

## FERROCENE

ANNUAL SURVEY COVERING THE YEAR 1979\*

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\* Ferrocene, Annual Survey Covering the Year 1978, see  
J. Organometal. Chem., 189 (1980) p. 163-250.

## 1. REVIEWS

A review of ferrocenylcarbocations has been included in volume 7 of the Journal of Organometallic Chemistry Library [1]. The chapters on "Structure and Bonding in Organic Iron Compounds", "Mass Spectra", "Magnetic Properties" and "Optical Activity" in the monograph "The Organic Chemistry of Iron", contained useful reviews of the relevant aspects of ferrocene chemistry [2].

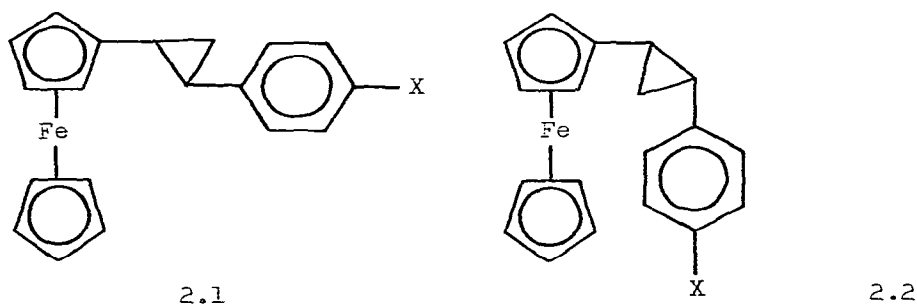
## 2. STRUCTURAL DETERMINATIONS

The crystal structure of ferrocene has been reinvestigated by neutron diffraction. Previous results, which had indicated significant nonplanarity of the cyclopentadienyl rings with the hydrogen atoms displaced towards the iron atom, were confirmed. The structure was found to be disordered and refinement of the structural analysis together with rigid-body-motion analyses of the thermal parameters indicated that the disorder of the cyclopentadienyl rings resulted from molecules in different orientations distributed at random throughout the crystal [3]. The molecular configuration of ferrocene has been determined in the ordered phase at 130°K. The configuration was characterised by an angle of 10° between the  $\eta$ -cyclopentadienyl ring orientations by the use of a triclinic face centred cubic lattice approximation [4].

An X-ray investigation of ferrocene at 293 and 193°K has provided evidence for a new interpretation of the disordered crystal structure of the molecule. Vibrational-ellipsoid patterns were obtained that were not compatible with pure rotational disorder of the cyclopentadienyl rings. The diffraction patterns of the high-temperature monoclinic structure (HT) and the low-temperature (<164°K) triclinic structure (LT), indicated that the formally centrosymmetric molecule in the disordered HT phase can be described approximately as an averaged superposition of the four molecules present in the primitive LT cell. On this basis, the molecular centre of symmetry for the HT space group is only statistical in nature and the crystallographic evidence for the staggered arrangement of the cyclopentadienyl rings in ferrocene will require revision [5]. The low temperature triclinic modification of ferrocene has been studied by X-ray

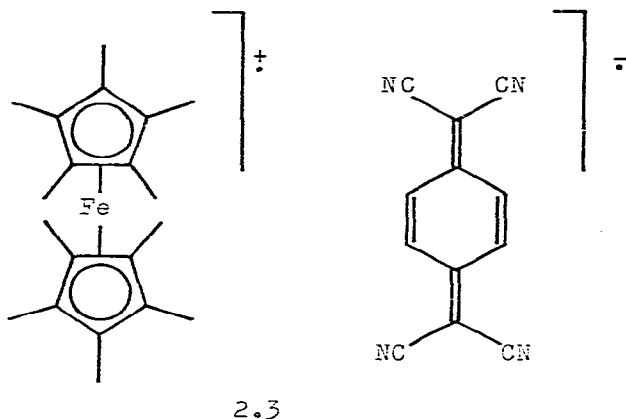
crystallography at 101, 123 and 148°K. Assuming a centrosymmetric space group  $F\bar{1}$ , the asymmetric unit consisted of two ferrocene molecules with almost regular pentagonal cyclopentadienyl rings. The rings were rotated by  $\sim 9^\circ$  from the eclipsed orientation [6].

The crystal and molecular structure of the ethyl ester of (Z)-2-ferrocenyl-2-methylcyclopropanecarboxylic acid has been determined by X-ray analysis. The  $\eta$ -cyclopentadienyl rings were almost parallel and twisted approximately  $3.8^\circ$  from the eclipsed conformation [7]. The ferrocenylcyclopropanes (2.1 and 2.2; X = OMe, Br) were formed by catalytic thermolysis of the appropriate ferrocenylpyrazolines. The crystal and molecular structure of one of these cyclopropanes (2.1; X = OMe) has been determined by X-ray crystallography [8]. The molecular structure of



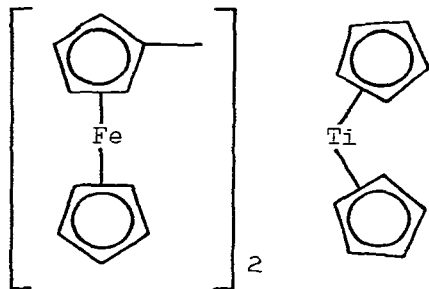
decamethylferrocene has been determined by gas phase electron diffraction. The Fe-C and cyclopentadienyl C-C distances were similar to those determined for ferrocene. The equilibrium conformation of decamethylferrocene was staggered by comparison with the eclipsed conformation for ferrocene. The ring C-methyl C bonds were bent out of the plane of the cyclopentadienyl group by  $3.4^\circ$  away from the metal atom [9].

The crystal and molecular structure of the paramagnetic 1:1 decamethylferrocenium 7,7,8,8-tetracyano-p-quinodimethanide dimer salt has been determined by X-ray analysis. The crystalline lattice consisted of isolated units of  $(\eta\text{-C}_5\text{Me}_5)_2\text{Fe}/\text{TCNQ}/\text{TCNQ}/-$



( $\eta$ -C<sub>5</sub>Me<sub>2</sub>)<sub>2</sub>Fe where TCNQ=7,7,8,8-tetracyano-p-quinodimethane, that is, dimers which were arranged in a regular manner [10]. The magnetic and Moessbauer properties of one-dimensional decamethylferrocenium TCNQ (2.3) have been investigated. At low temperatures the complex exhibited unusual magnetic properties and the results were consistent with a metamagnetic behaviour [11]. The charge transfer complex 1,1'-dimethylferrocenium bis(tetracyanoquinodimethane), [MeFc(TCNQ)<sub>2</sub>] has been characterized by X-ray crystallography, electrical conductivity, Raman spectroscopy and magnetic measurements. The magnetic susceptibility of MeFc(TCNQ)<sub>2</sub> followed the Curie-Weiss law and in the temperature range 4.2-76°K, was dominated by the ferrocenium cation. The cation was closely packed but did not show spin-spin interactions [12].

The crystal and molecular structure of the triclinic modification of 1,1'-ferrocenedicarboxylic acid has been determined by X-ray analysis. The structure was composed of hydrogen-bonded dimers and the carbon and hydrogen atoms attached to the  $\eta$ -cyclopentadienyl rings were displaced approximately 0.03Å out of the ring planes toward the iron atoms [13]. The crystal and molecular structure of 1,1'-bis(phenylglyoxyloyl)ferrocene has been determined by X-ray crystallography. The two ligands were centrosymmetric with respect to one another with the iron at the centre of symmetry [14]. The crystal and molecular structure of diferrocenyltitanocene (2.4) has been determined by X-ray crystallography. Each of the ferrocenyl groups and the titanocene group

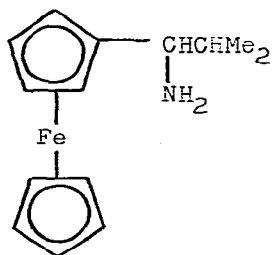


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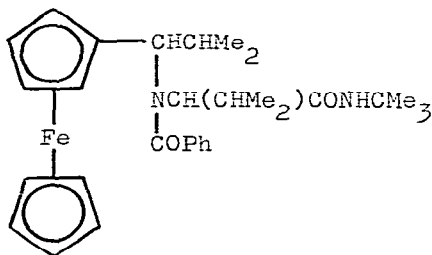
had an eclipsed conformation of the two cyclopentadienyl rings. The titanium-carbon  $\sigma$ -bond length was  $2.19\text{\AA}$  [15]. Iron oxychloride underwent direct intercalation by ferrocene and cobaltocene. X-ray studies showed that the Van der Waals gap between the  $\text{FeOCl}$  layers expanded by approximately  $5\text{\AA}$  to accommodate the metallocene [16].

### 3. STEREOCHEMISTRY OF FERROCENES

The (R)-form of the ferrocenylalkylamine (3.1), benzoic acid, iso-butylaldehyde and t-butylcyanide have been condensed together in a stereospecific four-component reaction to give a

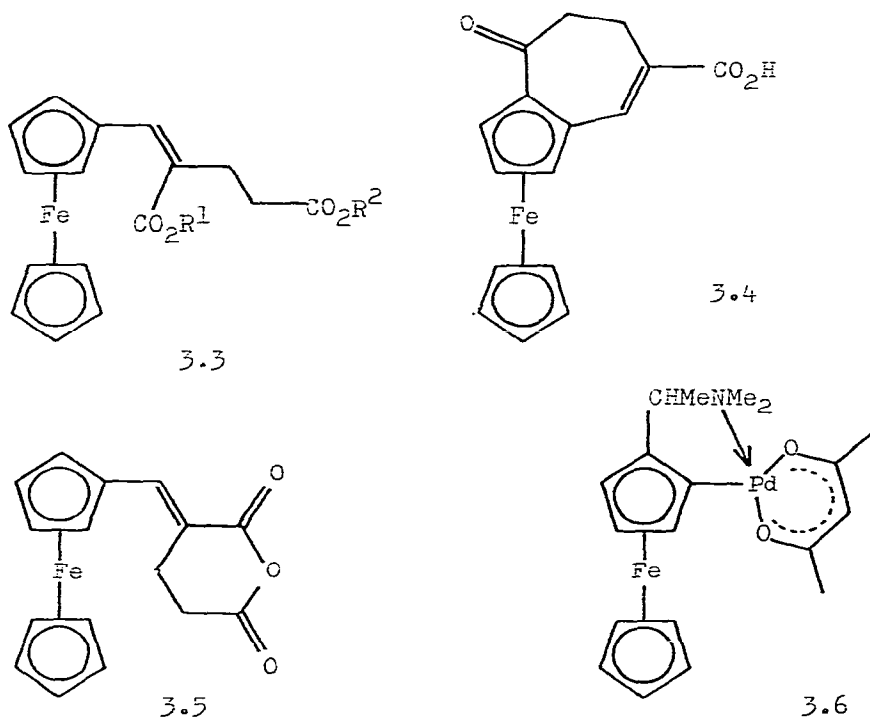


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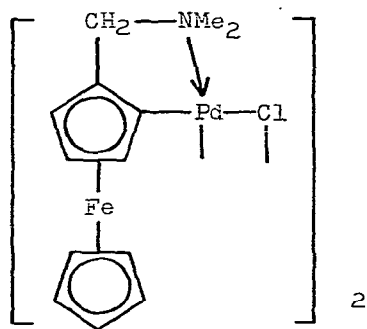
3.2

mixture of the (R,S)- and (R,R)-diastereoisomers of the derivative (3.2). The (R,S)-diastereoisomer was separated by chromatography and subjected to acidolytic cleavage with trifluoroacetic acid and thioglycolic acid to form PhCO-Val-NHMe<sub>3</sub> [17]. The condensation of formylferrocene with diethyl glutarate under Stobbe conditions in the presence of potassium t-butoxide gave the *E*-form of the unsaturated ester (3.3; R<sup>1</sup> = Et, R<sup>2</sup> = H) which was converted to the diester (3.3; R<sup>1</sup> = Et, R<sup>2</sup> = Me) with diazomethane. The configurational assignments made for the compounds (3.5) were supported by intramolecular acylation of the unsaturated ester (3.3; R<sup>1</sup> = Et, R<sup>2</sup> = H) to the cycloheptadienone (3.4) and by the conversion of the same unsaturated ester to the diacid (3.3; R<sup>1</sup> = R<sup>2</sup> = H), then to the anhydride (3.5) and finally to the cycloheptadienone (3.4) [18].

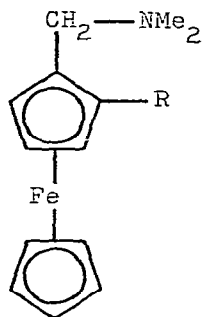


The crystal and molecular structure of the palladium complex (3.6) has been determined by X-ray analysis. The chiral carbon atom had the *R*-configuration and the substituted ferrocene

group had the S-configuration. The five-membered ring containing the palladium atom was nonplanar [19]. The optically active palladated ferrocene (3.7) has been transformed into chiral

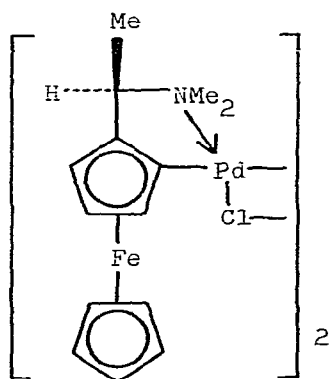


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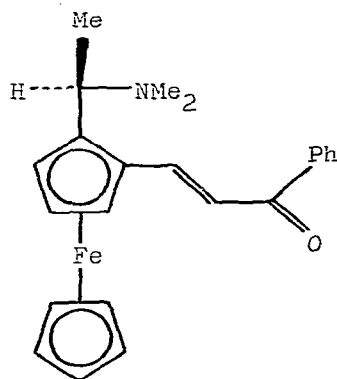


3.8

2-substituted (dimethylamino)methylferrocenes with good retention of optical activity. Treatment of the palladium complex (3.7) with  $\text{CH}_2=\text{CHAc}$  afforded the vinylferrocene (3.8;  $\text{R} = \text{CH}=\text{CHAc}$ ) which subsequently was reduced with  $\text{Et}_3\text{SiH}-\text{F}_3\text{CCO}_2\text{H}$  to the butylferrocene [3.8;  $\text{R} = (\text{CH}_2)_3\text{Me}$ ]. Carbonylation of the palladium complex (3.7) in methanol gave the methyl ester (3.8;  $\text{R} = \text{CO}_2\text{Me}$ ) [20]. The optically active palladated aminomethylferrocene (3.9) combined with phenylvinylketone and carbon monoxide to give



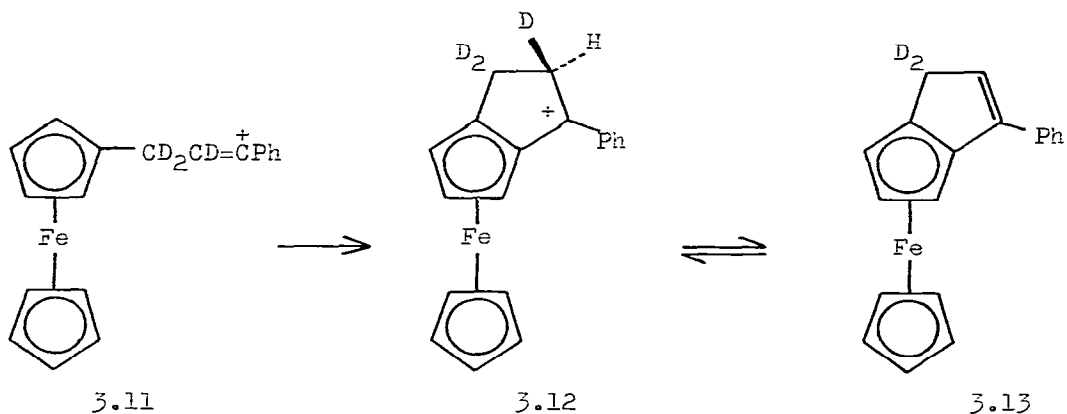
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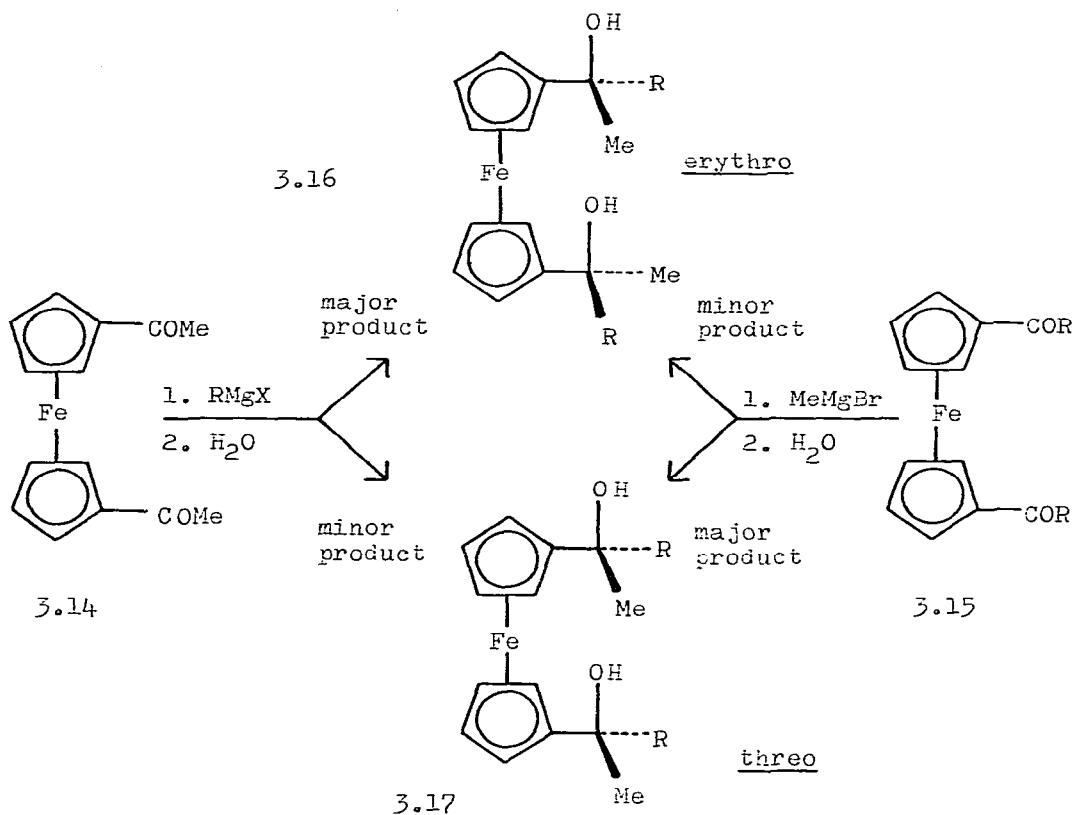
optically active 2-substituted aminomethylferrocenes such as the complex (3.10) [21].

A study has been made of the spontaneous conversion of the 3-ferrocenyl-1-phenylpropen-1-yl cation (3.11) into the ferrocenophanyl cation (3.12) followed by a reversible deprotonation to give the cycloalkene (3.13). It was concluded that the cation (3.11) was converted to the cyclic cation (3.12) by an inter-ionic 1,3-shift of an  $\eta$ -cyclopentadienyl  $\alpha$ -ring proton to C(2) of the homoannular bridge. The cyclic cation (3.12) then underwent deprotonation by stereospecific loss of the exo-proton adjacent to C<sup>+</sup> [22]. Two crystalline geometric isomers of 1,1'-bis( $\alpha$ -hydroxyethyl)ferrocene have been isolated and these were



identified as the meso and racemic modifications. In cyclization reactions 1,1'-bis( $\alpha$ -hydroxyethyl)ferrocene gave 7-oxa- and 7-thia-[3]ferrocenophanes with absolute stereospecificity [23]. The attack of 1,1'-diacylferrocenes by Grignard reagents to form tertiary alcohols showed marked stereoselectivity. Thus the addition of ethyl-, cyclohexyl-, benzyl-, and phenyl-magnesium halides to 1,1'-diacetylferrocene (3.14) gave the erythro-diols (3.16) as the major products, while the diketones (3.15) underwent addition with methylmagnesium bromide to give the threo-diols (3.17) as the main products. The stereoselectivity was ascribed to a preferential direction of attack by the Grignard relative to the intermediate hydroxy-ketone [24].



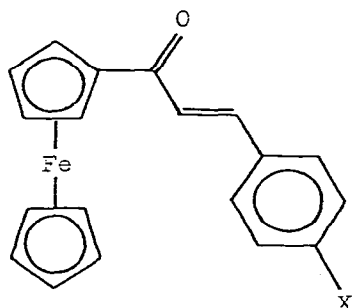


#### 4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

Moessbauer spectroscopy has been used to study the vibrational and thermodynamic properties of crystalline ferrocene and dilute solutions of ferrocene in the liquid crystals 4'-n-propylaniline, 4-n-hexyloxybenzylidene and terephthaloyl-bis-butylaniline [25]. Moessbauer spectra have been recorded for several bridged ferrocenes that contained one tetramethylene or pentamethylene bridge and ferrocenes that contained two bridges, one trimethylene and one tetramethylene, or both tetramethylene. It was shown that there was a linear correlation between the change of the iron to ring distances and the change of the Moessbauer parameters [26]. The Debye model has been used in a theoretical study of the temperature dependence of the Moessbauer free fraction in liquid crystal systems. Debye temperatures were obtained for ferrocene and diacetylferrocene and for their solutions in 4,4'-diheptyloxyazoxybenzene, 4,4'-dioctyloxyazoxybenzene, cholesteryl

myristate, and cholesteryl myristate with cholesteryl oleate. The mean square displacement of a Moessbauer probe inserted into the liquid crystal system has been determined [27].

The mass spectra of a series of methylferrocenes have been recorded and discussed. The fragmentation of methylferrocenes containing up to three methyl groups occurred mainly by elimination of neutral fragments corresponding to the initial methylcyclopentadienes and then to methylfulvenes. Symmetrical octa- and decamethyl-ferrocenes eliminated fragments that corresponded to methylcyclopentenes and tetramethylbenzene [28]. The mass spectra of eight alkylferrocenes; 1,1'-dimethyl-, ethyl-, 1,1'-diethyl-, 1,1'-di-n-propyl-, 1,1'-diisopropyl-, 1,1'-di-n-butyl-, 1,1'-di-t-butyl- and tetra-t-butyl-ferrocene have been recorded and discussed in detail [29]. The mass spectra of some ferrocenyl-chalcones (4.1; X = H, Br, OMe) and the corresponding cymantrenyl-chalcones have been recorded. The main processes of fragmentation of the ferrocenyl-chalcones involved cleavage of the metal- $\eta$ -cyclopentadienyl bond. It was concluded that the localization of

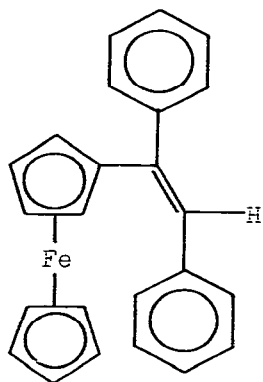


4.1

charge on the metal atom of  $\pi$ -complexes was an important factor in determining their fragmentation mode under electron impact [30]. The mass spectra of several benchtorenyl-, cymantrenyl- and ferrocenyl-carbinols have been recorded. Water was eliminated during the fragmentation of the molecules by a 1,2-elimination mechanism which involved transfer of the hydroxyl group to the metal atom [31].

The low-lying electron resonances in ferrocene, benzene and

naphthalene vapour have been determined by an electron impact procedure [32]. Ferrocene, adsorbed on the surface on an organo-metallic compound, has been investigated by IR spectroscopy [33]. The  $^1\text{H}$  NMR and electronic spectra of a series of alkenylferrocenes, including (E) and (Z) stereoisomers of some styrylferrocenes have been used to elucidate the structures of these molecules. The crystal and molecular structure of the ethenyl-ferrocene (4.2) was determined by X-ray analysis. The conformation of the molecule (4.2) indicated that there was minimal  $\pi$ -conjugation through the trans-stilbene and cis-styrylferrocene moieties [34].

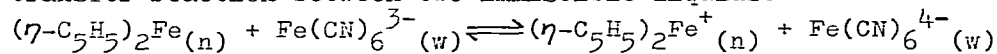


4.2

Dipole moment measurements on chloro-, 1,1'-dichloro-, bromo-, 1,1'-dibromo-, iodo-, and 1,1'-diiodo-ferrocene in the temperature range 5-130°C have been used to determine the energy barriers to rotation about the iron-cyclopentadienyl bond. Values obtained for the disubstituted ferrocenes at 10°C were as follows, 1,1'-dichloroferrocene, 480 cal mol<sup>-1</sup>; 1,1'-dibromoferrocene, 850 cal mol<sup>-1</sup>; 1,1'-diiodoferrocene, 950 cal mol<sup>-1</sup> [35]. The photonuclear reaction  $^{54}\text{Fe}(\gamma, 2n)^{52}\text{Fe}$  has been investigated for ferrocene in the solid phase and in solution and for solid ferrocinium picrate. The distribution of  $^{52}\text{Fe}$  between the parent compound, inorganic iron and unidentified products was measured. For ferrocene, the retention was dependent on the polarity of the solvent, in hexane the proportion of ferrocene was 37.6% while in diethyl ether the proportion was 10.2% [36].

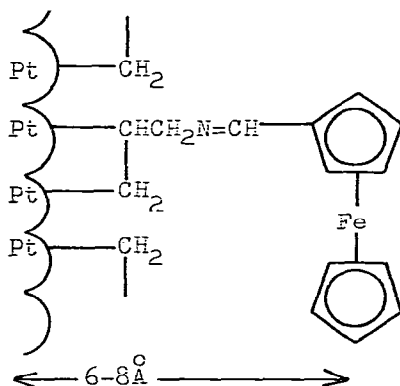
The oxidation potentials of a series of ferrocene

derivatives have been determined by rotating disc electrode voltammetry and cyclic voltammetry with a platinum electrode in methyl cyanide. Some of the molecules had two ferrocenyl moieties present and the formation of monocations and dications in these species was discussed [37]. Cyclic voltammetry with a four-electrode system has been used to investigate a charge transfer reaction between two immiscible liquids:



The hexacyanoferrate redox couple was in water (w) while the ferrocene-ferrocinium couple was in nitrobenzene (n). A qualitative understanding of the observed phenomena was obtained [38, 39].

Chronoamperometry has been used to study the electrochemical dissolution of ferrocene on a carbon electrode. The initial form of the ferrocene, discrete particles or a uniform deposit, determined the pattern of behaviour observed. The experimental results were in agreement with the previously derived theory for spherical particles or planar layers of solid. The dissolution process was found to be diffusion controlled [40]. Cleaned

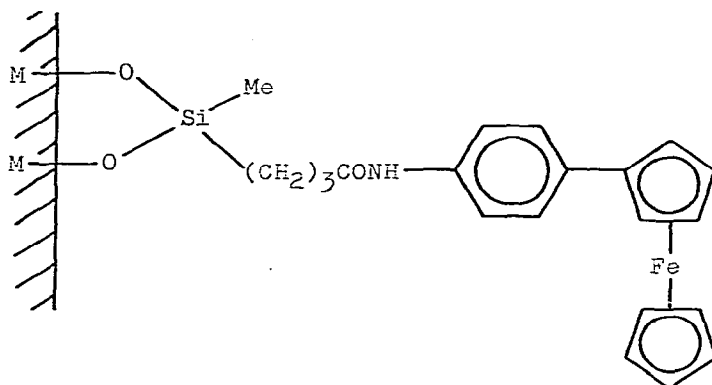


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platinum electrodes were immersed in an aqueous solution of allylamine and then treated with formylferrocene in the presence of a catalytic amount of hydrochloric acid. This gave a platinum-ferrocene electrode surface (4.3). Voltammetric measurements were carried out with the modified electrodes and the behaviour of the platinum-ferrocene electrode towards reactions involving dissolved species was examined. It was concluded that, under the conditions chosen, charge transfer occurred with the reactant at

a distance from the electrode where surface structural variations were not important [41].

Tin (IV) oxide, ruthenium (IV) oxide and platinum/platinum (II) oxide electrodes have been treated with 4-(methyldichlorosilyl)-butyryl chloride and then *p*-aminophenylferrocene to give surface coated electrodes (4.4; M = Sn, Ru, Pt). The electrochemical behaviour of the immobilized ferrocene molecules was investigated [42]. Platinum and gold electrode surfaces have been pretreated



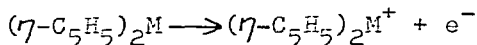
4.4

by anodization and then derivatized with (1,1'-ferrocenediyl)-dichlorosilane. Photoelectron spectroscopy of the surfaces showed Fe 2p  $3/2$  bands with binding energies consistent with ferrocene Fe and with large companion satellite peaks on the basis of a layer model. Relative Fe 2p  $3/2$  and electrode substrate intensities, platinum or gold were correlated with ferrocene coverage of the surface determined by cyclic voltammetry. It was shown that electrochemical charge transfer may occur through silylferrocene layers more than 100Å in thickness [43]. Pyrolytic graphite electrodes spontaneously bind  $\beta$ -ferrocenylethylamine at the surface. The coatings were regarded as polymeric condensation products between the amine groups and oxygen functions on the graphite and contained several monolayers with electroactive iron centres. The nature of the solvent containing the  $\beta$ -ferrocenylethylamine was important in determining the amount of electroactive material bound to the electrode [44]. Trichloro-*s*-triazine (cyanuric chloride) was bound to a pyrolytic graphite electrode via surface hydroxyl groups. The electrode was then

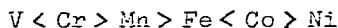
treated with hydroxymethylferrocene to attach the ferrocene group. The ferrocene modified electrode was characterised by cyclic voltammetry and differential pulse polarography [45].

Vinylferrocene has been immobilized on a reactive, deoxygenated glassy carbon surface formed by mechanical abrasion under nitrogen or by plasma etching under argon. Vinylferrocene was deposited as an electroactive ferrocene polymer on glassy carbon and on platinum by direct introduction into a radio-frequency plasma discharge. The modified electrodes formed in this way showed surface waves corresponding to  $3 \times 10^{-8}$  mol cm<sup>-2</sup> ferrocene [46].

The activity coefficients for ferrocene and 1,1'-diethylferrocene in cyclohexane, heptane and xylene at 25° have been obtained by an emf technique. The ferrocene solutions obeyed Henry's law and while the xylene solution showed ideal behaviour, the heptane solution showed a positive deviation from ideal behaviour [47]. The heat of formation of ferrocene at 298°K has been determined as 158+4 kJ mol<sup>-1</sup> and compared with the heats of formation of other metallocenes. The feasibility of the process:

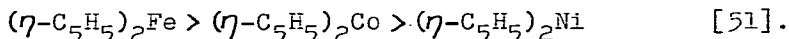


where M = V, Cr, Mn, Fe, Co, Ni, has been analyzed and shown to result from the interplay of exchange energy and ligand field stabilization energy terms in these low spin complexes. The order obtained:

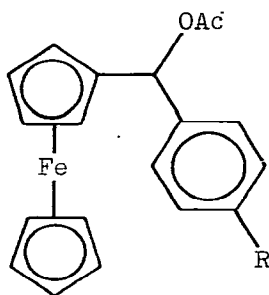


was associated with the special stability of half-filled and filled shells which occur at  $d^3$ ,  $d^6$ ,  $d^8$  and  $d^{10}$  because of the large ligand-field splitting [48]. Differential thermal analysis has been used to examine ferrocene crystals and the heat capacity was measured in the range from 15-300°K. A new low-temperature phase was found which was stable below 242°K [49]. It was concluded that the previously reported transition at 163.9°K [50] was a transition between metastable phases. The thermal decomposition in vacuo of vanadocene, chromocene, manganocene, ferrocene, cobaltocene and nickelocene has been investigated. Kinetic results have shown that the process is both homogeneous and heterogeneous and the decomposition products showed activity as catalysts. The thermal stability of the Group VIII metallocenes was determined by electronic structure rather than by thermodynamic factors,

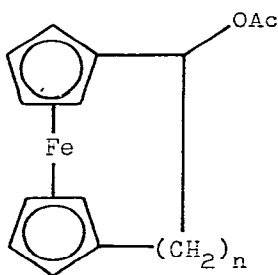
with the following order of stability:



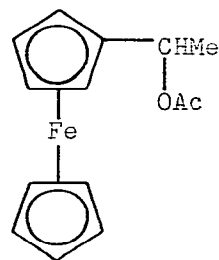
The thermal decomposition of 1,1'-diethylferrocene over alumina has been investigated. The 1,1'-diethylferrocene was adsorbed on to the alumina with the formation of the corresponding ferrocenium ion which decomposed to give a solid product. When the reaction vessel was supersaturated with hydrogen, metallic iron was formed [52]. The enthalpies of interaction of ferrocene in benzene solution with a number of electron acceptors have been measured at 298.15<sup>o</sup>K in an adiabatic calorimeter. The enthalpies measured for silicon (IV) chloride, germanium (IV) chloride, phosphorus (III) chloride, arsenic (III) chloride and sulphur dioxide were near to zero. However the mixing of ferrocene with liquid tin (IV) chloride, titanium (IV) chloride, antimony (V) chloride, VOCl<sub>3</sub> and with solid gallium (III) chloride and β-sulphur trioxide gave heats of formation for the complexes (kcal mol<sup>-1</sup>) of: -18.8, -11.9, -36.4, -20.7, -8.9 and -24.2 respectively [53]. First order rate constants for the solvolysis of the aryl(ferrocenyl)-methyl acetates (4.5; R = H, Me, CF<sub>3</sub>, OMe) have been measured. A linear correlation was obtained between relative rate constant and Hammett σ<sup>+</sup> substituent constants and pK<sub>R+</sub> values for the intermediate ferrocenyl-stabilized carbocations [54]. The ferrocenophar-1-yl acetates (4.6; n = 2, 3, 4) were obtained by treatment of the corresponding alcohols with acetic anhydride in pyridine. Solvolysis of the acetates (4.6) in 80% aqueous acetone has been



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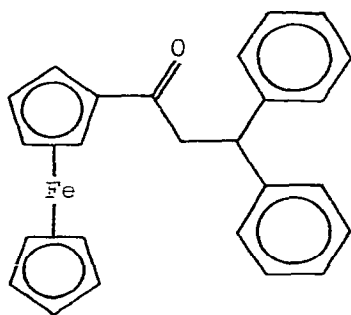


4.7

investigated kinetically using a titrimetric method. The first order rate constants obtained were compared with the value previously determined for 1-ferrocenylethyl acetate (4.7). Relative rate constants were (4.6;  $n = 2$ ) 0.0058; (4.7) 1.00; (4.6;  $n = 4$ ) 31.8; (4.6;  $n = 3$ ) 122 [55].

## 5. REACTIONS OF FERROCENE

The reaction of cyclopentadiene, dissolved in tetrahydrofuran, in the presence of [18]crown-6 as a phase transfer catalyst and potassium hydroxide, with iron (II) chloride gave ferrocene. Methyl-, benzyl-, propyl- and cyclohexyl-ferrocenes were prepared by similar phase transfer catalyzed reactions [56]. A convenient laboratory method for the preparation of ferrocene has been reported [57].  $\beta,\beta$ -Diphenylpropionylferrocene (5.1) has been prepared by treatment of ferrocene with the appropriate acid chloride in the presence of aluminium chloride [58]. Acylation of ferrocene

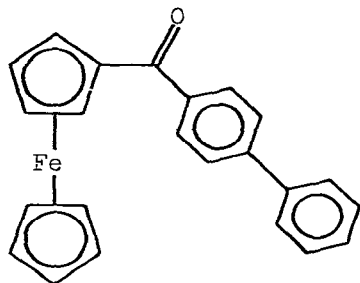


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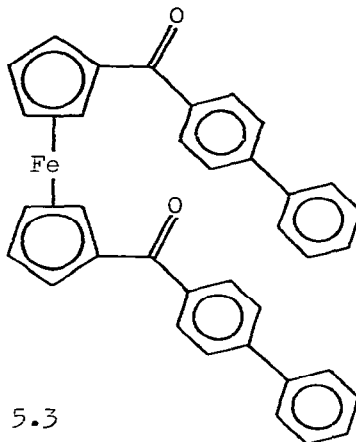
with 4-biphenyl carboxylic acid chloride in the presence of aluminium chloride gave the ferrocene derivatives (5.2 and 5.3). The ketone (5.3) was reduced to the corresponding diol [59].

The direct thiomethylation of ferrocene has been carried out using formaldehyde and a thiol as reagents in the presence of perchloric acid. The ferrocenylmethylsulphides (5.4;  $R = \text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{CH}_2\text{CO}_2\text{H}$ ,  $\text{C}_6\text{H}_4\text{-o-CO}_2\text{H}$ ) were obtained by this method [60]. The reaction of ferrocene, aniline and aluminium chloride gave the  $\eta$ -aniline complex (5.5) which was isolated as the hexafluorophosphate salt. Deprotonation of the cation (5.5) was most conveniently



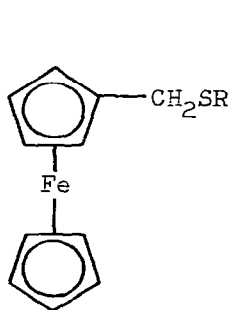


5.2

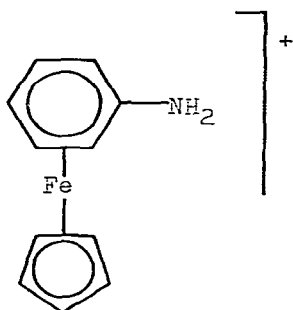


5.3

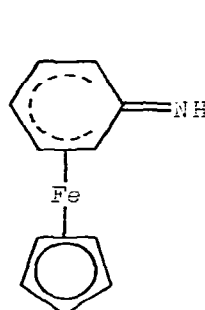
effected with sodamide in dichloromethane to give the air sensitive complex (5.6) [61]. Ferrocene underwent ligand exchange with



5.4



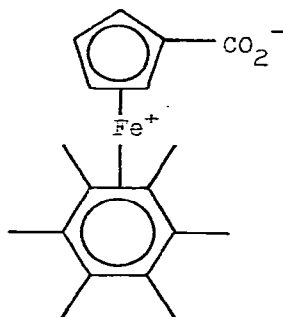
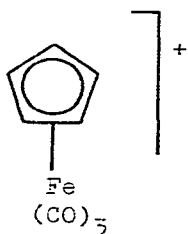
5.5



5.6

carbon monoxide in the presence of aluminium chloride to give the tricarbonyl( $\eta$ -cyclopentadienyl)iron cation (5.7). Several ferrocenophanes were isolated in low yields as minor products of the reaction [62]. Ferrocene underwent successive ligand exchange with arenes and carbon dioxide substitution in the presence of aluminium chloride. Arenes used were benzene, 2,4,6-trimethylbenzene, hexamethylbenzene and naphthalene. One of the products (5.8) has been used as a catalyst in the electrochemical reduction of nitrate to ammonia [63].

Ligand exchange between ferrocene and naphthalenes or anthracenes has been studied. In addition to the expected exchange



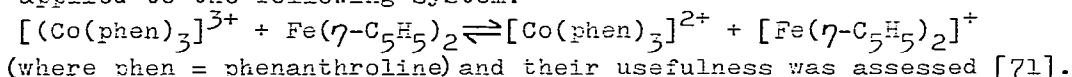
products, complexes were isolated which contained partially reduced naphthalene and anthracene ligands. The reduction mechanism involved abstraction of hydride ion by aluminium chloride from the complex to leave a carbenium ion which was stabilized by intramolecular electron transfer giving Fe (III) and a radical centre on the ligand. Hydrogen was then abstracted by the iron atom and transferred to the ligand [64]. Ferrocene underwent ligand exchange with pyrene in the presence of aluminium and aluminium chloride to give the ( $\eta$ -pyrene)( $\eta$ -cyclopentadienyl)-iron cation and the ( $\eta$ -pyrene)trans-bis( $\eta$ -cyclopentadienyl)iron dication. Reduction took place during the ligand exchange to give the ( $\eta$ -4,5-dihydropyrene)( $\eta$ -cyclopentadienyl)iron, and ( $\eta$ -4,5,9,10-tetrahydropyrene)( $\eta$ -cyclopentadienyl)iron cations as well as the ( $\eta$ -4,5,9,10-tetrahydropyrene)trans-bis( $\eta$ -cyclopentadienyl)iron dication [65]. Ferrocene and several ferrocene derivatives exploded when mixed with tetranitromethane. The reaction involved the initial formation of a charge-transfer complex, the radical  $\cdot\text{C}(\text{NO}_2)_3$  generated in this step then combined violently with ferrocene. Methanol and cyclohexane solutions of ferrocene were not attacked by tetranitromethane [66].

The deuteration of ferrocene and cymantrene was effected in the presence of a heterogeneous platinum catalyst and a homogeneous potassium tetrachloroplatinate (II) catalyst [67]. The formation of  $^{52}\text{Fe}$  in high specific activity was achieved conveniently by  $\gamma$ -irradiation of ferrocene containing  $^{54}\text{Fe}$  [68]. A solution of ferrocene or one of its derivatives in petrol was added to coal

at 150-325°. This treatment increased the magnetic susceptibility of the impurities in the coal [69].

## 6. FERROCINIUM SALTS

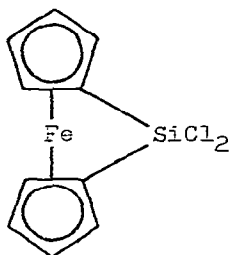
Redox potentials for the ferrocene-ferrocinium ion system have been determined in a series of water-acetic acid-sulphuric acid mixtures at different concentrations. An equation was derived which related the redox potential to the acetic acid and sulphuric acid concentrations [70]. The various equations used for the determination of activation parameters in electron-transfer reactions have been considered. The equations were applied to the following system:



Ferrocene and iodine at low concentrations in benzene have been subjected to flash photolysis. A sharp increase in absorbance at 625nm was observed 60 $\mu$ s after the flash onset. This corresponded to an increase in the concentration of ferrocinium iodide. The absorbance remained constant for a period of several ms but fell over a period of a few S. A mechanism for the reaction was proposed [72]. The oxidation of acetylferrocene and 1,1'-diacetylferrocene by cerium (IV) in sulphuric acid (H<sub>0</sub> range +1 to -3) involved an initial fast one-electron step to give the corresponding unstable ferrocinium ion. Further oxidation caused breakdown of the metallocene group, acetylferrocene was completely oxidized to Fe<sup>2+</sup> by two equivalents of cerium (IV) while 1,1'-diacetylferrocene required three equivalents of cerium (IV) for complete oxidation to Fe<sup>3+</sup>. The intermediate ferrocinium ions were increasingly stable in solutions of higher acidity and in the presence of the oxidizing agent [75]. Ferrocinium perchlorate and tetrafluoroborate decomposed under aqueous alkaline conditions. The stoichiometry of the reaction was dependent on the counter anion associated with the ferrocinium cation. The mechanism involved a rapid pre-equilibrium between ferrocinium and added inorganic anions (Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup>) followed by attack of hydroxide ion. The products were iron (III) hydroxide and an oxidized cyclopentadienide [74].

Ferrocene residues have been attached to the surfaces of n-type gallium arsenide semiconductors by using (1,1'-ferrocene-diyl)dichlorosilane (6.1) as the reagent. The surface attached

ferrocene groups were oxidized in an uphill sense on irradiation with light of energy greater than 1.4eV, the band gap of gallium arsenide. 50% conversion was achieved in the photooxidation at a



6.1

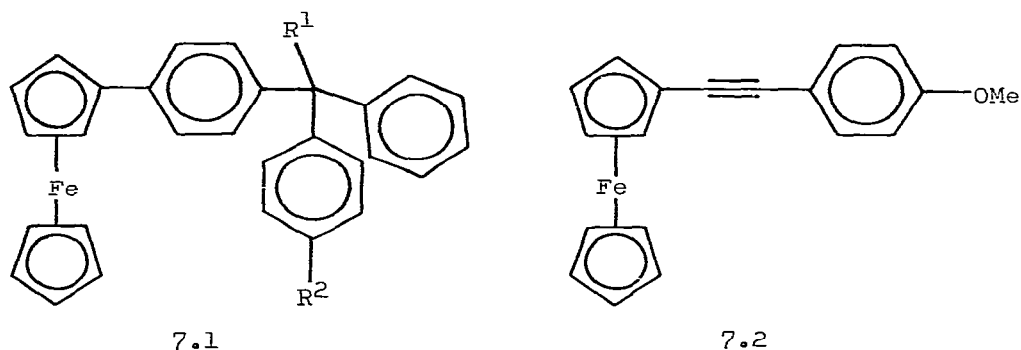
potential of  $\sim -0.25V$  vs. SCE, by contrast, conversion to this extent occurred at a potential of  $+0.40V$  at a reversible electrode. The surface-attached ferrocenium ion can be used to oxidize reducing agents in solution such as ferrocene and iodide [75]. The two electron reductants, biferrocene, diferrocenylmethane, bis(fulvene)diiron and N,N,N',N'-tetramethyl-p-phenylenediamine were oxidized contrathermodynamically to the corresponding dications at illuminated n-type silicon photoanodes. The ferrocenyl-silane (6.1) was attached to a silicon photoanode and this protected the surface from deleterious photoanodic  $SiO_x$  growth. Dichloro-diferrocenylsilane was attached to platinum and n-type silicon electrodes. The oxidizing power of the derivatized photoanodes was light intensity dependent [76].

The charge-transfer complex 1,1'-dimethylferrocenium bis-(tetracyanoquinodimethan), (TCNQ), has been characterized by X-ray crystallography. The structure consisted of chains of stacked TCNQ molecules and stacked ferrocenium ions. There were no intermolecular interactions in the ferrocenium chains. The magnetic and electrical properties of the complex were reported [77]. Decamethylferrocene (DMeFc) combined with TCNQ to give several salts including the green metamagnetic substance (DMeFc<sup>+</sup>)(TCNQ<sup>-</sup>). The structure of this salt was determined by X-ray methods and found to consist of parallel one-dimensional chains

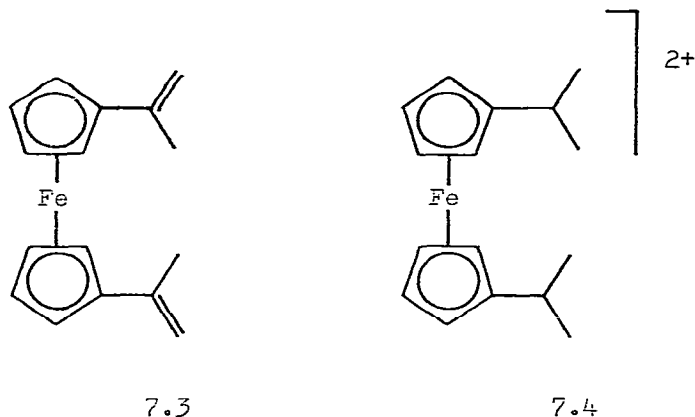
containing alternating  $\text{DMeFc}^+$  cations and  $\text{TCNQ}^-$  anions. The cyclopentadienyl rings of the ferrocenium cation were eclipsed and the anion had suffered partial oxidation to  $\alpha,\alpha$ -dicyano-*p*-toluoylcyanoide [78]. Moessbauer spectroscopy has been used to show that the monocation derived from diferrocenylacetylene was a mixed valence species while the monocation obtained from [2.2]ferrocenophane-1,13-diyne was an averaged valence species [79].

## 7. FERROCENYL CARBENIUM IONS

Reaction of the alcohols (7.1;  $\text{R}^1 = \text{OH}$ ,  $\text{R}^2 = \text{NMe}_2, \text{OMe}$ ) with sodium tetraphenylborate in acetic acid gave the corresponding carbenium ions. Treatment of the carbenium ions with piperidine gave the piperidine derivatives (7.1;  $\text{R}^1 = \text{piperidino}$ ,  $\text{R}^2 = \text{NMe}_2, \text{OMe}$ ) [80]. Ferrocenylacetylene was hydrolysed under acid



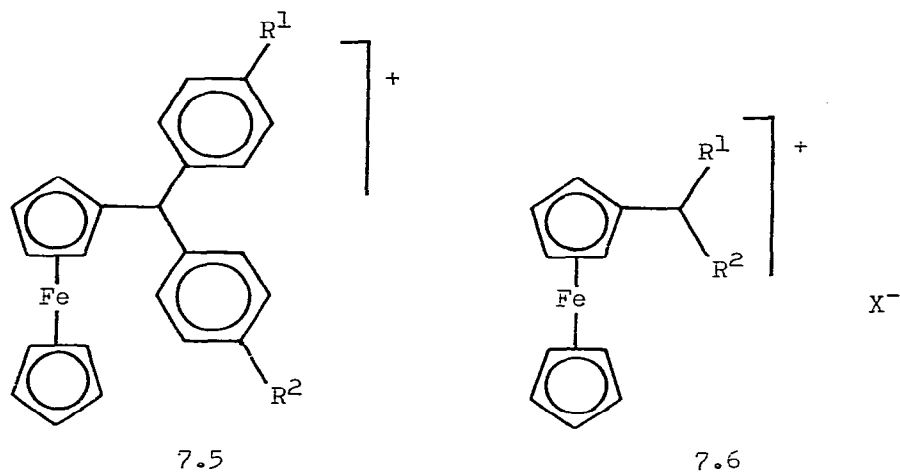
conditions 160 times faster than (*p*-methoxyphenyl)acetylene, the products were acetylferrocene and *p*-methoxyacetophenone. The acid hydrolysis of ferrocenyl(*p*-methoxyphenyl)acetylene (7.2) gave ferrocenyl(*p*-methoxybenzyl)ketone as the only product. These results confirmed the stability of the  $\alpha$ -ferrocenylcarbenium ion [81]. The divinylferrocene (7.3) has been converted to the ferrocenedicarbenium ion (7.4) with fluorosulphonic acid in liquid sulphur dioxide at  $-80^\circ\text{C}$ . An  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis of the dication (7.4) indicated that charge localization on the  $\alpha$ -carbon atoms was appreciably greater than in the corresponding tertiary monocarbenium ions. The structure proposed for the dication



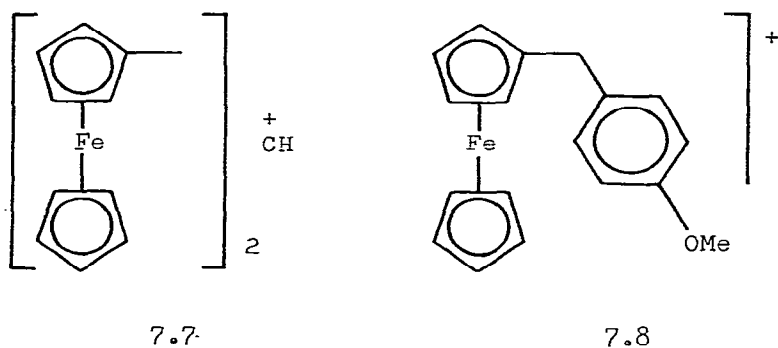
(7.4) contained a bent exocyclic bond to each  $\alpha$ -carbon with an overall anti-conformation to ensure minimal interannular electrostatic repulsions [82].

The spontaneous decomposition of ferrocenyldiarylmethylm ions (7.5;  $R^1 = R^2 = \text{H, OMe}$ ;  $R^1 = \text{H, } R^2 = \text{OMe, CF}_3$ ) to 6,6-diarylpentafulvenes has been investigated kinetically in aqueous acidic acetonitrile. The first order rate constants were dependent on the nature of the substituents  $R^1$  and  $R^2$  and on the ionic strength of the medium. Steric factors were implicated in control of the degradation but carbenium ion stability was not important [83]. The ferrocenylmethylcarbenium tetrafluoroborates [7.6;  $R^1 = R^2 = \text{H}$ ;  $R^1 = \text{H, } R^2 = \text{Me}$ ;  $R^1 = \text{H, } R^2 = \text{CH}(\text{Me})_2$ ;  $R^1 = \text{H, } R^2 = \text{Ph}$ ;  $R^1 = R^2 = \text{Me}$ ;  $R^1 = R^2 = \text{Ph}$ ;  $X = \text{BF}_4^-$ ] were prepared from the corresponding carbinols in diethyl ether, tetrahydrofuran and *t*-butyl methyl ether. The <sup>1</sup>H NMR spectra of the salts in CDCl<sub>3</sub> exhibited strong signals attributed to the ether used in the preparation. It was concluded that  $\alpha$ -ferrocenylmethylcarbenium ions underwent two types of solvation. One involved one molecule of ether per molecule of cation and had a large association constant whilst the other was a much weaker interaction [84].

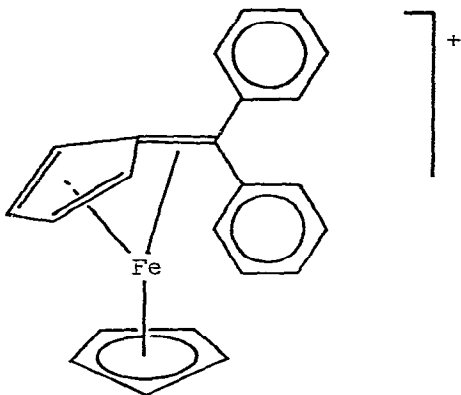
Secondary  $\alpha$ -hydrogen kinetic isotope effects in nucleophilic additions to ferrocenyl stabilized carbenium ions have been investigated. The results obtained from the solvolyses of the carbenium ions (7.7 and 7.8) in water and water-organic solvent mixtures suggested that there was appreciable C...O bond formation in the transition state for carbenium ion solvolysis [85]. The



crystal and molecular structure of ferrocenyldiphenylcarbenium tetrafluoroborate has been determined by X-ray crystallography.



The structure was regarded as an ( $\eta$ -cyclopentadienyl)( $\eta$ -fulvene)-iron cation (7.9) with the fulvene exocyclic double bond bent towards the iron at an angle of  $20.7^\circ$  and an Fe-C<sub>exo</sub> distance of 2.715Å [86]. Ferrocenylcarbinols have been treated with sulphuric acid and then ammonium hexafluorophosphate to form ferrocenylcarbenium salts such as the compounds (7.6; R<sup>1</sup> = H, R<sup>2</sup> = Me, Ph, ferrocenyl; R<sup>1</sup> = Ph, R<sup>2</sup> = Me, Ph; X = PF<sub>6</sub>). The salts (7.6) were attacked by nucleophiles including cyanide ion, azide ion and acetate ion to give the corresponding neutral  $\alpha$ -substituted ferrocenes. Thus the salt (7.6; R<sup>1</sup> = H, R<sup>2</sup> = Me)



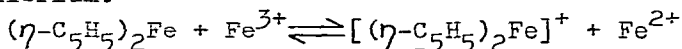
7.9

was attacked by cyanide to give  $\alpha$ -methylferrocenylacetonitrile [87].

## 8. FERROCENE CHEMISTRY

### (i) Photochemistry

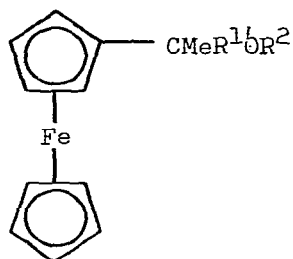
The triplet energy transfer from biacetyl to ferrocene has been studied in a range of solvents. The intensity of the phosphorescence was measured as a function of the ferrocene concentration. From the results it was concluded that resonance energy transfer did not take place but ordinary exchange methods occurred. The kinetics of energy transfer followed a Stern Volmer model and there was incomplete transfer per encounter in the less viscous solvents [88]. The mechanism of the reaction between *t*-butyl isocyanate and methanol photocatalysed by ferrocene and iron (III) chloride in carbon tetrachloride-dichloromethane mixtures has been investigated by kinetic, spectroscopic and quantum yield measurements. It was concluded that the ferrocene was involved in the equilibrium:



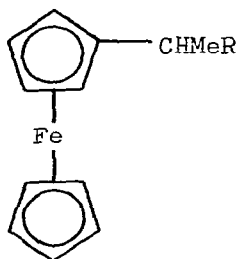
which regenerated the active  $\text{Fe}^{3+}$  [89]. The following halogenated compounds;  $\text{CCl}_4$ ,  $\text{PhCOCH}_2\text{Br}$ , *p*- $\text{BrC}_6\text{H}_4\text{COCH}_2\text{Br}$  and  $\text{Cl}_3\text{CCO}_2\text{Me}$  were dehalogenated by irradiation of alcoholic solutions containing ferrocene or iron (III) chloride. It was suggested that radicals from the alcohol solvent were involved in the reaction [90].

Vinylferrocene and *iso*-propylferrocene have been irradiated in methanol and ethanol to give ferrocenyloethers by way of ferro-

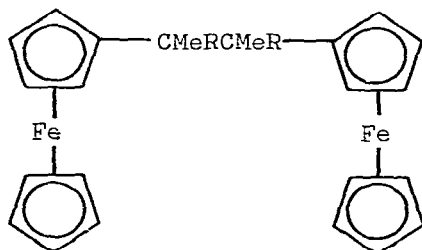




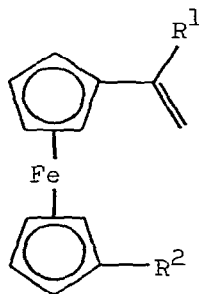
8.1



8.2



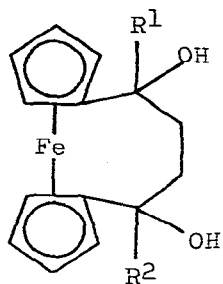
8.3



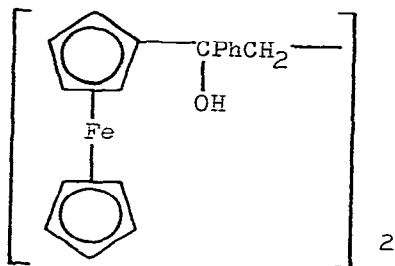
8.4

ferrocenyl carbocation intermediates. Vinylferrocene formed the ether (8.1;  $R^1 = H$ ,  $R^2 = Et$ ) while isopropylferrocene formed the products (8.1;  $R^1 = Me$ ,  $R^2 = Me, Et$ ). These compounds (8.1) were themselves labile under the conditions used and gave the alkylferrocenes (8.2;  $R = H$  and  $R = Me$ ) respectively. Binuclear products (8.3;  $R = H$  and  $R = Me$ ) respectively were also formed in the secondary reactions [91]. The photosensitized oxidation of the vinylferrocenes (8.4;  $R^1 = Me, Ph$ ,  $R^2 = CMe=CH_2$ ;  $R^1 = Ph$ ,  $R^2 = CPh=CH_2$ ) in dichloromethane in the presence of sodium copper-chlorophyllin sensitizer and oxygen gave the ferrocenophane diols (8.5;  $R^1 = Me, Ph$ ,  $R^2 = Me$ ;  $R^1 = R^2 = Ph$ ). However, the vinylferrocene (8.4;  $R^1 = Ph$ ,  $R^2 = H$ ) dimerized under the same conditions to give the diol (8.6). Singlet oxygen was implicated in the reactions [92].

The photolysis of several ferrocenyl ethers in methanol has been investigated and the products isolated were formed from  $\alpha$ -ferrocenyl free-radicals and  $\alpha$ -ferrocenyl carbocations. For example, for 2-ethoxy-2-ferrocenylpropane (8.7) it was postulated

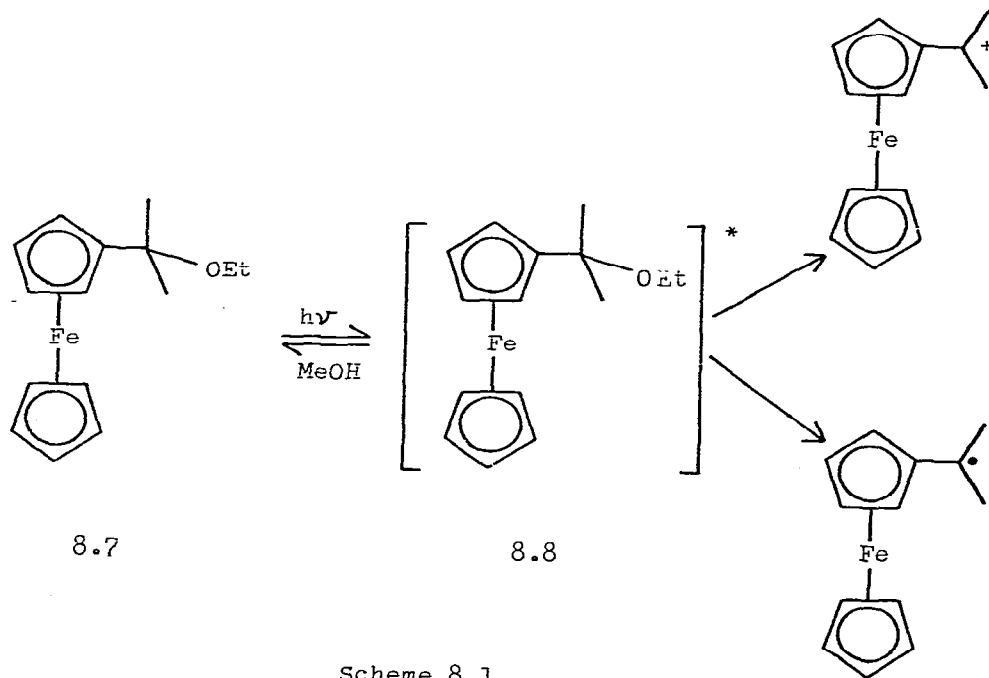


8.5



8.6

that photoexcitation afforded an excited state (8.8) which partitioned itself between two reaction paths (Scheme 8.1) [93].

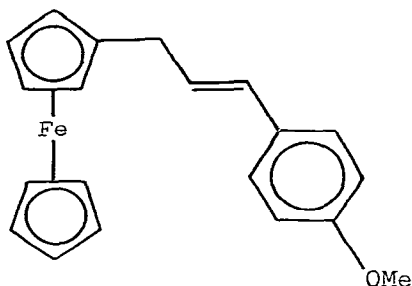


8.7

8.8

Scheme 8.1

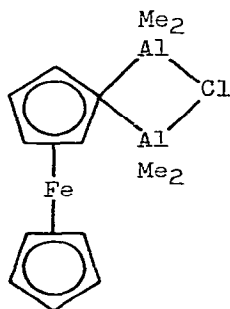
Irradiation of 3-ferrocenyl-1-p-methoxyphenylprop-1-ene (8.9) in methanol gave 3-ferrocenyl-p-methoxyphenylpropane, 3-ferrocenyl-1-methoxy-1-p-methoxyphenylpropane and 3-ferrocenyl-3-methoxy-1-p-methoxypropane. The mechanism of the reaction was investigated [94].



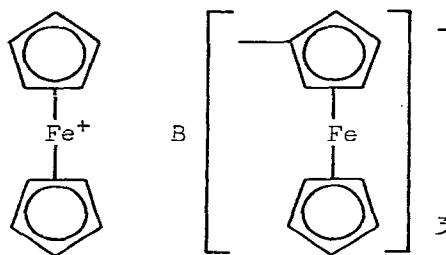
8.9

(ii) Derivatives containing other metals (metalloids)

The reaction of chloromercuriferrocene with trimethylaluminum in a sealed tube gave the ferrocenylalane (8.10). X-ray crystallographic characterization of the ferrocenylalane (8.10) showed that the two dimethylaluminum units were linked together by the chlorine atom and one carbon atom of a  $\eta$ -cyclopentadienyl ring. The angle of tilt of the two  $\eta$ -cyclopentadienyl rings was  $8.3^\circ$



8.10

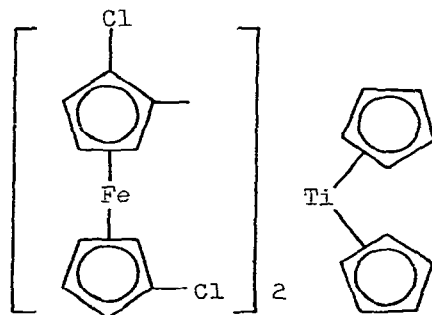
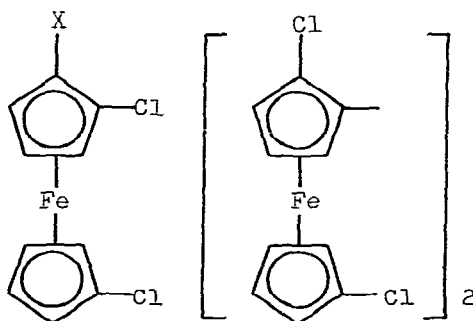
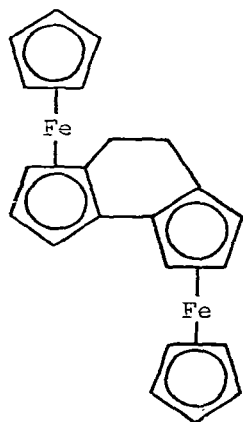
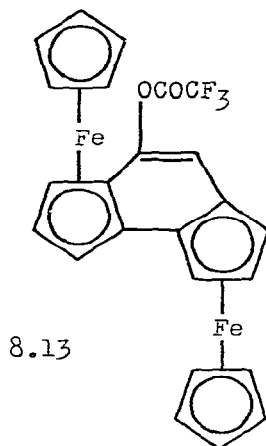
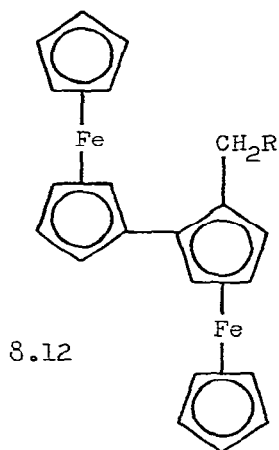


8.11

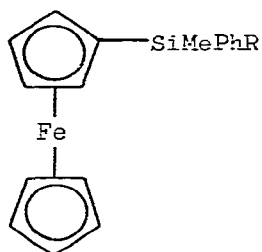
and there was no significant iron-aluminum interaction [95]. The reaction of excess ferrocenyllithium with tri-*n*-butylborane or boron trifluoride gave tris(ferrocenyl)borane and the zwitterion (8.11). The structure of the zwitterion (8.11) was determined by X-ray analysis. It was found that there was one sterically distinct ferrocenyl group and one electronically unique ferrocenyl moiety and these were not coincident. The electronic absorption spectrum of the molecule (8.11) indicated the presence of an intervalence electronic transition and it was suggested that the electron transfer proceeded via a through-space mechanism [96]. The interaction of ferrocenyllithium with  $[\text{CuBrPPh}_3]_4$  gave ferrocenylcopper. Treatment of the ferrocenylcopper with iodobenzene and benzoylferrocene gave phenylferrocene and benzoylferrocene respectively [97].

Lithioferrocene and 2-lithiodimethylaminomethylferrocene were coupled in the presence of tetrakis[iodo(tri-*n*-butylphosphine)-copper (I)] to give the biferrocene (8.12;  $\text{R} = \text{NMe}_2$ ). Treatment of the amine (8.12;  $\text{R} = \text{NMe}_2$ ) with methyl iodide gave the corresponding quaternary salt which gave the nitrile (8.12;  $\text{R} = \text{CN}$ ) on reaction with potassium cyanide. The nitrile (8.12;  $\text{R} = \text{CN}$ ) was hydrolysed to the corresponding acid and this acid was cyclized by trifluoroacetic acid anhydride to the trifluoroacetate (8.13). The latter compound (8.13) was hydrolysed with potassium hydroxide and the product was reduced to give the bridged biferrocene (8.14) [98]. Several halide complexes have been treated with 1,1'-dichloro-2-lithioferrocene to form the corresponding ferrocenyl derivatives [8.15;  $\text{X} = \text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ ,  $\text{AuPPh}_3$ ,  $\text{Mn}(\text{CO})_5$ ,  $\text{Ir}(\text{CO})(\text{PPh}_3)_2$ ]. A binuclear derivative (8.16) was formed in the same way. The compounds (8.15 and 8.16) were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy [99]. The treatment of ferrocene with lithium and 1,5-cyclooctadiene (COD) gave the lithio species  $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{COD})\text{Li}$  which was converted to the zinc salt  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{COD})]_2\text{Zn}$  with zinc chloride. This salt was in turn treated with ethylene and then lithium to give the derivative  $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_2\text{H}_4)\text{Li}$  [100]. Metallation of ferrocene in the presence of ethylene gave the complex  $(\text{C}_2\text{H}_4)_4\text{FeLi}_2$  which was characterized as the tetramethylethylenediamine adduct [101].

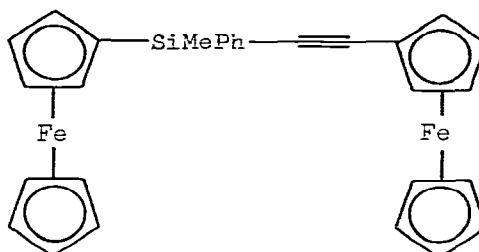
The ferrocenyl-silane (8.17;  $\text{R} = \text{H}$ ) was chlorinated with palladium (II) chloride to give the chloro-silane (8.17;  $\text{R} = \text{Cl}$ ). Reaction of this latter compound with 1-ferrocenyl-2-lithioacety-



lene gave the diferrocenyl derivative (8.18) [102]. The hydrosilylation of the ferrocenylacetylenes (8.19;  $n = 1, 2$ ;  $R = \text{Me, Et, Ph}$ ) with triethylsilane in the presence of a Speier's catalyst has been examined. The triethylsilyl group added to the carbon in the  $\alpha$ -position to the ferrocenyl group in the acetylenes (8.19;  $n = 1, 2$ ;  $R = \text{Me, Et}$ ) and to the  $\beta$ -carbon in the acetylenes (8.19;  $n = 1, 2$ ;  $R = \text{Ph}$ ). The addition of triphenylsilane under the same conditions took place in the opposite sense [103]. Hydrosilylation of the organogermanium ferrocenylacetylene (8.20;  $X = \text{GeEt}_3$ ) with  $\text{HSiPh}_3$  in the presence of a Speier's catalyst gave the adduct (8.21;  $X = \text{GeEt}_3$ ). Cleavage of the carbon-germanium bond also occurred to form the

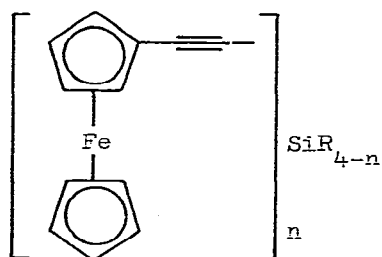


8.17

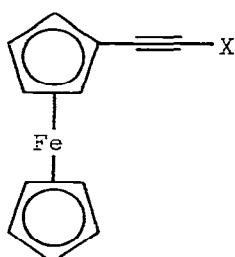


8.18

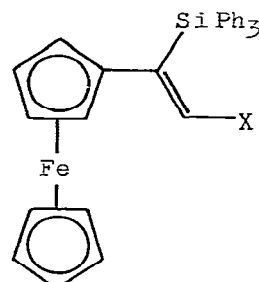
ferrocenylacetylene (8.20; X = SiPh<sub>3</sub>) and the disilylolefin (8.21; X = SiPh<sub>3</sub>), other related transmetalation and addition



8.19



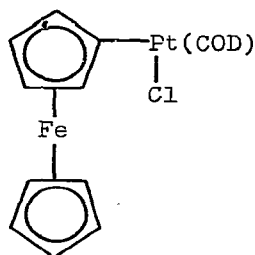
8.20



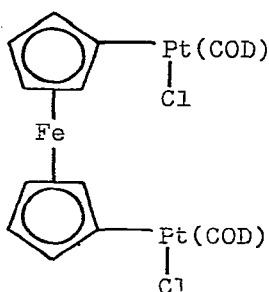
8.21

products were isolated from the reaction [104].

Treatment of trimethylstannylferrocene with [Pt(COD)Cl<sub>2</sub>] where COD = cycloocta-1,5-diene gave the ferrocene-platinum complex (8.22). A similar reaction with 1,1'-bis(trimethylstannyl)ferrocene gave the ferrocenyl platinum complex (8.23) [105]. The ferrocenyl-phosphine (8.24) catalysed the hydroformylation of 1-hexene to give complete conversion with high selectivity to *n*-hexanal [106]. Homogeneous catalytic asymmetric hydrogenation of olefins, ketones and imines by some rhodium-complexes of the ferrocenyl-phosphine (8.25; R = H, OH, NMe<sub>2</sub>)

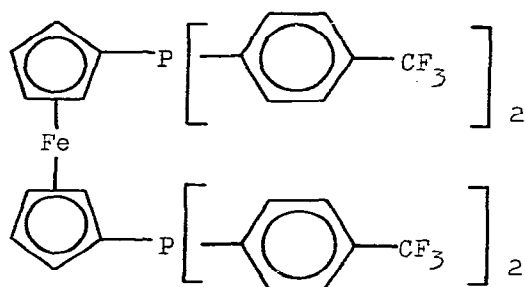


8.22

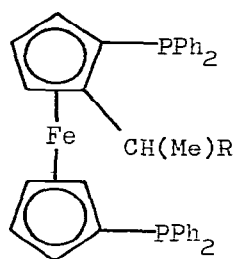


8.23

has been investigated. For example, the hydrogenation of the ketones  $R^1COR^2$  ( $R^1 = \text{Me, Et}$ ;  $R^2 = \text{Ph, Me}_3\text{C, Bu, CO}_2\text{H}$ ) gave 5-100% S- and R- $R^1\text{CH(OH)R}^2$  depending on the substituents [107].



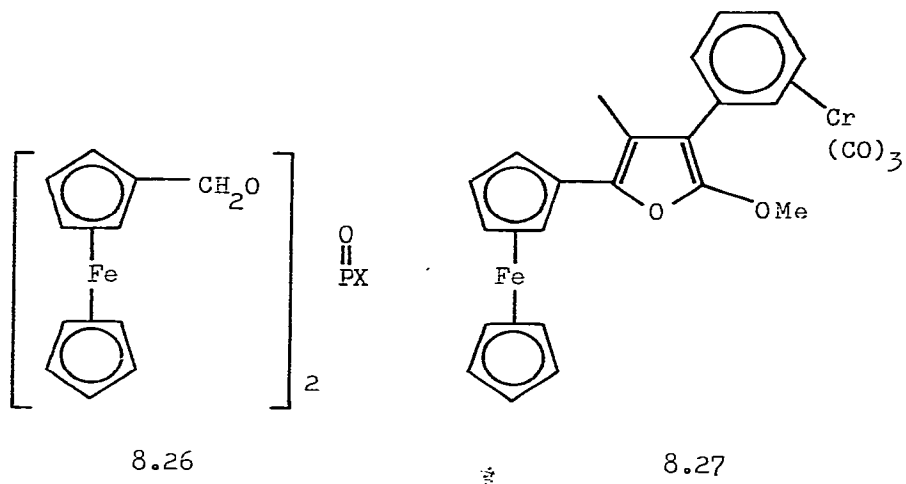
8.24



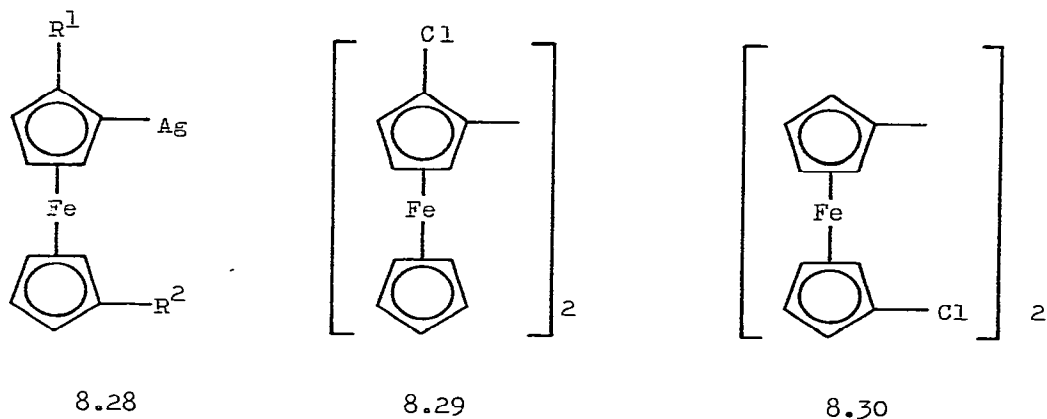
8.25

Dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium (II) has been used as a catalyst for the cross-coupling of sec-butylmagnesium chloride with bromobenzene,  $\beta$ -bromostyrene and 2-bromopropene to give the corresponding sec-butyl derivatives in very good yields [108]. The bis(ferrocenylmethyl)phosphonic acid (8.26;  $X = \text{H}$ ) has been treated with bis(dimethylamino)methane to form the phosphonate (8.26;  $X = \text{CH}_2\text{NMe}_2$ ) in 99% yield. The formation of twelve other phosphonates (8.26) was reported [109].

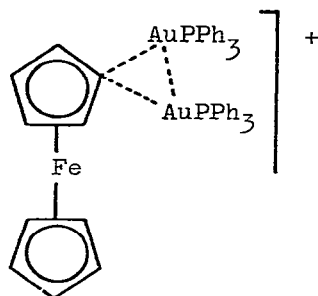
The ferrocenylfuran (8.27) has been formed by treatment of pentacarbonyl[ferrocenyl(methoxy)carbene]chromium with tolan in



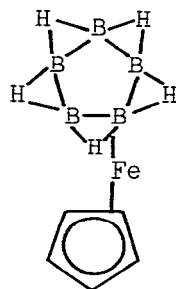
dibutyl ether. The crystal and molecular structure of the complex (8.27) has been determined by X-ray crystallography [110]. Treatment of the ferrocenyl-silver compounds (8.28;  $R^1 = \text{Cl}$ ,  $R^2 = \text{H}$ ;  $R^1 = \text{H}$ ,  $R^2 = \text{Cl}$ ) with iodine gave the bifero-cenyl derivatives (8.29 and 8.30) respectively [111]. The reaction of ferrocene with  $(\text{Ph}_3\text{PAu})_3\text{O}^+\text{BF}_4^-$  in the presence of hydrogen tetrafluoroborate gave the complex cation (8.31) [112]. The reaction of mercury (II) acetate with several alkylvinyl-substituted







8.31

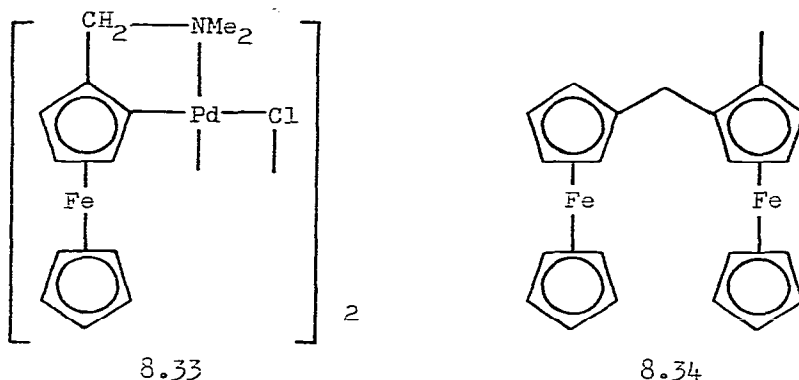


8.32

ferrocenes has been investigated. Two reactions occurred, addition to the olefinic linkage (methoxymercuration) and aromatic substitution of the  $\eta$ -cyclopentadienyl ring. Addition was the only reaction with vinyl- and  $\alpha$ -methylvinyl-ferrocenes and ring-substitution was the only reaction with  $\alpha$ -t-butylvinyl- and  $\beta,\beta$ -dimethylvinyl-ferrocenes. Both methoxymercuration and ring substitution occurred with trans- $\beta$ -methylvinylferrocene. Addition was of the Markownikov type and substitution occurred in the unsubstituted  $\eta$ -cyclopentadienyl ring. Kinetic data was obtained for these reactions [113]. The cyclopentadienide ion,  $B_5H_8^-$  and ferrous ion in THF at  $-78^\circ C$  combined to give a ferraborane which was converted by thermal isomerization to the ferrocene analogue (8.32) a violet air-sensitive solid [114].

(iii) Complexes of ferrocene-containing ligands

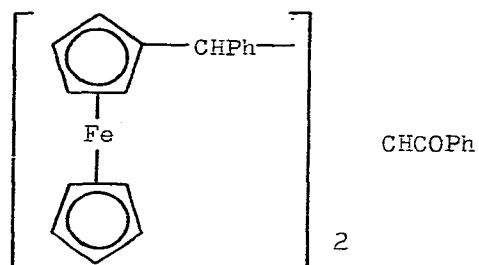
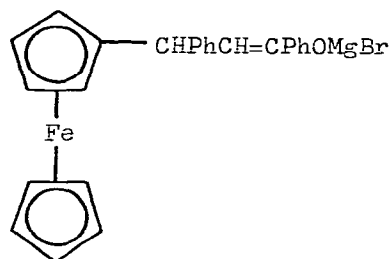
Complexes of the  $\beta$ -diketone ferrocenyltrifluoroacetone (FTFH) were obtained by reaction with the bis( $\eta$ -cyclopentadienyl)-metal dichlorides,  $(\eta-C_5H_5)_2MCl_2$ , where  $M = Ti, Zr, Hf, Nb$ . Two FTFH ligands were incorporated to give the complexes  $(\eta-C_5H_5)_M(FTF)_2Cl$ , where  $M = Ti, Zr, Hf, Nb$  [115]. Ferrocenylacetone, formed by treatment of acetylferrocene with ethyl acetate in the presence of strong bases, was used as a bidentate ligand towards copper (II) and iron (III) salts [116]. The metalation of (dimethylamino)methylferrocene with sodium tetrachloropalladate (II) in the presence of optically active N-acetyl-L-valine gave the optically active planar chiral 2-(dimethylamino)methylferrocenyl-



palladium chloride dimer (8.33) in high yield. The absolute rotation and optical purity of the dimer (8.33) were determined by conversion to 2-methylferrocenecarboxylic acid and to 2-methylferrocenecarbaldehyde [117]. The acetylhydrazone of acetylferrocene was attacked by palladium (II) chloride at the 2-position to give a cyclopalladated complex. The complex gave a pyridine adduct with a trans-N,N and trans-C,Cl geometry. Similar reactions were carried out with the acetylhydrazones of *p*-methylacetophenone and 2-acetylthiophen [118].

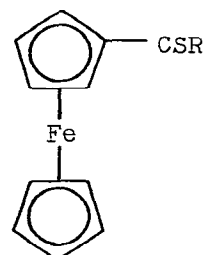
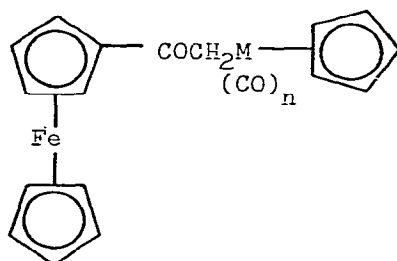
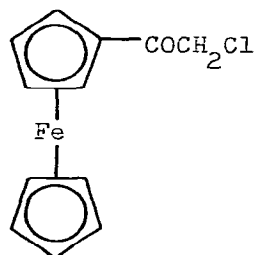
#### (iv) General Chemistry

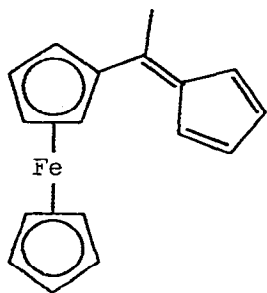
Ethylferrocene, methylferrocene and di-, tri- and tetra-methylferrocenes were obtained in yields of up to 78% by the cocondensation of iron atoms and the vapour of the appropriate ethyl- and methyl-cyclopentadienes at  $-196^{\circ}$  [119]. Oxidation of methylferrocene with manganese (III) acetate in acetic acid gave the diferrocenylmethane (8.34) together with the 3-methyl and 1'-methyl isomers [120]. Decamethylferrocene (DMeFc) combined with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) to form three charge transfer complexes, green (DMeFc)(TCNQ), purple (DMeFc)(TCNQ) and (DMeFc)(TCNQ)<sub>2</sub>. The two monoclinic 1:1 complexes were analyzed by X-ray methods, the green complex was found to have a one-dimensional structure while the purple form was made up of isolated dimers. The green complex contained paramagnetic (DMeFc)<sup>+</sup> and (TCNQ) groups and showed cooperative magnetic interactions [121]. The enolate salt (8.35), derived



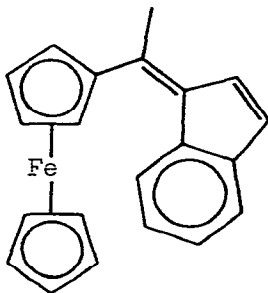
from the corresponding  $\beta$ -ferrocenyl-ketone, has been acylated with benzoyl chloride to form the binuclear ferrocenyl-ketone (8.36) as a mixture of diastereoisomers. A dibenzoyl intermediate was implicated in the reaction [122].

Reaction of the ferrocenyl-ketone (8.37) with  $\text{NaM}(\text{CO})_n(\eta\text{-C}_5\text{H}_5)$  where  $\text{M} = \text{Mo}, \text{W}, \text{Fe}$ ;  $n = 2, 3$  gave the corresponding ferrocenyl-methyl derivatives (8.38) [123]. Acetylferrocenes have been converted to thioketones (8.39;  $\text{R} = \text{Me}, \text{CMe}_3, \text{Ph}$ ) by reaction with  $\text{P}_4\text{S}_{10}$  in carbon disulphide [124]. Treatment of acetylferrocene with cyclopentadiene, indene and fluorene gave the ferrocenyl-fulvenes (8.40, 8.41 and 8.42) respectively [125].

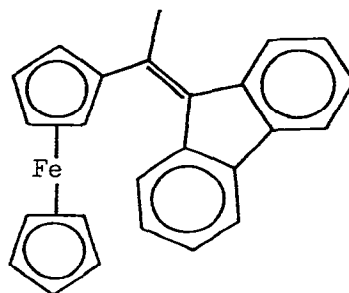




8.40

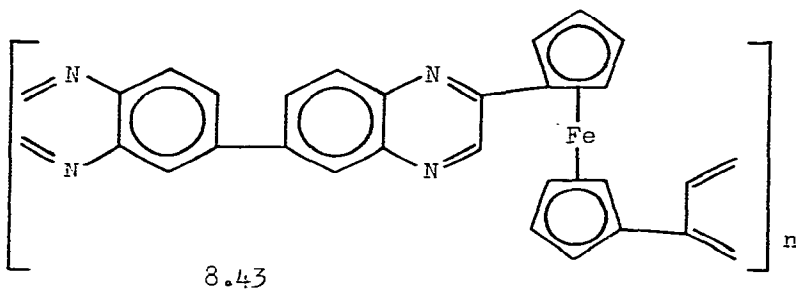


8.41

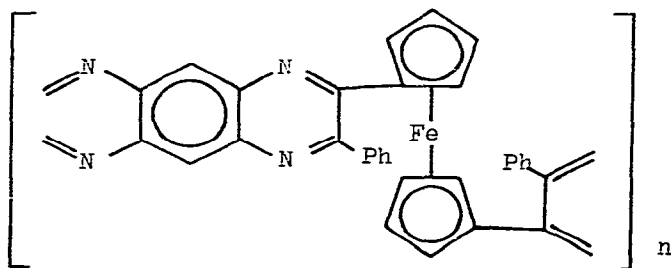


8.42

1,1'-Bis(glyoxalyl)ferrocene has been prepared by the selenium (IV) oxidation of 1,1'-diacetylferrocene and 1,1'-bis(phenylgly-



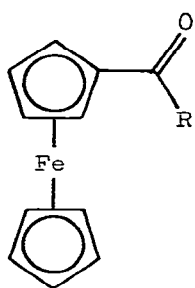
8.43



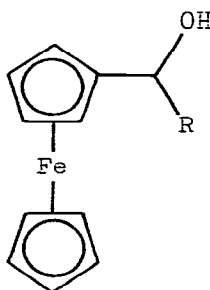
8.44

oxalyl)ferrocene was prepared by a similar route. The ferrocene bisglyoxalyls were condensed with 3,3',4,4'-tetraaminobiphenyl and 1,2,4,5-tetraaminobenzene to give polymers, for example (8.43 and 8.44). The properties of the polymers were investigated [126]. The reactions of 1,1'-bis(acetoacetyl)ferrocene have been examined [127]. Formylferrocene and some ferrocenyl-ketones (8.45;  $R = C_{1-15}$  alkyl, aryl,  $ClCH_2$ ,  $Cl_2CH$ ) have been prepared by oxidation of the corresponding ferrocenyl alcohol (8.46), ether (8.47) and olefin (8.48) with  $(R_3SiO)_2CrO_2$  ( $R = C_{1-4}$  alkyl, Ph). For example, the oxidation of ferrocenyl-methanol with  $(Ph_3SiO)_2CrO_2$  gave formylferrocene in good yields [128]. A related patent described the oxidation of 2,2,2-trichloro-1-ferrocenylethanol to give trichloroacetylferrocene [129].

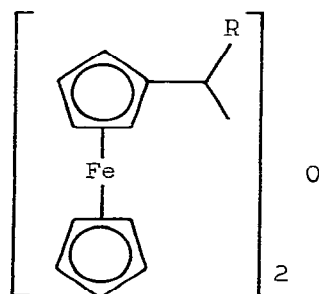
Formyl-, acetyl- and benzoyl-ferrocene have been condensed with diethylsuccinate under the conditions of the Stobbe reaction to give mixtures of the E and Z forms of the unsaturated ester



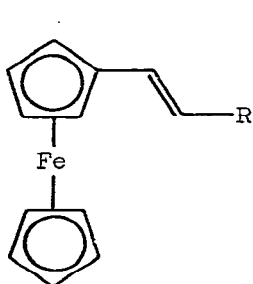
8.45



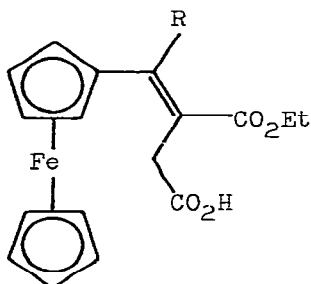
8.46



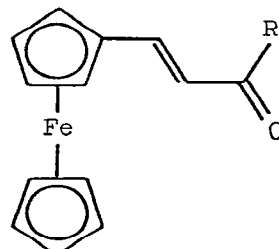
8.47



8.48

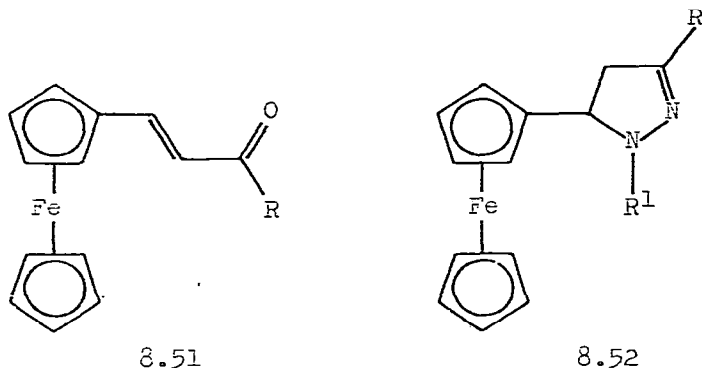


8.49



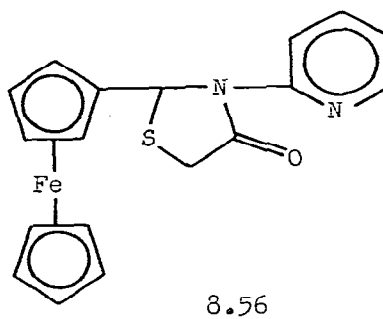
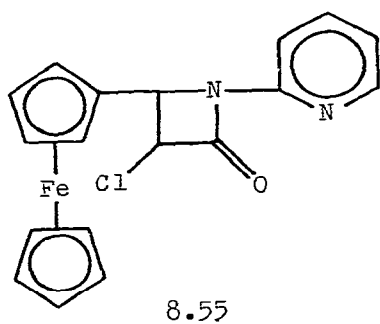
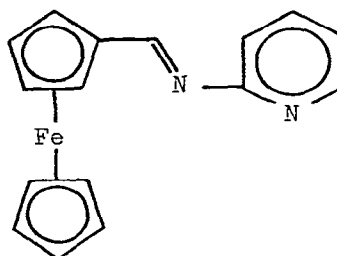
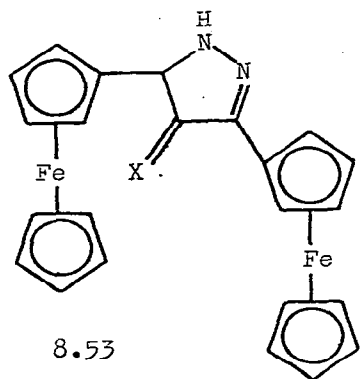
8.50

(8.49; R = H, Me, Ph) respectively [130]. Formylferrocene has been condensed with methylketones to form unsaturated ketones [8.50; R = Ph,  $(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)$ ,  $(\eta\text{-CH=CH.C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)$ ,  $(\eta\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ ,  $(\eta\text{-CH=CH.C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ ]. Some related aromatic and cymantrenyl compounds were reported [131]. Cyclization of the ferrocenyl derivatives (8.51; R = *p*-MeOC<sub>6</sub>H<sub>4</sub>; *p*-BrC<sub>6</sub>H<sub>4</sub>, ferrocenyl) with the hydrazines R<sup>1</sup>NHNH<sub>2</sub>, where R<sup>1</sup> = H, Ph, ferrocenyl, gave the corresponding ferrocenylpyrazolines (8.52) [132]. The ferrocenyl pyrazoline (8.53; X = H<sub>2</sub>) was condensed with benzaldehyde to form the benzal pyrazoline (8.53; X = CHPh).

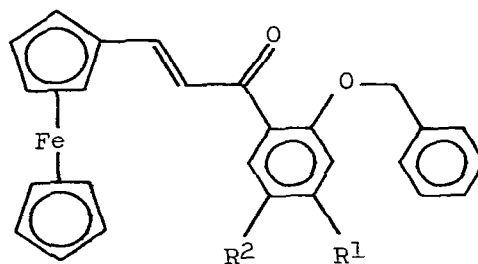
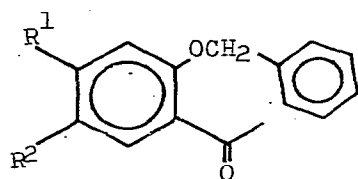


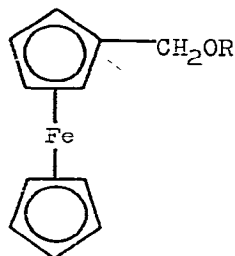
A mixed ferrocenyl cymantrenyl pyrazoline underwent the same reaction [133]. The reactions of ferrocenyl chalcones with diazomethane and, or benzenesulphonyl hydrazides gave ferrocenyl pyrazolines. The Michael reaction on ferrocenyl chalcones was used to prepare ferrocenyl-1,5-pentanediones and ferrocenyl- $\beta$ -ketosulphides [134].

The condensation of formylferrocene with 2-pyridinamine gave the corresponding Schiff's base (8.53). Cyclocondensation of the base (8.54) with ClCH<sub>2</sub>COCl or HSCH<sub>2</sub>CO<sub>2</sub>H gave the ferrocenyl- $\beta$ -lactam (8.55) and the ferrocenylthiazolidinone (8.56) respectively [135]. Formylferrocene was condensed with the acetophenone derivative (8.57; R<sup>1</sup> = R<sup>2</sup> = H, Me; R<sup>1</sup> = H, R<sup>2</sup> = Me, OMe, Cl, Br; R<sup>1</sup> = Me, OMe, R<sup>2</sup> = H) to give the trans form of the chalcone analogue (8.58) [136]. Ferrocenyl carbinol ethers (8.59; R = ethyl-octyl, allyl) were obtained by conversion of (dimethyl-amino)methylferrocene to a quaternary salt and then hydrolysis of this salt. Thus dichloroethane combined with the aminoferrocene

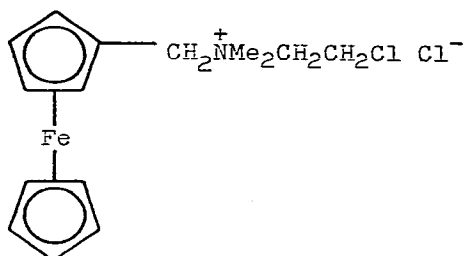


to form the salt (8.60) which was then hydrolyzed [137]. Ugi and Herrmann have reported a convenient "one-pot" synthesis of



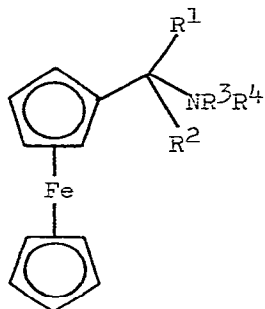


8.59

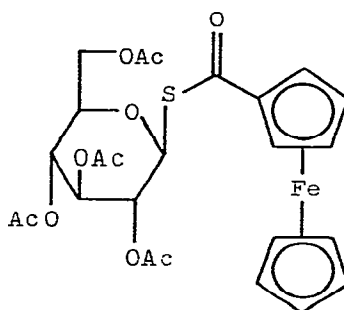


8.60

$\alpha$ -ferrocenylalkylamines. Ferrocene and a ketone or aldehyde,  $R^1R^2CO$ , were dissolved in a mixture of trichloroacetic acid and acetic acid, fluorosulphuric acid was added and the mixture was added to the amine,  $R^3R^4NH$ , in isopropyl alcohol at  $-78^\circ$



8.61



8.62

to give the corresponding ferrocenylalkylamine (8.61;  $R^1 = H$ , Me;  $R^2 = Me$ , *i*-Pr, *t*-Bu, cyclohexyl, Ph;  $R^3 = H$ , Me,  $R^4 = H$ , Me, *i*-Pr, *t*-Bu,  $CH_2Ph$ ) [138].

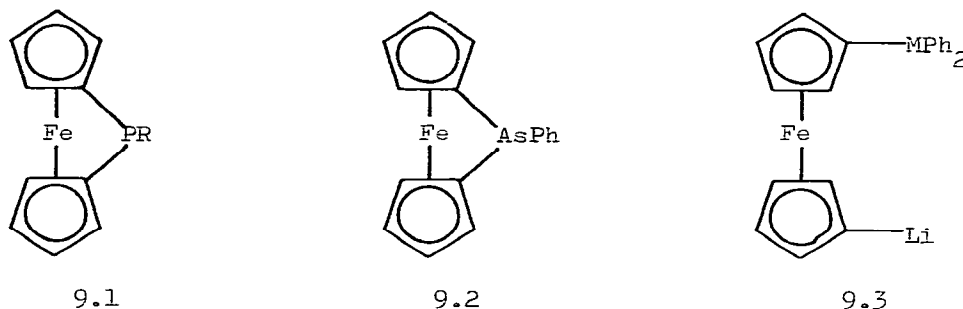
The thermal decomposition of ferrocenylmethyldimethylammonium perchlorate and picrate has been investigated [139]. The ferrocenyl group has been introduced as a substituent in glucopyranoses, thus ferrocenylcarbonyl chloride combined with 2,3,4,6-tetra-O-acetyl-1-thio- $\beta$ -D-glycopyranose to form the thioester (8.62). A similar amino-sugar, 1,3,4,6-tetra-O-acetyl-



-2-amino-2-deoxy- $\beta$ -D-glycopyranose, was attacked by (N,N-dimethyl-amino)methylferrocene methiodide at the nitrogen atom to give a diferrocenylmethyl derivative [140].

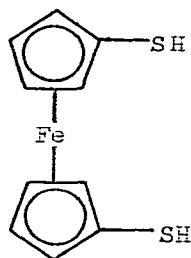
#### 9. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

Reaction of 1,1'-dilithioferrocenes with phenyl- or methyl-dichlorophosphine and phenyldichloroarsine gave the [1]ferrocenophanes (9.1, R = Ph, Me and 9.2) respectively. Treatment of the ferrocenophanes (9.1; R = Ph and 9.2) with phenyllithium gave

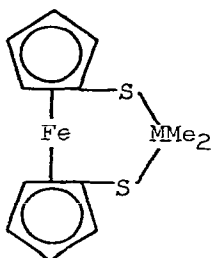


the lithio-ferrocene derivatives (9.3; M = P, As). These 1-lithio-1'-phosphino- (or -arsino-) -ferrocenes were treated with a series of electrophiles to give heteroannularly disubstituted ferrocenes in good yields [141]. Ferrocene-1,1'-dithiol (9.4) has been treated with dimethyl-silicon, -germanium and -tin dihalides in the presence of two moles of triethylamine to form the corresponding 1,3-dithia[3]ferrocenophanes (9.5; M = Si, Ge, Sn) in good yields. Variable temperature  $^1\text{H}$  NMR spectroscopy has been used to elucidate the fluxional behaviour of the compounds and to determine limiting conformations [142].

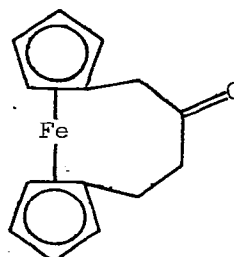
The equilibrium constants for the protonation of [4]ferrocenophan-7-one (9.6) and -6-one and for the ionization of [4]ferrocenophan-7-ol and -6-ol in aqueous sulphuric acid have been determined. The behaviour of these compounds as acid-base indicators has been studied and the results obtained indicated that the [4]ferrocenophane 7-carbenium ions were efficiently stabilized by the ferrocenyl group although the positive centre was remote from the



9.4



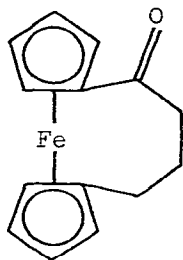
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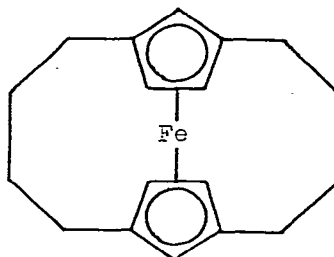
9.6

cyclopentadienyl ring [143].

The structure of [4]-ferrocenophan-1-one (9.7) has been determined by X-ray analysis. The planes of the  $\eta$ -cyclopentadienyl rings were essentially planar and the molecular configuration suggested that there was considerable steric strain in the bridging group. The strain was thought to occur at the carbonyl



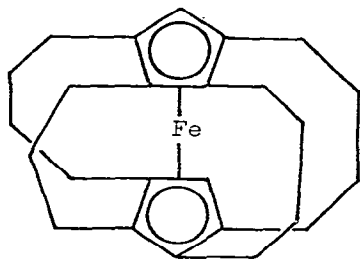
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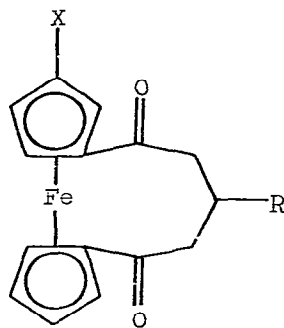
9.8

junction between the bridge and the  $\eta$ -cyclopentadienyl group [144]. The Moessbauer spectra of 1,1'-tetramethyleneferrocene and 1,1',3,3'-bis(tetramethylene)ferrocene (9.8) have been recorded. The crystal and molecular structures of this ferrocenophane (9.8) and of 1,1',2,2',4,4'-tris(trimethylene)ferrocene were determined by X-ray crystallography. The Moessbauer results were compatible with the ring tilting and iron-cyclopentadienyl ring bond

shortening confirmed by the X-ray analysis [145].

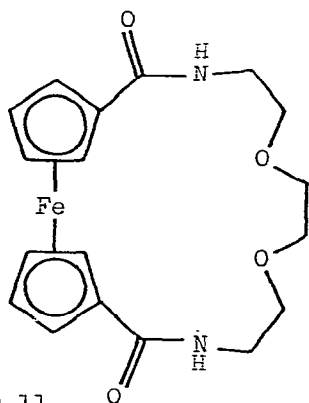


9.9

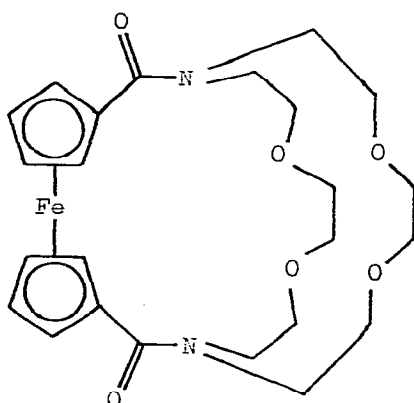


9.10

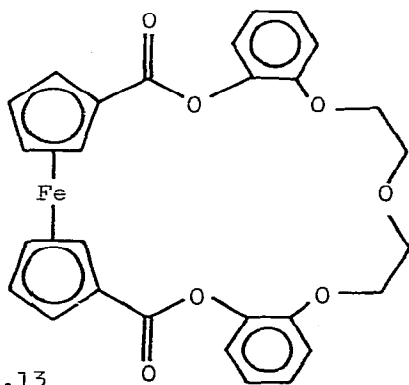
Yamakawa and co-workers have prepared the tetrabridged ferrocenophane (9.9) and the molecular structure was confirmed



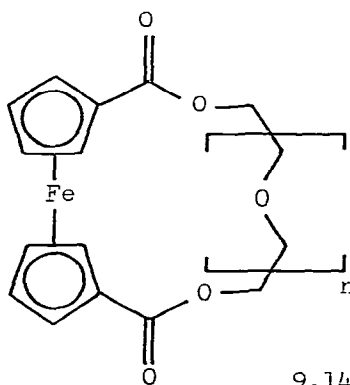
9.11



9.12



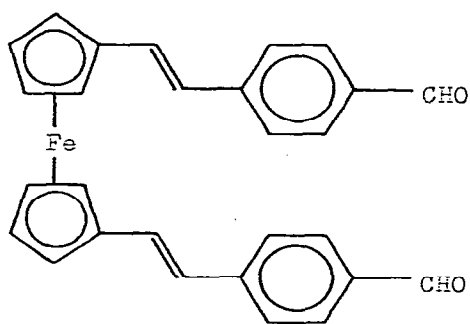
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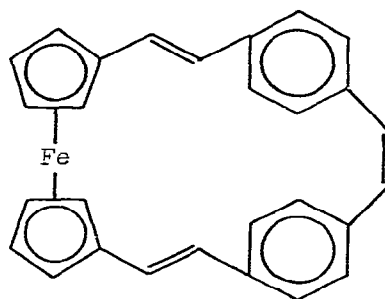
9.14

by X-ray analysis. The angle of tilt of the two  $\eta$ -cyclopentadienyl rings was  $5.68^\circ$  and the tetramethylene bridges took different conformations to each other [146]. Acetylation of chloro-, bromo- and methyl-ferrocene gave 3-chloro-, 3-bromo- and 3-methyl-1,1'-diacetylferrocene. These diacetylferrocenes were cyclized with RCHO, where R = Ph, CO<sub>2</sub>H, to give the corresponding ferrocenophanes (9.10; R = Ph, CO<sub>2</sub>H; X = Cl, Br, Me) [147]. The ferrocene crown ethers (9.11, 9.12, 9.13 and 9.14; n = 2,3) have been prepared. These bridged ferrocenes gave crystalline derivatives with lithium and sodium perchlorates [148].

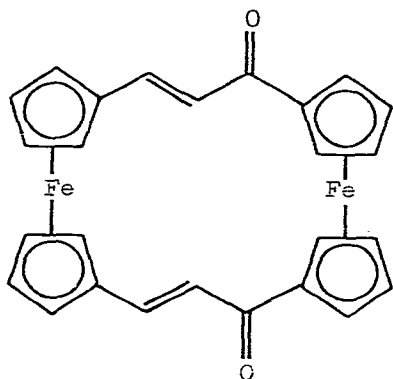
The paracycloferrocenophane (9.16) was formed by cyclization of the dialdehyde (9.15) using TiCl<sub>3</sub>/LiAlH<sub>4</sub>. The dialdehyde (9.15) was in turn obtained by treatment of 1,1'-diiodoferrocene with *p*-vinylbenzaldehyde. A diacetylene paracycloferrocenophane was formed in the same way [149]. Reaction of 1,1'-ferrocene-dicarboxaldehyde with 1,1'-diacetylferrocene in the presence of



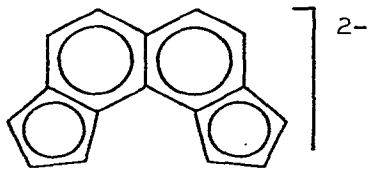
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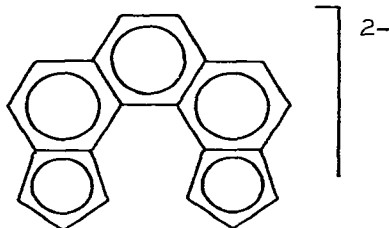
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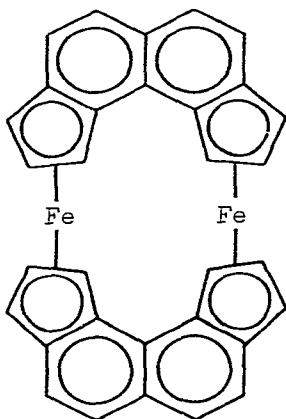
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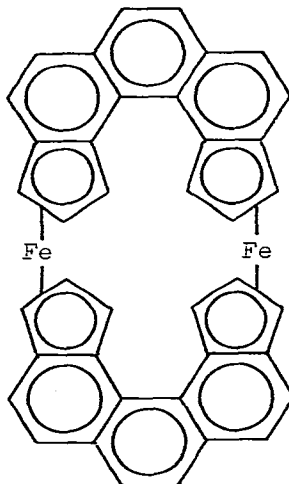
9.18



9.19



9.20



9.21

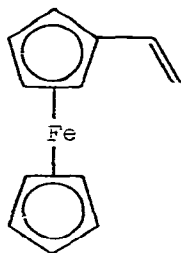
base gave the ferrocenophane (9.17)[150]. The dianions (9.18 and 9.19), formed from the appropriate hydrocarbons by treatment with *n*-butyllithium, were converted to the binuclear ferrocenophanes (9.20 and 9.21) on the addition of iron (II) chloride. The alternative polymeric products were not observed [151].

## 10. FERROCENE-CONTAINING POLYMERS

The electrical conductivity of plasma polymerized ferrocene films has been investigated. The results indicated the presence of an electron trap 0.45 eV below the conduction band [152]. The electrical properties of polyferrocene films deposited by glow-discharge polymerization have been investigated. The photocurrent was higher than the dark current and higher values of the photocurrent were obtained when the illuminated electrode was negatively biased. The effect of temperature on the dark

current was also investigated [153].

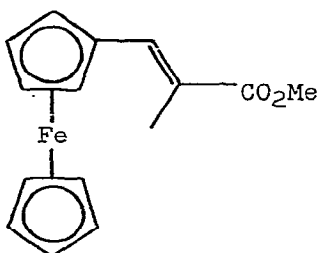
The 1,1'-dilithioferrocene-tetramethylethylenediamine complex underwent oxidative coupling in the presence of copper (II) halides to form polyferrocenylene in 30-45% yield. The yield was enhanced by thermal decomposition of the organocopper (I) intermediates in the absence of external oxidizing agents. The number-average molecular weight of the highest fractions was  $\leq 5000$ . In addition to linear polymers cyclization produced [0.0]ferrocenophane [154]. In a related study the same lithio-complex underwent polycondensation in the presence of copper (I). The reaction stoichiometry suggested that lithium ferrocenyl-cuprates were involved as intermediates. Copolymerization of the intermediates with 1,1'-diiodoferrocene was favoured over oxidative or thermal polymerization to give high yields (70-75%) and molecular weights (4000) for the products. Ferrocenophane byproducts were formed in only low (<1%) yield [155]. The condensation of 1,1'-dilithioferrocene with 1,1'-diiodoferrocene in 1,2-dimethoxyethane-tetrahydrofuran mixtures gave good yields of poly(ferrocene-1,1'-diyl). The addition of copper (II) or palladium (II) salts to the reaction mixture did not affect the degree of polymerization. The study of model reactions with ferrocenyllithium and iodoferrocene indicated the absence of a ferrocene mechanism and that propagation occurred without any loss of the heteroannular orientation of the substituents on the ferrocene nuclei [156]. Kalennikov and co-workers have reported a high yield preparation of poly(methyleneferrocenylene) by the bulk polymerization of ferrocene with formaldehyde in the presence of zinc chloride [157]. The formation of ceramic materials by



pyrolysis of crosslinked ferrocenes with continuous silicon carbide fibres has been surveyed [158].

Radical copolymerization of vinylferrocene (10.1) and 2-vinylnaphthalene gave a copolymer the composition of which indicated Mayo-Lewis reactivity ratios of 0.08 and 5.5 respectively. Fluorescence spectroscopy has shown emission from excited naphthalene monomer and naphthalene excimer with a decrease in total intensity as the ferrocene content increased. This was rationalized in terms of extensive intramolecular energy transfer from naphthalene to ferrocene groups and dynamic quenching of excited naphthalene monomer was more efficient than excimer formation [159]. Polymerized vinylferrocene was applied to platinum electrodes from radio frequency plasmas. The effects of methyl cyanide, water or aqueous ethanol on the electrochemistry of the thin polymer films has been investigated. It was concluded that the redox properties could be modified by the solvent [160]. The polymerizations of methyl methacrylate and acrylonitrile were initiated by the system poly(vinylferrocene)-carbon tetrachloride in the dark. The polymerizations proceeded via a radical mechanism and they were terminated by attack of a polarized monomer on the poly(vinylferrocene)-carbon tetrachloride charge transfer complex [161].

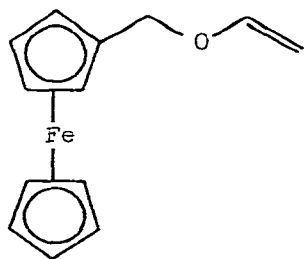
The  $\gamma$ -radiation initiated free radical copolymerization of ferrocenylmethyl methacrylate (10.2) with styrene, methyl methacrylate and ethyl acrylate in benzene has been investigated. Monomer reactivity ratios were calculated by the Tidwell-Mortimer method.  $Q$  and  $e$  values obtained from the copolymerization with styrene were 0.97 and 0.55 respectively [162]. The  $\gamma$ -ray induced polymer-



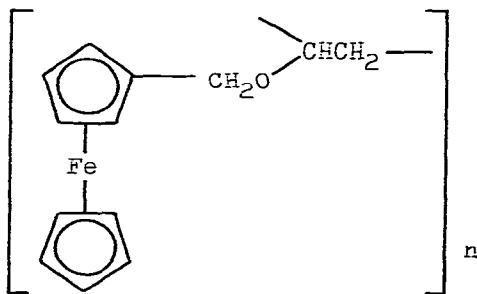
10.2

izations of ferrocenylmethyl methacrylate (10.2) and 1,1'-ferrocenyldi(methyl methacrylate) have been investigated. Polymerizations of the monomers were effected in the crystalline and amorphous states and also in benzene. Electron spin resonance spectra of the  $\gamma$ -irradiated monomers showed that ferrocene radicals and methacrylic radicals were formed simultaneously at low temperatures and with increasing temperature the ferrocene radicals disappear. It was concluded that the ferrocene group behaved as a radiation energy absorber [163]. The anionic homo- and co-polymerization of several transition metal containing vinyl monomers, including ferrocenylmethyl acrylate, has been investigated. Ferrocenylmethyl acrylate was homopolymerized in the presence of lithium aluminiumhydride and ethylmagnesium bromide at  $-78^{\circ}$  [164].

Unsaturated polyester moulding compositions containing vinylferrocenes have been used to give crack-free resins with efficient filling of detailed moulds. A typical formulation contained an epoxy methacrylate incorporating 20% styrene (100 parts), ethylvinylferrocene (20), glass fibre (25), calcium carbonate (200), silica sand (200) dicumyl peroxide (1) and zinc stearate (2). The mixture was moulded at  $150^{\circ}\text{C}$  for 3 min. under pressure [165]. Ferrocenylmethanol was converted to the vinyl ether (10.3) by heating with  $\text{BuOCH}=\text{CH}_2$  in the presence of mercury (II) acetate. The vinyl ether was then polymerized with boron trifluoride etherate to the linear macromolecule (10.4;  $n = 10-11$ ) [166]. Ferrocenylacetylene has been heated at  $190-300^{\circ}\text{C}$  in the presence of tri-iso-propylborane to form poly(ferrocenylacetylene) in 80%



10.3



10.4

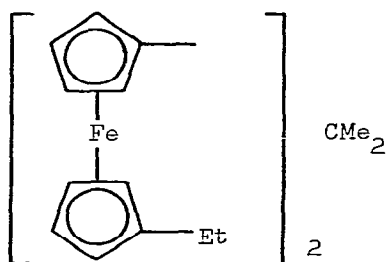


yield. The polymer had a paramagnetic concentration of  $10^{18}$ - $10^{19}$  spins  $g^{-1}$  and electrical conductivity  $10^{-10}\Omega^{-1}cm^{-1}$  [167]. Ferrocenylaniline, ferrocenylphenol, diacetylferrocene oxime and bis(hydroxyethyl)ferrocene underwent polycondensation with disulphur dichloride at 25-80°C in benzene to form poly(ferrocenyl disulphides) which contained the linkages -NHSS- and -OSS-. The polymers were stable in air to 200-250°C, had a paramagnetic centre concentration of  $10^{17}$ - $10^{19}$  spin  $g^{-1}$  and electrical conductivity of  $10^{-10}$ - $10^{-15}\Omega^{-1}cm^{-1}$  at 20°C [168].

## 11. APPLICATIONS OF FERROCENE

### (i) Ferrocene stabilizers and improvers

Low-density polyethylene has been stabilized by the addition of 2,2-bis(1,1'-diethylferrocenyl)propane (11.1) in the presence of other additives [169]. The reaction of chlorinated polythene



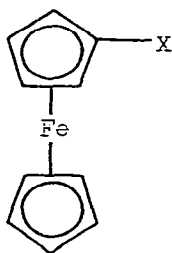
11.1

film with ferrocene proceeded by a fast substitution step followed by a slower diffusion controlled step. The photooxidation resistance of the ferrocene modified film was improved. The modified film was a good clear shield for the protection of vulnerable substrates against photodegradation [170]. The addition of 0.3-1 weight % ferrocene or a ferrocenyl ketone to petroleum-base cutting fluids increased the durability of cutting tools lubricated with the fluids [171].

### (ii) Ferrocene in analysis

Selenium (IV) has been estimated by reduction to selenium with ferrocene in acetic acid. The resulting ferrocinium ion

was then determined by colorimetry or by atomic absorption spectrophotometry. The technique was subject to interference by oxidizing agents [172]. The oxidation of ferrocene with tellurium (IV) has been studied in order to evaluate the reaction for the quantitative determination of tellurium. The reaction proceeded via the formation of tellurium (II) and the final product was metallic tellurium. A spectrophotometric procedure was devised for the determination of tellurium in cadmium telluride [173]. Ferrocene has been used in the electrochemical determination of molybdenum and vanadium in steel [174]. The electrochemical properties of the copper (II)-copper (I) and the ferrocene-ferrocenium ion systems were compared and the optimum conditions for the redox reaction between ferrocene and copper (II) were chosen. On the basis of these results a procedure was developed for the titrimetric determination of copper with ferrocene [175].

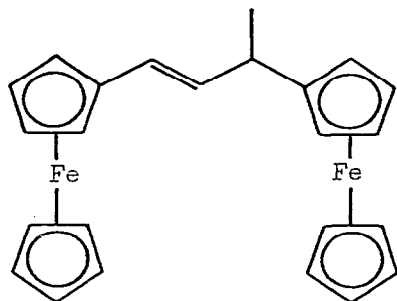


11.2

Substituted ferrocenes [11.2; X = Me, Bu, CH<sub>2</sub>OH, CHOHMe, CH<sub>2</sub>OMe, CO<sub>2</sub>Me, SiMe<sub>3</sub>, C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>, I] have been evaluated in sulphuric acid as redox titrants. The formal oxidation potentials were strongly dependent on the acid concentration with only very small substituent effects [176]. An electrochemical study has been made of carbon paste electrodes which contained an insoluble electroactive compound, such as iron (III) oxide and ferrocene, together with an electrolytic pasting liquid. The factors which affected the chronoamperometric and voltamperometric curves were evaluated. The electrodes were useful for the qualitative and quantitative analysis of solids [177].

(iii) Combustion control

The addition of ferrocene, mixed with an aliphatic alcohol and an organic hydroperoxide, to gasoline improved the octane number [178]. The effectiveness of mixtures of ferrocene and tricarbonyl-( $\eta$ -methylcyclopentadienyl)manganese as an antiknock reagent in gasoline have been investigated. The mixtures of the two organometallic compounds had a synergistic effect. The increases in the octane numbers caused by the mixtures were equal to or greater than those provided by the same weight of the cymantrene derivative. Tricarbonyl( $\eta$ -methylcyclopentadienyl)manganese was more effective than ferrocene as an antiknock reagent when the compounds were used by themselves [179]. The emission of nitrogen oxides from the combustion of fuel oil has been reduced by mixing the fuel with 0.1% ferrocene and 20% water. The efficiency of the boiler was not reduced [180]. The efficiency of combustion of heavy fuel oil has been improved by the addition of a small proportion of a transition metal compound and the introduction of a reducing agent into the flame. Thus, the addition of 0.14% ferrocene to the fuel and injection of ammonia into the flame reduced the concentration of  $\text{NO}_x$  by 28ppm [181]. The addition of ferrocene derivatives, for example 1,3-diferrocenyl-1-butene (11.3), improved the burning rate of propellants containing ammonium perchlorate and carboxy-terminated polybutadiene [182].



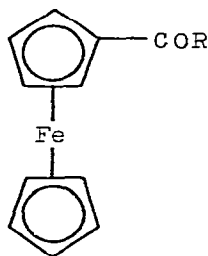
11.3

2-Ferrocenylethanethiol was treated with hydroxyl terminated polybutadiene and 2,2'-azobis(2-methylpropionitrile) to give a polymeric material that was useful as a binder for composite propellants. The propellants had stable burning properties [183]. The efficiency of dibromotetrafluoroethane as a fire

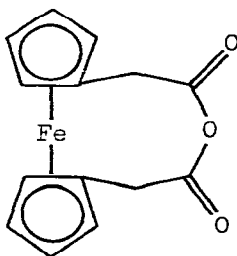
extinguisher was enhanced by the addition of a small proportion (0.05-0.50 weight %) of diethylferrocene [184].

(iv) Biochemical and biological applications

Ferrocene has been acylated with acyl chlorides to give the ketones [11.4; R = CH(CH<sub>2</sub>Me)(CH<sub>2</sub>)<sub>3</sub>Me, CHMeCH<sub>2</sub>CH<sub>2</sub>Me, (CH<sub>2</sub>)<sub>5</sub>Me, (CH<sub>2</sub>)<sub>7</sub>Me, (CH<sub>2</sub>)<sub>4</sub>CHMe<sub>2</sub>, CHMeCH<sub>2</sub>CMe<sub>3</sub>, CMe<sub>2</sub>CHMe<sub>2</sub>] which have been used in the treatment of iron deficiency anaemia [185]. 1,1'-Ferro-

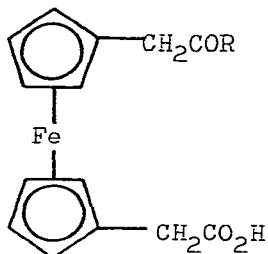


11.4

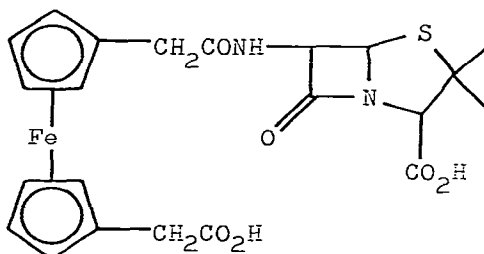


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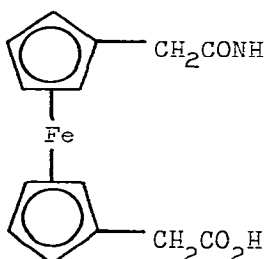
enediacetic acid anhydride (11.5) was prepared by treatment of the corresponding diacid with dicyclohexylcarbodiimide. Reaction of the anhydride (11.5) with amines gave the corresponding amides (11.6; R = NH<sub>2</sub>, PhCH<sub>2</sub>NH, C<sub>6</sub>H<sub>13</sub>N, morpholino). In a similar reaction, the anhydride (11.5) was treated with 6-aminopenicillanic acid (6-APA) or 7-aminocephalosporanic acid (7-ACA) to give the ferrocenyl-penicillin (11.7) and -cephalosporin (11.8) respectively. The anhydride (11.9) was also prepared and its reactions with 6-APA and 7-ACA were investigated [186]. The metabolism of ferrocene has been studied in vivo using rats and in vitro using rat liver microsomes. The biological activity of D,L-β-ferrocenyl-α-alanine (11.10) has been investigated and it was tested for its ability to: (i) support or inhibit the growth of L. mesenteroides, a phenylalanine requiring organism, (ii) inhibit the growth of CHO cells in culture and (iii) function as a substrate or inhibitor of phenylalanine hydroxylase and aromatic L-amino acid decarboxylase. The growth of L. mesenteroides, in the absence of phenylalanine, was not supported and there was no inhibition



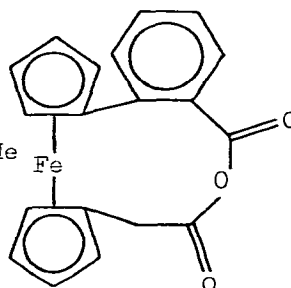
11.6



11.7



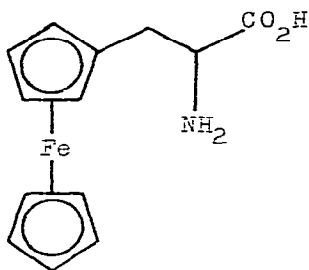
11.8



11.9

of growth in the presence of phenylalanine. The ferrocenyl-alanine was: (i) toxic to the CHO cells at a concentration of 0.45 mM, (ii) a noncompetitive inhibitor in the phenylalanine hydroxylase system and (iii) a competitive inhibitor of aromatic L-aminoacid decarboxylase with respect to phenylalanine [188].

The biological activity and metabolism of (+)-2-aminopropylferrocene succinate in mice has been investigated as an amphetamine analogue. In vitro the compound inhibited the metabolism of aminopyrene and *p*-nitroanisole but had no effect on the oxidation of *N,N*-dimethyloctylamine [189]. The metabolism and cytostatic effects of *N*-methyl-*N*- $\beta$ -chloroethylhydrazones of formyl-ferrocene and -ruthenocene have been investigated. Both the hydrazones exhibited cytostatic effects similar to those of the corresponding hydrazone of benzaldehyde [190]. A fertilizer containing 0.5% 3,5,5-trimethylhexanoylferrocene mixed with surfactants was used for supplying plants with iron. Treatment of chrysanthemums with the fertilizer controlled iron chlorosis and increased the



11.10

number of newly formed leaves [191].

## 12. REFERENCES

- 1 D. Seyferth, *Journal of Organometallic Chemistry Library*, Vol. 7, Elsevier, 1979.
- 2 E.A.K. von Gustorf, *The Organic Chemistry of Iron*, Vol. 1, Academic Press, 1978.
- 3 F. Takusagawa and T.F. Koetzle, *Acta Crystallogr., Sec. B*, B 35 (1979) 1074.
- 4 G. Clec'h, G. Calvarin, J.F. Berar and D. Andre, *C.R. Hebd. Seances Acad. Sci., Ser. C*, 287 (1978) 523.
- 5 P. Seiler and J.D. Dunitz, *Acta Crystallogr., Sect. B*, B 35 (1979) 1068.
- 6 P. Seiler and J.D. Dunitz, *Acta Crystallogr., Sect. B*, B 35 (1979) 2020.
- 7 Z. Kaluski, E. Skrzypczak-Jankun and M. Cygler, *Acta Crystallogr., Sect. B*, 35 (1979) 2699.
- 8 A.N. Nesmeyanov, E.I. Klimova, Yu. T. Struchkov, V.G. Andrianov, V.N. Postnov and V.A. Sazonova, *J. Organometal. Chem.*, 178 (1979) 543.
- 9 A. Almennigen, A. Haaland, S. Sandal, J. Brunvoll, J.L. Robbins and J.C. Smart, *J. Organometal. Chem.*, 173 (1979) 293.
- 10 A.H. Reis, L.D. Preston, J.M. Williams, S.W. Peterson, G.A. Candela, L.J. Swartzendruber and J.S. Miller, *J. Am.*

- Chem. Soc., 101 (1979) 2756.
- 11 G.A. Candela, L.J. Swartzendruber, J.S. Miller and M.J. Rice, *J. Am. Chem. Soc.*, 101 (1979) 2755.
  - 12 S.R. Wilson, P.J. Corvan, R.P. Seiders, D.J. Hodgson, M. Brookhart, W.E. Hatfield, J.S. Miller, A.H. Reis and P.K. Rogan, *NATO Conf. Ser.*, (Ser.) 6 (1978) 407; *Chem. Abstr.*, 91 (1979) 174588.
  - 13 F. Takusagawa and T.F. Koetzle, *Acta Crystallogr.*, Sect. B, B 35 (1979) 2888.
  - 14 K. Szulzewsky, I. Seidel, S. Kulpe, E. Hoehne, H. Raubach and U. Stoffer, *Krist. Tech.*, 14 (1979) 37.
  - 15 L.N. Zakharov, Yu. T. Struchkov, V.V. Sharutin and O.N. Suvorova, *Cryst. Struct. Commun.*, 8 (1979) 439.
  - 16 T.R. Halbert and J. Scanlon, *Mater. Res. Bull.*, 14 (1979) 415.
  - 17 R. Urban, D. Marquarding and I. Ugi, *Hoppe-Seyler's Z. Physiol. Chem.*, 359 (1978) 1541.
  - 18 M. Lacan and V. Rapic, *Croat. Chem. Acta*, 51 (1978) 273.
  - 19 L.G. Kuz'mina, Yu. T. Struchkov, L.L. Troitskaya, V.I. Sokolov and O.A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 1528.
  - 20 V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, *Dokl. Akad. Nauk SSSR*, 246 (1979) 124.
  - 21 A. Kasahara, T. Izumi and H. Watabe, *Bull. Chem. Soc. Jpn.*, 52 (1979) 957.
  - 22 W. Crawford and W.E. Watts, *J. Organometal. Chem.*, 185 (1980) 443.
  - 23 D.C. Van Landuyt, *Diss. Abstr.*, Int. B, 36 (1976) 3973, *Chem. Abstr.*, 92 (1980) 21920.
  - 24 P. Canonè, G. Foscolos and R. Harder, *J. Organometal. Chem.*, 178 (1979) 331.
  - 25 R.C. Hill, *Diss. Abstr. Int. B*, 39 (1978) 2382.
  - 26 M. Hillman and A.G. Nagy, *J. Organometal. Chem.*, 184 (1980) 433.
  - 27 V. Ya. Rochev, N.K. Kivrina and O.P. Kevdin, *Acta Phys. Pol. A*, A56 (1979) 137.
  - 28 E.I. Mysov, I.R. Lyatfov, R.B. Materikova and N.S. Kochetkova, *J. Organometal. Chem.*, 169 (1979) 301.
  - 29 B.V. Zhuk, G.A. Domrachev, N.M. Semenov, E.I. Mysov, R.B. Materikova and N.S. Kochetkova, *J. Organometal. Chem.*, 184 (1980) 231.

- 30 A.N. Nesmeyanov, D.V. Zagorevskii, Yu. S. Nekrasov, V.F. Sizoi, V.M. Postnov, A.M. Baran and E.I. Klimova, *J. Organometal. Chem.*, 169 (1979) 77.
- 31 Yu. S. Nekrasov, V.F. Sizoi, D.V. Zagorevskii and N.I. Vasyukova, *Org. Mass Spectrom.*, 14 (1979) 22.
- 32 E.P. Fesenko and L.P. Iogansen, (USSR), Deposited Doc. 1977, VINITI, 857; *Chem. Abstr.*, 90 (1979) 102929.
- 33 V.G. Kuleshov, B.V. Zhuk and G.A. Domrachev, *Khimiya Elementoorgan. Soedin.*, (Gor'kii), (1978) 88; *Chem. Abstr.*, 91 (1979) 163456.
- 34 C.J. Cardin, W. Crawford, W.E. Watts and B.J. Hathaway, *J. Chem. Soc., Dalton Trans.*, (1979) 970.
- 35 S. Sorriso, *J. Organometal. Chem.*, 179 (1979) 205.
- 36 L. Lindner and J.C. Kapteyn, *Radiochim. Acta*, 26 (1979) 97.
- 37 V. Ropic, I. Tabakovic, B. Skundric and M. Lacan, *Croat. Chem. Acta*, 51 (1978) 333.
- 38 Z. Samec, V. Marecek and J. Weber, *J. Electroanal. Chem. Interfacial Electrochem.*, 103 (1979) 11.
- 39 Z. Samec, V. Marecek and J. Weber, *J. Electroanal. Chem. Interfacial Electrochem.*, 96 (1978) 245.
- 40 R. Gavasso and E. Laviron, *J. Electroanal. Chem. Interfacial Electrochem.*, 102 (1979) 249.
- 41 M. Sharp, M. Petersson and K. Edstrom, *J. Electroanal. Chem. Interfacial Electrochem.*, 95 (1979) 123.
- 42 D.F. Smith, K. Willman, K. Kuo and R.W. Murray, *J. Electroanal. Chem. Interfacial Electrochem.*, 95 (1979) 217.
- 43 A.B. Fischer, M.S. Wrighton, M. Umana and R.W. Murray, Report 1979 TR-8, Order No. AD-A066631; from Gov. Rep. Announce. Index (U.S.), 79 (1979) 91.
- 44 K.B. Yap and F.C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, 100 (1979) 233.
- 45 A.M. Yacynych and T. Kuwana, *Anal. Chem.*, 50 (1978) 640.
- 46 R. Nowak, F.A. Schultz, M. Umana, H. Abruna and R.W. Murray, Report 1978, TR-6, Order No. AD-A061427, from Gov. Rep. Announce. Index (U.S.), 79 (1979) 90; *Chem. Abstr.*, 91 (1979) 29547.
- 47 A.A. Pendin, P.K. Leont'evskaya and E.F. Korobchenko, *Zh. Fiz. Khim.*, 53 (1979) 2228.
- 48 J.R. Chipperfield, J.C.R. Sneyd and D.E. Webster, *J. Organometal. Chem.*, 178 (1979) 177.



- 49 K. Ogasahara, M. Sorai and H. Suga, Chem. Phys. Lett., 68 (1979) 457.
- 50 J.W. Edwards, G.L. Kington and R. Mason, Trans. Faraday Soc., 56 (1960) 660; J.W. Edwards and G.L. Kington, Trans. Faraday Soc., 58 (1962) 1334.
- 51 L.M. Dyagileva, V.P. Mar'in, E.I. Tsyganova, J. Organometal. Chem., 175 (1979) 63.
- 52 B.V. Zhuk, H.M. Semenov and G.A. Domrachev, Zh. Obshch. Khim., 48 (1978) 2562.
- 53 V.G. Tsvetkov, L.M. Dyagileva, M.K. Safonova and Yu. A. Aleksandrov, Koord. Khim., 5 (1979) 772.
- 54 N. Cully and W.E. Watts, J. Organometal. Chem., 182 (1979) 99.
- 55 N. Cully, J. Park and W.E. Watts, J. Chem. Soc., Perkin Trans. 2, (1979) 947.
- 56 M. Salisova and H. Alper, Angew. Chem., 91 (1979) 858.
- 57 L. Poncini and J. Cook, Sch. Sci. Rev., 61 (1979) 91.
- 58 L. -C. Song, Hua Hsueh Tung Pao, (1979) 315; Chem. Abstr., 92 (1980) 6653.
- 59 L. -C. Song, Hua Hsueh Tung Pao, (1979) 313; Chem. Abstr., 92 (1980) 6652.
- 60 A. Ratajczak and B. Misterkiewicz, J. Organometal. Chem., 179 (1979) 181.
- 61 J.F. Helling and W.A. Hendrickson, J. Organometal. Chem., 168 (1979) 87.
- 62 E. Roman and D. Astruc, Inorg. Chem., 18 (1979) 3284.
- 63 E. Roman, R. Dabard, C. Moinet and D. Astruc, Tetrahedron Lett., (1979) 1433.
- 64 W.J. Pannekoek, Diss. Abstr. Int. B, 38 (1978) 3200.
- 65 C.C. Lee, K.J. Demchuk and R.G. Sutherland, Can. J. Chem., 57 (1979) 933.
- 66 A. Jaworska-Augustyniak and J. Wojtczak, Transition Met. Chem., (Weinheim, Ger.), 4 (1979) 207.
- 67 V.N. Setkina and T. Orlova, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2399.
- 68 L. Lindner and J.C. Kapteyn, Nuklearmedizin, Suppl. (Stuttgart), 16 (1978) 819; Chem. Abstr., 91 (1979) 165264.
- 69 Hazen Research Inc., Neth. Pat., 7800726, 1978, Jul. 25; Chem. Abstr., 90 (1979) 140022.

- 70 V.A. Balusov, Yu. D. Koreshkov, V.T. Solomatin, S.P. Gubin, and V.A. Drozdov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 457.
- 71 E. Pelizzetti, *Inorg. Chem.*, 18 (1979) 1386.
- 72 J.R.B. Hanna and S.R. Logan, *J. Photochem.*, 10 (1979) 267.
- 73 J. Holecek, K. Handlir and J. Klikorka, *Collect. Czech. Chem. Commun.*, 44 (1979) 1060.
- 74 J. Holocek, K. Handlir, J. Klikorka and D.B. Nguyen, *Collect. Czech. Chem. Commun.*, 44 (1979) 1379.
- 75 J.M. Bolts and M.S. Wrighton, *J. Am. Chem. Soc.*, 101 (1979) 6179.
- 76 A.B. Bocarsly, E.G. Walton, M.G. Bradley and M.S. Wrighton, *J. Electroanal. Chem. Interfacial Electrochem.*, 100 (1979) 283.
- 77 S.R. Wilson, P.J. Corvan, R.P. Seiders, D.J. Hodgson and M. Brookhart, Report 1979, TR-5, Order No. AD A064163; from Gov. Rep. Announce. Index (US), 79 (1979) 86; *Chem. Abstr.*, 91 (1979) 149656.
- 78 A.H. Reis, E. Gebert, J.S. Miller, J.J. Ritsko, W.R. Solanek, L. Kovnat, T.W. Cape and R.P. Van Duyne, *J. Am. Chem. Soc.*, 101 (1979) 7111.
- 79 M. Watanabe, S. Iijima, I. Motoyama and H. Sano, *J. Phys., Colloq. (Orsay. Fr.)*, (1979) 392.
- 80 A.N. Nesmeyanov, V.A. Sazonova, V.N. Postnov, N.M. Shchegalina and V.V. Stekol'nikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1978) 2175.
- 81 D. Kaufman, R. Kupper and T. Neal, *J. Org. Chem.*, 44 (1979) 3076.
- 82 C.R. Jablonski, *J. Organometal. Chem.*, 174 (1979) C3.
- 83 N. Cully, W.D. Quail and W.E. Watts, *J. Chem. Soc., Perkin Trans. 2*, (1979) 1148.
- 84 A. Cecon, G. Giacometti, A. Venzo, P. Paolucci and D. Benozzi, *J. Organometal. Chem.*, 185 (1980) 231.
- 85 C.A. Bunton, N. Carrasco and W.E. Watts, *J. Chem. Soc., Chem. Commun.*, (1979) 283.
- 86 U. Behrens, *J. Organometal. Chem.*, 182 (1979) 89.
- 87 G. Ortaggi and R. Marcec, *Gazz. Chim. Ital.*, 109 (1979) 13.
- 88 V. Carassiti, C.A. Bignozzi and F. Scandola, *Atti Accad. Sci. Ist. Bologna, Cl. Sci. Fis., Rend* 1976, 13 (1977) 123; *Chem. Abstr.*, 90 (1979) 143721.

- 89 L. Wilputte-Steinert, *Tetrahedron Lett.*, (1978) 4183.
- 90 L. Wilputte-Steinert, *Proc. IUPAC Symp. Photochem.*, 7 (1978) 361.
- 91 C. Baker and W.M. Horspool, *J. Chem. Soc., Perkin Trans. 1*, (1979) 1862.
- 92 M. Hisatome, T. Hashiyama and K. Yamakawa, *Tetrahedron Lett.*, (1978) 3759.
- 93 C. Baker and W.M. Horspool, *J. Chem. Soc., Perkin Trans. 1*, (1979) 2294.
- 94 C. Baker and W.M. Horspool, *J. Chem. Soc., Perkin Trans. 1*, (1979) 2298.
- 95 R.D. Rogers, W.J. Cook and J.L. Atwood, *Inorg. Chem.*, 18 (1979) 279.
- 96 D.O. Cowan, P. Shu, F.L. Hedberg, M. Rossi, T.J. Kistenmacher, *J. Am. Chem. Soc.*, 101 (1979) 1304.
- 97 A.N. Nesmeyanov, N.N. Sedova, V.A. Sazonova and S.K. Moiseev, *J. Organometal. Chem.*, 185 (1980) C6.
- 98 A. Davison and A.W. Rudie, *J. Organometal. Chem.*, 169 (1979) 69.
- 99 A.G. Osborne and R.H. Whiteley, *J. Organometal. Chem.*, 181 (1979) 425.
- 100 K. Jonas and L. Schieferstein, *Angew. Chem.*, 91 (1979) 590.
- 101 K. Jonas, L. Schieferstein, C. Krueger and Y. -H. Tsay, *Angew. Chem.*, 91 (1979) 590.
- 102 L.P. Asatiani, D.S. Zurabishvili and I.M. Gverdtsiteli, *Zh. Obshch. Khim.*, 48 (1978) 2386.
- 103 L.P. Asatiani, D.S. Zurabishvili and I.M. Gverdtsiteli, *Zh. Obshch. Khim.*, 49 (1979) 788.
- 104 L.P. Asatiani, D.S. Zurabishvili and I.M. Gverdtsiteli, *Zh. Obshch. Khim.*, 49 (1979) 1297.
- 105 Z. Dawoodi, C. Eaborn and A. Pidcock, *J. Organometal. Chem.*, 170 (1979) 95.
- 106 J.D. Unruh (Celanese Corp.) *Ger. Pat.*, 2834742, 1979, Mar. 1; *Chem. Abstr.*, 90 (1979) 203487.
- 107 M. Kumada and T. Hayashi, *Symp. Rhodium Homogeneous Catal.*, [Proc.]; (1978) 157.
- 108 T. Hayashi, M. Konishi and M. Kumada, *Tetrahedron Lett.*, (1979) 1871.
- 109 V.I. Boev and A.V. Dombrovskii, *Zh. Obshch. Khim.*, 49 (1979) 1246.

- 110 K.H. Doetz, R. Dietz and D. Neugebauer, *Chem. Ber.*, 112 (1979) 1486.
- 111 A.N. Nesmeyanov, V.A. Sazonova, N.N. Sedova and E.N. Stakheeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 2141.
- 112 A.N. Nesmeyanov, V.P. Dyachenko, K.I. Grandberg, A.N. Red'kin and E.G. Perevalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 2050.
- 113 B. Floris and G. Illuminati, *J. Organometal. Chem.*, 168 (1979) 203.
- 114 R. Weiss and R.N. Grimes, *Inorg. Chem.*, 18 (1979) 3291.
- 115 O.N. Suvorova, V.V. Sharutin and G.A. Domrachev, *Str., Svoistva Primen.  $\beta$ -Diketonatov Met.*, [Mater. Vses. Semin.], 3rd 1977 (Pub. 1978) 132; *Chem. Abstr.*, 91 (1979) 157339.
- 116 A.M. Shevchik, Yu. P. Losev and Ya. M. Paushkin, *Str., Svoistva Primen.  $\beta$ -Diketonatov Met.*, [Mater. Vses. Semin.], 3rd 1977 (Pub. 1978) 136; *Chem. Abstr.*, 91 (1979) 157858.
- 117 V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, *J. Organometal. Chem.*, 182 (1979) 537.
- 118 M. Nonoyama and M. Sugimoto, *Inorg. Chim. Acta*, 35 (1979) 131.
- 119 A.N. Nesmeyanov, G.A. Razuvaev, R.B. Materikova, G.A. Domrachev, V.D. Zinov'ev, N.P. Palitsyn and N.S. Kochetkova, *Zh. Obshch. Khim.*, 48 (1978) 2132.
- 120 T. Izumi, Y. Satou, Y. Yoshida and A. Kasahara, *Bull. Chem. Soc. Jpn.*, 52 (1979) 1551.
- 121 J.S. Miller, A.H. Reis and G.A. Cadela, *Lect. Notes Phys.*, 96 (1978, Pub. 1979), 313; *Chem. Abstr.*, 91 (1979) 193389.
- 122 A.N. Nesmeyanov, V.A. Sazonova and A.N. Pushin, *Dokl. Akad. Nauk SSSR*, 246 (1979) 886.
- 123 A.N. Nesmeyanov, E.G. Perevalova, L. I. Leont'eva and S.A. Eremin, *Dokl. Akad. Nauk SSSR*, 243 (1978) 1208.
- 124 D.N. Kursanov, V.N. Setkina and S.P. Dolgova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 869.
- 125 R.E. Bozak and B. Wilson, *Synth. React. Inorg. Met. -Org. Chem.*, 9 (1979) 513.
- 126 M. Vernois and H.L. Williams, *J. Appl. Polym. Sci.*, 23 (1979) 1601.
- 127 A.I. Vrublevskii, P.N. Gaponik, A.I. Lesnikovich and Yu. G. Orlik, 13 *Vses. Chugaev. Soveshch. po Khimii Kompleks. Soedin.*, 1978, (1978) 91; *From Ref. Zh. Khim.* (1979)

- Abstr. No. IV160; Chem. Abstr., 90 (1979) 204221.
- 128 J. Holecek, J. Klikorka, K. Handlir and V. Mraz, Czech. Pat., 175857, 1979, Jan. 15; Chem. Abstr., 90 (1979) 138026.
- 129 J. Holecek, J. Klikorka, K. Handlir and V. Mraz, Czech. Pat., 175900, 1979, Jan 15; Chem. Abstr., 90 (1979) 138027.
- 130 M. Lacan and V. Ropic, Croat. Chem. Acta, 51 (1978) 325, (published 1979).
- 131 A.N. Nesmeyanov, V.A. Sazonova, V.N. Postnov and A.M. Baran Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 902.
- 132 A.N. Nesmeyanov, E.I. Klimova and V.A. Sazonova, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 239.
- 133 A.N. Nesmeyanov, A.M. Baran, L. Eggert, V.N. Postnov, V.A. Sazonova, N.B. Bepalova, E.D. Babich and V.M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 1402.
- 134 K.M. Hassan, M.M. Aly and G.M. El-Naggar, J. Chem. Technol. Biotechnol., 29 (1979) 515.
- 135 K.M. Hassan, Z. Naturforsch., B; Anorg. Chem., Org. Chem.; 33B (1978) 1508.
- 136 I.G. Marchenko, A.V. Turov and V.P. Khilya, Dopov. Akad. Nauk Ukr. RSR, Ser. B; Geol., Khim. Biol. Nauki, (1979) 43; Chem. Abstr., 90 (1979) 152330.
- 137 V.A. Mironov, N.I. Verona and I.A. D'yakonova (Moscow Technological Institute of the Meat and Dairy Industry), USSR Pat., 667541, 1979, May 30; Chem. Abstr., 91 (1979) 108090.
- 138 R. Herrmann and I. Ugi, Angew. Chem., 91 (1979) 1023.
- 139 P.N. Gaponik, V.G. Guslev, K.K. Kovalenko and A.I. Lesnikovich, Khimiya i Khim. Tekhnol., (1978) 114; From Ref. Zh. Khim., (1978) Abstr. No. 23B1165; Chem. Abstr., 90 (1979) 121767.
- 140 M.J. Adam and L.D. Hall, J. Chem. Soc., Chem. Commun., (1979) 865.
- 141 D. Seyferth and H.P. Withers, J. Organometal. Chem. 185 (1980) C1.
- 142 A. Davison and J.C. Smart, J. Organometal. Chem., 174 (1979) 321.

- 143 G. Ortaggi, P. Riccio and I. Tritto, *J. Org. Chem.*, 44 (1979) 2920.
- 144 T.S. Cameron and R.E. Cordes, *Acta Crystallogr., Sect. B*, B55 (1979) 748.
- 145 A.G. Nagy and M. Hillman, Report (1978) KFK1-1977-105, from *Atomindex*, 10 (1979), Abstr. 435989.
- 146 M. Hisatome, Y. Kawaziri, K. Yamakawa and Y. Iitaka, *Tetrahedron Lett.*, (1979) 1777.
- 147 S. Toma, M. Pariciova and E. Solcaniova, *Acta Fac. Rerum Nat. Univ. Comenianaee, Chim.*, 26 (1978) 61; *Chem. Abstr.*, 90 (1979) 137966.
- 148 G. Oepen and F. Voegtler, *Liebigs Ann. Chem.*, (1979) 1094.
- 149 A. Kasahara, T. Izumi and I. Shimizu, *Chem. Lett.*, (1979) 1119.
- 150 A. Kasahara, T. Izumi and I. Shimizu, *Chem. Lett.*, (1979) 1317.
- 151 T.J. Katz and W. Slusarek, *J. Am. Chem. Soc.*, 101 (1979) 4259.
- 152 S.D. Phadke, *Indian J. Phys.*, 53A (1979) 389.
- 153 S.D. Phadke, R.N. Karekar and K. Sathianandan, *Proc. Nucl. Phys. Solid State Phys. Symp.*, 20C (1977) 146; *Chem. Abstr.*, 90 (1979) 96350.
- 154 E.W. Neuse and L. Bednarik, *Transition Met. Chem. (Weinheim, Ger.)*, 4 (1979) 87.
- 155 E.W. Neuse and L. Bednarik, *Transition Met. Chem. (Weinheim, Ger.)*, 4 (1979) 104.
- 156 E.W. Neuse and L. Bednarik, *Macromolecules*, 12 (1979) 187.
- 157 E.A. Kalennikov, Ya. S. Burvel, A.K. Zaloznyi, S.P. Gubin, R. Joonas, A. Ratsep and B.I. Kozyrkin, *USSR Pat.*, 647315, 1979, Feb. 15; *From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki*, (1979) 85; *Chem. Abstr.*, 90 (1979) 187625.
- 158 S. Yajima, *Kagaku Kojo*, 23 (1979) 38.
- 159 T. Nakahira, C. Minami, S. Iwabuchi and K. Kojima, *Makromol. Chem.*, 180 (1979) 2245.
- 160 P. Daum and R.W. Murray, *J. Electroanal. Chem. Interfacial Electrochem.*, 103 (1979) 289.
- 161 T. Ouchi, H. Taguchi and M. Imoto, *J. Macromol. Sci. Chem.*, A15 (1978) 719.
- 162 K. Tsubakiyama, T. Matsuo, T. Sasaki, K. Yoshida and K. Araki, *J. Polym. Sci., Polym. Chem. Ed.*, 17 (1979) 1829.

- 163 K. Tsubakiyama, T. Matsuo, T. Sasaki, K. Yoshida, T. Fujimura and K. Araki, *J. Polym. Sci., Polym. Chem. Ed.*, 17 (1979) 173.
- 164 C.U. Pittman and C.C. Lin, *J. Polym. Sci., Polym. Chem. Ed.*, 17 (1979) 271.
- 165 A. Nishikawa and H. Suzuki (Hitachi), *Jpn. Pat.*, 7941991, 1979, Apr. 03; *Chem. Abstr.*, 91 (1979) 40409.
- 166 V.S. Sukhinin, *Zh. Vses. Khim. O-va*, 24 (1979) 400; *Chem. Abstr.*, 91 (1979) 193391.
- 167 C. Simionescu, T. Lixandru, L. Tataru and I. Mazilu (Institutul Politehnic Iasi), *Rom. Pat.* 63714, 1978 Jun. 15; *Chem. Abstr.*, 91 (1979) 212018.
- 168 A.E. Vodop'yanova, Yu. P. Losev, Ya. M. Paushkin and M.A. Ksenofontov, *Dokl. Akad. Nauk BSSR*, 23 (1979) 458.
- 169 E.A. Kalennikov, U.S. Yuran, R.I. Dashevskaya and L. Ya. Belyavskaya, *Khim. Khim. Tekhnol (Minsk)*, 14 (1979) 90.
- 170 A. Gal, M. Cais and D.H. Kohn, *J. Appl. Polym. Sci.*, 22 (1978) 3449.
- 171 V.N. L'vov, P.A. Rutman, V.G. Safronov, E.B. Sokolova and G.P. Chalykh (All-Union Scientific-Research Institute of Natural Diamonds and Tools), *USSR Pat.* 649737, 1979 Feb. 28; *Chem. Abstr.*, 91 (1979) 60044.
- 172 V.A. Balusov, V.T. Solomatin, S.P. Gubin, A.P. Rysev and G.P. Tikhonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 921.
- 173 V.I. Ignatov, V.T. Solomatin and A.A. Nemodruk, *Zh. Anal. Khim.*, 34 (1979) 1544.
- 174 V.T. Solomatin, V.A. Balusov and T.F. Rybina, *Metody Instrument, Analiza Materialov, M.*, (1979) 75; *Chem. Abstr.*, 91 (1979) 116780.
- 175 V.I. Ignatov, V.T. Solomatin and A.A. Nemodruk, *Zh. Anal. Khim.*, 33 (1978) 2328.
- 176 S.P. Gubin, A.A. Pendin, V.A. Balusov and V.T. Solomatin, *Dokl. Akad. Nauk SSSR*, 248 (1979) 385.
- 177 M. Lamache, *Electrochim. Acta*, 24 (1979) 79.
- 178 T.S. Chao and E.H. Owston (Atlantic Richfield Co.) *US Pat.* 4104036, 1978, Aug. 1; *Chem. Abstr.*, 90 (1979) 74214.
- 179 D.H. Payne (du Pont de Nemours, E.I., and Co.) *US Pat.* 4139349, 1979, Feb. 13; *Chem. Abstr.*, 90 (1979) 189592.
- 180 T. Ueda, K. Hata, N. Kagawa and M. Tsuchiya (Nippon Zeon Co.), *Jpn. Pat.*, 7925904, 1979, Feb. 27; *Chem. Abstr.*, 91

- (1979) 60102.
- 181 A. Takahashi and T. Takeyama (Toray Industries), Jpn. Pat. 79 13510, 1979 Feb. 01; Chem. Abstr., 91 (1979) 94252.
- 182 C.I. Ashmore, C.S. Combs and W.D. Stephens (Thiokol Corp.) US Pat., 410869, 1978, Aug. 22; Chem. Abstr., 90 (1979) 74071.
- 183 C. Gotzmer and M.J. Cziesla (US Dept. of the Navy) US Pat., 4168362, 1979, Sep. 18; Chem. Abstr., 92 (1980) 8526.
- 184 L.D. Petrova, E.E. Kondenko, V.V. Azatyan, A.N. Baratov and S.G. Gabrielyan (All-Union Scientific-Research Institute of Fire Prevention), USSR Pat. 652944, 1979, Mar. 24; Chem. Abstr., 91 (1979) 7177.
- 185 R. Lattrell, H. Kief and H. Baehr (Hoechst), Ger. Pat. 2742201, 1979, Mar. 29; Chem. Abstr., 91 (1979) 57182.
- 186 E.I. Edwards, R. Epton and G. Marr, J. Organometal. Chem. 168 (1979) 259.
- 187 R.P. Hanzlik, P. Soine and W.H. Soine, J. Med. Chem., 22 (1979) 424.
- 188 W.H. Soine, Diss. Abstr. Int. B, 39 (1979) 3849.
- 189 R.P. Hanzlik, V. Kishore and R.E. Tessel, Xenobiotica, 8 (1978) 753.
- 190 M. Wenzel, M. Schneider and E. Liss, Z. Naturforsch., C; Biosci., 34C (1979) 670.
- 191 V. Mues and J. Niggemann (Bayer A. -G.) Ger. Pat., 2815930, 1979, Oct. 18; Chem. Abstr., 92 (1979) 21467.