FERROCENE
ANNUAL SURVEY COVERING THE YEAR 1986*

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1. REVIEWS

In the special issue to mark the appearance of Volume 300 of The Journal of Organometallic Chemistry Schloegl has reviewed recent advances in the stereochemistry of metallocenes. The first part of this excellent review dealt mainly with substituted ferrocenes and the second part with the stereochemistry of (η-arene)tricarbonylchromium complexes [1].

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* Annual survey covering the year 1985 see J. Organometal. Chem., 318 (1987) 231

A volume dealing with ferrocene compounds has been published as part of the 8th edition of the Gmelin Handbook of Inorganic Chemistry [2]. Ernst has reviewed metal-pentadienyl chemistry. The preparation and characterisation of open ferrocenes, half open ferrocenes, open ruthenocenes and related compounds was discussed [3].

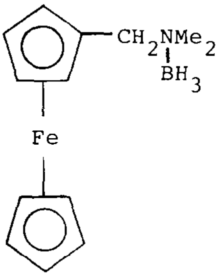
Geiger and Connelly have produced a review entitled "The Electron-Transfer Reactions of Polynuclear Organotransition Metal Complexes". In this review there was a section on sandwich compounds containing linked cyclopentadienyl or aryl groups. This included ferrocenes, ferrocenophanes, biferrocenes and ferrocene containing polymers [4].

Koridze has reviewed the structure and the mechanism of stabilization of ferrocenylcarbocations and related compounds [5]. The polymerization of vinylcyclopentadienyl, isoprenylcyclopentadienyl complexes and ferrocene derivatives has been reviewed by Pittman and Rausch [6]. The role of chiral ferrocenylphosphines in asymmetric synthesis has been surveyed by Sun [7].

The synthesis of optically active allylsilanes by asymmetric cross-coupling using chiral ferrocenylphosphine-palladium complexes as catalysts has been the suject of a survey by Hayashi [8]. The use of ferrocene derivatives as mediators in amperometric enzyme electrodes has been surveyed by Green and Hill [9]. Dombrowski, Baldwin and Sheats have reviewed the role of metallocenes including ferrocene in biochemistry, microbiology and medicine. The review covered three areas, (i) metallocene dihalides as anti-tumor agents (ii) metallocene derivatives as radiopharmaceutical agents and (iii) the general use of metallocenes in biochemistry, microbiology and medicine [10].

2. STRUCTURAL DETERMINATIONS

The crystal and molecular structure of acetylferrocene has been determined by X-ray analysis [11]. The crystal and molecular structure of the borane adduct (2.1) has been determined by X-ray crystallography [12]. 1,3-Diferrocenyl-1,3-butadiene underwent Diels Alder cycloaddition to N-phenylmaleimide to form the adduct (2.2) as a mixture of *endo*- and *exo*-isomers. The crystal and molecular structure of the *endo*-isomer was determined by X-ray crystallography [13].



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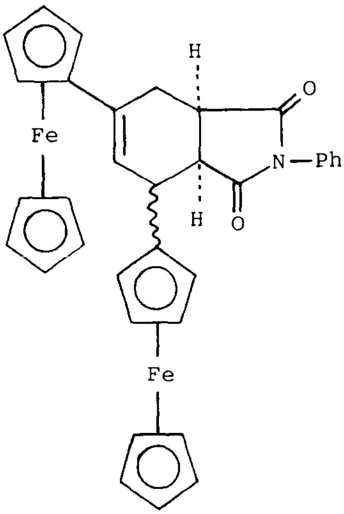

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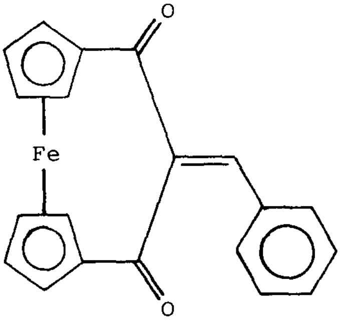
The crystal and molecular structure of 2-benzylidene[3]-ferrocenophane-1,3-dione (2.3) has been determined by X-ray crystallography. The two cyclopentadienyl rings were tilted by 13.57° with respect to one another and staggered by 34.1° [14]. The crystal structure of the ferrocenophane (2.4) has been determined by X-ray analysis. The η-cyclopentadienyl rings were



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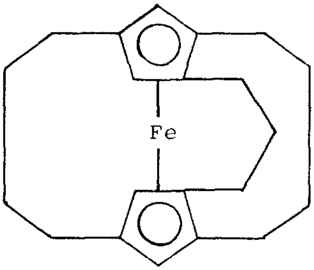

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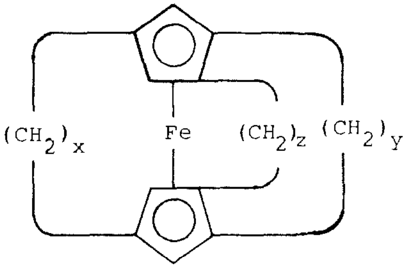

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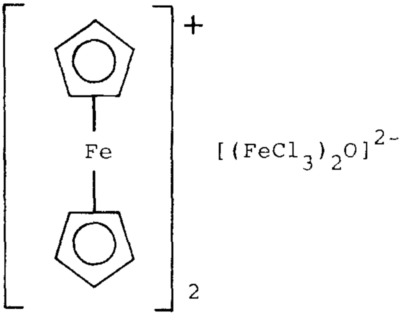
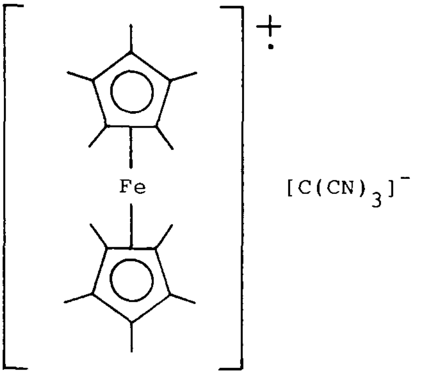
staggered amd the η-cyclopentadienyl-Fe distances were short when compared with those of tetramethylene-bridged ferrocenophanes. The electronic absorption spectra of the ferrocenophanes [2.4 and 2.5 (x,y,z = 3-5)] and the d-d absorption band in the visible region of the spectrum were correlated with the structural parameters [15].

X-Ray crystallography and Moessbauer spectroscopy have been used to characterize the ferrocenium salt formed by treatment of ferrocene with iron(III) chloride as ferrocenium μ-oxo-bis-[trichloroferrate(III)] (2.6) [16]. Carty and co-workers also characterised the salt (2.6) by X-ray crystallography. Thermal analysis of the complex (2.6) demonstrated that degradation in air took place in three successive steps [17].



2.6

The double salt $[(\eta\text{-}C_5H_5)_2Fe]^+[N(CH_2Ph)Et_3]^+[Cl_3FeOFeCl_3]^{2-}$ has been obtained by treatment of $[(\eta\text{-}C_5H_5)_2Fe]_2^+[Cl_3FeOFeCl_3]^{2-}$ with $[N(CH_2Ph)Et_3]_2^+[Cl_3FeOFeCl_3]^{2-}$ and was characterized by X-ray crystallography [18]. The crystal and molecular structure of the ferrocenium salt (2.7) has been determined by single-crystal X-ray analysis at -100°C. There were no cation-anion chains within the structure and the cation was ordered and had the expected bond lengths and angles [19].



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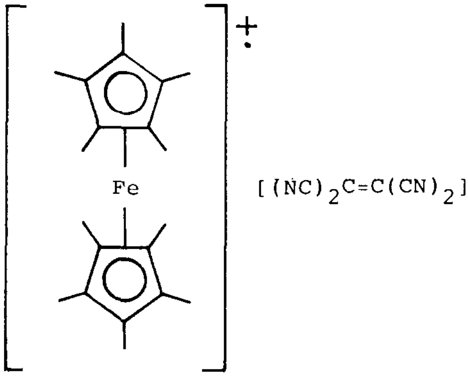

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The salt decamethylferrocenium tetracyanoethylenide (2.8) has been characterized by X-ray crystallography and found to consist of linear chains of alternating cations and anions. Magnetic susceptibility measurements confirmed that it showed predominantly ferromagnetic interactions [20]. The platinum(II) chloride complex of 1,1'-bis(diphenylphosphino)ferrocene has been characterized by X-ray crystallography. The complex was oxidized to the corresponding ferrocenium ion by $NOBF_4$ and it underwent a reversible electrochemical oxidation [21].

Ferrocene vapour combined with solid mercury(II) iodide to form the complex $(\eta\text{-}C_5H_5)_2Fe.7HgI_2$. The crystal structure of this complex has been determined by X-ray crystallography. Ferrocene molecules occupied holes in the cubic lattice formed by Hg and I atoms [22].

3. THEORETICAL STUDIES

The metal-ring distance in ferrocene has been calculated as 1.603Å using a linear combination of Gaussian-type orbitals

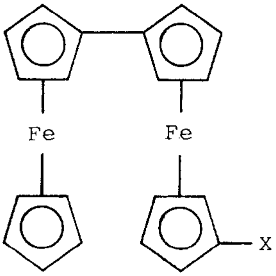
X_α approach. This compared with the experimental value of 1.650 Å [23]. The McConnell relationship has been used to calculate the diamagnetic anisotropy of the carbonyl groups in $M(CO)_3$ fragments, where M = Cr, Mo and W, similar calculations were carried out for ferrocene. The molecules were examined via 500-MHz ^1H NMR [24].

Chistyakov has reported a modification of the 2-dimensional electron-gas model for unsubstituted transition metal sandwich type complexes using the Virial theorem. Relationships between the electronic structures and the carbon-metal distances were given [25]. The average internal bond dissociation energies and the Wiberg parameters were almost constant for a series of bis(η-cyclopentadienyl)- and di(η-benzene)- 3d-transition metal complexes. It was concluded that there was a low ionic contribution to bond stability [26].

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

The Moessbauer spectra of a series of monohalo-biferrocenes (4.1; X = Cl, Br, I) have been recorded. The triiodide salts of the monocations of these biferrocenes showed a trapped valence state for the iron atoms. However, the monocations of the dihalo-biferrocenes (4.2; X = Br, I) showed an averaged valence state in the temperature range 4.2-298 K [27].

A Moessbauer spectroscopic study of the complex $[(\eta\text{-}C_5H_5)_2Fe]^+[(NC)_2C{=}C(CN)O]^-.[(\eta\text{-}C_5H_5)_2Fe]_{\frac{1}{2}}$ indicated that no thermal intervalence electron transfer occurred over the temperature range 80-345 K [28].



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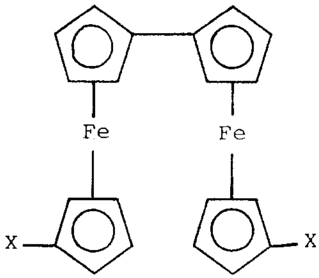

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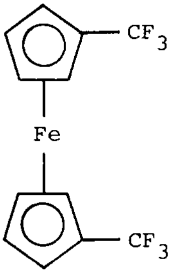
A Moessbauer study has been carried out on ferrocene mixed with human serum albumin, silica gel and Teflon. The sublimation of ferrocene from these mixtures was quicker in the presence of surface bound water molecules and this was accelerated by the presence of sulphate ions in the water [29]. ^{57}Fe Moessbauer spectra have been recorded for a 0.2% solution of 1,1'-diacetylferrocene in 4-octyloxyphenyl-4'-nonylbenzoate liquid crystals. The spectrum consisted of two quadrupole split doublets and it was suggested that some of the 1,1'-diacetylferrocene molecules had interacted chemically with the host 4-octyloxyphenyl-4'-nonylbenzoate [30].

Substituent effects in ferrocenylketones and ferrocene analogues of chalcones have been studied by Moessbauer spectroscopy and electrochemistry. The transmission coefficient of the vinylene group was determined and the effect of the ketone group on the electron distribution in the MO's was discussed [31].

The trifluoromethylcyclopentadienide anion has been treated with iron(II) chloride to give the corresponding 1,1'-bis(trifluoromethyl)ferrocene (4.3) which has been shown by ESCA spectroscopy to have an Fe($2p_{3/2}$) binding energy of 708.6 eV compared with 708.0 for ferrocene. Electrochemical oxidation of the ferrocene (4.3) gave an E° = 0.95 V compared with 0.31 V for ferrocene [32].

The effect of substituents on the electronic structure of a series of 1,1-disubstituted ferrocenes (4.4; R = C_2H_5, OCH_3, CN, $COCH_3$, CO_2CH_3, $OOCCH_3$, CH_2Ph, Ph) has been studied



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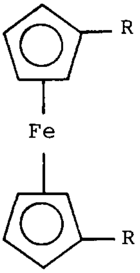

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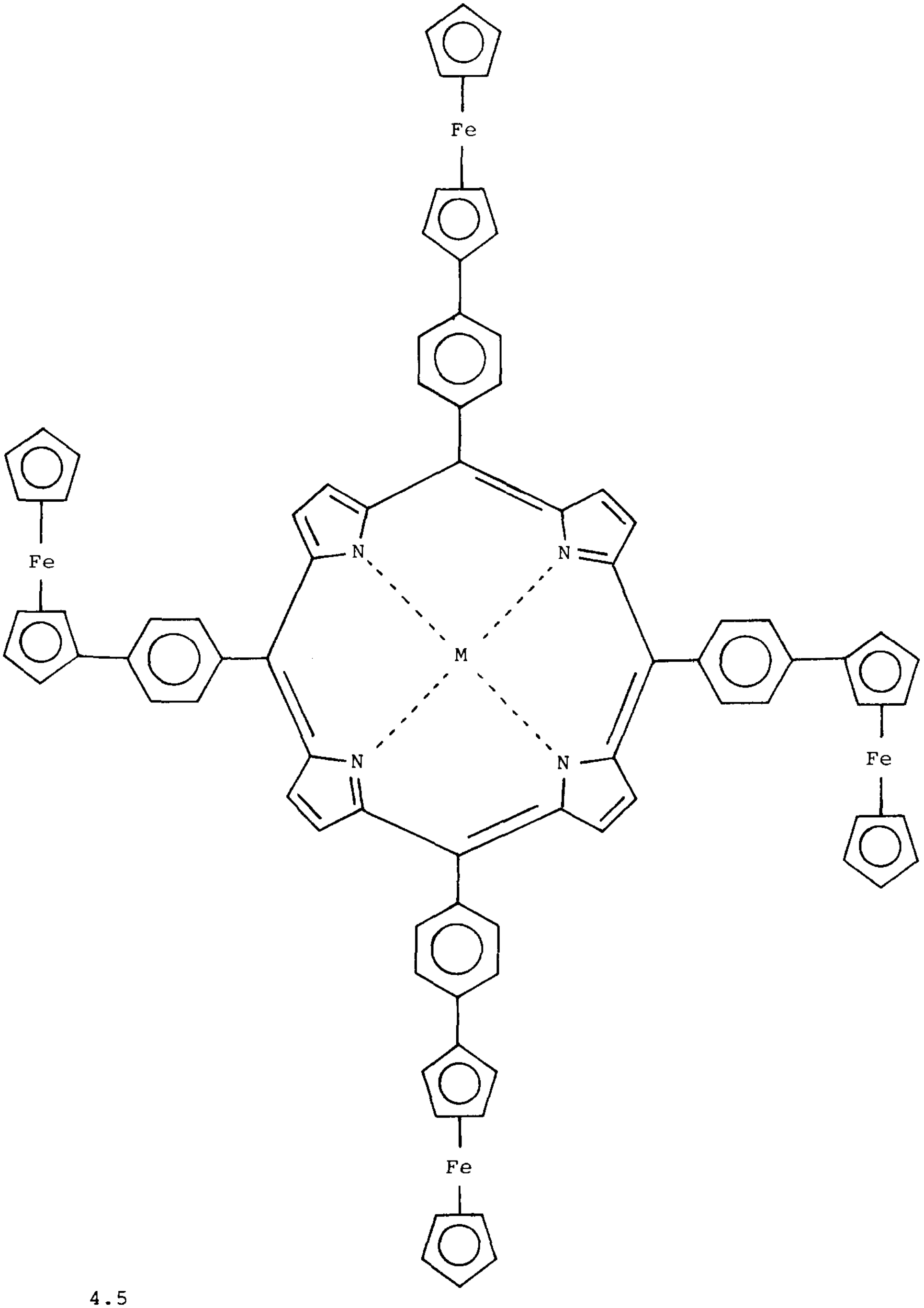
by photoelectron spectroscopy and by CNDO/2 calculations. The energy gap between the $^2\underline{E}_{2g}$ and $^2\underline{A}_{1g}$ ion states was affected only by the $COCH_3$ and CO_2CH_3 substituents. Splitting of the $\underline{e}_{1u}(\pi)$ level due to a reduction of the symmetry was the only effect observed in the photoelectron spectra. There was evidence of strong conjugation between the phenyl and the η-cyclopentadienyl π-orbitals in 1,1'-diphenylferrocene [33].

The photoelectron emission yield spectra for ferrocene solutions have been obtained by simulation calculation by using gas-phase UPS spectra. Comparisons with the experimentally determined spectra indicated that the threshold energy determined for the solution exhibited a narrow first band in the UPS spectrum corresponding to the vertical ionization process [34].

A three-photon dissociation of ferrocene gave atomic iron with an appreciable amount of recoil indicating that the process was nonconcerted and did not preserve a centre of symmetry. Evidence was also offered for dissociation by way of one or more repulsive electronic states [35]. The combined radiation of an excimer laser (248 and 351 nm) and a dye laser in the region 430-452 nm has been used to generate iron atoms by the multiphoton dissociation of ferrocene. State distributions and relative yields were investigated by multiphoton ionization. The amount of energy deposited in the ferrocene molecule before dissociation varied with the use of different wavelengths. Radiation at 248 nm gave iron in a large number of electronic states [36].

Excited iron atoms have been produced by collision of metastable $He(2^3S_1)$ with ferrocene which caused dissociative excitation of the metallocene. Analysis of the emission spectra of the excited iron atoms gave electronic-state distributions which were interpreted statistically to allow energy partitioning between the metal and the ligands. It was considered that the dissociative states were formed by electron rearrangement in the transient excited states of ferrocene produced by collision with $He(2^3S_1)$ [37].

The electronic absorption spectra of a series of arylferrocenes and the arylferrocenium pentacyanopropenide salts have been recorded. A Hammett correlation of the λ_{max} for the d-d transition bands of arylferrocenes was obtained only with strongly electron-withdrawing substituents. A good correlation



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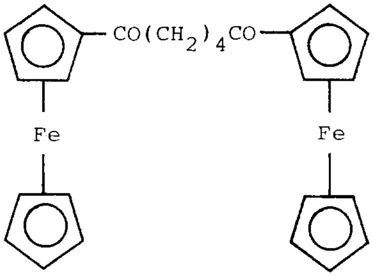
of λ_{max} with σ^+ constants was obtained for the arylferrocenium salts. The λ_{max} values also correlated well with the $E_{\frac{1}{2}}$ oxidation potentials measured via cyclic voltammetry [38].

The photoelectrochemical behaviour of n-SnS_2 has been investigated in aqueous methyl cyanide containing either ferrocene or thianthrene [39]. The ferrocenylphenylporphyrins (4.5; M = Hg, Zn) have been prepared and characterized by fluorescence and phosphorescence spectroscopy. Controlled potential oxidation of the porphyrins (4.5) gave the corresponding tetraferrocenium ion [40].

Doubly charged ion mass spectrometry has been applied to the examination of doubly charged ions produced by electron impact ionization of the metallocenes $(\eta\text{-}C_5H_5)_2M$, where M = Mn, Fe, Co, Ni. The ferrocene and cobaltocene spectra consisted of a single intense peak formed from the reactions of molecular doubly charged $[(\eta\text{-}C_5H_5)_2Fe]^{2+}$ and $[(\eta\text{-}C_5H_5)_2Co]^{2+}$ respectively [41]. The mass spectra of some dinuclear ferrocene derivatives, for example, the ketone (4.6) have been recorded and interpreted. Many of the fragmentation pathways originated in cleavages of the ferrocenyl groups [42].

The ionization potentials of gaseous ferrocene and symmetrically substituted chloroferrocenes have been measured by electron impact techniques. The ionization potentials increased as the number of chloro substituents increased and from the results it was concluded that the degree of overlap of the π-ring orbitals and the metal d- orbitals also increased [43].



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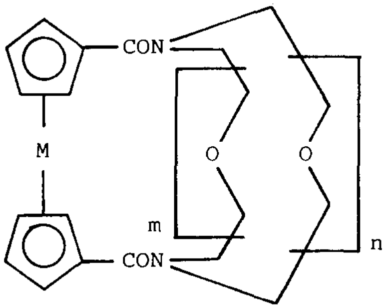
A dielectric relaxation study of 1,1'-diacetylferrocene in benzene and carbon tetrachloride has permitted the dipole moment and relaxation time at the microwave frequency to be determined. The contributions of several factors to the molar volume were obtained, information on the macroscopic isotropic characteristics and on solute-solvents interactions were calculated [44].

The ^{13}C NMR chemical shifts for 1,1'-diformyl- and 1,1'-dihydroxymethyl-ferrocene have been measured, assigned and compared with values calculated by the INDO method. A good correlation between experimental and theoretical values was obtained [45]. Self-diffusion, overall rotation of molecules and cyclopentadienyl ring rotation in the three phases of solid formylferrocene has been investigated by ^{1}H NMR spectroscopy and differential thermal analysis. Formylferrocene formed a rigid lattice at 77 K while above 130 K C_5 reorientation of the cyclopentadienyl rings about the C_5 axis was observed. Above 317 K in the plastic phase, the uniaxial as well as the overall rotations and self-diffusion of the molecule as a whole were observed [46].

^{1}H NMR studies have been carried out on the structural phase transitions and the molecular dynamics of the five-membered rings in solid ferrocene, azaferrocene and ruthenocene. The solid state properties of each phase detected and the mechanism of the phase transitions were discussed in relation to the ring dynamics [47].

The fluxional behaviour of the cryptands (4.7; M = Fe, n and m = 1, 2, 3, M = Ru, n = m = 2) has been studied by ^{1}H



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and ^{13}C NMR spectroscopy. These molecules exhibited restricted rotation about the Fe-CO-N bond system and the activation parameters for this process were determined [48].

Ferrocenes with long alkyl chain substituents bearing hydrophilic amide or ester groups were spread as monolayers on water and studied by pressure-area isotherms. Phase transitions from expanded to condensed monolayer forms were detected and it was considered that the conformation and packing of the ferrocene groups was dependent on the long-chain substituents present and on the phase state of the monolayers. The films showed high conductivity, a dielectric constant of 2.9 and an ionization potential of 5.3 eV [49].

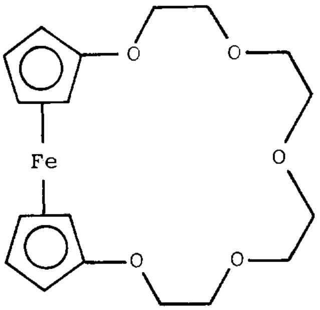
The adsorption of ethyl- and butyl-ferrocene on quartz, pyrolytic iron and pyrolytic chromium has been investigated at 100-224°. Physical adsorption occurred at high surface coverage on all the surfaces and charge-transfer complexes were formed at low surface coverage on the pyrolytic iron [50].

5. ELECTROCHEMISTRY AND PHOTOSENSITIVE ELECTRODES

The electrochemical oxidation of ferrocene, hydroquinone, catechol and N,N,N',N'-tetramethyl-p-phenylenediamine has been investigated at thin polypyrrole film electrodes via cyclic voltammetry and chronoamperometry. The results indicated that the polymer film was fairly porous and that there was an efficient conduction mechanism operating in the polypyrrole film [51].

The half-wave potentials have been determined for series of 2-ferrocenylimidazoles, 2-ferrocenylbenzimidazoles and 2-(ω-ferrocenylalkyl)benzimidazoles with a vibrating platinum electrode in a supporting electrolyte. The structures of the molecules significantly affected the half-wave potentials and the Taft parameters were calculated [52].

One-electron oxidation of 3-ferrocenylpropanoate, 4-ferrocenylbutanoate and 5-ferrocenylpentanoate gave the corresponding ferrocenium zwitterions. Rate constants have been measured for the reaction between these zwitterions and the hydrated electron to give values close to 3×10^{10} dm^3 mol^{-1} s^{-1}. These values indicated that the reactions were diffusion controlled as were the corresponding reactions for complexes formed between iron(III) and inorganic ligands [53].



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The electrochemical oxidation of pentaoxa[13]ferrocenophane (5.1) has been investigated. The addition of alkali metal cations to the solution of the ferrocenophane (5.1) caused a positive shift in the half-wave potential. This shift reflected an abrupt decrease in metal binding by the ferrocenium species as compared with that of the parent ferrocenophane (5.1) [54].

The electrochemical behaviour of ferrocenylamines has been investigated. Triferrocenylamine, with almost planar geometry around the nitrogen atom, had three reversible oxidation waves, the first of which was 0.31 V negative of the oxidation potential of ferrocene. From the results it was concluded that the resonance interaction between the ferrocenyl group and the lone pair of electrons on the nitrogen atom was an important factor in the electrochemical oxidation of the ferrocene moiety [55].

The cyclic voltammetric behaviour of the ferrocene/ferrocenium ion couple in methyl cyanide has been studied in the absence of an added electrolyte using a platinum wire quasi-reference electrode. At slow scan rates the usual sigmoidal shaped steady-state voltammograms were obtained on the forward oxidation scan but on the reverse reductive scan the voltammograms were not strictly sigmoidal and exhibited small peaks. This latter phenomenon was not found in the presence of an electrolyte and was attributed to ionic migration of the ferrocenium ion [56].

The alternating current voltammetry of ferrocene in methyl cyanide has been studied using carbon fibre microelectrodes [57].

The electrochemical oxidation of ferrocene on platinum has been investigated in a series of nonaqueous solvents. In some solvents slow decomposition of the ferrocenium ion occurred within the time scale of the cyclic voltammograms [58]. The behaviour of ferrocenium electrodes in the presence of molecular oxygen has been investigated [59].

The behaviour of electrodes based on ferrocene derivatives in the three component solutions, $NaBF_4$ - $PhSO_3Na$ - H_2O and NaCl - $PhSO_3Na$ - H_2O, has been examined [60]. The formal potentials of the ferrocene-ferrocenium ion system have been measured by cyclic chronovoltammetry at platinum and glassy-carbon electrodes in aqueous-organic solutions. The cathodic peak current varied with the concentration of the organic solvent and this variation was attributed to changes in the solution viscosity and, hence, the diffusion coefficient of the ferrocenium ion [61].

Cyclic chronovoltammetry has been used to examine the ferrocene-ferrocenium couple as a reference electrode in non-aqueous and mixed aqueous-organic solutions. The potential was independent of the solvent and the nature of the supporting electrolyte [62]. The ferrocene-ferrocenium reference electrode in aqueous ethanol containing HCl has been studied in the temperature range 10-60 °C by measurement of equilibrium potentials and by the method of anodic and cathodic polarization. The electrode reaction was reversible in oxygen-free solutions at $\geqslant$20 °C [63].

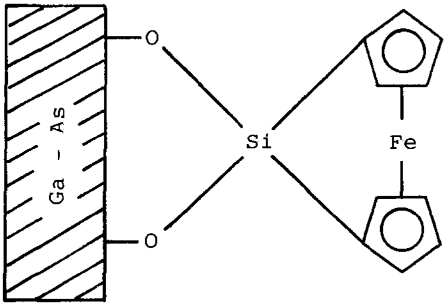
The ferrocene-ferrocenium couple has been used to make voltammetric comparisons between fluorinated vitreous carbon electrodes and freshly polished vitreous carbon electrodes [64]. The construction and characteristics of a full edge current flow thin-layer electrochemical cell that uses both internal (real) and external (auxiliary) references points has been described. When this cell was used for the ferrocene/ferrocenium ion couple, symmetrical cyclic voltammograms with negligible peak to peak separations were obtained at low scan rates in organic solvents [65].

In an electrochemical investigation cyclic voltammetry was studied at a band electrode and the relevant diffusion-electrochemical equations were evaluated via digital simulation. The simulated results agreed with voltammograms obtained for the oxidation of ferrocene at a band electrode [66]. Data for the cyclic voltammetry of ferrocene in dimethylacetamide has been used as an example to demonstrate the use of computer control in practical electrochemistry [67].

Ferrocene in methanol-tetrabutylammonium tetrafluoroborate has been studied with an instrument which performed oxidative and reductive single pulse coulostatic analysis [68]. n-Gallium-arsenide has been treated with (1,1'-ferrocenediyl)dichlorosilane to give the derivatized material (5.2). Surface attachment of ferrocene was verified by cyclic voltammetry under photoexcitation. The photoluminescent properties of the derivatized gallium arsenide surface were investigated [69].

The photoelectrochemistry of systems based on contacts between n-type silicon photoelectrodes and ferrocene-ferrocenium ion or iodine-iodide ion redox systems in polyethylene oxide have been investigated [70]. The electrocatalytic properties of poly(vinylferrocene) film electrodes have been investigated. The concentration of the electrolyte, the solvent and the thickness of the polymer film were all shown to be important [71].

The effect of ultraviolet radiation on polymerized vinylferrocene film electrodes has been investigated. Irradiation increased the peak current and the effects of film thickness, irradiation time and electrode position in the solution were also studied [72]. Transfer of an organized monolayer film of (ferrocenylmethyl)dimethyloctadecylammonium hexafluorophosphate on aqueous sodium sulphate to a hydrophilic gold electrode gave



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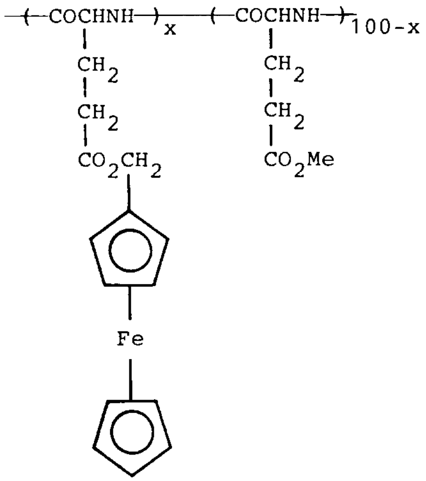
a "head-down" orientation of the polar head group on the electrode. Cyclic voltammetry of electrodes coated with monolayers in this way was studied for the effect of increasing transfer pressure [73].

The vinylferrocene-N-vinylcarbazole copolymer has been coated on a glassy carbon electrode by electrodeposition of the copolymer in the oxidized form. Cyclic voltammetry was used to examine the characteristics of the electrode. It was concluded that extensive cross-linking within the copolymer inhibited electron self-exchange between the ferrocene residues, restricted charge transfer through the polymer coating and suppressed diffusion of the counter ions [74].

When a current was passed through a dichloromethane solution containing tetrabutylammonium perchlorate and poly(vinylferrocene) an electroconductive film was deposited on one of the platinum electrodes [75]. The electrochemical behaviour of a gold-poly(vinylferrocene) electrode has been studied in sulphuric acid containing hydrochloric acid labelled with ^{36}Cl. Distorted cyclic voltammograms were obtained [76].

The effect of the nature and the concentration of counterions on the electrochemistry of poly(vinylferrocene) film electrodes has been studied. The changes in the peak potentials and currents with the nature and concentration of the counterions was explained in terms of salt formation between the ferrocenium ion and the counterions as well as the polyelectrolyte behaviour of the surface layer [77].

Glassy carbon electrodes coated with poly(vinylferrocene) have been used for the electrocatalytic oxidation of ascorbic acid. The catalytic peak currents were proportional to the concentration of ascorbic acid over the range $6 \times 10^{-2} - 6 \times 10^{-6}$ mol/dm^3 [78]. Copoly(γ-ferrocenylmethyl-L-glutamate/γ-methyl-L-glutamate) (5.3; x = 13, 45, 100) has been prepared by an ester exchange reaction of poly(γ-methyl-L-glutamate) with ferrocenylmethanol. The ferrocenyl containing polymers were cast onto a platinum minigrid sheet. Cyclic voltammetric studies of the cast films showed that the ferrocenyl groups underwent reversible oxidation-reduction. The permeability of the polypeptide films (5.3) was reversibly controlled by the electrochemical oxidation-reduction of the ferrocenyl groups [79]. The electrochemical transport of sodium ion across a dichloromethane



5.3

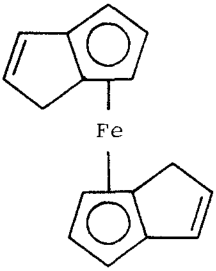
membrane containing pentaoxa[13]ferrocenophane (5.1) has been reported. It was concluded that electrochemically switched cation transport of this type was an efficient method for the conversion of electrical energy into a chemical concentration gradient [80].

The permeability of films of polycationic poly[tris(4-methyl-4'-vinyl)-2,2'-bipyridine)ruthenium] to ferrocene, ferrocenium ion, tetracyanoquinodimethane (TCNQ) and $TCNQ^-$ was measured in an Et_4NClO_4 electrolyte in methyl cyanide. The permeabilities varied with electrolyte concentration [81]. The cationic surfactant (11-ferrocenylundecyl)trimethylammonium bromide in an anionic micellar solution has been examined by cyclic voltammetry. It was concluded that the ferrocenyl residue incorporated in the micelle was active electrochemically in the presence of electrolytes but inactive in their absence [82].

The properties of ferrocene derivatives adsorbed on a high-order pyrolytic graphite (HOPG) electrode have been studied. The first- and second-order ferrocenium decay kinetics for several acetophenone, cyclohexanone and phenylphosphine derivatives of ferrocene on HOPG have been determined [83].

6. PREPARATIONS OF FERROCENES

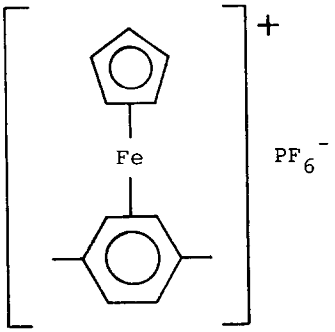
Lithiation of 1,5-dihydropentalene with n-butyllithium followed by treatment with iron(II) bromide produced the ferrocenophane (6.1). The ^1H and ^{13}C NMR and ultraviolet spectra of this compound were recorded together with the ESR spectrum of its cation [84].



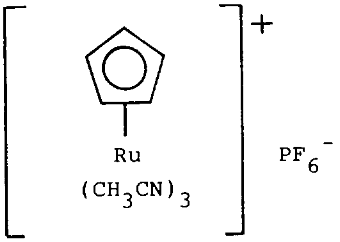
6.1

The reaction of the isodicyclopentadienide anion with bis-(2,4-pentanedionato)dipyridineiron(II) or ruthenium(III) chloride produced the corresponding metallocenes via exo-complexation of the ligands. The treatment of 4-(dimethylamino)isodicyclopentafulvene with the hexafluorophosphates (6.2 and 6.3) produced the corresponding metallocenes which were isolated as mixtures of the exo- and endo-isomers (6.4 and 6.5; M = Fe, Ru) after alkaline hydrolysis. The structure of the ether (6.6) was determined by X-ray analysis. This ether was obtained from the alcohol formed by reduction of the exo-isomer (6.4; M = Fe) [85].

Sodium cyclopentadienide combined with the esters $CH_3CO_2C_2H_5$, $PhCO_2Me$ and $MeO_2CCH_2CH_2CO_2Me$ in the presence of iron(II) chloride to produce 1,1'-diacetyl- and acetyl-ferrocene, 1,1'-dibenzoylferrocene and 1,1'-bis(β-carbomethoxypropionyl)ferrocene respectively [86]. Treatment of the helical hydrocarbon (6.7) with t-butyllithium followed by iron(II) chloride produced the optically active ferrocene (6.8; M = Fe) in good yield. When



6.2



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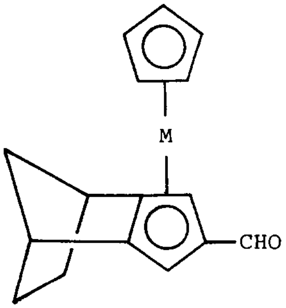

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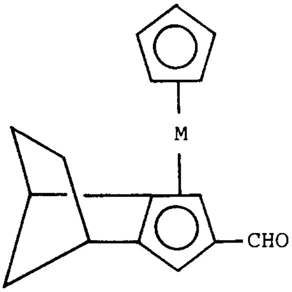

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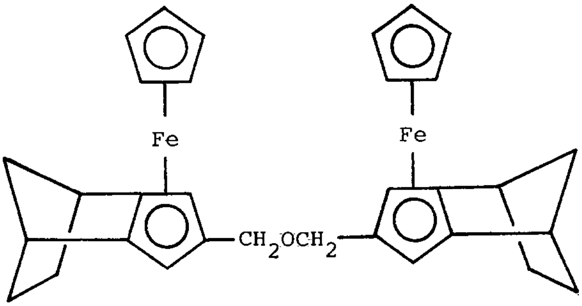

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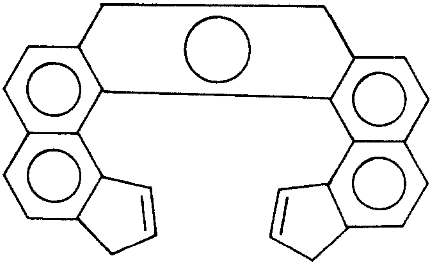

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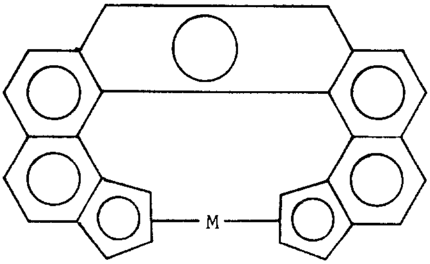
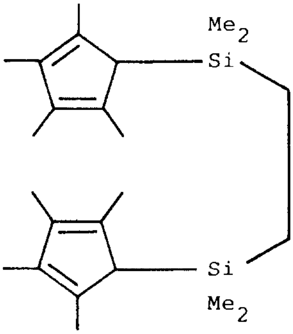


6.8

cobalt(II) bromide was used instead of the iron salt the analogous cobaltocenium hexafluorophosphate (6.8; M = $Co^+PF_6^-$) was obtained [87].

The cyclopentadiene (6.9) has been dilithiated and then treated with the metal halides MCl_2, where M = Fe, Ge or Sn, to produce the corresponding η-tetramethylcylopentadienyl compounds (6.10; M = Fe, Ge, Sn) [88]. The phosphacyclopentadienyl anions (6.11; R = H, Me, Ph; M = Li, K) removed the η^6-1,3,5-$Me_3C_6H_3$ group from the salt $[(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)(\eta\text{-}C_5H_5)Fe]PF_6$ to give the corresponding monophosphaferrocenes (6.12) [89].



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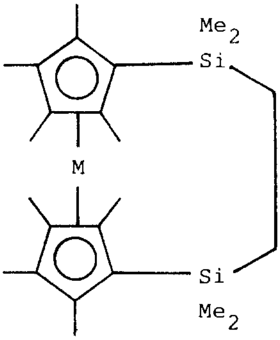
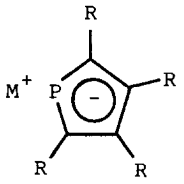
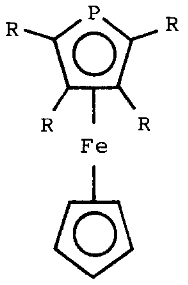


6.10

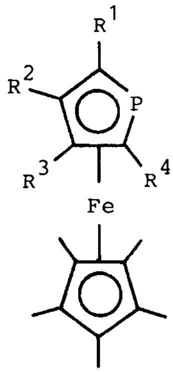
Nucleophilic attack of a metastable (η-cyclopentadienyliron) acetylacetonate by suitable phospholyl anions gave the phosphaferrocenes (6.13; $R^1 = R^2 = R^4 = H$, $R^3 = Me$; $R^1 = R^4 = H$, $R^2 = R^3 = Me$; $R^1 = R^2 = R^3 = R^4 = Ph$). Oxidation to the corresponding phosphaferrocenium ions has been investigated by cyclic voltammetry and one phosphaferrocene (6.13; $R^1 = R^2 = R^3 = R^4 = Ph$) has been characterized by X-ray crystallography [90].



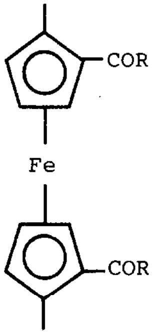
6.11



6.12



6.13



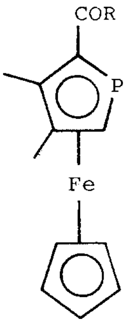
6.14

Electrolysis of methylcyclopentadiene with iron gave 1,1'-dimethylferrocene which underwent acylation with acetyl chloride to form the tetrasubstituted ferrocene (6.14; R = Me). Subsequent condensation with ethyl acetate gave the tetraketone (6.14; $R = CH_2COMe$) which formed complexes with Co(III), Ni(II), Pd(IV), Pt(IV), Ce(III) and Ce(IV) cations [91].

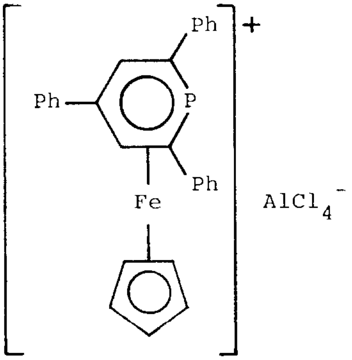
UV Irradiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ gave ferrocene with the loss of carbon monoxide. Low temperature irradiation allowed a monocarbonyl intermediate to be isolated [92].

7. REACTIONS OF FERROCENE

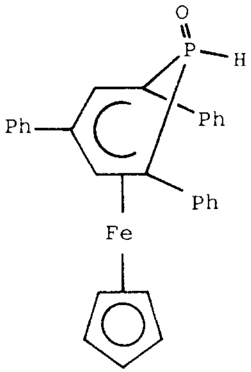
Friedel-Crafts acylation of 3,4-dimethylphosphaferrocene using F_3CSO_3H as an acid catalyst gave good yields of the 2-acetyl and 2-benzoyl derivatives (7.1; R = Me, Ph). Diphosphaferrocenes and ferrocenes were alkylated in the same way [93]. The ligand exchange of ferrocene with 2,4,6-triphenylphosphabenzene in the presence of aluminium chloride afforded the cationic complex (7.2) as a transient intermediate which was attacked by water



7.1



7.2

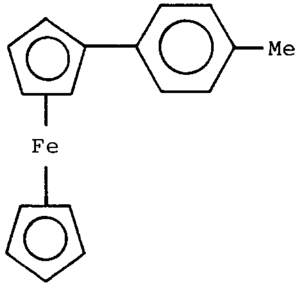


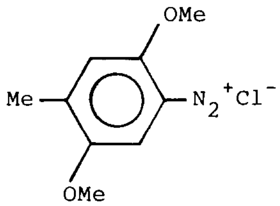
7.3

to produce the secondary phosphine oxide complex (7.3). The reactions of this latter compound were investigated [94]. The reaction of ferrocene with the arenes benzene, mesitylene, hexamethylbenzene or napthalene in the presence of aluminium chloride under an atmosphere of carbon dioxide produced the corresponding cation $[(\eta^5\text{-}C_5H_4CO_2H)Fe(\eta^6\text{-arene})]^+$ with a carboxylic acid substituent [95].

Hydrogenation of polyaromatics in the ligand exchange with a cyclopentadienyl ring of ferrocene has been investigated. Ligand exchange with substituted benzenes, napthalene and anthracene was discussed [96]. Treatment of ferrocene with carbonyl compounds in strongly acidic media produced α-ferrocenyl carbonyl compounds via the corresponding α-ferrocenylcarbenium ions. In this reaction 1,1'-dimethylferrocene was more reactive than ferrocene and substitution at the 2-position was favoured with sterically small electrophiles [97].

Ferrocene has been attacked by electrophilic reagents such as dioxane, sulphur trioxide, acetyltetrafluoroborate and mercury trifluoroacetate to give the ferrocenium cation as the major product [98]. Reaction of the benzene diazonium salt $\underline{p}$-$MeC_6H_4N_2X$ with ferrocene produced the corresponding substituted ferrocene (7.4). Treatment of this compound with the diazonium salt (7.5) gave the 1,1'-disubstituted ferrocene (7.6). Oxidation of the disubstituted ferrocene (7.6) with BBr_3 and Ag_2O produced the





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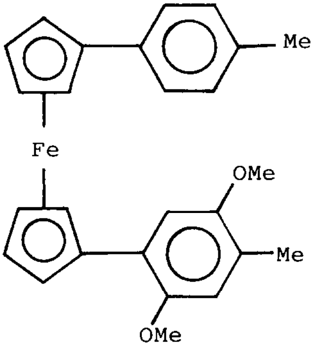
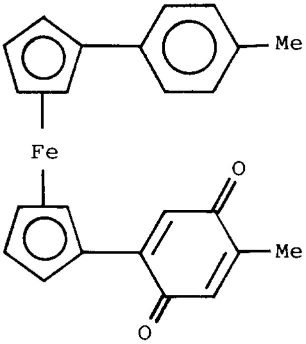


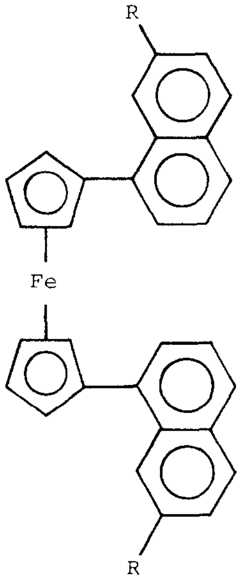


7.6

7.7

quinone (7.7) [99]. Arylation of ferrocene with the diazonium salt obtained from 8-aminonaphthalene-2-carboxylic acid produced the 1,1'-disubstituted ferrocene (7.8; R = CO_2H). This acid was converted to the aldehyde (7.8; R = CHO). Reductive coupling of the aldehyde with $TiCl_4$-Zn produced an unsaturated naphthaleno-ferrocenophane which was catalytically hydrogenated to give the corresponding ferrocenophane (7.9) [100].

Hydrogenolysis of ferrocenes under mild conditions, 10% Pd/C in acetic acid-perchloric acid or trifluoroacetic acid, produced the corresponding cyclopentanes [101]. Ferrocene formed an intercalation compound with the layer species $CdPS_3$. Moessbauer spectroscopy indicated that the ferrocene was ionized and three



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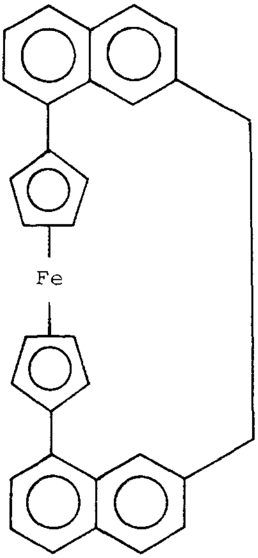


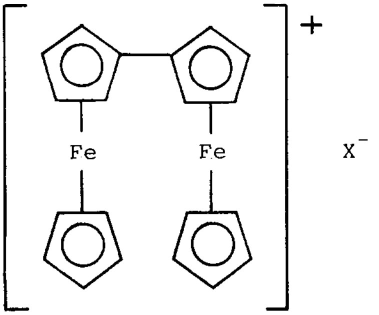
7.9

ferrocene moieties were detected each with a different extent of ionization. Differences in the ferrocene moieties were explained in terms of different environments provided by the host lattice [102].

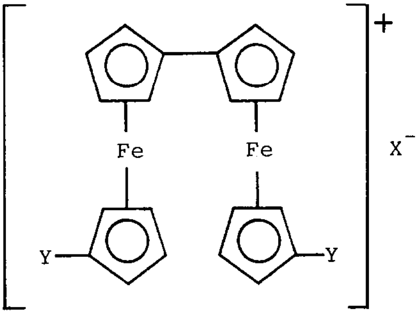
8. FERROCENIUM SALTS AND MIXED-VALENCE SALTS

The effect of changing the anion, X^- from $X = I_3$ to $X = I_2Br$, IBr_2 and PF_6 on the rate of intramolecular electron transfer in the mixed-valence biferrocenium salt (8.1) has been studied by EPR spectroscopy and Moessbauer spectroscopy. Powder X-ray diffraction showed that the three salts (8.1; $X = I_3$, I_2Br, IBr_2) were isostructural, however the Moessbauer results showed that electron transfer effects were shifted to much lower temperatures on moving from the I_3^- anion to the I_2Br^- anion. The importance of cation-cation and cation-anion interactions were discussed and a qualitative model was used to interpret the effect of anion replacement [103].

Substitution in the ferrocene residues of the biferrocenium salts (8.2; $X = I_3$, $Y = H$, Cl, Br, I; $X = Br_2I$; $Y =$ Cl, Br, I) with halogens also caused changes in the rate of electron transfer. An important factor was the packing arrangement in the solid state [104].



8.1

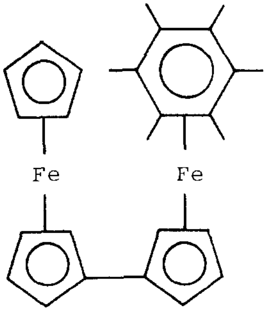


8.2

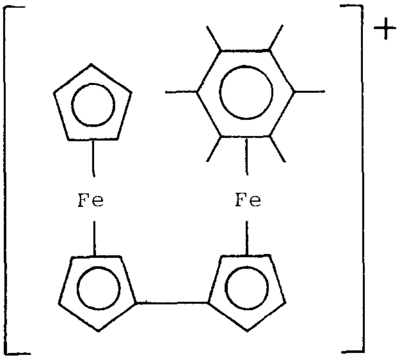
Biferrocene and several coupled, bridged ferrocenes have been prepared and evaluated as intervalence electron-transfer species in the form of the mixed-valence cations. Electrochemical, electronic and EPR studies have indicated that the inductive effects of substituents were more important than structural distortions caused by two-carbon and three-carbon bridges in determining the properties of the ferrocenophanes [105].

The ferrocenium, biferrocenium and 1',1'''-dihalobiferrocenium iodides have been studied by ^{129}I Moessbauer spectroscopy. Results for the mixed-valence biferrocenium iodides indicated that the rate of intramolecular electron transfer was dependent on the cation moiety in the solid state [106]. A Moessbauer and molecular orbital study of the mixed-valence iron complexes (8.3 and 8.4) has been carried out. The Moessbauer spectrum of complex (8.3) indicated that there were two types of iron atom present and hence this was a localized mixed-valence compound. The Moessbauer spectrum of complex (8.4) showed that the iron atoms were the same and it was concluded that this compound was a delocalized mixed-valence complex [107].

Reactivity of the charge transfer complex ferrocene:tetracyanoethene has been investigated. Various products were obtained depending on the reaction conditions including ferrocenium pentacyanopropenide, tricyanovinylferrocene and cyanoferrocene. Intervalent interaction of the iron centres in the mono-oxidized form of 1,2-diferrocene-1,2-diphenylethene (8.5) was found to be more effective than in similar biferrocene compounds. The



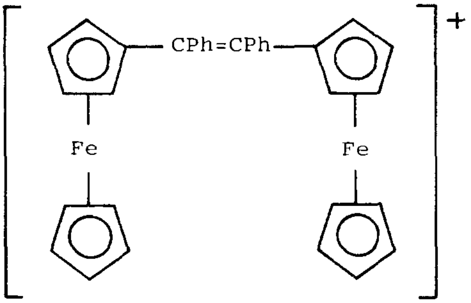
8.3



8.4

crystal and molecular structure of the species (8.5) indicated that the ferrocenyl groups were held in positions that maximized electron delocalization [108].

The structures of the mixed-valence 1',6'-diiodobiferrocenium triiodide (8.2; Y = I, X = I_3^-) and [1',6'-dichlorobiferrocenium]$^{2+}$(octaiodide)$^{2-}$ have been determined by X-ray analysis. The X-ray structural data was considered together with the variable-temperature ^{57}Fe Moessbauer, EPR and infrared spectra in an attempt to rationalize the rates of intramolecular electron transfer in these compounds. The different rates were attributed to differences in the symmetry of the solid-state environments [109].

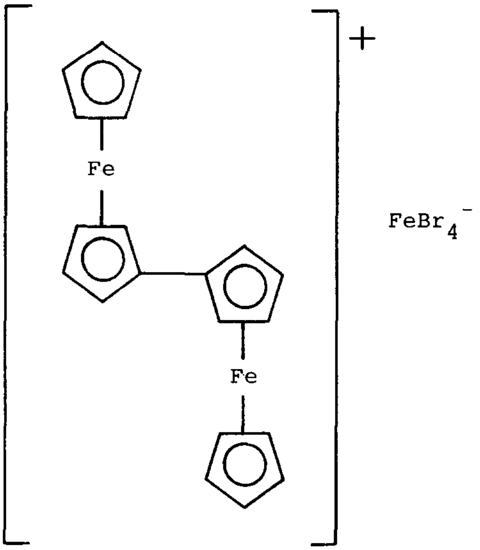


8.5

Biferrocenium tetrabromoferrate (8.6) has been characterized by X-ray crystallography. The cation adopted a trans-configuration but possessed no crystallographically imposed symmetry relating the two ferrocenyl environments. The Fe-ring distances at the two environments were typical of trapped Fe(II) and Fe(III) oxidation states [110].

Electron transfer has been investigated in mixed-valence cations derived from biferrocenes [111]. The crystal structures of dibutylbiferrocenium triiodide and iodotetramethyl[2]-ferrocenophanium triiodide have been investigated at 150,298 and 363 K. X-ray analysis at 298 K indicated that there were two types of iron atom present: 85% of the iron was bonded to iodide ions at 2.64 Å and 15% of them were Fe(III). These compounds were also investigated via Moessbauer spectroscopy [112].

The ferrocenium salts $[(\eta\text{-}C_5H_5)_2Fe]X$ ($X = BF_4$, PF_6, SbF_6) have been used as one electron oxidizing agent for the metallocenes $M(\eta\text{-}C_5H_5)_2$ (M = Cr, Co, Ni) and $Cr(\eta\text{-}C_6H_6)_2$. The corresponding cationic complexes $[M(\eta\text{-}C_5H_5)_2]BF_4$ and $[(\eta\text{-}C_6H_6)_2Cr]BF_4$ were obtained in almost quantitative yield. The metal-metal bond



8.6

in the dinuclear complexes $[(\eta\text{-dienyl})M(CO)_n]_2$ [M = Mo (n = 3); Fe (n = 2); Ni (n = 1)] and $Co_2(CO)_8$ was also cleaved by the ferrocenium cation to form cationic compounds [113].

Increasing methyl substitution of ferrocene caused an increase in the yield of ferrocenium ion on oxidation with sulphuric acid under dry argon. Di-, tetra-, hexa-, octa- and deca-methylferrocenium ions were isolated as the hexafluorophosphates [114]. Butyl- and propyl-ferrocenium cations have been used as substrates in the Belousov-Zhabotinskii reaction [115].

Electronic, infrared, Moessbauer and electron spin resonance spectroscopy have been used to show that the salts obtained by treatment of decamethylferrocene or cobaltocene with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) contain the $[DDQ]^{\dot{-}}$ radical anion rather than the $[DDQH]^-$ benzohydroquinone anion as had been previously suggested [116].

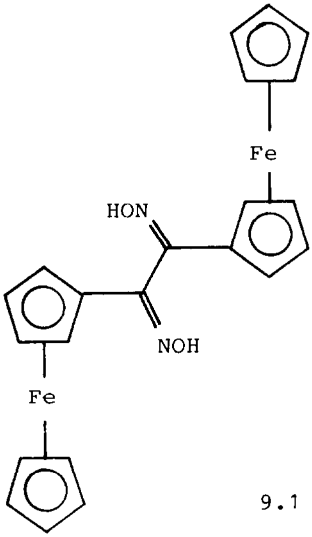
Ferrocenium tetrafluoroborate combined with nickelocenium tetrafluoroborate to form a macromolecule $\{[(C_5H_5)_2Fe(II)(C_5H_5)_2^- Ni(IV)](BF_4)_2\}_n$ for which a stacked structure was discussed. This may have consisted of alternate ferrocene and nickelocene residues in a single chain or parallel chains made up of ferrocene groups and nickelocene groups [117].

9. FERROCENE CHEMISTRY

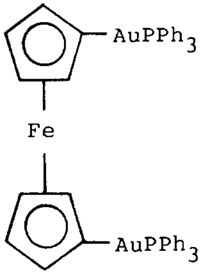
(i) Derivatives containing other metals (metalloids)

Lithioferrocene combined with anti-dichloroglyoxime to form diferrocenylglyoxime (FGOH) (9.1) which formed complexes with a metal:ligand ratio of 1:2. Several complexes were characterized with the stoichiometry $(FGO)_2.M(II)$, where M = Ni^{2+}, Pd^{2+}, Pt^{2+} and $(FGO)_2.ML_2$, where ML_2 = $[Co(III)Cl.py]^{2+}$, $[Pt(IV)Cl_2]^{2+}$ [118].

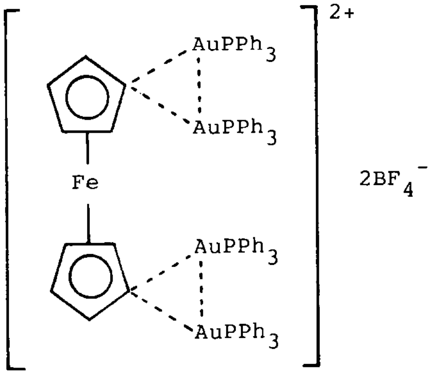
Lithiated ferrocene combined with $ClAuPPh_3$ to form the organogold compound (9.2) which was converted to the tetragold salt (9.3) with $[Ph_3PAu]^+BF_4^-$ [119]. 1,1'-Dilithioferrocene combined with sulphur to give the ferrocenophane (9.4) which was attacked by $[Ph_3PAu]^+BF_4^-$ to form $[(Ph_3PAu)_3S]^+BF_4^-$. Ferrocene-1,1'-dithiol was also prepared [120]. Reaction of $WOCl_4$ with three molar equivalents of ferrocenyllithium produced the triferrocenyl complex (9.5; X = Cl). The corresponding methoxide (9.5; X = OMe) was obtained by treatment of this


Fe
HON
NOH
Fe

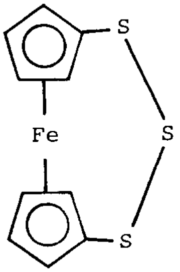
9.1


AuPPh3
Fe
AuPPh3

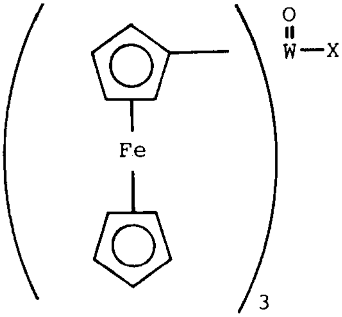
9.2


AuPPh3
AuPPh3
Fe
AuPPh3
AuPPh3
2+
2BF4−

9.3


S
Fe
S
S

9.4

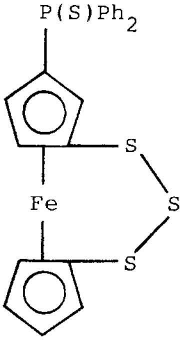

Fe
3
O
W—X

9.5

complex with potassium methoxide. Treatment of $WOCl_4$ with a sixfold excess of ferrocenyllithium gave a mixture containing the tetraferrocenyl compound (9.5; X = O-ferrocenyl) and the triferrocenyl complex (9.5; X = Bu). X-Ray crystallographic analysis of the tetraferrocenyl compound (9.5; X = O-ferrocenyl) showed a trigonal-bipyramidal structure with three ferrocenyl ligands in the equatorial positions and an axial ferrocenyloxy group coordinated trans to the oxo ligand [121].

(Diphenylphosphino)ferrocene has been metallated with n-butyllithium to form the heteroannular dilithio intermediate which combined with S_8 to form the [3]ferrocenophanes (9.6 and 9.7). The same dilithio intermediate combined with dichlorophenylphosphine to give [1]ferrocenophanes such as the diphosphine (9.8). The corresponding reaction with chlorodiphenylphosphine gave tris(tertiary phosphines) [122].

The ferrocenylthioethers (9.9; R^1 = H, R^2 = Me, Et, Me_2CH Me_2CHCH_2, isopentyl, Ph; R^1 = Me, R^2 = Me, Et, Me_2CH, Ph, CH_2Ph) and the ferrocenylselenoethers (9.10; R^1 = H, R^2 = Me, Ph, 4-chlorophenyl; R^1 = Me, R^2 = Ph; 9.11; R = Me, Ph and 9.12) have been prepared by the reaction of the appropriate lithioferrocene with RSSR or RSeSeR. The palladium(II) chloride complex of the thioether (9.9; R^1 = H, R^2 = Me_2CH) was a selective hydrogenation catalyst under homogeneous and heterogeneous conditions for the reduction of dienes to monoenes. The



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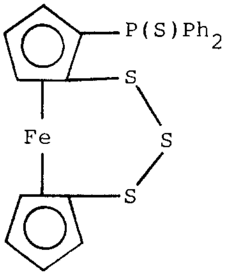

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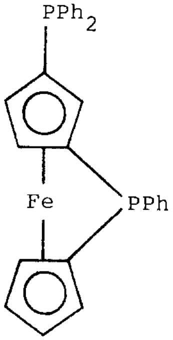

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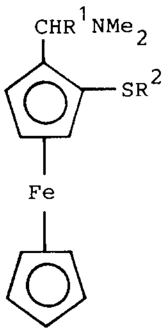

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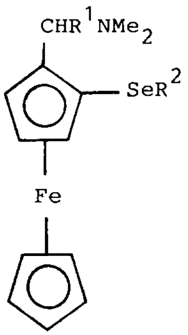

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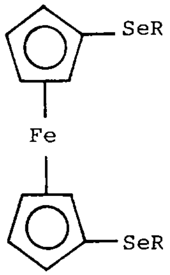

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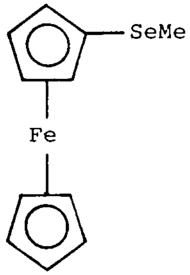
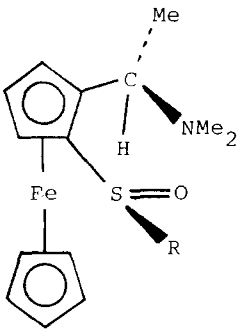


9.12

palladium(II) chloride complexes of (9.9; R^1 = Me, R^2 = Ph) and (9.10; R^1 = Me, R^2 = Ph) were effective as Grignard cross-coupling agents [123, 124, 125].

Thioethers (9.9; R^1 = H, R^2 = Me, Et, Pr^i, Bu^i, $pentyl^i$, Ph) have been prepared by lithiation of dimethylaminomethylferrocene and treatment of the 2-lithio intermediate with disulphides R^2SSR^2. The palladium(II) chloride complex of one thioether (9.9; R^1 = H, R^2 = Pr^i) has been investigated as a catalyst for the selective hydrogenation of 1,3-cyclooctadiene to cyclooctene [126].

A series of chiral sulphoxides (9.13 and 9.14; R = Me, CH_2Ph, CMe_3, 4-MeC_6H_4, $CH_2CH{=}CH_2$) and the corresponding sulphones



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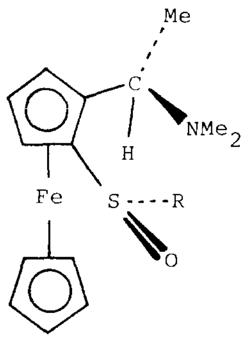

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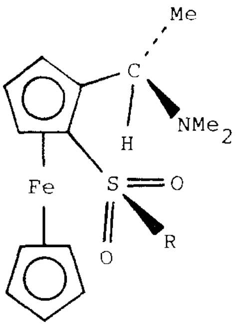

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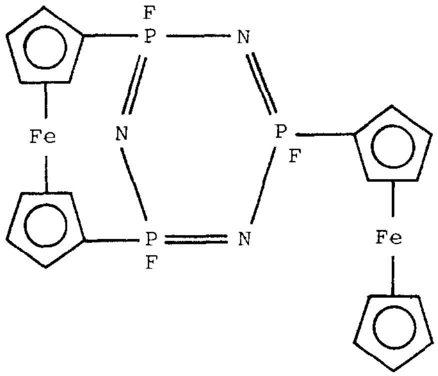
(9.15) have been prepared by the reaction of 2-lithio-1-(dimethylaminoethyl)ferrocene with the disulphides RSSR followed by oxidation. Many of the reactions proceeded with high stereoselectivity and the sulphoxides and sulphones were isolated as pure enantiomers [127].

Ferrocenyl or ruthenocenyl fluorocyclotri- and fluorocyclotetra-phosphazenes underwent displacement of fluorine with mono- and di-lithioferrocenes and with methyllithium or phenyllithium. The reaction products were influenced by steric hindrance and by the coordination of the incoming organolithium reagent with



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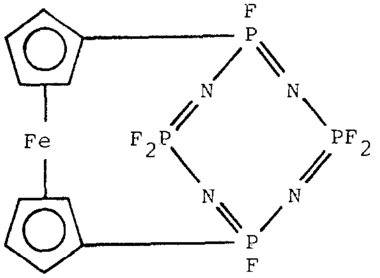


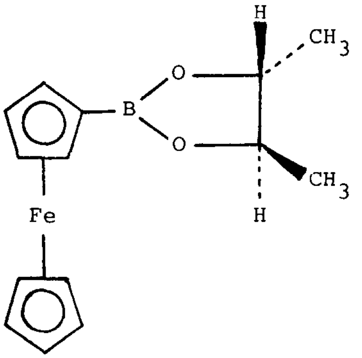
9.17

nitrogen atoms on the phosphazene. Among the four products characterized by X-ray crystallography were the cyclotri- (9.16) and cyclotetra-phosphazenes (9.17) [128].

The reaction of ferroceneboronic acid with 1,2-diols, 1,3-diols and related substrates in pyridine produced the corresponding cyclic ferroceneboronate derivatives. These derivatives afforded sharp symmetrical peaks in gas-liquid chromatography and their mass spectra showed abundant molecular ions. For example, a gas-liquid chromatographic separation of the ferroceneboronates (9.18 and 9.19) of one of the chiral forms of butane-2,3-diol and its meso- isomer was achieved [129].

The [2]ferrocenophane adducts of $CdCl_2$, $ZnCl_2$, $CoCl_2$ and CF_3CO_2H, where the e_{2g} electrons of the iron atom are donated to the Lewis acid, have been investigated [130]. Silylmetallocenes have been prepared by catalytic hydrosilylation of vinylferrocene-chlorosilane adducts, thus vinylferrocene combined with chlorodimethylsilane in the presence of H_2PtCl_6 to give, after reduction, the product (9.20) which was used as a vulcanization accelerator [131].

2-Lithio(dimethylaminomethyl)ferrocene has been condensed with tri(alkyl or aryl)chlorostannanes to give the corresponding 1,2-disubstituted ferrocenes (9.21; R = Me, Bu, Ph). The lithiation of dimethylaminomethylferrocene with excess butyllithium-tetramethylethylenediamine produced polylithiated species which were condensed with the same tri(alkyl or aryl)chlorostananes to give the polysubstituted ferrocenes (9.22; X = Y = SnR_3,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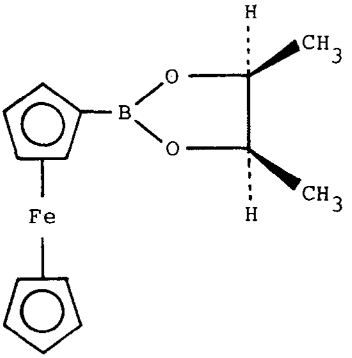
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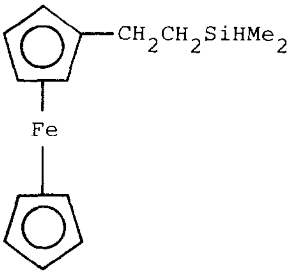
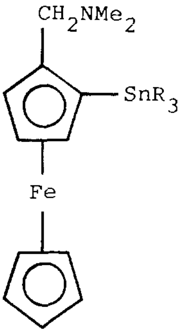


9.20

Z = H; X = Z = SnR_3, Y = H; X = Y = Z = SnR_3). The structures of the triorganostannyl derivatives were investigated by ^{1}H, ^{13}C and ^{119}Sn NMR together with ^{57}Fe and ^{119}Sn Moessbauer spectroscopy [132]. This duplicates, without acknowledgement, work reported in 1972 [133].

Cleavage of 1,1'-bis(triphenylstannyl)ferrocene (9.23) with trifluoroacetic acid in carbon tetrachloride gave a mixture of products including triphenylstannylferrocene, ferrocene and benzene. Mercuridestannylation with mercury(II) chloride gave only 1,1'-di(mercurichloro)ferrocene. Iodination gave a mixture of the mono- and bis-iodides (9.24 and 9.25) formed by Ph-Sn cleavage. Oxidation of the stannyl-ferrocene (9.23) by iron(III) chloride was also investigated [134].



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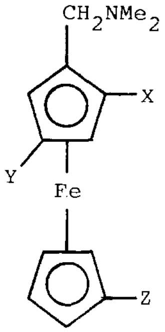

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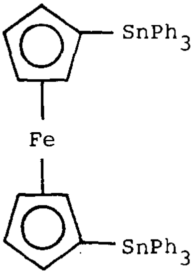

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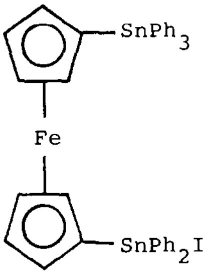

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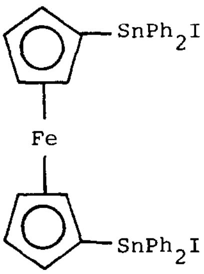

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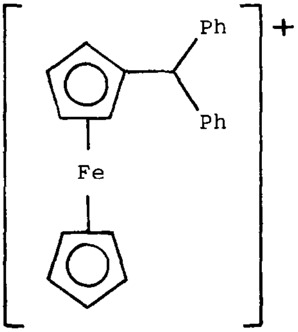
The α-ferrocenylcarbenium ion (9.26) has been attacked by tertiary phosphines to give the phosphonium ions (9.27; R_3 = Me_3, Et_3, n-Bu_3, $MePh_2$, Me_2Ph) [135]. ^1H NMR spectroscopy has been used to show that a correlation occurred between the spatial distribution of the $-NMe_2$ group in the diphenylphosphine (9.28) and the site of stereoselective lithiation [136]. The chiral ferrocenylphosphines (R)-(S)-[9.29; X = $NMeCH(CH_2OH)_2$, $N(CH_2CH_2OH)_2$, $NMeCH_2CH_2OH$] formed complexes with $(\eta\text{-}C_3H_5)PdCl$ which were effective as catalysts for the alkylation of (E)-PhCH(OAc)CH=CHPh with the nucleophiles NaCH(COMe)COR, where R = Me, Ph. Products with an enantiomeric excess of up to 92% were obtained and this selectivity was attributed to hydrogen bonding between the catalyst and the nucleophilic reagent [137].



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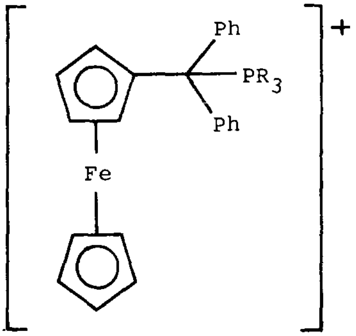

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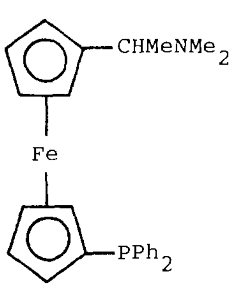

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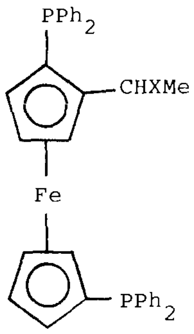

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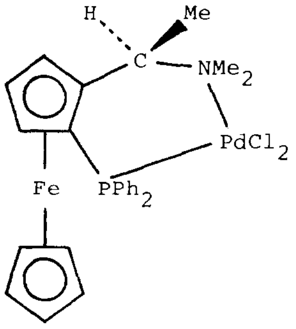
The stereospecific cross coupling of secondary alkyl Grignard reagents with Z- or E-1-bromo-2-phenylthioethene to give alkenyl sulphides has been catalyzed by the 1,1'-bis(diphenylphosphino)-ferrocene complex of palladium(II) chloride [138]. The chiral complex dichloro {(R)-N,N-dimethyl-1[(S)-2-(diphenylphosphino)-ferrocenyl]ethylamine} palladium(II) (9.30) has been used as a catalyst for the asymmetric cross-coupling of [(α-trimethyl-silyl)benzyl]- or [(α-trimethylsilyl)ethyl]-Grignard reagents with alkenyl bromides. The products were optically active allylsilanes with an asymmetric carbon bonded directly to a silicon atom [139].



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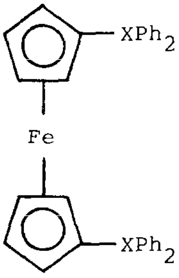
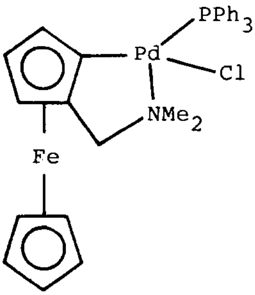


9.31

The chiral ferrocenylphosphine-palladium complex (9.30) has been used as a catalyst for the asymmetric hydrosilylation of 1-arylbutadienes with trichlorosilane to produce optically active allylsilanes, (Z)-1-aryl-1-silyl-2-butenes and their regioisomers [140]. The palladium(II) chloride complexes with the ligands (9.31; X = P, As) have been used as catalysts for the reaction of iodobenzene with phenylacetylene under an atmosphere of carbon monoxide in the presence of triethylamine to give the acetylenic ketone PhCOC≡CPh [141].

The protolysis of the palladium complex (9.32) with acetic acid in the presence of lithium chloride produced dimethylaminomethylferrocene and the dimer (9.33) [142]. Treatment of 1-chloropalladio-2-(dimethylaminomethyl)ferrocene with carbon monoxide in the presence of 2-O-benzylglycerin gave the optically active glyceride [(S)-9.34; R = H]. Reaction of this glyceride with triphenylchloromethane produced the tritylated complex [(S)-9.34; R = CPh_3]. The ferrocenyl group was removed from this latter compound by hydrolysis with aqueous sodium hydroxide [143].

The platinum(II) complex (9.35) of 1,1-bis(acetylhydrazone)-ferrocene has been used as an additive in vinylsiloxane rubber stock with enhanced overvulcanization resistance [144]. Molybdenum(II) and tungsten(II) complexes of 1,1'-bis(diphenylphosphino)ferrocene (DPF) have been prepared by treatment of $MI_2(CO)_3(MeCN)_2$, where M = Mo, W, with the ligand DPF to give $MI_2(CO)_3DPF$ as seven-coordinate complexes. The diferrocene



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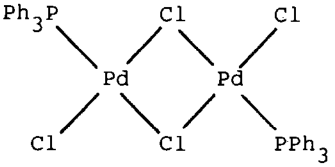

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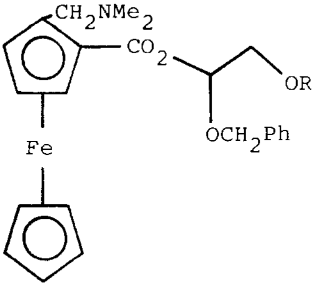
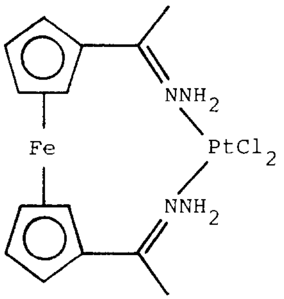




9.34

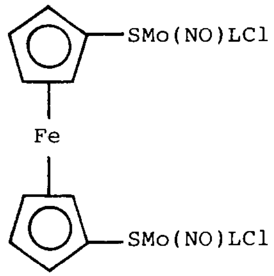
9.35

complex cis-$MoCl_2(CO)_2(DPF)_2$ was prepared and contained both monodentate and bidentate DPF ligands, the molybdenum atom was seven-coordinate [145].

The reaction of ferrocene dithiol with [Mo(NO)HB(3,5-$Me_2C_3N_2H)_3Cl_2$] in the presence of sodium hydride produced the trimetallic complex [9.36; L = HB(3,5-$Me_2C_3N_2H)_3$]. The electrochemical properties of this complex were investigated by cyclic voltammetry. It was concluded that the inductive effects of the molybdenum containing substituents were transmitted through the C-Fe-C atom chain [146].

Diferrocenyl trithiocarbonate (9.37) and 1,3-dithia[3]-ferrocenophane-2-thione (9.38) have been prepared by the reaction of 1,1'-thiocarbonyldiimidazole with ferrocenethiol and 1,1'-ferrocenedithiol respectively. Treatment of the ferrocenophane (9.38) with triphenylphosphine or trimethylphosphite produced the ethylene derivative (9.39) [147].

Esters of ferrocenedithiocarboxylic acid have been prepared by two procedures; the first involved alkylation with methyl iodide and ethyl iodide of the piperidinium salt (9.40) to give the products (9.41; R = Me, Et) and with dichloromethane and iodomethane to give the dinuclear diester (9.42). The second involved the treatment of ferrocenecarbonyl chloride with methanethiol to give the intermediate thioester which was sulphurated with P_4S_{10} to give the dithioester (9.41; R = Me). The corresponding reactions with dithiols gave dinuclear dithioesters [148].



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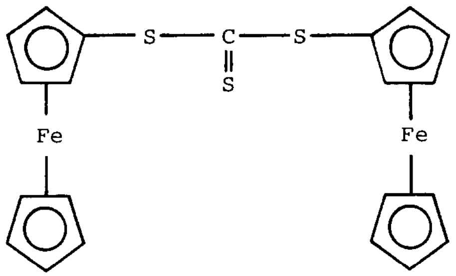

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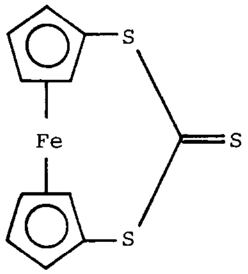

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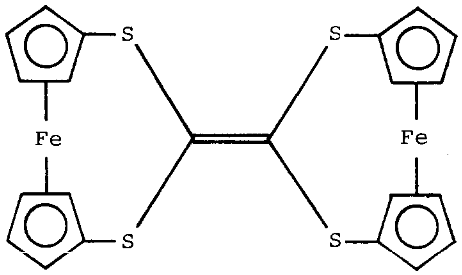

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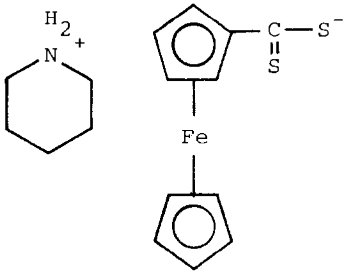
The reaction of 1,1'-bis(thiocyanatomercuri)ferrocene with $M(NCS)_2$, where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), afforded the corresponding tetrametallic complexes (9.43). These complexes together with their adducts with pyridine and 1,10-phenanthroline were investigated by physical methods. In the complexes (9.43; M = Co, Mn and Zn) the metal M was tetrahedrally coordinated and in the adducts all the metals (M) were octahedrally coordinated [149, 150].

Several lanthanide complexes (9.44; Ln = Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) have been obtained by treatment of 1-ferrocenyl-1,3-butandione with lanthanum(III) chloride [151].



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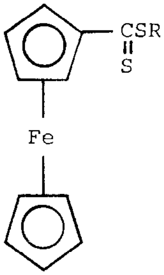

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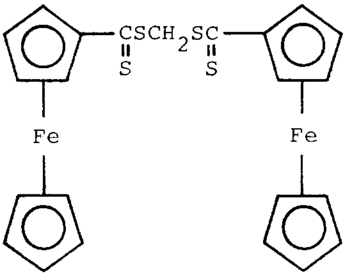

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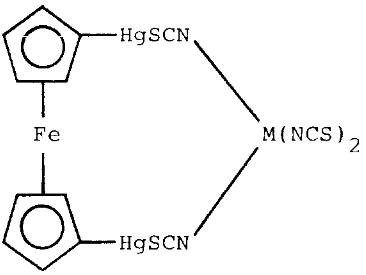

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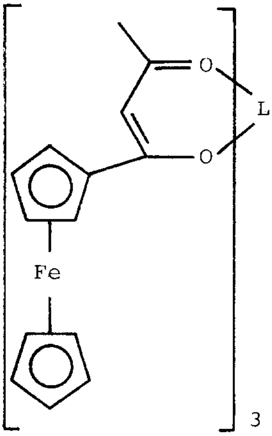

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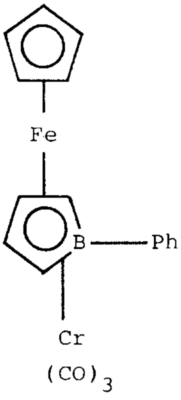


9.45

The anion of ferrocenoylacetone (FA) combined with lanthanide(III) chlorides to give the complexes $Ln(FA)_3(H_2O)_x$, where Ln = La, x = 2; Ln = Y, Nd, Sm-Gd, Dy-Lu, x = 1. The ligand was bidentate in these complexes [152]. The hetero-bimetallic triple decker sandwich complex (9.45) has been obtained from $Cr(CO)_3(NH_3)_3$ and the appropriate boraferrocene [153].

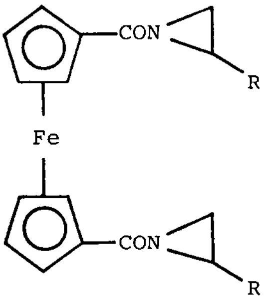
(ii) General chemistry

Ferrocenyl-γ- and -β-cyclodextrins have been prepared by the reaction of 6-0-2-naphthylsulphonyl-γ- or -β-cyclodextrin with potassium ferrocenylcarboxylate. The abilities of these ferrocenyl substituted cyclodextrins to form inclusion complexes with a variety of guest molecules in water was investigated. The binding ability of the γ-cyclodextrin derivative was much lower in water but higher in ethylene glycol than that of the corresponding ferrocenyl-β-cyclodextrin compound [154].

The inclusion of ferrocenecarboxylic acid and its carboxylate anion by β-cyclodextrin has been studied by induced circular dichroism. The result indicated that the arrangements of the acid and the anion were different from each other [155].

Oxidation of 1,1'-diacetylferrocene with NaOCl gave the corresponding dicarboxylic acid which was, in turn, converted to 1,1'-dichlorocarbonylferrocene with phosphorus pentachloride. Reaction conditions were optimized in each case [156].

Aziridines combined with 1,1'-ferrocenedicarbonyl chloride in dichloromethane-water mixtures to give the aziridine derivatives (9.46; R = H, Me, Et). Physical properties and thermal



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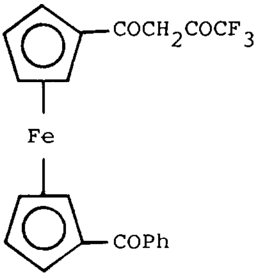
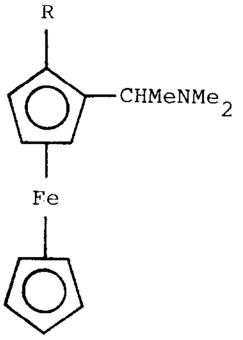


9.47

stability of the derivatives were determined [157]. 3-Aryl-1-ferrocenyl-2-propen-1-ones underwent Michael condensation with diethyl malonate to form diethyl(1-aryl-3-ferrocenyl-3-oxopropyl) malonates which were then saponified to the corresponding dicarboxylic acids. Decarboxylation of these acids gave 3-aryl-5-ferrocenyl-5-oxovaleric acids which were cyclized to 4-aryl-6-ferrocenyl-3,4-dihydro-2-pyrones using trifluoroacetic anhydride [158].

The treatment of 1-acetyl-1'-benzoylferrocene with CF_3CO_2Et produced the butanedione (9.47) which formed complexes with transition metal ions [159]. The dimethylaminoethylferrocene (9.48; R = H) underwent homoannular dilithiation with excess n-butyllithium and heteroannular dilithiation with n-butyllithium-tetramethylethylenediamine (TMEDA). The di-, tri- and tetra-substituted ferrocenes (9.48; R = $SiMe_3$, 9.49; R = H, $SiMe_3$) each underwent predominantly heteronuclear dilithiation with n-butyllithium-TMEDA. The lithioferrocenes (9.48 and 9.49; R = Li) were treated with chlorotrimethylsilane and chlorophosphines. The crystal and molecular structure of the tetra-substituted ferrocene (9.49; R = $SiMe_3$) has been determined by X-ray crystallography [160].

Chiral α-ferrocenylalkylamines have been obtained by resolution of the racemates, in some cases a single chiral reagent was effective in giving both enantiomers. α-Ferrocenylalkylamines with two chiral centres have been formed from α-ferrocenylalkyl carbenium ions by diastereoselective synthesis.



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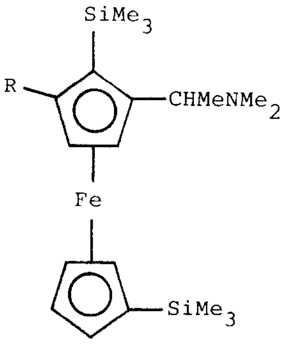


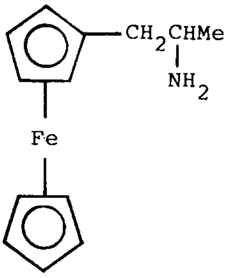
9.49

The chiral amines prepared in this way have been used as chiral inducing templates in the synthesis of peptides by stereoselective four-component condensation [161].

Ruthenocene and osmocene derivatives, which were useful as radiopharmaceutical diagnostic agents, have been prepared by ligand exchange reactions between ferrocene derivatives and labelled ruthenium or osmium halides. Thus the ferrocenylpropylamine (9.50) underwent exchange with $^{103}RuCl_3$ to give the corrresponding ruthenocene [162].

The ferrocenylalkenes (9.51; R = H, Me, t-Bu, Ph, 9.52; R = H, Me, Ph, 9.53; R = Me, Ph, 9.54; Ar = Ph, p-$MeOC_6H_4$, p-MeC_6H_4, p-BrC_6H_4, p-$NO_2C_6H_4$ and 9.55) have been subjected to hydroboration-alkaline hydrogen peroxide oxidation to give the corresponding 1- and 2-ferrocenylalkanols. The regioselectivity of the reaction was governed by both steric and electronic factors and this was a good general route to 2-ferrocenylalkanols [163].

The ferrocenylketimines (9.56; R = ferrocenyl, cymantrenyl) have been prepared by treatment of cyanoferrocene with RLi. The ketimine (9.56; R = ferrocenyl) was treated with acetic anhydride to give the N-acetyl derivative [164]. Reaction of the ferrocenyl-alcohols (9.57; R^1 = H, Me, Ph) with the amines R^2NHNO_2, where R^2 = Me, CH_2CH_2CN, gave the corresponding N-nitroferrocenylalkylamines (9.58). When ferrocenylmethanol (9.57; R^1 = H) was treated with N-nitrourea the N-ferrocenylmethylurea (9.59) was obtained. The same reaction with the alcohols



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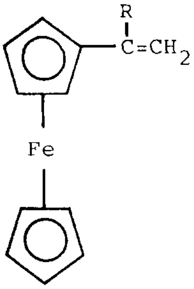

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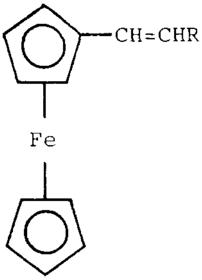

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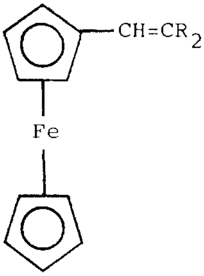

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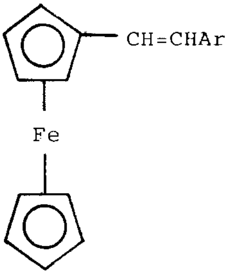

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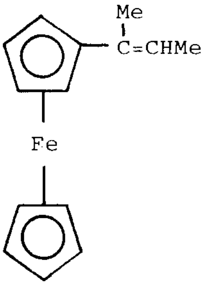
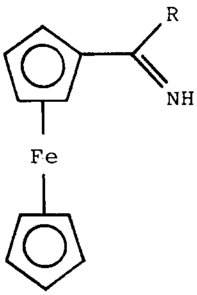


9.55

(9.57; R^1 = Me, Ph) afforded the corresponding N,N'-disubstituted ureas (9.60) [165].

Treatment of the alcohols (9.61; R = H, Me) with heterocyclic bases, for example, 2-methylpyridine in dichloromethane-aqueous perchloric acid or hydrogen tetrafluoroborate produced the corresponding salts (9.62; R = H, Me, X = ClO_4, BF_4) [166]. Reaction of amino acids or esters with formylferrocene and hydrogen over palladium(II) phthalocyanin gave the corresponding ferrocenylmethyl protected amino acids and esters (9.63; X = gly, R = H; X = ala, phe, R = Na; X = gly, ala, R = Me; X = phe, leu, val, R = CMe_3). These protected amino acids and esters were used in the synthesis of peptides [167].



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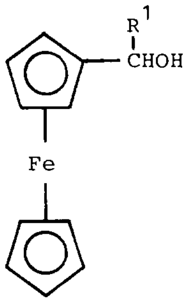

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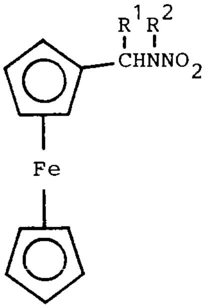

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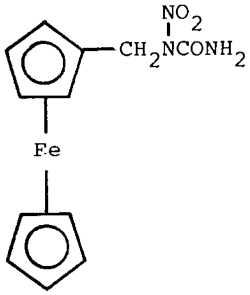

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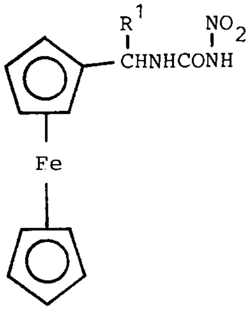

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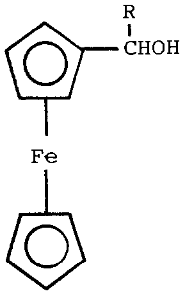

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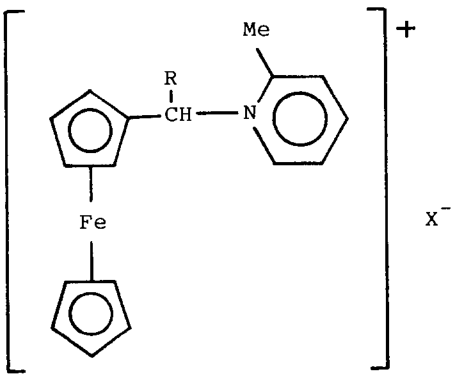

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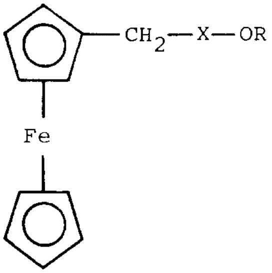

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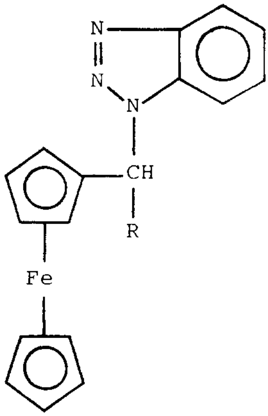


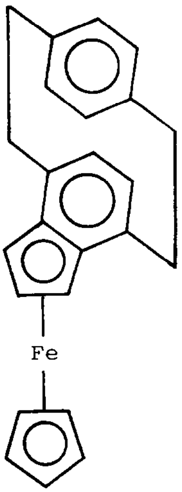
9.64

The ferrocenylmethylbenzotriazoles [9.64; R = H, Me, Ph, (η-C_5H_5)Fe(η-$C_5H_4CH{=}CH$-), 3-indolyl] have been prepared by reaction of the sodium benzotriazole salt with the corresponding ferrocenyl-alcohol in a two phase system of dichloromethane-45% aqueous hydrogen tetrafluoroborate [168].

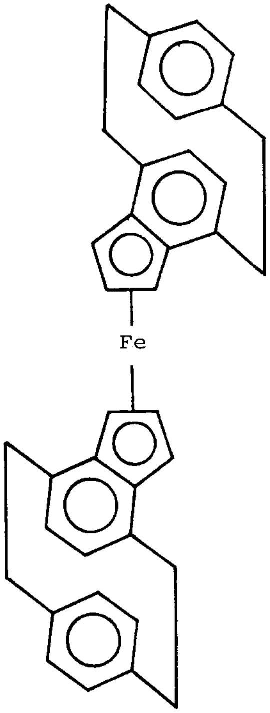
10. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

The multilayered ferrocenophanes (10.1 and 10.2) have been prepared by reaction between the anions of the appropriate ligands and iron(II) chloride. The ^1H NMR chemical shifts were discussed [169]. Condensation of 1,1'-bis(chlorocarbonyl)ferrocene with the diol $[(CH_2OCH_2CH_2)_2NCH_2CH_2OCH_2CH_2OH]_2$ gave the metallocene cryptand (10.3) which was shown by fast atom bombardment mass spectrometry to act as a selective binding agent towards the potassium ion. The corresponding ruthenocene cryptand showed similar properties [170].

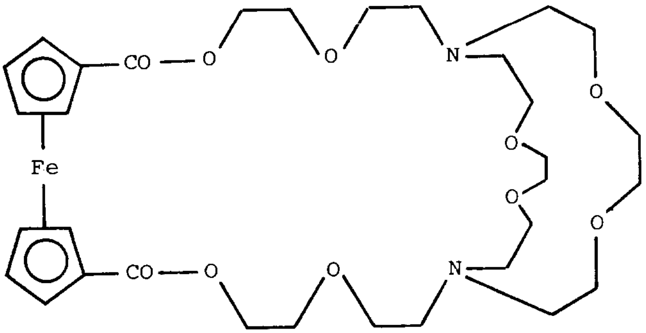
Polyoxa- and dioxapolythia[n]ruthenocenophanes were effective in the extraction of silver(I) ions while the corresponding ferrocenophanes decomposed under the same conditions [171]. Treatment of ferrocene with diazotized p-$H_2NC_6H_4CO_2Me$ and then with diazotized 2,5,4-$(MeO)_2(CO_2Et)C_6H_2NH_2$ produced the 1,1'-disubstituted ferrocene (10.4). This latter compound was used



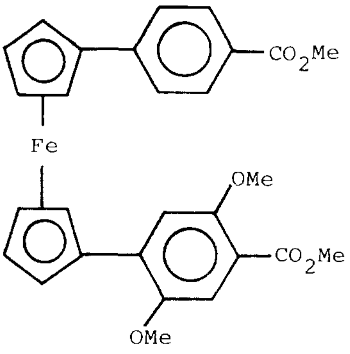
10.1



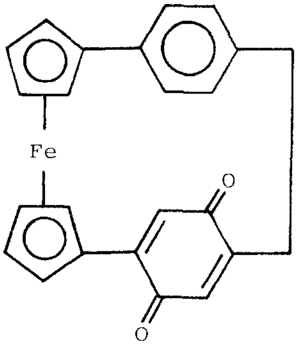
10.2



10.3



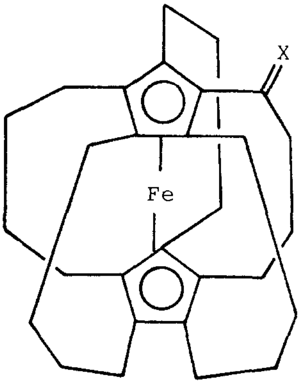
10.4



10.5

to prepare the ferrocenophane (10.5) [172]. Molecular spectroscopy has been used to show that the compound (10.5) had intramolecular charge-transfer properties [173].

The redox behaviour of several ruthenocenophanes has been studied by cyclic voltammetry and comparisons made with the corresponding ferrocenophanes. Rates of heterogeneous electron transfer on oxidation were smaller for the ruthenocenophanes. Negative shifts in the oxidation peaks were observed with an increase in the number of bridging methylene groups as with ferrocenophanes [174].



10.6

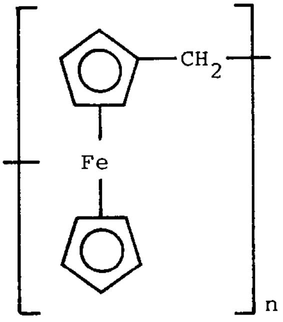
The symmetrical perbridged [4_5]ferrocenophane (10.6; X = H_2) has been prepared by reduction of the corresponding ketone (10.6; X = O) with lithium aluminium hydride-aluminium chloride. The crystal structure of the ferrocenophane (10.6; X = H_2) was determined by X-ray diffraction. The η-cyclopentadienyl rings were almost planar and in an eclipsed conformation. The overall shape of the molecule was almost spherical [175].

Ferrocenylcopper combined with benzoyl chloride to give a mixture of benzoylferrocene, diferrocene and ferrocene. Additives such as lithium bromide, sodium iodide, acetonitrile, triphenylphosphine and $CuBr.PPh_3$ caused the yield of benzoylferrocene to fall in each case [176].

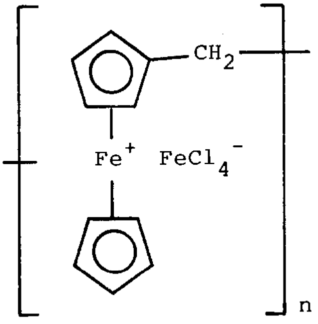
11. FERROCENE-CONTAINING POLYMERS

The oxidation of poly(ferrocenylenemethylene) (11.1) with a variety of oxidizing agents has been investigated. Ferrocenium tetrachloroferrate(III) oxidized the polymer (11.1) to give the pure poly(tetrachloroferrate) (11.2) which was soluble in water [177].

Neuse and Hart have investigated some oligo- and poly-(1,1'-ferrocenylenes) (11.3). The ferrocenylenes were prepared either by the palladium(II) chloride catalysed polycondensation of 1,1'-dilithioferrocene with 1,1'-diiodoferrocene or from 1,1'-dibromoferrocene and magnesium in tetrahydrofuran-dibromoethane. The latter coupling reaction proceeded less cleanly and the previously claimed higher selectivity for this route was not evident [178].



11.1



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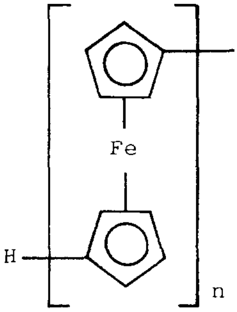
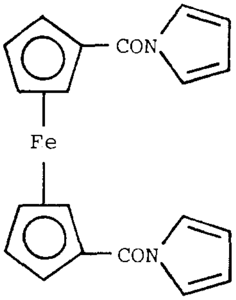


11.3



11.4

The polymerization of α-chloro-β-formyl-*p*-chlorostyrene and -*p*-bromostyrene has been initiated by a polymeric ferrocenium sulphate. Such a redox initiator was more efficient and gave higher yields than did thermal polymerization. The oligomers obtained had d.p. 4-11 and showed good thermal stability ≤ 260°C [179].

The reaction of 1,1'-ferrocenedicarbonyl chloride with N-3-aminopropylpyrrole in the presence of triethylamine produced the disubstituted ferrocene (11.4). Electrolysis of this pyrrole substituted ferrocene gave polymer films on the surface of the electrode. The nature of the polymer films was investigated by ESCA spectroscopy and cyclic voltammetry [180].

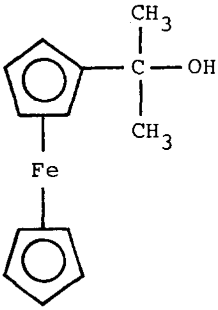
An unsuccessful attempt was made to electrochemically homopolymerize N-(2-ferrocenylethyl)pyrrole but it was copolymerized with pyrrole to give a polymer that contained some ferrocenium ions [181]. Ferrocene dicarboxaldehyde has been condensed with the bis-phosphonium salt of 1,4-bis(chloromethylbenzene) to give a vinylene polymer. The polymer was an insulator in the doped state but showed an increase in conductivity on treatment with arsenic pentafluoride. A convenient one-pot synthesis of ferrocene dicarboxaldehyde was developed [182].

The mechanical and thermal stability of poly(ethylene terephthalate) was improved by the incorporation of 0.1-0.4% 1,1'-diacetylferrocene [183]. Poly(ether urethanes) have been prepared with the incorporation of 1,1'-bis(β-aminoethyl)ferrocene and 1,1'-bis(hydroxyethyl)ferrocene as chain extenders. The disubstituted ferrocene residues were localized in the hard segments of these segmented polymers [184]. Acryloylferrocene has been copolymerized with 4-(1'-o-carboranyl)styrene at 185-190° in the presence of di(t-butyl)peroxide [185].

Poly(vinylamine) has been treated with ferrocenecarbonyl chloride to give polymers containing 0.7-21.0 mol% ferrocene. These polymers were investigated via physico-chemical methods and some copper complexes were prepared [186]. Treatment of acetylferrocene with a four molar excess of methylmagnesium iodide in tetrahydrofuran produced α-hydroxyisopropylferrocene (11.5) in good yield. The alcohol (11.5) was polymerized in the presence of tin(IV) chloride or boron trifluoride etherate. The polymerization proceeded by self-alkylation of the stable intermediate ferrocenylcarbenium ion to give oligomers that contained both homoannular and heteroannular links [187].

The formation of vinylferrocene polymer membrane electrodes via electrochemical polymerization of vinylferrocene has been investigated. The optimum conditions for the formation of electroactive poly(vinylferrocene) covered electrodes were determined. The electroactivity of the electrodes decreased with time in methyl cyanide and in air [188].

Plasma discharge polymerization of vinylferrocene produced a scratch-resistant electron beam of X-ray resist film. The film was used in the preparation of an integrated circuit [189]. A comprehensive ESCA examination has been carried out on plasma-polymerized films derived from ferrocene, vinylferrocene and dimethylaminomethylferrocene. The results indicated that ferrocene and vinylferrocene in the polymers maintained a carbon to iron



11.5

ratio characteristic of the parent compounds whereas dimethylaminomethylferrocene plasma polymer was richer in iron than the parent [190].

Wood has been treated with a 20% acetone solution of a mixture containing formaldehyde-furfurole-phenol copolymer (99%) and ferrocene or acetylferrocene (1%) in the presence of benzene-sulphonic acid as a catalyst. The wood was then soaked in water and dried to give a specimen with increased compression strength along the fibre [191].

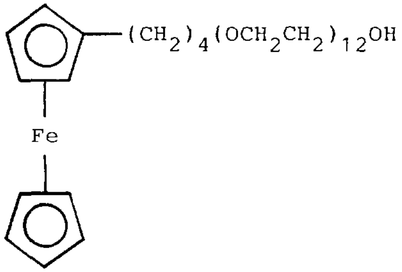
12. APPLICATIONS OF FERROCENE

(i) Ferrocene catalysts and photosensitizers

The cationic polymerization of vinyl ethers has been catalyzed by ferrocenium salts thus 1,4-butanediol divinyl ether was mixed with 1% 1:1 ferrocenium tetrachloroantimonate-hexachloroantimonate to give, after an induction period, a violent reaction forming a hard insoluble polymer [192].

An electrochromic display device has been prepared by using an electrolyte solution that contained heptyl viologen, tetraethylammonium perchlorate, acrylonitrile and ferrocene. This device exhibited a much lower threshold voltage than a control that contained no ferrocene [193]. Ferrocene has been incorporated into heat sensitive material used for coating paper [194].

Image recording materials based on ferrocene derivatives, diphenylamines and related amines have been used in pressure sensitive copying systems and thermal recording devices [195].



12.1

Acetyl- and α-hydroxylalkyl-ferrocene have been added to polyethylene film as sensitizers to increase the photodegradability and retention of required strength of the film [196].

Hydroxyalkylferrocenes have been prepared and used as nonionic and anionic surface-active agents. Thus 4-ferrocenyl-1-butanol was treated with ethylene oxide in the presence of $BF_3.OEt_2$ to give the product (12.1) which was effective in reducing surface tension [197].

(ii) Combustion control

The plasma vapour deposition of diamond from cyclohexane and hydrogen has been carried out in the presence of ferrocene and other organometallic compounds. The addition of ferrocene improved the quality of the diamonds obtained [198]. In a related patent ferrocene vapour was decomposed and remained in the plasma for 1-5 min in the presence of methane and hydrogen. The fine diamond powder obtained was suitable for use in lapping abrasives [199].

Ferrocene has been used with an organic compound to increase the growth yield in the manufacture of highly crystalline carbon fibres. A mixture containing H_2-H_2S-ferrocene-benzene in the proportions 85:2.5:0.7:11.8 was heated at 1095°C for 30 min to give carbon fibres [200].

The yield and quality of carbon fibres obtained from a hydrocarbon by vapour-phase growth carbonization were improved by decomposition of the hydrocarbon in the presence of ferrocene [201]. Carbon fibres have been prepared by the thermal decomposition of hydrocarbons, for example, benzene in a fluidized bed of ultra-fine iron particles formed by the decomposition of ferrocene [202].

The thermal decomposition of benzene in the presence of ferrocene and hydrogen produced carbon fibres [203]. In a related patent carbon fibres were prepared in a single step by the decomposition, in a d.c. arc plasma, of benzene mixed with argon in the presence of ferrocene. In the absence of ferrocene no carbon fibre formation was observed [204].

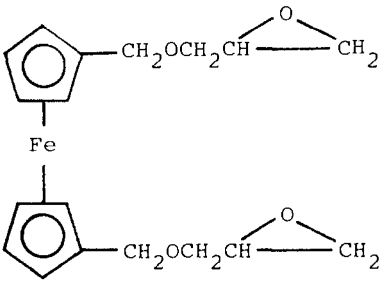
The role of ferrocene in the production of carbon fibres from hydrocarbons has been investigated [205]. Soot formation in vapourized toluene-isooctane flames containing 0-0.3% ferrocene has been investigated. The presence of ferrocene did not affect soot formation in the early stages of combustion and accelerated oxidative soot burnout in the later stages [206].

Smoke suppressants for kerosene and plastics have been prepared by the reaction of ferrocene with polybutene or with hydroxylated polybutadiene [207]. Ferrocene has been used as a smoke reducing agent in jet engine fuel [208].

The ferrocenium salt formed from ferrocene and antimony(V) chloride has been incorporated into rigid polyurethane foam to give good flame-retardant and smoke-suppressant properties in the moulded polymer [209]. Low-smoke, fire- and heat-resistant polyurethane foam has been prepared by the incorporation of ferrocene (0.05-10% as iron) [210].

Ferrocene has been incorporated in flame-retardant polymer compositions [211]. Polymers containing ethylenic unsaturation and silyl metallocene groups have been prepared and used as binders in propellant compositions. Thus polybutadiene was heated with [4-(dimethylsilyl)butyl]ferrocene to give a product in which 11.1% of the double bonds had been opened. A propellant mixture was prepared using the binder (13 parts), ammonium perchlorate (80 parts) and aluminium (2 parts) [212].

1,1'-Bis(trimethylsiloxymethyl)ferrocene behaved as a good bonding agent for ammonium perchlorate-hydroxyl terminated polybutadiene composite solid propellants. The silicon atoms were the active binding sites [213]. 1,1'-Bis(hydroxymethyl)ferrocene has been used to prepare 1,1'-bis(glycidoxymethyl)ferrocene (12.2) in good yield. The disubstituted ferrocene (12.2) behaved



12.2

as a bonding agent in composite solid propellants and also as a crosslinking agent for carboxyl-terminated polybutadiene which is a commonly used fuel binder in propellants [214].

The addition of n-butylferrocene as a catalyst to ammonium perchlorate based composite propellants greatly increased the burning rate. The rate-determining step in the burning reaction was investigated and it was concluded that the catalyst increased the rate of burning of individual ammonium perchlorate particles in the gas phase [215].

(iii) Biochemical and biological applications

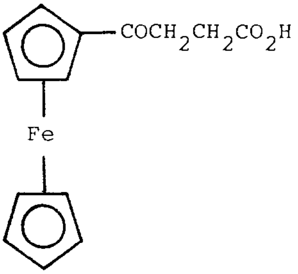
Enzyme electrodes have been prepared by the immobilization of glucose oxidase and ferrocene in cross-linked polyacrylamide gels. The electrode was stable in air and water and it gave a current response that was proportional to glucose concentrations up to 30 mM [216]. The ferrocene mediated oxidation of glucose by glucose oxidase has been used as the basis for an amperometric immunoelectrode. A lidocaine-ferrocenium ion complex behaved as the electron acceptor for glucose oxidase. The catalytic current produced in the oxidation was specifically inhibited upon binding the lidocaine(antigen)-ferrocene complex with antibody. The inhibition was reversed when free antigen was added. Overall, this was a ferrocene-mediated, homogeneous, competitive immunoassay, with an assay time of 15 min and a relative standard deviation of 3-6% [217].

Ferrocenecarboxylic acid has been used as a mediator in an amperometric sensor for D-galactose, glycolate or L-amino acids using the corresponding oxidases. Cyclic voltammetry was used to investigate the suitability of the electrode which responded to millimolar concentrations of the appropriate substrates [218].

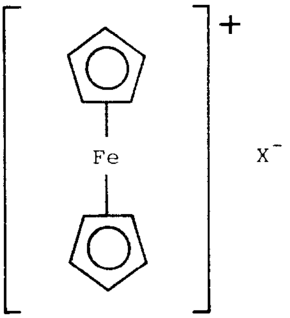
An electrochemical method has been described for the assay of ligands such as hormones, enzymes and antigens. In the method ferrocene was used as an electron transfer mediator [219]. The transport of lipophilic ions coupled to the transmembrane redox reaction mediated by t-amylferrocene has been studied in the liposome system [220].

Ferrocenoyl azide and 3-ferrocenylpropionyl azide have been condensed with alcohols, for example, hydroxy steroids to give urethanes. The derivatized alcohols were separated by hplc and detected electrochemically when the ferrocenyl group behaved as an electrophore. This method of derivatization was used for the characterization of the products formed from digoxigenin by in vitro bioconversion [221].

Ferrocene-carboxylic acid and -1,1'-dicarboxylic acid behaved as reversible competitive inhibitors of type I procollagen N-proteinase. The keto-acid (12.3) was a better inhibitor than the two simple carboxylic acids while ferrocenium tetrachloroferrate and hexafluorophosphate were very powerful inhibitors. The ferrocene derivatives showed high specificity and did not inhibit five other proteinases able to cleave N- and C-terminal propeptides or propeptide-like fragments from procollagen [222].



12.3



12.4

The antiproliferative activity of the ferrocenium salts [12.4; X = $CCl_3CO_2^-.CCl_3CO_2H$, $CCl_3CO_2^-.2CCl_3CO_2H$, $\frac{1}{2}(Cl_3FeOFeCl_3)^{2-}$, $FeCl_4^-$, 2,4,6-$(NO_2)_3C_6H_2O^-$] has been investigated against solid, growing Erhlich ascites tumor in vivo and in vitro. Tumor development was depressed markedly and the size of the tumor was reduced. In vitro, all the ferrocenium salts were equally effective at inhibiting cell growth but they were less effective than *cis*-diamminedichloroplatinum(II) [223].

Benzoylferrocenes have been used as microbiocides, thus 1-(3,4-dimethylbenzoyl)ferrocene was effective against *Colletotrichum lagenarium* and *Sphaerotheca fuliginea* on cucumbers [224].

13. REVIEWS

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