ORGANIC REACTIONS OF SELECTED π-COMPLEXES

ANNUAL SURVEY COVERING THE YEAR 1977*

GEORGE MARR and BERNARD W. ROCKETT

Department of Physical Sciences, The Polytechnic,

Wolverhampton, WV1 1LY (Great Britain)

CONTENTS

---

[*] Selected π-Complexes, Annual Survey covering the year 1976 see J. Organometal. Chem., 151(1978)193-312.

1. REVIEWS

Ittel and Ibers have discussed the coordination of unsaturated molecules to transition metals [1]. Howell has surveyed the recent chemistry of hydrocarbon-metal-η-complexes [2]. Abel and Stone have reviewed the literature of organometallic chemistry for 1975 [3].

The American Chemical Society has issued six tape cassettes and a manual entitled 'Organometallic Chemistry of the Transitio Elements' [4]. Tirouflet and Braunstein have made a general survey of the synthesis and reactivity of organometallic compoun of the transition elements [5]. The formation and reactivity of (η-alkenyl) transition metal complexes have been discussed [6]. Timms and Turney have comprehensively reviewed the metal atom synthesis of organometallic compounds. This was a good review that included a short section on the experimental methods used in this relatively new method of synthesis [7].

McGlinchey and Skell have surveyed the synthesis of organometallic and organic compounds by methods involving transition metal vapours [8]. Klikorka and Pavlik have discussed the structure, reactivity and applications of metallocenes [9]. In Methodicum Chimicum Volume 8 a critical survey is given of the methods available for the preparation of transition metal derivatives. There are four chapters that are particularly relevant to organometallic chemists. These are, Transition

Metal Carbonyls by King [10], Ferrocenes by Schloegl and Falk [11], Sandwich Compounds -A, Metallocenes by Rosenberg [12] and -B, Other Sandwich Compounds by Jasson [13].

The reactions of coordinated olefins and acetylenes have been reviewed by Green [14]. The electrochemistry of transition metal η-complexes has been reviewed by Denisovich and Gubin [15]. Connor has discussed the thermochemistry of organo-transition metal carbonyls including metallocenes, (η-arene)tricarbonylchromium compounds, cymantrene and tricarbonyl(η-diene)iron compounds [16]. New varieties of sandwich complexes have been the subject of a review by Werner [17].

Bruce has surveyed the rapidly developing area of cyclometallation reactions [18]. The vibrational spectroscopy of transition metal η-complexes has been the subject of an extensive review by Aleksanyan and Lokshin [19]. The chemistry of η-cyclopentadienyl and η-arene transition metal complexes has been surveyed [20]. Hunt has briefly reviewed the first twenty years of metallocene chemistry. The discovery of ferrocene was described together with other key compounds in the development of transition metal organometallic chemistry [21].

In a brief review on some aspects of organometallic chemistry Toma charted the progress made since the discovery of ferrocene. The article included a mention of bis(η-benzene)chromium and the use of organometallic-transition metal compounds in organic synthesis [22]. The utilization of arene-metal complexes in organic synthesis has been discussed by Semmelhack [23]. A review on high-performance liquid chromatography of metal-organic complexes included a section on η-arene metal carbonyls [24].

The reactions of tricarbonyl(η-chlorobenzene)chromium were reviewed [25]. A volume of the Journal of Less Common Metals was devoted to the proceedings of the Second Conference on the Chemistry and Uses of Molybdenum. One section was devoted to organomolybdenum complexes which included the plenary lecture presented by Green entitled "New Synthetic Routes in Organomolybdenum Chemistry" [26]. Efraty reviewed the chemistry of the (η-cyclobutadiene)metal complexes. In this excellent review most aspects of η-cyclobutadiene chemistry were examined in detail [27].

Alper reviewed the use of pentacarbonyliron in organic syntheses. In some of the reactions listed (η-diene)irontricarbonyl derivatives were isolated [28]. The chemistry of (η-diene)- and (η-enone)-tricarbonyliron compounds has been surveyed [29]. Sutherland has comprehensively reviewed the literature for (η-arene)(η-cyclopentadienyl)iron cations and related systems up to the end of 1975 [30]. King has reviewed the reactions of the macrocyclic alkadiynes 1,7-cyclododecadiyne 1,7-cyclotridecadiyne, 1,7- and 1,8-cyclotetradecadiyne and 1,8-cyclopentadecadiyne with the metal carbonyls $Fe(CO)_5$, $Fe_3(CO)_{12}$, $(\eta-C_5H_5)M(CO)_2$ (M = Co, Rh), $Co_2(CO)_8$ and $[(\eta-C_5H_5)NiCO]_2$ [31].

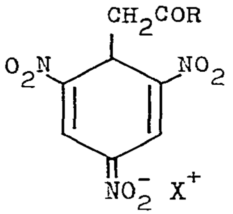
The chemistry of metallocarbenes, metallocarbynes, ylides, clusters and metallocarboranes has been discussed from an organo metallic viewpoint [32]. King has outlined the role of (η-pentamethylcyclopentadienyl)metal complexes in the synthesis of polynuclear metal carbonyls with multiple metal-metal bonding [33]. Haiduc and Popa reviewed metal complexes of η-ligands containing organosilicon groups. The organic ligands were classified according to the number of electrons contributed by the ligands to the metal and the particular effects of the σ-bonded organosilicon groups on the η-ligands were discussed [34].

Ligand substitution reactions of organometal carbonyls with Group V and Group VI donor ligands has been reviewed by Edwards [35]. The chemistry of thiocarbonyl complexes of transition metals has been reviewed by Yaneff. Complexes derived from cymantrene and benchrotrene were included [36]. Butler has reviewed the chemistry of the transition-metal thiocarbonyls and selenocarbonyls. The synthetic routes available to these relatively new classes of compounds were considered and a brief survey of their physicochemical properties were presented [37].

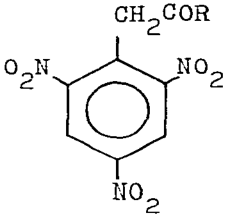
2. GENERAL RESULTS

In a series of related papers Mingos has reported a topological Huckel model for describing the bonding in η-organometallic complexes. He has developed a simplified MO method to account for the bond lengths in transition metal η^4-polyene complexes. The model has taken into account the insensitivity of the carbon-carbon bond lengths in the η-butadiene ligand to the number of benzene rings fused to it and the fixation of one double bond in the benzene ring adjacent to the butadiene group. Alternant bonding networks have been demonstrated for η^3- and η^4-olefin complexes. The electronic basis of the 18-electron rule has been indicated by application of the pairing theorem and the rule has been defined by the perturbation MO method. This method was also used to distinguish 18-electron rule isomers and to describe the fluxional characteristics of certain η^3- and η^4-olefin complexes [38, 39, 40].

A good correlation has been found between back donation of electrons from ligand to carbonyl and the oxygen 1s binding energy in complexes. Among the complexes studied were benchrotrene, cymantrene, (η-butadiene)tricarbonyliron, tricarbonyl(η-cycloheptatriene)iron and tetracarbonyl(η-cyclopentadienyl)vanadium [41]. Treatment of 1,3,5-trinitrobenzene with acetylcymantrene, acetylferrocene or acetylbenchrotrene in the presence of diethylamine or triethylamine gave the charged derivatives [2.1; R = (η-C_5H_4)Mn(CO)$_3$, (η-C_5H_4)(η-C_5H_5)Fe, (η-C_6H_5)Cr(CO)$_3$; X = Et_2NH_2, Et_3NH] respectively. Reaction of the organometallic compounds (2.1) with tropylium tetrafluoroborate in methyl cyanide gave the corresponding benzene derivatives (2.2) [42].



2.1

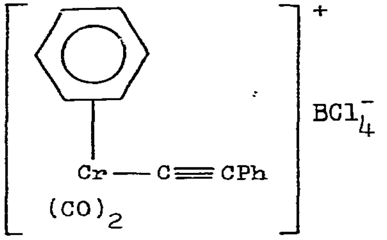


2.2

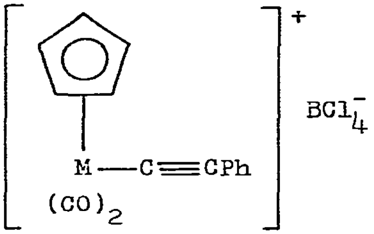
Treatment of the chromium, manganese and rhenium complexes (2.3 and 2.4; M = Mn, Re) with trimethylphosphine gave the corresponding cationic transition metal substituted phosphorus ylides (2.5 and 2.6; M = Mn, Re) [43]. Ligand field energy levels were calculated for d^6 metallocenes using the approximation of weak and strong ligand fields of $D_{\infty h}$ symmetry. The results were applied to the interpretation of the d-d spectra of ferrocene, ruthenocene and the cobalticinium cation and of some related carboranyl sandwich compounds. Determination of the ligand field parameters and the nephelauxetic ratios of individual complexes enabled the central atoms to be arranged in the nephelauxetic series:

Ni(IV) $\ll$ Ru(II) $\leqslant$ Co(III) $<$ Fe(II) $<$ Ni(II) $<$ Cr(III) $<$ V(II)

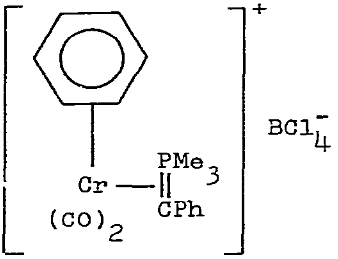
It was considered that central-field covalency and symmetry restricted covalency and made equal contributions to the nephelauxetic effect [44].



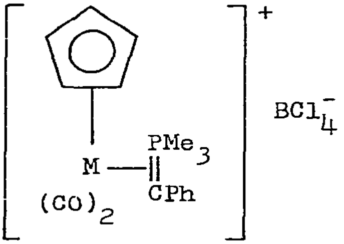
2.3



2.4



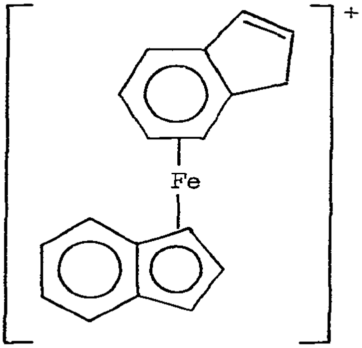
2.5



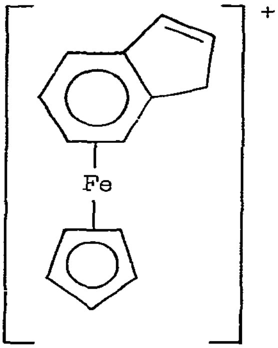
2.6

Phase transitions in chromocene, ferrocene, ruthenocene, cobaltocene and nickelocene were investigated by specific heat measurements. The phase transitions observed were: chromocene at 160-230 K with $\Delta S = 1.5\ JK^{-1}\ mol^{-1}$, ferrocene at 164 K with $\Delta S = 5.31\ JK^{-1}\ mol^{-1}$, nickelocene at 170-240 K with $\Delta S = 5.2\ JK^{-1}\ mol^{-1}$ [45]. Cobaltocene and ruthenocene, which have ordered structures at room temperature, were investigated by calorimetry and X-ray diffraction in the temperature range 77-300 K. They showed no phase transition which was in direct contrast to the disordered metallocenes, ferrocene, nickelocene and bis(η-cyclopentadienyl)chromium [46]. The thermal decomposition of bis(η-cyclopentadienyl)-chromium and -manganese has been investigated enabling an order of metallocene stability to be determined as V > Cr > Mn [47].

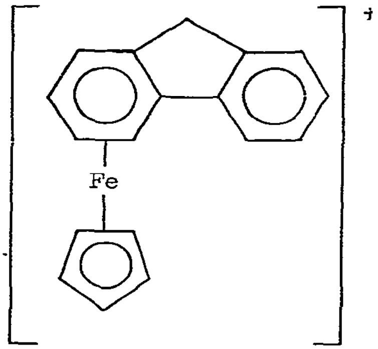
The negative ion mass spectra of (η-butadiene)tricarbonyliron, 1,1'-bis(trimethylsilyl)nickelocene and several other transition metal complexes were recorded. The stability of the negative molecular ions were governed by the effective positive charge on the metal atom [48]. Treatment of bis(η-indenyl)iron with protonic acids gave the cation (2.7). Similarly (η-cyclopentadienyl)(η-indenyl)iron on treatment with acid gave the cation (2.8). It was shown that in these reactions the proton was added to the 1-position of the η-indenyl ligand and the site of metal co-ordination was shifted from the 5-membered to the 6- membered ring. n-Butyllithium was effective in deprotonating the cations to give the initial neutral complexes. The fluorene cations (2.9 and 2.10) were prepared and the manganese complex (2.10) underwent thermal isomerization to give the neutral complex



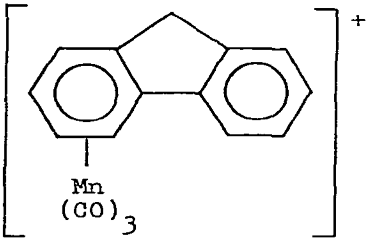
2.7



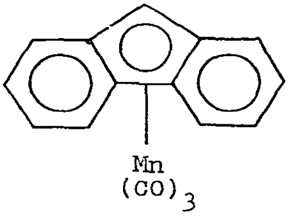
2.8



2.9



2.10

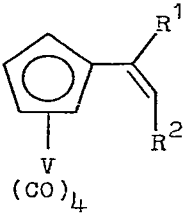


2.11

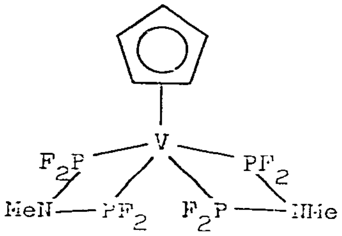
(2.11). The bonding in these complexes was discussed on the basis of ^1H and ^{13}C NMR spectra and X-ray crystallographic data [49]. In order to compare the ligating properties of the thiocarbonyl and carbonyl ligands Andrews has collected vibrational stretching frequencies for these ligands in a wide range of complexes including cymantrene and benchrotrene analogues. Force constant correlations led to the conclusion that the π-acceptor to σ-donor ratio varies more for thiocarbonyl than for carbonyl [50].

3. $(\eta-C_5H_5)V(CO)_4$

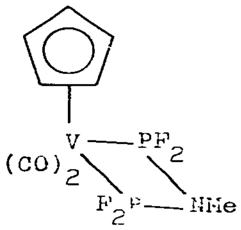
Several (η-alkenylcyclopentadienyl)tetracarbonylvanadium complexes (3.1; R^1 = H, Me, Et, Ph; R^2 = H, Me) have been synthesized by treatment of 6-alkylfulvenes with hexacarbonyl vanadium [51].



3.1

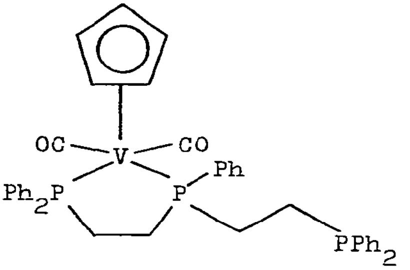


3.2

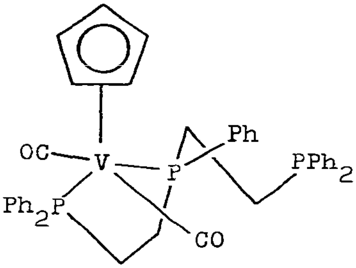


3.3

Irradiation of (η-cyclopentadienyl)tetracarbonylvanadium with methylaminobis(difluorophosphine) gave the first fully substituted (η- cyclopentadienyl)tetracarbonyl vanadium derivative (3.2). The intermediate vanadium dicarbonyl derivative (3.3) was obtained by altering the relative quantities of the reactants [52]. Irradiation of tetracarbonyl(η-cyclopentadienyl)vanadium in the presence of the ligand $PhP(CH_2CH_2PPh_2)_2$ gave the *cis*- and *trans*-complexes (3.4 and 3.5) respectively. The *trans*-complex (3.5) which was an isomeric mixture of two species with uncoordinated PPh_2 and PPh groups was formed by photo-induced configurational rearrangement of the *cis*- complex (3.4) [53].



3.4



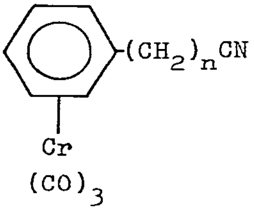
3.5

4. $(\eta-C_6H_6)Cr(CO)_3$

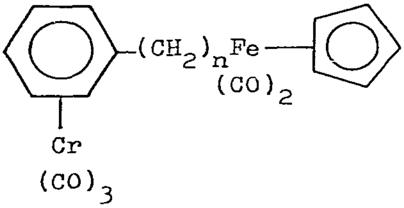
(i) Formation

Photochemical reaction of the metal carbonyls $M(CO)_6$ (M = Cr, Mo, W) with the cyanides RCN [$R = Ph(CH_2)_n$, n = 0 - 3; $2,4,6\text{-}Me_3C_6H_2(CH_2)_3$]gave the cyanide-metal bonded complexes $(RCN)M(CO)_5$. However, thermal reaction of the cyanides $Ph(CH_2)_nCN$ with hexacarbonylchromium gave the π-bonded complexes (4.1) [54]. The benchrotrene complexes (4.2; n = 0, 1) were formed by heating the appropriate ligand with hexacarbonylchromium in a diglyme-pentane mixture [55].

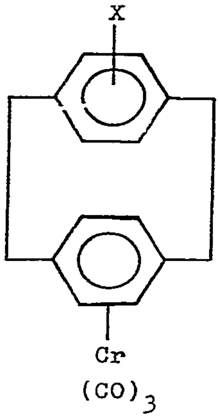
The tricarbonylchromium complexes (4.3, 4.4 and 4.5, no substituent X) and the corresponding bis(tricarbonylchromium)



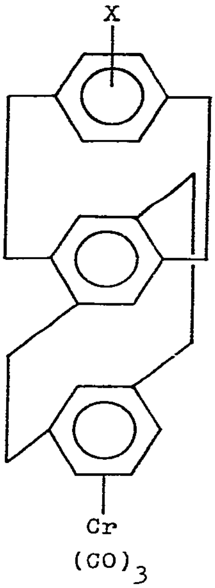
4.1



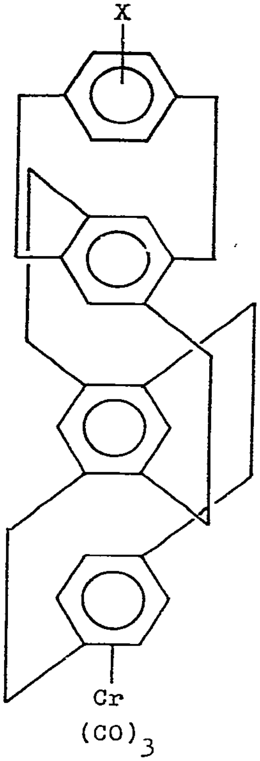
4.2



4.3



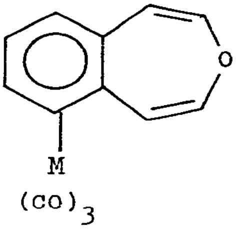
4.4



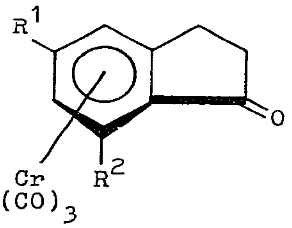
4.5

complexes 4.3, 4.4 and 4.5, X = $Cr(CO)_3$ were prepared by treatment of the cyclophanes with hexacarbonylchromium. The ^1H NMR, infrared and ultraviolet spectra of all the complexes were recorded and discussed in terms of electronic interactions [56]. Benzoxepin combined directly with acetonitrile or triglyme chromium, molybdenum and tungsten tricarbonyls to form the (η-benzoxepin) complexes (4.6; M = Cr, Mo, W) [57].

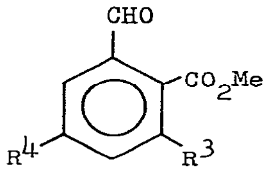
The (-)-indanone chromium complexes (4.7; $R^1 = R^2$ = H, Me, OMe) were condensed with the esters (4.8; $R^3 = R^4$ = H, Me) and then converted through a number of steps to the chiral 2,2'-spirobiindans (4.9). The chiralities and enantiomeric purities of the spirans (4.9) were deduced from those of the initial chromium complexes (4.7) [58]. Bis(tricarbonylchromium)complexes of dinuclear arenes were prepared either by direct reaction of



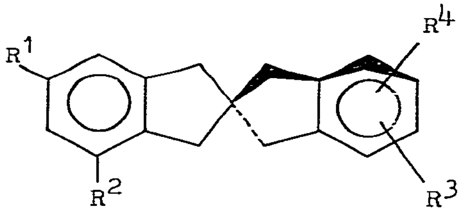
4.6



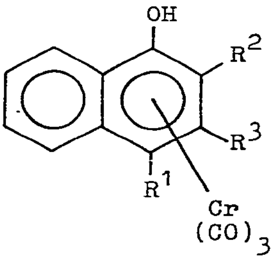
4.7



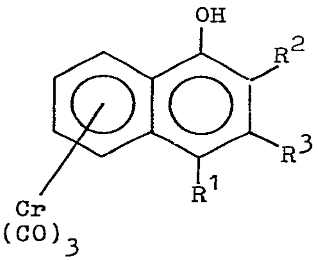
4.8



4.9



4.10



4.11

the arene with hexacarbonylchromium or by an exchange reaction with tricarbonyl(dimethylterephthalate)chromium. For example, deoxybenzoinbis(tricarbonylchromium) and *p*-methoxycarbonylbenzylmesitylenebis(tricarbonylchromium)were prepared and these complexes behaved as hydrogenation catalysts for acrylonitrile [59].

The carbenes $PhR^1C{:}Cr(CO)_5$ underwent stereoselective reaction with acetylenes $R^2C{\equiv}CR^3$ to give the naphthalene derivatives (4.10 and 4.11; R^1 = Ph, OMe; R^2 = Et, Me, Pr, Bu, Ph; R^3 = H, Me, Et, Ph, CO_2Et) [60]. Reaction of o- and m-$Ph(CH_2)_nCB_{10}H_{10}CR$ (R = H, Ph, $PhCH_2$, n = 0, 1) with hexacarbonylchromium gave the corresponding (η-arylcarborane)tricarbonylchromium complexes [61].

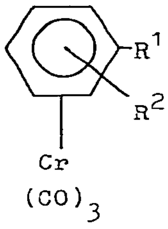
(ii) SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

The crystal and molecular structure of tricarbonyl(η-toluene)chromium has been determined by X-ray crystallography. The tricarbonylchromium group deviates from the eclipsed position with respect to the methyl substituent by only 2.2° [62]. The crystal structures of tricarbonyl(η-1,3,5-trimethylbenzene)-chromium and tricarbonyl(η-hexamethylbenzene)chromium were determined by X-ray analysis. Both molecules were close to C_{3v} symmetry, in the former molecule the carbonyl groups were eclipsed with respect to the methyl substituted carbon atoms, whilst in the latter the carbonyl groups were staggered with respect to the benzene ring atoms [63].

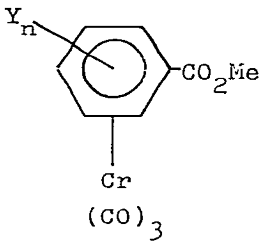
The structures of several η-complexes, including tricarbonyl-(η-diphenylfulvene)chromium have been determined by X-ray crystallography [64, 65]. The theoretical diffraction intensities for benchrotrene have been calculated by vibrational analysis and molecular mechanics. Comparisons with the experimental electron-diffraction patterns were made in order to determine the molecular conformation of least strain [66]. The helium (1α) photoelectron spectra of tricarbonyl(η-mesitylene)chromium and tricarbonyl(η-cycloheptatriene)chromium have been recorded and interpreted. Ionization energy assignments were made and Koopmans' theorem was violated for the d-orbital ionization in the (η-mesitylene) complex. Comparisons were made with the spectra of the corresponding molybdenum and tungsten complexes. The d-orbital ionization energies were almost independent of the nature of the metal [67].

ESCA was used to study the effect of substituents on the bonding in the chromium complexes (4.12; R^1 = H, R^2 = H, Me, Et, Pr, OMe, F, Cl; R^1 = R^2 = Me). The core ionization potentials of carbon and oxygen (C 1s, O 1s) increased and that of chromium (Cr 3s) decreased with increasing electron donor ability of the substituent R [68].

The thermodynamic dissociation constants of a series of (η-benzoic acid)tricarbonylchromium complexes were determined in aqueous ethanol. The pK_a^* values were correlated with the



4.12



4.13

electronic substituent parameters in terms of the Yukawa-Tsuno equation. It was concluded that when the aromatic system was attached to chromium it was less able to transmit electronic substituent effects [69].

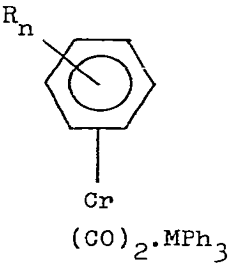
The ionization potentials of substituted benchrotrenes were correlated with the Taft inductive substituent constants. A good correlation was obtained with substituents containing carbon atoms while those with lone pair electrons formed a separate line. The force constants of the carbonyl stretching frequencies also gave a linear relationship with $\Sigma\sigma$. It was suggested that ionization occurred by loss of a chromium d_{xy} electron from a t_{2g} molecular orbital [70].

The electronic absorption spectra of benchrotrene and sixteen of its derivatives have been recorded and analyzed. The band at 314-330 nm arises from intramolecular charge transfer from chromium to the arene ligand and its extinction coefficient correlates with the substituent constant σp^{+} [71]. The IR spectra of thirty-seven tricarbonyl(η-methylbenzoate)chromium complexes {4.13; Y = alkyl, halogen, CO_2Me, OMe, NMe_2, Ph, Ph[$Cr(CO)_3$]; n = 1 - 3} have been measured and compared with the spectra of the free ligands. A poor correlation between ester carbonyl wave number and the electronic effect of the substituent was found whilst a fair correlation was found for the free aromatic ligands. The differences arose from differences in the conformational preferences of the tricarbonylchromium group in the presence of different substituents. The substituent constants σ_p and σ_m were determined for the tricarbonylchromium group. Local C_{3v} symmetry (A_1 + E) was used to assign the metal carbonyl stretching frequencies and the force constants obtained gave satisfactory correlations with substituent constan in terms of the Yukawa-Tsuno equation [72]. The ^{1}H NMR spectra of the ester complexes (4.13) were analyzed in order to determine the conformational preferences in these complexes. In many cases a single conformation was strongly preferred, and the position, electronic character and bulk of the ring substituents were important in deciding which conformation was adopted [73].

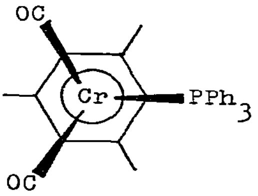
The ^{13}C NMR spectra of tricarbonyl(η-*p*-dimethylaminobenzaldehyde)chromium were recorded at different temperatures. The barrier to rotation ($\Delta G^{\neq}$ = 8.6 kcal mol^{-1}) around the bond between the formyl group and the complexed ring was determined by complete line shape analysis and compared with the corresponding value for the free arene ($\Delta G^{\neq}$ = 10.2 kcal mol^{-1}). The difference between the two values was attributed to a loss of conjugation in the complex and/or to an interaction between the formyl group and chromiumtricarbonyl moiety in the transition state [74].

The ^{13}C NMR spectra of 1-*p*-tolylethyl- and di-*p*-tolylmethyltricarbonylchromium cations were recorded in fluorosulphonic acid at -50° and compared with the spectra of the corresponding alcohols. For the cations the chemical shifts were explained in terms of structures in which the positive charge was localize mainly on the tricarbonylchromium group. It was concluded from a variable temperature study of the non-equivalent splittings of the *ortho* and *meta* carbon atoms and the carbonyl resonance that two motions around the aryl-methyl and the chromium-ring bonds characterized the dynamics of the ions [75].

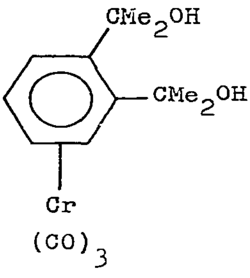
^{13}C NMR spectroscopy has been used to investigate deshielding of arene ring carbon atoms in the (η-benzene)dicarbonyl-



4.14



4.15

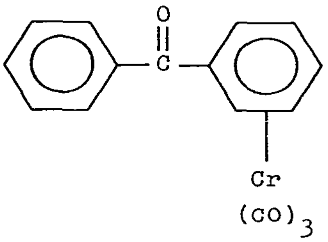


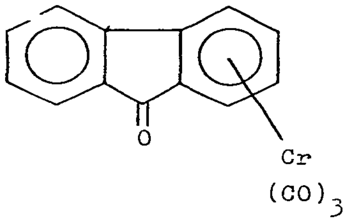
4.16

chromium complexes (4.14; R = Me, Bu^t; n = 1 - 3; M = P, As). Carbon atoms in the arene ring which were *trans* to phosphorus or arsenic in the preferred conformations of the molecules were deshielded as in the phosphine complex (4.15) [76].

The ^{1}H and ^{13}C NMR spectra of several mono- and *o*-disubstituted benchrotrenes have been measured and used to determine the effects of substituents on the stereochemistry where diastereotopy resulted from the presence of different types of chirality. For example the two *meso*-pseudosymmetrical isomers and the racemic-pseudosymmetrical isomer of the diol (4.16) were compared [77].

The ^{1}H and ^{13}C NMR spectra of the (η-arene)tricarbonylchromium complexes (4.17 and 4.18) have been measured, assigned and discussed. The large upfield shifts of the resonances of the directly coordinated rings were rationalised on the basis of CNDO calculations on benchrotrene [78].

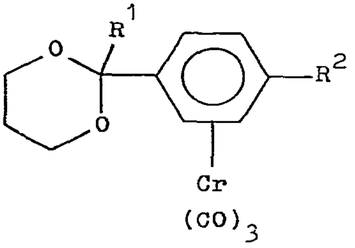

4.17


4.18

The self-consistent charge and configuration molecular orbital method and the Pople-Karplus equation were used to calculate ^{13}C NMR paramagnetic shielding constants for the isoelectronic series (η-benzene)tricarbonylchromium, tricarbonyl(η-cyclopentadienyl)manganese, (η-cyclobutadiene)tricarbonyliron, (η-allyl)tricarbonylcobalt and tricarbonyl(η-ethylene)nickel. A satisfactory explanation was given for the observed downfield shifts of the carbonyl ligands and the upfield shifts for the carbon atoms of the π-bonded organic ligands were rationalized [79]. The heats of thermal decomposition and of iodination were determined for a number of (η-arene)metal carbonyls. The following standard enthalpies of formation (kJ mol^{-1}) were obtained: $(\eta\text{-C}_6\text{Me}_6)\text{Cr(CO)}_3$ = -671 ± 13, (η-*nor*-$\text{C}_7\text{H}_8)\text{Cr(CO)}_4$ = -400 ± 13; $(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Mo(CO)}_3$ = -533 ± 13; $(\eta\text{-C}_6\text{Me}_6)\text{Mo(CO)}_3$ = -631 ± 8;

(η-cyclo-C_7H_8)Mo(CO)$_3$ = -297; (η-*nor*-C_7H_8)Mo(CO)$_4$ = -428 ± 10; (η-cyclo-C_7H_8)W(CO)$_3$ = -236 ± 8. It was concluded that the bond-enthalpy contribution, *D*(M—L), for a given ligand increas on ascending the series M = Cr→Mo→W, and for a given metal, *D*(M—L) increased on changing L along the series L = benzene→ mesitylene→hexamethylbenzene. It was suggested that the ther decomposition of some complexes took place in the condensed sta and involved the initial formation of polynuclear metal carbony and metal hexacarbonyls [80].

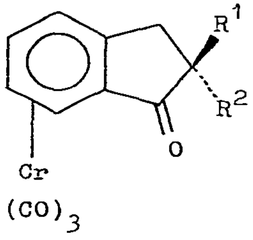
The stereochemistry of 2-benchrotrenyl-1,3-dioxanes (4.19; R^1 = H, Me, Ph; R^2 = H, Me) has been investigated by NMR spectroscopy and dipole moment measurements. It was found that the rotameric conformation of the molecule was determined by the steric requirements of the substituent on the benzene ligand [8



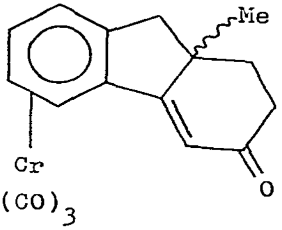
4.19

The tricarbonyl(η-indanone)chromium complex (4.20; R^1 = Me, R^2 = CH_2CH_2COMe) was cyclized under aldol conditions to form the enone complex (4.21; β-Me) in 91% yield. However, cyclization of the isomeric complex (4.20; R^1 = CH_2CH_2COMe, R^2 = Me) gave a mixture of the alcohols (4.22; R^1 = Me, R^2 = OH; R^1 = OH R^2 = Me) as the major products, >90% yield, together with a small proportion of the enone complex (4.21; α-Me), 5-10% yield The products (4.22) arose because of the unhindered *exo* face of the complex which facilitated attack at the activated C-3 position [82].

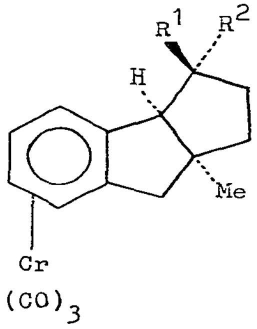
The α-alkylation of methyl arylacetates was facilitated by complexing the aryl ring with the tricarbonylchromium group. The reaction proceeded through an enolate anion which was generated by using 50% sodium hydroxide with a phase transfer catalyst such as cetyltrimethylammonium bromide or by using sodium hydride in N,N-dimethylformamide. Thus the ester comple



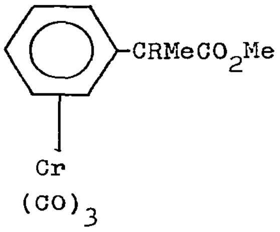
4.20



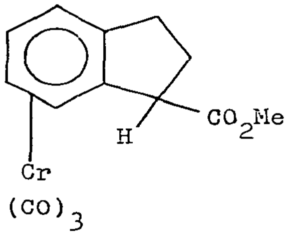
4.21



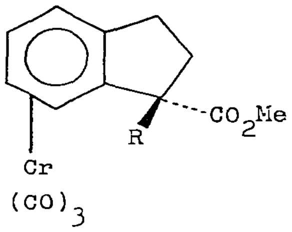
4.22



4.23



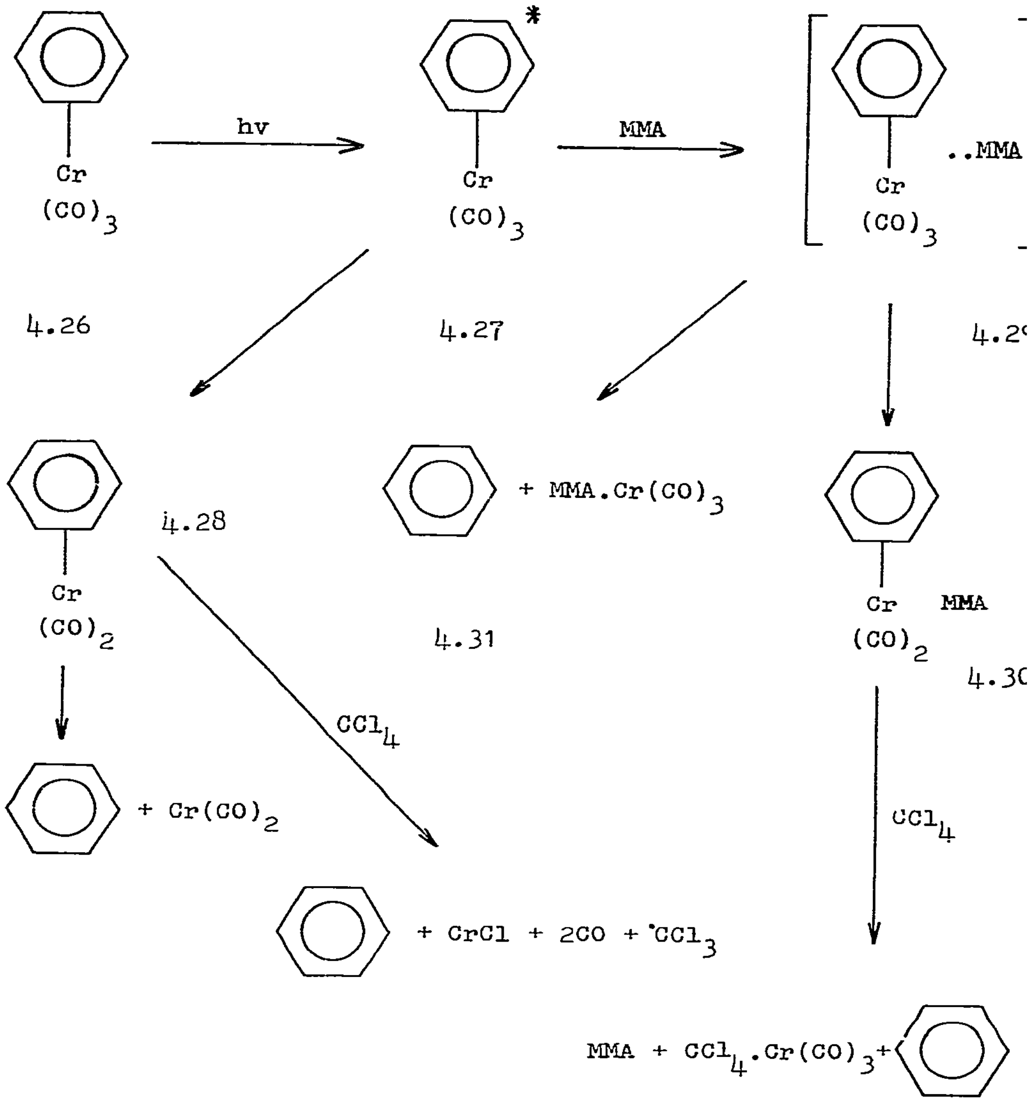
4.24



4.25

(4.23; R = H) was converted to the ester complexes (4.23; R = Me, $PhCH_2$, $CH_2{=}CHCH_2$, $HC{\equiv}CCH_2$). Alkylation of the *exo*- or *endo*-indane complexes (4.24) gave only the *exo*- product (4.25) [83].

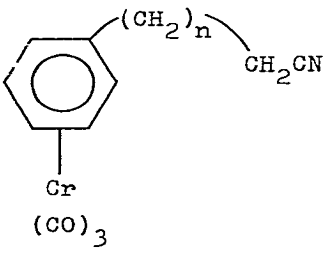
The photolysis of benchrotrene (4.26) in hydrocarbon solvents has been reinvestigated and the formation of an intermediate dicarbonyl complex (4.28) from the excited complex (4.27) confirmed. Subsequent decomposition to give benzene took place and this reaction was enhanced by the addition of carbon tetrachloride as indicated in Scheme 4.2. Photolysis in the presence of methyl methacrylate (MMA) afforded the exciplex (4.29) which then decomposed to the dicarbonyl intermediate (4.30) or to benzene and the chromium-methacrylate complex (4.31). When carbon tetrachloride was present it attacked the dicarbonyl intermediate (4.30) and enhanced the formation of benzene. The free radical polymerization of MMA in the presence of benchrotrene and carbon tetrachloride was investigated by kinetic methods [84].



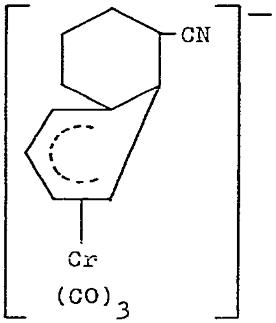
Scheme 4.2

(iii) GENERAL CHEMISTRY

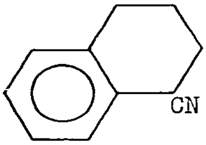
Stable organometallic polymers were obtained by treating polystyrene with tris(acetonitrile)tricarbonylchromium when tricarbonylchromium groups were linked to the phenyl residues of the polymer. The reactivity of the polymer decreased in the order: atactic > isotactic > crosslinked, while the replacement of chromium by molybdenum or tungsten led to unstable polymers [85]. Bis(η-benzene)chromium showed high photochemical stability by comparison with benchrotrene. Evidence was presented to show that (η-benzene)dicarbonylchromium was the intermediate in the photo-induced exchange of the benzene ligand in benchrotrene. Most of the energy absorbed by bis(η-benzene)chromium on irradiation was dissipated by rapid reversible isomerization or by rapid conversion of the excited state to the ground state [86]. Intramolecular nucleophilic addition of stabilized carbanions to the η-arene ligand in benchrotrenes has been observed. Thus the 5-phenylvaleronitrile complex (4.32; n = 3) was stirred with lithio-2,2,6,6-tetramethylpiperidide in THF to form the (η-alkylcyclohexadienyl)chromium intermediate (4.33) which, after oxidative quenching, afforded 1-cyanotetralin (4.34) in 89% yield. Under the same conditions, the lower homologue (4.32; n = 2) gave the [3.3]metacyclophane (4.35)[87].



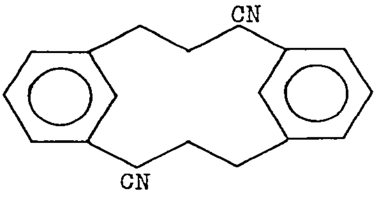
4.32



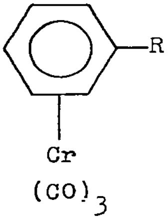
4.33



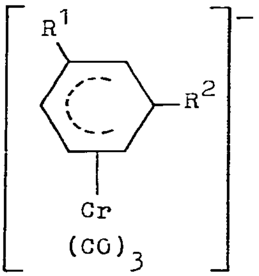
4.34



4.35



4.36



4.37

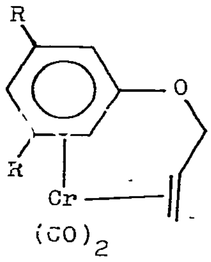
The addition of carbanions to substituted benchrotrenes (4.36; R = Me, OMe) gave (η-cyclohexadienyl)chromium complexes (4.37; R^1 = Me, OMe; R^2 = CH_2CN, CMe_2CN, $CH_2CO_2Bu^t$, $CMe_2CO_2Bu^t$) which were conveniently oxidized to the corresponding alkylbenzenes. The reaction shows high selectivity towards the formation of m-derivatives [88]. The epoxidation of cyclohexen by ethylbenzene hydroperoxide was found to be catalysed by (η-arene)tricarbonylmolybdenum complexes [89].

(η-Arene)tricarbonylmolybdenum complexes catalysed Friedel Crafts reactions such as alkylation, acylation, polymerization, sulphonation and dehydrohalogenation. If the reaction involved an aromatic hydrocarbon the molybdenum complex could be generat in situ by the addition of hexacarbonylmolybdenum or the preformed (η-arene)tricarbonylmolybdenum complex could be added. For example, the reaction of toluene with t-butylchloride in th presence of hexacarbonylmolybdenum gave p-(t-butyl)toluene in good yield [90].

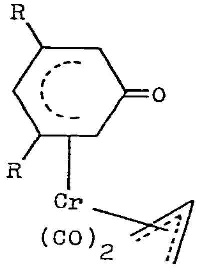
Tricarbonyl(η-naphthalene)chromium was an effective cataly for the addition of carbon tetrachloride to olefins to form 1,1,1,3-tetrachloroalkanes. The reaction involved the formatio of the active complex CCl_3.Cl Cr(THF)$(CO)_3$ through the intermediate (η-$C_{10}H_8$)(THF)Cr$(CO)_3$ [91]. Tricarbonyl(η-toluene)-molybdenum has been used as Friedel-Crafts catalyst for the alk ation, acylation and sulphonation of phenol, anisole, toluene and t-butylbenzene. The polymerization of benzyl-chloride and -fluoride was also catalyzed by the same complex [92].

(iv) ANALOGUES

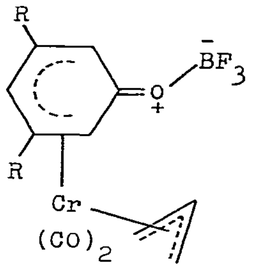
The polymerization of phenylacetylene in the presence of tricarbonyl(η-mesitylene)molybdenum was slow but on UV irradiat of the system, polymerization was greatly accelerated. It was proposed that irradiation of the catalyst caused displacement o a carbonyl group by the acetylene group of a monomer molecule. This η-acetylene complex then rearranged to a σ-acetylene compl which initiated polymerization [93]. The allyl phenyl ether complexes (4.38; R = H, Me) isomerized in benzene to give the corresponding η-allyl complexes (4.39). Treatment of the compl (4.38; R = H) with boron trifluoride etherate gave the boron trifluoride adduct (4.40) which was converted to the chromium complex (4.39; R = H) by reaction with diisopropylamine [94]. Mass spectrometry has been used to determine metal-ligand bond strengths in a series of (η-methylbenzoate)chromium complexes



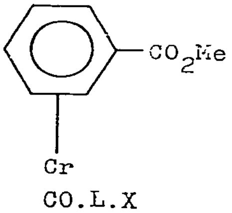
4.38



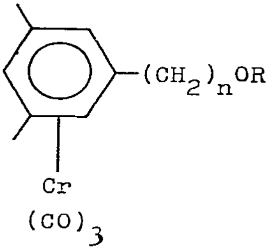
4.39



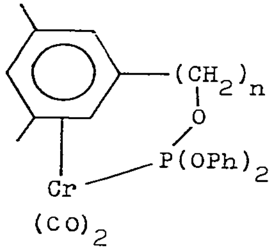
4.40



4.41



4.42

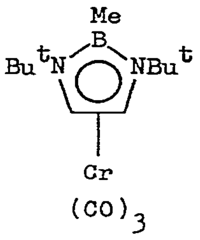


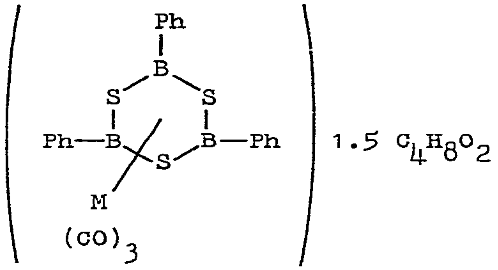
4.43

[4.41: L = CO; X = CS, PPh_3, PMe_2Ph, $P(OR)_3$; L = CS; X = $P(OR)_3$]. The thiocarbonyl group was shown to be a better σ-donor and π-acceptor than the carbonyl group [95]. The benchrotrene derivatives (4.42; n = 1 - 3; R = H) were converted to the phosphites (4.42; n = 1 - 3; R = $P(OPh)_2$ with $ClP(OPh)_2$ in pyridine and the phosphites were irradiated in benzene to give the chelate complexes (4.43; n = 1 - 3) [96].

The benchrotrene analogue (4.44) was formed by treatment of 1,3-di-t-butyl-2-methyl-Δ^4-1,3,2-diazaboroline with triacetonitriletricarbonylchromium [97]. Reaction of B,B',B"-triphenylborthiin with tricarbonyltri(methylcyanide)metal complexes $(MeCN)_3M(CO)_3$ (M = Cr, Mo, W) in dioxan gave the corresponding borthiin complexes (4.45). It was thought that the dioxan was bound to the borthiin ring via boron-oxygen bonds [98].

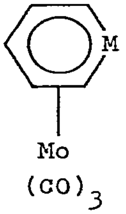
The σ- and π- coordination chemistry of the Group 5 heterobenzenes was investigated. Pentacarbonylphosphabenzenemolybdenum was prepared by ligand displacement from pentacarbonyltetrahydrofuranmolybdenum. The former complex was thermally stable up to

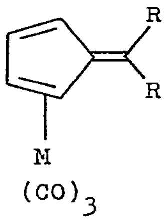




4.44

4.45





4.46

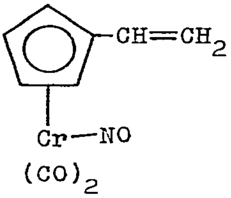
4.47

200^o and it did not lose CO to give the π-complex (4.46; M = P). The arsabenzene complex (4.46; M = As) was prepared by heating molybdenum carbonyl with arsabenzene in diglyme or by the boron trifluoride etherate catalysed ligand displacement from tricarbo tris(pyridine)molybdenum. The latter method was used to prepare the η-stibabenzene complex (4.46; M = Sb) [99].

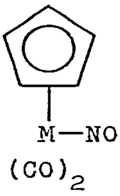
The (η-fulvene)metal complexes (4.47; R = alkyl, Ph; M = Cr, Mo, W) were obtained by treatment of the required fulvene with tris(acetonitrile)tricarbonyl-chromium, -molybdenum and -tungsten [100].

5. $(\eta\text{-}C_5H_5)Cr(CO)_2NO$

The chromium complex (5.1) was prepared by acetylation of dicarbonyl(η-cyclopentadienyl)nitrosylchromium followed by sodiu borohydride reduction of the ketone group and acid-catalysed dehydration. The monomer (5.1) was homopolymerized and copolyme



5.1



5.2

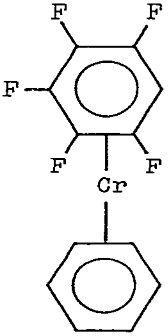
ized with styrene, N-vinylpyrrolidone and vinylcymantrene in the presence of azoisobutyronitrile as the initiator [101].

The infrared and Raman spectra of the nitrosyl complexes (5.2; M = Cr, Mo, W) were recorded and interpreted. The spectra of these compounds were compared with those of other nitrosyl complexes [102].

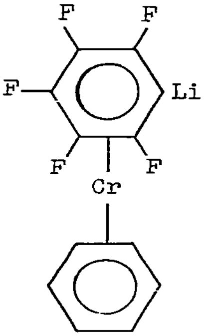
6. $(\eta\text{-}C_6H_6)_2Cr$

Cocondensation of chromium vapour with a mixture of pentafluorobenzene and benzene gave the air-stable chromium complex (6.1). Addition of t-butyllithium to the complex (6.1) gave the lithio derivative (6.2) which was condensed with a number of electrophiles. Infrared spectroscopy suggested that the $(\eta\text{-}C_6H_6)Cr$ moiety was electron-donating in character [103].

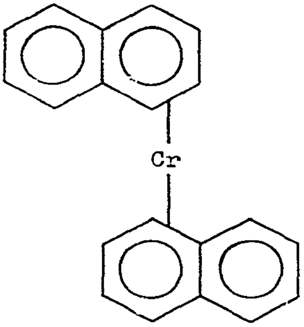
Bis(η-arene)chromium compounds were formed by the cocondensation of arenes with transition metal atoms. Convenient syntheses



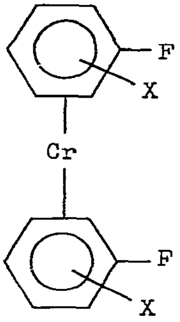
6.1



6.2



6.3

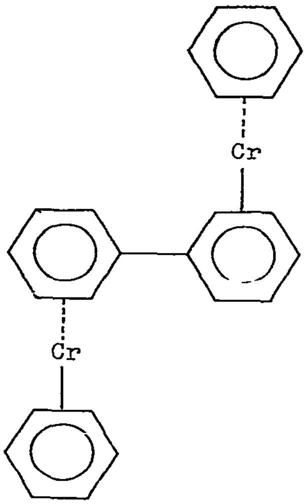


6.4

were devised for compounds bearing fluorine and trifluoromethyl substituents. The thermal stability of bis(η-benzene) transition metal complexes of first-row metals decreased with increasing atomic number of the metal [104, 105, 106]. Using metal vapour synthesis techniques chromium atoms were treated with naphthalene to give bis(η-naphthalene)chromium (6.3) and with 1-methylnaphthalene to give bis(η-1-methylnaphthalene)chromium. The latter compound was a mixture of isomers with either the C_6H_3Me or C_6H_4 ring unit coordinated to the metal. Bis(η-naphthalene)chromium underwent reaction easily with carbon monoxide at one atmosphere and room temperature to give first $(\eta\text{-}C_{10}H_8)Cr(CO)_3$ then $Cr(CO)_6$ [107, 108].

Fluoroarenes were cocondensed with chromium atoms to form a number of bis(η-arene)chromium complexes (6.4; X = *o*-, *m*-, *p*-; H, F, Cl, Me, CF_3). The correlation between the ^{19}F NMR chemical shifts of the complexes and those of the corresponding C_6F_5X compounds suggested that the electron withdrawing effect of an η-bonded chromium atom was similar to that of four ring-fluorine substituents. Nucleophilic attack by methoxide ion on bis(η-fluorobenzene)chromium gave bis(η-anisole)chromium [109].

The η-arenechromium analogue (6.5) of biferrocene was prepared by the reaction of lithiated bis(η-benzene)chromium with *o*-bromoanisole. Air oxidation of the chromium complex (6.5) gave a dication whose ESR spectrum in solution was characteristic of a diradical. It was concluded that the molecule (6.5) had a *trans* configuration [110]. Bis(η-ethylbenzene)chromium was prepared by the reductive Friedel-Crafts reaction and any impurities present were determined by mass spectral and gas

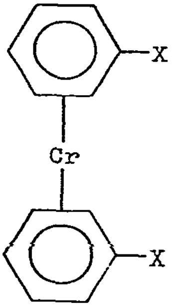


6.5

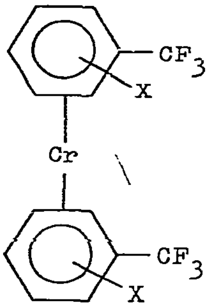
chromatographic methods [111]. Molybdenum(V) chloride was heated with ethylbenzene in the presence of aluminium chloride and aluminium to form bis(η-ethylbenzene)molybdenum [112].

An infrared spectroscopic study was made of the interaction of benzene and perdeuterobenzene with transition metal vapours at low temperatures. The spectra obtained from the products with chromium were compared with those of bis(η-benzene)chromium and bis(η-perdeuterobenzene)chromium. It was concluded that these complexes were not formed in the condensation [113]. Activation enthalpies for the reorientation of the hydrocarbon ligands in ferrocene, ruthenocene and di(η-benzene)chromium have been obtained from pulse NMR measurements. The values were compared with the calculated contribution from non-bonded interactions to the total potential for reorientation of the ligands. It was concluded that the observed potential barrier arose by combination of bonding forces within the molecule and crystal packing forces and did not arise from non-bonded interactions between the two ligands in a single molecule [114].

The electrochemical oxidation of several bis(η-arene)chromium complexes including the disubstituted (6.6; X = F, Cl, CF_3, OMe) and tetrasubstituted (6.7; X = m-CF_3, p-CF_3,p-Cl) complexes have been investigated by cyclic voltammetry. One-electron oxidation was observed in each case and a linear correlation was obtained



6.6



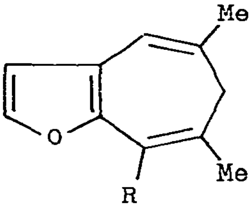
6.7

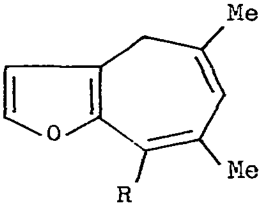
between the measured $E_{\frac{1}{2}}$ values and the Hammett σp parameters [11 Poly(methylsiloxane) stationary phases have been used for the gas chromatography of bis(η-arene)chromium compounds at 200°C. These stationary phases offered high capacity, they were useful for preparative gas chromatography and for the detection of small amounts of impurities in the chromium compounds [116].

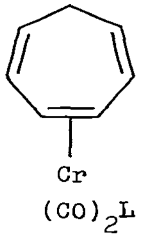
Bis(η-indenyl)chromium was deposited onto a silica support and this was used as a catalyst for the polymerization and copolymerization of ethylene. Ethylene was polymerized under pressure to give polyethylene containing nine parts per million chromium [117]. The thermal decompositions of bis(η-ethylbenzene chromium and (η-diethylbenzene)(η-ethylbenzene)chromium were investigated. The decompositions were shown to occur via both heterogeneous and homogeneous processes [118].

7. $[(\eta\text{-}C_7H_7)Cr(CO)_3]^+$ and $(\eta\text{-}C_7H_8)Cr(CO)_3$

Reactions of the furotropylidenes (7.1 and 7.2; R = H, Me) with hexacarbonylchromium gave the corresponding tricarbonylchromium complexes with the metal bonded to the seven-membered ring [119]. A carbonyl group in tricarbonyl(η-cycloheptatriene)-chromium was photochemically displaced by a group V ligand to give the chromium dicarbonyl derivatives [7.3; L = PMe_3, $P(OMe)_3$, $AsMe_3$]. These complexes exhibited temperature dependent ^1H, ^{13}C and ^{31}P NMR spectra arising from restricted motion of the η-cycloheptatriene ligand. Stereoisomers of the complexes were interconverted by this motion and the energy barriers to interconversion were determined [120]. The ^1H and ^{13}C NMR spectra of the complexes (7.4; M = Cr, Mo, W) were recorded. Two







7.1

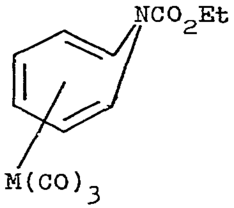
7.2

7.3

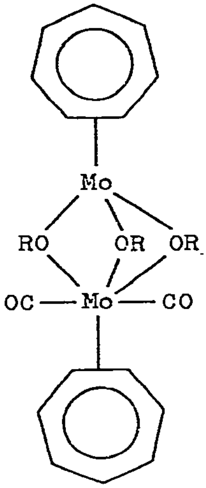
different ligand motions were activated thermally (1) rotation of the carbethoxy group around the C — N bond and (2) movement of the azepine ligand against the tricarbonylmetal group [121].

Reaction of (η-benzene)tricarbonylchromium complexes with mercury(II) chloride in ether gave the adducts $RC_6H_5Cr(CO)_3.nHgCl_2$ where R = H, NH_2, MeNH, Me_2N, $HOCH_2$ and n = 1 - 3 [122]. Treatmen of tricarbonyl(η-cycloheptatrienyl)molybdenum bromide with alkoxides or phenoxides gave the binuclear complexes (7.5; R = Me, Et, Ph, *p*-tolyl, *p*Cl-C_6H_4) with different oxidation states for the two molybdenum atoms and two types (η^3 and η^7) of cycloheptatrienyl ligand [123].

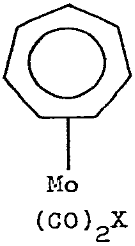
The tricarbonyl(η-cycloheptatrienyl)molybdenum cation was attacked by halogenotrimethylsilanes to form initially the halogenocomplexes (7.6; X = Cl, Br, I) which underwent further reaction to give the binuclear complexes (7.7; X = Cl, Br, I). Under mild oxidizing conditions these complexes gave the corresponding cations [124].



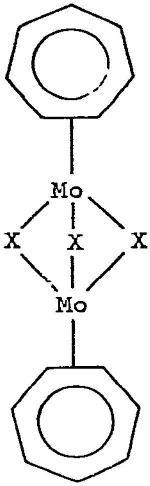
7.4



7.5

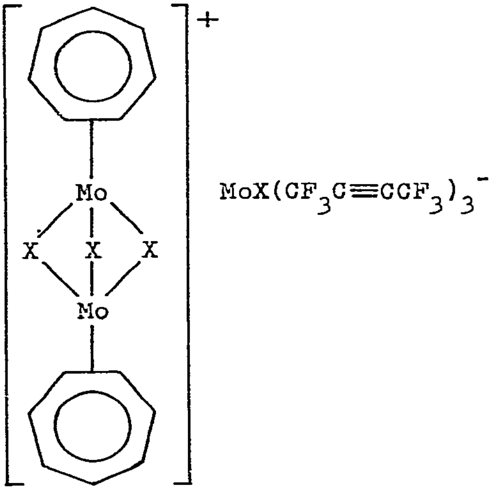


7.6

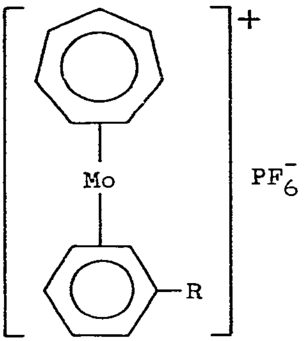


7.7

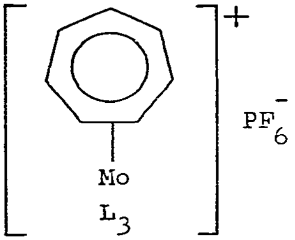
Heating halogenodicarbonyl(η-cycloheptatrienyl)molybdenum complexes with hexafluorobut-2-yne gave the ionic polynuclear complexes (7.8; X = Cl, Br, I). The chloro complex was



7.8



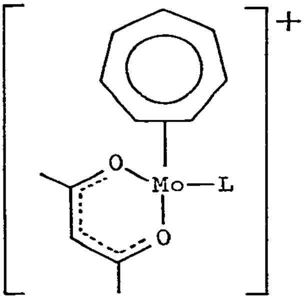
7.9



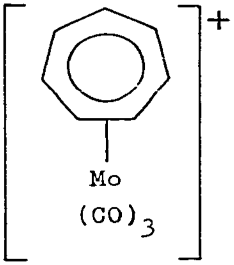
7.10

characterized by an X-ray diffraction study and ^{19}F NMR spectroscopy was used to demonstrate the fluxional nature of the complexes (7.8) [125]. The molybdenum complexes (7.9; R = H, Me) were treated with a series of ligands L (L = MeCN, PMe_2Ph, $PMePh_2$) when displacement of the arene group occurred to give the η-cycloheptatrienylmolybdenum complexes (7.10). The complexes (7.10) readily exchanged one or more of the ligands L when treated with other ligands [126].

Treatment of the cations (7.11) and (7.9; R = Me) with acetylacetone gave the seventeen-electron aqua-complex (7.12; L = H_2O) from which the water molecule was easily displaced by other ligands L where L = PEt_3, PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $AsMe_2Ph$, pyridine. The molecular and crystal structure of the aqua-complex (7.12; L = H_2O) was determined by X-ray analysis. In this cation the Mo(I) metal atom had approximately octahedral geometry [127].



7.12

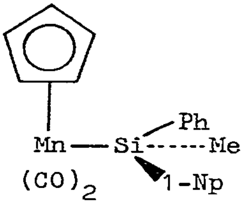


7.11

8. $(\eta\text{-}C_5H_5)Mn(CO)_3$

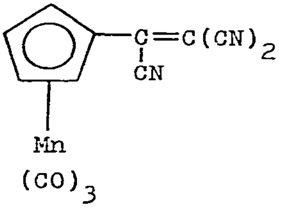
(i) FORMATION

Irradiation of cymantrene with 1-naphthyldimethylphenylsilan gave the manganese complex (8.1). Cleavage of the manganese - silicon bond in the complex (8.1) occurred either by nucleophili attack at silicon with inversion of configuration (lithium aluminium hydride, water or methanol) or by deinsertion with retention of configuration at the silicon atom followed by replacement of a ligand at manganese (triphenylphosphine or triphenylphosphite) or by decomposition of the manganese complex [128].



1-Np = 1-naphthyl

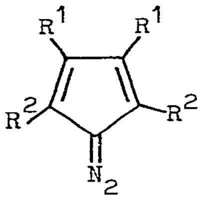
8.1



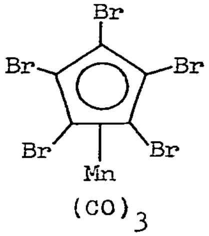
8.2

The reaction of thallium(I) tricyanovinylcyclopentadienide with bromopentacarbonylmanganese gave the tricarbonylmanganese derivative (8.2) [129]. A series of (η-benzoylcyclopentadienyl)-tricarbonylmanganese compounds was prepared together with the corresponding tricarbonylchromium derivatives. These complexes were examined by infrared, ^1H NMR and mass spectroscopy [130]. Reaction of the pentacarbonylmanganese halides $Mn(CO)_5X$ (X = Br, I) with the diazocyclopentadiene derivatives (8.3; $R^1 = R^2 = Br$; $R^1 = H$, $R^2 = I$) gave the corresponding cymantrene derivatives (8.4, 8.5 and 8.6) in good yields. Similarly, tricarbonyl(η-tetrachloroiodocyclopentadienyl)manganese was prepared from tetrachlorodiazocyclopentadiene [131].

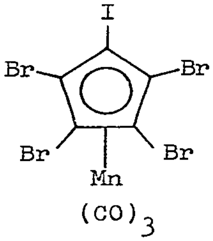
Treatment of cymantrene with chlorine and bromine at -40° gave the adducts (8.7; R = X = Cl) and (8.7; R = Br, X = Br_3) respectively. These adducts decomposed at 20° to give manganese (II) chloride, manganese(II) bromide, cymantrene, trichloro- and



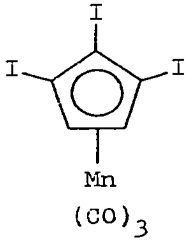
8.3



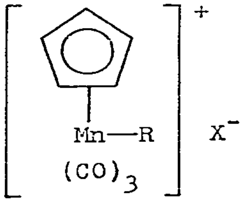
8.4



8.5

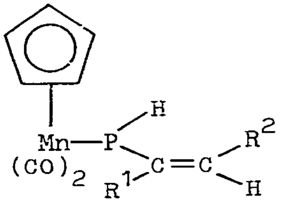


8.6



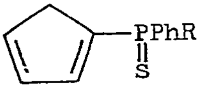
8.7

tribromo-cyclopentene and $[ClMn(CO)_4]_2$. Reaction of the adducts with sodium thiosulphate, tin(II) chloride, phenol, ferrocene and chloromercuriferrocene gave cymantrene [132]. Tricarbonyl-(η-trimethylsilylcyclopentadienyl)manganese was prepared by the reaction of sodium trimethylsilylcyclopentadienide with manganese (II) and carbon monoxide at 160° under pressure [133].

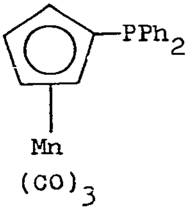


8.8

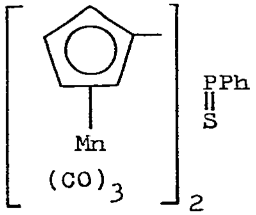
Dicarbonyl(η-cyclopentadienyl)(phenylphosphine)manganese underwent reaction stereospecifically with the acetylenes $R^1C{\equiv}CR^2$ (R^1 = H, R^2 = Ph; R^1 = R^2 = Ph; R^1 = H, R^2 = $SiMe_2C{\equiv}CH$ to give the corresponding phenylvinylphosphine complexes (8.8) [134]. The cyclopentadienylphosphine sulphide (8.9; R = Ph) was heated with manganese carbonyl to form the cymantrenyl phosphine (8.10) while the dicymantrenyl phosphine sulphide (8.11) was obtained from the bis(cyclopentadienyl)phosphine sulphide (8.9; R = 1-cyclopenta-1,3-dienyl) [135].



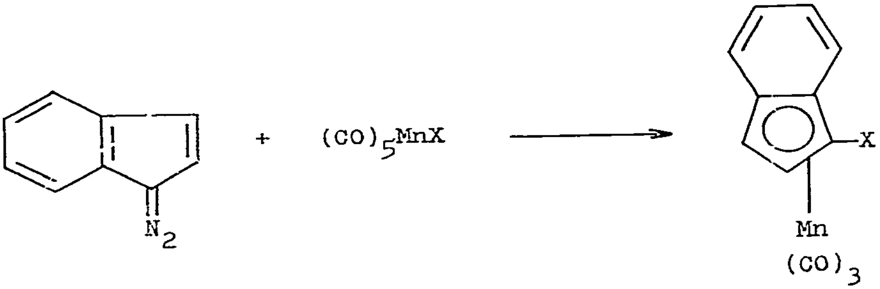
8.9



8.10



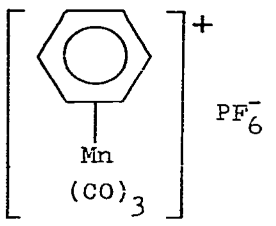
8.11



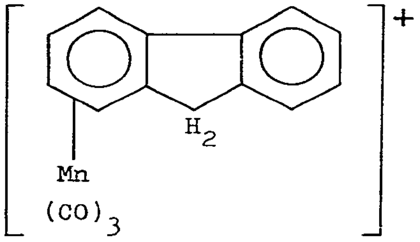
8.12

8.13

Reaction of the diazoindene (8.12) with a halopentacarbony manganese complex gave the corresponding cymantrene derivatives (8.13; X = Cl, Br, I) [136]. Treatment of tricarbonyl(η-methyl cyclopentadienyl)manganese with aluminium bromide in the preser of an aromatic hydrocarbon (benzene, toluene, xylene, mesityle gave the corresponding cationic (η-arene)- tricarbonylmanganes

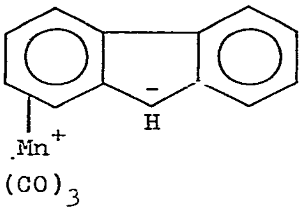


8.14

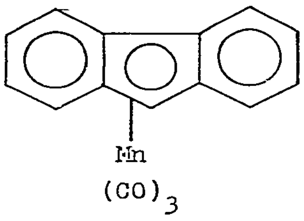


8.15

complex. For example with benzene the salt (8.14) was isolated [137]. The tricarbonyl(η-fluorene)manganese cation (8.15), prepared from fluorene and bromomanganese pentacarbonyl, underwent proton abstraction with triethylamine to form the deep red (η-fluorenyl)manganese complex (8.16). This complex was alkylated at C(9) by MeOSO$_2$F in hexane to give the *exo*-methyl derivative and reprotonated to the original cation (8.15) with trifluoroacetic acid, however, on standing the complex (8.16) rearranged irreversibly to the isomeric cymantrene derivative (8.17) [138].



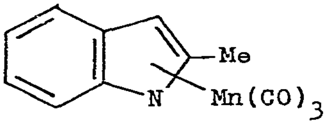
8.16



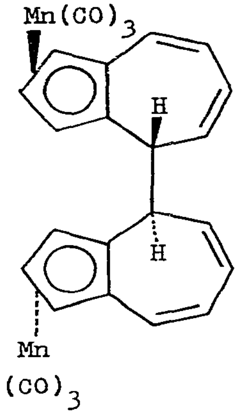
8.17

(ii) SPECTROSCOPIC AND PHYSICO-CHEMICAL PROPERTIES

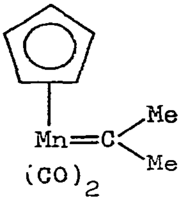
The crystal and molecular structure of tricarbonyl-η-(2-methylindolyl)manganese (8.18) was determined by X-ray diffraction. The manganese was bound to the heterocyclic ring with one of the carbonyl groups *trans* to the nitrogen atom [139]. The crystal and molecular structure of the (η-azulene)tricarbonylmanganese dimer has been determined by X-ray crystallography.



8.18



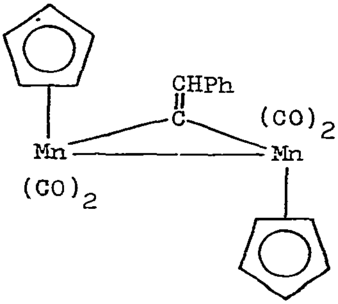
8.19



8.20

The molecule consisted of a 4,4'-diazulene ligand with each of the two five-membered rings bonded to a tricarbonylmanganese group (8.19) to form a chiral complex [140].

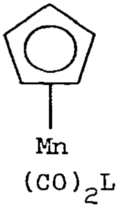
The structure of the carbene complex (8.20) was determined by X-ray analysis. The molecule exhibited pseudooctahedral coordination with the carbonyl groups and the carbene moiety at approximately 90° to each other. The η-cyclopentadienyl ring



8.21

was planar [141]. The crystal and molecular structure of the binuclear phenylvinylidene manganese complex (8.21) has been determined by X-ray crystallography [142].

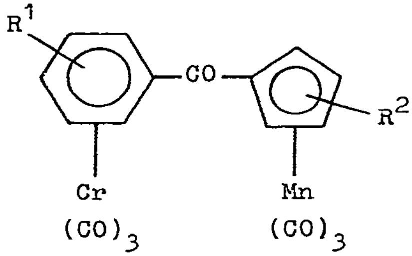
The electronic structure and structural dynamics of dicarbonyl(η-cyclopentadienyl)manganese, which is formed as an intermediate on photolysis of cymantrene, were considered in terms of the molecular orbital theory [143]. The electronic spectra and photosubstitution reactions of cymantrene and the related complexes (8.22; L = pyridine, substituted pyridine, aliphatic amine) have been studied. The low-energy region of the spectrum exhibited a strong M→π*L charge-transfer band when L was a pyridine. The complexes were photosensitive with efficiencies in the range 0.2-0.4 with the group L being replaced by 1-pentene, pyridine and substituted pyridine [144].



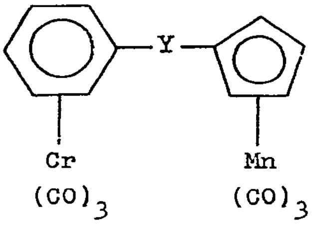
8.22

Several benchrotrene substituted acylcymantrenes (8.23; R^1 = H, Me, OMe; R^2 = H, Me) have been prepared together with some related mixed binuclear complexes (8.24; Y = CH_2, CH_2CO, CH_2CHOH, CH=CH). ^{1}H NMR spectroscopy was used to show that the electronic effect of the tricarbonyl chromium group was transmitted to the cyclopentadienyl ring through a carbonyl bridge but not through a methylene bridge. The IR carbonyl stretching frequencies of the tricarbonylmanganese group were affected slightly by the presence of the tricarbonyl chromium group [145].

The ^{1}H and ^{13}C NMR spectra of cymantrene have been obtained in nematic and isotropic solvents respectively. The direct and indirect H—H and ^{13}C—H coupling constants were determined and used to calculate the molecular geometry of the η-cyclopentadienyl ring and the distance between it and the planes of the carbonyl carbon atoms [146].

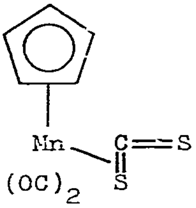


8.23

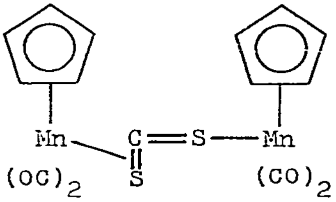


8.24

The temperature-dependence of the ^{13}C NMR spectrum of the carbon disulphide manganese complex (8.25) gave the energy barrier to free rotation of the carbon disulphide ligand as 9.5 kcal mol^{-1} while the free energy of activation for the degenerate σ—π isomerization of the same ligand in the binuclear complex (8.26) was 12.4 kcal mol^{-1} [147].

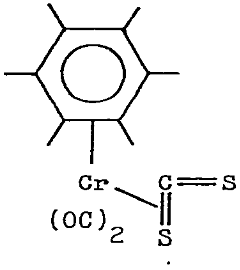


8.25

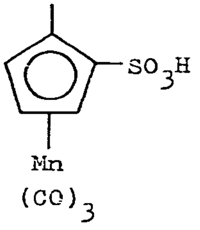


8.26

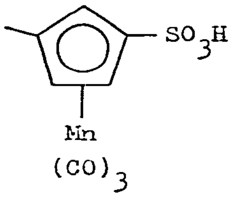
IR and ^{1}H NMR spectroscopy have been used to investigate the π-acceptor efficiency of the η^2-carbon disulphide ligand in complexes related to cymantrene (8.25) and benchrotrene (8.27). The ligand was found to be much more efficient than carbon monoxide [148]. The structures of isomers (8.28) and (8.29) which had been determined by ^{1}H NMR and chromatographic methods [149] were confirmed by an unambiguous chemical method. The influence of the methylthio group on the electrophilic substitution of 2-methyl- and 3-methyl-methylthiocymantrene was studied by Friedel-Crafts acetylation [150].



8.27



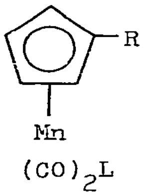
8.28



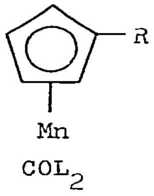
8.29

^{55}Mn and ^{35}Cl NQR data were obtained for cymantrenylmercurichloride and -bromide and bis(cymantrenyl)mercury. The presence of the mercury halide group had little effect on the quadrupole constants for manganese [151]. Cyclic voltammetry has been used to show that the (η-cyclopentadienyl)manganese complexes [8.30; R = H, Me; L = PR_3, $P(OR)_3$ and 8.31; R = H,Me; L = PR_3, $Ph_2PCH_2CH_2PPh_2$] underwent a reversible one electron oxidation. The relationship between the oxidation potential and the force constant for the carbonyl stretching vibrations was discussed [152].

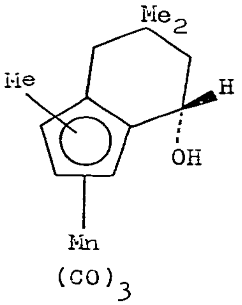
Plouzennec and Dabard have examined the reduction of 1,2-(α-oxotetramethylene)methylcymantrenes by borohydride and Grignard reagents. Formation of the secondary alcohol products (8.32) was stereospecific and the <u>endo</u>-configuration of the



8.30

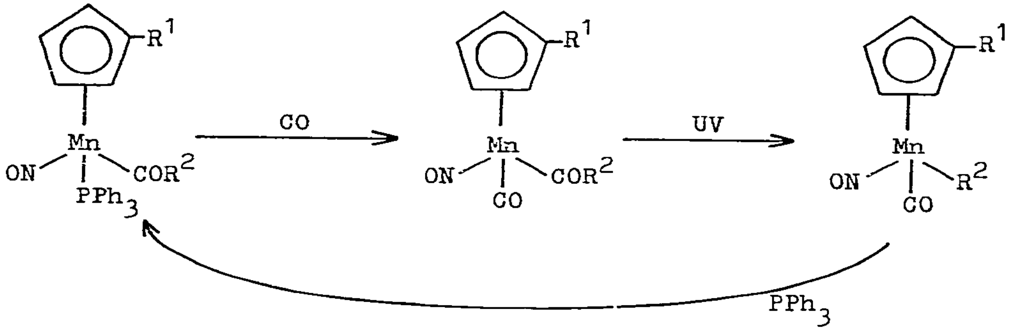


8.31



8.32

dominant products was confirmed by spectroscopy and chromatography. Reduction with lithium aluminium hydride was not stereospecific [153]. The optically active (η-cyclopentadienyl)manganese complexes (8.33; R^1 = H, Me; R^2 = Me, Ph) were carbonylated with displacement of the triphenylphosphine ligand to form the carbonyl(η-cyclopentadienyl)manganese intermediates (8.34; R^1 = H, Me; R^2 = Me, Ph). These intermediates underwent photochemical decarbonylation to the complexes (8.35; R^1 = H, Me; R^2 = Me, Ph) and slowly took up triphenylphosphine to form the original complexes (8.33). The slow final step allowed σ-alkyl and σ-aryl compounds to be ruled out as the chiral intermediates in the racemization and ligand exchange reactions of the triphenylphosphine complexes (8.33) [154].

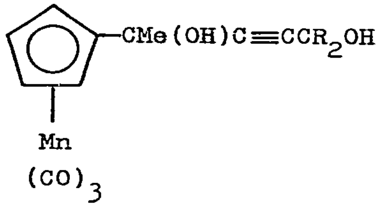


8.33 8.34 8.35

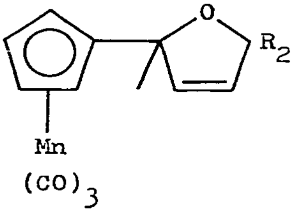
(iii) GENERAL CHEMISTRY

The cymantrenylacetylenes (8.36; R = alkyl, cycloalkyl) were hydrogenated over Raney nickel to give the corresponding olefins. Dehydration of these olefins with potassium hydrogen sulphate afforded the cyclic ethers (8.37). [155].

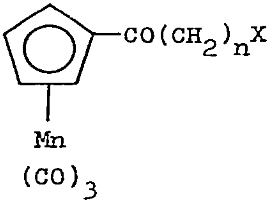
Friedel-Crafts reaction of cymantrene with acid chlorides was used to prepare the manganese complexes (8.38; n = 2,4, 6; X = Cl). Treatment of the latter complexes with potassium cyanide gave the corresponding cyanides (8.38; n = 2, 4, 6; X = CN) which when irradiated formed the dicarbonylmanganese complexes (8.39) [156]. Dicymantrenyl ketone was treated with cymantrenyllithium in THF at -50° to give tris(cymantrenyl)-



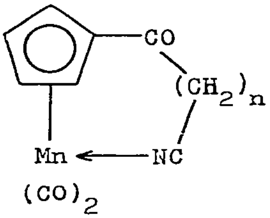
8.36



8.37



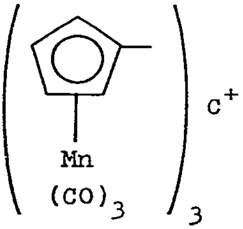
8.38



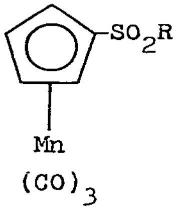
8.39

carbinol in 70% yield. The carbinol was converted to the tris(cymantrenyl)carbenium cation (8.40) in a mixture of trifluoroacetic acid and sulphuric acid [157].

Treatment of tricarbonyl(η-chlorosulphonylcyclopentadienyl)manganese with sodium azide or dimethylamine hydrochloride gave



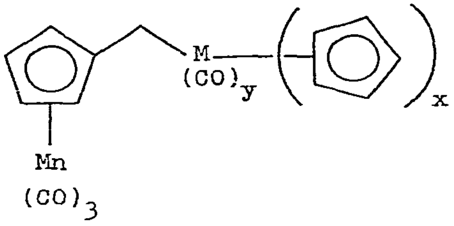
8.40



8.41

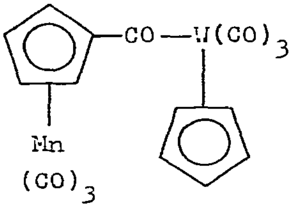
the azide (8.41; R = N_3) and amine (8.41; R = NMe_2) respectively Lithiation of the amine (8.41; R = NMe_2) at the 2- position was effected with methyl-lithium at -70°. The lithiated intermediate was condensed with a series of electrophiles to give 1,2-disubstituted tricarbonyl(η-cyclopentadienyl)manganese derivatives. The ^1H NMR and mass spectra of these compounds were discussed [158].

Cymantrene combined with boron triiodide to form bis-(diiodoboryl)cymantrene [159]. The (η-cyclopentadienyl)manganese complexes (8.42; M = Fe, x = 1, y = 2; M = Mo, W, x = 1, y = 3; M = Mn, Re, x = 0, y = 5) were prepared by the reaction of (η-C_5H_5)M$(CO)_y$Na with (tricarbonyl)(η-chloromethylcyclopentadienyl)manganese [160].

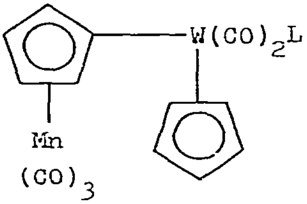


8.42

The cymantrenoyl tungsten complex (8.43) was formed by treating cymantrenoyl chloride with $NaW(CO)_3$(η-C_5H_5) in THF at -70°. Carbon monoxide was eliminated on heating in xylene to give the cymantrenyl tungsten complex (8.44; L = CO) which underwent ligand displacement on photolysis with triphenyl-



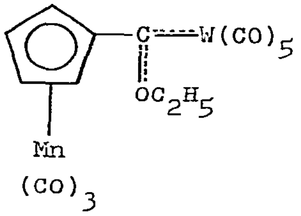
8.43



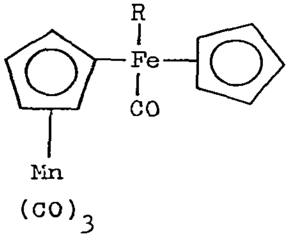
8.44

phosphine to form the derivative (8.44; L = PPh_3) [161].

Formation of the tungsten-carbene complex (8.45) from hexacarbonyltungsten, lithiocymantrene and $(C_2H_5)_3O.BF_4$ has been reported [162]. Reaction of the σ-cymantrenyl derivative (8.46; R = CO) with iodine gave tricarbonyl(η-iodocyclopentadienyl)manganese. The Fe—C σ-bond was cleaved also by mercury(II) bromide and trifluoroacetic acid. Irradiation of the complex (8.46; R = CO) in the presence of triphenylphosphine gave the manganese derivative (8.46; R = PPh_3) [163].



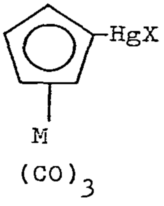
8.45



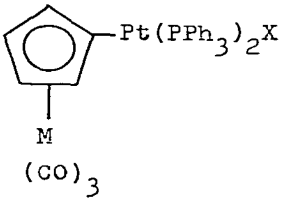
8.46

Reaction of the manganese or rhenium complexes (8.47; M = Mn, Re; X = Cl, Br) with tris(triphenylphosphine)platinum gave the corresponding platinum complexes (8.48) [164]. Reaction of lithiated derivatives (8.49; M = Mn, Re) with cis-dichlorobis-(triphenylphosphine)platinum(II) gave the corresponding σ-bonded platinum derivatives (8.50; M = Mn, Re) [165].

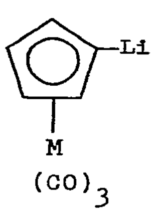
The effects of methylcymantrene on oxidative phosphorylation in rat hepatic mitochondria have been investigated. The complex



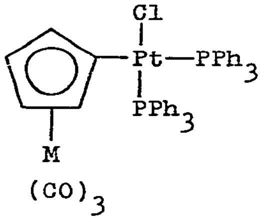
8.47



8.48



8.49



8.50

inhibited both electron transfer and energy transfer in mitochondria, it was more effective in inhibiting glutamate-maleate oxidation than the oxidation of succinate and tetramethylphenylenediamine-ascorbate [166].

The toxicological effects of methylcymantrene and related compounds on rat liver mitochondria have been investigated. These compounds were effective inhibitors of mitochondrial respiration and this effect was attributed to the tricarbonylmanganese group. Replacement of the methyl group by other substituents enhanced the inhibitory effect [167].

(iv) APPLICATIONS

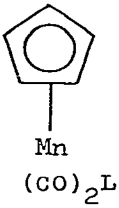
Silver-free photosensitive compositions have been prepared containing cymantrene, 1-5 parts, a binder such as polystyrene or cellulose triacetate, 1-10 parts and tetracyancethylene, 0.5-1 parts [168]. Cymantrene has been used to control soot formation in the combustion of light fuel oils in evaporating burners. The volatility and catalytic properties of the additive were factors contributing to its efficiency [169].

The fire resistance of wood was improved by treatment with a composition containing cymantrene, urea and phosphoric acid [170]. The fire resistance of fibreboard was increased by the incorporation of cymantrene [171].

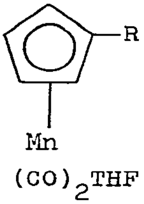
The addition of a mixture of cymantrene, thiophene, ethyl bromide, tricresyl phosphate and toluene to petrol reduced the concentration of carbon monoxide in the exhaust gases of an internal combustion engine. The combustion of cymantrene produced manganese(IV) oxide which catalyzed the oxidation of carbon monoxide to carbon dioxide. It was noted also that in the presence of cymantrene there was no significant increase in the concentration of nitrogen oxides in the exhaust gas [172].

(v) ANALOGUES

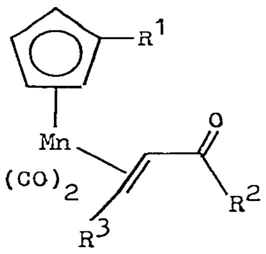
The THF(η-cyclopentadienyl)manganese complex (8.51; L = THF) was treated with cyclooctatetraene to form the (η-cyclooctatetraene)(η-cyclopentadienyl)manganese complex (8.51; L = C_8H_8). The crystal and molecular structure of this product was determined by X-ray crystallography confirming the η^2-mode of bonding for cyclooctatetraene [173].



8.51

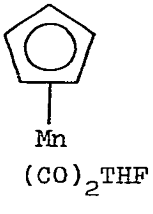


8.52

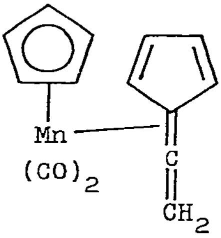


8.53

Irradiation of cymantrene and methylcymantrene in THF gave the intermediates (8.52; R = H, Me) which were converted to the enone-manganese complexes (8.53; R^1 = H, Me; R^2 = H, Me, OMe, Ph; R^3 = H, Me, Ph) on the addition of the appropriate enone. When the ligand was sorbic aldehyde (MeCH=CHCH=CHCHO) then coordination occurred only at the α-olefinic group [174]. The THF derivative of cymantrene (8.54) was treated with



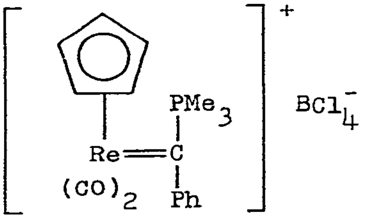
8.54



8.55

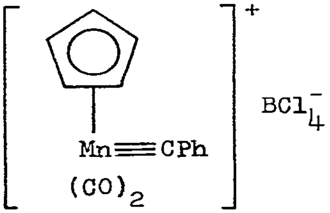
fulvenallene to yield the η-fulvenallene manganese complex (8.55) [175].

The crystal and molecular structure of dicarbonyl(η-cyclopentadienyl)phenylvinylidenemanganese has been determined by X-ray crystallography. The length of the manganese-carbon double bond linking the metal to the phenylvinylidene ligand was 1.68 Å [176]. The molecular structure of the rhenium complex (8.56) was determined by X-ray analysis. The double bond character of the Re—C(carbyne) bond was confirmed by a rhenium-carbon distance of 0.197 nm [177].

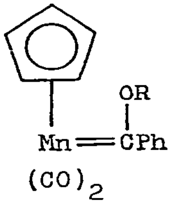


8.56

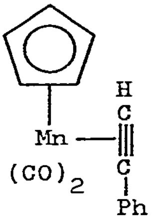
The phenylcarbyne complex (8.57) was treated with metal alkoxides, MOR [M = Li, Na, K; R = $(CH_2)_nMe$, n = 1-5, 7, $Me_2CHCH_2CH_2$, Me_2CH, EtMeCH, Me_3C, Ph, 2-$C_{10}H_7$, *p*-tolyl, *p*-ClC_6H_4, *o*-, *m*-, *p*-$MeOC_6H_4$] to give the carbene complexes (8.58) [178]. Irradiation of cymantrene in the presence of phenylacetylene in tetrahydrofuran gave an unstable complex



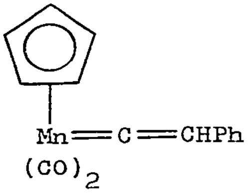
8.57



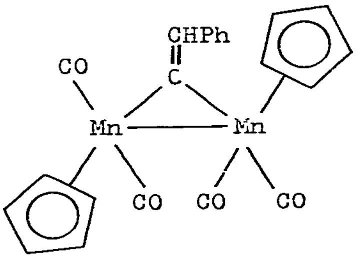
8.58



8.59



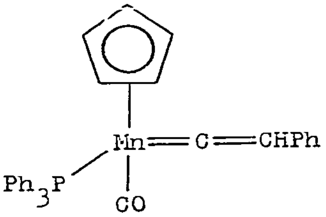
8.60



8.61

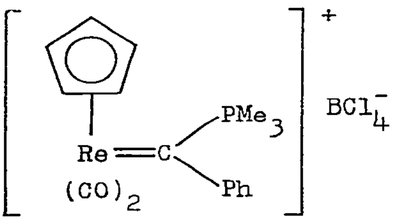
$(\eta\text{-}C_5H_5)_2Mn\ (C_{16}H_{10})(CO)_4$

8.62

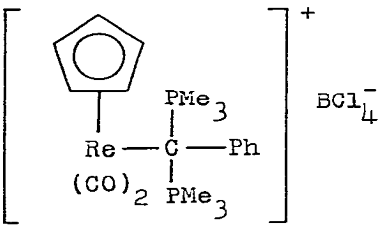


8.63

(8.59) together with three stable manganese compounds (8.60), 8.61 and 8.62). Conversion of a bridging vinylidene into a terminal ligand was achieved when the irradiation of complex (8.61) in the presence of triphenylphosphine gave the manganese



8.64



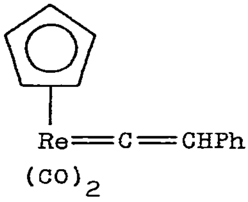
8.65

complex (8.63) together with dicarbonyl(η-cyclopentadienyl)-triphenylphosphinemanganese [179].

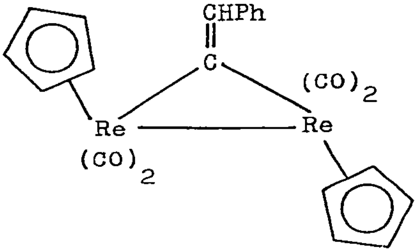
Reaction of the rhenium complex (8.64) with trimethylphosphine gave the thermolabile methanide complex (8.65) [180]. Irradiation of tricarbonyl(η-cyclopentadienyl)rhenium with phenylacetylene in tetrahydrofuran gave the rhenium complexes (8.66; 8.67, 8.68 and 8.69). The structure of the complex (8.69) was confirmed by X-ray analysis [181].

Dotz and Pruskil have treated the (η-cyclopentadienyl)-manganese carbene complexes (8.70; R^1 = Me, Ph; R^2 = OMe, Ph) with 1-diethylaminopropyne and have observed stereoselective insertion of the reagent into the manganese-carbene bond to form the diethylaminocarbene complexes (8.71; R^1 = Me, OMe, Ph; R^2 = OMe, Ph) [182].

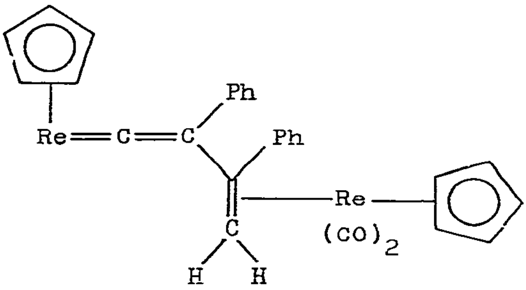
Irradiation of tricarbonyl(η-cyclopentadienyl)manganese in the presence of an excess of alkyl or aryl isocyanide gave the corresponding isocyanide complexes (8.72; R = Me, Ph,



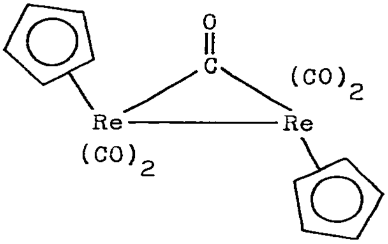
8.66



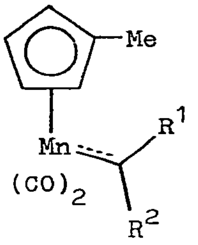
8.67



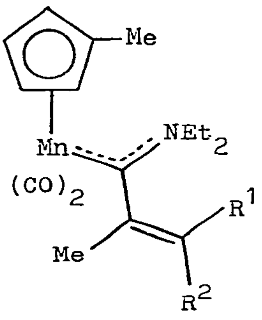
8.68



8.69



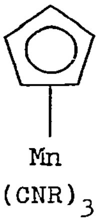
8.70



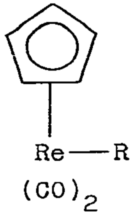
8.71

p-ClC_6H_4, C_6Cl_5). Cyclic voltammetry showed that all the isocyanide complexes underwent two sequential one-electron oxidations [183, 184].

Irradiation of tricarbonyl(η-cyclopentadienyl)rhenium in tetrahydrofuran gave the tetrahydrofuran complex (8.73; R = THF). Treatment of this complex (8.73; R = THF) with nitrogen under pressure gave the corresponding nitrogen complex (8.73; R = N_2).



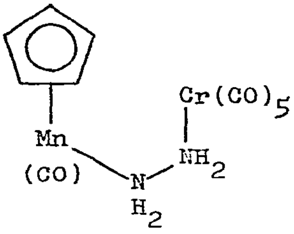
8.72



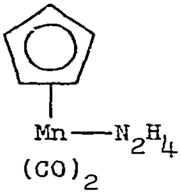
8.73

Reaction of the tetrahydrofuran compound (8.73; R = THF) with excess hydrazine gave the hydrazine complex (8.73; R = N_2H_4) which was oxidized easily to the nitrogen derivative (8.73; R = N_2). Irradiation of tricarbonyl(η-cyclopentadienyl)rhenium in hexane in the presence of ammonia produced the ammonia complex (8.73; R = NH_3) [185].

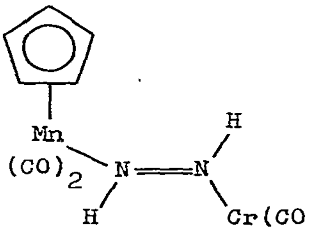
The heteronuclear hydrazine derivative (8.74) was prepared by reaction of the manganese complex (8.75) with pentacarbonyl-



8.74



8.75

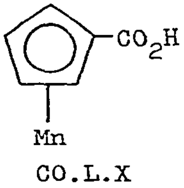


8.76

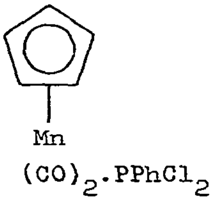
tetrahydrofuran chromium(0). Treatment of the complex (8.74) with hydrogen peroxide gave the first reported heteronuclear diazene-transition metal complex (8.76) [186].

The photochemical replacement of the carbonyl groups in cymantrene by phosphine or phosphite ligands to form the phosphorus complexes [8.77; L = CO; X = P(OR)$_3$, PPh$_3$; L = P(OR)$_3$ X = P(OR)$_3$, PPh$_3$] has been examined by ^{1}H NMR and IR spectroscop and by pK_a measurements in order to determine comparative ligand metal bond strengths. NMR spectroscopy was used to demonstrate the chirality of the manganese atom in pseudo-tetrahedral complexes with an asymmetric manganese atom [187].

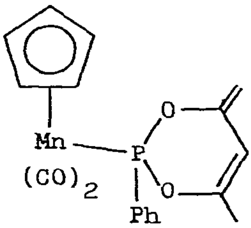
Treatment of the manganese-phosphine complex (8.78) with acetylacetone gave the complex (8.79) containing a modified phosphine ligand with a new coordination form of acetylacetone [188].



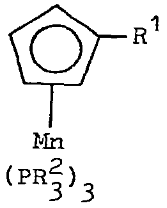
8.77



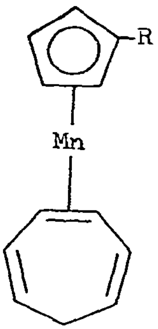
8.78



8.79



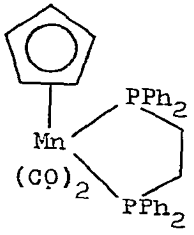
8.80



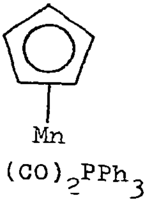
8.81

Werner and Juthani have described convenient procedures for the synthesis of phosphine and phosphite analogues of cymantrene (8.80; R^1 = H, Me; R^2 = Me, OMe, OEt). Bis(η-cyclopentadienyl)manganese or the (η-cycloheptatriene)manganese complexes (8.81; R = H, Me) were treated directly with the appropriate phosphorus compound [189].

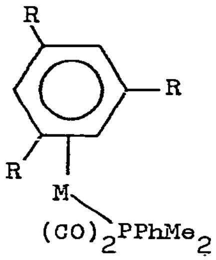
The effect of aprotic acids on the diphosphine-manganese complex (8.82) has been studied by spectroscopy and electroconductivity. Treatment with π-acids such as tetracyanoethylene and π-complexes such as $(\eta\text{-}C_5H_5)TiX_3$ gave the cation-radical of the complex (8.83). Oxidation of the central manganese atom also occurs when halides of aluminium, titanium, tin or mercury are used as the aprotic acids. Manganese complexes of lower basicity such as cymantrene, pentaethylcymantrene and the phosphine complex (8.83) were less basic and were not oxidized by π-acids but formed charge-transfer complexes [190].



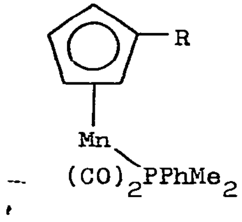
8.82



8.83



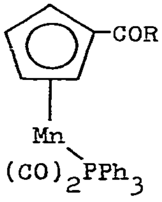
8.84



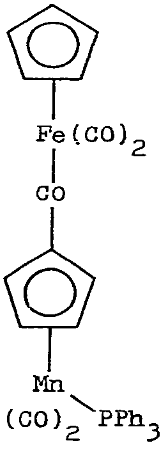
8.85

The phosphine complexes (8.84; R = H, Me; M = Cr, Mo, W) and the manganese-phosphine complexes (8.85; R = H, Me) were protonated quantitatively at the metal atom by an excess of CF_3SO_3H. Two isomers which underwent rapid nondissociative interconversion were detected by ^1H NMR spectroscopy for each protonated complex. $\Delta G^{\neq}$ for the isomerization was in the range 11-15 kcal mol^{-1}. The mechanism favoured by the authors involved interchange between square pyramidal and trigonal bipyramidal species where both the η-hydrocarbon and phosphine ligands occupied axial positions [191].

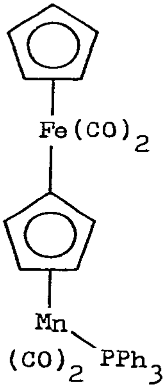
Hydrolysis of the ester (8.86; R = OMe) followed by chlorination gave the acid chloride (8.86; R = Cl) which when treated with $(\eta-C_5H_5)(CO)_2FeNa$ gave the mixed transition metal complex (8.87). This complex (8.87) when heated in xylene



8.86

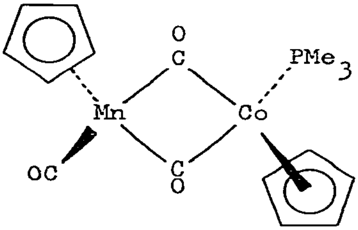


8.87

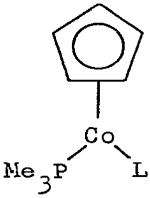


8.88

eliminated carbon monoxide to give the σ—π complex (8.88) [192]. Reaction of tricarbonyl(η-cyclopentadienyl)manganese or dicarbonyl(η-cyclopentadienyl)tetrahydrofuran manganese with (η-cyclopentadienyl)bis(trimethylphosphine)cobalt gave the dinuclear complex (8.89). Treatment of this complex (8.89) with a Lewis base L [L = PMe$_3$, PPh$_3$, P(OMe)$_3$, maleic anhydride, diphenylacetylene)] gave cymantrene together with the corresponding cobalt complex (8.90) [193].



8.89

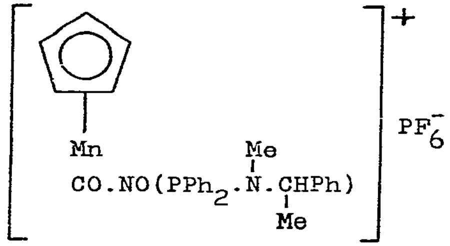


8.90

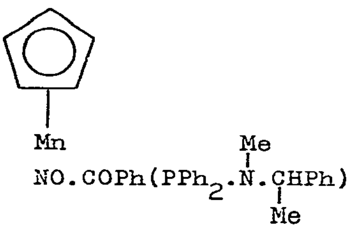
Treatment of the optically active (η-cyclopentadienyl)-manganese phosphine complex (8.91) with phenyllithium gave the benzoyl complex (8.92) in addition to the phenyl adduct (8.93) both of which were optically active. The ring addition product (8.93) was configurationally stable whilst the benzoyl complex (8.92) epimerized by a first order process. The reaction proceeded through a chiral intermediate which was formed by dissociation of the phosphine ligand [194].

Dicarbonyl(η-cyclopentadienyl)triphenylphosphine manganese was treated with mercury(II) acetate and calcium chloride to give the mercurichloride derivative (8.94; X = HgCl). This product was attacked by Pt(PPh$_3$)$_3$ to form the platinum complex [8.94; X = PtCl(PPh$_3$)$_2$] [195].

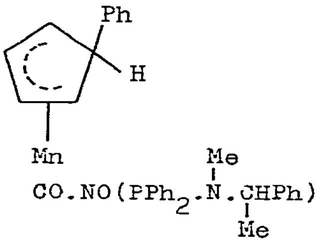
Treatment of cymantrene with the ligand Me$_2$AsNMe$_2$ gave the manganese complex (8.95). The dimethylamino group was removed by treatment with hydrochloric acid to give the chlorodimethylarsine derivative (8.96; R = Cl). The complex (8.96; R = Cl) was treated with the sodium salts of transition metal carbonyl anions to give the corresponding arsenic derivatives [8.96; R = Mn(CO)$_5$, Re(CO)$_5$, Co(CO)$_4$, Mo(CO)$_3$(η-C$_5$H$_5$), W(CO)$_3$(η-C$_5$H$_5$), Fe(CO)$_2$(η-C$_5$H$_5$)]. Three of these complexes



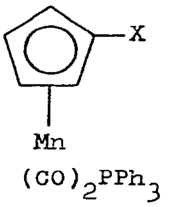
8.91



8.92



8.93

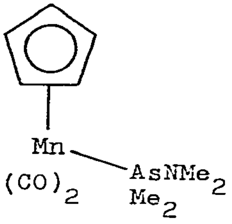


8.94

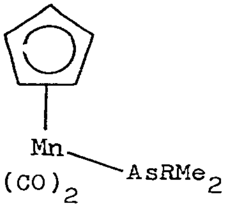
eliminated carbon monoxide thermally or on irradiation to give the corresponding bridged dinuclear complexes [8.97; M = $Mn(CO)_4$, $Re(CO)_4$, $Co(CO)_3$]. Treatment of the bridged complexes (8.97) with a phosphine PR_3 [PR_3 = $P(OMe)_3$, PPh_3, PMe_3, Me_2PNMe_2] gave the corresponding ring opened product (8.98) [196].

The acetylation of tricarbonyl(η-pyrrolyl)manganese under Friedel-Crafts conditions gave the binuclear complex (8.99), the structure of which was confirmed by X-ray crystallography. A mechanistic scheme for the formation of the complex was proposed [197].

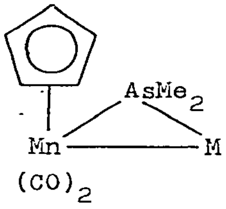
Thiocarbonyl complexes of manganese and rhenium (8.100; R = H, Me; M = Mn, Re) have been obtained by UV irradiation of the appropriate tricarbonyl(η-cyclopentadienyl)metal compound in THF with carbon disulphide and triphenylphosphine. When the starting material was cymantrene and the addition of triphenylphosphine was delayed then additional products were obtained including the phosphine (8.101) and the binuclear



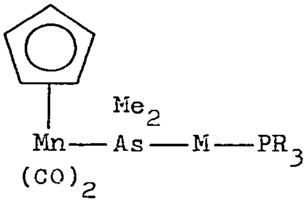
8.95



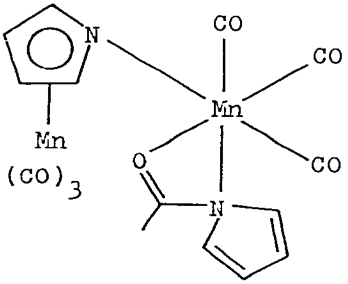
8.96



8.97

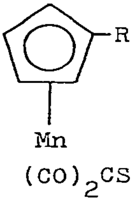


8.98

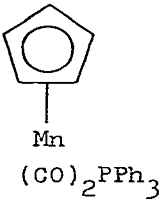


8.99

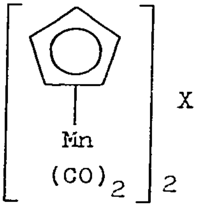
complexes (8.102; X = CS, CS_2) [198]. The manganese complexes (8.103; R = H, Me) were treated with potassium iodide to give the corresponding iodomanganese derivatives (8.104). The reactions of these latter complexes with zinc dust, trifluoro-



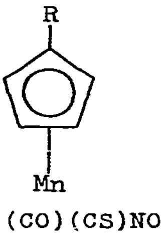
8.100



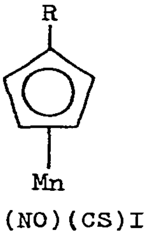
8.101



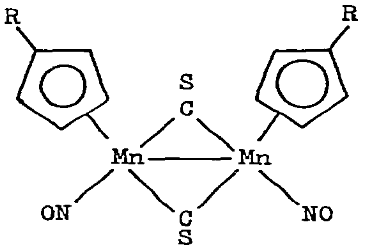
8.102



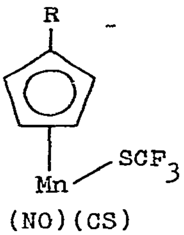
8.103



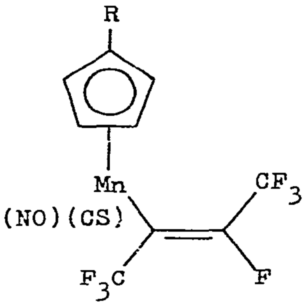
8.104



8.105

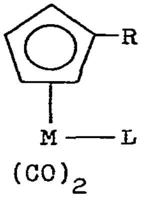


8.106

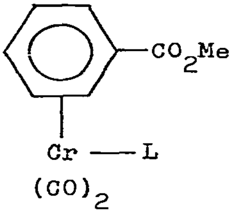


8.107

methylthiosilver and trans-perfluoro(1-methylpropenylate)silver gave the manganese complexes (8.105; 8.106 and 8.107) respectively [199]. The η-cyclopentadienyl-metal complexes (8.108; M = Mn, R = H, Me; L = THF; M = Re, R = H, L = THF) and the chromium complex (8.109; L = tetrahydrofuran) were treated with



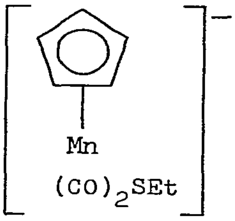
8.108



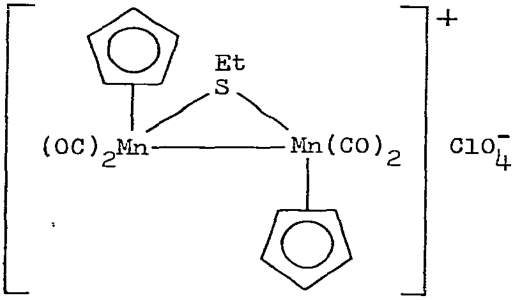
8.109

carbon diselenide in the presence of triphenylphosphine to give the selenocarbonyl complexes (8.108; L = CSe) and (8.109; L = CSe) repectively. The selenocarbonyl complexes were air stable and from spectroscopic data it was concluded the CSe was a better net electron-withdrawing (σ-donor and π-acceptor) group than CO and CS [200].

The thioethylmanganese anion (8.110), formed by displacement of THF by the thioethyl group in the appropriate parent complex was oxidized with perchloric acid to the binuclear sulphur-bridged complex (8.111). The structure of this product was confirmed by X-ray crystallography [201].



8.110

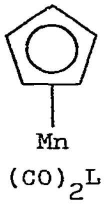


8.111

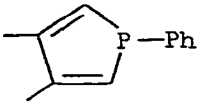
Interaction of the manganese complexes [8.112; L = PPh_3, $AsPh_3$, $SbPh_3$, $P(\underline{iso}\text{-}C_3H_7)_3$, $P(C_6H_{11})_3$] with an excess of tin(IV) chloride gave a series of adducts containing two molecules of tin(IV) chloride. The crystal and molecular structure of the adduct $(\eta\text{-}C_5H_5)Mn(CO)_2PPh_3.2SnCl_4$ was determined by X-ray analysis. It had an ionic structure $[(\eta\text{-}C_5H_5)Mn(CO)_2(PPh_3)SnCl_3]^+SnCl_5^-$ and the coordination environment of the manganese atom was a distorted square pyramid with the $\eta\text{-}C_5H_5$ ligand at the apex. It was concluded that in the complexes (8.112) the manganese atom was the site of attack by aprotic acids and that it was the most basic site of the molecule [202].

Heating the P-phenylphosphate (8.113) with manganese carbonyl in xylene gave the phosphacymantrene (8.114) which underwent Friedel-Crafts acetylation with acetyl chloride to give the mono-acetyl derivative [203].

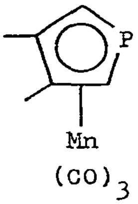
Thermolysis of 4,4-dimethyl-1-phenyl-1-bora-2,5-cyclohexadiene with either manganese or rhenium carbonyl gave the



8.112

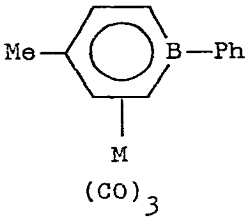


8.113

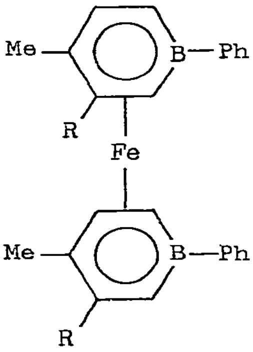


8.114

borabenzene derivatives (8.115; M = Mn, Re). Thermal reaction of tricarbonyl(4,4-dimethyl-1-phenyl-1-bora-2,5-cyclohexadiene)-iron gave a mixture of the iron complexes (8.116; R = H, Me)[204



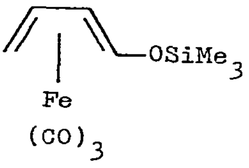
8.115



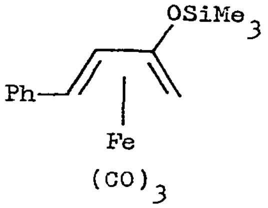
8.116

9. (Acyclic-η-diene)Fe(CO)$_3$ and (η-trimethylenemethane)-Fe(CO)$_3$ complexes

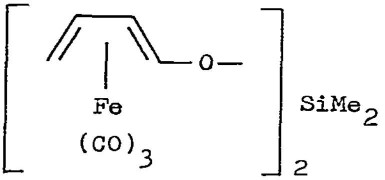
Triiron dodecacarbonyl was heated with siloxybutadienes to give iron tricarbonyl complexes such as the siloxybutadienes (9.1, 9.2 and 9.3) [205]. Nonacarbonyldiiron was heated with hexa-1,3,5-triene to give the (η-hexatriene)iron complex (9.4). The uncoordinated olefin group was attacked by boranes to form the alcohol (9.5; X = OH; Y = H) while oxidation with osmium tetroxide gave the diol (9.5; X = Y = OH). Protonation of the triene complex (9.4) gave the (η-hexadienyl)iron cation (9.6) which was not deprotonated to the original complex [206].



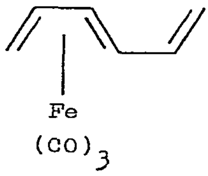
9.1



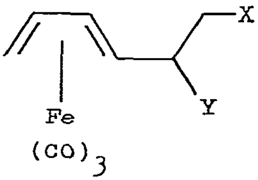
9.2



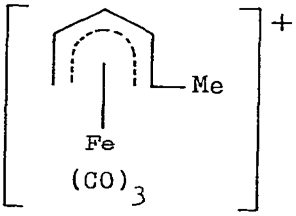
9.3



9.4



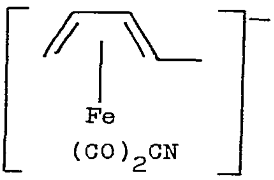
9.5



9.6

Tricarbonyl(η-diene)iron complexes were converted to the anionic nitrile complexes, $[(\text{diene})Fe(CO)_2CN]^-$ on treatment with sodium bis(trimethylsilyl)amide. Thus tricarbonyl(η-1,3-pentadiene)iron was converted to the nitrile complex (9.7) [207].

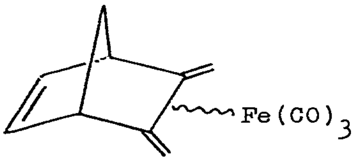
Ruh and Von Philipsborn have synthesised (η-butadiene)-tricarbonylruthenium and investigated the character of the



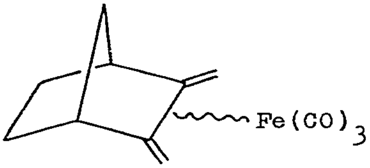
9.7

ligand by ^1H and ^{13}C NMR spectroscopy. Close similarities with the corresponding iron complex were observed [208].

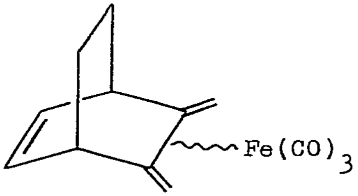
Reaction of diironenneacarbonyl with 2,3-dimethylidene-5-bicyclo[2.2.1]heptene, -bicyclo[2.2.1]heptane, -bicyclo-[2.2.2]octene and -bicyclo[2.2.2]octane gave the tricarbonyliro complexes (exo- and endo-9.8, -9.9, -9.10) and (9.11) respectively. Hydrogenation of the free double bond in the exo- and endo- complexes (9.8) occurred from the exo- side as shown by deuteration experiments [209].



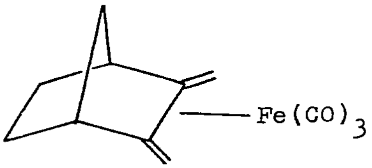
9.8



9.9



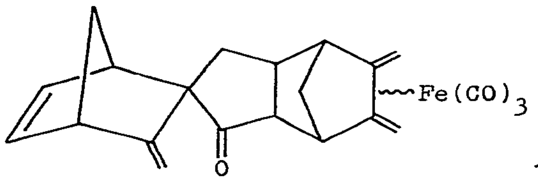
9.10



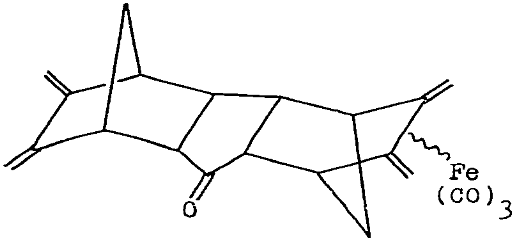
9.11

From the reaction of 2,3-dimethylidene-5-bicyclo[2.2.1]-heptene with diironenneacarbonyl the pentacyclic ketones (9.12) and (9.13) were isolated also [210]. Irradiation of 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene with iron pentacarbon gave initially the tetracarbonyliron complex (9.14) and then the diiron complex (9.15). Under more vigorous conditions oxygen was abstracted from the ligand and rearrangement occurre to give the tricarbonyliron and hexacarbonyldiiron complexes (9.16 and 9.17) [211].

Several tricarbonyliron products have been obtained from 5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene and iron carbonyl

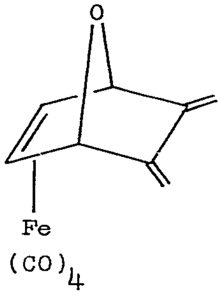


9.12

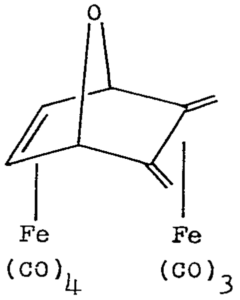


9.13

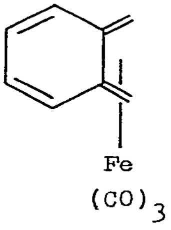
Irradiation of the ligand with pentacarbonyliron at -80° gave the *exo*-tricarbonyliron complex (9.18) while heating with nonacarbonyldiiron gave the *endo*-*exo*-diiron complex (9.19) in addition to the first complex (9.18). Treatment of the ligand with (η-benzalacetone)tricarbonyliron at 60° gave the *diexo*-



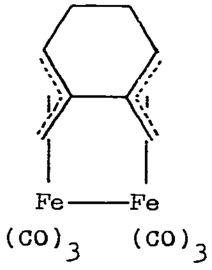
9.14



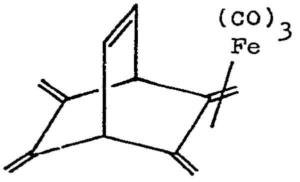
9.15



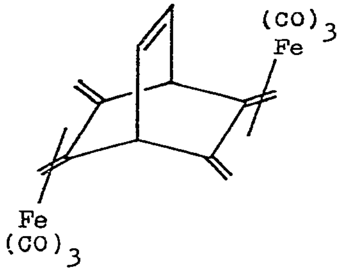
9.16



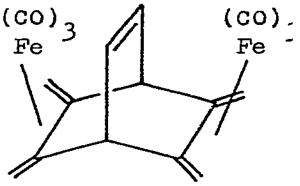
9.17



9.18



9.19



9.20

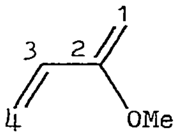
diiron complex (9.20) as well as the complex (9.18) obtained in the previous reactions [212].

^{1}H NMR spectra of (η-1,3-butadiene)tricarbonyliron orientated in a nematic liquid crystal solvent were analysed. The proton skeleton was found to be non-planar and the distance of the anti-protons from the plane defined by the remaining four protons was 0.77 Å. The results indicated also that there was some rehybridisation of the terminal carbons towards sp^3 [213].

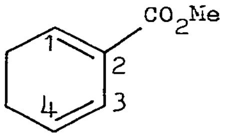
Substituent effects in relation to π-bond order distributi were investigated by ^{13}C NMR in tricarbonyl(η-diene)iron complexes. For the uncomplexed ligands (9.21 and 9.22) the result were compatible with contributions to the structures from the resonance forms (9.23 and 9.24). On complex formation it was concluded that there was greater π-bond order in the 2,3 bond than in the 1,2 (or 3,4) bond. This was explained in terms of the mesomeric interactions (9.25 and 9.26) which suggested that the canonical form (9.27) contributed to the bonding in the π-complexes [214, 215].

High pressure liquid chromatography was used to separate cis- and trans- dienone-irontricarbonyl complexes (9.28 and 9.29). The column packing was silica with methylene chloride as the mobile phase. A similar separation was achieved with ψ-endo- and ψ-exo- dienol-irontricarbonyl complexes [216].

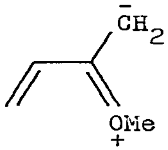
A kinetic study of the attack of 1,3-dimethoxy- and 1,3,5-trimethoxy- benzene on tricarbonyl(η-pentadienyl)iron cations (9.30; R^1 = Ph, p-MeOC$_6$H$_4$, Me; R^2 = Me) demonstrated that the reactions do not go to completion. The mechanism involved initial rearrangement to a trans-(η-pentadienyl)iron cation (9.31) which was then attacked by the reagent to form a cationi



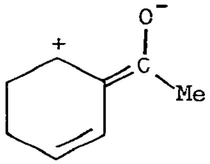
9.21



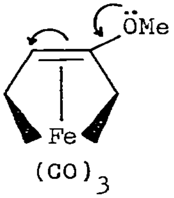
9.22



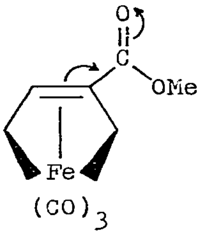
9.23



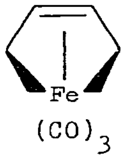
9.24



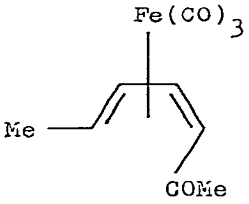
9.25



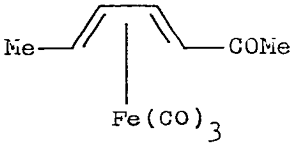
9.26



9.27



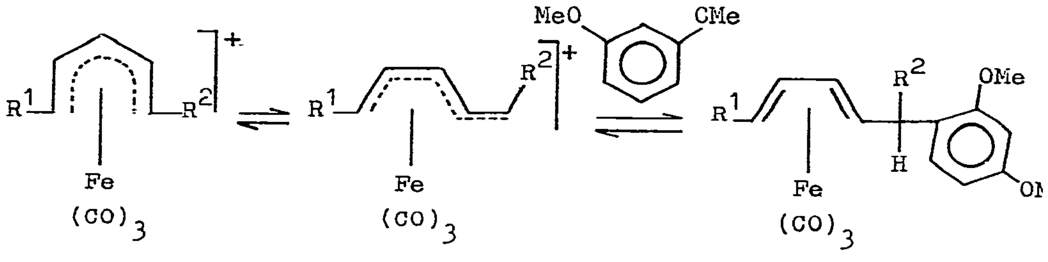
9.28



9.29

(η-diene)iron adduct and this in turn eliminated a proton to give the neutral (η-diene)iron products (9.32) [217].

The mechanism of the displacement of a carbonyl group in the tricarbonyliron complexes (9.33; R = H, *p*-Me, *p*-Cl, *p*-Br, *p*-I, *p*-OMe, *p*-NMe$_2$) by triphenylphosphine or tri(n-butyl)-phosphine was investigated. The rate of substitution by the phosphine ligands was first order in the complex concentration



9.30 9.31 9.32

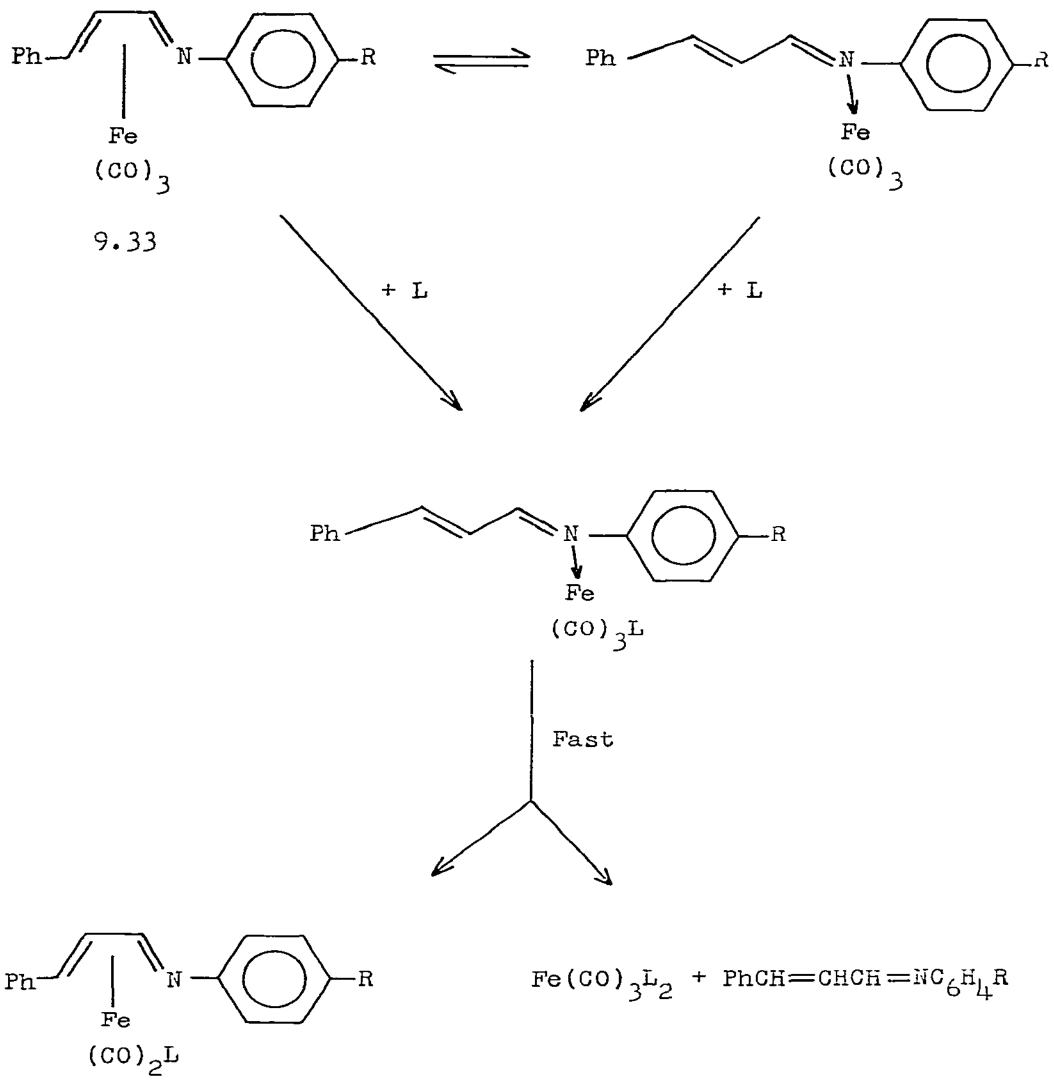
and the pseudo-first-order rate constants varied with the ligand concentration. From the results it was concluded that the reaction mechanism had two paths (Scheme 9.1) [218].

The reaction between the tricarbonyliron complexes (9.34; R = H, m-OMe, p-Cl) and triphenylantimony was investigated, the equilibrium constants and the forward and reverse rate constants for the reaction were determined. The reaction between the tricarbonyliron complexes (9.34; R = H, p-NMe_2, m-OMe, p-OMe, p-Me, p-Cl) and triphenylphosphine was investigated. For triphenylantimony it was concluded that the reaction proceeded via a dissociative equilibrium of the η^4-complexes (9.34) to η^2-unsaturated complexes (9.35) [219].

Reaction of the benzylideneacetone complex (9.36) with carbondisulphide followed by the addition of a phosphite gave the carbon disulphide complexes [9.37; L = $P(OPh)_3$, $P(OEt)_3$], The carbon disulphide behaved as a two electron ligand [220].

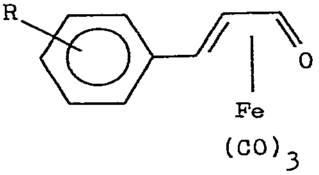
The muconate-iron complex (9.38) was heated with the ligands 2,2-bipyridyl, 2-benzoylpyridineanil and 2-benzoylpyridine-p-methoxyanil when one of the diethylmuconate groups was replaced by one of the 1,4-diaza-1,3-diene ligands. The iron complex (9.39) was irradiated with the same 1,4-diaza-1,3-diene ligands when two of the carbonyl groups were replaced by one of the ligands. The crystal structure of the complex (9.40) was determined by X-ray analysis. The complex (9.40) approximated to a square pyramid with one of the nitrogen atoms of the 2,2'-bipyridyl ligand occupying the apical position [221].

Green and his colleagues have reported further results on the reactions of unsaturated fluorocarbons with η-organometallic complexes. Thus, irradiation of hexafluorobut-2-yne

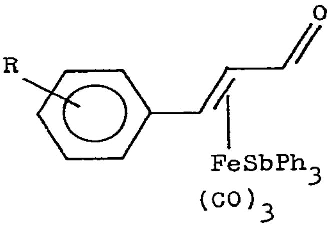


Scheme 9.1

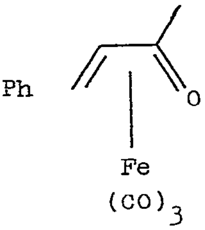
with (η-butadiene)- and (η-2,3-dimethylbutadiene)-tricarbonyliron gave the oxidative coupling products (9.41; R = H, Me) respectively. Similar reactions with both iron and ruthenium complexes were also described [222].



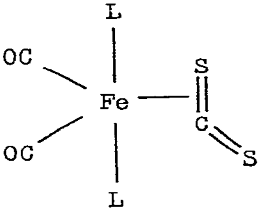
9.34



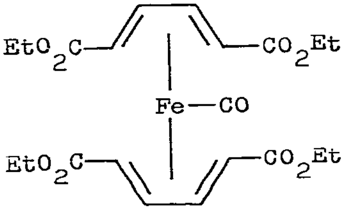
9.35



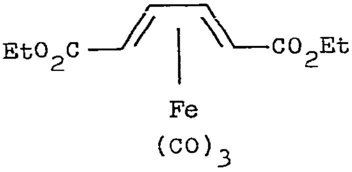
9.36



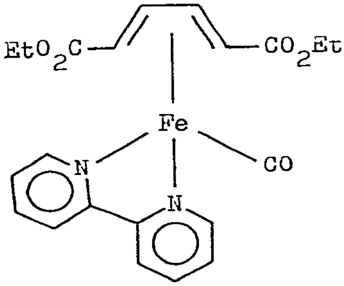
9.37



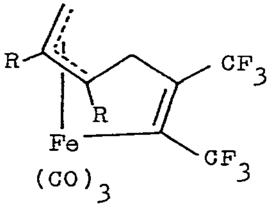
9.38



9.39



9.40



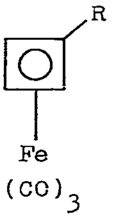
9.41

Cyclic hydrocarbons have been formed by intramolecular coupling of bis[tricarbonyl(η-dienyl)iron] cations prepared from (η-butadiene)tricarbonyliron and diacid chlorides [223].

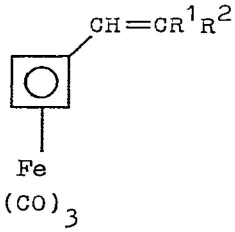
ESCA spectra were recorded for tricarbonyl(η-trimethylenemethane)iron and (η-butadiene)tricarbonyliron. The C 1s spectrum was consistent with a high positive charge on the central carbon atom of the η-trimethylenemethane ligand. It was concluded that the overall donor and acceptor characteristics of η-trimethylenemethane and η-butadiene were similar with a slightly larger degree of back-bonding to η-butadiene [224].

10. (η-C_4H_4)Fe$(CO)_3$

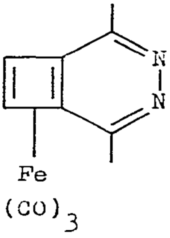
The formation of α,β-unsaturated derivatives of tricarbonyl(η-cyclobutadiene)iron has been reported. The aldehyde (10.1; R = CHO) underwent the Wittig reaction to form the vinyl compound (10.2; $R^1 = R^2 = H$). The acrylate (10.2; R^1 = Br, $R^2 = CO_2Me$)



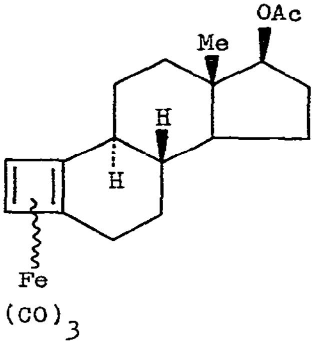
10.1



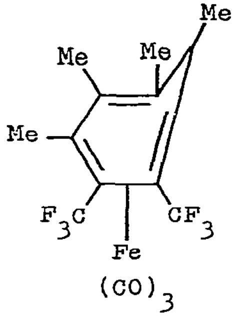
10.2



10.3



10.4

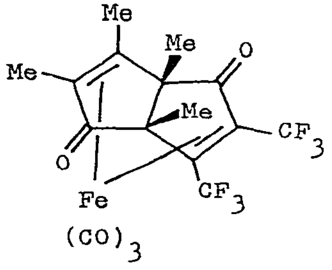


10.5

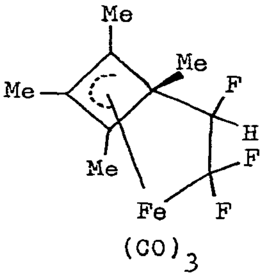
was formed in the same way and converted to the acetylene (10.1; R = $C\equiv C.CO_2Me$) with potassium t-butoxide [225].

The tricarbonyl(η-pyridazinocyclobutadiene)iron complex (10.3) was formed from tricarbonyl(η-1,2-diacetylbutadiene)iron and hydrazine in acetic acid. The diacetyl compound was reduced with sodium borohydride and Grignard reagents to form the corresponding diols [226]. The stereospecific synthesis of two isomeric iron tricarbonyl estradiene complexes (10.4) has been reported [227].

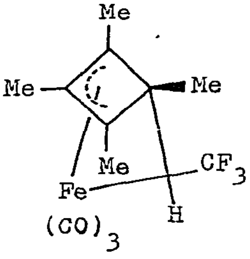
Irradiation of a mixture of tricarbonyl(η-tetramethylcyclobutadiene)iron and hexafluorobut-2-yne gave the tricarbonyliron



10.6



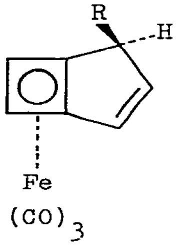
10.7



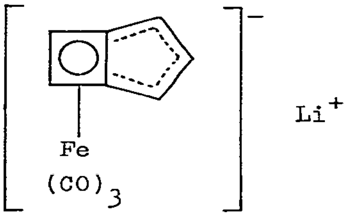
10.8

complexes (10.5 and 10.6). The structures of these two complexes were determined by X-ray crystallography and the mechanisms of formation were discussed. Irradiation of a mixture of trifluoroethylene and tricarbonyl(η-tetramethylcyclobutadiene)iron afforded a mixture of the two isomeric η-cyclobutenyl complexes (10.7 and 10.8) [228].

The (η-cyclobutadiene)iron complex (10.9; R = H) was converted to the anionic complex (10.10) on treatment with n-butyllithium in THF at -78°. Reactions with nucleophiles gave derivatives of the original neutral complex, thus methyl iodide gave the exo-methyl complex (10.9; R = Me) [229].



10.9

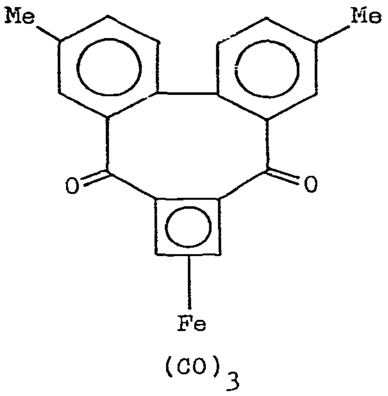


10.10

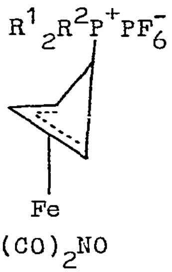
^{1}H NMR spectra of a series of tricarbonyl(η-cyclobutadiene)iron compounds were recorded in deuteriochloroform. The chemical shifts of the H-2 and H-4 protons in the η-cyclobutadiene ring were correlated with substituent constants derived from Hammett and modified-Hammett linear free energy equations. It was concluded that a substituent modified the electron density at the ring positions adjacent to it in much the same way as it would in benzene. Also, the substituent had a significant influence on electron density at the carbon atom directly across the ring [230].

The proton coupled ^{13}C NMR spectrum of η-butadienetricarbonyliron was analysed in detail. The data were interpreted in terms of a nonplanar C,H skeleton with the C—C bond lengths nearly equal and with the terminal carbon atoms showing some rehybridization towards sp^3 [231].

The crystal structure of the substituted η-cyclobutadiene complex (10.11) was determined by X-ray analysis. The



10.11



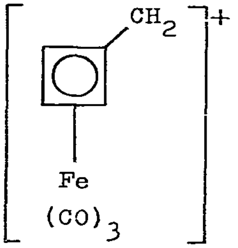
10.12

eight-membered ring was flattened from a boat conformation and the six-membered rings were twisted from coplanarity by an angle of 74° [232].

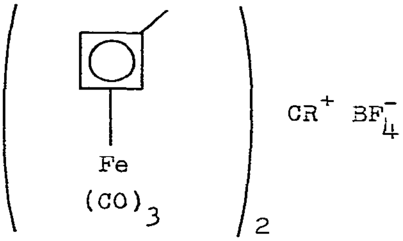
The nucleophilic addition of the tertiary phosphines $(R^1)_2R^2P$ ($R^1 = R^2$ = Me, Et, n-Pr, n-Bu, Ph; R^1 = Me, R^2 = Ph; R^1 = Ph, R^2 = Me) to dicarbonyl(η-cyclobutadiene)nitrosyliron hexafluorophosphate gave the exo-phosphonio derivatives (10.1 [233]. The high stability of the (η-cyclobutadienyl)iron carbenium ion (10.13) was demonstrated by determination of the forward and reverse solvolysis rates for (η-chloromethylcyclobutadiene)tricarbonyliron in aqueous acetone. Several bis-tricarbonyl(η-cyclobutadienyl)iron methyl fluoroborates (10.1 R = H, Ph, Me, cyclopropyl) were characterized and the barrie to free rotation about the cyclobutadienyl ring-carbinyl carb bond estimated by ^{1}H NMR spectroscopy [234].

Grubbs and Pancoast have degraded the optically active (η-cyclobutadiene)iron complex containing a dienophile in t side chain (10.15) in order to investigate the mechanism of oxidative decomposition of these complexes. The product (10.1 showed high retention of optical activity and suggested that in intermolecular trapping experiments free achiral cyclobutadiene was an intermediate [235].

Kaplan and Roberts have used the cyclobisacylation of p,p'-dimethylbiphenyl (10.17) with the (η-cyclobutadiene diac

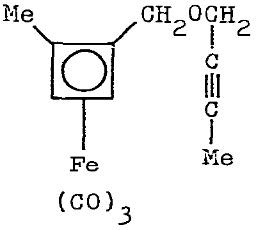


10.13

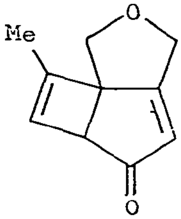


10.14

chloride)iron complex (10.18) as a route to a dibenzo derivative of bicyclo[6.2.0]decapentaene as the tricarbonyliron complex (10.19). The complex (10.19) was a twisted, rigid, enantiomerically stable bridged biphenyl. With 2,7-di-tert-butylfluorene as the reagent the planar complex (10.20) was obtained.



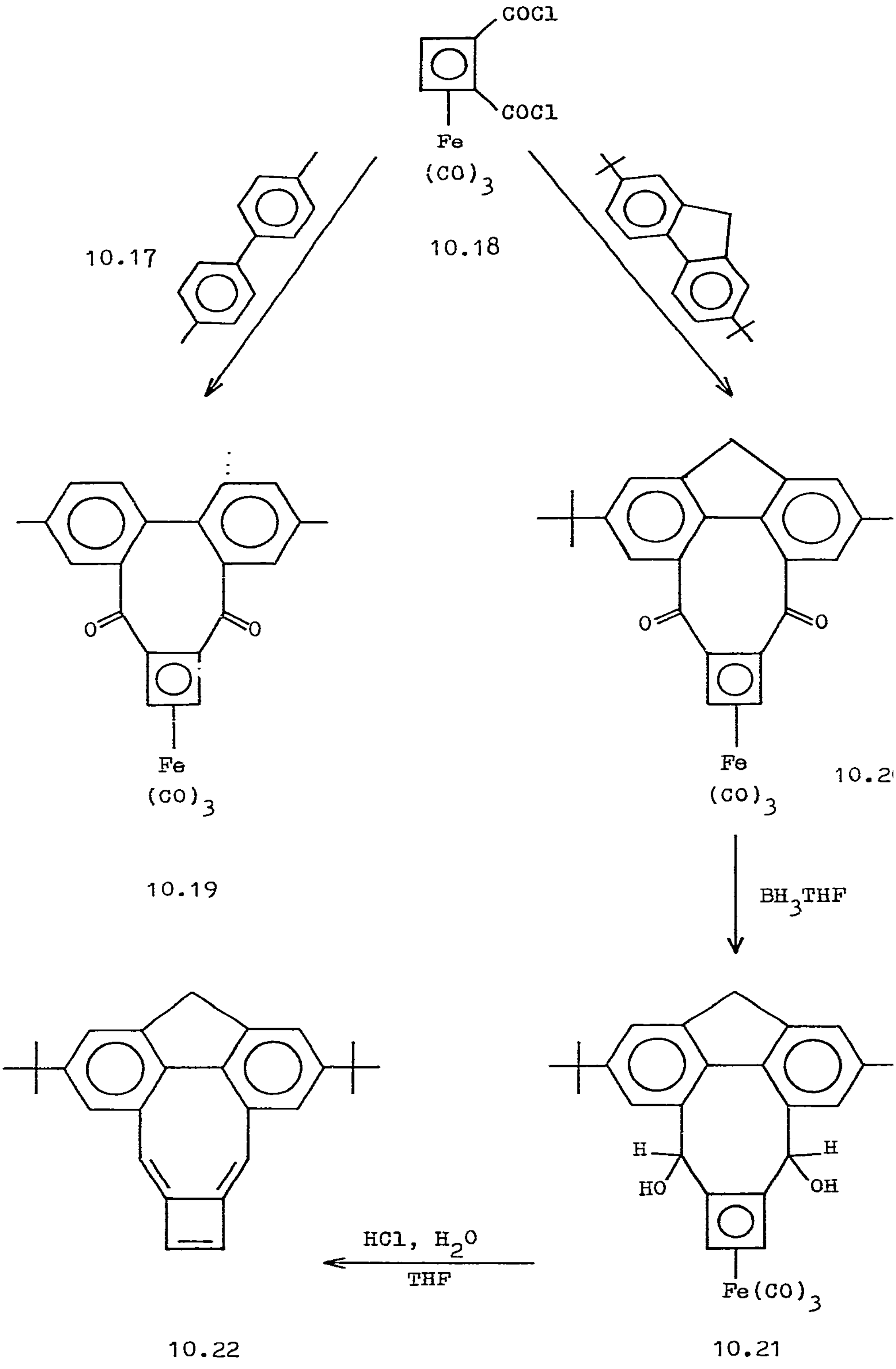
10.15

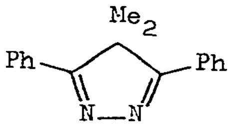


10.16

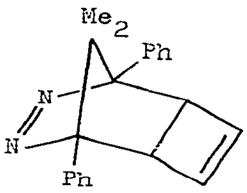
Hydride reduction of the two diketone complexes (10.19 and 10.20) led to the corresponding cis,syn-diols, thus the diketone (10.20) gave the diol (10.21) which was degraded to the free hydrocarbon (10.22) with aqueous hydrochloric acid [236].

Alkyne substituents were introduced to the tricarbonyl(η-cyclobutadiene)iron nucleus by treatment of tricarbonyl(η-bromoethylcyclobutadiene)iron with alkynols. Each complex was then oxidized with cerium(IV) salts to liberate the free ligand which underwent intramolecular Diels-Alder addition to give the isolated products. When the complex was optically active then oxidative degradation afforded an optically active product of high optical purity [237].

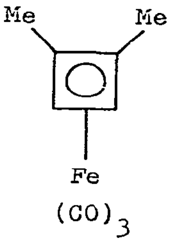

COCl
COCl
Fe
(CO)$_3$
10.17
10.18
Fe
(CO)$_3$
10.19
O
O
Fe
(CO)$_3$
10.2
O
O
BH$_3$THF
HCl, H$_2$O
THF
10.22
H
HO
H
OH
Fe(CO)$_3$
10.21



10.23

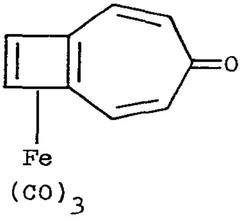


10.24

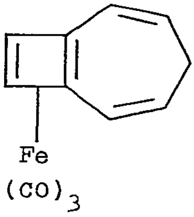


10.25

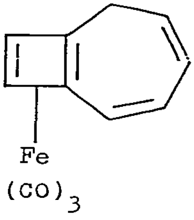
Tricarbonyl(η-cyclobutadiene)iron was added to a solution of the tetrasubstituted isopyrazole (10.23) in acetone and the resulting complex was oxidatively degraded with cerium(IV) to form the free ligand (10.24). This ligand was then converted quantitatively to 3,3-dimethyl-2,4-diphenyltricyclo[3.2.0.$0^{2,4}$]-hept-6-ene by irradiation in ether [238].



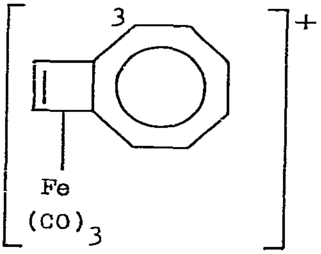
10.26



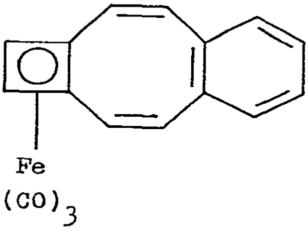
10.27



10.28



10.29

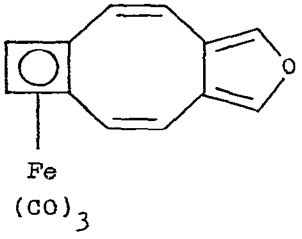


10.30

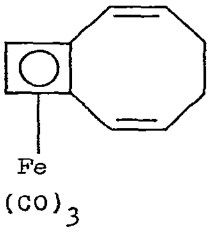
The photochemical reactions of tricarbonyl(1,2-dimethylcyclobutadiene)iron (10.25) with a number of acetylenes have been investigated. For example, irradiation of the complex (10.25) with acetylene gave o- and p-xylene; with propyne 1,2, and 1,2,4-trimethylbenzene were isolated while 2-butyne formed 1,2,3,4- and 1,2,4,5-tetramethylbenzene. Possible mechanisms were presented to explain the formation of these products [239

Tricarbonyl(η-cyclobutadiene-1,2-dicarbaldehyde)iron was subjected to a bis-Wittig reaction with the ylid derived from $[(Ph_3\overset{+}{P}CH_2)_2CO]2Cl^-$ to form the (η-cyclobutatropone)iron compl (10.26). A similar reaction afforded a mixture of the isomeri (η-bicyclononatetraene)iron complexes (10.27 and 10.28) which were converted with trityl hexafluorophosphate to the (η-cyclobutatropylium)iron cation (10.29). ^{1}H NMR spectroscopy indica that the most important canonical form for the cation (10.29) was one with the positive charge on carbon-3 [240].

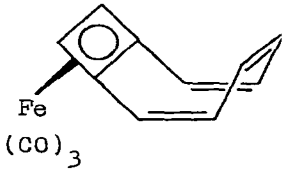
Independently, Kaplan and Roberts have used a similar rou to tricarbonyliron complexes of benzo-, furo-, dihydro- and tropono-bicyclo[6.2.0]decapentaene (10.30, 10.31, 10.32 and 10.26) respectively. Conformational analysis of the parent complex suggested preference for the conformer where the metal was on the convex face of a tub form of the ligand (10.33) [24



10.31



10.32

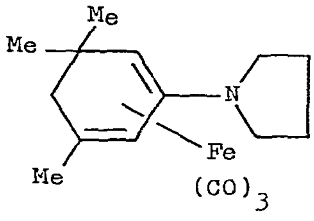


10.33

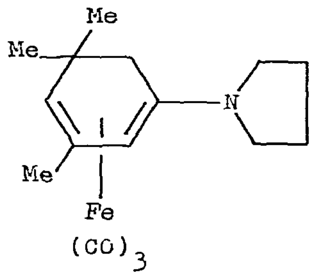
11. (Cyclic-η-diene)Fe(CO)$_3$ Complexes

(i) FORMATION

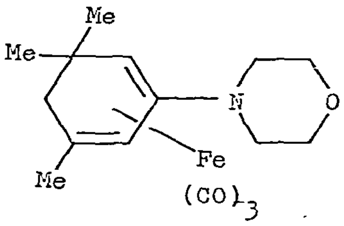
Reaction of the morpholine and pyrrolidine dienamines of 3,5,5-trimethylcyclohex-2-en-1-one with iron carbonyl each gav a mixture of two tricarbonyl(η-dienamine)iron complexes (11.1, 11.2 and 11.3, 11.4) respectively. The complexes (11.1 and 11.3) where the dienamine system was cross-conjugated were



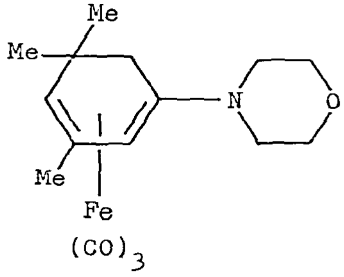
11.1



11.2



11.3



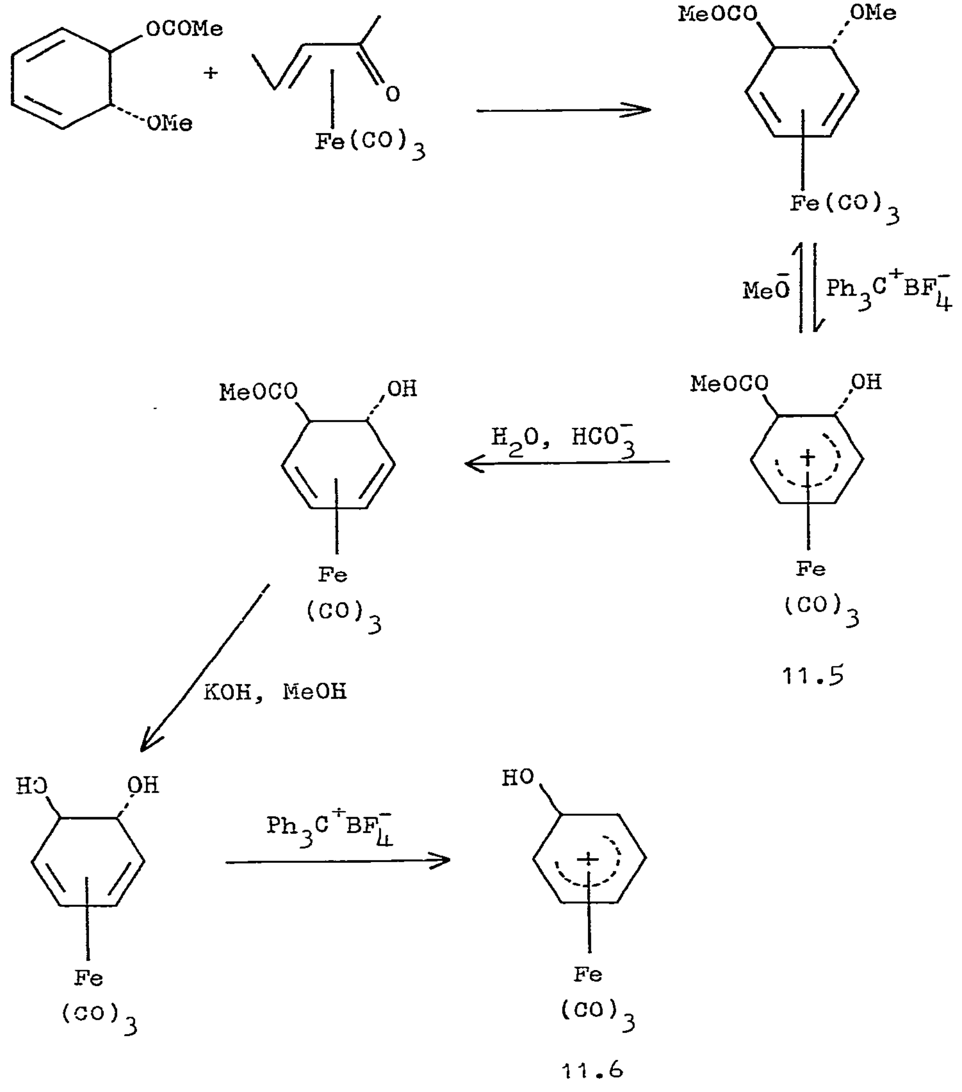
11.4

more stable than the complexes (11.2 and 11.4) where the dienamine was linearly conjugated [242].

Berchtold and Ashworth have reported the stereospecific synthesis of tricarbonyl(η-*endo*-6-acetoxy-1,3-cyclohexadienyl)-iron fluoroborate (11.5) and tricarbonyl(η-*endo*-6-hydroxy-1,3-cyclohexadienyl)iron fluoroborate (11.6) (Scheme 11.1) [243].

Several tricarbonyl(η-1,3-cyclohexadiene)iron complexes were prepared and their properties were investigated [244]. The addition of heterocyclic aromatic molecules such as furan and pyrrole to tricarbonyl(η-cyclohexadienyl)iron cations gave the tricarbonyl(η-cyclohexadiene)iron complexes (11.7; R = C_4H_3O, C_4H_4N). The reaction followed second order kinetics indicating electrophilic attack on the heterocycle by the cation. The relative reactivities of several other heterocyclic aromatic reagents in this reaction have been explored [245].

Friedel-Crafts acetylation of tricarbonyl(η-cyclohexa-1,3-diene)iron gave a 4/1 mixture of the 5-*exo*- and 5-*endo*-

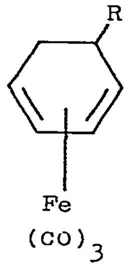


Scheme 11.1

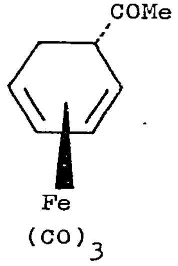
acetyl complexes (11.8 and 11.9) respectively, as the major products [246].

Attack of cyanide ion on the (η-cyclohexadienyl)iron catio (11.10) took place specifically at the most electron-deficient end of the dienyl system and it was also stereospecific forming the <u>exo</u>-cyanide complex (11.11) [247].

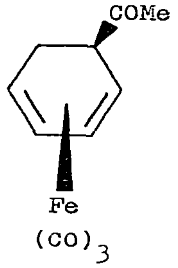
Treatment of the bullvalene bis(tricarbonyliron) complex (11.12) with carbon monoxide gave the tricarbonyliron complex (11.13). Oxidative decomposition of the complex (11.13) with



11.7

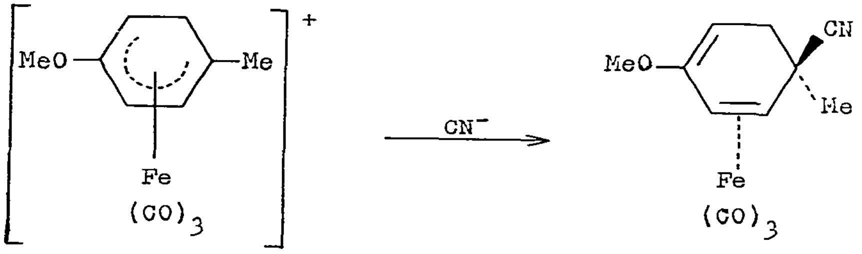


11.8



11.9

iron(III) chloride gave the thermally unstable ketone (11.14) which isomerized by a Cope rearrangement to give the tricyclic derivative (11.15) [248].



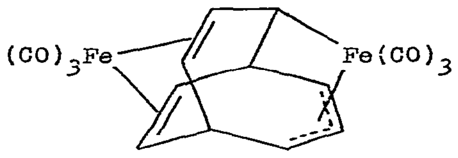
11.10

11.11

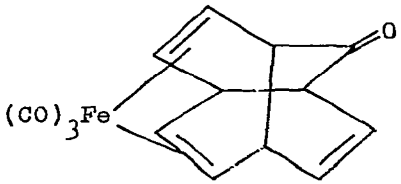
Bicyclo[6.1.0]nona-2,4,6-triene was treated with diiron nonacarbonyl to give a 9:1 mixture of the isomeric η-cyclononatetraene complexes (11.16 and 11.17). The complex (11.17) rearranged on heating to form the dihydroindene complex (11.18) [249].

The reaction of tricarbonyl(η-cyclooctatetraene)iron with the triazolinediones (11.19; R = Me, Ph) gave the corresponding tricarbonyliron derivatives (11.20; R = Me, Ph) together with the barbaralone derivatives (11.21; R = Me, Ph) [250].

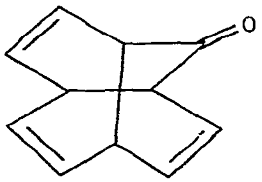
The tricarbonyliron complex (11.23) was formed when the tetracarbonyliron derivative (11.22) was heated in benzene [251]. Triiron dodecacarbonyl was treated with 2-methylthiophane to form the ferrathiacyclohexadiene complex (11.24) which was characterised by X-ray crystallography. The preparation



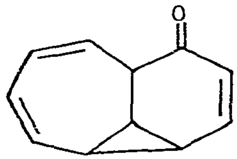
11.12



11.13



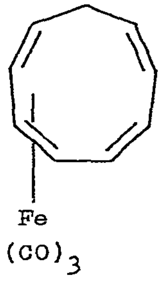
11.14



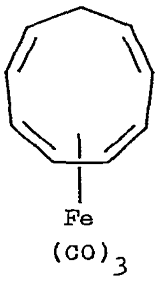
11.15

of two isomers of the methyl substituted tricarbonyl[tricarbonyl (ferracyclopentadiene)]iron was described together with their mass spectra and NMR spectra [252].

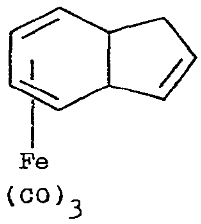
Victor, Usieli and Sarel have continued their studies of cyclopropyl-olefins and -acetylenes as ligands for iron with an investigation of the reaction between dicyclopropylacetylene and iron carbonyls under thermal and photolytic conditions.



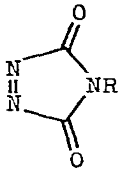
11.16



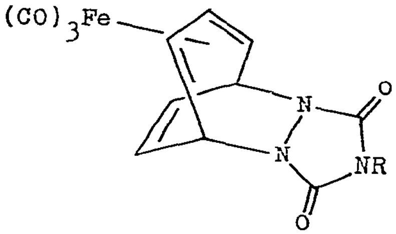
11.17



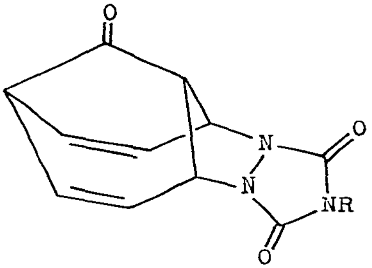
11.18



11.19



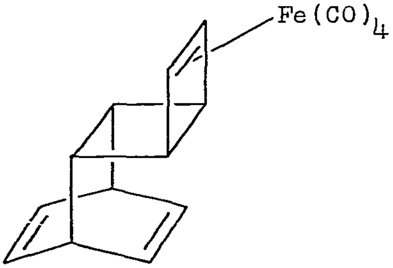
11.20



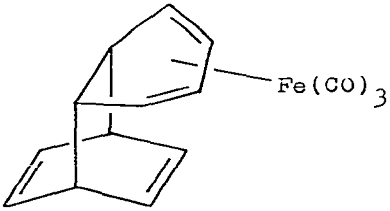
11.21

Complex mixtures of products were obtained, the nature and proportions of which were dependent on the carbonyl used and the reaction conditions. Thus irradiation of iron pentacarbonyl and dicyclopropylacetylene in a 2:1 molar ratio gave the ferroles (11.25, 11.26, 11.27 and 11.28) as the principal products together with three other complexes, two of which were unidentified [253].

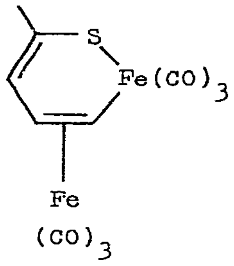
Iron atoms were cocondensed with thiophenes at -196° and the co-condensate was allowed to warm to room temperature under an atmosphere of carbon monoxide. Desulphurization of the thiophene occurred with the formation of tricarbonylferrole iron tricarbonyl compounds (11.29; R = H, Me) [254].



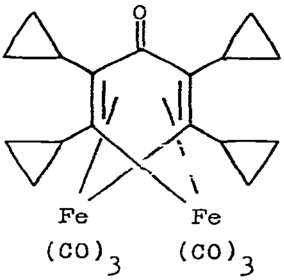
11.22



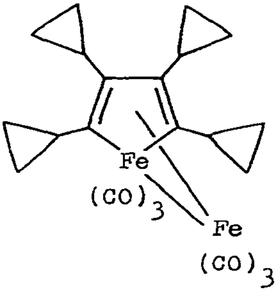
11.23



11.24



11.25

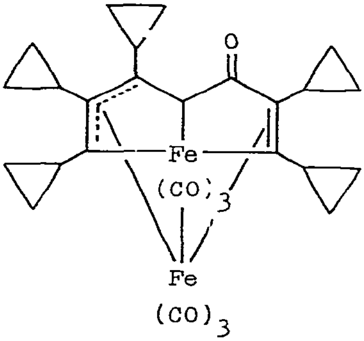


11.26

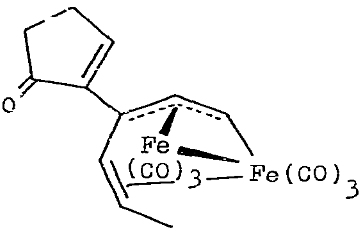
The iron-borole complexes (11.30 and 11.31) were formed by treating pentaphenylborole with diiron nonacarbonyl and 1-phenyl-2-ethyl-4,5-dihydroborepin with iron pentacarbonyl respectively [255].

The tricarbonyl(η-cyclopentadiene)iron complexes (11.32; R = Me, CH_2Ph, CH_2Cl, Cl; M = Si, Ge) were obtained by photolysis of the free ligand with iron pentacarbonyl. Substitution reactions at germanium in the η-germacyclopentadiene complexes demonstrated the high reactivity of the germanium-carbon bond [256].

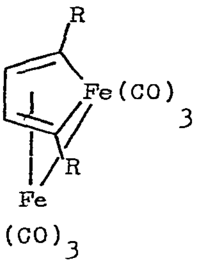
The crystal and molecular structure of the (η-boracyclodiene)iron complex (11.33) has been determined by X-ray crystallography [257].



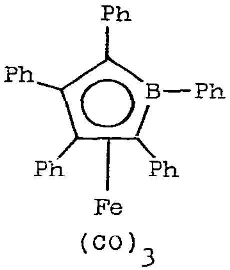
11.27



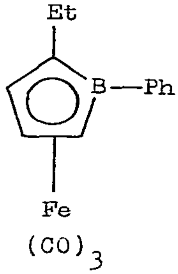
11.28



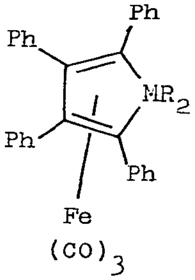
11.29



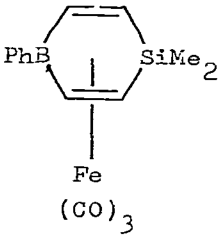
11.30



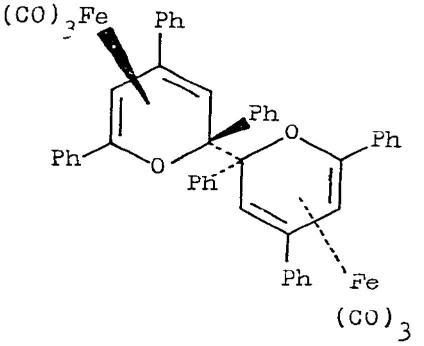
11.31



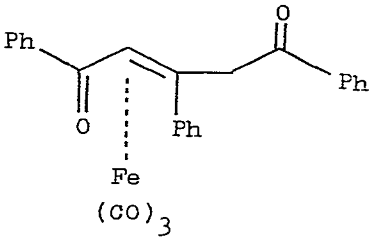
11.32



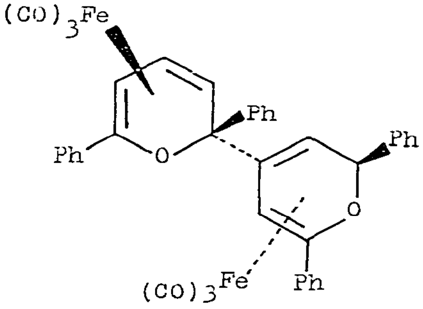
11.33



11.34



11.35



11.36

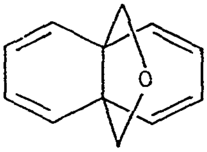
Treatment of 2,4,6-triphenylpyrylium iodide with an excess of diiron enneacarbonyl gave the bis(tricarbonyliron) complex (11.34), which was produced by the reductive coupling of two pyrylium moieties, and a small amount of the tricarbonyliron complex (11.35). Similarly, the reaction of 2,6-diphenylpyryli iodide with diiron eneacarbonyl gave the bis(tricarbonyliron) complex (11.36) [258].

(ii) SPECTROSCOPIC AND PHYSICO-CHEMICAL PROPERTIES

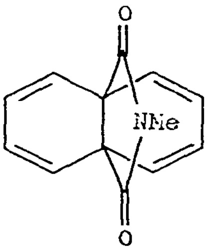
The variable temperature ^{13}C NMR spectrum of tricarbonyl-(η-cycloheptatriene)iron was examined and only a little broadening occurred before the molecule decomposed. However, on application of the Forsen-Hoffman spin saturation method the molecule was shown to be fluxional. It was not clear from the results whether tricarbonyl(η-cycloheptatriene)iron was fluxional via either a 1,2 or a 1,3 shift mechanism [259].

^{13}C and ^{1}H NMR spectroscopy were used to study the configurations of a series of mono- and bis-tricarbonyliron complexes of the propellanes (11.37 and 11.38). Praseodymium induced ^{13}C-shifts of the ironcarbonyl carbon atoms and the shifts of the central carbon atom of the complexed diene system were particularly useful in helping to decide whether the configuration of the tricarbonyliron group was exo or endo [260

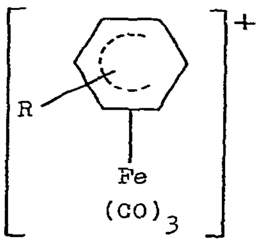
The ^{13}C NMR spectra of eleven 1-, 2-, and 3-substituted tricarbonyl(η-cyclohexadienyl)iron cations (11.39; R = H, Me, OMe, CO_2Me) were assigned and the substituent effects were compared with those in the corresponding cyclohexadienyl cation Chemical shifts for the methoxy compounds (11.39; R = OMe) suggested that canonical forms with a positive charge on oxygen or on the ring carbon atom bound to oxygen were of major



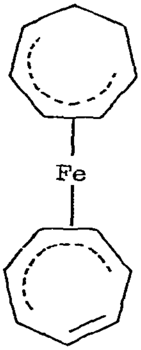
11.37



11.38



11.39

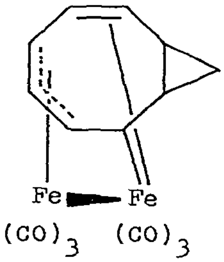


11.40

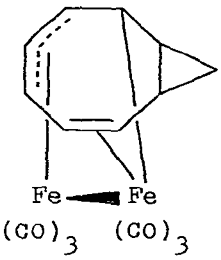
importance in the electronic structure of these cations. Product distribution in nucleophilic addition to the cations (11.39) was discussed in terms of the chemical shifts observed for the carbon atoms at which addition occurred [261].

The fluxional behaviour of the iron complex (11.40) was investigated by variable temperature ^{13}C and ^{1}H NMR spectroscopy. A 1,2-shift mechanism of the η-cycloheptatrienyl group with respect to the central iron atom was proposed [262].

The fluxional behaviour of the (η-bicyclo[6.1.0]nonatriene)-diiron complex (11.41) has been investigated by variable temperature ^{1}H and ^{13}C NMR spectroscopy. The low temperature limiting spectra were consistent with the asymmetric skew-type structure of the crystalline solid (11.41 and 11.42). At higher temperatures a "twitching" process was implicated in the interchange between the two forms. The twitch was followed by scrambling



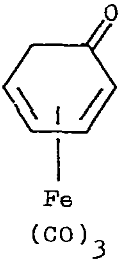
11.41



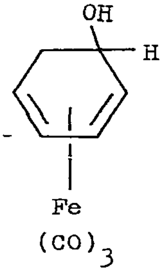
11.42

of the carbonyl groups first on the allyl-bound iron atom and then on the second iron atom. The free energy of activation for the twitch was determined as ΔG‡ = 7.4 kcal mol^{-1} [263].

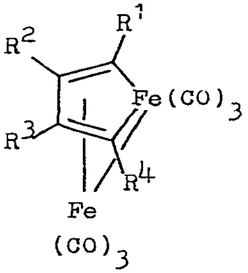
The mass spectra of the tricarbonyliron complexes (11.43 and 11.44) were recorded. It was concluded that the radical cations $[(C_6H_6O)Fe]^{+\bullet}$ formed by both the complexes had different structures over that part of the energy distribution that gave rise to decompositions in the ion source [264].



11.43

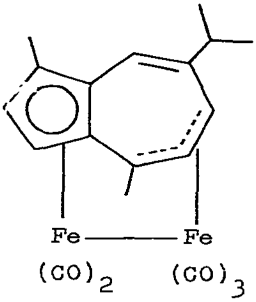


11.44

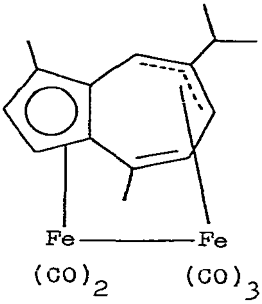


11.45

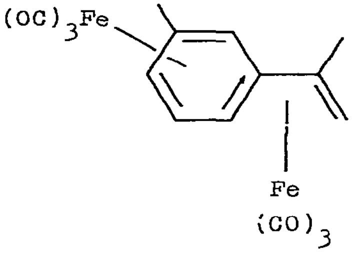
Mass spectrometry has been used to determine the stabilities of the complexes (11.45) which were prepared from triiron dodecacarbonyl and substituted acetylenes. Stability was determined by the electron releasing power of the substituents [265]. The crystal and molecular structure of 2,2'-bithienylhexacarbonyldiiron has been determined by X-ray crystallography. One thiophene ring remained free while the second had an iron tricarbonyl group inserted to give a metallocycle with a second, pendant, iron tricarbonyl group [266].



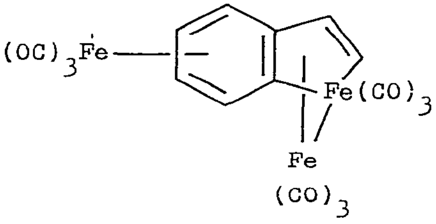
11.46



11.47



11.48

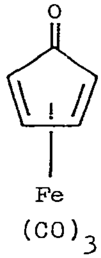


11.49

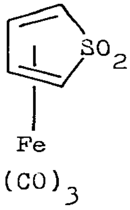
The crystal and molecular structures of the isomeric pentacarbonyl(η-guaiazulene)diiron complexes (11.46 and 11.47) have been determined by X-ray crystallography. Their fluxional behaviour has been studied by ^{13}C NMR spectroscopy and the carbonyl scrambling processes were very similar to those observed in pentacarbonyl(η-azulene)diiron [267].

The crystal and molecular structures of the (η-dimethylstyrene)diiron complex (11.48) and the (η-ferraindene)diiron complex (11.49) have been determined by X-ray methods. The η-dimethylstyrene complex (11.48) consisted of two planar (η-isoprene)tricarbonyliron groups that intersected at an angle of 34.3°. The two tricarbonyliron groups occupied trans positions with respect to one another. The (η-*cis*-butadiene)tricarbonyliron groups in the (η-ferraindene) complex (11.49) had dimensions closely in accord with those observed previously [268].

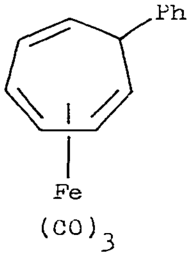
A single crystal X-ray diffraction study has confirmed the structure of tricarbonyl(η-cyclopentadienone)iron (11.50). The



11.50



11.51



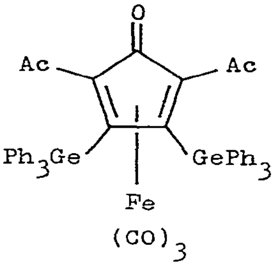
11.52

ketone group is 19.9° out of the plane of the butadiene moiety [269]. The crystal and molecular structure of tricarbonyl(η-3 dimethylthiophen-1,1-dioxide)iron (11.51) has been determined by X-ray methods. The compound is structurally analogous to tricarbonyl(η-butadiene)iron although the sulphur atom is bent out of the plane of the butadiene moiety by 26.9° [270].

The crystal and molecular structure of tricarbonyl(η-<u>exo</u>-7-phenylcycloheptatriene)iron (11.52) has been determined by X-ray crystallography [271].

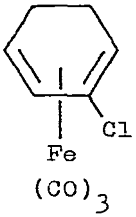
(iii) GENERAL CHEMISTRY

The (η-germylcyclopentadienone)iron complex (11.53) was formed from diiron nonacarbonyl and $Ph_3GeC{\equiv}CAc$ [272].

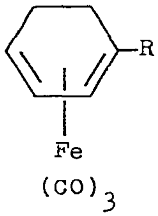


11.53

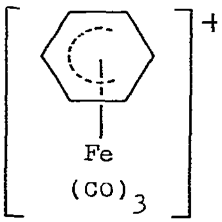
2-Chloro-1,3-cyclohexadiene was treated with triiron dodecacarbonyl to form a mixture of the two isomeric (η-cyclohexadiene)iron complexes (11.54 and 11.55; R = Cl) which was converted to tricarbonyl(η-cyclohexadiene)iron (11.55; R = H) with sulphuric acid. This complex was, in turn, oxidized



11.54



11.55

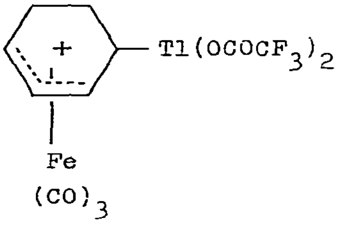


11.56

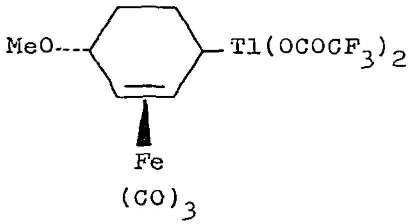
smoothly to the (η-cyclohexadienyl)iron cation (11.56). The aldehyde complex (11.55; R = CHO) underwent condensation reactions to form derivatives such as the nitrile (11.55; R = CH=CHCN) [273].

Electrophilic substitution of tricarbonyl(η-cyclohexa-1,3-diene)iron with thallium(III) trifluoroacetate in methanol gave a mixture of the methoxides (11.59 and 11.60) and the alcohol (11.61). It was proposed that the η-allyl intermediate (11.57) was formed initially and that this was attacked by methoxide ion to give the η-cyclohexene intermediate (11.58) which in turn lost thallium(I) trifluoroacetate and trifluoroacetic acid to give the product [274].

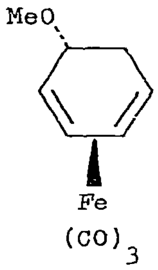
The tricarbonyl(η-cyclohexadienyl)iron cation (11.62) combined with alkoxides at room temperature to give the (η-*exo*-cyclohexadiene)iron compound (11.63; R = OMe, OEt, OPr^n). The *exo*-methoxy product (11.63; R = OMe) isomerized rapidly on heating to give a mixture of the *endo*- and *exo*-isomers in the ratio 3:2. The same mixture was obtained by heating the



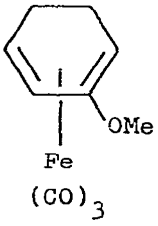
11.57



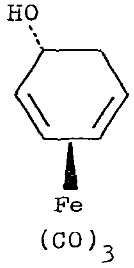
11.58



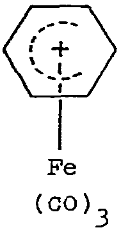
11.59



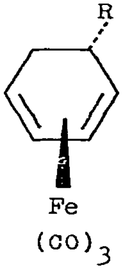
11.60



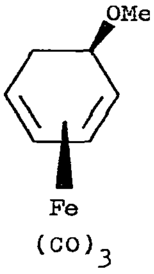
11.61



11.62



11.63

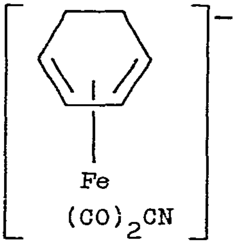


11.64

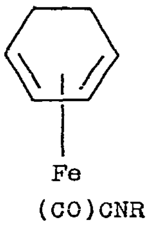
endo-isomer (11.64) under reflux with acidified methanol. An ^{1}H NMR shift reagent was used to show that the relatively slow isomerization of the endo-isomer was caused by steric hindrance to protonation [275].

Tricarbonyl(η-1,3-cyclohexadiene)iron was converted to the anionic cyano complex (11.65) with $NaN(SiMe_3)_2$ and was in turn protonated to the isocyanic acid derivative (11.66; R = H) and alkylated with $(Et_3O)BF_4$ to the isonitrile complex (11.66; R = Et). Similar reaction sequences were reported for (η-butadiene)tricarbonyliron and (η-cyclooctatetraene)tricarbonyliron [276].

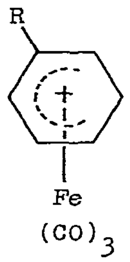
The attack of mixed alkylcuprates, $Li(R^1R^2Cu)$, where R^1 = Me, $CH_2{=}CH$, Bu, Bu^t, Pr^i and R^2 = $CH_2{=}CH$, Bu, OBu^t, SPh on tricarbonyl(η-cyclohexadienyl)iron cations (11.67; R = H, Me) has been investigated. When the reagent contained the thiophenyl group together with a bulky alkyl group such as iso-propyl or t-butyl then alkylation of the cation occurred to give a mixture of the two isomeric (η-cyclohexadiene)iron



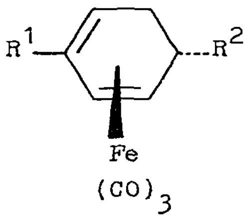
11.65



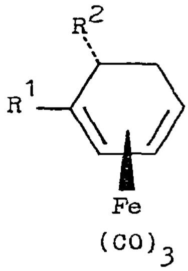
11.66



11.67



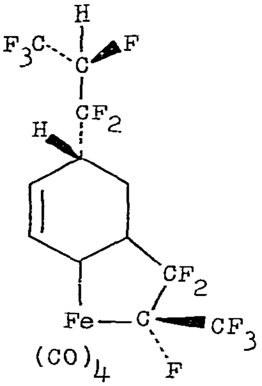
11.68



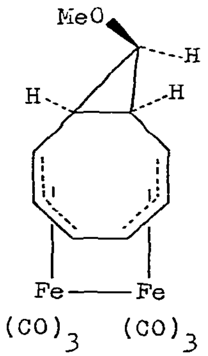
11.69

complexes (11.68 and 11.69). The ratio of these two products was sensitive to the nature of the reagent but the dominant product in each case was the 2,5-disubstituted complex (11.68) [277].

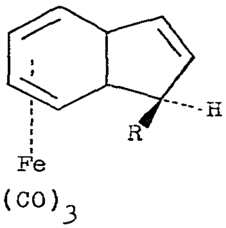
The kinetics of substitution of dicarbonyliodo(η-cyclohexa-1,3-dienyl)- and dicarbonyliodo(η-cyclohepta-1,3-dienyl)- iron complexes by phosphite ligands was investigated. The variation in rate with the size of the attached ring was η-cyclohexadienyl >η-cycloheptadienyl >η-cyclopentadienyl. Detailed solvent studies showed that for the 6- and 7- membered ring compounds the transition state was more polar than the ground state which was opposite to that found for the η-cyclopentadienyl complexes [278].



11.70

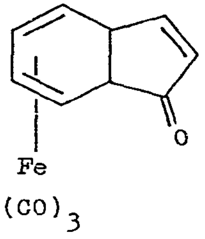


11.71

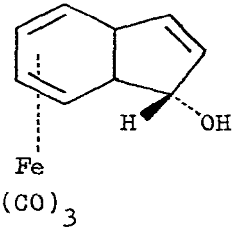


11.72

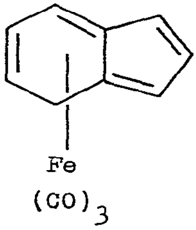
The addition of hexafluoropropene to tricarbonyl(η-cyclo 1,3-diene)iron took place in the molar ratio 2:1 with the fluoropropene adding endo to the iron atom. The structure of the ferraindene product (11.70) was determined by X-ray cryst lography and a mechanism was proposed for its formation [279]



11.73

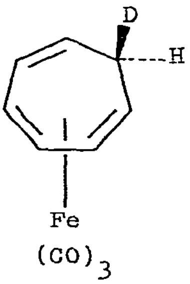


11.74

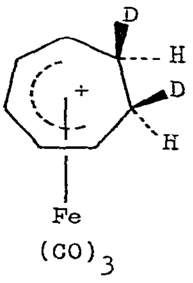


11.75

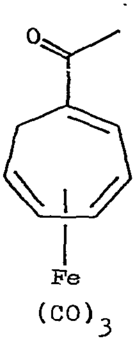
Diiron nonacarbonyl combined with 9-anti-methoxy-cis-bicyclo[6.7.0]nonatriene to form the binuclear complex (11.71 of the initial bicyclic ring system together with the (η-dihydroindene)iron complex (11.72; R = OMe). The latter was esterified with trifluoroacetic acid to give the ester (11.72; R = $OCOCF_3$) which was then saponified on alumina to the alcoho (11.72; R = OH). This compound was in turn oxidized to the indenone complex (11.73) which led to the endo-alcohol (11.74) When any one of the complexes (11.72; R = OMe, OH, $OCOCF_3$) was extracted from dichloromethane into concentrated sulphuric acid and then quenched with water, the homopentalene complex (11.75) was obtained [280].



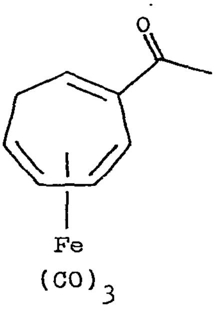
11.76



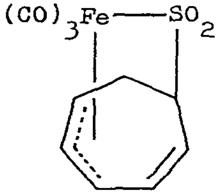
11.77



11.78

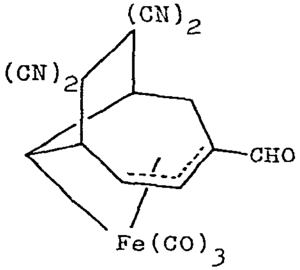


11.79

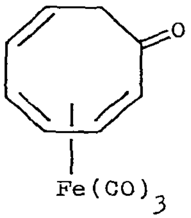


11.80

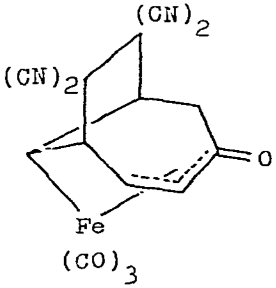
Treatment of the tricarbonyliron derivative (11.76) with deuterated trifluoroacetic acid gave the cation (11.77) where deuterium addition had occurred exclusively exo to iron [281]. The site of addition of a proton and tetracyanoethylene to some



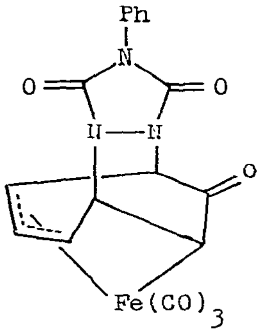
11.81



11.82



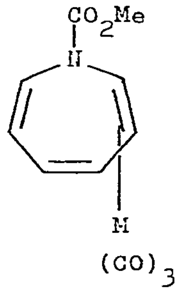
11.83



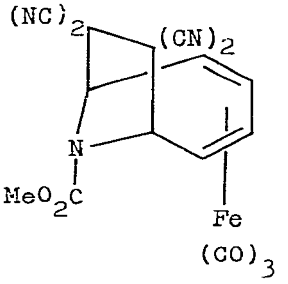
11.84

η-cycloheptatrienetricarbonyliron complexes was investigated. Tetracyanoethylene underwent 1,3-addition to the uncoordinated side of the ring in the acetyl derivatives (11.78 and 11.79), whereas the proton added to the coordinated double bond in the 2-acetyl complex (11.79). When tricarbonyl(η-cycloheptatriene)-iron was dissolved in sulphur dioxide the adduct (11.80) separated [282].

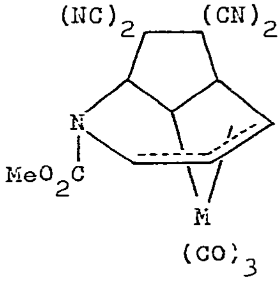
Treatment of tricarbonyl[η-(6-formyl-cycloheptatriene)]iron with tetracyanoethylene gave the adduct (11.81). The adduct was formed by initial electrophilic attack of tetracyanoethylene at the C—1 position of the coordinated double bond followed by ring closure at C—3. In a similar reaction with tetracyanoethylene the η-cyclooctatrienone complex (11.82) gave the cycloadduct (11.83). Tricarbonyl(η-tropone)iron underwent 1,5-cycloaddition with N-phenyl-triazolinedione to give the complex (11.84) [283]



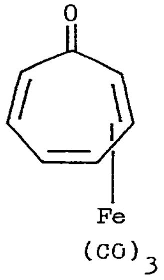
11.85



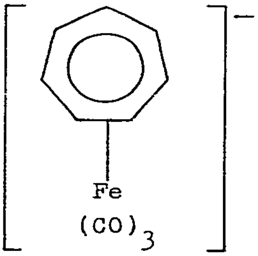
11.86



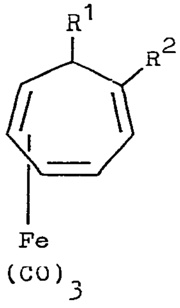
11.87



11.88



11.89

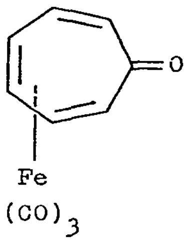


11.90

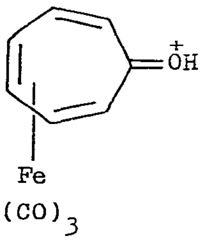
The cycloaddition of olefins and ketones bearing electronegative substituents to (η-azepine)- and (η-cycloheptatrienone)-iron and -ruthenium carbonyls has been compared with cycloaddition to the free ligands. The (η-azepine)iron complex (11.85; M = Fe) combined with tetracyanoethylene over 30 min at room temperature to form the (η-diene)iron complex (11.86) as the major product by 1,6-addition together with the (η-allyl)iron complex (11.87; M = Fe) as a minor product by 1,3-addition. Hexafluoroacetone gave the 1,3-adduct with the same (η-azepine) complex (11.85; M = Fe) and its ruthenium analogue (11.85; M = Ru) also gave the products of 1,3-addition with hexafluoroacetone, tetracyanoethylene (11.87; M = Ru) and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene. Tricarbonyl-(η-cycloheptatrienone) iron (11.88) underwent slow cycloaddition with hexafluoroacetone and tetracyanoethylene to give 1,3-adducts. The mechanism of the reactions has been discussed in terms of the Woodward Hoffmann topological rule [284].

The tricarbonyl(η-cycloheptatrienide)iron anion (11.89) combined with the ester $\mathrm{ClCO_2Me}$ to form the isomeric η-cycloheptatriene ester complexes (11.90; $R^1 = CO_2Me$, $R^2 = H$; $R^1 = H$, $R^2 = CO_2Me$). The triethylsilyl and triethylgermanyl derivatives (11.90; $R^1 = Et_3Si$, Et_3Ge, $R^2 = H$) respectively were obtained by using triethylchlorosilane and triethylgermanium chloride as the reagents [285].

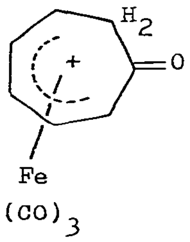
Tricarbonyl(η-tropone)iron (11.91) was protonated on the oxygen atom with trifluoroacetic acid in dichloromethane at -78° to form the blood-red cation (11.92). On warming to 0° the cation isomerized to the carbon protonated complex (11.93). The 7-methyltropone complex was also protonated [286, 287]. The reaction of tricarbonyl(η-tropone)iron with diphenyl-



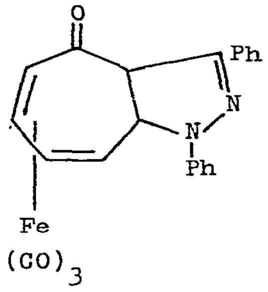
11.91



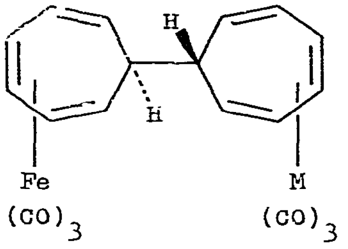
11.92



11.93



11.94

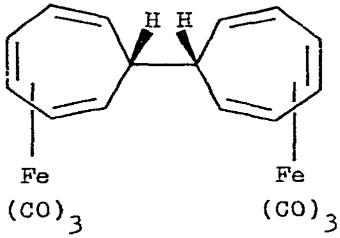


11.95

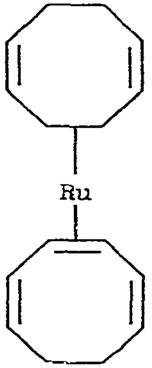
nitrilimine gave the adduct (11.94) as the major product. Treatment of the adduct (11.94) with cerium(IV) gave the free ligand [288].

Tricarbonyl(η-cycloheptatriene)iron combined with tricarbonyl(η-cycloheptatriene)-chromium, -molybdenum and -tungsten to give the mixed exo-binuclear complexes (11.95; M = Cr, Mo, W). The same iron complex was treated with allyl bromide to give the endo-diiron complex (11.96). Elimination of $M(CO)_3$, where M = Cr, Mo, W, from the complexes (11.95) and subsequent treatment with (η-benzylideneacetone)tricarbonyliron gave the exo-diiron complex (11.95; M = Fe) [289].

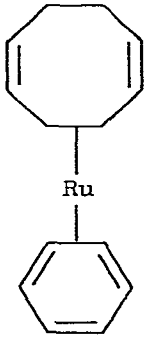
The (η-cyclooctadiene)ruthenium complex (11.97) underwent several reactions involving ligand exchange, ligand reduction and aromatisation in the presence of hydrogen. Thus the (η-benzene)ruthenium complex (11.98) was formed with benzene and hydrogen at room temperature [290].



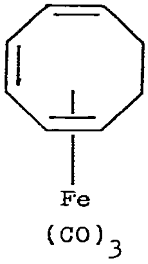
11.96



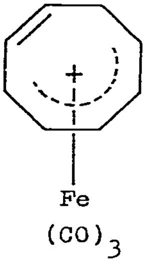
11.97



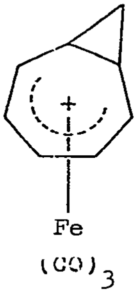
11.98



11.99



11.100

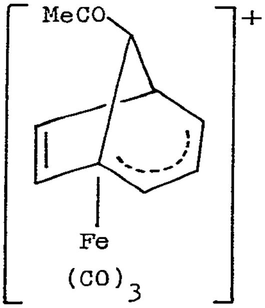


11.101

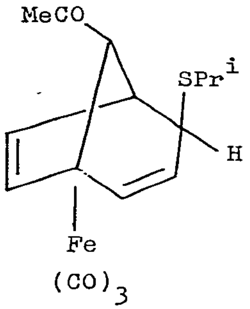
Tricarbonyl(η-cyclooctatetraene)iron was reduced quantitatively to the η-cyclooctatriene complex (11.99) by electrolysis in the presence of trimethylammonium bromide as a proton donor. Reduction with potassium in THF gave the same product in 30% yield. The mechanism of reduction was investigated by cyclic voltammetry [291].

Tricarbonyl(η-cyclooctatetraene)iron was protonated in a mixture of fluorosulphonic acid and fluorosulphonyl chloride at -120° to form the dienyl cation (11.100). When the solution was allowed to warm to -60° the cation rearranged to the tricarbonyl(η-bicyclo[5.1.0]octadienyl)iron cation (11.101) by electrocyclic ring closure [292].

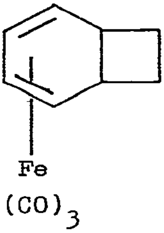
Acetylation of tricarbonyl(η-cyclooctatetraene)iron under Friedel-Crafts conditions gave the (η-bicyclo[3.2.1]octadienylium)-iron complex (11.102) which was characterised structurally by X-ray crystallography and was converted to the η-diene complex (11.103) with iso-propylthiol and butyllithium. The reaction of the cation with nucleophiles was also reported [293].



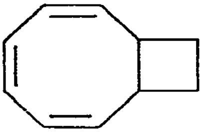
11.102



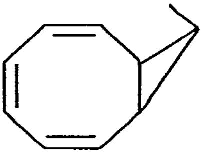
11.103



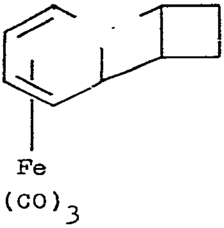
11.104



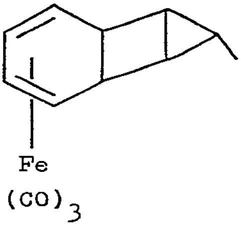
11.105



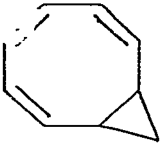
11.106



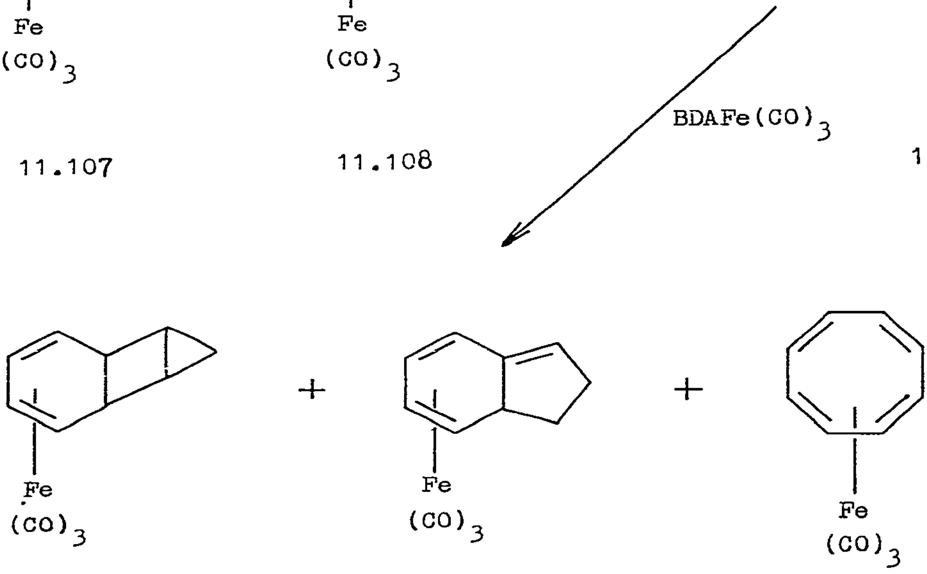
11.107



11.108



11.109



11.110 11.111 11.112

A kinetic study of the reaction between cyclooctatriene and (η-benzylideneacetone)tricarbonyliron, BDAFe(CO)$_3$, to give the tricarbonyliron complex of bicyclo[4.2.0]octadiene (11.104) has confirmed that the rate determining step is the ring closure of the triene to the tautomeric bicyclodiene. The low concentrations of the tautomeric dienes present in equilibrium with trienes (11.105 and 11.106) were also trapped selectively with (η-benzylideneacetone)tricarbonyliron to form the complexes (11.107 and 11.108). However, bicyclo[6.1.0]nonatriene (11.109) gave a mixture of complexes containing tri-, di- and mono-cyclic ligands (11.110, 11.111 and 11.112) [294].

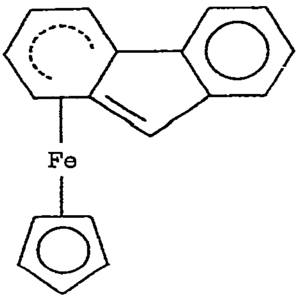
The thermal reactions of (η-benzylideneacetone)tricarbonyliron with cyclooctatriene, bicyclo[6.1.0]nonatriene and syn-9-methylbicyclo[6.1.0]nonatriene gave (η-bicyclo[4.2.0]octadiene)tricarbonyliron, (η-tricyclo[4.3.0.0]-nona-2,4-diene)tricarbonyliron and tricarbonyl(η-syn-8-methyltricyclo[4.3.0.0]nona-2,4-diene)iron respectively as the major products. A kinetic study was carried out on the reaction of (η-benzylideneacetone)tricarbonyliron with 1,3-cyclohexadiene to give tricarbonyl(η-cyclohexadiene)iron. It was suggested that this reaction proceeded by dechelation of the carbonyl group to give a sixteen electron iron complex which was then trapped by cyclohexadiene [295].

12. $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6H_6)]^+$

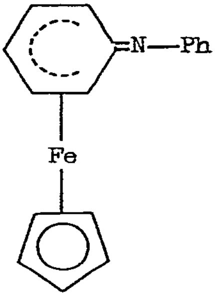
Several (η-arene)(η-cyclopentadienyl)iron(II) salts (arene = diphenylamine, carbazole, benzimidazole, triphenylmethane, fluorene) were prepared by heating the arene, ferrocene, aluminium chloride and aluminium in decalin. Treatment of the η-arene complexes with either bis(trimethylsilyl)amide or sodamide in ammonia gave the corresponding η-cyclohexadienyl compounds (12.1, 12.2, 12.3 and 12.4) [296].

The formation of (η-benzene)iron sandwich cations (12.5; R = Me, NO_2, OMe) in the gas phase has been reported. Ferrocene was mixed with the arene in an ion cyclotron resonance spectrometer at low pressure. The reaction proceeded through attack of the cation $(\eta\text{-}C_5H_5)Fe^+$ on the neutral arene [297]. Treatment of 1,1'-bis(3-phenylpropyl)ferrocene with aluminium chloride and aluminium gave the η-benzene complex (12.6) whose structure was confirmed by X-ray analysis [298].

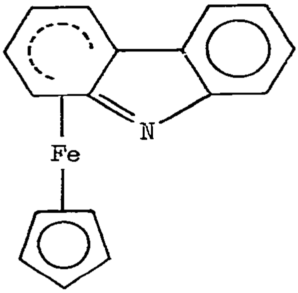
Determination of the crystal and molecular structure of the (η-fluorenyl)iron complex (12.7) by X-ray crystallography has led to its formulation as a zwitterion with a positive charge on iron and a negative charge principally on C(9). The complex behaves as a nucleophile towards alkyl halides to give the exo-9-alkyl derivatives. Thus methyl iodide gave the salt (12.8); other related reactions were reported [299].



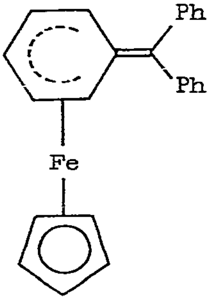
12.1



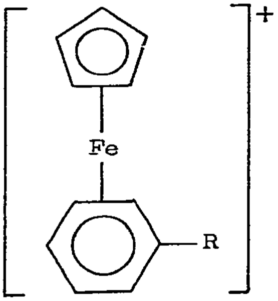
12.2



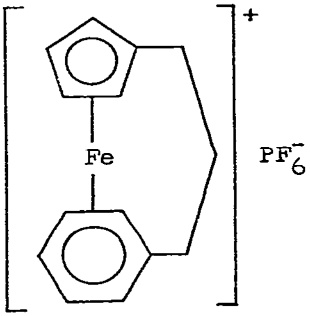
12.3



12.4

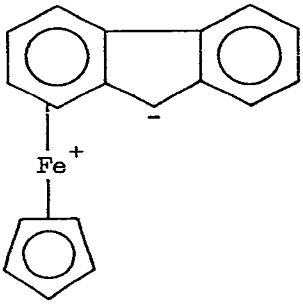


12.5

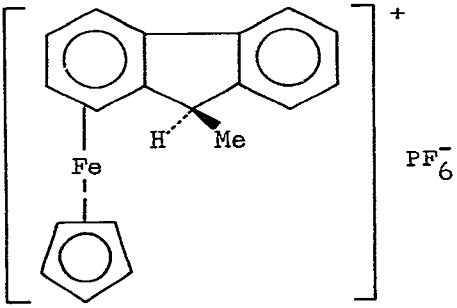


12.6

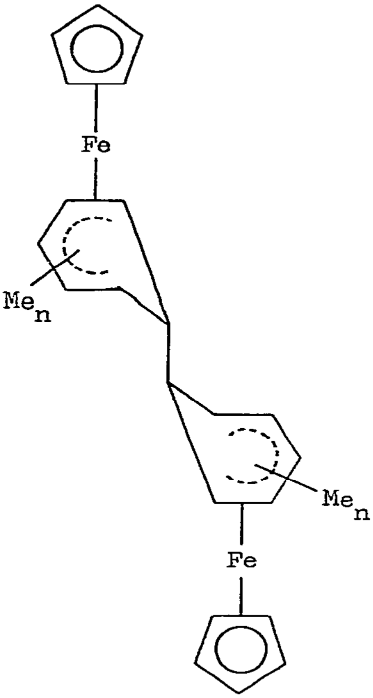
Electrochemical reduction of (η-benzene)(η-cyclopentadienyl)-iron cations gave the binuclear (η-cyclohexadienyl)iron complexes (12.9; n = 1—5) through dimerization of the intermediate radical. When the initial cation was unsubstituted the metal ligand bonds



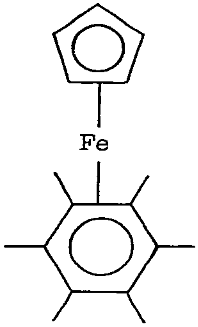
12.7



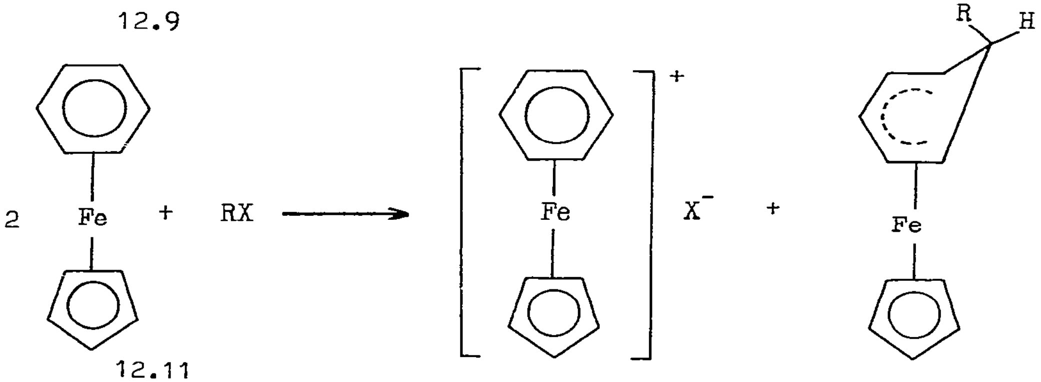
12.8



12.9

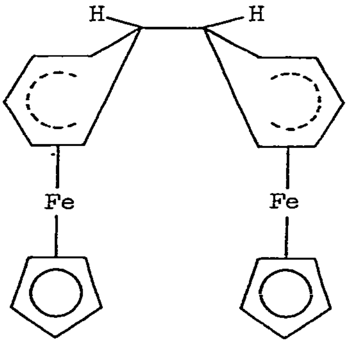


12.10



12.11

Equation 1



12.12

were cleaved to form benzene and cyclopentadiene and when the cation carried six methyl groups the first formed mononuclear radical (12.10) was stable [300].

The reaction of (η-benzene)(η-cyclopentadienyl)iron with the proton donors RH [RH = HCl, PhSH, $(MeCO)_2CH_2$, H_2O, MeOH] gave $[(\eta-C_6H_6)Fe(\eta-C_5H_5)]R$ [301].

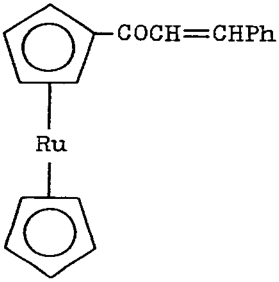
(η-Benzene)(η-cyclopentadienyl)iron (12.11) dimerized at 20° in pentane to give the complex (12.12). The dimer (12.12) was moderately stable to air oxidation and on pyrolysis it gave ferrocene and benzene as the main products. The reaction of the iron complex (12.11) with organic halides RX (RX = CCl_4, Ph_3CCl, $PhCH_2Cl$, EtBr, PhBr, PhCl) gave a salt and the substituted (η-cyclohexadienyl)(η-cyclopentadienyl)iron derivative (Equation 1) [302].

13. $(\eta-C_5H_5)_2Ru$

The ruthenocene and ferrocene complexes $(\eta-C_5H_5)_2Ru.HgX_2$ (X = Br, Cl), $[(\eta-C_5H_5)_2Ru]_2Hg_2Cl_4$, $(\eta-C_5H_5)_2Fe.7HgX_2$ and $[(\eta-C_5H_5)_2Fe]_2Hg_2Cl_4$ were prepared and their infrared and ultraviolet spectra were recorded. Charge-transfer absorptions between ruthenium or iron and mercury occurred at 280 and 360 nm respectively. Irradiation of the complexes within the charge-transfer bonds caused oxidation of the metallocene to the corresponding metallocinium ion together with the formation of mercury(I) [303].

Ruthenocene has been used to quench the triplet states of organic compounds. Those compounds with triplet energies <24000 cm^{-1} showed a decrease in the efficiency of quenching as the triplet energy decreased while those with triplet energies >24000 cm^{-1} were quenched at a diffusion controlled rate. The large Stokes shift between absorption by, and emission from, the lowest triplet state of ruthenocene indicated that it was geometrically distorted [304].

The free energy barriers for rotation of the acetyl groups in acetylruthenocene and 1,1'-diacetylruthenocene were determined as 33.1 and 32.3 kJ mol^{-1} respectively by the use of ^1H and ^{13}C NMR spectroscopy [305]. The quenching of triphenylene phosphorescence in poly(methylmethacrylate) at 77 K by ruthenocene and ferrocene was investigated. Transfer of energy to ruthenocene was shown to occur by an exchange mechanism, while transfer to ferrocene occurred mainly by a dipole-dipole mechanism with a weaker transfer channel due to the polymer



13.1

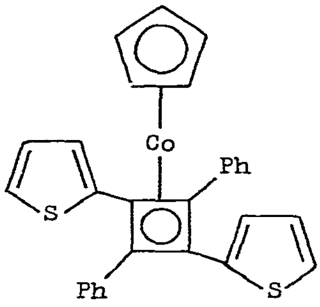
matrix [306]. ^{103}Ru and ^{59}Fe labelled ruthenocene and ferrocene carboxylic acids were administered to mice. The organ distribution and the quantity of label excreted were determined. The metallocenes were excreted ninety times faster than $^{103}RuCl_3$ and $^{59}FeCl_3$. The presence of free iron in the urine and retention of radioactivity in the blood indicated that the ferrocene derivative was degraded in vivo but the ruthenocene compound was not broken down [307].

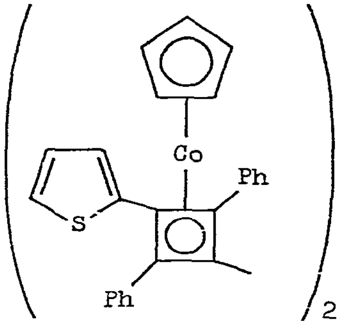
The acylruthenocene (13.1) labelled with ^{103}Ru was injected into mice and found to accumulate principally in the thymus gland [308]. Cinnamoyl-[^{103}Ru]-ruthenocene was injected intravenously into rats and mice. The excretion rates and organ distributions of the labelled metallocene and $^{103}RuCl_3$ were determined. The latter compound was evenly distributed in the body whilst the former was concentrated in the liver, lungs and spleen. After intraperitoneal injection of cinnamoyl-[^{103}Ru]-ruthenocene, a high thymus affinity was found and autoradiography showed that the site of ^{103}Ru was in the thymocytes [309].

^{103}Ru-labelled ruthenocene was administered to rats by interperitoneal injection. The ruthenocene was hydroxylated and conjugated with glucoronic acid and the conjugate was excreted in the urine [310].

14. $(\eta-C_4H_4)Co(\eta-C_5H_5)$

Reaction of dicarbonyl(η-cyclopentadienyl)cobalt with phenyl-2-thienylacetylene gave the cobalt complex (14.1) as the major product together with triphenyltri-2-thienylbenzene,





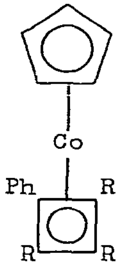
14.1

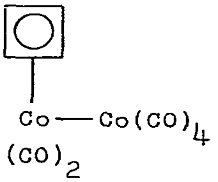
14.2

three isomeric cyclopentadienone-cobalt complexes and the dimer (14.2) [311].

Lee and Brintzinger have carried out a general study of the interactions between (η-cyclopentadienyl)cobalt carbonyls and acetylenes and have observed the formation of (η-cyclopentadienyl)(η-tetraphenylcyclobutadiene)cobalt in good yield from the binuclear complex $(\eta\text{-}C_5H_5)_2(\eta\text{-PhC}{\equiv}\text{CPh})Co_2(CO)$ [312]. Mono- and bis-(phenylethynyl)ferrocenes were treated with the complexes $(\eta\text{-}C_5H_5)CoPPh_3(RC{\equiv}CR)$ and $(\eta\text{-}C_5H_5)Co(PPh_3)_2$ and several (η-ferrocenylcyclobutadiene)cobalt complexes (14.3; R = Fc, Ph, CO_2Me) were isolated [313].

The structure of hexacarbonyl(η-cyclobutadiene)dicobalt (14.4) was determined by X-ray analysis. The η-cyclobutadiene ring was bound to the cobalt atom of a $Co(CO)_2$ moiety which, in turn, was linked to a $Co(CO)_4$ fragment through the metal





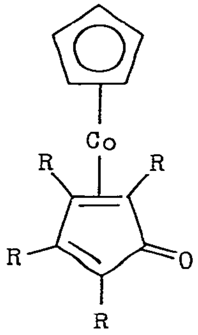
14.3

14.4

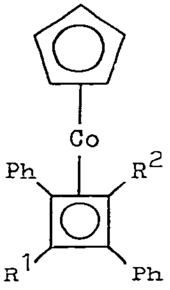
atoms. Apparently to decrease repulsion between the η-cyclobutadiene ring and the $Co(CO)_4$ group, the ring was tilted with the result that the η-C_4H_4—Co interaction was unsymmetrical [314].

Cyclic voltammetry was used to examine the reduction of (η-cyclopentadienone)(η-cyclopentadienyl)cobalt complexes (14.5; R = Ph, C_6F_5). Reversible one-electron reduction was observed to form stable anion radicals; the ESR spectra of these species were consistent with a high degree of metal character in the orbital receiving the electron [315].

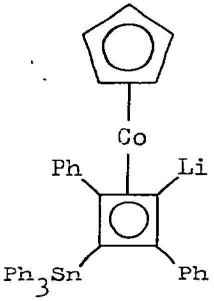
Reaction of the η-cyclobutadiene-cobalt complex (14.6; $R^1 = R^2 = SnPh_3$) with two molar equivalents of phenyllithium gave only the monolithio derivative (14.6; $R^1 = SnPh_3$, $R^2 = Li$) which was condensed with chlorotrimethylsilane. A further substituent was introduced by treatment of the complex (14.6; $R^1 = SnPh_3$, $R^2 = SiMe_3$) with phenyllithium followed by condensation of the lithio-intermediate (14.7) with an electrophile [316].



14.5



14.6

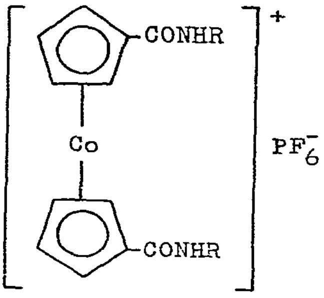


14.7

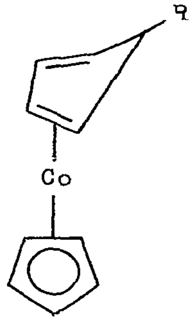
15. (η-C_5H_5)$_2$Co and [(η-C_5H_5)$_2$Co]$^+$

All the homologues of the $(Me)_nC_5H_{6-n}$ series were treated with sodium amide in liquid ammonia to give the corresponding anions $(Me_nC_5H_{5-n})^-$. Treatment of the anions with hexaamminecobalt(II) chloride gave symmetrically substituted polymethylcobalticinium cations. These ions were isolated as their hexafluorophosphate salts [317].

The ^{13}C NMR spectra of alkylcobalticinium ions have been obtained and the effect of increasing size of the alkyl group on the chemical shift has been compared with the effect in the



15.1



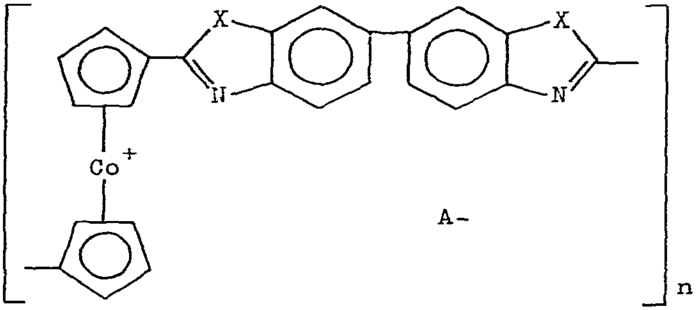
15.2

isoelectronic alkylferrocenes. The two series showed similar sensitivities to alkyl substitution [318].

Condensation of the 1,1'-dicarboxycobalticinium cation with amines and hydrazines gave the corresponding amides and hydrazides (15.1; R = Ph, p-ClC_6H_4, 2-naphthyl, PhNH, PhCONH) [319]. Cobaltocene anions were formed by electrochemical reduction in THF and treated with electrophiles to form the (η-cyclopentadiene)(η-cyclopentadienyl)cobalt derivatives (15. R = CH_2Br, CH_2Ph, CHClPh, CCl_3) in quantitative yield. Produc obtained from the oxidation of these derivatives by air, acid and by the triphenylmethyl cation were dependent on the natur of the substituents. Derivatives with exo-hydrogen or an exo-carbomethoxy group gave the corresponding cobalticinium ions while those with an exo-methyl or -phenyl group suffered degradation [320, 321].

Cobaltocene was attacked by lithium and 1,5-cyclooctadie in THF at 0^{c} to form the complex bis(-1,5-cyclooctadiene)-CoLi$(THF)_2$ [322]. Cobaltocene catalysed the cycloaddition of acetylenes to nitriles to give 2-substituted pyridines in goo yields [323].

The thermal decomposition of cobaltocene at 500° and 45-280 mm Hg followed first order kinetics. The principal products were hydrogen, cyclopentadiene and methane [324]. Cobaltocene has been used as a selective initiator in the polymerization of vinyl monomers such as acrylonitrile, acrol butadiene and isobutyl vinyl ether. The nature of the solven and the presence of organic halides were factors which affect the mechanism of initiation [325]. Low molecular weight amid linked cobalticinium copolymers were obtained by low temperat

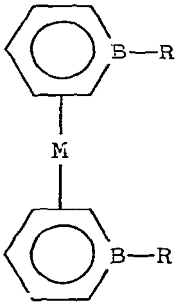


15.3

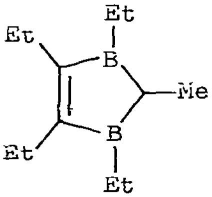
solution polymerization. The copolymers underwent thermal cyclization to form benzimidazole-cobalticinium copolymers (15.3; X = NH, S; A^- = PF_6, Cl) [326].

The borabenzene salts $K[C_5H_5BR]$ (R = Me, Ph) were prepared from the cobalt complex (15.4; M = Co) by treatment with potassium cyanide. Addition of chromium(III) chloride or chromium(II) chloride-tetrahydrofuran to the borabenzene salts gave the chromium complexes (15.4; R = Me, Ph; M = Cr) [327].

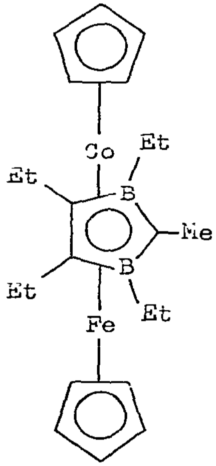
The triple-decker sandwich compound (15.6) containing both iron and cobalt was formed by heating the diborolene



15.4



15.5

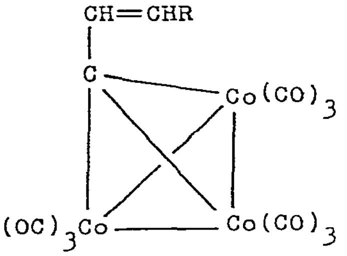


15.6

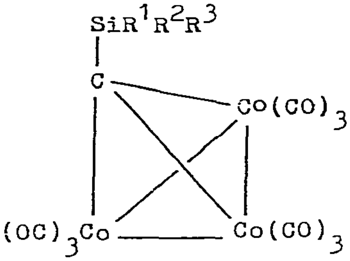
ligand (15.5) with dicarbonyl(η-cyclopentadienyl)cobalt and dicarbonyl(η-cyclopentadienyl)iron dimer in diglyme [328].

16. COBALT-CARBON CLUSTER COMPOUNDS

The synthesis of vinylmethylidynetricobalt nonacarbonyl compounds (16.1; R = H, Me, Me_3Si, MeCO) from dicobalt octacarbonyl and vinyltrihalogenomethanes in dry THF has been reported. The vinyl complexes (16.1) were protonated with hexafluorophosphoric acid to give the α-cluster carbenium ions which showed high stability and were converted to several derivatives [329].



16.1

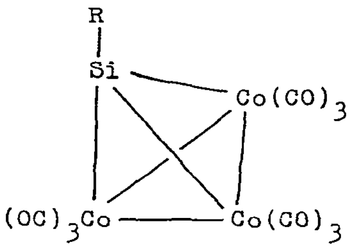


16.2

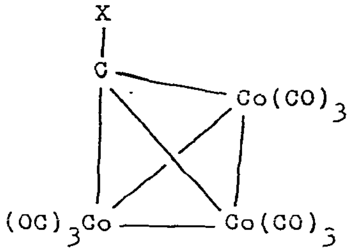
The reaction of methylidynetricobalt nonacarbonyl with silicon hydrides was used to prepare a series of silyl-substituted methylidynetricobalt nonacarbonyls (16.2; $R^1 = R^2 = R^3$ = Et, n-Pr, Ph). The products derived from the reactions with trichlorosilane, dichloromethylsilane and chlorodimethylsilane were converted to the corresponding methoxy- or hydroxysilyl derivatives (16.2; $R^1 = R^2$ = Me, R^3 = OMe; $R^1 = R^2$ = Me, R^3 = OH; R^1= Me, $R^2 = R^3$ = OMe; R^1 = Me, $R^2 = R^3$ = OH; $R^1 = R^2$ R^3 = OMe; $R^1 = R^2 = R^3$ = OH). Some reactions of these silanols were investigated [330].

Silicon analogues of methylidenetricobalt nonacarbonyl cluster complexes have been prepared by treating the tetracarbonylcobaltate anion with trichlorosilanes. The methyl- (16.3; R = Me) and vinyl- (16.3; R = $CH{=}CH_2$) cluster complexes were obtained in this way [331].

The acetylene complexes, $XC{\equiv}CX.Co_2(CO)_6$ where X = Cl, Br, I were heated with octacarbonyldicobalt to form the binuclear cluster complex $[CCo_3(CO)_9]_2$ (16.6) [332].

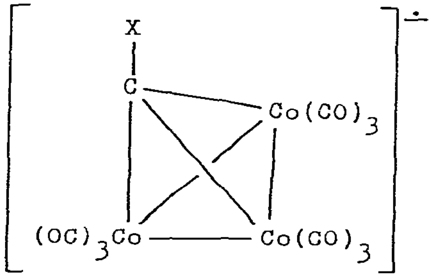


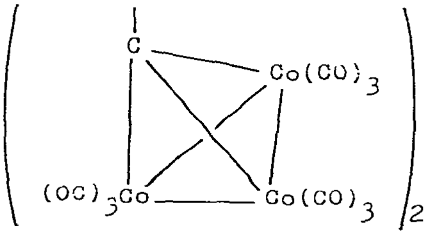
16.3



16.4

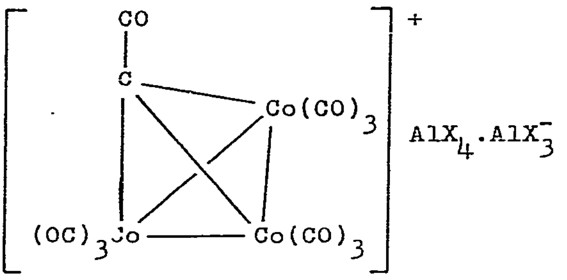
Polarography and cyclic voltammetry have been used to investigate the reduction of methylidynetricobalt enneacarbonyl complexes (16.4; X = F, Cl, Br, H, Me, Ph, CF_3, Me_3Si) in acetone. The half-wave values for one-electron reduction to the radical anion fell in the range -0.2 to -0.5V vs. the silver-silver chloride standard electrode and were correlated with the charge density on the cobalt atoms in the neutral cluster complex. Reduction to the dianion caused breakdown of the cluster [333]. The radical-anions (16.5; X = F, Cl, Br, H, Me, Et, CF_3, CF_3CH_2) were also obtained by reduction of the appropriate neutral cluster compound with sodium or cesium in ether. The ESR spectra of the highly stable radical anions allowed the assignment of the unpaired electron to a non-degenerate, delocalized, metal-centred orbital. $\underline{A}^{Co}$ was not sensitive to the nature of the apical substituent and hyperfine interactions with the apical carbon and substituents were absent [334]. Treatment of (η-dihaloacetylene)hexacarbonyldicobalt compounds with cobalt carbonyl or sodium tetra-



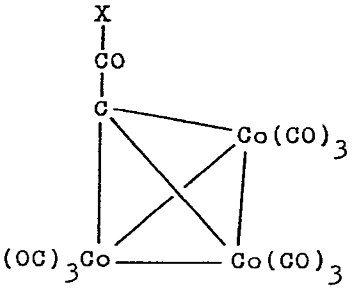


16.5

16.6



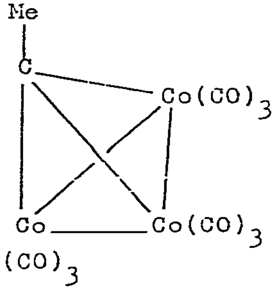
16.7



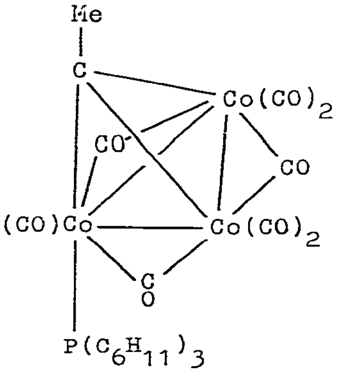
16.8

carbonylcobaltate (-1) gave the dicluster (16.6) [335].

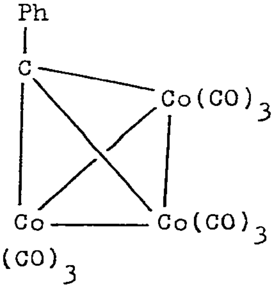
Aluminium halides were effective in converting bromo- and chloro-methylidynetricobalt nonacarbonyl to the corresponding acylium haloaluminate (16.7; X = Br, Cl) in good yield. These salts were attacked by a wide variety of nucleophiles such as alcohols, phenols, amines, thiols, tetraalkyltins, reactive aromatics and silicon hydrides to form the corresponding α-functional alkylidynetricobalt nonacarbonyl compounds (16.8; X = RO, ArO, R_2N, RS, R, Ar, H). Formation of the acylium haloaluminate (16.7) required the efficient transfer of carbon monoxide from other molecules of the starting material [336]. The Clemmensen reduction was used to convert acyl- and vinylic-methylidynetricobalt nonacarbonyl complexes to the corresponding saturated alkylidynetricobalt nonacarbonyls. Treatment of the acyl-substituted cobalt clusters with diborane in tetrahydrofuran gave a mixture of the corresponding alcohol and alkyl derivatives [337].



16.9



16.10



16.11

Reaction of the cobalt-cluster compound (16.9) with tricyclohexylphosphine gave the cobalt complex (16.10). The structure of this complex was determined by X-ray analysis. In the reaction one axial carbonyl of the parent $CCo_3(CO)_9$ unit had been replaced by the phosphine and the equatorial carbonyls had rearranged so that three of them formed bridges across the sides of the Co_3 triangle [338].

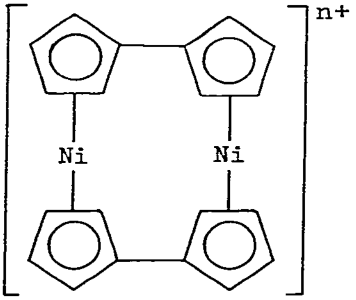
The methylidynetricobaltnonacarbonyl complex (16.11) has been used as a homogeneous hydroformylation catalyst for 1-pentene [339]. Cobalt carbonyl cluster complexes have been evaluated as catalysts for the dimerization of bicycloheptadiene. Small cluster complexes and those bearing a negative charge were the most efficient. The order of activity for the substituted methylidene nonacarbonyl tricobalt clusters $RCCo_3(CO)_9$ was

$$R = H > Me > Ph > CF_3$$

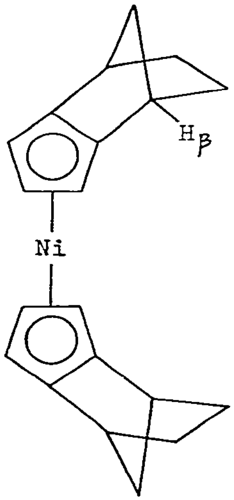
which suggested that the size of the substituent was less important than its electronegativity [340].

17. $(\eta\text{-}C_5H_5)_2Ni$

The [0]nickelocenophane (17.1; n = 0) was obtained as a red-brown air-sensitive solid by treatment of the fulvalene dianion with nickel acetylacetonate in THF at -78°. It was oxidised with iron(III) chloride in benzene to the dication



17.1



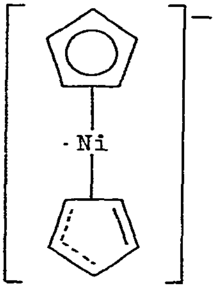
17.2

(17.1; n = 2) isolated as the red-brown hexafluorophosphate. Orange solutions of the dication (17.1; n = 2) were unstable towards reduction to the purple mixed-valence cation (17.1; n = 1). The electronic and infrared absorption spectra of the complexes were used to support the proposal that they were electronically and structurally distinct from the corresponding metallocenes [341].

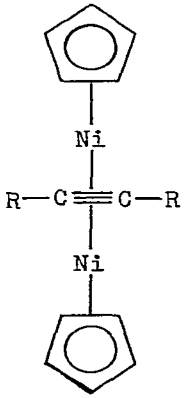
The metal-ligand vibrations in ferrocene and nickelocene were investigated by IR and Raman spectroscopy. The lower ring tilt vibration frequency in nickelocene was rationalized in terms of electronic and vibronic effects on the bond force constant. The effect of charge-transfer on the bonding was found to be less important in nickelocene than in ferrocene [342].

The crystal and molecular structure of the nickelocene (17.2) has been determined by X-ray crystallography and ^1H NMR contact shifts have been measured. The relationship betwee the H_β contact shift and the dihedral angle made by C_α—H_β and the ring carbon p_z axis was explored [343]. Nickelocene combined with the phosphinoacetylene $Ph_2PC{\equiv}CCF_3$ to give six isolable products one of which has been characterised by X-ray crystallography and contains a CpNi—NiCp moiety bound to the acetylenic bond of the ligand [344].

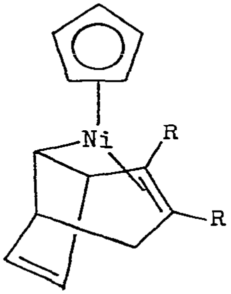
The mass spectra of nickelocene and 1,1'-di(isopropyl)-nickelocene were recorded. The spectra indicated that a large



17.3



17.4

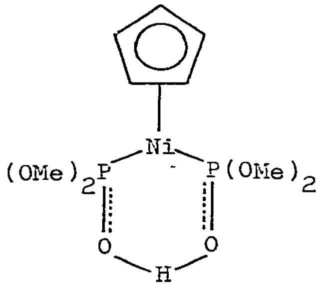


17.5

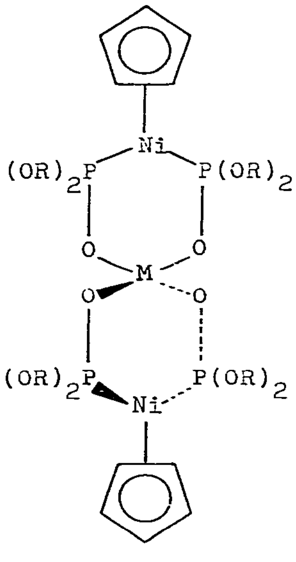
number of rearrangement processes occurred and that a large number of nickel containing species were present. The introduction of the isopropyl groups increased the degree of rearrangement [345]. Working under high-vacuum conditions electrochemical experiments (cyclic voltammetry, dc polarography and coulometry) were carried out on nickelocene, vanadocene and chromocene. Nickelocene was reduced to give the anion $[(\eta\text{-}C_5H_5)_2Ni]^-$ which was detected by cyclic voltammetry. The anion $[(\eta\text{-}C_5H_5)_2Ni]^-$ is a twenty-one electron compound and it was suggested that it had a "slipped sandwich" structure (17.3) to relieve the high electron density around the metal [346].

The pyrolysis of nickelocene in the gas phase at 340-420° was investigated and found to involve an activation energy of 21.4 kcal mol^{-1}. The principal hydrocarbon product was cyclopentadiene and a radical mechanism with both homogeneous and heterogeneous pathways was proposed [347].

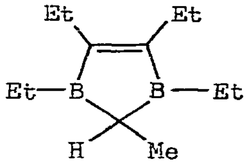
Nickelocene was degraded by acetylenes to give mixtures of the (η-cyclopentadienyl)nickel complexes (17.4 and 17.5; R = H, CO_2H, methyloxycarbonyl). One of the racemates (17.5) was resolved into its enantiomers [348]. Nickelocene was heated with excess dimethylphosphonate to give the nickel complex (17.6). Reaction of the complex (17.6) with ammonia followed by either cobalt(II) chloride or zinc chloride gave the trinuclear complexes (17.7; M = Co, Zn) which were regarded



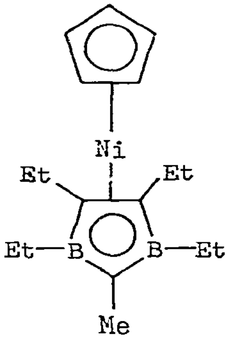
17.6



17.7



17.8

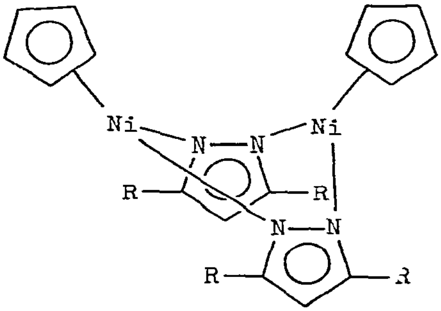


17.9

as "supersandwich" compounds [349]. The kinetics of hydrosilylation of olefins with alkylchlorosilanes in the presence of nickelocene was investigated. The hydrosilylations obeyed Markovnikov's rule to give the α-adducts. For styrene, the rate of addition of the silane was $HSiCl_3 > HSiMeCl_2 > HSiMe_2Cl > HSiMeEt_2$ [350].

Nickelocene was heated with the 1,3-diborolene (17.8) to give the diamagnetic nickel complex (17.9) which was structurally analogous to nickelocene [351]. Nickelocene was used to prepare a number of (η-cyclopentadienyl)bis(ligand)nickel(I) complexes. Pure compounds were isolated when 1,2-bis(diphenylphosphino)ethane, 1,1'-bipyridyl and di-n-butylphenylphsophine were used as the ligands [352].

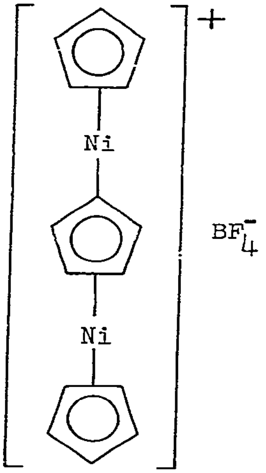
The reaction of nickelocene with 3,5-dialkylpyrazoles gave red diamagnetic complexes (17.10; R = Me, Et, i-Pr). In the ^1H NMR spectra of the complexes (17.10; R = Me, i-Pr) the



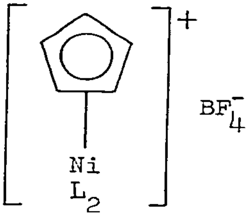
17.10

position of the resonance for the η-cyclopentadienyl group was temperature dependent. This behaviour was interpreted in terms of an equilibrium between the dimer and a paramagnetic monomer. The reaction of nickelocene with pyrazole and with 3-methylpyrazole gave polymeric bis(pyrazolates) in which both η-cyclopentadienyl groups had been displaced from the nickel [353].

Treatment of the tripledecker sandwich complex (17.11) with the alkynes diphenylacetylene, phenylacetylene and di(carboxymethyl)acetylene gave nickelocinium tetrafluoroborate and the corresponding binuclear complexes $(\eta\text{-}R^1C_2R^2)[Ni(\eta\text{-}C_5H_5)]_2$. Reaction of nickelocinium tetrafluoroborate with trimethyl and triphenylphosphite gave the corresponding nickel complexes [17.12; L = $P(OMe)_3$, $P(OPh)_3$] and treatment with nickelocene gave the complex (17.11) [354].



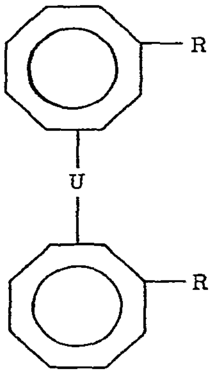
17.11



17.12

18. URANOCENE

A series of monosubstituted cyclooctatetraenes were prepared, reduced to the corresponding anions and treated with uranium(IV) chloride to give the disubstituted uranocenes [18.1, R = OMe, OEt, t-BuO, $OCH_2CH{=}CH_2$, NMe_2, CH_2NMe_2, $(CH_2)_3NMe_2$, NMe_3I, CH_2NMe_3I, Et, n-Bu, t-Bu, $(CH_2)_4Me$]. The ether (18.1; R = OMe) and the salt (18.1; R = NMe_3I) when treated with alkyllithium reagents gave the corresponding dialkyluranocenes. It was suggested that these compounds were formed by a metallation chain reaction involving a cyclooctatrienyneuranium intermediate [355].



18.1

REFERENCES

1 S. D. Ittel and J. A. Ibers, Adv. Organometal. Chem., 14 (1976) 33 .

2 J. A. Howell, Organometal. Chem., 5 (1976) 292.

3 E. W. Abel and F. G. A. Stone, Organometallic Chemistry, Vol. 5, A Review of the Literature Published during 1975, Chem. Soc., London, England (1976) 520 pp.

4 P. Treichel, Amer. Chem. Soc. Sound Recording, Chem. Abstr., 87 (1977) 6178.

5 J. Tirouflet and P. Braunstein, Actual. Chim., (1975) 4.

6 B. A. Dolgoplosk, E. I. Tinyakova, S. I. Beilin, G. N. Bondarenko, O. P. Parenago, N. N. Stefanovskaya, V. M. Frolov, O. K. Sharaev and V. A. Yakovlev, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2498.

7 P. L. Timms and T. W. Turney, Adv. Organometal. Chem., 15 (1977) 53.

8 M. J. McGlinchey and P. S. Skell, Cryochemistry, (1976) 167.

9 J. Klikorka and I. Pavlik, Sb. Ved. Pr., Vys. Sk. Chemickotechnol., Pardubice, 34 (1975) 27.

10 R. B. King, Method. Chim., 8 (1976) 421; Edited by K. Niedenzu and H. Zimmer, Academic Press, New York.

11 K. Schloegl and H. Falk, Method. Chim., 8 (1976) 469; Edited by K. Niedenzu and H. Zimmer, Academic Press, New York.

12 H. Rosenberg, Method. Chim., 8 (1976) 500; Edited by K. Niedenzu and H. Zimmer, Academic Press, New York.

13 J. R. Wasson, Method. Chim., 8 (1976) 543; Edited by K. Niedenzu and H. Zimmer, Academic Press, New York.

14 M. Green, Ann. N. Y. Acad. Sci., 295 (1977) 160.

15 L. I. Denisovich and S. P. Gubin, Usp. Khim., 46 (1977) 50; Chem. Abstr., 86 (1977) 97843.

16 J. A. Connor, Top. Curr. Chem., 71 (1977) 71.

17 H. Werner, Angew. Chem., 89 (1977) 1.

18 M. I. Bruce, Angew. Chem., 89 (1977) 75.

19 V. T. Aleksanyan and B. V. Lokshin, Itogi Nauki Tekh., Str. Mol. Khim. Svyaz; Chem. Abstr., 86 (1977) 98122.

20 T. S. Abram and W. E. Watts, Organometal. Chem., 5 (1976) 352.

21 C. B. Hunt, Educ. Chem., 14 (1977) 110.

22 S. Toma, Chem. Listy, 71 (1977) 478.

23 M. F. Semmelhack, J. Organometal. Chem. Libr., 1 (1976) 361.

24 H. Veening, Prog. Anal. Chem., 6 (1973) 165; Chem. Abstr., 87 (1977) 77747.

25 M. Yoshifuji, Gendai Kagaku, 73 (1977) 14.

26 M. L. H. Green, J. Less-Common Met., 54 (1977) 159.

27 A. Efraty, Chem. Rev., 77 (1977) 691.

28 H. Alper, inOrganic Syntheses via Metal Carbonyls, Edited by I. Wender and P. Pino, Wiley, New York 1977.

29 M. Brookhart, C. R. Graham, G. O. Nelson, O. Gregory and G. Scholes, Ann. N. Y. Acad. Sci., 295 (1977) 254.

30 R. G. Sutherland, J. Organometal. Chem. Libr., 3 (1977) 311.

31 R. B. King, J. Indian Chem. Soc., 54 (1977) 169.

32 J. Tirouflet, P. Dixneuf and P. Braunstein, Actual. Chim., (1975) 3.

33 R. B. King, Coord. Chem. Rev., 20 (1976) 155.

34 I. Haiduc and V. Popa, Adv. Organometal. Chem., 15 (1977) 113.

35 D. A. Edwards, Organometal. Chem., 5 (1976) 205.

36 P. V. Yaneff, Coord. Chem. Rev., 23 (1977) 183.

37 I. S. Butler, Acc. Chem. Res., 10 (1977) 359.

38 D. M. P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 20.

39 D. M. P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 26.

40 D. M. P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 31.

41 W. L. Jolly, S. C. Aranzino and R. R. Rietz, Inorg. Chem., 16 (1977) 964.

42 M. I. Kalinkin, G. D. Kolomnikova, V. E. Puzanova, M. M. Gol'din, Z. N. Parnes and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1852.

43 F. R. Kreissl, P. Stueckler and E. W. Meineke, Chem. Ber., 110 (1977) 3040.

44 V. Cerny, I. Pavlik and É. Kustkova-Maxova, Collect. Czech. Chem. Commun., 41 (1976) 3232.

45 C. Pommier and C. Azokpota, Journ. Calorimetric Anal. Therm., [C,R.], 3-6 (1976) 8 pp.
46 C. Azokpota, C. Pommier, J. F. Berar and G. Calvarin, J. Organometal. Chem., 135 (1977) 125.
47 L. M. Dyagileva, V. P. Mar'in and E. I. Tsyganova, Dokl. Akad. Nauk SSSR, 236 (1977) 886.
48 A. Sh. Sultanov, U. M. Dzhemilev, M. S. Miftakhov, V. I. Khvostenko and G. A. Tolslikov, Zh. Obshch. Khim., 47 (1977) 1336.
49 J. W. Johnson, Diss. Abstr. Int. B, 37 (1977) 4454.
50 M. A. Andrews, Inorg. Chem., 16 (1977) 496.
51 K. Hoffmann and E. Weiss, J. Organometal. Chem., 131 (1977) 273.
52 R. B. King and K.-N. Chen, Inorg. Chim. Acta, 23 (1977) L19.
53 I. Muller and D. Rehder, J. Organometal. Chem., 139 (1977) 293.
54 A. N. Nesmeyanov, V. S. Kaganovich, V. V. Krivykh and M. I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 156.
55 A. N. Nesmeyanov, I. V. Polovyanyuk and L. G. Makarova, Dokl. Akad. Nauk SSSR, 230 (1976) 1351.
56 H. Ohno, H. Horita, T. Otsubo, Y. Sakata and S. Misumi, Tetrahedron Lett., (1977) 265.
57 C. G. Kreiter and S. Ozkar, J. Organometal. Chem., 129 (1977) C14.
58 A. Meyer, H. Neudeck and K. Schloegl, Chem. Ber., 110 (1977) 1403.
59 H. Reinke and G. Oehme, J. Prakt. Chem., 318 (1976) 959.
60 K. H. Doetz and R. Dietz, Chem. Ber. 110 (1977) 1555.
61 G. K. Magomedov, A. S. Frenkel, V. N. Kalinin and L. I. Zakharkin, Izv. Akad. Nauk SSSR, Ser. Khim.,(1977) 949.
62 F. van Meurs and H. van Koningsveld, J. Organometal. Chem., 131 (1977) 423.
63 D. E. Koshland, S. E. Myers and J. P. Chesick, Acta Crystallogr., Sect. B, B33 (1977) 2013.
64 V. G. Andrianov and Yu. T. Struchkov, Zh. Strukt. Khim., 18 (1977) 318.
65 G. G. Aleksandrov, V. G. Andrianov, N. G. Bokii, N. I. Kirillova, L. G. Kuz'mina, T. N. Sal'nikova and Yu. T. Struchkov, Tezisy Dokl.-Vses. Chugaevsko Soveshch. Khim. Kompleksn. Soedin., 12th, 2 (1975) 227.

66 L. Schaefer, Kem. Kozl., 45 (1976) 321; Chem. Abstr., 86 (1977) 105772.

67 M. Gower, L. A. P. Kane-Maguire, J. P. Maier and D. A. Sweigart, J. Chem. Soc., Dalton Trans., (1977) 316.

68 C. Azokpota, Y. Limouzin, J. C. Maire, C. Pommier, A. Baldy and R. Ouaki, J. Microsc. Spectrosc. Electron, 1 (1976) 273.

69 F. Van Meurs, A. J. Hoefnagel, B. M. Wepster and H. Van Bekkum J. Organometal. Chem., 142 (1977) 299.

70 L. S. Levitt and B. W. Levitt, J. Inorg. Nucl. Chem., 38 (1976) 1907.

71 G. A. Razuvaev, V. A. Kuznetsov, A. N. Egorochkin, A. A. Klimov, A. N. Artemov and N. I. Sirotkin, J. Organometal. Chem., 128 (1977) 213.

72 F. Van Meurs, J. M. A. Baas and H. Van Bekkum, J. Organometal. Chem., 129 (1977) 347.

73 F. Van Meurs and H. Van Bekkum, J. Organometal. Chem., 133 (1977) 321.

74 B. P. Roques, J. Organometal. Chem., 136 (1977) 33.

75 M. Acampora, A. Ceccon, M. Dal Farra, G. Giacometti and G. Rigatti, J. Chem. Soc., Perkin Trans. 2 (1977) 483.

76 W. R. Jackson, C. F. Pincombe, I. D. Rae, D. Rash and B. Wilkinson, Aust. J. Chem., 29 (1976) 2431.

77 J. Tirouflet, J. Besancon, F. Mabon and M. L. Martin, Org. Magn. Reson., 8 (1976) 444.

78 M. Coletta, G. Granozzi and G. Rigatti, Inorg. Chim. Acta, 24 (1977) 195.

79 D. A. Brown, J. P. Chester, N. J. Fitzpatrick and I. J. King, Inorg. Chem., 16 (1977) 2497.

80 D. L. S. Brown, J. A. Connor, C. P. Demain, M. L. Leung, J. A. Martinho-Simoes, H. A. Skinner and M. T. Zafarani Moattar, J. Organometal. Chem., 142 (1977) 321.

81 H. Keller, C. Krieger, E. Langer, H. Lehner and K. Schlögl, Monatsh. Chem., 108 (1977) 113.

82 G. Jaouen and A. Meyer, Tetrahedron Lett., (1976) 3547.

83 H. DesAbbayes and M. A. Boudeville, J. Org. Chem., 42 (1977) 4104.

84 C. H. Bamford, K. G. Al-Lamee and C. J. Konstantinov, J. Chem. Soc., Faraday Trans. 1, 73 (1977) 1406.

85 A. Munoz-Escalona and G. Di Filippo, Makromol. Chem., 178 (1977) 659.

86 A. K. Gilbert, J. M. Kelly, M. Budzwait and E. Koerner von Gustorf, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 1091.

87 M. F. Semmelhack, Y. Thebtaranonth and L. Keller, J. Amer. Chem. Soc., 99 (1977) 959.

88 M. F. Semmelhack and G. Clark, J. Amer. Chem. Soc., 99 (1977) 1675.

89 V. A. Sapunov, I. Yu. Litvintsev, G. I. Magomedov and I. Margitfal'vi, Kinet. Katal., 18 (1977) 626.

90 M. F. Farona and J. F. White (University of Akron), US Pat., 4038324, 1977, July 26; Chem. Abstr., 87 (1977) 184685.

91 O. Gandolfi and M. Cais, J. Organometal. Chem., 125 (1977) 141.

92 M. F. Farona and J. F. White (University of Akron), US Pat., 3984483, 1976 Oct. 5; Chem. Abstr., 86 (1977) 89350.

93 L. M. Svanidze, E. A. Mushina, A. M. Sladkov, N. I. Sirotkin, A. K. Artemov, I. R. Gol'ding, T. G. Samedova, G. N. Bondarenko and B. E. Davydov, Vysokomol. Soedin., Ser. B, 19 (1977) 51.

94 W. S. Trahanovsky and R. A. Hall, J. Am. Chem. Soc., 99 (1977) 4850.

95 G. Simonneaux, G. Jaouen, R. Dabard and P. Guenot, J. Organometal. Chem., 132 (1977) 231.

96 A. N. Nesmeyanov, V. V. Krivykh. P. V. Petrovskii and M. I. Rybinskava, Dokl. Akad. Nauk SSSR, 231 (1976) 110.

97 G. Schmid and J. Schulze, Angew. Chem., 89 (1977) 258.

98 H. Noth and U. Schuchardt, J. Organometal. Chem., 134 (1977) 297.

99 A. J. Ashe and J. C. Colburn, J. Amer. Chem. Soc., 99 (1977) 8099.

100 F. Edelmann and U. Behrens, J. Organometal. Chem., 134 (1977) 31.

101 E. A. Mintz, M. D. Rausch, B. H. Edwards, J. E. Sheats, T. D. Rounsefell and C. U. Pittman, J. Organometal. Chem., 137 (1977) 199.

102 B. V. Lokshin and E. B. Nazarova, Koord. Khim., 3 (1977) 857.

103 A. Agarwal, M. J. McGlinchey and T.-S. Tan, J. Organometal. Chem., 141 (1977) 85.

104 H. F. Efner, Diss. Abstr., Int. B, 37 (1977) 3413.

105 H. F. Efner, W. B. Fox, R. R. Smardzewski and D. E. Tevault, Inorg. Chim. Acta, 24 (1977) L93.

106 H. F. Efner, D. E. Tevault, W. B. Fox and R. R. Smardzewski, J. Organometal. Chem., 146 (1978) 45.

107 E. P. Kundig and P. L. Timms, J. Chem. Soc., Chem. Commun., (1977) 912.

108 C. Elschenbroich and R. Moeckel, Angew. Chem., 89 (1977) 908.

109 T.-S. Tan, Diss. Abstr. Int. B, 37 (1976) 1683.

110 C. Elschenbroich and J. Heck, Angew. Chem., 87 (1977) 497.

111 Yu. B. Zverev, Gidridy, Galedy Metalloorg. Soedin. Osoboi Chist., (1976) 123.

112 L. S. Zborovskaya, T. N. Aizenshtadt, A. N. Artemov and A. S. Emel'yanova, Khim. Elementoorg. Soedin., 4 (1976) 92.

113 V. T. Aleksanyan and T. S. Kurtikyan, Koord. Khim., 3 (1977) 1548.

114 A, J. Campbell, C. A. Fyfe, D. Harold-Smith and K. R. Jeffrey, Mol. Cryst. Liq. Cryst., 36 (1976) 1.

115 G. J. Essenmacher, Diss. Abstr. Int. B, 37 (1977) 3401.

116 A. I. Bruk, N. T. Karabanov, M. B. Nedosnivina and D. A. Vyakhirev, Zh. Anal. Khim., 32 (1977) 1380.

117 F. J. Karol (Union Carbide Corp.) US Pat., 4015059, 1977, Mar. 29; Chem. Abstr., 87 (1977) 6662.

118 Yu. A. Aleksandrov, L. M. Dyagileva and E. I. Tsyganova, Zh. Obshch. Khim., 47 (1977) 1554.

119 M. El Borai, R. Guilard, P. Fournari, Y. Dusausoy and J. Protas, Bull. Soc. Chim. Fr., (1977) 75.

120 M. Djazayeri, C. G. Kreiter, H. M. Kurz, M. Lang and S. Oezkar, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 1238.

121 C. G. Kreiter and S. Oezkar, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 32B (1977) 408.

122 G. I. Magomedov, A. I. Gusev, A. S. Frenkel, V. G. Syrkin, L. I. Chaplina and S. N. Gurkova; Koord. Khim. 2 (1976) 257.

123 B. Kanellakopulos, D. Noethe, K. Weidenhammer, H. Wien and M. L. Ziegler, Angew. Chem., 89 (1977) 271.

124 M. Bochmann, M. Green, H. P. Kirsch and F. G. A. Stone, J. Chem. Soc., Dalton Trans., (1977) 714.

125 R. Bowerbank, M. Green, H. P. Kirsch, A. Mortreux, L. E. Smart and F. G. A. Stone, J. Chem. Soc., Chem. Commun., (1977) 245.

126 E. F. Ashworth, J. C. Green, M. L. H. Green, J. Knight, R. B. A. Pardy and N. J. Wainwright, J. Chem. Soc., Dalton Trans., (1977) 1693.

127 M. Green, H. P. Kirsch, F. G. A. Stone and A. J. Welch, J. Chem. Soc., Dalton Trans., (1977) 1755.

128 E. Colomer, R. Corriu and A. Vioux, J. Chem. Res. S (Synopses), (1977) 168.

129 M. B. Freeman, L. G. Sneddon and J. C. Huffman, J. Amer. Chem. Soc., 99 (1977) 5194.

130 C.-K. Chu, Diss. Abstr. Int. B, 37 (1977) 760.

131 W. A. Herrmann and M. Huber, J. Organometal. Chem., 140 (1977) 55.

132 V. V. Korol'kov, L. M. Epshtein, E. V. Shumilina and T. P. Tolstaya, Vestn. Mosk. Univ., Ser. 2: Khim., 18 (1977) 98; Chem. Abstr., 87 (1977) 85116.

133 E. A. Chernyshev, A. S. Dmitriev, N. M. Zharkova, Yu. K. Molokanov and O. N. Fursa, Khim. Prom-st. (Moscow), (1977) 498.

134 G. Huttner, H. D. Mueller, P. Friedrich and U. Koelle, Chem. Ber., 110 (1977) 1254.

135 F. Mathey and J.-P. Lampin, J. Organometal. Chem., 128 (1977) 297.

136 W. A. Herrmann, B. Reiter and M. Huber, J. Organometal. Chem., 139 (1977) C4.

137 P. Bachmann, K. R. Repp and H. Singer, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 32B (1977) 471.

138 P. M. Treichel and J. W. Johnson, Inorg. Chem., 16 (1977) 749.

139 J. A. D. Jeffreys and C. Metters, J. Chem. Soc., Dalton Trans., (1977) 1624.

140 M. R. Churchill, R. A. Lashewycz and F. J. Rotella, Inorg. Chem., 16 (1977) 265.

141 P. Friedrich, G. Besl, E. O. Fischer and G. Huttner, J. Organometal. Chem., 139 (1977) C68.

142 G. G. Aleksandrov, A. B. Antonova, N. E. Kolobova and Yu. T. Struchkov, Koord. Khim., 2 (1976) 1561; Chem. Abstr 86 (1977) 63949.

143 P. Hoffmann, Angew. Chem., 89 (1977) 551.

144 P. J. Giordano and M. S. Wrighton, Inorg. Chem., 16 (1977) 160.

145 N. J. Gogan and C.-K. Chu, J. Organometal. Chem., 132 (1977) 103.

146 C. L. Khetrapal, A. C. Kunwar and A. Saupe, Mol. Cryst. Liq. Cryst., 35 (1976) 215.

147 M. Herberhold, M. Suess-Fink and C. G. Kreiter, Angew. Chem., 89 (1977) 191.

148 M. Herberhold and M. Suess-Fink, Angew. Chem., 89 (1977) 192.

149 C. Sergheraert, P. Marcincal and E. Cuingnet, J. Organometal. Chem., 120 (1976) 329.

150 C. Sergheraert, P. Marcincal and E. Cuingnet, J. Organometal. Chem., 139 (1977) 283.

151 A. N. Nesmeyanov, V. V. Korol'kov, E. V. Bryukhova, S. I. Kuznetsov, T. P. Tolstaya and G. K. Semin, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1099.

152 N. G. Connelly and M. D. Kitchen, J. Chem. Soc., Dalton Trans., (1977) 931.

153 M. Le Plouzennec and R. Dabard, J. Organometal. Chem., 133 (1977) 359.

154 H. Brunner and W. Steger, Bull. Soc. Chim. Belg., 85 (1976) 883.

155 L. P. Asatiani and I. M. Gverdtsiteli, Soobshch. Akad. Nauk Gruz. SSR, 87 (1977) 369.

156 A. N. Nesmeyanov, L. M. Korneva and M. I. Rybinskaya, Koord. Khim., 3 (1977) 1394.

157 A. G. Ginzburg, V. N. Setkina, D. N. Kursanov and Sh. G. Kasumov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 2398.

158 R. G. Sutherland and A. K. V. Unni, J. Chem. Soc., Perkin Trans., 2, (1977) 703.

159 W. Ruf, T. Renk and W. Siebert, Z. Naturforsch., B, Anorg. Chem., Org. Chem., 31B (1976) 1028.

160 A. N. Nesmeyanov, N. E. Kolobova, Z. P. Valueva, M. Ya. Solodova and K. N. Anisimov, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1138.

161 A. N. Nesmeyanov, E. G. Perevalova, E. V. Shumilina and L. I. Leont'eva, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2380.

162 E. O. Fischer, V. N. Postnov and F. R. Kreissl, J. Organometal. Chem., 127 (1977) C19.

163 A. N. Nesmeyanov, E. G. Perevalova, L. I. Leont'eva and E. V. Shumilina, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1142.

164 V. I. Sokolov, G. Z. Suleimanov, V. V. Bashilov, T. Kh. Kurbanov and I. A. Amiraslanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1894.

165 G. Z. Suleimanov, T. Kh. Kurbanov, O. A. Reutov and M. M. Mamedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 967.

166 N. Autissier, P. Dumas, J. Brosseau and A. Loireau, Toxicology, 7 (1977) 115.

167 N. Autissier, B. Gautheron, P. Dumas, J. Brosseau and A. Loireau, Toxicology, 8 (1977) 125.

168 V. A. Nefedov and V. V. Titov, USSR Pat. 542970, 1977 Jan. 15; Chem. Abstr., 86 (1977) 113741.

169 K. Keszthelyi, F. Tatrai and E. Vamos, Period. Polytech., Chem. Eng., 21 (1977) 79.

170 E. D. Mersov, I. M. Gol'dberg, E. I. Borzenko, M. S. Lashchaver and A. A. Leonovich (Scientific-Industrial Enterprises of the Wood Tile Industry), USSR Pat. 546472, 1977, Feb. 15; Chem. Abstr., 86 (1977) 157335.

171 E. D. Mersov, E. I. Borzenko and N. G. Maksimova (Scientific-Industrial Enterprises of the Wood Tile Industry), USSR Pat. 537844, 1976 Dec. 5; Chem. Abstr., 86 (1977) 92203.

172 V. G. Chalabov, O. A. Gabrielyan and A. M. Pogosyan, Nauchn. Soobshch. - Nauchno - Issled. Proektn. Inst.. Tsvetn. Metall. Armniprotsvetmet (1975) 45, Chem. Abstr., 87 (1977) 87440.

173 I. B. Benson, S. A. R. Knox, R. F. D. Stansfield and P. Woodward, J. Chem. Soc., Chem. Commun., (1977) 404.

174 M. Giffard, E. Gentric, D. Touchard and P. Dixneuf, J. Organometal. Chem., 129 (1977) 371.

175 F. Edelmann and U. Behrens, J. Organometal. Chem., 128 (1977) 131.

176 G. G. Aleksandrov, A. B. Antonova, N. E. Kolobova and Yu. T. Struchkov, Koord. Khim., 2 (1976) 1684.

177 F. R. Kreissl and P. Friedrich, Angew. Chem., 89 (1977) 553.

178 E. O. Fischer, E. W. Meineke and F. R. Kreissl, Chem. Ber., 110 (1977) 1140.

179 A. B. Antonova, N. E. Kolobova, P. V. Petrovsky, B. V. Lokshin and N. S. Obezyuk, J. Organometal. Chem., 137 (1977) 55.

180 F. R. Kreissl, K. Eberl and P. Stueckler, Angew. Chem., 89 (1977) 657.

181 N. E. Kolobova, A. B. Antonova, O. M. Khitrova, M. Yu. Antipin and Yu. T. Struchkov, J. Organometal. Chem., 137 (1977) 69.

182 K. H. Dotz and I. Pruskil, J. Organometal. Chem., 132 (1977) 115.

183 P. M. Treichel and H. J. Mueh, Inorg. Chim. Acta, 22 (1977) 265.

184 H. J. Mueh, U.S. NTIS, AD Rep. 1976, AD-A031753, 195 pp; Gov. Rep. Announce. Index (U.S.) 77 (1977) 94.

185 D. Sellmann and E. Kleinschmidt, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 32B (1977) 795.

186 D. Sellmann and K. Joedden, Angew. Chem., 89 (1977) 480.

187 M. Le Plouzennec, F. Le Moigne and R. Dabard, J. Organometal. Chem., 132 (1977) 409.

188 J. Von Seyerl, D. Neugebauer and G. Huttner, Angew. Chem., 89 (1977) 896.

189 H. Werner and B. Juthani, J. Organometal. Chem., 129 (1977) C39.

190 B. V. Lokshin, E. B. Nazarova and A. G. Ginsburg, J. Organometal. Chem., 129 (1977) 379.

191 T. C. Flood, E. Rosenberg and A. Sarhangi, J. Amer. Chem. Soc., 99 (1977) 4334.

192 A. N. Nesmeyanov, E. G. Perevalova, L. I. Leont'eva and E. V. Shumilina, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1156.

193 K. Leonard and H. Werner, Angew. Chem., 89 (1977) 656.

194 H. Brunner and W. Steger, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 1493.

195 O. A. Reutov, V. I. Sokolov, G. Z. Suleimanov, V. V. Bashilov and I. A. Amiraslanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2147.

196 U. Richter and H. Vahrenkamp, J. Chem. Res. S (Synopses) (1977) 156.

197 N. I. Pyshnograeva, V. N. Setkina, V. G. Andrianov, Yu. T. Struchkov and D. N. Kursanov, J. Organometal. Chem., 128 (1977) 381.

198 I. S. Butler, N. J. Coville and D. Cozak, J. Organometal. Chem., 133 (1977) 59.

199 A. Effraty, R. Arneri and W. A. Ruda, Inorg. Chem., 16 (1977) 3124.

200 I. S. Butler, D. Cozak and S. R. Stobart, Inorg. Chem., 16 (1977) 1779.

201 J. C. T. R. Burckett-St. Laurent, M. R. Caira, R. B. English R. J. Haines and L. R. Nassimbeni, J. Chem. Soc., Dalton Trans., (1977) 1077.

202 A. G. Ginzburg, N. G. Bokyi, A. I. Yanovsky, Yu. T. Struchkov, V. N. Setkina and D. N. Kursanov, J. Organometal. Chem., 136 (1977) 45.

203 F. Mathey, Tetrahedron Lett., (1976) 4155.

204 G. E. Herberich and E. Bauer, Chem. Ber., 110 (1977) 1167.

205 G. A. Tolstikov, M. S. Miftakhov, Yu. B. Monakov and S. I. Lomakina, Zh. Obshch. Khim., 46 (1976) 2630.

206 B. F. G. Johnson, J. Lewis, D. G. Parker and S. R. Postle, J. Chem. Soc., Dalton Trans., (1977) 794.

207 H. Behrens, M. Moll, W. Popp and P. Wuerstl, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 32B (1977) 1227.

208 S. Ruh and W. Von Philipsborn, J. Organometal. Chem., 127 (1977) C59.

209 U. Steiner, H. J. Hansen, K. Bachmann and W. Von Philipsborn, Helv. Chim. Acta, 60 (1977) 643.

210 U. Steiner and H. J. Hansen, Helv. Chim. Acta, 60 (1977) 191.

211 T. Boschi, P. Vogel and R. Roulet, J. Organometal. Chem., 133 (1977) C36.

212 T. Boschi, P. Narbel, P. Vogel and R. Roulet, J. Organometal. Chem., 133 (1977) C39.

213 P. Diehl, A. C. Kunwar and H. Zimmermann, J. Organometal. Chem., 135 (1977) 205.

214 A. J. Pearson, Aust. J. Chem., 30 (1977) 407.

215 A. J. Pearson, Aust. J. Chem., 29 (1976) 1679.

216 D. G. Gresham, C. P. Lillya, P. C. Uden and F. H. Walters, J. Organometal. Chem., 142 (1977) 123.

217 T. G. Bonner, K. A. Holder, P. Powell and E. Styles, J. Organometal. Chem., 131 (1977) 105.

218 G. Bellachioma and G. Cardaci, J. Chem. Soc., Dalton Trans., (1977) 2181.

219 G. Cardaci and G. Bellachioma, Inorg. Chem., 16 (1977) 3099.

220 H. Le Bozec, P. Dixneuf, N. J. Taylor and A. J. Carty, J. Organometal. Chem., 135 (1977) C29.

221 M. A. De Paoli, H.-W.Fruhauf, F.-W. Grevels, E. A. Koerner Von Gustorf and W. Riemer, J. Organometal. Chem., 136 (1977) 219.

222 M. Bottrill, R. Davies, R. Goddard, M. Green, R. P. Hughes, B. Lewis and P. Woodward, J. Chem. Soc., Dalton Trans., (1977) 1252.

223 R. S. Sapienza, Diss. Abstr. Int. B, 37 (1977) 3950.

224 J. W. Koepke, W. L. Jolly, G. M. Bancroft, P. A. Malmquist and K. Siegbahn, Inorg. Chem., 16 (1977) 2659.

225 E. E. Nunn, Aust. J. Chem., 29 (1976) 2549.

226 I. G. Dinulescu, E. G. Georgescu and M. Avram, J. Organometal. Chem., 127 (1977) 193.

227 F. I. Carroll, H. H. Seltzman and F. M. Hauser, Tetrahedron Lett., (1976) 4237.

228 A. Bond, M. Bottrill, M. Green and A. J. Welch, J. Chem. Soc., Dalton Trans., (1977) 2372.

229 J. T. Bamberg and R. G. Bergman, J. Amer. Chem. Soc., 99 (1977) 3173.

230 P. L. Pruitt, E. R. Biehl and P. C. Reeves, J. Chem. Soc., Perkin Trans. 2, (1977) 907.

231 K. Bachmann and W. Von Philipsborn, Org. Magn. Reson., 8 (1976) 648.

232 W. Stallings and J. Donohue, J. Organometal. Chem., 139 (1977) 143.

233 A. Efraty, S. S. Sandhu, R. Bystrek and D. Z. Denney, Inorg. Chem., 16 (1977) 2522.

234 N. J. Grice, Diss. Abstr. Int. B, 38 (1977) 2181.

235 R. H. Grubbs and T. A. Pancoast, J. Amer. Chem. Soc., 99 (1977) 2382.

236 F. A. Kaplan and B. W. Roberts, J. Amer. Chem. Soc., 99 (1977) 518.

237 T. A. Pancoast, Diss. Abstr. Int. B, 38 (1977) 2187.

238 L. A. Paquette and L. M. Leichter, Org. Photochem. Synth., 2 (1976) 52.

239 P. L. Pruitt, E. R. Biehl and P. C. Reeves, J. Organometal. Chem., 134 (1977) 37.

240 M. B. Stringer and D. Wege, Tetrahedron Lett., (1977) 65.

241 F. A. Kaplan and B. W. Roberts, J. Amer. Chem. Soc., 99 (1977) 513.

242 Md. G. Ahmed, P. W. Hickmott and M. Cais, J. Chem. Soc., Dalton Trans., (1977) 1557.

243 R. W. Ashworth and G. A. Berchtold, J. Amer. Chem. Soc., 99 (1977) 5200.

244 V. I. Ivanov, M. Slupczynski and F. S. Bayauova, Issled. v Obl. Neftekhimii, (1970) 32; Chem. Abstr., 87 (1977) 6152.

245 G. R. John, C. A. Mansfield and L. A. P. Kane-Maguire, J. Chem. Soc., Dalton Trans., (1977) 574.

246 B. F. G. Johnson, J. Lewis and D. G. Parker, J. Organometal. Chem., 141 (1977) 319.

247 A. J. Pearson, J. Chem. Soc., Chem. Commun., (1977) 339.

248 R. Aumann, Chem. Ber., 110 (1977) 1432.

249 M. Airoldi, G. Deganello and J. Kozarich, Inorg. Chim. Acta, 20 (1976) L5.

250 H. Olsen, Acta Chem. Scand. Ser. B, B31 (1977) 635.

251 W. Grimme and E. Schneider, Angew. Chem., 89 (1977) 754.

252 P. Hubener and E. Weiss, J. Organometal. Chem., 129 (1977) 105.

253 R. Victor, V. Usieli and S. Sarel, J. Organometal. Chem., 129 (1977) 387.

254 T. Chivers and P. L. Timms, Can. J. Chem., 55 (1977) 3509.

255 G. E. Herberich, J. Hengesbach, U. Koelle and W. Oschmann, Angew. Chem., 89 (1977) 43.

256 P. Jutzi and A. Karl, J. Organometal. Chem., 128 (1977) 57.

257 G. E. Herberich, E. Bauer, J. Hengesbach, U. Koelle, G. Huttner and H. Lorenz, Chem. Ber., 110 (1977) 760.

258 R. P. Hughes, J. Organometal. Chem., 141 (1977) C29.

259 B. E. Mann, J. Organometal. Chem., 141 (1977) C33.

260 K. Bachmann, W. Von Philipsborn, C. Amith and D. Ginsburg, Helv. Chim. Acta, 60 (1977) 400.

261 A. J. Birch, P. W. Westerman and A. J. Pearson, Aust. J. Chem., 29 (1976) 1671.

262 J. R. Blackborow, R. H. Grubbs, K. Hildenbrand, E. A. Koerner von Gustorf, A. Miyashita and A. Scrivanti, J. Chem. Soc., Dalton Trans., (1977) 2205.

263 G. Deganello, L. K. K. Li Shing Man and J. Takats, J. Organometal. Chem., 132 (1977) 265.

264 J. Calleja, R. Davis and I. A. O. Ojo, Org. Mass Spectrom., 12 (1977) 109.

265 E. Sappa, Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat., 109 (1975) 623; Chem. Abstr., 86 (1977) 54617.

266 G. Le Borgne and D. Grandjean, Acta Crystallogr., Sect. B, B33 (1977) 344.

267 F. A. Cotton, B. E. Hanson, J. R. Kolb, P. Lahuerta, G. G. Stanley, B. R. Stults and A. J. White, J. Amer. Chem. Soc., 99 (1977) 3673.

268 F. H. Herbstein and M. G. Reisner, Acta Crystallogr., Sect. B, B33 (1977) 3304.

269 K. Hoffmann and E. Weiss, J. Organometal. Chem., 128 (1977) 237.

270 K. Hoffmann and E. Weiss, J. Organometal. Chem., 128 (1977) 389.

271 J. A. D. Jeffreys and C. Metters, J. Chem. Soc., Dalton Trans., (1977) 729.

272 A. A. Ioganson, A. M. Sladkov and L. D. Lezhava, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2391.

273 N. S. Nametkin, V. D. Tyurin, M. Slupczynski, V. I. Ivanov and A. I. Nekhaev, Rocz. Chem., 50 (1976) 1499.

274 B. F. G. Johnson, J. Lewis and D. G. Parker, J. Organometal. Chem., 127 (1977) C37.

275 A. L. Burrows, B. F. G. Johnson, J. Lewis and D. G. Parker, J. Organometal. Chem., 127 (1977) C22.

276 H. Behrens, M. Moll and P. Wuerstl, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 1017.

277 A. J. Pearson, Aust. J. Chem., 30 (1977) 345.

278 D. A. Brown and S. K. Chawla, Inorg. Chim. Acta, 24 (1977) 71.

279 R. Goddard and P. Woodward, J. Chem. Soc., Dalton Trans., (1977) 1161.

280 A. Eisenstadt, Tetrahedron Lett., (1976) 3543.

281 M. Brookhart, K. J. Karel and L. E. Nance, J. Organometal. Chem., 140 (1977) 203.

282 D. Cunningham, P. McArdle, H. Sherlock, B. F. G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1977) 2340.

283 Z. Goldschmidt and Y. Bakal, Tetrahedron Lett., (1977) 955.

284 M. Green, S. M. Heathcock, T. W. Turney and D. M. P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 204.

285 H. Behrens, K. Geibel, R. Kellner, H. Knoechel, M. Moll and E. Sepp, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 1021.

286 M. S. Brookhart, C. P. Lewis and A. Eisenstadt, J. Organometal. Chem., 127 (1977) C14.

287 C. P. Lewis, Diss. Abstr. Int. B, 38 (1977) 692.

288 M. Bonadeo, C. De Micheli and R. Gandolfi, J. Chem. Soc., Perkin Trans., 1, (1977) 939.

289 G. Deganello and T. Boschi, Chim. Ind. (Milan), 58 (1976) 654.

290 P. Pertici, G. P. Simonelli, G. Vitulli, G. Deganello, P. L. Sandrini and A. Mantovani, J. Chem. Soc., Chem. Commun., (1977) 132.

291 N. El. Murr, M. Riveccie, E. Laviron and G. Deganello, Tetrahedron Lett., (1976) 3339.

292 G. A. Olah, G. Liang and Yu. Simon, J. Org. Chem., 42 (1977) 4262.

293 A. D. Charles, P. Diversi, B. F. G. Johnson, K. D. Karlin, J. Lewis, A. V. Rivera and G. M. Sheldrick, J. Organometal. Chem., 128 (1977) C31.

294 C. R. Graham, G. Scholes and M. Brookhart, J. Amer. Chem. Soc., 99 (1977) 1180.

295 C. R. Graham, Diss. Abstr. Int. B, 38 (1977) 606.

296 J. F. Helling and W. A. Hendrickson, J. Organometal. Chem., 141 (1977) 99.

297 P. H. Hemberger and R. C. Dunbar, Inorg. Chem., 16 (1977) 1246.

298 A. N. Nesmeyanov, M. V. Tolstaya, M. I. Rybinskaya, G. B. Shul'pin, N. G. Bokii, A. S. Batsanov and Yu. T. Struchkov, J. Organometal. Chem., 142 (1977) 89.

299 J. W. Johnson and P. M. Treichel, J. Amer. Chem. Soc., 99 (1977) 1427.

300 C. Moinet, E. Roman and D. Astruc, J. Organometal. Chem., 128 (1977) C45.

301 A. N. Nesmeyanov, N. A. Vol'kenau, V. A. Petrakova and U. S. Kolesov, Dokl. Akad. Nauk SSSR, 235 (1977) 366.

302 A. N. Nesmeyanov, N. A. Vol'kenau and V. A. Petrakova, J. Organometal. Chem., 136 (1977) 363.

303 O. Traverso, C. Chiorboli, U. Mazzi and G. L. Zucchini, Gazz. Chim. Ital., 107 (1977) 181.

304 A. P. Chapple, J. P. Vikesland and F. Wilkinson, Chem. Phys. Lett., 50 (1977) 81.

305 J. Sandstrom and J. Seita, Acta Chem. Scand., Ser. B B31 (1977) 86.

306 J. P. Vikesland and F. Wilkinson, J. Chem. Soc., Faraday Trans. 2, 73 (1977) 1082.

307 M. Wenzel, E. Nipper and W. Klose, J. Nucl. Med., 18 (1977) 367.

308 M. Wenzel and W. Klose, Klin. Wochenschr., 55 (1977) 559.

309 M. Wenzel, R. Herken and W. Klose, Z. Naturforsch., C: Biosci., 32C (1977) 473.

310 A. J. Taylor and M. Wenzel, Naturwissenschaften, 64 (1977) 273.

311 A. Clearfield, R. Gopal, M. D. Rausch, E. F. Tokas, F. A. Higbie and I. Bernal, J. Organometal. Chem., 135 (1977) 229.

312 W.-S. Lee and H. H. Brintzinger, J. Organometal. Chem., 127 (1977) 93.

313 K. Yasufuku and H. Yamazaki, J. Organometal. Chem., 127 (1977) 197.

314 P. E. Riley and R. E. Davis, J. Organometal. Chem., 137 (1977) 91.

315 H. van Willigen, W. E. Geiger and M. D. Rausch, Inorg. Chem., 16 (1977) 581.

316 D. Seyferth and S. C. Vick, J. Organometal. Chem., 139 (1977) 209.

317 A. N. Nesmeyanov, R. B. Materikova, I. R. Lyatifov, T. Kh. Kurbanov, E. V. Leonova and N. S. Kochetkova, J. Organometal. Chem., 136 (1977) C55.

318 A. N. Nesmeyanov, E. V. Leonova, E. I. Fedin, N. S. Kochetkova, P. V. Petrovskii and A. I. Lutsenko, Dokl. Akad. Nauk SSSR, 237 (1977) 143.

319 E. W. Neuse and L. Bednarik, Synthesis, (1977) 480.

320 N. El Murr and E. Laviron, Can. J. Chem., 54 (1976) 3350.

321 N. El Murr and E. Laviron, Can. J. Chem., 54 (1976) 3357.

322 K. Jonas, R. Mynott, C. Krueger, J. C. Sekutowski and Y.-H. Tsay, Angew. Chem., 88 (1976) 808.

323 P. Hardt (Lonza Ltd.) Ger. Pat., 2615309, 1977, Mar. 24; Chem. Abstr., 87 (1977) 23068.

324 L. M. Dyagileva, E. I. Tsyganova and O. N. Druzhkov, Zh. Obshch. Khim., 47 (1977) 2397.

325 T. Otsu and Y.-U. Mun, J. Macromol. Sci., Chem., A11 (1977) 1783.

326 E. W. Neuse, G. Horlbeck, H. W. Siesler and K. Yannakou, Polymer, 17 (1976) 423.

327 G. E. Herberich and W. Koch, Chem. Ber., 110 (1977) 816.

328 W. Seibert and M. Bochmann, Angew. Chem., 89 (1977) 895.

329 D. Seyferth, C. S. Eschbach, G. H. Williams and P. L. K. Hung, J. Organometal. Chem., 134 (1977) 67.

330 D. Seyferth and C. L. Nivert, J. Amer. Chem. Soc., 99 (1977) 5209.

331 H. J. Haustein and K. E. Schwarzhans, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 1719.

332 G. Varadi and G. Palyi, Inorg. Chim. Acta, 20 (1976) L33.

333 A. M. Bond, B. M. Peake, B. H. Robinson, J. Simpson and D. J. Watson, Inorg. Chem., 16 (1977) 410.

334 B. M. Peake, B. H. Robinson, J. Simpson and D. J. Watson, Inorg. Chem., 16 (1977) 405.

335 G. Varadi and G. Palyi, Magy. Kem. Foly., 83 (1977) 323.

336 D. Seyferth, G. H. Williams and C. L. Nivert, Inorg. Chem., 16 (1977) 758.

337 D. Seyferth, C. S. Eschbach and M. O. Nestle, Synth. React. Inorg. Met.-Org. Chem., 7 (1977) 269.

338 T. W. Matheson and B. R. Penfold, Acta Crystallogr., Sect. B, B33 (1977) 1980.

339 R. C. Ryan, C. U. Pittman and J. P. O'Connor, J. Amer. Chem. Soc., 99 (1977) 1987.

340 G. A. Catton, G. F. C. Jones, M. J. Mays and J. A. S. Howell, Inorg. Chim. Acta, 20 (1976) L41.

341 J. C. Smart and B. L. Pinsky, J. Amer. Chem. Soc., 99 (1977) 956.

342 K. Yokoyama, S. Kobinata and S. Maeda, Bull. Chem. Soc., Jpn., 49 (1976) 2182.

343 W. T. Scroggins, Diss. Abstr. Int. B, 37 (1976) 1250.

344 R. J. Restivo, G. Ferguson, T. W. Ng and A. J. Carty, Inorg. Chem., 16 (1977) 172.

345 O. N. Druzhkov, Yu. A. Andrianov and L. M. Dyagileva, Zh. Obshch. Khim., 47 (1977) 1836.

346 J. D. L. Holloway, W. L. Bowden and W. E. Geiger, J. Amer. Chem. Soc., 99 (1977) 7089.

347 L. M. Dyagileva, O. N. Druzhkov and Yu. A. Andrianov, Zh. Obshch. Khim., 47 (1977) 82.

348 H. Brunner and W. Pieronczyk. Bull. Soc. Chim. Belg., 86 (1977) 725.

349 H. Werner and T. N. Khac, Angew. Chem., 89 (1977) 332.

350 V. O. Reikhsfel'd, T. P. Khvatova, M. I. Astrakhanov and G. I. Saenko, Zh. Obshch. Khim., 47 (1977) 726.

351 J. Siebert and M. Bochmann, Angew. Chem., 89 (1977) 483.

352 A. N. Williamson, Diss. Abstr. Int. B, 37 (1977) 5075.

353 A. B. Blake, D. F. Ewing, J. E. Hamlin and J. M. Lockyer, J. Chem. Soc., Dalton Trans., (1977) 1897.

354 H. Werner, B. Ulrich and A. Salzer, J. Organometal. Chem., 141 (1977) 339.

355 C. A. Harmon, D. P. Bauer, S. R. Berryhill, K. Hagiwara and A. Streitwieser, Inorg. Chem., 16 (1977) 2143.