ORGANIC REACTIONS OF SELECTED π-COMPLEXES

ANNUAL SURVEY COVERING THE YEAR 1981[*]

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1. Reviews

Jonas has reviewed the chemistry of alkali metal-transition metal π-complexes. This review contained a section on the preparation of transition metal-olefin and alkali metal-transition metal-olefin complexes from metallocenes, mainly cobaltocene and ferrocene, by reductive elimination of the cyclopentadienyl ligand [1].

Froboese has reviewed the antitumor activity of metallocenes [2]. Watts has reviewed the chemistry of η-cyclopentadienyl, η-arene and related complexes published in 1979 [3].

Deeming has presented a brief review of the recently published chemistry of π-bonded organometallics [4].

Howell has reviewed the chemistry of hydrocarbon-metal π-complexes published in 1979 [5]. The role of σ-π rearrangement of organotransition metal complexes has been reviewed in the context of organometallic catalysis [6].

2. General Results

Several decamethylmetallocenes (2.1; M = V, Cr, Co, Ni) and decamethylmetallocene cations (2.2; M = Cr, Co, Ni, n = 1; M = Ni, n = 2) have been prepared and their electronic properties studied. NMR, IR spectroscopy, magnetic susceptibility and, in some cases, X-ray crystallography have been used to show that the compounds (2.1) and cations (2.2) were D_{5d} or D_{5h} with low-spin configurations. Reversible, one-electron redox reactions have been demonstrated by cyclic voltammetry for the systems:

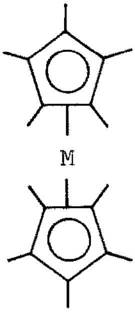
$$(\eta\text{-Me}_5\text{C}_5)_2\text{M} \longrightarrow [(\eta\text{-Me}_5\text{C}_5)_2\text{M}]^+$$

where M = Cr, Mn, Fe, Co, Ni

$$[(\eta\text{-Me}_5\text{C}_5)_2\text{Mn}]^- \longrightarrow (\eta\text{-Me}_5\text{C}_5)_2\text{Mn}$$

$$[(\eta\text{-Me}_5\text{C}_5)_2\text{Ni}]^+ \longrightarrow [(\eta\text{-Me}_5\text{C}_5)_2\text{Ni}]^{2+}$$

The decamethylmetallocenes were, in general, more easily oxidized to the corresponding cations than were the free metallocenes. ^{1}H and ^{13}C NMR and UV spectra for several decamethylmetallocenes have been recorded [7].



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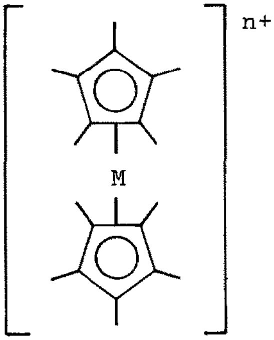

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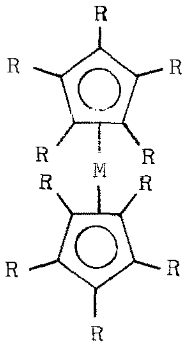
Several complexes of pentakis(methoxycarbonyl)cyclopentadiene, $HC_5(CO_2Me)_5$, have been reported. The fully-substituted metallocenes (2.3; M = Mn, Fe, Co, Ni; R = CO_2Me) were obtained by treatment of the free ligand with the appropriate metal(II) acetate. The complexes (2.3) are water soluble and are fully ionized in water. The structure of the ruthenium complex (2.4) has been determined by X-ray crystallography [8].

The frequencies and forms of the normal vibrations in symmetry coordinates have been calculated for the metallocenes $(\eta\text{-C}_5\text{H}_5)_2\text{M}$, where M = Mg, Ca, V, Cr, Mn, Fe, Ru, Os, Ni. The nature of the metal exerted only a small influence on the shape of the normal vibrations. Force constants for the vibration were calculated [9].



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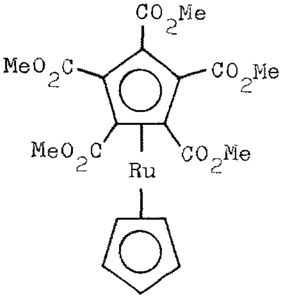


2.4

The ^{19}F NMR spectra of the 3- and 4-fluorophenyl derivatives of ferrocene, ruthenocene and osmocene were recorded. The Taft equation was used to obtain inductive substituent constants of -0.032, -0.042 and 0.062 and resonance substituent constants of -0.107, -0.097 and 0.095 respectively for the metallocenyl groups. The fluorophenyl derivatives of tricarbonyl(η-cyclopentadienyl)-manganese and -rhenium were prepared also and examined [10].

The cross polarization method has been used to obtain high-resolution solid-state ^{13}C NMR spectra of ferrocene, ruthenocene, bis(η-benzene)chromium and related sandwich compounds. The shielding tensor anisotropy reflected the character of the bonding. Motion was observed in several of the compounds and has been used to assign the shielding tensor principal directions [11].

The dynamics of ring rotation in ferrocene, nickelocene and ruthenocene have been studied by incoherent quasi-elastic neutron scattering. At temperatures above the 164°K phase transition the activation energy for ring rotation in ferrocene fell to 4.4 ± 0.5 kJ mol^{-1} (approximately half the low temperature value). At room temperature the η-cyclopentadienyl rings in nickelocene behaved the same as in ferrocene but in ruthenocene they reoriented less frequently and resembled those of ferrocene below 164 °K [12].

The proton affinities for twenty organotransition metal complexes including benchrotrene, methylcymantrene, ferrocene, ruthenocene and nickelocene have been determined in the gas phase by ion cyclotron resonance spectroscopy. The site of protonation has been determined in several cases [13].

Microsolution optical spectroscopy has been used to monitor the fate of metal atoms deposited into cryogenic solutions. The interactions of iron, cobalt, nickel and zirconium vapours with ligands such as COD and toluene were examined and reaction intermediates proposed on the basis of the optical spectra obtained [14].

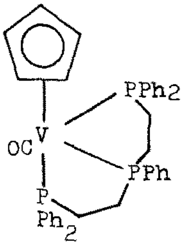
A theoretical study using INDO SCF MO calculations has been carried out in order to make comparisons between the cyclopentadienyl, borabenzene and benzene ligands in sandwich complexes of chromium, manganese and iron. Ground state differences were found within both the borabenzene series and cyclopentadienyl series of complexes and also between the two series. The differences were rationalized in terms of a simple ligand field model [15].

The Thouless instability conditions in a series of polydecker organometallic sandwich compounds have been investigated by semiempirical INDO calculations. Hartree-Fock fluctuations of the singlet, non-singlet and non-real type were found. The reasons for the various instability conditions were analyzed [16].

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

The solid state structure of the (η-cyclopentadienyl)vanadium complex (3.1) has been determined by X-ray crystallography. In solution, IR, ^{31}P and ^{51}V NMR spectroscopy showed that the molecule was fluxional down to 200 °K [17].

The photoreactions between tetracarbonyl(η-cyclopentadienyl)-vanadium and the ligands $Ph_2ECH_2EPh_2$ (E = P, As, Sb) have been investigated. The complexes (3.2 and 3.3; E = P, As, Sb) were isolated and investigated by ^{51}V NMR. The crystal and molecular



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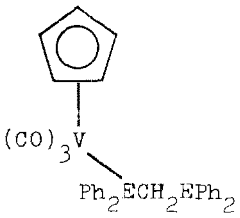

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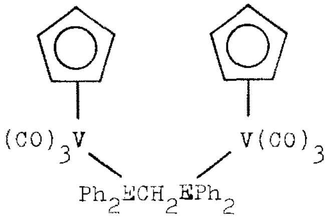
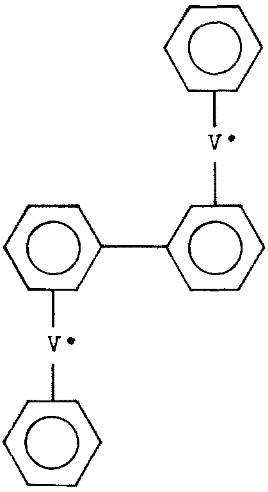


3.3

structure of $(\eta\text{-}C_5H_5)V(CO)_3As_2Ph_4$ was determined by X-ray analysis [18].

The binuclear diradical (3.4) was obtained by coupling of bis(η-benzene)vanadium, the product was characterized by ESR spectroscopy [19].

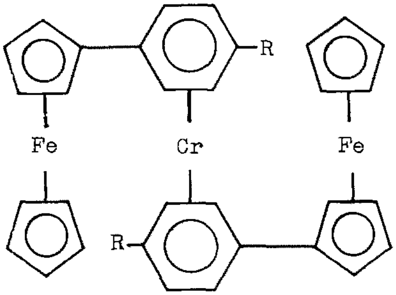


3.4

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

(i) Formation

The condensation of chromium vapour with phenyl- or p-tolylferrocene produced the bis(η-arene)chromium complexes (4.1; R = H or Me) respectively [20].



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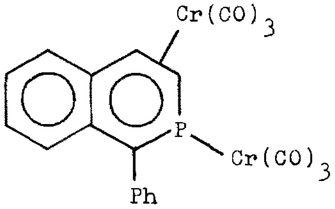


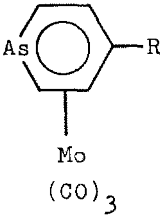
4.2

Treatment of hexacarbonylchromium with 1-phenyl isophosphinoline produced the bis(tricarbonylchromium) complex (4.2) [21].

Reaction of tricarbonyltris(methyl cyanide)metal complexes with 4-R-λ^3-arsenines and 2-aryl-4-R-λ^3-arsenines gave the corresponding tricarbonylmetal complexes (4.3; R = Ph, cyclohexyl, t-Bu, Et) and (4.4; R = Ph, cyclohexyl, t-Bu; M = Cr, Mo, W) [22]. The preparation of some oligomeric (η-arene)transition metal tricarbonyl complexes has been reported [23].

Steroidal hormones containing benzene rings, such as estradiol, estrone-3-methyl ether and estrone have been treated with chromium, molybdenum and tungsten hexacarbonyls to form the tricarbonylmetal complexes, such as the tricarbonylchromium complex (4.5). The kinetics of formation was monitored [24].

Benchrotrene and related complexes (4.6; R = H, Me, M = Cr, Mo, W) have been obtained in high yield by heating the free



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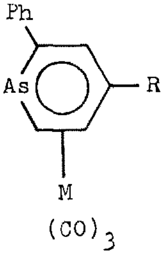

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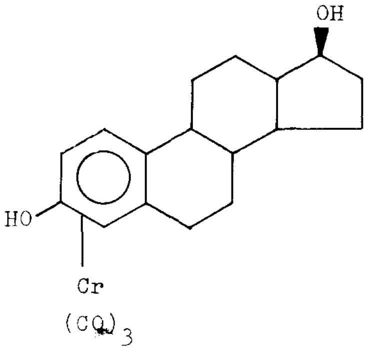

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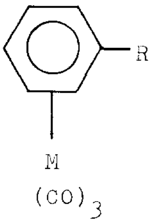
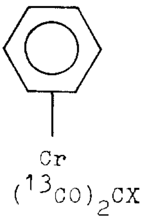


4.6

ligand with the appropriate metal hexacarbonyl at 150-170 °C in the autoclave with a pyridine, picoline or thiophene catalyst [25].

The synthesis of ^{13}CO labelled benchrotrene and benchrotrene derivatives has been reported. The multistep exchange reaction was photochemically induced and >90 atom % ^{13}C enrichment was achieved by using ^{13}CO as the reagent for replacement of the three carbonyl groups. The corresponding labelled thiocarbonyl and selenocarbonyl complexes (4.7; X = S, Se) were obtained in similar reactions [26].

The reaction of triphenylbismuth with triamminetricarbonylchromium produced the π-complexes (4.8, 4.9 and 4.10; M = Bi). Similar products (4.8, 4.9 and 4.10; M = Sb) were obtained by



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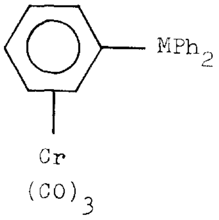

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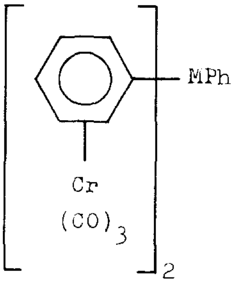

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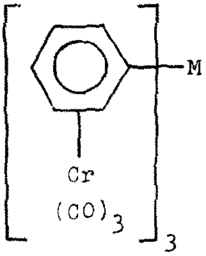
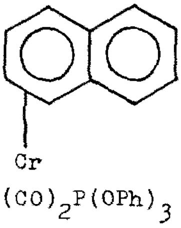


4.10

treatment of the chromium complex with triphenylantimony in the presence of boric acid [27].

4. (ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structure of the (η-naphthalene)-chromium complex (4.11) has been determined by X-ray crystallography. The molecule exhibited an octahedral arrangement about chromium and had a short Cr-P bond. Cr-naphthalene bond distances were similar to those found in the corresponding tricarbonyl complex. The structure of a related (η-phenanthrene)chromium complex was also reported [28].



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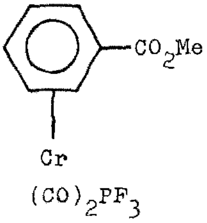
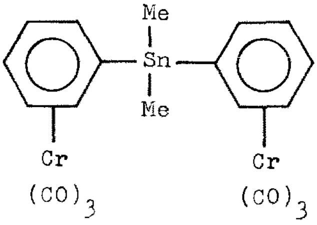


4.12

The crystal and molecular structures of hexaethylbenzene and of its tricarbonylchromium, tricarbonylmolybdenum and dicarbonyl-(triphenylphosphine)chromium complexes have been determined by X-ray analysis. The structure of the triphenylphosphine complex differed from the others in that all six of the ethyl groups were arranged such that the methyl moiety projected towards the uncomplexed side of the ring and the molecule assumed a staggered conformation [29].

The crystal and molecular structure of the dicarbonyltrifluorophosphinechromium complex (4.12) has been determined by X-ray crystallography. The chromium-phosphorus distance, 2.132 Å was the shortest found to date and suggested that the trifluorophosphine ligand was a good π-electron acceptor [30].

The structure of the tricarbonylchromium complex (4.13) has been determined by X-ray analysis. In the lattice the molecule was distorted in that one of the $Cr(CO)_3$ groups could be on either side of the phenyl ring to which it was bonded. The geometry around the tin atom was approximately tetrahedral [31].



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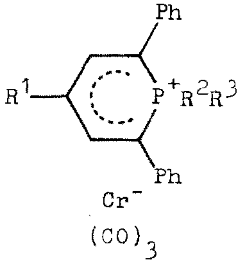
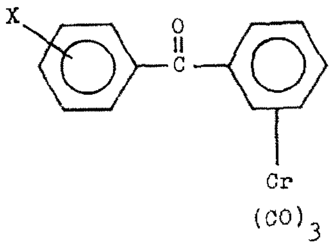


4.14

X-ray crystallography and NMR spectroscopy have provided strong evidence that the (η-phosphorin)chromium complexes (4.14; R^1 = Ph, CMe_3; R^2, R^3 = Me, Et, CMe_3, OMe, NEt_2, F) have a zwitterionic structure [32].

The benchrotrene complexes (4.15; X = *p*-Me, *o*-Me, *p*-OMe, *p*-F, *p*-Cl and 4.16; R = *o*-Me, *p*-Me) have been prepared and the IR and ^1H NMR spectra recorded and interpreted. Substituents in the uncomplexed benzene ring in complex (4.15) had little effect on the stretching frequencies of the tricarbonylchromium group. Some electron delocalization between the two arene rings was indicated by the NMR spectra [33].

^{95}Mo NMR spectra of $LMo(CO)_3$ complexes (L = η-cycloheptatriene, η-mesitylene, η-*o*, *m* and *p*-xylene, η-toluene, η-cyclopentadienyl) have been recorded and discussed. The chemical shift was related



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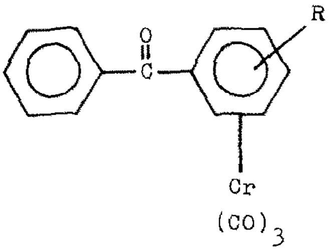

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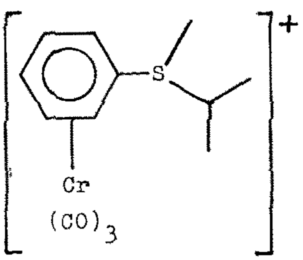
to the molybdenum-arene bond strength [34].

As part of an investigation into the origin of magnetic nonequivalence of methyl groups in iso-propylsulphonium cations, $[XSMeCHMe_2]^+$, the crystal and molecular structure of the benchrotrenesulphonium cation (4.17) has been determined by X-ray crystallography. Two alternating conformational units were characterized with the S-Me group either trans-gauche or gauche-gauche with respect to the isopropyl group. The results were used to interpret the diastereotopic NMR shifts [35].

The radical anion benchrotrene complexes (4.18; R^1 = H, o-Me, p-Me, p-OMe, p-Cl, p-F; R^2 = H; R^1 = H, R^2 = o-Me, p-Me) have been prepared by potassium reduction of the parent complexes and investigated by ESR spectroscopy. The results confirmed delocalization of unpaired electron density over the ligand system [36].



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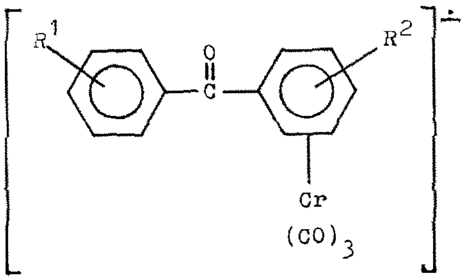

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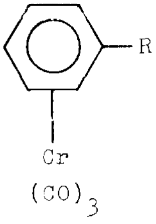

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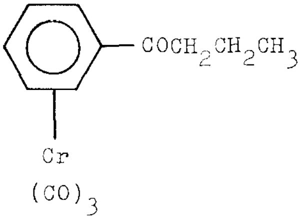

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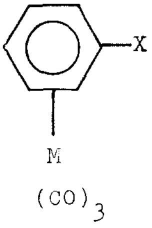
Dipole moments and molar Kerr constants at 589 nm have been determined for a number of benchrotrene complexes (4.19; R = CHO, COMe, CO_2Me, OMe, NH_2, NHMe, NMe_2). These results, together with evidence from IR spectroscopy indicated that the preferred conformations of the substituents were similar in both the complexes (4.19) and the free ligands [37].

In the mass spectrum of the chromium complex (4.20) several hydrogen transfer processes occurred and these were studied by deuterium labelling of the propyl group in the 1-, 2- or 3-position. Propylene elimination was either specific (McLafferty rearrangement) or mainly random, depending on the pressure of carbon monoxide at the decomposing ion. In another rearrangement hydrogen was transferred from the 1-position of the propyl group to the ester carbonyl carbon atom [38].

The electron impact mass spectra of four benchrotrene complexes (4.21; M = Cr, X = OMe, OBu^n, CO_2Me, CO_2Bu^n) and of the



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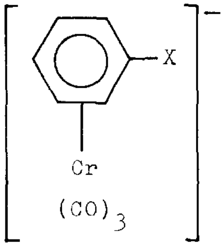

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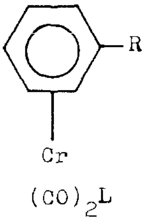


4.23

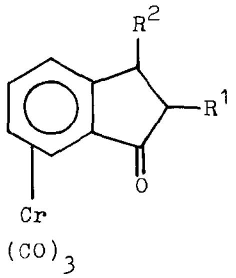
analogous tungsten complexes (4.21; M = W, X = OMe, OBu^n, CO_2Me CO_2Bu^n) have been recorded and analysed in detail to give complete fragmentation diagrams. Differences between the tungsten and chromium complexes were attributed to the stronger electrophilic character of tungsten and its tendency to attain higher oxidation states [39].

The mass spectra of negative ions formed by the dissociative electron capture (DEC) of π-complexes have been recorded and interpreted. Among the complexes examined were (η^6-benzene)-, (η^6-indene)-, (η^6-fluorene)- and (η^6-azafluorene)-tricarbonylchromium. The $[M-H]^-$ ion from (η^6-indene)tricarbonylchromium underwent a process of recoordination of the chromium atom from the benzene to the cyclopentadienyl ring [40].

Mass spectra of the benchrotrene negative ions (4.22; X = H, Cl, F, I, OMe, NMe_2) obtained by DEC have been obtained. The first maxima of the resonance of the ions $[M-CO]^-$ was shown to have a linear dependence on the Hammett σ_p constants [41].

The favoured conformations in the gas phase of several benchrotrenes such as [4.23; R = CO_2Me, $CH(CMe_3)_2$, COMe, L = CO; R = CO_2Me, L = CS] have been determined by the EHT method and compared with solid state conformations obtained by X-ray crystallography. The conformations were similar in most cases [42].

Kinetic isotope effects have been determined for the sodium borohydride and sodium borodeuteride reduction of (η-indanone)-tricarbonylchromium complexes (4.24) with substituents on carbons 2 and 3. The maximum effect $\underline{k}_H/\underline{k}_D$ = 2.46 was found when R^1 = H, R^2 = exo-Me and this corresponded to a shift of the transition



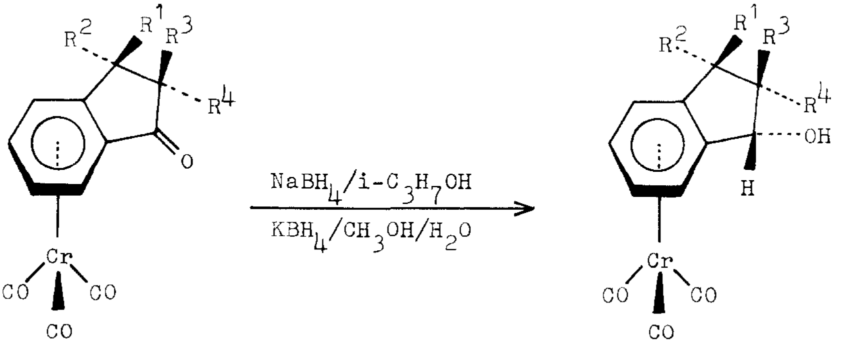
4.24

state from a late to an early position by increased steric hindrance [43].

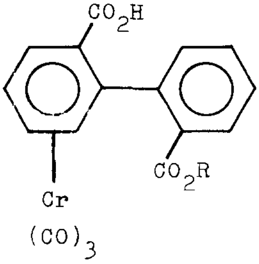
Hydrogen-deuterium exchange in the benchrotrene complexes (4.23; R = H, L = PPh_3, ferrocenylPPh_2, CO) has been studied in EtOD-EtONa and in CF_3CO_2D. Rate constants determined for exchange of the η-C_6H_6 hydrogens demonstrated that the ferrocenylPPh_2 ligand was a stronger electron donor than the PPh_3 ligand in basic media. Only a small difference in the exchange rates for the complexes (4.23; R = H, L = ferrocenylPPh_2, CO) were observed [44].

Hydrogen-deuterium exchange in the benchrotrene complexes (4.23; R = Ph, $PhCH_2$, $PhCH_2CH_2$, PhCO, PhO, L = CO, PPh_3) in CF_3CO_2D has been studied and rate constants obtained. In the complexes (4.23; L = PPh_3) the change in ring substituent had no effect on the rate of exchange, in sharp contrast to the same reaction in the free binuclear arenes. The o-, m-, and p-positions in the coordinated ligands for the complexes (4.23; L = PPh_3) had similar reactivities [45].

The reduction of endo- and exo-α- and β-alkylindanonetricarbonylchromium complexes [4.25; R^1 = Me, Et, CH(Me)$_2$, $R^2 = R^3 = R^4$ = H; R^2 = Me, Et, CH(Me)$_2$, $R^1 = R^3 = R^4$ = H; R^3 = Me, Et, CH(Me)$_2$, $R^1 = R^2 = R^4$ = H; R^4 = Me, Et, CH(Me)$_2$, $R^1 = R^2 = R^3$ = H] by sodium or potassium borohydride in iso-propanol or methanol gave only the corresponding endo-alcohols (4.26). The organic



4.25 4.26



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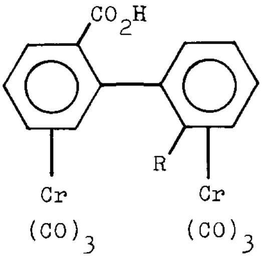

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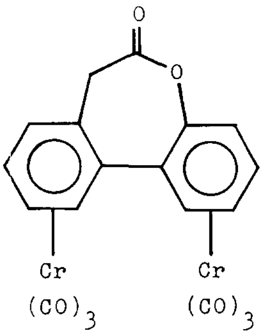
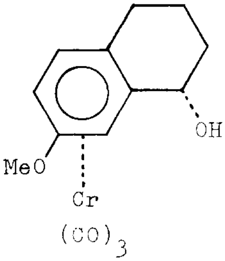


4.29

ligand was removed quantitatively from these complexes to give cis- and trans-indanols [46].

The optically active diphenic acid complexes (+)-(4.27; R = H, Me) and (-)-(4.28; R = CO_2H) have been obtained by resolution using the cinchonidinium salts although enantiomeric purities were only ≤8%. The aldehyde (4.28; R = CHO) underwent kinetic resolution with a chiral lithium aluminium hydride complex to give the aldehyde (+)-(4.28; R = CHO), the alcohol (-)-(4.28; R = CH_2OH) and the lactone (4.29). The optical yield was 33%. The CD spectra of the optically active products were obtained and used to assign the chirality by comparison with benchrotrene complexes of known absolute configuration [47].

The methoxybenchrotrene complex (4.30) underwent regiospecific lithiation at the 4-position and then electrophilic substitution with carbon dioxide to give, after demetalation and methylation the 4-substituted arene (4.31) in 91% yield. Several related reactions were reported [48].



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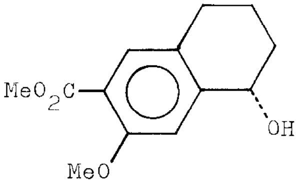
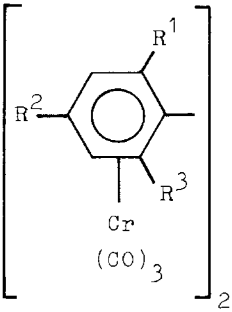


4.31

4. (iii) General Chemistry

The electrochemical oxidation of the tricarbonylchromium complexes (4.32; $R^1 = R^3 = H$, $R^2 = H$, OMe, NMe_2; $R^1 = R^3 = Me$, $R^2 = Me$, OMe, H) and (4.33; $R^1 = R^3 = Me$, $R^2 = H$, Me; $R^1 = R^3 = H$, $R^2 = SiMe_3$) gave stable cations on the cyclic voltametric time scale. Oxidation of the mono-complexes (4.33) gave stable cations while the bis-complexes (4.32) gave stable dications. The stability of the cations was increased by the introduction of electron donating groups into the 2,4 and 6 positions of the phenyl rings [49].

A series of chromium complexes containing functionalised isocyanide ligands (4.34; $R^1 = CO_2Me$, OMe, Me, Et, $CHMe_2$, CMe_3,



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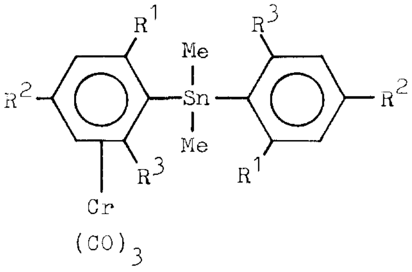

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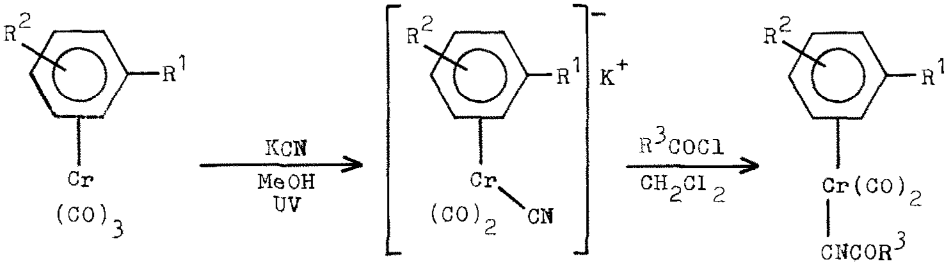
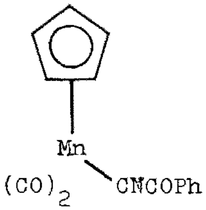


4.34

Scheme 4.1



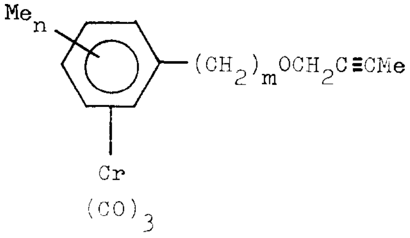
4.35

NMe_2, R^2 = *o*, *m*, *p*-H, *o*, *m*-Me, R^3 = Ph, NMe_2, OEt, SEt) has been prepared (Scheme 4.1). The manganese complex (4.35) was prepared similarly. Infrared and mass spectroscopic studies showed that the presence of a carbonyl group α to the nitrogen resulted in the ligand being a better electron acceptor than CO [50].

Ultraviolet irradiation of the tricarbonylchromium complexes [4.36; n = m = o; n = 2(2,3-Me_2), m = 1,2; n = 3(2,4,6-Me_3), m = 2,3] induced intramolecular cyclization to produce the corresponding dicarbonylchromium compounds (4.37) [51].

Irradiation of the tricarbonylchromium complexes (4.38; $R^1 = R^2 = R^3$ = H, Me; $R^1 = R^2$ = Me, R^3 = CH_2OH, CH_2CH_2OH) with CH_2=$CHCHR^4OR^5$ (where R^4 = H, CH_2CH_2Ph; R^5 = H or allyl) gave the corresponding cationic η-allylchromium complexes (4.39) [52].

UV irradiation of benchrotrene with allyl alcohol and its derivatives in the presence of hydrofluoroboric acid gave



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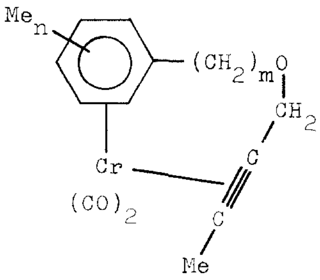
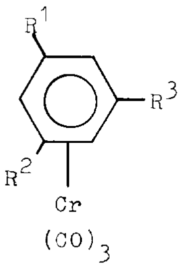


4.37

(η-arene)(η-allyl)chromium cationic complexes (4.40; R^1 = OH, H, 1,3,5-Me_3, 3,5-Me_2, CH_2OH; R^2 = H, CH_2CH_2Ph). Similar complexes were obtained by cleavage of chelate dicarbonylchromium complexes such as the benchrotrene (4.41) and by proton cleavage with simultaneous irradiation of allyl substituted benchrotrenes such as the ether (4.42). Several related reactions were reported [53].

A kinetic study of the reduction of the η-acetophenone complexes [4.23; R = COMe, L = CO, CS, $P(OMe)_3$, $P(OPh)_3$, PPh_3, PBu_3] by sodium borohydride has been carried out. The reactivity of arene ligand was controlled electronically by the $Cr(CO)_2$**L** group [54].

The rate of deprotonation of fluorene and its tricarbonylchromium complex (4.43) by potassium hydride has been determined.



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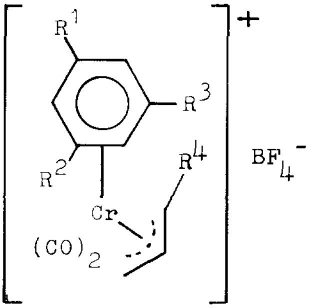

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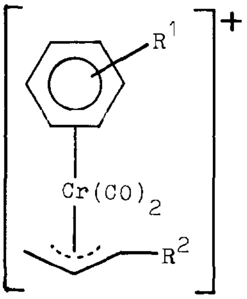

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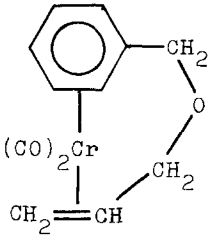

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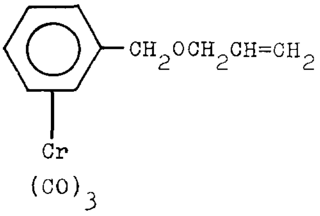
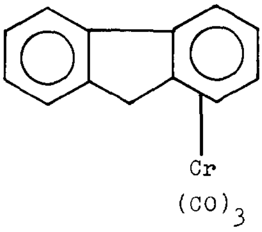


4.42

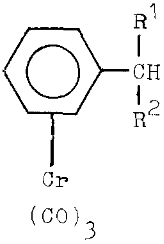
^{1}H and ^{13}C spectra showed that for the anion generated at -20 °C the $Cr(CO)_3$ group was bound to one of the benzene rings but when the anion was formed at room temperature the $Cr(CO)_3$ group was bound mainly to the cyclopentadienyl ring [55].



4.43

Treatment of the tricarbonylchromium complexes (4.44, $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = R^2 = Me$) in dimethylsulphoxide with potassium t-butoxide followed by condensation with an aldehyde R^3CHO ($R^3 = H$, Ph) produced the corresponding alcohols (4.45). The strong electron withdrawing character of the $Cr(CO)_3$ group had enhanced the reactivity of the benzylic position towards attack by the base [56].

The reaction of benchrotrenic ketones with Grignard reagents was studied. Mixtures of secondary and tertiary alcohols were



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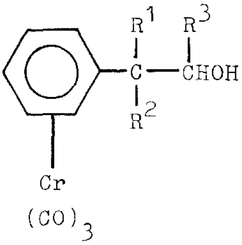

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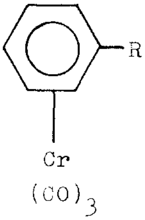
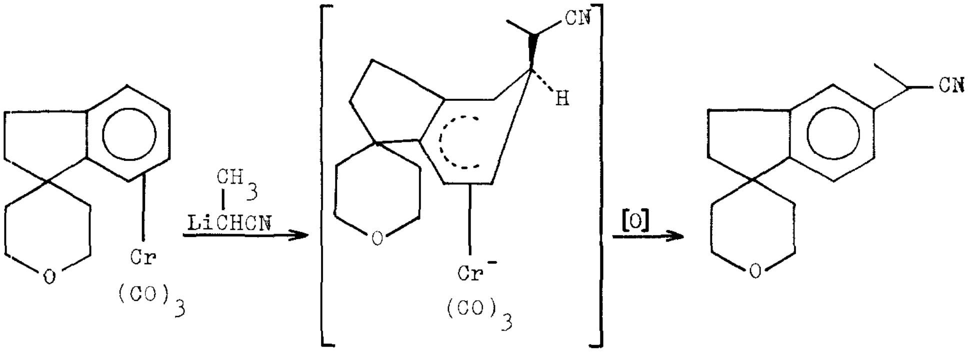


4.46

formed and a mechanism was proposed to account for the formation of the secondary alcohols. This involved participation of the metal atom in hydrogen transfer [57].

The tricarbonylchromium complexes (4.46; R = H, OMe, F, Cl) have been lithiated with n-butyllithium at low temperatures. Metallation of the substituted arene complexes occurred exclusively at the ortho-position. The lithiated intermediates were condensed with a series of electrophiles [58].

The reaction of LiCH(CH$_3$)CN with the tricarbonylchromium complex (4.47) has been investigated. The major product obtained after oxidative removal of the tricarbonylchromium group (Scheme 4.2)

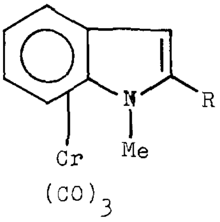


4.47

Scheme 4.2

corresponded to nucleophilic addition on an arene carbon atom which was in an eclipsed position with respect to the carbonyl group of the $Cr(CO)_3$ unit of the most stable conformer [59].

Treatment of tricarbonyl(η^6-1-methylindole)chromium with n-butyllithium-tetramethylethylenediamine followed by ethylchloroformate produced the 2-ethoxycarbonyl substituted product (4.48; R = CO_2Et) in good yield. Lithiation of the 2-substituted indole complex (4.48; R = $SiMe_3$) followed by condensation with ethylchloroformate afforded the 7-ethoxycarbonyl derivative (4.49) as the major product together with some tricarbonyl(η^6-4-ethoxycarbonyl-1-methyl-2-trimethylsilylindole)chromium [60].



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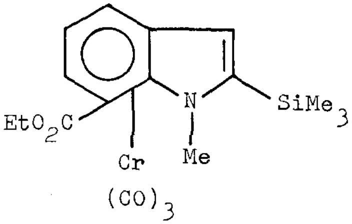
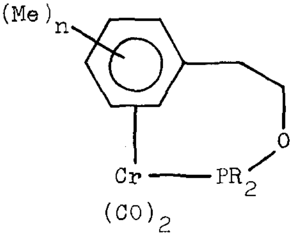


4.49

The reactions of (η-benzene)dicarbonyltriphenylphosphinechromium with aprotic acids, for example mercury(II) and tin(IV) chloride, have been investigated. Complexes were formed at the chromium atom which was the position in the molecule with the

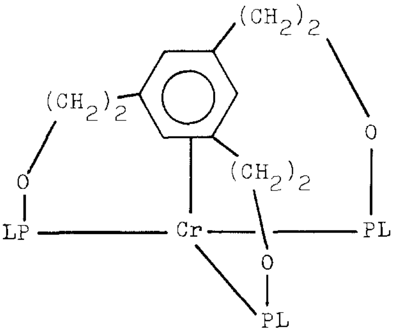


4.50

highest basicity. The IR spectra of the complexes showed high carbonyl frequencies [61].

The chromium complexes [4.50; R = Ph; n = 2 (3,5-Me_2), n = 3 (2,4,6-Me_3)] have been obtained by treatment of the corresponding complexes (4.50; R = F, PhO) with phenyllithium without any ring cleavage [62].

The chromium complexes (4.51 and 4.52; L = o-OC_6H_4O) have been prepared in good yields by the reaction of [η-1,3,5($HOCH_2CH_2)_3C_6H_3$]-$Cr(CO)_3$ or [η-1,3,5-$Me_2C_6H_3CH_2CH_2OH$]$Cr(CO)_3$ with LPCl and triethylamine followed by ultraviolet irradiation [63].



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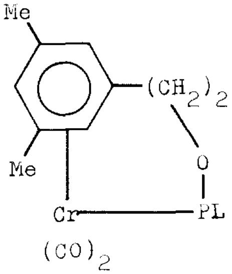
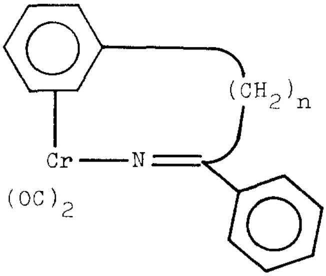


4.52

Treatment of the bridged benchrotrene complexes (4.53; n = 2, 3) with alkyllithium reagents gave the chiral amines $Ph(CH_2)_nCRPhNHPh$, where n = 2, R = Me, Bu; n = 3, R = Me [64].



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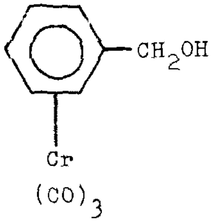
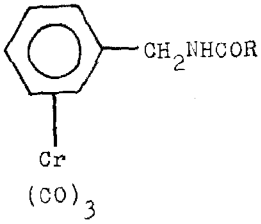


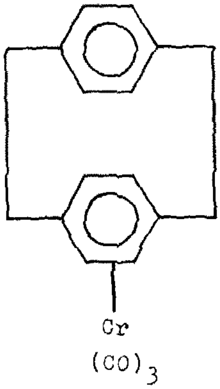


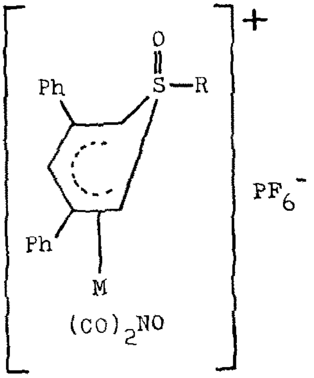
4.54

4.55

The reaction of benzylcarbenium ion with nitriles to give amides was facilitated by stabilization of the carbenium ion through complexation with the tricarbonylchromium group. Thus the (η-benzylalcohol)chromium complex (4.54) was attacked by the nitriles, RCN, where R = Me, Pr, $CH=CH_2$, CH_2Cl, Ph, $PhCH_2$, $2Me.C_6H_4$, to give the corresponding amides (4.55) [65].

The charge-transfer complex formed between tricarbonyl(η-[2.2]paracyclophane)chromium (4.56) and 1,3,5-trinitrobenzene in 1,2-dichloroethane has been investigated. It was concluded that there was direct interaction of the 1,3,5-trinitrobenzene with the chromium d orbital [66].





4.56

4.57

Benchrotrene in acetonitrile was attacked by a nitromethane solution of (NS)PF_6, obtained in situ from $N_3S_3Cl_3$ and $AgPF_6$, to form the cationic thionitrosyl complex $[Cr(NS)(NCMe)_5]^{2+}$ [67].

Tricarbonyl-chromium, molybdenum and -tungsten complexes of 1-alkyl-3,5-diphenylthiabenzene 1-oxides have been oxidized with $NO^+PF_6^-$ in dichloromethane at -78 °C to give the cationic dicarbonylnitrosyl complexes [4.57; M = Cr, Mo, W, R = $CH(CH_2Ph)_2$, $CH(SiMe_3)_2$; M = Cr, R = Me, Et, CH_2CH_2Ph, CH_2HgMe] [68, 69].

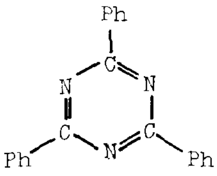
Benchrotrenes bearing one, two or three methoxy groups on the benzene ring were effective catalysts for the hydrogenation of methyl sorbate to methyl hexenoate [70].

The reaction of furan with t-butyl chloride in the presence of an (η-arene)tricarbonylmolybdenum compound as catalyst produced 2-t-butylfuran and 2,5-di-t-butylfuran. The catalyst was virtually deactivated after twelve hours and up to 150 alkylation events occurred per molybdenum atom [71].

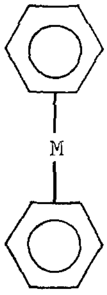
5. $(\eta\text{-}C_6H_6)_2Cr$

The reaction of benzonitrile with chromium vapour gave bis(η-benzonitrile)chromium as the major product together with some 2,4,6-triphenyltriazine (5.1), formed by cyclotrimerization of benzonitrile. In a similar reaction of bromobenzene with chromium only insignificant amounts of cationic bis(η-arene)chromium compounds were isolated [72].

The structures of bis[η-1,4-(trifluoromethyl)benzene]chromium, bis[η-1,3-(trifluoromethyl)benzene]chromium and bis[η-1-chloro-3-(trifluoromethyl)benzene]chromium have been determined by X-ray



5.1

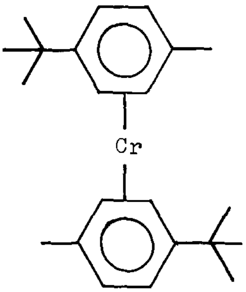


5.2

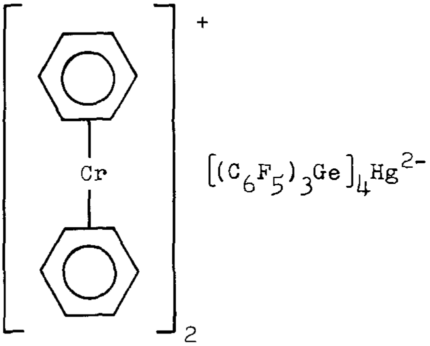
analysis. The results suggested that the CF_3 group did not behave as a strongly σ-electron-withdrawing group and that the polar effect of CF_3 was a "through space" rather than a "through the bond" effect [73].

The heats of thermal decomposition and iodination for the bis-(η-benzene) complexes (5.2; M = Mo, W) have been determined by microcalorimetry in the temperature range 520-523 $^{\circ}$K. The standard enthalpies of formation at 25 $^{\circ}$C were obtained as 235.3 and 242.2 kJ mol^{-1} for the complexes (5.2; M = Mo, W) respectively. Metal-ligand mean bond dissociation enthalpies were derived as 247.0 and 304.0 kJ mol^{-1} for benzene and toluene respectively [74].

Hindered rotation about the metal-ligand bond in the chromium complex (5.3) has been studied by ^1H and ^{13}C NMR spectroscopy [75].



5.3



$[(C_6F_5)_3Ge]_4Hg^{2-}$

5.4

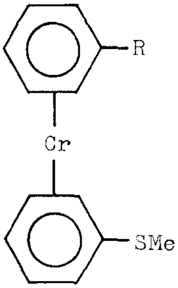
The redox reactions of twenty bis(η-arene)chromium complexes have been studied via the rotating disc electrode technique in dimethylsulphoxide. The half-wave potentials correlated well with the meta-substituent constants. It was concluded that the electronic effects of the substituents were largely transferred to the metal atom by an inductive mechanism [76].

Bis(η-ethylbenzene)chromium has been treated with hydrogen peroxide in ether or methanol. A yellow solid was isolated and ESR spectroscopy showed that there were peroxide linkages present [77].

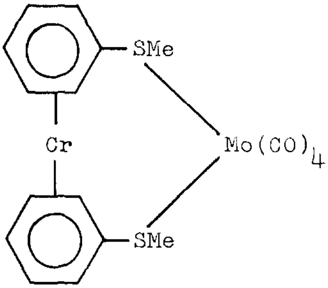
Bis(η-benzene)chromium was oxidized by treatment with bis[tris(pentafluorophenyl)germyl]mercury in glyme to give the salt (5.4) in 95% yield [78].

The lithiation of bis(η-benzene)chromium followed by treatment with dimethyldisulphide gave the η-methylthiobenzene derivatives

(5.5; R = H and SMe). The ESR spectra of the η-methylthiobenzene derivatives and their corresponding radical cations were determined. The reaction of bis(η-methylthiobenzene)chromium (5.5; R = SMe) with tetracarbonyl(η-norbornadiene)molybdenum gave the ligand replacement product (5.6) which underwent rapid conformational interconversion at room temperature [79].



5.5



5.6

The self-exchange rates and activation parameters in the $(\eta^6\text{-arene})_2\mathrm{Cr}/[(\eta^6\text{-arene})_2\mathrm{Cr}]^+$ systems (where arene = toluene, benzene, methoxybenzene, biphenyl, ethylbenzoate and chlorobenzene) have been measured by an electron spin resonance line broadening technique. Cyclic voltammetry was used to investigate the one-electron reduction of a series of $[(\eta^6\text{-arene})_2\mathrm{Cr}]^+$ complexes. It was concluded that the electron exchange reactions proceeded by the outer sphere mechanism and probably by the side to side transition state. All the results indicated that the electron densities about chromium were affected by inductive effects and these accounted for the variations in the exchange rates [80].

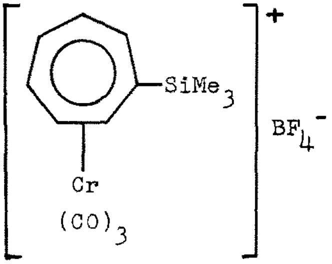
The oligomerization of perfluoropropylene in the presence of bis(η-arene)chromium complexes (arene = benzene, diphenyl, 1,3,5-trimethylbenzene, hexamethylbenzene) as catalysts has been investigated. Dimers, trimers and two defluorotrimers were identified in the mixture of oligomers. The relative order of activity of the chromium complexes was: bis(η-1,3,5-trimethylbenzene)chromium > bis(η-benzene)chromium > bis(η-biphenyl)-chromium > bis(η-hexamethylbenzene)chromium [81].

Bis(η-benzene)chromium has been used as a catalyst for the oligomerization of perfluoropropylene to dimers and trimers.

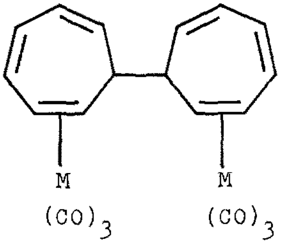
One mole of the complex was effective in converting 50 mole of the monomer [82].

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

Desilylation of the cycloheptatrienyl complex (6.1) produced the binuclear cycloheptatriene complex (6.2; M = Cr) [83].



6.1

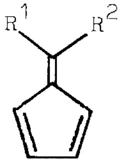


6.2

Ultraviolet irradiation of tricarbonyl(η-1,3,5-cycloheptatriene)chromium with the monosubstituted fulvenes [6.3; R^1 = H, R^2 = $OCOCH_3$; R^1 = H, R^2 = $N(Me)_2$] gave the corresponding dicarbonylchromium complexes in the exo- and endo- forms (6.4 and 6.5). The disubstituted fulvenes (6.3; R^1 = R^2 = OMe, R^1R^2 = $-SCH_2CH_2S-$, R^1 = Me, R^2 = Ph) produced the corresponding dicarbonylchromium derivatives (6.4). A similar reaction with the fulvene $C_5H_4{=}NNMe_2$ produced the (η^3-cycloheptatrienyl)chromium complex (6.6), the product of hydride transfer from the cycloheptatriene to the nitrogen atom of the fulvene [84].

The crystal and molecular structures of the (η-cycloheptatriene)-molybdenum and -tungsten complexes (6.7; M = Mo, X = Te; M = W, X = Se) together with the dimolybdenum complex, $(\eta\text{-}C_7H_7)Mo(\mu\text{-}SePh)_3\text{-}Mo(CO)_3$, have been determined by X-ray crystallography. Bond lengths and bond angles were reported [85].

Tellurium dioxide was activated by evaporation in a metal evaporator and treated with the molybdenum complex (6.8). Reaction occurred to produce the first TeO_2 insertion product (6.9; M = Te). Sulphur dioxide and selenium dioxide were inserted also into the molybdenum-carbon bond to give the dicarbonylmolybdenum complexes (6.9; M = S, Se) [86].



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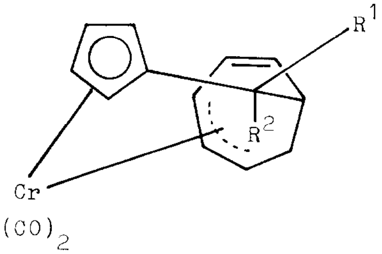

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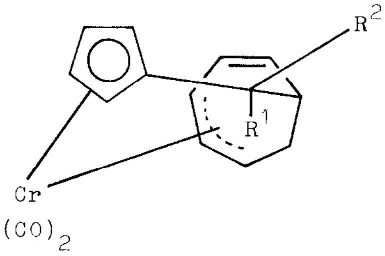

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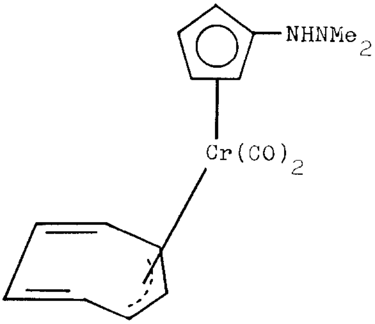

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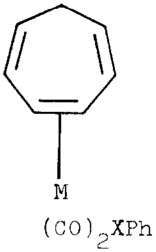

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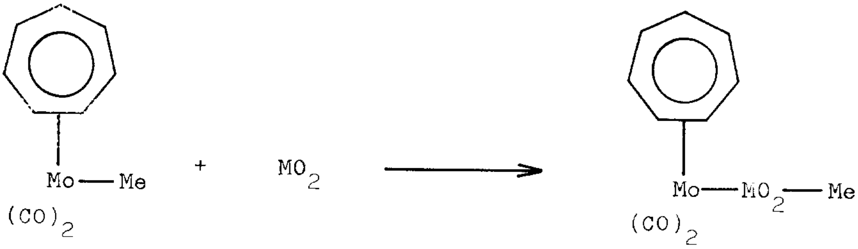
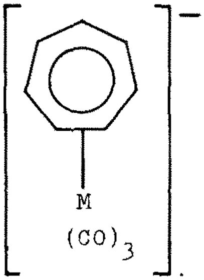


6.8

6.9

The tropylium complexes (6.10; M = Cr, Mo, W) were coupled by treatment with carbonylmetallates, for example, $[(\eta\text{-}C_5H_5)Mo(CO)_3]^-$ and $[Re(CO)_5]^-$, to give the corresponding bis(2,4,6-cycloheptatrien-1-yl) complexes (6.2; M = Cr, Mo, W) [87].

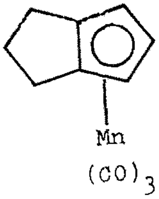


6.10

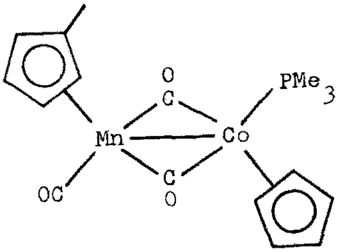
7. $(\eta\text{-}C_5H_5)Mn(CO)_3$

(i) Formation

The manganesetricarbonyl complex (7.1) was formed from cyclooctatetraene and $[HMn(CO)_4]_3$. This dehydrogenative transannular ring closure of cyclooctatetraene was rationalized in terms of a disrotatory electrocyclization of a cyclooctadienyl moiety [88].



7.1



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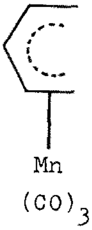


7.3

In an investigation of the formation and thermolysis of tetramethyldiphosphine bridged carbonyl complexes the cymantrene derivative, $(\eta\text{-}C_5H_5)Mn(CO)(\mu\text{-}Me_2PPMe_2)Cr(CO)_4$, was obtained [89].

Some cyclopropane derivatives of cymantrene have been prepared from the corresponding pyrazoline complexes [90].

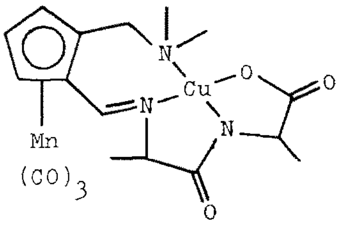
Several reactions of the mixed cobalt-manganese complex (7.2) have been reported. Phosphorus and sulphur ligands as reagents gave methylcymantrene and a cobalt complex [91].

Bromomanganesepentacarbonyl has been attacked by 2,4-pentadienyltrimethyltin in boiling THF to form tricarbonyl(η^5-pentadienyl)manganese (7.3) in 52% yield. This complex was an open analogue of cymantrene, it decomposed slowly in air in the solid state [92].

7. (ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structure of cymantrene has been reexamined by X-ray analysis. The results indicated some localized C-C bonding with bond distances in the ring between 1.400 and 1.439 Å. Vibrational studies on cymantrene also supported a breakdown of the fivefold symmetry of the ring outside of the crystalline environment [93].

The crystal and molecular structure of the cymantrene Schiff base complex (7.4) has been determined by X-ray crystallography and the absolute configuration confirmed as S, the Mn and Cu atoms were trans with respect to the plane of the cyclopentadienyl ring [94].



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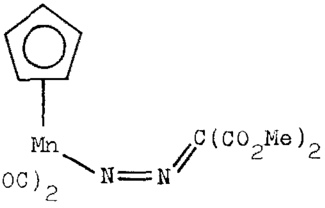
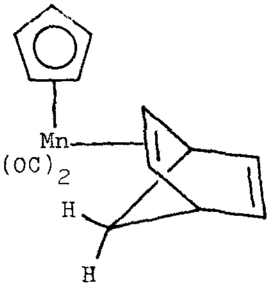


7.5

Dimethyldiazomalonate combined with the THF complex of cymantrene, (η-C_5H_5)Mn(CO)$_2$THF, to give the diazoalkane complex (7.5). X-Ray crystallography demonstrated that the complex contained a monodentate diazomalonate group bonded through the terminal nitrogen and with the diazo group bent at the central nitrogen [95].

The crystal and molecular structure of the cymantrene analogue (7.6) has been determined by X-ray crystallography. Norbornadiene was coordinated to manganese in an exo configuration and was a two-electron donor. The manganese-bridgehead methylene hydrogen distance was 2.97 Å and indicated a lack of CH•••Mn interaction [96].

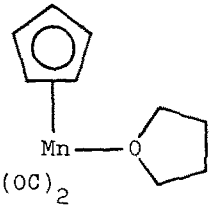
Cyclooctatetraene attacked the cymantrene complex (7.7) to form the (η^2-cyclooctatetraene)manganese complex (7.8) the structure of which has been determined by X-ray crystallography. Analogous



7.6

complexes containing η^2-cycloheptatriene and η^2-cycloocta-1,3,6-triene were also prepared [97].

The crystal and molecular structure of the (η-cyclopentadienyl)manganese complex (7.9) has been determined by X-ray



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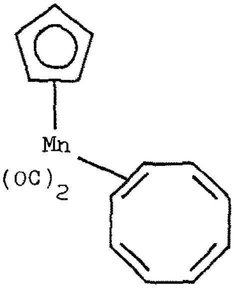

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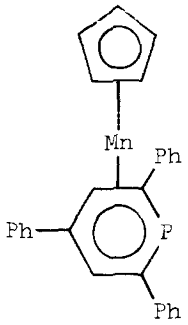
crystallography. The metal atom was sandwiched between the η-C_5H_5 and the η-$C_5PH_2.Ph_3$ rings [98].

Gas phase He I, He II and Mg Kα photoelectron spectra have been recorded for the complexes $[\eta\text{-}C_5H_{5-n}(CH_3)_n]M(CO)_3$ where n = 0, 1, 5 and M = Mn, Re. The influence of the methyl groups was monitored by the shifts in both core and valence ionization energies. The magnitudes of the valence ionization energy shifts were relatively large which indicated a considerable change in the electronic



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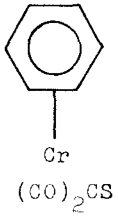

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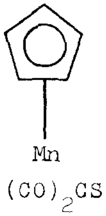


7.11

structure of these compounds. It was concluded that electronic effects were as important as steric effectsin determining reactivity differences between substituted and unsubstituted η-cyclopentadienyl complexes. It was concluded also that considerable rhenium to carbonyl π back-bonding occurred [99].

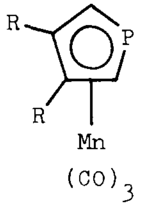
The He I and He II valence photoelectron spectra of the complexes $[\eta\text{-}C_5H_{5-n}(CH_3)_n]Mn(CO)_2L$ where n = 1, 5 and L = C_2H_4, C_3H_6 have been recorded and interpreted. It was found that the ionizations and stability of the complexes were sensitive to the geometry changes that arose due to the introduction of the olefin. These distortions were associated with a lower carbon-carbon bond strength and an increased metal-olefin bond strength through increased π-donor/π^*-acceptor interactions [100].

Gas phase core electron binding energies were obtained by an X-ray photoelectron spectroscopic study of a series of thiocarbonyl complexes which included the chromium and manganese compounds (7.10 and 7.11). The binding energies of the metal atom and the carbonyl groups was approximately constant when one of the carbonyl groups was replaced by a thiocarbonyl group. It was concluded that the electron distribution within the complex was largely unaffected by the change in the ligand. The greater donor character of the thiocarbonyl ligand being compensated for by an increase in back bonding [101].

The mass spectrometric fragmentation of thirteen monosubstituted (η-cyclopentadienyl)tricarbonylrhenium complexes has been examined.

In general the complexes underwent decarbonylation, dehydrogenation and breakdown of the cyclopentadienyl ring [102].

The IR and Raman spectra of phosphacymantrene and dimethylphosphacymantrene (7.12; R = H, Me) have been recorded in the solid and liquid states. The spectra of the corresponding deutero complexes have also been obtained. A complete vibrational assignment has been made and has shown that the η-C_4H_4P ring was more electrophilic and a weaker π-electron donor than the η-C_5H_5 ring [103].

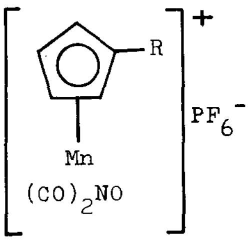


7.12

7. (iii) General Chemistry

Caulton has reviewed the coordination chemistry of the manganese and rhenium fragments (η-C_5H_5)M(CO)$_2$ [104].

Reaction of the dicarbonylmanganese complexes (7.13; R = H, Me) with the stereochemically rigid diisocyanides (L-L) 1,3- and 1,4-



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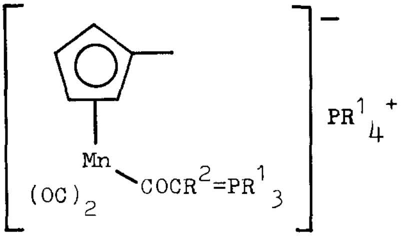

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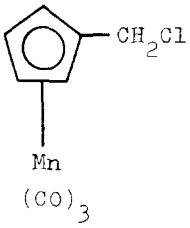
diisocyanobenzene, 4,4'-diisocyanobiphenyl and 4,4'-diisocyanodiphenylmethane afforded mixtures of oligomers of the type $[(RC_5H_4MnNO)_n(L\text{-}L)_{n+1}]^{n+}[PF_6^-]_n$ [105].

Methylcymantrene underwent addition with Wittig reagents, $R^1_3P{=}CHR^2$, where R^1 = Me, R^2 = H and R^1 = Et, R^2 = Me, to form the products (7.14; R^1 = Me, R^2 = H; R^1 = Et, R^2 = Me) [106].

Treatment of the chloromethyl derivative (7.15) with $NaOCH_2C{\equiv}CH$ gave the dicarbonylmanganese complex (7.16). A similar reaction was used to prepare the cymantrenyl derivative (7.17) [107].

The Friedel-Crafts reaction on t-butyl derivatives of cymantrene has produced the ester (7.18). The structure of the complex (7.18) was confirmed by X-ray analysis [108].

Several cymantrenylthioketone complexes [7.19; R = Me, Ph, ML = $W(CO)_5$; R = Ph, ML = $Mn(CO)_2(\eta\text{-}C_5H_5)$] have been prepared by



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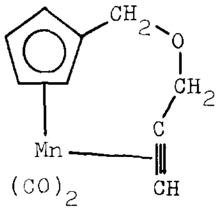

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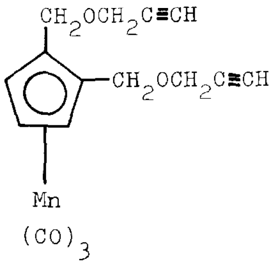

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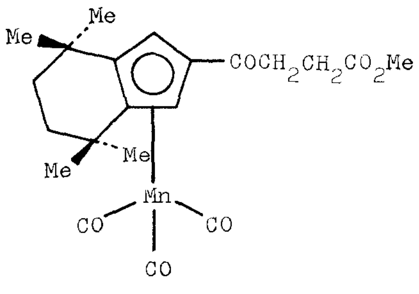

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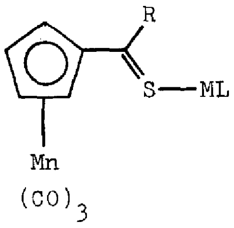
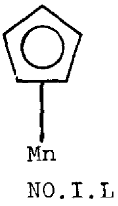


7.19

treating the cymantrenylthioketone with the appropriate metal carbonyl [109].

The thermally unstable nitrosyl complex (7.20; L = CO) underwent coupling in the presence of zinc amalgam to give the dimer $[(\eta\text{-}C_5H_5)Mn(CO)NO]_2$ while with phosphines the derivatives [7.20; L = PPh_3, $P(OPh)_3$, $P(C_6H_{11})_3$] were obtained. By contrast, attack with hard Lewis bases such as pyridine, dimethyl sulphoxide and acetone caused decomposition with the binuclear complex (7.21; X = I) as the only nitrosyl containing product. Other members of the same series (7.21; X = Br, Cl, NO_2, Me, Et) were obtained by nucleophilic attack of X^- on the cation $[(\eta\text{-}C_5H_5)Mn(CO)_2(NO)]^+$ [110].

Treatment of formylcymantrene with chloroform in the presence of water and a phase transfer catalyst, for example triethylbenzylammonium chloride, produced α-cymantrenylglycolic acid [111].



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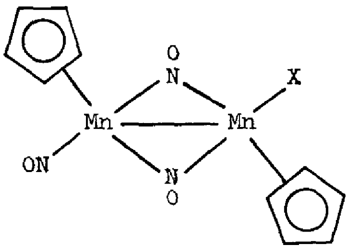

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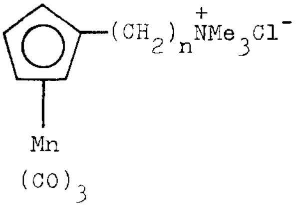

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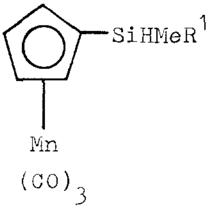

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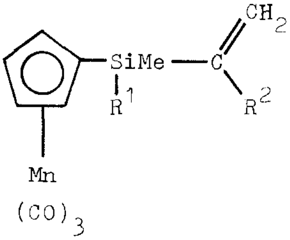

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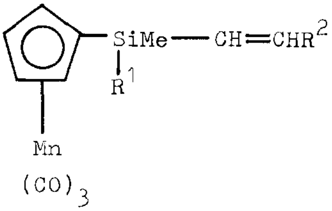

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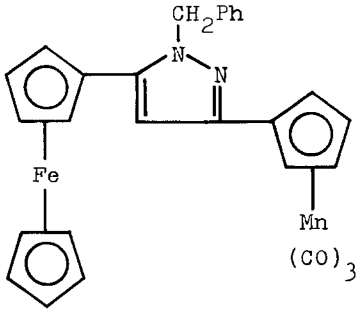
The cymantrenylammonium chlorides (7.22; n = 3, 5, 7) have been prepared by treatment of the corresponding alkyl chlorides with trimethylamine. The use of these ammonium salts as cationic surfactants was investigated [112].

Cymantrenylsilanes (7.23; R^1 = Me, Ph) were effective in the hydrosilylation of acetylenes $HC\equiv CR^2$, where R^2 = CMe_2OH, 1-hydroxycyclohexyl, in the presence of Speier's catalyst to give a mixture of the two isomeric products (7.24 and 7.25; R^1 = Me, Ph; R^2 = CMe_2OH, 1-hydroxycyclohexyl) in yields of 14-22% and 44-59% respectively [113].

The benzylpyrazoles (7.26 and 7.27) have been prepared by reaction of the corresponding pyrazolines with benzaldehyde. These reactions proceeded via oxidation of the pyrazoline to pyrazole accompanied by simultaneous reduction of the benzaldehyde [114].



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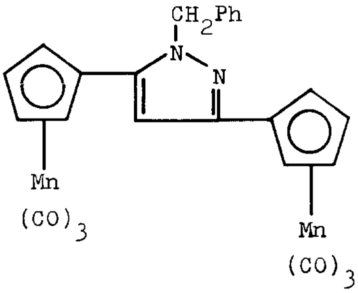

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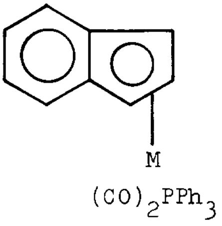

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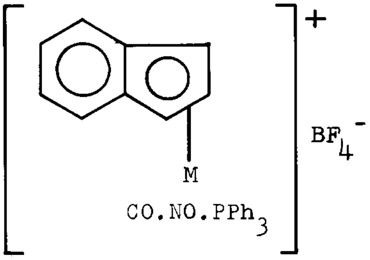

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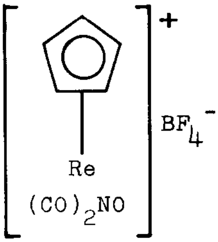

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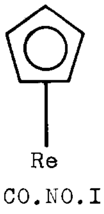

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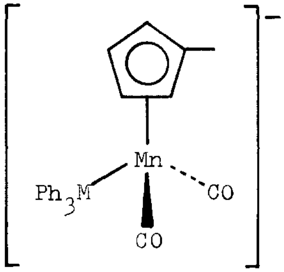
Treatment of the η^5-indenyl complexes (7.28; M = Mn, Re) with NO_2BF_4 gave the corresponding salts (7.29; M = Mn, Re). The indenyl ligand was removed from the complex (7.29; M = Mn) by treatment with KX, where X = Br, I, CN, to give $Mn(NO)_2PPh_3X$. In a similar reaction the treatment of the cation (7.30) with potassium iodide or iodine produced the complex (7.31) [115].

The triphenylgermanyl and triphenylsilyl substituted anions (7.32; M = Si, Ge) have been alkylated with methyl iodide and benzyl bromide to give the dicarbonylmanganese complexes (7.33; M = Si, Ge, R = Me, CH_2Ph). The ^1H NMR spectra of the benzyl derivatives showed a sharp singlet for the CH_2 groups which indicated that carbonyls were arranged diagonally to one another assuming that the molecule had a square pyramidal geometry [116].



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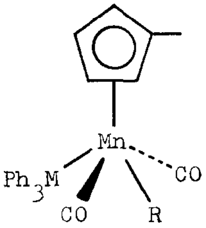

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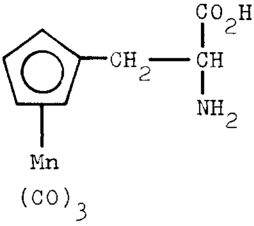

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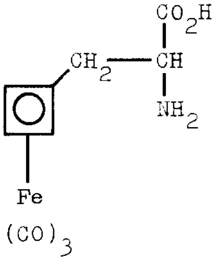
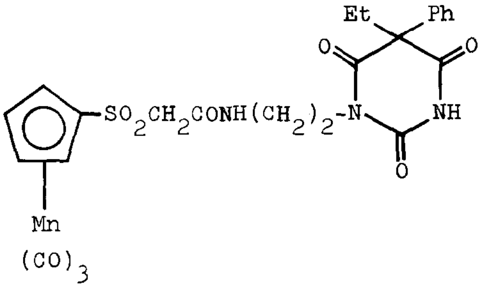


7.35

The metallocene analogues of phenylalanine, D,L-β-cymantrenyl alanine (7.34) and D,L-β-tricarbonyl(η-cyclobutadienylalanine)iron (7.35) have been prepared [117].

Cais and Tirosh have reported the preparation of the manganese labelled phenobarbitone haptens (7.36 and 7.37) via (cymantrenylsulphonyl)acetic acid and 2-(cymantrenylsulphonyl)-ethylamine respectively. Atomic absorption spectroscopy was used to determine manganese concentrations in buffered solutions of the metallohapten containing immunoassay concentrations of anti-phenobarbitone antisera. The results indicated the feasibility of quantitative detection of manganese in the 10^{-9} g ml^{-1} range [118].



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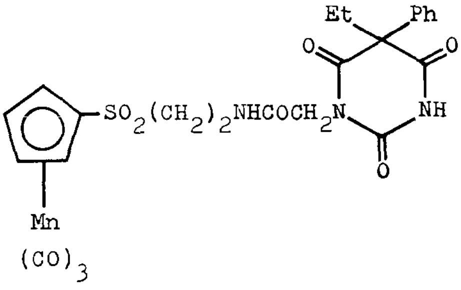


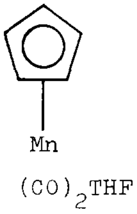
7.37

η^5-Cyclopentadienyl-, η^5-indenyl- and η^5-fluorenyl-tricarbonylmanganese have been shown to exhibit approximately the same reactivity towards photosubstitution of a carbonyl group by triphenylphosphine [119].

Cymantrene and methylcymantrene have been subjected to photolysis in glassy matrices at 77 ^{o}K. Cymantrene gave the species $(\eta\text{-}C_5H_5)Mn(CO)_2$, $(\eta\text{-}C_5H_5)Mn(CO)$ and, when ethers were present, $(\eta\text{-}C_5H_5)Mn(CO)_2(\text{ether})$ and $(\eta\text{-}C_5H_5)Mn(CO)(\text{ether})_2$. Methylcymantrene gave similar species although both substrates underwent slower photolysis than the d^6 hexacarbonyls. Rather similar behaviour on photolysis was observed for the complexes $(\eta\text{-}C_6H_6)Cr(CO)_3$, $(\eta\text{-}C_5H_5)Mn(CO)_2CS$, $[\eta\text{-}C_4(CF_3)_4S(C_6F_5)]Mn(CO)_3$

and $(\eta\text{-}C_5H_5)Fe(CO)_2I$ [120].

The photochemically generated THF complex (7.38) has been attacked by allyl alcohol and the product subjected to prototrophic elimination of water with $HPF_6\text{-}Ac_2O$ to form the cationic (η-allyl)manganese complex (7.39). Several methylated derivatives were formed in the same way [121].



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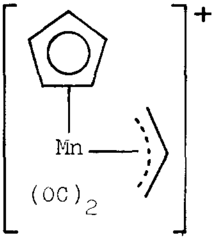
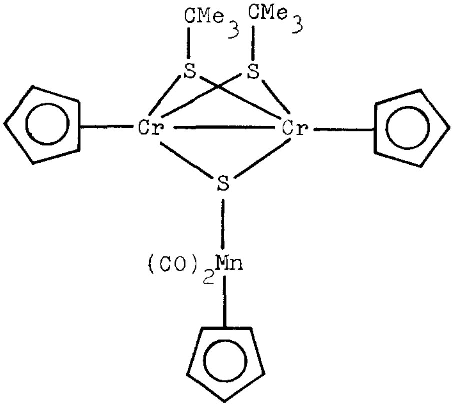


7.39

Irradiation of cymantrene with $(\eta\text{-}C_5H_5CrSCMe_3)_2S$ produced the complex (7.40) and the structure of this molecule was determined by X-ray analysis [122].

Irradiation of methylcymantrene with diphenylsilane gave the dicarbonylmanganese complex (7.41; X = H). Treatment of this



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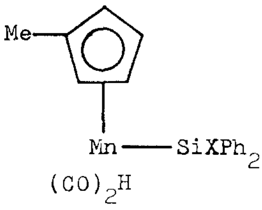
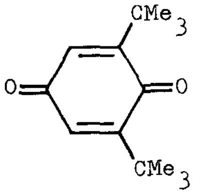


7.41

complex with $[Ph_3C]BF_4$ in dichloromethane or with carbon tetrachloride in the presence of phosphorus(V) chloride gave the halogen derivatives (7.41; X = F and Cl) respectively. Reaction of the latter complexes with carbon monoxide under pressure led to methylcymantrene and the corresponding monohalogenodiphenylsilane [123].

Reaction of lithiocymantrene with the quinone (7.42) produced the alcohol (7.43) which was reduced with zinc-hydrochloric acid to give the corresponding phenol (7.44). Oxidation of this phenol gave the tricarbonylmanganese radical complex (7.45). A similar series of reactions was performed starting from lithiobenchrotrene [124].

Lithiation of (dimethylamino)methylcymantrene using n-butyllithium at -70 °C gave the lithio intermediate (7.46; X = Li)



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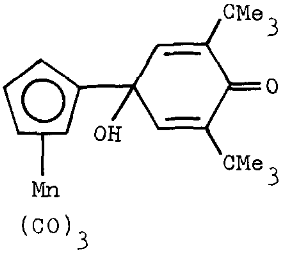

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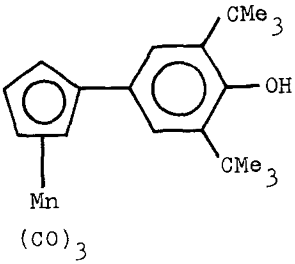

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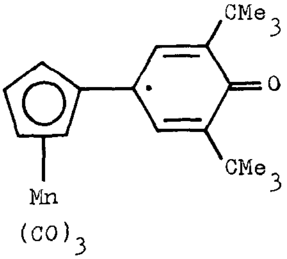
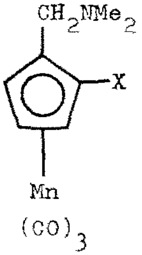


7.45

and this was treated with deuterium oxide, dimethylformamide and chlorodiphenylphosphine to form the 1,2-disubstituted cymantrenes (7.46; X = D, CHO, PPh_2) respectively. Hydroxymethylcymantrene underwent similar metallation and attack by electrophilic reagents to form 2-substituted derivatives while diphenylphosphinocymantrene gave 1,3-disubstituted products under similar conditions. The orientation of the reactions was confirmed by chemical methods and by ^1H and ^{13}C NMR spectroscopy [125].



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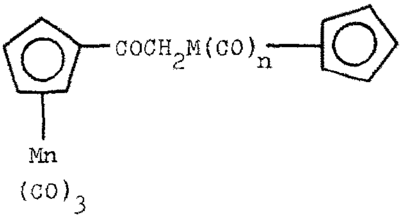
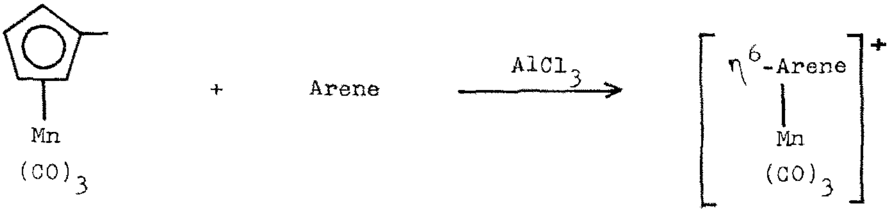


7.47

The cymantrenylchloroacetyl complex $(\eta\text{-}C_5H_4.COCH_2Cl)Mn(CO)_3$, has been treated with the sodio complexes, $NaM(CO)_n(\eta\text{-}C_5H_5)$, where M = Fe, W, Mo and n = 2, 3 to form the α-metallated ketones (7.47; M = Fe, W, Mo, n = 2, 3) [126].

Methylcymantrene (7.48) underwent ligand exchange with methyl substituted benzenes in the presence of aluminium chloride to form

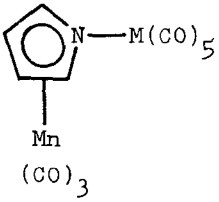


7.48

7.49

the cations (7.49; arene = benzene, toluene, *p*-xylene, *o*-xylene, *m*-xylene, mesitylene, durene, tetramethylbenzene, pentamethylbenzene, hexamethylbenzene) [127, 128].

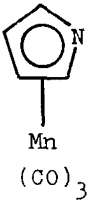
UV irradiation of tricarbonyl(η-pyrrolyl)manganese with the metal carbonyls $M(CO)_6$ produced the corresponding pyrrolyl complexes (7.50) [129].



7.50

Metallation of (η-pyrrolyl)manganesetricarbonyl (7.51) with n-butyllithium and subsequent quenching with D_2O gave a trinuclear complex (7.52) formed by attack of the metallating agent at a carbonyl group. Deuterium was not taken up into the product (7.52), the molecular structure of which was determined by X-ray crystallography [130].

Picric acid attacked (η-pyrrolyl)manganesetricarbonyl (7.51)



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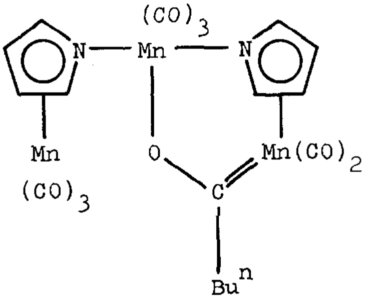

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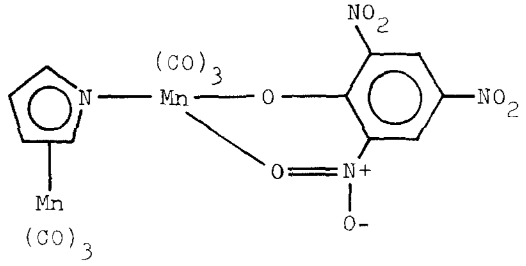

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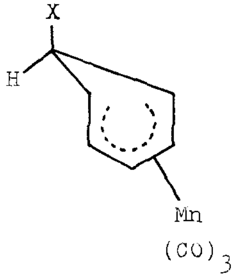
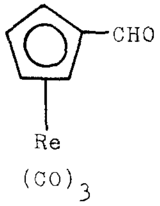


7.54

to form a binuclear complex (7.53) the molecular structure of which has been determined by X-ray crystallography [131].

The kinetics of nucleophilic attack by anions on the (η-benzene)tricarbonylmanganese cation, to give the corresponding neutral species (7.54; X = N_3, OH, CN), were investigated. The overall rate trend $N_3^- \gg OH^- \gg CN^-$ was unusual and it was similar to that for anion addition to free carbenium ions [132].

Tricarbonyl(η-lithiocyclopentadienyl)rhenium has been treated with dimethylformamide in THF at -70 °C and then ammonium chloride at -10 °C to give the formyl derivative (7.55). Several reactions of this product (7.55) were described including reduction with lithium aluminium hydride to the corresponding methanol derivative [133].



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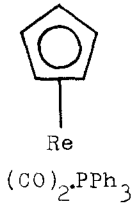

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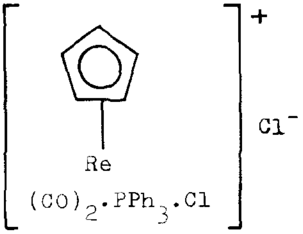
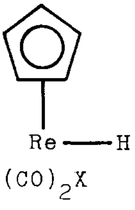


7.57

Chlorination of the rhenium complex (7.56) with chlorine or thionyl chloride produced the salt (7.57). Similar reactions were carried out with tricarbonyl(η-cyclopentadienyl)rhenium [134].

The dicarbonylhydridorhenium complexes [7.58; X = $SiPh_3$, $Si(CH_2Ph)_3$, $SiPh_2H$] have been prepared by ultraviolet irradiation of tricarbonyl(η-cyclopentadienyl)rhenium with the appropriate silane. The hydrides (7.58; X = $SiPh_3$, $GeCl_3$, $GeBr_3$, $SnCl_3$) were obtained by protonation of the corresponding anions (7.59) [135].



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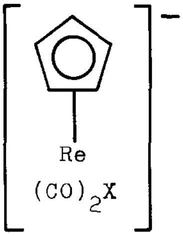
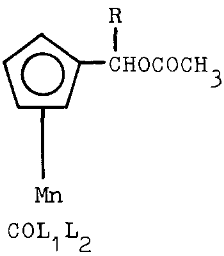


7.59

The hydrolysis and methanolysis of the manganese and rhenium complexes [7.60; R = H, Me, Ph; L^1L^2 = $(CO)_2$, $(CO)(PEt_3)$, $(CO)(PPh_3)$, $Ph_2PCH_2CH_2PPh_2$] and (7.61) have been studied. The carbenium ions generated in these reactions were stabilized better by phosphine ligands than by the carbonyl group on manganese. The stabilizing abilities of manganese and rhenium were the same [136].



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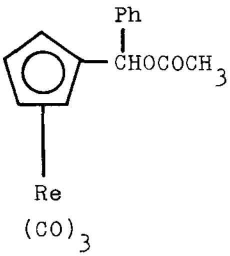
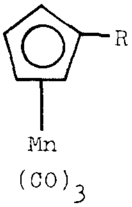


7.61

7. (iv) Applications

^{3}H-Methylcymantrene, orally administered to rats, was efficiently absorbed, metabolized and excreted in the urine as the alcohol (7.62; R = CH_2OH) and as the carboxylic acid (7.62; R = CO_2H). In vitro, the same complex was metabolized by rat liver microsomes by a cytochrome P 450-dependent process [137].



7.62

The toxicity of methylcymantrene in rats has been investigated. The LD_{50} dose was 50 mg/kg for oral administration and 23 mg/kg for i.p. administration. Histological examination of rats treated with methylcymantrene revealed pathological changes in the lungs, liver and kidney. Phenobarbital pretreatment protected rats from the lethal effects of 2.5 times the LD dose [138].

Polymer-bounddinitrogen complexes were prepared by treating vinylpyrrolidinone-tricarbonyl(η-vinylmethylcyclopentadienyl)-manganese-styrene copolymers with nitrogen under pressure (3 atmospheres). These dinitrogen complexes were more stable than the corresponding monomer model dicarbonyldinitrogen (η-methylcyclopentadienyl)manganese [139].

No significant chain transfer was observed on polymerization of styrene in the presence of cymantrene or poly(η^5-vinylcylopentadienyl)tricarbonylmanganese [140].

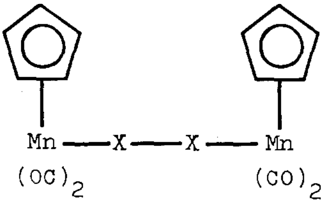
Cymantrene has been incorporated with advantage into a fire extinguishing composition [141].

Extensive fleet trials of methylcymantrene as a gasoline antiknock additive have been subjected to statistical analysis in order to provide mathematical models for the effect of the additive. Hydrocarbon emissions increased linearly with additive concentration while catalyst converter efficiency was increased in the presence of methylcymantrene [142].

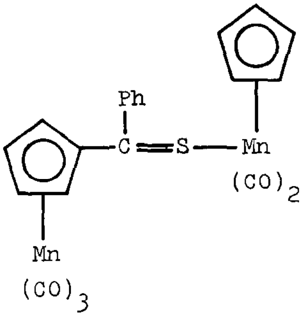
Methylcymantrene has been determined at ng/m^3 concentrations in air. The sample was trapped in a small segment of a gas chromatography column and measured by gas chromatography using an electrothermal atomic absorption spectrometry detector. The limit of detection was found to be 0.05 ng/m^3 [143].

8. Polynuclear (η-C_5H_5)Mn(CO)$_3$ Complexes

The THF derivative of cymantrene, (η-C_5H_5)Mn(CO)$_2$(OC$_4$H$_8$) combined with COS and COSe to form the binuclear complexes (8.1; X = S, Se). An X-ray crystallographic investigation of the sulphur compound (8.1; X = S) confirmed that the molecule was centrosymmetric with a planar Mn-S-S-Mn unit [144].



8.1



8.2

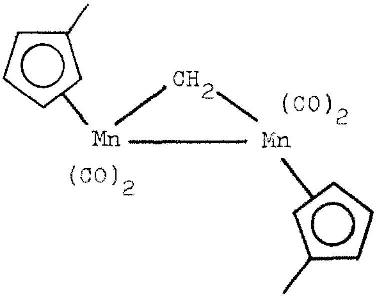
The ^{13}C NMR spectra of cymantrenylphenylthioketone and the binuclear complex (8.2) have been recorded and interpreted. The structure of the complex (8.2) was determined by X-ray analysis [145].

The electronic structure of the cluster complex μ-CH$_2$-[(η-C_5H_5)Mn(CO)$_2$]$_2$ has been investigated by vapour-phase photoelectron spectroscopy and by quantum mechanical calculations. The molecular orbitals used in formation of the cyclic Mn-CH$_2$-Mn bridge were discussed [146, 147]. The crystal and molecular structure of the same complex has been determined by X-ray crystallography. The molecule contains two <u>trans</u>-(η-C_5H_5)Mn(CO)$_2$

groups joined by a bridging methylene group. The manganese-manganese interatomic distance was 2.799 Å [148].

The He I photoelectron spectrum in the ionization energy range below 11 ev has been recorded for the bridged complex (8.3) and compared with the spectra of methylcymantrene and $(\eta\text{-}C_5H_4Me)Mn(CO)_2(\eta\text{-}C_2H_4)$. It was concluded that the Mn-Mn bond in (8.3) was an important factor in the stability of this compound [149].

The irradiation of cymantrene with $HC{\equiv}CCO_2Me$ in tetrahydrofuran gave the dicarbonylmanganese derivatives (8.4 and 8.5) as the major products. Treatment of the manganese complex (8.4) with hydrogen chloride produced the corresponding η-olefin derivative (8.6) [150].



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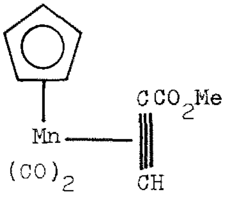

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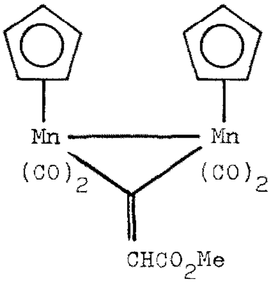

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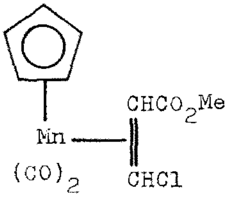

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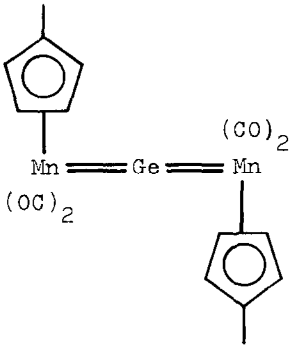

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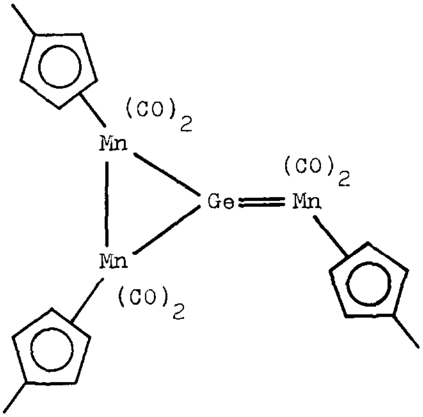
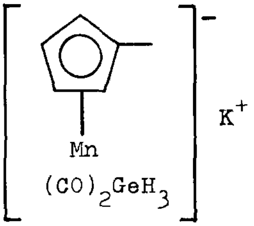


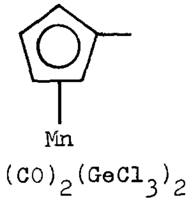
8.8

Treatment of the hydride $K[(\eta\text{-}MeC_5H_4)Mn(CO)_2GeH_3]$ with acetic acid gave the trinuclear complex (8.7) which has been characterized by X-ray crystallography. The molecule is centrosymmetric and contains a linear Mn=Ge=Mn moiety with Mn-Ge double bonds. Treatment of the same hydride with mercury(II) gave the trimanganese germanium complex (8.8) which contained a Mn-Ge double bond in addition to a triangular Mn_2Ge ring [151].

Reaction of methylcymantrene with GeH_3K gave the potassium salt (8.9) which when treated with germanium tetrachloride produced the neutral complex (8.10) [152]. Treatment of the salt (8.9) with mercury(II) chloride gave the tetramercury derivative (8.11) [153].



8.9



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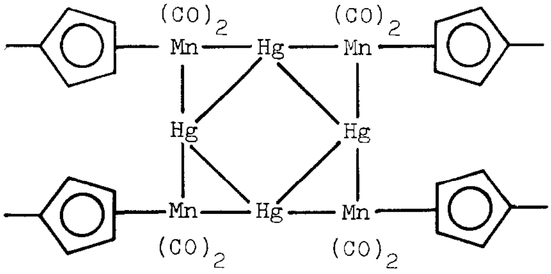


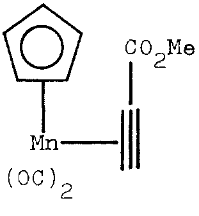
8.11

9. Carbene and Carbyne (η-C_5H_5)Mn(CO)$_3$ Complexes

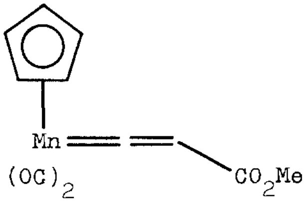
The methylpropiolate complex (9.1) was attacked by organolithium compounds, RLi, where R = Me, Bu^t, Ph, to give the carbene complex (9.2) in 50% yield [154].

Treatment of the methylcymantrene complex (9.3) with MeO_3SF gave the phosphorylid-carbene complex (9.4; R = H) and then the salt (9.5) in the presence of an excess of MeO_3SF. The product (9.5) was attacked by $Me_3P{=}CH_2$ to give the phosphorylid-carbene complex (9.4; R = Me) [155].

The reaction of dicarbonyl(η-methylcyclopentadienyl)-



9.1



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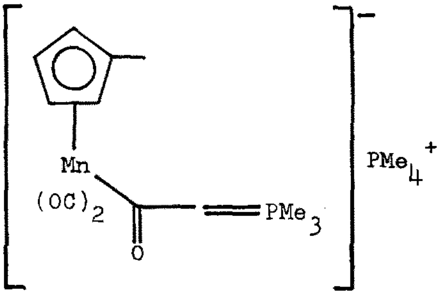

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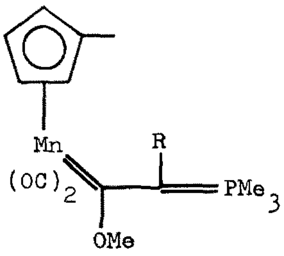

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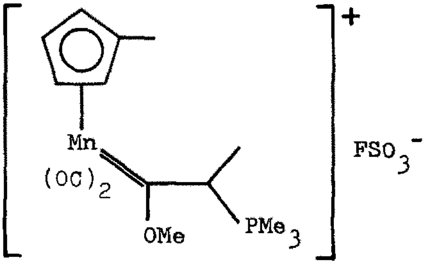


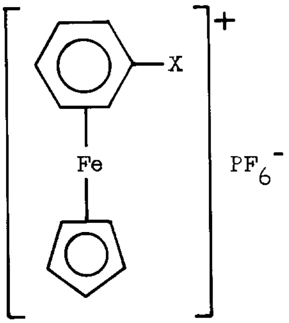
9.5

(diorganylallenylidene)manganese compounds with t-butyllithium followed by protonation or methylation gave the vinylidene complexes (9.6; R = H, Me; and 9.7). The structure of the complex (9.8) was determined by X-ray analysis [156].

The carbene complex (9.9), obtained by treatment of $Ph_2C{=}W(CO)_5$ with $(\eta$-$C_5H_5)Mn(CO)_2THF$, underwent photolysis to form tetraphenylethylene, diphenylmethane and 1,1,2,2-tetraphenylethane [157].

Treatment of the manganese complexes (9.10; R = $C{=}CHCO_2Me$, η-$CH{\equiv}CCO_2Me$, $C{=}C{=}CPh_2$) with nonacarbonyldiiron gave the corresponding tetracarbonyliron derivatives (9.11; $R^1 = H$, $R^2 = CO_2Me$; $R^1 = CO_2Me$, $R^2 = H$; $R^1R^2 = CPh_2$) [158].

The electronic structures and bonding capabilities of the



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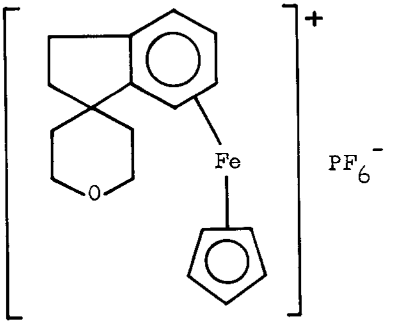

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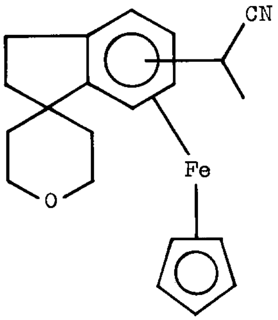

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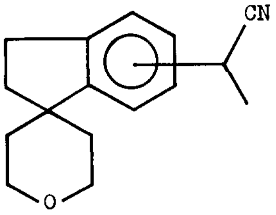

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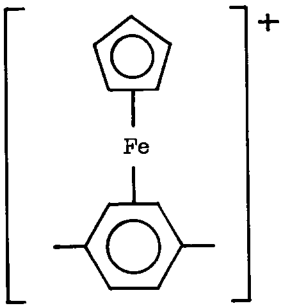

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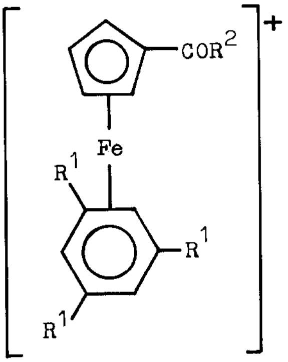
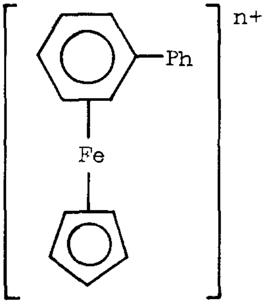


14.23

Reduction of the (η-benzene)(η-cyclopentadienyl)iron cation (14.24; n = 1) with sodium amalgam gave the neutral complex (14.24; n = 0) in addition to the (η-cyclohexadienyl)iron complex (14.25) [272].



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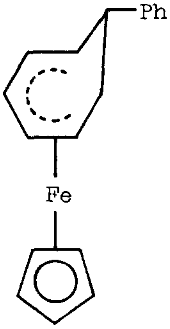


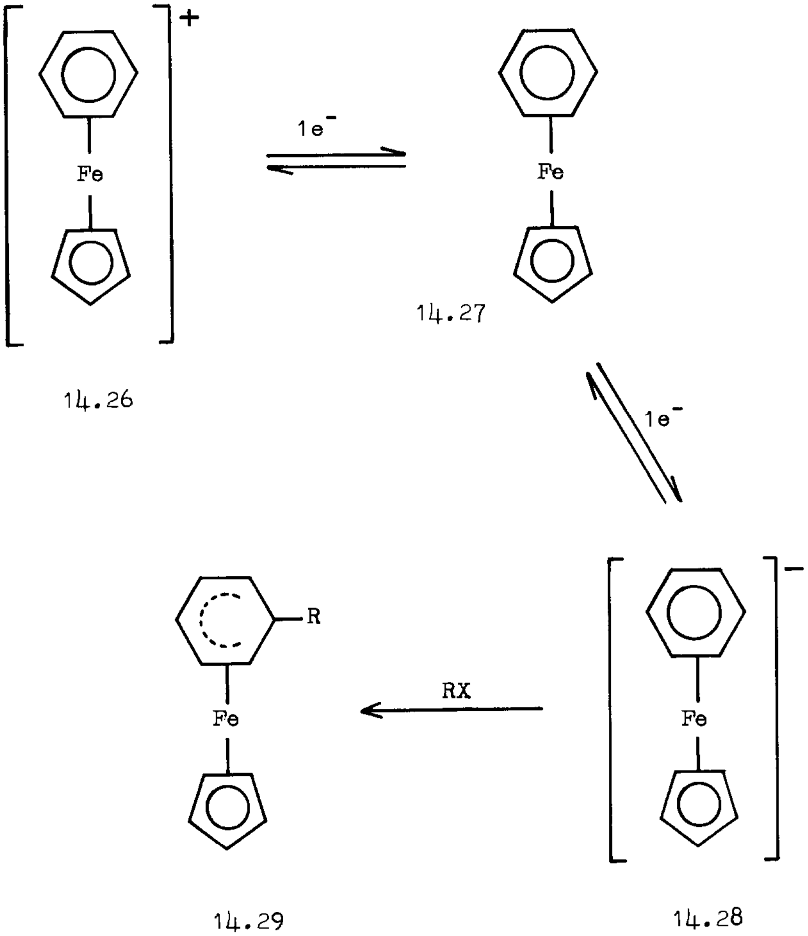
14.25

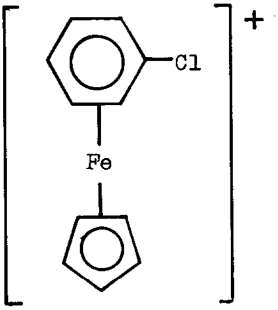
Electrochemical reduction of the (η-arene)iron cation (14.26) gave successively the neutral radical (14.27) and the anion (14.28) which was attacked by iodobenzene and methyl iodide to form the (η-cyclohexadienyl)iron complexes (14.29; R = Ph, Me). Several related reactions were reported [273].

The electrochemical reduction of (η^6-arene)(η^5-cyclopentadienyl)iron cations in basic media has been studied. One-electron reversible electroreduction occurred to give the corresponding radicals, that is the neutral 19 electron d^7 complexes (η^6-arene)(η^6-C_5H_5)Fe(I). The behaviour of the radicals depended on the nature and the number of the substituents on the rings and also on the medium. With all the radicals catalytic reduction of the medium occurred together with radical dimerization or decomposition liberating Fe(0) or Fe(II) [274].

The (η-chlorobenzene)iron cation (14.30) has been reduced with sodium amalgam at -10 °C to give neutral (η-chlorobenzene)-(η-cyclopentadienyl)iron which dimerized in air and in aqueous sodium borohydride [275].

Hydrogen atom abstraction with oxygen from the neutral (η^6-hexamethylbenzene)iron complex (14.31) gave the (η^5-benzyl)-iron complex (14.32) which has been characterized by X-ray crystallography. The exocyclic methylene is bent away from the





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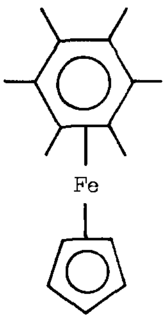
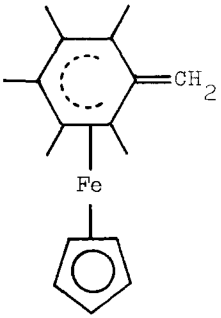
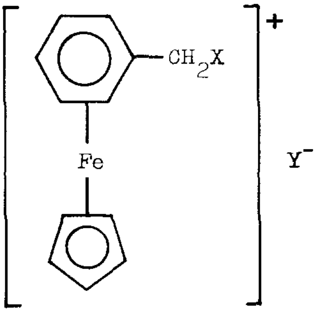


14.31



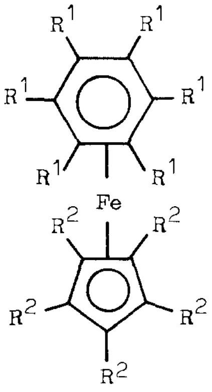
14.32



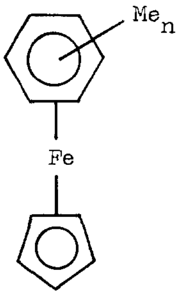
14.33

iron atom and out of the plane of the six-membered ring. The complex (14.32) acted as a nucleophile to organic and organometallic halides, PhCOCl, Ph_2PCl, Me_3SiCl, $Mn(CO)_5Br$, (η-C_5H_5)$Fe(CO)_2Cl$, to form the (η-arene)iron salts [14.33; X = COPh, PPh_2, $SiMe_3$, $Mn(CO)_5$, $Fe(CO)_2$(η-C_5H_5), Y = Cl, Br] [276].

The peralkyl (η-arene)iron complexes (14.34; R^1 = Me, Et, R^2 = H; $R^1 = R^2$ = Me) have been obtained by sodium amalgam reduction of the corresponding cations. The green compounds (14.34) were characterized as d^7 19-electron complexes of Fe(I) by spectroscopic and magnetic techniques. The methylated (η-arene)iron complexes (14.35; n = 1 to 5) dimerize thermally



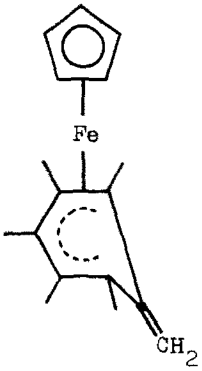
14.34



14.35

at -20 °C through the arene ring. The complexes (14.34 and 14.35) were effective redox catalysts [277].

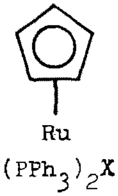
The complexes $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6Me_6)$, $\eta\text{-}C_5Me_5Fe(\eta\text{-}C_6Me_6)$, $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6Me_5CH_2)]_2$ and $(\eta\text{-}C_5H_5Fe(\eta\text{-}C_6Et_6)$ underwent rapid reaction with oxygen to give the corresponding η-cyclohexadienyl complexes with doubly bonded exocyclic methylene groups. For example, $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6Me_6)$ produced the η-cyclohexadienyl complex (14.36). This latter complex underwent nucleophilic substitution with, for example, CH_3I, PhCOCl, Me_3SiCl, Ph_2PCl $(\eta\text{-}C_5H_5)Fe(CO)_2Cl$, $(\eta\text{-}C_5H_5)Mo(CO)_3I$, $Mn(CO)_5Br$, $Cr(CO)_6$ and nucleophilic addition with, for example, CO_2, CS_2 and $[(\eta\text{-}C_5H_5)Fe(CO)_3]^+$ [278].



14.36

15. $(\eta\text{-}C_5H_5)_2Ru$ and $(\eta\text{-}C_5H_5)_2Os$

Treatment of the ruthenium complexes (15.1, X = H, Cl) with cyclopentadiene gave ruthenocene [279].



15.1

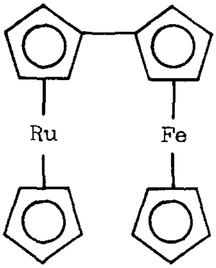
Ruthenocene underwent an irreversible oxidation, $E_{p/2}$ = +0.68 V, 100 mV s^{-1}, on voltammetry in an 0.8:1 molar ratio $AlCl_3$:n-butylpyridinium chloride melt using vitreous carbon electrodes. In acidic melts with an excess of $AlCl_3$ ruthenocene was oxidized by a multistep sequence which was sensitive to the composition of the melt [280].

The ^{13}C NMR chemical shifts for several ruthenocenophanes including [4]ruthenocenophan-2-one and [3]ruthenocenophan-1-one have been measured and compared with the values for the corresponding ferrocenophanes [281].

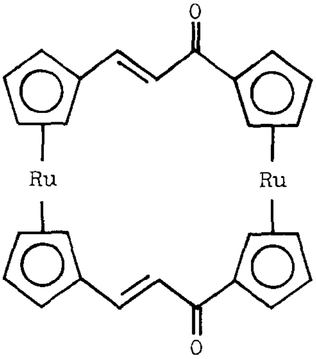
The reduction of 1,1'-diacetylruthenocene with sodium borohydride in the presence of aluminium chloride, borontrifluoride or sulphuric acid produced 1,1'-diethylruthenocene [282].

Irradiation of ruthenocene in ethanol-polychloromethane solutions led to photochemical substitution with the product depending on the nature of the polychloromethane. Carbon tetrachloride caused ethoxycarbonylation of ruthenocene, chloroform caused formylation and dichloromethane caused ethoxymethylation. In addition to substitution, carbon tetrachloride favoured oxidation with the formation of $[(\eta-C_5H_5)_2Ru]^+RuCl_4^-$ and cyclopentenes containing chloro and trichloromethyl substituents [283].

Ferrocenylruthenocene (15.2) has been obtained by Ullmann coupling of iodoruthenocene with a large excess of iodoferrocene in the melt. Mass spectrometry of the complex (15.2) indicated lower metal-ligand bond strength for iron than for ruthenium [284].



15.2



15.3

The [3.3](1,1')- and [5,5](1,1')-ruthenocenophanes and the ferrocenoruthenocenophane homologues have been prepared. For example, the reaction of 1,1'-ruthenocenedicarboxaldehyde with 1,1'-diacetylruthenocene in ethanol in the presence of sodium ethoxide gave the ruthenocenophane (15.3) in good yield [285].

Vinylruthenocene has been homopolymerized and solution copolymerized with methylacrylate, styrene and vinylpyrrolidine in the presence of azobisisobutyronitrile as catalyst. The polymers were benzene soluble with molecular weights of 3.13×10^3-1.3×10^5 and molecular weight distributions of 3.1-13.2. The polymers were investigated by thermogravimetric analysis [286].

Polyruthenocenylene oligomers have been prepared by the coupling of the 1,1'-dilithioruthenocene-1,2-bis(dimethylamino)-ethane complex in the presence of copper(II) chloride [287].

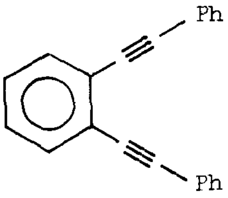
Hydroxylase activity in rats and mice has been studied using ^{103}Ru-ruthenocene. Greater hydroxylation was observed in male than in female animals and after pretreatment with barbiturates. The distribution of ^{103}Ru in lung and kidney after administration of ^{103}Ru-ruthenocene was affected by barbiturate pretreatment [288].

^{103}Ru-Labelled ruthenocenecarbaldehyde was treated with glucosamine, galactosamine and mannosamine to give the corresponding Schiff bases which were reduced at the C=N bond and the aldehyde group. ^{14}C-Labelled glucosamine was also condensed with ruthenocenecarbaldehyde to give the corresponding labelled amino sugar derivative of ruthenocene [289].

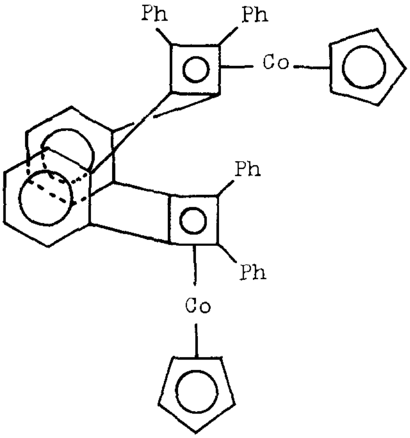
The metabolism of ruthenocene derivatives of amino-sugars labelled with ^{103}Ru has been investigated. The derivatives were concentrated in the kidney and liver of tumour-bearing mice and excretion was rapid as the unmetabolized amino-sugar. The stability of the ruthenocene group was demonstrated by these results [290].

16. $(\eta\text{-}C_4H_4)Co(\eta\text{-}C_5H_5)$

Dicarbonyl(η-cyclopentadienyl)cobalt combined with 1,2-bis(phenylethynyl)benzene (16.1) to form 1,2,4-triphenyl-3-(*o*-phenylethynylphenyl)biphenylene as the major product together with the (η-cyclobutadiene)cobalt and (η-cyclopentadienone)cobalt



16.1



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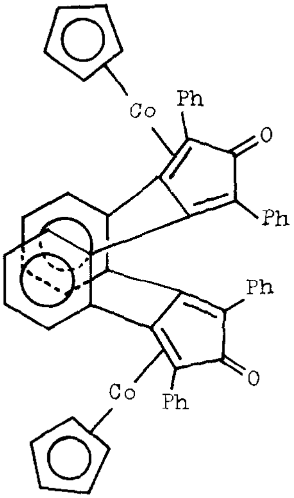
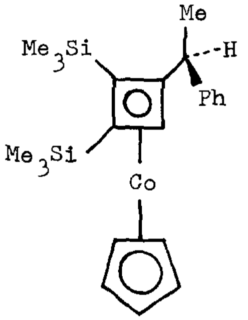


16.3

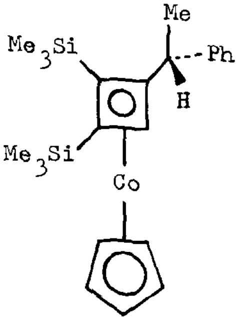
complexes (16.2 and 16.3) respectively. The structure of the (η-cyclobutadiene)cobalt complex (16.2) has been confirmed by X-ray crystallography. The related reaction of dicarbonyl-(η-cyclopentadienyl)rhodium and the ligand (16.1) was reported [291].

Coupling constants, $^1J(C_1-C_2)$ and $J(C_2\text{-H})$ have been obtained by ^{13}C NMR spectroscopy for (η^4-diphenylmethoxycyclobutadiene)-tricarbonylcobaltium hexafluorophosphate. The value obtained for the former was the lowest reported for 1-bond coupling between trigonal carbon atoms. The value for the latter was high and was in accordance with values previously reported for substituted (η-cyclobutadiene)tricarbonyliron complexes [292].

High performance liquid chromatography has been used for the separation of closely related (η-cyclobutadiene)-



16.4



16.5

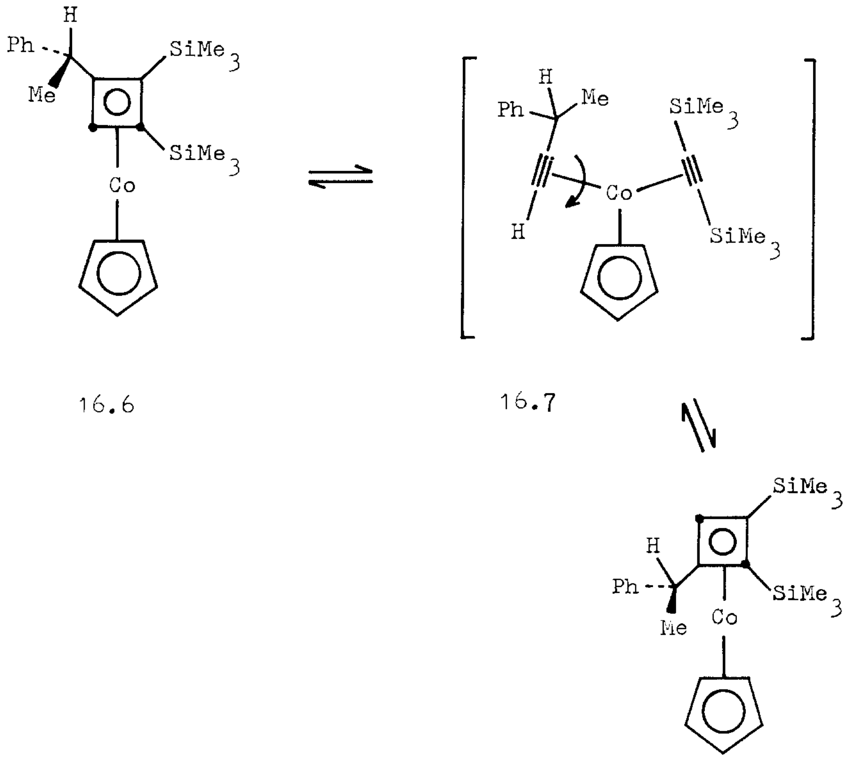
(η-cyclopentadienyl)cobalt complexes such as diastereoisomers and structural isomers. Reversed phase chromatography has been used with octadecylsilyl-modified silica as a stationary phase and polar mobile phases saturated with argon. Thus the diastereoisomers (16.4 and 16.5) which were inseparable by TLC were conveniently separated using acetonitrile/water (9/1) [293, 294].

Cyclic voltammetry and polarography have been used to show that (η-cyclobutadiene)(η-cyclopentadienyl)cobalt underwent reversible electrochemical oxidation [295].

The mechanism of formation of η^4-cyclobutadiene-metal compounds, by the interaction of transition metal complexes with alkynes, has been investigated. Compounds of the type (16.6 and 16.8) were subject to flash vacuum pyrolysis and extensive equilibration between these two compounds was observed. From the results it was concluded that the cobalt complexes (16.6 and 16.8) reversibly isomerized through the intermediate (16.7) by single alkyne rotation [296].

Gas phase rearrangement of the (η-cyclobutadiene)cobalt complex (16.9; $R^1 = R^2 = SiMe_3$, $R^3 = R^4 = C{\equiv}CH$) gave the product (16.9; $R^1 = R^2 = C{\equiv}CSiMe_3$, $R^3 = R^4 = H$). It was considered that the corresponding rearrangement of the complex (16.9; $R^1 = R^2 = H$, $R^3 = R^4 = C{\equiv}CH$) could involve the intermediate (16.10) [297].

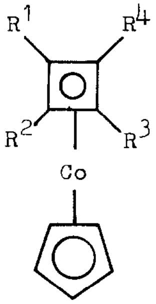
The treatment of the η-tetraphenyl-cobalt complex (16.11) with lithium tetrachloropalladate(II) in the presence of sodium acetate gave the ortho-palladated compound (16.12). The reactions of this latter compound with carbon monoxide and



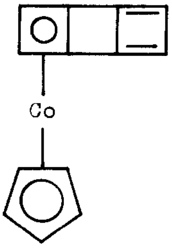
16.6

16.7

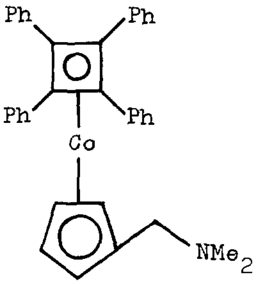
16.8



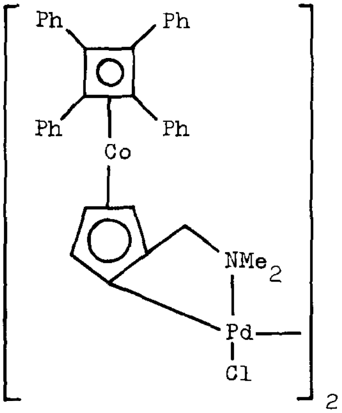
16.9



16.10



16.11



16.12

olefins were examined [298].

A complete product analysis for the reaction of dicarbonyl-(η-cyclopentadienyl)cobalt with 1,6-bis(trimethylsilyl)-1,5-hexadiyne has been carried out. Eighteen metal complexes were characterized and these were formed by oligomerization of the diyne to give mixed cyclobutadienes, cyclopentadienones and biscarbyne clusters [299].

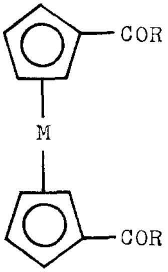
(η^4-Cyclooctadiene)- and (η^4-cyclooctatetraene)-(η-cyclopentadienyl)cobalt have been investigated electrochemically. For both the complexes the 1,5-bonded isomer was thermodynamically more stable in the neutral compounds and less stable in the anions on reduction [300].

17. $(\eta\text{-}C_5H_5)_2Co$ and $[(\eta\text{-}C_5H_5)_2Co]^+$

Cobaltocene has been obtained in 52% yield by heating cyclopentadiene with cobalt(II) ethoxide and diethylamine [301]. In a similar preparation cobalt(II) ethoxide was treated with cyclopentadiene in the presence of sodium cyclopentadienide [302].

Reaction of sodium cyclopentadienide with ethyl formate, methyl acetate or methylcarbonate afforded the substituted sodium cyclopentadienide derivatives (17.1; R = H, Me and OMe) respectively. Reaction of the organosodium reagents (17.1; R = Me, OMe) with cobalt(II) chloride or nickel(II) bromide produced the corresponding cobaltocene and nickelocene

17.1



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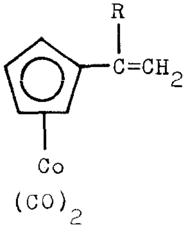
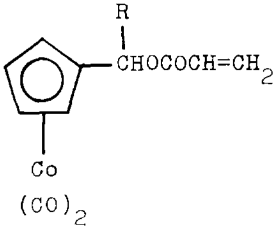


17.3

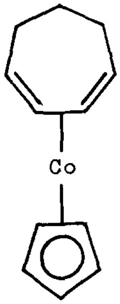


17.4

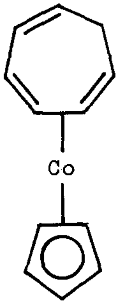
derivatives (17.2; M = Co, Ni; R = Me, OMe). The sodium cyclopentadienide derivatives (17.1; R = H, Me, OMe) were used as precursors in the preparation of the new organometallic monomers (17.3 and 17.4) [303, 304].

The reaction of dicarbonyl(η-cyclopentadienyl)cobalt with cyclohepta-1,3-diene and cyclohepta-1,3,5-triene gave the corresponding cobalt complexes (17.5 and 17.6). Hydride abstraction from complex (17.5) or protonation of complex (17.6) gave the stable cation (17.7). Proton abstraction from complex (17.6) with n-butyllithium produced the anion (17.8) [305].

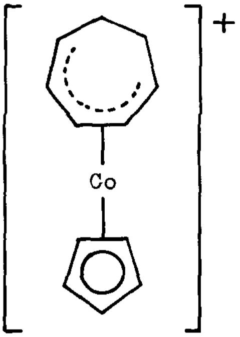
Reaction of dicarbonyl(η-cyclopentadienyl)cobalt with 1,4- or 1,3-cyclohexadiene gave the (η^4-1,3-cyclohexadiene)-cobalt complex (17.9). Hydride abstraction produced the dication



17.5



17.6



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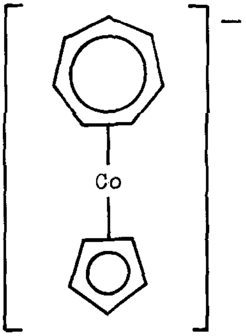
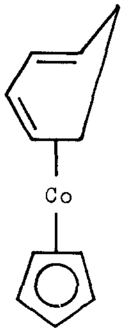


17.8

(17.10). Treatment of the dication (17.10) with sodium methoxide or sodium cyclopentadienide gave double, vicinal and stereospecific (<u>exo</u>) addition to the benzene ring in accord with the Davies-Green-Mingos rules [306].

The photolysis of (η-C_5H_5)Co(CO)$_2$ in an aromatic solvent such as benzene or toluene afforded the corresponding (η-C_5H_5)Co(η-arene) and (η-C_5H_5)Co(η-arene)$_2$ complexes. The benzene complex (η-C_5H_5)Co(η-C_6H_6) combined with 2-butyne to give the hexamethylbenzene derivative (η-C_5H_5)Co(η-C_6Me_6) but failed to catalyse the formation of free hexamethylbenzene from an excess of 2-butyne [307].

Decamethylcobaltocene has been prepared from ($MeOCH_2CH_2OMe$)-$CoBr_2$ and lithium pentamethylcyclopentadienyl and it readily underwent reaction with the electrophiles RX (MeI, PhI, $ClCH_2I$,



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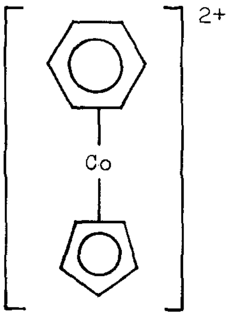
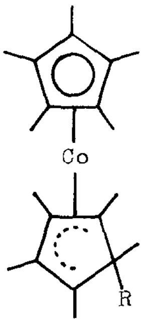


17.10

MeOCH$_2$Cl, MeCHClI) to give the products of oxidative addition (17.11). This reaction with the chloroiodoalkanes gave the corresponding exo-chloroalkyl derivatives (17.11) and these compounds underwent solvolytic ring expansion to form the η-cyclohexadienyl cations (17.12; R = H, Me) [308].

The η^4-cyclopentadiene compounds (17.13; R^1 = Ph, Me; R^2 = Me) rearranged when heated in methylcyclohexane to give the corresponding cobalt complexes (17.13; R^1 = H, R^2 = Ph, Me). Treatment of these complexes with ammonium hexafluorophosphate or triphenylmethyl hexafluorophosphate produced the corresponding cobaltocenium salts (17.14; R = Ph, Me) [309].

Several reactions of di(η-cyclopentadienyl)dicobalttetraiodide have been reported including reduction with sodium amalgam to form cobaltocene [310].



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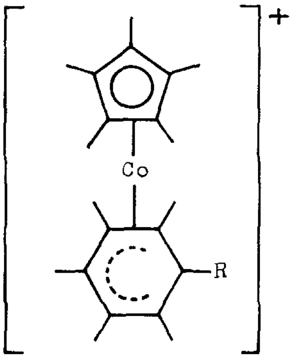

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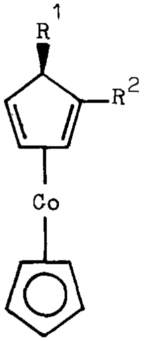

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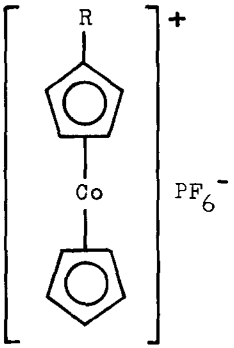
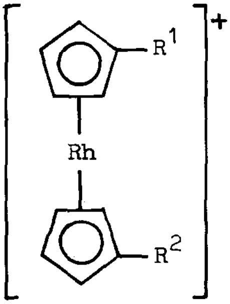


17.14

Thallium-cyclopentadienide and -methylcyclopentadienide were treated with rhodium(III) chloride to give the rhodocenium cations (17.15; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = R^2 = Me$). Oxidation of the latter two complexes with potassium permanganate produced the corresponding acids which were converted to the acid chlorides (17.15; $R^1 = H$, $R^2 = COCl$; $R^1 = R^2 = COCl$). Treatment of the acid chlorides with sodium azide gave the amides (17.15; $R^1 = H$, $R^2 = CONH_2$; $R^1 = R^2 = CONH_2$) [311].

The reaction of tetraacetatodirhodium with pentakis-(methoxycarbonyl)cyclopentadiene unexpectedly produced the rhodocenium salt (17.16) where two of the CO_2Me groups in each ring had been replaced by H. The structure of the salt (17.16) was determined by X-ray analysis. Both the C_5-rings were η^5-bonded and they were fully staggered which allowed the bulky



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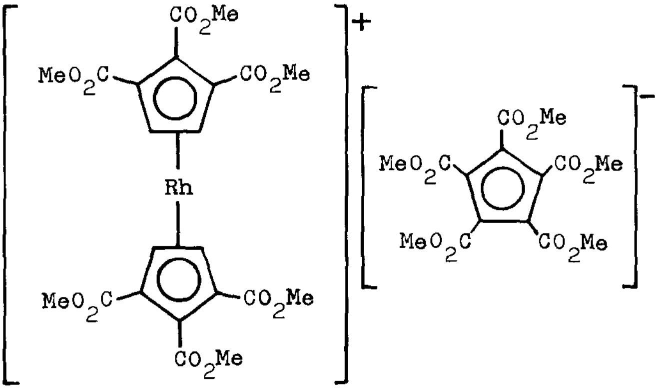
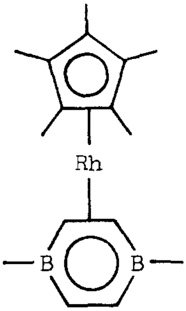


17.16

CO_2Me groups to intermesh [312].

Addition of the η-diborabenzene complex (17.17) to trifluoroacetic acid at -80 °C produced the triple-decked sandwich complex (17.18; n = 2) in high yield. This thirty valence electron complex was electrochemically reduced to the corresponding singly charged 31 electron cation (17.18; n = 1) [313].



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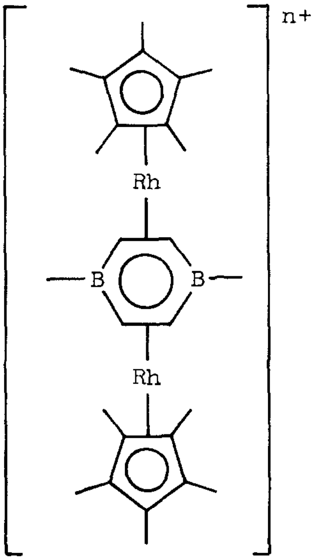
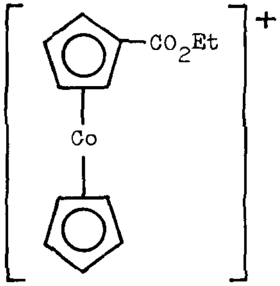


17.18

The ^1H and ^{13}C NMR spectra of a series of sym-methylcobaltocenium hexafluorophosphates have been recorded and interpreted. The spectra were compared with those of the ferrocene analogues. It was concluded that the distribution of electron density over the metallocene molecules was dominated by the central metal atom [314].

Electrochemical reduction of the cobaltocenium cation (17.19) in acid solution gave the hydroxymethylcobaltocenium cation (17.20) isolated as the tetraphenylborate salt in 60% yield [315].

Attack of the cobaltocenium cation with methyl- or phenyllithium gave the corresponding exo-substituted (η-cyclopentadiene)cobalt complexes (17.21; R = Me, Ph) which underwent endo-hydride abstraction with triphenylmethylium tetrafluoroborate to give the substituted cobaltocenium cations (17.22; R = Me, Ph) respectively [316].



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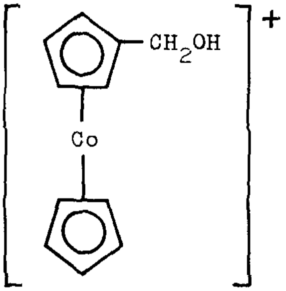
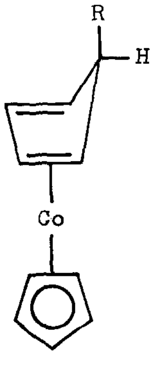


17.20

Cobaltocenium halides were prepared by oxidizing cobaltocene with 0.01-0.03 M bromine or iodine in a hydrocarbon-tetrahydrofuran solvent mixture at 0-5 ° in an inert atmosphere [317].



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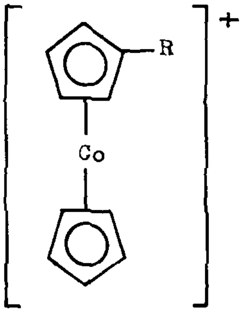


17.22

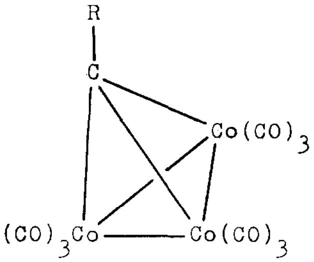
The intercalation compound $Zr(HPO_4)_{1.5}(PO_4)_{0.5}[(\eta-C_5H_5)_2Co]_{0.5}$ has been obtained by treatment of cobaltocene with $Zr(HPO_4)_2.H_2O$ [318].

Nesmeyanov and co-workers have reported a method for improving the strength and yield of 1,1'-diacetylcobaltocenium hexafluorophosphate copolymers [319].

Mercaptoorganosiloxanes were used, with cobaltocene as catalyst, to prepare one-package sealing compositions which were stable in the absence of oxygen and were cured in the presence of oxygen [320].

18. Cobalt-carbon Cluster Compounds

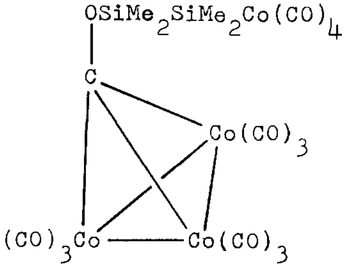
The cobalt-carbon cluster compounds [18.1; R = CH_2CO_2Me, $CH(CO_2Me)_2$] were formed unexpectedly by the reaction of methyl acetylenecarboxylate or di(methyl) acetylenedicarboxylate with $Co_2(CO)_8$ [321].



18.1

Prolonged reaction of sodium tetracarbonylcobaltate with $(ClMe_2Si)_2$ gave the cobalt cluster compounds (18.2 and 18.3) [322].

The alkylidynecobalt nonacarbonyl complexes (18.4; X = Cl, Br, H) have been prepared in a one step process. Cobalt(II) nitrate in aqueous ammonia was reduced with sodium dithionite under an atmosphere of carbon monoxide at room pressure in the presence of a benzene solution of the halocarbon containing cetyltrimethylammonium bromide as the phase transfer catalyst.



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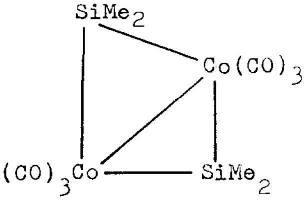

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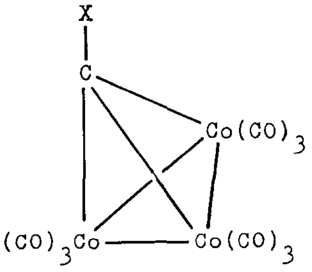

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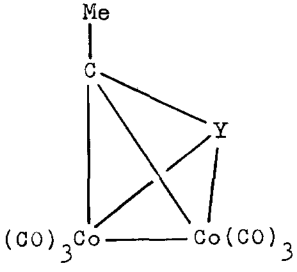


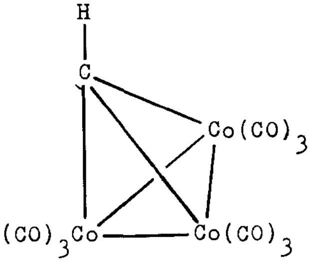
18.5

The cobalt cluster complex was isolated from the organic layer after two hours [323].

An unsuccessful attempt has been made to prepare alkylidynetrirhodium complexes by the reaction of $Na[Rh(CO)_2(PPh_3)_2]$ with halocarbons. The major product was $RhX(CO)(PPh_3)_2$, where $X = Cl, Br$ [324].

The methyl substituted cluster complex [18.5; $Y = Co(CO)_3$] has been treated with (η-cyclopentadienyl)metal carbonyls to give the derivatives [18.5; $Y = Mo(\eta\text{-}C_5H_5)(CO)_3$, $W(\eta\text{-}C_5H_5)(CO)_3$, $Fe(\eta\text{-}C_5H_5)CO$, $Ni(\eta\text{-}C_5H_5)$] [325].

Treatment of the cobalt complex (18.6) with the hydrides R_3MH ($M = Si$, $R_3 = Me_3$, Ph_3, Me_2Cl, $MePhCl$; $M = Ge$, $R_3 = Ph_3$, Et_3, Ph_2Cl, Et_2Cl) produced the corresponding silicon and germanium derivatives (18.7). Alcoholysis of chlorosilane



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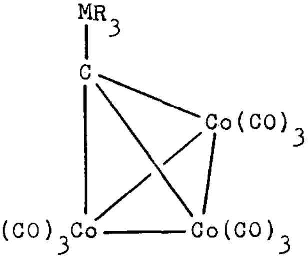
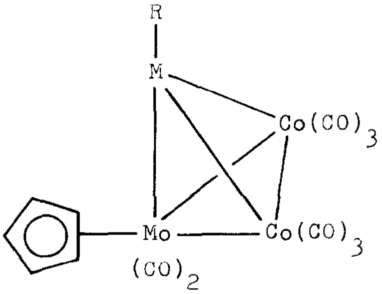


18.7

derivative (18.7; MR_3 = SiMePhCl) gave the corresponding alkoxy derivatives. These alkoxy compounds underwent reaction with i-Bu_2AlH or Et_2OBF_3 to give the corresponding silicon hydride or fluoride [326].

The silicon- and germanium-cluster complexes (18.8; M = Si, Ge, R = Me, Ph) have been formed by metal exchange with a preformed cluster or by synthesis from dicobalt octacarbonyl and (η-C_5H_5)$(CO)_3MoSiH_2Me$ [327].

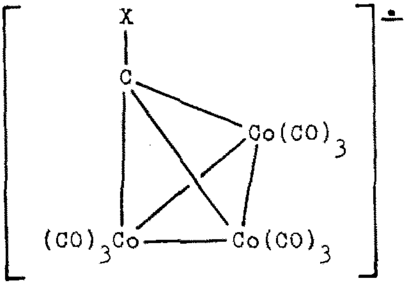


18.8

The crystal and molecular structure of the methylidyne-nonacarbonyltricobalt cluster complexes (18.4; X = Cl, $C_6H_2Me_3$) have been determined by X-ray crystallography. The chloro complex (18.4; X = Cl) shows the expected structure while the mesityl complex (18.4; X = $C_6H_2Me_3$) shows interaction between the o-methyl group of the substituent and the neighbouring carbonyl ligands forcing the latter into the Co_3-plane and imparting some bridging character [328].

Ultraviolet photoelectron spectra and molecular orbital calculations on the cobalt complexes (18.1; R = H, Me, OMe, Cl, Br, I) have been reported. It was suggested that the apical carbon was electron rich and that the π-system was sufficiently flexible to behave as either a donor or acceptor. It was concluded that the CR group was best described as sp hybridized [329].

The He(I) photoelectron spectra of the cobalt cluster complexes (18.4; X = F, Cl, Me) have been measured and interpreted on the basis of qualitative arguments. The results were consistent with the interpretation of the cluster as an electron



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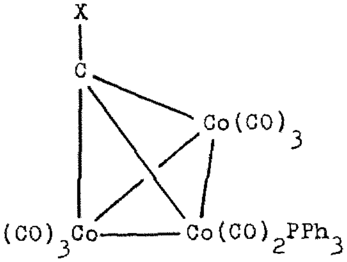
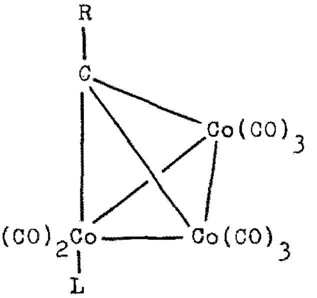


18.10

sink which underwent π-interaction with the substituent X [330].

The radical anion cluster complex (18.9; X = Ph, Cl) was obtained by electrochemical reduction and underwent nucleophilic substitution with phosphines and phosphites to form products such as the triphenylphosphine (18.10) [331].

Treatment of the tricobalt clusters [18.11; R = $CONMe_2$, Cl, H, Ph, Me; L = CO, PMe_3, $P(OMe)_3$] with Me_2AsNMe_2 gave intermediate substitution products which were highly susceptible to hydrolysis and derivatives (18.12) of the bidentate ligand $(Me_2As)_2O$ were isolated. The same compounds (18.12; L = CO) were obtained by direct substitution of the cobalt clusters (18.11; L = CO) by $(Me_2As)_2O$ together with the corresponding di- and tri-substituted products [332].



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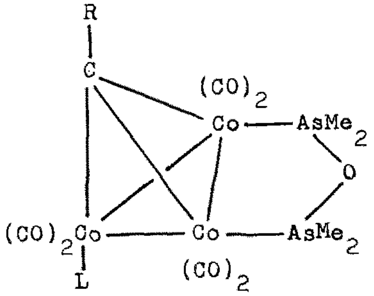

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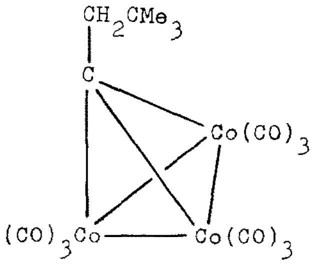

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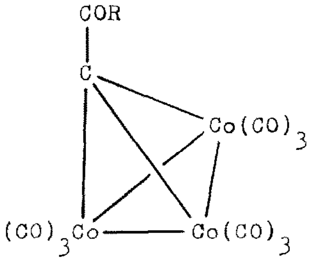
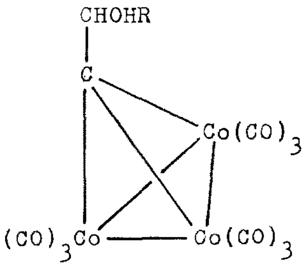


18.14

The cobalt cluster compound (18.13) underwent reaction with hydrogen in aromatic solvents to give 3,3-dimethylbutene, 2,2-dimethylbutane and 4,4-dimethylpentanal. The hydrogenation was inhibited by the presence of carbon monoxide [333].

Acyl- and aroyl-methylidynetricobaltnonacarbonyl cluster complexes (18.14; R = H, Me, Et, Bu^n, 4-Br.C_6H_4, 4-Cl.C_6H_4, 4-F.C_6H_4, 4-Me.C_6H_4, Ph) underwent reduction with hydrogen in refluxing benzene to give either the α-hydroxyalkylidyne complexes (18.15) or the completely reduced alkylidyne complexes (18.16) or in some cases a mixture of the two products. When the reagent was trifluoroacetic acid then the alkylidyne clusters (18.16) were the exclusive products. Thermal decarbonylation of the complexes (18.14) gave the corresponding alkyl- and aryl-methylidyne cluster complexes (18.1; R = Et, Bu^n, Pr^i, 4-Br.C_6H_4,



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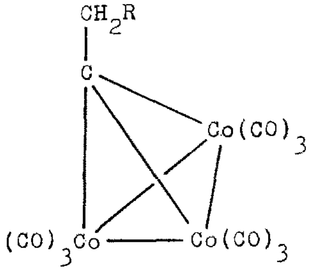
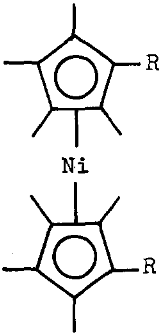


18.16

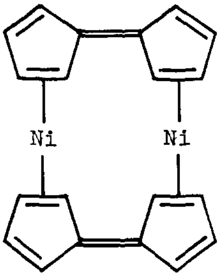
$4\text{-Cl.}C_6H_4$, $4\text{-F.}C_6H_4$, $4\text{-Me.}C_6H_4$, Ph, $4\text{-Me}_2N.C_6H_4$, ferrocenyl, 2-pyrrolyl) [334].

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

The nickelocenes (19.1; R = H, Et) have been prepared by reaction of the corresponding lithium cyclopentadienide with nickel chloride. 1.65 THF 335 .



19.1



19.2

Treatment of nickel(II) chloride with bis(η-cyclopentadienyl)-magnesium gave nickelocene in 72% yield [336].

The cluster complex $(\eta\text{-}C_5H_5)_3Ni_3(CO)_2$ was degraded by heating with triphenylphosphine in THF to give a mixture of nickelocene, $(PPh_3)_3Ni(CO)$ and $(PPh_3)_2Ni(CO)_2$. The reaction mechanism was discussed [337].

The disordered phase of nickelocene at 295 °K was investigated by an X-ray diffraction study and compared with that of ferrocene. The results showed that the evolution of the disordered phase of nickelocene and ferrocene between 295° and 5 °K was different [338].

The structure of bis(η-fulvalene)dinickel (19.2) has been determined by X-ray crystallography. The C-C bond distances were found to show localization of multiple C-C bonding as in the neutral ligand [339].

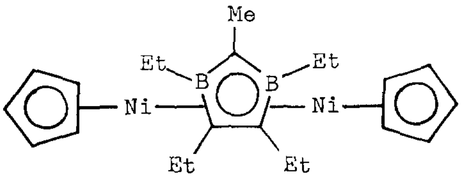
The collison free molecular multiphonon dissociation (MPD) and molecular multiphonon ionization (MPI) of nickelocene induced by the light of a tunable dye laser in the wavelength region 3750-5200 Å has been investigated. Four reactive processes were identified, two-photon molecular MPI for $\hbar\omega \geqslant$ 3.10 eV, 3-photon MPI for $\hbar\omega$ = 3.10-2.10 eV, 2-photon MPD for $\hbar\omega \geqslant$ 2.86 and 3-photon MPD for $\hbar\omega$ = 2.8-1.9 eV [340].

Multiphoton dissociation of nickelocene and ferrocene has been studied in effusive and in supersonic molecular beams. Mass spectrometric ion detection showed almost exclusive generation of bare metal ions produced by resonant and non-resonant mechanisms [341].

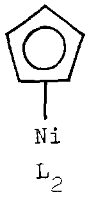
The Raman and infrared spectra (10-400 cm^{-1}) of nickelocene and ferrocene and the corresponding perdeuterated compounds have been recorded at 30-300 ^{o}K. The temperature dependence of the low frequency spectra (10-200 cm^{-1}) and quasi-elastic neutron scattering were discussed in terms of dynamic disorder which resulted from conformational fluctuations [342].

The ^{1}H, ^{11}B and ^{13}C NMR spectra of the paramagnetic triple-decker sandwich complex (19.3) have been recorded and analysed. The complex behaved like a metallocene and the unpaired electron was equally distributed over both nickel atoms [343].

The electrochemistry of nickelocene at 40 ^{o}C in an aluminium chloride-1-butylpyridinium chloride (BPC) melt has been studied. In neutral melts, 1:1 molar ratio $AlCl_3$:BPC, nickelocene underwent a reversible one-electron charge-transfer reaction with $E_{\frac{1}{2}}$ = -0.165 V vs. Al reference. Both nickelocene and the nickelocenium ion were found to be unstable in chloride rich solvents. In acidic melts, > 1:1 molar ratio $AlCl_3$:BPC, spontaneous oxidation to the nickelocenium ion was observed with reversible formation of a stable dication at $E_{\frac{1}{2}}$ = +0.912 V vs. Al.



19.3



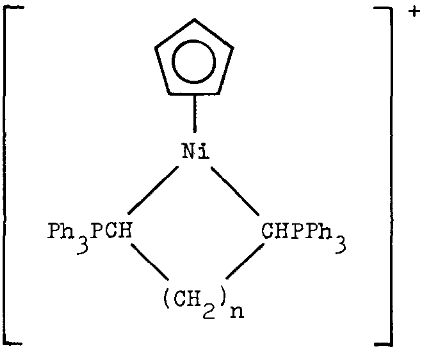
19.4

The electronic spectra of nickelocene species in the +2, +3 and +4 oxidation states have been obtained in the melts [344].

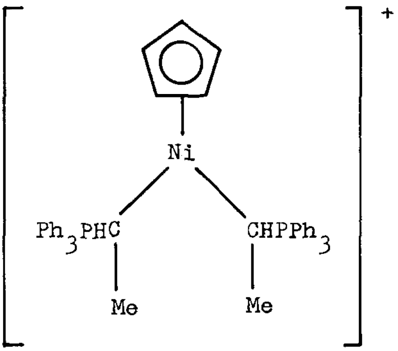
Nickelocene has been used in the preparation of the phosphine complexes [19.4; L = PPh_3, $Ph(n\text{-}Bu)_2P$, $PhMe_2P$, Ph_2MeP, $(n\text{-}Bu)_3P$, Et_3P; L_2 = diphos, o-phen, bipy]. The mechanism of substitution of nickelocene was discussed [345].

Reaction of nickelocene with the bis-ylids $Ph_3PCH(CH_2)_n$-$CHPPh_3$ (n = 1-3) gave the corresponding chelate complexes (19.5). Treatment of nickelocene with the mono-ylids ethylidenetriphenylphosphorane and triphenylphosphoniumcyclopentadienylid afforded the cations (19.6 and 19.7) respectively [346].

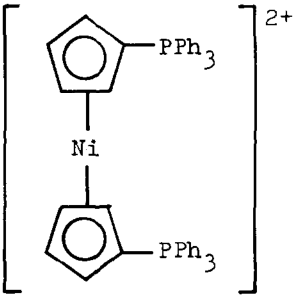
Reaction of nickelocene with $HP(O)(OR)_2$, (R = Me, Et) produced the corresponding nickelbis(phosphonate) complexes



19.5



19.6



19.7

$(\eta\text{-}C_5H_5)Ni\{[P(OR)_2O]_2H\}$ which contained a six-membered $NiPO_2H$ ring with a symmetrical O-H-O hydrogen bond [347].

The reaction of nickelocene with $Ru_3(CO)_{12}$ gave $[(\eta\text{-}C_5H_5)Ru(CO)_2]_2$, $\eta\text{-}C_5H_5NiRu_3(CO)_9$ and with $HRu(CO)_9C_2Bu^t$ the hydride $HRu_3(CO)_9C_2Bu^t$ [348].

$(\eta^2$-Alkenyl)$(\eta^5$-cyclopentadienyl)nickel complexes were prepared from nickelocene by treatment with alkenylmagnesium halides, isopropylmagnesium bromide and alkadienes or with methylenecycloalkanes [349].

λ^3-7-Phosphanorbornenes have been prepared by reduction of the corresponding phosphorus sulphides with nickelocene in the presence of propyl iodide [350].

Slocum and co-workers have demonstrated the potential of π-bonded organometallic polymers in catalyst design. The reaction of cobaltocene with the tetracyclone ligand produced (η-cyclopentadienyl)(η-tetracyclone)cobalt and the same reaction with nickelocene afforded bis(η-tetracyclone)nickel [351].

20. $(\eta\text{-}C_8H_8)_2U$

Activated uranium prepared by the reduction of uranium(IV) chloride with sodium-potassium alloy in dimethoxyethane, has been treated with cyclooctatetraene to form uranocene in 40% yield [352].

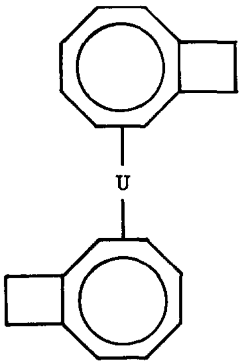
Uranocene has been prepared by treating uranium with cyclooctatetraene at room temperature. The thermal behaviour of uranocene was investigated. Between 575-680 °K it sublimed and above 680 ° decomposition occurred to give uranium and cyclooctatetraene [353].

Lithium hexaalkyluranate(IV) complexes combined with cyclooctatetraene to form uranocene in good yield [354].

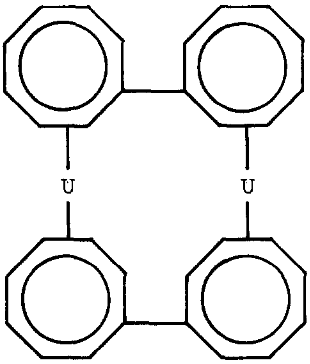
The substituted uranocene (20.1) has been prepared by the reaction of uranium(IV) chloride with the cyclobutenocyclooctatetraene dianion [355].

Bis(η-bicyclooctatetraenyl)diuranium, "biuranocenylene" (20.2) has been obtained, together with 1,1'-bis(cyclooctatetraenyl)uranocene, by treatment of bicyclooctatetraenyl with potassium in THF and then uranium(IV) chloride [356].

Uranocene has been reduced with lithium naphthalenide in tetrahydrofuran to give $[U(C_8H_8)_2]^-Li_n^+$.THF. NMR and ESR data



20.1



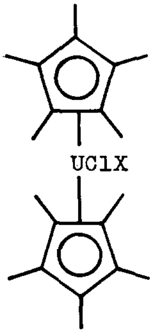
20.2

indicated that this anion had a sandwich structure and that U(III) was present [357].

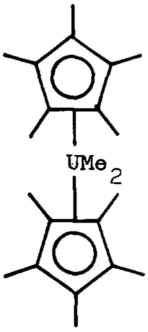
The reaction of uranocene with iodine gave $UC_{16}H_{12}I_4$ which could be sublimed under reduced pressure. The infrared spectrum of the product indicated the presence of a C-I bond and possible use of this compound for the preparation of ultra pure uranium was discussed [358].

Oxidative-addition takes place at uranium in the bis(η-pentamethylcyclopentadienyl)uranium complex (20.3; X = THF) with alkyl halides, such as Bu^nCl, $PhCH_2Cl$ and Me_3CCH_2Cl, to form the complexes (20.3; X = Cl, Bu^n, CH_2Ph, CH_2CMe_3). The stoicheiometrics of the reactions were examined [359].

The bis(η-cyclopentadienyl)uranium complex (20.4) was an effective hydrogenation and polymerization catalyst for alkenes [360].



20.3



20.4

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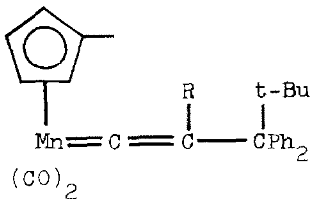

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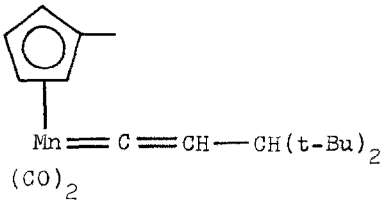

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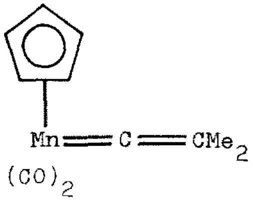

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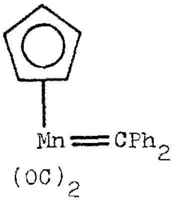

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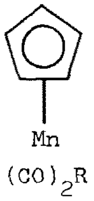

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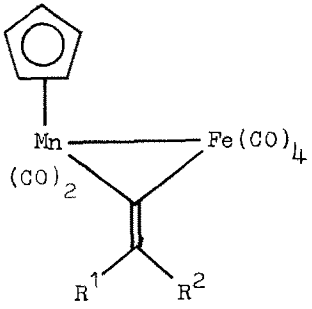
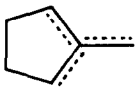


9.11

carbyne ligands CMe^+, $CSiMe_3^+$, CPh^+ and $CNEt_2^+$ and the metal-containing fragments $(\eta\text{-}C_5H_5)Mn(CO)_2$ and $Cr(CO)_5$ have been investigated by a nonparametrised molecular orbital method. Calculations were carried out on four carbyne complexes made from these fragments: $(\eta\text{-}C_5H_5)Mn(CO)_2CMe^+$, $(\eta\text{-}C_5H_5)Mn(CO)_2SiMe_3^+$, $(\eta\text{-}C_5H_5)Mn(CO)_2CPh^+$ and $(CO)_5CrCNEt_2^+$. It was concluded that the orientation of nucleophilic attack on these complexes seemed to be frontier controlled and that the gross positive charge of the substrate molecule enhanced its overall reactivity towards nucleophiles [159].

10. (η-Trimethylenemethane)Fe$(CO)_3$ Complexes

Molecular orbital theory has been used in a theoretical investigation of the energies of low lying electronic states in the 2-methylenecyclopentane-1,3-diyl ligand (10.1) [160].



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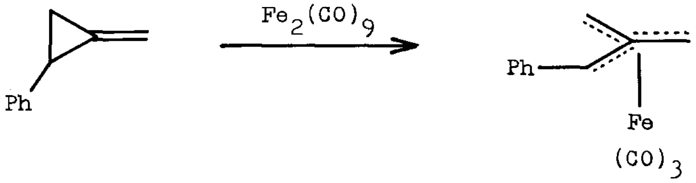

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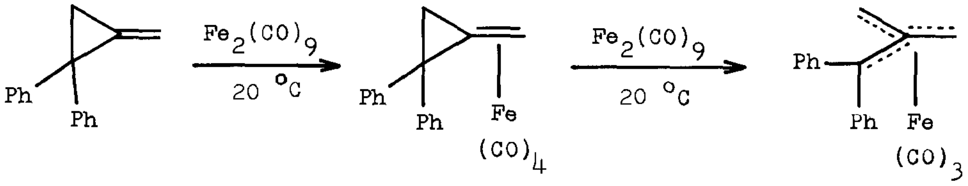


10.4

10.5

10.6

The stereochemistry of ring opening of 2-phenylmethylenecyclopropane (10.2) to tricarbonyl(η-phenyltrimethylenemethane)-iron (10.3) has been elucidated by stereospecific deuterium labelling. The reaction of 2,2-diphenylmethylenecyclopropane (10.4) with nonacarbonyldiiron gave the tetracarbonyliron complex (10.5), identified by X-ray crystallography, which underwent ring opening to form the (η-trimethylenemethane)iron complex (10.6). The stereochemistry of the reaction mechanism was shown to be consistent with frontier molecular orbital symmetry considerations [161].

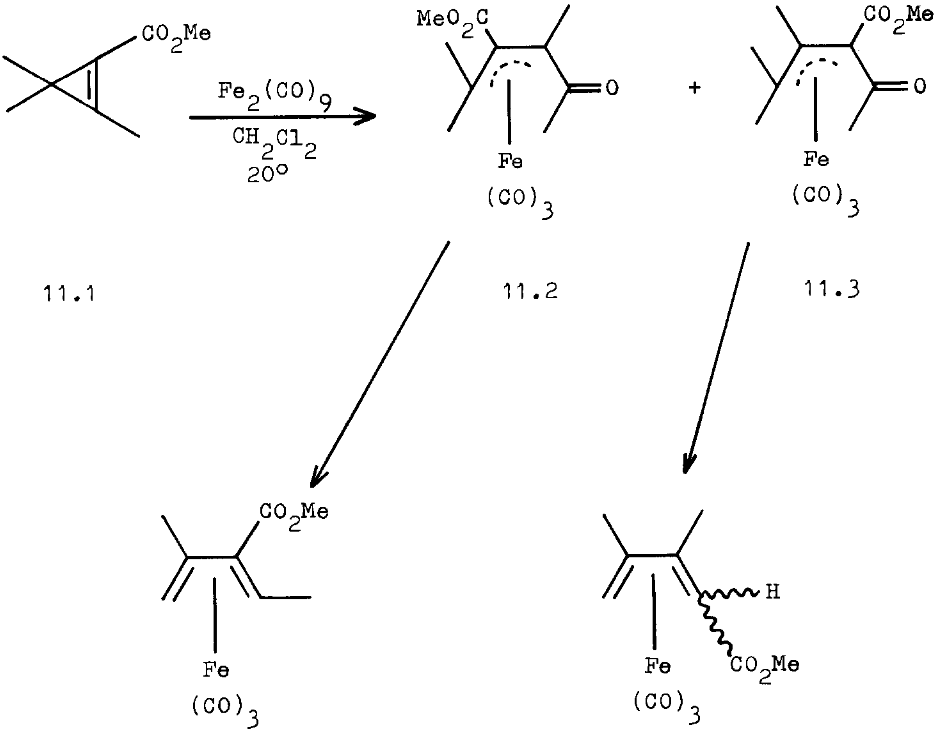
11. (Acyclic-η-diene)$Fe(CO)_3$ Complexes

UV irradiation of pentacarbonyliron with a mixture of 1,3-dienes and silanes gave mixtures of isomeric hydrosilylation products. The reaction proceeded by way of intermediate (η^3-anti-butenyl)tricarbonyliron-trialkylsilicon complexes which were accessible by photoinduced addition of R_3SiH to (η-butadiene)-tricarbonyliron and which on heating gave similar mixtures of isomeric butenyltrialkylsilicon derivatives [162].

Treatment of the cyclopropenic ester (11.1) with enneacarbonyldiiron led initially to the η-allylcarbonyl complexes (11.2 and 11.3). When these compounds were heated decarbonylation and hydrogen migration occurred to produce the tricarbonyliron complexes (11.4 and 11.5). From this and related work it was concluded that (η^3:η^1-allylcarbonyl)tricarbonyliron complexes were converted easily into (tricarbonyl)(η^4-diene)iron compounds whenever the possibility of hydrogen migration existed [163].

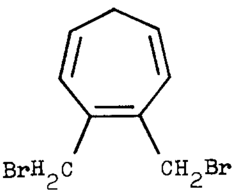
Reaction of the dibromide (11.6) with $Fe_2(CO)_9$ produced the (η-3,4-dimethylene-1,5-cycloheptadiene) complex (11.7). Treatment of the latter complex (11.7) with n-butyllithium followed by water, deuterium oxide or benzaldehyde gave the tricarbonyliron complexes [11.8; R = H, D, CH(OH)Ph] respectively [164].

Tricarbonyl(η-2-pyrone)iron combined with two nucleophiles in succession to form substituted (η-butadiene)tricarbonyliron complexes. Thus treatment with n-butyllithium and then methyllithium gave tricarbonyl[η-(2E,4E)-2,4-decadien-6-one]iron. Several reactions of this type were reported and a mechanism was proposed [165].



11.1 11.2 11.3

11.4 11.5



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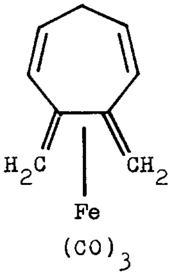

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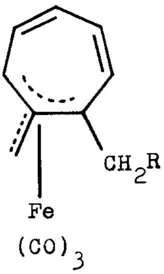
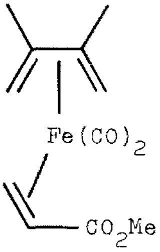


11.8

Irradiation of 2,3-dimethyl-1,3-butadiene with (η-CH_2=$CHCO_2Me$)$Fe(CO)_4$ gave the η^4-diene-iron complex (11.9). Reaction of the complex (11.9) with carbon monoxide at $\geqslant -30$ °
produced a mixture of the tricarbonyliron complexes (11.10; R^1 = H, R^2 = CO_2Me; R^1 = CO_2Me, R^2 = H) [166].



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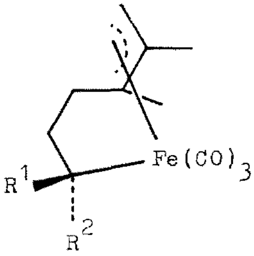
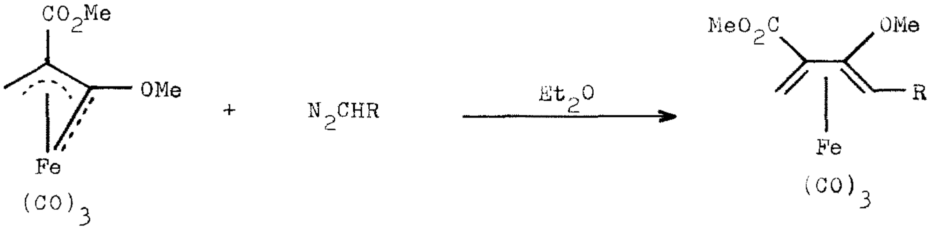


11.10

The (η^3-vinylcarbene)iron complex (11.11) was attacked by diazo compounds, N_2CHR, where R = H, CO_2Et, Ph, to form the (η-butadiene)iron complexes (11.12; R = H, CO_2Et, Ph). The mechanism appeared to involve insertion of the methylene group of the diazo reagent into the carbene carbon-iron bond [167].

The main product from the reaction of 2,3,5,6-tetrakis-(methylene)-7-oxabicyclo[2.2.1]heptane with $Fe_2(CO)_9$ was the bis(tricarbonyliron)complex (11.13). The structure of this complex was determined by X-ray analysis. The addition of



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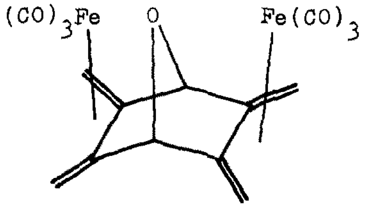

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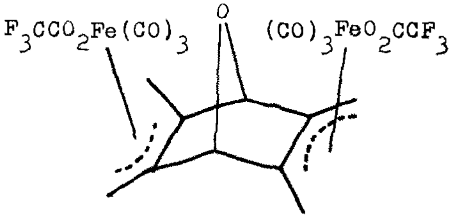


11.14

trifluoroacetic acid to the complex (11.13) gave initially a η^3-allyl complex then the <u>trans</u>-bis(η^3-allyl)isomer (11.14) with high regioselectivity [168].

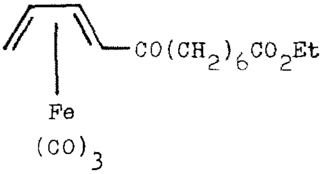
The electronic structure of the complexes (η-diene)$_2$Fe(CO), where diene = butadiene, dimethylbutadiene and 1,3-cyclohexadiene, has been investigated by He(I) photoelectron spectroscopy. The first seven bands in each spectrum were assigned using INDO calculations based on the ΔSCF procedure and the transition operator model. Bonding in the ground state of the parent complex (η-butadiene)$_2$Fe(CO), was discussed [169].

The natural isotope abundance ^{57}Fe NMR spectra of thirty-five organoiron complexes, principally cyclic and acyclic (η-diene)-Fe(CO)$_3$, have been measured at 2.9 MHz by direct detection. The ^{57}Fe chemical shift range observed was 3000 ppm and most resonances were at higher frequency than that of pentacarbonyliron which was used as a secondary standard. The ^{57}Fe shielding was discussed qualitatively in terms of charge distribution in the complexes with very large deshielding effects being observed for cationic olefinic ligands. The shielding in (η-diene)iron complexes was dependent upon ligand geometry and decreased with an increase in C-C-C bond angle or with an increase in ligand ring size [170].

Moessbauer spectroscopy was used to study the dynamic properties of (η-butadiene)tricarbonyliron films on exfoliated graphite [171].

The infrared and Raman spectra of (η-butadiene)- and (η-hexadeuterobutadiene)-tricarbonyliron have been recorded and interpreted [172].

Tricarbonyliron has been used as a protecting group for 1,3-dienes in the stereospecific synthesis of insect pheromones. Thus (η-butadiene)tricarbonyliron was treated with $ClCO(CH_2)_6CO_2Et$ and $AlCl_3$ under Friedel-Crafts conditions to form the (η-diene)-iron complex (11.15) which was converted to the acetate (11.16) in two steps. Decomplexation with trimethylamine N-oxide gave the free pheromone, (E)-9,11-dodecadienyl acetate, of the red bollworm moth. Several related pheromones were obtained in the same way [173].



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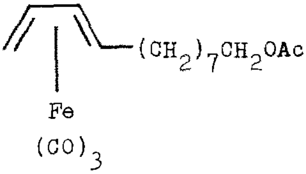
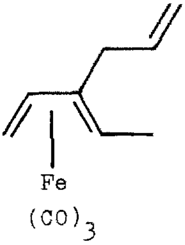


11.16

Cationic polymerization of the (η-butadiene)iron complex (11.17) with boron trifluoride etherate gave a methanol insoluble polymer while the monomer (11.18) obtained by thermal



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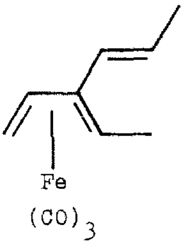


11.18

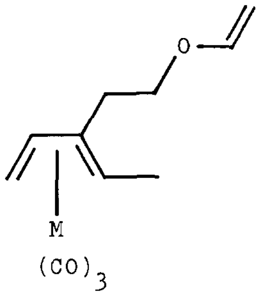
isomerization of the complex (11.17) was inert to cationic polymerization. Polymers derived from related (η-pentadiene)-iron and -ruthenium complexes were chemically modified to contain the η-allyl group and metal-metal bonds. 1,2-Polybutadiene and 3,4-polyisoprene combined with pentacarbonyliron and dodecacarbonyltriiron to yield polymers with (η-diene)iron groups in the main chain [174].

The (η-butadiene)-iron and -ruthenium complexes (11.19; M = Fe, Ru) have been prepared as monomers and were polymerized with cationic initiators to give high molecular weight polymers (11.20; M = Fe, Ru). These polymers were then protonated using dry hydrogen chloride to form (η-allyl)metaltricarbonyl groups [175].

The tricarbonyliron derivative (11.21) has been resolved and used to prepare the optically active complexes (11.22 and 11.23). These complexes were used to prepare chiral electrophilic cyclopropanes [176].

The carboxaldehyde complex (11.24) has been treated with hydroxylamines to form the nitrones (11.25; R = Me, Ph) which underwent 1,3-cycloaddition with olefins to form the corresponding isoxazolidine complexes [177].

The electronic effects in the tricarbonyl(η^4-diene)iron derivative (11.26) have been evaluated by pK_a measurements on this compound and on the uncomplexed diene ligand. The results



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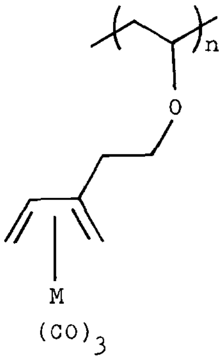

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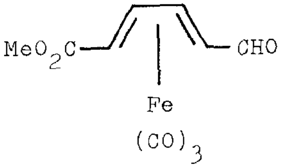

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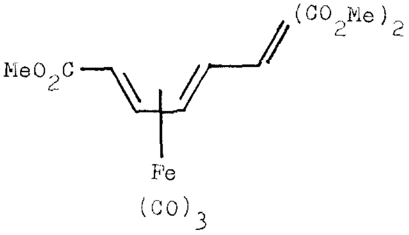

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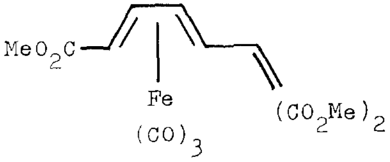
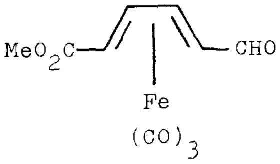


11.23

indicated that the $Fe(CO)_3$ group was electron releasing and that it reduced the electron-withdrawing properties of the diene system by disruption of the conjugation of the dienyl group with the aromatic ring [178].



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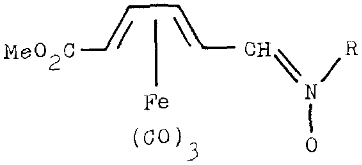

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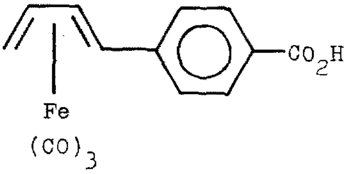
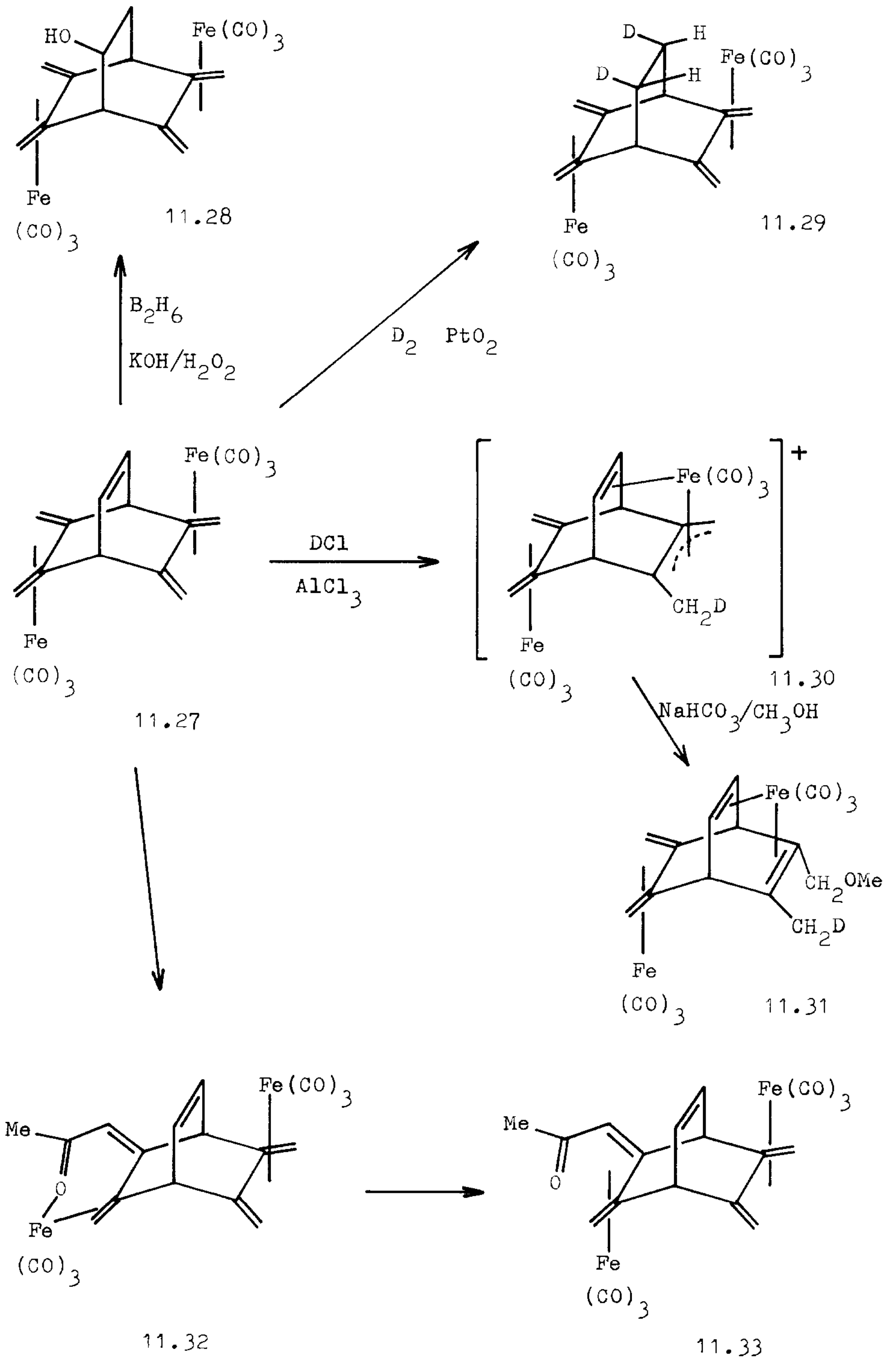


11.26

Enneacarbonyldiiron attacked the pentaene 5,6,7,8-tetrakis-(methylene)bicyclo[2.2.2]oct-2-ene in hexane-methanol to form the endo,exo-bis(tricarbonyliron) complex (11.27) and the structure of this complex has been determined by X-ray crystallography. The asymmetric arrangement of the two Fe$(CO)_3$ groups was used to induce either stereospecific functionalization of the uncoordinated endocyclic olefinic bond or stereo- and regiospecific functionalization of one of the two coordinated s-cis-butadiene groups of the complex. Thus hydroboration/oxidation of the complex (11.27) gave the endo,exo-bis(tricarbonyliron)-bicyclooctane-2-ol (11.28) while cis-deuteration was achieved with D_2/PtO_2 in hexane to form the endo, exo-complex (11.29). Protonation of the initial complex (11.27) with $HCl/AlCl_3/CH_2Cl_2$ gave the η^3-dienyl cation (11.30) which was quenched with $NaHCO_3/CH_3OH$ to form the tetraene complex (11.31) by 1,4-addition [179]. Stereospecific acetylation of the same complex (11.27) with $CH_3COCl/AlCl_3$ in dichloromethane afforded exclusively the endo-derivative (11.32) which isomerized in solution to the thermodynamically preferred form (11.33). The crystal and molecular structure of the complex (11.32) was confirmed by X-ray crystallography. Several related reactions were reported [180].

The acetolyses of the brosylates (11.34, 11.35 and 11.36) have been studied by ^{1}H NMR spectroscopy. The acetolysis of the complex (11.35) was too slow to detect and that of the complexes (11.34 and 11.36) occurred with retention of configuration. From the results it was concluded that homoconjugative stabilization of a carbocation by an exocyclic η-diene-Fe$(CO)_3$ group can compete with its destabilizing inductive effect [181].


HO
Fe(CO)3
Fe
(CO)3
11.28
D
H
D
H
Fe(CO)3
Fe
(CO)3
11.29
B2H6
KOH/H2O2
D2 PtO2
Fe(CO)3
Fe
(CO)3
11.27
DCl
AlCl3
Fe(CO)3
CH2D
Fe
(CO)3
+
11.30
NaHCO3/CH3OH
Fe(CO)3
CH2OMe
CH2D
Fe
(CO)3
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O
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(CO)3
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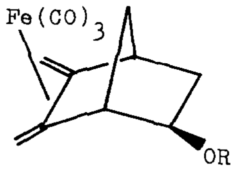

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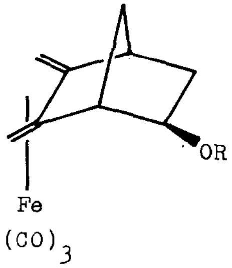

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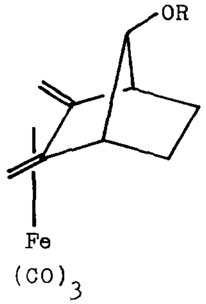
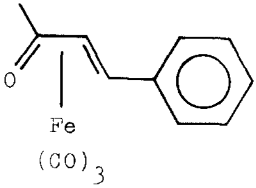


11.36

Reaction of the tricarbonyliron complex (11.37) with Me_2AsM [M = $Mn(CO)_4PMe_3$, $Fe(CO)_2(\eta\text{-}C_5H_5)$, $Mo(CO)_3(\eta\text{-}C_5H_5)$, $Mo(CO)_2(\eta\text{-}C_5H_5)PMe_3$, $W(CO)_3(\eta\text{-}C_5H_5)$, $W(CO)_2(\eta\text{-}C_5H_5)PMe_3$] gave, for example, the tetracarbonyliron complexes [11.38; M = $Mn(CO)_3PMe_3$, $Mo(\eta\text{-}C_5H_5)(CO)_2$], (11.39) and $(\eta\text{-}C_5H_5)(CO)_3WAs\text{-}Me_2Fe(CO)_3AsMe_2L$ [L = $Fe(CO)_2(\eta\text{-}C_5H_5)$, $Mo(CO)_2(\eta\text{-}C_5H_5)PMe_3$] [182].

The (η-butadiene)iron and (η-heterobutadiene)iron complexes (11.40; X = CH, N; L = CO, PPh_3, $AsPh_3$, $SbPh_3$) combined with 1,2-bis(diphenylphosphino)ethane (diphos) to form the derivatives $Fe(CO)_2$(diphos)diphos. A kinetic study of the reaction suggested an (η^1-butadiene)iron intermediate [183].

Friedel-Crafts acylation of the hexacarbonyldiiron complex (11.41) with acetyl chloride or benzyl chloride produced the corresponding tricarbonyliron complexes (11.42; R = Me, Ph) [184].



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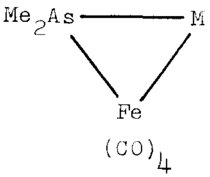

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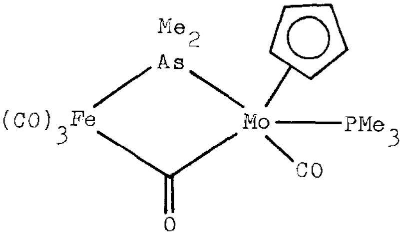

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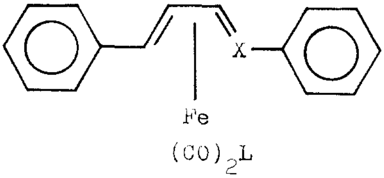

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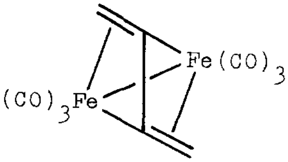

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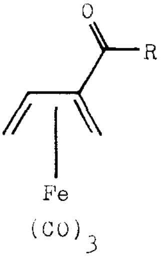

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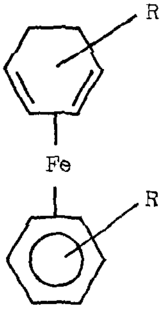
12. $(\eta\text{-}C_4H_4)Fe(CO)_3$

Cocondensation of arenes with iron atoms at -196 °C gave the complexes $Fe_x(arene)_y$ which combined with hydrogen to form the mixed (η-arene)(η-cyclohexadiene)iron complexes (12.1; R = H, Me, CMe_3, Me_3). When cyclopentadiene replaced hydrogen as the reagent then the (η-cyclohexadienyl)iron complexes (12.2; R = H, Me, CMe_3, Me_2) were formed [185].



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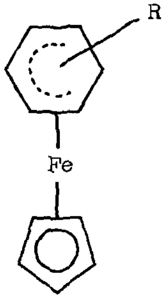
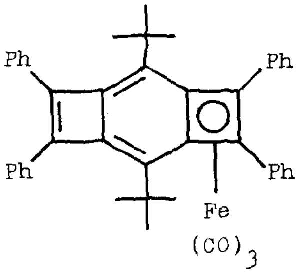


12.2

The reaction of 1,2-di-t-butyl-3,4,5,6-tetramethylbenzocyclobutadiene with nonacarbonyldiiron produced the two tricarbonyliron complexes (12.3 and 12.4). The structures of these complexes were confirmed by X-ray analysis [186, 187].

The crystal and molecular structure of tricarbonyl(η-1,2-di-t-butyl-3,4,5,6-tetramethylbenzocyclobutadiene)iron has been



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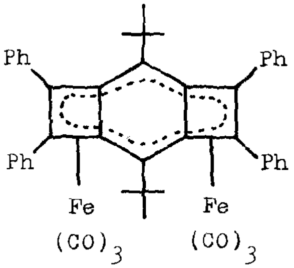


12.4

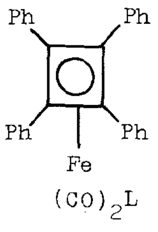
determined by X-ray analysis. The tricarbonyliron group was coordinated in a tetrahapto mode to the cyclobutadiene ring but the complex was not regarded as a pure cyclobutadiene complex because the iron was shifted away from the middle of the 4-membered ring due to the tendency of the benzene ring to retain some of its resonance energy [188].

Atom superposition and electron delocalization (ASED) molecular orbital theory has been used to determine a structure of tricarbonyl(η-cyclobutadiene)iron that was in close agreement with electron diffraction results [189].

The IR and Raman spectra of (η-cyclobutadiene)tetracarbonylmolybdenum in both the solid and liquid phases have been recorded and interpreted [190].

Photolysis of (η-butadiene)tricarbonyliron isolated in a carbon monoxide matrix at 12 °K gave tricarbonyl(η-cyclopentadienone)iron [191].

The (η-tetraphenylcyclobutadiene)iron complexes [12.5; L = PPh_3, $P(OMe)_3$] underwent reversible one-electron oxidation at a platinum electrode in dichloromethane to form the corresponding paramagnetic radical cations [12.6; L = PPh_3, $P(OMe)_3$]. The same cations (12.6) were generated by oxidation of the complexes (12.5) with $AgBF_4$ and $[N(4\text{-}Br.C_6H_4)_4]PF_6$ in dichloromethane and were characterized as the tetrafluoroborate or hexafluorophosphate salts. The cations (12.6) were implicated as intermediates in the formation of the cation (12.7) from the corresponding neutral (η-tetraphenylcyclobutadiene)iron complex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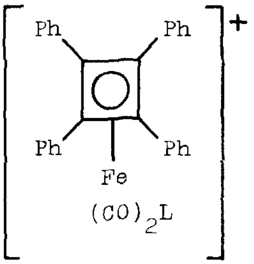
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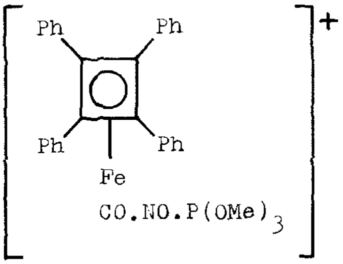
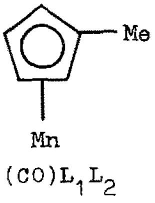

12.7

and silver nitrate and in similar oxidations. Several related reactions of iron and ruthenium complexes were reported [192].

Irradiation of monosubstituted tricarbonyl(η-cyclobutadiene)-iron complexes in the presence of propyne gave isomeric mixtures of substituted toluenes. The presence of electron-withdrawing groups on the metal complex produced mixtures rich in the ortho isomer while electron-releasing groups favoured the para isomer [193].

(η-Benzocyclobutadiene)dicarbonylnitrosyliron hexafluorophosphate was prepared by the reaction of (η-benzocyclobutadiene)-tricarbonyliron with nitronium or nitrosonium salts. The former complex underwent facile reaction with R_3M (M = P, As; R = Me, Ph) to afford the η-benzocyclobutenyliron complexes $[(R_3MC_8H_6)\text{-}Fe(CO)(NO)MR_3]^+PF_6^-$ by a two step process involving nucleophilic addition and carbonyl substitution. In the same thesis the mass spectra of the manganese complexes (12.8; L_1 = CO, L_2 = Ph_3P, Ph_3As, Ph_3Sb; L_1 = CS, L_2 = Ph_3P, Ph_3As, Ph_3Sb) were also discussed [194].



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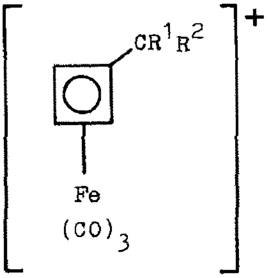


12.9

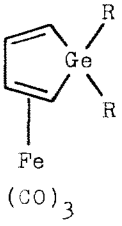
A Hammett-Deno indicator acidity study using trifluoroacetic acid-water solutions was used to determine $p\underline{K}_{R}{}^{+}$ values for a series of tricarbonyl(η-cyclobutadiene)iron carbocations (12.9; R^1 = H, Ph, Me, R^2 = Ph, p-MeC_6H_4, Me). These carbocations were less stable than the corresponding ferrocene systems but more stable than a variety of similar organic and organometallic carbocations [195].

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

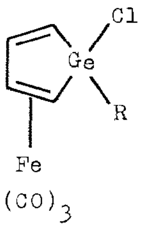
(i) Formation

Reaction of the acetylenes PhC≡CMPh$_3$ (M = Si, Ge, Sn, Pb) with Fe$_2$(CO)$_9$ gave the complexes η^4-LFe(CO)$_3$ where L = 2,5-bis(triphenylsilyl)-3,4-diphenyl-; 2,5-diphenyl-3,4-bis(triphenylgermyl)-; 2,4-bis(triphenylstannyl)-3,5-diphenyl- and diphenylbis(triphenylplumbyl)-cyclopentadienone respectively. The Ph$_3$M groups were removed by treatment with hydrochloric acid to give the corresponding tricarbonyl(η-diphenylcyclopentadienone)iron complexes [196].

The η-germacyclopentadiene-iron complexes (13.1, R = Et, Ph, *p*-MeC$_6$H$_4$, *p*-Me$_2$NC$_6$H$_4$, C$_6$F$_5$) have been prepared by reaction of the corresponding germacyclopentadiene with pentacarbonyliron. Treatment of the tricarbonyliron complexes (13.1, R = Me, CH$_2$Ph, *p*-MeC$_6$H$_4$, *p*-Me$_2$NC$_6$H$_4$) with tin tetrachloride gave the corresponding *exo*- chloro derivatives (13.2). Decomplexation of the η-germacyclopentadiene ligands was effected with Me$_3$NO and TiCl$_4$. Further reactions of the tricarbonyl(η-germacyclopentadiene)iron complexes were described [197].

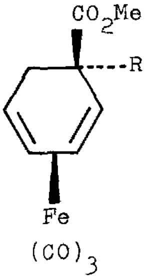


13.1



13.2

1,4-Cyclohexadienes with *gem*- substituents have been treated with pentacarbonyliron to form the corresponding (1,3-cyclohexadiene)iron complexes in order to elucidate directing effects in the reactions. Alkyl groups exerted classical steric hindrance while the CO$_2$Me group directed attack by forming an intermediate complex with the entering tricarbonyliron group. Thus the complexes (13.3; R = Me, Ph, CH$_2$Ph) were formed as the exclusive products by treatment of the corresponding 1,4-cyclohexadienes



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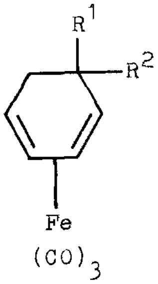
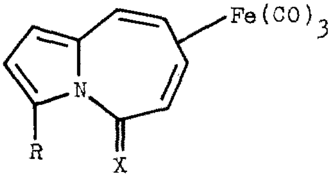


13.4

with pentacarbonyliron while the products (13.4; $R^1 = CO_2Me$, $R^2 = CH_2CO_2Me$; R^1 = Me, R^2 = Ph) were each obtained as mixtures of two stereoisomers [198].

The 3a-azoniaazulene complexes [13.5; R = H, CHO, $CH{=}CHCOCH_3$, $CH{=}C(COCH_3)_2$, X = O; R = H, X = CHCN and 13.6] were prepared in high yield by treatment of the free ligands with enneacarbonyl-



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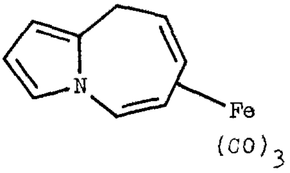

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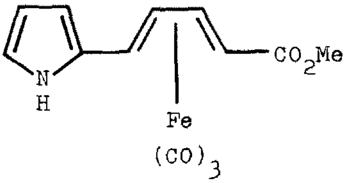
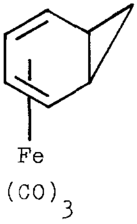


13.7

diiron. The tricarbonyliron complex (13.7) was prepared also [199].

Treatment of *syn*- or *anti*-tricyclo[3.2.0.0]hept-6-ene with nonacarbonyldiiron produced the corresponding tetracarbonyliron complexes. Reaction of these complexes with nonacarbonyldiiron produced the *anti*- and *syn*-norcaradieneiron complexes (13.8 and 13.9) respectively. When the complexes (13.8 and 13.9) were heated they both rearranged to give tricarbonyl(η^4- cycloheptatriene)iron [200].



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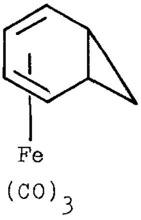


13.9

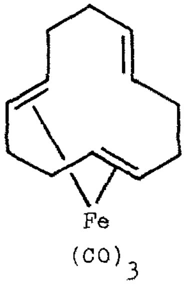
Thermal reaction of 1,5-cyclooctadiene with $Fe_2(CO)_9$ produced tricarbonyl(η-1,5-cyclooctadiene)iron [201].

1,5,9-Cyclododecatriene was heated with nonacarbonyldiiron in an ampoule and the tricarbonyliron complex (13.10) was isolated from a mixture of products [202].

Reaction of 1-phenyl- or 1-t-butyl-3,4-dimethylphosphole with the phosphole-iron complexes (13.11 and 13.12) respectively produced the corresponding dimers (13.13; $R^1 = R^2 = Ph$; $R^1 = R^2 =$ t-Bu; $R^1 = Ph$, $R^2 =$ t-Bu). The structure of the complex (13.13; $R^1 = R^2 = Ph$) was determined by X-ray analysis. The two phosphole rings adopted a head to tail disposition and they were strongly folded [203].

Bis(η^5-heptamethylindenyl)iron has been prepared from heptamethylindene and iron(II) chloride [204].

The (η-cyclohexadienyl)iron cation (13.14) underwent regioselective cyclopentylation with 1,2-bis(trimethylsiloxy)cyclopent-1-ene followed by dehydration and dehydrogenation with breakdown of the complex to form the 2-arylcyclopentenone (13.15). Several similar syntheses were reported [205].



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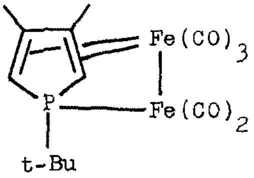

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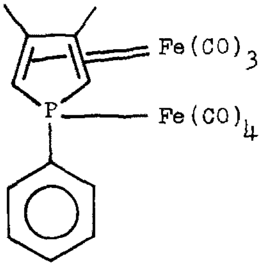

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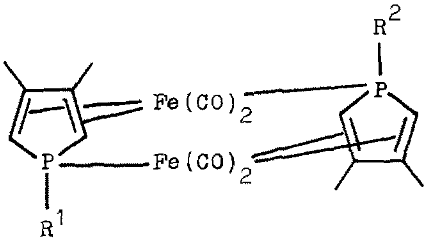
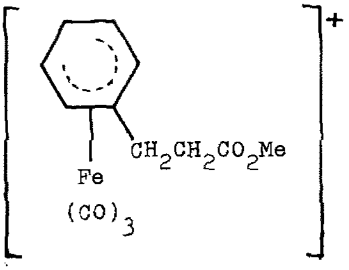


13.13

The rates of reaction of pentane-2,4-dione with a range of tricarbonyl(η^5-cyclohexadienyl)iron cations (13.16; R = H, Me, OMe) and for example (13.17; R^1 = Me, $R^2 = R^3$ = H; $R^1 = R^3$ = H, R^2 = Me; $R^1 = R^3$ = H, R^2 = OMe; R^1 = CO_2Me, $R^2 = R^3$ = H) have been obtained under pseudo-first-order conditions. The rates



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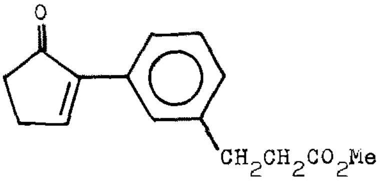

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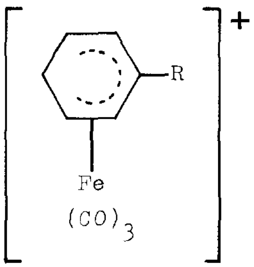

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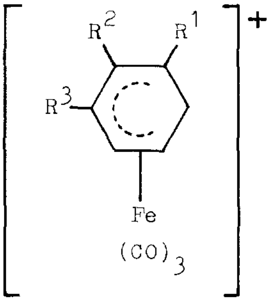
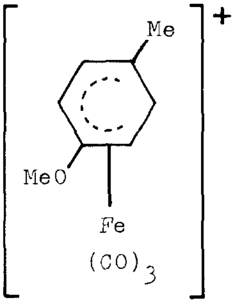


13.17

were affected by the nature of the substituent and by the position. For example, a 2-methoxy group caused retardation and a 3-methoxy group a slight acceleration [206].

The (η-cyclohexadienyl)iron cation (13.18) combined with enolate anions at the methylated dienylium terminus in a highly



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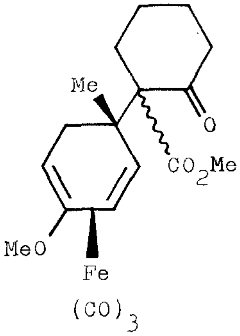

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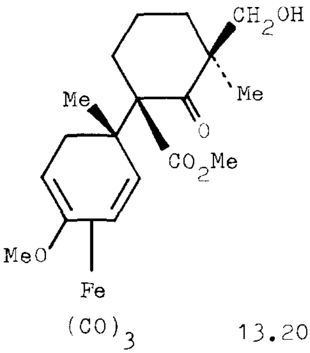
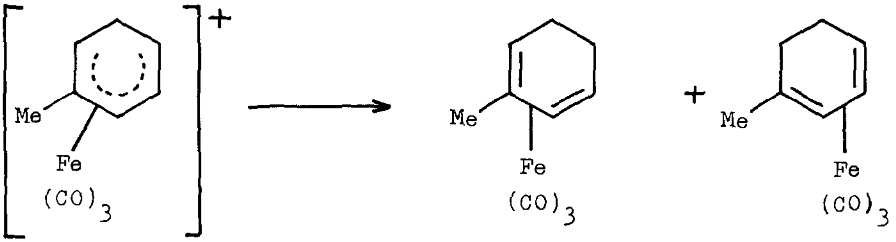


13.20

regioselective reaction which was of importance in steroid and terpene synthesis. Thus the enolate anion methyl 2-oxocyclohexanecarboxylate gave the product (13.19) in 97% yield. The complex (13.20) was obtained in the same way and X-ray crystallography was used to determine the crystal and molecular structure [207].

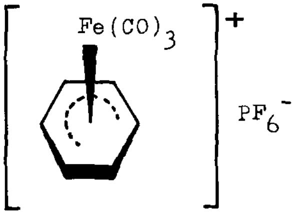
Reduction of the tricarbonyliron cation (13.21) to the cyclohexadiene complexes (13.22 and 13.23) by a series of metal hydrides became less regioselective at lower temperatures. In contrast reduction by 9-borobicyclononane became more regioselective as the temperature was lowered [208].



13.21 13.22 13.23

The absolute configuration of the salt (13.24) has been defined and it has been used for the asymmetric synthesis of the γ-disubstituted cyclohexenone (13.25) [209].

Alkylation of the (η-cyclohexadienyl)iron cations (13.26; R^1 = H, Me, OMe) with alkyllithiums, R^2Li, where R^2 = Me, Pr^i,



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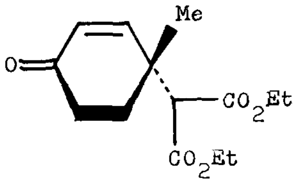

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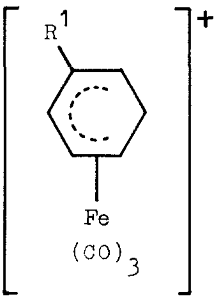

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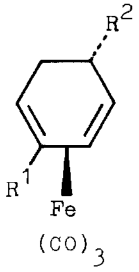

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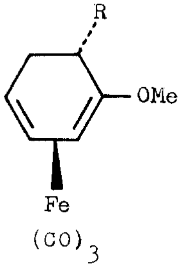


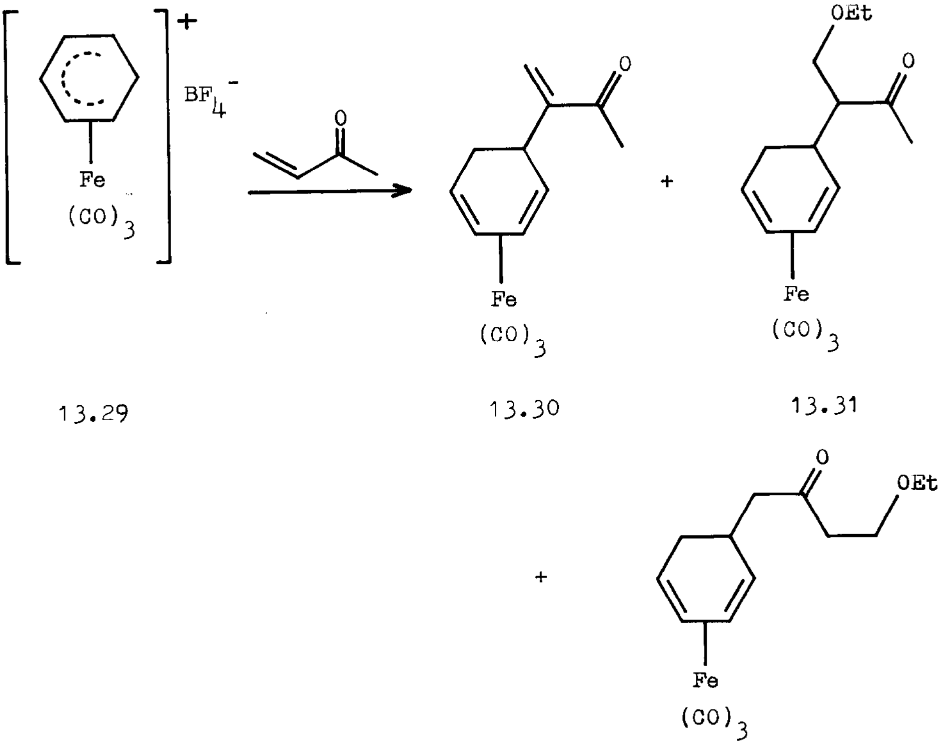
13.28

Bu^n, Bu^t, in chloroform at -78 °C gave the corresponding (η-cyclohexadiene)iron products (13.27; R^1 = H, Me, OMe; R^2 = Me, Pr^i, Bu^n, Bu^t). In addition to this product, the cation (13.26; R^1 = OMe) gave with Pr^iLi, Bu^nLi and Bu^tLi, the isomeric products (13.28; R = Pr^i, Bu^n, Bu^t) and the expected regioselectivity was not observed [210].

Tricarbonyl(η-cyclohexadienyl)iron tetrafluoroborate (13.29) was attacked by carbon nucleophiles to give addition products. Thus methylvinyl ketone gave a mixture of the ketones (13.30, 13.31 and 13.32) rather than the expected tricarbonyl-5-exo-(2-oxobut-3-enyl)cyclohexa-1,3-dieneiron. The anion of nitromethane also underwent addition to form a 5-exo-nitromethyl derivative [211].

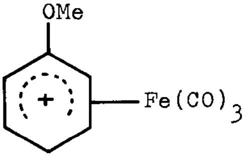
The cation (13.33) has been shown to be synthetically equivalent to the 5-cyclohex-2-enone cation. Treatment of the cation (13.33) with a variety of nucleophiles gave a mixture of isomers of the complex (13.34) and subsequent removal of the tricarbonyliron group produced the corresponding 5-substituted cyclohex-2-enone (13.35) [212].

Tricarbonyliron complexes have been used to provide a route to compounds containing the quaternary carbon atom corresponding to C-20 in Aspidosperma alkaloids. The (η-cyclohexadienylium)-iron cations (13.36; R = OAc, $O_3S.C_6H_4.Me$-4, phthalimido) were treated with $NaCH(CO_2Me)_2$ to give the (η-cyclohexadiene)iron complexes (13.37; R = OAc, $O_3S.C_6H_4.Me$-4, phthalimido) as the principal products. Decomplexation of the product (13.37; R = phthalimido) and treatment with aqueous methanolic oxalic acid gave the derivative (13.38) [213].



13.29 13.30 13.31

13.32



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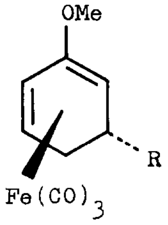

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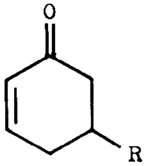
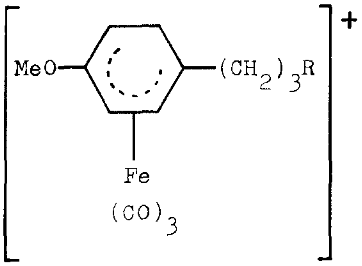


13.35

The cations $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$, where dienyl = C_6H_7, C_6H_6OMe-2 and C_7H_9, combined with *p*-toluidine in acetonitrile to form adducts such as the (η-cyclohexadiene)iron complex (13.39). A kinetic study of the reaction suggested that a two-step



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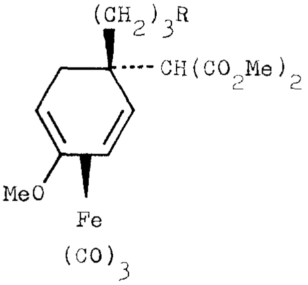

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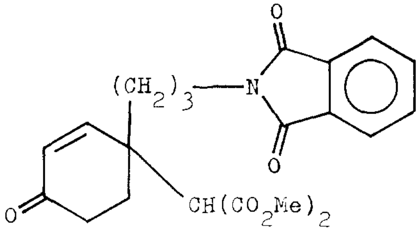

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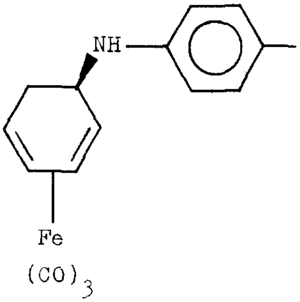
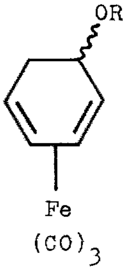


13.39

mechanism was operating with initial reversible addition of p-toluidine to the dienyl ring followed by rapid loss of a proton [214].

Tricarbonyl(η-cyclohexadienylium)iron tetrafluoroborate was attacked by anions, RO^-, to give the (η-cyclohexadiene)iron complexes (13.40; R = H, Me, Bu^t, Ph, $SiMe_3$) in addition to binuclear products. Yields were determined by the nature of the group R and the reaction conditions [215].

The cation (13.42) has been treated with 1,3,5-, 1,2,3-, 1,2,4-trimethoxy- and 1,3- and 1,4-dimethoxy-benzene to give the corresponding η-diene complexes. For example, 1,2,4-trimethoxybenzene gave the tricarbonyliron derivative (13.41). Rate data were obtained for these reactions and were interpreted in terms



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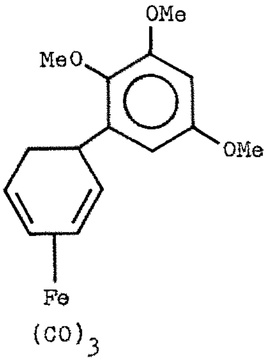
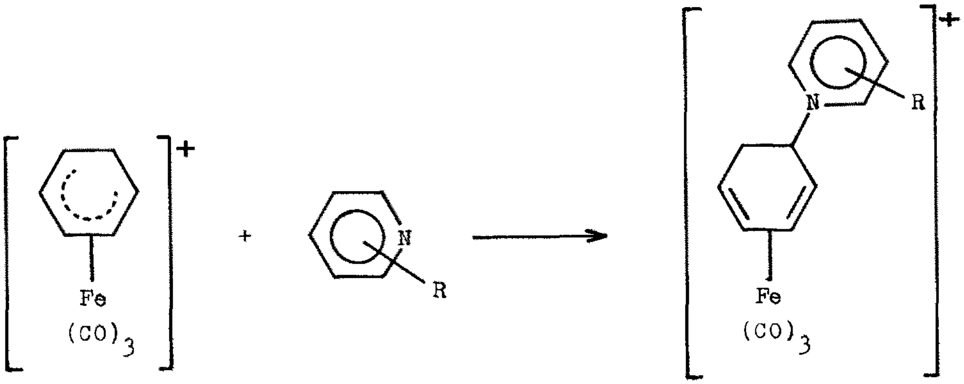


13.41

of an electrophilic substitution mechanism that involved rapid preequilibrium formation of a π-complex followed by rate determining rearrangement to a Wheland-type σ-complex. Rapid proton loss than gave the products [216].

The nucleophilic attack of substituted pyridines on the tricarbonyl(η-cyclohexadienyl)iron cation (13.42) has been the subject of a kinetic investigation. The products were pyridinium adducts (13.43; R = H, 2-Me, 3-Me, 4-Me, 2,5-Me_2, 2,6-Me_2, 3,5-Me_2, 2,4,6-Me_3, 4-Ph, 2-CN, 3-Cl). The rate of the second order reactions showed a marked dependence on pyridine basicity. However, blocking of the 2- and 6-positions of the pyridine by methyl groups caused steric retardation. The corresponding

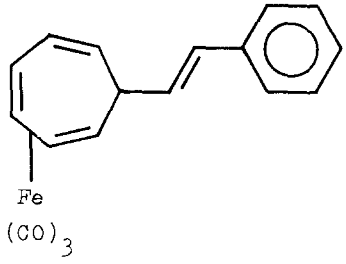


13.42

13.43

reactions of the cations $[(\eta^5\text{-}2\text{MeOC}_6H_6)Fe(CO)_3]^+$ and $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]^+$ were compared [217].

The tropylium ion $[C_7H_7]^+$ attacked tricarbonyl(η-cyclooctatetraene)iron to form the neutral complex (13.44) which contained a η-styrylcycloheptatriene ligand. Mechanistic proposals indicated that the cycloheptatriene ring in the complex (13.44) was derived from the cyclooctatetraene ring while the phenyl group was formed from the tropylium ion. The crystal and molecular structure of the complex (13.44) was confirmed by X-ray crystallography [218].

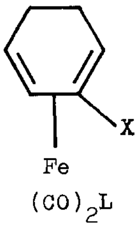


13.44

Reaction of the closo-carbaborane $2,3\text{-Me}_2\text{-}2,3\text{-}C_2B_9H_9$ with (η-1,5-cyclooctadiene)(η-cyclopentadienyl)iron in benzene, toluene, o-xylene or with an excess of naphthalene in petroleum-ether produced the corresponding (η^6-arene)-closo-carbaferraborane complex. The structure of the η^6-toluene complex was established by X-ray crystallography [219].

13. (ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structures of the (η-cyclohexadiene)iron complexes (13.45; X = H, OMe, L = CO) have been determined by X-ray crystallography. The ^{13}C NMR spectra of these and the related complexes [13.45; X = H, OMe, L = $P(OMe)_3$, $AsPh_3$, PPh_3] have been recorded and interpreted in terms of depopulation of the diene LUMO as the π-acceptor strength of L decreased rather than the expected enhanced population of the orbital. An explanation has been proposed using a pictorial MO model [220].



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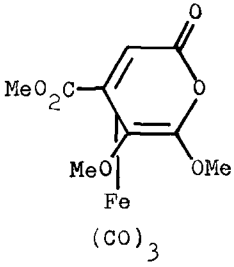

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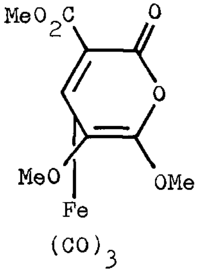


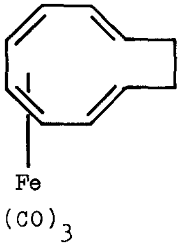
13.47

The crystal and molecular structure of bis[tricarbonyl-(η-cyclopentadienone)iron]hydroquinone has been determined by X-ray methods. The molecule contains two tricarbonyl(η-cyclopentadienone)iron groups linked to hydroquinone by hydrogen bonds [221].

The structure of (η^5-1-methyl-4-isopropylcyclohexadienyl)-tricarbonyliron hexafluorophosphate has been determined by X-ray analysis. The cyclohexadienyl ring had a sofa conformation [222].

The thermal rearrangement of the (η-2-pyrone)iron complex (13.46) to the isomer (13.47) has been investigated. The crystal and molecular structures of both complexes (13.46 and 13.47) have been determined by X-ray crystallography and a mechanism involving a (η^3-vinylcarbene)iron intermediate and a novel 1,4-oxygen shift has been proposed [223].

The crystal and molecular structures of the (η-cyclodeca-

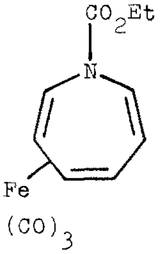


13.48

tetraene)iron complex (13.48) has been determined by X-ray crystallography. The tricarbonyliron group was bonded to the *cis*, *cis*-3,5-diene unit of the ligand [224].

The ESR spectra of (η-1,3-cyclooctatetraene)(η-C_5H_5)Co^-, (η-1,3-cyclooctatetraene)-$Fe(CO)_3^-$ and -$Fe(CO)_2PPh_3^-$ have been recorded and interpreted. It was concluded that the odd electron resided in the cyclooctatetraene portion of the molecule. The ESR spectra for (η-1,5- and 1,3-cyclooctadiene)(η-C_5H_5)Co^- showed that the unpaired electron was predominantly metal centred [225].

The application of Frontier Orbital theory to cycloaddition reactions of some tricarbonyliron complexes has been investigated. ^1H NMR spectroscopy showed that the reaction of tetracyanoethylene with the azepine complex (13.49) gave initially the



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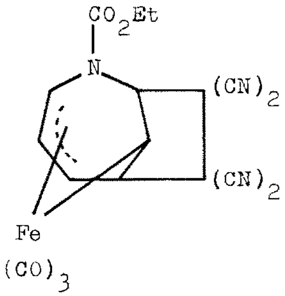

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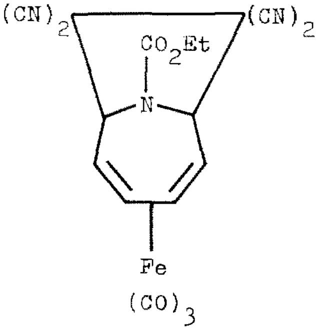

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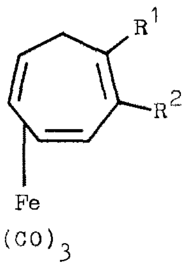


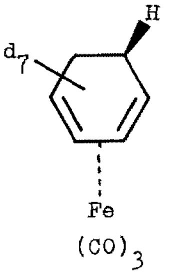
13.52

1,3-addition product (13.50) which isomerized to the 1,6-addition product (13.51). The initial formation of the 1,3-addition product was in agreement with Frontier Orbital theory [226].

A kinetic study has been made of the addition of tetracyanoethylene to (η-cycloheptatriene)iron complexes (13.52; R^1 = H, COMe, CHO, R^2 = H, R^1 = H, R^2 = COMe) and to tricarbonyl(η-cycloheptatrienone)iron in several solvents. The tricarbonyliron group activated the complex and the reaction mechanism involved neither ionic nor free radical intermediates. In one case (13.52; R^1 = CHO, R^2 = H) two parallel reactions were in competition [227].

The thermal isomerization of tricarbonyl(η-cyclohexadiene-5-*exo*-*h*-d_7)iron (13.53) at 134 °C has been studied in order to elucidate the mechanism of 1,5-hydrogen shifts. Identical initial rates of ^1H incorporation into the 1- and 2-positions of the cyclohexadiene ring were observed. These findings are consistent only with a mechanism involving two sequential 1,3-shifts of deuterium *endo* to the metal [228].

Oxidative cyclization of the (η-cyclohexadiene)iron complex (13.54) with anhydrous iron(III) chloride on silica gel gave the tricarbonyliron complex (13.55) containing a tricyclic ligand. This reaction was in contrast to the behaviour of alcohols and (η-diene)iron complexes towards iron(III) chloride [229].



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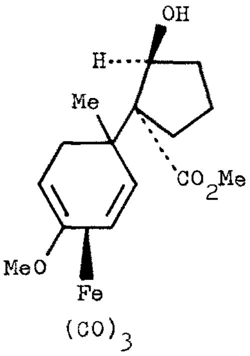

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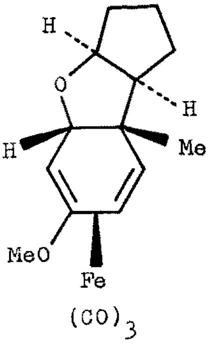
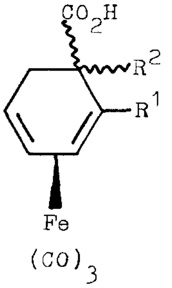


13.55

The (η-cyclohexadiene)iron complex (13.56; R^1 = H, CO_2Me, R^2 = β-H) underwent acid catalyzed decarbonylation with concentrated sulphuric acid to form the (η-cyclohexadienylium)-iron cation (13.57; R = H, Me). However, the complex (13.56; R^1 = H, R^2 = α-H) was unaffected. The mechanism of the reaction was discussed [230].



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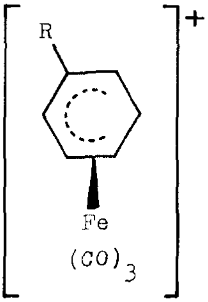


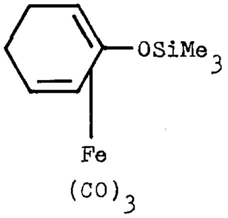
13.57

13. (iii) General Chemistry

Birch and co-workers have discussed the concept of superimposed lateral control of reactivity, stereochemistry and structures, by attachment of transition metal carbonyl derivatives to olefinic systems. The reactions of substituted tricarbonyl-(η-cyclohexa-1,3-diene)iron derivatives especially the derived dienyliron salts which were defined as equivalents of specifically substituted aryl cations or as cyclohex-2-enone cations, were discussed in some detail [231].

Elimination of both the hydride and the trimethylsilyl group from the diene complexes (13.58 and 13.59) occurred when they were treated with triphenylmethyl tetrafluoroborate to give the corresponding tricarbonyliron complexes (13.60 and 13.61) [232].

Reaction of dispiro[2.0.2.4]deca-7,9-diene with (benzylidene-acetone)tricarbonyliron or $Fe_2(CO)_9$ gave the tricarbonyliron complex (13.62; L = CO). Related complexes [13.62; L = PPh_3, $P(OPh)_3$] and some cyclohexadiene derivatives were prepared also. The tricarbonyliron complex (13.62; L = CO) underwent reaction with tetrafluoroboric acid to give the first complex (13.63) of an ethylenebenzenium ion [233].



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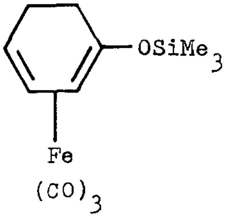

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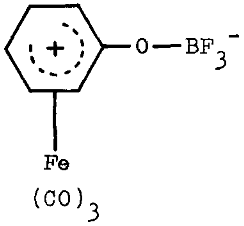

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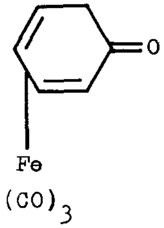

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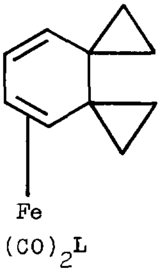

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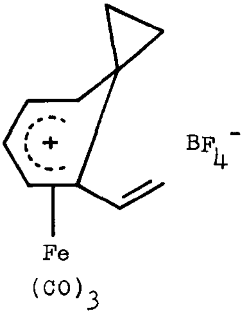
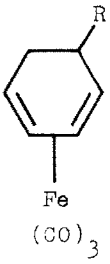


13.63

Reactions of the π-enyl complexes $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$, $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]BF_4$, $[(\eta^5\text{-}C_7H_7)Fe(CO)_3]BF_4$, $\{[(5.1.0)\eta^5\text{-}C_8H_9]Fe(CO)_3\}BF_4$, $[(\eta^3\text{-}C_4H_7)Fe(CO)_3]BF_4$ and $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ with selected anionic nucleophiles have been investigated [234].

The η-cyanocyclohexadiene complex (13.64; R = CN) was treated with hydrogen chloride and methanol to give the methyl iminoester (13.65). Treatment of the iminoester (13.65) with base gave the amide (13.64; R = $CONH_2$) and condensation with the appropriate nitrogen compounds afforded the heterocyclic derivatives 2-(2-cyclohexadienyl-2,2-irontricarbonyl)-imidazoline-2, -benzoxazole, -benzimidazole and 2-phenyl-5-(5-cyclohexadienyl-5,5-irontricarbonyl)-1,3,4-oxadiazole. Some reactions of η-cyanocyclohexadiene derivative (13.66) were also investigated [235].



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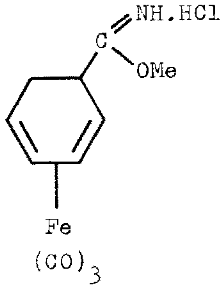

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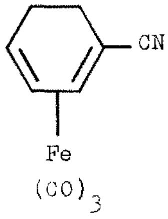
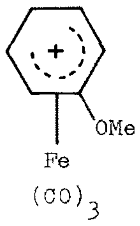


13.66

The symmetrical 3-methoxy cation (13.67) has been prepared from tricarbonyl(η-1,3-dimethoxycyclohexa-1,3-diene)iron by treatment with trifluoroacetic acid. The cation (13.67) was shown to be synthetically equivalent to a meta-methoxybenzene cation or to a 5-cation of cyclohex-2-enone. The preparation



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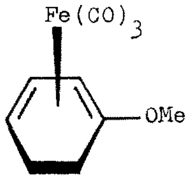

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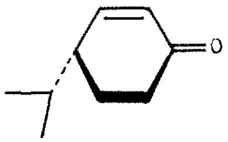
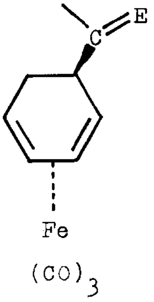


13.69

of tricarbonyl(η-cyclohexa-2,4-dienone)iron was also described and nucleophilic reactions at the 1-position of this complex were investigated [236].

Stereospecific reactions of tricarbonyl(η-cyclohexadienyl)-iron salts, derived from unsymmetrically substituted tricarbonyl-(η-cyclohexadiene)iron complexes, have been used to direct the formation of new chiral centres at carbon and so to define absolute configurations by chemical correlation with the terpenes cryptone and phellandrene. For example, (1S)-(+)-tricarbonyl-(η-1-methoxy-1,3-cyclohexadiene)iron (13.68) has been correlated with (R)-(-)-cryptone (13.69) [237].

The (η-cyclohexadiene)iron complex (13.70; E = CH_2), obtained by a Wittig reaction on the (η-acetylcyclohexadiene)iron complex (13.70; E = O), was protonated with fluoroboric acid to give the salt (13.71). Acetylation of the same complex, (13.70; E = CH_2), with one mole of an equimolar mixture of $AlCl_3$ and



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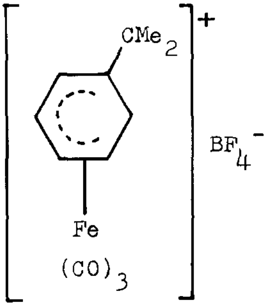

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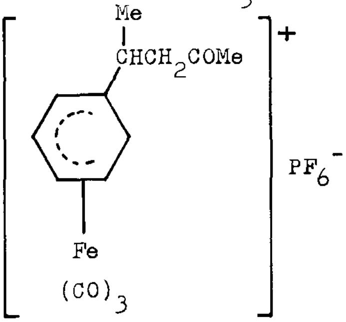

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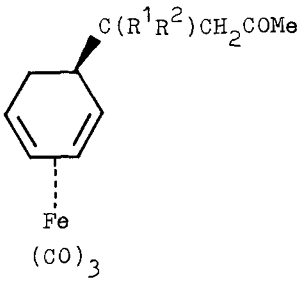
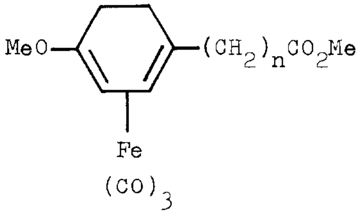


13.73

MeCOCl gave three products, the salt (13.72) and the (η-cyclohexadiene)iron complexes (13.73; R^1 = Me, R^2 = Cl; R^1R^2 = $=CH_2$) in yields of 14, 26 and 4.5% respectively [238].



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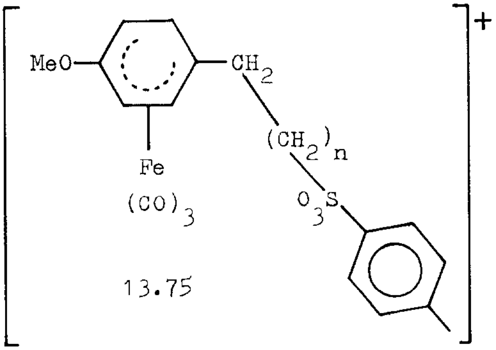

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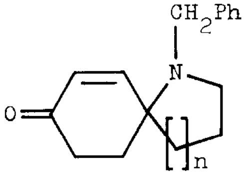

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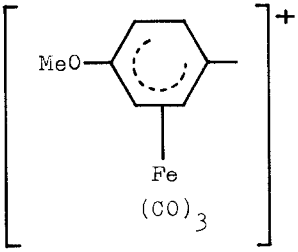

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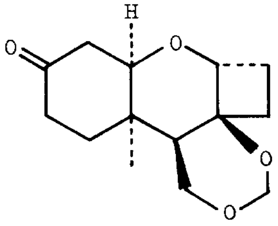

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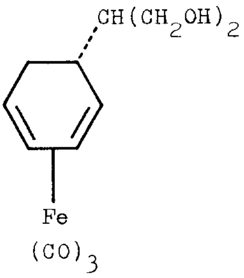

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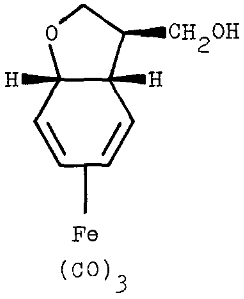

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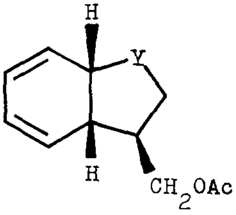


13.81

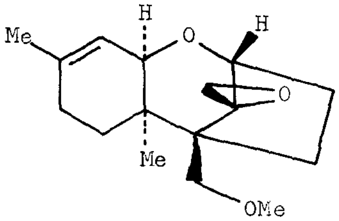
(η-Cyclohexadienylium)iron complexes have been used as intermediates in the synthesis of azospirocyclic compounds. Thus the (η-cyclohexadiene)iron complexes (13.74; n = 1, 2) were converted to the (η-cyclohexadienylium)iron intermediates (13.75; n = 1, 2) by sequential reduction, tosylation and hydride abstraction. The intermediates (13.75; n = 1, 2) were treated with benzylamine and subjected to demetallation and hydrolysis to give azaspirocyclic enones (13.76; n = 1, 2) [239]. In a related sequence of reactions the (η-cyclohexadienylium)iron complex (13.77) was stereospecifically converted to the trichothecane intermediate (13.78) [240].

Stereospecific cyclization of the (η-cyclohexadiene)iron complex (13.79) using $Tl(O_2CCF_3)_3$ in the presence of sodium carbonate gave the cis-hydrindene complex (13.80) which underwent acetylation and decomplexation to form the product (13.81; Y = O). A similar cyclization was used to obtain the product [13.81; Y = $C(CO_2Me)_2$] [241].

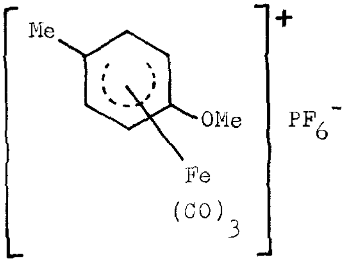
A stereocontrolled total synthesis of a 12,13-epoxytrichothecene analogue (13.82) has been achieved using the hexafluorophosphate salt (13.83). The synthetic route described illustrated the usefulness of the $Fe(CO)_3$ group for diene and dienol ether protection [242].

The conversion of the diastereoisomers (13.84; R = α- or β-CO_2Me) to steroid precursors has been described [243].

Oxidation of the complexes (13.85; α-CO_2Me, OR = α-OH; β-CO_2Me, OR = β-OH) was effected with either thallium(III)



13.82



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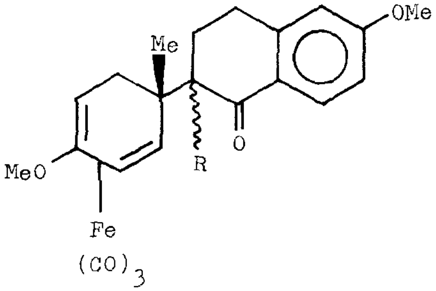
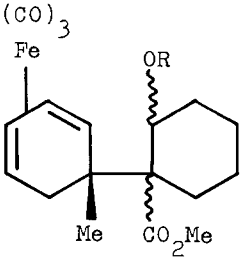


13.84

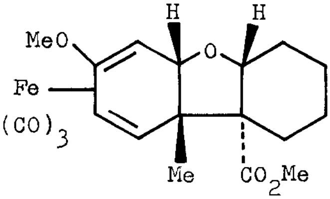
trifluoroacetate or iron(III) chloride on silica gel to give the corresponding cyclic derivatives (13.86 and 13.87). The latter complexes and related compounds were readily converted into 4,4-disubstituted cyclohexa-2,5-dienones [244].

Nucleophilic addition to the tricarbonyl(η-cycloheptadienylium)iron cation by phosphines gave either 5-exo or 5-endo isomers of phosphine-substituted tricarbonyl(η-cyclohepta-1,3-diene)iron. In dichloromethane, direct attack at the ring gave the 5-exo isomer and in methyl cyanide the 5-endo isomer was formed probably via a metal-assisted pathway [245].

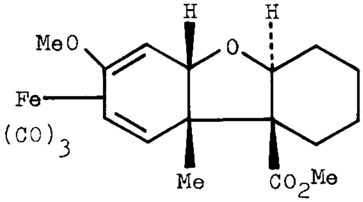
Catalytic amounts of acid or base were effective in isomerizing the bicyclo[5.2.0]nona-2,4-dien-8-one complex (13.88) to the cycloheptatriene complex (13.89). Mechanisms involving



13.85



13.86



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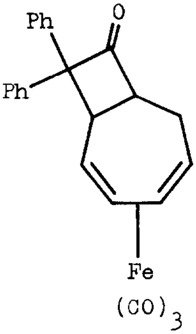
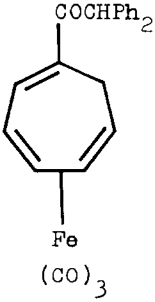


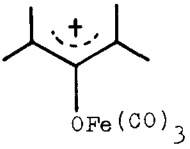
13.88



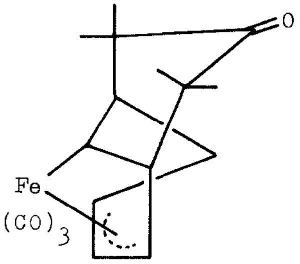
13.89

vinylcycloheptatriene intermediates were used to explain the reactions [246].

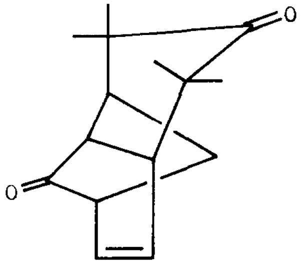
The 2-oxyallylcation (13.90), generated from 2,4-dibromo-2,4-dimethylpentan-3-one and enneacarbonyldiiron when treated with tricarbonyl(η^4-cycloheptatriene)iron, gave a 1:1 adduct (13.91) whose structure was confirmed by X-ray analysis. The oxidative degradation of the adduct (13.91) with o-chloranil



13.90



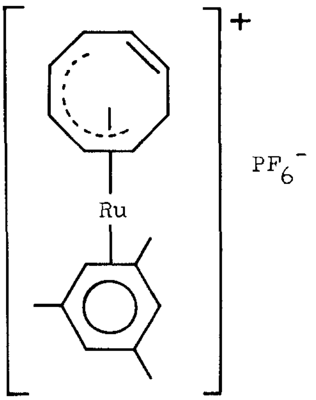
13.91



13.92

gave the iron-free compound (13.92) which had inserted a carbonyl group. Similar reactions were carried out with tricarbonyl[8-(4-chlorophenyl)-8-azaheptafulvene]iron and tricarbonyl[(N-ethoxycarbonyl)azepine]iron [247,248].

Protonation with HPF_6, HBF_4 or CF_3CO_2H of (η-arene)-(η-cyclooctatetraene)ruthenium complexes gave the corresponding



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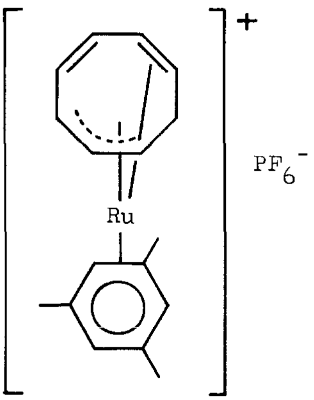


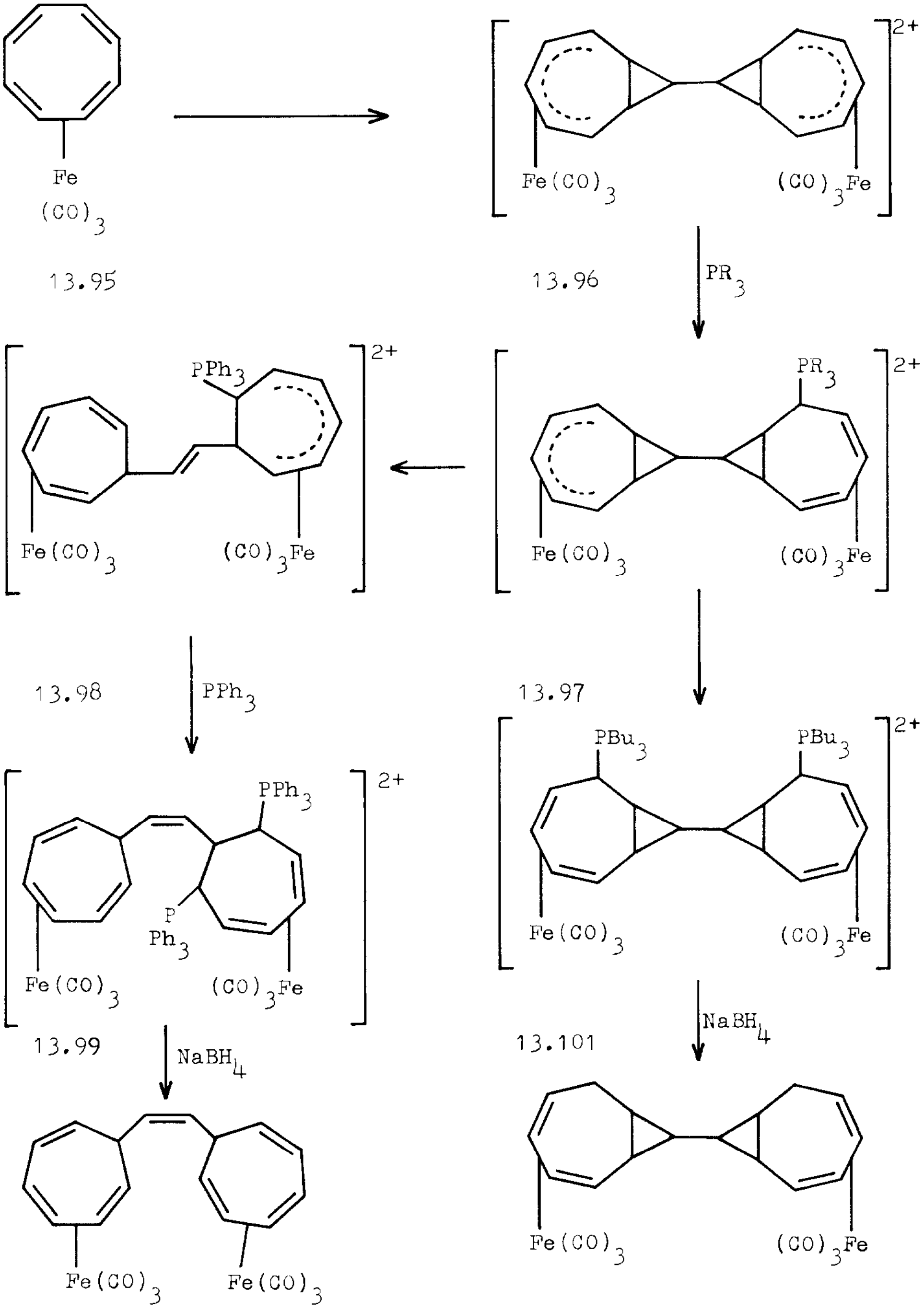
13.94

$[(\eta\text{-arene})(1\text{-}5\text{-}\eta\text{-}C_8H_9)Ru]^+$ cations (arene = mesitylene, hexamethylbenzene or t-butylbenzene) which were isolated as PF_6 or BF_4 salts. The mesitylene and hexamethylbenzene species isomerized on warming in organic solvents to $[(\eta\text{-arene})\text{-}(1\text{-}3\text{:}6\text{-}7\text{-}\eta\text{-}C_8H_9)Ru]^+$. The structures of the isomeric η-cyclooctatrienyl complexes (13.93 and 13.94) were determined by X-ray analysis [249].

Oxidative dimerization of tricarbonyl(η-cyclooctatetraene)iron (13.95) gave the dication (13.96) which was attacked by triphenylphosphine to form the (η-bicyclooctadiene)(η-bicyclooctadienyl)diiron cation (13.97; R = Ph) and this rearranged to the intermediate (13.98) before undergoing further addition of triphenylphosphine to give the bis-phosphonium salt (13.99). Both triphenylphosphine groups were displaced by hydride on treatment with sodium borohydride to yield the binuclear (η-cycloheptatriene)iron complex (13.100). The crystal and molecular structure of the bis-phosphonium salt (13.99) was determined by X-ray crystallography. When triphenylphosphine was replaced by tributylphosphine then the dication (13.97; R = Bu) gave the bis-phosphonium salt (13.101) which was reduced with sodium borohydride to the (η-bicyclooctadiene)iron complex (13.102) [250].

The (η-cyclooctatetraene)iron complex (13.95) underwent electrochemical or chemical oxidation to the reactive radical cation (13.103) which was followed by isomerization to the bicyclic species (13.104) and dimerization to the binuclear dication (13.105; L = CO). The crystal structure of the cation $[13.105;\ L = P(OPh)_3]$ as the PF_6^- salt has been determined by X-ray crystallography. Borohydride ion reduced the cation (13.105; L = CO) to the neutral complex (13.102) while bromide ion caused reductive C-C coupling to form the complex (13.106). This last product (13.106) was converted to the binuclear complex (13.107) with enneacarbonyldiiron [251].

Ligand substitution and nucleophilic reactivity in tricarbonyl(η-cyclooctadienylium)iron (13.108) has been studied. Attack by cyanide ion gave the carbonitrile (13.109) and the (η-cyclooctatriene)iron complex (13.110) while triphenylphosphine gave the phosphonium salt (13.111). Methoxide ion led to the (η-cyclooctadiene)iron complex (13.112) while iodide gave the (η-cyclooctadienyl)iron complex (13.113) which was converted



13.95

13.96

13.97

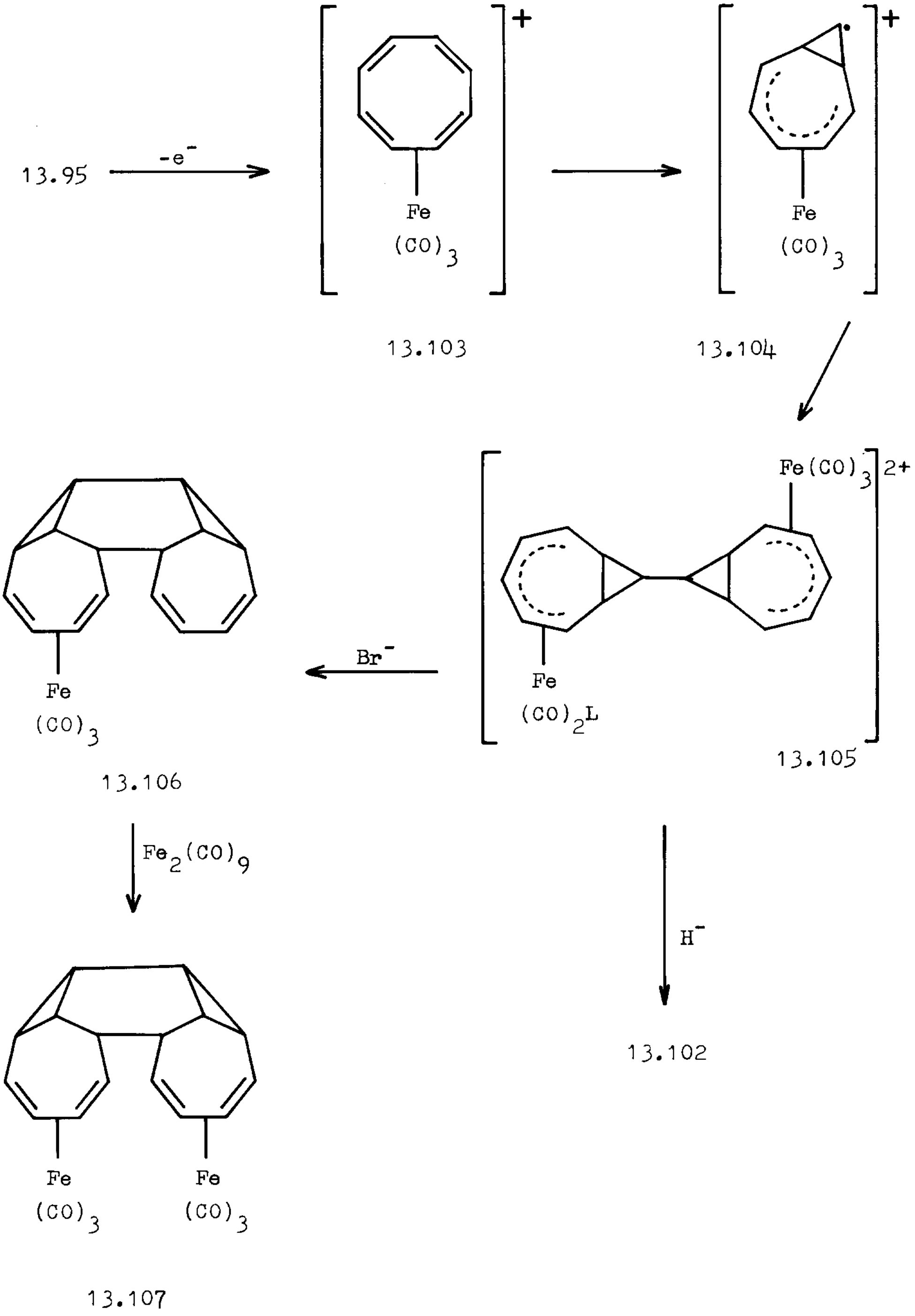
13.98

13.99

13.100

13.101

13.102



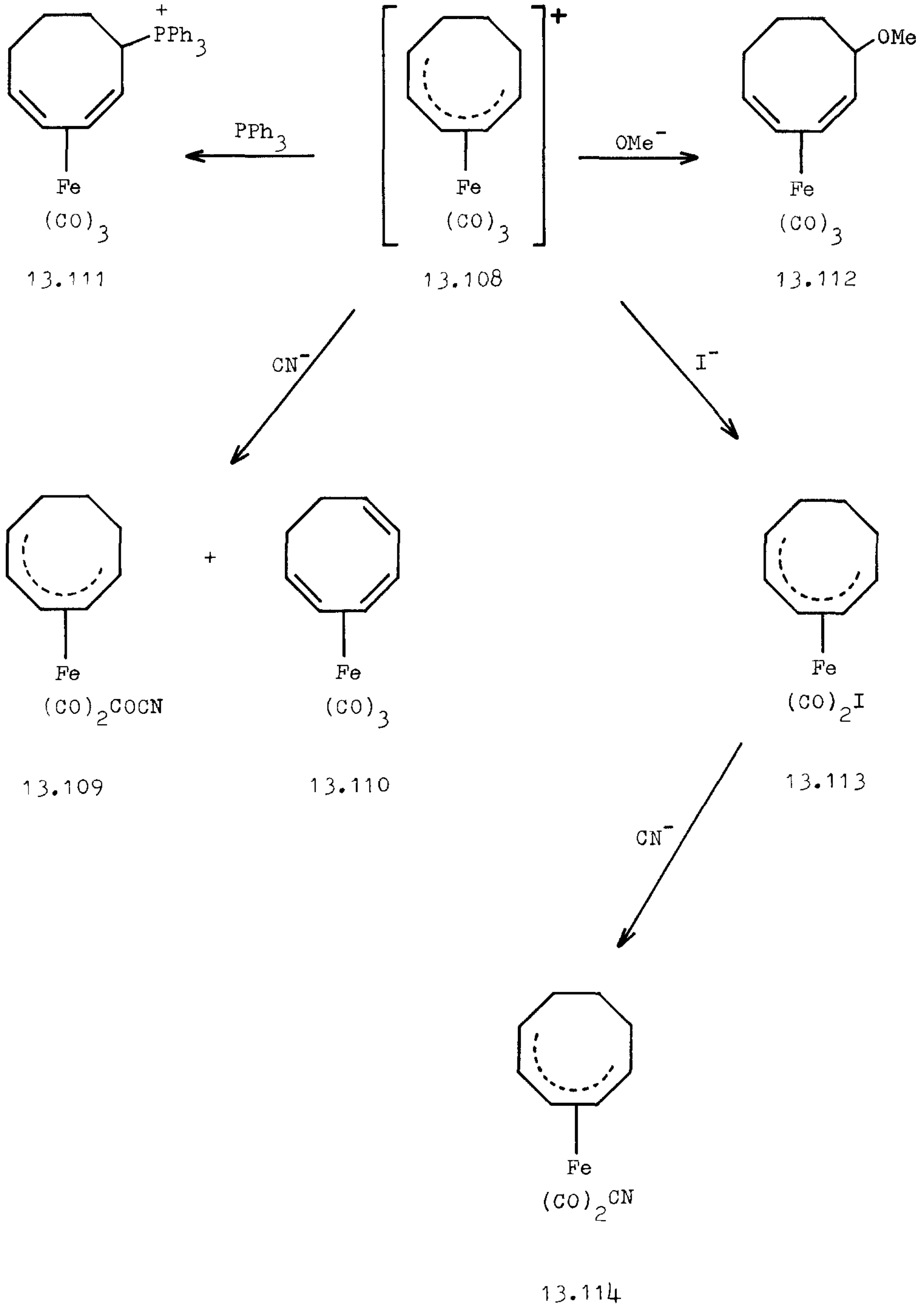
13.103

13.104

13.105

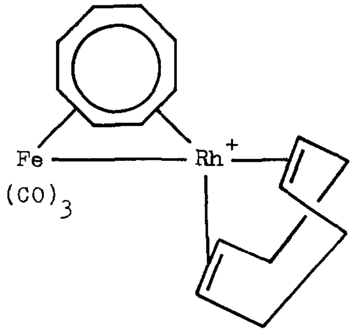
13.106

13.107

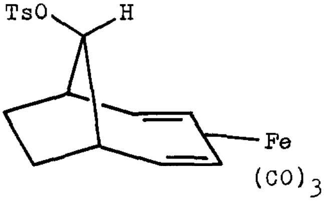

PPh3
OMe−
CN−
I−
CN−
+PPh3
Fe
(CO)3
13.111
Fe
(CO)3
13.108
OMe
Fe
(CO)3
13.112
Fe
(CO)2COCN
13.109
+
Fe
(CO)3
13.110
Fe
(CO)2I
13.113
Fe
(CO)2CN
13.114

with cyanide ion to the product (13.114). Several related reactions were reported [252].

The electron rich cyclooctatetraene complexes (η^4-C_8H_8)-Fe(CO)$_3$, (η^4-C_8H_8)(η^5-C_5H_5)Co and (η^4-C_8H_8)(η^5-C_5H_5)Rh have been treated with unsaturated cationic derivatives of rhodium, iridium and palladium to form dimetallic products. For example, reaction of the iron complex with η^4-cyclooctadienerhodium tetrafluoroborate gave the cation (13.115). All the complexes prepared were characterised by ^{13}C NMR spectroscopy [253].



13.115



13.116

(η^4-Cyclooctadiene)(η^6-cyclooctatriene)ruthenium has been shown to behave as a selective hydrogenation catalyst with some polyenes. For example, cycloheptatriene was hydrogenated at room temperature under one atmosphere of hydrogen and it was possible, by variation of the solvent, to form monoenes [254].

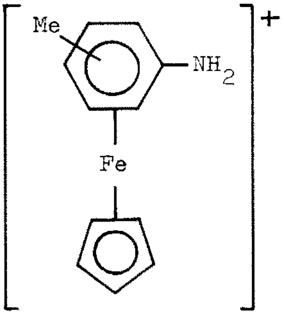
The rates of solvolysis of the complex (13.116) and the corresponding free ligand have been measured. The presence of the tricarbonyliron group increased the rate of methanolysis. This was believed to be the first example where iron complexation had increased the rate of reaction at a remote site where there was no possibility of direct metal participation [255].

14. [(η-C_5H_5)Fe(η-C_6H_6)]$^+$

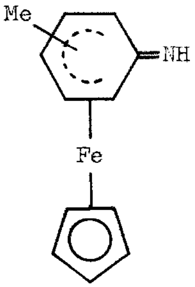
The ligand-exchange reaction between arenes and ferrocene has been utilized for the selective complexation of aromatics in petroleum. The aromatics were identified by pyrolytic mass spectral analysis and by thin layer chromatography of the

(η^6-arene)(η^5-cyclopentadienyl)iron cations formed in the exchange reaction. There was good agreement between the two sets of data [256].

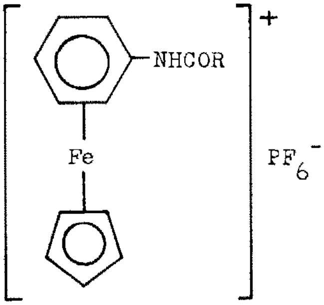
Ligand exchange reactions between ferrocene and *o*-, *m*- and *p*-toluidine gave the corresponding (η-cyclopentadienyl)-(η-toluidine)iron cations (14.1) which underwent deprotonation with potassium t-butoxide in THF to form the zwitterionic complexes (14.2). These complexes (14.2) were effective as nucleophiles in reactions with methyl iodide, carbon disulphide, acetyl chloride, propionyl chloride and benzoyl chloride. The products (14.3; R = Me, Et, Ph) were obtained from the three acid chlorides [257].



14.1

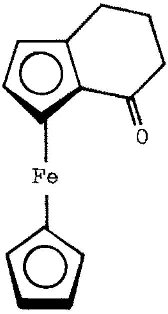


14.2

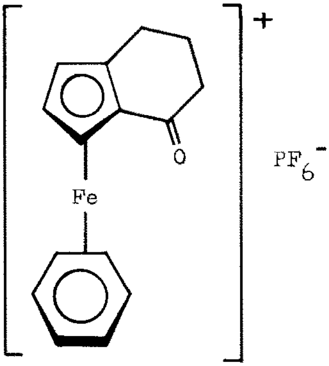


14.3

Ligand exchange in (+)-1,2-(α-ketotetramethylene)ferrocene (14.4) was carried out in benzene in the presence of aluminium chloride. Retention of configuration occurred and the optically



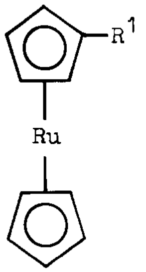
14.4



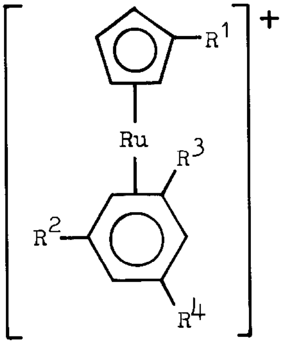
14.5

active salt (14.5) was isolated with an optical purity close to 100% [258].

Ligand exchange has been effected in a series of ruthenocenes (14.6; R^1 = Et, COMe, H) by treatment with an aromatic hydrocarbon in the presence of aluminium chloride-aluminium powder. The corresponding cations (14.7; R^1 = Et, COMe, H; R^2 = R^3 = H, R^4 = H, Cl, Me; R^2 = R^3 = R^4 = Me) were formed and these were isolated as the hexafluorophosphate salts [259].

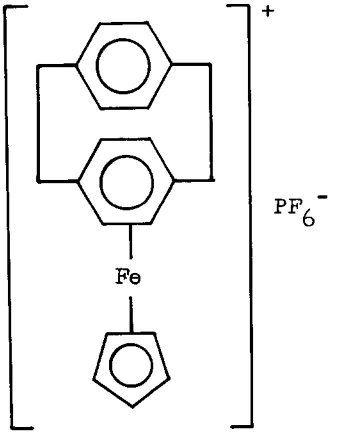


14.6

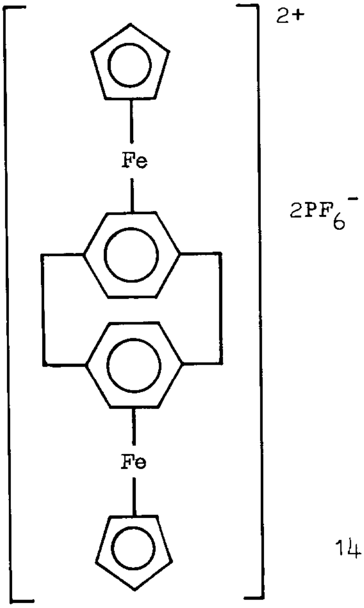


14.7

Ferrocene has been attacked by [2.2]paracyclophane in the presence of aluminium chloride and aluminium powder to form



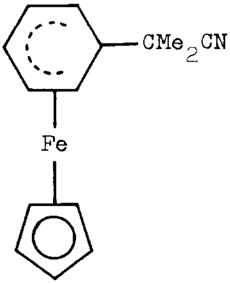
14.8



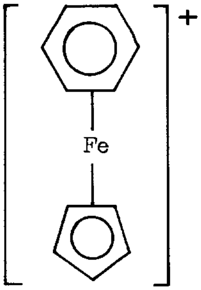
14.9

the (η-paracyclophane)iron complexes (14.8 and 14.9) [260].

Oxidation of the (η-cyclohexadienyl)iron complex (14.10) with N-bromosuccinimide gave a mixture of the (η-benzene)iron cation (14.11) and the free ligand PhCMe$_2$CN in the ratio 1:5. When cerium(IV) was the oxidizing agent then a mixture of the cation (14.11) and benzene was obtained in the ratio 1:1. Oxidation of (η-benzene)(η-toluene)iron with cerium(IV) gave toluene as the only product [261].



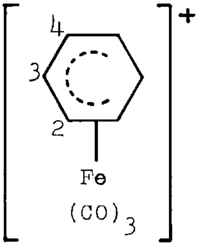
14.10



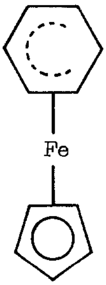
14.11

The electronic absorption spectra of a series of (η-arene)-(η-cyclopentadienyl)iron cations, where arene = benzene, toluene, mesitylene, tetralin, biphenyl, naphthalene and phenanthrene, and the corresponding neutral complexes have been recorded and interpreted [262].

Bonding in the (η-cyclohexadienyl)iron complexes (14.12 and 14.13) has been compared in a ^{13}C NMR investigation.



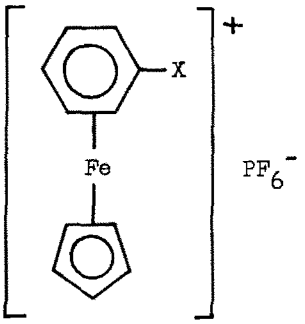
14.12



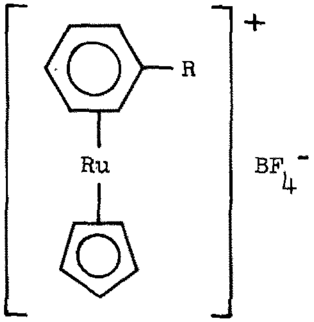
14.13

In the tricarbonyliron complex (14.12) the least shielded carbons were C(2,4) while in the (η-cyclopentadienyl)iron complex (14.13) C(2,3,4) were similar [263].

The ^{13}N NMR spectra for seventeen (η-arene)(η-cyclopentadienyl)iron salts (14.14; X = H, Me, Et, Pr^i, Bu^t, Ph, OPh, COPh, OMe, CO_2H, NH_2, NH_3^+, NMe_2, CN, NO_2, F, Cl) have been measured and analyzed in detail. The chemical shifts were interpreted qualitatively on the basis of ligand-metal interactions. ^{13}C NMR spectra were recorded for seventeen polysubstituted arene complexes, $[(\eta\text{-arene})(\eta\text{-}C_5H_5)Fe]PF_6$ [264].



14.14

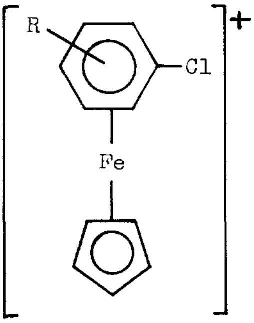


14.15

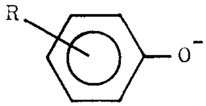
Nucleophilic replacement of chlorine in (η-chlorobenzene)-(η-cyclopentadienyl)ruthenium tetrafluoroborate occurred when it was treated with methanol, piperidine or ammonia to give corresponding ruthenium complexes (14.15; R = MeO, piperidino, NH_2) [265].

The nucleophilic displacement of chloride by phenoxides (14.17; R = H, 3-, 4-Me, 4-Ph, 3-CO_2Me, 3-Cl, 4-Br) in the (η-benzene)iron complex cations (14.16; R = H, 2-, 3-Me) has been the subject of a kinetic investigation. Hammett ρ values were determined for the three cations (14.16) as 3.16, -3.55 and -3.01 respectively. The reaction mechanism was interpreted in terms of Meisenheimer-type intermediates [266].

The azido complex (14.18; X = N_3) has been prepared by the reaction of the η^6-chlorobenzene derivative (14.18; X = Cl) with sodium azide. Pyrolysis in vacuum or irradiation of the complex (14.18; X = N_3) gave (η^6-aniline)(η^5-cyclopentadienyl)-iron hexafluorophosphate (14.18; X = NH_2) together with some



14.16



14.17

cyanoferrocene. The formation of these products was explained in terms of a phenylnitrene complex [267].

The addition of LiCH(CH_3)CN to the cation (14.19) gave initially a (η^5-cyclohexadienyl)(η^5-cyclopentadienyl)-iron complex which was oxidized by N-bromosuccinimide to the intermediate (14.20) and then to a mixture of the cyanides (14.21) [268].

Photolysis of the cation (14.22) in the presence of 6- or 2-electron donor ligands resulted in replacement of the η-*p*-xylene ligand with one 6-electron or three 2-electron donor ligands. The 6-electron donor ligands were cycloheptatriene, η^6-cyclooctatetraene and 2,2-paracyclophane and the 2-electron donors were trimethyl- and triethyl-phosphite [269].

Irradiation of (η^5-cyclopentadienyl)(η^6-*p*-xylene)iron hexafluorophosphate and [2.2]paracyclophane in dichloromethane by visible light gave the iron complex (14.8). When ferrocene was heated with [2.2]paracyclophane in the presence of aluminium powder and aluminium chloride the dication (14.9) was formed [270].

The ketones (14.23; R^1 = H, R^2 = Me, Ph; R^1 = R^2 = Me; R^1 = Me, R^2 = Ph) have been transformed into the corresponding secondary alcohols or pinacols by cathodic reduction on mercury. Acids were reduced similarly to give the corresponding primary alcohols. The electroreduction was activated by the cationic organoiron group and it was regiospecific on the functional group rather than on the ring, in contrast to the reduction with chemical reagents [271].