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FERROCENE

ANNUAL SURVEY COVERING THE YEAR 1988*

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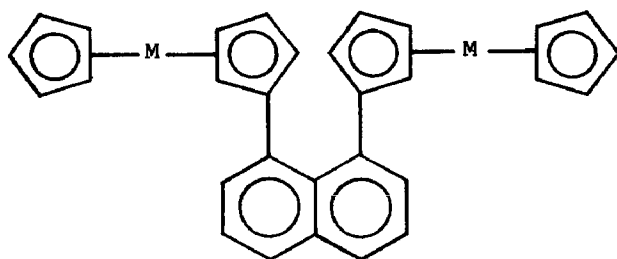
*Annual Survey covering the year 1987 see *J. Organomet. Chem.*, 357 (1988) 247.

1. REVIEWS

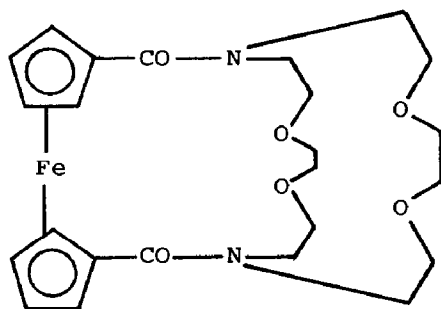
The solid state properties of organometallic compounds have been surveyed by Green, Qin and O'Hare. Organometallic charge-transfer salts, such as ferrocenium tetracyanoquinodimethane, were discussed in some detail [1].

2. STRUCTURAL DETERMINATIONS

The crystal structures of *o*-, *m*- and *p*-nitrophenylferrocenes have been determined. All three compounds consisted of discrete molecules with Fe-C distances in the range 1.997-2.120 Å. The presence of the nitro group led to different conformations in the three structures [2].



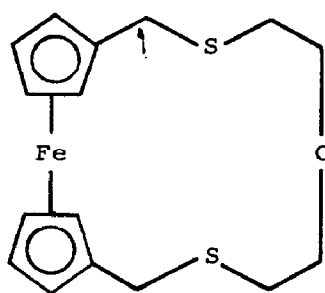
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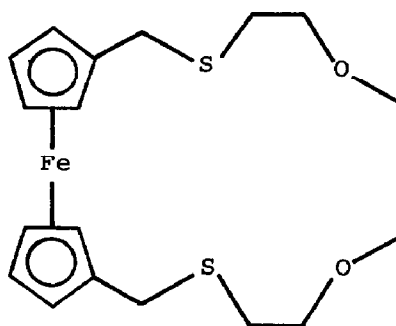
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The crystal and molecular structure of 1,8-diruthenocenylnaphthalene (2.1; M = Ru) has been determined and compared with the structure of the corresponding ferrocene compound (2.1; M = Fe). The two compounds (2.1; M = Fe, Ru) were very similar in structure. Changes in the geometry of the compound (2.1; M = Fe) on conversion to the monocation indicated a decrease in electron density on the cyclopentadienyl rings on oxidation [3].

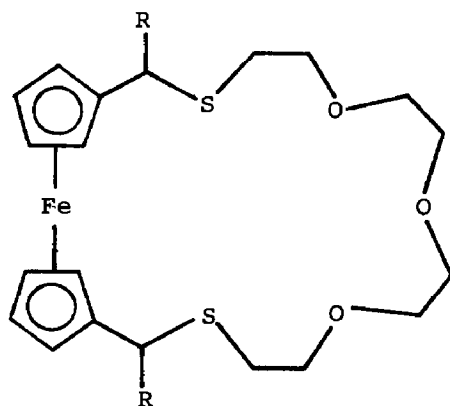
X-ray crystallography has been used to determine the crystal and molecular structure together with the absolute configuration of [1-(N,N-dimethylamino)ethyl]ferrocene tartrate dihydrate [4]. The structure of the complex tris(ferrocenyl)boron-pyridine has



2.3



2.4



2.5

been determined by X-ray analysis. As expected from previous results the geometry around the boron atom was distorted tetrahedral [5].

The crystal and molecular structure of the ferrocenyl cryptand (2.2) has been determined by X-ray analysis. The ferrocenyl group had planar η -cyclopentadienyl rings which were very nearly parallel. The two rings were rotated from an eclipsed orientation by 6.4° [6]. The crystal structures of the dithiaferrocenophanes (2.3, 2.4 and 2.5; R = H, Me) have been determined by X-ray analysis. In all the molecules the two η -cyclopentadienyl rings were almost parallel and they adopted an eclipsed conformation. The electrochemical behaviour of these compounds was also examined [7, 8].

3. THEORETICAL STUDIES

Several basis sets have been examined for a range of organometallic compounds, including ferrocene, and used to derive a compact and accurate basis set for total geometry optimisation. Differences between calculated and experimental metal-ligand bond distances were discussed [9]. Calculated geometries for complexes formed between ferrocene and α -, β -, and γ -cyclodextrin have been obtained from a molecular mechanics force field approach. The interaction of 3-ferrocenylacrylate esters with β -cyclodextrin and the acylcyclodextrin obtained have been studied by docking calculations. The increased reactivity of the *p*-nitrophenyl ester when it entered the cyclodextrin cavity was ascribed to the formation of a distorted ester in the acylcyclodextrin [10].

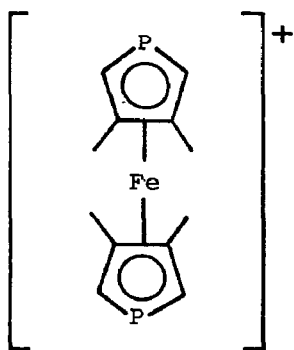
4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

Mixtures of helium and organometallic compounds in vapour form have been subject to an electrodeless high-frequency discharge and the emission spectra studied. Benchtrene and ferrocene were among the compounds examined. Ferrocene gave a metal atom and two radicals [11]. The optical absorption of gaseous ferrocene, 1,1'-dichloro-, 1,1'-dibromo and 1,1'-dimethyl-ferrocene has been measured using synchrotron radiation. Ligand field parameters were estimated from this data [12].

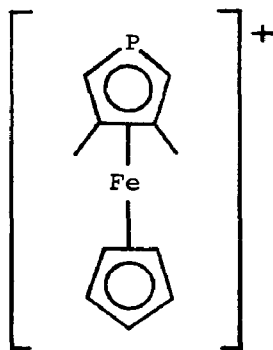
An inductively coupled plasma atomic emission spectrometer has been interfaced to a supercritical fluid chromatograph for elemental detection. The performance was evaluated by injecting

ferrocene solutions onto the column and monitoring the iron emission line at 259.94 nm. The interface was used for the separation of a mixture of ferrocenes [13].

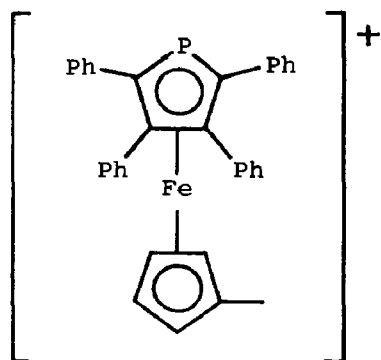
The Moessbauer spectra of a series of 1,1'-dialkyferrocenium triiodides have been recorded and interpreted [14]. Masuda and Sano have given an explanation for the temperature dependence of the quadrupole splitting values in the Moessbauer spectra of mixed valence biferrocenium triiodides. The temperature dependence was explained in terms of an order-disorder transition related to the valence state of the two iron atoms in the biferrocenium ions [15].



4.1



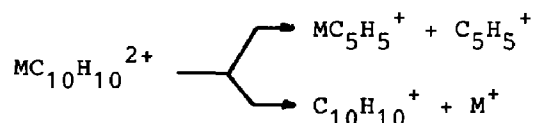
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4.3

An ^{57}Fe Moessbauer study has been carried out on the phosphaferricenium ions (4.1, 4.2 and 4.3) which were generated by treatment of the parent metallocenes with organic oxidants. On oxidation of the phosphaferricenium ions the quadrupole splitting did not collapse but remained relatively large which was in direct contrast to the ferrocene-ferricenium ion system. The phosphaferricenium ions were relatively unstable and disproportionated to give iron(II) as the initial product [16].

The decomposition of gaseous ferrocene, 1,1'-dichloroferrocene and 1,1'2,2'-tetrachloroferrocene has been investigated using photon and electron induced ionization mass spectroscopy. Elimination reactions in the decompositions of the chloroferrocenes were identified [17]. The charge separation reactions (coulomb explosion) of the ferrocene, cobaltocene and nickelocene dications, generated by electron impact ionization in the gas phase in a mass spectrometer, have been investigated. The dications all behaved similarly in their unimolecular decomposition reactions to give rise to the charge separation products shown below:



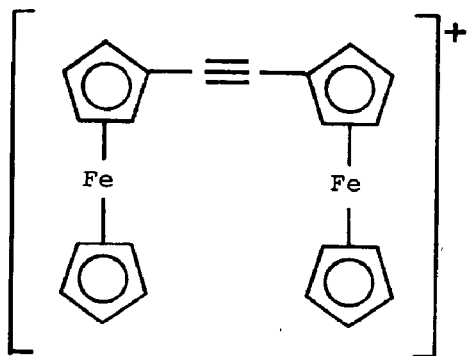
The intercharge distances of the exploding dications in the transition structures were calculated [18].

The mechanism of formation of negative molecular ions from the metallocenes $(\eta\text{-C}_5\text{H}_5)_2\text{M}$, where $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$, by dissociative electron capture has been investigated [19]. An extensive series of ferrocene derivatives has been studied by gas-phase ultraviolet photoelectron spectroscopy, mass spectrometry and cyclic voltammetry. The results indicated that there was a linear correlation between the first ionization energies of the compounds in the gas phase and the electrochemical oxidation potentials in solution [20].

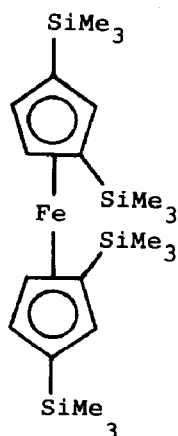
The infrared spectra of a series of substituted ferrocenes were recorded and analysed. Assignment of the ring-mode vibrations was attempted. Also included in this paper was an improved preparation for 1,2,3,4,5-pentamethylferrocene which was formed by the irradiation of dicarbonyl(η^5 -pentamethylcyclopentadienyl)iron halides with sodium cyclopentadienide [21].

Infrared spectroscopy has been used to show that the basicity of formyl oxygen atoms in a series of complexes decreased in the order: $(\eta\text{-C}_5\text{H}_5)\text{Rh}(2,5\text{-norbornadiene-2-carboxaldehyde}) > \text{formylferrocene} > \text{formylcymantrene}$ [22]. Shubina and co-workers have carried out an infrared spectral and X-ray single crystal study of hydrogen bonds and the structures of nonamethylferrocenyl- and ferrocenyl-carbinols in the solid state. The molecules associated predominantly via intermolecular $\text{OH}\cdots\text{O}$ bonds. In some of the nonamethylferrocenylcarbinols intermolecular $\text{OH}\cdots\pi\text{-C}_5\text{Me}_5$ hydrogen bonds were also formed. The most stable intermolecular hydrogen bonds were formed by the primary alcohols [23]. In a related paper the character of intramolecular hydrogen bonds in ferrocenyl- and nonamethylferrocenyl-carbinols was determined from their infrared spectra and on the basis of molecular mechanics calculations. The intramolecular hydrogen bonds $\text{OH}\cdots\text{Fe}$ were formed when the steric requirements of the substituents at the carbinol carbon atom and the $\eta\text{-cyclopentadienyl}$ rings made the corresponding conformations energetically favourable [24].

A study has been carried out on the effect of pressure induced freezing on the energy of the intravalence-transfer band of the mixed valence salt (4.4). The salt was dissolved in CD_3CN and the near infrared electronic spectrum was recorded



4.4

 I_3^- 

4.5

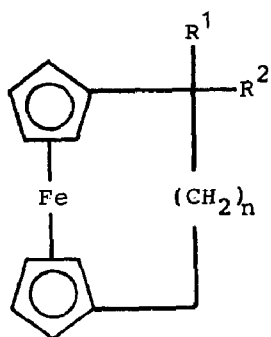
at pressures below and above freezing point of the solution. The peaks shifted significantly to lower energy but less than predicted [25].

^1H NMR Spectroscopy has been used to study the conformation of *o*-substituted phenylferrocenes. In *o*-hydroxy- and *o*-alkyl-phenylferrocenes the cyclopentadienyl ring to aryl group bonds were twisted and the conformations of the substituents were endo. With *o*-chloro- and *o*-nitro-phenylferrocene the exo-conformation was preferred. These results were explained in terms of (i) van der Waals repulsion between the α -proton on the η -cyclopentadienyl ring and the ortho-substituent and (ii) interaction between the d -electrons on the iron atom and the substituent [26].

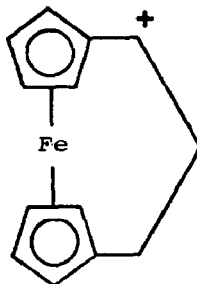
Variable temperature ^1H NMR spectroscopy has been used to demonstrate restricted rotation about the metal-ligand bond in tetrakis(trimethylsilyl)ferrocene (4.5) [27]. Conformational effects in ferrocenes with bulky 1,1'-substituents have been investigated by dipole moment measurements and by ^1H and ^{13}C NMR spectroscopy. Severe restriction to rotation was observed in 1,1'-bis(triphenylmethyl)ferrocene while 1,1'-di-*t*-butylferrocene was found to consist of a mixture of five antiprismatic conformers [28].

Rate constants for the electron self-exchange of cobaltocenium ion-cobaltocene and for decamethylcobaltocene have been determined by the NMR line-broadening technique. The results were compared with those obtained for the ferrocenium ion-ferrocene couple. The results provided direct evidence for the importance of orbital-overlap factors in outer-sphere redox reactivity [29]. The ^{13}C -NMR spectra of a series of (*o*-substituted phenyl)ferrocenes have been recorded and interpreted [30].

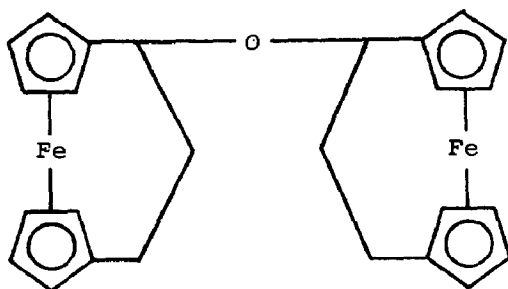
^{13}C and ^{57}Fe NMR spectra of the ferrocenophanes (4.6; $n = 1, 2$; $\text{R}^1\text{R}^2 = \text{H}_2, \text{O}$; $\text{R}^1 = \text{H}, \text{R}^2 = \text{OH}$; 4.7 and 4.8) have been recorded and interpreted. In the carbocation (4.8) there was evidence of direct interaction between the α -carbon atom and the iron [31]. Deuterium NMR studies have been carried out on the thiourea-deuterated ferrocene (3:1) clathrate and the deuterated ferrocene-cyclodextrin inclusion complexes [32].



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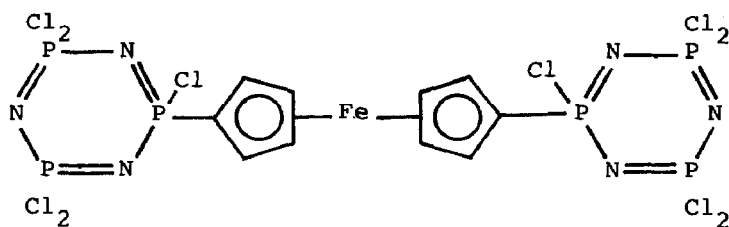
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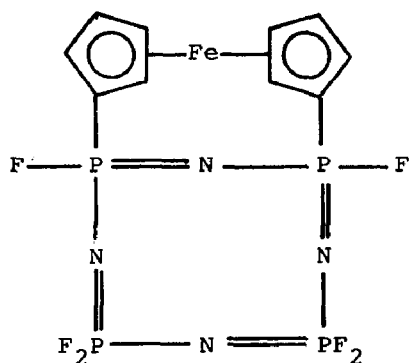
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5. ELECTROCHEMISTRY AND PHOTSENSITIVE ELECTRODES

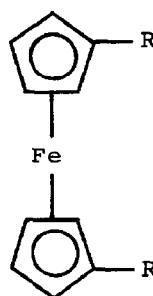
The reaction entropy for the electroreduction of bis(biphenyl)chromium has been compared with the values obtained for the ferrocene/ferrocenium and bis(benzene)chromium(o)/-bis(benzene)chromium(I) couples [33]. The oxidation-reduction chemistry of a number of ferrocenyl cyclic phosphazenes, for example the phosphazenes (5.1 and 5.2), have been studied by cyclic voltammetry at platinum disc electrodes. The transannular linked ferrocenyl-phosphazenes had shifts in oxidation peak potentials approximately twice those of the pendent analogues. It was concluded that each phosphorus atom in the phosphazene skeleton had equal electron withdrawing properties and that



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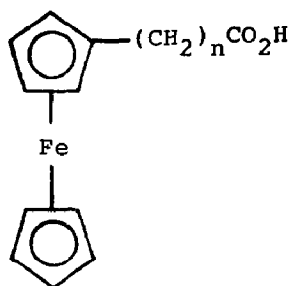


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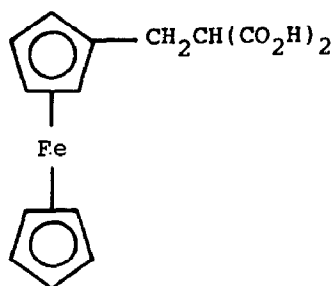
the inductive effects of the phosphazene operating via each η -cyclopentadienyl ring were cumulative [34].

A series of 1,1'-disubstituted-ferrocenes (5.3; R = CH₂OH, COCH₃, CO₂CH₃, CHO, CO₂H) has been studied by cyclic voltammetry. A linear relationship was obtained between the redox potentials and the Hammett σ constants for the substituents [35]. 1,1'-Ferrocendicarboxylic acid has been investigated via cyclic voltammetry. The redox process was quasi-reversible and became less reversible in the pH range 6-11 [36].

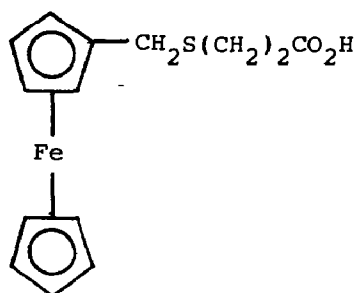
The ferrocenyl-carboxylic acids (5.4; n = 0-3 and 5.5) and the sulphur containing acids (5.6 and 5.7) have been



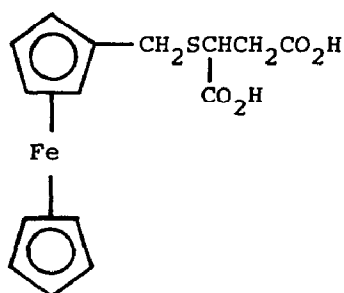
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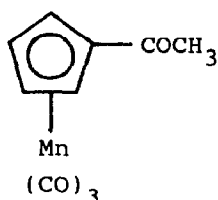
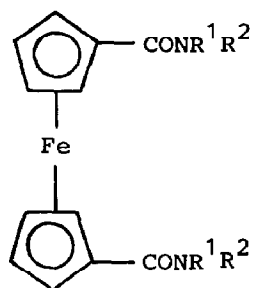
5.6



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investigated via cyclic voltammetry. Most of the carboxylic acids were less susceptible to oxidation than ferrocene [37]. The electrochemical behaviour of the cyclodextrin-ferrocene-carboxylic acid inclusion complex has been studied by cyclic voltammetry. The electrocatalytic oxidation of NADH by ferrocene-carboxylic acid was enhanced by β -cyclodextrin [38].

An electrochemical investigation has been carried out on the porphyrins $(P)Ge(\text{ferrocenyl})_2$ and $(P)Ge(C_6H_5)(\text{ferrocenyl})$ where P was the dianion of octaethylporphyrin or tetraphenylporphyrin. In the neutral species delocalization of electron density occurred from the porphyrin macrocycle onto the



ferrocenyl group. In the electrooxidized species $[(P)Ge(C_6H_5)-(ferrocenyl)]^+$ delocalization of positive charge occurred from the ferrocenyl group onto the porphyrin macrocycle [39].

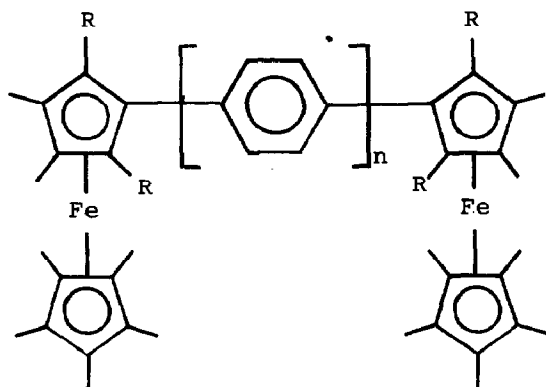
The ferrocene oxidation wave in the ferrocene amides (5.8; $R^1 = H, Me$; $R^2 = Me, Ph$; $R^1 = R^2 = Et$) has been shifted to more positive potentials by the addition of the lithium ion to the acetonitrile solution [40]. The electrical conductivities of poly(ethynylferrocene) and several other polymers doped with a series of reagents have been determined. High conductivities were found with those polymers doped with iodine [41].

1,1'-Diacetylferrocene and manganese carbonyl have been used in the electrochemical synthesis of acetylcymantrene (5.9). The electrochemical reduction of acetylferrocene, acetylcymantrene and (η -acetophenone)tricarbonylchromium in methyl cyanide gave the corresponding cyanoalkyl compounds [42].

6. PREPARATIONS OF FERROCENE

Ferrocene has been synthesised electrochemically in good yield (86%) in hexamethylphosphortriamide solutions containing lithium chloride [43]. The dilithiosalts of *p*-phenylene- and *p*-biphenylene-bridged cyclopentadienyls were treated with (η - C_5Me_5)(2,4-pentanedionato)iron to give the corresponding substituted ferrocenes (6.1; $R = H, Me$; $n = 1, 2$). The electrochemistry of these compounds was investigated [44].

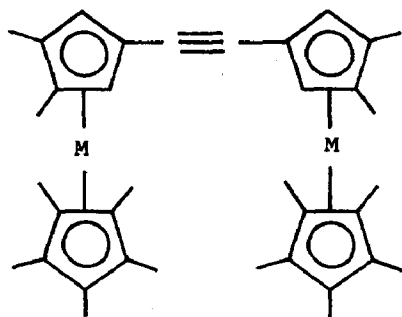
In related work (η - C_5Me_5)(2,4-pentanedionato)-iron or -nickel was treated with lithiocyclopentadienyls to give the corresponding



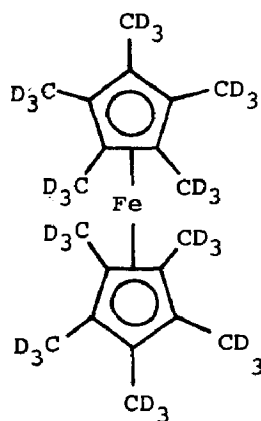
6.1

substituted ferrocenes (6.2; $M = \text{Fe}, \text{Ni}$) [45]. Deuterio(pentamethylcyclopentadiene), $\text{C}_5(\text{CD}_3)_5\text{H}$, has been prepared on a large scale by heating $\text{C}_5(\text{CH}_3)_5\text{H}$ with C_6D_6 under a D_2 atmosphere in the presence of $(\eta\text{-C}_5\text{Me}_5\text{H})_2\text{ScD}$ as the catalyst. The deuterated ferrocene (6.3) was prepared via a stoichiometric ligand exchange between $[\eta\text{-C}_5(\text{CD}_3)_5]_2\text{ScCl}$ and bis(pentane-2,4-dionato)iron(II) [46].

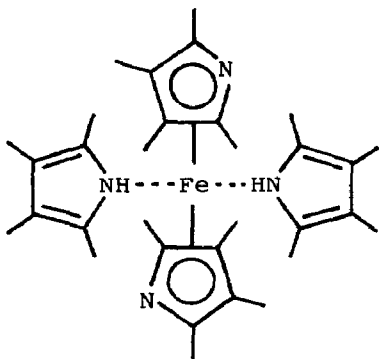
Treatment of $\text{C}_4\text{Me}_4\text{NLi}$ with iron(II) chloride in tetrahydrofuran produced $(\eta^1\text{-C}_4\text{Me}_4\text{N})_2\text{Fe}\cdot 2\text{THF}$, which on hydrolysis



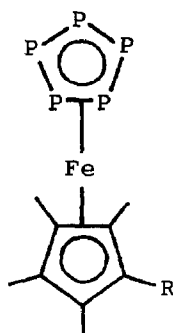
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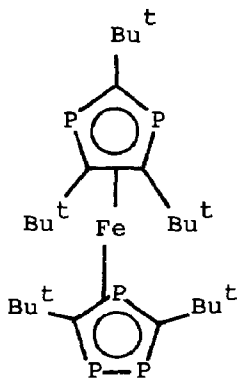
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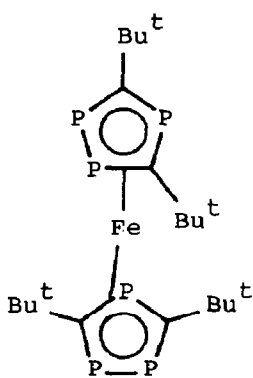
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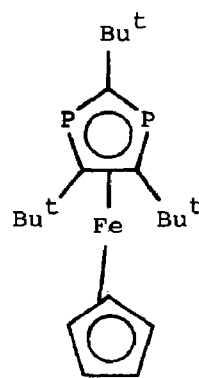
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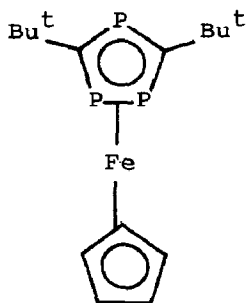
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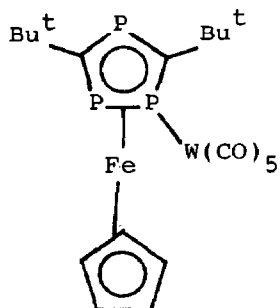
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6.8



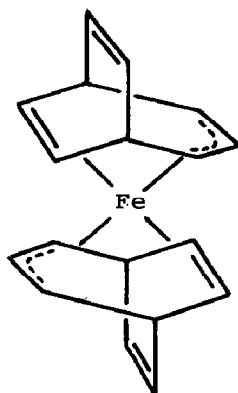
6.9



6.10

gave the complex (6.4) [47]. Sodium pentaphosphacyclopentadienide has been formed by the reaction of white phosphorus with sodium in tetrahydrofuran in the presence of 18-crown-6. Reaction of the corresponding lithium salt LiP_5 with iron(II) chloride in the presence of lithium pentamethylcyclopentadienide produced the complex (6.5; $\text{R} = \text{Me}$) [48]. In a related piece of work white phosphorus and $[(\eta\text{-C}_5\text{Me}_4\text{R})\text{Fe}(\text{CO})_2]_2$, where $\text{R} = \text{Me}$ and Et , were heated together and the corresponding mixed sandwich complexes (6.5) were formed. The structure of the complex (6.5; $\text{R} = \text{Et}$) was determined by X-ray analysis [49].

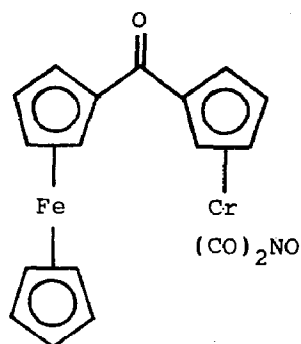
Treatment of iron(II) chloride with a mixture of lithium cyclopentadienide and the lithium salts of the $\text{C}_2(\text{t-Bu})_2\text{P}_3$ and $\text{C}_3(\text{t-Bu})_3\text{P}_2$ anions produced the corresponding di- and tri-phosphorus analogues of ferrocene (6.6-6.9). The pentacarbonyltungsten complex (6.10) was prepared and characterised by X-ray analysis [50]. The $(\eta\text{-bicyclononatrienyl})$ iron complex (6.11) has been prepared and characterized by X-ray crystallography. It was regarded as a ferrocene analogue with separated allyl and olefin systems [51].



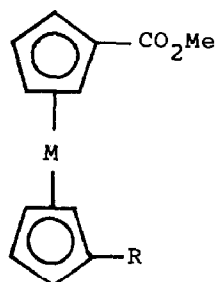
6.11

7. REACTIONS OF FERROCENE

The Friedel-Crafts acylation of ferrocene with derivatives of dicarboxylic acids has been investigated. Thus the methyl ester chlorides of 1,3- and 1,4-benzenedicarboxylic acids have been used as acylating agents. Hydrolysis of the methyl esters



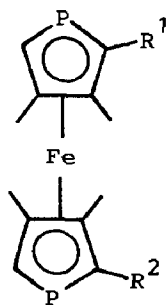
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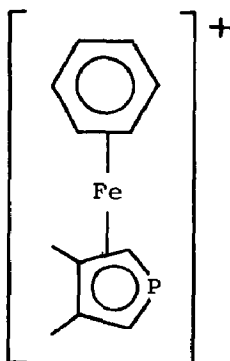
7.2

to the carboxylic acids was described [52]. Ferrocene has been used in ligand exchange reactions with arenes to give (η -arene)-(η -cyclopentadienyl)iron cations [53]. The cynichrodenylferrocenyl ketone (7.1) has been prepared from ferrocene and the carbonylchloride of dicarbonyl(η -cyclopentadienyl)nitrosylchromium. The ketone (7.1) has been converted to the corresponding α -ferrocenylcarbenium ion and reduced with lithium tetrahydridoaluminate or Grignard reagents to 6-ferrocenylfulvenes [54].

Substituted ferrocenes underwent ligand exchange on heating with $^{103}\text{RuCl}_3$ to give the corresponding labelled ruthenocenes which were used as radiopharmaceutical diagnostics. Thus the ferrocenes (7.2; M = Fe, R = H, CO₂Me) were converted to the



7.3



7.4

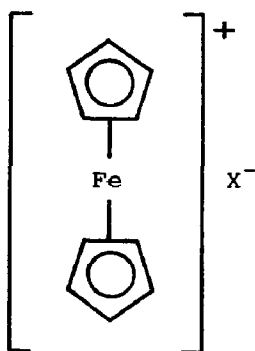
ruthenocenes (7.2; $M = {}^{103}\text{Ru}$, $R = \text{H}, \text{CO}_2\text{Me}$) [55]. The tropanol esters of the carboxylic acids of ferrocene, ${}^{103}\text{Ru}$ -ruthenocene and ${}^{103\text{m}}\text{Rh}$ -rhodocinium have been prepared [56].

The aluminium chloride cleavages of 3,3',4,4'-tetramethyl-diphosphaferrocene (7.3; $R^1 = R^2 = \text{H}$) and the acyl derivatives (7.3; $R^1 = \text{COCH}_3$, $R^2 = \text{H}$; $R^1 = \text{COPh}$, $R^2 = \text{H}$; $R^1 = R^2 = \text{COCH}_3$, COPh) have been investigated in benzene. The diphosphaferrocene (7.3; $R^1 = R^2 = \text{H}$) did not produce any of the η^6 -benzene cleavage compound and both the mono acyl derivatives (7.3; $R^1 = \text{COCH}_3$, $R^2 = \text{H}$; $R^1 = \text{COPh}$, $R^2 = \text{H}$) produced the same cationic product (7.4). The reactivity of the diacyl compounds (7.3; $R^1 = R^2 = \text{COCH}_3$, COPh) was low and the desired cationic products were not isolated [57].

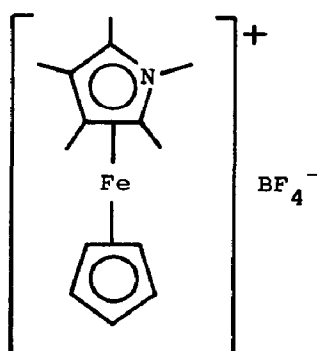
Pyrolysis of ferrocene and nickelocene produced thin films of iron and nickel which adhered well to stainless steel and nickel. The thermodynamics of the gaseous deposition of these metallocenes was examined [58].

8. FERROCENIUM SALTS AND MIXED-VALENCE SALTS

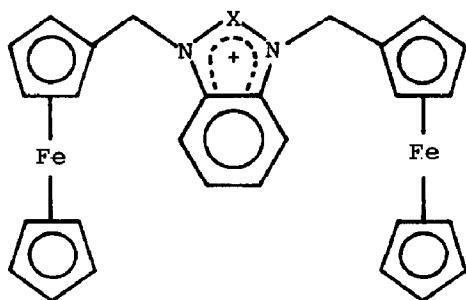
Ferrocene was oxidized in nitromethane containing hydrogen fluoride by phosphorus or antimony pentafluoride to give the corresponding ferrocenium salts [8.1; $X = \text{PF}_6, \text{SbF}_6$] [59]. Molybdenum, tungsten and uranium hexafluorides in Freon 11 have been used to oxidize ferrocene to the ferrocenium cation as the hexafluoromolybdate(v), -tungstate(v), and -uranate(v) salts [60].



8.1



8.2

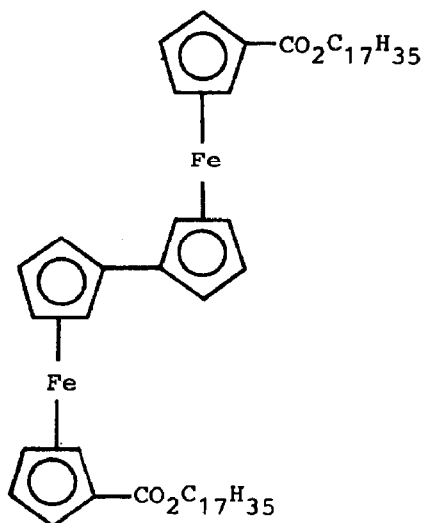


8.3

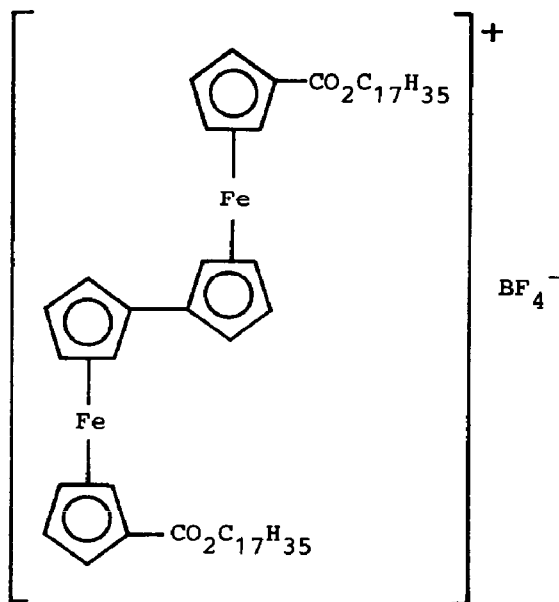
Pentamethylpyrrole combined with the salt $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{SMe}_2)_3]\text{BF}_4$ to form the azaferrocenium tetrafluoroborate (8.2) [61]. α -Ferrocenylcarbinols have been treated with azoles and fluoroboric acid in dichloromethane to form α -ferrocenylalkyl derivatives of azoles such as the cations (8.3; X = CH, N, PhCH_2C) [62]. The kinetics of oxidation of the ferrocenium ion to cyclopentenedione in acidic cerium(IV) sulphate in the presence of oxygen has been investigated. The rate determining step was the decomposition of an unstable ferrocenium ion-oxygen complex by the cerium(IV) sulphate [63].

The kinetics of oxidation of ascorbic acid by copper(II) and the ferrocenium ion have been investigated. In this reaction the ferrocenium ion behaved as a typical outer-sphere oxidant and the results obtained from the two oxidizing systems were compared [64]. The ferrocenium ion has been used to oxidize an $(\eta\text{-cyclooctatetraene})\text{rhodium}$ complex and investigate the mechanism of the reaction [65].

1,6'-Bis(stearoyloxy)biferrocene (8.4) has been prepared by the Ullmann coupling of 1'-iodo- or -bromo-1-stearoyloxyferrocene. Oxidation of the biferrocene(8.4) with benzoquinone and boron trifluoride-ether gave the salt (8.5). The Langmuir-Blodgett film of the biferrocene (8.4) was prepared and in the film the $\eta\text{-cyclopentadienyl}$ rings were orientated perpendicular to the film surface. The mixed-valence salt (8.5) formed a stable monolayer on water [66].



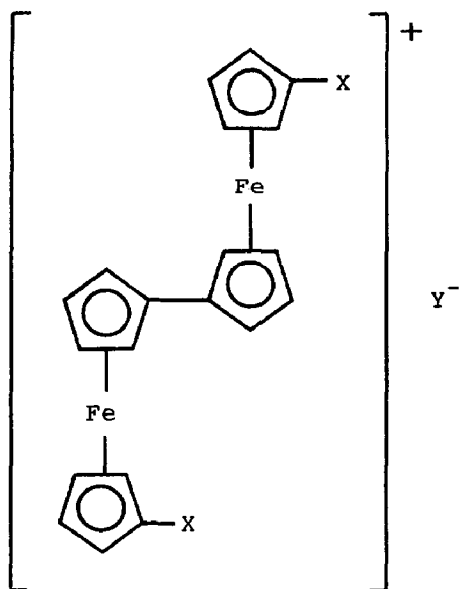
8.4



8.5

The effect of alkyl substitution in the ferrocenium cation of TCNQ salts has been studied by IR spectroscopy [67]. Changes in electron localization within the TCNQ stacked anions were observed [68]. The ferromagnetic behaviour of the charge-transfer salt decamethylferrocenium tetracyanoethanide and related compounds has been reviewed [69]. Irradiation promoted the reaction of the ferrocenium cation in acetonitrile in the presence of benzyl alcohol, benzhydrol and 1-propanol. Ligand-metal charge-transfer excitation induced a redox reaction giving reduction of the ferrocenium ion and oxidation of the alcohol. The ligand field transition excitation induced a dehydration and decomposition process [70].

Pressure effects on the intervalence-transfer bands of the biferrocenium salts (8.6; $\text{X} = \text{H}$, $\text{Y}^- = \text{I}_3^-$, PF_6^- ; $\text{X} = \text{I}$, $\text{Y}^- = \text{I}_3^-$, IBr_2^- ; $\text{X} = \text{Br}$, Et, n-Bu, $\text{Y} = \text{I}_3^-$) intercalated into

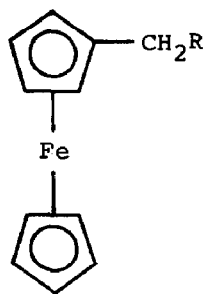


8.6

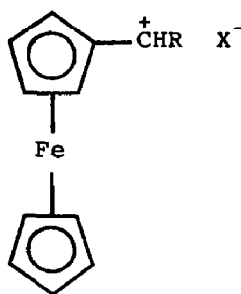
a clay have been investigated. Three different types of pressure response were found. These responses appeared to reflect the different solid-state environments of alternating stacks of cations and anions together with segregated stacks of cations and cations intercalated into the clay interlammellar regions [71].

9. FERROCENYL CARBENIUM IONS

The structure of α -metallocenylcarbocations, including α -ferrocenylcarbocations, has been discussed and the mechanism by which the cationic centre was stabilized has been reviewed. The significance of permethylated metallocenes in these studies has been emphasised [72]. Treatment of a series of alkylferrocenes for example, (9.1; R = Me, Ph, ferrocenyl) with Ph_3CX , where X = BF_4 , ClO_4 , produced the corresponding α -ferrocenylcarbenium ion salts (9.2) [73].



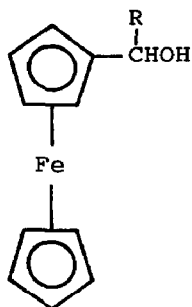
9.1



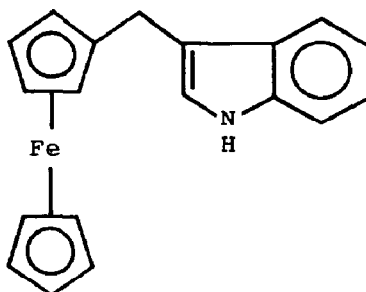
9.2

The treatment of nucleophilic substrates, for example triphenylphosphine, indole and pyridine, with the ferrocenyl alcohols (9.3; R = H, Me, Ph) in different media to give α -ferrocenylalkylated products has been investigated. For example, the reaction of ferrocenylmethanol with indole afforded the 3-substituted product (9.4) [74]. The mechanism of dehydrogenation of α -hydroferrocenes has been investigated. 3-(Ferrocenylmethyl)-indole (9.4) transferred an electron to ferrocenium tetrafluoroborate or to silver perchlorate to give a cation radical which transferred a hydrogen atom to a trityl radical to produce the salt (9.5) [75].

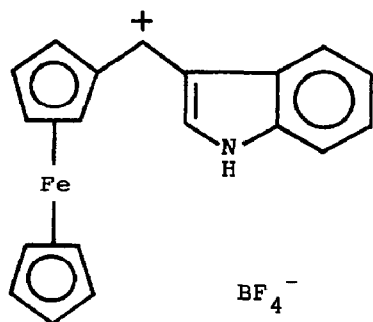
A comparison of the behaviour of the iron-subgroup cations



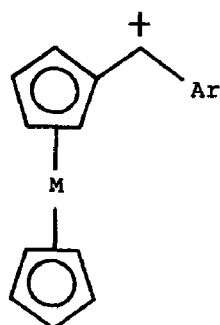
9.3



9.4



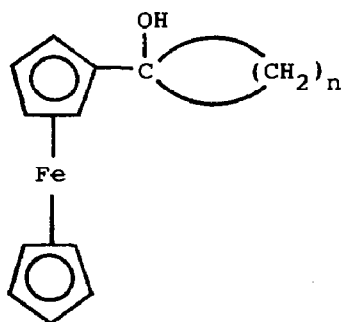
9.5



9.6

(9.6; M = Fe, Ru, Os; Ar = Ph, C₆H₂Me₃, C₆F₅) has been carried out. The ruthenium and osmium containing cations were more stable than their iron counterparts. Comparison of ¹H and ¹³C NMR data indicated that the shielding of ¹H and ¹³C nuclei by the carbenium centre -CH⁺ increased on going from Fe → Ru → Os. The results also implied that direct participation by the metal atom in the stabilization of the carbenium ion increased from iron to osmium [76].

The condensation of lithioferrocene with cycloalkanones produced the corresponding hydroxycycloalkylferrocenes (9.7; n = 3-9, 11, 14). The stability constants pK_R⁺ of the carbocations derived from these hydroxycycloalkylferrocenes were



9.7

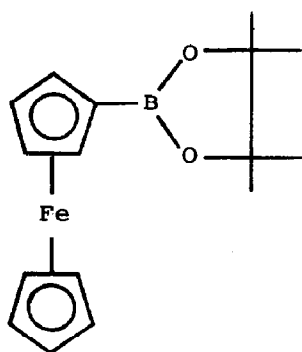
determined and the solvolysis of the corresponding acetates was also investigated. The maximum stability of the cations was shown by the species with five and eight membered rings. The rates of solvolysis of the acetates showed a good correlation with pK_{R^+} of the corresponding carbocations [77]. The ferrocenyl obaltocenium and ferrocenylenedicobaltocenium cations have been characterized as the hexafluorophosphate salts [78].

10. FERROCENE CHEMISTRY

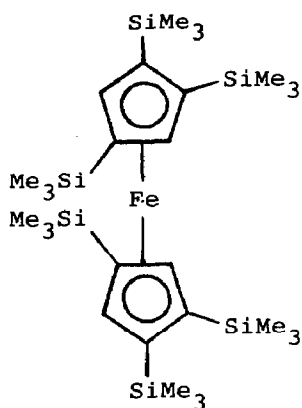
(i) Derivatives containing other metals (metalloids)

Cyclic ferroceneboronates have been used as derivatives for the gas chromatographic separation and characterization of diols and related compounds. The boronates were readily prepared by heating ferroceneboronic acid with a diol in dry pyridine. For example, the reaction of ferroceneboronic acid with pinacol gave the stable boronate (10.1) in high yield. A series of low molecular diols was analysed as their boronates with ferroceneboronic acid [79].

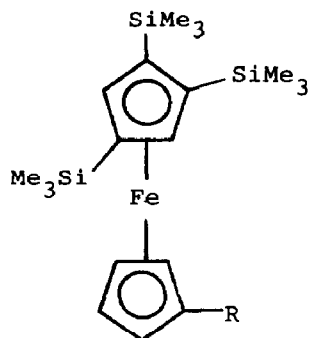
Reaction of tris(trimethylsilyl)cyclopentadienyllithium with iron(II) halides produced the hexasubstituted ferrocene (10.2). The trimethylsilyl-substituted ferrocenes (10.3; R = H, Me) were also prepared. X-ray analysis of the hexasubstituted ferrocene (10.2) showed that the cyclopentadienyl rings were eclipsed and that the molecule had relatively long (2.082 Å) Fe-C(ring) distances [80]. The reaction of acetylferrocene with dilithium derivatives of phenylcyclopolysilanes produced



10.1



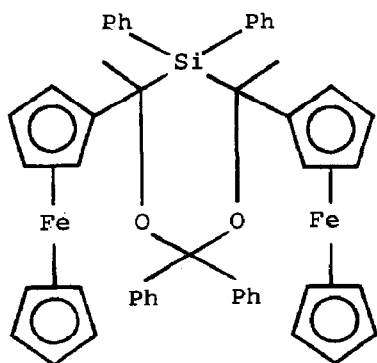
10.2



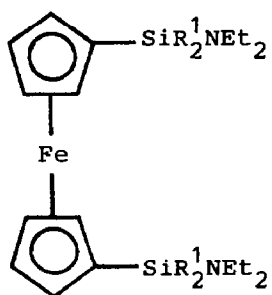
10.3

the diferrocenyl derivative (10.4) as one of the products [81]. Reaction of 1,1'-bis[dialkyl(diethylamino)silyl]ferrocenes (10.5; $R^1 = \text{Me, Et}$) with aliphatic alcohols or triorganosilanol gave the 1,1'-disubstitutedferrocenes (10.6; $R^2 = \text{Me, Et, octyl}$) and (10.7; $R^2 = \text{Me, Et, Ph}$) respectively. Hydrolysis of the siloxane (10.7; $R^1 = \text{Me}$) gave the ferrocenophane (10.8) [82].

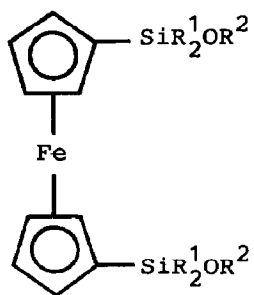
Deprotonation of the salt (10.9) by *n*-butyllithium followed by the addition of 4-nitrobenzaldehyde produced the cis- and trans-isomers (10.10 and 10.11). The structure of the cis-isomer (10.10) was determined by X-ray analysis. This compound



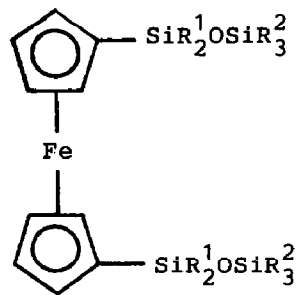
10.4



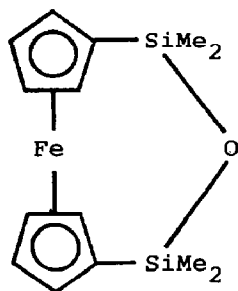
10.5



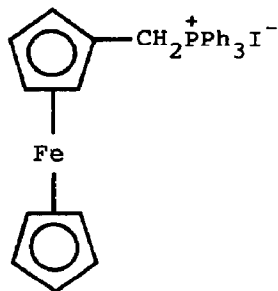
10.6



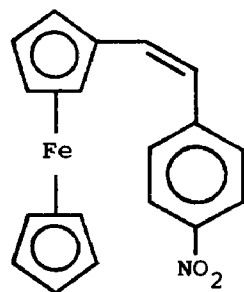
10.7



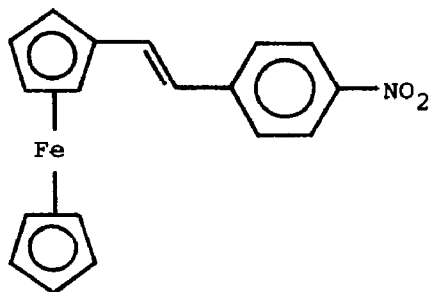
10.8



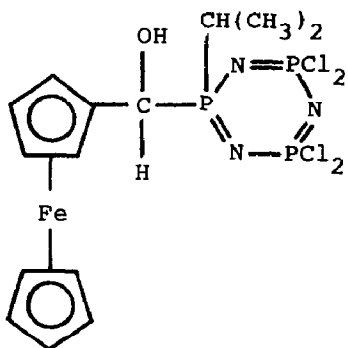
10.9



10.10



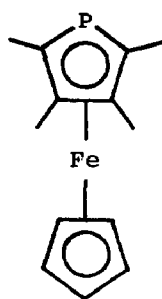
10.11



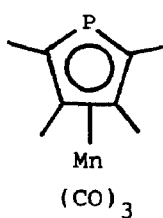
10.12

exhibited a large second-order optical nonlinearity [83]. Diferrocenylphosphine and ferrocenylphenylphosphine have been used as ligands to replace a carbonyl group in benchtorene and cymantrene by photolysis [84].

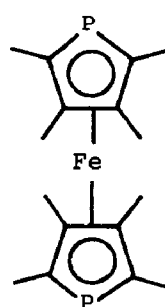
The structure of 4,4,6,6-tetrachloro-2-[ferrocenyl(hydroxy)-methyl]-2-isopropyl-1,3,5,2 λ^5 , 4 λ^5 ,6 λ^5 -triazatriphosphorine (10.12) has been determined by X-ray analysis. The N_3P_3 ring had an envelope conformation and the η -cyclopentadienyl rings were almost eclipsed [85]. Reaction of 1-phenyl-2,3,4,5-tetramethylphosphole with $[(\eta-C_5H_5)Fe(CO)_2]_2$ and $Mn_2(CO)_{10}$ produced the ferrocene and cymantrene analogues (10.13 and 10.14)



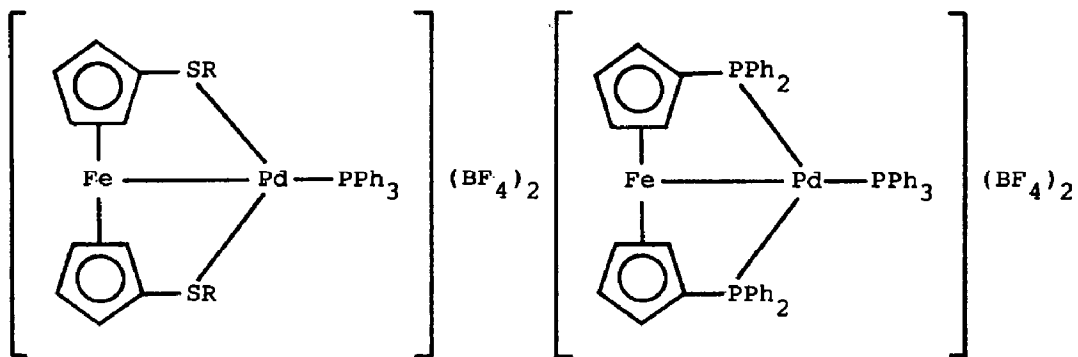
10.13



10.14



10.15

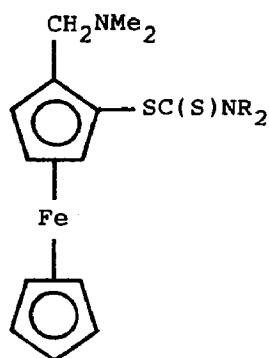


10.16

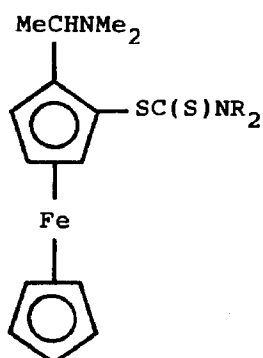
10.17

respectively. Cleavage of the P-Ph bond of the phosphole was achieved with lithium and reaction of the resultant phospholy anion with iron(II) chloride afforded bis(η^5 -2,3,4,5-tetramethylphospholy)iron (10.15) as fairly air-stable bright red crystals [86].

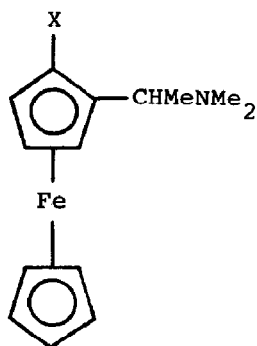
Reaction of 1,1'-bis[(alkyl- or phenyl-)thio]- and 1,1'-bis(diphenylphosphino)-ferrocenes with $(\text{CH}_3\text{CN})_4\text{Pd}(\text{BF}_4)_2$ in the presence of triphenylphosphine afforded the corresponding 1:1 complexes (10.16; R = Me, *i*-Pr, *i*-Bu, CH_2Ph , Ph and 10.17). Spectral data suggests the presence of an Fe-Pd dative bond in these complexes [87].



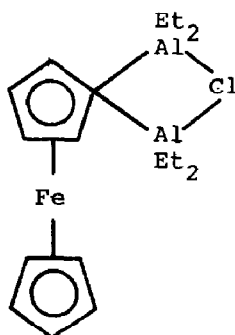
10.18



10.19



10.20



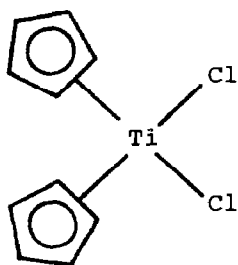
10.21

The condensation of 1-lithio-2-dimethylaminomethylferrocene or 1-lithio-2-dimethylaminomethylferrocene with tetraalkylthiuram disulphides produced the corresponding dialkylthiocarbamoylthio compounds (10.18 and 10.19; R = Me, Et) [88]. Lithiation of optically active *N,N*-dimethyl-1-ferrocenylethylamine (10.20; X = H) followed by reaction with disulphides gave the chiral ferrocenyl sulphide ligands (10.20; X = MeS, EtS, Me₂CHS, BuS, Me₂CHCH₂S, Me₃CS, isopentylS, PhS, PhCH₂S, 4-Me.C₆H₄.S, 4-Cl.C₆H₄.S). The ligands formed complexes with palladium(II) and platinum(II) chlorides and these were used as asymmetric Grignard cross-coupling catalysts. The structure of one ligand (*R,S*)-(10.20 X=SMe) was determined by X-ray crystallography [89].

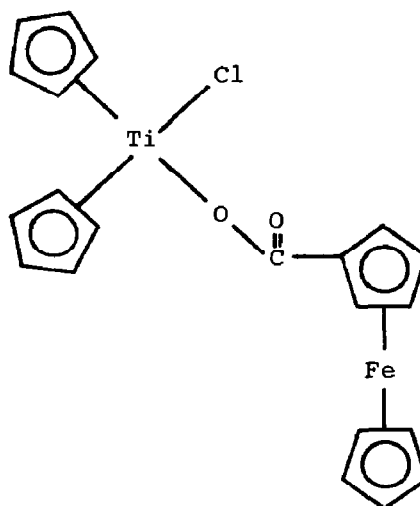
Reaction of ferrocenylmercurichloride with triethylaluminium produced the ferrocenylalane (10.21). This latter compound was characterized by X-ray analysis. The Al-Cl-Al-C ring was planar and there was no significant Al-Fe interaction [90].

The reactions of ferrocenyl-carboxylic acids with the titanium complex (10.22) have been investigated. For example, the reaction with ferrocenylcarboxylic acid in the presence of sodium amide produced the bimetallic compound (10.23) [91].

The osmium cluster complex, Os₃(CO)₁₀(MeCN)₂ combined with azaferrocene to give the addition product (10.24) under mild conditions [92]. Reaction of ferrocenylethyne with Os₃H₂(CO)₁₀ produced the complex (10.25) together with two other ferrocene containing metal carbonyl compounds. Thermolysis of the complex (10.25) produced the triosmium containing cluster (10.26).



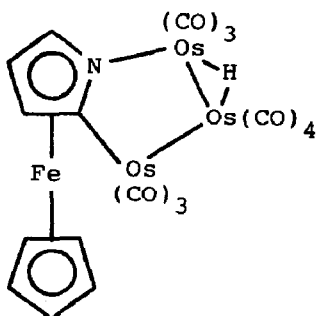
10.22



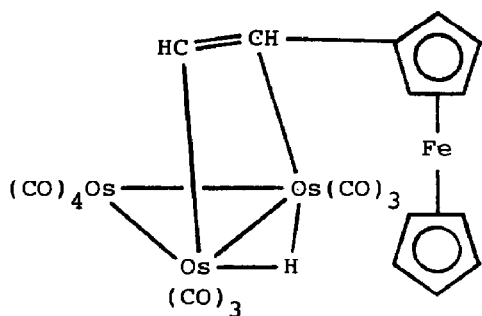
10.23

Further reactions of this cluster compound were investigated [93].

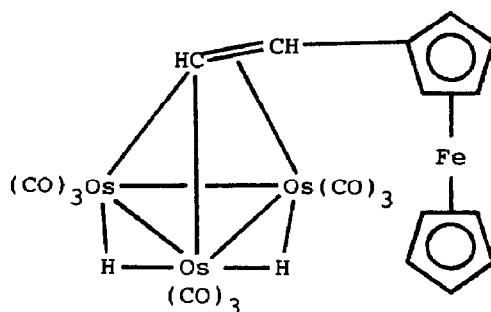
Treatment of bromoferrocene with *n*-butyllithium followed by $\text{CuBr} \cdot \text{PPh}_3$ gave the polymeric ferrocenylcuprate (10.27). Reaction of this cuprate with organolithium or Grignard reagents RM , where $\text{R} = \text{Ph}, \text{Me}, 4\text{-Me}_2\text{NC}_6\text{H}_4, (\eta\text{-}2\text{-Me}_2\text{NCH}_2\text{C}_5\text{H}_3)\text{Fe}(\eta\text{-C}_5\text{H}_5)$, $\text{M} = \text{Li}, \text{MgBr}$, gave the corresponding cross-coupled products (10.28) [94]. A series of copper and silver derivatives of ferrocene and cymantrene have been prepared and subjected to X-ray analysis. For example, the silver complex (10.29) was prepared by the treatment of 2-lithiodimethylaminomethylferrocene



10.24



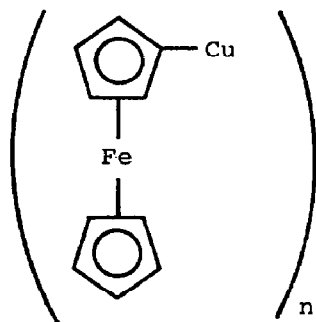
10.25



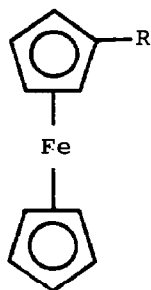
10.26

with $\text{AgNO}_3 \cdot 3\text{PPh}_3$. The copper complex (10.30) was prepared by a similar reaction [95].

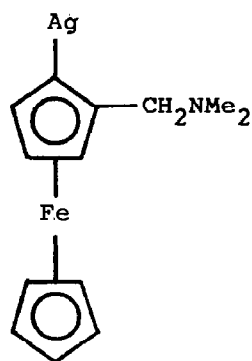
Trithia- and tetrathiaferrocenophanes formed copper(I) complexes on treatment with copper(II) tetrafluoroborate [96]. The crystal structures of 1,1'-bis(diphenylphosphino)ferrocene and the nickel complex (10.31) have been determined by X-ray analysis. The geometry around the nickel atom in the complex (10.31) was approximately tetrahedral with a larger Cl-Ni-Cl angle of 125° due to repulsion of the Cl atoms [97]. The nickel(II) bromide complex of (S)-1-[(R)-2-(diphenylphosphino)-



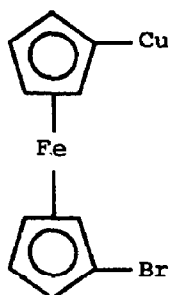
10.27



10.28



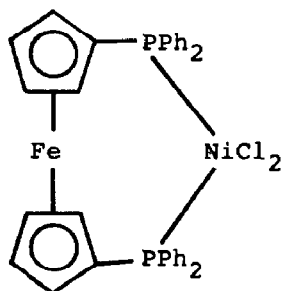
10.29



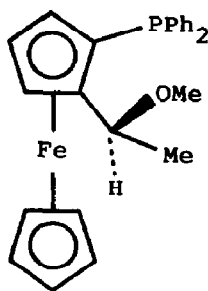
10.30

ferrocenylethyl methyl ether (10.32) has been used as a catalyst for the cross-coupling of naphthyl Grignard reagents with naphthyl bromides to give asymmetric 1,1'-binaphthyls in good yield [98].

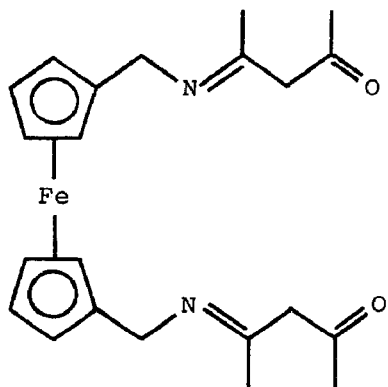
Acetylacetone has been treated with 1,1'-bis(aminomethyl)-ferrocene to give the derivative (10.33) which has been used as a binucleating ligand in reactions with cyclopalladated complexes of benzo[h]quinoline and *N,N*-dimethylbenzylamine [99]. The reaction of the platinum and palladium complexes (10.34; $M = \text{Pt}, \text{Pd}$) with silver tetrafluoroborate in different solvents has been used to prepare the corresponding bridged complexes (10.35; $X = \text{OH}, \text{Cl}$). The structure of the μ -hydroxo compound (10.35; $M = \text{Pt}, X = \text{OH}$) has been determined by X-ray analysis.



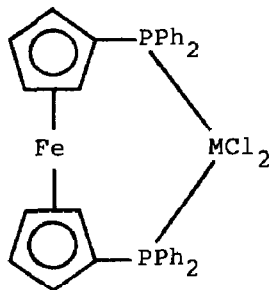
10.31



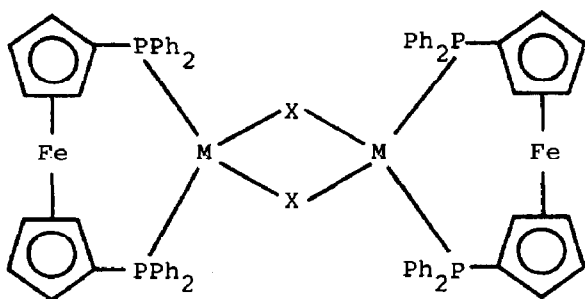
10.32



10.33



10.34

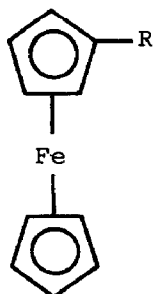


10.35

The ligand geometry around the platinum atoms was distorted square planar [100]. Mercury(II) halides formed complexes with ferrocene, biferrocene and [2]ferrocenophane. Moessbauer and ^{13}C NMR spectroscopy indicated direct mercury-iron bonding [101].

10. (ii) Photochemistry

Irradiation of the ferrocene-tetracyanoethylene complex in solution produced cyanoferrocene. When the same reaction was carried out in the solid state cyanoferrocene and 1,2-diferrocenyl-1,1,2,2-tetracyanoethane were produced [102]. The photochemical properties of ferrocene, cobaltocene and nickelocene and their complexes with 2,2,2-trichloroethanol



10.36

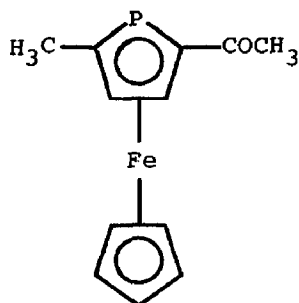
in solution have been investigated. When exposed to near ultra-violet and argon laser irradiation the ferrocene solutions were stable. In the presence of 2,2,2-trichloroethanol photooxidation occurred to give the ferrocenium ion [103].

The photolysis of substituted ferrocenes (10.36; R = H, COMe, COEt, CHMeOH) in the presence of N-t-butyl-2-phenylnitrene has given radicals which were studied by ESR spectroscopy [104]. The quantum yield for the generation of the T_1 state of ferrocene and the lifetime of the state have been measured using the sensitized isomerization of D-glucose phenylosazone [105].

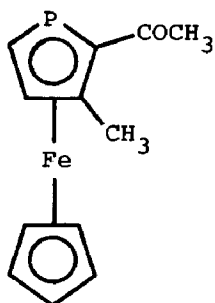
10. (iii) General chemistry

Acetylation of 2-methylphosphaferrocene with $CF_3SO_3H/-(CH_3CO)_2O$ afforded only the 2,5-isomer (10.37). Acetylation of 3-methylphosphaferrocene produced both isomers (10.38 and 10.39) resulting from α -acetylation. The effect of the methyl group on acetylation was very similar to that found in methylferrocene. The reactivity of phenylphosphaferrocenes was also investigated [106].

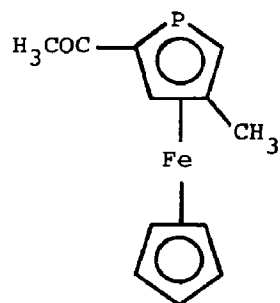
The complete oxidation of metallocenes including ferrocene and related compounds with hydroperoxides, Me_3COOH and $HOOH$ has been studied. Carbon dioxide was a primary product [107]. Diferrocenylcyclopropanes have been treated with trityl tetrafluoroborate, to give the products of cyclopropane ring opening, thus the cyclopropane (10.40) gave the salt (10.41) [108]. The metalation of alkynes with mercury(II) acetate has been



10.37



10.38

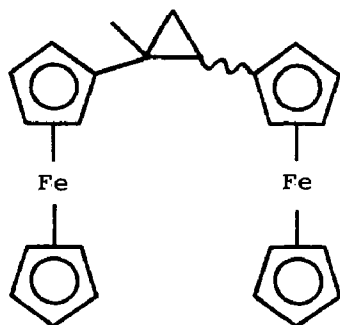


10.39

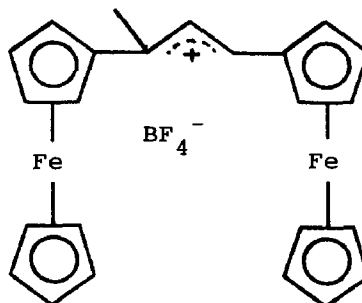
systematically investigated. Ethynylferrocene was one of the substrates examined [109].

The reaction of ethynylferrocene with arenesulphenyl chlorides proceeded by substitution of the acetylenic proton rather than electrophilic addition to the triple bond. For example, treatment of ethynylferrocene with *p*-chlorobenzenesulphenyl chloride gave initially *p*-chlorophenylthio(ferrocenyl)ethyne (10.42) in good yield. Further reaction produced the olefins (10.43 and 10.44). A mechanistic scheme was proposed for this reaction [110].

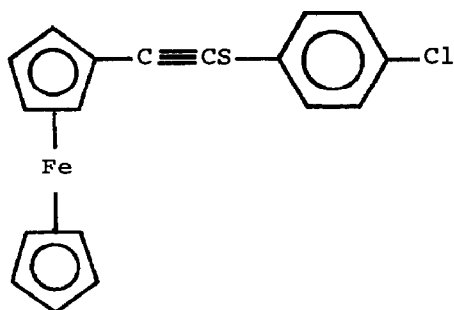
Reaction of (3,3-dicyano-2-ferrocenylallyl)(η -cyclopentadienyl)dicarbonyliron (10.45) with iodine produced the alkenes



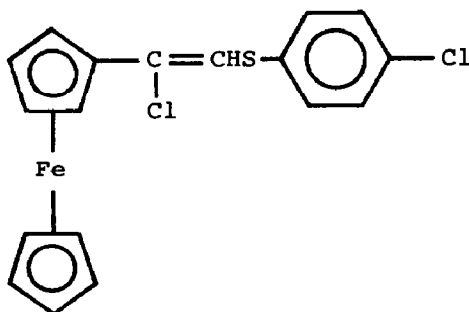
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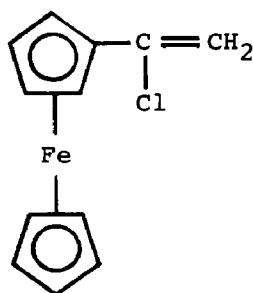
10.41



10.42



10.43

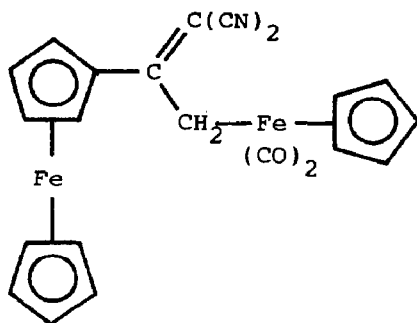


10.44

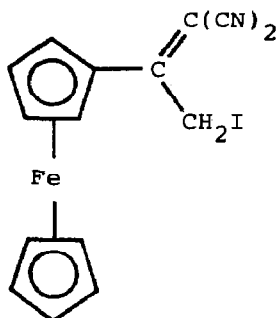
(10.46 and 10.47) as the ferrocene containing products. Treatment of the complex (10.45) with lithiocymantrene or lithium aluminium hydride gave the alkene (10.48) as the ferrocene containing product [111].

Diels-Alder reaction of the 1,3-diferrocenyl-1,3-alkadienes (10.49; $R^1 = R^2 = H$; $R^1 = Me, R^2 = H$; $R^1 = H, R^2 = Me$) with the maleimides (10.50; $R = Ph, PhCH_2$) gave the corresponding condensation products (10.51) as a mixture of *exo*- and *endo*-isomers [112]. Electron transfer from the potassium salt of cyclooctatetraene to the nitro-olefin (10.52) gave the dimer (10.53) in almost quantitative yield [113].

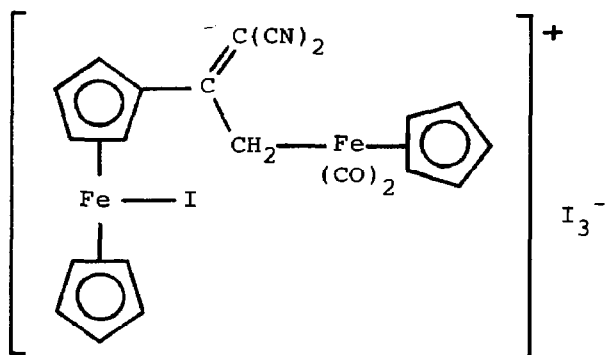
Reduction of the ester (10.54; $R = CO_2Me$) with lithium aluminium hydride produced the alcohol (10.54; $R = CH_2OH$).



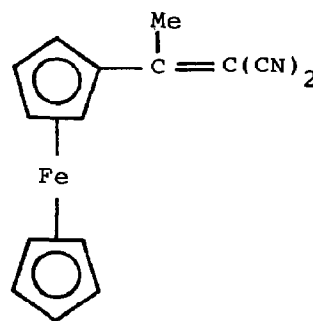
10.45



10.46



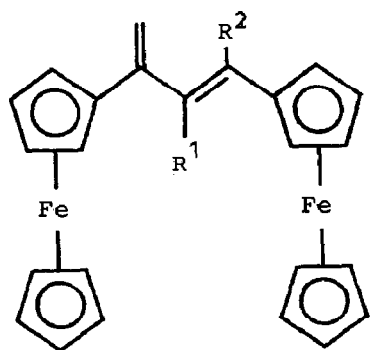
10.47



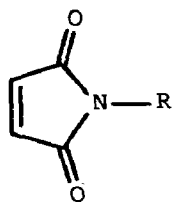
10.48

Chlorination of this alcohol with PCl_3 in the presence of pyridine gave the alkyl halide (10.54; $\text{R} = \text{CH}_2\text{Cl}$). The reactions of this alkyl halide with oxygen, sulphur, nitrogen and carbon nucleophiles produced the corresponding ferrocenylmethyl derivatives [10.54; $\text{R} = \text{CH}_2\text{OPh}$, CH_2SPh , CH_2NMePh , $\text{CH}_2\text{CH}(\text{COMe})_2$, $\text{CH}_2\text{C}(\text{CO}_2\text{Et})_2\text{NHCHO}$] [114].

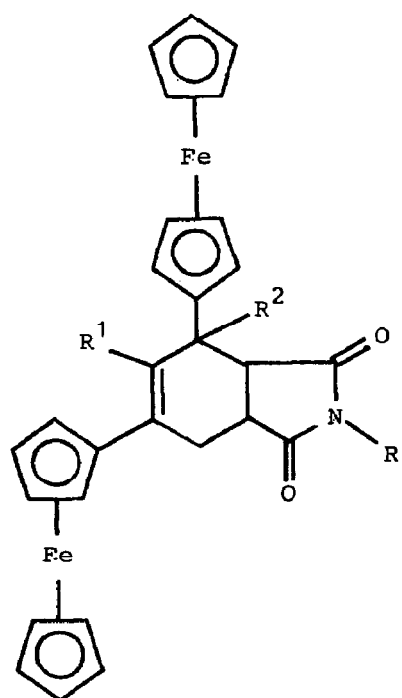
The nonamethylferrocenyl-carbinols (10.55; $\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, C_6F_5 , α -naphthyl) have been prepared by treating the parent aldehyde with the corresponding organolithium agents RLi . The ^1H NMR spectra of the carbinols and their cations were recorded [115].



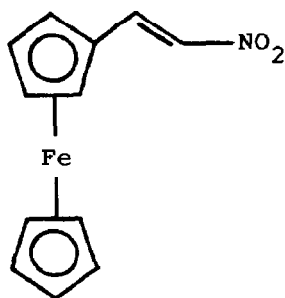
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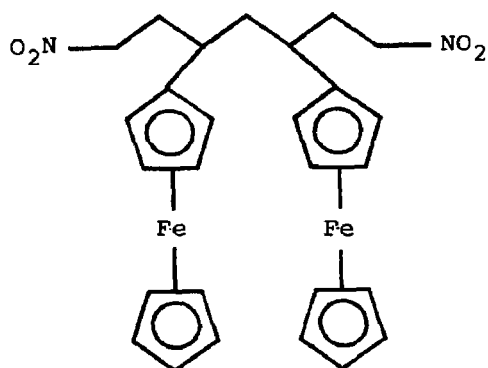
10.50



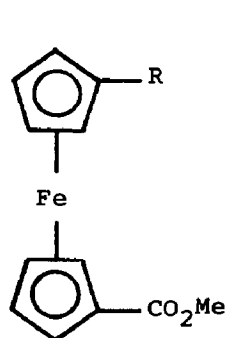
10.51



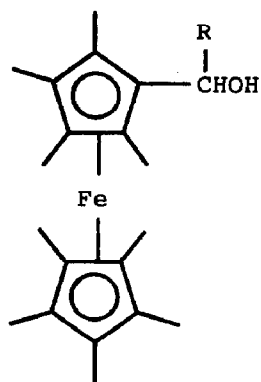
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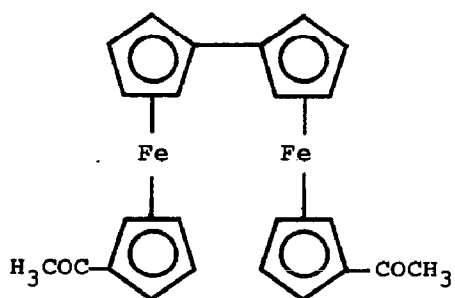
10.53



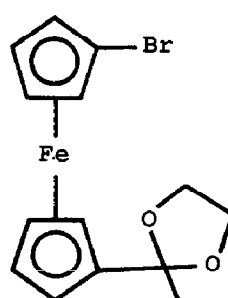
10.54



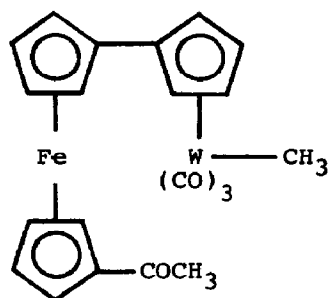
10.55



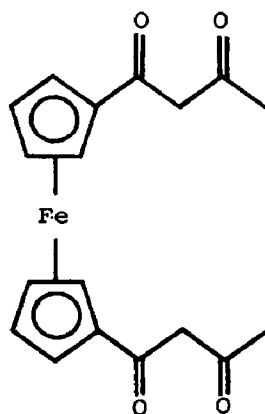
10.56



10.57



10.58



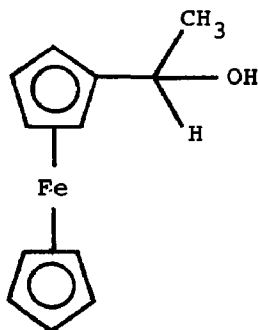
10.59

The diacetylferrocene (10.56) was prepared by a Grignard coupling reaction of the bromo-ferrocene (10.57). The biferrocene (10.56) was electrochemically reduced and the reduction mixture was treated with $W(CO)_3(PrCN)_3$ and methyl iodide to give the heterobimetallic fulvalene complex (10.58). The electrochemical properties of the complex (10.58) were investigated [116]. Reaction of 1,1'-diacetylferrocene with ethylacetate in the presence of sodium amide gave the ketone (10.59) [117].

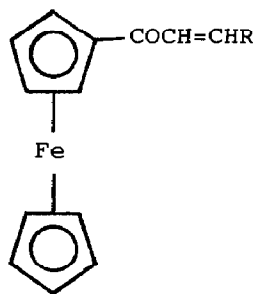
Formylferrocene and acetylferrocene were included in a series of aldehydes and ketones that were treated with alkyl-uranium compounds which were being used as selective nucleophilic reagents. For example, the treatment of formylferrocene with $[(Me_3Si)_2N]_3UCH_3$ followed by hydrolysis gave the alcohol (10.60) in 92% yield [118].

Homoionic forms of montmorillonite have been used as catalysts for the Diels-Alder cycloaddition of acryloylferrocene to 1-phenyl-1,3-butadiene. The reactions showed high yields and high selectivity by comparison with the aluminium chloride catalyzed reaction [119]. Friedel-Crafts acylation of ω -phenyl-alkanoylferrocenes with cinnamoyl chloride led to attack at the unsubstituted cyclopentadienyl ring while acylation with phenylpropionyl chloride caused substitution in the benzene ring [120].

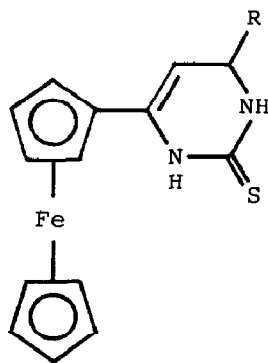
Formylferrocene has been treated with 1-oximino-2-hydroxyl-amino-1-phenyl-2-methylpropane and the product oxidized with lead(IV) oxide in methanol to give a spin labelled ferrocene [121].



10.60



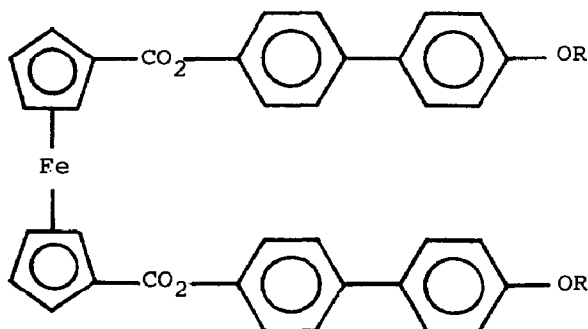
10.61



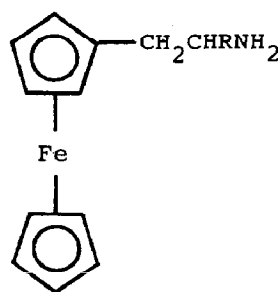
10.62

Ultrasound accelerated the base catalyzed addition of thiourea to the ferrocenyl-chalcone analogues (10.61; R = Ph, *p*-tolyl, *p*-anisyl, 3,4-methylenedioxyphenyl, *p*-ClC₆H₄) to give the corresponding pyrimidines (10.62) [122].

Frederic and Toma have described the preparation of eleven analogues of chalcones, where an organometallic group was attached to the β -carbon of the chalcone double bond. The organometallic species included ferrocene and substituted ferrocenes [123]. The coupling of 1,1'-di(chlorocarbonyl)ferrocene with 4-alkoxy-4-biphenols has been used to prepare a series of ferrocene diesters (10.63; R = C₄H₉, C₅H₁₁, C₆H₁₃, C₇H₁₅, C₈H₁₇, C₉H₁₉, C₁₀H₂₁, C₁₁H₂₃), some of which exhibited liquid-crystal phases [124].



10.63



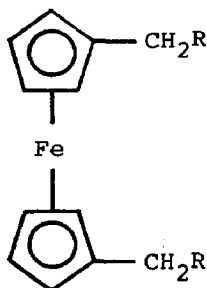
10.64

Nitrovinylferrocenes have been reduced with lithium aluminium hydride to give the corresponding ferrocenylaminoalkanes (10.64; R = H, Me, Et) which were amphetamine analogues. The ferrocene compounds (10.64) were converted to ^{103}Ru labelled ruthenocenes by reaction with $^{103}\text{RuCl}_3$ [125]. Treatment of 1,1'-di(chloromethyl)ferrocene with $\text{HCONHCH}(\text{CO}_2\text{Et})_2$ in the presence of sodium hydride produced the ester [10.65; R = $\text{C}(\text{CO}_2\text{Et})_2\text{NHCHO}$]. Saponification of this ester followed by decarboxylation gave the ferrocenyl-alanine derivative [10.65; R = $\text{CH}(\text{NHCHO})\text{CO}_2\text{H}$] [126].

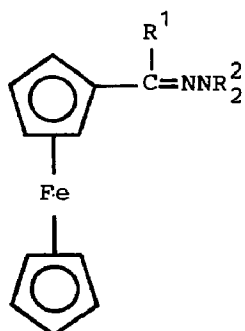
The condensation of acetyl- or 1,1'-diacetyl-ferrocene with a series of substituted hydrazines $\text{H}_2\text{NNHCOC}_6\text{H}_4\text{R}$, where R = H, 3- NO_2 , 3-Br, 4-OMe, 4- NMe_2 , afforded the corresponding hydrazones. Complexes of these hydrazones with Ni, Cu, Zn, Cd, Hg and Pd were prepared. The metal complexes were examined by infrared spectroscopy and their magnetic properties were studied [127].

The condensation of formyl-, acetyl- or benzoyl-ferrocene with hydrazines produced the corresponding hydrazones (10.66; $\text{R}^1 = \text{H}, \text{CH}_3, \text{Ph}$; $\text{R}^2 = \text{H}, \text{CH}_3$). Reaction of these hydrazones with cobalt salts gave polymeric complexes that contained six-coordinate cobalt and terminal hydrazone ligands [128]. Reaction of 1,1'-diacetylferrocene with the hydrazines $\text{RC}(\text{X})\text{NHNH}_2$, where X = S, R = NHNH_2 ; X = O, R = $\text{NH}_2, \text{Ph}, \text{p-O}_2\text{NC}_6\text{H}_4$, produced the corresponding condensation products (10.67) [129].

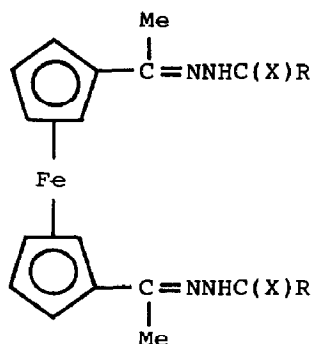
Dimethylaminomethylferrocene has been lithiated and then treated with disulphides, RSSR , and diselenides, RSeSeR , to



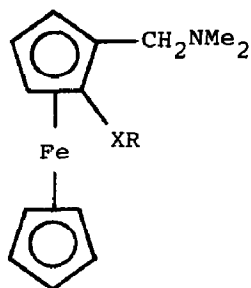
10.65



10.66



10.67



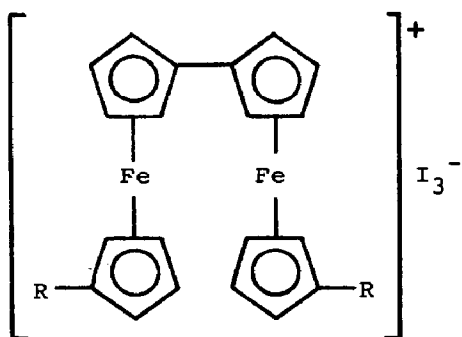
10.68

give the chalconide derivatives (10.68; X = S, Se; R = Pr, Bu, EtMeCH, Me₃C, PhCH₂, 4-Me.C₆H₄, 4-Cl.C₆H₄) which formed complexes with platinum(II) chloride and palladium(II) chloride. These complexes were selective homogeneous and heterogeneous catalysts for the reduction of dienes to monoenes [130].

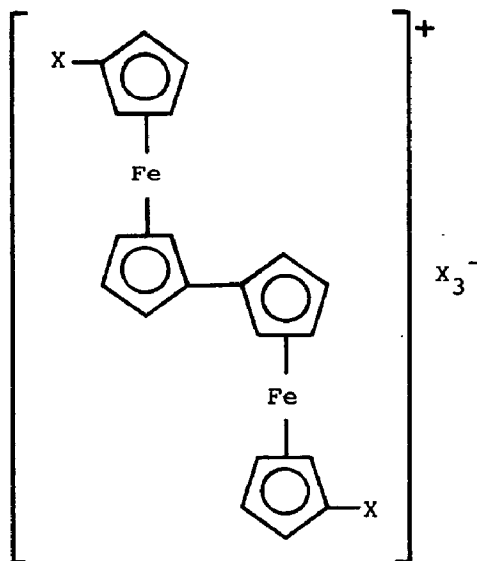
11. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

Moessbauer and ESR spectroscopy have been used to study mixed valence behaviour in the biferrocenium salts (11.1). One crystal form of the salt (11.1; R = n-butyl) showed trapped-valence behaviour at low temperatures and mixed-valence character at higher temperatures while a second crystal form showed only a trapped-valence state at all temperatures. In the same way the isobutyl derivative (11.1; R = iso-butyl) showed temperature dependent behaviour and the salt (11.1; R = pentyl) exhibited only trapped-valence character [131].

The effects of cooperative intermolecular interactions on the electronic delocalization in mixed valence biferrocenium trihalides (11.2; X = H, Et, n-Pr, n-Bu, Cl, Br, I; X₃⁻ = I₃, Br₂I) have been investigated. A model was proposed for these systems and the model successfully explained data obtained via Moessbauer spectroscopy, heat capacity measurements, X-ray crystallography and infrared spectroscopy [132]. The condensation of formylferrocene with a series of ketones produced the corresponding ferrocenylidene ketones, for example, condensation with acetone gave the ketone (11.3). In the same paper it was



11.1

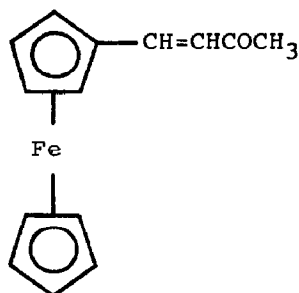


11.2

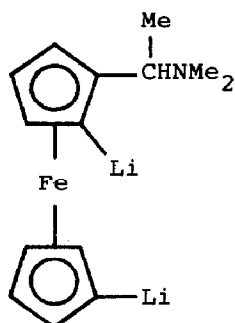
reported that the treatment of lithioferrocene with methylbenzoate or phthalic anhydride gave a mixture of ferrocene and biferrocene [133].

The reaction of the dilithio-ferrocene (11.4) with tetrachlorosilane produced the ferrocenophane (11.5). X-ray analysis indicated that the tilt angle between the η -cyclopentadienyl rings was 19.0° . Treatment of the ferrocenophane (11.5) with methanol produced the 1,2-disubstituted ferrocene (11.6) together with other products [134]. A kinetic study of the formation of dihydrogen from the reaction of [1.1]ferrocenophane (11.7), 3,3'-trimethylene[1.1]ferrocenophane and 2,2'-trimethylene[1.1]ferrocene with acids has been carried out using tensiometry and spectrometry. The results were consistent with a three-step mechanism for the formation of hydrogen. A very fast initial protonation, a slower second protonation and the elimination of hydrogen as the rate determining step [135].

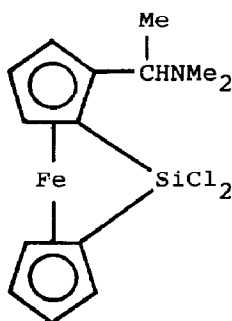
The [2]meta- and [2]para-cycloferrocenophanes (11.8 and 11.9) respectively have been prepared by cyclocondensation. X-ray crystallographic structure investigations indicated that the benzene ring in each cyclophane was distorted but the cyclopentadienyl rings maintained planarity [136]. The (η -indenophane)-iron complex (11.10) has been formed by treatment of the free



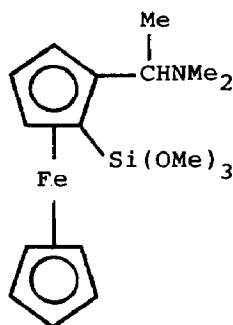
11.3



11.4



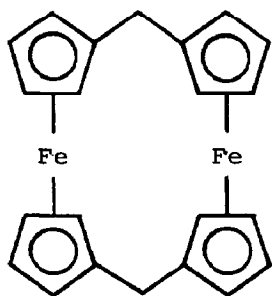
11.5



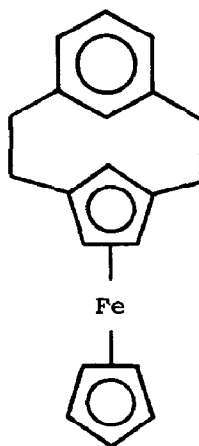
11.6

indenophane ligand with iron(II) chloride and lithium cyclopentadienide. This complex (11.10) was in turn treated with methyl-lithium and iron(II) chloride to give the multidecker metallocenophane (11.11) [137].

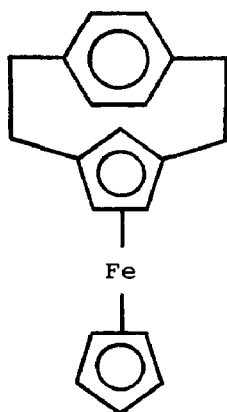
The one-electron oxidation product of as-indacenebis(cyclopentadienyliron) as the triiodide salt has been studied by Moessbauer spectroscopy. At low temperatures the spectra of Fe(II) and Fe(III) were observed indicating a trapped-valence species while at room temperature the spectrum indicated an averaged-valence species. Comparisons were made with dihalo- and dialkylbiferrocenium triiodides [138]. The bis[(η -pentamethylcyclopentadienyl)metal] η -pentalene complexes (11.12;



11.7



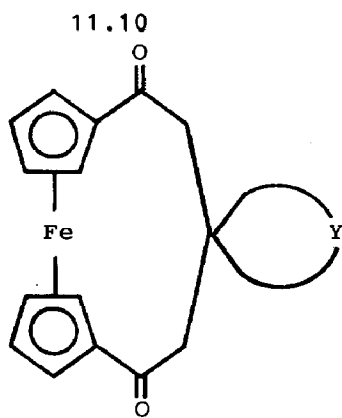
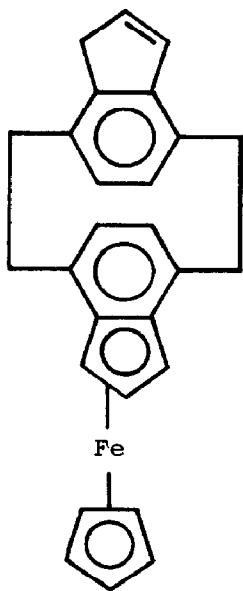
11.8



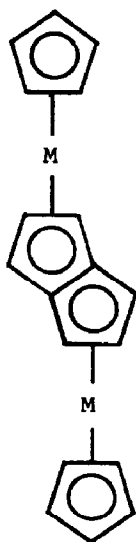
11.9

M = Fe, Co, Ni) have been prepared and characterized by electrochemistry and X-ray crystallography. An extended Hückel molecular orbital diagram for the iron complex (11.12; M = Fe) was constructed [139].

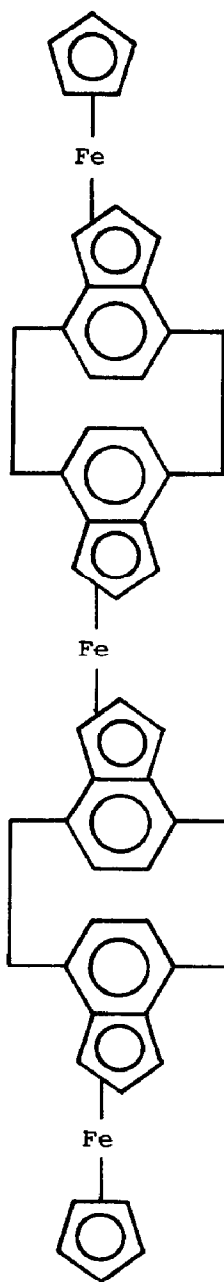
Condensation of 1,1'-diacetylferrocene with cyclohexanone, alkyl- or phenyl-cyclohexanones and cycloheptanone produced the corresponding 3-spiro[5]ferrocenophane-1,5-diones [11.13; Y = (CH₂)₃, CH₂CHMeCH₂, CH₂CHEtCH₂, CH₂CH(i-Pr)CH₂, CH₂CH(t-Bu)CH₂, CH₂CHPhCH₂, CH₂CMe₂CH₂, CHMe(CH₂)₂, CHPh(CH₂)₂, CH₂ $\overline{\text{CH}(\text{CH}_2)_4}$ CH, (CH₂)₄]. The NMR spectra of these ferrocenophanes were recorded and discussed [140]. Reaction of 1,1'-bis(p-hydroxymethylphenyl)-ferrocene with triphenylphosphine produced the ferrocenophane



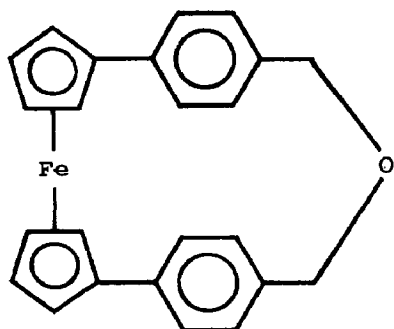
11.13



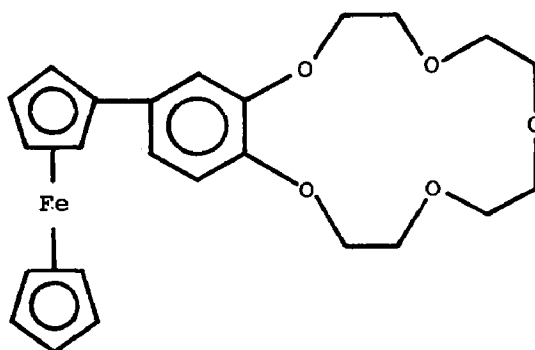
11.12



11.11



11.14



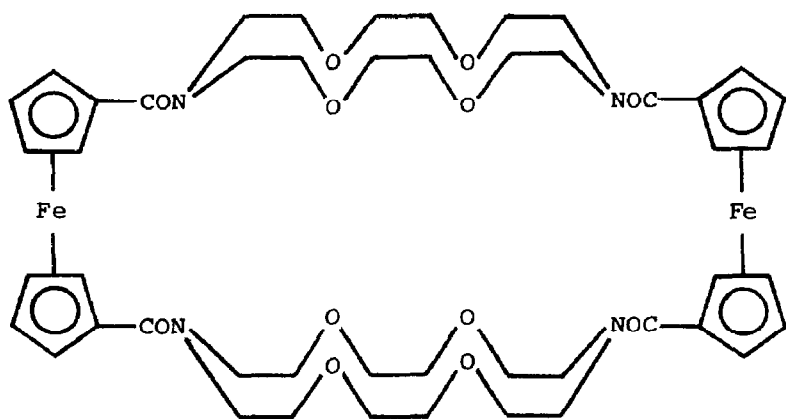
11.15

(11.14). ^1H NMR spectroscopy indicated that this molecule was fluxional and in dynamic equilibrium between eclipsed and staggered conformations [141].

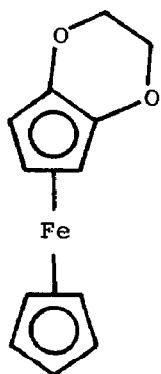
Ferrocene crown ethers such as the benzo-15-crown-5 (11.15) have been prepared from the ferrocenium ion and the diazonium salt of the corresponding amine. The binding of Na^+ , K^+ and Mg^{2+} to the crown ether (11.15) caused the oxidation wave of the ferrocene to be shifted to more positive potentials. The magnitude of the shift was related to the charge/radius ratio of the cationic guest. The crystal and molecular structure of the sodium salt of the crown ether (11.15) has been determined by X-ray crystallography [142].

The metallocene bridged cryptand (11.16) has been characterized by X-ray crystallography and shown to contain a large cryptand cavity. This was in agreement with the complexing properties observed for the species [143]. The reaction of 1,2-di(hydroxymethyl)ferrocene with α,ω -alkanedithiols in the presence of trifluoroacetic acid gave mononuclear dithia- and binuclear tetrathia-ferrocenophanes. Ethylene glycol combined with 1,2-ferrocenediol to form the dioxoferrocenophane (11.17). The cyclic tetramer (11.18) was formed in the same reaction [144].

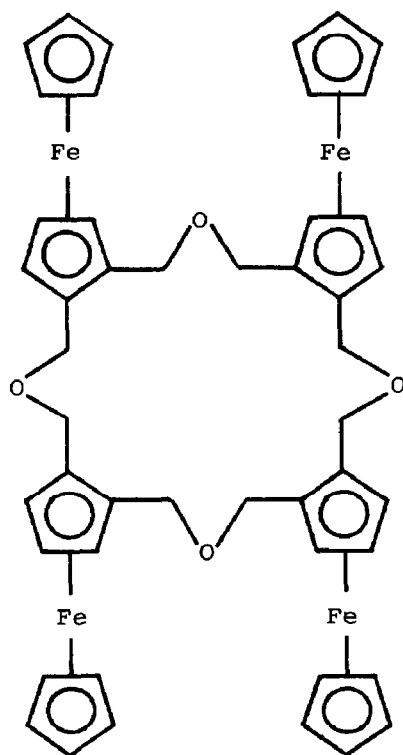
Ferrocenecarbonyl chloride has been condensed with calix[4]-arene to give the bis-ferrocene calix[4]arene (11.19). X-Ray



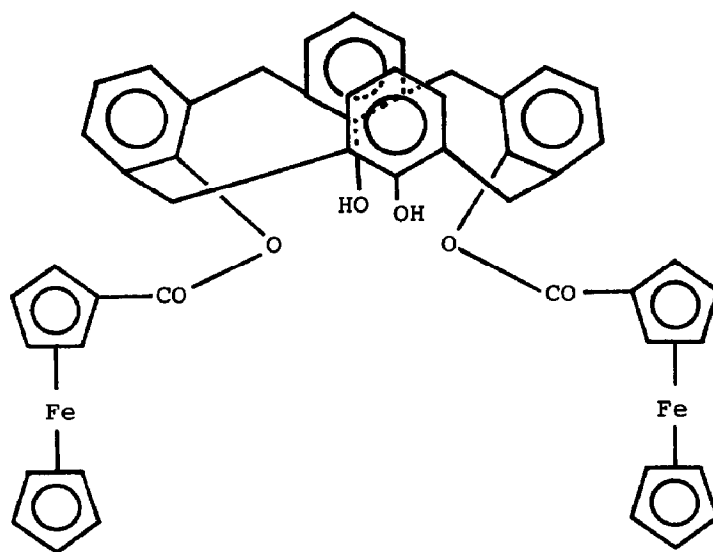
11.16



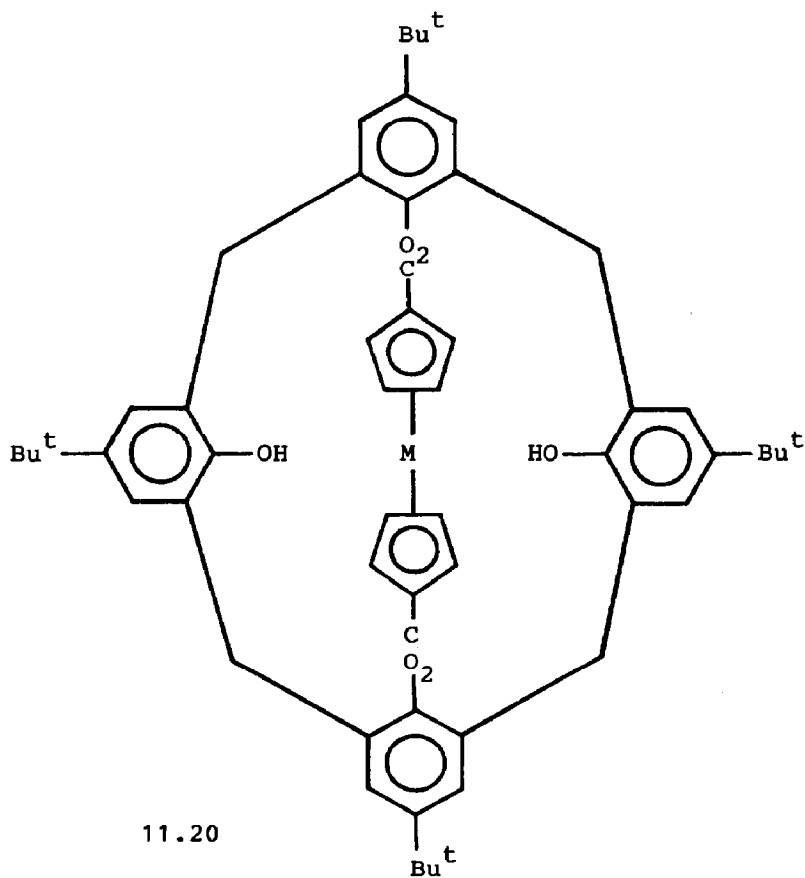
11.17



11.18



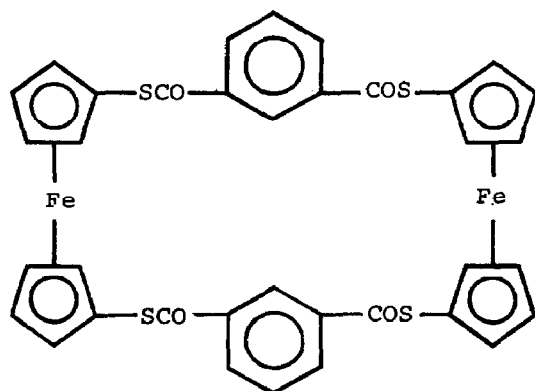
11.19



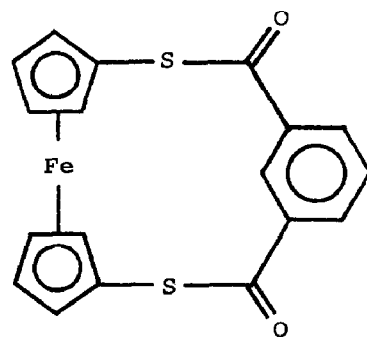
11.20

crystallography was used to demonstrate the cone conformation of the molecule [145]. The metallocene calix[4]arenes (11.20; M = Fe, Ru) have been prepared by treatment of the parent calix-arene with 1,1'-bis(chlorocarbonyl)metallocenes [146].

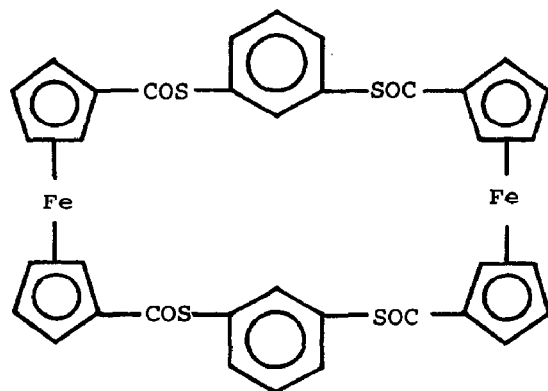
A number of sulphur-containing ferrocenophanes have been prepared from ferrocene-1,1'-dithiol or ferrocene-1,1'-bis(carbonylchloride). Thus the ferrocenophanes (11.21 and 11.22) were obtained from ferrocene-1,1'-dithiol and the corresponding diacid chloride while the ferrocenophanes (11.23 and 11.24) were formed from ferrocene-1,1'-bis(carbonylchloride) and the appropriate aromatic dithiol [147].



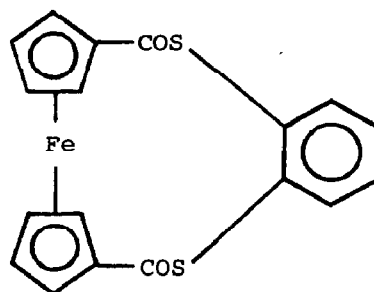
11.21



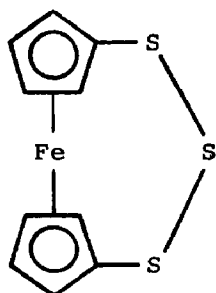
11.22



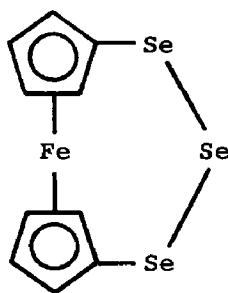
11.23



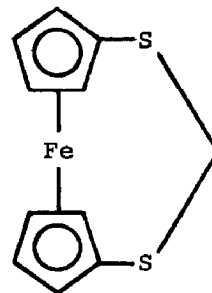
11.24



11.25



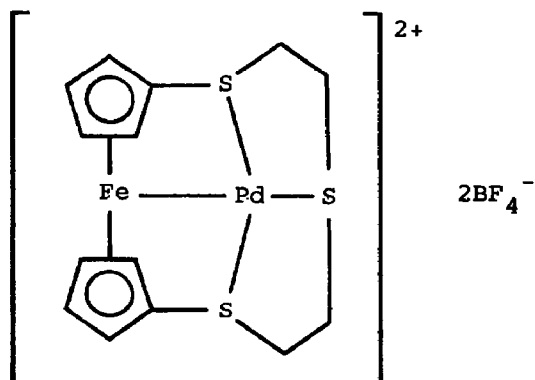
11.26



11.27

The oxidation potentials of 1,2,3-trithia- (11.25), 1,2,3-triseleno- (11.26) and 1,3-dithia[3]-ferrocenophane (11.27) have been determined. These ferrocenophanes had high oxidation potentials relative to ferrocene, 1,1'-bis(methylthio)ferrocene and methylene bridged [3]-ferrocenophane. The photoelectron spectrum of 1,2,3-trithiaferrocenophane (11.25) indicated that the d-electrons of iron were attracted by the sulphur bridge [148].

Trithia[n]- and tetrathia[n]-ferrocenophanes combined with palladium(II) tetrafluoroborate to form 1:1 complexes. Thus



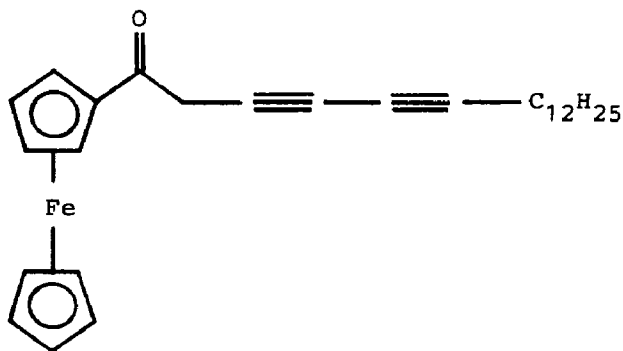
11.28

the complex (11.28) was shown by spectroscopy to have an iron-palladium bond [149]. The μ_3 -benzynes complex, $\text{Ru}_3(\text{CO})_7-(\mu_3-\eta^2-\text{C}_6\text{H}_4)[\mu_2\text{-PPh}(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)]_2$ has been formed by heating the carbonyl complex $\text{Ru}_3(\text{CO})_{10}[\text{PPh}_2(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)]_2$. The product was characterized by X-ray crystallography. The ferrocenyl groups were trans with respect to the plane of the Ru_3 triangle [150].

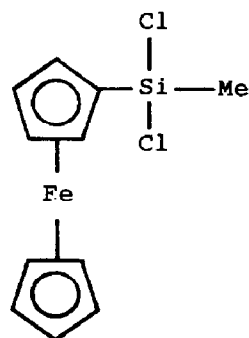
12. FERROCENE-CONTAINING POLYMERS

The alkynes RC_2H , where $\text{R} = \text{Ph}$, $n\text{-Bu}$, were polymerized instantaneously at 20° in the presence of 1% $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$ and 0.01% $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]^+\text{PF}_6^-$ as the catalyst [151]. Pressure-area isotherms and electronic spectroscopy have been used to study the photopolymerization of heptadeca-2,4-diynylferrocene-carboxylate (12.1) as a monolayer on water. Molecular packing determined the polymerization behaviour [152].

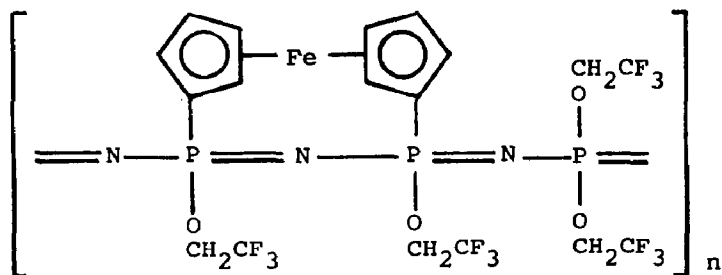
Ferrocene containing polysilanes have been prepared and the film forming properties examined. The reaction of these polymers with tetracyanoquinodimethane, tetracyanoethylene, chloranil and iodine gave charge transfer complexes. The properties of these complexes were investigated [153]. The copolymerization of ferrocenylmethyldichlorosilane (12.2) with phenylmethyldichlorosilane has been used to produce high molecular weight polymers. The photostability of these polymers was investigated [154].



12.1

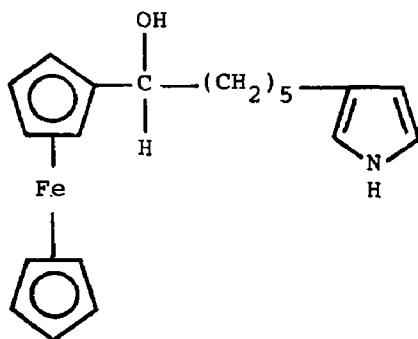


12.2



12.3

The electrochemical oxidation and reduction of ferrocene substituted polyphosphazenes (12.3) has been studied by cyclic voltammetry and chronoamperometry [155]. Electrochemical copolymerization of pyrrole with 3-(6-ferrocenyl-6-hydroxyhexyl)-pyrrole (12.4) afforded a polymer containing controllable concentrations of ferrocene. The polymer films were deposited on electrodes and electrochemical properties were investigated. Cyclic voltammetry showed two different redox processes corresponding to the reduction-oxidation of the polypyrrole polymer backbone and the ferrocene moiety [156].

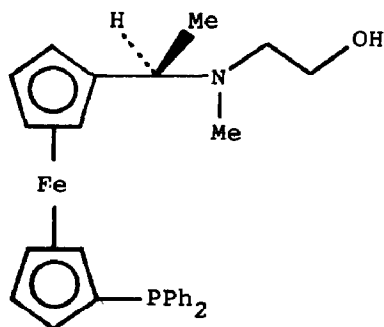


12.4

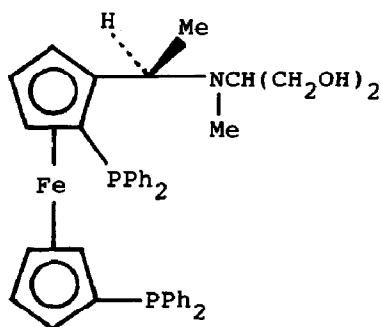
13. APPLICATIONS OF FERROCENE

(i) Ferrocene catalysts and photosensitizers

Dithiourethanes underwent arylation with aryldiazonium tetrafluoroborates in acetone containing ferrocene. A radical mechanism was indicated [157]. Catalytic asymmetric allylation of sodium enolates of β -diketones with allyl acetate has been shown to proceed with high enantioselectivity in the presence of palladium catalysts containing functionalized chiral ferrocenylphosphine ligands, to give optically active ketones. The most effective ligand was the ferrocenylphosphine (13.1) [158].



13.1



13.2

Asymmetric cyclization of 2-butenylene dicarbamates has been catalyzed by chiral ferrocenylphosphine-palladium complexes. The highest stereoselectivity was obtained when the ferrocenylphosphine (13.2) was used as the ligand [159].

13. (ii) Combustion control

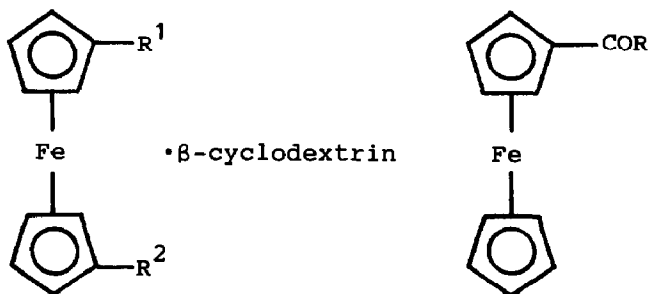
Ferrocene and substituted ferrocenes have been incorporated in polyisocyanate foams. The foams exhibited good heat resistance, improved flame resistance and emitted little smoke on combustion [160]. The temperature sensitivity of the burning rate of composite propellants has been investigated. The addition of 2,2-bis(ethylferrocenyl)propane reduced the temperature sensitivity [161].

13. (iii) Clathrate complexes

Enantioselective reduction of the carbonyl groups in the acylferrocene— β -cyclodextrin complexes (13.3; $R^1 = \text{COCF}_3$, $R^2 = \text{H}$; $R^1 = R^2 = \text{COCH}_3$) has been achieved with sodium borohydride to give the corresponding optically active alcohols [13.3; $R^1 = \text{CH(OH)CF}_3$, $R^2 = \text{H}$; $R^1 = R^2 = \text{CH(OH)CH}_3$] [162]. The acylferrocenes (13.4; $R = \text{H, Me, CF}_3$) together with some diacylferrocenes have been used to form inclusion complexes with α -, β -, and γ -cyclodextrins. The complexes were examined by circular dichroism and the induced Cotton effects were shown to correspond to the metallocene chromophores [163].

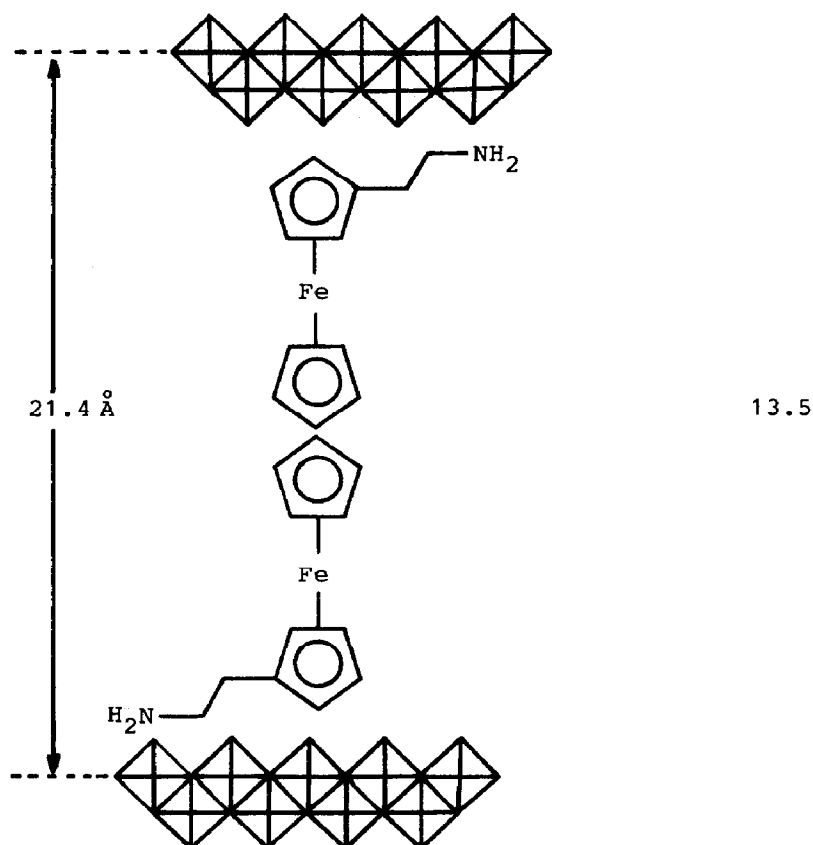
The complex formed by methyl ferrocenylacrylate and β -cyclodextrin has been studied by molecular modelling calculations. Reactivity of the ester was linked with twisting of the ester group out of full conjugation [164]. A series of inclusion compounds of ferrocene and its derivatives with α , β and γ -cyclodextrins have been prepared. β and γ -cyclodextrin formed 1:1 inclusion compounds whilst α -cyclodextrin formed 2:1 (host:guest) complexes with ferrocene and monosubstituted ferrocenes. The α - or β -cyclodextrin:ferrocene complexes were thermally stable up to 100° in vacuo [165].

Several aminoferrocenes have been prepared and intercalated into MoO_3 . For example, ferrocenylethylamine formed bilayers (13.5), as indicated by the stoichiometry and the large inter-layer separations. Diagram (13.5) is a representation of the



13.3

13.4



structure of the intercalate $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_2)]_{0.6}\cdot\text{MoO}_3$ [166]. Molecular nitrogen formed complexes with metallocenes at 16 K, $(\text{C}_5\text{H}_5)_2\text{M}\cdot\text{N}_2$ and $(\text{C}_5\text{Me}_5)_2\text{M}\cdot\text{N}_2$, where $\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$. At 80 K polymeric complexes were formed [167].

13. (iv) Ferrocene in analysis

α -Hydroxyethylferrocene has been used in the determination of iron in ores. The iron ore was dissolved in a mixture of hydrochloric and nitric acids to give a solution of Fe(III). α -Hydroxyethylferrocene was added and the corresponding ferrocenium ion was generated. The concentration of α -hydroxyethylferrocenium ion was estimated spectrophotometrically and the total iron present in the ore was determined [168].

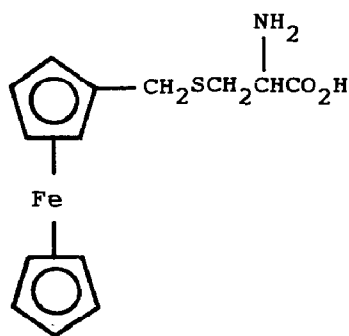
Ferrocene has been used as a reagent in the spectrophotometric determination of ferric oxide in cement. On addition of ferrocene to the iron(III) the ferrocenium ion was generated

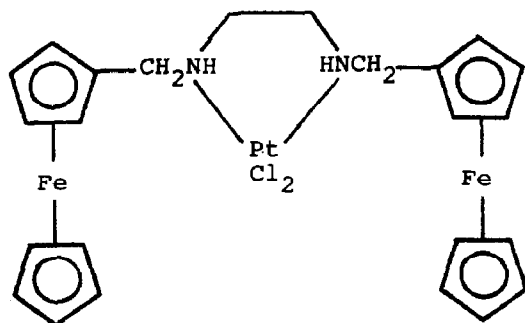
and then estimated [169]. Liquid chromatography on a polyamide column with aqueous α -cyclodextrin as the mobile phase has been used to resolve 1-ferrocenylethanol and similar compounds into the enantiomers [170].

13. (v) Biochemical and biological applications

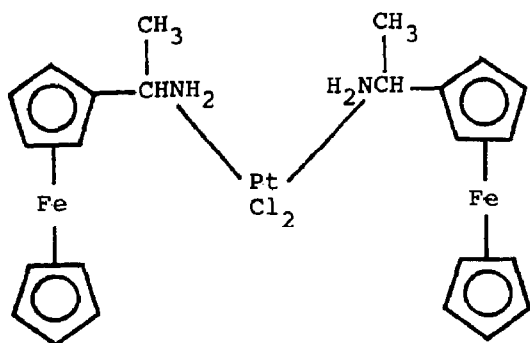
Glucose oxidase and ferrocenecarboxylate have been immobilised in a conducting polypyrrole film to form a simple biosensor used for the measurement of glucose [171]. Drey and Stewart have reported the preparation of S-ferrocenylmethyl-L-cysteine (13.6) from ferrocenylmethanol and L-cysteine in the presence of trifluoroacetic acid. The ferrocenylmethyl protected amino-acid (13.6) was used in the synthesis of glutathione [172].

The chemical reactivity and tribological properties of ferrocene sulphides as lubricant additives have been discussed [173]. Ferrocene containing platinum complexes have been prepared as potential antitumour agents. N,N'-Di(ferrocenylmethyl)ethane-diamine was prepared by condensing formylferrocene with 1,2-diaminoethane followed by reduction of the product with lithium aluminium hydride. Addition of the ligand to K_2PtCl_4 gave the complex (13.7). The addition of 1-ferrocenylethylamine hydrochloride to K_2PtCl_4 produced the complex (13.8). The antitumour activity of the complexes (13.7 and 13.8) was not reported [174].





13.7



13.8

REFERENCES

1. M. L. H. Green, J. Qin and D. O'Hare, *J. Organomet. Chem.*, 358 (1988) 375.
2. R. M. G. Roberts, J. Silver, B. M. Yamin, M. G. B. Drew and U. Eberhardt, *J. Chem Soc., Dalton Trans.*, (1988) 1549.
3. R. Arnold, B. M. Foxman, M. Rosenblum and W. B. Euler, *Organometallics*, 7 (1988) 1253.
4. Y. G. Luo, R. J. Barton and B. E. Robertson, *Can. J. Chem.*, 65 (1987) 2756.

5. M. Soriano-Garcia, A. Toscano, T. Lopez and A. Campero-Celis, *J. Crystallogr. Spectrosc. Res.*, 17 (1987) 719; *Chem. Abstr.*, 110 (1989) 23925.
6. P. D. Beer, C. D. Bush and T. A. Hamor, *J. Organomet. Chem.*, 339 (1988) 133.
7. I. Bernal, E. Raabe, G. M. Reisner, R. A. Bartsch, R. A. Holwerda, B. P. Czech and Z. Huang, *Organometallics*, 7 (1988) 247.
8. I. Bernal, G. M. Reisner, R. A. Bartsch, R. A. Holwerda and B. P. Czech, *Organometallics*, 7 (1988) 253.
9. R. L. Williamson and M. B. Hall, *Int. J. Quantum Chem., Quantum Chem. Symp.*, 21 (1987) 503; *Chem. Abstr.*, 109 (1988) 22992.
10. F. M. Menger and M. J. Sherrod, *J. Am. Chem. Soc.*, 110 (1988) 8606.
11. A. M. Ob'edkov, B. V. Zhuk and G. A. Domrachev, *Metalloorg. Khim.*, 1 (1988) 592.
12. P. A. Dowben, D. C. Driscoll, S. Ranjeet and N. M. Boag, *Organometallics*, 7 (1988) 305.
13. C. Fujimoto, H. Yoshida and K. Jinno, *J. Chromatogr.*, 411 (1987) 213.
14. S. Nakashima, M. Katada, I. Motoyama and H. Sano, *Bull. Chem. Soc. Jpn.*, 60 (1987) 2253.
15. Y. Masuda and H. Sano, *Bull. Chem. Soc. Jpn.*, 60 (1987) 2674.
16. R. M. G. Roberts, J. Silver and A. S. Wells, *Inorg. Chim. Acta*, 126 (1987) 61.
17. S. Barfuss, M. Grade, W. Hirschwald, W. Rosinger, N. M. Boag, D. C. Driscoll and P. A. Dowben, *J. Vac. Sci. Technol. A*, 5 (1987) 1451.
18. T. Drewello, C. B. Lebrilla, H. Schwarz and T. Ast, *J. Organomet. Chem.*, 339 (1988) 333.
19. V. I. Khvostenko, N. L. Asfandiarov and G. A. Tolstikov, *Dokl. Akad. Nauk SSSR*, 292 (1987) 840.
20. A. M. Al-Saeed, E. A. Seddon, K. R. Seddon, A. A. Shimran, S. Tompkins, M. C. Grossel and J. P. Knychala, *J. Organomet. Chem.*, 347 (1988) C25.
21. L. Phillips, A. R. Lacey and M. K. Cooper, *J. Chem. Soc., Dalton Trans.*, (1988) 1383.

22. L. E. Vinogradova, I. T. Chizhevskii, N. V. Rastova, N. E. Kolobova and L. A. Leites, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1987) 890.
23. E. S. Shubina, L. N. Epstein, A. I. Yanovsky, T. V. Timofeeva, Yu. T. Struchkov, A. Z. Kreindlin, S. S. Fadeeva and M. I. Rybinskaya, *J. Organomet. Chem.*, 345 (1988) 313.
24. E. S. Shubina, L. M. Epstein, T. V. Timofeeva, Yu. T. Struchkov, A. Z. Kreindlin, S. S. Fadeeva and M. I. Rybinskaya, *J. Organomet. Chem.*, 346 (1988) 59.
25. W. S. Hammack, H. G. Drickamer, M. D. Lowery and D. N. Hendrickson, *Inorg. Chem.*, 27 (1988) 1307.
26. T. Hayashi and Y. Okada, *Nippon Kagaku Kaishi*, (1987) 208; *Chem. Abstr.*, 108 (1988) 38063.
27. J. Okuda, *J. Organomet. Chem.*, 356 (1988) C43.
28. Y. Okada, N. Nakai, N. Nakamura and T. Hayashi, *Nippon Kagaku Kaishi*, (1987) 1567.
29. R. M. Nielson, M. N. Golovin, G. E. McManis and M. J. Weaver, *J. Am. Chem. Soc.*, 110 (1988) 1745.
30. Y. Okada and T. Hayashi, *Nippon Kagaku Kaishi*, (1988) 162; *Chem. Abstr.*, 110 (1989) 39124.
31. A. A. Koridze, P. V. Petrovskii, N. M. Astakhova and N. E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1987) 1504.
32. N. J. Cayden, C. M. Dobson, S. J. Heyes and P. J. Wiseman, *J. Inclusion Phenom.*, 5 (1987) 65.
33. J. S. Jaworski, *Polyhedron*, 6 (1987) 2151.
34. R. A. Saraceno, G. H. Riding, H. R. Allcock and A. G. Ewing, *J. Am. Chem. Soc.*, 110 (1988) 980.
35. X. You, C. Li, J. Chen, Q. Chao, X. Pen and A. Dai, *Kexue Tongbao (Foreign Lang. Ed.)*, 32 (1987) 1410; *Chem. Abstr.*, 110 (1989) 39116.
36. J. G. Ibanez, C. S. Choi and R. S. Becker, *J. Electrochem. Soc.*, 134 (1987) 3083.
37. N. F. Blom, E. W. Neuse and H. G. Thomas, *Transition Met. Chem. (London)*, 12 (1987) 301.
38. T. Osa, *Stud. Org. Chem. (Amsterdam)*, (1987) 30; *Chem. Abstr.*, 109 (1988) 38097.
39. Q. Y. Xu, J.-M. Barbe and K. M. Kadish, *Inorg. Chem.* 27 (1988) 2373.

40. P. D. Beer, H. Sikanyika, C. Blackburn and J. F. McAleer, *J. Organomet. Chem.*, 350 (1988) C15.
41. A. Furlani, C. Napoletano, R. Paolesse and M. V. Russo, *Synth. Met.*, 21 (1987) 337.
42. M. G. Peterleitner, L. I. Denisovich and D. N. Kravtsov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1988) 442.
43. G. S. Tsurtsuniya, M. V. Chankashvili and T. P. Agladze, *Elektrokhimiya*, 23 (1987) 1679.
44. E. E. Bunel, P. Campos, J. Ruz, L. Valle, I. Chadwick M. Santa Ana, G. Gonzalez and J. M. Manriquez, *Organometallics*, 7 (1988) 474.
45. E. E. Bunel, L. Valle, N. L. Jones, P. J. Carroll, M. Gonzalez, N. Munoz and J. M. Manriquez, *Organometallics*, 7 (1988) 789.
46. D. O'Hare, J. Manriquez and J. S. Miller, *J. Chem. Soc., Chem. Commun.*, (1988) 491.
47. N. Kuhn, E. M. Horn, R. Boese and N. Augart, *Angew. Chem.*, 100 (1988) 1433.
48. M. Baudler, S. Akpapoglou, D. Ouzounis, F. Wasgestian, B. Meinigke, H. Budzikiewicz and H. Muenster, *Angew. Chem.*, 100 (1988) 288.
49. O. J. Scher, T. Brueck and G. Wolmershaeuser, *Chem. Ber.*, 121 (1988) 935.
50. R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Organomet. Chem.*, 340 (1988) C37.
51. J. Blumel, F. H. Kohler and G. Muller, *J. Am. Chem. Soc.*, 110 (1988) 4846.
52. S. Kaluz and S. Toma, *Gazz. Chim. Ital.*, 117 (1987) 529.
53. H. O. Doggweiler and V. Desobry (Ciba-Geigy A. G.), *Eur. Pat. Appl. EP 270490*, 1988 Jun. 8; *Chem. Abstr.*, 109 (1988) 129310.
54. Y. P. Wang, R. S. Shyu, J. M. Hwu and Y. H. Li, *Proc. Natl. Sci. Counc. Repub. China, Part A: Phys. Sci. Eng.*, 11 (1987) 110.
55. M. Wenzel, *Ger. Pat.*, DE 3441095, 1986 May 7; *Chem. Abstr.*, 107 (1987) 237019.
56. M. Wenzel and Y. Wu, *J. Labelled Compd. Radiopharm.*, 25 (1988) 53.
57. R. M. G. Roberts and A. S. Wells, *Inorg. Chim. Acta*, 126 (1987) 67.

58. G. T. Stauf, D. C. Driscoll, P. A. Dowben, S. Barfuss and M. Grade, *Thin Solid Films*, 153(1987) 421; *Chem. Abstr.*, 108 (1988) 42258.
59. W. Schumann, *Chem.-Ztg.*, 111 (1987) 111.
60. K. Moock, L. Turowsky and K. Seppelt, *J. Fluorine Chem.*, 37 (1987) 253.
61. E. M. Horn, E. Zauder, D. Blaeser and R. Boese, *Angew. Chem.*, 100 (1988) 572.
62. N. S. Kochetkova, V. I. Boev, V. N. Babin, R. B. Materikova, L. B. Popova and V. M. Bondarenko (Institute of Hetero-organic Compounds, Academy of Sciences), USSR Pat. SU 1320212, 1987 Jun. 30; *Chem. Abstr.*, 107 (1987) 237018.
63. A. A. Pendin, P. K. Leont'evskaya, O. L. Suverneva, I. V. Rozenkova and B. P. Nikol'skii, *Dokl. Akad. Nauk SSSR*, 293 (1987) 1411.
64. B. G. Cox, W. Jedral and J. Palou, *J. Chem. Soc., Dalton Trans.*, (1988) 733.
65. L. Brammer, N. G. Connelly, J. Edwin, W. E. Geiger, A. G. Orpen and J. B. Sheridan, *Organometallics*, 7 (1988) 1259.
66. M. Sato, H. Nakahara, K. Fukuda and S. Akabori, *J. Chem. Soc., Chem. Commun.*, (1988) 24.
67. M. Pawlak, W. Pukacki, A. Graja, M. Lequan and R. M. Lequan, *Potsdamer Forsch. Paedagog. Hochsch. "Karl Liebknecht" Potsdam, Naturwiss. Reihe*, 51 (1987) 142.
68. M. Pawlack and A. Graja, *Synth. Met.*, 24 (1988) 145.
69. A. J. Epstein, S. Chittipeddi, A. Chakraborty and J. S. Miller, *J. Appl. Phys.*, 63 (1988) 2952.
70. B. Divisia-Blohorn and M. Paltrier, *Inorg. Chim. Acta*, 131 (1987) 65.
71. U. Sinha, M. D. Lowery, W. W. Ley, H. G. Drickamer and D. N. Hendrickson, *J. Am. Chem. Soc.*, 110 (1988) 2471.
72. M. I. Rybinskaya, A. Z. Kreindlin and S. S. Fadeeva, *J. Organomet. Chem.*, 358 (1988) 363.
73. V. I. Boev, *Zh. Obshch. Khim.*, 57 (1987) 633.
74. V. I. Boev and A. V. Dombrovskii, *Zh. Obshch. Khim.*, 57 (1987) 938.
75. V. I. Boev, *Zh. Obshch. Khim.*, 57 (1987) 713.
76. M. I. Rybinskaya, A. Z. Kreindlin, S. S. Fadeeva and P. V. Petrovskii, *J. Organomet. Chem.*, 345 (1988) 341.
77. G. Ortaggi, *Gazz. Chim. Ital.*, 117 (1987) 75.

78. K. E. Schwarzhans and W. Stolz, *Monatsh. Chem.*, 118 (1987) 875.
79. C. J. W. Brooks and W. J. Cole, *J. Chromatogr.*, 399 (1987) 207.
80. J. Okuda and E. Herdtweck, *Chem. Ber.*, 121 (1988) 1899.
81. V. V. Korshak, S. L. Sosin, Yu. E. Ovchinnikov, T. M. Frunze, V. V. Dement'ev, B. A. Antipova, V. E. Shklover and Yu. T. Struchkov, *Dokl. Akad. Nauk SSSR*, 292 (1987) 1141.
82. V. I. Buziashvili, L. M. Khananashvili, B. K. Kabanov, T. N. Nikol'skaya and O. V. Kuz'min, *Zh. Obshch. Khim.*, 58 (1988) 88.
83. M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy, D. Bloor, P. V. Kolinsky and R. J. Jones, *Nature (London)* 330 (1987) 360.
84. V. I. Losilkina, N. K. Barenetskaya, V. S. Tolkunova, A. I. Krylova, V. D. Vil'chevskaya and V. N. Setkina, *Zh. Obshch. Khim.*, 57 (1987) 852.
85. A. Meetsma, P. L. Buwalda and J. C. Van de Grampel, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, C44 (1988) 58.
86. F. Nief, F. Mathey, L. Ricard and F. Robert, *Organometallics*, 7 (1988) 921.
87. M. Sato, M. Sekino and S. Akabori, *J. Organomet. Chem.*, 344 (1988) C31.
88. L. H. Shen, M. O. Okoroafor and C. H. Brubaker, *Organometallics*, 7 (1988) 825.
89. M. O. Okoroafor, D. L. Ward and C. H. Brubaker Jr., *Organometallics* 7 (1988) 1504.
90. G. H. Robinson, S. G. Bott and J. L. Atwood, *J. Coord. Chem.*, 16 (1987) 219.
91. Y. Ma and C. Ma, *Lanzhou Daxue Xuebao, Ziran Kexueban*, 23 (1987) 136; *Chem. Abstr.*, 110 (1989) 39118.
92. A. J. Arce, C. Acuna and A. J. Deeming, *J. Organomet. Chem.*, 356 (1988) C47.
93. A. A. Koridze, O. Kizas, P. V. Petrovskii, N. E. Kolobova and G. M. Mikheeva, *Dokl. Akad. Nauk SSSR*, 293 (1987) 117.
94. N. N. Meleshonkova, M. Se Phan and S. K. Moiseev, *Zh. Obshch. Khim.*, 57 (1987) 2606; *Chem. Abstr.*, 110 (1989) 24056.

95. F. M. Spiridonov, S. K. Moiseev, N. N. Meleshonkova and V. A. Sazonova, *Koord. Khim.*, 13 (1987) 1458; *Chem. Abstr.*, 110 (1989) 8368.
96. M. Sato, S. Akabori, M. Katada, I. Motoyama and H. Sano, *Chem. Lett.*, (1987)1847.
97. U. Casellato, D. Ajo, G. Valle, B. Corain, B. Longato and R. Graziani, *J. Crystallogr. Spectrosc. Res.*, 18 (1988) 583.
98. T. Hayashi, K. Hayashizaki, T. Kiyoi and Y. Ito, *J. Am. Chem. Soc.*, 110 (1988) 8153.
99. M. Onishi, K. Hiraki, S. Wada and Y. Ohama, *Polyhedron*, 6 (1987) 1243.
100. B. Longato, G. Pilloni, G. Valle and B. Corain, *Inorg. Chem.*, 27 (1988) 956.
101. M. Watanabe, Y. Masuda, I. Motoyama and H. Sano, *Chem. Lett.*, (1987) 1981.
102. J. Meng and T. Matsuura, *Gaodeng Xuexiao Huaxue Xuebao*, 8 (1987) 623; *Chem. Abstr.*, 108 (1988) 204790.
103. A. Jaworska-Augustyniak and J. Wojtczak, *Transition Met. Chem. (London)*, 12 (1987) 167.
104. H. Ji, G. Xu, L. Sun and S. Shi, *Huaxue Tongbao* (1987) 26; *Chem. Abstr.*, 109 (1988) 110608.
105. A. Jaworska-Augustyniak, J. Karolczak, A. Maciejewski and J. Wojtczak, *Chem. Phys. Lett.*, 137 (1987) 134.
106. R. M. G. Roberts and A. S. Wells, *Inorg. Chim. Acta*, 130 (1987) 93.
107. A. N. Lineva, V. M. Fomin, L. N. Martynova, A. V. Lunin, V. N. Lataeva and Yu. A. Aleksandrov, *Zh. Obshch. Khim.*, 57 (1987) 2646.
108. E. I. Klimova, A. N. Pushin and V. A. Sazonova, *Zh. Obshch. Khim.*, 57 (1987) 2336.
109. M. Bassetti and B. Floris, *J. Chem. Soc., Perkin Trans. 2*, (1988) 227.
110. B. Floris and G. Illuminati, *J. Chem. Soc., Perkin Trans. 2*, (1986) 1811.
111. L. I. Leont'eva, B. Won, D. N. Kravtsov and E. G. Perevalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1986) 2302.
112. A. N. Pushin, E. I. Klimova and B. A. Sazonova, *Zh. Obshch. Khim.*, 57 (1987) 1102.

113. Z. V. Todres and T. M. Tsvetkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1987) 1553.
114. S. Kaluz and S. Toma, *Collect. Czech. Chem. Commun.*, 52 (1987) 2717; *Chem. Abstr.*, 110 (1989) 24058.
115. A. Z. Kreindlin, S. S. Fadeeva, P. V. Petrovskii and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1988) 170.
116. R. D. Moulton and A. J. Bard, *Organometallics*, 7 (1988) 351.
117. C. Zhao and Y. Zhang, *Lanzhou Daxue Xuebao, Ziran Kexueban*, 23 (1987) 147, *Chem. Abstr.*, 108 (1988) 94733.
118. A. Dormond, A. Aaliti and C. Moise, *J. Org. Chem.*, 53 (1988) 1034.
119. S. Toma, P. Elecko, J. Gazova and E. Solcaniova, *Collect. Czech. Chem. Commun.*, 52 (1987) 391.
120. S. Toma and M. Salisova, *Collect. Czech. Chem. Commun.*, 52 (1987) 1520.
121. V. I. Ovtshcharenko, W. Huber and K. E. Schwarzahns, *Monatsh. Chem.*, 118 (1987) 955.
122. S. Toma, M. Putala and M. Salisova, *Collect. Czech. Chem. Commun.*, 52 (1987) 395.
123. J. Frederic and S. Toma, *Collect. Czech. Chem. Commun.*, 52 (1987) 174.
124. J. Bhatt, B. M. Fung, K. M. Nicholas and C.-D. Poon, *J. Chem. Soc., Chem. Comm.*, (1988) 1439.
125. M. Wenzel, D. Preiss and G. Gunther, *J. Labelled Compd. Radiopharm.*, 25 (1988) 121.
126. S. Kaluz and S. Toma, *Collect Czech. Chem. Commun.*, 53 (1988) 638.
127. V. A. Kogan, A. N. Morozov and V. V. Lukov, *Zh. Neorg. Khim.*, 33 (1988) 133.
128. J. Markopoulos, O. Markopoulou, D. Bethell and D. Nicholls, *Inorg. Chim. Acta*, 122 (1986) L15.
129. K. Iyanar, S. Prema and K. Kishore, *J. Chem. Eng. Data*, 33 (1988) 220.
130. M. O. Okoroafor, L. H. Shen, R. V. Honeychuck and C. H. Brubaker Jr., *Organometallics*, 7 (1988) 1297.
131. S. Nakashima, Y. Masuda, I. Motoyama and H. Sano, *Bull. Chem. Soc. Jpn.*, 60 (1987) 1673.
132. T. Kambara, D. N. Hendrickson, T. Y. Dong and M. J. Cohn, *J. Chem. Phys.*, 86 (1987) 2362.

133. M. A. I. Salem, A. Y. Mohammed and S. El-Nagdy, *J. Chem. Soc. Pak.*, 9 (1987) 35; *Chem. Abstr.*, 108 (1988) 150656.
134. I. R. Butler, W. R. Cullen and S. J. Rettig, *Can. J. Chem.*, 65 (1987) 1452.
135. S. Michaile, M. Hillman and J. J. Eisch, *Organometallics*, 7 (1988) 1059.
136. M. Hisatome, M. Yoshihashi, K. Yamakawa and Y. Itaka, *Bull. Chem. Soc. Jpn.*, 60 (1987) 2953.
137. H. Hopf and J. Dannheim, *Angew Chem.*, 100 (1988) 724.
138. H. Sano, M. Katada, Y. Masuda and I. Motoyama, *Kyoto Daigaku Genshiro Jikkensho [Tech. Rep.] 1987, KURRI-TR-296, "Chobisai Sogo Sayo" Senmon Kenkyukai Hokoku, 1 15; Chem. Abstr.*, 109 (1988) 63686.
139. E. E. Bunel, L. Valle, N. L. Jones, P. J. Carroll, C. Barra, M. Gonzalez, N. Munoz, G. Visconti, A. Aizman and J. M. Manriquez, *J. Am. Chem. Soc.*, 110 (1988) 6596.
140. J. Mirek, S. Rachwal, T. Gorecki, B. Kawalek, P. Milart and E. Szneler, *J. Organomet. Chem.*, 344 (1988) 363.
141. A. Kashara, T. Izumi, S. Tanno and T. Kikuchi, *Yamagata Daigaku Kiyo, Kogaku*, 19 (1987) 137; *Chem. Abstr.*, 108 (1988) 94724.
142. P. D. Beer, H. Sikanyika, C. Blackburn, J. F. AcAleer and M. G. B. Drew, *J. Organomet. Chem.*, 356 (1988) C19.
143. M. C. Grossel, M. R. Goldspink, J. P. Knychala, A. K. Cheetham and J. A. Hriljac, *J. Organomet. Chem.*, 352 (1988) C13.
144. A. Ratajczak and J. Krzykowski, *Gazz. Chim. Ital.*, 117 (1987) 533.
145. P. D. Beer, A. D. Keefe and M. G. B. Drew, *J. Organomet. Chem.*, 353 (1988) C10.
146. P. D. Beer and A. D. Keefe, *J. Inclusion Phenom.*, 5 (1987) 499.
147. M. Herberhold, C. Dornhofer, H. I. Hayen and B. Wrackmeyer, *J. Organomet. Chem.*, 355 (1988) 325.
148. H. Ushijima, T. Akiyama, M. Kajitani, K. Shimizu, M. Aoyama, S. Masuda, Y. Harada and A. Sugimori, *Chem. Lett.*, (1987) 2197.
149. M. Sato, K. Suzuki and S. Akabori, *Chem. Lett.*, (1987) 2239.

150. W. R. Cullen, S. T. Chacon, M. I. Bruce, F. W. B. Einstein and R. H. Jones, *Organometallics*, 7 (1988) 2273.
151. M.-H. Desbois and D. Astruc, *J. Chem. Soc., Chem. Commun.*, (1988) 472.
152. A. Fukada, T. Koyama, K. Hanabusa, H. Shirai, H. Nakahara and K. Fukuda, *J. Chem. Soc., Chem. Comm.*, (1988) 1104.
153. Z. Du, X. Wen and J. Lin, *Shandong Daxue Xuebao, Ziran Kexueban*, 22 (1987) 115; *Chem. Abstr.*, 108 (1988) 56695.
154. K. Pannell, J. M. Rozell and J. M. Zeigler, *Macromolecules*, 21 (1988) 276.
155. R. A. Saraceno, G. H. Riding, H. R. Allcock and A. G. Ewing, *J. Am. Chem. Soc.*, 110 (1988) 7254.
156. T. Inagaki, M. Hunter, X. Q. Yang, T. A. Skotheim and Y. Okamoto, *J. Chem. Soc., Chem. Commun.*, (1988) 126.
157. R. K. Freidlina, L. V. Yashkina and B. V. Kopylova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1987) 2328.
158. T. Hayashi, K. Kanehira, T. Hagihara and M. Kumada, *J. Org. Chem.*, 53 (1988) 113.
159. T. Hayashi, A. Yamamoto and Y. Ito, *Tetrahedron Lett.*, 29 (1988) 99.
160. K. Moriya, T. Sasahara, T. Ikegami and S. Takao, (Nippon Urethane Service Co. Ltd.,) *Jpn. Kokai Tokkyo Koho JP 62190212*; *Chem. Abstr.*, 108 (1988) 76460.
161. N. Kubota and S. Miyazaki, *Propellants, Explos., Pyrotech.*, 12 (1987) 183.
162. V. I. Sokolov and V. L. Bondareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1987) 460.
163. V. I. Sokolov, V. L. Bondareva and I. F. Golovaneva, *J. Organomet. Chem.*, 358 (1988) 401.
164. H. J. Thiem, M. Brandl and R. Breslow, *J. Am. Chem. Soc.*, 110 (1988) 8612.
165. A. Harada, Y. Hu, S. Yamamoto and S. Takahashi, *J. Chem. Soc., Dalton Trans.*, (1988) 729.
166. K. Charakondur, M. L. H. Green, J. Qin, M. E. Thompson and P. J. Wiseman, *J. Chem. Soc., Chem. Commun.*, (1988) 223.
167. I. I. Grinval'd, B. V. Lokshin, V. P. Mar'in, L. I. Vyshinskaya and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 296 (1987) 111.

168. S. Jiang and X. Yun, *Huaxue Shiji*, 9 (1987) 301; *Chem. Abstr.*, 108 (1988) 105507.
169. S. Jiang and X. Yun, *Huaxue Shiji*, 9 (1987) 232; *Chem. Abstr.*, 108 (1988) 100099.
170. A. Harada, K. Sacki and S. Takahashi, *J. Inclusion Phenom.*, 5 (1987) 601.
171. C. Iwakura, Y. Kajiya and H. Yoneyama, *J. Chem. Soc., Chem. Comm.*, (1988) 1019.
172. C. N. C. Drey and A. S. J. Stewart, *Pept. Proc. Eur. Pept. Symp.*, 19th, 1986, (Pub. 1987) 65; *Chem. Abstr.*, 108 (1988) 56593.
173. C. Kajdas, J. R. Dabrowski, R. M. Matveevskii and I. A. Buyanovskii, *Trybologia*, 18 (1987) 11; *Chem. Abstr.*, 108 (1988) 97481.
174. E. W. Neuse, M. G. Meirim and N. F. Blom, *Organometallics*, 7 (1988) 2562.