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FERROCENE
ANNUAL SURVEY COVERING THE YEAR 1989*

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CONTENTS

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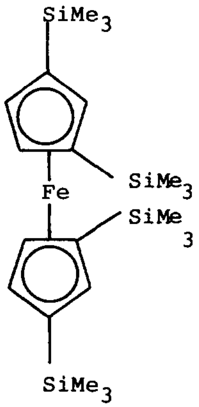
* Annual Survey covering the year 1988 see J. Organomet. Chem., 392 (1990) 93

1. STRUCTURAL DETERMINATIONS

The tetrakis(trimethylsilyl)ferrocene (1.1) has been characterised by X-ray crystallography. The trimethylsilyl groups were staggered with the cyclopentadienyl rings nearly eclipsed [1]. Diferrocenylmercury(1.2) has been prepared by treatment of ferrocenylmercurichloride with cysteine. The crystal and molecular structure of the hydrate (1.2).H_2O was determined by X-ray crystallography, the cyclopentadienyl rings were eclipsed [2]. The diacetylene compound (1.3) has been characterized by X-ray crystallography [3]. The crystal and



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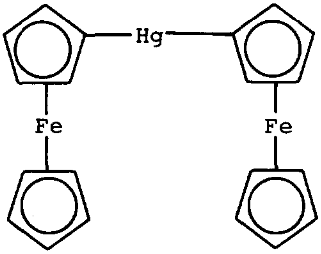

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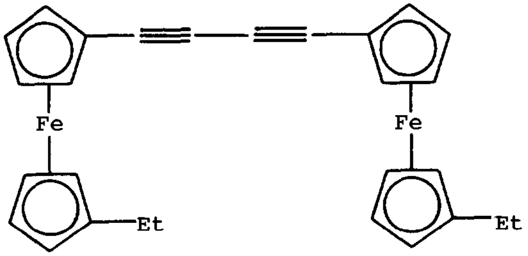

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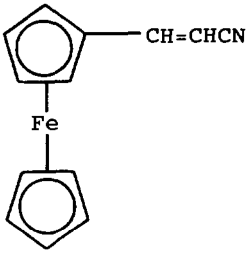

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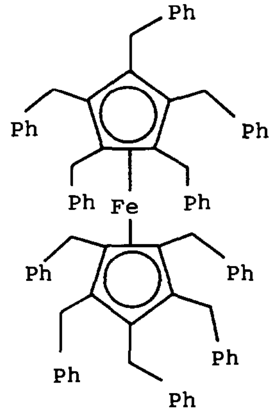
molecular structure of cis-β-ferrocenylacrylonitrile (1.4) has been determined by X-ray crystallography. The nitrile group was found to be displaced away from the plane of the cyclopentadienyl ring [4].

Reaction of iron(II)chloride with $LiC_5(CH_2Ph)_5$ gave decabenzylferrocene (1.5). X-Ray analysis indicated the η-cyclopentadienyl rings were staggered and that all five phenyl groups of each ligand were on the same side of the ring [5].



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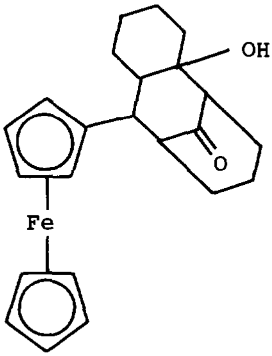

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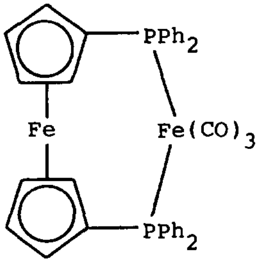

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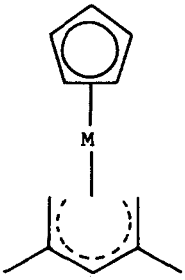
Claisen-Schmidt condensation of formylferrocene with a large excess of cyclohexanone produced 8-ferrocenyl-2-hydroxytricyclo[7,3,1,$0^{2,7}$]tridecan-13-one (1.6). The structure of this complex was determined by X-ray analysis [6]. Reaction of decamethylferrocene with perfluoro-7,7,8,8-tetracyano-p-quinodimethane ($TCNQF_4$) led to the isolation of two phases with 1:1 and 2:1 stoichiometry. The structure of the black 2:1 complex, $\{[(\eta\text{-}C_5Me_5)_2Fe]^{+\cdot}\}_2\ [TCNQF_4]^{2-}$, was determined by X-ray analysis. The dianion was nonplanar with the $-C(CN)_2$ groups forming a plane and the C_6 ring forming a second plane with a dihedral angle of 33.3° [7]. (η-Maleic acid)tetracarbonyliron has been treated with 1,1'-bis(diphenylphosphino)-ferrocene to give the complex (1.7) which has been characterized by X-ray crystallography [8].

2. THEORETICAL STUDIES

INDO calculations showed that the metallocenes $(\eta\text{-}C_5H_5)_2M$, where M = Ti, V, Cr, Fe, Co and Ni, could form complexes with methane and acetylene [9]. The molecular hyperpolarizibility of ruthenocene and other metallocenes including ferrocene has been measured and compared with the value for a liquid ferrocene derivative. The third order coefficient, γ had a value 2 to 3 times greater than that of nitrobenzene. The observed n_2 was considered to be electronic in origin [10]. Molecular graphics techniques have been used to model the nucleophilic and electrophilic addition reactions to organometallic species including ferrocene [11]. The kinetics of the reaction of several α-hydroxylated ferrocenes with thioglycollic acid has been studied [12]. The half-open ruthenocene and osmocene complexes (2.1; M = Ru, Os) have been prepared by reduction of $RuCl_3nH_2O$ and Na_2OsCl_6 in the presence of slightly less than one equivalent of cyclopentadiene and an excess of 2,4-dimethyl-1,3-pentadiene. An X-ray diffraction study of the ruthenium complex indicated a structure analogous to that of the isomorphous iron compound. INDO-MO calculations were used to correlate the energy levels and the wave functions of bis(η-pentadienyl)iron, (η-cyclopentadienyl)(η-pentadienyl)iron and ferrocene. The He(I) and He(II) photoelectron spectra of (η-cyclopentadienyl)-(η-2,4-dimethylpentadienyl)-iron, -ruthenium and -osmium were recorded [13].



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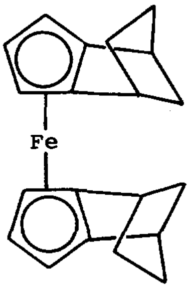
3. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

A 2D ^1H NMR study of the isodicyclopentadiene derivative (3.1) has shown that all possible isomers, *exo*, *exo*; *exo*, *endo*; *endo*, *endo* were present although the *exo*, *exo* distribution was favoured [14]. ^{13}C NMR spectroscopy and cyclic voltammetry have been used to investigate the effects of electron-withdrawing and electron donating substituents on the distribution of electron density in phenylferrocene and the olefins (3.2, 3.3 and 3.4) [15]. Formylferrocene was used to prepare the substituted acetylene (3.5). Reaction of this latter compound with hexacarbonyldicobalt or $Mo_2(\eta\text{-}C_5H_5)_2(CO)_4$ produced the corresponding metallocarbonyl clusters [3.6; M_2 = $Co_2(CO)_6$, $Mo_2(\eta\text{-}C_5H_5)_2(CO)_4$]. Treatment of these complexes with HBF_4 afforded the corresponding salts (3.7) which were studied by NMR and IR spectroscopy. It was concluded that in the cobalt cluster [3.7; M_2 = $Co_2(CO)_6$] the ferrocenyl group dominated in the stabilization of the carbenium ion. Whilst in the molybdenum complex [3.7; M_2 = $Mo_2(\eta\text{-}C_5H_5)_2(CO)_4$] the molybdenum cluster played the principal role in stabilizing the cation [16].



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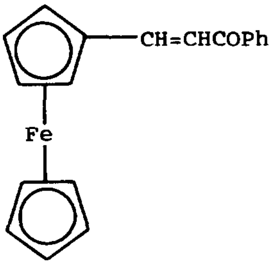

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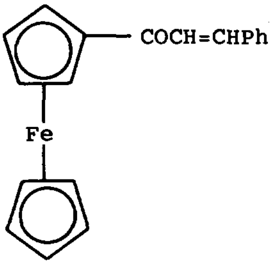

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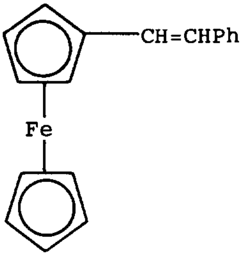
Adducts of ferrocenyl ruthenocene with mercury(II) chloride and iodine, ferrocenyl ruthenocenyl ketone with mercury (II) chloride, tin(IV) chloride and iodine have been studied by high resolution solid state ^{13}C NMR and ^{57}Fe Moessbauer spectroscopy. The results suggested the presence of Ru-Hg and Ru-I bonds in the adducts [17,18]. The ^1H and ^{13}C NMR spectra of



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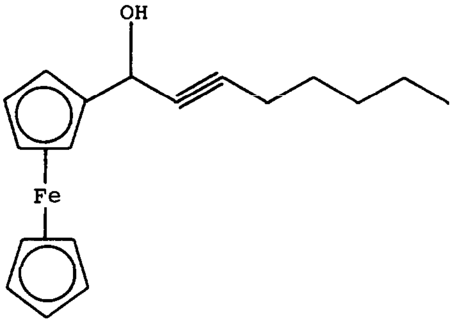

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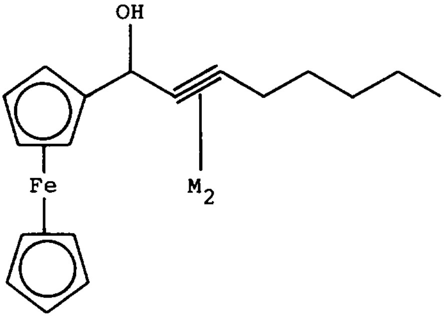

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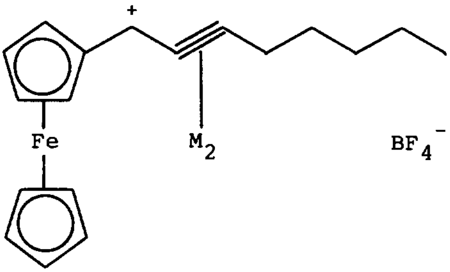

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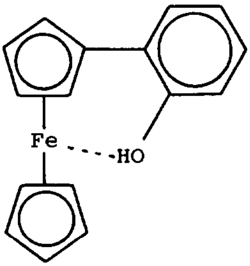

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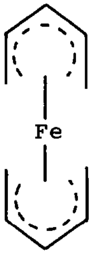

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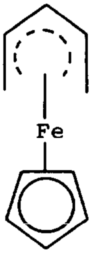

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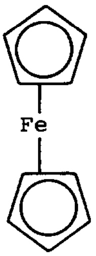
the phenol (3.8) and several analogues have been recorded in a series of aprotic polar solvents. As the polarity of the solvent increased the strength of intramolecular OH-d orbital type hydrogen bond decreased [19]. Open (3.9), half-open (3.10) and closed (3.11) ferrocenes have been prepared and compared by ^{13}C and ^{57}Fe NMR spectroscopy. On moving from closed to half-open and then open ferrocenes there was a deshielding of the iron nucleus by about 700 and 1100ppm [20].



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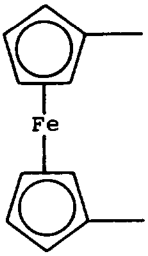

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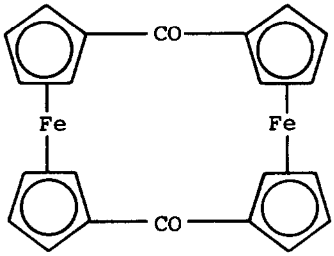

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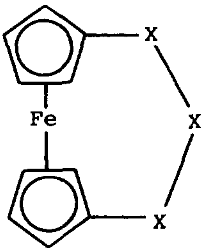
The FT-IR and laser Raman spectra of 1,1'-dimethylferrocene (3.12) have been recorded and assigned. The force constants of manganocene, ferrocene and cymantrene have been obtained by G-F matrix, qualitatively assigned and translated to the 1,1'-dimethylferrocene molecule (3.12) [21].

IR spectroscopy has been used to show that phenol and t-butanol formed hydrogen bonds with 1,1' -diethylferrocene [22]. The position of charge-transfer bands have been determined in the electronic spectra of charge-transfer complexes of a series of ferrocene derivatives with diiodomethane, triiodomethane and tetraiodomethane. The nature of the iodo-methane was more important than the substituent on ferrocene in determining the position of the band [23]. Bands in the vapour-phase UV spectra of ferrocene and 1,1'-dimethylferrocene have been assigned to the Rydberg $3d_{(a1g)} \rightarrow R4p$ transition [24]. Induced Cotton effects have been determined for ferrocene, acetyl-, trifluoroacetyl- and formyl-ferrocene, 1,1'-diacetylferrocene and two ferrocenophanes in α-, β- and γ-cyclodextrins. The results obtained contradicted the hypothesis of Harada and Takahashi about the dependence of the sign of the induced Cotton effect on the orientation of the ferrocene in the cyclodextrin cylinder [25,26].

A range of metallocenes and related derivatives including hexamethylferrocene have been studied by mass spectrometry and fragmentation pathways confirmed [27]. A comprehensive pulsed mass spectrometric study of ferrocene has been carried out. The ionization energy was found to be 157.1 kcal mol^{-1} and the proton affinity was 207 kcal mol^{-1}. The results obtained exhibited some features that were unusual in gas-phase ion chemistry. These included the following: very low solvation energies; slow proton transfer with small or no temperature coefficient and entropy driven proton transfer from cluster ions. These features were associated with the iron atom being the site of protonation and with steric hindrance to the access to the metal [28]. The carbon 1s oscillator strength spectra of ferrocene, cobaltocene and nickelocene have been obtained from inelastic electron scattering spectra by using conditions in which electric dipole transitions were dominant [29].

A series of ferrocenylamines and ferrocenylphosphines has been studied by ^{57}Fe Moessbauer spectroscopy and the results were compared with those obtained by ^{13}C NMR spectroscopy and cyclic voltammetry. A difference was observed in the interaction between the ferrocenyl unit and the exocylic nitrogen and phos-



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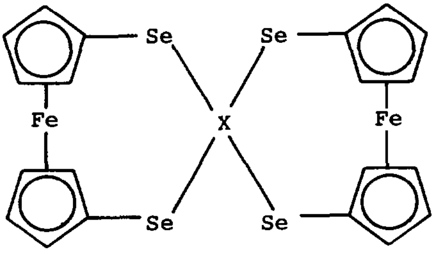

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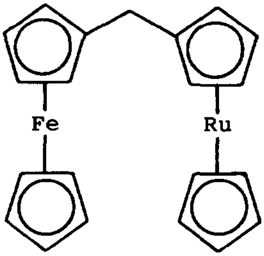
phorus atoms [30]. Reaction of [1.1]ferrocenophane-1,12-dione (3.13) with iodine or dichlorodicyanobenzoquinone (DDQ) gave dimagnetic [1.1]ferrocenophane-I_2 and -DDQ adducts. Paramagnetic {[1.1]ferrocenophanium-1,12-dione}$^+Br_3^-$ was formed on reaction with bromine. ^{57}Fe-Moessbauer spectroscopy and other physico-chemical data confirmed that iodine and DDQ formed molecular complexes and bromine gave a trapped-valence type mixed-valence salt with [1.1]ferrocenophane -1,12-dione [31]. Trisferrocenylborane has been synthesised and studied by IR and Moessbauer spectroscopy [32]. Substituted ferrocenes and several other organometallic compounds have been doped with iodine and investigated as semiconductors. The formation of low-spin Fe(II) species was implicated in the carrier transport system by Moessbauer spectroscopy, IR and ^{13}C CPMAS NMR studies [33].

The oxidation potentials and Moessbauer parameters for several ferrocenophanes such as (3.14; X = S, Se) and spiro compounds such as (3.15; X = Si, Sn) have been reported [34]. Ferrocenylruthenocene, ferrocenylruthenocenylmethane (3.16) and biruthenocene formed adducts with iodine, tin (IV) chloride and mercury(II) chloride. Bonding in these adducts was investigated by ^{13}C CPMAS NMR and ^{57}Fe and ^{119}Sn Moessbauer spectroscopy. Direct interaction was observed between iron or ruthenocene and the central atom in the Lewis acid [35]. The behaviour of a



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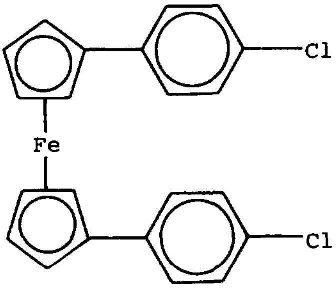
series of α-phosphaferrocenyl alcohols in CF_3CO_2H has been examined by ^{31}P NMR and ^{57}Fe Moessbauer spectroscopy. Dehydration occurred and carbenium ions were formed. These had lower stability than the corresponding α-ferrocenyl carbenium ions [36]. Ferrocenyl(η-arene)(η-cyclopentadienyl)iron complexes with 36, 37 and 38 electrons have been examined by Moessbauer spectroscopy. Coupling between 19e subunits was elucidated and related to electron transfer to the bridge in the mixed valence states [37].



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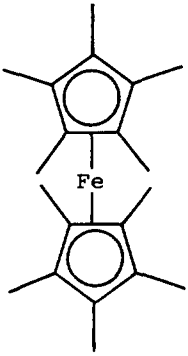

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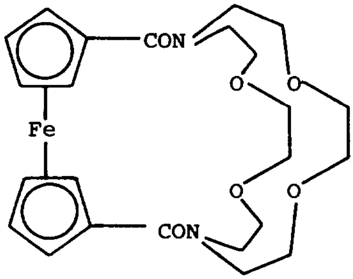
A series of ferrocene derivatives and (η-benzene)tricarbonylchromium complexes have been characterised by X-ray photoelectron spectroscopy. The binding energies of the 2p electrons indicated that the actual oxidation states of the iron and chromium atoms were close to zero. The metal core electron levels were unchanged by substituents on the η-cyclopentadienyl and η-benzene rings [38]. The He(I) photoelectron spectra of 1,n-dithia[n]ferrocenophanes (n = 3-8, 10) and 1,1'-bis(methylthio)ferrocene have been recorded. The energy gap between $^2A_1(a_1{}^1e_2{}^4)$ and $^2E_2(a'_1{}^2e'_2{}^3)$ ion states was decreased by the perturbation of the coplanarity of ligand planes and by a conjugative interaction of sulphur lone pairs with ferrocene orbitals [39]. The dipole moments of several chlorophenyl derivatives of ferrocene, such as the bis(4-chlorophenyl)ferrocene (3.17), have been measured and the conformations of the compounds determined [40].

The kinetics of quenching of tris(2,2'-dipyridine)-chromium(III) ions by a series of ferrocenes and ferrocenium ions has been investigated by laser flash photolysis. Ferrocenium ion quenching proceeded by energy transfer and it was dependent on the donor-acceptor distance, as expected for an electron--exchange mechanism. The ferrocenes were effective quenchers and the reactions partitioned themselves between electron transfer and energy transfer. The tris(2,2'-bipyridine)chromium (II) ions and the ferrocenium ions, formed by electron-transfer quenching, underwent rapid back electron transfer [41]. The pK_a value of 4-nitro-2,3,5,6-tetrafluorophenol was determined and the phenolic esters of trans-ferrocenylacrylic acid and ferrocenylcyclopropanecarboxylic acid were prepared. The relationship between pK_a and the rates of β-cyclodextrin catalysed hydrolysis of the esters was investigated. The kinetics of hydrolysis followed a Hammett linear free energy relationship [42]. The one-electron reduction of substituted benzenediazonium salts has been investigated using decamethylferrocene (3.18) as the reducing agent. Rate constants were measured and a linear Hammett plot was obtained [43].

4. ELECTROCHEMISTRY

The bimetallic ferrocene complex $Fe(\eta\text{-}C_5H_4S)_2Mo(NO)[HB(3,5\text{-}Me_2C_3N_2H)]$ has been studied by cyclic voltammetry and shown to have an anomalous cathodic oxidation potential [44].



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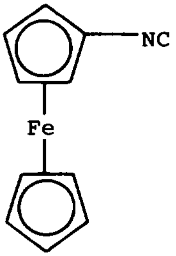

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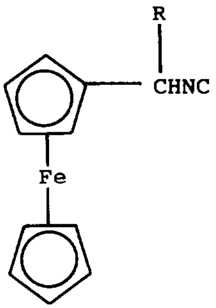
Complexes of the cryptand (4.1) with alkaline-earth and lanthanide metal cations have been investigated by cyclic voltammetry. The results obtained were used to calculate values of $\underline{K}_2$ for the association of the oxidized cryptand with the metal cations. A linear correlation was obtained between ln$\underline{K}_2$ and the ratio of ionic radius/ionic charge. This supported the idea that the stability of the oxidized cryptate depended mainly upon charge repulsion between the oxidized cryptand and the complexed metal ion [45]. The kinetics of electron transfer between ferrocene, 1,1'-diethylferrocene or 1,1'-distearoylferrocene in 1,2-dichloroethane and hexacyanoferrate(III) ion in water has been studied by convolution potential sweep voltammetry. The potential and the concentration of reactants had no effect on the rate constant of electron transfer from the organic to the aqueous phase. The reaction was complicated by the decomposition of the ferrocenium ion in the dichloroethane [46]. The efficient reduction of dioxygen with ferrocene and a series of alkylferrocenes was catalysed by metalloporphyrins or $[Co(TIM)]^{3+}$, where TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, in the presence of perchloric acid in methyl cyanide. Electron transfer from the ferrocenes to the metalloporphyrins was rate determining and the rate was independent of the concentration of dioxygen and perchloric acid. The rate of electron transfer from the ferrocenes to $[Co(TIM)]^{3+}$ was increased by the presence of dioxygen and perchloric acid. The rates of the electron transfer reactions were discussed in terms of the Marcus theory to distinguish between other-sphere and inner-sphere electron transfer processes [47]. The reduction potentials of five alkyl-substituted ferrocenes have been determined in a N-(n-butyl)pyridinium chloride-aluminium chloride molten salt. The reduction potentials varied over a range of 1.6V which was greater than had been observed for similar ferrocenes in other nonaqueous solvents. A close correlation of $\sigma\overset{o}{\underline{p}}$ constants with reduction potentials was observed [48].

An electrochemical study has been carried out on the ferrocenylisocyanides [4.2 and 4.3; R = H, (1R, 2S, 5R)-2-isopropyl-5-methylcyclohexyl] and their complexes with the $Cr(CO)_5$ group. The cyclic voltammograms of these chromium complexes



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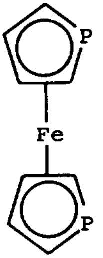

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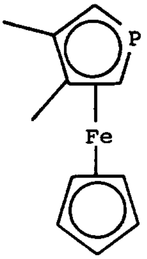

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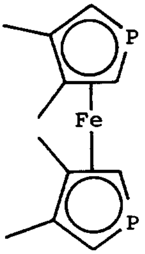
exhibited two successive one-electron quasi-reversible anodic waves which were assigned to the stepwise oxidation of the two metal atoms. The ferrocenyl redox centre was easier to oxidize than the coordinated $Cr(CO)_5$ moiety [49]. A comparative electrochemical study of the oxidation of ferrocene and the three phosphaferrocenes (4.4, 4.5 and 4.6) has been carried out in the presence of nucleophilic reagents. The phosphaferrocenium cations were less stable to nucleophilic attack than the ferrocenium ion. The phosphorus atoms were responsible for this situation as they were strong electron-attractors and especially effective as π-acceptors [50].



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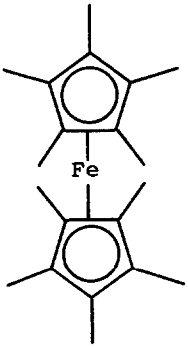

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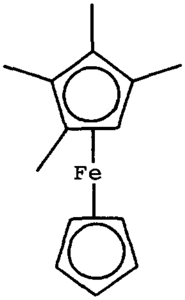
The reaction of 4-ferrocenylaniline with MoI$_2$(NO)[(dimethyl-3,5-pyrazolyl)borate]$_3$ in the presence of base gave 4-ferrocenylanilidonitrosyl[tris(dimethyl-3,5-pyrazolyl)boratomolybdenum]. No transmission of electronic effects between the two nuclei was detected by electrochemical investigation and this was attributed to the presence of an electron-rich group in the bridging ligand [51]. A vinylferrocene-vinylpyrrolidone copolymer has been deposited on to a platinum electrode. Coulometric and ellipsometric techniques were used to characterize the surface film [52]. Ferrocene-cobaltocenium ion charge-transfer complex formation has been observed at the interface of a bilayer film containing the two metallocenes under the influence of an electrical field [53]. Decamethylferrocene (4.7) has been used as the electroactive species in a study of diffusional transport to nanoscopic band electrodes [54].

5. PREPARATIONS OF FERROCENE

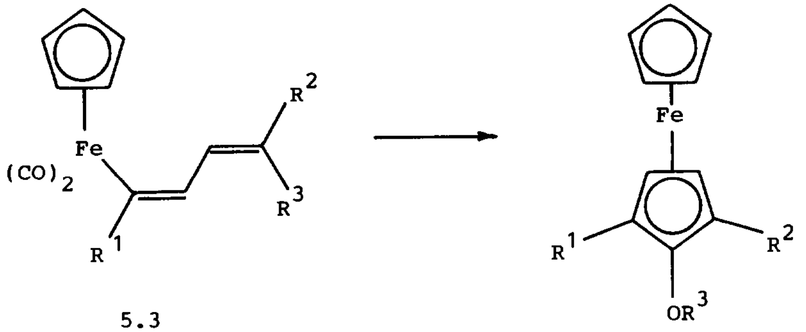
The cocondensation of iron atoms with cyclopentadiene and alkynes at 77K gave ferrocene together with substituted ferrocenes due to the incorporation of the alkyne skeleton into an η-cyclopentadienyl ring. For example, the cocondensation of equimolar quantities of cyclopentadiene, iron atoms and 2-butyne produced ferrocene and 1,2,3,4-tetramethylferrocene (5.1) in a 2:1 ratio. It was postulated that coordinatively unsaturated alkylidyne complexes (5.2; R = H, alkyl) were intermediates in these reactions [55]. Ferrocene was obtained



5.1

5.2

as a minor product from the photolysis of disilanyliron(II)-carbonyl complexes such as (η-C_5H_5)$Fe(CO)_2SiMe_2SiMe_3$ [56]. The low temperature pyrolysis of [(η-C_5H_5)(Et_3P)(CO)Fe]$_2$ and [(η-C_5H_5)(Et_3P)(CO)FeTe]$_2$ has been used to produce iron monotelluride and iron ditelluride respectively. Ferrocene was one of the by-products in these reactions [57]. Ferrocene was formed as a minor product in the reaction between lithium cyclopentadienide and $Fe(NPh_2)_2$ [58]. Reaction of



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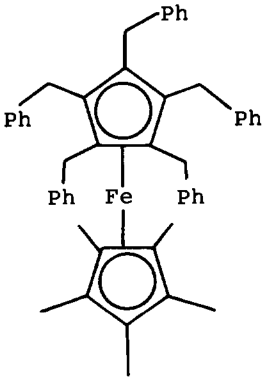

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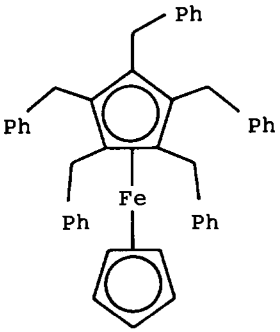
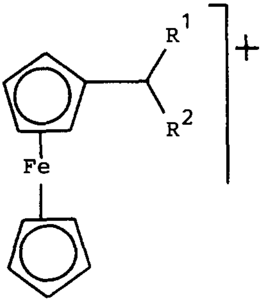


5.6

1-lithio-1,3-butadienes with (η-C_5H_5)Fe(CO)$_2$I produced the corresponding η^1-buta-1,3-dienyl complexes (5.3; $R^1 = R^2$ = Ph, R^3 = H; $R^1 = R^3$ = H, R^2 = Ph; $R^1 = R^3$ = H, R^2 = CH_3, $R^1 = R^2$ = Ph, R^3 = D). Irradiation of these complexes afforded the corresponding hydroxyferrocenes (5.4) in excellent yields. The mechanism of this reaction was investigated [59]. Reaction of lithium pentabenzylcyclopentadienide with iron(II) chloride produced decabenzylferrocene. The pentabenzylferrocenes (5.5 and 5.6) were also prepared via (η-C_5R_5)Fe(acetylacetonate), where R = Me, benzyl. X-Ray analysis of decabenzylferrocene indicated that all ten phenyl-groups were pointing away from the iron atom [60].

6. REACTIONS OF FERROCENE

Ferrocene has been treated with aldehydes and ketones in sulphuric acid to give the intermediate ferrocenylcarbenium ions (6.1; $R^1 = R^2$ = H, Me; R^1 = H, R^2 = Me, Ph; R^1 = Ph, R^2 = Me) which led to a variety of other products [61].



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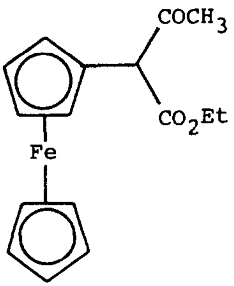
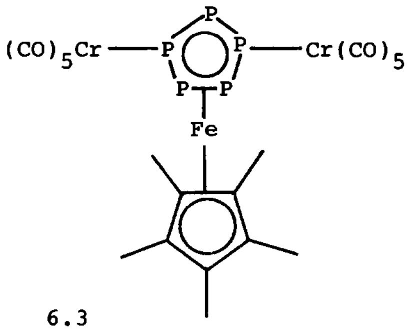


6.2

Reaction of ferrocene with $MeCOCH_2CO_2Et$ and concentrated sulphuric acid at -5° gave the ester (6.2) in good yield [62]. Ferrocene underwent ligand exchange with polyaromatic ligands such as triphenylene, perylene, biphenyl, phenanthrene, dihydrophenanthrene and pyrene to give the corresponding (η-cyclopentadienyl)(η-polyarene)iron cations [63]. The reaction between metallocenes including ferrocene and carbon monoxide at low temperatures has been examined by IR spectroscopy [64].



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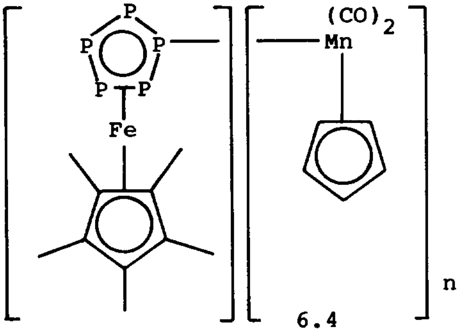

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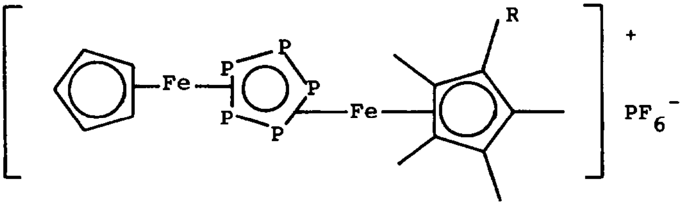
An iron carbide film has been deposited from ferrocene vapour by using an electron cyclotron resonance plasma technique [65].



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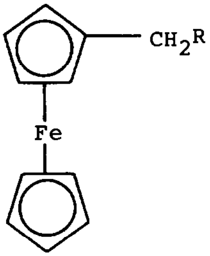
An iron carbonitride film has been formed on a glass substrate from ferrocene and hydrogen, and a hydrogen-nitrogen plasma [66]. Reaction of pentaphosphaferrocene with $[Cr(CO)_5(THF)]$ or $[(\eta\text{-}C_5H_5)(CO)_2Mn(THF)]$gave the corresponding chromium and manganese complexes (6.3 and 6.4; n = 1-4). Irradiation of pentaphosphaferrocene or $(\eta\text{-}C_5Me_4Et)Fe(\eta\text{-}P_5)$ with $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]PF_6$ gave the cationic triple-decker compounds (6.5; R = Me and Et) respectively [67].

7. FERROCENIUM SALTS AND MIXED-VALENCE SALTS

Oxidation of the ferrocenyl-carboxylic acids [7.1; R = CO_2H, CH_2CO_2H, $(CH_2)_2CO_2H$, $CH(CO_2H)_2$, $S(CH_2)_2CO_2H$, $SCH(CO_2H)CH_2CO_2H$) with p-benzoquinone-HCl-$FeCl_3$ produced the corresponding hydrophilic salts (7.2) [68]. Ferrocenium charge transfer salts of the form $[Fe(\eta\text{-}C_5Me_5)_2]^+[Ni(X_2R)_2]^-$ have been prepared and evaluated as three-dimensional ferromagnetic solids. Two of the salts prepared, where X_2R = 2-thioxo-1,3-dithiole-4,5-dithiolate and 1,2-benzenediselenolate, have been characterized by X-ray crystallography [69]. Reaction of the ferrocenium salt (7.3) with K_2OsCl_6 and K_2PtCl_6 gave the corresponding ferrocenium salts $[(\eta\text{-}C_5H_5)_2Fe]_2$ - $OsCl_6$ and -$PtCl_6$. Thermolysis of these salts produced ferrocene [70]. The ferrocenium ion



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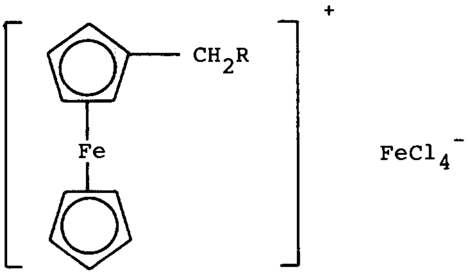

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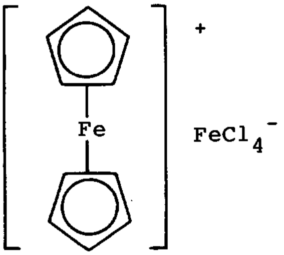

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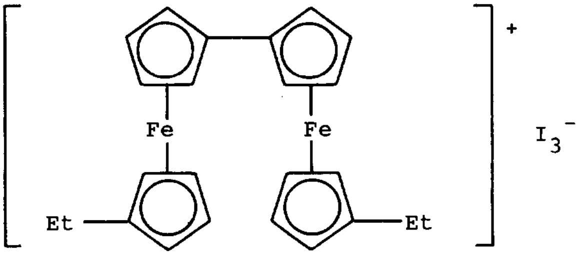


7.4

has been used as an oxidizing agent for (η-cyclopentadienyl)-nitrosylmanganese complexes [71].

Rate constants and activation parameters for the electron self-exchange in the cobaltocenium/cobaltocene couple have been compared with the ferrocenium/ferrocene couple in 13 organic solvents. The data were used to make a systematic comparison of solvent dielectric relaxation effects on the barrier crossing frequency for outer sphere reactions [72]. The crystal structure of the biferrocenium salt (7.4) has been determined at 298 and 140°K. The biferrocenium cations and the triiodide anions sat on a crystallographic centre of symmetry at both temperatures and the two ferrocenyl units were crystallographically equivalent [73]. Ferrocene-ferrocenium electron self--exchange in CD_3CN has been studied at elevated pressures by ^1H NMR spectroscopy. Rate constants and thermodynamic parameters were reported and discussed on the basis of theoretical models [74].

NMR line broadening has been used to study electron self exchange in the cobaltocenium/cobaltocene couple. Comparisons were made with the ferrocenium/ferrocene couple. The slower self-exchange kinetics observed for the ferrocene couple indicated high ligand-delocalized character of the Ze(Ig) orbital in the cobaltocene couple compared with the 4e(2) or 8a(Ig) orbital in the ferrocene couple [75]. The linear charge transfer complexes $[(\eta\text{-}C_5Me_4H)_2Fe]^{\dot{+}}[TCNE]^{\dot{-}}$ and $[(\eta\text{-}C_5Me_4H)_2Fe]^{\dot{+}}[TCNQ]^{\dot{-}}$ have been studied by EPR and Moessbauer spectroscopy. The ferromagnetic behaviour was discussed [76].

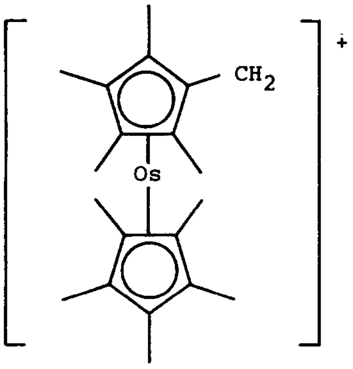
8. FERROCENYL CARBONIUM IONS

Rybinskaya and co-workers determined the structure of the osmocenylcarbonium ion salt (8.1) by X-ray analysis. It was concluded that in nonamethylmetallocenylcarbonium ions the ability of the central metal atom to stabilize the α-carbenium cation increased in the order Fe<Ru<Os [77].

9. FERROCENE CHEMISTRY

(i) Derivatives containing main group metals and metalloids

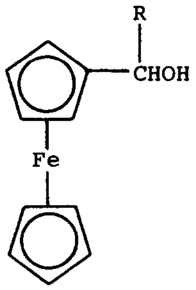
Treatment of the ferrocenyl-alcohols (9.1; R = H, Me) with Me_3SiNEt_2 produced the corresponding trimethylsilyl



$BPh_4^-.CH_2Cl_2$

8.1

derivatives (9.2). In a similar reaction between the alcohol (9.1; R = Me) and $PhSiMe(NEt_2)_2$ the di(ferrocenyl) compound (9.3) was obtained in good yield [78]. Reaction of ferrocenylmethanol with the methylchlorosilanes $Me_{2+n}SiCl_{2-n}$ or the



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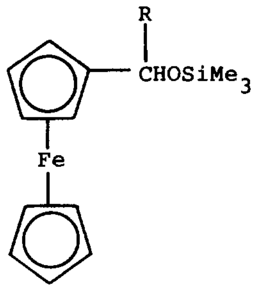

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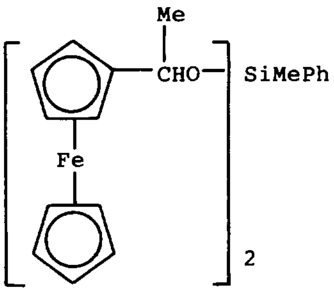
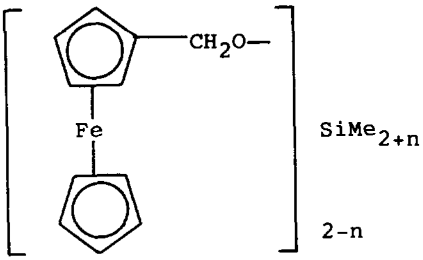


9.3

dimethylaminomethylsilanes $Me_{2+n}Si(NEt_2)_{2-n}$ produced the corresponding ferrocenylsiloxanes (9.4) [79]. Oxidation of 1,1'-bis-(diphenylphosphino) ferrocene with Me_3SiN_3 produced the trimethylsilyliminophosphine (9.5). Reaction of this molecule with tungsten(VI) fluoride afforded the ferrocenophane (9.6) [80]. Charge-transfer complex formation between tetrabromomethane and the silylferrocenes (9.7, 9.8; X = NH, O and 9.9; X = NH, O) has been investigated by absorption spectroscopy. The



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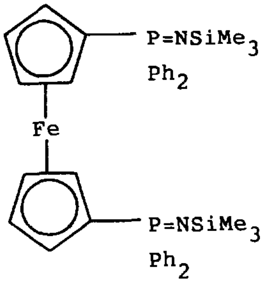

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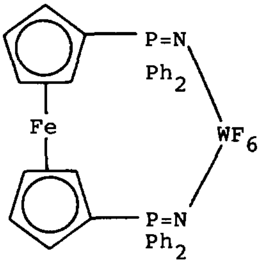

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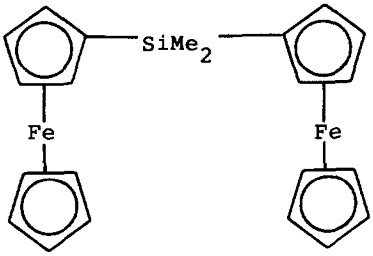

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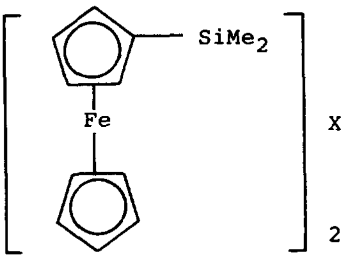

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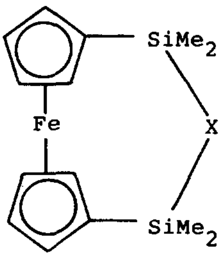

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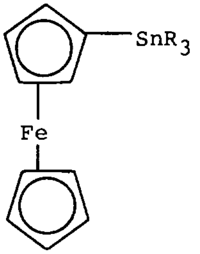

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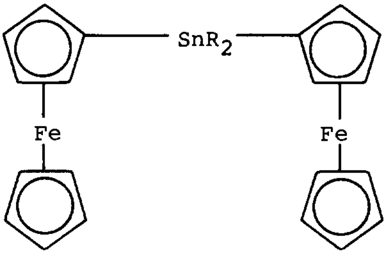
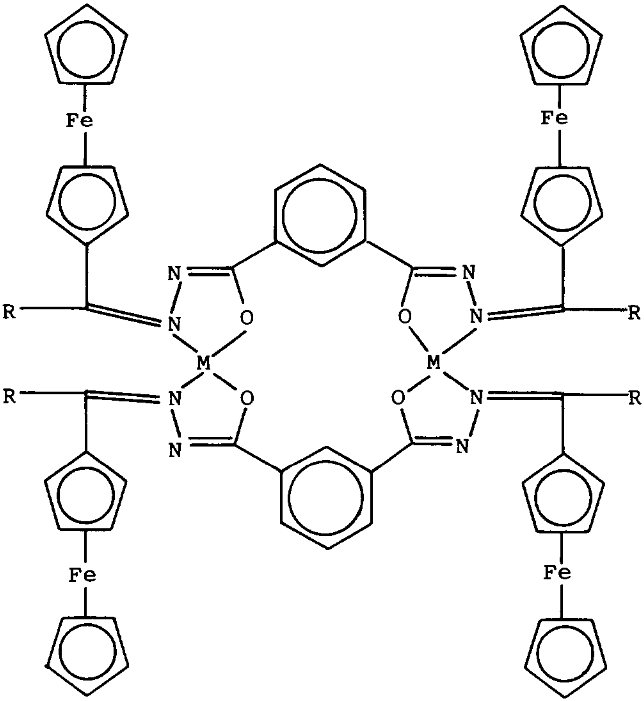


9.11

complexes were 1:1 with diferrocenyl species showing a stronger tendency to form complexes [81].

Laser-flash photolysis and ferrocene quenching studies of (TPP)Ge(R)$_2$, where TPP is the dianion of meso-tetraphenylporphyrin and R is either C_6H_5 or $CH_2C_6H_5$, indicated that the triplet states of the porphyrin complexes were photoreactive. In contrast, the complexes (TPP)Ge(C_6H_5)Fc and (TPP)Ge(Fc)$_2$, where Fc is the σ-bonded ferrocenyl group, were photostable. An energy transfer from the porphyrin triplet state to the ferrocenyl group was thought to be involved in the photostability of these two complexes [82]. Diferrocenylmercury has been treated with bis-triorganotin sulphides and diorganotin sulphides to give triorganostannylferrocenes and diorganostannylferrocenes (9.10 and 9.11; R = Me, Bu, C_6H_5) respectively [83]. The oxo- and thio-aroylhydrazones of formyl- and acetyl-ferrocene were treated with metal acetates to give the corresponding chelate complexes (9.12 and 9.13; R = H, Me; M = Co, Ni, Cu, Zn, Hg) [84].

Condensation of 1,1'-diacetylferrocene with benzoylhydrazine gave the corresponding hydrazide (9.14). This compound produced the metal complexes (9.15; M = Co, Ni, Zn, Cd, Cu, Mn and 9.16; M = Co, Ni, Cd, Mn) on reaction with the corresponding metal(II) acetates and chlorides respectively [85]. Reaction of acetylferrocene with $PhCONHNH_2$ gave the hydrazone (9.17). Treatment of this hydrazone with the metal chlorides MCl_3, where



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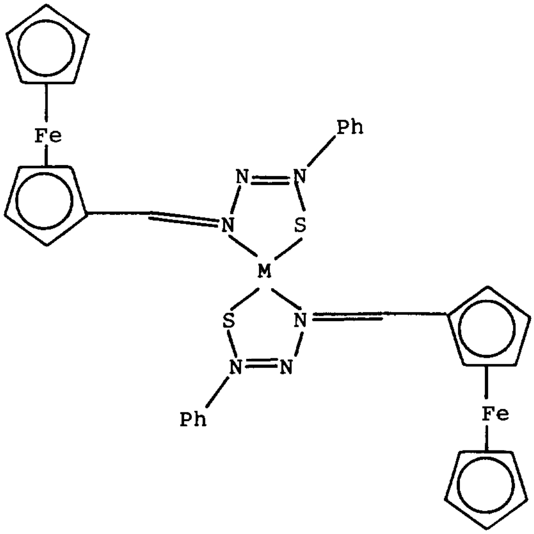

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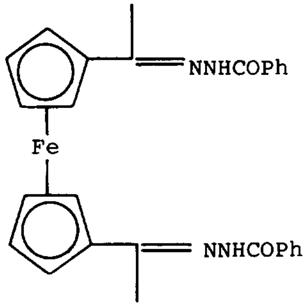

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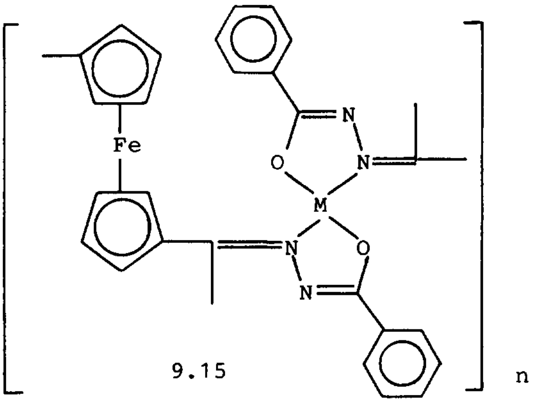

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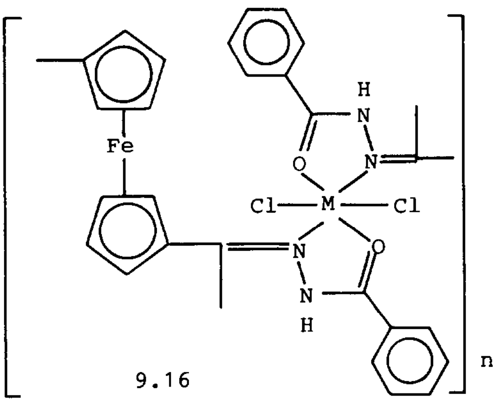

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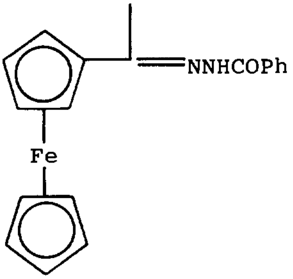
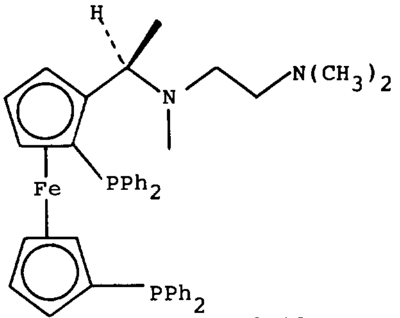


9.17

M = La, Ce, Pr, Sm, Eu, Gd, Tb, Tm and Lu, in the presence of triethylamine gave the corresponding hydrazone-metal complexes [86]. Similar reactions of the same ligand and the characterisation of the metal complexes via ^{13}C-CP-MAS NMR and ^{57}Fe-Moessbauer spectroscopy were reported in another paper [87]. The infrared and ultraviolet spectra, thermal analytical data and conductivity measurements indicated that the hydrazone ligand coordinated with the metal ions in the keto form [88].

As part of a study on the nature of the stereoselective step in the gold(I)-catalyzed aldol reaction the effect of the ferrocenyl-amine ligand (9.18) in this type of reaction was investigated. It was concluded that the central chirality of the stereogenic carbon atom in the ferrocenyl side chain



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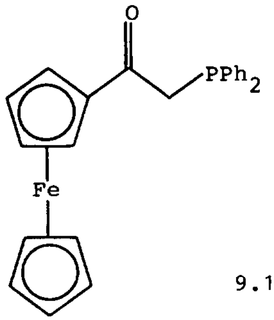

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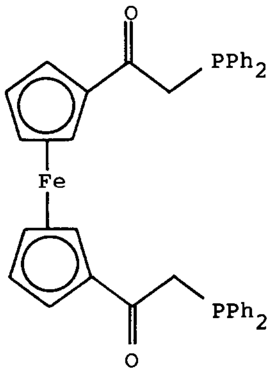

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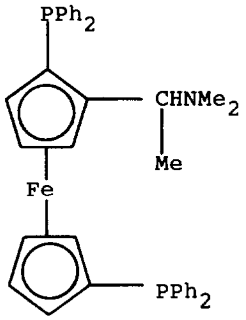
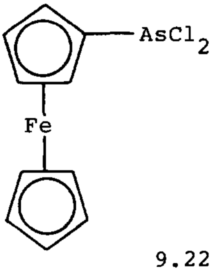


9.21

strongly affected the stereochemistry of the product. The results also suggested that the planar chirality and central chirality found in the ligand (9.18) may act in a cooperative or noncooperative manner [89]. Reaction of the lithium enolates derived from acetylferrocene and 1,1'-diacetylferrocene with diphenylchlorophosphine gave the ketophosphines (9.19 and 9.20) respectively. The structure of the ketophosphine (9.19) was determined by X-ray analysis. Both the ketophosphines formed transition metal complexes and several were prepared and characterised [90]. Several derivatives of the ferrocene-diphosphine ligand (9.21) have been prepared by introducing substituents into the phenyl rings [91].

Reaction of the chloroarsine (9.22) with 2,4,6-tri-tert-butylphenylphosphine produced the phosphorane (9.23). Treatment of this latter compound with $(Ph_3P)_2Pt(\eta\text{-}C_2H_4)$ afforded



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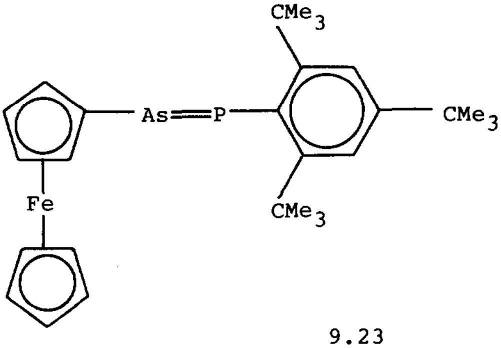

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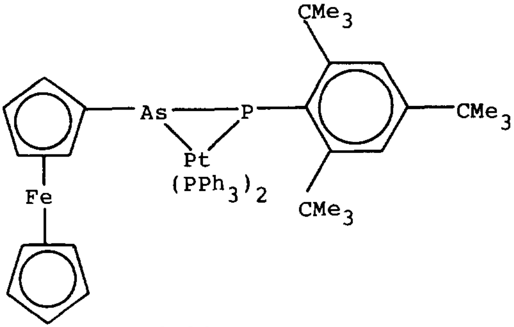

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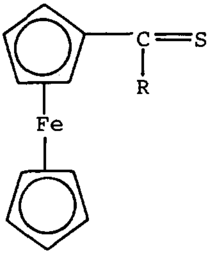

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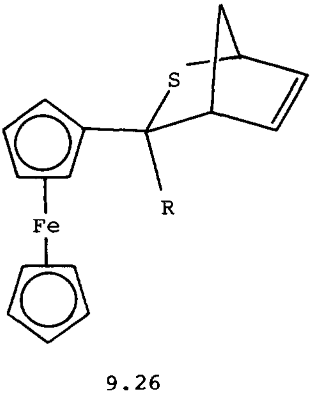

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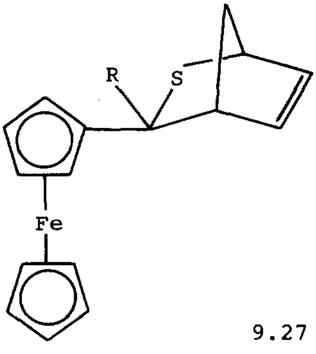
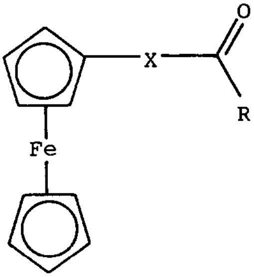


9.27

the complex (9.24) which contained a three membered ring containing arsenic, phosphorus and platinum [92]. Diels-Alder reaction of the thioketones (9.25; R = Me, Ph) with cyclopentadiene produced the corresponding exo- and endo-thiabicycloheptenes (9.26 and 9.27) [93]. A series of nine ferrocene



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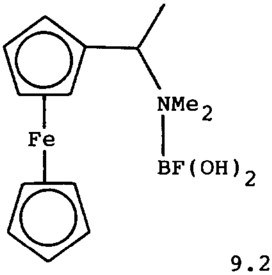

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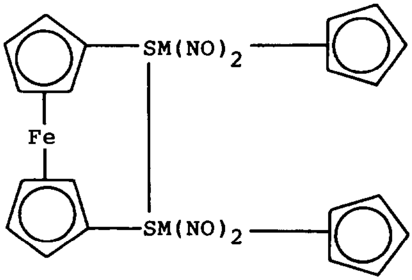
chalcogenol derivatives (9.28; X = S, Se, Te; R = C_6H_5, 2-thienyl, ferrocenyl) have been prepared together with the corresponding 1,1'-dichalcogenol compounds. The ^1H and ^{13}C NMR spectra were discussed [94]. The enthalpy of complex formation between sulphur dioxide and (R)-N,N-dimethylaminoethylferrocene has been measured as 21.5 kcal mol^{-1}. The adduct contained a sulphur-nitrogen bond. Boron trifluoride



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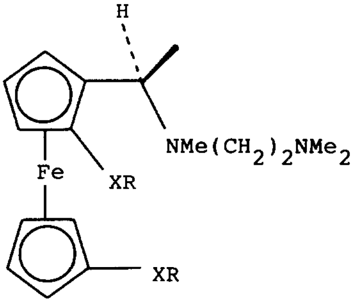
reacted with the same amine to give the partly hydrolyzed adduct (9.29) which has been characterized by X-ray crystallography [95].



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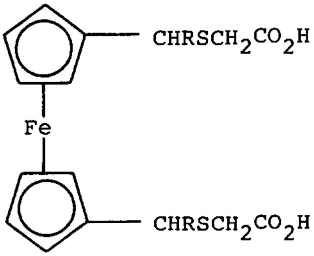
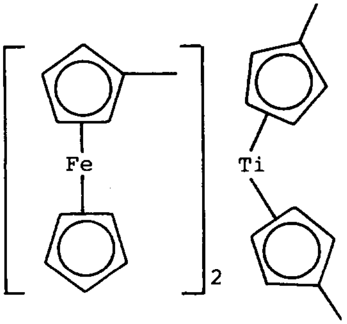


9.32

Several trinuclear complexes containing the ferrocene-1,1'-dithiolato bridge have been prepared including the chromium, molybdenum and tungsten complexes (9.30; M = Cr, Mo, W). The ferrocenylthiolato ligands were more powerful electron donors than methyl- and phenyl-thiolato ligands [96]. Dilithiation of the R-(+)-1-ferrocenylethylamine and reaction with a disulphide or diselenide gave the chiral thio- and seleno-ferrocenylamines (9.31; X = S, R = Ph, CH$_2$Ph; X = Se, R = Ph) [97]. The 1,1'-bis[(carbomethoxy)thioalkyl]ferrocenes (9.32; R = Me, Et, Pr, Pr^i, C$_6$H$_5$) have been prepared and characterized by IR and ^{1}H NMR spectroscopy [98].

(ii) Derivatives containing transition metals

Ferrocenyllithium combined with the (η-cyclopentadienyl)-titanium reagents (η-C$_5$H$_4$Me)$_2$TiCl$_2$, (η-C$_5$H$_5$)TiCl$_3$ and (η-C$_5$Me$_5$)TiCl$_3$ to give the ferrocenyl complexes (9.33, 9.34 and 9.35) respectively. The zirconium complex (9.36) was made in the same way and was characterized by X-ray crystallography [99]. 1,1'-Bis(diphenylphosphino)ferrocene gave a mixture of heterometallic products with hexacarbonylchromium which were oxidized with trimethylamine-N-oxide [100]. Reaction of two equivalents of ferrocenyldiphenylphosphine with MI$_2$(CO)$_3$(CH$_3$CN)$_2$,



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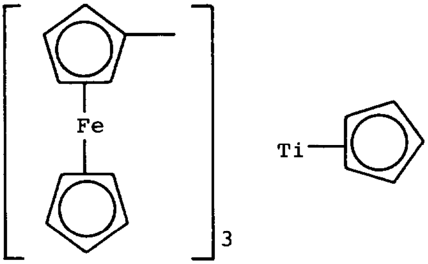

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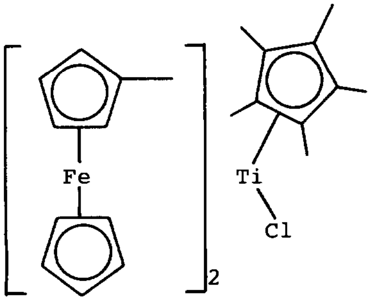

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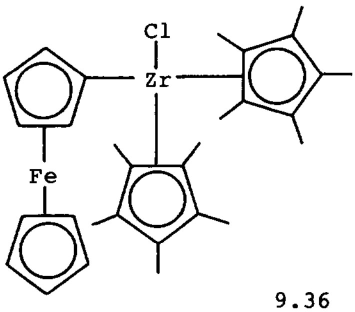

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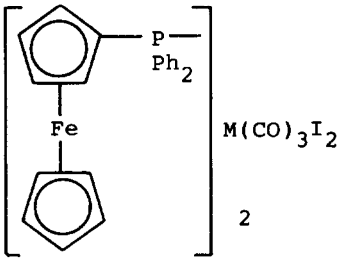

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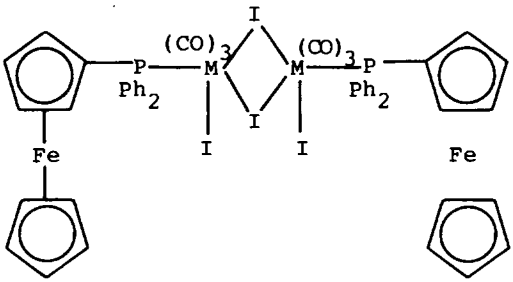

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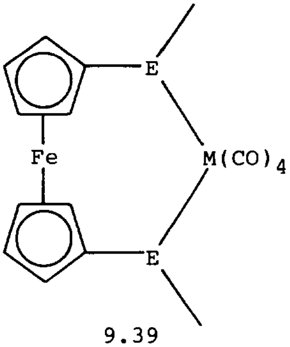
where M = Mo or W, produced the corresponding seven-coordinate complexes (9.37) via displacement of the methyl cyanide ligands. When the same reaction was carried out with one equivalent of ferrocenyldiphenylphosphine the dimer (9.38) was isolated. Several other reactions of ferrocenyldiphenylphosphine were reported [101]. The [3]ferrocenophanes (9.39; E = S, M = Cr, Mo, W; E = Se, M = Cr, Mo, W) were prepared and the ^{1}H, ^{13}C- {^{1}H} and ^{77}Se- {^{1}H} NMR spectra were recorded and interpreted. The crystal structure of the tungsten complex (9.39; E = Se, M = W) was determined by X-ray analysis. The η-cyclopentadienyl rings were eclipsed with the ring planes parallel [102].



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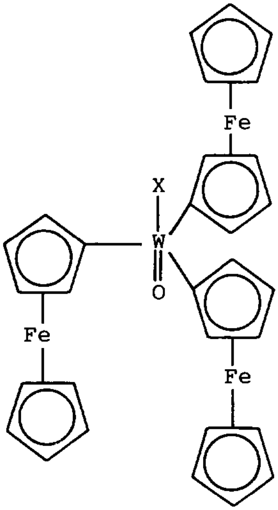
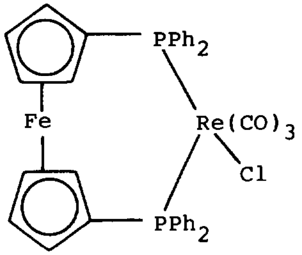


9.40

Ferrocenyllithium combined with $WOCl_4$ to give the triferrocenyltungsten complex (9.40; X = Cl) which was converted to the derivatives (9.40; X = F, OMe, OEt, OBu^{n}, OBu^{t}, O-ferrocenyl)[103]. The rhenium complexes (9.41, 9.42, 9.43, 9.44 and 9.45) have been prepared and the structures of the complexes (9.41 and 9.44) were determined by X-ray analysis. The electrochemical properties of the complexes were investigated and they all exhibited ferrocene-based reversible oxidations. The carbonyl stretching frequencies of all the complexes shifted to higher energy upon oxidation and the magnitude of the shifts was related to the number of bonds separating the ferrocenyl group from the rhenium atom [104]. Sodium phenylborataferrocene has been treated with $ReBr(NCMe)_2(CO)_3$ to form the triple-



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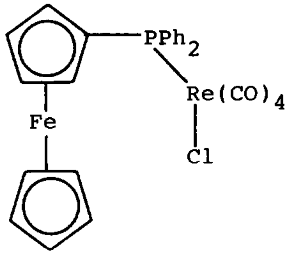

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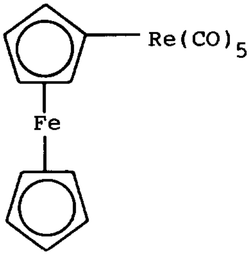

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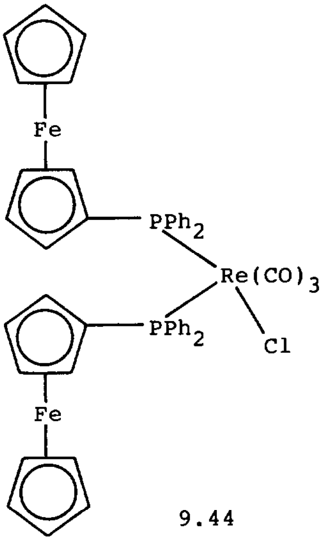

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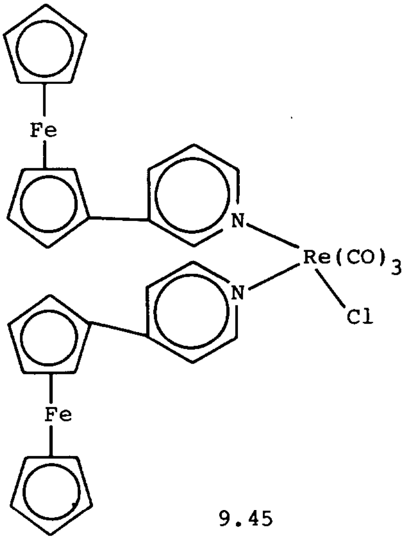
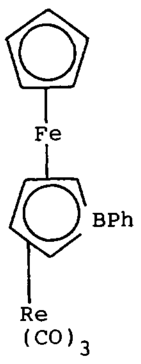


9.45

decker heteronuclear complex (9.46) [105]. Triple-decker sandwich complexes (9.47; M = Nb, Ta) containing the boraferrocene group have been prepared [106]. The ruthenium complex, $RuCl(PPh_3)_2(\eta-C_5H_5)$, underwent exchange of triphenylphosphine with 1,1'-bis(diphenylphosphino)ferrocene to give the ruthenium-ferrocenephosphine complex (9.48) [107].

The ferrocenyldiketone (9.49), FDKH, has been used to prepare the metal complexes $(FDK)_3Fe$ and $(FDK)_2Cu$, these products were used as catalysts for the combustion of ammonium perchlorate [108]. Protonation of the alkenylidene complexes $Os_3H_2(CO)_9(C{=}CHR)$, where R = ferrocenyl, phenyl or H, with



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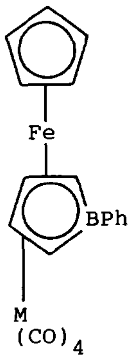

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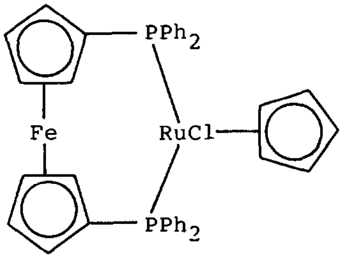
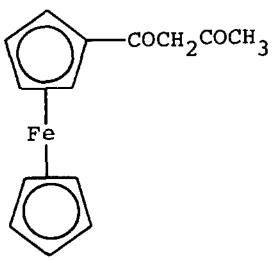


9.48

with CF_3CO_2H at -30 to -10° has been investigated. Protonation occurred at the carbene α-carbon atom [109]. A ferrocenyl alkyne cluster complex $Os_3(\mu_3\text{-CHCferrocenyl})(\mu\text{-CO})(CO)_9$ has been prepared [110]. Ferrocenylphenylacetylene combined with octacarbonyldicobalt to give the binuclear cobalt cluster complex $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4C{\equiv}CC_6H_5)Co_2(CO)_6$ [111]. Ferrocenylphosphines and ferrocenylarsines have been used to prepare 3-, 4-, 5- and 8-membered inorganic ring systems with ferrocenyl and ferrocenylene substituents. Linear, polymeric and oligomeric



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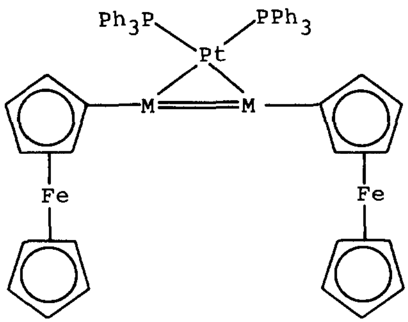

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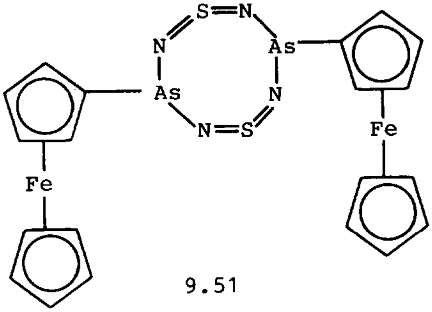

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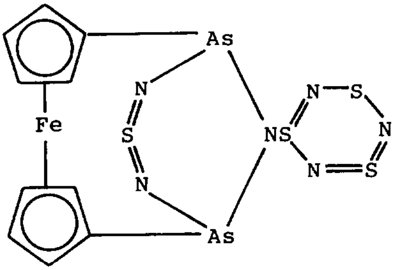

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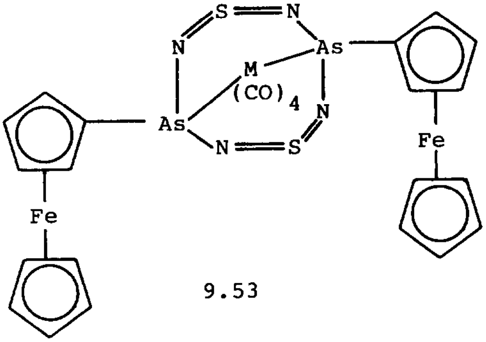

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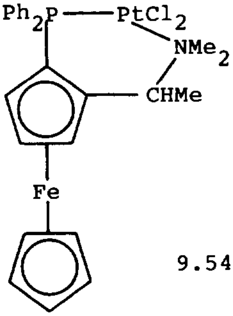
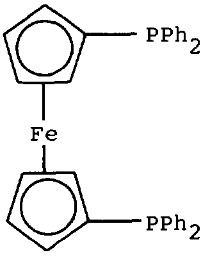


9.54

ferrocenylphosphines and ferrocenylarsines combined with $(Ph_3P)_2Pt(C_2H_4)$ to give P_2Pt and As_2Pt three-membered ring systems. Among the compounds prepared in this study were the platinum phosphines (9.50; M = P, As), the eight-membered diarsenic ring compound (9.51), and the ferrocenophane (9.52). Complexation of the diarsenic compounds (9.51) with (η-norbornadiene)metal carbonyls gave the derivatives (9.53; M = Cr Mo) [112].

The asymmetric hydrosilylation of acetophenone with Ph_2SiH_2 has been carried out with the platinum(II) chloride complex (9.54) [113]. A series of platinum(II) complexes containing the ligand (9.55) have been prepared and characterized.



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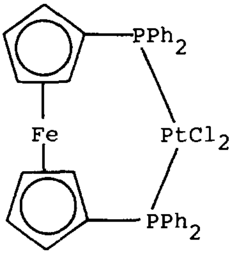

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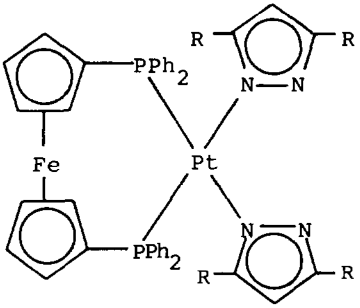
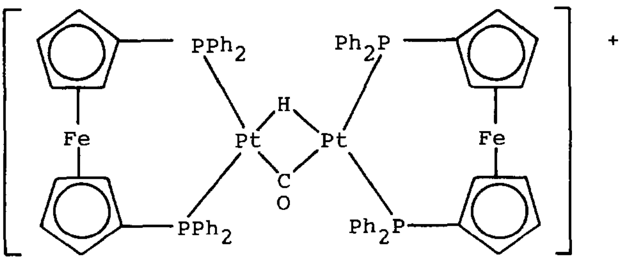


9.57

For example, reaction of the dichloro-complex (9.56) with pyrazoles produced the corresponding bis(pyrazole) compounds (9.57; R = H, Me). The hydride complex (9.58) was prepared and characterized by X-ray analysis [114]. The ferrocenyl platinum complexes (9.59; E = S, Se; X = Cl, Br, I) have been prepared and studied by variable temperature NMR spectroscopy. Activation energies for inversion were calculated [115]. The palladium complex (9.60) has been prepared and its reactions with styrene, methylpropenoate and 2-ferrocenylpropene were examined [116].



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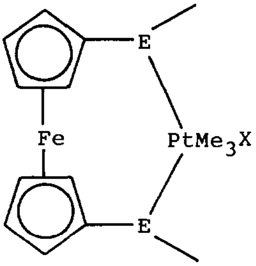

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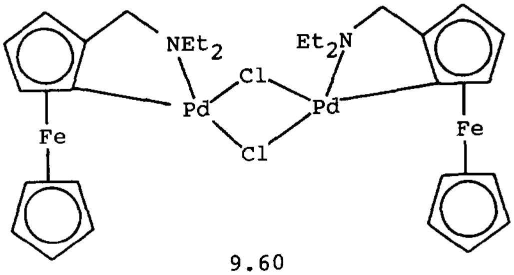

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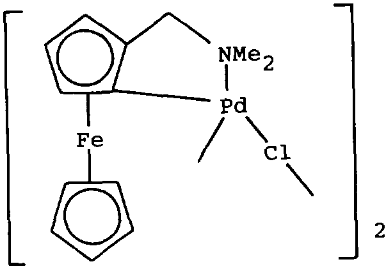

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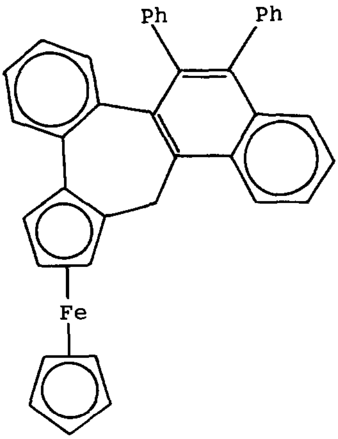

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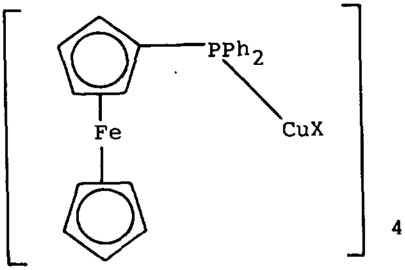
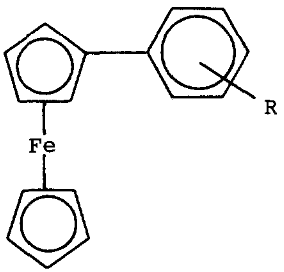


9.63

The palladium(II) chloride complex (9.61) underwent alkyne insertion at 20°C to give, for example, the ferrocene (9.62) with diphenylacetylene [117]. A chiral ferrocenyl-



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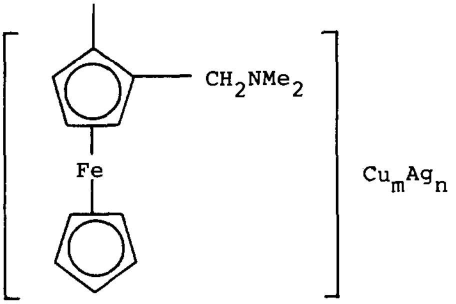
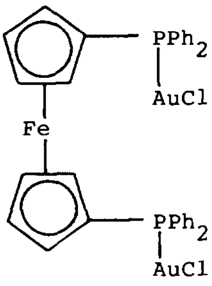


9.65

phosphine-palladium complex has been used as a catalyst for the cycloaddition of $PhSO_2CH_2C(CH_2OCO_2Et)=CH_2$ with $MeCOCH=CH_2$ and $MeOCOCH=CH_2$ to give optically active methylenecyclopentane compounds [118]. Reaction of copper(I) chloride or bromide with an equimolar quantity of ferrocenyldiphenylphosphine produced the tetrameric complexes (9.63; X = Cl, Br). When the same reaction was carried out with an excess of the ligand



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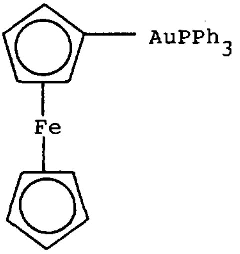

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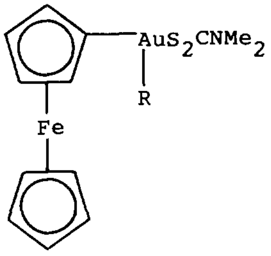
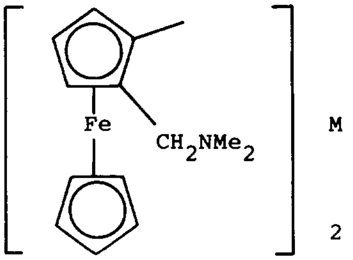


9.68

a mononuclear complex was isolated. Irradiation of the copper(I) complexes (9.63) and 2,5-norbornadiene at 366nm resulted in valence isomerization of the 2,5-norbornadiene to quadricyclene. ^{31}P NMR studies indicated that the key photoactive species in the isomerization was a ground state copper-2,5-norbornadiene adduct [119]. Reaction of ferrocenylcopper with the aryliodides RC_6H_4I, where R = H, o-CN, p-CH_3CO, -NO_2, -OMe, -CH_3, -CHO, -Br, gave the corresponding arylferrocenes (9.64) together with ferrocene and biferrocene. The reaction of ferrocenylcopper with a series of substituted benzaldehydes was also studied [120].

Treatment of 2-lithiodimethylaminomethylferrocene with $CuBr(PPh_3)$ and $AgNO_3(PPh_3)_3$ gave the complexes (9.65; m+n = 4) [121]. The ferrocene-gold complex (9.66) has been characterized by X-ray crystallography and by ^{57}Fe and ^{197}Au Moessbauer spectroscopy [122]. The ferrocenylgold compound (9.67) has been treated with $(Me_2NCS_2)_2$ and with $PhAu(S_2CNMe_2)_2$ to give the products (9.68; R = ferrocenyl, Ph) [123].



9.69

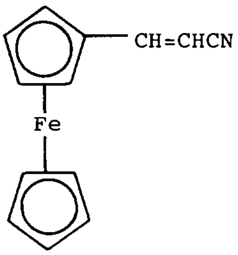
Reaction of 1-lithio-2-dimethylaminomethylferrocene with $ZnCl_2$, $CdBr_2$ and $HgCl_2$ afforded the corresponding metal complexes (9.69; M = Zn, Cd, Hg). 1-Mercurichloro-2-dimethylaminomethylferrocene was prepared by a similar route [124]. The complexes formed by mercury(II) chloride, bromide, iodide and tetrafluoroborate with ferrocene, methylferrocene biferrocene and ferrocenophanes have been investigated by ^{57}Fe Moessbauer and ^{13}C NMR spectroscopy. Direct mercury-iron bonding was demonstrated [125].

(iii) Photochemistry

Ferrocene has been photodissociated with 193nm excimer laser radiation. Most of the dissociation occurred by the incoherent absorption of two photons followed by the sequential elimination of the two η-cyclopentadienyl groups. Some dissociation also occurred by the absorption of a single proton which produced $(\eta\text{-}C_5H_5)Fe$ in an excited state [126]. Photolysis of ferrocene and aminomethylferrocenes has been studied by ESR spin-trapping techniques. The primary photolysis processes gave the radicals $(C_5H_5Fe)^\bullet$, $(C_5H_5)^\bullet$, $(RC_5H_4)^\bullet$ [127]. Ferrocene, ruthenocene and osmocene formed electron donor-acceptor complexes with the solvents carbon tetrachloride, chloroform, dichloromethane and tetrachloroethane. Irradiation of these complexes in the presence of spin traps led to the detection of nitroxide radical adducts of chlorocarbon radicals. The ability of ferrocene to trap transient chlorocarbon radicals in electron transfer processes was demonstrated [128].

(iv) General Chemistry

Alkoxy-anions attacked β-ferrocenylacrylonitrile (9.70) to form the nitrile stabilized carboanion (9.71) while cyclooctatetraene dianion gave the anion-radical (9.72) [129]. Fifteen ferrocene derivatives such as (9.73; R^1 = H, Me, R^2 = $\underline{p}\text{-}O_2NC_6H_4$, $\underline{p}\text{-}C_6H_4CHO$) with second-order optical nonlinearities have been prepared. The structure of the complex



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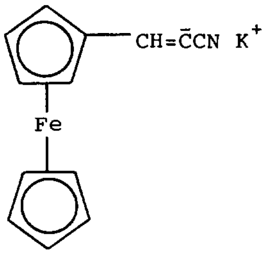

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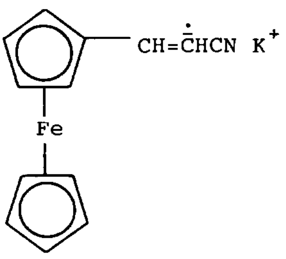
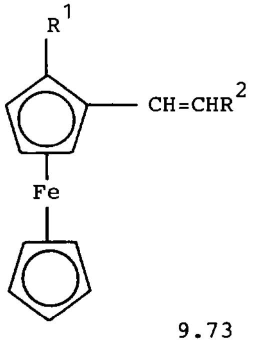


9.72

(9.73; $R^1 = H$, R^2 = p-$O_2NC_6H_4$) was determined by X-ray analysis [130]. Condensation of ferrocenylacetate with 4-methoxybenzaldehyde gave the olefin (9.74) which on condensation with amino-1,2,4-triazole, 2-aminobenzimidazole, 3-amino-1-phenyl-2-pyrazolin-5-one or guanidine hydrochloride produced the corresponding cyclic products (9.75, 9.76, 9.77 and 9.78) [131].



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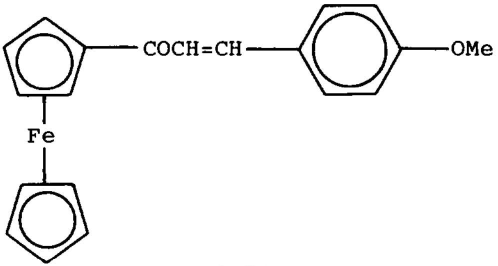
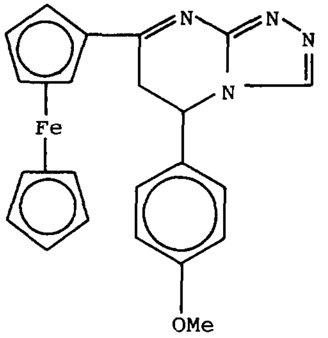


9.74

Enantiometrically pure α-ferocenylalkylamines have been prepared by using chiral terpenes,α- and β-pinene and camphor without a resolution stage [132].

Reaction of aryliminodimagnesium reagents [$ArN(MgBr)_2$] with nitro- and aroyl-ferrocenes produced the azoxyferrocenes (9.79), the azoferrocenes (9.80) and the N-(ferrocenylarylmethylene)-anilines (9.81; Ar = 4-RC_6H_4 where R = H, Cl, Me, OMe). These products were the same as those obtained in similar types of reactions with nitrobenzenes and benzophenones [133]. The ferrocenylhydrazone ligand (9.82) has been used to prepare chelate complexes with lanthanide(III) chlorides containing Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu [134]. Several ferrocenylcarbonylhydrazones (9.83; R = 4-NO_2, 4-OH, 2-Cl, 2-NO_2, 2-OH) have been prepared from ferrocenylcarbonylhydrazine and the corresponding aldehydes. The hydrazones (9.83) were converted to the corresponding nickel(II) complexes [135].

The diazonium salt formed from 4-nitro-1-aminonaphthalene has been treated with zinc chloride and ferrocene to give 4-nitro-1-ferrocenylnaphthalene which was subsequently reduced



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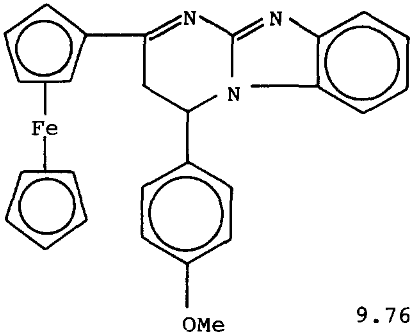

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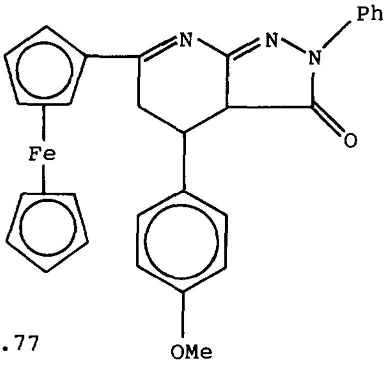

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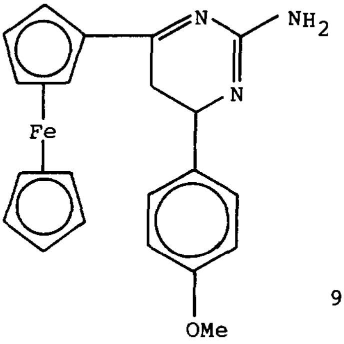

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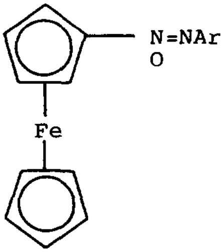

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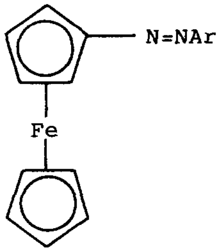

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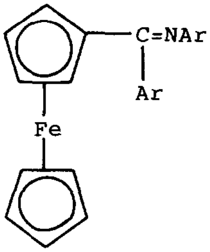

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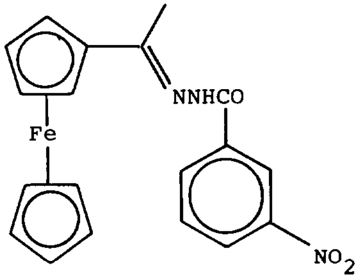

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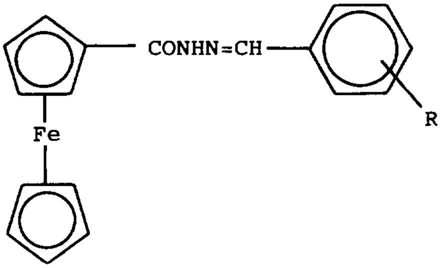
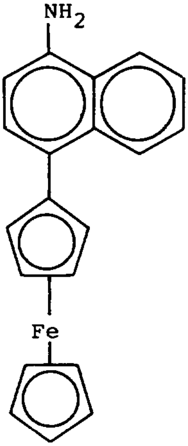
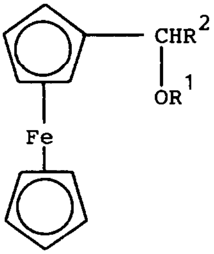


9.83

to 4-amino-1-ferrocenylnaphthalene (9.84) [136]. Acetylferrocene and acylferrocenes have been used to prepare unsymmetrical 1,1'-diacylferrocenes. 1-Acetyl-1'-palmitoylferrocene and 1-benzoyl-1'-palmitoylferrocene have been prepared in this way from palmitoylferrocene [137]. Several ferrocenylcarbinol ethers (9.85; R^1 = Me, Et, Pr, Bu, allyl; R^2 = H, Me) have been prepared from the corresponding ferrocenylcarbinols [138]. Reduction of the ketone (9.86) with lithium aluminium hydride in ether gave the alcohol (9.87) in quantitative yield after





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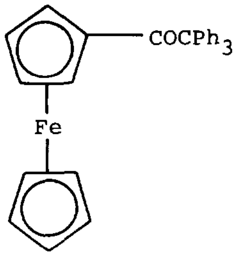

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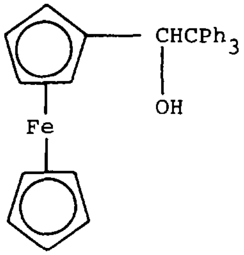
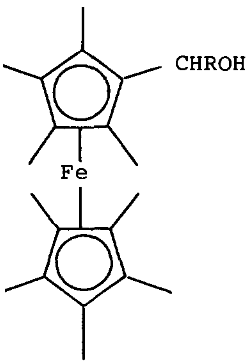


9.87

fifteen minutes. If the reaction mixture was left overnight some cleavage of the C_α-C_β bond occurred and a measureable quantity of ferrocenylmethanol was produced together with triphenylmethane [139].

Oxidation of the alcohols [9.88; R = Me, Ph, ferrocenyl, cymantrenyl, C_6F_5,2,4,6-$Me_3C_6H_2$] with barium permanganate in ether gave the corresponding aldehydes (9.89 and/or 9.90) [140]. Oxidation of 1,2-bis(hydroxymethyl)ferrocene with horse liver alcohol dehydrogenase gave only the (1R,2S)-(hydroxymethyl)-aldehyde (9.91). While 1,2-diformylferrocene underwent reduction



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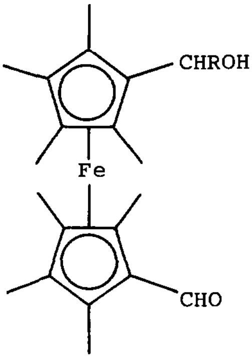

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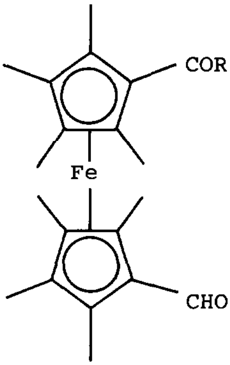

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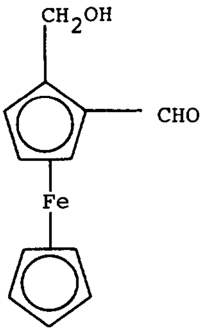

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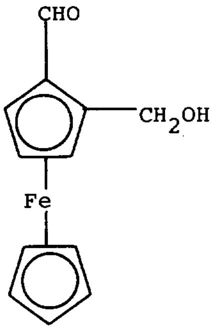
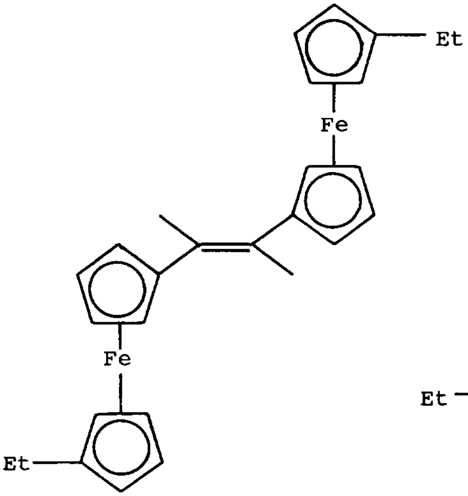


9.92

to the (1S,2R)-(hydroxymethyl)aldehyde (9.92) [141]. The geometrical isomers (9.93 and 9.94) were prepared and the structure of the isomer (9.93) was determined by X-ray analysis. The mixed valence cations obtained from the two isomers (9.93 and 9.94) had similar physical properties and it was concluded that intramolecular electron transfer in these compounds was associated with *cis*→*trans* and *trans*→*cis* isomerizations [142]. The ease of oxidation of (*o*-substitutedphenyl)ferrocenes (9.95; R = Me, OMe, COMe, CO_2Me, OH, Cl) with air in acid solution has



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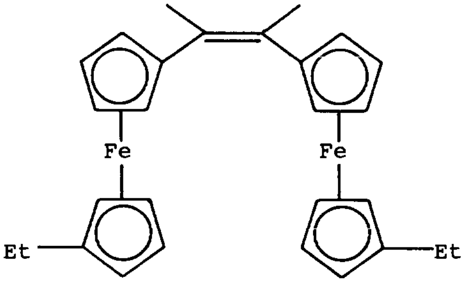
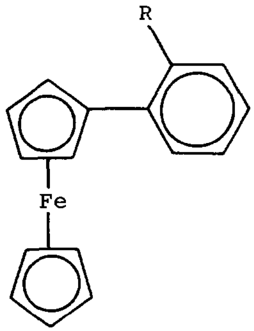
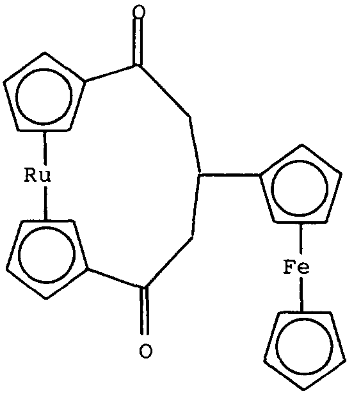


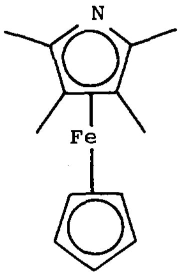
9.94

been measured and compared with the corresponding *p*-isomers. Higher reactivity was observed for the *o*-OMe, *o*-COMe and *o*-CO_2Me compounds while the *o*-Me and *o*-OH isomers were less reactive than the *p*-isomers [143].





1,1'-Disubstituted ferrocenes have been treated with arenes in the presence of zirconium(IV) chloride and aluminium to give (η-arene)(η-cyclopentadienyl)iron cations which were used as photochemical initiators for cationic polymerization [144]. Toma and co-workers have reported the preparation of some ruthenocenophanes including the ferrocene derivative (9.96). The ability of these compounds to act as oxidizing agents was



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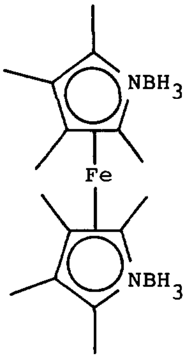


9.98

investigated [145]. Deprotonation of the pyrrole complex $[(\eta\text{-}C_5H_5)Fe(C_4Me_4NH)]BF_4$ gave 2,3,4,5-tetramethyl-1-azaferrocene (9.97). The nitrogen atom had basic properties similar to those of alkylpyridines and formed adducts with Lewis acids. X-Ray analysis showed that complex (9.97) was isosteric wih pentamethylferrocene and had an eclipsed conformation [146]. The bis[trihydro(tetramethylpyrrolyl)borate]iron complex (9.98) has been prepared and characterized by X-ray crystallography as a species with characteristic metallocene orientation, it was isosteric with decamethylferrocene [147].

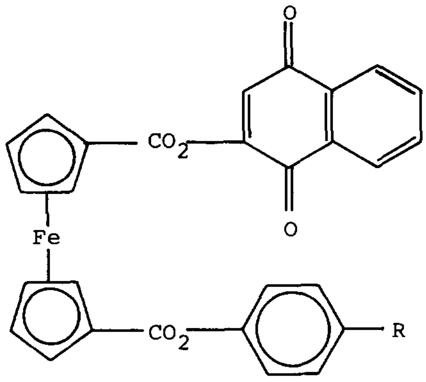
10. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

Condensation of 1,1'-bis(chlorocarbonyl)ferrocene with one molar equivalent of 5-(p-hydroxyphenyl)-10,15,20-triphenylporphyrin followed by 2-hydroxynaphthoquinone gave the mono-porphyrin (10.1) and the bis-porphyrin (10.2) [148]. The synthesis and structure of mono- and bis-ferrocenyl calix[4]arene hydrophobic receptor molecules has been studied and their electrochemical properties examined [149]. The preparation of the side-by-side biferrocenes (10.3 and 10.4) has been reported and one of them (10.3) was characterized by X-ray crystallography [150]. Reduction of [1.1]ferrocenylruthenocenophane-1,12-dione has been used to prepare [1.1]ferrocenylruthenocenophane and both of these compounds reacted with $BF_3.Et_2O$ containing benzoquinone to give black monocationic salts containing the [1.1]ferrocenylruthenocenophanium and [1.1]ferrocenylruthenocenophane-1,12-dionium ions. Intramolecular electron transfer between the ruthenium and iron atoms was indicated by ^{57}Fe Moessbauer spectroscopy [151].

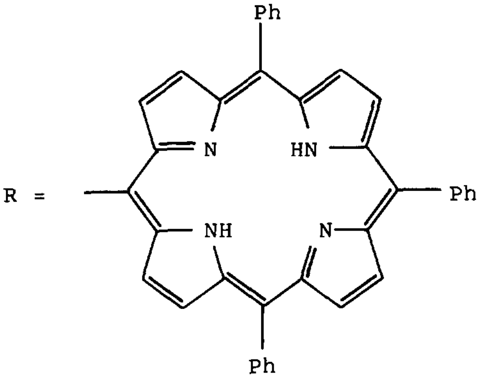
Several (η-fulvalene)diiron complexes (10.5; $R^1 = R^2 = I$; R^1 = Me, Et, R^2 = H; $R^1 = R^2$ = Me) have been prepared by ligand exchange between biferrocene and the appropriate arene in the presence of aluminium chloride and aluminium. The (η-hexamethylbenzene)diiron complex (10.6) showed three reversible waves by cyclic voltammetry [152]. The temperature dependence of the ^1H NMR spectrum of the carbanion of [1,1]ferrocenophane (10.7) indicated that a symmetrical double-well potential determined the dynamic equilibrium of the proton as follows:

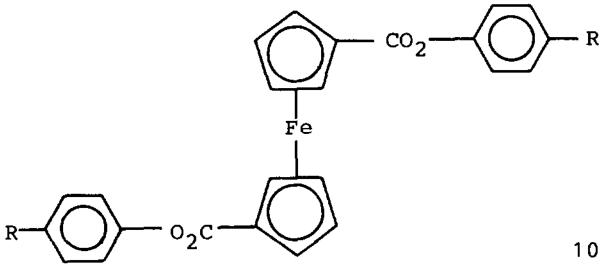
$$[C^{-}\cdots\cdots H{-}C] \rightleftharpoons [C{-}H\cdots\cdots{}^{-}C]$$

Kinetic isotope effects and isotopic perturbation have been used to determine the nature of the hydrogen bond [153]. The



10.1





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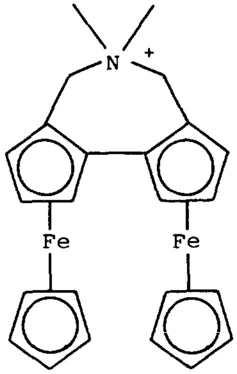

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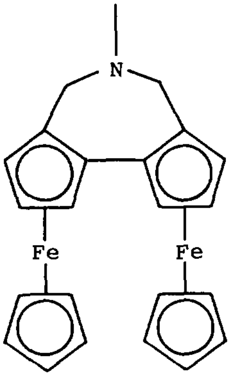

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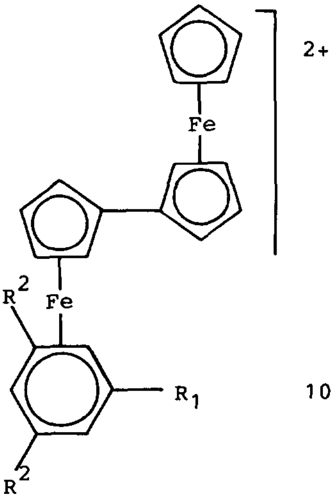
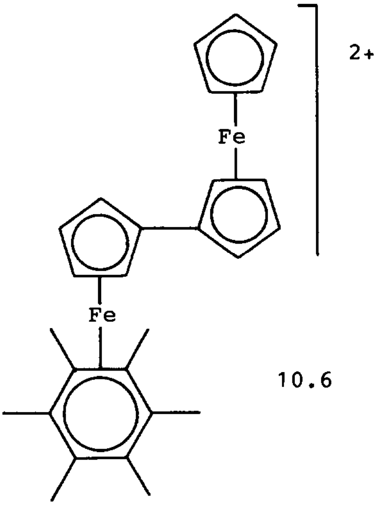


10.5



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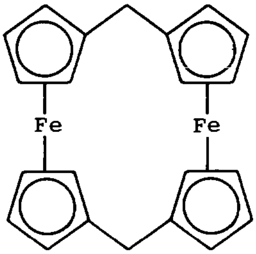
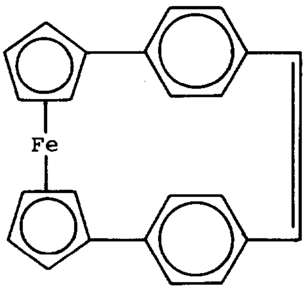


10.7

ferrocenophane (10.8) was prepared from 2-thia[3]paracyclo[0](1,1')ferroceno[0]paracyclophane by a Stevens rearrangement followed by a Hoffmann elimination [154]. Ferrocenecarboxaldehyde has been condensed with dithiols in the presence of Lewis acids to give ferrocenyl thioacetal crown ligands [10.9; X = O, OCH_2CH_2O, $O(CH_2CH_2O)_n$ where n = 2-4; X = S, $OCH_2CH_2SCH_2CH_2O$]. The complexation of these ligands (10.9) with cations such as Na^+, K^+, Ag^+, Tl^+, Cu^{2+}, Pb^{2+} and Zn^{2+}



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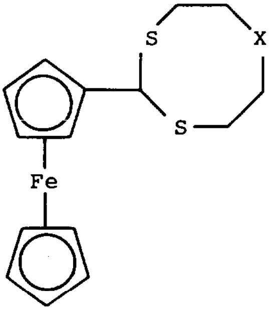
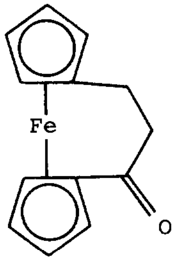


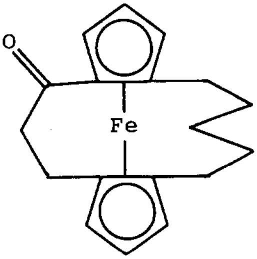
10.9

was studied by picrate extraction into chloroform and by cyclic voltammetry [155]. Several related dithia crown ligands with 7-, 8-, 11-, 14-, 17- and 20-membered rings have been prepared [156].

Addition of β-cyclodextrin to the ferrocenophane (10.10) gave a 1:1 inclusion complex. Treatment of the complex with sodium borohydride gave the corresponding alcohol and the extent of asymmetric induction was approximately 5% [157]. The structure of [5]-α-oxo[3](1,2)ferrocenophane (10.11) has been determined by conversion to the bis(pentamethylene) bridged compound (10.12) by bridge enlargement [158]. The (1,2,3,4) ferrocenophane (10.13) with four pentamethylene bridges has been prepared by formation of a three carbon bridge on [5_3](1,2,4)ferrocenophane and then insertion of two methylene



10.10



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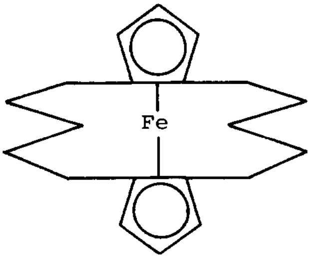

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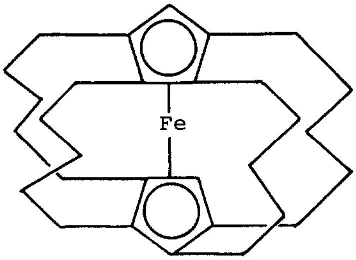

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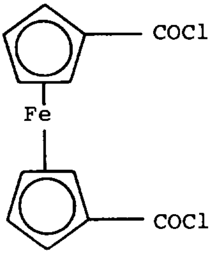

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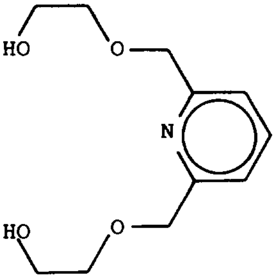

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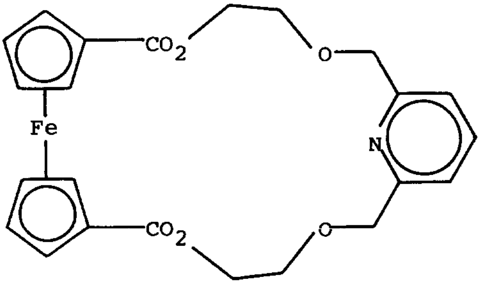
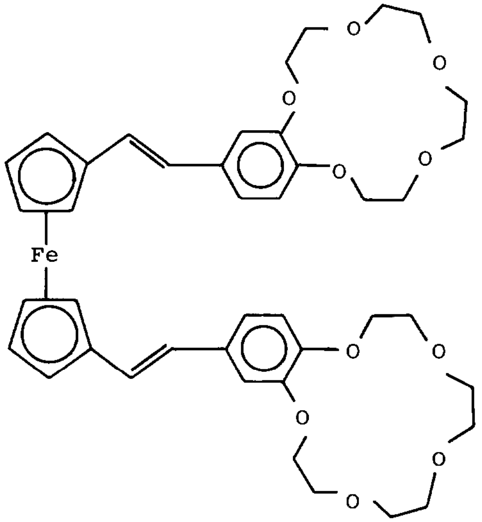


10.16

groups. The crystal and molecular structure of the complex has been determined by X-ray crystallography [159]. The reaction of 1,1'-ferrocenedicarbonyl dichloride (10.14) with the dihydroxydiether (10.15) gave the pyridino crown ether (10.16). The corresponding [6] crown and [8]crown ethers were prepared in the same way. These products were selective ligands for Ag^+, In^{3+} and Zr^{4+} [160].

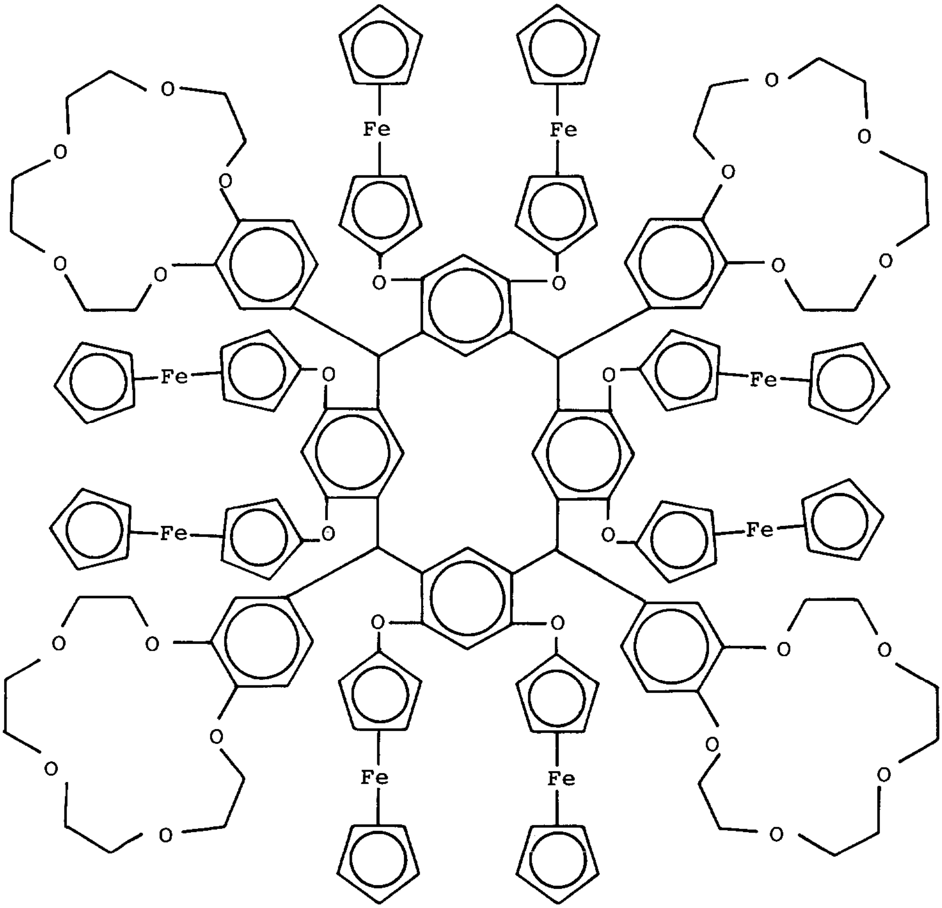
The ferrocenyl crown ether (10.17) has been prepared and shown to respond electrochemically to the potassium cation in the presence of sodium and magnesium ions [161]. The synthesis and electrochemical characteristics of the macrocyclic benzo crown ether (10.18) have been reported. The species (10.18) contained eight redox-active ferrocenyl groups and was able to bind dipyridinium and sodium cations [162]. The binding of ammonium ions to the diaza- and triaza-crown ethers (10.19 and 10.20) gave large anodic shifts of the ferrocene-ferrocenium redox couple [163]. The lipophilic macrocyclic compound (10.21) with eight redox active ferrocene centres has been prepared [164]. A ^1H and ^{13}C NMR spectroscopic study



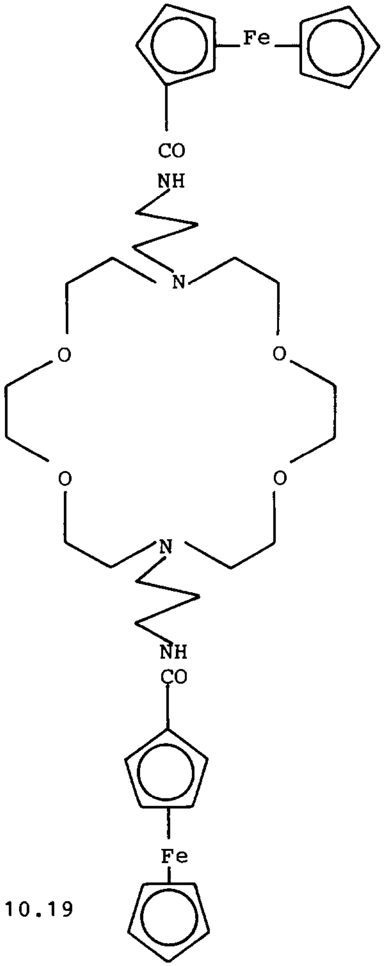
10.17

of some $[S_3]$-bridged ferrocenophanes, for example, the aminoferrocenophane (10.22) has been carried out. The ^{13}C spectrum of this complex was completely assigned [165].

Biferrocene has been used to prepare the fulvalene cation (10.23) together with the hexamethylbenzene analogue. The cyclic voltammograms at -35°C in dimethylformamide showed four reversible waves corresponding to 35e, 36e, 37e and 38e species. The 35e to 37e complexes were isolated using conventional redox reagents while the fourth, the 38e complex was detected only by cyclic voltammetry. The 35e and 37e complexes were localised mixed-valence species, Fe(II), Fe(III) and Fe(I), Fe(II) respectively [166]. The mechanism of the thermal electron localization-delocalization transition in mixed valence biferrocenium trihalides has been investigated by a statistical mechanics model. Good agreement was obtained with experimentally determined values [167]. Treatment of bromoferrocene with triphenylmethanol in the presence of aluminium



10.18



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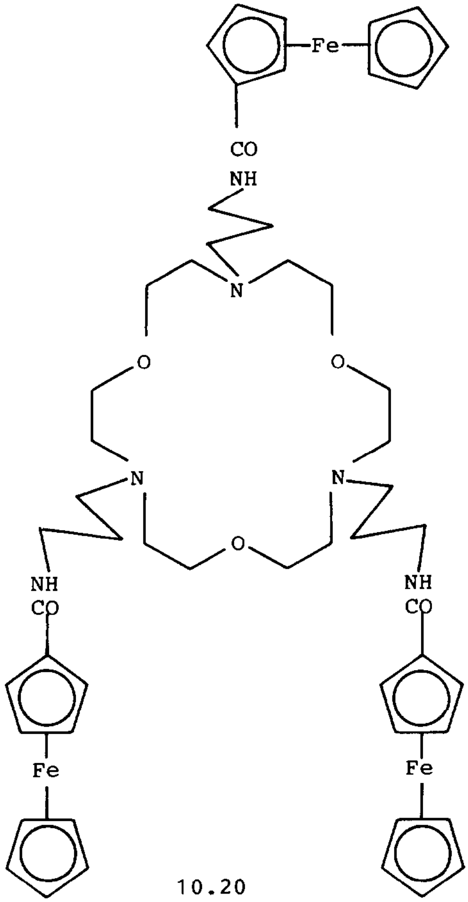
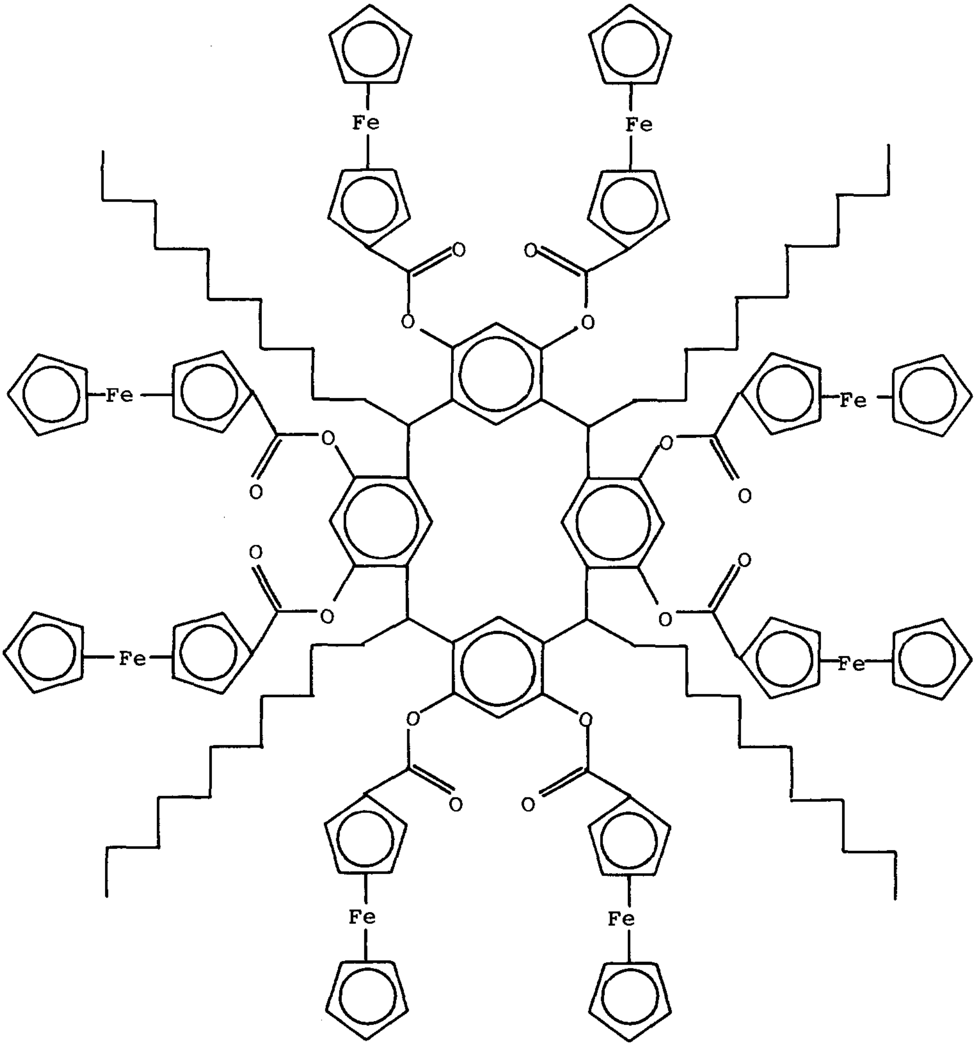


10.20

chloride gave the heteroannularly disubstituted ferrocene (10.24). When this latter compound was heated with activated copper the biferrocene (10.25) was formed. The triiodide salt (10.26) was prepared and investigated electrochemically and via Moessbauer spectroscopy. The Moessbauer spectrum indicated the presence of both valence localized and delocalized species [168].

The bis(p-bromobenzyl)biferrocenium pentaiodide (10.27) has been characterized by X-ray crystallography and by Moessbauer spectroscopy. It was suggested that the degree of delocalization of negative charge in the pentaiodide unit



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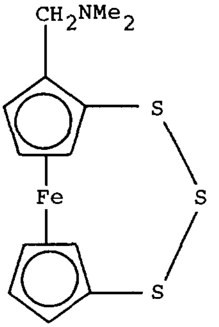

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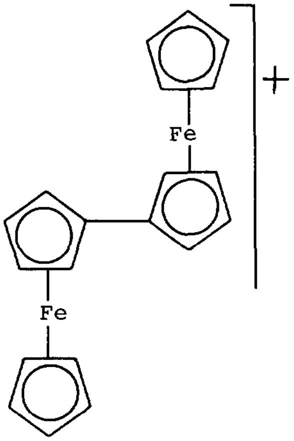

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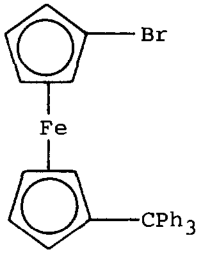
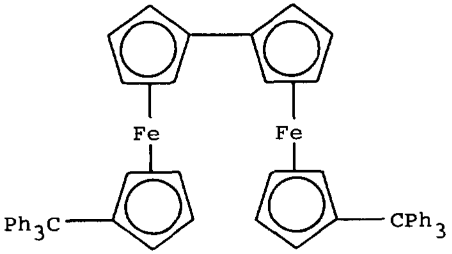


10.24

controls the intra-molecular electron transfer in the mixed-valence biferrocenes [169]. Several dihalogenobiferrocenium salts [10.28; X = H, Br, I; Y = $FeCl_4$; X = H, Br; Y = $(CuBr_2)_2$; X = I; Y = $CuBr_2$] have been examined by ^{57}Fe Moessbauer spectroscopy. Differences were observed between the iron valence states and the temperature dependent behaviour in the salts (10.28) and the corresponding biferrocenium triodide salts [170]. The mixed-valence salts (10.29; X^1 = Cl, Br; X^2 = I) with two different halogen substituents have



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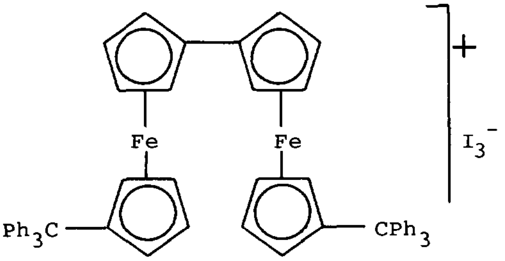

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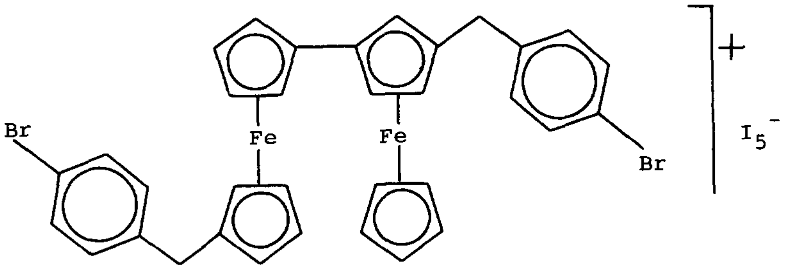
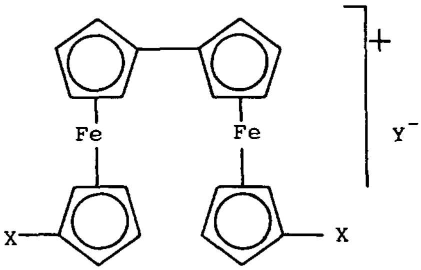


10.27

been studied by ^{57}Fe Moessbauer spectroscopy and found to show averaged valence behaviour even at very low temperatures such as 4.2K. This behaviour accorded with the previously observed behaviour of salts with similar substituents (10.29; $X^1 = X^2$ = Br, I) [171].

ESR spectroscopy has been used to investigate the valence states of 1',1'''-dialkyl- and 1',1'''-bis(methylbenzyl)-biferrocenium triiodides. Temperature dependence of the mixed-valence state of 1',1'''-diisobutylbiferrocenium triiodide was found in the crystal state and a trapped-valence state was found



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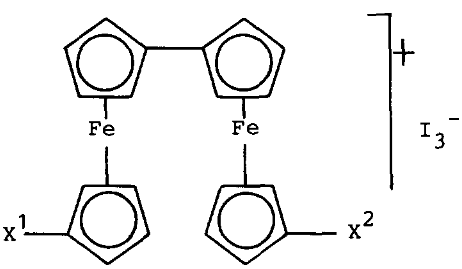
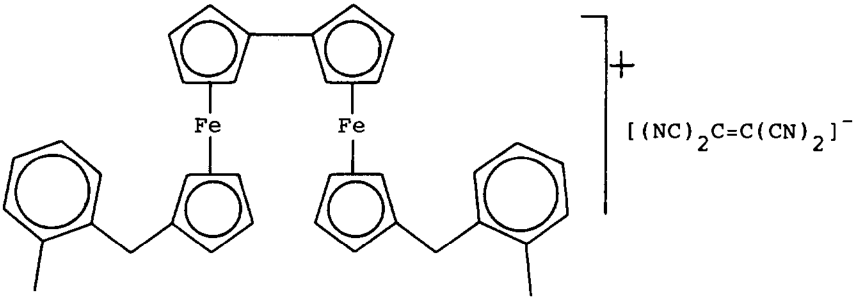
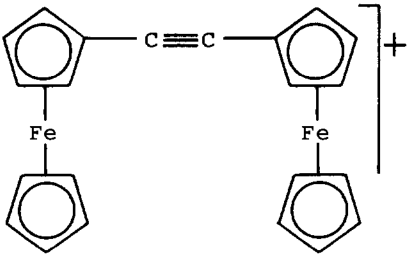


10.29



10.30

in a dispersed state [172]. Temperature dependence in the mixed valence state complex (10.30) has been examined by Moessbauer spectroscopy. The trapped- and averaged-valence states were found to coexist at higher temperatures and the relative areal intensity of the averaged valence state increased at higher temperatures [173]. The effect of solvent on the intervalence electron-transfer energies for the cations of biferrocene, bis(ferrocenyl)acetylene (10.31) and bis(ferrocenyl)-butadiyne (10.32) has been investigated by measurement of outer-shell electron-transfer reorganisation energies [174].



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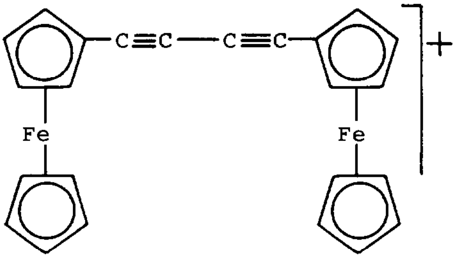
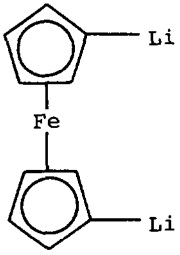


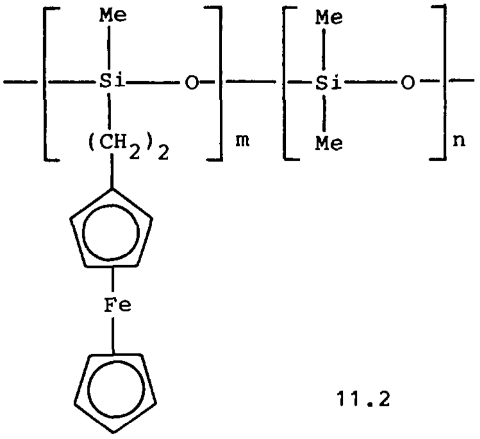
10.32

11. FERROCENE-CONTAINING POLYMERS

Treatment of polystyrene polymers with lithioferrocene and 1,1'-dilithioferrocene (11.1) caused the ferrocene group to be incorporated into the polymer [175]. Cyclic voltammetry has been used to show that siloxane polymers (11.2) containing pendant ferrocenyl groups retain the electrochemical properties of the metallocene [176].



11.1

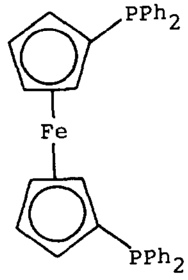


11.2

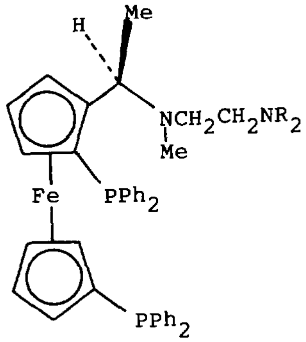
12. APPLICATIONS OF FERROCENE

(i) Ferrocene catalysts and photosensitizers

Hydroformylation catalysts have been prepared by treatment of the bis(diphenylphosphine)ferrocene (12.1) with $Rh_2(\mu\text{-}SCMe_3)_2(CO)_4$. The catalyst contained the $Rh_2(\mu\text{-}SCMe_3)_2$ bridging group and the catalytic behaviour of several complexes was assessed [177]. Gold(I) complexes of the chiral ferrocenylphosphine ligands (12.2; NR_2 = morpholino, piperidino, diethylamino, dimethylamino) have been used as catalysts in the asymmetric synthesis of β-hydroxy-α-alkylamino acids [178]. The optically active ferrocenylphosphines [12.3; X = $NMeC(CH_2OH)_3$ $NMeCH(CH_2OH)_2$, $N(CH_2CH_2OH)_2$, $NMeCH_2CH_2OH$] have been shown to be effective ligands for the palladium catalyzed asymmetric alkylation of 1,3-disubstituted 2-propenyl acetate with sodium acetylacetonate and related nucleophiles. Gold(I) complexes



12.1



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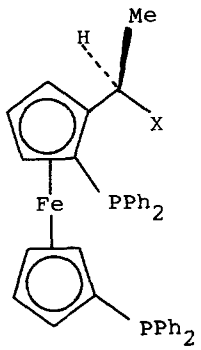
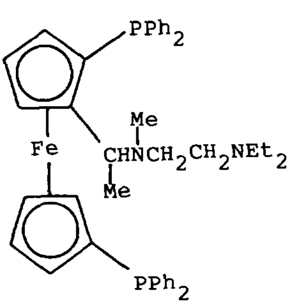


12.3

of the chiral ferrocenylphosphine ligands (12.2; R = Me, Et) were good catalysts for the reaction of methyl isocyanoacetate with aldehydes to give optically active trans-4-methoxycarbonyl-5-alkyl-2-oxazolines with high enantioselectivity in high yields [179].

Reaction of bis(cyclohexylisocyanide)gold in the presence of the ferrocenyl-phosphine (12.4) with $CNCH_2CO_2Me$ and benzaldehyde produced the (4R, 5R)- (10.4%) and (4S, 5R)-4-methoxycarbonyl-5-phenyl-2-oxazolines (84.6%). The latter



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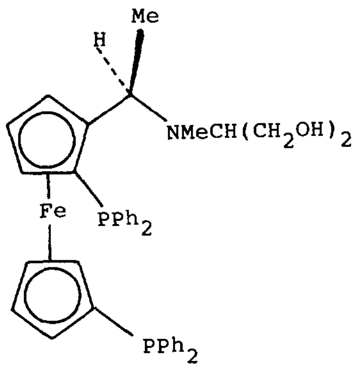
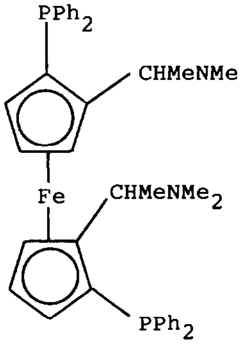


12.5

oxazoline was used to prepare L-(-)-*threo*-β-phenylserine in high yield [180]. The chiral catalyst prepared from bis-(cyclohexylisocyanide)gold(I) tetrafluoroborate and (R)-N-methyl-N-[2-(1-piperidino)ethyl-1-[(S)-1',2-bis(diphenylphosphinoferrocenyl]ethylamine has been used to promote aldol condensation of cyanoamides such as $CNCH_2CONMe_2$ with aldehydes under high enantio- and dia-stereoselectivity. The products were converted to optically active *threo*-β-hydroxyamino acids [181]. The use of metal complexes of ferrocenylphosphines as catalysts in the hydrogenation of olefins to optically active arylacetic acid derivatives has been described. For example, these catalysts were used in the reduction of 2-(4-chlorophenyl)-3-methylcrotonic acid to (S)-2-(4-chlorophenyl)-3-methylbutyric acid [182].



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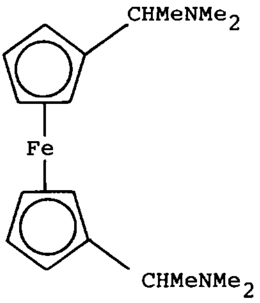
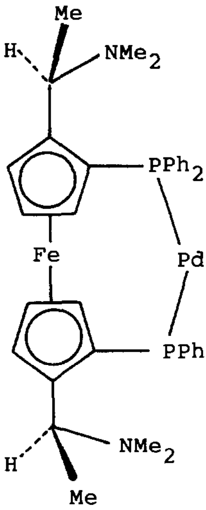


12.7

The asymmetric allylic amination of allyl compounds has been carried out in the presence of palladium complexes of chiral ferrocenylphosphine ligands such as the amine-diol (12.5) [183]. A new chiral ferrocenylphosphine ligand (12.6) has been prepared with C_2 symmetry and a functional group on the side chain. The $PdCl_2$ complex was prepared and shown to have square planar geometry [184]. Lithiation of the amine (12.7), which consisted of a mixture of the *dl*- and *meso*-isomers, with n-butyllithium followed by chlorodiphenylphosphine gave the corresponding ferrocenylbisphosphines. The mixture of *dl*-optical isomers was resolved and the (+)-isomer



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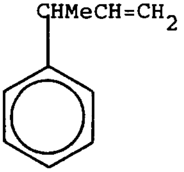

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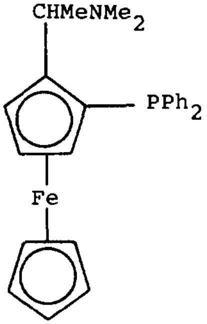
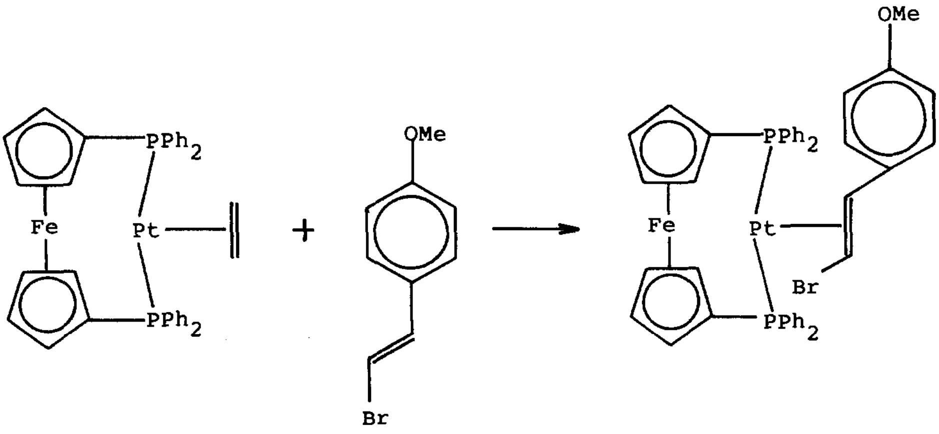


12.10

was used to prepare the palladium complex (12.8). This complex was a good catalyst for the asymmetric cross-coupling of bis(1-phenylethyl)zinc with vinyl bromide to give (R)-3-phenylbut-1-ene (12.9) quantitatively [185]. A chiral ferrocenylphosphine-nickel complex has been used as a catalyst for the asymmetric synthesis of a ternaphthalene [186].

Cationic palladium(II) complexes of the ferrocenylphosphines (12.1 and 12.10) have been prepared. The complexes of the ligand (12.1) were good homogeneous catalysts for the hydrogenation of olefins at 30° and one atmosphere pressure of hydrogen [187]. Stereoselectivity was observed in the catalytic

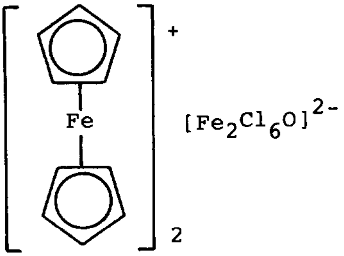


12.11 12.12 12.13

hydrogenation of several chiral 1,2-disubstituted ferrocenes with carboxyl and tertiary amine groups [188]. Reaction of the η^2-ethylene complex (12.11) with the halide (12.12) gave the isolable alkene complex (12.13). This complex catalysed the cross-coupling of arylmagnesium halides and arylethenyl bromides under mild conditions [189].

(ii) <u>Combustion control</u>

Acylation of ferrocene with 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid anhydride under Friedel-Crafts conditions and incorporation of the product into poly(vinyl chloride) gave a flame-retardant and smoke-suppressant material [190]. The ferrocenium salt (12.14) and the



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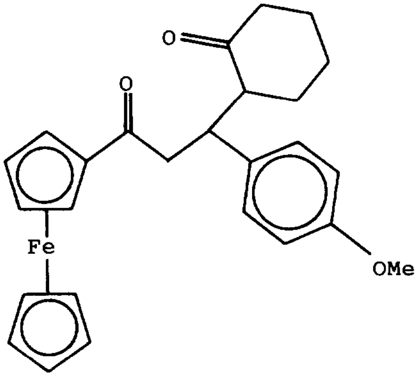

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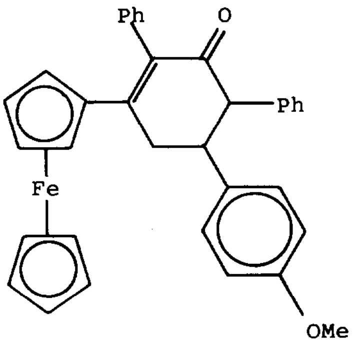

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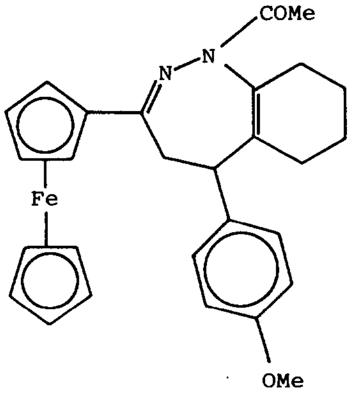

12.17

pyridinium analogue were heated in the temperature range 18-200° and the Moessbauer spectra of the products were recorded. At 200° the salt (7.5) was reduced to a mixture of iron(II) compounds. It was concluded that the use of ferrocenium as a smoke suppressant apparently had no advantage over that of ferrocene, as it was converted to ferrocene when heated in air in the presence of light [191].

(iii) Clathrate complexes

A zeolite-host lattice is formed from $[Fe(CN)_6]^{3-}$ and Me_3Sn units. Treatment of moist $[(Me_3Sn)_3Fe(CN)_6]_\infty$ with ferrocene gave a ferrocenium intercalate $[(\eta\text{-}C_5H_5)_2Fe(Me_3Sn)_3 Fe(CN)_6]_\infty$ when this intercalate was heated 0.5 equivalents of ferrocene were recovered [192]. A series of metallocenes $(\eta\text{-}C_5H_5)_2M$, where M = Cr, Fe and Co, and some substituted metallocenes have been impregnated into a range of ion-exchanged Y and A zeolites. These metallocenes were studied by optical, vibrational and paramagnetic resonance spectroscopy. The intrazeolite chemistry and the dynamics of $(\eta\text{-}C_5H_5)_2M\text{-}[(\eta\text{-}C_5H_5)_2M]^+$ redox pairs were investigated [193]. Some ferrocene-cyclodextrin inclusion complexes have been studied by cyclic voltammetry [194].

(iv) Biochemical and biological applications

Kovacic and co-workers have ascertained the electrochemical characteristics of various organometallic complexes with anti--cancer properties. The compounds and ions investigated included the ferrocenium ion, ruthenocene, the cobaltocenium ion, nickelocene and titanocene dichloride [195]. Acetylferrocene has been used in the preparation of the antimicrobial reagents (12.15; 12.16 and 12.17) [196].

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