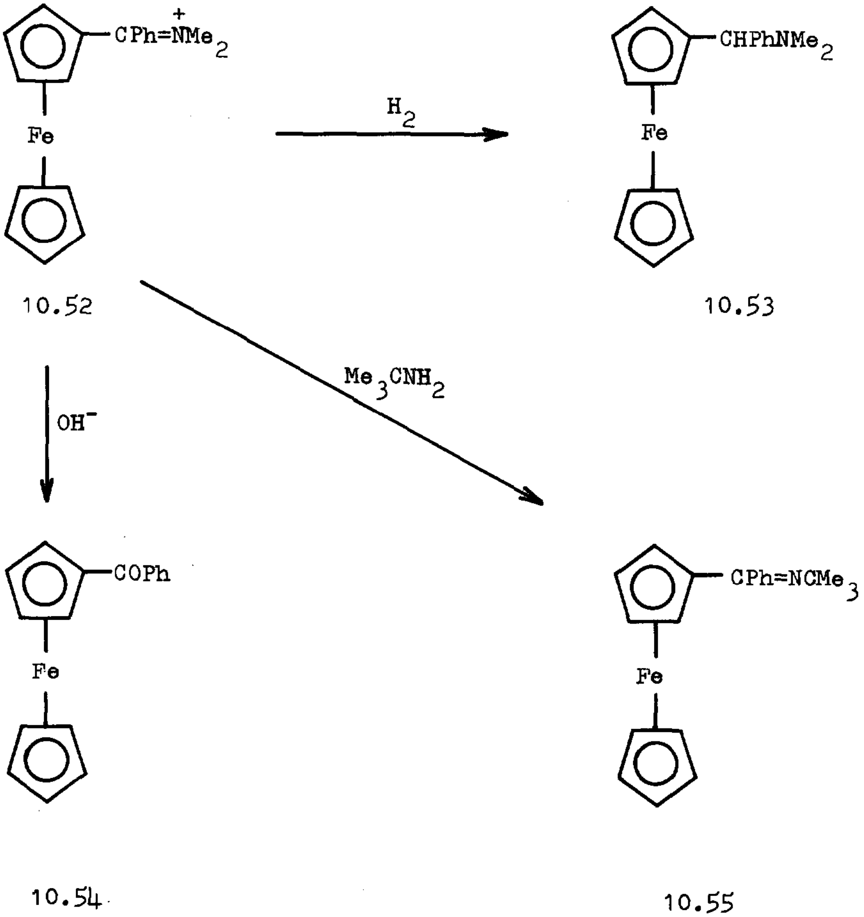
10.51

(ii) General Chemistry

The photoreactions of vinylferrocene with carbon tetrachloride and tetrachloroethene in cyclohexane have been studied. Irradiation at $\lambda = 300$ nm and $\geqslant 300$ nm caused photodecomposition and quantum yields of the photoproducts were determined. From the UV spectra it was concluded that intermolecular charge-transfer complex formation between vinylferrocene and the halogenated solvent was the first stage of the reaction [118].

The photolysis of acetylferrocene in carbon tetrachloride-cyclohexane and tetrachloroethylene-cyclohexane mixtures has been studied. Charge-transfer complexes were formed between the acetylferrocene and the chlorinated solvents. The equilibrium constants and molar extinction coefficients for these complexes were calculated. The photodecomposition products were identified and included cyclopentadiene, cyclohexyl chloride and iron chloride. Quantum yields were calculated [119].

Ferrocenyliminium cations underwent hydrogenation to the corresponding tertiary amines, hydrolysis with base to the corresponding aldehydes or ketones and conversion to the imines with primary amines. Thus the cation (10.52) was converted to



10.52

10.53

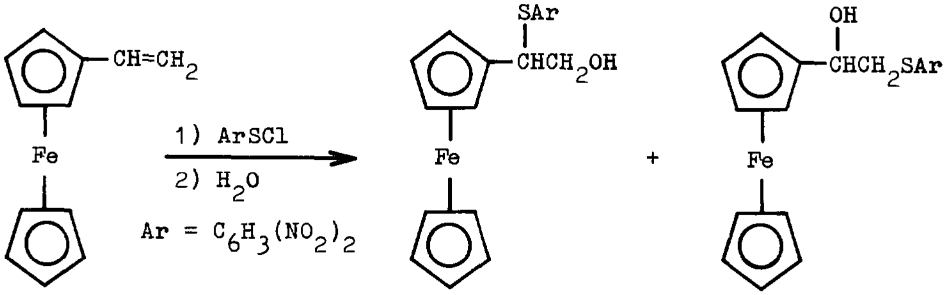
10.54

10.55

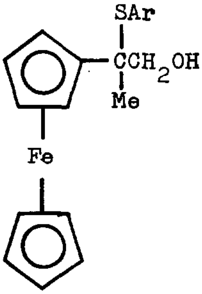
the tertiary amine (10.53), to benzoylferrocene (10.54) and to the imine (10.55) with t-butylamine [120].

Decamethylferrocene has been found to resist reduction by $Co_2(CO)_8$ at 200°C under pressure and in the presence of carbon monoxide and hydrogen. Ferrocene was reduced under the same conditions [121].

Vinylferrocene (10.56) and its methyl-substituted derivatives have been treated with 2,4-dinitrobenzenesulphenyl chloride to give the products of addition to the double bond. Vinylferrocene in acetic acid solution gave two addition products (10.57 and 10.58) after hydrolysis whereas ∝-methylvinylferrocene in dichloromethane produced one addition product (10.59) [122].



10.56 10.57 10.58



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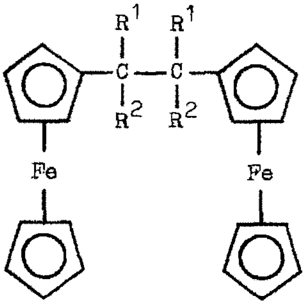
Titanium-induced reductive coupling of the lithium salts of the ferrocenyl carbinols $FcCR^1R^2OH$, where R^1 = H, Me, CMe_3, Ph, ferrocenyl, R^2 = Me; R^1 = ferrocenyl, R^2 = α-naphthyl, gave the corresponding 1,2-diferrocenylethanes (10.60) [123].



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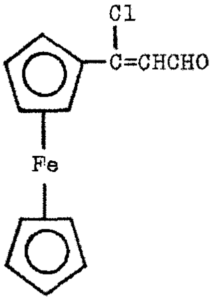
Cyclization of β-chloro-β-ferrocenylacrolein (10.61) with the amines m-$H_2NC_6H_4R$, where R = OMe, OH, produced the corresponding quinoline derivatives (10.62). The substituted pyridines (10.63; R^1 = R^2 = Ph, Me; R^1 = Me, R^2 = OEt; R^1R^2 = $CH_2CMe_2CH_2$) were produced in similar reactions [124].

The treatment of the ferrocenylmethanols (10.64; R^1 = H, Me, R^2 = H, Me) with nucleophiles in the presence of dichloromethane and aqueous acids gave the corresponding ferrocenylmethyl derivatives in 50-99% yield. Thirteen compounds were prepared [125].

Treatment of ferrocenylmethylchloride or the salt (10.65) with urea produced the ferrocenylmethyl derivative (10.66). Reaction of the complex (10.65) with thiourea afforded the salt (10.67) [126].

Chlorocarbonylferrocene combined with aziridine to form 2-ferrocenyl-2-oxazoline (10.68; X = H) and this compound underwent regiospecific lithiation with n-butyllithium to form the 2-lithio intermediate (10.68; X = Li) which was treated with iodomethane and chlorotrimethylsilane to give the derivatives (10.68; X = Me, $SiMe_3$). The oxazoline group was degraded to the carboxyl group by acid hydrolysis [127].



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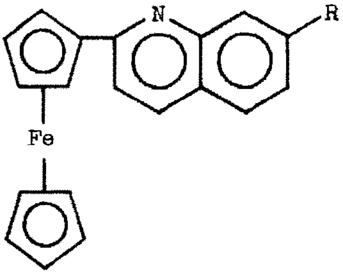

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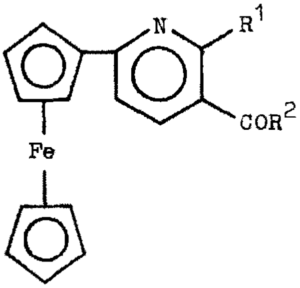

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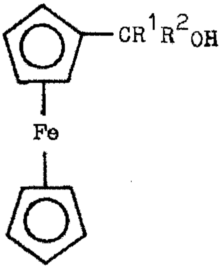

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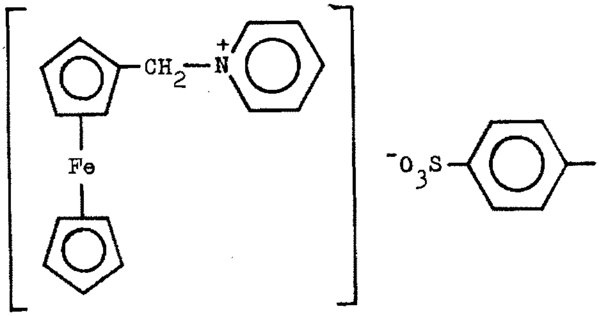
Bis(ferrocenylmethyl)ether (10.69) has been prepared in high yield by the treatment of ferrocenylmethanol with p-$RC_6H_4SO_2Cl$ (R = H, Me) in 30% aqueous benzene in the presence of the phase transfer catalyst $PhCH_2\overset{+}{N}Et_3Cl^-$ [128].

Formylferrocene has been treated with chloroform in the presence of the interphase catalyst $PhCH_2\overset{+}{N}Et_3Cl^-$ to give α-ferrocenylglycolic acid in 54% yield, 1,3-diferrocenyl-1-propen-3-one was also obtained [129].

Treatment of formylferrocene azine with dodecacarbonyltriiron produced the dione (10.70) [130].

The ferrocenylketones (10.71; R = H, Me, CCl_3, Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-$Me_3CC_6H_4$, 3,4-$Cl_2C_6H_3$) were obtained by oxidation



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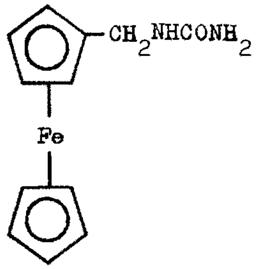

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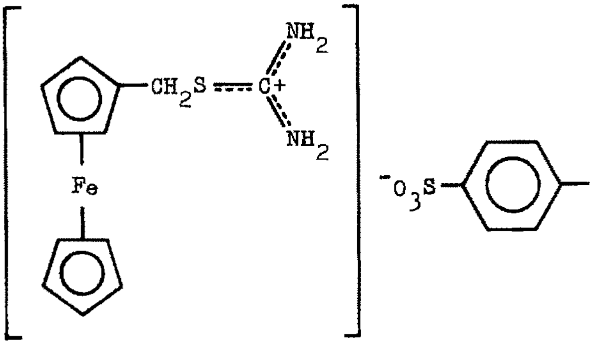

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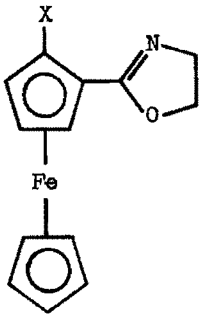

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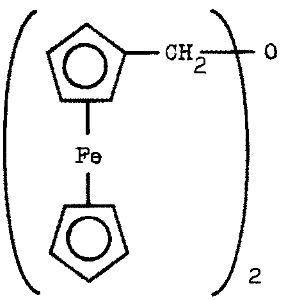

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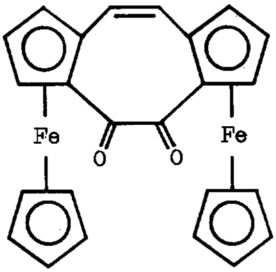

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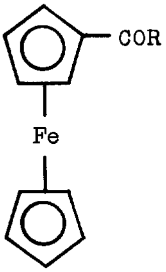


10.71

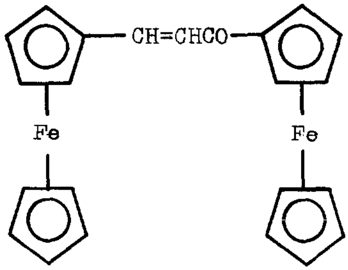
of the corresponding secondary alcohols with bis(triphenylsilyl)-chromate(VI), $(Ph_3SiO)_2CrO_2$. Yields were in the range 66-82% [131].

It was suggested that the reaction proceeded via a two-step mechanism in which the transesterification of the initial components was followed by a rate determining redox decomposition of the intermediate CrO_2 ester [132].

The chalcone analogue (10.72) underwent cyclic condensation with hydrazine to form the dihydropyrazole (10.73) which gave the diferrocenyl cyclopropane (10.74) on heating with Pt-C-KOH. Methyl derivatives of the unsaturated ketone (10.72) underwent parallel reactions [133].

A kinetic study of the cyclization of the 1-alkenoyl-1'-acylferrocenes (10.75; R^1 = H, Me, Et, $CHMe_2$, Ph, CMe_3; R^2 = H, Me) in the presence of sodium methoxide demonstrated that the rate of reaction was markedly dependent on the steric effects imposed by substituents R^1 and R^2. A parallel study showed that substitution at the double bond of the alkenoylferrocene (10.76; R^1, R^2 = H, Me, R^3 = H, Me, CMe_3, R^4 = H, Ph) had only a small effect on the cyclization. The results were interpreted in terms of the transition state for the process [134].

Some ferrocenyl- and ruthenocenyl- analogues of chalcones have been acetylated under Friedel-Crafts conditions. The ferrocenyl-ketone (10.77; Mp = 1-methylpyrrol-2-yl) was acetylated on the methylpyrrol group whereas the isomer (10.78) was



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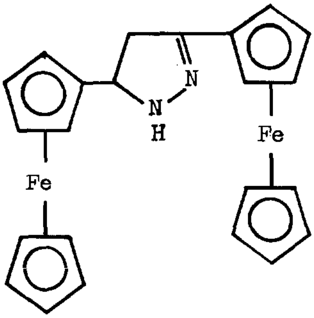

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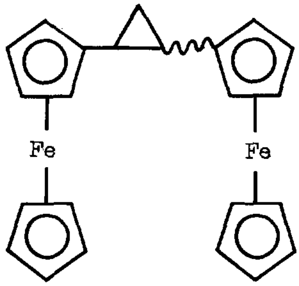

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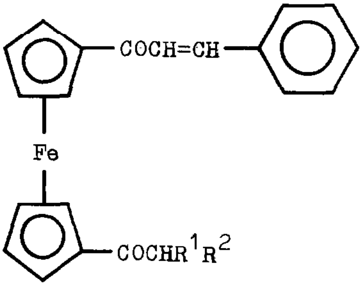

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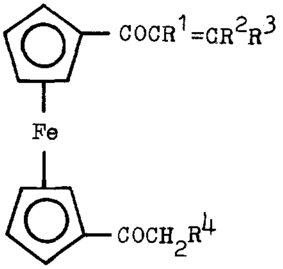

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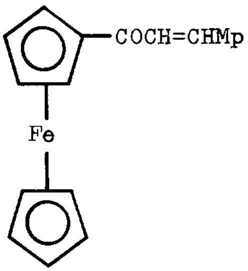

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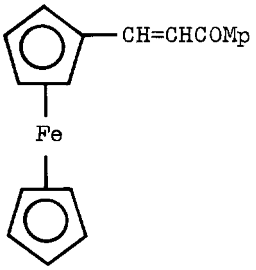
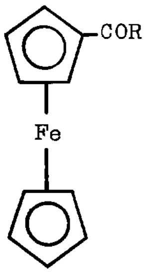


10.78

acetylated at all possible positions [135].

The reduction of some ferrocene containing β-unsaturated ketones has been studied [136].

The ferrocenylketones (10.79; R = Me, Et, $CHMe_2$, Ph, CF_3 and 10.80) have been reduced stereoselectively by Cervinka's complex (quinine-lithium aluminium hydride) to give the corresponding (R)-(-)-alcohols in good yields [137].



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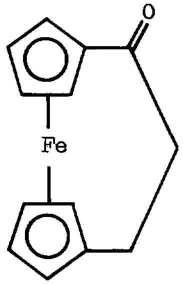

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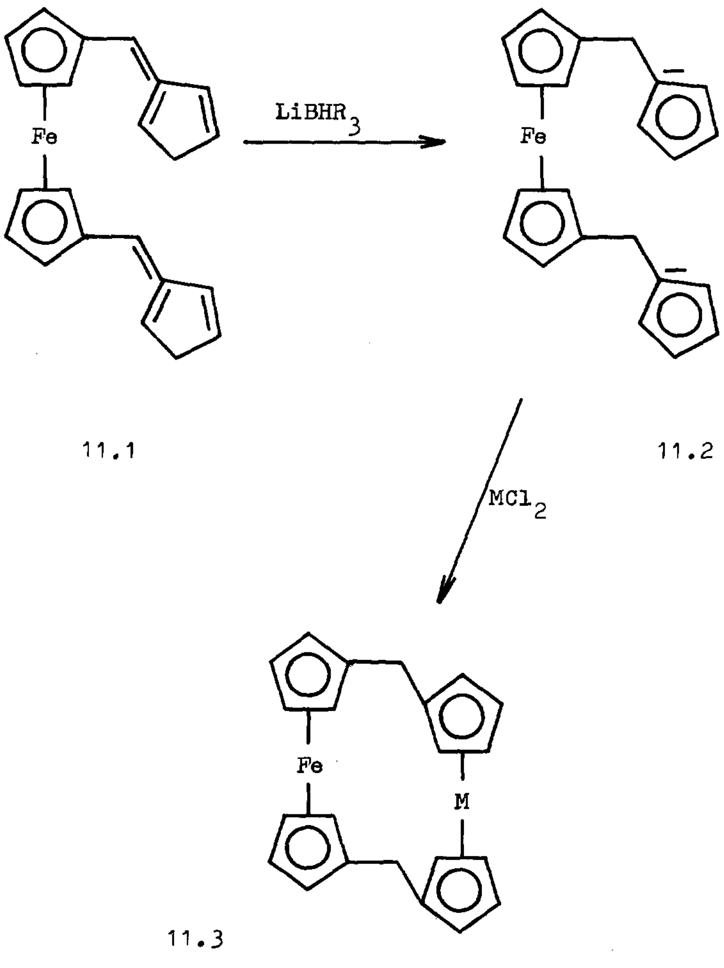
11. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

The structure of biferrocene has been redetermined by X-ray crystallography. The crystal was monoclinic and disorder in it was recognized as the remnant of an ordered low temperature phase [138].

Bis(fulvenyl)ferrocene (11.1) has been treated with $LiBHR_3$ to form the 1,1'-bis(cyclopentadienylmethyl)ferrocene dianion (11.2) which combined with iron(II) chloride and with ruthenium (II) chloride to give the [1.1]metallocenophanes (11.3; M = Fe, Ru) respectively [139]. Cyclic voltammetry of these two products confimed two reversible one-electron oxidations for [1.1]ferrocenophane (11.3; M = Fe) but the mixed metallocenophane (11.3; M = Ru) showed a ferrocene centred one-electron reversible oxidation together with a ruthenocene centred two-electron irreversible oxidation [140].

Ferrocene-1,1'-dicarboxaldehyde has been treated with $TiCl_4$-$LiAlH_4$ in THF containing tributylamine to give the ferro-



11.1

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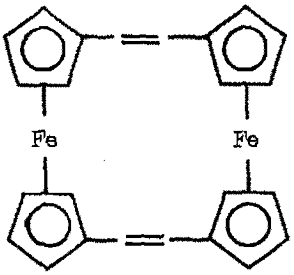

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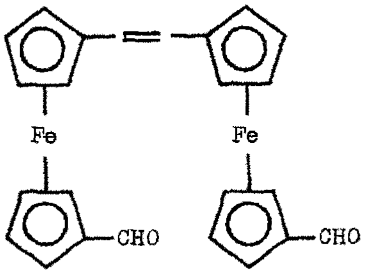
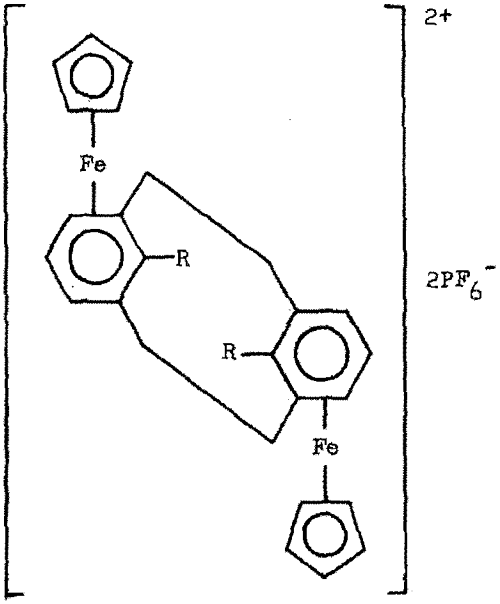


11.5

cenophane (11.4) and the diferrocenylethylene (11.5). Several related reactions were reported [141].

Treatment of ferrocene with anti-[2.2]metacyclophanes in the presence of aluminium chloride and aluminium produced the corresponding (η^6-cyclophane)(η^5-cyclopentadienyl)iron(II) complexes (11.6; R = H, Me) [142].



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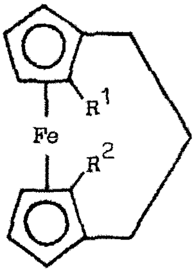
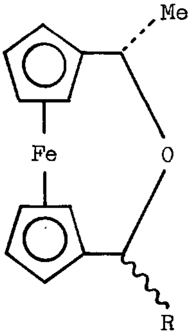


11.7

The [3]ferrocenophane (11.7; $R^1 = R^2 = H$) has been metalated with BuLi-TMEDA to give mono- and di-lithiation at the 2-, 3-, 2,2' and 3,3' positions. The lithio intermediates were converted to the bromo-, iodo- and methyl carboxylate derivatives. Typical products were the bromoferrocene (11.7; $R^1 = Br$, $R^2 = H$) and the diiodoferrocene (11.7; $R^1 = R^2 = I$) [143].

Steric hindrance in the heteroferrocenophanes (11.8; R = α, β-Me) and (11.9; X = S, CH_2) has been studied by ^{13}C NMR spectroscopy. The conformations of some of the ferrocenophanes were determined [144].



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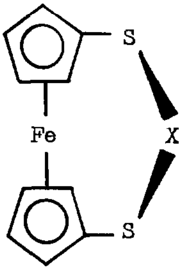
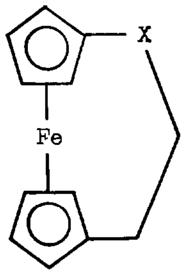


11.9

Moessbauer spectroscopy has been used to show that the [3]ferrocenophanes (11.10; X = C=O, CHOH) were ring-tilted. The low quadrupole splitting value for the [4]ferrocenophane (11.11; X = C=O) was attributed to interaction between the carbonyl group and iron, no evidence was found for protonation of this ketone in trifluoroacetic acid or 80% sulphuric acid. The alcohol (11.11; X = CHOH) had Moessbauer parameters close to those for ferrocene [145].

The oxidation of [n]ferrocenophanes with barium permanganate has been studied. α-Oxo compounds were only produced when $n > 3$ and the yield of product increased when n = 4 and 5. In doubly-bridged [n][3]ferrocenophanes the longer bridge was preferentially oxidized when $n > 3$. Oxidation of the ferrocenophanes (11.12; n = 3, 4, 5) gave the corresponding ketones (11.13) [146].

Bridge enlargement of α-oxo[3]ferrocenophane derivatives



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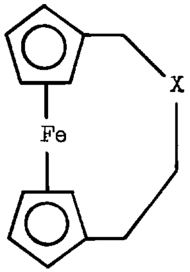

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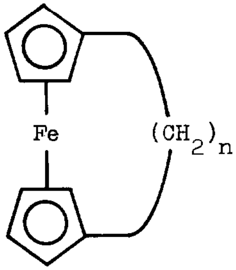

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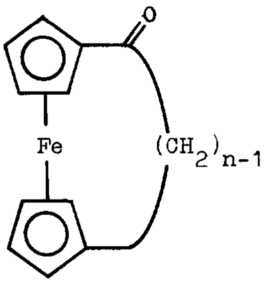
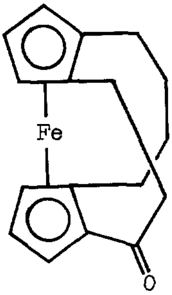


11.13

has been achieved by treatment with diazomethane in the presence of boron trifluoride etherate. For example, the treatment of [4](1,1')-α-oxo[3](2,2')ferrocenophane (11.14) with diazomethane in the presence of boron trifluoride as the catalyst produced α-oxo-[4][4]ferrocenophane (11.15). This reaction was used, followed by reduction of the ketone group, to prepare several new multibridged ferrocenophanes with tetramethylene bridges [147].

Treatment of [4_4]ferrocenophanepropionic acid (11.16) with polyphosphate ester produced the tetrabridged ferrocenophane trimer 6,9,12-trioxo[3.3.3](1,1')[4](2,2')[4](4,4')[4](5,5')-ferrocenophane. The structure of the trimer was determined by



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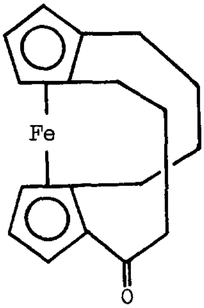
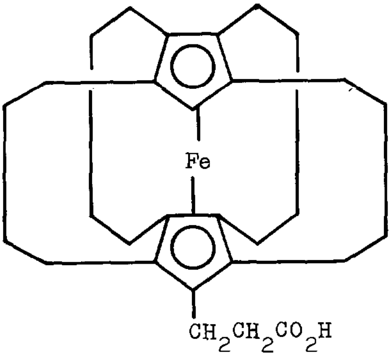


11.15

X-ray analysis and the tetramethylene bridges were shown to have a screw conformation [148].



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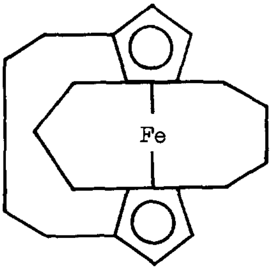
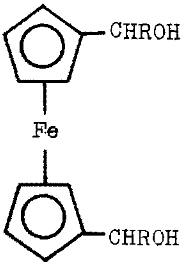


11.17

The crystal and molecular structure of the [4][3][4]-ferrocenophane (11.17) has been determined by X-ray crystallography. The two cyclopentadienyl rings were almost eclipsed with a dihedral angle between the rings of 10.4° [149].

Treatment of the ferrocenyl- alcohols (11.18; R = H, Me) with the thiols $HSCH_2CH_2O(CH_2CH_2O)_nCH_2CH_2SH$, where n = 1, 2, gave the corresponding diastereomeric oxathiaferrocenophanes (11.19). The individual stereoisomers of the diastereomeric ferrocenophane (11.19 ; R = Me) were separated by preparative thin-layer chromatography [150].



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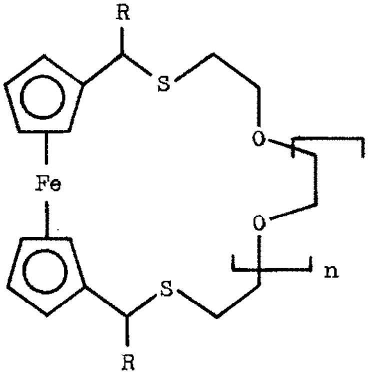


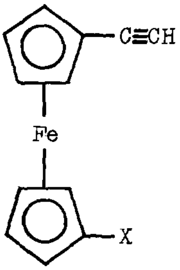
11.19

12. FERROCENE-CONTAINING POLYMERS

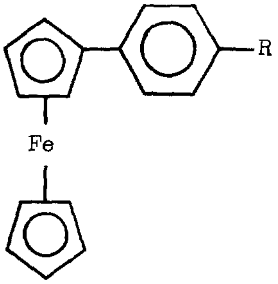
Moessbauer evidence for the structure of linear, saturated polymers formed by radical polymerization of 1,1'-divinylferrocene was consistent with cyclopolymers containing a three-carbon bridged ferrocene group in the main chain. Polymers formed in the presence of cationic initiators appeared to contain unstrained ferrocene groups consistent with five-carbon bridged bicyclic units or a ladder structure [151].

Dicarbonylferrocenes have been polymerized with biuret to form poly(ferrocenyleniminoimides) and with aromatic diamines to form poly(ferrocenylenazomethines). These new ferrocene polymers have been studied by DTA and thermogravimetry and it was found that the poly(ferrocenylenazomethines) showed good thermal stability at 200°C. Thermal stability was decreased by the presence of -O-, -S- and -S-S- bridges in the diamine comonomers [152, 153].

Polyenes, polyiminoimides and Schiff polybases containing ferrocene residues have been obtained by polymerization and by polycondensation. Among the monomers used were ethynylferrocene (12.1; X = H), 1-chloro-1'-ethynylferrocene (12.1; X = Cl), the ferrocenylstyrene (12.2; R = CCl=CHCHO), the phenylacetylene (12.2; R = C≡CH) and the acetophenone (12.2; R = COMe). Polymers with linear or three-dimensional structures were obtained and



12.1



12.2

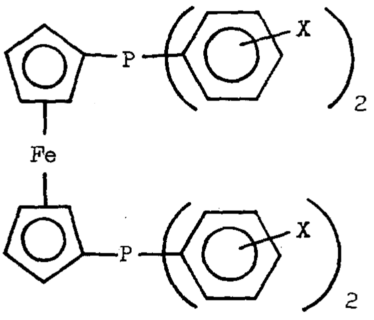
exhibited good thermal stability and semiconducting properties [154].

The preparation of some elastomers containing ferrocene has been reported [155].

13. APPLICATIONS OF FERROCENE

(i) Ferrocene catalysts and photosensitizers

Rhodium-phosphine catalyzed hydroformylation has been studied using 1,1'-bis(diphenylphosphino)ferrocenes (13.1; X = H, *p*-Cl, *m*-F, *p*-CF_3) as the ligands. The most selective catalyst had three phosphorus atoms bound to each rhodium and this was thought to be a dirhodium complex. The introduction of electron



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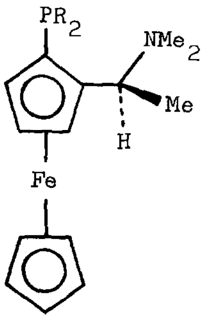


13.2

withdrawing substituents onto the ligand produced higher reaction rates and higher linear:branched aldehyde ratios [156].

$Pd(OAc)_2$-(S)-(R)-N,N-dimethyl-1-[1',2-bis(diphenylphosphino)ferrocenyl]ethylamine has been used as a catalyst for the asymmetric cyclization of methyl (E)-oxo-9-phenoxy-7-nonenoate to the corresponding cyclohexanone at 30°C for 0.7 h [157].

The chiral ferrocenyldiphenylphosphine (13.2; R = Ph) has been used as a ligand to form a complex with nickel(II) chloride which was effective as a catalyst for the stereoselective coupling of Grignard reagents, RCHMeMgCl, where R = Et, hexyl, Ph, with vinyl bromide and related bromides. The presence of the dimethylamino group was essential for high stereoselectivity in the reactions [158].

Secondary alcohols of high optical purity have been obtained by asymmetric hydrogenation of enol diphenylphosphinates in the presence of a cationic rhodium complex of (R)-1-[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethanol [159]. See also Section 10 (i), references 94 to 97.

Optically active ferrocenylphosphines (13.2; R = Ph, CMe_3) formed cationic complexes with rhodium(I) which were active in catalyzing the asymmetric hydrogenation of acetamidoacrylic acid derivatives and itaconic acid. The t-butyl complex (13.2; R = CMe_3) was the more efficient catalyst. Attempts to protect an alcohol function α to the ferrocenyl group with the (β-methoxyethoxy)methyl group were not successful [160].

The hydroformylation of olefins has been achieved in the presence of a platinum complex such as $PtCl_2(PhCN)_2$, and a group IV b compound with a ferrocene derivative, for example, tin(II) chloride with 1,1'-bis(diphenylphosphino)ferrocene. Thus 1-pentene was converted at 100 atm to a mixture of aldehydes including $Me(CH_2)_4CHO$ [161].

Polyethylene sheets containing a small proportion of ferrocene have been subjected to laser irradiation in order to produce films containing submicron iron particles. The radiation was soft focussed to give black spots 0.5-1 cm diameter in predetermined positions. The material had potential applications in data storage [162].

Polyethylene containing biferrocene 0.001-0.2 mol/kg underwent photooxidative degradation on UV irradiation. The reaction was characterized by an induction period which was followed by autocatalytic degradation. The length of the induction period was determined by the concentration of biferrocene. Degradation was inhibited by the presence of undecomposed biferrocene and sensitized by the organic decomposition products from the metallocene [163].

Biferrocene, at a level of 0.05-0.1%, was an effective sensitizer for the photodegradation of polyethylene film. The decrease in elongation of the film after aging was used as a measure of the degradation. The service life of the film was controlled by the amount of sensitizer added [164].

Polyacrylate films containing 1,1'-dimethylferrocene have been used to overcoat Se-SeTe xerographic photoreceptors for conventional electrophotography. The electrical properties of the films were unaffected by changes in temperature and relative humidity [165].

A light-sensitive composition has been developed for the copying of illustrations, for reproduction of micrographs, for integrated circuit masks and for photoresistors. A typical formulation was ethylferrocene 10%, tetrabromomethane 6%, β-naphthol-indole mixture 0.5% and ethanol to 100%. The composition was applied to a paper support exposed to a tungsten lamp and the image developed by heating at 60-100°C for one minute to give a brown copy [166].

A multifilament X-ray photon counter has been developed with a primary ionization chamber filled with xenon containing 0.1% ethylferrocene [167].

(ii) Ferrocene Stabilizers and Improvers

The effectiveness of binuclear ferrocene derivatives as light stabilizers in polythene was enhanced by the presence of sulphur containing antioxidants. It was suggested that the antioxidants significantly decreased the concentration of polymeric hydroperoxides which interacted with the iron atom of the ferrocene additive [168].

The presence of 0.25-1.0% 2,2'-bis[1,1'-diethyl-(*o*-methoxybenzoyl)ferrocenyl]propane in polyolefins increased their stability to ultraviolet radiation [169].

The thermoplastic properties of cross-linked polyethylene were improved and premature cross-linking was prevented by the addition of ferrocene 0.5-1, diphenylguanidine 0.5-1 and

$Ph_2Si(OH)_2$ 1.5-2 wt % [170].

Compositions containing a polymerizable vinyl compound, an organic peroxide and ferrocene were rapidly curable and were used as heat resistant adhesives for bonding speaker voice coil bobbins to vibration cones [171].

Thermogravimetric analysis has been used to determine the efficiency of ferrocene, acetylferrocene, ferrocenemethanol, 1,1'-diethylferrocene and [3]ferrocenophane as stabilizers for rigid poly(vinyl chloride) and polyethylene. The size, rather than the nature, of the substituent was important in determining the efficiency of the substituted ferrocene and the best stabilizer was [3]ferrocenophane [172].

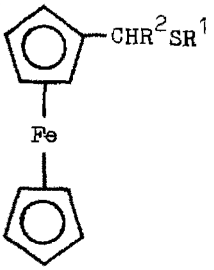
The strength of vulcanized rubbers derived from chloroprene rubber stock was increased by the use of diacetylferrocene-1,1'-dioxime (0.5-10%) as the vulcanizing agent [173].

Ferrocenylalcohols have been added to paraffin lubricating oils in order to improve the antiwear properties. The additives caused a favourable change in the pressure coefficient of viscosity at pressures >275 MPa [174].

The effect of ferrocenes in lubricating oils has been studied [175].

Ferrocene has been incorporated with a neutral emulsifying agent and an antioxidant in stabilizing compositions for aqueous heavy oil emulsions [176].

Several ferrocenylsulphides including the phenyl derivatives (13.3; R^1 = Ph, CH_2Ph; R^2 = H) have been prepared and evaluated



13.3

as extreme-pressure and antiwear additives in lubricating oils. The thermal stability of the additives was correlated with wear and seizure load parameters. The most effective sulphide was the propyl compound (13.3; R^1 = Ph, R^2 = Pr^i) [177].

Trace amounts of phosphate acid diesters have been shown to behave as cure rate inhibitors for ferrocene-containing propellants [178].

Homogeneous aluminium coatings less than 20μ thick were deposited on copper, iron, titanium, graphite and glass ceramic by pyrolysis of triisobutylaluminium vapour at 180-190°. The addition of ferrocene increased coating adhesion and reflectance [179].

(iii) Ferrocene in analysis

Spectrophotometric and colorimetric methods have been developed for the determination of ferrocene and its derivatives in polyethylene films when they are used as photosensitizers for photodegradation. The colorimetric method involved estimation of the complex formed between iron and 1,10-phenanthroline. The results showed that virtually complete decomposition of the photosensitizer occurred when the polymer films were exposed to ultraviolet irradiation in the open for two-three months [180].

Ferrocene has been used for the amperometric determination of iron(III) in brass. The first stage was to remove the copper by electrodeposition. The determination of iron(III) was carried out in sulphuric acid-acetone using a platinum indicator electrode with 1 mM ferrocene in ethanol as the titrant [181].

A similar method has been reported for the determination of iron in manganese ores, blast-furnace slags and dolomites. Initially the sample was dissolved in a mixture of hydrochloric acid and hydrogen peroxide. Sulphuric acid was added and amperometric or potentiometric titration of iron(III) was carried out with ferrocene in propanol [182].

A procedure has been developed for the amperometric titration of iridium(IV) with ferrocene. The best results were obtained in 1:1 water-ethanol containing 3-6 M hydrochloric acid. It was possible to determine iridium in the presence of some 'platinum metals' [183].

Rhenium(VII) has been determined in alloys containing Hf, Nb and W by amperometric titration with 0.01 M diethylferrocene.

The cell employed a platinum indicator electrode and an alkaline permanganate reference electrode. Molybdenum interfered with the determination. [184].

The use of an electrode based on the diethylferrocene-diethylferrocenium perchlorate couple for the determination of perchlorate has been explored. Comparisons were made of the experimental and calculated values of deviations from the electrode function [185].

The optimum conditions were determined for the potentiometric titration of copper with ferrocene in aqueous solution. A method was developed for the determination of copper and iron in aluminium alloys [186].

An ion-selective electrode for the determination of tetraphenylborate has been constructed with heterogeneous electroactive material consisting of crystalline ferrocenium tetraphenylborate and a solution of the corresponding ferrocene in nitrobenzene [187].

(iv) Combustion control

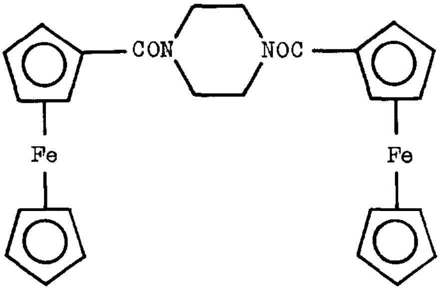
Diferrocenylketone has been used as a burning rate modifier in a solid propellant based on ammonium perchlorate and hydroxy-terminated polybutadiene. The burning rate was increased in the presence of the ferrocene derivative and the stability of the propellant was unaffected [188].

The pot-life of ammonium perchlorate propellants bonded by hydroxy-terminated polybutadiene was determined with a plastograph. The addition of butylferrocene decreased the pot-life [189].

Ferrocene and n-butylferrocene have been added to solid propellants based on ammonium perchlorate and carboxyl-terminated polybutadiene. Thermal decomposition and combustion of the propellants has been investigated. The presence of ferrocenes increased both the rate of thermal decomposition and the burning rate. The burning rate was proportional to the amount of added ferrocene while a maximum rate for n-butylferrocene was achieved at 2.5% addition [190].

2,2-(Diethylferrocenyl)propane, which is non-volatile, has been used instead of n-butylferrocene as a burning rate modifier in a composite propellant [191].

Diferrocenoylpiperazine (13.4) has been prepared by treatment of ferrocenecarbonylchloride with piperazine at room



13.4

temperature. Ammonium perchlorate composite propellants in crystalline form were coated with the burning-rate modifier (13.4). Under these conditions migration of the piperazine (13.4) was decreased [192].

Hypergolic hybrid solid propellants which ignited spontanesously in red fuming nitric acid have been prepared and classified. One such propellant contained urotropin, p-toluidine, ferrocene and an epoxy resin binder [193].

The addition of a small proportion of finely ground ferrocene to poly(vinyl chloride) was effective in reducing smoke formation during combustion in the temperature range 400-800°C. Smoke was reduced by 20% under smouldering conditions and by 50% under flaming conditions. The char yield was increased [194].

A nonvolatile smoke suppressant for plastics has been prepared by treating ferrocene with polybutadiene (molecular weight 150-2000) in the presence of aluminium chloride. When the smoke suppressant was added to polystyrene, the polymer burned without forming black smoke [195].

Ferrocene and ferrocene derivatives have been evaluated as antiknock agents for gasoline. Carbonyl and halogen derivatives were more efficient than ferrocene although the solubility in gasoline was low [196].

(v) Biochemical and biological applications

The enzymic hydroxylation of ruthenocene and osmocene by mouse liver microsomes has been studied. The reaction required oxygen, and NADPH was a more effective cofactor than NADH which suggested hydroxylation by the microsomal cytochrome P 450 system. No metabolism occurred at 0° or in the absence of the added coenzyme. In buffer at pH 7.4 at 37°, in the absence of microsomes, ruthenocene and osmocene were more stable than ferrocene [197].

The pure enantiomers t-butyloxycarbonyl(3-ferrocenyl)-D-alanine (Boc-D-Fer-OH) and t-butyloxycarbonyl-(3-ferrocenyl)-L-alanine (Boc-L-Fer-OH) have been used to prepare the (D-Fer^4, Leu^5)- and (L-Fer^4,Leu^5)-enkephalins via the solid phase method. The opiate receptor affinities of these enkephalin analogues were lower than that of [Leu]-enkephalin but they were more potent than most other position-4 analogues. The D-analogue was significantly more potent than the L-analogue [198].

In similar work the diastereoisomers of [Fer^4,Leu^5]-enkephalin have been prepared and then separated by reversed phase high pressure liquid chromatography. The binding of these peptides to enkaphalin receptors was discussed [199].

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