FERROCENE
ANNUAL SURVEY COVERING THE YEAR 1987*

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CONTENTS

1. REVIEWS

The chemistry of surface active nonionic ethoxylated ferrocenylalkanols and anionic ferrocenylalkanol sulphate salts have been the subject of a brief review [1]. The

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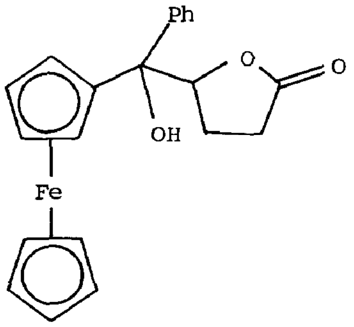
history, current status and pharmacology of non-platinum group antitumour metallocenes has been surveyed [2]. O'Connor and Casey have produced a review on ring-slippage chemistry of transition metal η-cyclopentadienyl and η-indenyl complexes. Very little ferrocene chemistry was discussed but the article is of interest to all in this field [3].

2. STRUCTURAL DETERMINATIONS

The crystal and molecular structure of 4-(ferrocenylhydroxyphenylmethyl)-4-butanolide (2.1) has been determined by X-ray crystallography. The hydroxyl hydrogen atom was directed towards the iron atom rather than towards the oxygen atoms of the lactone ring [4]. The crystal and molecular structure of O-(2-cyanoethyl)benzoylferrocene (2.2) has been determined by X-ray crystallography. The molecule (2.2) adopted a cis-configuration about the C-N double bond [5]. The crystal and molecular structure of the ferrocenylsulphonamido derivative (2.3) has been determined by X-ray analysis [6]. The crystal and molecular structure of the O-substituted ferrocenyloxime (2.4) has been determined. The ferrocenyl and OC_2H_4CN groups were linked to the C=N moiety with a cis-configuration [7]. The crystal and molecular structure of 1-ferrocenyl-1-(methylphenylcymantrenyl) silylethylene has been determined by X-ray crystallography [8].



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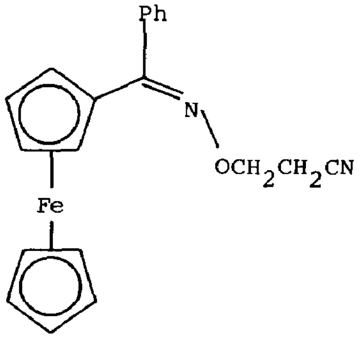

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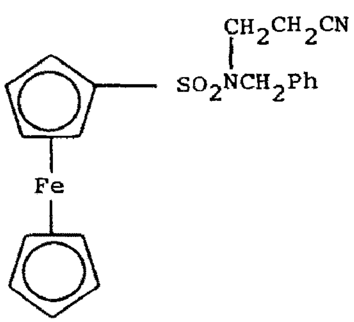

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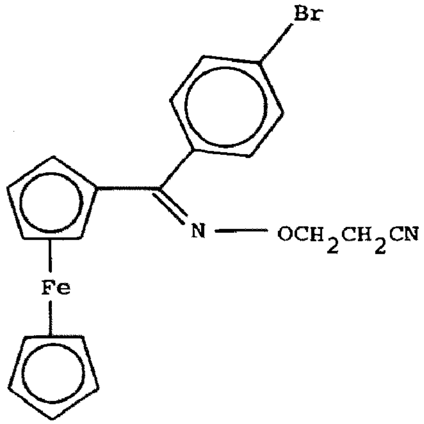

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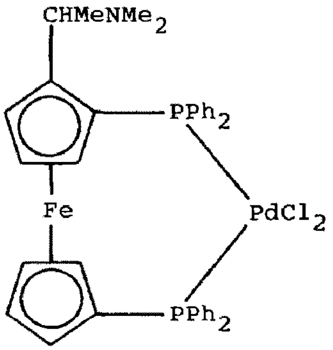
The crystal structure of trichloroacetic acid solvated ferrocenium trichloroacetate has been determined by X-ray analysis. The η-cyclopentadienyl rings exhibited rotational disorder. The anion was composed of two equivalent monodentate trichloroacetate anions bridged by a proton. It was concluded that the salt should be formulated as ferrocenium hydrogen bis(trichloroacetate) [9]. Octaphenylferrocene,



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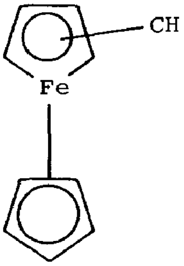
formed from iron (II) chloride and Li(C_5HPh_4), has been characterized by X-ray crystallography. Variable temperature ^{1}H NMR spectroscopy was used to demonstrate free rotation of the phenyl groups at 20°C with ordering of the same groups at low temperatures [10]. The crystal and molecular structure of the palladium chloride complex (2.5) of (S)-N,N-dimethyl-1-[(R)-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine has been determined by X-ray crystallography. The complex (2.5) was square planar with two cis-chlorine atoms and two phosphorus atoms bound to palladium. The aminoalkyl side chain was responsible for fixing the chiral conformation of the chelate complex [11].

3. THEORETICAL STUDIES

EHMO and ab initio calculations have been made with the use of an STO-3G basis set on the stability of an alternative ferracyclopentadiene structure (3.1) for ferrocene. The non-classical structure (3.1) was 6.0 eV higher in energy than the classical structure, this difference was reduced by half when a CH group in the cyclopentadienyl ring was replaced by BH^- [12].



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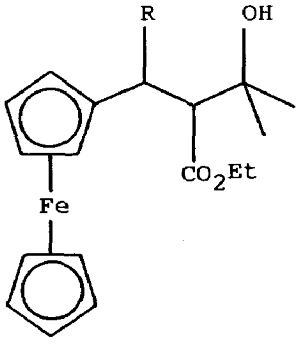
The electronic structure and bonding in metallocenes has been analyzed by the EHMO method. The effects of σ-, π- and δ-bonding on the stability of the compounds was discussed [13]. The coupled Hartree-Fock-perturbation theory-extended basis-CNDO method, extended for transition metal compounds, has been used to calculate the polarizability and second hyperpolarizability of ferrocene. The polarizability calculated in this way was close to the experimentally determined value [14]. The electronic structure of open-ring pentadienyl sandwich complexes of Ti, V, Cr and Fe has been the subject of a theoretical study using the EHMO method. Calculated conformation angles were found to be in agreement with experimental values [15].

A theoretical analysis of the electrocatalytic oxidation of NADH by the ferrocenecarboxylic acid-β-cyclodextrin complex has indicated that very small amounts of the complex were effective in the oxidation of NADH [16]. The geometrical configurations of ligands in a series of π-complexes, including sandwich compounds, have been calculated using a molecular mechanics method [17]. Decamethylferrocenium tetracyanoethanide has been characterized with a ferromagnetic ground state by a study of the temperature and magnetic field dependence of the magnetization and susceptibility of a single crystal. A general Hubbard model was used to describe the ferromagnetic exchange interactions in the species [18].

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

Moessbauer spectroscopy has been used to examine the lattice dynamics in mono- and di-substituted acetyl-, ethyl- and carboxy-ferrocenes. Some tin complexes of acetylferrocenes were also examined. An harmonic oscillation model was used to discuss the lattice vibrations in acetyl- and carboxy-ferrocenes and in the tin complexes [19]. Moessbauer spectroscopic studies have been carried out on molecular rotation and lattice dynamics of cyclodextrin clathrates of ferrocene, methyl-, ethyl- and formyl-ferrocene [20]. Bis(methylbenzyl)bi-



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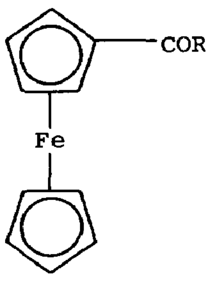

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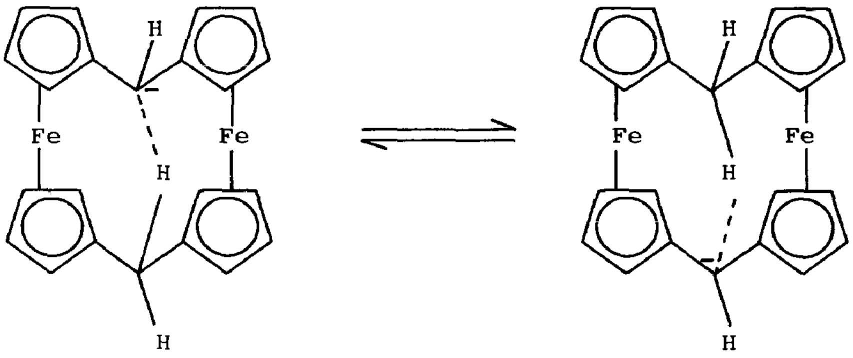
ferrocenes have been prepared, converted to the corresponding monocations and examined by Moessbauer spectroscopy for trapped-valence and averaged valence behaviour [21]. Moessbauer spectroscopy has been used to investigate complex formation between ferrocenophanes and biferrocene with tin(IV) chloride and bromide. Iron-tin bonding was indicated in the [2]ferrocenophane : 1.5 tin(IV) halide complexes while the [3]ferrocenophane and biferrocene adducts were regarded as ferrocenium salts [22].

Fourier transform ion cyclotron resonance has been used to investigate the thermal electron transfer reactions in the gas phase for a series of metallocenes and metallocenium cations [23]. Mass spectrometry has been used to investigate electron-transfer kinetics in ferrocene, ruthenocene and cobaltocene. The Franck-Condon barriers associated with self exchange were predicted by proposals for the inner-sphere reorganisation energy of the electron-transfer processes [24]. The infrared absorptions for the hydroxyl groups in the alcohols (4.1; R = Ph, ferrocenyl) have been interpreted in terms of C=O----HO-, -OH-----π-aromatic and -OH------π-C_5H_5 hydrogen bonding. The existence of iron-----hydroxyl type hydrogen bonding was not required to explain the spectra [25]. The application of micro-Raman spectroscopy to the examination of organometallic compounds has been investigated. The spectra of several ferrocene compounds for example (4.2; R = Me, Ph, CH_2Ph) and some (η^6-arene)$Cr(CO)_3$ compounds were recorded. This technique required much lower laser powers than normally used in Raman spectroscopy. It was concluded that the spectra of compounds considered to be unstable to long periods of laser irradiation could be recorded successfully [26].

Nakai and co-workers have carried out a ^{13}C NMR study of the dynamic structure of the thiourea-ferrocene inclusion compound [27]. Variable temperature ^1H NMR spectroscopy has been used to study the carbanion (4.3) prepared from [1.1]ferrocenophane and n-butyllithium in [$^2H_8$]tetrahydrofuran. The results indicated that the carbanion was asymmetrically hydrogen bonded and that it underwent degenerate rearrangement to the alternative structure (4.4) [28]. The ^{13}C spectra of a series of 1-aryl-2-ferrocenylethylenes have been recorded and interpreted. The olefin group reduced the transfer of



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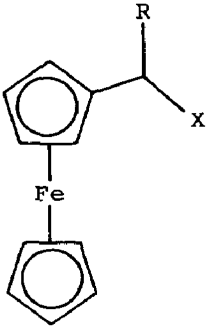
substituent effects from the aryl moiety to the ferrocenyl group. The effect of these substituents on the β-position of the CH=CH bridge was greater than in the corresponding stilbenes [29]. Proton spin-lattice relaxation has been used to study the energy barriers to molecular rotation in the low-temperature phase of ferrocenecarbaldehyde. The principal relaxation was assigned to rotation of the unsubstituted cyclopentadienyl ring. The activation energy was determined as 15.3 kJ mol^{-1} [30]. Optical resolution of the racemic ferrocene derivatives (4.5; R = alkyl, X = OH, alkoxy, $OCOCH_3$, NH_2, NMe_2) has been achieved by liquid chromatography



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on polyamide packings using cyclodextrin as the mobile phase [31].

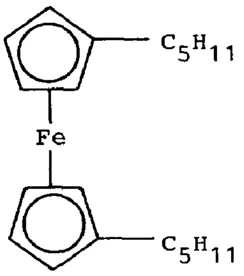
Thirty-two substituted ferrocenes have been separated by reversed phase HPLC with octadecylsilane as the stationary phase and aqueous methanol as the mobile phase [32]. Di-, hexa-, octa- and deca-methylferrocene and diethylferrocene gave hydrogen bonded complexes with perfluoro-t-butanol in liquid xenon. The enthalpy of complex formation was determined [33]. The heat capacities of the inclusion compound $(\eta\text{-}C_5D_5)_2Fe.3(NH_2)_2CS$ and the salts $[(\eta\text{-}C_5H_5)_2Fe]^+PF_6^-$ and $[(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Fe]^+PF_6^-$ have been measured by adiabatic calorimetery. The inclusion compound exhibited five phase transitions and those at 145.8 and 160.6 K were responsible for the onset of reorientational order-disorder of the molecular axis of $(\eta\text{-}C_5D_5)_2Fe$ in the clathrate cavity. Ferrocenium hexafluorophosphate had three phase transitions. The higher-temperature transition was assigned to the reorientational order-disorder mechanism of the molecular axis of the ferrocenium ion in a pseudo-cavity formed by the PF_6^- anions [34]. The solvation of ferrocene has been studied in aqueous-organic media. Ferrocene solubility in mixed solvents and solvent activity coefficients have been used to derive the solvation excess of the organic component in the solvation sphere of ferrocene. The solvation radius of ferrocene was found to be similar to that obtained from crystallographic results [35].

5. ELECTROCHEMISTRY AND PHOTOSENSITIVE ELECTRODES

(i) General

The electrochemical behaviour of ferrocene in methyl cyanide has been investigated. The electrode became rapidly covered with a passive film of an insoluble ferrocene complex salt which hindered the electron transfer process [36]. The oxidation of ferrocene in acetonitrile has been studied using very small electrodes, 20 to 500 Å wide and 0.5 to 1 cm long. Transport equations were found to break down as the electrode width approached the molecular dimensions of the redox active species [37]. The reversible one-electron oxidation of ferrocene in methyl cyanide has been used in an investigation into the application of transient electrochemical techniques to inlaid ultra-microelectrodes [38]. The oxidation of ferrocene in toluene-methyl cyanide has been used in a study of voltammetric measurements made with microelectrodes in low-conductivity systems [39]. The electrochemical oxidation of ferrocene on platinum electrodes has been carried out in ethanol, dimethylformamide, propylene carbonate and aqueous solutions of these solvents using sodium perchlorate as the supporting elecrolyte. The ferrocenium ion decomposed slowly in these solutions [40].

The oxidation of ferrocene to the ferrocenium ion in aqueous media has been studied by voltammetry and chronocoulometry in order to determine the conditions under which the reaction could be used as a standard voltammetric reference process. It was important to ensure that the effects of adsorption were minimal [41]. An optically transparent thin-layer electrochemical cell has been used to investigate infrared spectral changes during the electrochemical oxidation of ferrocene [42]. The electrochemical oxidation of ferrocene was studied in an investigation of polythiophene and polybithiophene coated electrodes [43].



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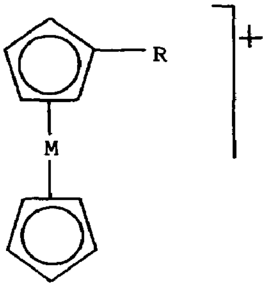

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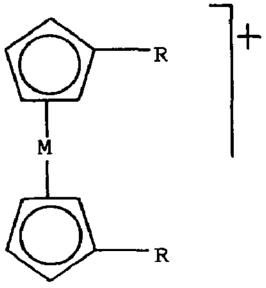

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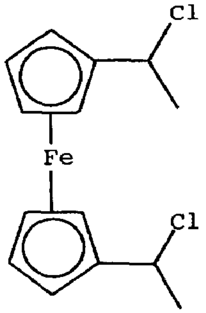
The electrochemistry of ferrocene at a platinum disc electrode has been examined in near-critical carbon dioxide containing water. A well defined voltammetric wave was obtained for ferrocene [44]. The electrochemical oxidation of ferrocene has been compared with that of tetrathiafulvalene in aqueous micelles and dodecane-in-water emulsions. The diffusion processes of these molecules were compared [45]. Ferrocene in dimethylsulphoxide and saturated aqueous potassium hexacyanoferrate(II) stabilized antimony(III) sulphide photoelectrodes in photovoltaic cells. The behaviour of these cells on irradiation with light was investigated [46]. The electrochemical oxidation of ferrocenyl substituted 1,4-dihydropyridines has been examined at a rotating ring-disc electrode. Two stages were observed corresponding to formation of the ferrocenium ion and then deprotonation of the dihydropyridine ring [47].

The transfer of the ferrocenium ion across water-organic solvent interfaces has been studied by cyclic voltammetry. The standard Gibbs energy of ion transfer was calculated from the voltammetric data [48]. Electrode systems based on amyl- and 1,1′-diamyl-ferrocene (5.1) have been investigated [49]. Modified tin(IV) oxide electrodes have been prepared using zeolite Y which have been ion-exchanged with the complexes $[M(bipyridyl)_3]^{2+}$, where M = Ru or Os, and a metallocene cation (5.2; M = Co, Fe; R = H, Me, NH_2, CO_2Me, CH_2NMe_2 or 5.3; M = Co, Fe; R = H, Me, NH_2,CO_2Me, CH_2NMe_2). The electrodes were examined by cyclic voltammetry. The results indicated that rapid electron transfer from the electrode occurred almost entirely via the $[M(dipyridyl)_3]^{2+}$ complex [50].

A platinum electrode has been modified by the adsorption of an electroactive surfactant, (ferrocenylmethyl)dimethyloctadecylammonium hexafluorophosphate, as a monolayer. The electrochemical characteristics of the film were dependent on the nature of the electrolyte from which it was deposited [51]. The output of a cadmium sulphide/poly(vinylferrocene)/gold solid state cell was dependent on the concentration of oxidized sites in the polymer film. When illuminated the polymer layer was partly oxidized and the photocurrent increased linearly with the increase in light intensity [52]. The reduction of ferrocene has been included in a study of electrochemical kinetics at microelectrodes in media of low ionic strength. A small increase in diffusion coefficient was observed with a decrease in ionic strength and the amplitude of the current was independent of the ionic strength [53].

(ii) Polymer-film coated electrodes

The redox thermodynamics of thin films of plasma polymerized vinylferrocene deposited on different substrates have been investigated via controlled potential coulometry [54]. The electrochemical properties of thin films (<200nm) of linear polyvinylferrocene (LPVF) deposited on polished electrodes have been studied in Bu_4NClO_4-MeCN solutions. The redox behaviour was quite complex. This behaviour was attributed to large potential-dependent changes in film ion concentration and to the high degree of structural freedom due to the lack of cross-linking in the LPVF film [55]. Impedance plots have been obtained for poly(vinylferrocene) films coated on platinum electrodes. Three regions were observed corresponding to kinetic control, diffusion control and charge saturation as the frequency decreased. Diffusional charge transport and exchange current density were dependent on the oxidation state of the polymer [56]. The electrochemistry of glassy carbon electrodes coated with argon plasma polymerized vinylferrocene has been investigated. The effects of etching the electrodes with argon and oxygen plasmas prior to deposition of the polymer film were investigated. The presence of vinylferrocene monomer in the polymer films was detected [57].



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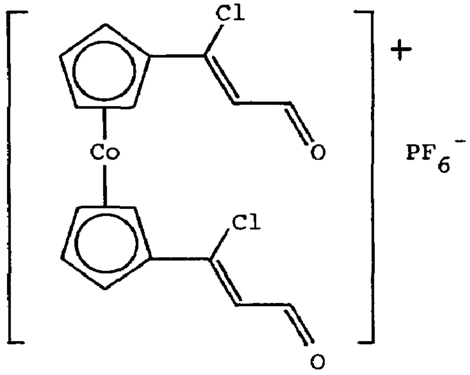

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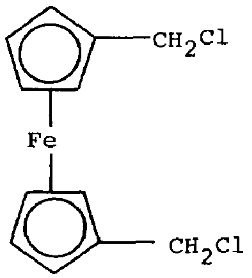
The quartz crystal microbalance technique has been used to study the ion and solvent populations in thin films of poly(vinylferrocene) on electrodes as a function of redox state in different supporting electrolytes. In electrolytes containing the perchlorate and hexa-fluorophosphate anions the oxidation of the polymer film occurred with no change in solvent content in the film. With chloride containing electrolytes multiple peaks were observed in the voltammetry of the polymer film as a result of the electrochemically induced dissolution or delamination of the film [58]. An investigation has been carried out on electron transfer processes at open circuit polyvinylferrocene films using rotating disc electrodes. The bimolecular rate constant was determined for the single electron transfer process $[\text{polyvinylferrocene}]^+/[\text{Fe(CN)}_6]^{4-}$ [59]. Durst and co-workers have developed a cross-linked poly(vinylferrocene) modified reference electrode suitable for use in nonaqueous solvents. The cross-linking agent used was triallyltrimellitate and the useful lifetime of the electrode was 24h in acetonitrile and methanol but less in solvents where ferrocene was highly soluble [60]. The sorption of calcium cations and sulphate anions into a poly(vinylferrocene) film on an electrode surface has been studied by a radiotracer technique [61].

Liquid crystal doped films of polyvinylferrocene have been prepared. The incorporation of 4-pentyl-4'-cyano-biphenyl in polyvinylferrocene substantially changed the rate of charge transport through the polymer film. The temperature dependence of this effect was large above and below the nematic/isotropic transition temperature (36°C) of 4-pentyl-4'-cyano-biphenyl [62]. The potential use of polyvinylferrocene as an electrode-active material in rechargeable batteries has been investigated. The charge-discharge curves for the polymer electrodes were quite flat with high coulombic efficiencies. The presence of graphite



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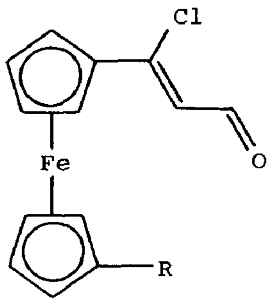

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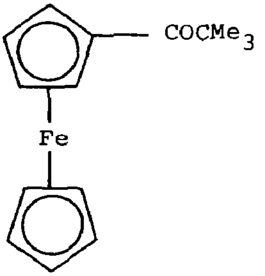
powder in the polyvinylferrocene electrodes increased the discharge rate [63]. Nishihara and co-workers have developed a chemical diode that consisted of ferrocene and cobaltocenium polymer electrode films and which functioned in the gas phase. In this device a polymer film formed from the chloroethylferrocene (5.4) and a film formed by electroreduction of the salt (5.5) were used [64].

Charge-transfer kinetics for the reduction of organic redox species have been investigated at glassy carbon electrodes, coated with films of electropolymerized 1,1'-bis(chloromethyl)-ferrocene, via rotating disc voltammetry. It was concluded that charge-transfer complex formation between the organic electron acceptor molecules in solution and the ferrocene sites in the polymer film was the rate-determining step in the electron transfer process [65]. The chloroferrocenes (5.6 and 5.7; R = H, CCl=CHCHO) have been reduced on glassy-carbon and indium tin oxide coated glass electrodes to give stable electroactive polymer films. The films were shown by cyclic voltammetry to control the reversibility of redox reactions of nitrobenzene and benzoquinones at the electrodes [66].

6. PREPARATION OF FERROCENE

Flash vacuum pyrolysis (FVP) of the dinuclear complex $(\eta\text{-}C_5H_5)_2Fe_2(CO)_4$ at 500° produced the tetranuclear complex $(\eta\text{-}C_5H_5)_4Fe_4(\mu_3\text{-}CO)_4$ (16.7%) and ferrocene (65.3%). At higher temperatures ferrocene was the only product. FVP of pivaloylferrocene (6.1) at 675° and 700° produced isobutene. The minimum temperature for the isobutene product was 675° and the temperature range over which it was a significant product was only 40° [67]. The solubility of ferrocene in protic and aprotic solvents and the continuous electrosynthesis of ferrocene have been the subjects of a brief review [68]. Cyclopentadienyl anion generation during the electrochemical reduction of molecular oxygen in dimethyl sulphoxide has been investigated. As part of this study the synthesis of ferrocene was carried out at a controlled potential [69]. The 1,1'-disubstitued ferrocenes (6.2; X = C, Si, Ge, Sn, Pb) have been prepared from the appropriate cyclopentadienide ions and iron(II) chloride. The products (6.2) were characterized by ^{1}H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb NMR spectroscopy and the electronegativity



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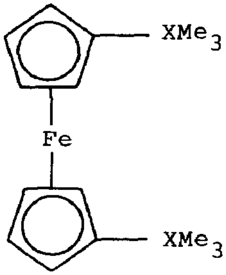

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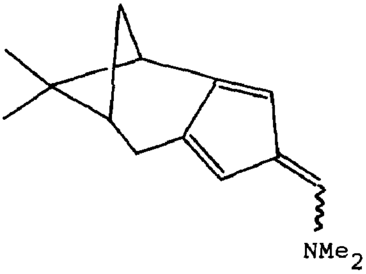

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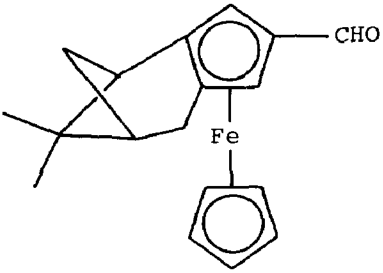
of the element X was correlated with chemical shift and coupling constant [70].

Ferrocenes have been formed from the homochiral dimethyltricyclodecadiene (6.3) and its derivatives. Thus, the isomeric ferrocenes (6.4 and 6.5) were obtained by ligand exchange with the (η-1,4-dimethylbenzene)(η-cyclopentadienyl)-iron cation [71]. Katz and Sudhakar have reported the preparation of some helicenes, for example, the siloxane (6.6), which were suitable for the preparation of helical metallocenes [72]. The ferrocene analogue (6.7) was obtained by thermal isomerization of (η^5-cyclopentadienyl)(η^6-fluorenyl)iron [73].



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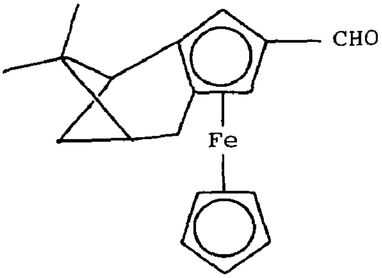

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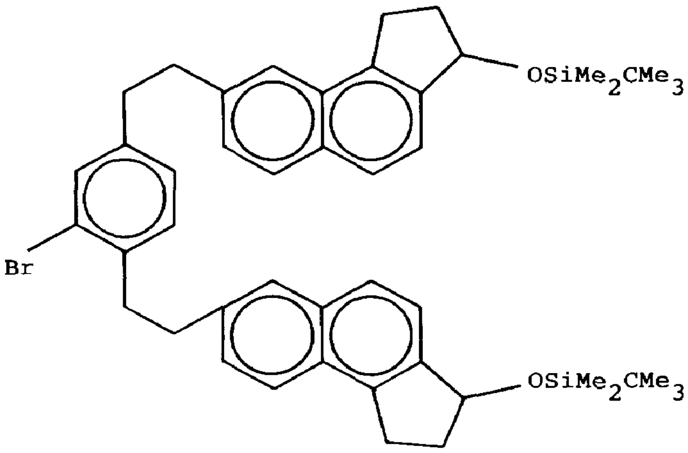

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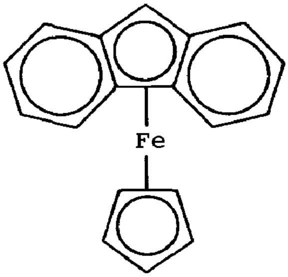

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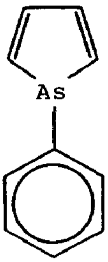

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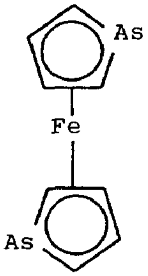
Condensation of the phenylarsole (6.8) with iron(II) chloride in the presence of lithium afforded diarsaferrocene (6.9). Deuteration and acetylation of diarsaferrocene were investigated [74]. The pentaphosphaferrocene (6.10) has been prepared by heating $[(\eta\text{-}C_5Me_5)Fe(CO)_2]$ with phosphorus in xylene [75].

7. REACTIONS OF FERROCENE

Ferrocene has been treated with halogen substituted benzoyl chlorides to give the corresponding halogenobenzoylferrocenes



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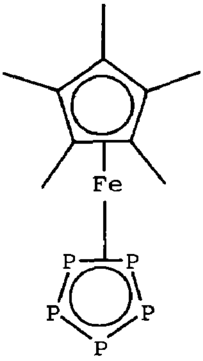
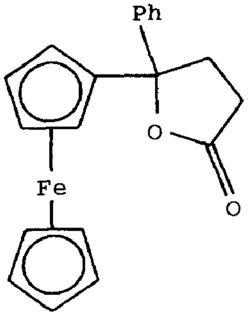


6.10

[76]. Ferrocene formed complexes with the bromopropanes Br_3CCH_2CHBrR, where R = CN, CF_3, CO_2H, CO_2Me, Me, $SiMe_3$. The first four substituents were electron withdrawing and caused a bathochromic shift of the UV charge-transfer. The last two substituents caused the opposite effect [77]. The



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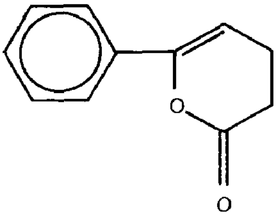

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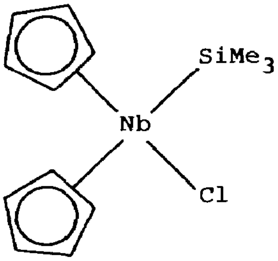
oxidation of ferrocene in chloroform and hydrochloric acid by selenious acid has been used as the basis of a method for the spectrophotometric determination of selenium [78]. Friedel--Crafts alkylation of ferrocene with the lactone 4-phenyl-4-(3-butenolide) afforded 4-ferrocenyl-4-phenyl-4-butanolide (7.1) which was unstable in air. When the same reaction was carried out with the lactone (7.2) a complicated mixture of products was obtained. In this reaction the formation of an intermediate β-ferrocenylcarbenium ion was suggested [79]. Ferrocene, ruthenocene and cymantrene have been acylated with the acid chlorides $PhCO(CH_2)_nCOCl$. When n = 3-8 unsymmetrical substitued diketones were isolated in the reactions with ferrocene [80]. The kinetics of the reversible oxidation and oxidative degradation of ferrocene by molecular oxygen have been investigated. The ferrocene was dissolved in heptane and broguht into contact with aqueous 0.1M HCl-1.0M KCl containing dissolved oxygen. Ferrocenium ions were formed reversibly and iron ions were formed irreversibly [81].

8. FERROCENIUM SALTS AND MIXED-VALENCE SALTS

Photocurrent spectra of $GaAs/Al_{0.38}Ga_{0.62}As$ lattice--matched superlattice electrodes were recorded in photoelectrochemical cells that contained nonaqueous electrolytes. The spectra were compared with those of the ferrocenium and cobtaltocenium ions [82]. The ferrocenium ion has been used to oxidize η^2-acetaldehyde complexes of molybdenum [83]. Oxidation of the niobium compound (8.1) with ferrocenium hexafluorophosphate produced a complex mixture of products [84]. The ferrocenium ion has been used as an oxidizing agent for $(\eta\text{-}C_5Me_5)Fe(CO)Me(Ph_2PCH_2CH_2PPh_2)$ and $(\eta\text{-}C_5Me_5)FeMe(PMe_3)_2$



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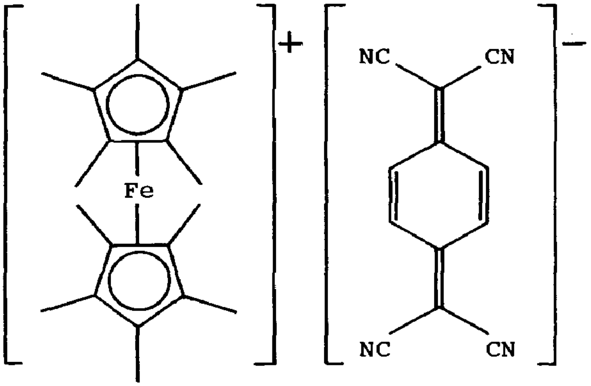
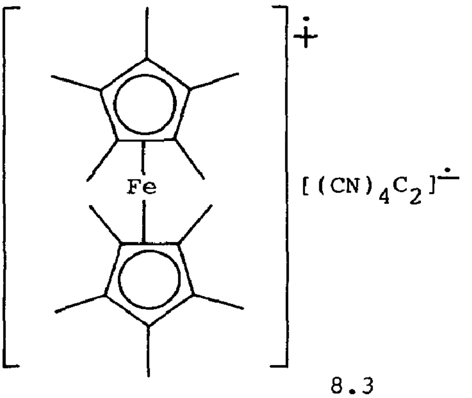


8.2

which were converted to the corresponding mono-cations. The reactions were part of a study of stable 17-electron iron(III)-methyl complexes [85]. Ferrocenium hexafluorophosphate in the presence of triphenylphosphine has been used as an oxidizing agent for (η-alkoxysilylcyclopentadienyl)iron complexes [86].

The oxidation of ferrocene in zeolite cavities to the ferrocenium cation has been studied by resonance Raman spectroscopy. The size and position of co-cations within the cavities were important in determining the extent of oxidation [87]. Adsorption of t-butylferrocene on to the surface of manganese dioxide led to formation of the corresponding ferrocenium ion while adsorption of acetylferrocene was followed by degradation [88]. Stop flow techniques have been used to investigate the kinetics of ferrocenium triiodide formation from ferrocene and iodine in benzene. The reaction was first order in ferrocene, second order in iodine and the Arrhenius activation energy was 10.7 kJmol^{-1}. When substituted ferrocenes were used, electron donating substituents increased the rate of reaction whilst electron withdrawing substituents retarded it [89].



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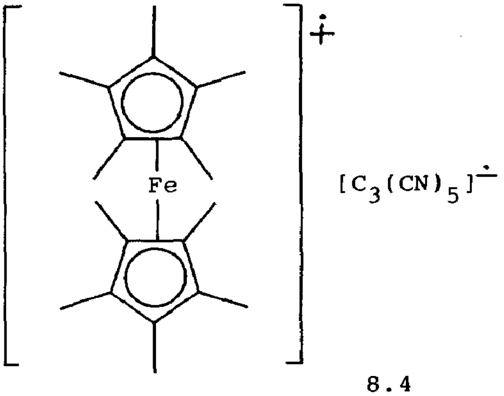


8.4

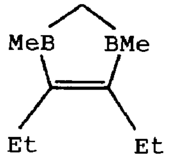
The reaction between decamethylferrocene (DMFE) and 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) has been investigated in detail. Three major products were characterized: a 1-D metamagnetic salt [DMFE]$^+$[TCNQ]$^{\dot{-}}$ (8.2), a paramagnetic dimeric salt [DMFE$^+$]$_2$[TCNQ$^-$]$_2$ and a conducting salt [DMFE]$^+$[TCNQ]$_2^-$. The crystal and molecular structures of the two 1:1 complexes were determined by X-ray crystallography. The metamagnetic salt (8.2) consisted of one-dimensional chains of alternating cations and anions: DMFE. TCNQ. DMFE. TCNQ···· . The paramagnetic dimeric salt contained discrete stacks of DMFE, TCNQ, TCNQ, DMFE dimer units, there was no one-dimensional stacking [90]. The reaction of decamethylferrocene with tetracyanoethylene in methyl cyanide produced the salts (8.3 and 8.4). The structure of these salts were obtained by X-ray analysis and then magnetic properties were measured via the Faraday technique. Both the salts were ferromagnetic and contained low-spin iron(III) [91].

The reaction of ferrocene with 7,7,8,8-tetracyanoperfluoro-p-quinodimethane ($TCNQF_4$) produced the ferrocenium salts $[Fe(\eta\text{-}C_5H_5)_2][TCNQF_4]$ and $[Fe(\eta\text{-}C_5H_5)_2]_2[TCNQF_3]_3$. The structures of these salts were investigated by X-ray analysis and ^{57}Fe Moessbauer spectroscopy [92]. Photoelectron spectroscopy and x-ray absorption near edge structure have been used to investigate the iron valence states in mixed-valence binuclear ferrocenes. Differences were observed in $1s \longrightarrow 3d$ transitions between trapped--valence and averaged-valence monocations of binuclear ferrocenes [93].

9. FERROCENE CHEMISTRY

(i) Derivatives containing other metals (metalloids)

The diborole (9.1) combined with tricarbonylbis(cis-cyclooctene)iron to form the paramagnetic tetradecker ferrocene analogue (9.2) which was characterized by X-ray crystallography [94]. The 1,1'-dilithioferrocene-TMEDA complex combines with sulphur or selenium in a mixture of THF and toluene to give the intermediate (9.3; X = S, Se). This species combined with electrophiles to give the corresponding heterodichalconated ferrocenes. Thus acid gave the dithiol and diselenol (9.4; X = S, Se) while sulphur or selenium gave the ferrocenophane (9.5; X = Y = S, Se), diiodomethane also gave a ferrocenophanes (9.6; X = S, Se), benzoyl chloride and benzyl chloride gave the benzoyl (9.7; X = S, Se) and benzyl (9.8; X = S, Se) complexes respectively [95]. Ferrocenyllithium combined with tellurium to give the intermediate (9.9; R = Li) which was oxidized in air to give diferrocenylditelluride (9.10). This compound (9.10) was treated with organolithium reagents, RLi, to form the ferrocenyltellurides (9.9; R = ferrocenyl, n-Bu, o-, p-anisyl. Bis(ferrocenyltelluro)methane was also prepared (9.11) [96].



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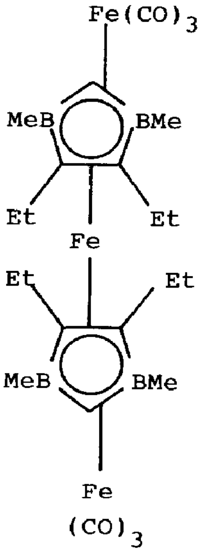

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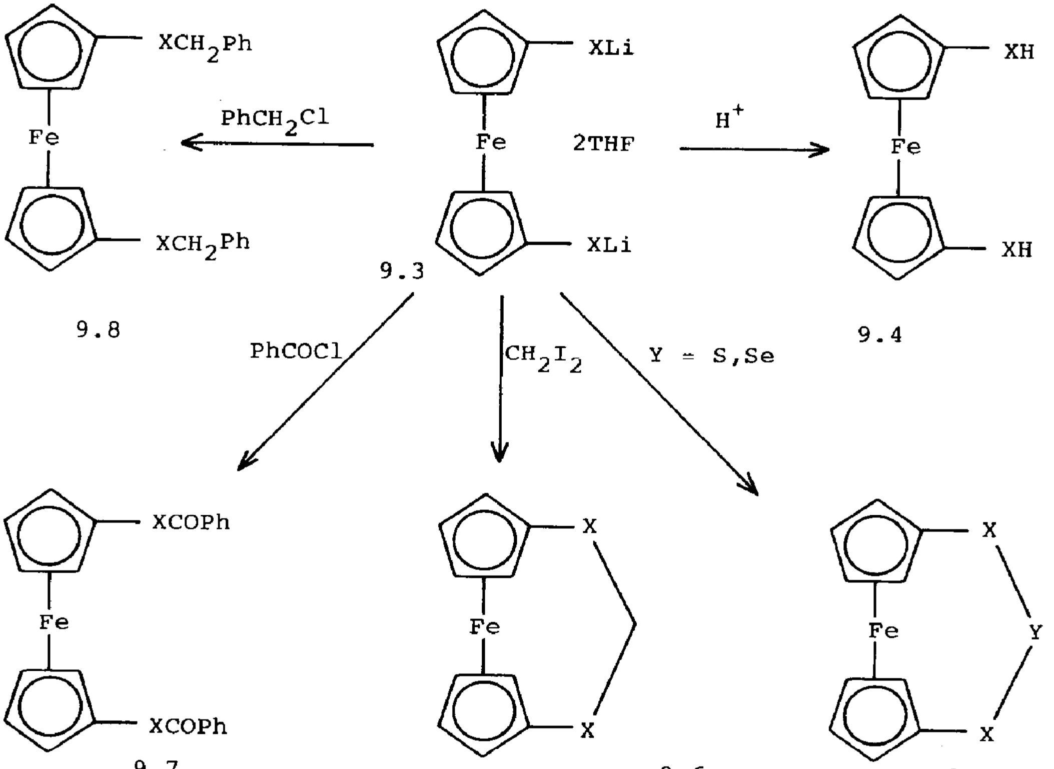

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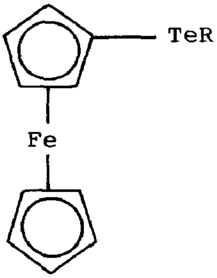
9.5

Phenol formed complexes by hydrogen bonding with ferrocenyldiphenylphosphine, diferrocenylphenylphosphine and triferrocenylphosphine. The thermodynamic properties of these complexes have been evaluated, ΔH values in the range -4.8 to -5.9 kcal mol^{-1} were obtained. Values for the corresponding phosphine oxide complexes were in the range -7.8 to 9.8 kcal mol^{-1}. An increase in the number of ferrocenyl groups caused an increase in the strength of the phenol-phosphine hydrogen bond [97]. Reaction of the diphosphonium iodide (9.12) with tetracyanoquinodimethane (TCNQ) produced the corresponding salt (9.13) which was a conductor of electricity [98]. A series of achiral and chiral ferrocenylphosphines has been prepared and their ability to form complexes with transition metals has been investigated. The catalytic properties of the rhodium complexes for the hydrogenation of a range of olefins was examined [99]. The synthesis of 1-ferrocenylphospholes has been studied, thus the phosphole (9.14) was attacked by ferrocene to give the 2-ferrocenylphospholene (9.15). A similar reaction with the bromophospholene (9.16) gave, after oxidation of phosphorus with CS_2 or H_2O/CH_2Cl_2, the 1-ferrocenylphospholene (9.17; X = S, O) respectively. Thermolysis of 1-cyclopentadienylphosphole tetracarbonyliron complexes gave phosphaferrocenes, thus the complex (9.18) was heated in xylene to give the phosphaferrocenes (9.19 and 9.20) [100].



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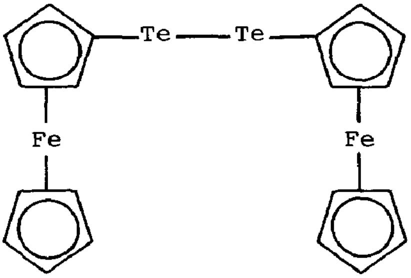

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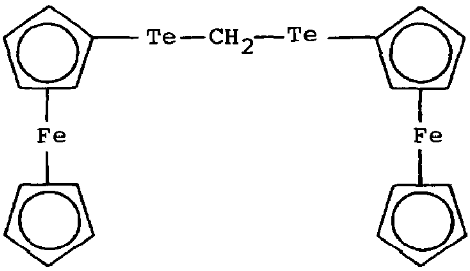

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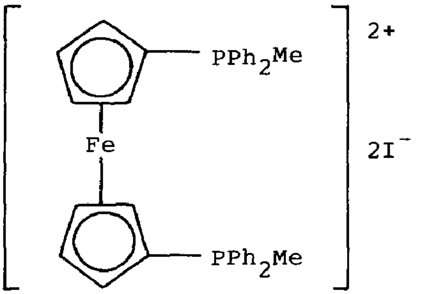

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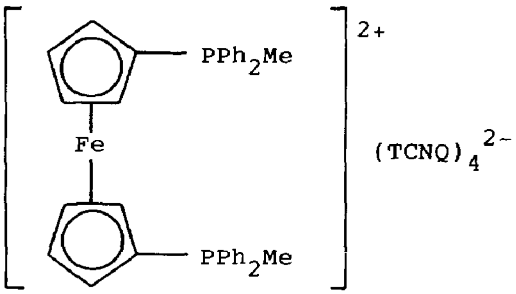

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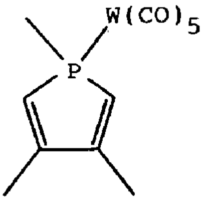
Substituted (η-benzene)(η-cyclopentadienyl)iron cations combined with phospholyl anions to give the substituted phosphaferrocenes (9.21; R^1 = H, 3-Me, 3,4-Me_2, 2,3,4,5-Ph_4; R^2= Me, COMe, $COCMe_3$, COPh, CO_2H, CH_2NMe_2) [101]. Freidel-Crafts acylation of 3,3',4,4'-tetramethyldiphosphaferrocene has produced the acetyl (9.22; R^1 = Ac, R^2 = H, Ac) and the benzoyl (9.22; R^1 = PhCO, R^2 = H, PhCO) derivatives. Diastereomers of the diacylated compounds were observed and separated. Protonation in CF_3CO_2H or 70% H_2SO_4 was investigated by NMR and Moessbauer spectroscopy. The acyl groups were protonated to give mono- and di-protonated species [102]. Protonation of diphosphaferrocenes in trifluoromethanesulphonic acid has been studied by ^{57}Fe Moessbauer spectroscopy and by ^{1}H and ^{31}P NMR spectroscopy. Iron-protonation was preferred over phosphorus-protonation in, for example, 2,2',5,5'-tetraphenyldiphosphaferrocene (9.20). The iron-bonded proton underwent fast exchange and was often difficult to observe by ^{1}H NMR spectroscopy [103]. Complexes formed by the diphosphaferrocenes (9.23 and 9.20) have been investigated. Adduct formation occurred on the addition of boron trifluoride etherate to the diphosphaferrocene (9.23) and ^{31}P NMR spectroscopy indicated that complex formation occurred at phosphorus. The addition of silver(I) and copper(I) salts to the complexes (9.23 and 9.20) resulted in the formation of stable adducts which were isolated. Moessbauer spectroscopy indicated that in these adducts bonding occurred at the iron atom [104].



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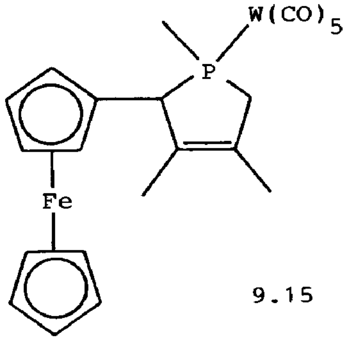

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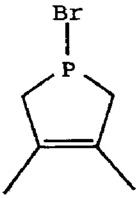

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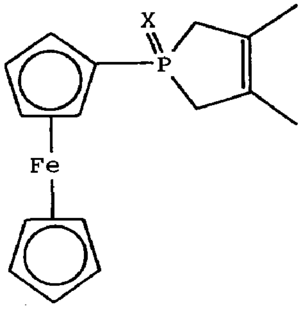

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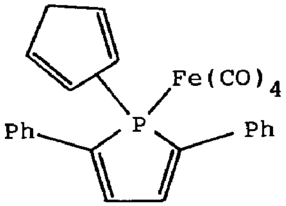

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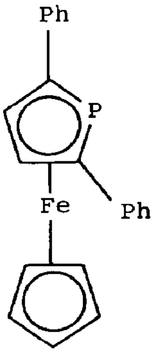

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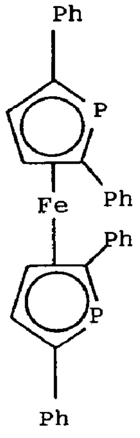

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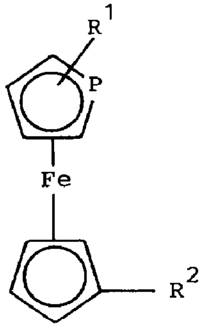

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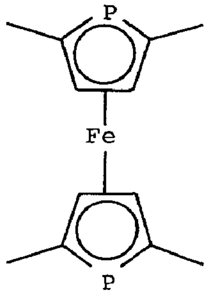

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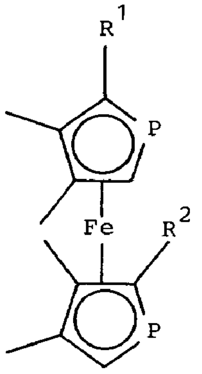

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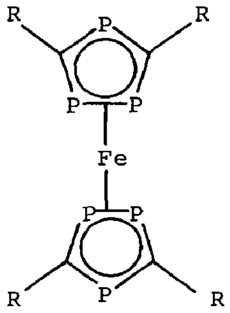
Iron(II) chloride combined withthe salt [Li(1,2-dimethoxyethane)$_3$]$^+$ [C$_2$t-Bu$_2$P$_3$]$^-$ to give the hexaphosphorus analogue of ferrocene (9.24; R = t-Bu) together with a small proportion of the pentaphosphorus species (9.25; R = t-Bu). X-ray crystallography was used to confirm the eclipsed sandwich structure for each of these compounds. The two polyphosphorus compounds (9.24 and 9.25) were green, air stable sublimable solids [105]. Phosphaferrocenes in CF_3SO_3H have been shown to undergo protonation at iron by ^1H NMR and Moessbauer spectroscopy [106]. An acid-base reaction has been used to achieve the intercalation of dimethylaminomethylferrocene into α-$Sn(HPO_4)_2.H_2O$. Ferrocene was intercalated with α-$VOPO_4.2H_2O$ by a redox topotactic process



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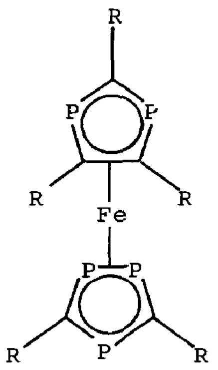

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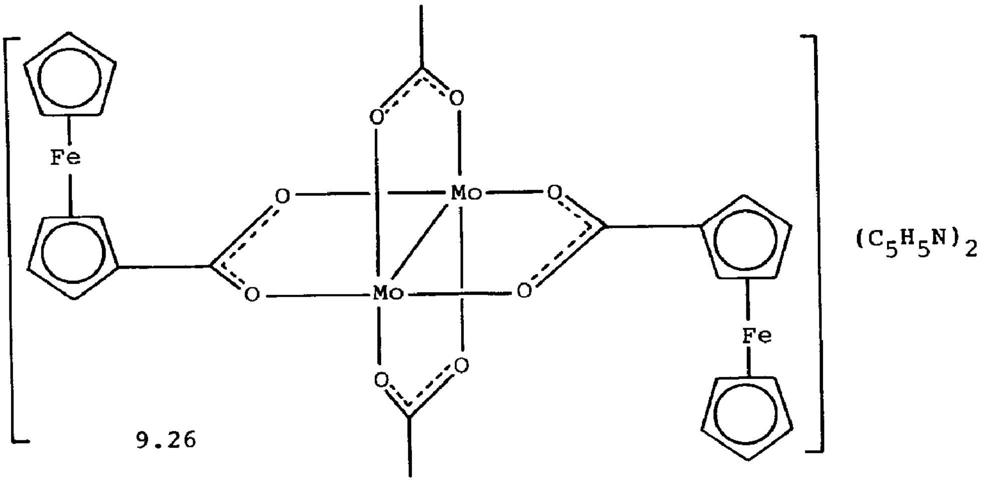

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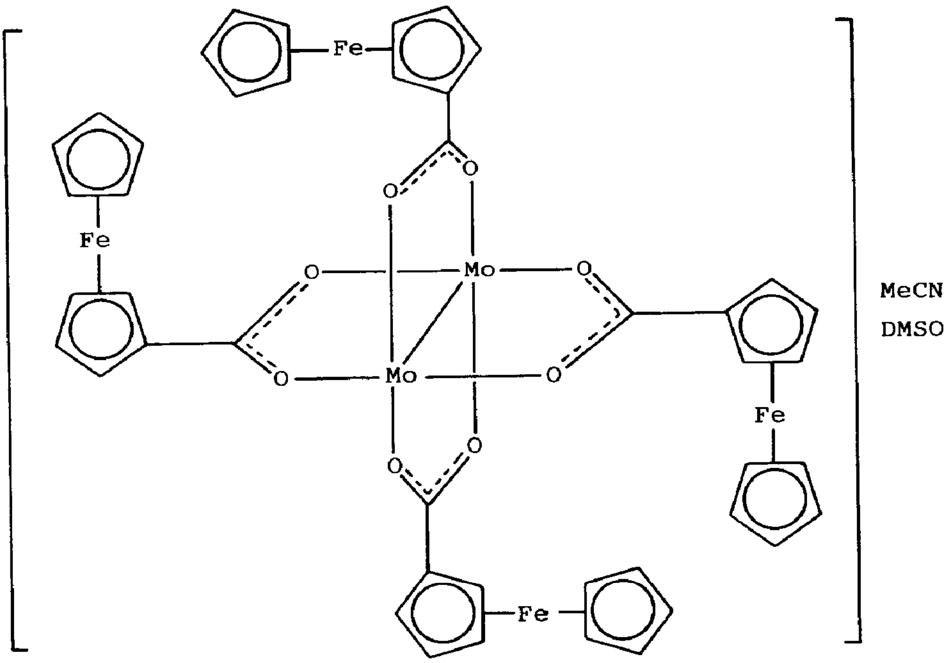
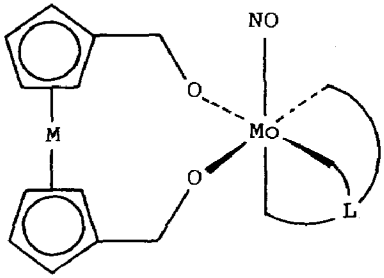


9.27

[107]. The complexes (9.26 and 9.27) have been prepared by ligand exchange on $Mo_2(O_2CCH_3)_4$ by ferrocenecarboxylic acid. The structures of the complexes were determined by X-ray analysis. Complex (9.26) was an intermediate in the complete carboxylate exchange reaction. The complexes (9.26 and 9.27) were investigated electrochemically [108].

1,1'-Bis(hydroxymethyl)-ferrocene and -ruthenocene have been treated with $[Mo(NO)LI_2]$; L = (hydro)tris(3,5-dimethylpyrazolyl)-borate, in the presence of triethylamine to give the corresponding molybdenum complexes (9.28; M = Fe, Ru). The trimetallic complex (9.29) was prepared by the reaction of ferrocenylmethanol with $[Mo(NO)LI_2]$ in the presence of triethylamine. The electrochemical properties of the complexes (9.28 and 9.29) were investigated by cyclic voltammetry [109]. Ferrocenyllithium combined with $(\eta\text{-}C_5H_5)W(NO)_2Cl$ to give the ferrocenyltungsten complex (9.30; X = NO) which was characterized by X-ray crystallography. Oxidation by air in dichloromethane gave the ferrocenyldioxotungsten complex (9.30; X = O) [110]. Decamethyl-ferrocene, -ruthenocene and -osmocene have been combined with the (η-benzene)(η-cyclopentadienyl)iron cation to form 30-electron triple-decker sandwich complexes [111]. Ferrocene derivatives of tricobalt-carbon cluster complexes have



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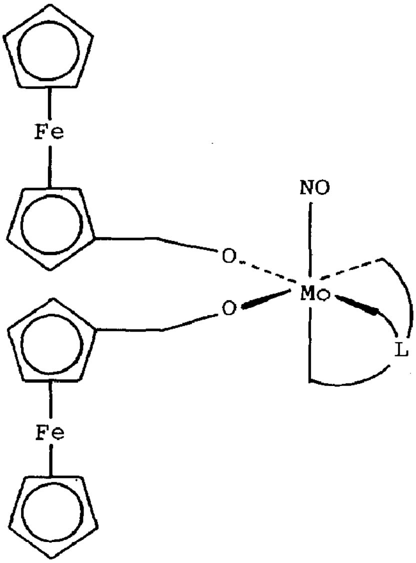

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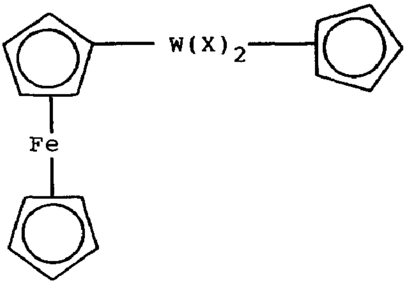

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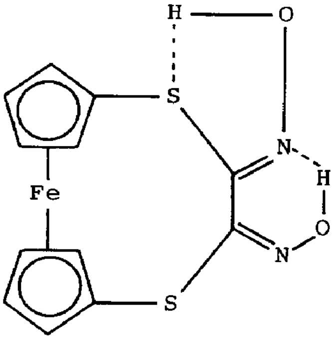
been prepared and subjected to spectroscopic and redox analysis. Thus, the amide $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)NHCOCCo_3(CO)_9$ did not show any transmission of electronic effects between the iron and cobalt centres. Oxidation at the ferrocene centre and reduction at the tricobalt-carbon centre were reversible [112]. The reaction of disodium 1,1'-ferrocenedithiolate with anti--dichloroglyoxime produced the amphi- and anti- isomers (9.31 and 9.32). The anti-isomer (9.32) formed a red complex (9.33) with nickel(II) chloride [113].

Aminoferrocene combined with anti-dichloroglyoxime to give bis(ferrocenylamino)glyoxime (9.34). This compound had an s-trans structure and gave a stable insoluble complex with nickel(II) [114]. The [10]ferrocenophane dioxime (9.35) has been prepared by treatment of S,S'-bis(aminoethyl)(1,1')-dithiaferrocene with anti-dichloroglyoxime. The dioxime (9.35) formed a nickel(II) complex with nickel(II) chloride in ethanol [115]. Ferrocenylamine has been condensed with salicylaldehyde to give the hydroxybenzylideneimine derivative (9.36) which formed complexes with cobalt(II) and zinc(II) [116]. The structure of the palladium complex (9.37) has been determined by x-ray analysis. The Fe-Pd distance was 2.878Å which indicated a weak dative Fe ⟶ Pd bond. The lack of reactivity of the complex with PPh_3, CO and NO supported the dative bond formulation [117]. The disodium salts of 1,1'-ferrocenediol and 1,1'-ruthenocene diol have been treated with $Pd(PPh_3)_2Cl_2$ to give the corresponding palladium complexes (9.38; M = Fe, Ru). The complexes



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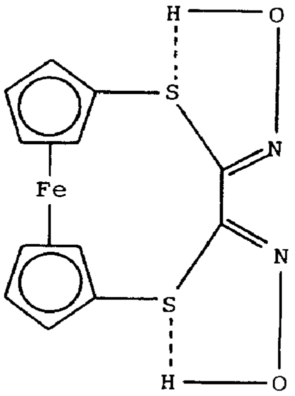

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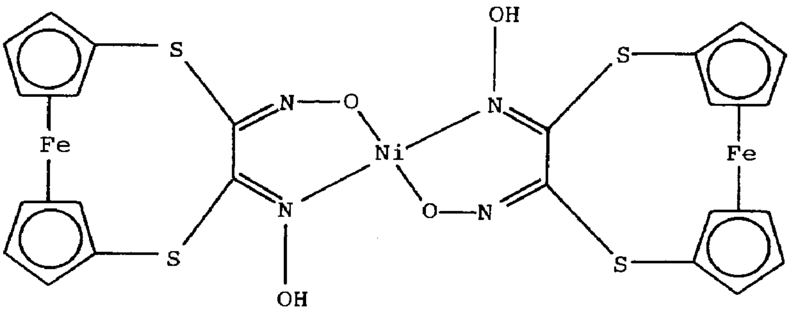

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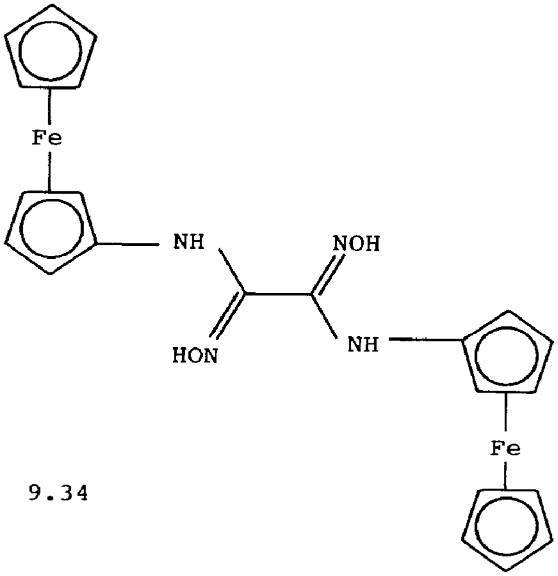

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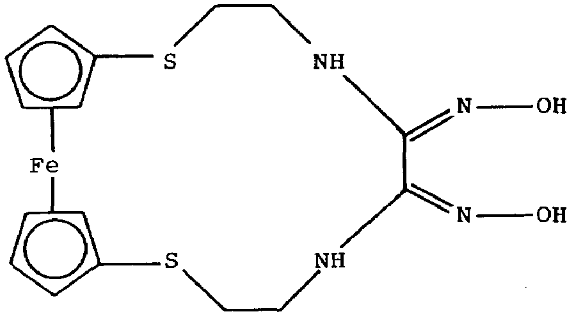

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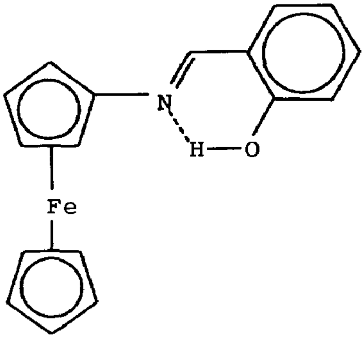

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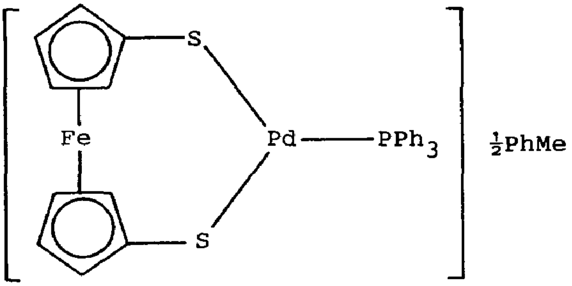

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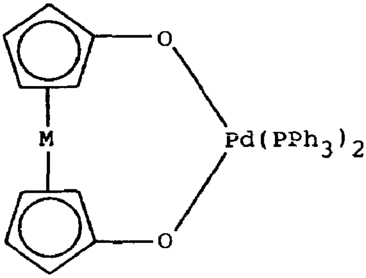
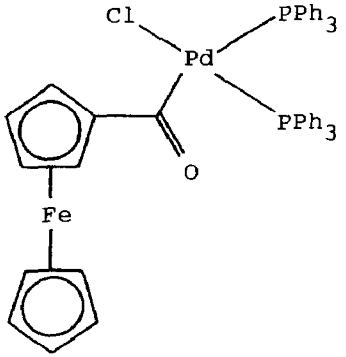


9.38

(9.38) were shown by X-ray crystallography to be isomorphous. The short Ru-Pd and Fe-Pd bond distances together with the large ^{1}H NMR chemical shift differences between the α- and β-hydrogens on the cyclopentadienyl rings provided evidence for metal-metal dative bonding [118].

Addition of ferrocenylcarbonyl chloride to tetrakis-(triphenylphosphine)palladium(0) produced the stable palladium complex (9.39). Reaction of this complex with poly(1-pyrazolyl)-borates gave the corresponding poly(1-pyrazolyl)borato complexes which were shown to be fluxional molecules by ^{1}H NMR spectroscopy. The reactions of the complex (9.39) with 1,10-phenanthroline and 2,2'-bipyridine were also investigated and the electrochemical properties of the poly(1-pyrazolyl)borato complexes were examined [119]. Reaction of the sulphides and selenides (9.40;



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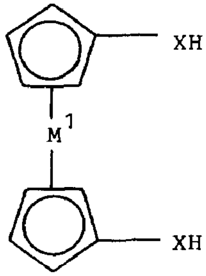

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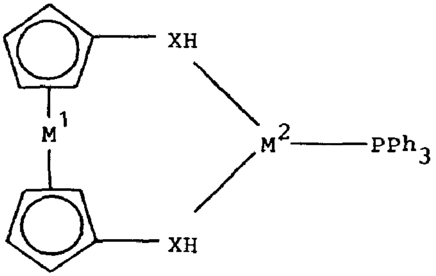
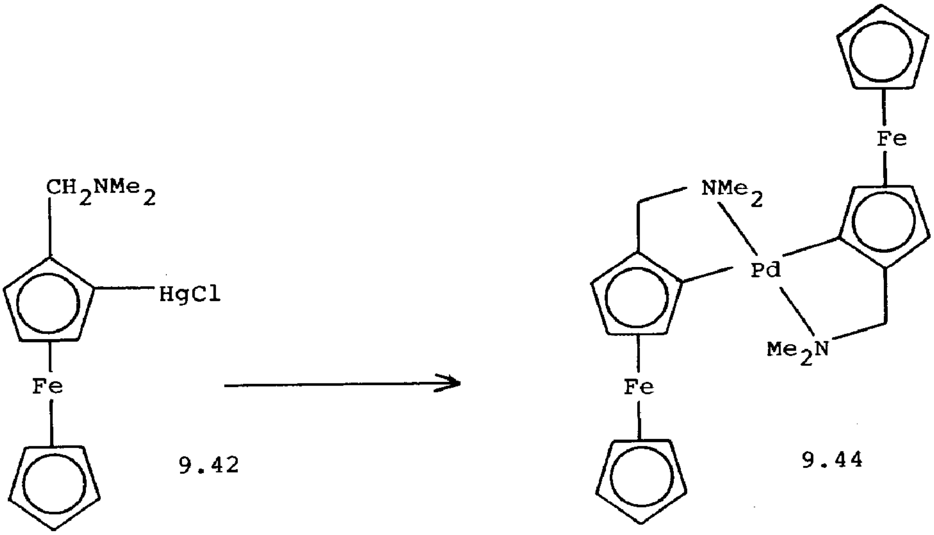


9.41

M^1 = Fe, Ru; X = S, Se) with tetrakis(triphenylphosphine)-platinum(O) produced the corresponding mono(triphenylphosphine) complexes (9.41; M^2 = Pt). The analogous palladium compounds (9.41; M^2 = Pd) were prepared by a similar route. The structure of the platinum complex (9.41; M^1 = Fe, M^2 = Pt; X = S) was determined by x-ray analysis. The short Fe—Pt distance of 2.935 Å indicated electronic interaction between the two metals [120]. 1-Chloromercuri-2-dimethylaminomethylferrocene (9.42) underwent transmetalation with $Pt(PPh_3)_3$ to form the platinum complex (9.43) while reaction with triphenylphosphine and then with Pd_2(dibenzylideneacetone)$_3$ gave the metallabicyclic complex (9.44) [121].

Reaction of 1,1'-di(mercurithiocyanato)ferrocene (9.45) with copper(II) or zinc isothiocyanate produced the complexes $[Fe(\eta\text{-}C_5H_4HgSCN)_2M(NCS)_2]$ where M = Cu or Zn. Treatment of the



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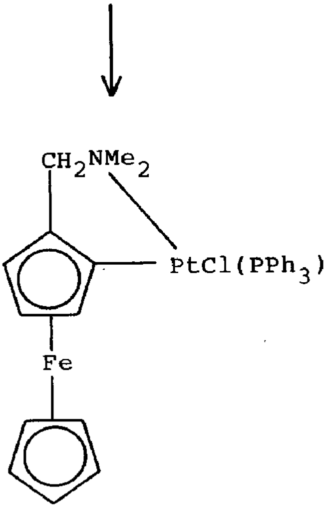

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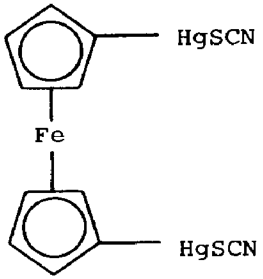

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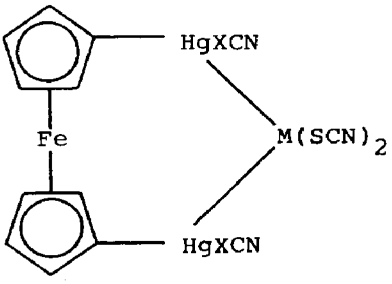


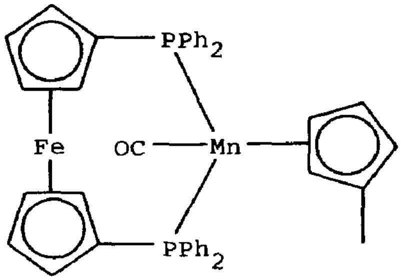
9.46

dithiocyanate (9.45) with $M(NCS)_2L_2$, where L = morpholine, M = Co, Cu, Ni and L_2 = 1,2-diaminoethane, M = Ni, Cu, Zn, afforded the corresponding complexes $[Fe(\eta\text{-}C_5H_4HgSCN)_2M(NCS)_2L_2]$. Spectroscopy indicated that the cobalt and zinc complexes were tetrahedral and the nickel and copper complexes were octahedral [122]. In a closely related study, transition metal thiocyanates combined with ferrocene-1,1'-bismercury(II) thiocyanate and selenocyanate to form the trimetallic complexes (9.46; M = Co, Ni, Cu, Zn; X = S, Se) which in turn formed adducts with pyridine and 1,10-phenanthroline [123]. The electron-transfer reactions between ferrocene or 1,1'-dimethylferrocene and copper(II) pyridyl complexes have been the subject of a kinetic study. Equilibrium formation of a precursor complex was indicated [124].

(ii) Photochemistry

Photolysis of methylcymantrene with 1,1'-bis(diphenylphosphino)ferrocene in benzene gave the manganese-bridged ferrocene (9.47) which has been characterized by X-ray crystallography [125]. Photolysis of the (σ-allyl)iron complex (9.48) gave the corresponding (π-allyl)iron complex (9.49) with the loss of carbon monoxide [126]. Photolysis of the methiodides (9.50 and 9.51) produced the dihydropyridine derivatives (9.52 and 9.53) respectively [127]. The composition of metallic deposits obtained by the photodecomposition of a mixture of ferrocene and nickelocene vapour were varied by selecting the laser wavelength to match features in the absorption spectra of the organometallic molecules. For example, iron:nickel ratios of 92:8 and 65:35 were produced by using 193nm and 337nm laser lines respectively [128].

The incorporation of 0.1-0.5% 1,1'-diacetylferrocene into poly(ethylene terephthalate) films increased their resistance to ultraviolet irradiation. The photostabilizing properties of 1,1'-diacetylferrocene were attributed to its ability to absorb at 200-300nm [129]. Ferrocene and tetrabromomethane formed a 1:1 charge-transfer complex in heptane and dimethylformamide. Stability constants and molar extinction coefficients were determined and were discussed in terms of the photosensitivity of polystyrene films containing ferrocene and tetrabromomethane [130]. The UV-visible absorption spectra for several ferrocenylbenzenes (9.54; R = H, OH, Me, OH_2) and ferrocenylnaph-



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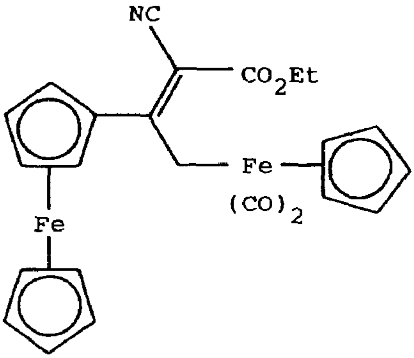

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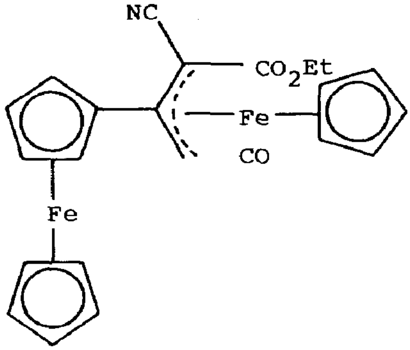

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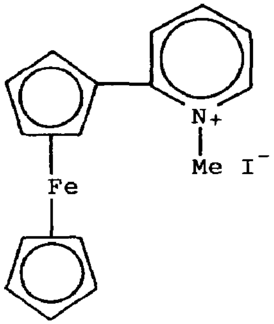

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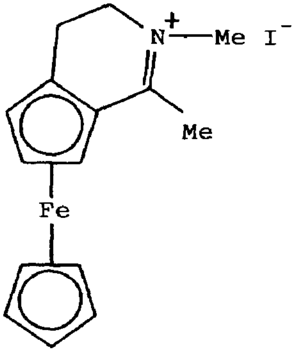

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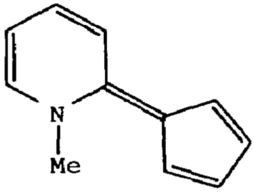

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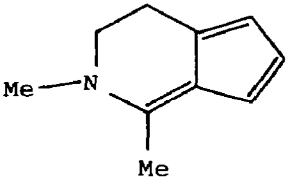

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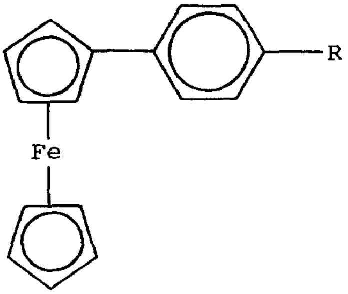

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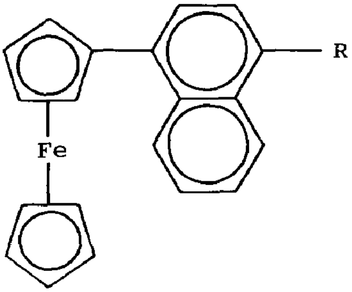

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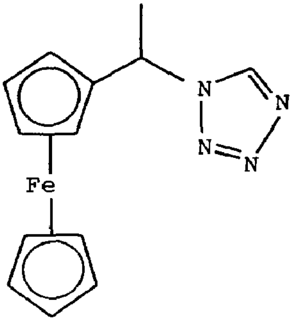
thalenes (9.55; R = H, NH_2, NO_2) as charge-transfer complexes with tetrabromomethane have been measured and interpreted. Bathochromic shifts were observed for electron donor substituents and hypsochromic shifts for electron acceptor substituents [131]. A Moessbauer spectroscopy study has been carried out on charge--transfer complex formation between ferrocene and carbon tetrabromide [132].

(iii) General chemistry

Hydroxymethylferrocenes combined with ethyl malonate, ethyl formamidomalonate, acetylacetone and aniline in the presence of calcium bentonite and calcium montmorillonite to give ferrocenylmethyl derivatives in 40-60% yield [133]. 5-Aryltetra-



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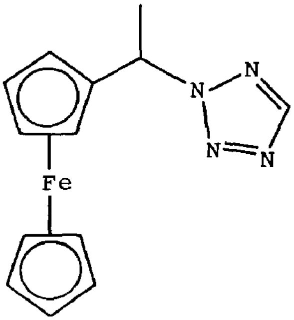

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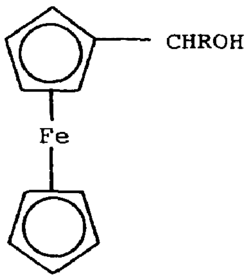
zoles combined with ferrocenemethanol, 1-ferrocenylethanol and 1-ferrocenylbenzylalcohol to form the corresponding (2-ferrocenylalkyl)-5-aryltetrazoles in good yield. Ferrocenylcarbene cations and tetrazolate anions were implicated in the reaction mechanism [134]. The reaction of ferrocenyl-alcohols with tetrazoles and 1,2,4-triazoles has been investigated. For example, the treatment of 1-ferrocenylethanol with tetrazole afforded the substituted tetrazoles (9.56 and 9.57) [135]. The ferrocenyl methanols (9.58; R = H, Me, Ph) attacked 5-aryltetrazoles in acetic acid to give the corresponding 2-(ferrocenylalkyl)-5--aryltetrazoles [136]. α-Ferrocenylcarbinols (9.59; R = H, Me, Et, cycloalkane) combined smoothly with mercaptosuccinic acid to form the dicarboxylic acids (9.60; R = H, Me, Et, cycloalkane) one of which was used in the resolution of tertiary alcohols [137].

Treatment of acetylferrocene with aniline and phosphorus oxychloride in dimethylformamide gave the enamine (9.61). The addition of acetylferrocene to a mixture of titanium tetrachloride and dimethylamine produced the enamine (9.62). The use of this enamine in the synthesis of 3-ferrocenyl-2H-thiete (9.63) and the corresponding sulphone (9.64) was described [138]. Several oximino derivatives of ferrocene have been prepared from 1,1'-diacetylferrocene, in one case further reaction with base gave the bisoxadiazole (9.65) [139]. The reaction of formylferrocene with 2,3-bis(hydroxylamino)-2,3-dimethylbutane followed by oxidation of the product with PbO_2 produced the nitronyl-



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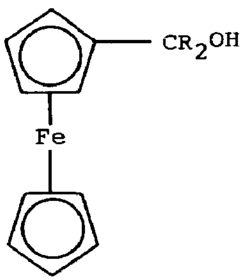

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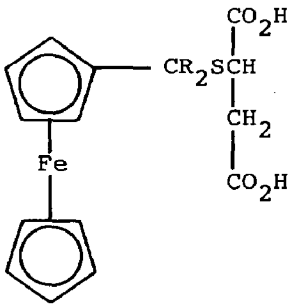

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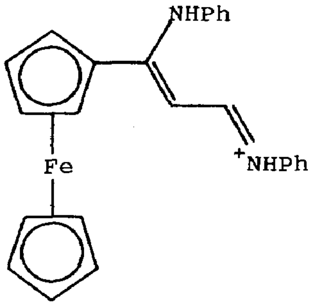

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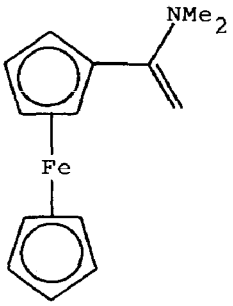

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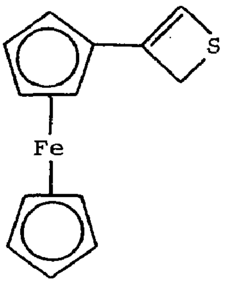

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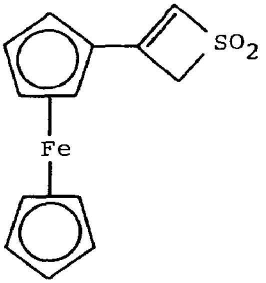

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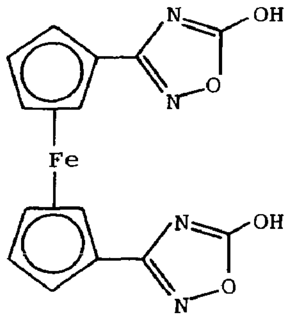
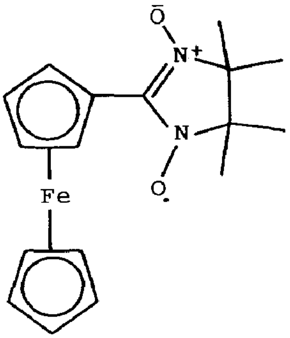


9.65

nitroxide derivative (9.66) [140]. Highly regioselective hydroformylation of vinylferrocene has been achieved in the presence of rhodium or platinum catalysts to give 2-ferrocenylpropionaldehyde as the major product together with some 3-ferrocenylpropionaldehyde [141]. Ferrocenylketoaziridines have been prepared by treatment of ferrocenylacid chlorides with aziridines in the presence of potassium carbonate [142].

Several isocyanide derivatives of ferrocene (9.67; R = H, Me, i-Pr, t-Bu, CH_2OMe) have been prepared by dehydration of the N-substituted formamides. The products were characterized by cyclic voltammetry and spectroscopy. Seven chiral ferrocene isocyanides were also prepared and configurational assignments were made [143]. The 1-ferrocenyl-2-methylpropyl group has been used as a chiral auxilliary in the synthesis of the benzophenanthridine alkaloids [(+)-9.68] and (-)-corynoline. The



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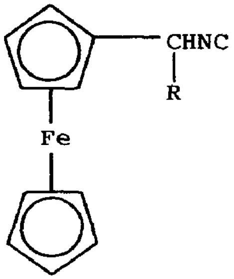

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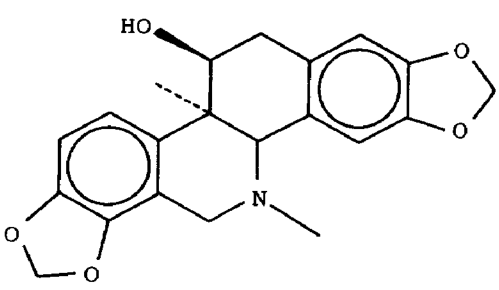
key step in the preparation of the alkaloid (9.68) was the condensation of the Schiff base [(R)-(-)-9.69] with the anhydride [(±)-9.70] to give the amide (9.71) together with some of the amine (9.72) [144]. The ferrocenylphenylanils (9.73; X = 2-, 3-, 4-NO_2,4-OMe) have been cyclized with acetoacetic ester to form the esters (9.74; X = 2-, 3-, 4-NO_2, 4-OMe). These products (9.74) underwent oxidation at iron or quaternization at nitrogen [145].

The Michael addition of thiols and carbanions to acryloyl- and cinnamoyl-ferrocene was catalyzed by potassium fluoride--alumina. Thus the thiols RSH combined with acryloylferrocene to give the products (9.75; R = Ph, CH_2CO_2Et, CH_2CO_2H) [146]. The arenesulphenyl chlorides R^1SCl, where R^1 = 4-RC_6H_4 (R = MeO, Me, Cl, H, NO_2); 2,4-$(NO_2)_2C_6H_3$, added to the alkynylferrocene (9.76; R^2 = Ph) to give the corresponding alkenes (9.77 and 9.78). Similar additions were carried out with the alkynes [9.76; R^2 = ferrocenyl, $(CH_2)_2Me$] to give the corresponding alkenes. The overall second order rate constants were obtained for these reactions and the results were consistent with an intermediate possessing a partial positive charge on the carbon atom adjacent to the ferrocenyl group [147]. Reaction of the ferrocenyl salts (9.79; R^1 = Me, Ph) with $[R^2C(NO_2)_2]K$, where R^2 = H, Me, NO_2, afforded the corresponding (nitroalkyl)-ferrocenes (9.80 and 9.81) [148].



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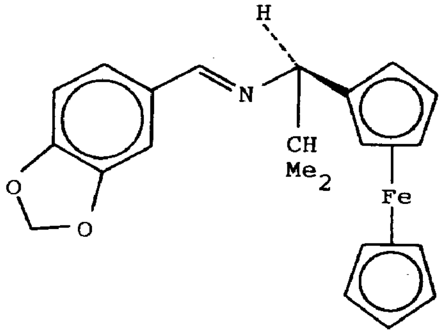

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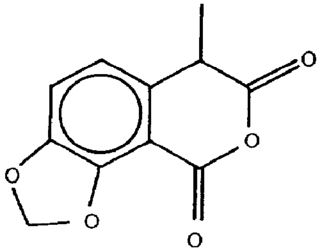

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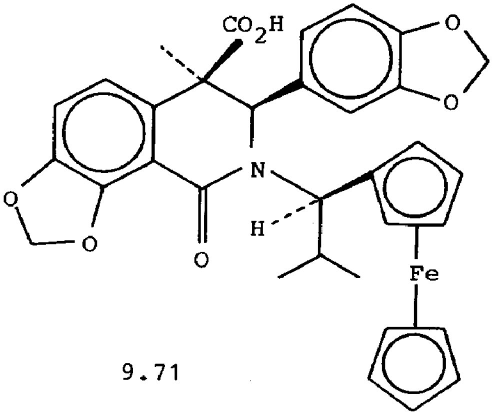

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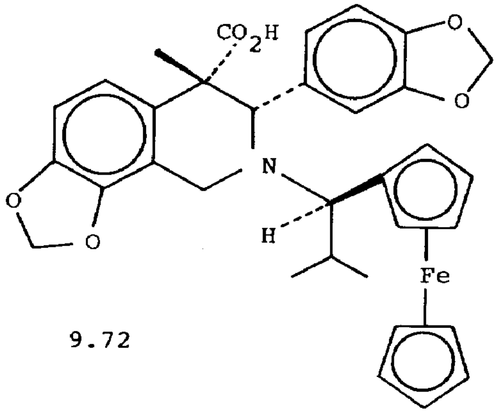

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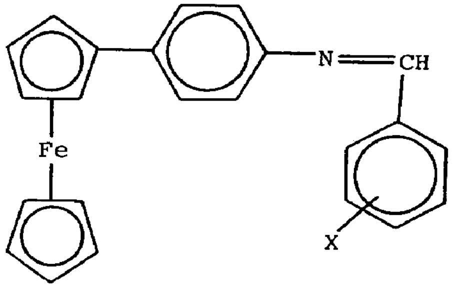

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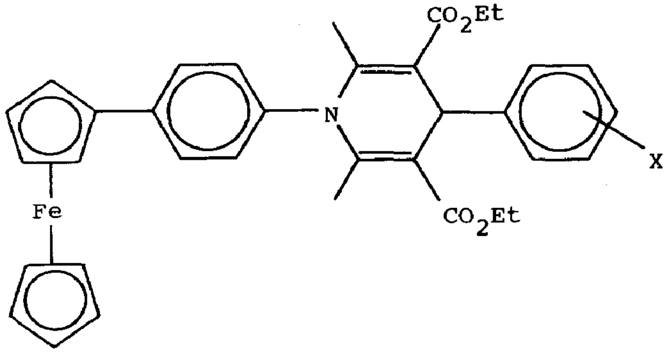

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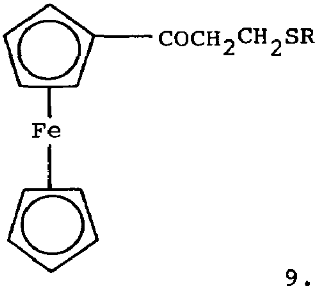

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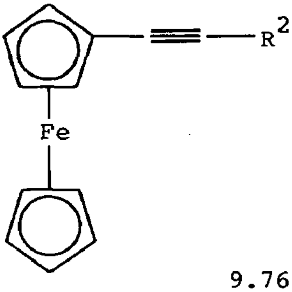

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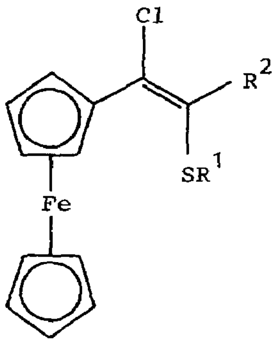
The ferrocenyldiphenylallyl cation (9.82) was attacked by small nucleophiles, such as methoxide ion, at the tertiary carbon centre to give products such as the methoxide (9.83) and by large nucleophiles, such as dimethylaniline, at the secondary carbon centre to give the amine (9.84) [149]. Zinc chloride and iodide catalyzed the reaction of 1-acetoxy-1-ferrocenylethane (9.85) with the double bond of enoxysilanes, such as the pinacolone derivative (9.86) to give the corresponding α-alkylated derivatives such as the ketone (9.87). Secondary carbenium ions were involved as intermediates [150]. 1,2-Disubstituted ferrocenes [9.88; R^1 = H, R^2 = NMe_2; R^1 = $(CH_2)_5CO_2Et$, R^2 = $(CH_2)_6Me$] have been degraded by hydrogenolysis over palladium on charcoal to give trans-cyclopentanes (9.89) as the main products [151]. An investigation has been carried out on the kinetics and mechanism of decomposition of ethylferrocene on



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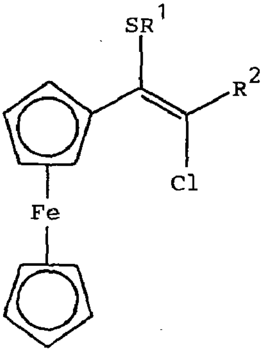

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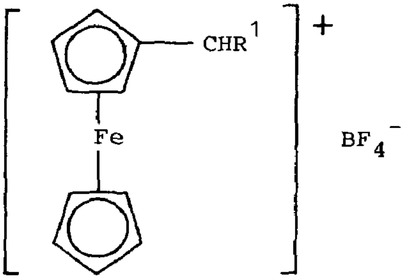

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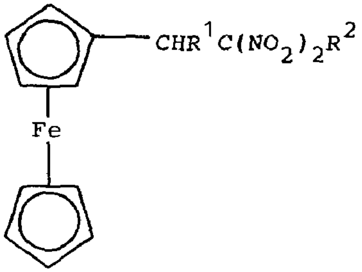

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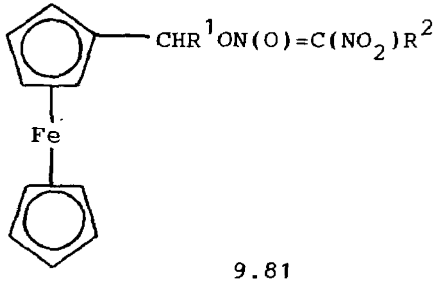

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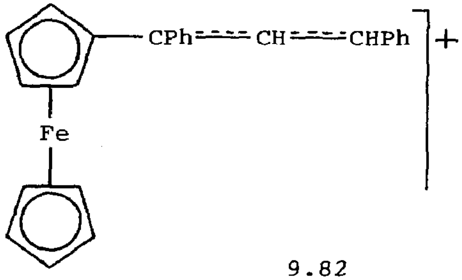

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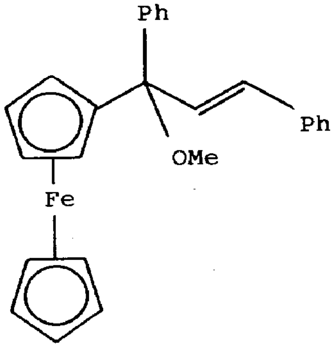

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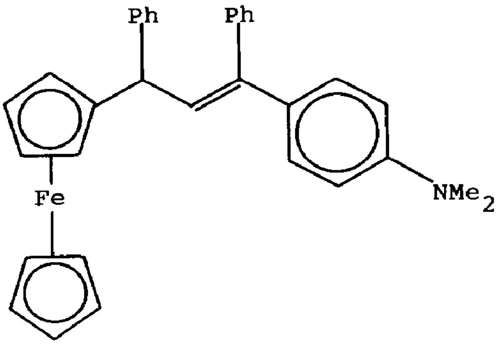

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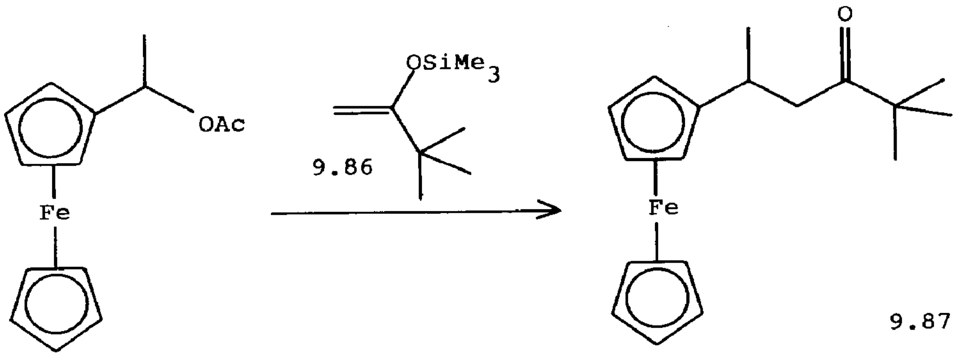

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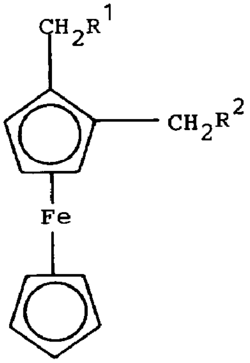

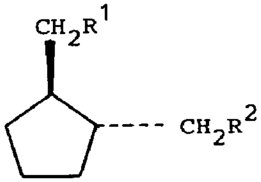

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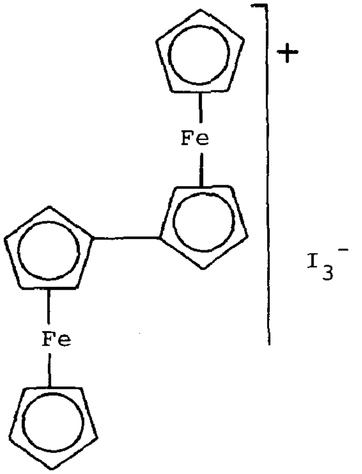
quartz-supported catalysts formed from pyrolyzed bis(η-ethylbenzene)chromium and diisopropylnickelocene [152].

10. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

Biferrocenyl has been prepared in high yield (78%) by the reaction of lithioferrocene with p-xylenedibromide. The isolation of biferrocenyl and ferrocene from this reaction indicates that ferrocenyl radicals were generated and supported a Wurtz-type radical mechanism for the formation of biferrocenyl [153]. Nitrobenzene or dichloromethane solutions of mixed-valence biferrocenium triodide (10.1) showed a concentration dependence of the energy of the intervalence transfer band in the electronic spectrum. This effect was explained by ion aggregation



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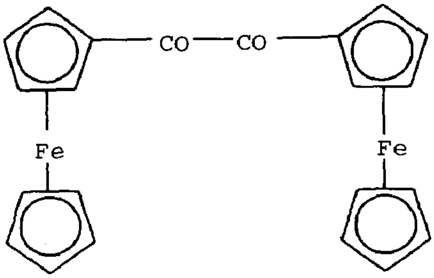

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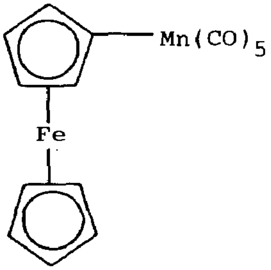

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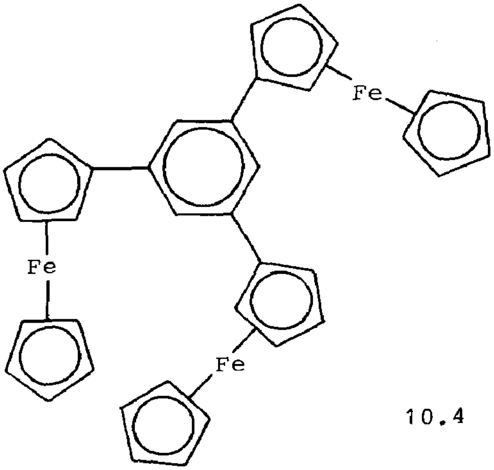
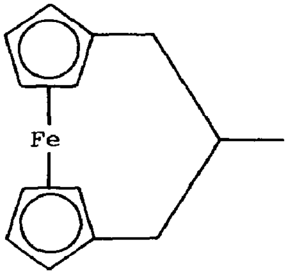


10.4

in solution and which was made up of ion-paired cations and non-ion-paired cations in varying proportions [154]. Heat capacity measurements at constant pressure on the biferrocenium triiodide (10.1) have shown that a phase transition occurred at the temperature where the trapped-valence state changed to the high temperature average-valence state. Distortion in the triiodide anion was investigated by IR and Raman spectroscopy [155].

Biruthenocene and ferrocenylruthenocene each combined with tin(IV) chloride to give an adduct in which Moessbauer spectroscopy indicated covalent Ru-Sn bonding [156]. Mercury(II) chloride formed stable adducts with biferrocene and ferrocenylruthenocene. Moessbauer spectroscopy was used to examine biferrocene--$2HgCl_2$ and ferrocenylruthenocene-$5HgCl_2$ and the presence of direct interaction between iron and mercury was indicated with a chelating effect between Fe-Fe or Fe-Ru [157]. Treatment of biruthenocene with iodine gave a stable diamagnetic adduct and in a similar reaction with ferrocenylruthenocene a less stable diamagnetic adduct was obtained. ^1H NMR and ^{57}Fe-Moessbauer spectroscopic data indicated direct interaction between the ruthenium and iodine atoms in the adducts [158]. Ferrocenyllithium combined with pentacarbonylmanganese bromide to form ferrocenylpentacarbonylmanganese (10.2), diferrocenoyl (10.3) was obtained by way of a side reaction. The ferrocenyl group in the manganese complex (10.2) was slowly split off in protic solvents. Thus the methyl ester of ferrocene carboxylic acid was obtained in methanol while ferrocenecarboxaldehyde was formed in acetonitrile [159].

Di- and tri-ferrocenylbenzenes were effective photocatalysts for the evolution of hydrogen from ethanol in the methylviologen-triethanolamine-colloidal platinum catalyst system using visible light irradiation. The most efficient metallocene was 1,3,5-triferrocenylbenzene (10.4) [160]. The protonation of bridge alkylated [3]-, [4]- and [5]-ferrocenophanes, such as the methylferrocenophane (10.5), has been studied by ^1H NMR spectroscopy. Long-lived iron protonated species were obtained in HBF_3OH. Oscillation of the cyclopentadienyl rings and the bridges was slowed or inhibited by the bridge substituents. Iron-proton chemical shifts were sensitive to bridge length but not to bridge substituents [161]. Cyclization of ferrocene-1,



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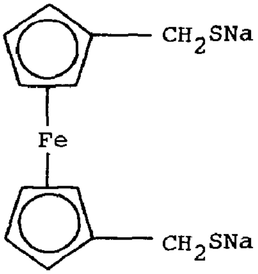

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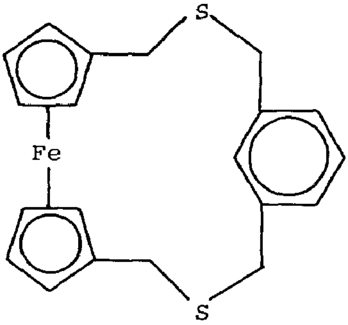

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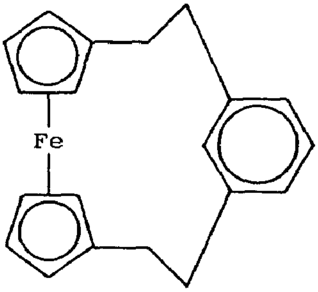

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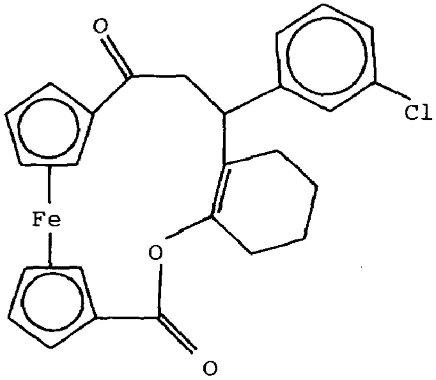
1'-diols has been used to produce β-oxatrimethylene bridged ferrocenes which also contained trimethylene bridges. X-ray



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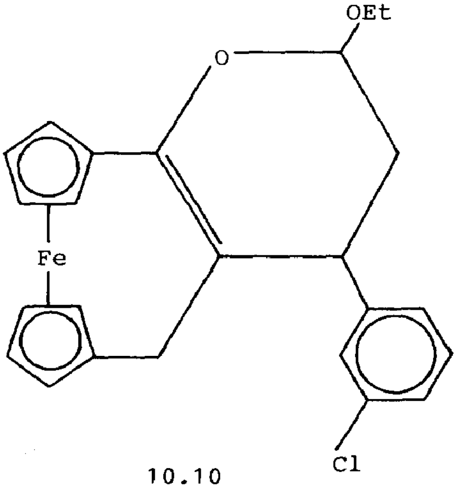
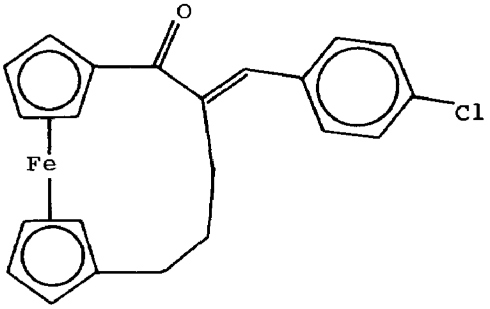


10.10

crystallography and cyclic voltammetry were applied to the characterization of the products. Interaction between the bridge oxygen atom and the iron atom was observed [162].

A kinetic study has been carried out on the formation of hydrogen gas from the reaction of ferrocenophanes with strong acids, the mono- and di-hydrates of boron trifluoride [163]. Dibromo-m-xylene combined with the dithiolato (10.6) to form the ferrocenophane (10.7) which was treated $LiN(CHMe_2)_2$ and methyl iodide followed by nickel to give the ferrocenophane (10.8). The structures of the two products (10.7 and 10.8) were confirmed by x-ray crystallography. The 9-H atom of the benzene ring in (10.8) was close to the iron atom and showed a large downfield chemical shift as a result of the anisotropic effect of the ferrocene moiety [164]. The reaction of 2-(3-chlorobenzylidene)-



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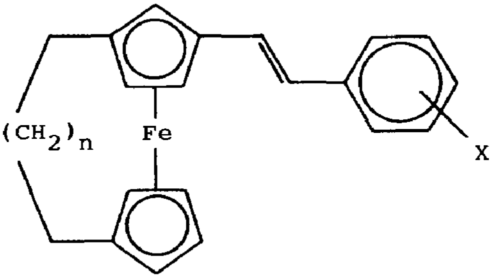

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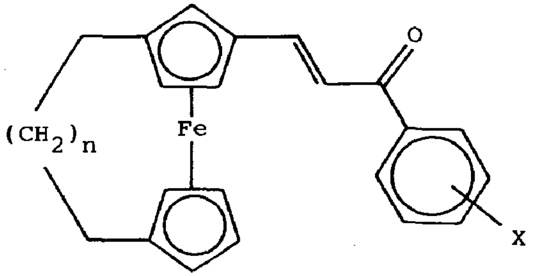

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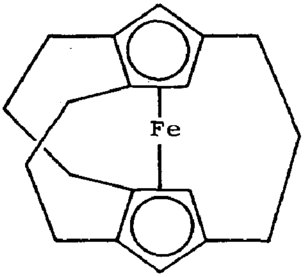
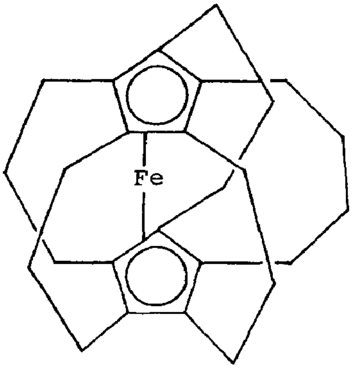


10.14

[3]ferrocenophane-1,3-dione with 1,3-cyclohexanedione, in the presence of 18-crown-6 and potassium carbonate, produced the bridge-expanded product (10.9). In a similar reaction with vinylethyl ether the cycloadduct (10.10) was obtained [165].

The reactivity of [m]ferrocenophanones, where m = 3, 4, 5, to 4-chlorobenzaldehyde under aldol conditions has been examined. Both the length of the bridge and the position of the ketone group were important in the reaction. The [3]- and [4]-ferrocenophan-1-ones gave only β-hydroxyketones while [5]ferrocenophan-1-one gave the α,β-unsaturated ketone (10.11) in addition to the β-hydroxyketone. The manganese dioxide oxidation of [m]ferrocenophanes gave the corresponding ketones and diketones [166]. Several arylferrocenophanyl-ethylenes and -propanones (10.12, 10.13; n = 1, 3; X = H, 3-Cl, 4-OMe, 4-CN) have been



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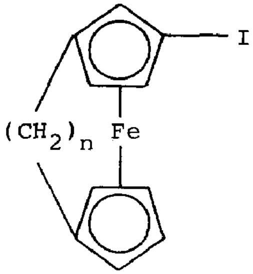

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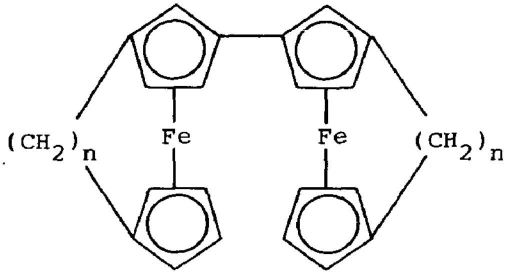

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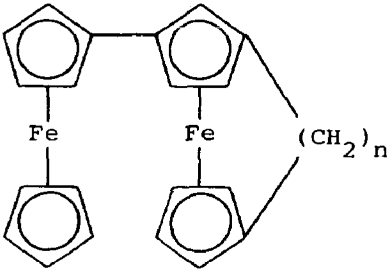
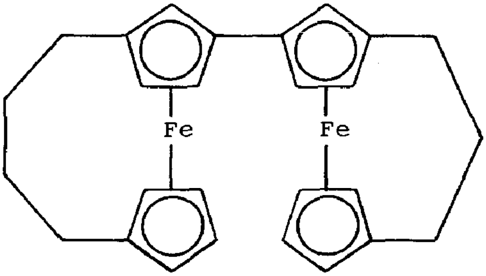


10.18

prepared and studied by electronic absorption spectroscopy. The d-d band wavelength varied with the substituent X but the bridge did not produce a specific effect [167]. The ferrocenophane (10.14) was the starting material for the preparation of $[4][3_4](1,2,3,4,5)$ferrocenophane (10.15), the first example of a bridged ferrocene with four trimethylene chains. The d-d* absorption band of this latter molecule appeared at an unusually short wavelength 345nm [168].

Ullmann coupling of the iodoferrocenophanes (10.16; n = 3,4) produced the corresponding biferroceneophanes (10.17). Cross-coupling of the ferrocenophanes (10.16; n = 3,4) with ferrocenylzinc chloride in the presence of a Pd catalyst gave the unsymmetrical ferrocenylferrocenophanes (10.18; n =3,4). The unsymmetrical biferrocenophane (10.19) was prepared by a similar route. The ferrocenophanes (10.17, 10.18 and 10.19; n = 3,4) were investigated via cyclic voltammetry [169]. The anion derived from the benzoindenophane (10.20) has been used to prepare the ferrocenophanes (10.21 and 10.22). The structures of these ferrocenophanes were determined by x-ray analysis. In both molecules the position of the iron atom was not directly above the centre of the substituted η-cyclopentadienyl ring but was displaced away from the six-membered rings [170]. Reaction of the phosphorus bridged ferrocenophane (10.23) with lithium cyclopentadienide in the presence of tetramethylethylenediamine followed by water or $(\eta\text{-}C_5H_5)Fe(CO)_2I$ afforded the products of bridge cleavage (10.24 and 10.25) respectively. Treatment of the ferrocenophane (10.23) with $(\eta\text{-}C_5H_5)Fe(CO)_2Na$ produced phosphine complex (10.26). The structures of the complexes (10.25 and 10.26) were determined by x-ray analysis [171].

The reaction of 1,2- or 1,3-bis(hydroxymethyl)ferrocene with $4\text{-}MeC_6H_4SO_3CH_2(CH_2OCH_2)_nCH_2O_3SC_6H_4Me\text{-}4$ (n = 1-5) has produced the crown ethers (10.27; n =2-5) and (10.28). The ability of these crown ethers to complex with a range of metal ions has been investigated [172]. Lithiated (diphenylphosphino)ferrocene has been treated with sulphur to give a mixture of the two [3]ferrocenophanes (10.29 and 10.30) which were characterized by x-ray crystallography. ^1H NMR spectroscopy has been used to show that the ferrocenophane (10.29) existed in solution as a mixture (60:40) of diastereomers depending



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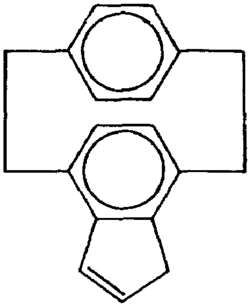

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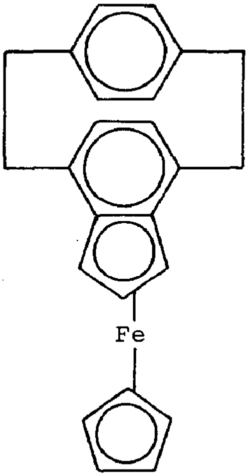

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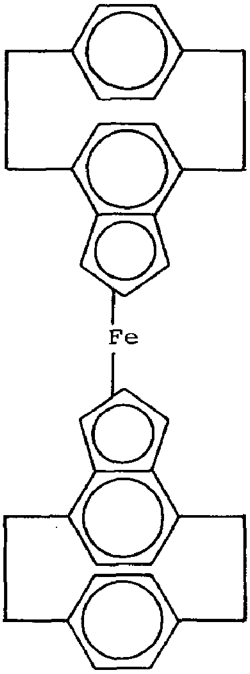
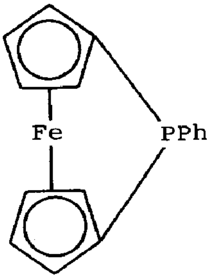


10.22

on the orientation of the S_3 bridge. The isomer (10.30) was mainly one diastereomer [173].

The tetrathia[n]ferrocenophanes-transiton metal complexes (10.31 and 10.32; n = 0,1, M = Cu, Ag, X = ClO_4, m = 1; M = Hg, Pd, X = Cl, m = 2) have been prepared and characterized. Spectroscopic evidence indicated that there was little interaction between the iron atom of the ferrocene group and the complexed metal ions [174]. The trithia[7]- and trithia[9]-ferrocenophanes (10.33; n = 1,2) formed complexes with copper(I), silver(I), mercury(II) and palladium(II) salts. Thus, the



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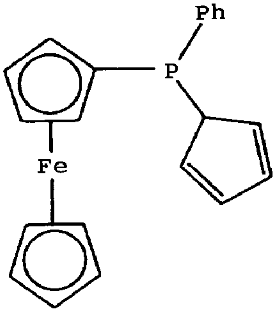

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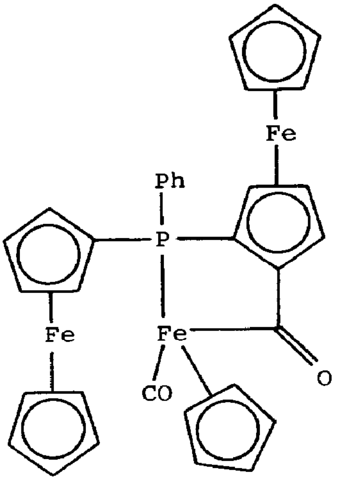

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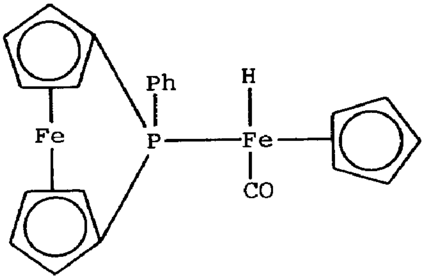

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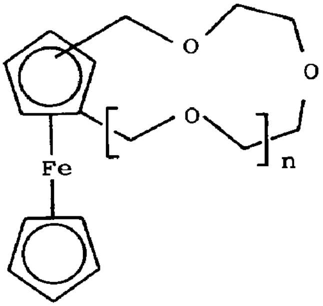

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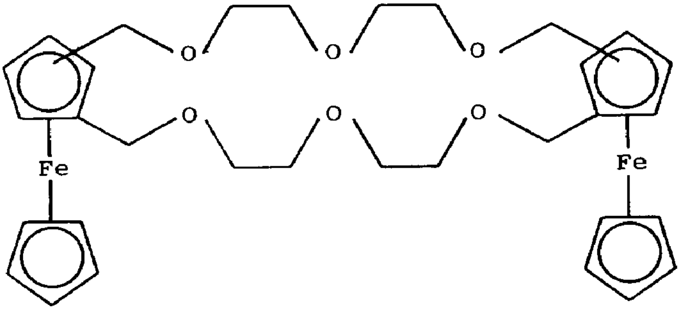

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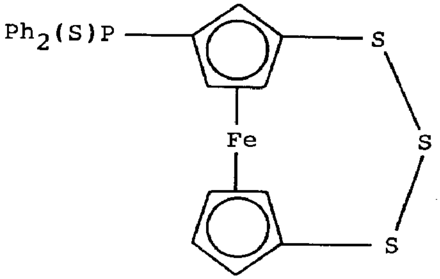

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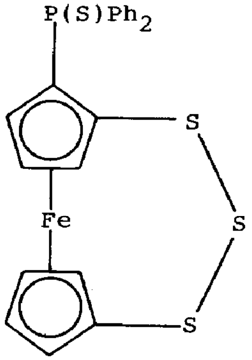

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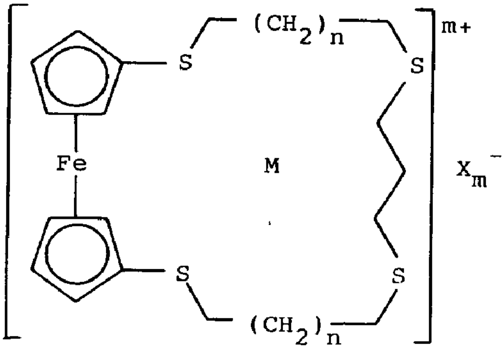

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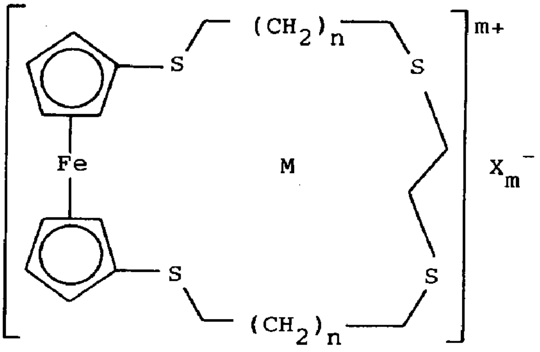

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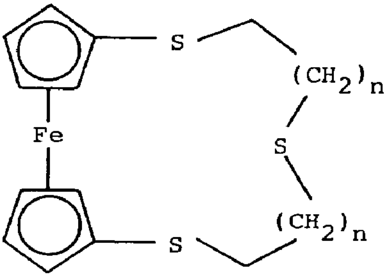

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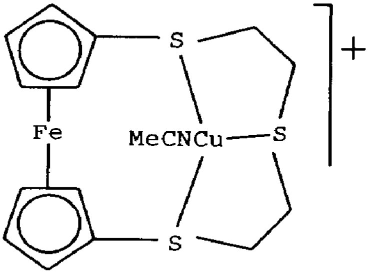
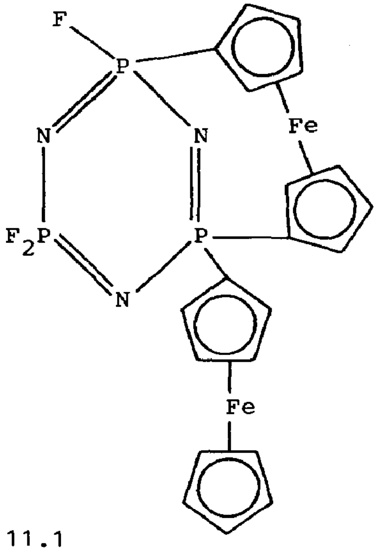


10.34

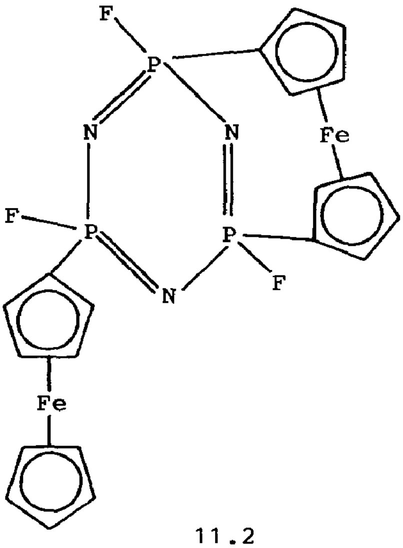
ferroceneophane (10.33; n = 1) combined with $Cu(BF_4)_2$ and copper in acetonitrile to give the cationic complex (10.34) [175].

11. FERROCENE-CONTAINING POLYMERS

Vinylferrocene vapour underwent polymerization in a low-temperature plasma to form thin polymer films which increased in thickness at the rate of 20 mm min^{-1}. The presence of ferrocene groups in the product was confirmed and the vinyl groups were active in the polymerization [176]. 1,1'-Divinylferrocene



11.1



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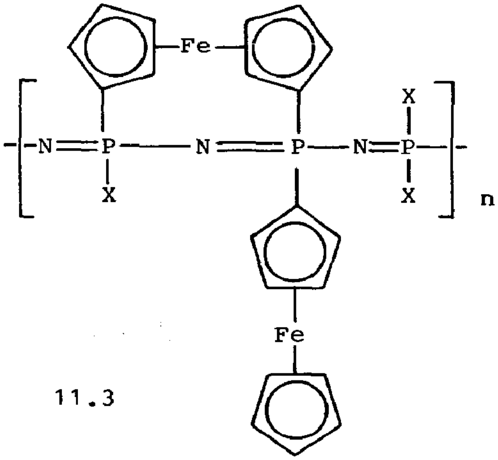

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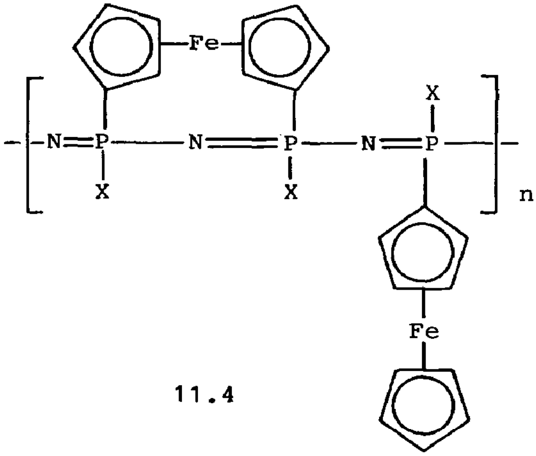


11.4

has been copolymerized with styrene in the presence and absence of divinylbenzene to give ferrocene containing polymers. The properties of these polymers were investigated [177]. Dimethylaminomethylferrocene vapour has been plasma polymerized in argon onto electrodes. The polymer film was characterized by ESCA and the electrochemistry was investigated. The cyclic voltammetric responses decayed on continuous cycling [178]. The metallocenylphosphazenes (11.1 and 11.2) polymerized when heated in the molten state to give the corresponding polymers (11.3 and 11.4; X = F). Treatment of these hydrolytically unstable polymers with sodium trifluoroethoxide produced the hydrolytically stable polymers (11.3 and 11.4; X = OCH_2CF_3) [180].

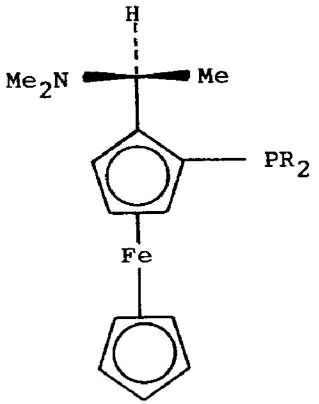
Poly(methylphenylphosphazene) has been metalated with n-butyllithium and then treated with acetylferrocene or ferrocenecarbaldehyde to give a polymer with pendant ferrocene groups [179].

12. APPLICATIONS OF FERROCENE

(i) Ferrocene catalysts and photosensitizers

Reduction of 1,1'-bis(diphenylphosphine)ferrocenepalladium dichloride gave a species which was used in situ as a catalyst for the cross coupling of alkyl iodides with Grignard reagents. Thus $4\text{-}MeOC_6H_4MgBr$ was treated with methyl iodide and $(Me_2CHCH_2)_2AlH$ in the presence of the catalyst to give the cross coupled product $4\text{-}MeOC_6H_4Me$ as well as the homo-coupled species $4\text{-}MeOC_6H_4.C_6H_4OMe\text{-}4$ [181]. Platinum(II) chloride complexes of the ferrocenyl-phosphines (12.1; R = Ph, $CHMe_2$ and 12.2) were effective catalyst precursors for the hydrosilylation of the ketones PhCOR [R = Me, $(CH_2)_2Me$, $CHMe_2$] by diphenylsilanes to give the corresponding alcohols in high yields. The optical yields of these alcohols were low. The reduction of acetyl- and benzoyl-ferrocene were also investigated. The structure of the catalyst (12.3) was determined. The platinum had cis square planar coordination with significant distortion toward tetrahedral geometry [182].

Ferrocene derivatives have been linked to aldehyde functionalised cross-linked polystyrene and the platinum and palladium derivatives used as catalysts. Thus the (S,R)-diphenylphosphinoferrocene (12.1) was dilithiated with n-butyllithium and TMEDA and then combined with the polymer to give the products (12.4 and



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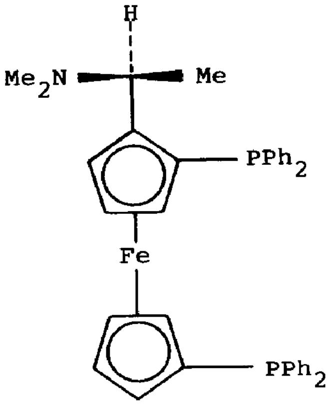

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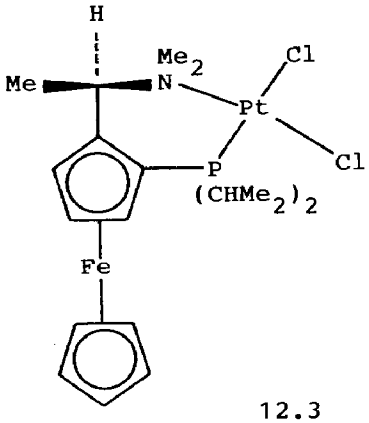

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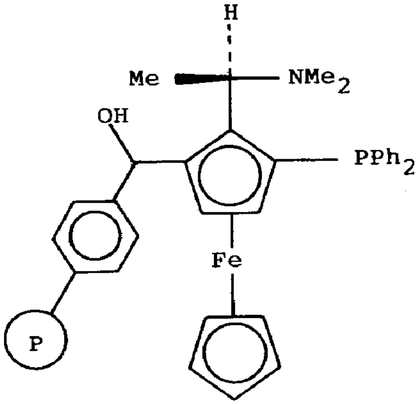

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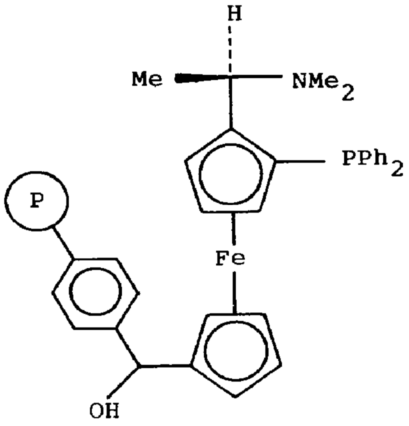

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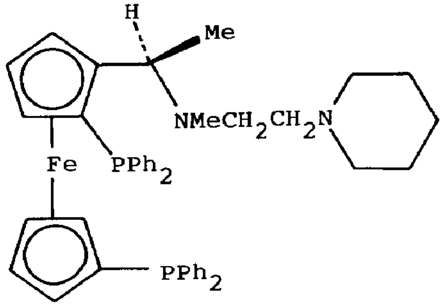
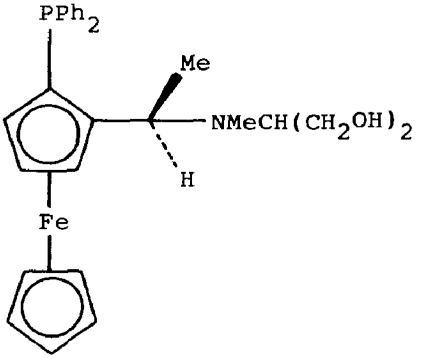
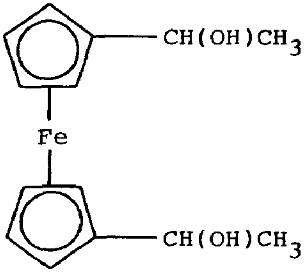


12.6

12.5) in which chirality was induced at the linking carbon atom. The palladium complex was effective in catalyzing the stereoselective α-addition of trichlorosilane to styrene. The catalysts were recycled without loss of stereoselectivity but the optical yield was reduced [183]. The asymmetric hydrogenation of trisubstituted acrylic acids has been catalyzed by rhodium complexes of chiral (aminoalkyl)ferrocenylphosphine compounds such as the diphosphine (R)-(S)- (12.6). High stereoselectivity was obtained and the catalysts were of high activity [184].



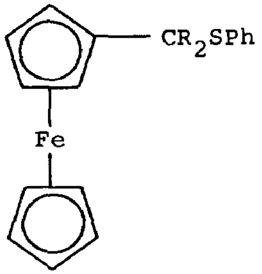
12.7



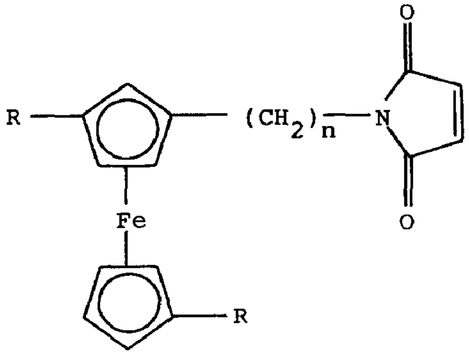
12.8

The chiral ferrocenylphosphine (12.7) formed a palladium complex which was effective as a catalyst for the regiospecific allylic alkylation of racemic 1,3-disubstiuted 2-propenyl acetates. Products of high optical purity were obtained with up to 95% enantiomeric excess [185].

A wide range of metallocenes, including ferrocenes, have been used as polymerization catalysts for α-olefins [186]. Ferrocene, acetylferrocene and 1,1'-bis(α-hydroxyethylferrocene) (12.8) behaved as catalysts for the oxidation of cumene and the decomposition of cumene hydroperoxide. The ferrocenyl-alcohol (12.8) was the most effective catalyst in both the reactions [187]. 1,1'-Diacetylferrocene disemicarbazide, 0.25-0.5 parts, in the presence of metal oxides behaved as a vulcanizing agent in polychloroprene rubber. The addition of 2-3 parts of the disemicarbazide in the absence of metal oxides resulted in a high rate of vulcanization and high scorch resistance. The semicarbazide groups underwent reaction with the rubber to cause crosslinking [188]. The incorporation of 1.5-1.7 mol % of ferrocene into



12.9



12.10

isoprene rubber by copolymerization with suitable ferrocene derivatives increased the resistance of the rubber to thermal and photochemical aging [189]. Ferrocenium tetrachloroferrate(III) has been used as a hardener in furan resins. The physicomechanical properties of these glass-fibre reinforced resins were superior to those crosslinked with iron(III) chloride [190].

The ferrocenylmethyl sulphides (12.9; R = H, Me, Et, Pr) have been used as additives in lubricating oil. In friction tests the seizure load and wear characteristics of the oil were improved [191]. Octanoylferrocene and related compounds have been used as photosensitizers for photodegradable polyethylene film. Thus, film containing 0.1% octanoylferrocene underwent complete degradation after exposure to sunlight for three months on seedbeds [192].

(ii) Combustion control

Pressure pyrolysis at <600°C of divinylbenzene-ferrocene and divinylbenzene-vinylferrocene copolymers has been used to obtain cementite-dispersed carbon. Magnetization measurements on the products indicated that bonding of ferrocene to the polymer matrix by the two-carbon unit was effective in giving a fine dispersion of cementite particles in the carbon formed [193]. The effect of ferrocene on a sooting flame, produced by burning a prevaporized mixture of toluene and isooctane, has been investigated by laser-optical diagnostic techniques. Ferrocene completely suppressed the visible soot plume [194]. The pyrolysis of hydrocarbons to form carbon fibres was improved by the presence of organometallic compounds. Thus ferrocene (6%) was used with benzene in a reactor at 1150° to give carbon fibres 1-2mm in length [195]. The addition of a small proportion of ferrocene to premixed ethylene flames enhanced soot formation over a range of carbon:oxygen ratios by factors of 1.2-13.5. Iron oxide particles acted as nuclei for carbon deposition [196].

Ferrocene and ferrocene derivatives have been extracted from ammonium perchlorate-aluminium high burn rate propellants by the use of compressed carbon dioxide in the near critical liquid state (NCL). The NCL carbon dioxide was introduced into a pressure vessel containing the cooled propellant and the two allowed to remain in contact for an extended period of time. 2,2-Bis(ethylferrocenyl)propane was recovered by this procedure in a yield of 99.8% [197]. 1,3-Diferrocenyl-1-butene has been used as a combustion catalyst in high-energy composite rocket fuels [198]. Ferrocene derivatives such as 1,1'-bis(1-oxopropyl)ferrocene and 1,1'-bis(1-hydroxypropyl)ferrocene have been used as additives to solid propellants [199].

(iii) Ferrocene in analysis

2-Ferrocenylethylamine has been condensed with steroid glucuronides in the presence of a water soluble carbodiimide and 1-hydroxybenzotriazole. The derivatized glucuronides were determined by high performance liquid chromatrography with electrochemical detection. This method was suitable for the estimation of estrogen glucuronyltransferase activities and estrogen glucuronides in pregnancy urine [200]. The ferrocenylmaleimides (12.10; R = H, n = 0; R = CH_3, n = 0; R = H, n = 2) have been prepared and evaluated for precolumn derivatization of thiol compounds in high performance liquid chromatography with dual electrode coulometric detection. N-Acetyl-L-cysteine was used as a model compound and N-(ferrocenyl)-maleimide (12.10; R = H, n = 0 was found to be the preferred reagent. The method was applicable to the determination of glutathione in biological specimens [201]. A series of fatty acid has been condensed with 3-bromoacetyl-1,1'-dimethylferrocene in the presence of 18-crown-6 and potassium fluoride to give the corresponding esters. The esters were analysed by high performance liquid chromatography with electrochemical detection. This method was shown to be suitable for the determination of fatty acids in human serum [202].

Copper(II) dissolved in thiocyanate solution has been determined by potentiometric titration with ferrocene in ethanol or propanol. The differential determination of iron(III) was carried out in the absence of thiocyanate ion. The method was suitable for the estimation of copper and iron in aluminium base alloys [203]. A method has been devised for the determination of osmium using ferrocene as a reducing agent. The osmium was oxidized to osmium(VIII) and potentionmetrically titrated with a solution of ferrocene [204]. A ferrocene modified platinum electrode has been used for the voltammetric determination of ascorbic acid in natural fruit juices [205].

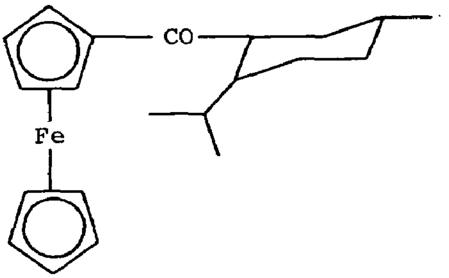
(iv) Biochemical and biological applications

The bio-electrochemistry of redox proteins, including the role of ferrocenes as mediators, has been surveyed by Hill [206]. An amperometric glucose sensor has been developed on the basis of mediated electron transfer between immobilized glucose oxidase and a graphite base electrode. A sensing strategy was provided where entrapped 1,1'-dimethylferrocene, under potentiostatic control, behaved as an alternative electron acceptor to oxygen. Glucose concentrations measured by the sensor in plasma samples showed significant correlations with values measured by a laboratory glucose analyzer [207]. Ferrocene-mediated amperometric glucose microelectrodes have been tested *in vitro* and as subcutaneous implants in pigs. A rapid linear response proportional to concentration was obtained *in vitro* and tissue glucose was related blood glucose [208, 209].

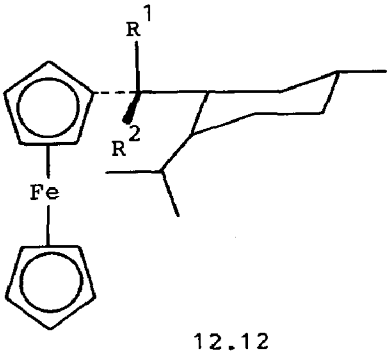
Ferroceneacetic acid has been coupled covalently to glucose oxidase to give a mediator modified enzyme which underwent direct oxidation at an electrode. The modified enzyme showed good reactivity towards glucose, a low overpotential for oxidation and good storage stability [210]. Enzymes have been determined electrochemically by reaction with a substrate that was converted to a mediator and which facilitated the reaction between a redox substrate and a redox enzyme. The redox reaction was measured by a suitable electrode [211]. Enzyme electrodes have been developed using carbon paste or foil compositions containing 1,1'-dimethylferrocene and immobilized enzymes or enzymes held at the carbon electrode by use of a polycarbonate or dialysis membrane. The amperometric ferrocene-mediated electrodes were interfaced to microprocessors to permit computer control of processes [212]. Three bioelectrochemical assays for total cholesterol have been developed in which ferrocene derivatives behaved as mediators of electron transfer between an enzyme and an electrode. In one assay the ferrocenium ion behaved as an electron acceptor from cholesterol oxidase, the ferrocene produced was reoxidized electrochemically. In another assay cholesterol dehydrogenase was used to oxidize cholesterol. The third assay involved the detection of hydrogen peroxide which was formed from the oxidation of cholesterol by cholesterol oxidase in the presence of oxygen. Horseradish peroxidase was used to reduce the hydrogen peroxide and subsequent electron transfer from the electrode to the enzyme occurred via the ferrocene mediator [213].

The use of ferrocenes as electron transfer mediators in electrochemical asssys using enzyme electrodes has been discussed. The assays for glucose, cholesterol and lidocaine were used as illustrations [214]. Pyrolytic graphite electrodes derivatized with organosilyl groups have been used to study protein-electrode interactions. Azurin and cytochrome c were examined in the presence of the redox couples hexaammine ruthenium(III), hexacyanoferrate(III) and ferrocenecarboxylic acid [215]. N-(Phenylboronyl)ferrocenecarboxamide has been used in an electrochemical assay for cis-diols. For example, glycosylated haemoglobin was treated with N-(phenylboronyl)ferrocenecarboxamide, glucose oxidase was added and a cyclic voltammogram was used to construct a calibration curve of current against glucosylated haemoglobin [216]. The oxidation of hydroxyethylferrocene by [2-pyridylmethylbis(2-ethylthioethyl)amine]copper(II) has been the subject of a kinetic investigation in order to determine the effect of the 2-ethylthioethyl ligand on the rate of electron transfer. The sulphur ligand was not found to have any special effect in the enhancement of electron transfer reactivity [217].

The ferrocenyl ketone (12.11) has been converted to chiral ferrocenylalkylamines by reduction to the alcohol, formation of the ferrocenylcarbenium ion, addition of azide and reduction to the primary amine. The amines (12.12; $R^1 = H$, $R^2 = NH_2$, $R^1 = NH_2$, $R^2 = H$) were obtained in this way and were used to form chiral peptide models [218]. The kinetics of oxidation of a high-potential iron-sulphur protein from Chromatium vinsosum by



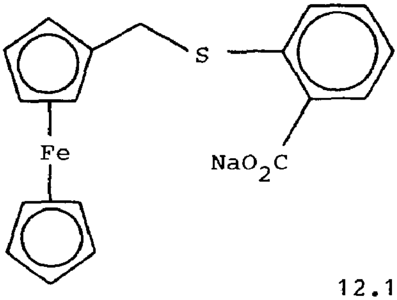
12.11



12.12

the ferrocenium ion, 1,1'-dimethylferrocenium ion, chloromercuriferrocenium ion, hydroxymethylferrocenium ion or the phenylferrocenium ion have been investigated spectrophotometrically at 480 nm. Second order rate constants for protein oxidation were obtained and no rate saturation was observed at high ferrocenium ion concentration [219]. The oxidation of spinach plastocyanin by ferrocenium ions has been the subject of a kinetic investigation in the presence of redox active inhibitors. Electrons appeared to be transferred from two locations on the surface of the plastocyanin. Partitioning of the oxidizing agent between the two sites was determined by the charge on the oxidizing agent, the hydrophobic character of the ligand and the pH of the medium [220].

Direct electrical communication was achieved between the flavine adenine dinucleotide centres of glucose oxidase and carbon, gold or platinum electrodes by the attachment of approximately twelve ferrocenecarboxylic acid groups, via amide links, to each glucose oxidase molecule. More than 50% of the catalytic activity of the enzyme was retained after treatment with ferrocene carboxylic acid [221]. The structure of a 2:1 complex formed between deoxychloic acid, a bile acid, and ferrocene has been investigated by X-ray analysis. The ferrocene was accommodated in the channel of deoxychloic acid as a guest molecule [222]. Two ferrocenyl groups have been linked together through the central germanium atom in a metalloporphyrin. Cyclic voltammetry and electronic absorption spectroscopy have been used to show the ease of oxidation of the complex and delocalization of charge on to the metalloporphyrin bridge [223]. Platinum(II) complexes such as the cation cis-$[Pt(1,1'\text{-diphenylphosphino})ferrocene.X_2]^{2+}$, where X = DMF, DMSO, combined with nucleosides to give 1:1 adducts. The nucleosides appeared to be bonded through N(3) [224].



12.13

The effect of ferrocene, 1,1'-dibenzoylferrocene, 1-benzoyl-1'-[1-phenyl-1-hydroxy-3(1-hydroxycyclohexyl)-2-propynyl]ferrocene and 1-ferrocenyl-1-phenyl-1,3-dihydroxy-4-methyl-2-pentyne on 5'-nucleotidase activity and lipid fluidity in human erythrocyte membranes has been investigated. The ferrocene compounds decreased membrane fluidity and enzyme activity [225]. The effect of the sodium salt of S-(ferrocenylmethyl)thiosalicylic acid (12.13) on the germination and growth of cereal grains and seedlings has been investigated. The salt (12.13) was taken up by the seedlings and used for chlorophyll synthesis. Germination of the seeds, seedling growth and α-amylase activity were inbitited but proteinase, catalase and peroxidase activity were stimulated. The salt (12.13) also exhibited mycostatic activity to the pathogenic fungi Fusarium avenaceum, Mortierella camerdensis and M. humilis [226]. A series of ^{103}Ru-ruthenocene derivatives has been prepared by treatment of the corresponding ferrocene with $^{103}RuCl_3$. The use of the ^{103}Ru-ruthenocenes as radio-diagnostic agents was investigated [227]. The acute toxicity of several substituted ferrocenes has been determined in rats, rabbits and monkeys. Acetylferrocene was the most toxic with an oral LD of <5mg kg^{-1} for female rats and 10-100mg kg^{-1} for monkeys. It was also highly toxic by eye or skin application [228].

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