FERROCENE
ANNUAL SURVEY COVERING THE YEAR 1983*

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CONTENTS

1. REVIEWS

Kauffman has recorded the events that led to the discovery of ferrocene and the confirmation of its structure and aromatic character [1]. The chemistry of ferrocenyl stabilized carbocations has been the subject of a brief review [2]. The chemistry of chelate complexes containing organo-

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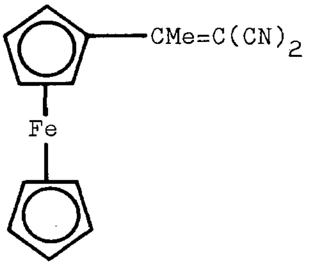
* Annual Survey covering the year 1982 see J. Organometal. Chem., 257 (1983) 209

metallic ligands with arene and cyclopentadienyl groups has been surveyed by Rybinskaya and Krivykh [3]. The organometallic derivatives of ferrocene have been reviewed [4].

2. STRUCTURAL DETERMINATIONS

X-ray analysis of the metastable triclinic phase of ferrocene was carried out at 130K on a single crystal cooled through the transition temperature of 164K. When the triclinic phase was obtained by cooling a crystal from room temperature its structure consisted of a mixture of molecular packings, face-centred and P1 symmetry [5]. The same group of workers investigated the disordered structure of ferrocene at room temperature by X-ray diffraction and lattice energy calculations [6]. The crystal and molecular structure of the dicyanovinylferrocene (2.1) has been determined by X-ray crystallography [7]. Vinylferrocene has been attacked by tris(3-iodopentane-2,4-dionato)cobalt(III) in the presence of triphenylphosphine and palladium(II) to form the two isomeric ferrocenyl dihydrofurans (2.2 and 2.3). The compounds (2.2 and 2.3) were characterized by X-ray crystallography and the mechanism by which they were formed was discussed [8]. The structure of the helical ferrocene (2.4) has been determined by X-ray analysis. This structure represents the first ferrocene where the two η-cyclopentadienyl rings are linked by unbroken



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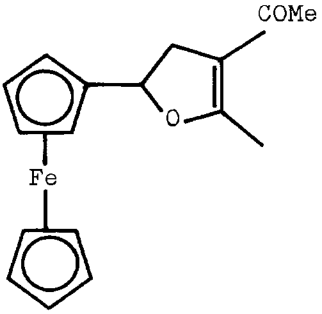

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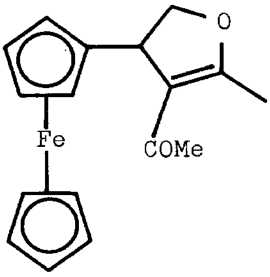

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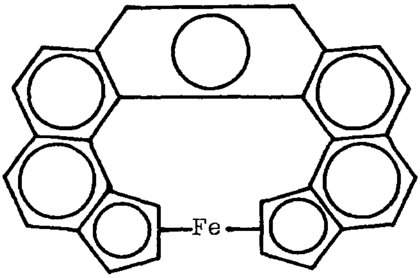
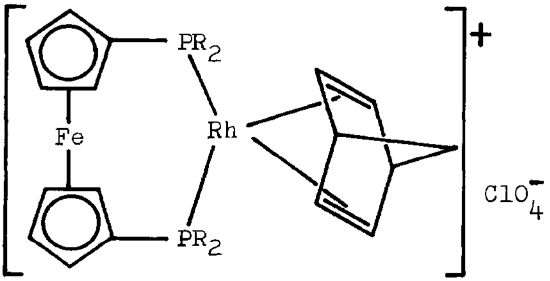


2.4

conjugation [9].

The crystal and molecular structure of benzyldiphenylferrocenylphosphonium chloride has been determined by X-ray analysis. The results indicated that it was possible for the filled ha_g molecular orbital of the ferrocenyl group to overlap with an empty 3d orbital of phosphorus. The implications of this overlap on the rates and stereochemistry of the Wittig reactions of (carbomethoxymethylene)diphenylferrocenyl- and (carbomethoxymethylene)diferrocenylphenyl-phosphorane with benzaldehyde were considered [10]. The structure of the ferrocenylphosphine-rhodium complex (2.5; R = CMe_3) has been determined by X-ray analysis. The rhodium atom was shown to be in a distorted square planar environment. The behaviour of the complexes (2.5, R = CMe_3, Ph) as homogeneous catalysts in the hydrogenation of $CH_2{=}CRCO_2H$, where R = $NHCOCH_3$, CH_2CO_2H, and $PhCH{=}CRCO_2H$, where R = $NHCOCH_3$, Me, was investigated [11]. The crystal structure of the ferrocenyl quaternary ammonium salt $[(\eta\text{-}C_5H_5)Fe(C_5H_4CH_2NMe_3)]_2B_{10}H_{10}$ has been determined by X-ray analysis [12]. The crystal and molecular structure of (ferrocenylmethyl)(η-cyclopentadienyl)dicarbonyliron has been determined by X-ray methods [13].

The crystal and molecular structure of the ferrocene (η-cyclopentadienyl)iron complex (2.6) and of three related complexes have been determined by X-ray crystallography [14]. Several methyl-substituted bis(η-pentadienyl)iron complexes, including the dimethyl derivative (2.7) have been prepared and



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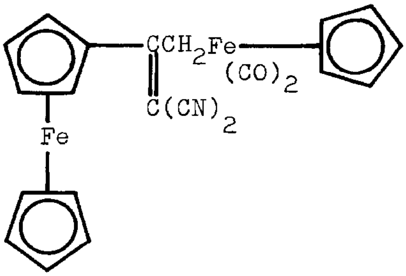
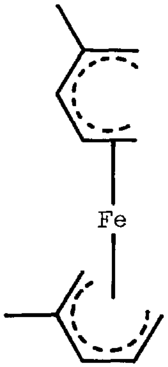


2.6

characterized as red air-stable compounds. The crystal and molecular structure of one complex (2.7) has been determined by X-ray crystallography. The molecule adopted a gauche-eclipsed ligand conformation with metal-carbon bond distances a little greater than those in ferrocene. Physico-chemical properties of the complexes were similar to those of ferrocene [15].



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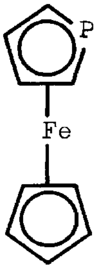

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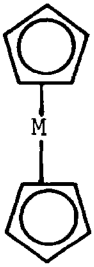
3. THEORETICAL STUDIES

The effect of substituent groups and of ligand replacement on the frontier orbitals in ferrocene has been examined. Replacement of a cyclopentadienyl ligand by arene caused major changes in the e_1 (antibonding) interaction which was decreased and in the back-bonding e_2 (bonding) interaction which was increased. The introduction of methyl substituents caused a minor increase in the e_1 interaction and a minor decrease in the e_2 interaction. The introduction of acetyl groups caused the opposite effect [16]. A force field study of ring orientation in ferrocene and ruthenocene has been carried out. Minima in the intermolecular strain energy corresponded to the observed conformations only if the relative orientation in all the neighbouring molecules was assumed to change with that of the reference molecule [17]. The bonding and reactivity of phosphaferrocene (3.1) and diphosphaferrocene have been studied by nonparametrized MO calculations. The ligands were shown to form π-bonds with the metal d orbitals and the calculated electron density distribution in phosphaferrocene (3.1) was in accordance with the observed distribution. Charge control was important in determining the regioselective character of electrophilic substitution in phosphaferrocenes. Lone pair electrons associated with phosphorus were localized on that atom but did not confer nucleophilic properties on phosphorus since the lone pair was not in a frontier MO [18]. INDO-(crystal orbital)calculations have been used to obtain the energy band structure and density of electronic states in polyferrocenylene [19].

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

Intercalation compounds of ferrocene, lithium and pyridine derivatives in the layered transition metal oxyhalides MOX, where X = Cl, Br, M = V, Cr; X = Cl, M = Fe have been prepared and characterized by X-ray diffraction, voltammetric, ^1H NMR and Moessbauer methods [20]. Solutions of monosubstituted ferrocenes and biferrocene in freon mixtures have been subjected to γ-irradiation at 78°K. The monocations produced from biferrocene and phenylferrocenes showed an absorption band that was assigned to electron transfer from ferrocenyl or phenyl to the iron atom [21]. Butylrubber containing ^{57}Fe-enriched ferrocene tracer has been studied by γ-resonance spectroscopy. The temperature dependence of the Moessbauer parameters, probability of resonance absorption, band widening, quadrupole splitting and chemical shift, were determined [22]. The energies of the low-lying, unstable negative ion states of the 3d metallocenes (4.1; M = V, Cr, Mn, Fe, Co, Ni) have been determined by electron transmission spectroscopy. For the complexes (4.1; M = Fe, Co, Ni) calculations employing the multiple scattering X_α method with stabilization permitted the assignment of the observed states to electron capture into the metal 3d, $4e_{1g}$ orbital or cyclopentadienyl π^* orbitals [23].



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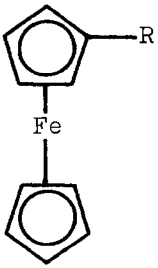

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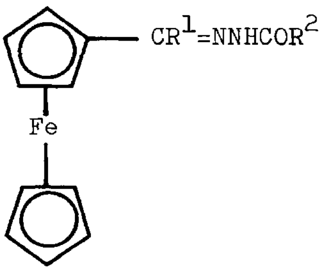

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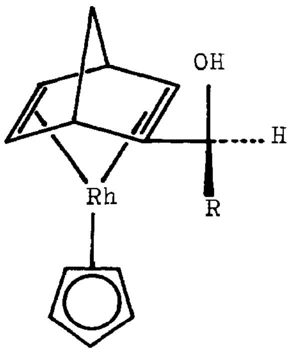
Open-shell, vanadocene and chromocene, and closed-shell, ferrocene, metallocenes have been studied by electron transmission spectroscopy. The spectra were interpreted by the use of multiple scattering X_α calculations [24]. ESCA spectroscopy has been used to investigate the electronic effects of methylsubstitution in titanocene, zirconocene, hafnocene and ferrocene. The binding energies of the inner shell electrons were significantly altered thus the introduction of ten methyl groups into a metallocene was equivalent to a one-electron reduction of the metallocene [25].

The mass spectra of the substituted ferrocenes [4.2; R = $COCH_3$, CH_3, CHO, CO_2H, CH_2OH, COPh, $CH_2N(CH_3)_2$] have been reinvestigated making intensive use of the metastable ions. The observed primary fragmentations of the molecular ions were different in some respects from those previously suggested [26]. Acetyl- and benzoyl-ruthenocene and 1,1'-diacetylruthenocene have been studied by mass spectrometry. The high metal-ligand bond strengths led to extensive fragmentation of the ligands by comparison with ferrocene [27]. The mass spectra of eight ferrocenyl aroylhydrazones (4.3; R^1 = H, Me; R^2 = Ph, substituted Ph, pyridyl) have been measured and interpreted in terms of skeletal and hydrogen rearrangements and bond cleavages [28]. The gas phase reactions of Fe^+, Co^+ and Ni^+ with cyclic hydrocarbons have been investigated by Fourier transform mass spectrometry. The intermediate $[Fe(C_5H_6)]^+$ cation combined readily with cyclopentane and underwent multiple dehydrogenations to give the ferrocenium cation $[(C_5H_5)_2Fe]^+$ [29]. Zagorevskii and co-workers have reported a correlation between mass spectra data and *endo*-*exo*-stereoisomerism in the rhodium complexes (4.4; R = ferrocenyl, methyl and 4.5; *exo*-isomers shown) [30].



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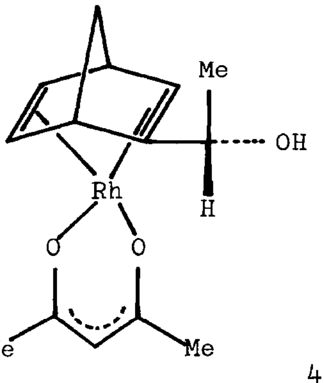

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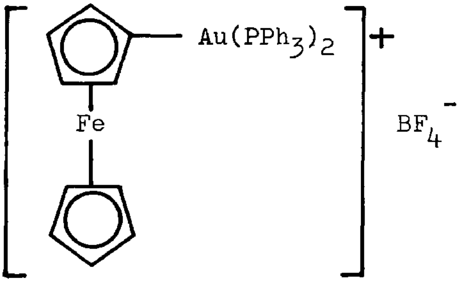
Photoionization efficiency curves have been recorded for ferrocene vapour between 1900 and 590 Å. The parent ion $[(\eta\text{-}C_5H_5)_2Fe]^+$ had an appearance potential of 6.747 eV and the fragments $[(\eta\text{-}C_5H_5)Fe]^+$ and Fe^+ appeared at 13.162 and 13.506 eV respectively [31]. Ferrocene and bis(η-arene)chromium complexes have been ionized on a tungsten oxide surface.

Ferrocene formed a molecular ion but no fragment ions were observed. The ion current increased with temperature and at approximately 1150K the coefficient of surface ionization was 8×10^{-3} [32].

A Moessbauer study of anisotropic molecular diffusion has been carried out with 1,1'-diacetylferrocene dissolved in liquid crystals of p-methoxybenzylidene-p-butylaniline or dissolved in a eutectic mixture of cyano biphenyls and terphenyls over the temperature range 80-300K. The Moessbauer effect disappeared and reappeared as the temperature was changed [33]. ^{197}Au- and ^{57}Fe-Moessbauer spectra have been recorded for the ferrocenyl-gold complex (4.6). The data was consistent with the presence of Au(I) and Fe(II) in the complex [34]. A series of



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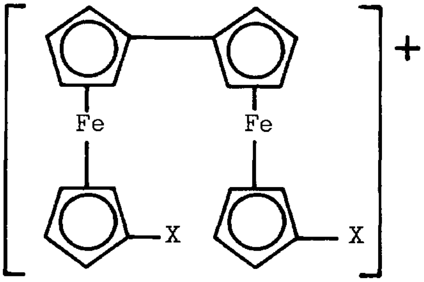

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1,1'-diacetylferrocene complexes of the Lewis acids $AlCl_3$, $SnCl_4$, $FeCl_3$ and $TiCl_4$ has been studied by Moessbauer spectroscopy. All the complexes exhibited a lowering of quadrupole splitting relative to the uncomplexed ligand. The decreases in quadrupole splitting were discussed in terms of the stereochemistry of the complexes [35]. The dynamic properties of polymers based on vinylferrocene have been investigated by Moessbauer spectroscopy. Acrylonitrile-vinylferrocene copolymer exhibited an anomalous decrease of the recoil-free fraction between 80 and 130K accompanied by line broadening and motional narrowing. The results were interpreted in terms of anharmonic hindered motion of the ferrocenyl group [36].

A Moessbauer and electrochemical study has been carried out on the haloferrocenes (4.7; X = Cl, Br, I). The Moessbauer spectra of the cations (4.7; X = Br, I) indicated average valence states for the iron atoms but the cation (4.7; X = Cl) showed a trapped valence state for the iron atoms. No difference was found in the half-wave potentials of these molecules [37].

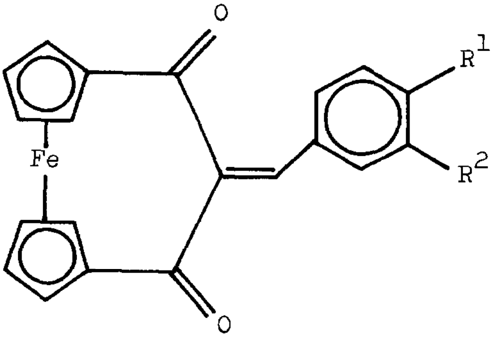
The ^{57}Fe Moessbauer spectra of a series of ferrocene derivative-α- and β-cyclodextrin clathrates have been recorded at 78-320K. For example, the spectrum of the formylferrocene-α-cyclodextrin clathrate consisted of a doublet at low temperatures which collapsed on heating to a singlet of reduced intensity. This variation in the spectrum was interpreted in terms of reorientation of the formylferrocene in the cavity of α-cyclodextrin as the temperature increased [38]. Moessbauer spectroscopy has been used to study oxidation interaction and irreversible phase transitions between layers of ferrocenium ion-iron oxychloride intercalates of the type $[(\eta\text{-}C_5H_5)_2Fe]^+[(6\text{-}7FeOCl)]^-$ with ^{57}Fe labelled ferrocenes. At low temperatures the unstable dynamic equilibria, Eq. 4.1 and Eq. 4.2 in the

$$\text{Ferrocene} \rightleftharpoons [\text{Ferrocenium}]^+ + e^- \qquad \text{Eq. 4.1}$$

$$Fe^{3+}OCl^- + e^- \rightleftharpoons [Fe^{2+}\ \underline{\text{para}}\ OCl]^- \text{ or } [Fe^{2+}\ \underline{\text{antiferro}}\ OCl]^- \qquad \text{Eq. 4.2}$$

guest and host layers respectively gave rise to irreversible phase transitions [39].

The ^{57}Fe chemical shift in ferrocenes has been used as a sensitive indicator of ring tilting with increased tilting being shown by high field shifts [40]. The effective polarization anisotropy, the electric quadrupole moment and the magnetic anistropy of ferrocene and ruthenocene in cyclohexane have been determined at 25°C. The results have been used to show that these metallocenes were more polarizable in directions parallel to the ligand-metal-ligand axes. It was indicated that metal-ligand bonding resulted in transfer of electronic charge from the metal to the cyclopentadienyl rings [41]. The ^{13}C and ^{1}H NMR spectra of the benzylideneferrocenophanediones (4.8; R^1 = H, Cl, Br, NMe_2, OMe, Me, NO_2, CN, R^2 = H; R^1 = H, R^2 = Cl, Br) have been recorded and interpreted. A correlation of the carbonyl carbon chemical shift with the Hammett constants was found for both Z- and E-CO groups [42]. Electron



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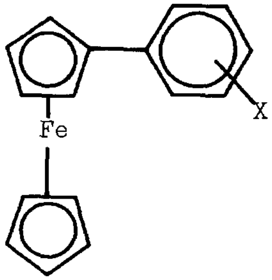

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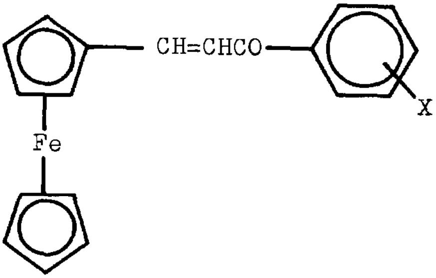

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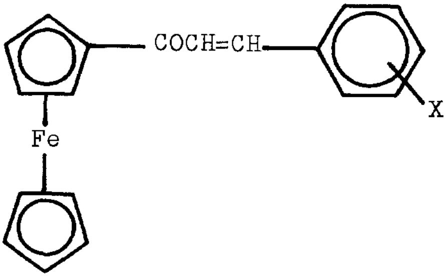

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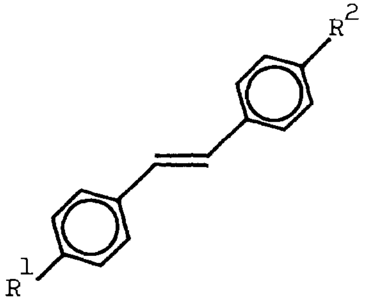
density distributions in the phenyl-ring substituted ferrocenes (4.9, 4.10, 4.11; X = H, m-CHO, p-OMe) have been measured using cyclic voltammetry and ^{13}C NMR spectroscopy. The effects of substituents on electron density distributions was discussed [43].

The ^{57}Fe NMR spectra of 28 mono- and di-substituted ferrocenes with natural abundance ^{57}Fe have been recorded using ferrocene as an internal reference. The resonances observed were mainly on the high-frequency side of the reference. The shielding effect of substituents was discussed and ring tilting was shown to be important in determining ^{57}Fe shifts [44].
A complete molecular dynamics study of acetylferrocene has been carried out in p-xylene by dielectric relaxation measurements

at 100 MHz-38 GHz and 293-323K at low concentrations. No intermolecular association or interation of any type was observed between the solute molecules. The acetylferrocene molecule exhibited one sharp absorption band in the GHz-region and this was assigned either to rotation around the molecular axis perpendicular to the two η-cyclopentadienyl rings or to molecular reorientation. Debye-like behaviour was observed [45]. Similar measurements were made on benzoyl- and 1,1'-dibenzoyl-ferrocene in p-xylene. The results obtained were similar to those observed for acetylferrocene [46]. The effect of substituents on the wavenumbers of carbonyl valence vibrations in ferrocene derivatives has been investigated. On application of the Seth-Paul-Van Duyse equation a linear correlation was found between the wavenumbers of C=O vibration and $X^+(R)$ constants of structural fragments [47]. A series of metallocenes, which included ferrocene, has been studied by vibrational spectroscopy, quasielastic neutron scattering and calorimetry. An attempt to classify the different order-disorder phase transitions showed that the determination of activation energies, residence times and geometries of the solid state reorientational motion of aromatic rings could only be derived when the three techniques were considered together [48].

Diphenylchloromethane has been photolysed in the presence of ferrocene and the reaction studied by picosecond absorption spectroscopy. The ferrocenium ion and the diphenylmethyl radical were formed within 35ps of the photolysis and decayed at the same rate by ferrocenium oxidation of the diphenylmethyl radical to give ferrocene and the diphenylmethyl cation [49]. Electrodes reversible to dipropyl- and octyl-ferrocenium cations have been constructed and used to determine the solubilities of dipropyl- and octyl-ferrocene in water [50]. A stopped-flow kinetic study of the electron-transfer reaction between ferrocene and $[Co(1,10\text{-phenanthroline})]^{3+}$ has shown that anionic micelles catalyze the transfer while cationic and non-ionic micelles inhibit the process [51]. The reaction between vinylferrocene and $Tl(OAc)_3$ to form 1-ferrocenyl-1,2-dimethoxyethane has been the subject of a kinetic study. The intermediate methoxythallation species was hydrolysed under the reaction conditionsused to give the observed product. Under the same reaction conditions β-methylvinylferrocene gave both addition and substitution products [52].

The effect of ferrocene on the photoisomerization of substituted trans-stilbenes has been investigated. The concentration of the cis-isomer formed at equilibrium in the photoisomerization of the trans-isomer (4.12; R^1 = MeO, R^2 = NO_2) was decreased by the presence of ferrocene. This was taken to indicate the participation of a triplet state. Ferrocene had no effect on the photoisomerization of the trans-stilbenes [4.12; R^1 = NMe_2, R^2 = $P(O)Ph_2$, Br] [53]. The vapour pressures of benzoyl- and 1,1'-dibenzoyl-ferrocene have been measured by a torsion-effusion technique. The pressure-temperature equations were derived and second-law treatment of the data produced the heats of sublimation [54]. When single crystals of ferrocene were cooled below the λ-type phase transition at 163.9K, crystal disintegration occurred with explosive violence. The strain energy released at the disintegration was 1.10 $kJmol^{-1}$. The disintegration was explained in terms of an energy transfer from the strain energy accumulated in the domain boundaries in a form of elastic energy to the kinetic energy of disintegrated crystallites [55]. The phase transitions of ferrocene-d_{10} have been examined. The high-temperature phase was easily undercooled to give a λ-type transition at 164.1K in the metastable state. The stable low-temperature phase was obtained by annealing the undercooled high-temperature phase at 190K. A first-order phase transition occurred between the stable low-temperature and high-temperature phases at 251K [56]. A new low-temperature crystalline phase of azaferrocene stable at <281K has been found from the measurements of proton spin-lattice relaxation



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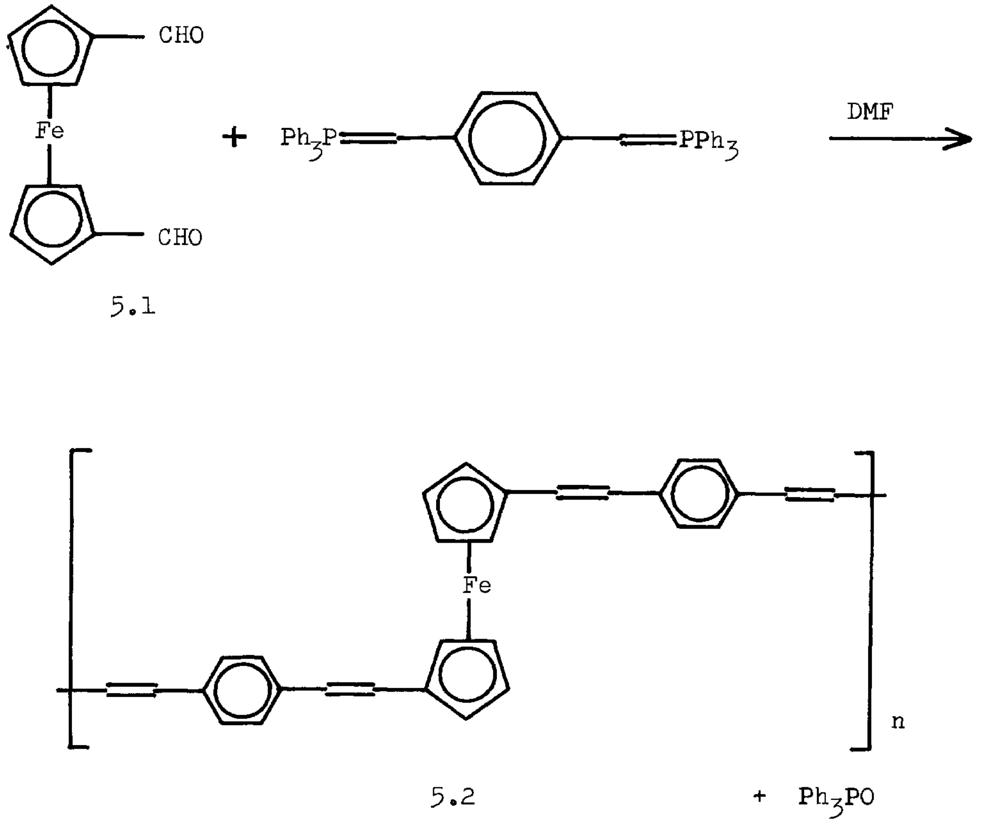
time and differential thermal analysis [57].

5. ELECTROCHEMISTRY AND PHOTOSENSITIVE ELECTRODES

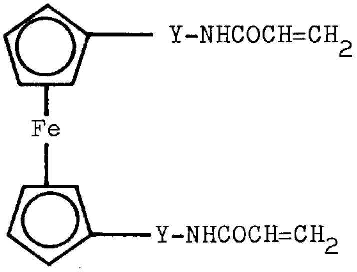
The operation of electrodes chemically modified by coating with polymer films has been the subject of a review. Polyferrocenes were among the polymers used [58]. Cyclic neopolarographic methods have been used to study a plasma-polymerized vinylferrocene-film chemically modified electrode [59]. Small band gap semiconductor electrodes, such as n-Si and In_2O_3 glass electrodes, have been chemically modified by using the surface-active properties of chromium complexes of redox couple carboxylic acids. Ferrocene was used to modify electrodes by this procedure with the chromium complex serving to anchor the active ferrocene group. Electrode stability in photoelectrochemical photovoltaic cells was enhanced in this way [60]. n-Type silicon electrodes in methanol with 0.2M 1-hydroxyethylferrocene, 0.5mM 1-hydroxyethylferrocenium ion and 1.0M lithium perchlorate exhibited efficiences of 10.1% for the conversion of sunlight into electricity. A high open-circuit voltage of 0.53V was also achieved [61].

An electrochemical cell has been constructed using n-type gallium arsenide or p-type silicon rotating disc electrodes and tetrabutylammonium perchlorate with ferrocene in acetonitrile. The properties of the electrodes were examined as a function of light intensity and rotation velocity [62]. The electrochemical behaviour of a gold modified n-silicon photoelectrode in ferrocene-Et_4NClO_4-C_2H_5OH and $K_4Fe(CN)_6$-$NaClO_4$ solutions has been examined by cyclic voltammetry. The values of the under potentials were 0.31V in the presence of ferrocene and 0.22V in the presence of potassium hexacyanoferrate(II) [63]. The photoassisted generation of hydrogen from water has been carried out by using as the cathode a semiconductor exposed to light. The cathode was a p-type single crystal silicon wafer which was coated with a ferrocenophane containing polymer. The polymer was prepared by the treatment of poly(chloromethylstyrene) with a lithioferrocenophane [64]. The stability has been determined of two-layer ferrocene-polypyrrole coated (111) single-crystal silicon electrodes in aqueous photoelectrochemical cells containing the Fe^{3+}/Fe^{2+} and I/I^- redox couples [65].

1,1'-Diformylferrocene (5.1) has been used to prepare poly(1,1'-ferrocenylene vinylene phenylene vinylene) (PFVPV) (5.2). PFVPV was an insulating material with a high resistivity but on oxidation (doping) with iodine, bromine or arsenic (V)



fluoride it became a semiconductor with conductivities ranging from 10^{-4} to $10^{-9} \Omega\, cm^{-1}$. Iodine doped material underwent an instantaneous two-fold increase in conductivity when illuminated with a 75W tungsten lamp [66]. Ferrocene monomers such as the unsaturated ketones (5.3; Y = C_1-C_{10} alkylene, carboxyl, alkylenoxy) have been converted to crosslinked polymers and used to form a gel in an electrolyte. Two electrodes, one of which was a semiconductor, were immersed in the electrolyte and illuminated to form a photovoltaic device [67, 68]. The poor



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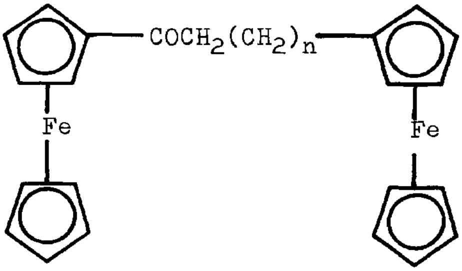
charge transfer characteristics of nickel electrodes used for the oxidation and reduction of the ferrocene-ferrocenium couple have been attributed to oxidative instability. This difficulty has been overcome by chemical derivatization of the electrode surface using 1,1'-ferrocenediyldichlorosilane [69]. Vinylferrocene has been plasma polymerized on glassy carbon electrodes which had been etched previously by an argon plasma. The electrochemical properties of the electrodes were studied via cyclic voltammetry. On an electrode covered with a thin film of polymer the redox reaction between ferrocene and the ferrocenium ion proceeded without hindrance of electrochemical charge transport. In the presence of thicker films the reactions were diffusion limited [70].

A series of decamethylmetallocenes $(\eta\text{-Me}_5C_5)_2M$, where M = V, Cr, Mn, Co, Ni, has been prepared and their structures investigated. Alkylation of the η-cyclopentadienyl ring enhanced its ligand field strength and all the metallocenes investigated were low spin. Cyclic voltammetry studies verified the reversibility and one electron nature of the following process where M = Cr, Mn, Fe, Co, Ni:

$$(\eta\text{-Me}_5C_5)_2M \rightleftharpoons [(\eta\text{-Me}_5C_5)_2M]^+ + e^- \qquad [71]$$

The incorporation of an ionic dye (croconate violet) into poly(vinylpyridine) coated polycrystalline tin (IV) oxide electrodes produced significant changes in the kinetics of electrooxidation of soluble ferrocene derivatives [72]. A reversible cyclic voltammogram for the one-electron reduction of ferrocene in 1,2-dimethoxyethane has been recorded under conditions that enabled the ferrocene anion to exist for several minutes. The formal rate constant of the ferrocene $^{o/-}$ electrode at -45^{o}C was approximately 1.7×10^{-3} cm s^{-1} which was compared with that of ferrocene $^{+/o}$ which was 10^{-1} cm s^{-1}. From these results it was postulated that the ferrocene anion had one bent *tetrahapto*- and one planar *pentahapto*-cyclopentadienyl ligand [73]. Several diferrocenyl compounds including the ketones (5.4; n = 0, 1 and 5.5) have been the subject of an electrochemical study using platinum electrode voltammetry. The difference between the first and second half-wave potentials varied by >40mV in solvents such as methanol, acetone, acetonitrile, dichloromethane and nitromethane. Iron-to iron through space interaction was not important [74].



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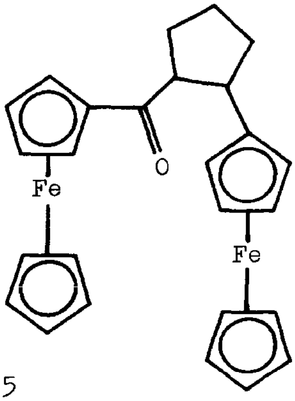
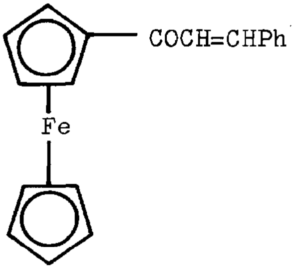


5.5

The effect of carbonyl groups on the redox potentials and Moessbauer spectra has been investigated in formylferrocene, acetylferrocene, ferrocenylphenylketone and the ketones (5.6 and 5.7). A carbonyl group α to the η-cyclopentadienyl ring increased the oxidation potential. The results indicated that approximately 50% of the inductive effect of the carbonyl group in ketone (5.7) reached the ferrocenyl group through the ethylene moiety. The quadrupole splittings in the Moessbauer spectra of the ketoferrocenes were smaller than that of ferrocene but the isomer shifts were approximately the same [75]. The charge-transfer kinetics of ferrocene at platinum and vitreous



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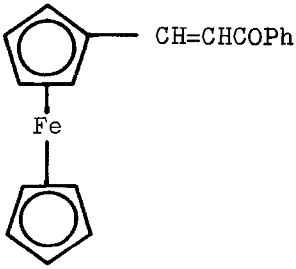
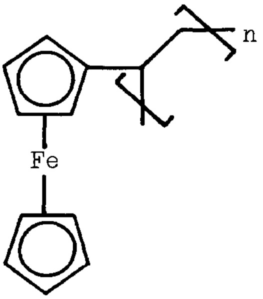


5.7

carbon electrodes have been determined by potential step chronocoulometry. The formal rate constants were independent of the electrode and of the supporting electrolyte which was $LiClO_4$, Et_4NClO_4 or Et_4NBF_4 [76]. Oxidation-reduction, diffusion and solubility properties of several ferrocenylalkyl quaternary ammonium salts have been investigated in water, methyl cyanide and room-temperature aluminium chloride-1-butylpyridinium chloride melt electrolytes. In the basic melts nucleophilic chloride ion attack of ferrocenium ion charge-transfer products occurred. In acid melts, the quaternary salts decomposed and underwent an intramolecular electron transfer from the carbenium ion to the metal centre [77]. The effect of β-cyclodextrin on the rate of electron-transfer between ferrocenecarboxylic acid and glassy carbon electrodes has been investigated. It was concluded that the acid could be included in β-cyclodextrin and the iron atom was located in the cavity [78]. The rate of heterogeneous hole transfer between a laser-excited single--crystal zinc oxide electrode and ferrocene in a non-aqueous solvent has been determined at 10^4 s $^{-1}$ as a first-order constant of the hole [79]. The contact angle has been measured between water in the form of a drop of 0.1M potassiumchloride and poly-(vinyl ferrocene) (5.8) as a film on the surface of a platinum electrode. The dynamic contact angle decreased as the electrode potential passed through the ferrocene oxidation wave but did not increase during the reduction wave [80].

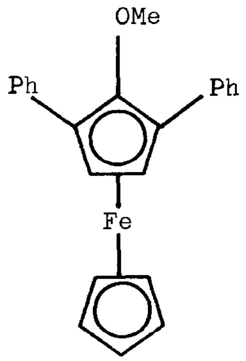


5.8

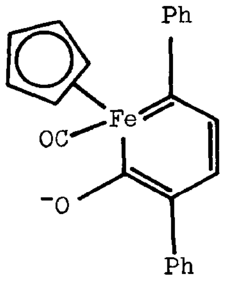
6. PREPARATIONS OF FERROCENE

An improved method for the preparation of ferrocene has been reported. A catalytic amount of polyethylene glycol (2 mmol) was dissolved in dimethylsulphoxide, powdered sodium hydroxide (15g) iron (II) chloride tetrahydrate (33 mmol) and 1,3-cyclopentadiene (67 mmol) were added. The mixture was stirred for one hour to give ferrocene (approximately 61%) [81]. The reaction of iron atoms with 2-butyne, 2-pentyne, 3-hexyne, methylphenylacetylene and propyne have been investigated. All of these alkynes, except propyne, produced iron complexes. Structural characterisation of the iron complexes indicated that they were substituted ferrocenes [82]. The reaction of (E, E)--PhCLi=CHCH=CLiPh with (η-C_5H_5)$Fe(CO)_2I$ produced 1,3-diphenyl-2--methoxyferrocene (6.1). It was postulated that this reaction proceeded via the ferrabenzene (6.2) [83].

The helicene (6.3) has been synthesized in a 13-step process from 2,7-dibromonaphthalene and converted to the helical ferrocene (2.4) by way of the corresponding dianion which was treated with $FeCl_2$.2THF [84]. The basicity of the pentamethylcyclopentadienide ion has been determined and is appreciably greater than that of the cyclopentadienide ion. This difference has been related to the differences in chemistry between (η-cyclopentadienyl)transition metal complexes and the corresponding (η-pentamethylcyclopentadienyl) complexes. The effects of methylation on indene and fluorene ligands were also discussed [85].



6.1



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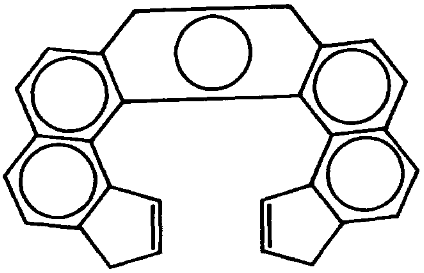
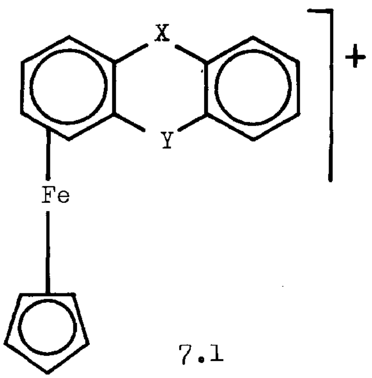


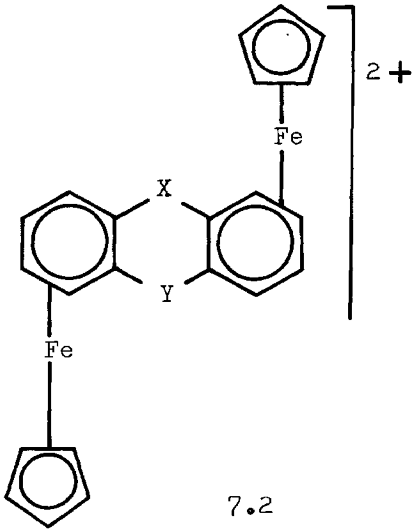
6.3

7. REACTIONS OF FERROCENE

A study has been carried out on the alkylation of ferrocene by olefinic hydrocarbons [86]. The reaction of ferrocene with ethyl radicals, generated from diethylmercury at 205-230°, produced ethylferrocene and diethylferrocene [87]. Ferrocene in concentrated hydrochloric acid has been treated with diazonium salts prepared from heterocyclic amines to give ferrocenylheterocycles. Mono- and 1,1'-di-substituted ferrocenes with 2-methyl-5- and -6-benzothiazolyl, 2,3,3-trimethyl-5-indolenyl, 2-methyl-5- and -8-quinolyl groups were obtained [88]. A series of (η^6-arene)(η^5-cyclopentadienyl)iron cations has been prepared from ferrocene and subjected to a spectroscopic study [89]. Ligand exchange reactions between ferrocene and dibenzodioxin,



7.1



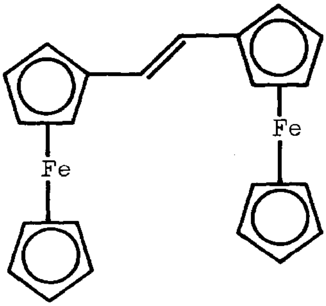
7.2

phenoxathiin or phenoxazine produced the (η^6-heterocycle)(η^5--cyclopentadienyl)iron cations (7.1; X=Y=O; X=S, Y=O; X = NH, Y=S) respectively. This method of preparation of these complexes was compared with an alternative route. When a large excess of ferrocene was used in the ligand exchange reaction the corresponding (η^6, η^6-heterocycle)bis(η^5-cyclopentadienyl) dications (7.2) were obtained [90].

Graphite-acceptor compounds have been used as oxidizing agents towards ferrocene. Thus stage 5 graphite fluoroborate smoothly oxidized ferrocene and provided the basis of a reversible intercalation process [91]. Tetranitromethane underwent detonation when mixed with ferrocene in solution in organic solvents. Thus tetranitromethane, 0.01g, was mixed with a 20% solution of ferrocene, 0.2ml, when an explosion occurred. The gases evolved contained nitrogen, oxygen, carbon dioxide, nitrogen dioxide and nitrous oxide [92]. The hydrocarbon ligands in bis(pentadienyl)iron have been displaced by trifluorophosphine to form pentakis(trifluorophosphine)iron [93].

8. FERROCENIUM SALTS AND MIXED-VALENCE SALTS

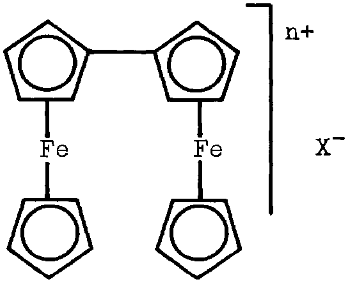
Ferrocenium tetrafluoroborate has been prepared in 93% yield from ferrocene and $HBF_4.OEt_2$ in nitromethane [94].



8.1

The heterogeneous oxidation of ferrocene on manganese (IV) oxide in saturated hydrocarbon solutions has been studied [95]. A solution of ferrocene and bismuth(III) bromide in acetone was oxidized by molecular oxygen in the presence of sunlight to the ferrocenium salt $[(\eta\text{-}C_5H_5)_2Fe]_4[Bi_4Br_{16}]$ which formed a blue-black crystalline precipitate. The salt was characterized by X-ray crystallography [96].

The near-IR spectra have been recorded for nineteen mixed-valence π-bond bridged and σ-bond bridged di-, tri- and tetra-ferrocene compounds. Intervalence electron transfer was evident



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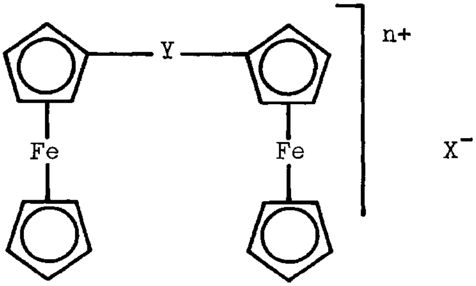
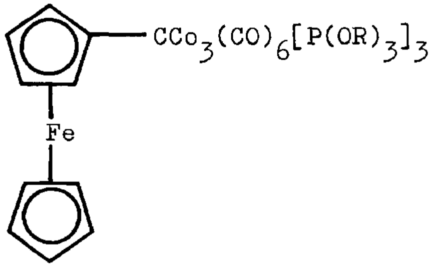


8.3

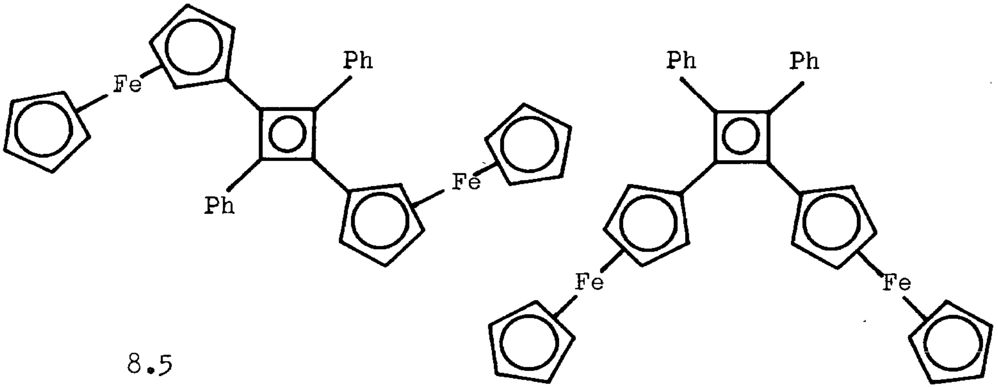
in all of the π-bond bridged and some of the σ-bond bridged species. The near-IR transition in the π-bond bridged derivatives was attributed to a through-bond mechanism while the transition in the σ-bond bridged compounds was attributed to a through space mechanism. Among the compounds exhibiting the electron transfer transition were, 1,2-diferrocenylethene (8.1), azoferrocene, 1,1-diferrocenylethene and diferrocenylketone [97]. The biferrocenes (8.2; n = 1, 2) and the bridged ferrocenes (8.3; Y = Hg, PPh, CH=CH, CMe=CMe, CPh=CPh, CH=NN=CH, CMe=NN=CMe, n = 1, 2) have been studied by cyclic voltammetry, IR and electronic spectroscopy, and Moessbauer spectroscopy. Several of the complexes including (8.2; n = 1; 8.3; Y = CPh=CPh, n = 1, X = I_3, tetracyanoquinodimethane, 2,3-dichloro-5,6-dicyanobenzoquinone) were characterized as mixed-valence compounds at room temperature [98]. Cyclic voltammetry and



8.4

visible and near-infrared spectroscopy have been used to examine electron transfer inthe ferrocene-tricobalt carbon cluster complexes (8.4; R = Me, Ph). Both complexes formed a redox series 2+/+/0/- with specific electrode potentials, however only the cationic species were stable. Chemical oxidation and electrolysis were used to obtain the cationic species, it was found that both the ferrocenyl moiety and the Co_3C cluster behaved as redox sites in the dications [1+,1+]. The mixed-valence cations [1+,0] had localized valence sites and the observed intervalence transitions were consistent with the Hush model for a class II species displaying unsymmetrical optical electron transfer [99].

Decomposition of the charge-transfer complex $(\eta\text{-}C_5H_5)_2\text{-}Fe\text{-}C_2(CN)_4$ in ethyl acetate gave the salt $[(\eta\text{-}C_5H_5)_2Fe]^+_{1.5}$ $[(NC)_2C{=}CCNO]^{\overline{\cdot}}$ which was considered to be a ternary phase of the type $[D^+][D_{0.5}A^-]$, where D and A are donor and acceptor molecules respectively. The crystal structure was determined and it was found to be composed of one-dimensional segregated stacks of; (i) ferrocenium ions and (ii) alternating 1:2:1 ferrocene: (tricyanoethenolate)$_2$:ferrocene stacks [100]. The cis- and trans-isomers (8.5 and 8.6) underwent two successive redox reactions at almost the same potentials in the range 0.30-0.55V and these were attributed to the Fe(II)-Fe(III) couples. The 1+ and 2+ ions of both isomers gave rise to a band in the near infrared indicative of intervalent transfer. It was concluded that the intervalent transfer arose from a Co(I)-Fe(III) interaction in the 2+ ions because Fe-Fe interaction was not possible [101].

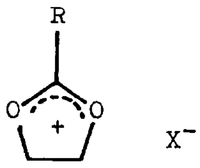


8.5

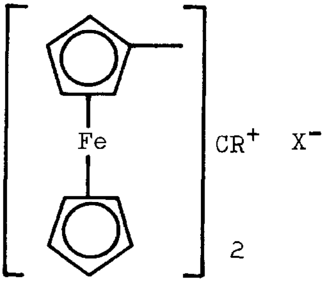
8.6

9. FERROCENYL CARBENIUM IONS

Several diferrocenylcarbenium salts (9.2; R = H, Me, Et, Ph, X = BF_4,ClO_4) have been prepared by heating ferrocene with the salt (9.1; R = H, Me, Et, Ph, X = BF_4, ClO_4) in acetic acid.



9.1



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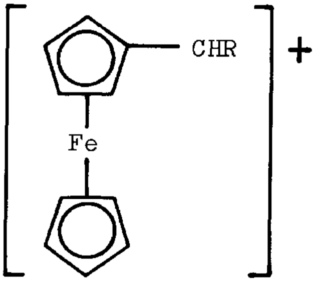


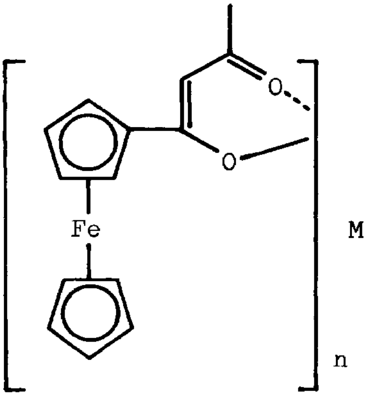
9.3

The salts (9.2) underwent alkaline hydrolysis to the corresponding diferrocenylmethanols [102]. The $^{13}C\{^{57}Fe\}$ NMR double resonance technique has been used to investigate direct metal participation in the stabilization of ^{57}Fe-enriched ferrocenyl carbocations. The ^{57}Fe resonances spanned a 1200 ppm range and provided a sensitive tool for the evaluation ofiron participation. Factors active in producing the large chemical shift differences were the shielding effect caused by rehybridization of the iron non-bonding d-orbitals and deshielding caused by the electron withdrawing effect of the substituent in the cyclopentadienyl ligand. Among the species studied were the cations (9.3; R = H, Me, Ph) [103]. A large secondary α-deuterium kinetic isotope effect has been found on hydrolysis of ferrocenylmethylquinolinium chloride in water and aqueous methyl cyanide. It was concluded that there was no significant bonding between the iron atom and the α-carbon atom in the ferrocenylmethylquinolinium ion [104].

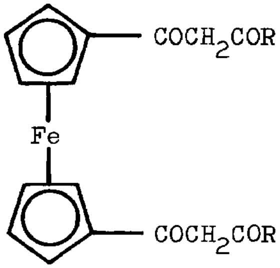
10. FERROCENE CHEMISTRY

(i) Derivatives containing other metals (metalloids)

A series of transition metal complexes [10.1; M = Fe(II), n = 3; M = Cu(II), Mn(II), n = 2] has been prepared by the reaction of acetoacetylferrocene with $Fe(NO_3)_3$, $Cu(OCOCH_3)_2$ and $Mn(OCOCH_3)_2$ respectively [105]. Ferrocenyl-β-diketonate ligands (10.2; R = Me, CF_3) have been used to prepare titanium, zirconium and hafnium complexes. The bis(η-cyclopentadienyl)-titanium complexes (10.3; R = Cl, CH_2NMe_2) were also prepared.

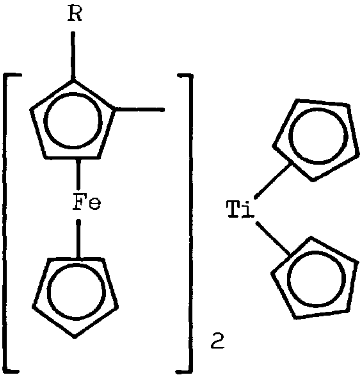


10.1



10.2

The complexes were characterized by mass spectrometry [106]. Reaction of the ferrocenyl-hydrazones (10.4; R^1 = H, Me; R^2 = Ph, *p*-Cl-, *p*-NO_2-, *p*-HO-C_6H_4, 4-pyridyl) with copper(II) acetate produced the corresponding copper(II) complexes (10.5) [107]. Reaction of the ferrocenylhydrazones (10.6; R = Ph,



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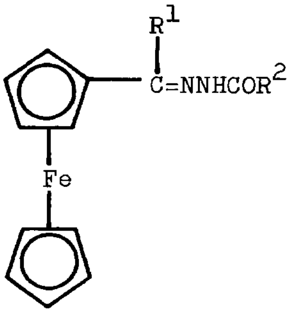
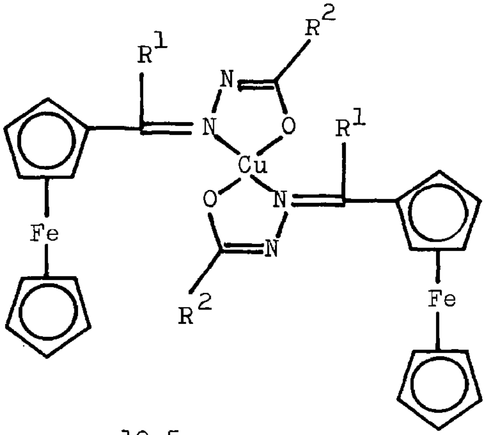


10.4

4-ClC_6H_4, 2-$O_2NC_6H_4$, 2-HOC_6H_4, pyridyl) with tin(II) chloride or R_2SnO, where R = Bu, octyl, produced the corresponding co-ordination complexes (10.7; R^1 = Ph, 4-ClC_6H_4, 2-$O_2NC_6H_4$, 2-HOC_6H_4, pyridyl; R^2 = Cl, Bu, octyl) [108]. The same ferrocenyl-hydrazones (10.6) also formed stable complexes with triphenyltin acetate. The structure of the complex depended



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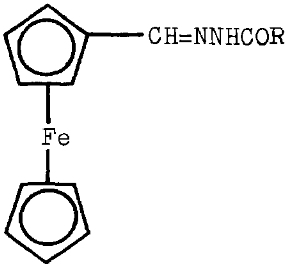
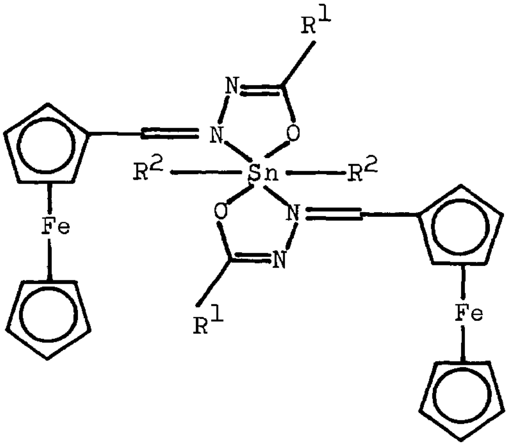


10.6

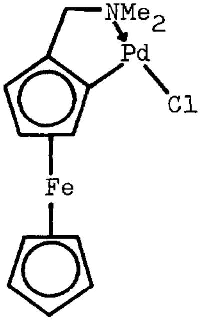
on the substituent R. Both octahedral and trigonalbipyramidal tin(IV) complexes were formed together with acetoxy bridged species [109].

Terminal olefins have been hydrogenated under mild conditions by using dichloro(triphenylphosphine)[1-(N,N-α-dimethylaminoethyl)-2-diphenylphosphinoferrocene]ruthenium(II) as a catalyst [110]. Several substituted ferrocenylnitriles have been



10.7

prepared and used as ligands to form $(NH_3)_5Ru(II)$nitrile complexes in which intervalence transfer was investigated by electronic absorption spectroscopy. A weakly coupled Class II description was used to account for the observed behaviour [111]. The



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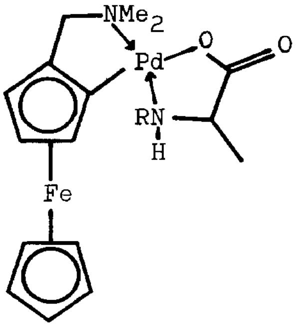
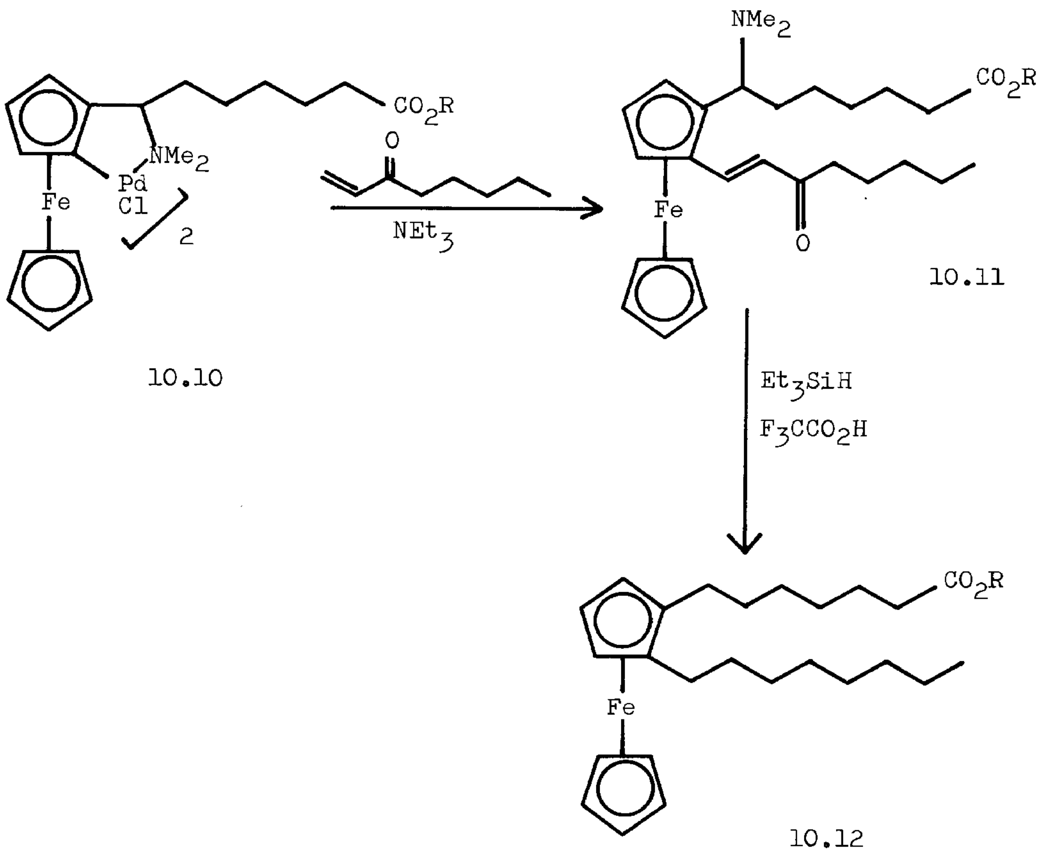


10.9

hydroformylation of allyl alcohol has been carried out using several rhodium-phosphine catalysts. 1,1'-Bis(diphenylphosphinyl)ferrocene was found to be one of the efficient phosphines in the catalyst [112]. The hydroformylation of 1-hexene in the presence of $HRhCO(PPh_3)_3$-bidentate phosphine ligand catalysts has been investigated. A good linear Hammett free-energy relationship was obtained for 1,1'-bis(diarylphosphino)ferrocenes with electron withdrawing substituents. These catalysts gave higher rates and selectivities to linear aldehyde formation [113].

The (±)- and (-)- ferrocene-palladium complex (10.8) has been treated with the sodium salts of several amino acids, $RNHCHMeCO_2Na$, to form the amino acid and dipeptide complexes (10.9; R = H, NH_2CH_2CO, $NH_2CHMeCO$) [114]. The optically active ferrocene analogue of prostanoic acid (10.12) has been prepared from the ferrocene-palladium complex (10.10) by way of the intermediate keto-ester (10.11) [115]. Organozinc reagents, prepared from the reaction of secondary alkyl Grignard reagents (ArRCHMgCl, where Ar = Ph, *p*-MeC_6H_4; R = Me, Et) and excess zinc halides were treated with vinylbromide in the presence of the chiral ferrocenylphosphine-palladium complex (10.13) as a catalyst. The asymmetric cross coupling products (10.14;



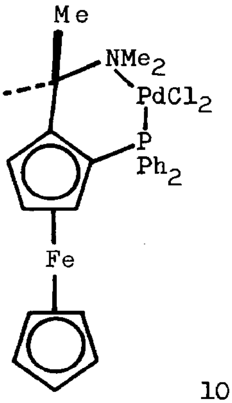
10.10

10.11

10.12

R^1 = H, Me, R^2 = Me, Et) were obtained in up to 86% enantiomeric excess [116]. The enantiomeric dipalladium complex (10.8) formed complexes with amino acids including glycine, L-lysine, L-aspartic acid and L-cysteine. The glycine complex combined with sodium glycinate to form a hexacoordinated palladium diglycine complex [117]. The benzoylation of ferrocenylcopper produced benzoylferrocene and some biferrocenyl. Acylation with the acid chlorides XC_6H_4COCl, where X = p-Br, p-MeO, m-NO_2, p-NO_2, produced the corresponding ferrocenylketones (10.15). Treatment of ferrocenylcopper with adipoyl chloride gave the diferrocenyl derivative (10.16) [118].

Slow crystallization of the dilithioferrocene-tetramethylethylenediamine (TMEDA) adduct (10.17) from ether solution produced $[(\eta\text{-}C_5H_4Li)Fe(\eta\text{-}C_5H_3LiCH(Me)NMe_2)]_4[LiOEt]_2[TMEDA]_2$.



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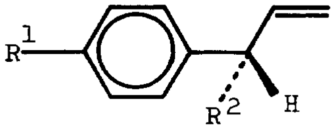
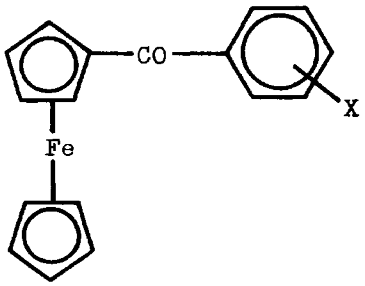


10.14

The structure of this latter complex was determined by X-ray analysis. The structure consisted of discrete molecules possessing exact C_2 symmetry; each containing four ferrocene moieties, ten lithium atoms, two TMEDA units and two ethoxy groups. Each of the five independent lithium atoms achieved a distorted tetrahedral coordination in a different way. An extremely short Li-C bond (2.04Å) was observed [119].



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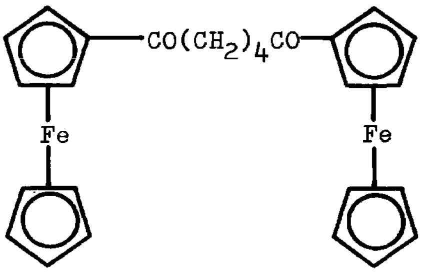
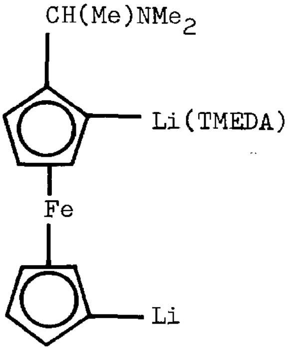


10.16

Treatment of the 1,1'-dilithioferrocene (10.18) with mercury(II) chloride produced the ferrocenophane (10.19) [120]. Lithiation of 1,2,3,4,5-pentamethylferrocene (10.20) followed by condensation with tetrachlorosilane produced the ferrocenophane (10.21).



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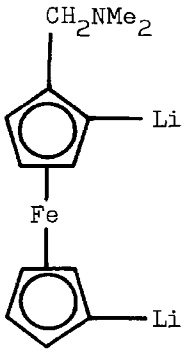
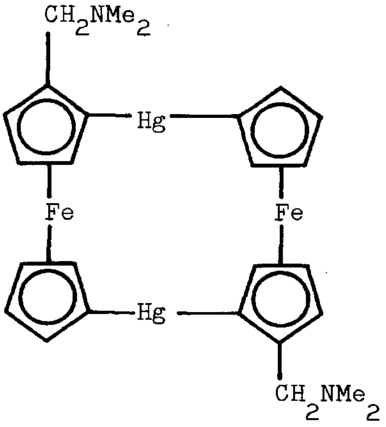


10.18

This ferrocenophane was used to derivatize the surface of platinum and n-type silicon electrodes. The functionalized platinum electrodes exhibited persistent cyclic voltammetry waves consistent with a surface-confined redox couple. These electrodes effected the one-electron reduction of horse heart ferricytochrome $\underline{C}$ (cyt $\underline{C}_{ox}$) to ferrocytochrome $\underline{C}$ (cyt $\underline{C}_{red}$) The functionalized n-type silicon photoanodes effected the uphill oxidation of cyt $\underline{C}_{red}$ upon illumination and effected cyt $\underline{C}_{ox}$ reduction in the dark. The derivatized electrodes were durable



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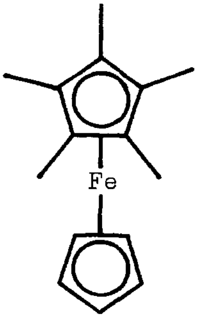

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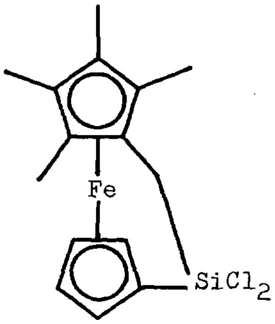

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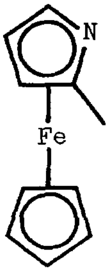
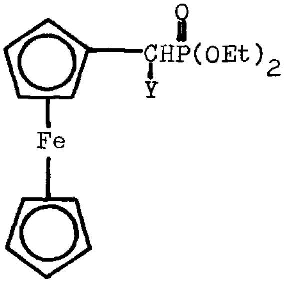


10.22

and lost little activity with repeated use [121]. Metalation of azaferrocene with n-butyllithium gave a mixture of 2- and 1'-lithio- and the 2,1'-dilithio-intermediates which were characterized by treatment with methyliodide to give the corresponding methyl- and dimethylazaferrocenes. The predominant product was the 2-methyl compound (10.22) [122].

The phosphonoferrocene (10.23; Y = OH) has been treated with triphenylphosphine in HBF_4 or in $HClO_4$ and CH_2Cl_2 to form the phosphonium salts (10.23; Y = $PPh_3^+BF_4^-$, ClO_4^-) respectively



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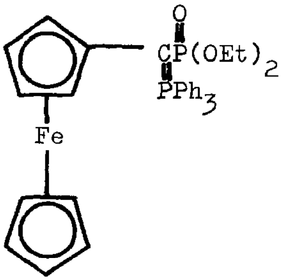

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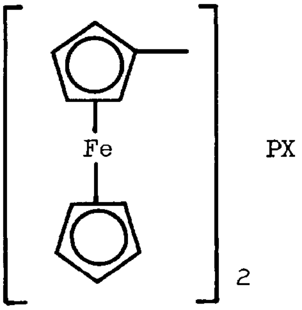

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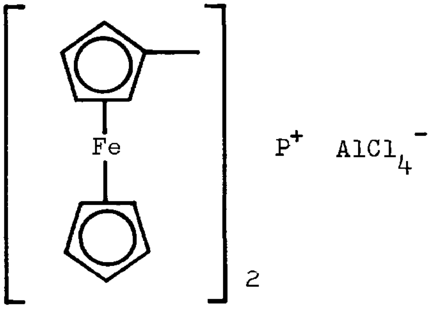
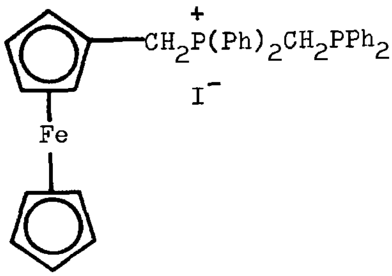


10.26

which were converted by sodium carbonate to the ylide (10.24) [123]. The ferrocenylphosphorus(III) chloride (10.25; X = Cl) has been treated with aluminium chloride to form the salt (10.26) which was confirmed as a ferrocenyl compound by Moessbauer spectroscopy. The chloride (10.25; X = Cl) was reduced to the secondary phosphine (10.25; X = H) with lithium aluminium hydride. Several related transformations were reported [124, 125]. The reaction of bis(diphenylphosphino)methane with ferrocenyltrimethylammonium iodide produced the phosphonium salt (10.27) which was converted into the ylide (10.28). Reaction of this ylide with sodium amide or potassium hydride produced the alkali metal complexes (10.29; M = Na, K). These complexes were soluble in some organic solvents and the NMR spectra of the solutions indicated an interaction between the alkali metal cations and the ferrocenyl group. The reaction of ferrocenylmethylchloride with bis(diphenylphosphino)methane produced the diquaternary salt (10.30). The reaction of this salt with strong bases was investigated [126].

Mono- and di-phosphaferrocenes, including the tetraphenyl compound (10.31) have been studied by ^{1}H and ^{31}P NMR and Moessbauer spectroscopy. Introduction of a phosphorus atom into the cyclopentadienyl ring caused a reduction in quadrupole splitting by comparison with ferrocene. The diphosphaferrocene (10.31) underwent phenyl ring protonation in CF_3SO_3H and the high quadrupole splitting for this species was interpreted in terms of iron participation in the stabilization of the



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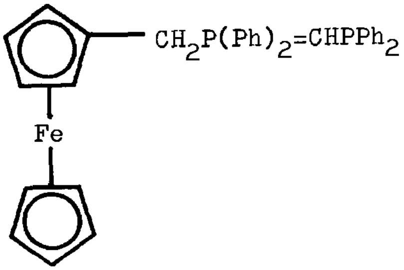

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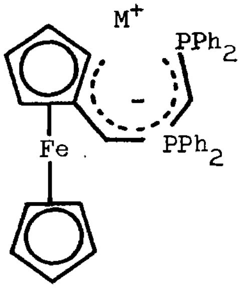

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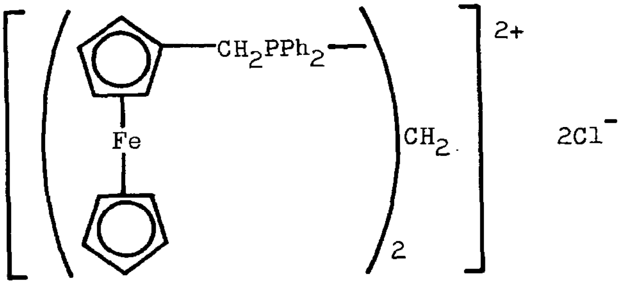
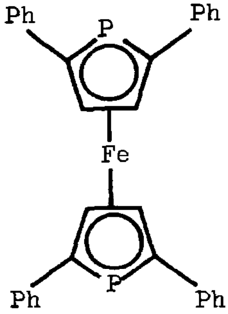


10.30

σ-complex [127]. The preparation of the 1,4-dibora-2,5-cyclohexadiene)metal complexes $(FcBC_6H_4BFc)M(CO)_4$, where



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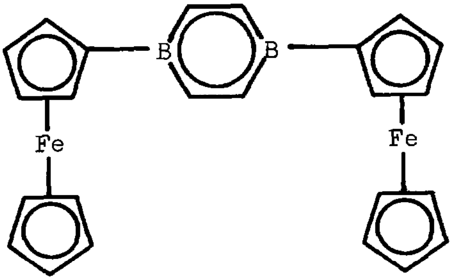
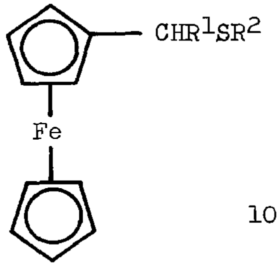


10.32

M = Cr, Mo, W, and $(FcBC_6H_4BFc)M(CO)_3$, where M = Fe, Ru, Os, has been described. In all these complexes the 1,4-diborabenzene moiety (10.32) behaved as a strongly back-donating η^6-bonded ligand [128].

(ii) General Chemistry

The ferrocenylmethylthio-carboxylic acids (10.33; R^1 = H, R^2 = CH_2CO_2H, $C_6H_4.CO_2H$-2) have been converted to formylferrocene by oxidation with manganese dioxide. Reduction of the carboxylic acids (10.33; R^1 = H, R^2 = $C_6H_4.CO_2H$-2; R^1 = Me, R^2 = CH_2CO_2H) gave methyl- and ethyl-ferrocene



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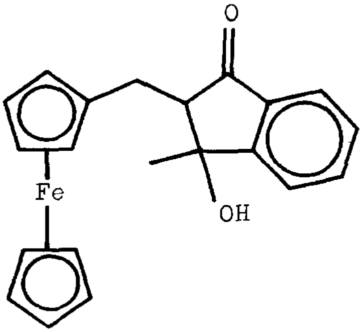

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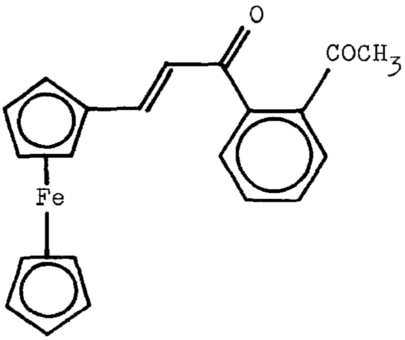
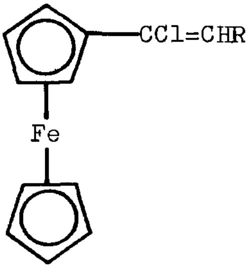


10.35

respectively [129]. The base catalysed condensation of formylferrocene with o-$(CH_3CO)_2C_6H_4$ produced the cyclic ketone (10.34), in the presence of acid the olefin (10.35) was obtained. Similar acid and base catalysed condensations were carried out with o-$CH_3COC_6H_4C_6H_4COCH_3$-o and 1,8-diacetylnaphthalene [130]. Treatment of acetylferrocene with $POCl_3$ and Me_2NCHO gave a



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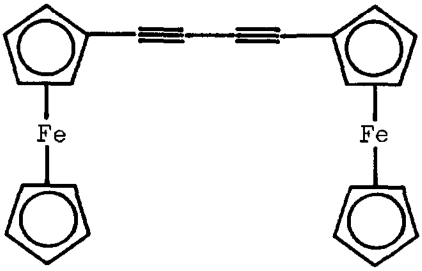
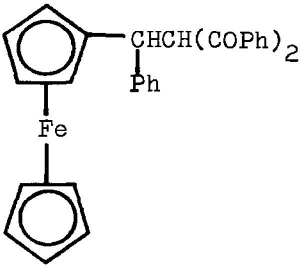


10.37

mixture of the chlorovinylferrocenes (10.36; R = H, CHO) which gave ferrocenylacetylene with sodium hydroxide. Ferrocenylacetylene was coupled in the presence of copper(II) to form the diacetylene (10.37) [131]. Decomposition of the dicarbonyl compound (10.38) with 1:1 $MgBr_2$-$Mg(OMe)_2$ or MeOMgBr produced



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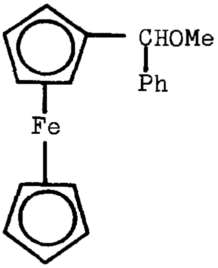

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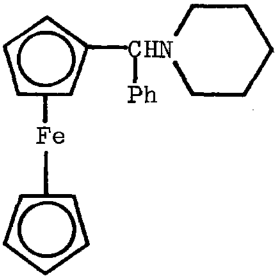
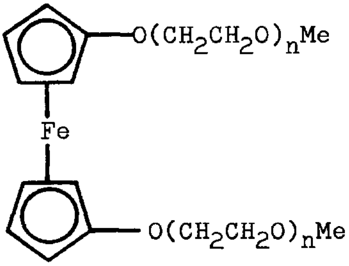


10.40

the ether (10.39) as the major product. In a similar decomposition with $C_5H_{10}NMgBr$ the amine (10.40) was obtained [132]. Ferrocene polyethers (10.41; n = 0-3) have been prepared by treatment of 1,1'-diacetoxyferrocene with the halides $Me(OCH_2CH_2)_nX$, where X = halogen. The polyether (10.41; n = 3) was effective in the extraction of unipositive cations. The order of efficiency was:

$$Ag^+ > Tl^+ > Cs^+ > K^+ > Li^+ > Na^+$$

The diferrocenyl polyethers (10.42; n = 2-4) were obtained by treatment of the potassium salt of hydroxyferrocene with the dibromides $Br(CH_2CH_2O)_nCH_2CH_2Br$ in DMF. These polyethers (10.42) were not useful as extractants for metal cations [133].



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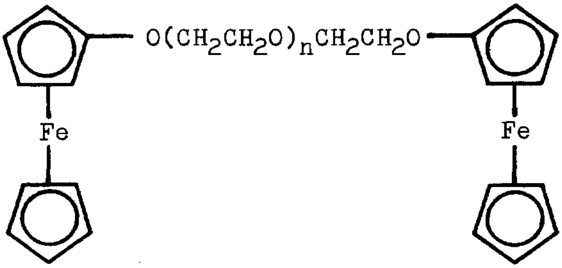
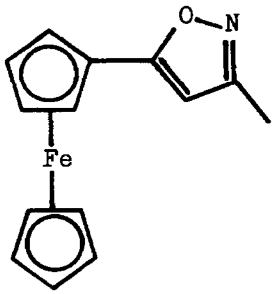


10.42

β-Dicarbonyl derivatives of ferrocene have been used to prepare the ferrocenylheterocycles (10.43; 10.44 and 10.45; R = H, Me, Ph) [134]. Ferrocenylmethyl compounds (10.46; R = Me, Ph, ferrocenyl) have been oxidised to the corresponding ketones (10.47; R = Me, Ph, ferrocenyl) with bis(triphenylsilyl)chromate(VI), $(Ph_3SiO)_2CrO_2$. Ferrocenylethenes were oxidatively cleaved by the same reagent to aldehydes [135]. Oxidation of the alcohols (10.48; R = H, Me, Ph, substituted Ph, OMe, CMe_3) to the corresponding ketones (10.47; R = H, Me, Ph, substituted Ph, OMe, CMe_3) has been investigated using $[Bu_4N]_2[Cr_2O_7]$, $[PhNH_3][CrO_3Cl]$ and $[Bu_4N][MnO_4]$ as the reagents [136]. Acylferrocenes have been treated with thioglycollic acid and the ethyl ester to form the dithio compounds (10.49; R^1 = H, Me, Ph; R^2 = H, Et). 1,1'-Diacylferrocenes



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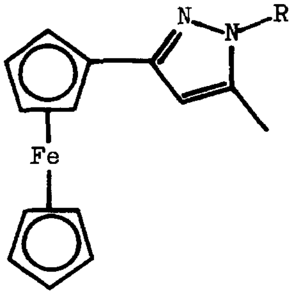

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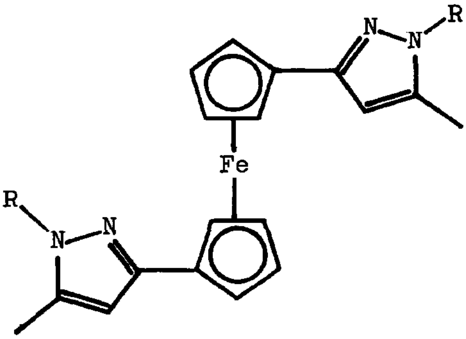

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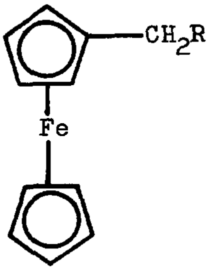
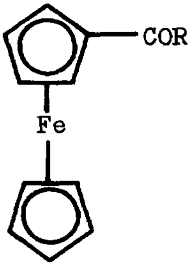


10.46

underwent the same reaction. Reduction of the compounds (10.49) with lithium aluminium hydride gave the corresponding diols



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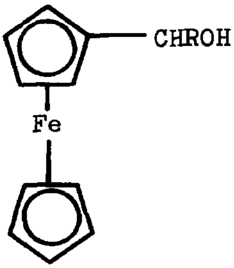

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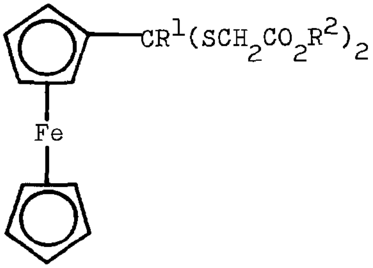

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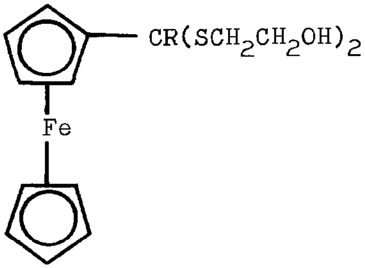
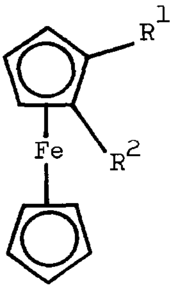


10.50

(10.50; R = H, Me, Ph) [137].

The catalytic hydrogenation of diacetylferrocene to diethylferrocene on nickel-aluminium-metal catalysts (metal = Ti,Fe-Ti, Cr-Ti, Cu) has been investigated. One of the most active catalysts was obtained when M = Ti [138]. Hydrogenation of diacetylferrocene on a nickel-rhenium catalyst in propan-2-ol at 78°C under one atmosphere pressure of hydrogen gave 85-98% diethylferrocene [139]. Enantiomeric and diastereomeric 1,2-disubstituted ferrocenes, for example the alcohol [10.51; R^1 = Me, R^2 = $(CH_2)_7OH$] have been prepared from the ester [10.51; R^1 = $CO(CH_2)_5CO_2Et$, R^2 = H] via reduction, amination,



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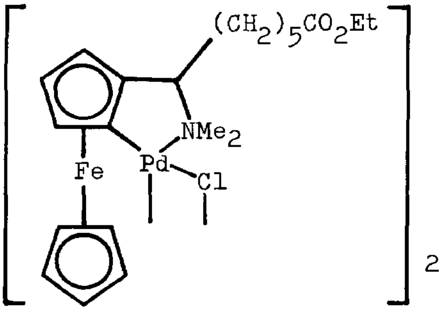

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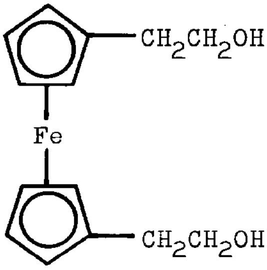

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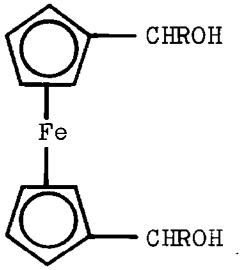

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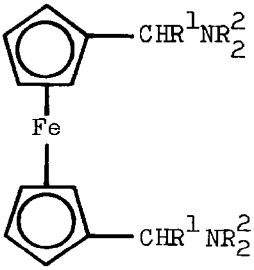
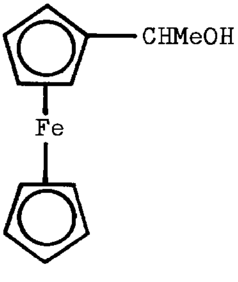


10.55

cyclopalladation with sodium tetrachloropalladate(II) to give the dimer (10.52) followed by carbonylation and reductive amination [140]. The reaction of 1,1'-bis(hydroxymethyl)-ferrocene with phosphorus(III) chloride followed by potassium cyanide produced 1,1'-bis(cyanomethyl)ferrocene. Hydrolysis of this cyanide and reduction of the diacid obtained gave the diol (10.53) in 56% total yield. The cyanide was also used to prepare 1,1'-bis(β-aminoethyl)ferrocene [141].

Ferrocenemethanols such as the secondary alcohols (10.54; R = Me, Ph) have been converted to the corresponding tertiary amines (10.55; R^1 = Me, Ph, R^2 = Me; R^1 = Ph, R^2 = Et) by



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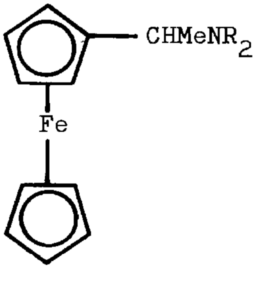

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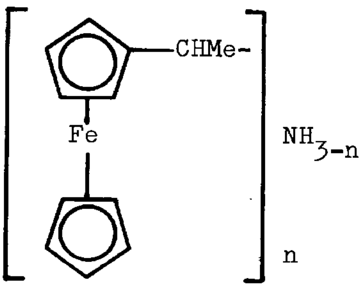

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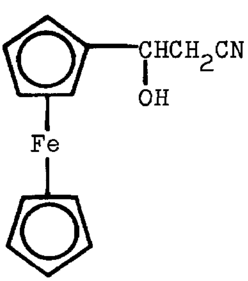

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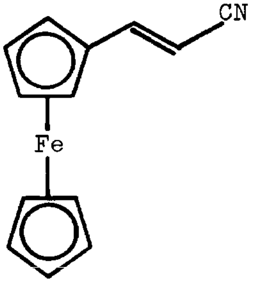

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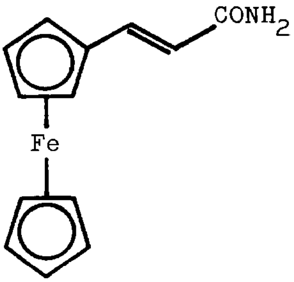
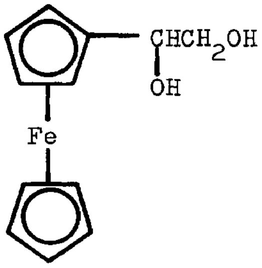
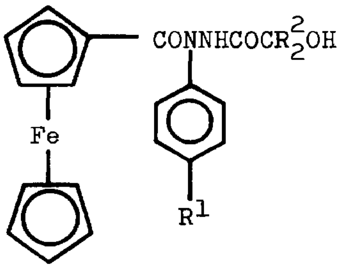


10.61

treatment with hydrogen bromide and then dimethylamine or diethylamine [142]. Treatment of 1-ferrocenylethanol (10.56) with dimethylamine and dicyclohexylamine in the presence of hydrogen bromide gave the tertiary ferrocenylethylamines (10.57; R = Me, C_6H_{11}). When the reagent was ammonia a mixture of the primary, secondary and tertiary amines (10.58; n = 1, 2, 3) was obtained. Use of the optically active amine d-(+)-$PhMeCHNH_2$ led to the formation of diastereoisomeric ferrocenylethylamine products [143]. Dehydration of the alcohol (10.59) with $SnCl_2$-HCl gave 96% of the <u>trans</u>- isomer of the olefin (10.60). When a mixture of the <u>cis</u>- and <u>trans</u>-isomers was treated with



10.62



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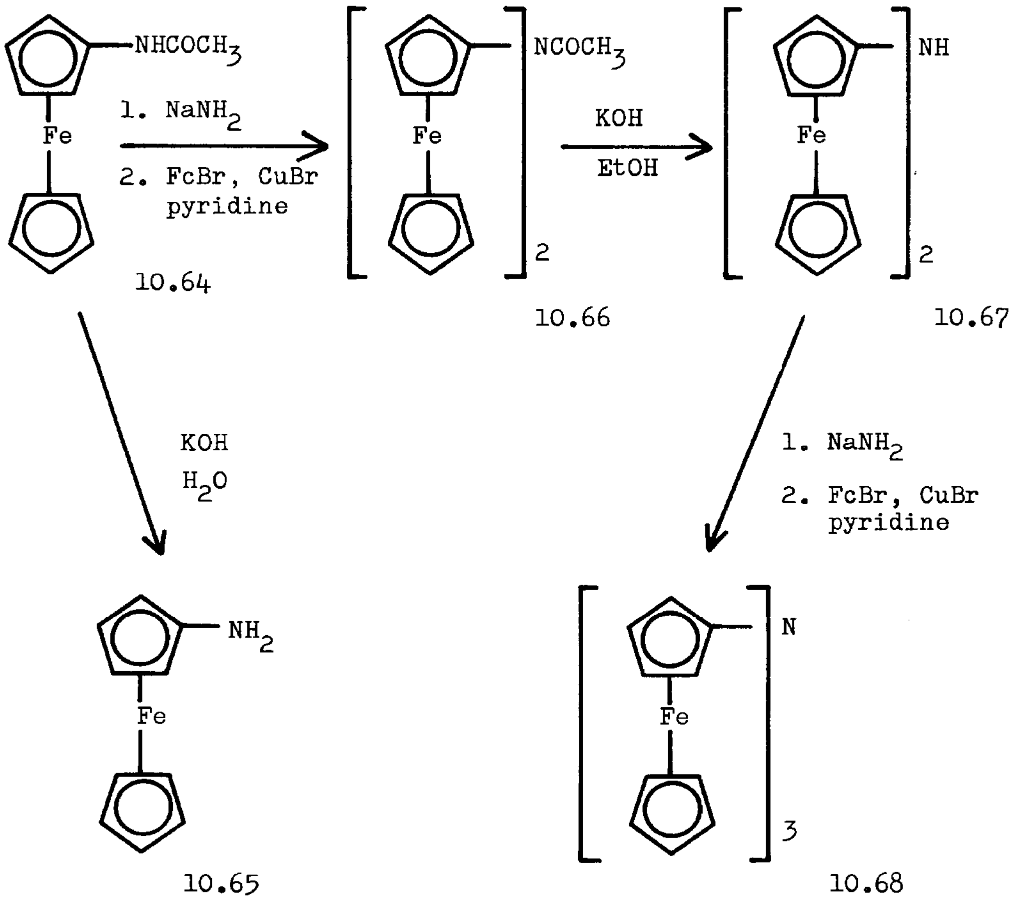
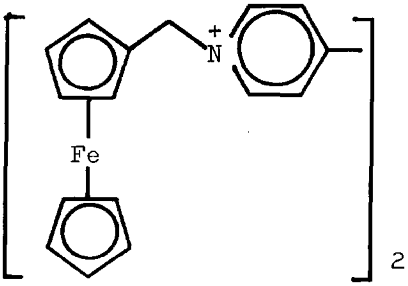


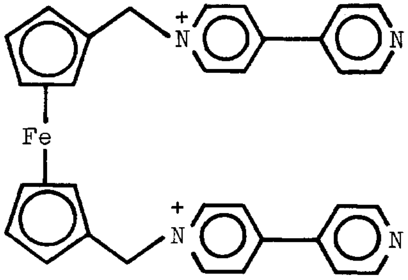
10.64 10.66 10.67 10.65 10.68

$SnCl_2$-HCl, 94-5% of the trans-isomer was produced (10.60). Reaction of the cis- and trans-isomers with H_2O_2-KOH produced the cis- and the trans-acrylamide (10.61) [144]. Oxidation of vinylferrocene with tetrabutylammonium permanganate in dichloromethane produced the diol (10.62) [145]. The hydrazides (10.63; R^1 = H, R^2 = Et, Br, Ph; R^1 = Me, R^2 = Ph) have been prepared from ferrocenoyl chloride and p-$R^1C_6H_4$-$NHNHCOCR^2_2OH$ [146].

The reaction of bromoferrocene with the sodium salt of an amine or amide in the presence of copper(I) bromide/pyridine has been used as a general method for the preparation of ferrocenylamines. Ferrocenylamine (10.65) was prepared by the



10.69

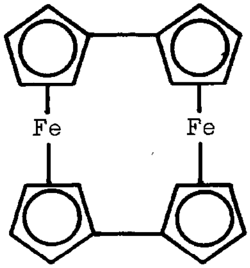


10.70

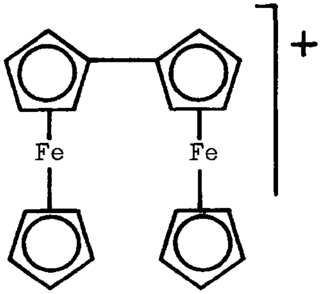
hydrolysis of N-ferrocenylacetamide (10.64). The secondary (10.67) and tertiary (10.68) ferrocenylamines were obtained from the same starting material (10.64) through the intermediate diferrocenylamide (10.66) [147]. The reaction of chloromethyl- and 1,1'-bis(chloromethyl)-ferrocene with 4,4'-bipyridine produced the corresponding ferrocenylmethyl derivatives (10.69 and 10.70) [148]. Inhibition by aliphatic alcohols of the photooxidation of ferrocenyl-substituted carboxylic acids has been reinvestigated. The aliphatic alcohol has been shown to act as a scavenger for OH radicals which were involved in the oxidation process [149].

11. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

The electronic structures of biferrocene and biferrocenylene (11.1) have been examined by He(I) photoelectron spectroscopy. The results were compared with calculations using semiempirical INDO MO methods which predicted large reorganization effects for ionization events of highly localized MOs with major iron 3d amplitudes. The time of hole exchange in the 1+ and 2+ cations derived from biferrocene and the complex (11.1) has been estimated. This has allowed the binuclear ferrocenes to be classified in a way that corresponds to the theoretical models used for mixed valence species [150]. The crystal and molecular structure of a picrate hemihydroquinone salt of the [0.0]ferrocenophanium cation (11.2) has been determined by X-ray crystallography. The Fe-Fe distance was



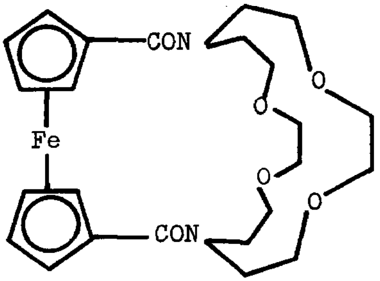
11.1



11.2

34 pm shorter than in the neutral ferrocenophane which indicated some Fe-Fe interaction in addition to the interaction between the cyclopentadienyl rings [151]. Adducts of [2]ferrocenophane and 1,1,2-tetramethyl[2]ferrocenophane with mercury(II) salts were prepared by treating the ferrocenophanes with HgX_2 where X = Cl, I, CN. Moessbauer spectroscopy suggested that there was strong direct interaction between the iron and mercury atoms [152]. Ferrocene, [2]ferrocenophane and [3]ferrocenophane combined with tin(IV) chloride to form adducts. The red-orange [2]ferrocenophane adducts showed an unusually large ^{57}Fe Moessbauer quadrupole splitting which was interpreted in terms of direct Fe-Sn bonding. The ferrocene and [3]ferrocenophane adducts were dark green and contained the ferrocenium and [3]ferrocenophanium cations [153].

Intramolecular reductive coupling of 1,1'-bis(o-formylphenyl)-ferrocene using low valent titanium reagents gave syn- and anti-[0]orthocyclo[2]orthocyclo[0](1,1')ferrocenophan-7-ene. These and related ferrocenophanes prepared by similar reactions were examined by NMR and UV spectroscopy for π-electronic interactions between the two benzene rings [154]. Treatment of 1,1'-bis(chlorocarbonyl)ferrocene with diaza-18-crown-6 gave the ferrocene cryptates (11.3 and 11.5). The yields and proportions of these products were determined by the reaction temperature. The same reagent combined with ethylene glycol bis(aminophenyl)ethers to give the macrocyclic ferrocenophanes (11.4; n = 0, 1, 2). Structural features of the products



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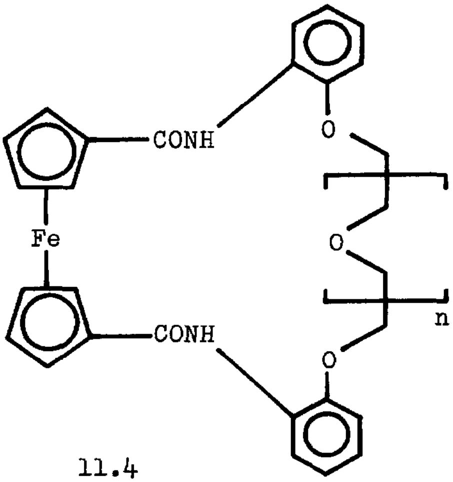
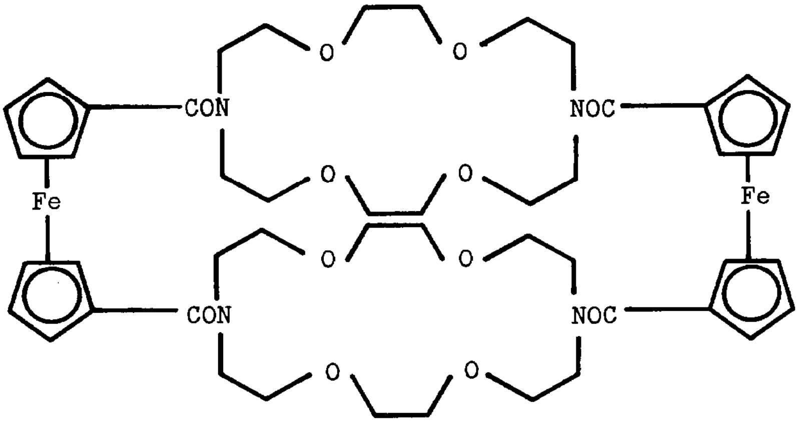


11.4

(11.3 and 11.4) and dynamic processes within the molecules were examined by ^1H and ^{13}C NMR spectroscopy [155, 156]. The diacetate (11.6; R = COMe) has been treated with the dichloroethers, $ClCH_2(CH_2OCH_2)_nCH_2Cl$, where n = 0-3, in the presence of potassium hydroxide to form the chloroethers (11.6; R = $CH_2(CH_2OCH_2)_nCH_2Cl$. These were then attacked by sodium sulphide to give the polyoxathiaferrocenophanes (11.7; n = 0-3) and the binuclear polyoxadithiaferrocenophanes (11.8; n = 0-3). The ferrocenophane (11.7; n = 3) was effective in extracting unipositive cations with the following order of efficiency:

$Tl^+ \gg Rb^+ > K^+ > Cs^+ > Na^+ > Li^+$ [157].

The polyoxaferrocenophanes (11.9; n = 0, 1, 2, 3, 4) were prepared in one-step by reaction of 1,1'-diacetoxyferrocene with the appropriate ether $ClCH_2(CH_2OCH_2)_nCH_2Cl$. The ferrocenophane (11.9; n = 4) formed crystalline 1:1 complexes with lithium, sodium and potassium thiocyanates. Spectroscopic data indicated that in these complexes there was possibly some interaction between the iron atom and the complexed alkali metal cation [158]. The polyoxa-ferrocenophanes (11.10 and 11.11; n = 2, 3, 4) and (11.12; n = 1, 2) have been prepared from 1,1'-bis(hydroxymethyl)ferrocene. The complexing ability of these compounds with alkali and transition metal cations was investigated [159]. The cyclization of 1-acetyl-1'-(p-chlorocinnamoyl)ferrocene to the ferrocenophane (11.13) was catalysed by a variety of acid catalysts [160]. The base catalyzed condensation of 1,3-



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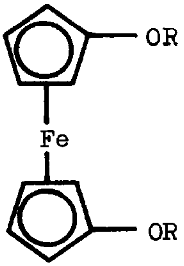

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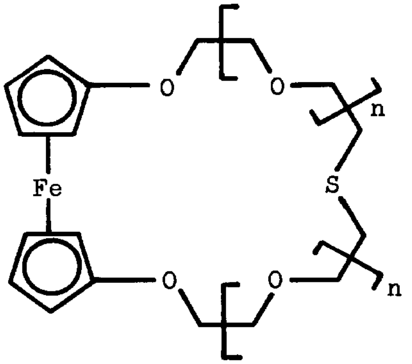
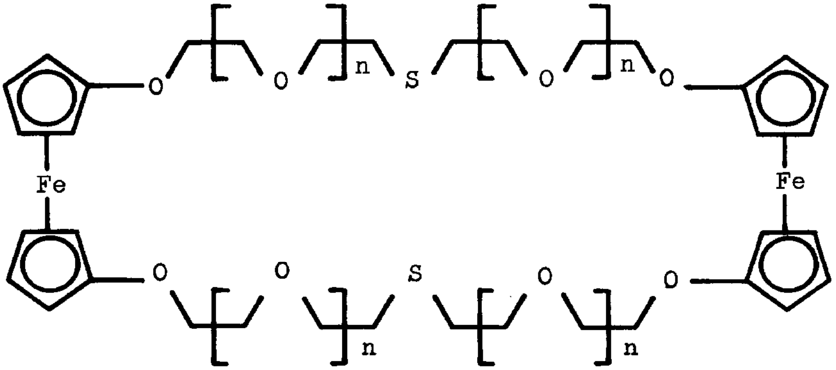


11.7

-ferrocenediacarbaldehyde with 1,3-diacetylferrocene using the high dilution technique produced the ferrocenophane (11.14).



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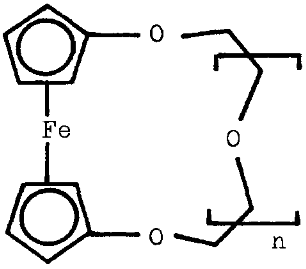
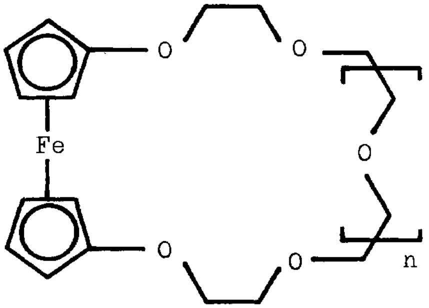


11.9



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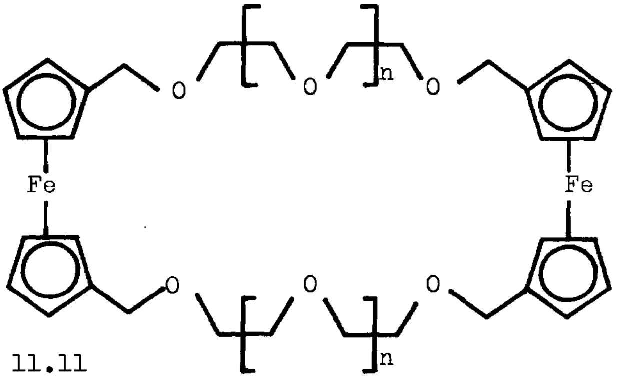

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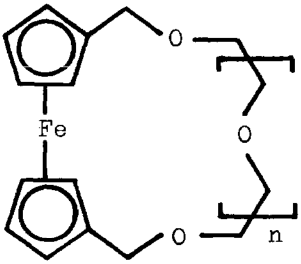
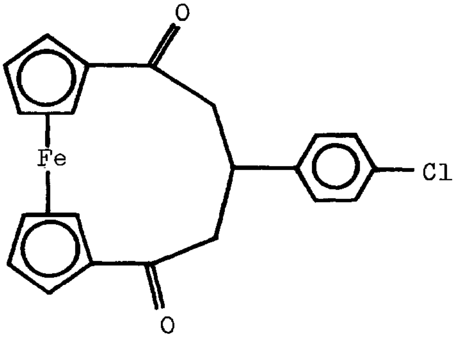


11.12

This compound was reduced with $LiAlH_4$-$AlCl_3$ and then catalytically hydrogenated to give [3.3](1,3)-ferrocenophane [161].

The stereochemistry of the reaction of Grignard reagents with the 3-aryl- and 3-alkyl-[5]ferrocenophane-1,5-diones (11.15; R^1 = Ph, p-$MeOC_6H_4$, Me_2CHCH_2, Et) has been investigated. The reaction was completely stereospecific giving the corresponding alcohols (11.16 and 11.17; R^2 = Me, Et, n-Pr, i-Pr, CH_2=$CHCH_2$, t-Bu) where the introduced alkyl groups were cis to substituents at C(3). The chair conformation, with strong intramolecular hydrogen bonding predominated in the hydroxyketones (11.16) and this was the only conformer present in the dihydroxy derivatives (11.17) [162] A series of ferrocenophanes, in which the two η-cyclopentadienyl rings were linked by biphenyl rings, have been prepared via intramolecular coupling



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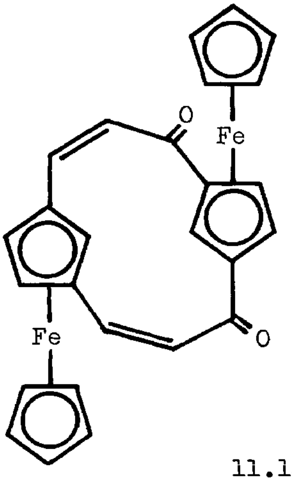
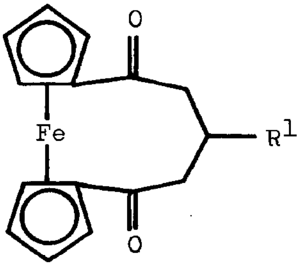


11.14

of the corresponding formyl compounds with a $TiCl_4$-Zn reagent. For example reductive coupling of the dialdehydes (11.18; R^1 = CHO, R^2 = H; R^1 = H, R^2 = CHO) produced the biphenyl derivatives (11.19 and 11.20) respectively. The structures of these and related compounds were examined by spectroscopy [163]. Several ferrocenophanes including the acetylenes (11.21 and 11.22) have been prepared by reductive coupling of the corresponding aldehydes. UV-visible spectroscopy was used to investigate transannular electronic interactions [164].



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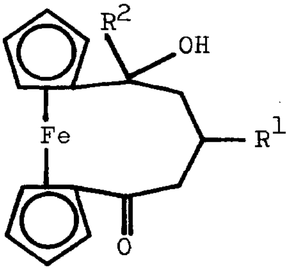

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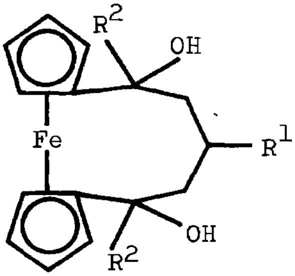

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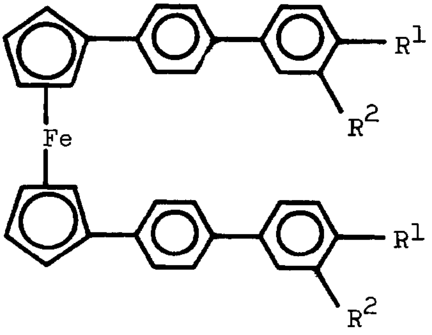

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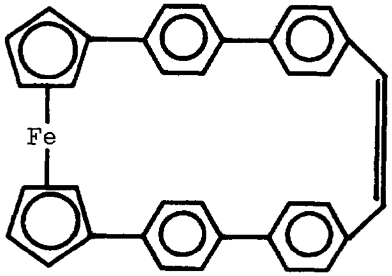

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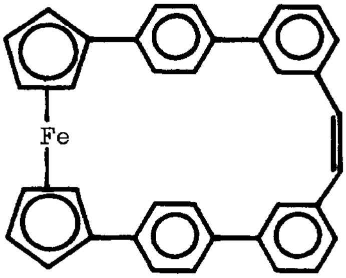

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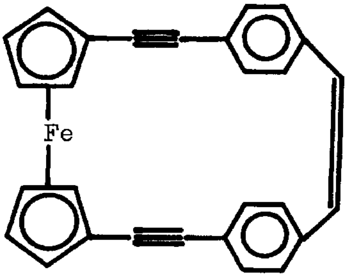
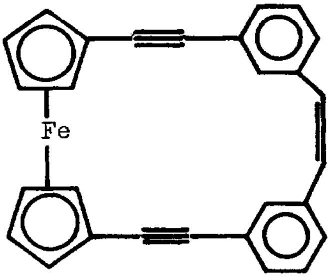


11.21

The pentabridged ferrocenophanes (11.23 and 11.24) have been prepared from the propionic acid (11.25). The structures of the ferrocenophanes (11.23 and 11.24) were confirmed by X-ray analysis. The crystal and molecular structures of both compounds were almost identical and both contained a rotational disorder about the axis of five fold symmetry through the two η-cyclopentadienyl rings [165]. Formylferrocene has been condensed with the appropriate formylparacyclophane to give the cyclophane complex (11.26) and the diparacyclophane complex (11.27) has been obtained by complexation of the appropriate ligand with iron [166]. The reaction of tetrakis(triphenylphosphine)palladium(0) with 1,2,3-trithia[3]ferrocenophane produced the heterobinuclear species (11.28). The structure of this complex was determined by X-ray analysis. The ferrocene



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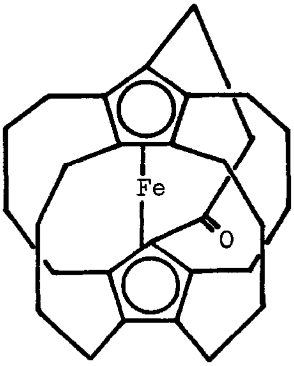

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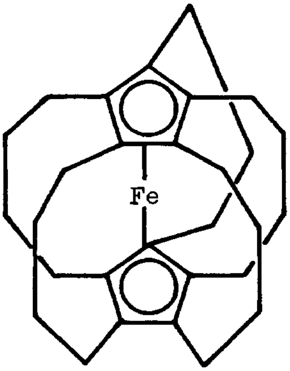

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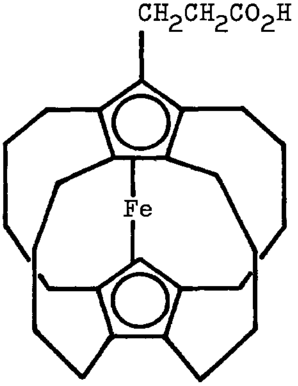
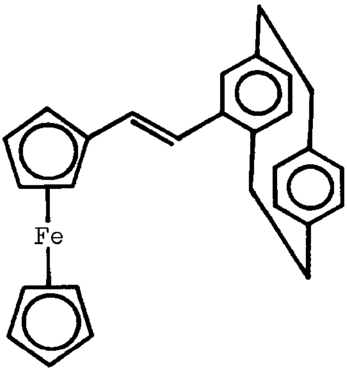


11.25

moiety was slightly bent and the geometry about the palladium atom was a distorted square plane [167]. Trithiaferrocenophane (11.29) has been treated with dodecacarbonyltriiron to form the dithiolatodiiron complex (11.30) [168].

1,1'-Ferrocenedithiol has been used to prepare the polythiaferrocenophanes [11.31, X = $(CH_2)_2$, $(CH_2)_2$ $S(CH_2)_2$, $(CH_2)_2S(CH_2)_nS(CH_2)_2$, n = 2,3; $(CH_2)_3S(CH_2)_nS(CH_2)_3$, n = 2, 3]. The spectroscopic properties of these compounds were discussed [169]. The [5]ferrocenophane (11.32) has been obtained by treatment of ferrocene-1,1'-dithiol with pentaerythritol tetrabromide. Bridge reversal in the complex (11.32) has been examined by ^{1}H NMR spectroscopy [170]. Diastereomeric oxathiaferrocenophanes, for example the complex (11.33), have



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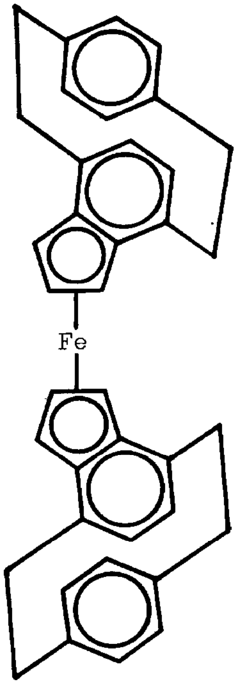

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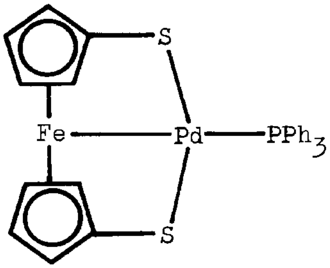

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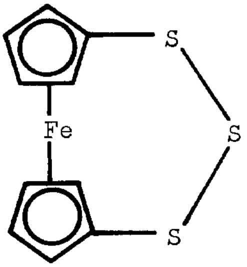

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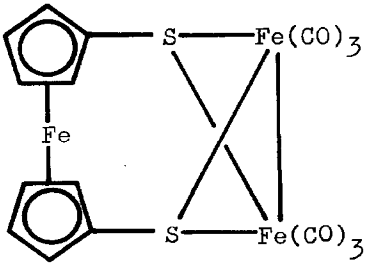

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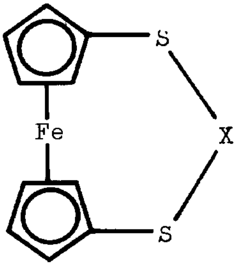

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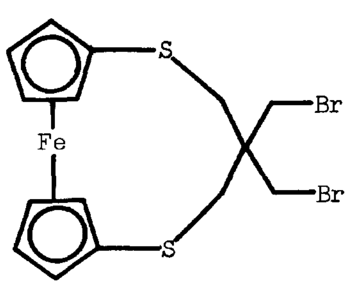

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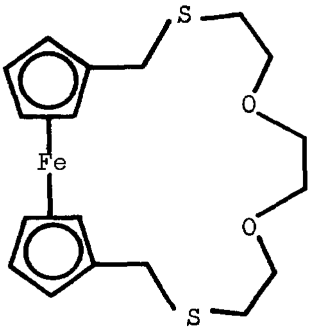

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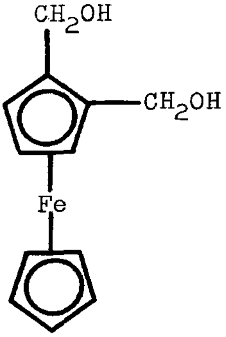
been prepared by reaction of 1,1'-bis(hydroxymethyl)ferrocene with dithiols containing ether linkages [171]. 1,2-Bis(hydroxy-



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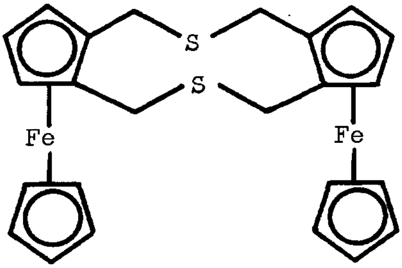

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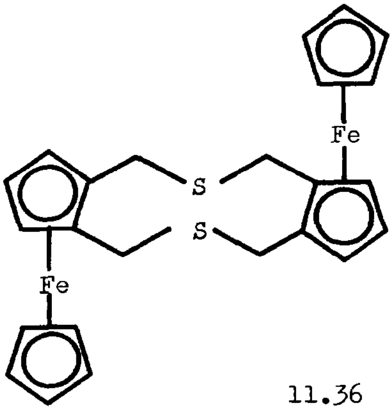

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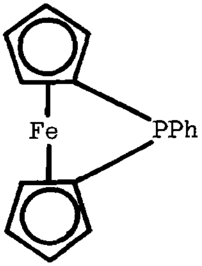

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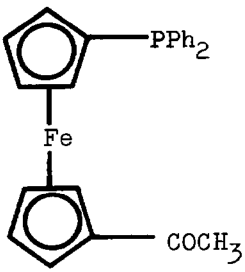

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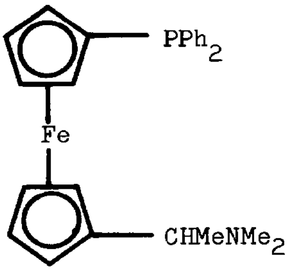

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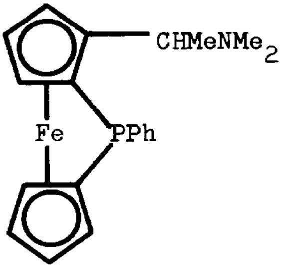
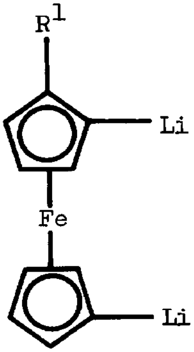


11.40

methyl)ferrocene (11.34) has been attacked by hydrogen sulphide to form the dithiaferrocenophanes (11.35 and 11.36) [172].

The cleavage of the [1]-ferrocenophane (11.37) with phenyllithium produced 1-lithio-1'-diphenylphosphinoferrocene which was coupled with acetyl chloride to produce the heteroannularly substituted acetylferrocene (11.38). Reduction of this ketone produced the corresponding alcohol and attempts were made to convert this to the amine (11.39), but the yields were small. An alternative synthetic route to the amine (11.39) was devised. The ferrocenophane (11.40) was treated with



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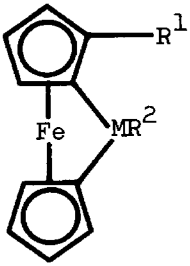
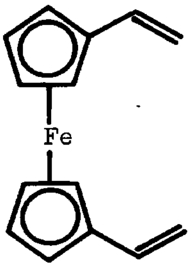


11.42

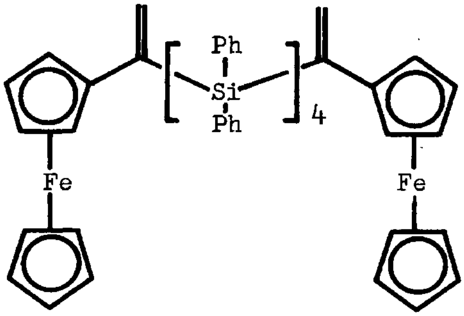
phenyllithium at low temperatures and on hydrolysis the amine (11.39) was produced in good yield [173]. Treatment of the 1,1'-dilithioferrocenes [11.41; R^1 = H, $CHMeNMe_2$, $CH(CHMe_2)NMe_2$] with R^2MCl_2($PhPCl_2$, $PhAsI_2$, Me_3CPCl_2) produced the corresponding [1]ferrocenophanes (11.42). The crystal structures of these compounds were determined. The mean tilt of the η-C_5H_5 rings in the phosphorus bridged compounds was 27.0° and for the arsenic derivatives 22.9° [174].

12. FERROCENE-CONTAINING POLYMERS

Radical polymerization of 1,1'-divinylferrocene (12.1) gave a homopolymer which was shown by ^{13}C NMR and Moessbauer spectroscopy to be a cyclopolymer containing a three-carbon bridged ferrocene unit. When cationic polymerization was used then the polymer had an acyclic structure [175]. Divinylbenzene and vinylferrocene have been copolymerized at 680°C and 125 MPa and the resulting copolymer was subjected to pressure pyrolysis to give carbon containing finely dispersed iron. The pyrolysis conditions used determined the morphology of the carbons which consisted of fibrils, spheres and polyhedra [176]. The rate of intramolecular electron exchange between pendant ferrocenyl groups in poly(vinylferrocene) has been determined by an NMR line broadening technique. The rate constant was determined



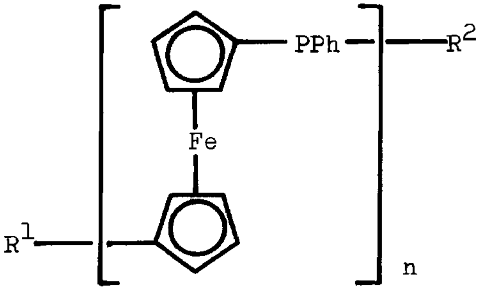
12.1



12.2

as 6.4×10^8[177]. Electroactive plasma polymerized vinylferrocene (PPVF) films have been deposited on glassy carbon electrodes for use in electrochemical X-ray photoelectron spectroscopic and ellipsometric studies. Ferrocene residues in the PPVF film surface were found to be appreciably oxidized to ferrocenium. Equilibrium charge-potential measurements demonstrated that the activities of ferrocene and ferrocenium were proportional to the square of their concentrations and were independent of the solvent used [178].

1,1'-Diisopropenylferrocene underwent cationic homopolymerization in the presence of trifluoroacetic acid or boron trifluoride etherate to give a polymer with a number average molecular weight of 8100-14700. Some residual unsaturation in the polymer was identified by ^1H and ^{13}C NMR spectroscopy and some mixed valence, Fe(II)-Fe(III), material was also present [179]. Adducts of crystalline poly(1,1'-ferrocenylene) with various electron acceptors such as iodine, 2,2'-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile and tetracyanoethylene have been prepared. The magnetic susceptibilities and Moessbauer spectra indicated partial oxidation of iron(II) to iron(III). The electrical conductivities of the adducts were relatively high [180]. The preparation and polymerization of the monomers $R^1R^2C{=}CH_2$ and $(H_2C{=}CR^1)_2Z$ (R^1 = ferrocenyl, R^2 = m-carbonyl, Z = 1,7-m-carboranediyl) have been investigated.



12.3

Treatment of acetylferrocene with $Li(SiPh_2)_4Li$, followed by dehydration, produced the monomer (12.2). The polymerization of this monomer was also studied [181].

Products from the reaction between ferrocenyllithium and methylphenylchlorosilane underwent addition to $Me_2Si(C\equiv CH)_2$ and $Ph_2Si(C\equiv CH)_2$ in the presence of an H_2PtCl_6 catalyst. The oligomeric products were characterized by thermogravimetry and DTA at temperatures of up to 1000°C in oxygen [182]. The 1,1'-ferrocenylenephenylphosphine oligomers (12.3; $R^1 = H$, $R^2 = Ph$, $n = 1$-4; $R^1 = Ph_2P$, $R^2 = Ph$, $n = 1, 2$) combined with octacarbonyldicobalt to form complexes in which the phosphine ligands were chelating and tridentate when appropriate. The complexes were evaluated as catalysts for the hydroformylation of 1-hexene, they exhibited similar reactivity and selectivity to cobalt-triphenylphosphine catalysts. Cobalt complexes formed from the polymeric phosphines (12.3; $R^1 = H$, $R^2 = OH$) with molecular weight 8,900-161,000 amu showed catalytic activity that was molecular weight dependent [183].

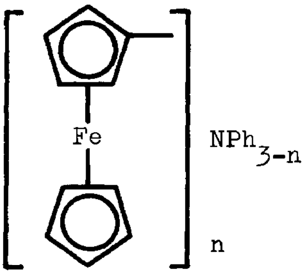
13. APPLICATIONS OF FERROCENE

(i) Ferrocene Catalysts and Photosensitizers

The photochemical and subsequent dark reactions of the ferrocene-tetrabromomethane system in polymer layers have been investigated. A mechanism was proposed and the sensitometric characteristics of this ferrocene based photoimaging system were determined [184]. The ferrocene-tetrabromomethane system has been used as the basis of a photoimaging film which was suitable for the preparation of offset printing plates [185]. A light sensitive composition has been prepared from triethylferrocene or tri-t-butylferrocene with carbon tetrabromide and a toning compound [186]. A similar composition with high light sensitivity in the long wavelength region was based on polymethylferrocenes [187]. A light sensitive composition containing ferrocene, dibenzylaniline and tetrabromomethane in a polystyrene binder gave different photoproducts on exposure to light of different wavelengths [188]. Light sensitive compositions with good contrast and relatively low cost have been developed. They contained a mixture of mono-, di- and tri-t-butylferrocene or a mixture of mono-, di-, tri- and tetra-isopropylferrocene together with tetrabromomethane and a toning compound [189].

In a related patent the composition contained methyl, ethyl or propyl acetylferrocenecarboxylate as the metallocene component. Low temperatures for development and short development times were claimed [190].

Ferrocenyldiphenylamine, diferrocenylphenylamine and triferrocenylamine (13.1; n = 1, 2, 3) respectively, have been dissolved in polystyrene or a polycarbonate and used to form electrophotographic layer materials with photoconductor properties [191]. Condensation polymers, such as poly(oxy-2,6--dimethyl-1,4-phenylene), have been solubilized by treatment with Cs salts, such as the Cs salt of ferrocene carboxylic acid.



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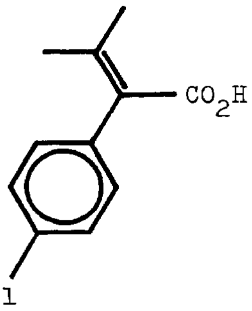

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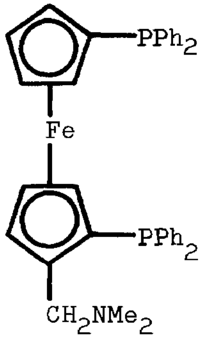


13.3

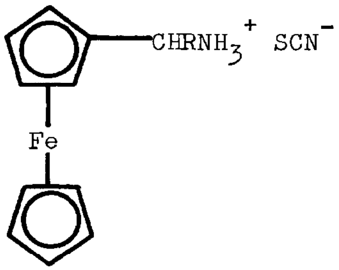
Irradiation at 435nm of the solubilized polymer films in the presence of dibromotetrachloroethane caused rapid darkening consistent with cation formation [192]. Asymmetric hydrogenation of the tetra-substituted olefinic acids $R^1R^2C{=}CR^3CO_2H$ ($R^1 = R^2 = Me$, $R^1R^2 = CH_2CH_2$, $R^3 = aryl$) has been achieved with a catalyst system containing a coordination complex of rhodium, ruthenium or iridium and a chiral ferrocenyl-, ruthenocenyl-, osmocenyl- or pyrrolidinyl-phosphine ligand. For example, the olefin (13.2) was asymmetrically hydrogenated at 700 p.s.i. and 80°C using a catalyst system containing $[(\eta\text{-norbornadiene})RhCl]_2$, the chiral ferrocenylphosphine (R,S)-(13.3), silver tetrafluoroborate and triethylamine [193].

A catalyst has been prepared, for use in the synthesis of ammonia, by the adsorption of potassium vapour and ferrocene on active carbon. The catalyst had much higher activity at lower temperatures than a conventional iron catalyst. A linear correlation was observed between the ferrocene concentration and the activity increase. A Moessbauer study indicated the presence of ferromagnetic Fe_3C and α-Fe with the α-Fe being the active centre [194]. 1-Benzoyl-1'-o-chlorobenzoylferrocene has been used as an intermediate in the preparation of 1'-benzylferrocenecarbinol which was converted to the tricarbonylchromium complex and evaluated as a catalyst [195].

(ii) Ferrocene Stabilizers and Improvers

Several ferrocene derivatives have been tested for their ability to prevent the ultraviolet induced aging of corrosion-protective films of low-pressure polyethylene on steel. The addition of acetyl-1,1'-diethylferrocene oxime to the polymer gave maximum resistance to ultraviolet aging and maximum protection of the steel from atmospheric corrosion [196]. A study has been carried out on the relaxation of stresses in modified polyethylenes. The mechanical properties of the polymer were improved by the addition of ferrocene [197]. Ferrocene has been used in the treatment of polyethylene and polypropylene wastes which were subsequently recovered [198]. The effect of ferrocene derivatives and cymantrene on the heat and radiation resistance of silicone rubbers has been investigated. α-Methyl-β,β-dicyanovinylferrocene, 1,1'-tetramethylsiloxanylferrocenophane and cymantrene increased the heat and radiation resistance with the ferrocenophane being the most effective [199]. The incorporation of the ferrocenylamine thiocyanates (13.4; R = H, Me) into neoprene rubber produced vulcanizates with increased strength [200].

A small proportion of ferrocene or acetylferrocene and benzenesulphonic acid has been mixed with a formaldehyde-furfural-phenol copolymer and acetone to give a composition suitable for the treatment of wood. Samples modified in this way showed a loss in compressive strength and a low mass loss on accelerated aging [201]. Ferrocene or acetylferrocene, 0.5-1.5%, has been added to the same copolymer which was then used to retard the aging of wood [202]. A related patent described the modification of wood by the incorporation of the same copolymer containing a small proportion of benzenesulphonic acid and ferrocene to give a fracture-resistant



13.4

material [203]. The addition of 0.05 wt.% of ferrocene derivatives to 1:1 water-lubricating oil mixtures reduced the rate of emulsification when air was blown through the mixture [204]. A stabilizer for fuel oil-water emulsions has been developed that contained ferrocene together with a combustible emulsifier, benzyl alcohol, an oil soluble magnesium salt and a surfactant [205]. A series of ferrocenyl-alcohols and eight ferrocenyl-sulphides have been tested as antiwear additives in paraffin oil. The results were discussed in terms of the stability of the ferrocenyl-carbenium ions that were formed readily by the alcohols and the sulphides [206]. Metallocene copolymers, such as styrene-vinylferrocene copolymer, with a ferrocene plasticizer have been used to form the basis of charge-carrier transport materials for electrophotography [207]. γ-Hematite magnetic thin films have been formed by evaporating ferrocene in an oxidizing atmosphere, depositing the film on a heated substrate and then heat treating it in a reducing atmosphere [208]. The gas carburization of steel products in the presence of ferrocene vapour speeded up the process at a lower temperature [209].

(iii) Ferrocene in Analysis

Vanadium has been determined in steels containing 0.14-2.12% vanadium by amperometric titration with ferrocene. Vanadium and iron were determined in nickel-based alloys by potentiometric titration with ferrocene in 5-6M sulphuric acid.

Strong oxidizing agents such as chromium(VI) and manganese(VII) interfered but large excesses of iron(III), molybdenum(VI) and copper(II), relative to the vanadium(V) concentrations, did not interfere [210]. The concentrations of vanadium(IV) and vanadium(V) present together in vanadium catalysts have been determined by a titrimetric method using a solution of ferrocene in propanol. Initially the vanadium(V) was determined amperometrically or potentiometrically in a 5-6M sulphuric acid solution. After the addition of phosphoric acid the vanadium (IV) was determined by continuing the titration [211]. Iron(III) and vanadium(IV) were determined in the presence of each other by amperometric or potentiometric titration with 0.01M ferrocene. Methods were developed for determining iron and vanadium in different alloys [212]. Ferrocenometric techniques have been used for the determination of standard reference materials [213].

Ferrocene has been proposed as a primary iron standard in volumetric analysis since it may be purified easily, it is resistant to oxidation and it is not hygroscopic [214]. Ferrocene has been determined by potentiometric titration with iron(III) chloride in methanol containing perchloric acid [215]. Gold(III) has been determined by potentiometric titration with a 0.01M ferrocene solution. Copper and a four fold excess of silver did not interfere [216]. Ferrocene has been used as a reducing agent for palladium(II) and silver(I) in aqueous-organic solutions. A gravimetric procedure, using ferrocene, has been developed for the determination of these elements in palladium--silver alloys [217].

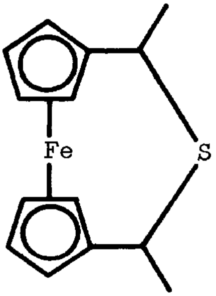
A ferrocene-modified platinum electrode has been used as a potentiometric sensor for L-ascorbic acid in an aqueous glycine buffer at pH 2.2. In recovery experiments with pure L-ascorbic acid the relative standard deviation was 1.9% and in the analysis of fresh orange juice the relative standard deviation was 6.1% [218]. A kinetic investigation of the oxidation of NADH by ferrocenium salts has provided an estimate of the $E^{o\prime}$ value (1.05 V vs. NHE) for the one-electron no proton couple $NADH/NADH^{+}$ [219].

(iv) Combustion Control

The addition of metallocenes and related compounds was effective in reducing the smoke and hydrogen chloride evolved in the thermal degradation of poly(vinyl chloride). Nickelocene and dicyclopentadienyltitanium dichloride were more efficient in smoke suppression than ferrocene [220]. The combustion velocity of ammonium perchlorate based solid propellants for rocket igniters has been improved by using dibutylferrocene as a catalyst in place of Fe_2O_3 [221]. The use of diesel fuel containing 20-30 ppm of ferrocene was effective in replacing carbon deposits with catalytic iron oxide on the combustion surfaces of diesel engines. Subsequent operation with a lower concentration of ferrocene, 10-15 ppm maintained the iron oxide layer [222].

(v) Biochemical and Biological Applications

The toxicity of the ferrocene hematinic (13.5) and its effects on the liver and adrenal cortex of the dog, rat and monkey have been investigated. The hematinic (13.5) was administered orally at dosages ranging from 0 to 500mg/kg/day to dogs, for two weeks, and to monkeys and rats, for six weeks. High-dose rats had distended abdomens due to enlarged livers while high-dose dogs and monkeys exhibited the following signs: emesis, depression, ataxia, anorexia and a high number of deaths [223]. The effect of the ferrocenyl group on the antimicrobial activity of β-lactamic antibiotics has been investigated and the reaction conditions determined for the preparation of 1,1'-ferrocenyldicarboxamidopenicillanic acid (13.6) and 1,1'-ferrocenyldicarboxamidocephalosporanic acids (13.7; R = CH_2OCOMe, $CH_2S.CN_2CS.Me$) [224]. The ferrocene analogues of the



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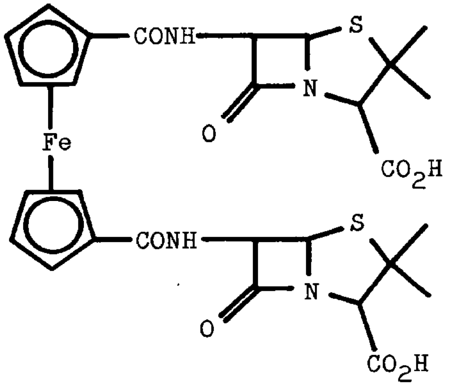

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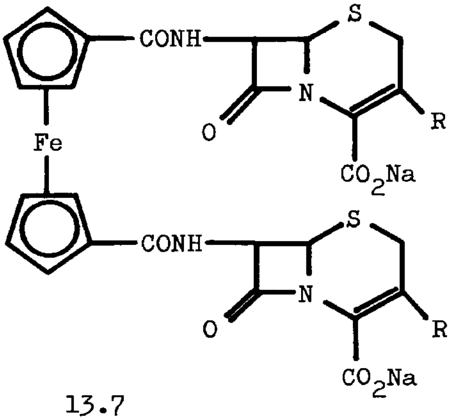
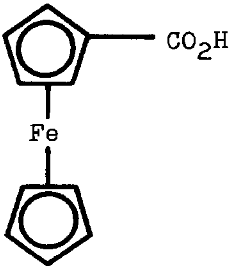


13.7

antiinflammatory agents tolmetin, fenbufen, flurbiprofen and fenclofenac have been prepared and tested for biological activity. The compounds exhibited little or no antiarthritic or platelet antiaggregatory activity [225].

Analogues of enkephalin, substance P(SP) and bradykinin containing ferrocenylalanine, cymantrenylalanine and tricarbonyl-(η-cyclobutadiene)ironalanine have been prepared by solid-phase synthesis. The properties of these molecules were compared with those of the corresponding phenyl containing derivatives [226].



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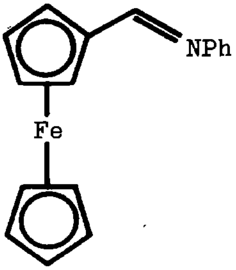

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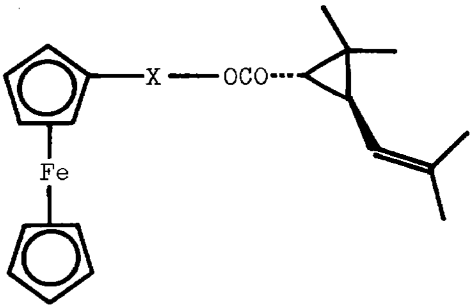
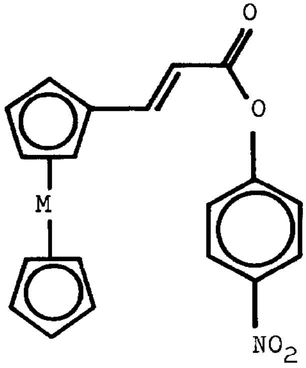


13.10

Biologically active peptides have been labelled with metallocenes by treatment of the peptide, bound to a solid phase substrate, with ferrocenecarboxylic acid (13.8) or cymantreneacetic acid followed by cleavage with HF-anisole [227]. Drug derivatives, such as p-succinamidophenobarbital, have been combined with ferrocenylmethylamine to form haptens which were in turn treated with bovine serum albumin and used to obtain antibodies for metalloimmunoassay [228].

Ferrocenylmethanol and α-ferrocenylethanol have been treated with eleven nitrogen containing heterocycles, triphenylphosphine, dialkylsulphides and the ferrocenylimine (13.9) in the presence of HBF_4 or $HClO_4$ to give a series of onium compounds. These compounds had bactericidal and fungicidal activity against Staphylococcus and Candida species [229]. A number of ferrocene derivatives containing alkyl, aryl, acyl and carboxyl substituents have been tested as fungicides. For example, benzoylferrocene controlled Sphaerotheca fullginea on cucumbers [230]. Ferrocenylpyrethroids (13.10; X = CH_2CH_2, $CH_2CH{=}CH$, $CH_2CH_2SCH_2$, o-$CH_2.C_6H_4SCHMe$) have been obtained by the esterification of (+)-trans-chrysanthemic and (±)-2,2-dichloro-1-methylcyclopropanecarboxylic acids with the appropriate ferrocenylalcohols. The products (13.10) showed insecticidal activity against houseflies [231].

The p-nitrophenyl ester of (E)-ruthenoceneacrylic acid (13.11; M = Ru) was shown to react in a complex to acylate β-cyclodextrin, but with a poorer binding and rate constant than



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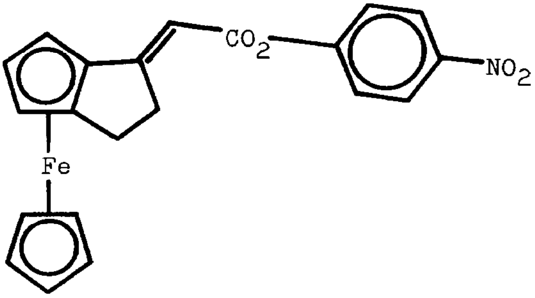

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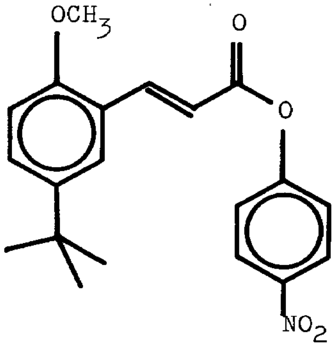

13.13

for the corresponding ferrocene compound (13.11; M = Fe). The cyclopentenyl ester (13.12) was prepared and found to be an excellent substrate for the cyclodextrin reaction [232]. The effect of pressure on rates of transacylation of the p-nitrophenylesters (13.11 and 13.13) in the presence of β-cyclodextrin was also investigated [233].

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