ORGANIC REACTIONS OF SELECTED π-COMPLEXES

ANNUAL SURVEY COVERING THE YEAR 1980*

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* Organic Reactions of Selected π-Complexes, Annual Survey Covering the Year 1979 see J. Organometal. Chem., 207 (1981) 343.

1. Reviews

To mark the publication of Volume 200 of The Journal of Organometallic Chemistry selected organometallic chemists were invited to contribute papers. These included, "The use of atoms of the Group IV, V and VI transition metals for the synthesis of zerovalent arene compounds and related studies" by M.L.H. Green [1]; "Nucleophilic addition to transition metal complexes" by P.L. Pauson [2] and "The way to novel sandwich-type complexes" by H. Werner [3]. As part of a US government report King has summarised the reactions of alkyliminobis(difluorophosphines) with the carbonyls of Cr, Mo, W, Fe, Co and Ni and the (η-cyclopentadienyl)metal carbonyls of V, Mo, W, Mn and Fe [4]. Jonas and Krueger have reviewed the chemistry of alkali metal-transition metal π-complexes. A section on the preparation of these compounds from ferrocene, cobaltocene and nickelocene was included [5].

Pearson has reviewed recent developments in the chemistry of tricarbonyl(η-diene)iron complexes [6]. Birch has surveyed the stereospecific and regiospecific formation and reactivity of some substituted tricarbonyl(η-cyclohexadiene)iron complexes [7].

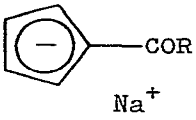
2. General Results

A theoretical investigation of bonding in the metallocenes $(\eta\text{-}C_5H_5)_2V$, $(\eta\text{-}C_5H_5)_2Mn$, $(\eta\text{-}C_5H_5)_2Fe$, $(\eta\text{-}C_5H_5)_2$ Ru and

$(\eta\text{-}C_5H_5)_2Ni$ has indicated that the bond orders of the C-C bonds reflect the extent of π-bonding which in turn determines the strength of the metal-ligand bond. Pauling's bond distance-bond order relationship was used to determine the bond orders of the C-C bonds and the number of π-electrons in the metal-ligand bonds were derived. The values were correlated with observed dissociation energies which allowed the estimation of the energies of the highest occupied molecular orbitals, these energies were then used to predict the metal-ligand distances [8]. The carbon 1s, nitrogen 1s and oxygen 1s binding energies of fifty five transition metal carbonyl and nitrosyl compounds have been subjected to correlative analysis. The carbon 1s and oxygen 1s binding energies of the carbonyl complexes were linearly related to the C-O stretching force constants and similarly for the nitrosyl complexes the nitrogen 1s and oxygen 1s binding energies were linearly related to the N-O stretching force constants. The data showed that the transfer of electron density to the CO and NO groups weakened the C-O and N-O bonds. Also, that in back bonding to CO more charge was transferred to the carbon atoms than to the oxygen atoms and for NO similar amounts of charge was transferred to the nitrogen and oxygen atoms [9].

The frontier molecular orbital method was used to analyze bonding in transition metal π-complexes. A simple model was proposed but when it was applied to tricarbonyl(cross-conjugated dienyl)iron cations it failed [10]. The application of the Extended Hueckel Theory to organometallic molecules has been examined. A new population analysis, which gave good results, was applied to di(η-benzene)chromium, (η-benzene)tricarbonyl-chromium and ferrocene [11]. Apparatus has been described for the synthesis of organometallic compounds by cocondensation of metal atoms and the vapour of the ligand. The liquid reaction product was monitored spectrophotometrically to determine the extent of reaction and the liquid could be recycled [12]. A related patent described apparatus which differed in that the pressure in the evaporator section (10^{-4} torr) could be maintained below that in the reaction chember ($>10^{-3}$ torr) [13].

A route to functionally substituted (η-cyclopentadienyl)-transition metal complexes has been reported. It permitted the synthesis of complexes which were difficult to form by electrophilic substitution of the parent system. The procedure involved the formation of formyl-, acetyl- and methoxycarbonyl-cyclopentadienylsodium (2.1; R = H, Me, OMe respectively), by treatment of cyclopentadienylsodium with ethyl formate, methyl acetate and dimethyl carbonate respectively. These intermediates were then treated with transition metal salts and transition metal carbonyls to form the functionally substituted complexes. Thus the sodium salt (2.1; R = Me) was treated with cobalt chloride to give 1,1'-diacetylcobaltocene. The formation of chromium, molybdenum, tungsten, rhodium and nickel complexes was also described [14]. A series of metallofulvalene complexes (2.2; M = V, Cr, Ni; Z = 0) has been synthesized and characterized. The complexes (2.2) were regarded as electronically delocalized systems and were formally analogous to the metallocenes. Each of the complexes has been obtained in three oxidation states (2.2; M = V, Cr, Ni; Z = 0, 1, 2). The crystal and molecular structures of two of the complexes (2.2; M = V, Ni; Z = 0) have been determined by X-ray crystallography [15].



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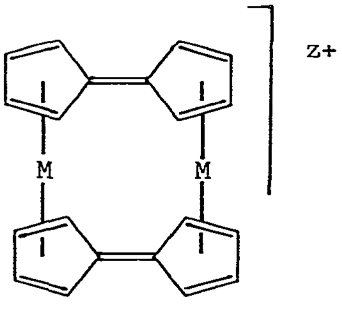

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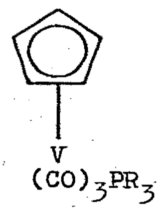
Reaction of C_5D_5Na with a metal chloride has been used to prepare the perdeuterated metallocenes, $(\eta\text{-}C_5D_5)_2M$, where M = V, Cr, Mn, Fe, Co, Ni. The infrared and mass spectra of the perdeuterated species were recorded and discussed [16]. In the mass spectra of cymantrene, benchotrene, tricarbonyl(η-cyclopentadienyl)rhenium, tetracarbonyl(η-cyclopentadienyl)vanadium and ferrocene obtained by their simultaneous evaporation with organic molecules and deuteroanalogues, protonated (deuterated) molecular and fragment ions were detected. These were formed as a result of (i) ion-molecule reactions in the ionization chamber at pressures of 10^{-5}-10^{-4}mn Hg and (ii) the interaction of neutral molecules of the π-complex and the organic compound before their ionization [17].

Stainless-steel porous-layer open tubular (PLOT) columns were prepared with Dexsil and other stationary phases that were suitable for the separation of organometallic compounds. Ferrocene, ruthenocene and osmocene were separated as were dicarbonyl-(η-cyclopentadienyl)nitrosyl-chromium, -molybdenum and -tungsten. Plate numbers in excess of 10,000 were obtained demonstrating the excellent behaviour of these compounds on PLOT columns [18]. Metallocenes containing chromium, molybdenum, manganese, iron or nickel have been used as sources of metal impurities in the doping of semiconductor materials during vapour-phase epitaxy. The impurity distribution was found to change sharply from one film to another in semiconductors based on GaAs, InP, Si, CdS and PbSe [19].

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

The ^{31}P and ^{51}V NMR spectra of the vanadium complexes [3.1; $PR_3 = PH_2Ph$, PMe_3, $P(n\text{-}Bu)_3$, $PMePh_2$, PPh_3, $P(OMe)_3$, $P(OPh)_3$] have been recorded. The shielding of the ^{51}V atom decreased with decreasing ligand strength (electronegativity of R) and increasing spatial requirement for the PR_3 ligand [20]. Photolysis of (η-cyclopentadienyl)vanadium tetracarbonyl in the presence of triphenylphosphine using monochromatic radiation gave the complex (3.1; $PR_3 = PPh_3$). The mechanism involved photodissociation of



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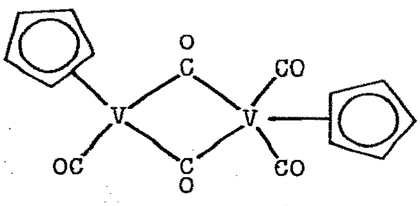


3.2

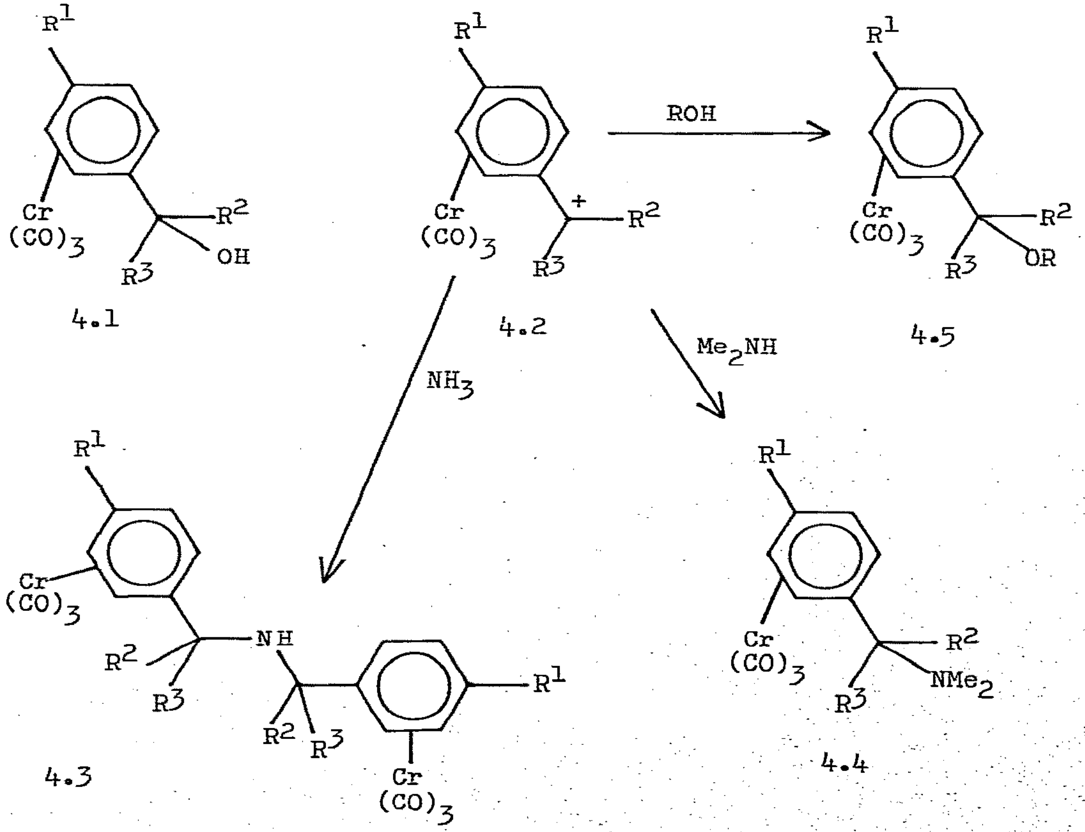
the excited starting material to give a vanadium tricarbonyl intermediate which then underwent nucleophilic attack by the phosphine [21].

The UV irradiation of tetracarbonyl(η-cyclopentadienyl)-vanadium with MeSSMe in THF gave a mixture of the binuclear complexes $[(\eta\text{-}C_5H_5)V.SMe(CO)_2]_2$, 21-68% yield and $[(\eta\text{-}C_5H_5)V(SMe)_2]_2$, 8-59% yield. The proportions of the two products varied with the reaction time [22]. The photolysis of tetracarbonyl(η-cyclopentadienyl)vanadium in tetrahydrofuran gave the dimer (3.2). The thermal and photochemical reactions of the dimer (3.2) were examined [23, 24].

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

(i) Formation

The formation of the tricarbonylchromium complexes (4.1; R^1 = OMe, $R^2 = R^3$ = H; R^1 = OMe, R^2 = H, Me; R^1 = OMe, $R^2 = R^3$ =



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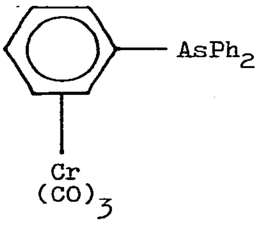
Me; $R^1 = R^2 = H$, $R^3 = Ph$) from the corresponding benzyl alcohols enhanced the stability of the carbenium (4.2) ions generated from these alcohols. Treatment of these carbenium ions with ammonia, amines or alcohols (R = Me, Et) gave the corresponding amines and ethers (4.3, 4.4, 4.5). This method was used to control the stereochemistry of nucleophilic attack in indane and tetralin [25]. Reaction of triphenylarsine with hexacarbonylchromium produced the tricarbonylchromium complex (4.6). The structure of the chromium complex (4.6) has been determined by X-ray analysis. The geometry about chromium was of the symmetrical "three-legged piano-stool" type with a Cr to As distance of 3.73 Å which indicated that there was no bonding between these two atoms [26].

Several chromium tricarbonyl complexes of phenylsilanes such as the benzylsilane complex (4.7) and the bimetallic complex (4.8) have been synthesized. Some chemical reactions of the complexed ligands were reported [27]. Tricarbonyl(η-phenalene)chromium (4.9) has been obtained by treatment of the free hydrocarbon ligand with $(MeCN)_3Cr(CO)_3$. Complexation of the metal to ring A occurred exclusively [28]. The reaction of 2,6,15,19-tetrathia [7.7]paracyclophane with hexacarbonylchromium gave five products (4.10, 4.11, 4.12, 4.13 and 4.14). The formation of these products was discussed and a radical mechanism was proposed for the elimination of the 1,3-propanedithia unit which was required for the formation of the complexes (4.12, 4.13 and 4.14) [29]. Ladder polyphenylsilsesquioxane and a linear polydiphenylsiloxane were treated with hexacarbonylchromium to give the corresponding tricarbonylchromium complexes. These silicone polymer complexes catalyzed stereo-



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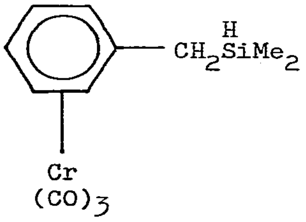

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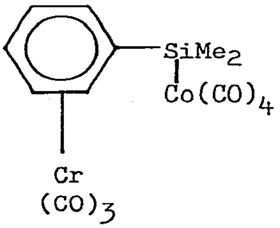

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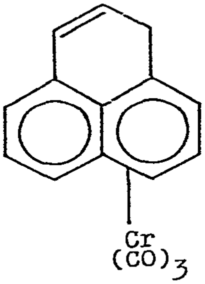

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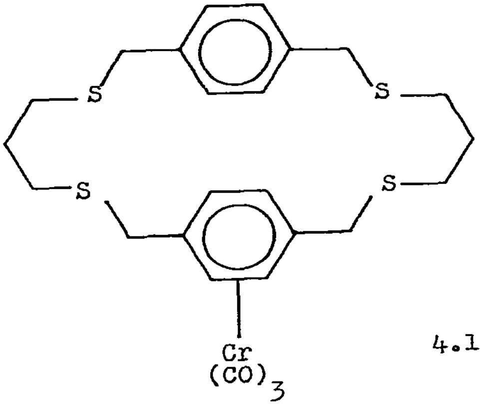

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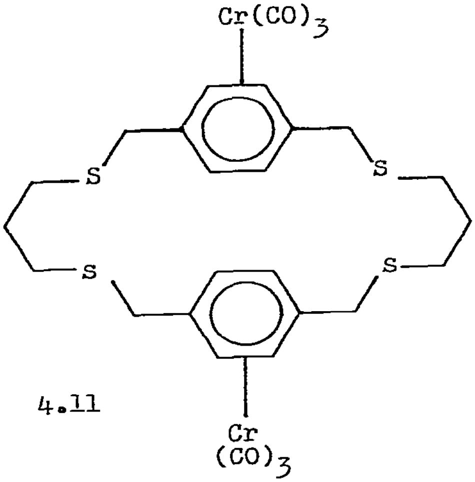

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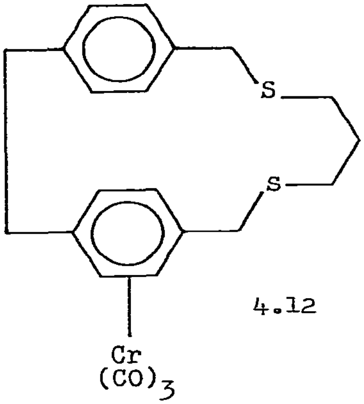

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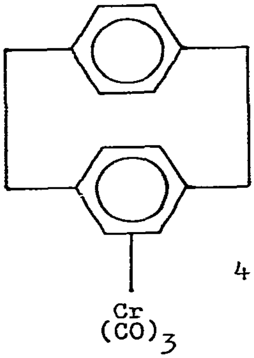

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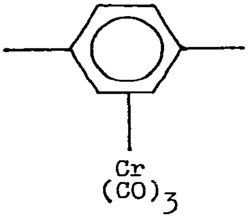
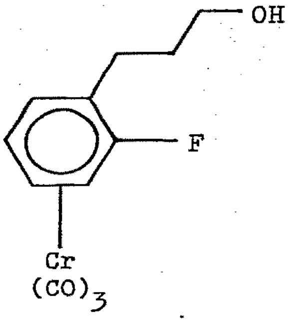


4.14

selective hydrogenation of methyl sorbate to cis-3-hexenoate in cyclohexane and tetrahydrofuran [30].

The tricarbonylchromium complex (4.15) was prepared from the parent fluoro alcohol by reaction with tricarbonyltris(pyridine)-



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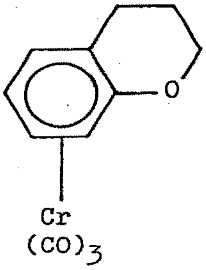

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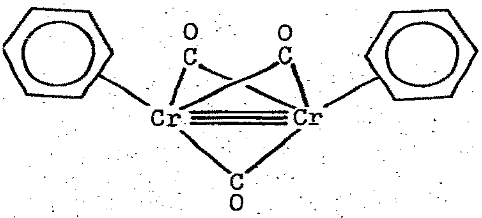
chromium in the presence of boron trifluoride-ether. Addition of potassium t-butoxide to the complex (4.15) resulted in cyclization to give the chroman complex (4.16). Treatment of the latter complex with iodine gave the uncomplexed chroman in quantitative yield [31]. When (η-benzene)dicarbonyl(methyl cyanide)chromium was heated in benzene the chromium complex (4.17) with a $\mathrm{Cr{\equiv}Cr}$ triple bond was formed [32]. Heating chromium hexacarbonyl with di-n-butyl ether at reflux temperature gave a mixture of o-, m-, and p-dimethylbenchrotrenes. In the same way dipentyl ether and chromium hexacarbonyl gave a mixture of isobutyl- and 1-methyl-3--propyl-benchrotrene. Dipropyl ether and dihexyl ether were inert towards the carbonyl. Carbon amides may act as catalysts in promoting the reaction [33]. Regiospecific attack of 1,4-enynes,



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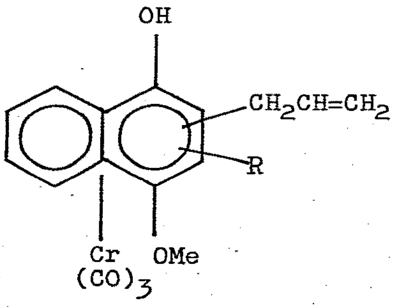
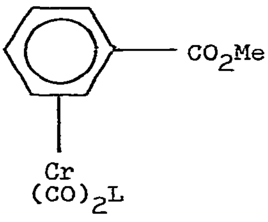


4.18

$RC\equiv CCH_2CH=CH_2$, where R = Me, Et, Pr, Bu, on pentacarbonyl(methoxyphenylcarbene) chromium (0) gave the tricarbonylchromium complexes (4.18; R = Me, Et, Pr, Bu) which were degraded to the free ligands or the corresponding naphthaquinones on silica gel. Oxidation of the complexes (4.18) with Ag_2O gave only the corresponding naphthaquinones or their tricarbonylchromium complexes [34].

(ii) Spectroscopic and Physico-chemical Studies

The electronic effects of the ligands CO, CS and CSe in the benchrotrene complexes (4.19; L = CO, CS, CSe) have been compared by theoretical calculations and by spectroscopic and structural investigations. The strength of the ligand-metal bond and the electron withdrawing power of the ligand decreased in the order CSe > CS > CO with the largest difference between CS and CO. CS was the most efficient π-electron acceptor and σ-electron donor [35].



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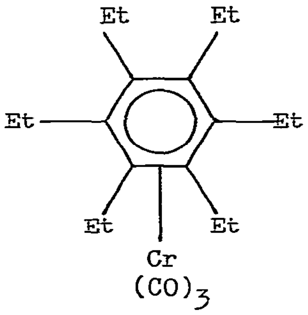

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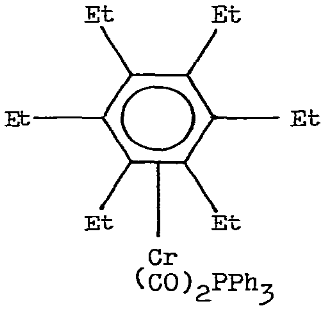

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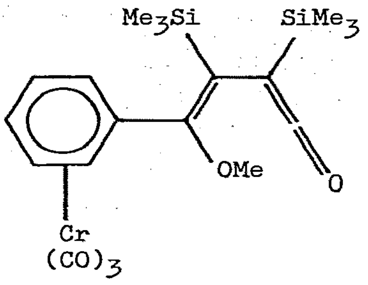
The crystal and molecular structures of the two chromium carbonyl complexes (4.20 and 4.21) have been determined by X-ray analysis. In complex (4.20) the hexaethylbenzene ligand closely resembled the ground state conformation of the free arene with an alternation of the ethyl groups above and below the mean plane of the benzene ring. However, in complex (4.21) all six ethyl groups were on the side of the benzene ring remote from the metal [36]. The crystal and molecular structure of the benchrotrenylketene (4.22) has been determined by X-ray diffraction. The structure showed little evidence for conjugation between the phenyl ring and the vinylketene group [37].



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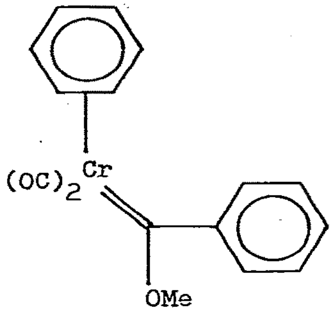

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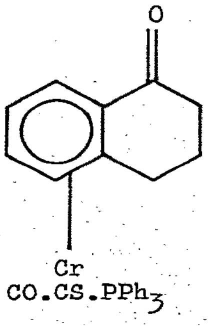
The crystal and molecular structure of (η-benzene)dicarbonylmethoxyphenylcarbenechromium (4.23) have been determined by X-ray crystallography. The chromium-carbene carbon interatomic distance was the shortest reported to date at 1.93 Å. Bond lengths and bond angles around the carbene carbon atom were discussed in terms of the π-donor ability of the three groups and competition between them for the carbene positive charge [38]. The structure of the (η-tetralone)chromium complex (4.24) has been determined by X-ray analysis. The Cr-C(S) bond was shorter than the Cr-C(O) bond due to the greater degree of π-back-bonding associated with the thiocarbonyl ligand [39]. The (η-diazaborin)chromium complexes (4.25; R = H, Me) were obtained by treatment of the free ligands



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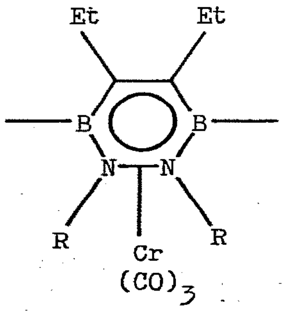

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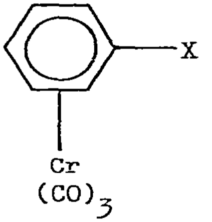
which were isoelectronic and isostructural with benzene, with $(MeCN)_3Cr(CO)_3$ or $Cr(CO)_6$ in acetonitrile. The X-ray crystal structure of the complex (4.25; R = H) confirmed that the metal-ring atom bond distance was determined by the nature of the ring atom [40]. The photoelectron spectra of the tricarbonyl-chromium and -molybdenum complexes of mesitylene have been measured. The electronic structures of the ligands were found to be insensitive to the nature of the metal [41].

The mass spectra of several substituted benchrotrenes (4.26; X = H, alkyl, aryl, OMe, NH_2, NMe_2, CO_2Me, halogeno) have been recorded and interpreted in terms of the quasi-equilibrium theory. The nature of the groups X in the complexes (4.26) did not affect decarbonylation of the molecular ions. A linear relationship was observed between log $[Cr]^+/[(XC_6H_5)Cr]^+$ and the number of degrees of freedom of the ion $[(XC_6H_5)Cr]^+$ [42]. The ion-molecule reactions



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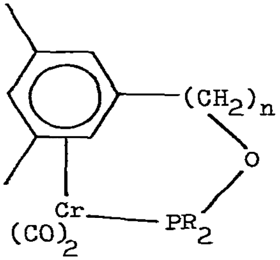

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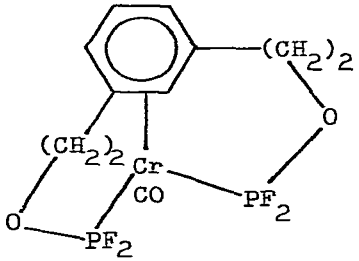

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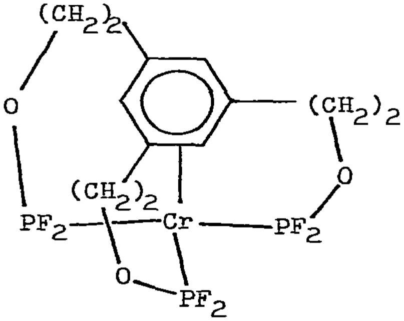

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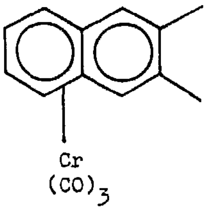
that occurred in a mass spectrometer were studied for the combined vaporization of the (η-arene)tricarbonylchromium complexes (η-arene = C_6H_6, C_6H_5Cl, $C_6H_5NMe_2$, C_4H_4S, C_4H_4Se) and the (η-cyclopentadienyl)metal carbonyls, (η-C_5H_4R)$M(CO)_n$, where M = Mn, R = H, Cl, Br, COMe, n = 3; M = Re, R = H, n = 3; M = V, R = H, n = 4, with various aromatic (PhR; R = H, NH_2, Cl, OH, CH_2Cl, NO_2) and heterocyclic compounds. In all cases secondary ions of the type $(ArCrL)^+$ or $(C_5H_4RML)^+$ where L is an aromatic or heterocyclic compound, were formed [43]. The mass spectra of the (η-arene)-chromium complexes (4.27; R = OPh, n = 1-5; R = Ph, n = 2; R = OEt, n = 2, 3; R = F, n = 2; 4.28 and 4.29), some related complexes and of the tricarbonylchromium precursors to these compounds were recorded and interpreted. The mass spectra of the complexes (4.27, 4.28 and 4.29) showed the presence of molecular ions which decomposed by the simultaneous ejection of the two carbonyl groups. The subsequent fragmentation was controlled by the nature of the substitutuent on the phosphorus atom [44].

Electron impact and chemical ionization mass spectra have been compared for a range of benchrotrene complexes including methyl- and acetyl-benchrotrenes, the naphthalene complex (4.30) and the diphenylpropane related complexes (4.31: M = C, Si, Ge, Sn, Pb). The MH^+ ion was the base peak for all of the simple benchrotrene complexes using chemical ionization while $[M-3CO]^+$ or $^{52}Cr^+$ dominated the mass spectra with electron impact ionization. The diphenyl complexes (4.31) gave chemical ionization molecular ion clusters, but the base peaks arose by fragmentation of the Group



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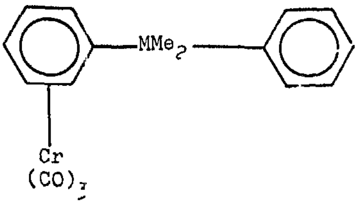
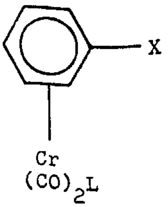


4.31

IV element-benzene bond. Electron impact ionization of these complexes was characterized by loss of carbon monoxide and the formation of Cr^+ ions [45]. Gas phase reactions of a series of (η-arene)tricarbonylchromium complexes, where η-arene = benzene, toluene, methylbenzoate and acetophenone and (η-cycloheptatriene)-tricarbonyl complexes of chromium, molybdenum and tungsten with Brønsted acid reagent ions H_3^+, CH_5^+, t-$C_4H_9^+$ and $(NH_3)_nH^+$ have been investigated. These reactions were carried out in a mass spectrometer and they depended on the Brønsted acid strengths of the ions and on the basicity of the metal complexes. Processes were identified which involved either metal or ligand proton attachment together with charge exchange, electrophilic addition and rearrangement [46].

The neutron inelastic scattering spectrum of (η-benzene)tricarbonylchromium has been measured between 10 and 2000 cm^{-1}. A new valence force field was determined and when this was used to calculate the neutron spectrum, good agreement with the observed optical frequencies and neutron intensities was obtained [47]. Methods have been developed for the accurate determination of chromium in organochromium compounds. After oxidation the chromium was determined spectrophotometrically as Cr(VI) with diphenylcarbazide [48]. The IR spectra of a number of benchrotrene analogues such as the complexes (4.32; X = Et, CO_2Me, L = CS; X = COMe, L = PPh_3, $AsPh_3$; X = CO_2Me, L = CNCOPh) were recorded in the carbonyl stretching region. The activity of several complexes (4.32) in the hydrogenation of norbornadiene was evaluated and it was inferred that changes in the IR spectra of the complexes in THF solution may be used as a guide to the catalytic activity. It was suggested that centrochiral complexes of stoichiometry (η-Arene)$CrCOL^1L^2$ may be useful as hydrogenation catalysts in asymmetric synthesis [49]. The IR and Raman spectra of tricarbonyl(η-cycloheptatriene)-chromium, -molybdenum and -tungsten have been used to determine the CO force constants. The results obtained allowed an almost complete assignment of the metal-ligand vibrations; ν(CO), δ(MCO), ν(MC), ν(M-ring), ring-tilt and δ(CMC) [50].

The ^1H NMR spectra of the tricarbonylchromium complexes (4.33, 4.34 and 4.35) were recorded and the nonexponential relaxation of the methyl signals was analysed. Correlation times for internal rotation of the methyl group and local reorientation were determined [51]. Bis(tricarbonylchromium)diphenylmethane has been treated with excess potassium t-butoxide to give the anion (4.36).



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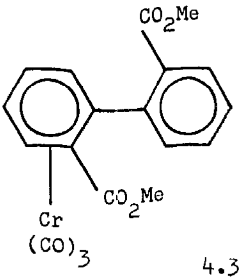

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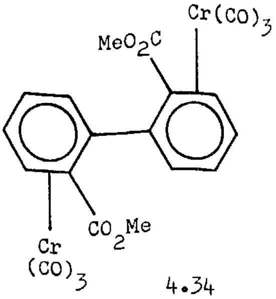

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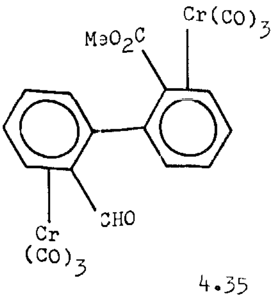

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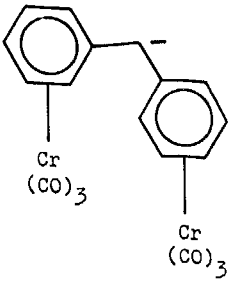
^{13}C and ^{1}H NMR chemical shift coupling constant data indicated that the carbanion (4.36) was stabilized by delocalization of negative charge on to the carbonyl moieties. The cation (4.37) was studie



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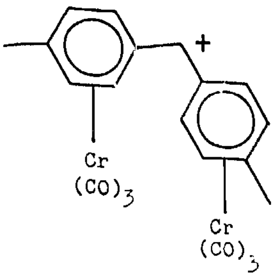
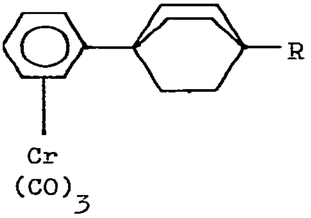


4.37

also and there was no evidence to suggest any interaction between the chromium and the α-carbon atom [52]. The ^{13}C and ^{19}F NMR spectra of the tricarbonylchromium complexes (4.38; R = H, F, Cl, Br, OAc, COMe, OMe, Me, t-Bu, 4.39; R = H, F, OAc, OMe, Me, and 4.40; R = H, F, OMe) were recorded and interpreted. The substituent chemical shifts (SCS) permitted an unambiguous evaluation of the polar factors governing ^{13}C and ^{19}F SCS in (η-arene) $Cr(CO)_3$ complexes. It was concluded that a qualitative description of the η-arene-$Cr(CO)_3$ bond in terms of only the π-electrons of the arene ring was preferred and that there was little participation by the σ-electrons [53].



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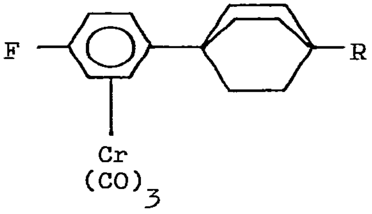

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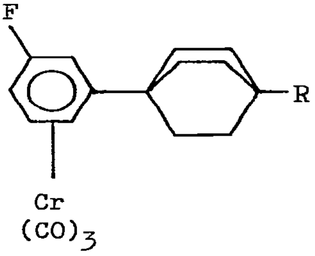

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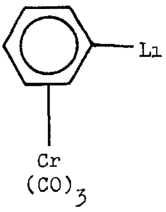
The ^{13}C NMR spectra of (η-fluorene)-, (η-3-methylfluorene)- and (η-6-methylfluorene)-tricarbonylchromium complexes were described by the "fingerprint" method, ^{13}C spin-lattice relaxation time measurements and an additive calculation of carbon chemical shifts of the methyl-substituted complexes [54]. The preferred conformations of mono- and bis-(tricarbonylchromium) complexes of dimethyl-1,1'-biphenyl-2,2'-dicarboxylate were determined via ^{1}H NMR spectroscopy using the lanthanide induced shift technique. The mono- and bis-(tricarbonylchromium) complexes of methyl-2'-methyl-1,1'-biphenyl-2-carboxylate were used as model compounds. In all the complexes the torsional angle between the two rings was approximately 90° with the substituents, $Cr(CO)_3$, CO_2Me and Me occupying one of the different octants [55]. The formation of charge-transfer complexes by benchrotrene and twenty substituted benchrotrenes with π-acceptor molecules including tetracyanoethylene, chloranil, trinitrobenzene and trinitrophenol has been investigated by UV-visible absorption spectroscopy. Tetracyanoethylene formed molecular complexes which were of the π,π-type. The character of the donor-acceptor interaction between the tricarbonylchromium group and the arene ligand depended on the positive charge value on the benzene ring which was identifiable by the electron affinity of the acceptor. Thus for the powerful π-acceptor tetracyanoethylene, the tricarbonylchromium group is an electron-donor relative to the benzene ring while the same group is an electron-acceptor for trinitrobenzene [56].

(iii) General Chemistry

Lithiobenchotrene (4.41) has been prepared by the reaction of benchotrene with n-butyllithium in tetrahydrofuran at -20°C. When the lithio-derivative (4.41) was quenched with methyl iodide or iodine, (η-toluene)- and (η-iodobenzene)-tricarbonylchromium respectively were obtained. When the lithio-derivative was warmed



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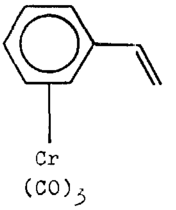

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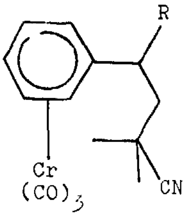

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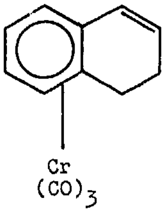
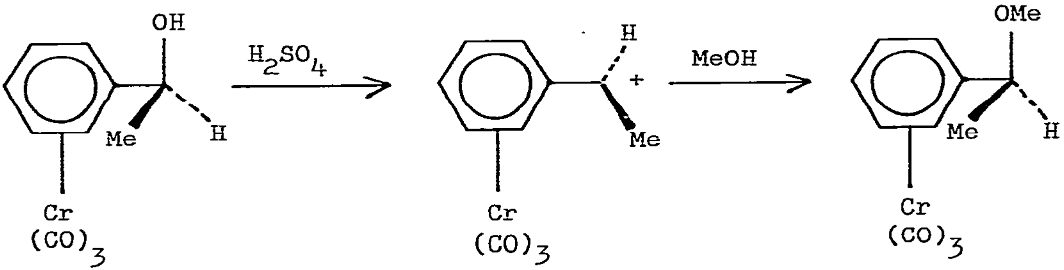


4.44

to 0°C in the presence of excess n-butyllithium, n-butylbenzene was formed in high yield [57]. The addition of 2-lithio-2-methylpropionitrile to tricarbonyl(η^6-styrene)chromium (4.42) at -30° gave the complex (4.43; R = H) after hydrolysis. If an electrophile was added before hydrolysis a substituent was introduced into the α-position. For example, the addition of methyl iodide or acetyl chloride gave the complexes (4.43; R = Me and COMe) respectively. Similar reactions were carried out with other



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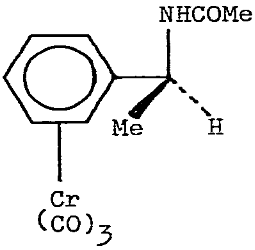

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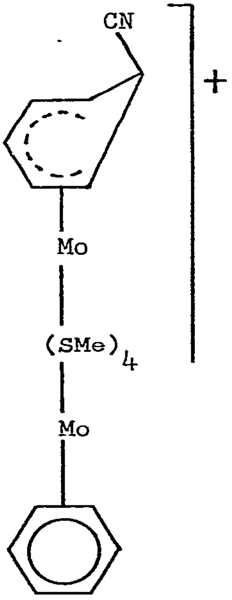

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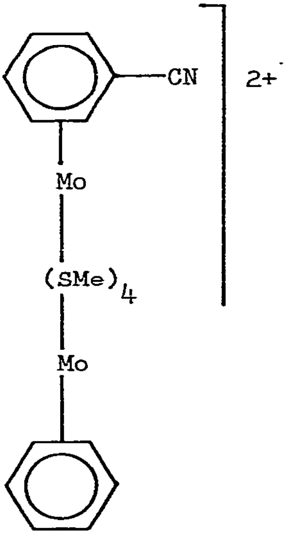
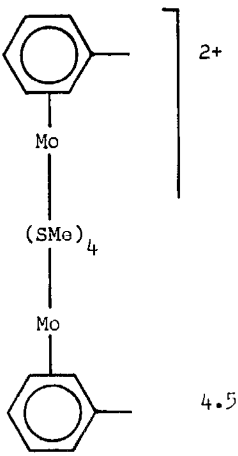


4.49

organolithium reagents and with other tricarbonylchromium complexes, for example with the η^6-dihydronaphthalene derivative (4.44) [58]. Treatment of the (S)-(+)-1-phenylethanol complex (4.45) of optical purity 89% with methanol and sulphuric acid gave the ether (S)-(-)- (4.46) of 64% optical purity. Therefore this reaction proceeded with retention of configuration and 72% conversion of optical purity. The amide (4.47) was prepared in a similar manner and it was obtained with 92% optical purity [59].

Exhaustive electrolysis of the (η-cyanocyclohexadienyl)molybdenum complex (4.48) at a controlled potential of + 1.2V in propylene carbonate gave the (η-benzonitrile)molybdenum complex (4.49 The reaction involved two-electron oxidation followed by rapid elimination of a proton [60]. The binuclear (η-toluene)molybdenum dication (4.50) underwent oxidation with $KMnO_4$ in hydrochloric acid at -10°C to give a dication of stoichiometry $[Mo_2(MeC_6H_5)_2(SMe)_3OSMe]^{2+}$. IR and NMR spectroscopy confirmed that oxidation had taken place at the sulphur atom [61]. The carbene complexes



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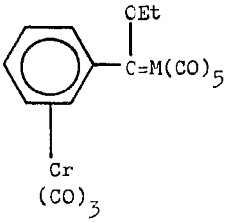

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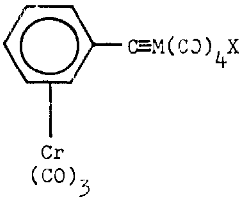

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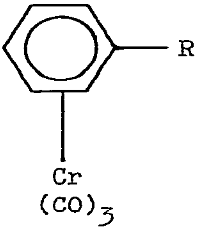
(4.51; M = Cr, Mo, W) have been prepared by treatment of tricarbonyl(η^6-phenyllithium)chromium with $M(CO)_6$, where M = Cr, Mo, W, followed by alkylation with $(Et_3O)^+BF_4^-$. Reaction of the carbene complexes (4.51; Cr, W) with boron halides, BX_3 (X = Cl, Br), gave the carbyne complexes (4.52; M = Cr, W; X = Cl, Br) [62].

Nucleophilic and electrophilic substitution in (η-arene)tricarbonylchromium complexes has been investigated by the application of extended Hueckel molecular orbital calculations and qualitative considerations from perturbation theory. It was found that the regioselectivity of attack on the arene should be controlled by the substituent on the arene and the conformation of the tricarbonylchromium moiety. It was shown that arene carbons which were eclipsed with respect to the carbonyl group were more prone to nucleophilic attack whilst electrophilic substitution occurred more readily at the staggered arene carbon atoms [63].



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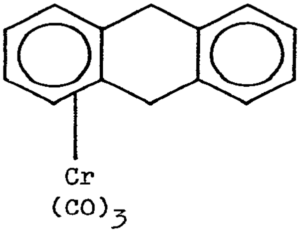
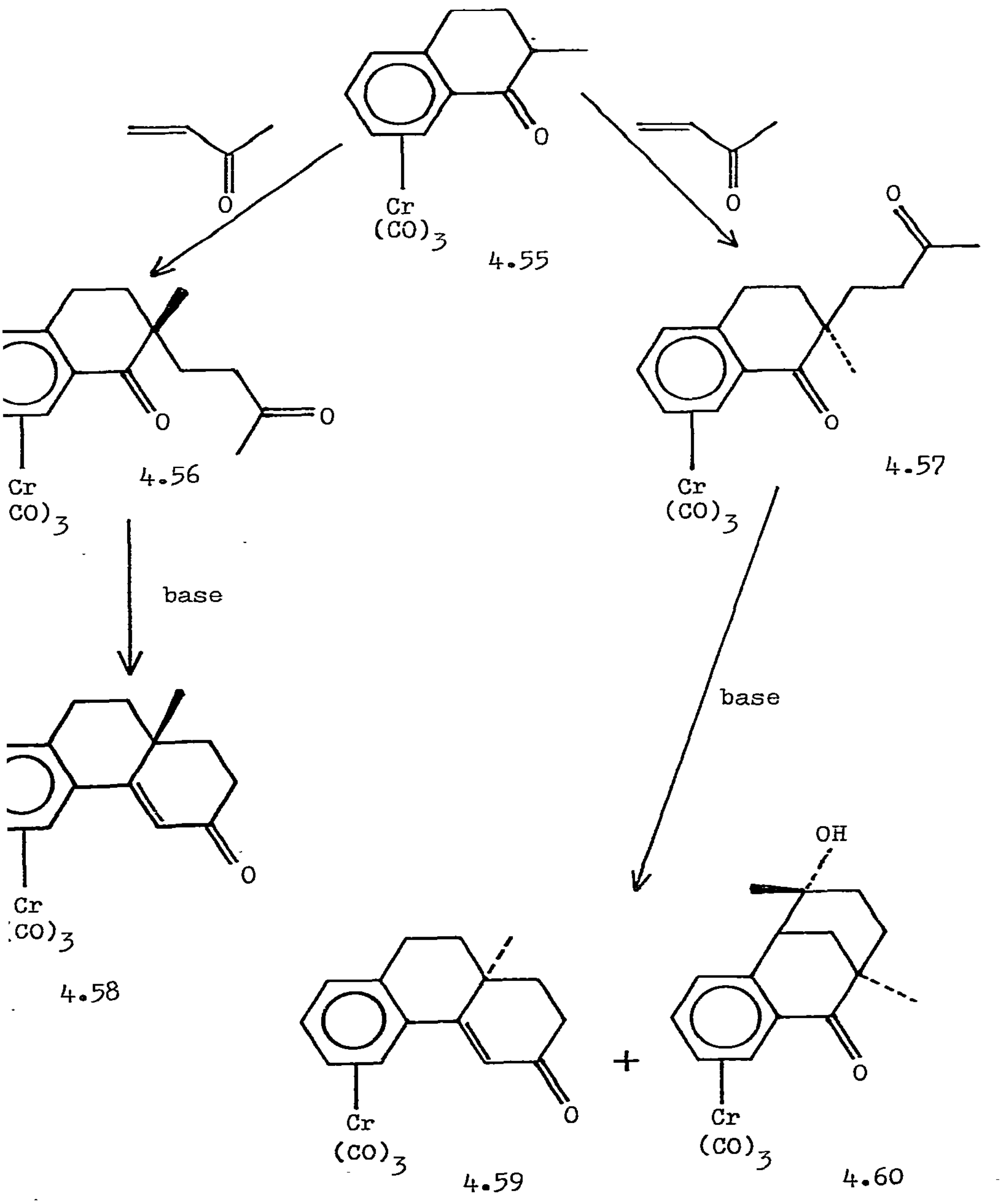


4.54

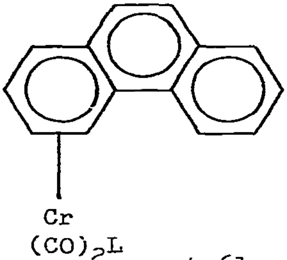
Base-catalysed hydrogen-deuterium exchange in the benchrotrene complexes (4.53; R = Me, CH_2Ph, CH_2CH_2Ph, CH=CHMe and 4.54) took place fastest for the hydrogens adjacent to the complexed benzene ring. A mechanism involving conjugative stabilization using the tricarbonylchromium group was suggested. The exchange reactions for the benchrotrene complexes (4.53; R = OMe, NMe_2, CMe_3 and CO_2Et) were explained in terms of the conformation of the complexes [64]. Jaouen and co-workers showed that the complexation of the tricarbonylchromium unit to certain aromatic hydrocarbons enhanced the benzylic position towards attack by superoxide ion in dimethylsulphoxide. For example, the reaction of tricarbonyl-(η^6-diphenylmethane)chromium with KO_2 in dimethylsulphoxide at 90°C gave benzophenone in 59% yield [65]. Photolysis of (η^6-arene)-tricarbonylchromium complexes, where arene = PhH, PhMe, 1,3,5-$Me_3C_6H_3$, with diphenylacetylene in tetrahydrofuran gave (η^2-PhC≡CPh)$_3$Cr(CO). Benchotrene underwent a similar reaction with Ph_3GeC≡CPh to give

η^2-Ph$_3$GeC≡CPh)$_3$Cr(CO) [66].

A scheme has been developed for the stereospecific synthesis f optically active benzobicyclic systems using (η-indanone)- and η-tetralone)-chromiumtricarbonyl complexes. Thus a mixture of



the exo- and endo-isomers of the methyltetralone complex (4.55) was treated with methylvinylketone to form the 3-oxobutyl derivatives (4.56 and 4.57) in the ratio 13:87. Cyclization of the exo-methyl isomer (4.56) in methanolic Triton B and benzene gave the α-enone complex (4.58) in 91% yield while cyclization of the endo-methyl isomer (4.57) afforded a small proportion of the aldol condensation product (4.59) together with the keto-alcohol (4.60) as the major product [67]. The dicarbonyl(η-phenanthrene)chromium complexes [4.61; L = PEt_3, PBu_3, PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P(OBu)_3$, $SbPh_3$] and the dicarbonyl(η-naphthalene)chromium complexes (4.62; X = Et, Bu, Ph, OPh) have been formed from the corresponding tricarbonyl complexes by photosubstitution. The complexes (4.61 and 4.62) were investigated as catalysts for the hydrogenation of norbornadiene and found to be less efficient than the corresponding tricarbonyl complexes. The difference was ascribed to steric shielding of the chromium by the bulky PR_3 group which inhibited diene-chromium interaction. The crystal and molecular structures



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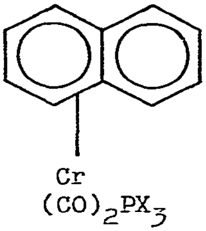

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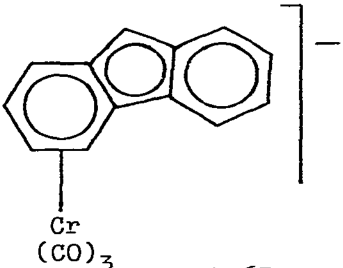

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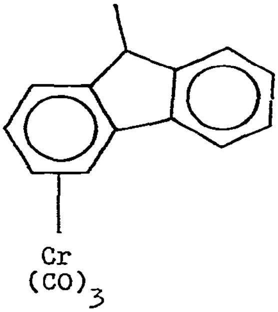

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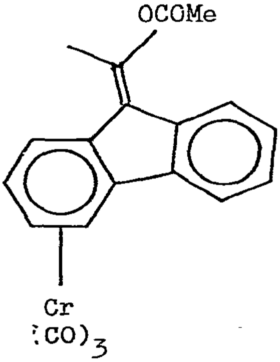

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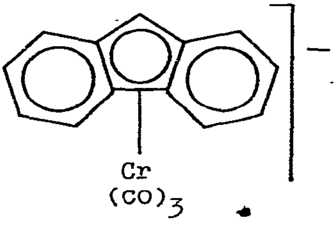
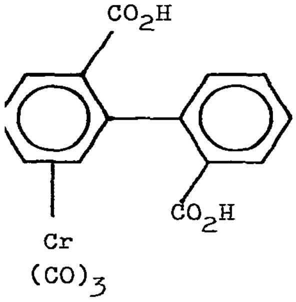


4.66

of two complexes (4.61; L = PEt_3 and 4.62; X = OPh) were determined by X-ray crystallography and supported this proposal [68].

Treatment of tricarbonyl(η-fluorene)chromium with an excess of potassium t-butoxide in THF at -70°C gave the anion (4.63) which combined with methyl iodide to form the C(9)-methyl derivative (4.64). A second methyl group was introduced at C(9) by treatment of the derivative (4.64) with potassium t-butoxide and then methyl iodide. Acylation of the anion (4.63) with acetyl chloride at -70° gave the enol form of the acetate of tricarbonyl(9-acetylfluorene)chromium (4.65). When the anion (4.63) was allowed to warm from -70°C to -20°C then rearrangement to the (η^5-fluorene)chromium anion (4.66) took place [69].



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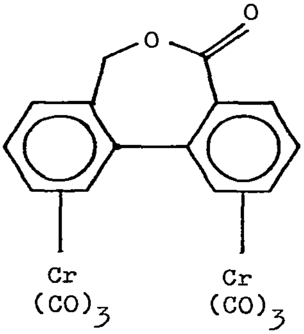
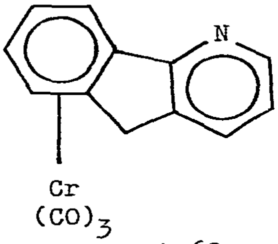


4.68

Diphenic acid and its monomethyl ester have been converted to the corresponding mono- and bis-tricarbonylchromium complexes, such as the diacid complex (4.67), by way of the trimethylsilyl esters and subsequent hydrolysis. The complexes were then reduced to the hydroxymethyl derivatives with diborane. Configurational assignments for these last derivatives were made by IR and ^1H NMR spectroscopy. The _trans_-bis(tricarbonylchromium) complex (4.68) was formed in the same way as the diphenic acid complexes and was used in ring opening and cyclization reactions [70].

The reactions of 2- and 4-azafluorenes and methyl derivatives of these compounds with hexacarbonylchromium have been studied. 2-Azafluorene forms a $Cr(CO)_5$ N-donor complex while the other compounds form (η-arene) chromiumtricarbonyl complexes with the benzene ring rather than pyridine bonded to the metal. The product



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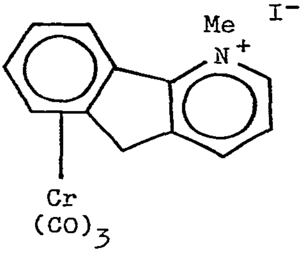

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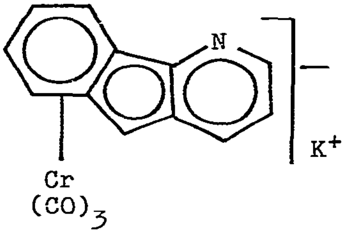

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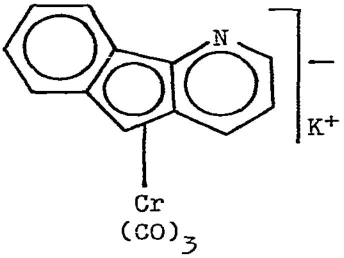

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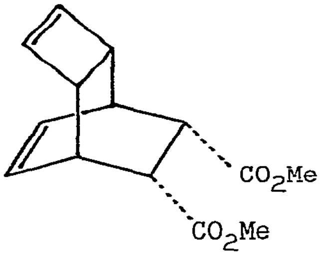
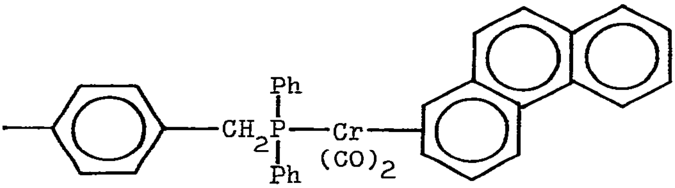


4.73

(4.69) obtained from 4-azafluorene underwent addition with methyl iodide to form the corresponding quaternary ammonium salt (4.70) while deprotonation with an excess of t-BuOK gave a mixture of the (η^6-arene)chromiumtricarbonyl anion (4.71) and the (η^5-cyclopentadienyl)chromium tricarbonyl anion (4.72) [71]. The hydrogenation of the ester (4.73) in the presence of tricarbonyl(η-phenanthrene)-chromium as the homogeneous catalyst was stereospecific and highly regioselective with the cis-endo-1,2-addition of hydrogen [72]. Irradiation of tricarbonyl(η-phenanthrene)chromium with polystyrene--CH_2PPh_2 polymer beads gave the dicarbonyl(η-phenanthrene)substituted polymer (4.74). The polymer beads (4.74) were examined by scanning electron microscopy. Large pore beads allowed the reagents to react throughout the polymer, whereas small pore sizes permitted penetration of the reagents only to a limited extent [73]. Benchrotrene and its carboxymethyl derivative have been irradiated with



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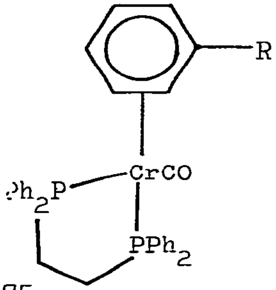


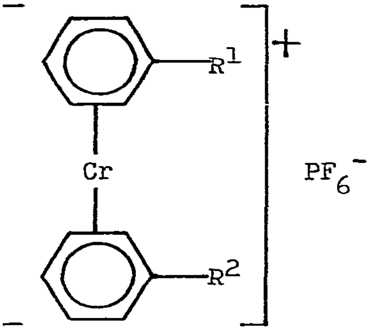
4.75

e ligand $Ph_2P(CH_2)_2PPh_2$ to form the complexes (4.75; R = H,
$)_2$Me). A similar reaction was carried out with tricarbonyl-
-mesitylene)chromium [74].

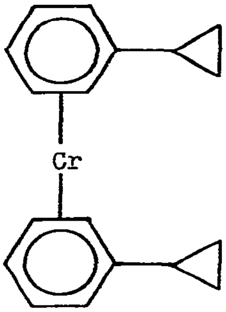
$(\eta-C_6H_6)_2Cr$

The cocondensation of chromium vapour with chlorobenzene followed
oxidation and treatment with sodium hexafluorophosphate gave the
-chlorobenzene)chromium complex (5.1; $R^1 = R^2 = Cl$). The
action of this latter complex with sodium methoxide in methanol-
thyl cyanide produced the (η-methoxybenzene) complexes (5.1;
= MeO, $R^2 = Cl$; $R^1 = R^2 = MeO$) [75]. The reactions of metal
oms with various organocyclopropanes have been examined including
e cocondensation of chromium atoms with cyclopropylbenzene when
s(η-cyclopropylbenzene)chromium (5.2) was formed [76]. The
pour of [3.3]paracyclophane has been cocondensed with chromium
oms to form the cyclophane-chromium complex (5.3) which was
idized in air to give the corresponding radical cation isolated
the hexafluorophosphate salt [77].

Bis(η-naphthalene)chromium (5.4) has been formed by condensation
chromium atoms into a solution of naphthalene in diglyme at
0°C. The 1-methyl- and 1,4-dimethyl-naphthalene complexes were
tained in the same way. The parent complex (5.4) was highly
active and one naphthalene ligand was displaced by carbon
noxide at 0°C to form the benchrotrene analogue (5.5). Similar
actions were achieved with PF_3, $P(OMe)_3$ and PMe_3 while isocyanides



5.1



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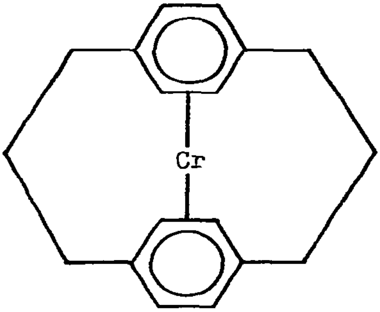
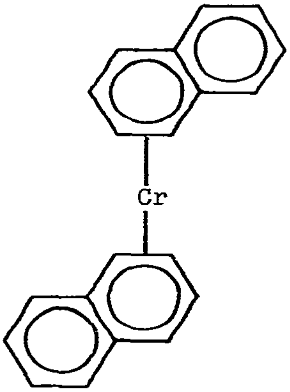


5.3

displaced both arene ligands [78]. The infrared and Raman spectra of $(\eta$-$C_6H_6)Cr(\eta$-$C_6F_6)$ and $(\eta$-$C_6D_6)Cr(\eta$-$C_6F_6)$ were analyzed and about half of the forty six normal modes in each molecule were assigned.



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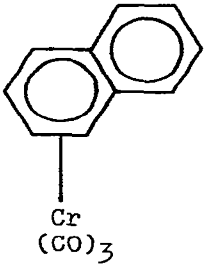

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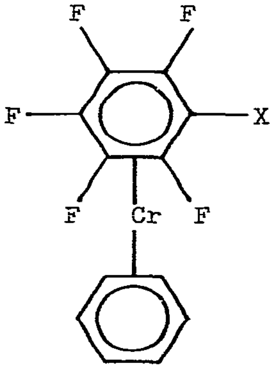
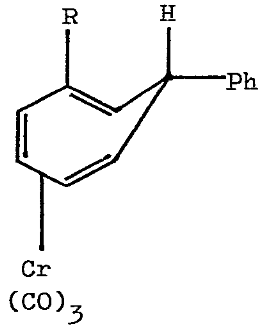


5.6

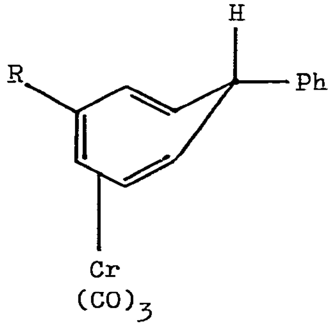
The assignments fitted in with the idea of π-electron migration from the η-C_6H_6ring to the η-C_6F_6 ring [79]. The ^{19}F NMR spectra of a series of bis(η-arene)chromium complexes [5.6; X = PPh_2, $SiMe_3$, Ph, SMe, CO_2Et, $CONHC_6H_4F$, CO-C_4H_3O, H, CH(OH)-ferrocenyl, F] were recorded, interpreted and compared with the spectra of the corresponding C_6F_5X molecules. On complexation the ^{19}F chemical hifts were shielded by 30-50 ppm [80].

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

Treatment of the (η-arene)tricarbonylchromium complexes 4.53; R = H, Et, Ph, CH_2Ph, CH_2OH, OMe, NMe_2) with benzyl hloride-lithium diisopropylamide led to stereospecific ring xpansion and the corresponding endo-(η-cycloheptatriene)complexes 6.1a and 6.1b) were obtained [81]. Field desorption mass pectrometry was used to characterize tricarbonyl(η^6-cycloheptatriene)chromium, molybdenum and tungsten. The only peaks observed were he molecular $[P]^{+\bullet}$ ions and the less intense $[P + 1]^+$ and $[P + 2]^+$ ons. There was a complete absence of fragment ions [82]. ricarbonyl(η-cycloheptatriene)chromium underwent [4s + 6s] cyclo-ddition with butadiene in the presence of UV light to form η-bicyclo[4.4.1]undeca-1,3,7-triene)tricarbonylchromium in 29% ield [83]. Butadiene has been irradiated together with tri-arbonyl(η-cycloheptatriene)chromium in pentane to form (η-bicyclo-4.4.1] undeca-2,4,8-triene)-tricarbonylchromium in 29% yield [84].

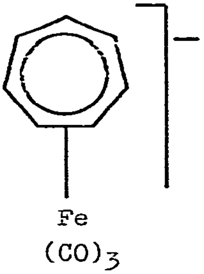


6.1a

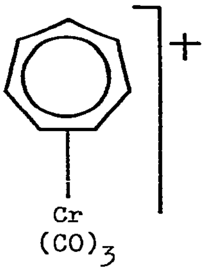


6.1b

The (η-cycloheptatrienyl)ferrate anion (6.2), generated from he corresponding (η-cycloheptatriene)iron complex, has been used s a nucleophile to attack the (η-cycloheptatrienyl)metal cations 6.3; M = Cr, Mo, W) and form the binuclear complexes (6.4; = Cr, Mo, W). The products (6.4) exhibited exo-stereochemistry 85]. The mechanism of displacement of cycloheptatriene from ricarbonyl(η-cycloheptatriene)-chromium, -molybdenum and -tungsten y benzonitrile has been investigated. Results for the chromium



6.2



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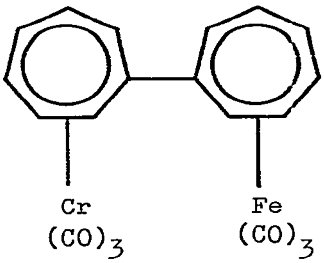
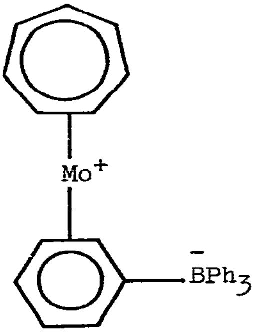


6.4

complex indicated a first-order dependence on the concentration of complex and benzonitrile while results for the molybdenum complex show first-order dependence on the complex and second-order dependence on benzonitrile. The tungsten complex showed intermediate behaviour. A mechanism was suggested in which the cycloheptatriene was attacked successively by benzonitrile ligands [86]. Reaction of dicarbonyl(η-cycloheptatrienyl)iodomolybdenum with sodium tetraphenylborate gave the zwitterionic complex (6.5). Cyclic voltammetry of the molybdenum complex (6.5) indicated several stable oxidation states. This complex also behaved as a homogeneous catalyst in the hydrogenation of cyclohexene and phenylacetylene [87].



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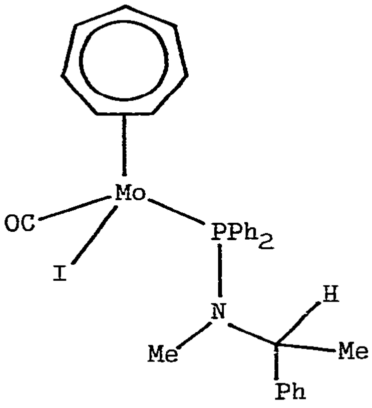

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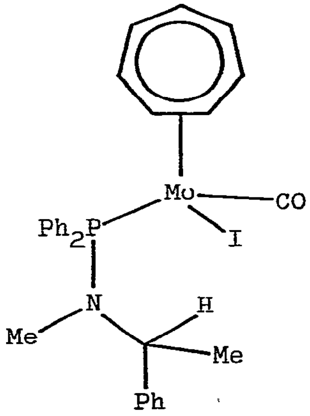
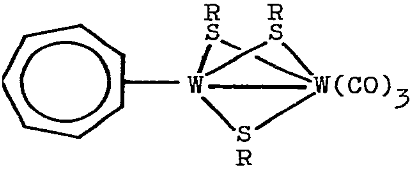


6.7

Treatment of dicarbonyl(η^7-cycloheptatrienyl)iodomolybdenum with (S)(+)-$Ph_2PN(Me)CH(Me)Ph$ gave the corresponding monocarbonyl complex as two diastereoisomers (6.6 and 6.7). An X-ray structure analysis on complex (6.6) showed that the absolute configuration at molybdenum was (R) [88]. The hydrocarbon ligand in tricarbonyl-(η-cycloheptatriene)molybdenum and -tungsten has been displaced by 3,5-dimethylpyrazolyl phosphines to give the corresponding pyrazolylphosphine complexes [89]. Treatment of tricarbonyl(η-cycloheptatriene)molybdenum with tetraethylthiuram disulphide in daylight gave $Mo(S_2CNEt_2)_3$. When the same reaction was carried out in the dark $Mo(S_2CNEt_2)_4$ was formed [90]. Reaction of dicarbonyl(η^7-cycloheptatrienyl)iodotungsten with the thiolates $Pb(SR)_2$ (R = Et, n = Bu) or the selenol PhSeH gave the dinuclear (6.8) and trinuclear (6.9) coordination compounds or their analogues with



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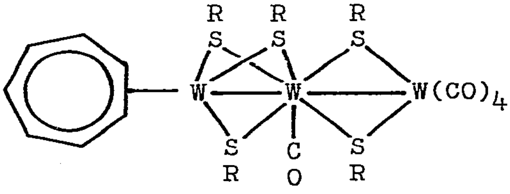


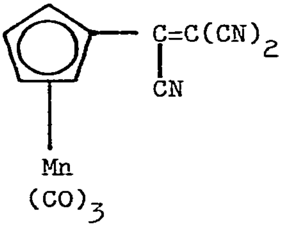
6.9

SePh in the place of SR [91].

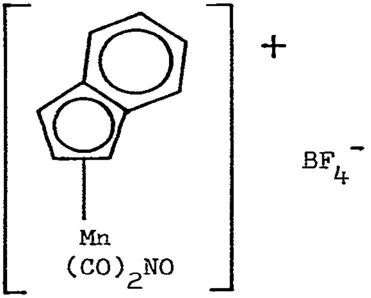
7. $(\eta$-$C_5H_5)Mn(CO)_3$

(i) Formation

Tricarbonyl(η-cyclopentadienyl)manganese has been prepared in high yield by stirring titanium (IV) chloride, manganese (II) chloride, magnesium and cyclopentadiene in tetrahydrofuran at room temperature for forty hours, followed by carbonylation with carbon monoxide at 180°C and eighty atmospheres for three hours [92]. Cyclopentadienylthallium (I) combines with tetracyanoethylene at room temperature to form thallium (I) tricyanovinylcyclopentadienide, $Tl^+[C_5H_4C(CN)C(CN)_2]^-$ in good yield. This reagent was attacked by bromopentacarbonylmanganese in THF to form the cymantrene complex



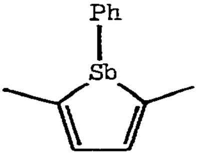
7.1



7.2

(7.1) in 31% yield. Several related reactions were reported [93].

(η^5-Indenyl)- and (η^5-fluorenyl)-tricarbonyl-manganese and -rhenium have been prepared by treatment of the methylcyanide complexes $(MeCN)_2M(CO)_3X$ where M = Mn, Re; X = Cl, Br, with indenyl- and fluorenyl-potassium. Reaction of the η^5-indenyl complex with NO_2BF_4 gave the corresponding nitrosyl derivative (7.2) [94]. Hydrostannation of 2,4-hexadiyne with dibutyltin dihydride gave 1,1-dibutyl-2,5-dimethylstannole which when treated with phenylantimony dichloride gave 1-phenyl-2,5-dimethylstibole (7.3). Treatment of the cyclic diene (7.3) with lithium followed by reaction with bromopentacarbonylmanganese or iron (II) chloride gave the corresponding cymantrene (7.4) and ferrocene (7.5) analogues.



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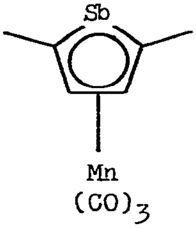

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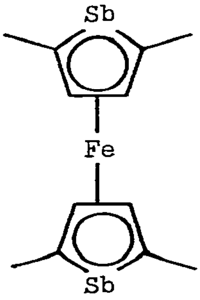
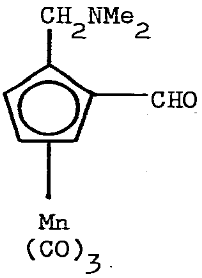


7.5

The ^{1}H and ^{13}C NMR spectra of these compounds were recorded and discussed [95].

(ii) Spectroscopic and Physico-chemical Studies

The 1,2-disubstituted cyamantrene (7.6) was resolved into the enantiomers by enantiospecific formation of stable copper complexes with chiral dipeptides. The absolute configuration of the enantiomers was determined by X-ray analysis [96]. α-Aminoethylcymantrene (7.7) has been resolved into its enantiomers by means of (+)-*d*-tartaric acid. The molecular structure and absolute configuration of (+)-(*R*)-α-(N-acetylamino)ethylcymantrene, prepared from (-)- (7.7), was established by X-ray analysis [97]. The crystal and molecular structure of chlorotris(cymantrenyl)tin has been determined by X-ray analysis. The tin atom was in the planes of two of the η-cyclopentadienyl groups and the angles between the rings were 69, 69 and 73° [98].



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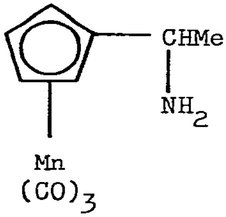
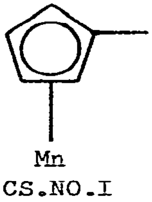


7.7

The structure of the manganese complex (7.8) has been determined by X-ray crystallography. The three unidentate ligands and the centre of the η-cyclopentadienyl ring surrounded the manganese atom in a distorted tetrahedral arrangement. By comparing the bond lengths with those found in related complexes it was concluded that $\mathrm{Mn{-}C(S)} \simeq \mathrm{Mn{-}C(O)} > \mathrm{Mn{-}N(O)}$ [99]. The crystal and molecular structure of μ-[oxybis(dimethylphosphane)]bis-[dicarbonyl(η-cyclopentadienyl)manganese(I)] has been determined by X-ray analysis [100]. The mass spectra of the manganese complexes (7.9; R = H, Me) were recorded and the appearance



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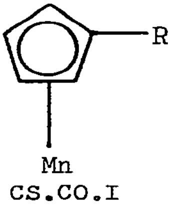
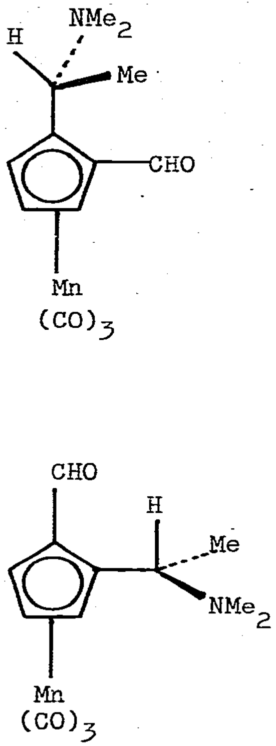


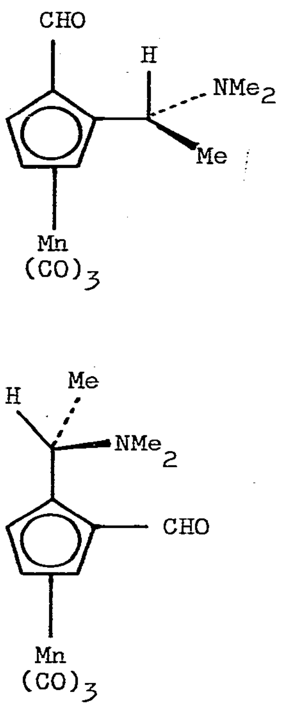
7.9

potentials of the manganese containing ions with intact ligands were determined. The primary fragmentations in the spectra were assigned and it was concluded that the strength of the manganese-ligand bonds in the fragment ions followed the order $I > RC_5H_4 > CS \gg NO$ [101]. The mass spectra of dimethylaminoalkyl derivatives of ferrocene and cymantrene, the corresponding methiodides and deutero analogues have been recorded and interpreted. It was shown that mass spectrometry could be used for the quantitative determination of the total deuterium content in these aminoalkyl derivatives [102].

The Fourier-transform ion-cyclotron-resonance mass spectra of cymantrene and related complexes have been measured. Cymantrene underwent condensation with the elimination of carbon monoxide and the mechanism of the process was discussed [103]. Liquid chromatography has been used to examine the chromatographic properties of copper (II) chelates formed from the Schiff bases obtained by condensation of a dipeptide with a 1,2-disubstituted cymantrene containing both planar and central chirality. Metallation of [α(N,N-dimethylamino)ethyl]cymantrene (R,S) with n-butyllithium and treatment with dimethylformamide gave a mixture of diastereoisomers (7.10a and 7.10b) in the ratio 7:2. The isomers (7.10a) were separated from the isomers (7.10b) by liquid chromatography of the copper chelates of their dipeptides. Metallocene chirality was important in the separation but central chirality did not contribute to the separation [104]. Reaction of dicarbonyl(η-cyclopentadienyl)-tetrahydrofuranmanganese with the (η^2-CS_2)iron derivatives [7.11;

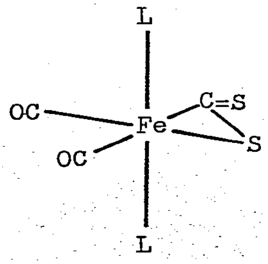


7.10a



7.10b

L = P(OMe)$_3$, PMe$_2$Ph, PMe$_3$, PPh$_3$] gave the corresponding manganese complexes (7.12). The structure of the complex (7.12; L = PMe$_2$PH was determined by X-ray analysis. The FeCS$_2$Mn moiety was nearly planar [105].



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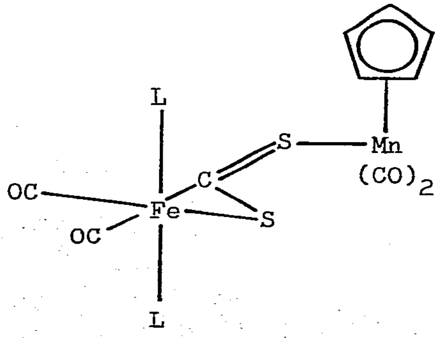
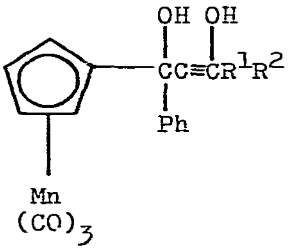


7.12

(iii) General Chemistry

Reaction of benzoylcymantrene with the Grignard reagents $BrMgC{\equiv}CR^1R^2(OMgBr)$ [$R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Et$; $R^1R^2 = (CH_2)_4$, $(CH_2)_5$] gave the corresponding diols (7.13) [106].



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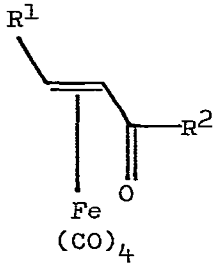

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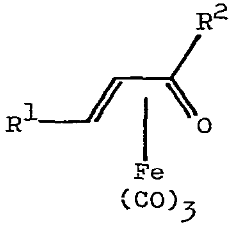
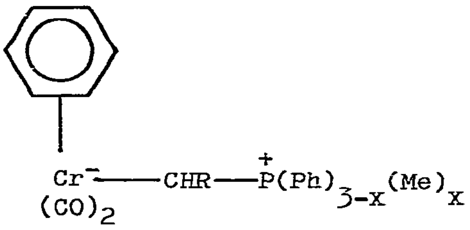


7.15

Reaction of the α,β-unsaturated ketones $R^1CH{=}CHCOR^2$ [$R^1 = (\eta\text{-}C_5H_4)Mn(CO)_3$, $R^2 = (\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)$, Ph, $(\eta\text{-}(C_5H_4)Mn(CO)_3$; $R^1 = Ph$, $R^2 = (\eta\text{-}C_5H_4)Mn(CO)_3$] with nonacarbonyldiiron gave the corresponding tetracarbonyliron (7.14) and tricarbonyliron (7.15) complexes whilst treatment with dodecacarbonyltriiron gave only the corresponding tricarbonyliron complexes (7.15) in high yields [107]. Reaction of $(\eta\text{-}C_6H_6)Cr(CO)_2THF$ and $(\eta\text{-}MeC_5H_4)Mn(CO)_2THF$ with methylene- and benzylidene-phosphoranes gave the stable complexes (7.16; R = H, Ph, x = 0-3 and 7.17; R = H, Ph, x = 0-3) respectively. The ^1H NMR, ^{31}P NMR and infrared spectra of these compounds were recorded and discussed [108].



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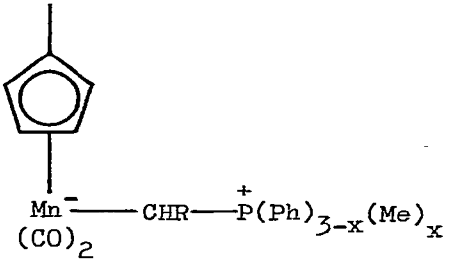
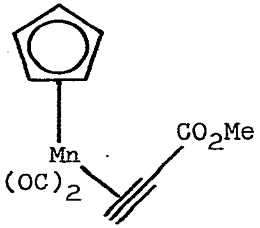
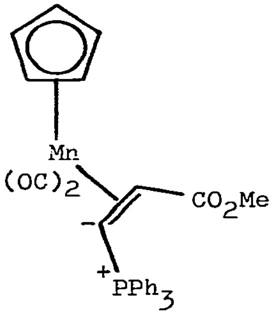


7.17

The acetylene complex of cymantrene (7.18) has been treated with triphenylphosphine in pentane to form the phosphorylide complex (7.19) in 85% yield [109]. The acetylenes, $RC\equiv CH$ where R = Et_3Si, Ph_3Si, Ph, ferrocenyl, underwent hydrosilylation in the presence of Speiers catalyst to form mixtures of adducts.



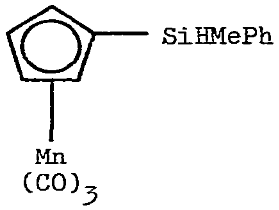
7.18



7.19

Thus hydrosilylation of ferrocenylacetylene with the cymantrenylsilane (7.20) gave a mixture of the β-adduct (7.21) in 68% yield and the α-adduct (7.22) in 17% yield [110]. Tricarbonyl(η-cyclopentadienyl)rhenium has been used as a starting material for synthesis of triphenylsilyl carbene and carbyne complexes. The initial stages involved treatment with $LiSiPh_3$ and alkylation with $MeSO_3F$ to form the triphenylsilyl complex (7.23) [111].

Reaction of the η-cyclopentadienyl complexes (7.24; M = Mn, R^1 = Me; M = Re, R^1 = H) with diazonium salts produced the corresponding aryldiazenido complexes (7.25; R^2 = CF_3, F, H). The structure of the complex cation (7.25; M = Mn, R^1 = Me, R^2 = CF_3) was determined by X-ray analysis. The cation had the "piano stool" geometry with the aryldiazenido ligand coordinated to the metal in a "singly bent" configuration. The complexes (7.25; M = Mn, R^1 = Me, R^2 = CF_3; M = Re, R^1 = H, R^2 = CF_3) underwent reaction with a variety of nucleophiles to form the corresponding dinitrogen complexes (7.26) [112, 113]. Photolysis of the THF complex (7.27) with tolunitrile gave the nitrile complex (7.28) which on subsequent treatment with dimethylmethylenephenylphosphorane gave the phosphorane (7.29; R = $CH{=}PPhMe_2$) which was hydrolysed to the imine complex (7.29; R = Me) [114]. Several cymantrenyl-



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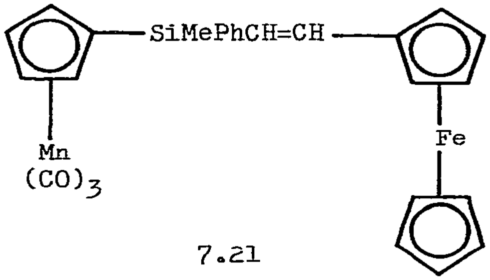

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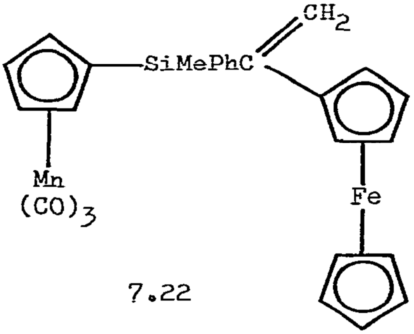

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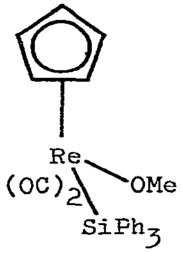
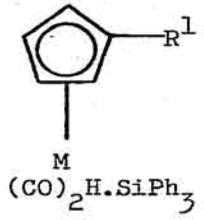


7.23

carbenium ions [7.30; R^1, R^2 = H, Me, Et, Ph; L^1, L^2 = CO, PEt_3, PPh_3, $P(OEt)_3$, $P(OPh)_3$; $L^1L^2 = Ph_2P(CH_2)_nPPh_2$ where n = 2, 3] have been prepared from the corresponding cymantrenylmethanols and investigated by IR and ^{31}P NMR spectroscopy. Formation of the carbenium ions involved a change in geometry by which the α-carbon atom moved closer to the manganese atom. In the presence of a phosphorus containing ligand the number of carbonyl bands observed in the IR exceeded the number theoretically expected. When two phosphorus atoms were present they were found to be magnetically nonequivalent [115].

Treatment of the rhenium complexes (7.31; R = Me, CH_2OH) with trimethylphosphine produced the corresponding η^1-cyclopentadiene complexes (7.32) [116]. Cymantrene has been converted to the THF intermediate (7.27) by irradiation at room temperature and the THF ligand was displaced by a phosphorin to give the σ-phosphorin complex (7.33). Subsequent irradiation of this complex (7.33)



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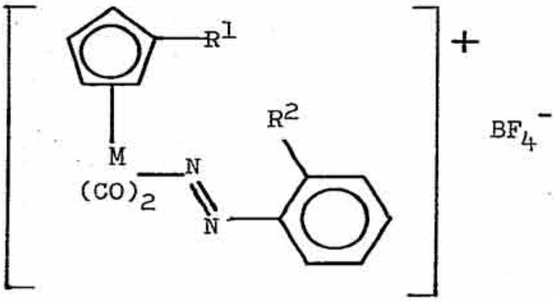

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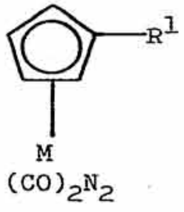

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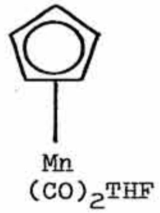

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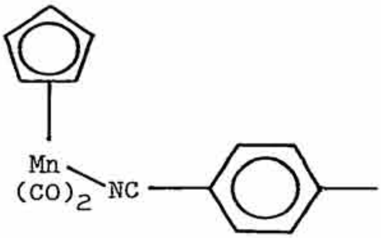

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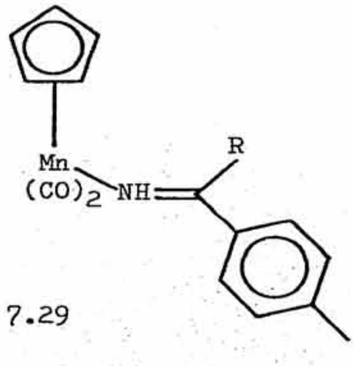

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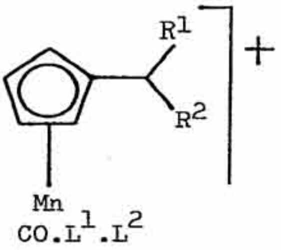
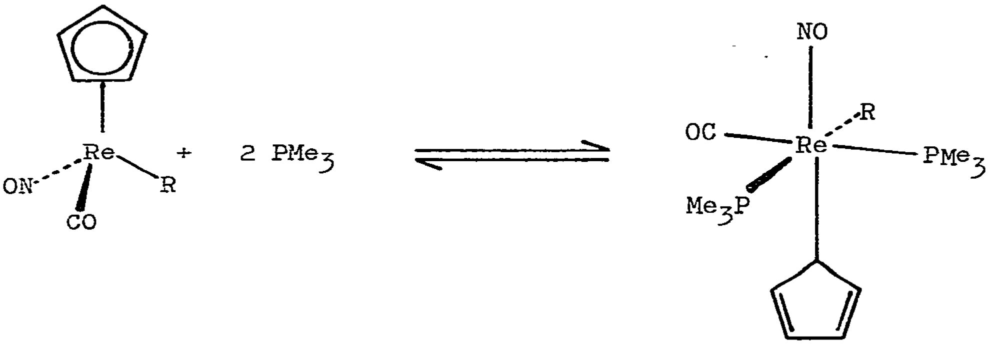


7.30

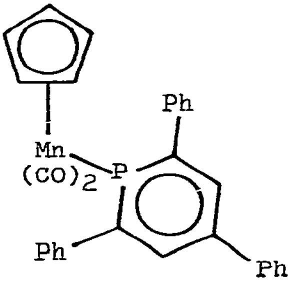
gave the $(\eta^6$-phosphorin)manganese complex (7.34). Several similar reactions were described [117]. The triphenylphosphine complexes (7.35; M = Mn, Re) underwent halogenation with chlorine or bromine to form salts such as the tribromide (7.36; M = Mn, Re; X = Br;



7.31

7.32

Y = Br$_3$) and the chloride (7.36; M = Re; X = Cl; Y = Cl) [118]. The cationic cymantrene analogues (7.37; R = H, Me; L = CO;



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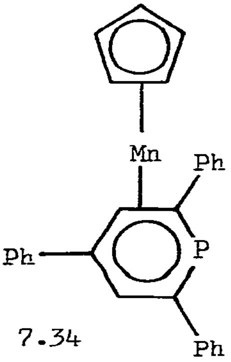

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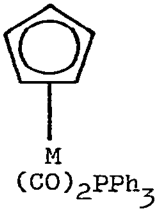

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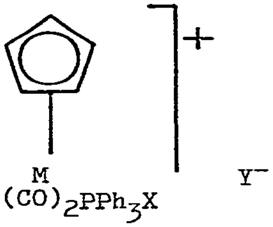

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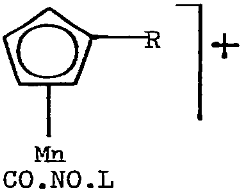

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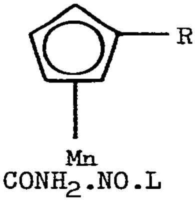
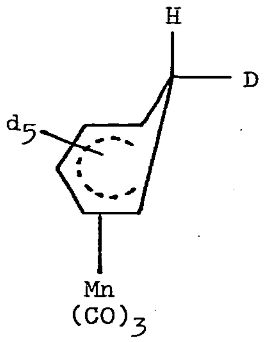


7.38

R = H, L = PPh_3, $AsPh_3$, CNMe, CNEt) combined with liquid ammonia to form the neutral carbamoyl complexes (7.38; R = H, Me, L = CO; R = H, L = PPh_3, $AsPh_3$, CNMe, CNEt). The carbamoyl ligand was converted to a carboxylic ester group on treatment with an alcohol [119].

The thermal isomerization of (η-6-exo-^{1}H-cyclohexadienyl-d_6)-manganesetricarbonyl (7.39) has been the subject of a detailed kinetic study. The reaction was first order k = 1.1×10^{-5} s^{-1} at 145°C, $\Delta G^{\ddagger} = 34$ kcal mol^{-1} for the isomerization of the single 6-exo hydrogen to vinylic ring sites. The mechanism involved insertion of manganese into the endo-C-D bond to give an intermediate (η^4-benzene)manganesetricarbonyl deuteride which formed (η-cyclohexadienyl)manganesetricarbonyl or underwent 1,2-manganese shift to give scrambling of ^{1}H to new sites [120]. The reaction of arenes with bromopentacarbonylmanganese followed by addition of aqueous hydrogen hexafluorophosphate gave the manganese complexes [7.40; R = H; 1,4-$(MeO)_2$; 4-Cl; Me; 1,3,5-Me_3, Me_5, Me_6] in good yields. Reduction of some of these complexes gave the corresponding η^5-cyclohexadienyl compounds (7.41; R = H, Cl, Me). Tricarbonyl(η^5-6-exo-methylcyclohexadienyl)manganese and tricarbonyl-(η^5-6-exo-phenylcyclohexadienyl)manganese were prepared by treatment of the η^6-benzene complex (7.40; R = H) with methyl- and phenyl-lithium respectively. These η^5-6-exo-methyl and -phenyl-cyclohexadienyl derivatives underwent hydrogen migration which involved a shift of the 6-endo-hydrogen via a metal hydride intermediate [121].



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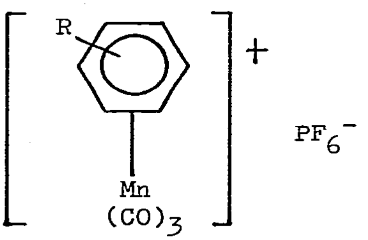

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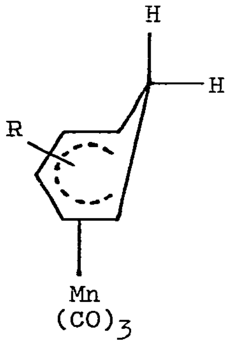


7.41

(iv) Applications

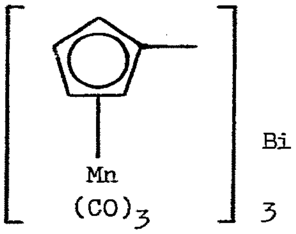
The effect of added methylcymantrene on the ignition of kerosene in air has been examined. Changes in the induction time for ignition were observed and these changes were dependent on the concentration of the additive [122]. The addition of tetrahydrofuran to gasoline, containing tricarbonyl(η^5-methylcyclopentadienyl)-manganese as the antiknock agent, reduced the exhaust hydrocarbon emissions and combustion-chamber deposits of the engine [123]. Methylcymantrene has been mixed with the dimer of an unsaturated C_{16-18} carboxylic acid and added to gasoline as an antiknock. A substantial decrease in hydrocarbon emission was achieved in vehicles using this fuel composition [124].

Ethyl cymantrene has been evaluated as a gasoline antiknock. The effect of this compound on spark plug life, combustion chamber deposits, catalytic converters and exhaust emissions has been examined. Its use at $\geq$0.03g Mn/gal. in gasoline was found to have an adverse effect on the control of the emission of hydrocarbons from the exhaust [125]. Tricarbonyl(η-methylcyclopentadienyl)manganese (0.1-1.0 wt. %) together with an oxygenated compound (0.01-1.5 wt. %) for example, tetrahydrofuran, acetone, undecanol or propionaldehyde, were added to diesel fuel as combustion improvers. The exhaust smoke was greatly reduced in the presence of these additives [126]. Tributyltincymantrene was less efficient as an antiknock in gasoline than trimethylsilylcymantrene, cymantrene, trimethylleadpentacarbonylmanganse and tetraethyllead. The tin complex was formed from lithiocymantrene and tributyltinchloride [127].

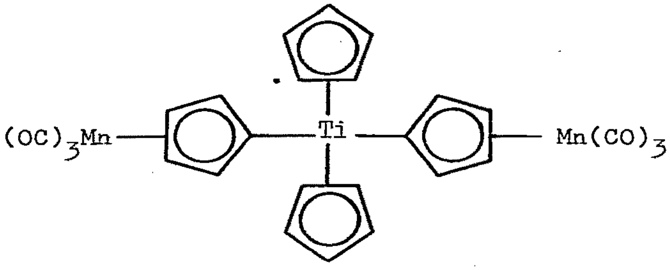
8. Polynuclear (η-C_5H_5)$Mn(CO)_3$ Complexes

The chemistry of polynuclear cymantrene complexes has been the subject of a considerable increase in activity during 1980 and reports of work in the area have been collected together in this section. Some overlap occurs between this topic and "carbene and carbyne complexes of cymantrene" surveyed in Section 9.

The crystal and molecular structure of the nitrogen-bridged binuclear cymantrene complex $[(\eta\text{-}C_5H_4Me)Mn(CO)_2]_2\mu\text{-}N_2$ has been determined by X-ray crystallography. The N-N interatomic distance was found to be 111.8 pm [128]. The crystal and molecular structure of tris(cymantrenyl)bismuth (8.1) has been determined by X-ray analysis. The η-cyclopentadienyl rings were planar and



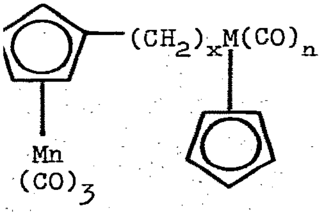
8.1



8.2

the bismuth atom was 0.26Å out of the ring planes [129]. The reaction of lithiocymantrene with dichlorobis(η-cyclopentadienyl)-titanium gave the titanium complex (8.2), the structure of which has been determined by X-ray analysis [130]. The mass spectra of the cymantrene derivatives (8.3 and 8.4; M = Fe, n = 2, x = 0,1; M = Mo, n = 3, x = 0,1; M = W, n = 3, x = 0,1) have been recorded and interpreted. It was concluded from the high intensity of the $[(\eta\text{-}C_5H_5)W(CO)_3Mn]^+$ and $[(\eta\text{-}C_5H_5)Fe(CO)_2Mn]^+$ ions in the spectra that it might be possible to synthesise compounds of this type [131].

The redox potentials of the manganese complexes (8.5; x = 1, L = N_2, N_2H_4, NH_3; x = 2, L = N_2H_2) have been measured. The N_2 complex was reduced more easily than the corresponding carbonyl



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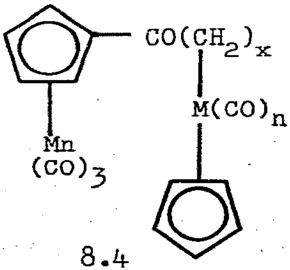

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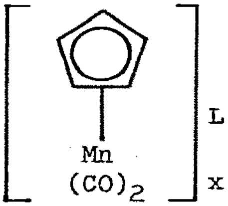
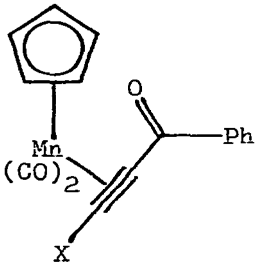


8.5

complex. The hydrazine complex was oxidised to the binuclear diazene complex and then to the dinitrogen complex [132]. The THF derivative of cymantrene, $(\eta\text{-}C_5H_5)Mn(CO)_2THF$, combined with phenylethynylketone, $PhCOC{\equiv}CH$, at 20°C to form the mixed cyclopentadienyl-acetylene complex (8.6; X = H) together with a small proportion of binuclear complex (8.7). The acetylenic hydrogen in the complex (8.6; X = H) was replaced by chlorine using hydrogen chloride as the reagent and by acetate using acetic acid as the reagent to form the derivatives (8.6; X = Cl, OCOMe) respectively [133].



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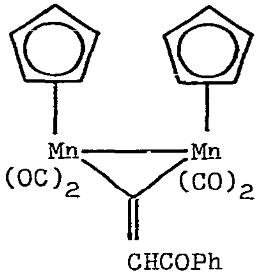
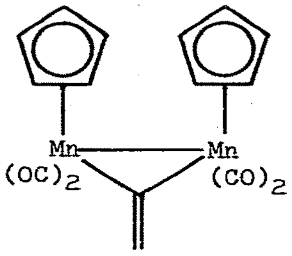


8.7

The chemistry of the binuclear manganese complex (8.8) with a vinylidene ligand has been studied. The complex (8.8) underwent protonation at vinylidene in trifluoroacetic acid to give the salt (8.9) and was attacked by $LiEt_3BH$ in THF followed by methyl iodide to form the allene complex (8.10) which was characterized by X-ray crystallography [134]. The THF derivative of cymantrene (7.27) combined with antimony (III) chloride to form either the cyclic (8.11) or the open chain (8.12) trimetallastibine complexes depending on the reaction conditions used. The two complexes (8.11 and 8.12) were each characterized by X-ray crystallography [135]. Ultraviolet irradiation of methyl cymantrene in tetrahydrofuran followed by addition of $[W{\equiv}C(4\text{-}C_6H_4Me)(CO)_2(\eta\text{-}C_5H_5)]$ gave the manganese complex (8.13). Similarly, irradiation of $(\eta\text{-}C_6Me_6)Cr(CO)_3$ in tetrahydrofuran followed by the addition of the same tungsten complex gave the chromium complex (8.14). The structure of the latter compound was determined by X-ray analysis [136].



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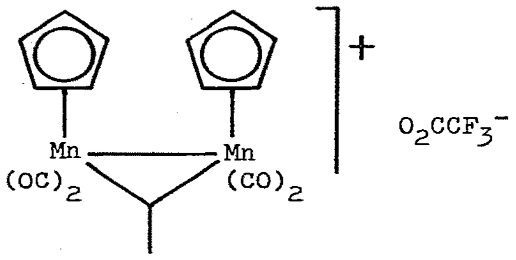

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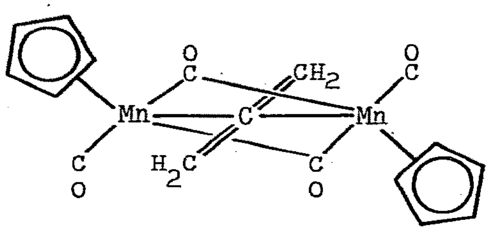

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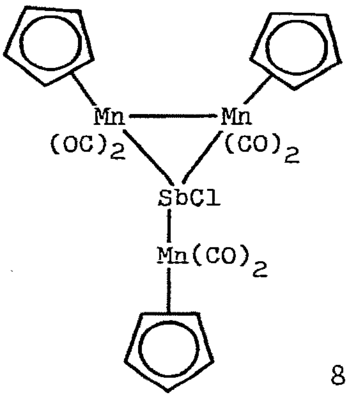
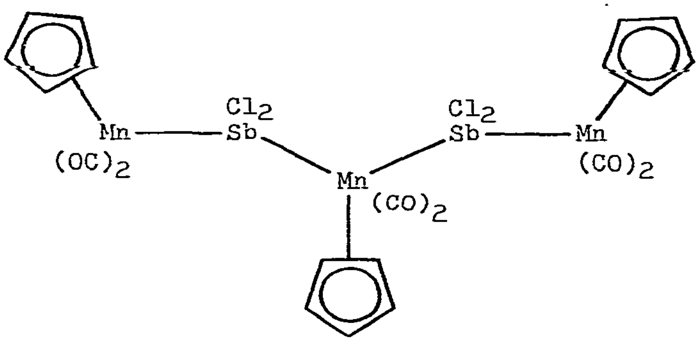


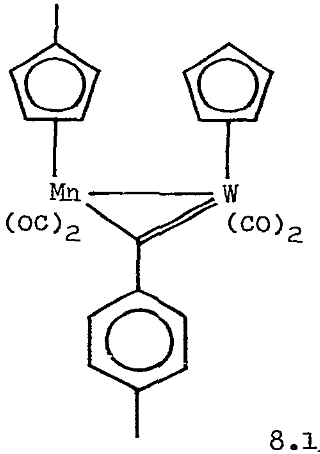
8.11

Irradiation of tricarbonyl(η-pyrrolyl)manganese with dicarbonyl(η-cyclopentadienyl)iron iodide gave a trinuclear complex (8.15) in which two tricarbonyl(η-pyrrolyl)manganese groups behaved as coordinating ligands to a third manganese atom. The crystal and molecular structure of the complex was confirmed by X-ray crystallography [137]. Reaction of dicarbonyl(η-cyclopentadienyl)tetrahydrofuranmanganese with the methanediazo complexes (8.16; M = Mo, W) gave the corrresponding thermally stable bridged compounds (8.17) where the methanediazo groups acted as bridging ligands via their basic nitrogen atoms [138]. Cymantrenyllithium was coupled with a series of ferrocene-lithium



8.12

compounds (8.18; R = H, Cl, CH_2NMe_2) in the presence of copper (II) chloride, to give the corresponding dimers (8.19) [139].



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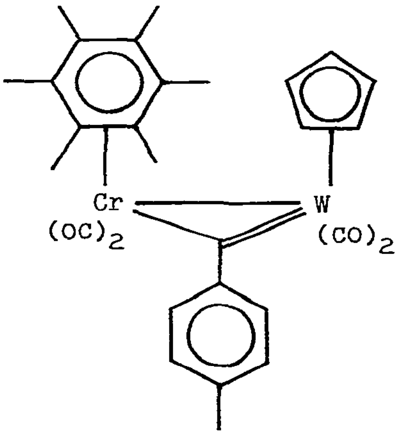
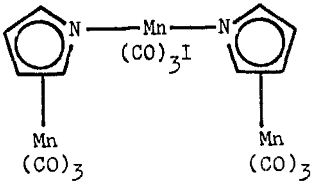


8.14

Cleavage of metal-metal bonds in arsenic bridged transition metal complexes resulted in the formation of functional dinuclear complexes containing the MAsM'PCl and MAsM'PP frameworks. Thus the cymantrene complex (8.20) was cleaved by Me_2PCl to give the product (8.21). This and related complexes were coupled under hydrolytic conditions or in the presence of metal carbonyls to give tetranuclear and pentanuclear derivatives respectively [140]. The nucleophilic cleavage of the manganese to cobalt bond in the



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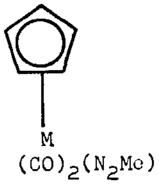

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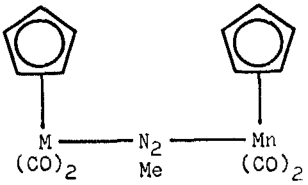

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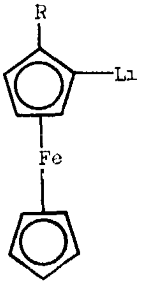
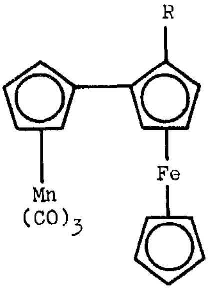


8.18

singly bridged dinuclear complex (8.20) by a series of dimethylarsenic-metal complexes gave the corresponding trinuclear compounds.



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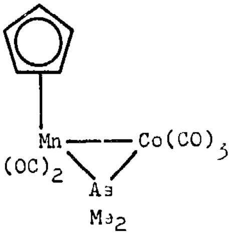

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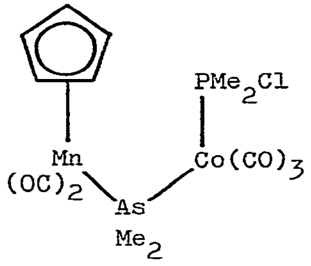

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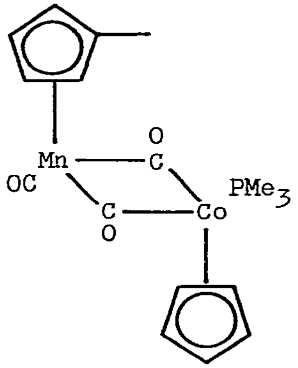

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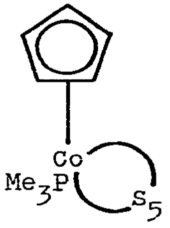


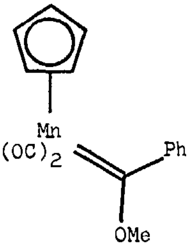
8.23

A series of trinuclear complexes was formed by the cleavage of iron-cobalt, manganese-cobalt, iron-iron and iron-manganese in several arsenic or phosphorus singly bridged dinuclear complexes [141]. The methylcymantrene derivative (8.22) has been treated with sulphur, S_8, to give the metallapentathiaheterocycle (8.23) [142].

9. Carbene and Carbyne $(\eta\text{-}C_5H_5)Mn(CO)_3$ Complexes

The synthesis and properties of cymantrenyl carbene and carbyne complexes have attracted an increase in activity in 1980 and research in this area has been brought together as a separate section.

The manganese carbene complex (9.1) was attacked by $\underline{d}^{10}$ transition metal species such as Ni^0, Pd^0 and Pt^0 to form heteronuclear dimetal compounds with bridging carbene ligands [143]. Transition metal carbene derivatives of cymantrene have been formed from carbene starting materials through intermediate transition metal carbynes. Thus the methylcymantrene complex (9.2; X = OMe) was treated with boron trichloride to form the cationic carbyne complex (9.3) and this, in turn, was treated with thiocyanate ion as a nucleophile to yield the carbene thiocyanate (9.2; X = SCN). Several related reactions were described [144]. The crystal structure of $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2]_2(\eta^2\text{-}C_{10}H_8)$ (9.4), a carbene addition product of dicarbonyl(η^5-methylcyclopentadienyl)tetrahydrofuranmanganese has been determined by X-ray analysis. It was



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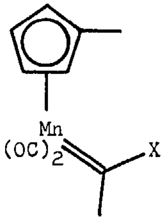

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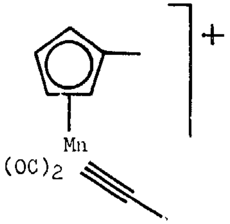
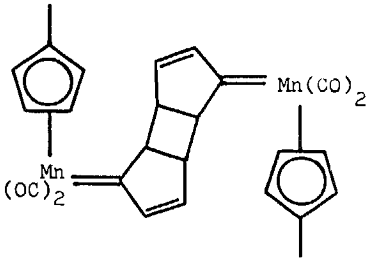


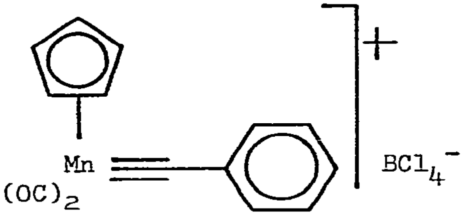
9.3

claimed that this was the first example of an oligocyclic dicarbene which was stabilized by complex formation [145].



9.4

Reaction of the carbyne-manganese complex (9.5) with the isocyanides RNC, where R = Me, cyclo-C_6H_{11}, t-Bu gave the corresponding thermolabile keteniminyl complexes (9.6) [146]. Treatment of the acetylene complex (9.7) with an organo-lithium compound, RLi, where R = Me_3C, CH_2Ph, cyclohexyl, Ph, gave the corresponding carbenes (9.8) which decomposed thermally to produce the dimers (9.9). Reaction of the acetylene complex (9.7) with methyllithium gave the carbene (9.10; $R^1 = R^2 = Me$) [147]. By contrast the acetylene complex (9.7) was attacked by organolithium reagents in equimolar proportion at -20 to -50°C in ether to form the vinyl-



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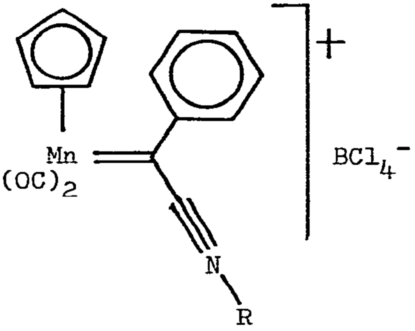
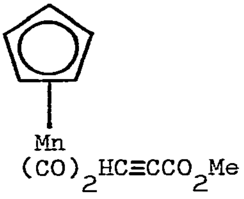


9.6

idene complex (9.11) in 38% yield. However, when the organolithium reagent (RLi) was in excess the tertiary alcohol (9.12;



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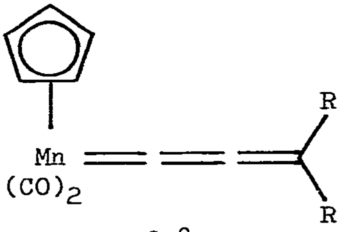

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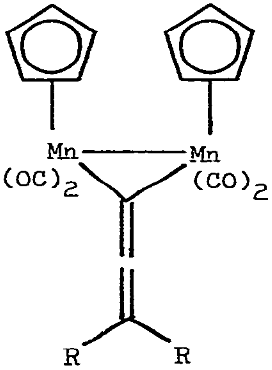

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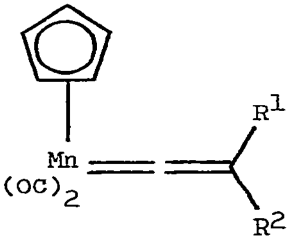

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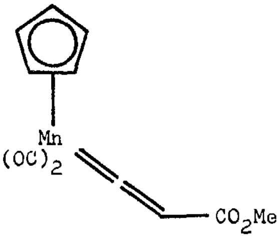
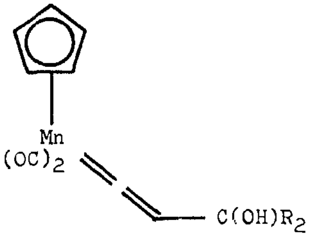


9.11



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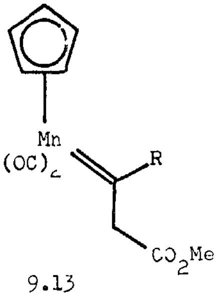
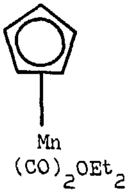


9.13

R = Bu^t, Ph) was formed. Treatment of the vinylidene complex (9.11) with excess organolithium reagent also gave the alcohol (9.12) and this was dehydrated to the cumulene (9.8; R = Bu^t, Ph) [148]. The reaction of dicarbonyl(η^5-cyclopentadienyl)methylpropiolate)manganese with different proportions of t-butyllithium followed by HCl or MeOSO$_2$F produced the vinylidene complexes [9.10; R^1 = H, Me; R^2 = CO$_2$Me, Me$_3$CCO, (Me$_3$C)$_2$COH]. The carbene complexes (9.13; R = NH$_2$, OMe) were also prepared [149].

The cymantrene-allenylidene complex (9.8) combined with the cymantrene-ether reagent (9.14) to form diorganoallenylidene compounds of the [(η-C$_5$H$_5$)Mn(CO)$_2$]$_2$ fragment (9.9; R = Bu^t, C$_6$H$_{11}$, C$_6$H$_5$, C$_6$H$_5$CH$_2$) [150]. The manganese carbyne complex (9.5) combined with NaRe(CO)$_5$ to give the binuclear phenylketenyl complex



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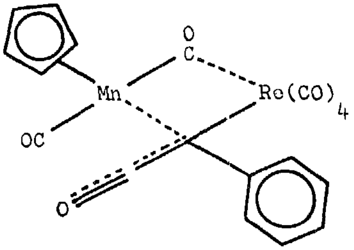
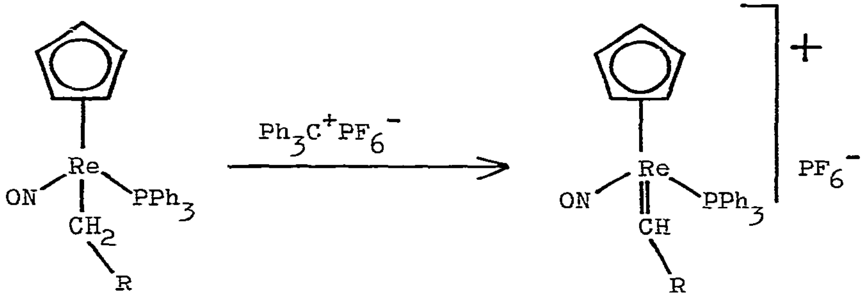
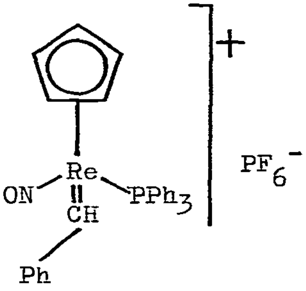


9.15

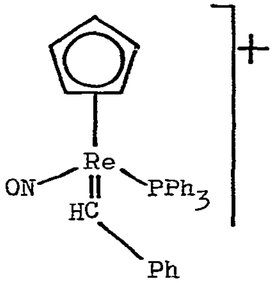
(9.15). X-ray crystallography demonstrated that the Mn-Re bond was bridged by the α-carbon atom of the alkylphenylketenyl group and semi-bridged by a carbonyl group [151]. Hydride abstraction from the (η-cyclopentadienyl)rhenium alkyls (9.16; R = Ph, Me, Et) to form the cationic alkylidene complexes (9.17; R = Ph, Me, Et)



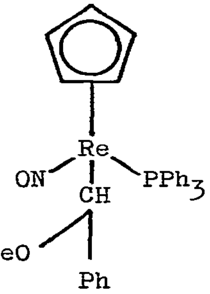
9.16 9.17



9.18a



9.18b

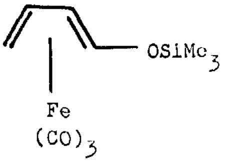


9.19

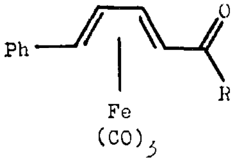
is both regiospecific and stereospecific. Attack occurred only at the α-carbon and one diastereotopic α-hydride was preferred over the other [152]. Addition of sodium methoxide to either one of the two geometric isomers of the benzylidene complex (9.18A and 9.18B) gave the corresponding rhenium complex (9.19) in which a new chiral centre had been generated stereospecifically or with high stereoselectivity. Treatment of either isomer of the complex (9.19) with Ph_3CPF_6 caused chemospecific abstraction of the methoxy group and stereospecific regeneration of the isomers of the complex (9.18) [153].

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

Several 1,3-butadienes with trimethylsilyl substituents, including 1-(trimethylsiloxy)-1,3-butadiene, 5-(trimethylsilyl)-1,3-pentadiene and 2-(trimethylsiloxy)-1,3,5-pentatriene combined with diiron enneacarbonyl in benzene to form the corresponding tricarbonyliron complexes. Thus 1-(trimethylsiloxy)-1,3-butadiene gave the complex (10.1) [154]. Substituted (η-butadiene)- and (η-1,3-cyclohexadiene)tricarbonyliron complexes have been



10.1



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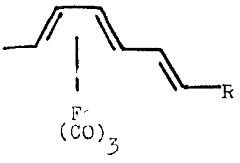
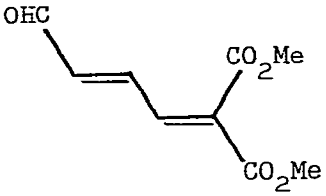


10.3

prepared by treatment of the appropriate α,β-unsaturated alcohols with iron carbonyls [155]. Cymantrenyl- and ferrocenyl-butadienes have been converted to the corresponding iron tricarbonyl complexes [10.2; R = (η-C_5H_4)Fe(η-C_5H_5), CH=CH(η-C_5H_4)Fe(η-C_5H_5), (η-C_5H_4)-$Mn(CO)_3$, CH=CH(η-C_5H_4)$Mn(CO)_3$; 10.3; R = (η-C_5H_4)Fe(η-C_5H_5), (η-C_5H_4)$Mn(CO)_3$] by treatment with triiron dodecacarbonyl [156]. Reaction of the diene (10.4) and the triene (10.5) with pentacarbon iron gave the complexes (10.6 and 10.7) respectively. Further reaction of compound (10.6) with $Ph_3P=CHCO_2Me$ gave the isomeric η-diene complexes (10.8 and 10.9) [157].

Photochemical reaction of $Os_3(CO)_{12}$ with butadiene gave (η-1,3-butadiene)tricarbonylosmium. The ^1H and H-coupled ^{13}C NMR spectra for this complex were compared with those of the analogous iron and ruthenium complexes. The data indicated that there was an increase in distortion from planarity of the C,H-skeleton at the terminal diene carbon atoms in the sequence Fe < Ru < Os [158]. Extended photolysis of pentacarbonyliron in 2,3-dimethylbutadiene caused the diene to dimerize and then form



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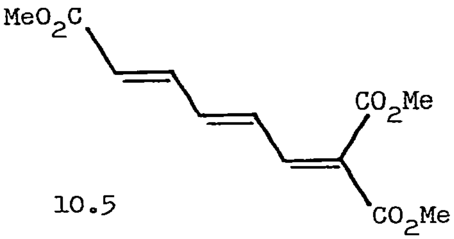

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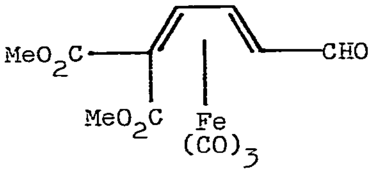

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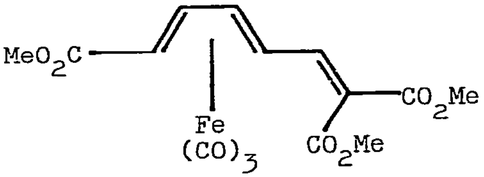

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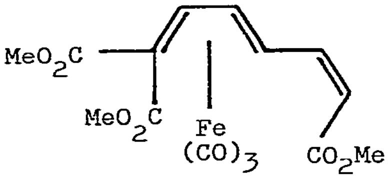

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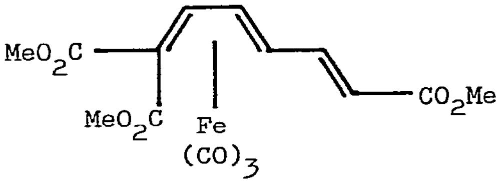
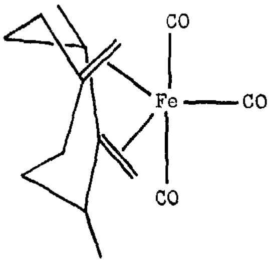
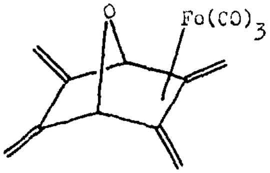


10.9

the tricarbonyliron complex (10.10). The complex (10.10) had trigonal bipyramidal geometry with the exocyclic double bonds and a carbonyl group lying exactly in the equatorial coordination plane [159]. The ligand 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]-heptane combined with iron pentacarbonyl and diiron enneacarbonyl to give several (η-diene)tricarbonyliron complexes. When the solvent was hexane, benzene or acetonitrile then the *exo*-complex (10.11), the diiron complexes (10.12 and 10.13) and the rearranged product (10.14) were obtained. When the solvent was methanol then the *endo*-complex (10.15) was obtained in addition to the other products. The structures of the *endo*-complex (10.15) and the



10.10



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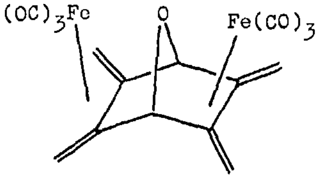

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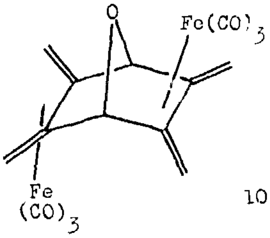

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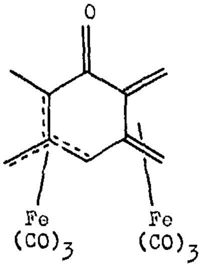

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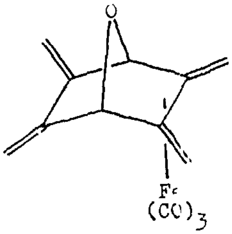
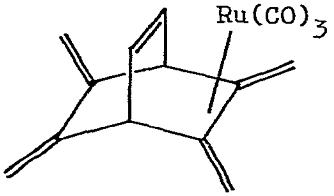


10.15

rearranged complex (10.14) were confirmed by X-ray crystallography [160].

Reaction of 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene with $Ru_3(CO)_{12}$ gave the *exo*- and *endo*-tricarbonylruthenium



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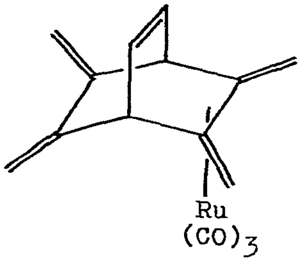

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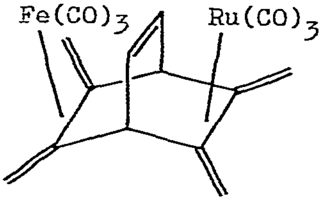

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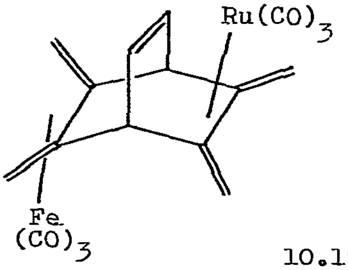

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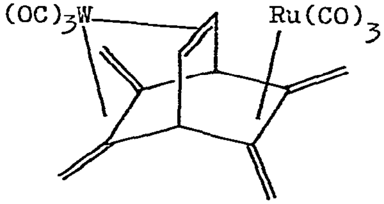
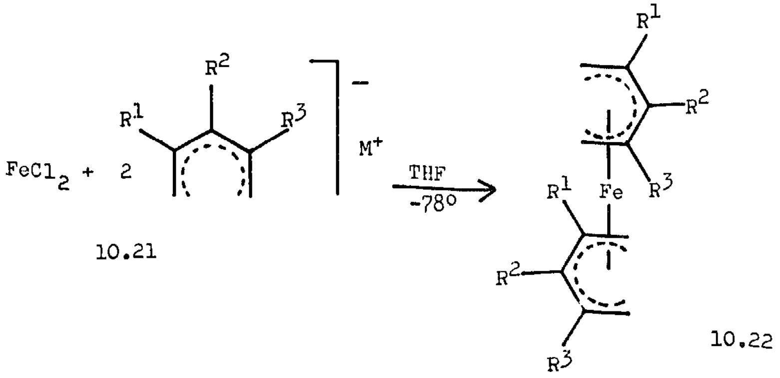


10.20

complexes (10.16 and 10.17). The tricarbonyliron complexes (10.18 and 10.19) were prepared also and coordination of all five double bonds was achieved by the reaction of the complex (10.16) with tricarbonyltris(methyl cyanide)tungsten to form the exo-isomer

(10.20) [161]. Reaction of iron (II) chloride with an ionic pentadienyl ligand (10.21; $R^1 = R^2 = R^3 = H$; $R^1 = R^3 = Me$, $R^2 = H$; $R^1 = R^3 = H$, $R^2 = Me$; $R^1 = R^2 = Me$, $R^3 = H$; M = Li, K) gave the corresponding bis(η^5-pentadienyl)iron complexes (10.22), "open ferrocenes". The methyl substituted complexes were similar to ferrocene, being hydrocarbon soluble, sublimable, stable at room temperature and air stable for at least several hours. The infrared spectra were devoid of C=C stretching bands which suggested a η^5 mode of bonding. X-ray analysis showed these compounds to be "open sandwiches" [162]. The (η^3-vinylcarbene)tricarbonyliron complex (10.23) was attacked by cyclohexylisonitrile to form the (η^4-vinylketenimine)tricarbonyliron complex (10.24). The structure of this product was confirmed by X-ray crystallography. Methylation of the complex (10.24) with $SFO_2(OMe)$ in methylene dichloride afforded the N-methylated derivative (10.25) [163].



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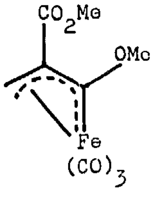

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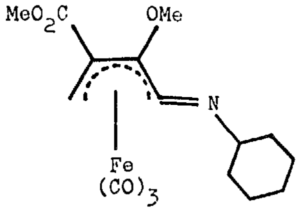

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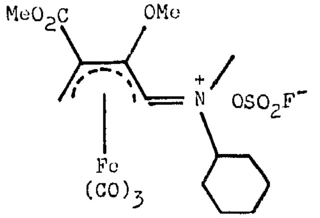
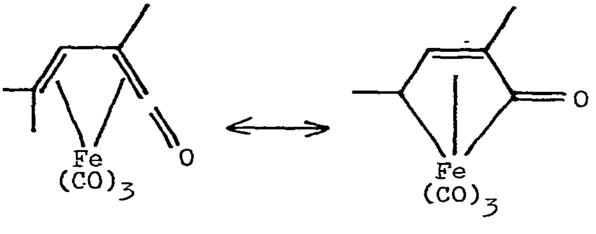


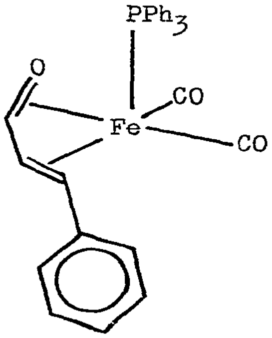
10.25

A ^{13}C NMR investigation of several diene-isonitrile complexes (η^4-diene)Fe(CO)$_2$CNR, where diene = butadiene, 2,3-dimethylbutadiene, penta-1,3-diene, cyclohexa-1,3-diene and cyclohepta-1,3-diene and R = Me, SiMe$_3$, GeMe$_3$, SnMe$_3$, has indicated that these complexes are fluxional in solution. A conformational preference was observed at low temperatures where one CO group occupied the apical position of a square pyramid while the CNR ligand together with a CO ligand and the olefin were in basal positions. The pseudorotation process was discussed on the basis of $\Delta G^{\ddagger}$ values for the CO-CNR ligand exchange [164]. In a related paper the mass spectra of the complexes were discussed. Elimination of the intact isonitrile ligand, the olefin ligand and sequential loss of CO was common to all of the complexes while fragmentation of the olefin ligands showed important differences [165]. The ring opening of 1,3,3-trimethylcyclopropene with diiron nonacarbonyl gave the (η-pentadienone)iron complex (10.26). X-ray crystallographic analysis of the molecular structure indicated that the 1-ferracyclopent-3-en-5-one canonical form (10.26b) made a large contribution to the structure. The alternative diene canonical form (10.26a) was also important [166].

The crystal structure of dicarbonyl(η^4-cinnamaldehyde)triphenyl phosphine iron (10.27) was determined by X-ray analysis. The molecule displayed square-pyramidal coordination with the PPh$_3$ group in the apical position [167]. Quantitative structure--resonance theory and previously described graph-theoretical



10.26a 10.26b



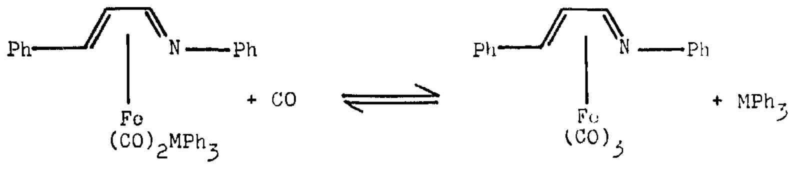
10.27

algorithms have been used to describe eighteen tricarbonyl(η^4-diene)-iron complexes as resonance hybrids of valence-bond structures. Resonance energies have been calculated and the values obtained were in agreement with the experimental properties of the complexes [168]. The photoelectron spectra of eighteen tricarbonyl(η-diene)-iron complexes and the corresponding free diene ligands have been recorded. Comparisons between the spectra of the ligands and the complexes enabled perturbation energies to be calculated for the interaction of the two π orbitals of the diene with the tricarbonyl-iron group. Only slight variations in perturbation energy were observed in the series, $\Delta\pi_1$, = 0.89 ± 0.07 eV, $\Delta\pi_2$ = 0.22 ± 0.06 eV These values were used to estimate the π ionization energies for the transient ligands cyclobutadiene, 8.29 and 11.95 eV, and trimethylenemethane, 8.36 and 11.79 eV [169].

The ligand exchange reaction:

$(\eta^4\text{-enone})\mathrm{Fe(CO)_3} + \text{diene} \rightleftharpoons (\eta^4\text{-diene})\mathrm{Fe(CO)_3} + \text{enone}$

where enone = benzylideneacetone, cinnamaldehyde, chalcone and dypnone and diene = 1,4-diphenylbutadiene, cyclohexadiene, cycloheptadiene, cycloheptatriene and cyclooctatetraene, was a stepwise process with rate-determining dechelation of the enone CO group followed by coordination of the diene as an η^2-ligand and then displacement of the enone ligand [170]. The ligand-substitution reaction in the (η-butadiene)iron complex (10.28; M = P, As, Sb) with carbon monoxide to form the irontricarbonyl complex (10.29) has been investigated by rate and equilibrium studies. The mechanism involved a dissociative equilibrium of the initial complex (10.28) to give an intermediate σ-bonded irontricarbonyl complex. Differences in the basicity of the ligands, PPh$_3$, AsPh$_3$

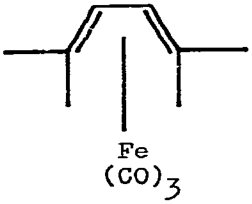


10.28

10.29

and $SbPh_3$ were responsible for the differences observed in the equilibrium and rate constants [171]. Several (η-diene)irontricarbonyl complexes have been converted to the nitrile anions $[(\eta\text{-diene})Fe(CO)_2CN]^-$ with $NaN(SiMe_3)_2$ and then to the neutral isonitrile complexes (η-diene)$Fe(CO)_2CNR$, where diene = butadiene, 1-methylbutadiene, 2-methylbutadiene, 1-ethylbutadiene, 2,3-dimethylbutadiene, cyclohexadiene, cycloheptadiene, cyclooctatetraene, 2,5-dimethylhexa-1,3-diene and R = Me, Et with $(R_3O)BF_4$ and to the neutral complexes (η-diene)$Fe(CO)_2CNMR_3$ where M = Si, Ge, Sn, Pb and R = Me, Et with R_3MCl [172].

The attack of methylamine on (η-butadiene)iron complexes has been examined as part of a study of the synthesis of δ-lactones. The complex (10.30) was converted to the trans-ferralactam (10.31) together with the cis-isomer [173]. A study of the thermal decomposition of tricarbonyliron lactones has shown that (η-diene)iron complexes may be formed in some cases. Thus the lactone (10.32) in THF gave the complex (10.33) in 54% yield [174]. The photolysis of tricarbonyl(η-2,3-diemthylbutadiene)iron and (η-butadiene)tricarbonyliron in argon and xenon matrices at 10°K has been investigated. Both complexes underwent loss of carbon monoxide as the major photoreaction while (η-butadiene)tricarbonyliron also underwent decomplexation to form (η^2-butadiene)tricarbonyliron. The same product was formed in the photolysis of (η^2-butadiene)tetracarbonyliron and it was subsequently transformed to (η^4-butadiene)tricarbonyliron. Photolysis of the two original tricarbonyl(η^4-1,3-diene)iron complexes in a nitrogen matrix gave (η^4-1,3-diene)$Fe(CO)_2N_2$ [175].



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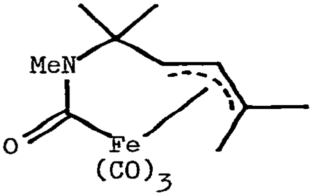
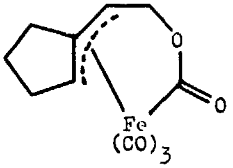


10.31

Photolysis of (η-butadiene)tricarbonyliron derivatives, bis(η-butadiene)carbonyliron complexes and tricarbonyl(η-cyclo-



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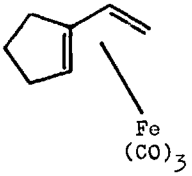
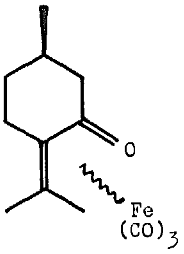


10.33

butadiene)iron in the presence of excess trimethylphosphite resulted in both carbonyl displacement and diene replacement.



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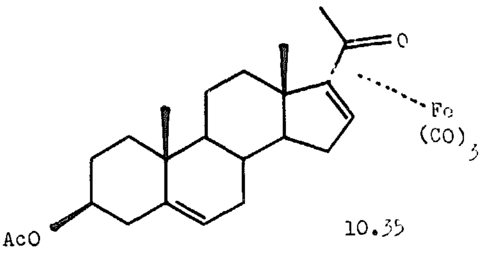

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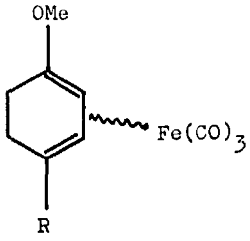

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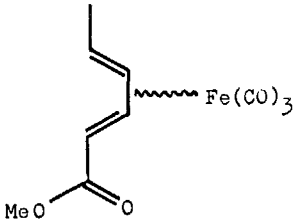
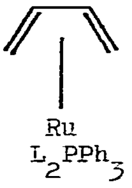


10.37

Quantum yields for the two reactions (Φ_{CO} and Φ_D respectively) were determined and were found to be substantially less than 1.0. Quantum yields increased with decreasing wavelength down to 313 nm. Values for Φ_{CO} were greater than values for Φ_D and the ratio Φ_{CO}/Φ_D increased with decreasing wavelength. The reaction mechanism was considered to involve an intermediate (η^2-diene)iron complex [176]. The (η-butadiene)tricarbonyliron complexes, $LFe(CO)_3$, where L = isoprene, 2,5-dimethyl-1,3-hexadiene, 1,3-cycloheptadiene, were attacked by $NaN(SiMe_3)_2$ to give the anions $[LFe(CO)_2CN]^-$. These anions and the corresponding anions where L = butadiene, 2,3-dimethylbutadiene, 1,3-pentadiene, 1,3-cyclohexadiene and cyclooctatetraene were found to be fluxional in solution. The low temperature isomer was a square pyramid with the basal positions occupied by two carbon atoms of the diene, one CO molecule and the CN^- ligand [177].

The tricarbonyliron complexes of the chiral enones (10.34) and (-)-3β-acetyloxypregna-5,16-diene-20-one (10.35) have been prepared. Treatment of these complexes (10.34 and 10.35) with 1-methoxycyclohexa-1,3-diene, 1-methoxy-4-methylcyclohexa-1,3-diene and methyl sorbate gave the corresponding optically active tricarbonyliron complexes (10.36; R = H, Me) and (10.37) [178]. Treatment of bis(η^4-butadiene)triphenylphosphineruthenium with an excess of $P(OMe)_3$, $P(OCH_2)_3CMe$ or PF_2NMe_2 resulted in displacement of one molecule of butadiene to give the corresponding ruthenium complexes [10.38; L = $P(OMe)_3$, $P(OCH_2)_3CMe$, PF_2NMe_2]. Reaction of (η^6-benzene)(η^4-1,3-cyclohexadiene)ruthenium with $P(OMe)_3$ or



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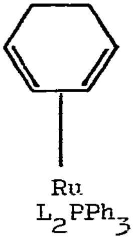
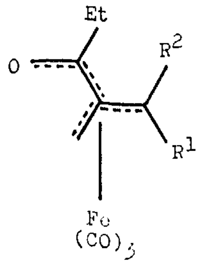


10.39

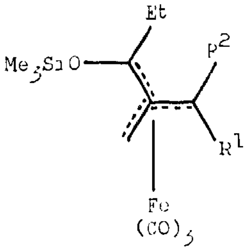
P(OCH$_2$)$_3$CMe gave the corresponding (η-1,3-cyclohexadiene)-ruthenium complexes [10.39; L = P(OMe)$_3$, P(OCH$_2$)$_3$CMe]. The variable temperature ^{31}P NMR spectra of these complexes were recorded and interpreted [179].

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

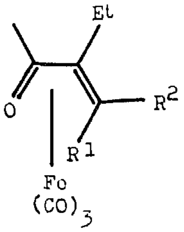
The thermal conversion of tetracarbonyl(η-cyclobutene)iron complexes to (η-butadiene)tricarbonyliron species and of tetracarbonyl(η-methylenecyclopropane)iron complexes to tricarbonyl(η-trimethylenemethane)iron compounds have been investigated theoretically by the Extended Hueckel MO method. A qualitative frontier MO picture was derived that allowed the reactions to be classified as allowed or forbidden. It further showed that for allowed disrotatory ring-opening the rotational mode that bent the breaking σ-bond towards the metal was preferred. Whereas for forbidden disrotatory reactions bending of the σ-bond away from the metal was the lower energy process [180]. Some results on the ring opening of tetracarbonyl(η-phenylmethylenecyclopropane)iron were presented in support of the theoretical proposals [181]. Treatment



11.1



11.2



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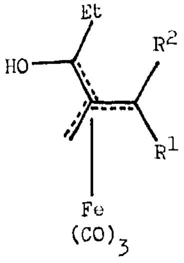
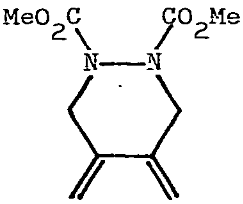


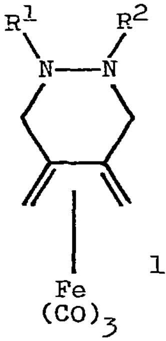
11.4

of the allenes, $CH_2=C=CR^1R^2$, where $R^1 = R^2$ = H, Me; R^1 = H, R^2 = Ph, with an alkylferrate, formed from sodium tetracarbonylferrate and ethyl bromide, gave the corresponding complex anions (11.1). Reaction of the anions (11.1) with trimethylchlorosilane gave the η^4-trimethylenemethane complexes (11.2) which underwent reaction with trifluoroacetic acid to form the η-heterodiene complexes (11.3) [182 and 183]. Further work by Roustan and co-workers showed that protonation of the complex anions (11.1) by acetic acid gave the corresponding (η^4-hydroxytrimethylenemethane)-iron complexes (11.4) which isomerized easily to give a mixture of (η^4-heterodiene)-iron tricarbonyl complexes [184]. Oxidation of these latter compounds with trimethylamine oxide released the α,β-unsaturated ketone, the most substituted ketone predominated [185].

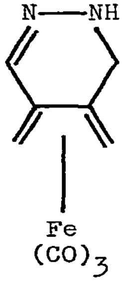
The unstable butadiene (11.5) has been stablized by treatment with enneacarbonyldiiron to form the tricarbonyliron complex (11.6; $R^1 = R^2 = CO_2Me$) which on hydrolysis with potassium hydroxide gave



11.5



11.6



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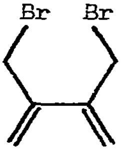

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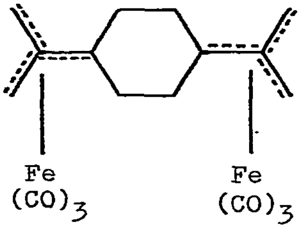

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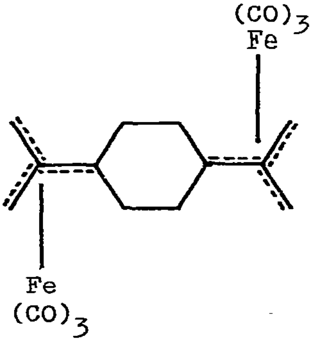
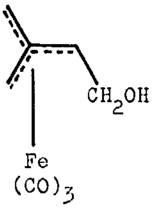
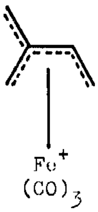


11.10

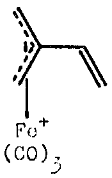
successively the monoester (11.6; $R^1 = CO_2Me$, $R^2 = H$) and the hydrazine (11.6; $R^1 = R^2 = H$.. Air oxidation of the first formed complex (11.6; $R^1 = R^2 = CO_2Me$) gave the pyridazine complex (11.7). The dibromide (11.8) attacked enneacarbonyldiiron with the formation of the trimethylenemethane complexes (11.9 and 11.10) in addition to an (η-allyl)iron complex. Protonation and deprotonation of the complexes (11.9 and 11.10) converted them to (η-diene)iron complexes [186]. The (cross-conjugated η-dienyl)iron cation (11.12) has been the subject of an experimental and theoretical study of its structure. The cation (11.12) was formed from the (η-trimethylenemethane)iron complex (11.11) in a mixture of fluorosulphonic acid and liquid sulphur dioxide at -78°C and examined in the temperature range -65 to -20°C by NMR spectroscopy. The cation (11.12) behaved as a coordinatively saturated species and showed an energy barrier to rotation about the C_2-C_3 bond of >13 kcal mol^{-1}. These observations exclude the η^3 structure (11.13)



11.11



11.12



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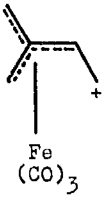

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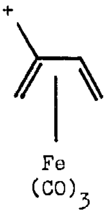
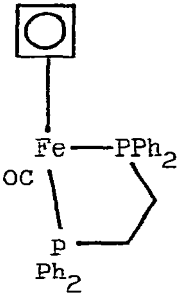


11.15

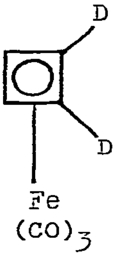
predicted by simplified (one-interaction) frontier orbital model and instead favour the η^4 structures (11.14 and 11.15). An Extended Hueckel treatment suggested similar energies for the three structures (11.13, 11.14 and 11.15) [187].

12. (η-C_4H_4)Fe(CO)$_3$

The crystal and molecular structure of the (η-cyclobutadiene)-iron complex (12.1) has been determined by X-ray crystallography at -35°C. The electron-withdrawing carbonyl group was bound more strongly to iron than in the parent (η-cyclobutadiene)irontricarbonyl complex by virtue of the electron donor capacity of the phosphine ligands. Stereochemical results for ten (η-cyclobutadiene)-metal complexes characterized by X-ray methods have been analyzed in terms of distortions from idealized symmetrical structures [188].



12.1



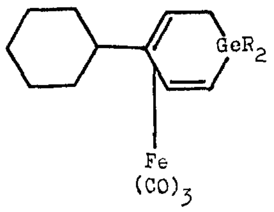
12.2

Oxidation of (η-cyclobutadiene-1,2-d^2)irontricarbonyl (12.2) gave an equimolar mixture of methyl (Z)-3-cyanoacrylate trapped products derived from the two isomeric forms of the free cyclobutadiene intermediate confirming the square form of the ligand ring in the complex (12.2). Trapped cyclobutadiene products from organic precursors were not obtained as equimolar mixtures [189].

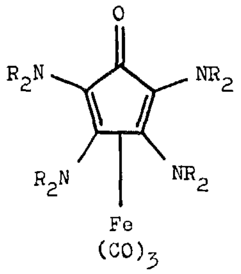
13. (Cyclic-η-diene)Fe(CO)$_3$ Complexes

(i) Formation

The formation and reactions of 1,1-disubstituted-1-germacyclohexa-2,4-dienes have been reported. These dienes combined with iron pentacarbonyl to form the iron tricarbonyl complexes

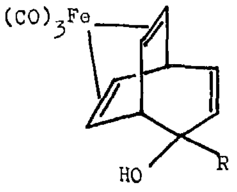


13.1



13.2

(13.1; R = Me, Et, Ph)[190]. Diaminoacetylenes, $R_2NC{\equiv}CNR_2$, where R = Me, Et, obtained by pyrolysis of cyclopropenones, combined with pentacarbonyliron to form the (η-cyclopentadienone)-iron complexes (13.2; R = Me, Et) [191]. Reaction of bicyclo [3.2.2] tertiary alcohols with $Fe_2(CO)_9$ gave the corresponding η-diene complexes, for example, complexes (13.3 and 13.4; R = Me, Ph). Treatment of these compounds (13.3 and 13.4) with hydrogen tetrafluoroborate in acetic anhydride produced (η-bicyclo-[3.2.2]dienyl)tricarbonyliron cations [192]. The stereospecific synthesis of (η-5,6-disubstitutedcyclohexadiene)iron complexes has been reported. Thus a mixture of the two diastereoisomeric forms of the alcohol (13.5) was converted with thallium (III) trifluoro-



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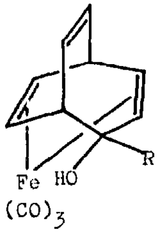
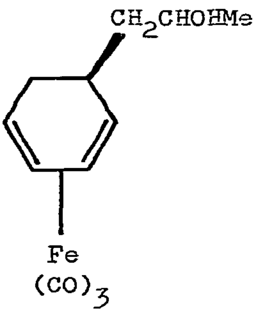
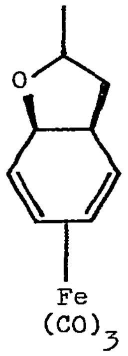


13.4

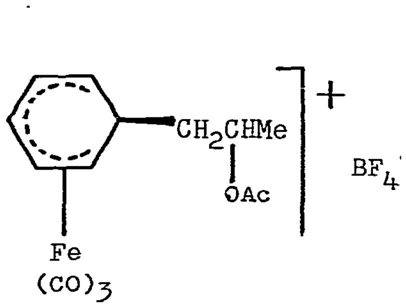
acetate to the complex (13.6) as a single diastereoisomer and thence to the (η-cyclohexadienyl)iron salt (13.7) with tetrafluoroboric acid. The salt (13.7) combined with dimethyl sodiomalonate to form the disubstituted complex (13.8) as a single diastereoisomer [193].



13.5



13.6



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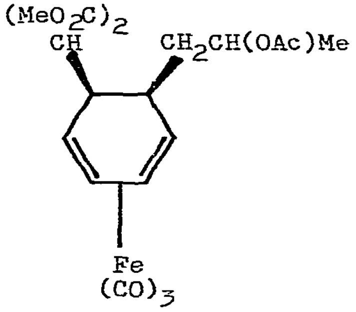

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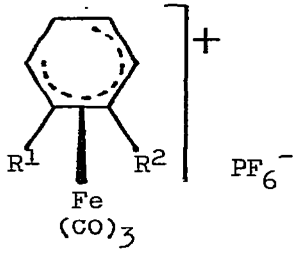

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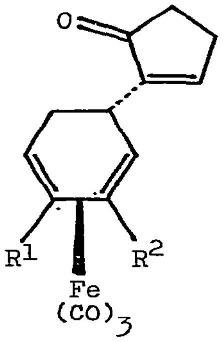
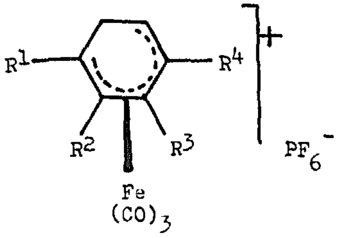


13.10

Treatment of the η-cyclohexadienyl complexes [13.9; R^1 = H, R^2 = H, Me; R^1 = OMe, Me, R^2 = H; R^1R^2 = $(CH_2)_4$] with 1,2-bis-(trimethylsiloxy)-1-cyclopentene at -20°C in methyl cyanide gave, after treatment with hydrogen chloride in methanol, the corresponding 2-substituted 2-cyclopenten-1-ones (13.10) [194].

Reaction of a series of tricarbonyl(η-cyclohexadienyl)iron complexes [13.11; $R^1 = R^2 = R^3 = R^4$ = H; $R^1 = R^3 = R^4$ = H, R^2 = Me;



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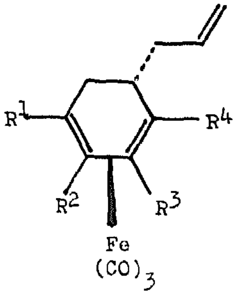
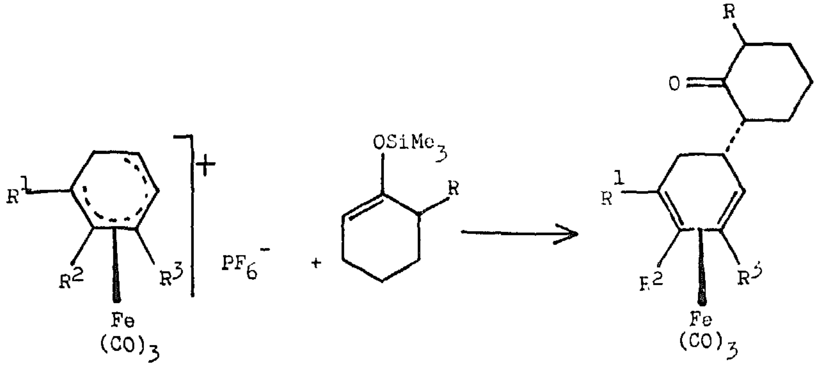
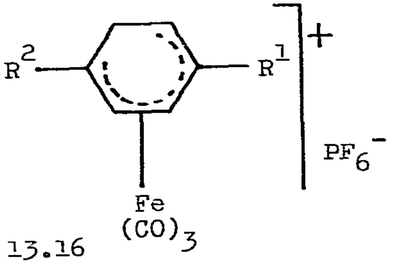


13.12

$R^1 = R^2 = R^4 = H$, $R^3 = OMe$; $R^1 = CO_2Me$, $R^2 = Me$, $R^3 = R^4 = H$; $R^1 = R^4 = H$, R^2-$R^3 = (CH_2)_4$] with allyltrimethylsilane gave the corresponding substituted η-cyclohexadiene complexes (13.12) [195]. In the same way reaction of the cyclohexadienyl complexes (13.13; $R^1 = R^2 = R^3 = H$; $R^1 = R^3 = H$, $R^2 = OMe$; $R^1 = CO_2Me$; $R^2 = H$, $R^3 = Me$) with trimethylsilyl enol ethers derived from cyclohexanone and 2-methylcyclohexanone (13.14; R = H, Me) gave the corresponding η^4-cyclohexadiene complexes (13.15)[196]. Reaction of the tricarbonyliron complexes (13.16; $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = OMe$, $R^2 = H$) with either sodium or potassium nitromethanate



13.13 13.14 13.15



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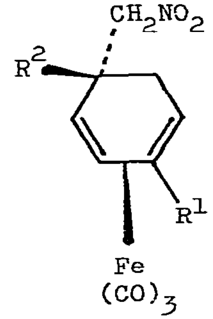

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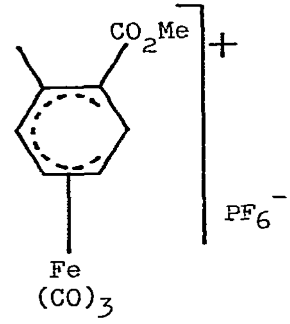

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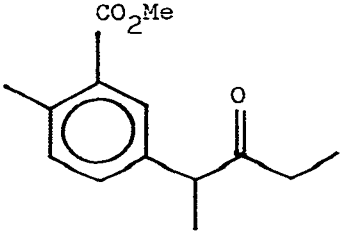

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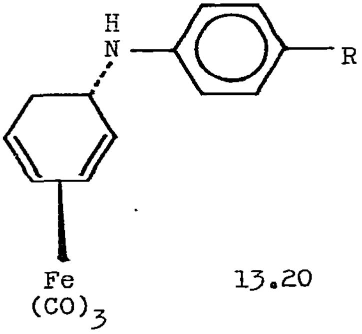

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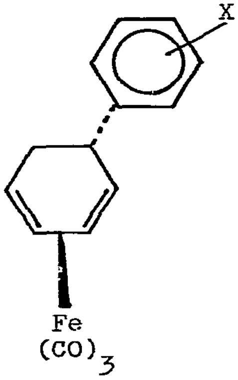

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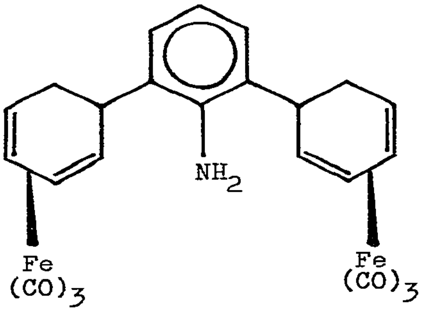
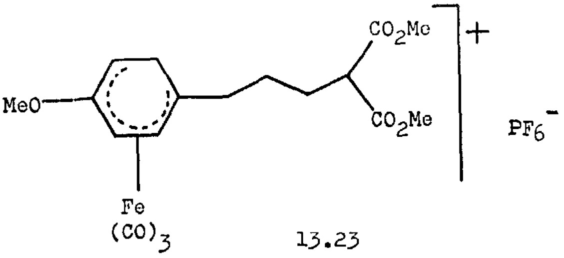


13.22

gave the corresponding η-cyclohexadiene complexes (13.17) [197].

The nucleophilic addition of silyl enol ethers to (η-cyclohexadienylium)iron salts has been used as a route to 2-substituted carbonyl arenes. Thus the (η-cyclohexadienylium)iron salt (13.18)



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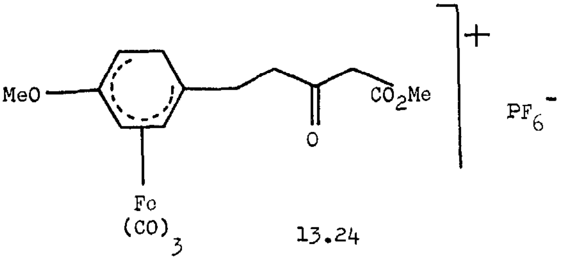

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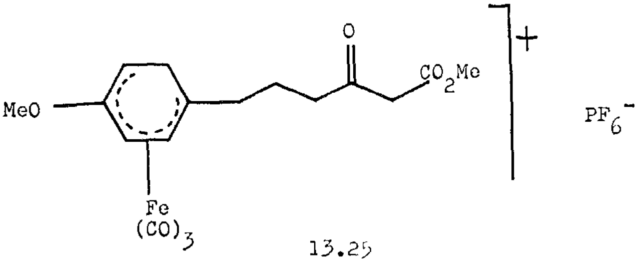

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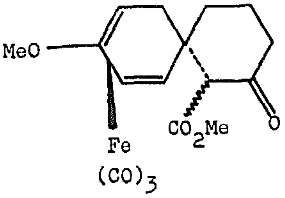
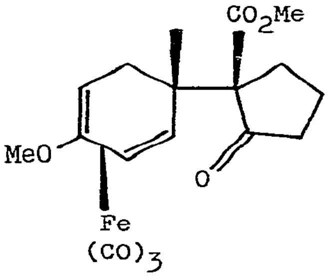


13.26

was treated with MeCH=CEtOSiMe$_3$ to give the corresponding (η-cyclohexadiene)iron complex which underwent decomplexation and dehydrogenation to form the arene (13.19) [198]. Treatment of tricarbonyl(η^5-cyclohexadienyl)iron tetrafluoroborate with aniline, *p*-toluidine or *p*-anisidine in acetonitrile at room temperature gave the corresponding N-alkylated products (13.20; R = H, Me, OMe). When the same reaction was carried out with aniline at the reflux temperature of acetonitrile C-alkylation *ortho* and *para* to the amine occurred to give the tricarbonyl iron complexes (13.21; X = *o*-NH_2, *p*-NH_2; 13.22) [199]. An unsuccessful attempt has been made to spirocyclize the tricarbonyliron complexes (13.23 and 13.24). However the η-cyclohexadienyl complex (13.25) readily cyclized to give tricarbonyl [η-7—10-(methyl 9-methoxy-2-oxospiro[5.5]undeca-7,9-diene-1-carboxylate)]iron (13.26) as a pair of diastereoisomers [200].

Reaction of tricarbonyl(4-methoxy-1-methylcyclohexa-2,4-dienyl)iron hexafluorophosphate with the potassium enolate of methyl 2-oxocyclopentanecarboxylate gave an equimolar mixture of the diastereoisomers (13.27 and 13.28) in quantitative yield. The potential of this reaction for constructing the carbocyclic framework present in trichothecanes was investigated. The structure of the isomer (13.27) was determined by X-ray analysis [201]. The tricarbonyl(η-cycloheptadienylium)iron cation underwent nucleophilic addition with ethoxide ion at 0°C to form the nuetral carboalkoxy complex (13.29). On raising the temperature the complex spontaneously rearranged to give the 5-*exo*-ethoxy complex (13.30) [202].



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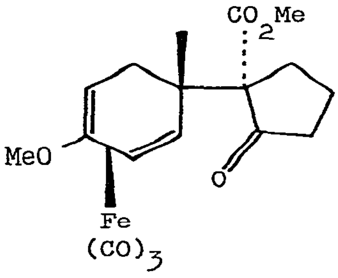

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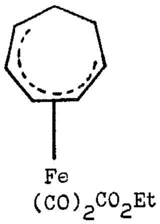

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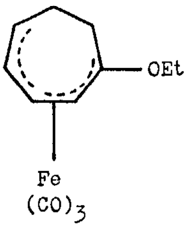
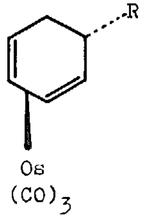


13.30

Reduction of tricarbonyl(η-cyclohexadienyl)-osmium with sodium borohydride gave the 1,3-diene complex (13.31; R = H) and the σ-η-allyl derivative (13.32; R = H). Reaction of the initial dienyl complex with cyanide gave similar products (13.31, R = CN and 13.32; R = CN). However, all other nucleophiles such as alcohols, thiols, amines, phosphines and other carbon nucleophiles produced only the corresponding 1,3-diene products (13.31) [203].



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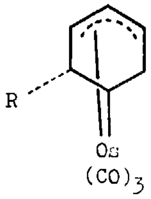
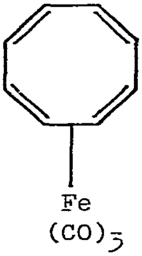


13.32

(ii) Spectroscopic and Physico-chemical Studies

The highest occupied molecular orbitals of tricarbonyl(η-cyclooctatetraene)iron (13.33) have been derived from those of (η-butadiene)tricarbonyliron and used together with INDO calculatio to interpret the He (I) photoelectron spectrum of the complex (13.33). The first five bands of the spectrum were assigned on this basis [204]. As part of a theoretical study of the reaction path for bisethylene metallocyclopentane interconversion where two olefin groups are coordinated to a trigonal bipyramidal irontricarbonyl moiety, the previously reported conversion of (η-cyclo-



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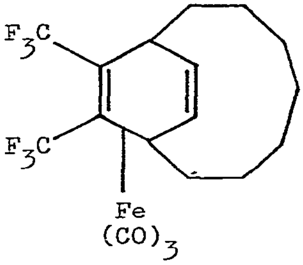
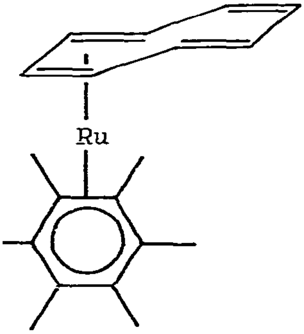


13.34

octa-1,3-diene)irontricarbonyl and perfluoropropene to a metallocyclopentene has been reconsidered [205]. The irontricarbonyl complex (13.34) was formed from the free ligand and used to elucidate the structure of the latter by ^{1}H NMR spectroscopy and X-ray crystallography [206]. The cyclooctatetraene (COT) complexes (η^6-arene)(η^4-COT)M, where M = Fe, Ru, Os and arene = PhH, 1,3,5-$C_6H_3Me_3$, C_6Me_6, have been prepared by treatment of (η-arene)-metal halides or bis(η-arene)metal cations with COT^{2-}. The crystal



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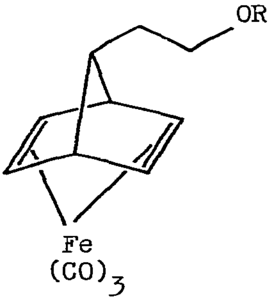
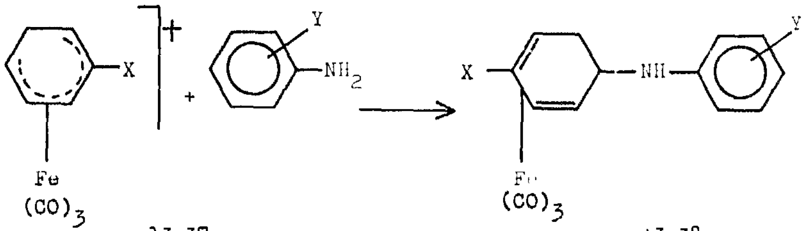


13.36

and molecular structure of the ruthenium complex (13.35) has been determined by X-ray crystallography. The Ru-C(diene) interatomic distances are shorter than in (η-COT)Ru(CO)$_3$ and variable temperature ^{1}H and ^{13}C NMR spectroscopy has shown that the COT ring is highly fluxional by comparison with the corresponding tricarbonyls [207].

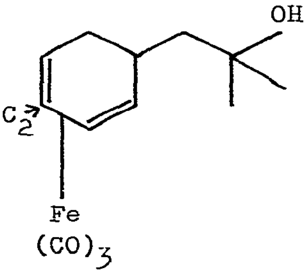
Acetolysis of the norbornadiene complex (13.36; R = SO$_2$Me) to form the derivative (13.36; R = COMe) proceeded 5 x 10^{-5} times as fast as that of the free ligand and indicated that complexation of the ligand reduced double bond participation in the rate-determining and product-determining steps of the reaction [208]. The second-order rate constants, k_1, have been determined for the addition of anilines and pyridines to tricarbonyl(η-dienyl)iron cations. Thus the cations (13.37) were attacked by aniline and substituted anilines giving the (η-cyclohexadiene)iron complexes (13.38). The Bronstead relationship, log k_1, = αpK_a + constant, was obeyed for the addition of anilines to the cation (13.37; X = MeO) and of pyridines to the cation (13.37; X = H). The rate constants, k_1, were shown to be strongly dependent on amine basicity. The results were interpreted in terms of a "hard" character for the dienyl ligands in the cations (13.37) [209]. Dehydration of the alcohol (13.39) with p-toluenesulphonic acid gave a mixture of products which, on repeated treatment with p-toluenesulphonic acid gave tricarbonyl-2-(2-methyl-prop-1-enyl)cyclohexa-1,3-dieneiron (13.40) in high yield. The presence of a methoxy group at the 2-position prevented isomerization of the coordinated diene into conjugation with the olefin, with the side chain remaining in the



13.37

13.38

Y = H, 2-Me, 3-Me, 4-Me, 4-OMe, 3-Cl, 4-Cl



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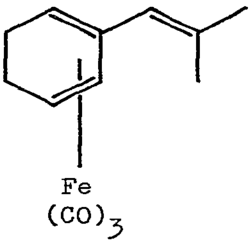

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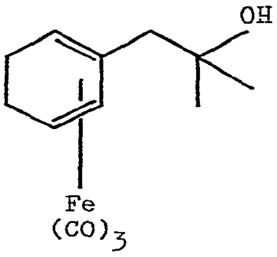


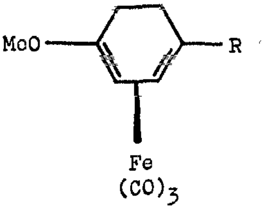
13.41

5-*exo*-position [210].

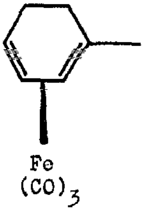
The mass spectra of the η-cyclohexadiene complexes (13.39 and 13.41) were recorded. Both exhibited a McLafferty rearrangement mechanism for an arene fragment bearing a coordinated iron atom [211]. The gas phase protonation of (η-butadiene)-, (η-cyclobutadiene)-, (η-cycloheptatriene)-, (η-cyclooctatetraene)-irontricarbonyl and related complexes by a series of Bronstead acid reagents H_3^+, CH_5^+, t-$C_4H_9^+$, $(NH_3)_nH^+$ has been investigated. The reactions and mass spectra were discussed in terms of the relative acid strengths of the protonating reagent ions. These results were compared with the conditions used for protonation of the same complexes in the solution phase [212]. Iron in tricarbonyl(η-cyclohexadiene)iron complexes has been determined by atomic absorption spectrometry. Dimethylformamide solutions were used and the effects of molecular structure of the complexes together with flame parameters were evaluated [213]. Phase selective alternating current polarography has been used to determine the electron-transfer parameters of tricarbonyl(η^4-cyclooctatetraene)iron in dimethylformamide in the presence of tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The results obtained were compared with those for uncoordinated cyclooctatetraene. It was concluded that there were no large structural changes on reduction [214].

(iii) General Chemistry

The absolute configurations of the η-cyclohexadiene complexes (13.42; R = H, Me) were obtained by chiral transfer of $Fe(CO)_3$ to the two methoxycyclohexa-1,3-dienes from the complex of

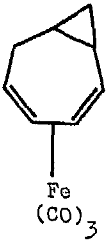


13.42



13.43

(+)-pulegone and conversion of the complexes into the known terpenes, cryptone and phellandrene [215]. Tricarbonyl(η-1-carboxycyclohexa-1,3-diene)iron was resolved into its optically pure (+)- and (-)- isomers. Reduction of the (+)- isomer with BH_3-Me_2S and BF_3-Et_2O gave the (-)-1-methyl complex (13.43) [216]. The methylene group, generated under Simmons-Smith conditions from diiodomethane and zinc-copper couple, attacked the uncoordinated double bond in tricarbonyl(η-cycloheptatriene)iron to form the η-bicyclo[5.1.0]octadiene complex (13.44). A similar reaction with tricarbonyl(η-cyclooctatetraene)iron gave the η-tricyclo[8.1.0.0] undecadiene complex (13.45) by the addition of these equivalents of methylene [217].



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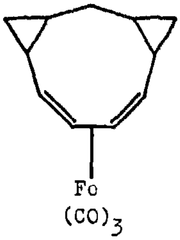

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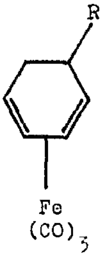
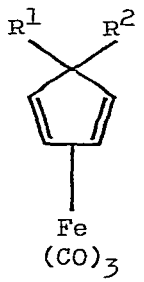


13.46

Reaction of the tricarbonyliron complex (13.46; R = H) with bromoform (as reactant and solvent), sodium hydroxide and benzyltriethylammonium chloride or tricaprylmethylammonium chloride, as the phase transfer catalyst, afforded the dibromomethyl complex (13.46; R = $CHBr_2$) formed by insertion of dibromocarbene into a saturated carbon-hydrogen bond. (η-Acyclic diene)carbonyliron complexes containing a secondary or tertiary C-H bond also experienced dibromocarbene insertion in the presence of a phase transfer catalyst [218]. Irradiation of the tricarbonyliron complexes [13.47; $R^1 = R^2 = Me$, $R^1R^2 = (CH_2)_4$] was atudied at 10^oK in an argon matrix. Cleavage of carbon-carbon bonds occurred to give the η^5-cyclopentadienyl systems (13.48) [219]. The (η-bicyclononatrienol)tricarbonyliron complex (13.49) rearranged in the presence of iron-pentacarbonyl to give the (η-bicyclononatrienone)tricarbonyliron complex (13.50) rather than the expected product. A mechanism involving an intermediate ion pair with $[HFe(CO)_4]^-$ was proposed. The structure of the product (13.50) was confirmed by X-ray crystallography [220].



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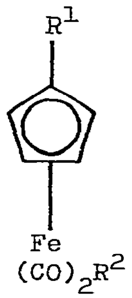
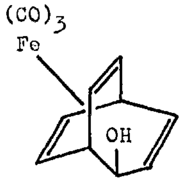


13.48

Tricarbonyl(η-tropone)iron combined with thiols in the presence of boron trifluoride etherate to form the corresponding alkyl- and aryl-thio derivatives (13.51; R = Me_2CH, Ph). A difunctional reagent, $HSCH_2CH_2SH$, underwent a similar reaction to give a binuclear product [221]. Mechanistic studies were carried out on the reactions of 5-exo-substituted tricarbonyl(η-cyclohexadiene)iron compounds (13.52; R = OMe, OEt NMe_2) and the tricarbonyl(η-cyclohexadienyl)iron cation. It was concluded that the conditions necessary for endo addition to the η-cyclohexadienyl ring were:



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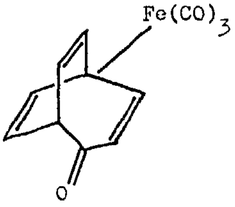

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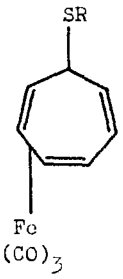
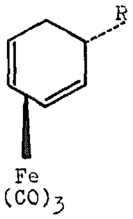


13.51

1, addition to the exo face must be reversible in the presence of acid, 2, the endo form must be sufficiently stable thermodynamically and 3, its formation must not be inhibited by the size of the nucleophile [222]. The (η^4-spirononadiene)iron complex (13.53) was attacked by diiron nonacarbonyl in boiling benzene with cleavage of an unstrained C-C bond and formation of the bridged (σ-alkyl-η^5--cyclopentadienyl)iron complex (13.54) which subsequently underwent insertion of tetracarbonyliron into the Fe-alkyl bond. 5,5-Dialkylcyclopentadienes also took part in this reaction and crossover experiments together with stereochemical studies indicated an intramolecular reaction mechanism with migration of the endo-alkyl group [223]. Tricarbonyl[η-5-exo-(isopropenyl)cyclohexa-1,3-diene]iron (13.55) has been prepared from tricarbonyl[η-5-exo-cyano(cyclohexa-1,



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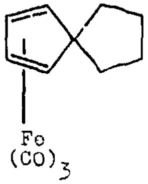

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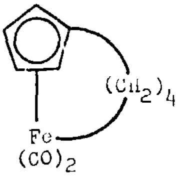

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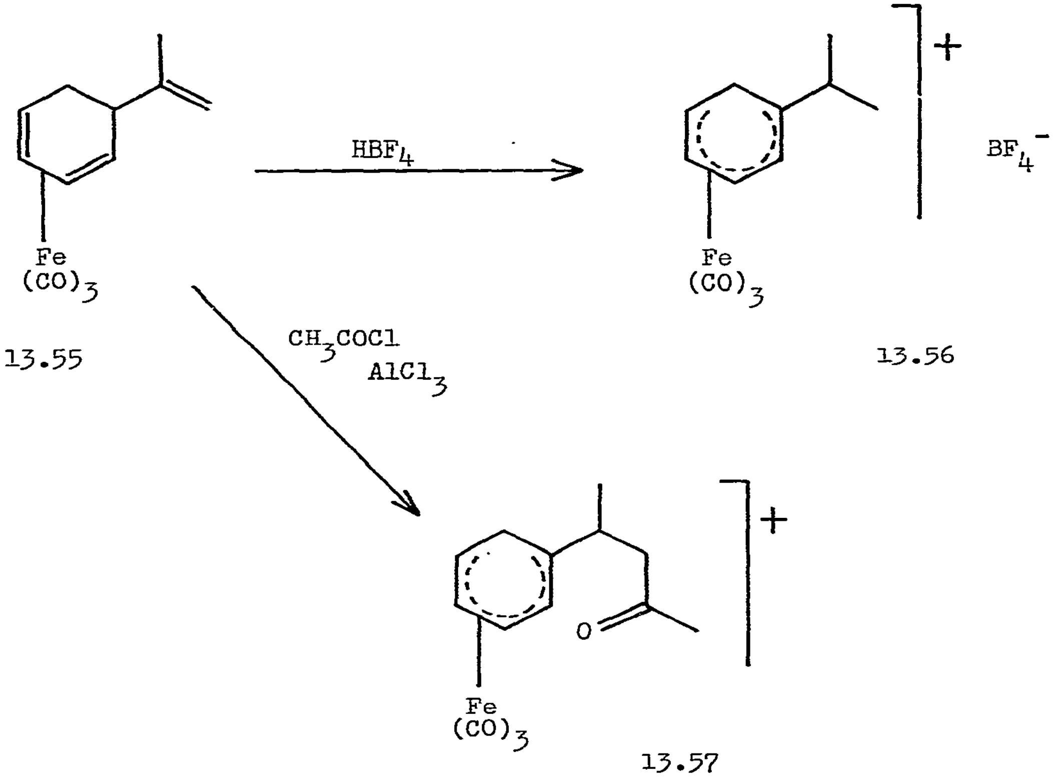
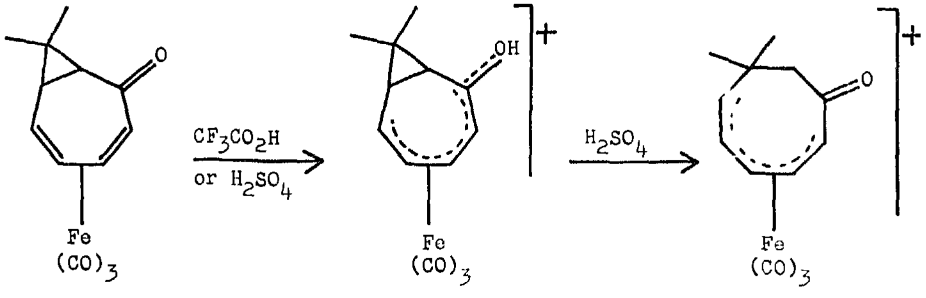


3-diene)]iron by treatment with methylmagnesium iodide followed by a Wittig reaction on the resultant acetyl complex. Protonation and acetylation of the complex (13.55) gave the 1-substituted η-cyclohexadienyl cations (13.56 and 13.57) respectively [224].

The (η-homotropone)iron tricarbonyl complex (13.58) dissolved in trifluoroacetic acid to give the oxygen-protonated cation (13.59). When sulphuric acid was the solvent then the cation (13.59) underwent rearrangement to form the carbon-protonated cation (13.60). The reaction mechanism was investigated by deuterium labelling and the preferred site of protonation of the (η-cyclooctatrienone)iron complex (13.60) was confirmed as C(2). The corresponding reactions of some closely related complexes were described [225]. Reaction of the cationic ruthenium complexes (13.61; N-N=1,10-phenanthroline, 2,2'-bipyridyl; $PR_3=PMe_2Ph,PMePh_2$) with various nucleophiles, Y^-, where Y = H, CN, OH, gave the corresponding stable η^5-cyclohexadienyl complexes (13.62) [226]. Several (η-cyclohexadiene)iron complexes, such as the ether (13.63), have been converted to the

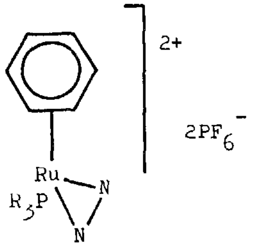


13.58

13.59

13.60

corresponding (η-cyclohexadienylium)iron cations, such as the complex (13.64), with triphenylmethylium tetrafluoroborate. The complex (13.64) underwent a highly regiospecific reaction with sodiomalononitrile to form the 1,4,4-trisubstituted cyclohexadiene complex



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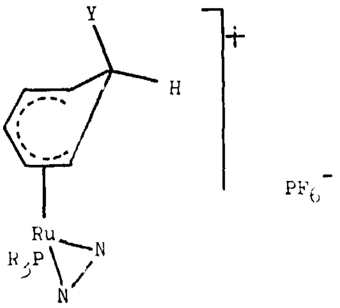
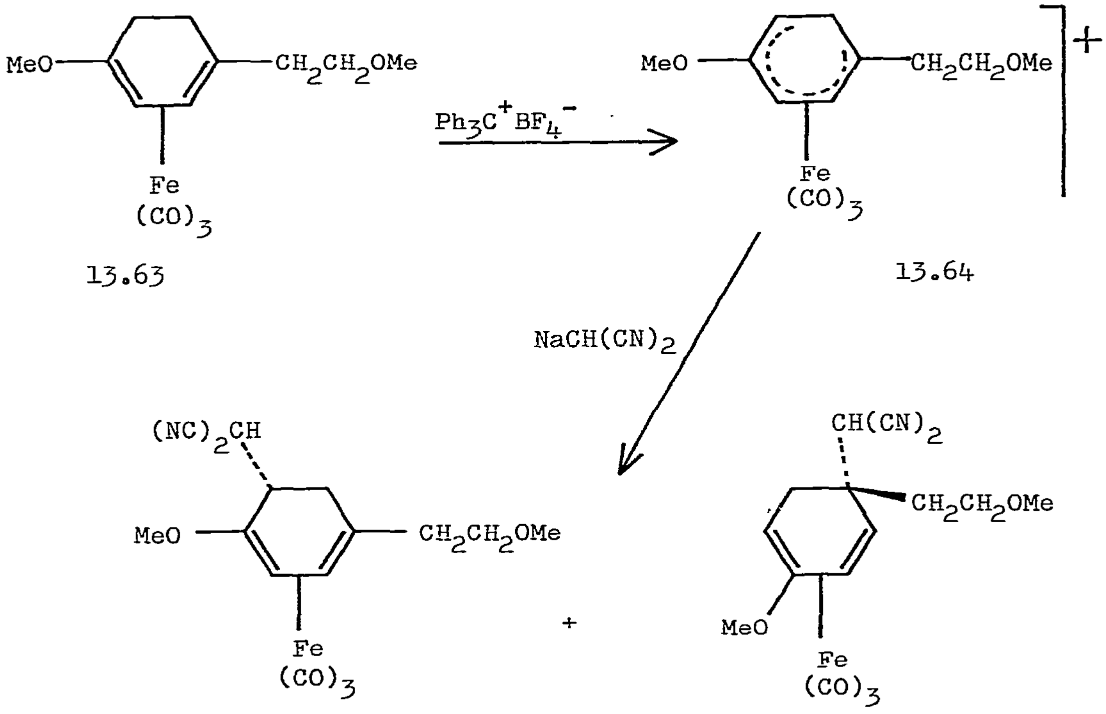


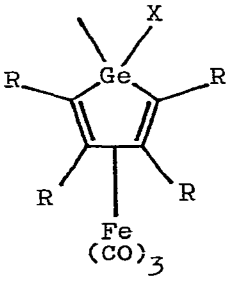
13.62

(13.65) and the 1,2,4-trisubstituted cyclohexadiene complex (13.66) in the ratio 90 : 10. The product (13.65) was a potential 4,4-disubstituted cyclohexenone precursor [227]. The cationic (η-germacyclopentadiene)iron complexes (13.68; R = H, Ph) have been obtained by abstraction of a hydride ion or a halide ion from the corresponding neutral complexes (13.67; R = H, X = F; R = Ph, X = H, F, Cl). Structure and bonding in the complexes (13.68)



13.63 13.64 13.66 13.65

were discussed [228].



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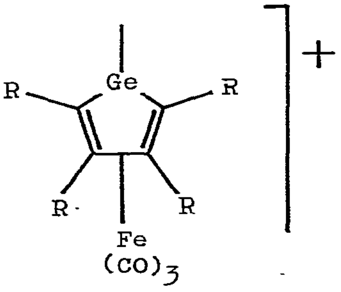
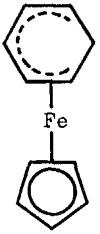


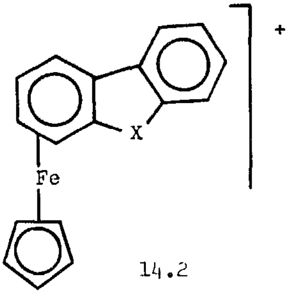
13.68

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

The cocondensation of iron atoms and benzene on to a liquid nitrogen cooled surface gave a highly reactive mixture which, when treated with cyclopentadiene gave the η^5-cyclohexadienyl complex (14.1) and a small quantity of ferrocene. Isotopic labelling



14.1



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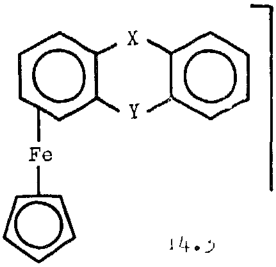

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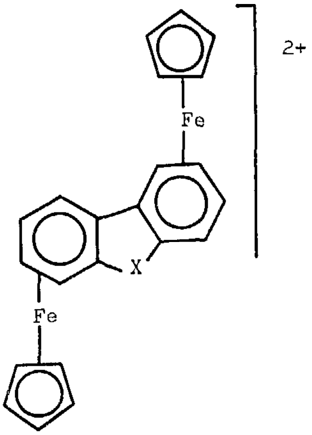

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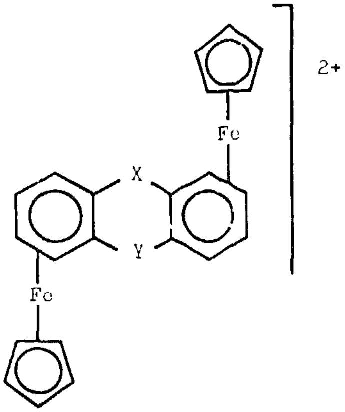
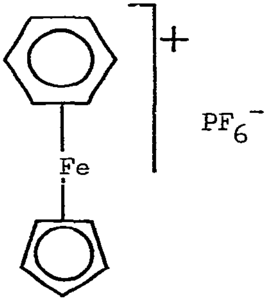


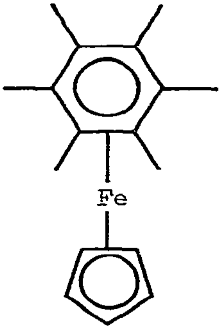
14.5

experiments indicated that hydrogen transfer from cyclopentadiene to coordinated benzene occurred *exo* with respect to the metal and was intermolecular in nature [229]. Ferrocene underwent ligand exchange with heterocyclic analogues of fluorene and anthracene in the presence of aluminium and aluminium chloride to give mononuclear and dinuclear (η-arene)(η-cyclopentadienyl)iron complexes. Dibenzofuran gave the cations (14.2; X = O, 14.4; X = O), dibenzothiophene gave the complexes (14.2; X = S, 14.4; X = S) while carbazole gave only the binuclear complex (14.4; X = NH). Xanthene gave the products (14.3; X = CH_2, Y = O, 14.5; X = CH_2 Y = O), thioxanthene afforded the cations (14.3; X = CH_2, Y = S, 14.5; X = CH_2, Y = S) phenothiazine led to the species (14.3; X = NH, Y = S, 14.5; X = NH, Y = S), while phenazine gave only the binuclear product (14.5; X = Y = NH) [230].

The unrestricted Hartree-Foch method in the INDO approximation with modified parametrization has been used to study the electronic structure of the $(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)Fe^+$ ion and its carboxyl and amino derivatives. Comparisons with the analogous derivatives of ferrocene were made. An unsymmetrical charge distribution was found between the two rings, with the greater positive charge on the arene ring. This difference was manifested in the acidic and basic properties of the rings which was confirmed both by direct calculations of acidic dissociation energy and by experimental observation [231]. The ^{57}Fe Mössbauer spectrum of the (η-cyclohexatriene)iron complex (14.6) has been measured in the temperature range 4.2-350°K. As the temperature was raised the initial quadrupole doublet changed to a four-peak spectrum and then to a single peak spectrum. The last change corresponded to a phase change in the solid. The changes observed were reversed on cooling the sample. The organometallic cation was assumed to lie at an eight-coordinate



14.6



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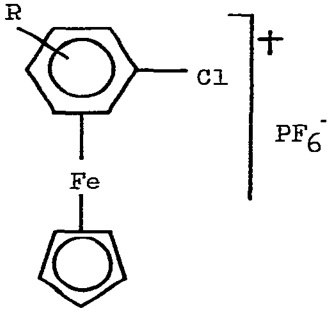
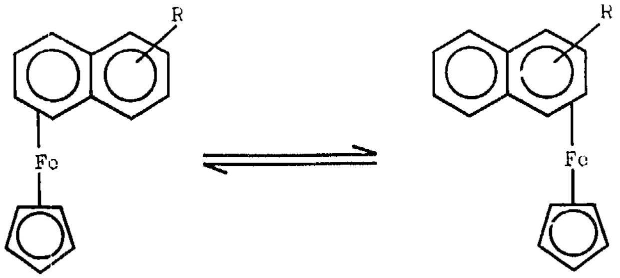


14.8

site made up from eight PF_6^- groups. Reorientations within this site were proposed to account for the spectral changes observed [232].

Moessbauer spectra of (η-benzene)(η-cyclopentadienyl)iron complexes have been recorded in the temperature range 4.2-293°K. The green complex (14.7) was a paramagnetic 19 electron $\underline{d}^7$ species which exhibited Jahn-Teller distortion. The observation of quadrupole doublets at temperatures below 185°K indicated a phase transition [233]. The kinetics and mechanism of the reaction of (η^6-chlorobenzene)(η^5-cyclopentadienyl)iron hexafluorophosphate with piperidine in dioxane, benzene and chlorobenzene was investigated. The reaction was first order in the π-complex and second order in piperidine [234]. The second order rate constants and the activation parameters were determined for the substitution reaction of the iron complexes (14.8; R = o-, m- or p-Me, p-CO_2Na, H) with sodium methoxide in methanol. The reactivity of the complexes increased in the order (14.8; o-Me < m-Me < p-Me < CO_2Na < H) and this was different from that for the uncoordinated ligands [235].

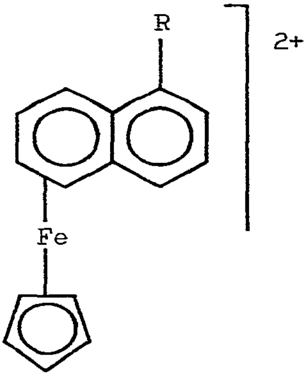
The anomalous temperature behaviour, averaging of the g-Factor anisotopy, in the EPR spectrum of (η-cyclopentadienyl)(η-naphthalene)iron was investigated by studies on the complexes (14.9; R = α-Me, β-F). The latter two compounds showed splitting of the g_{11} signals into two components which corresponded to two dissimilar isomers (14.9a and 14.9b) at temperatures above 77°K [236]. The ESR spectra of the dications (14.10; R = H, Me) were studied at 77°K. The $g_{||}$ and $g_\perp$ values were measured and the splitting of the



14.9a

14.9b

degenerate $\underline{e}_{2g}$ orbitals were calculated. The splitting of the $\underline{e}_{2g}$ orbitals in the dications was far smaller than the splitting of the $\underline{e}^{*}_{1g}$ orbitals in the corresponding neutral complexes [237].



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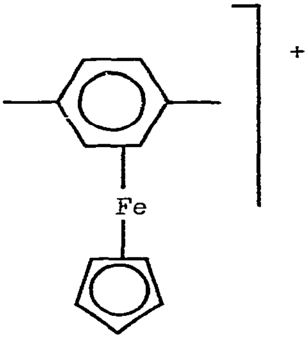

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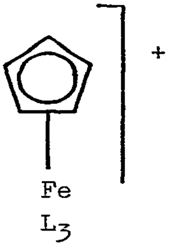
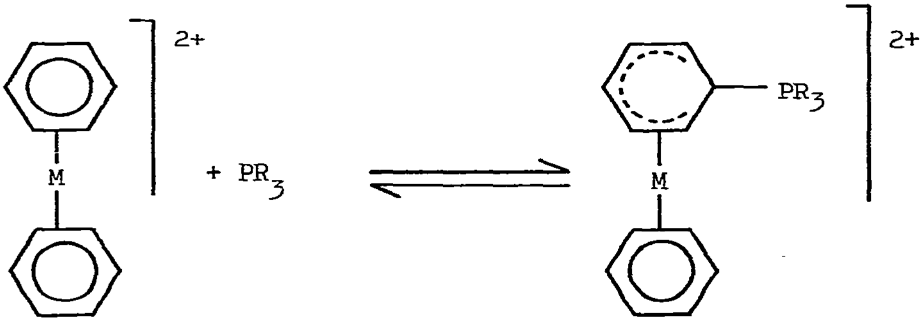


14.12

Visible-light irradiation of the complex cation (14.11) in the presence of suitable ligands gave the products of η-arene ligand replacement [14.12; $L_3=(\underline{p}\text{-CNC}_6H_4Me)_3, (CO)_3$, hexamethylbenzene, triphos]. The quantum yields for the formation of the complexes (14.12) were high [238].

The nucleophilic addition of tertiary phosphines to the bis-(η-benzene)metal (II) cations (14.13; M = Fe, Ru, Os) to give the corresponding η-cyclohexadienyl complexes (14.14; R = Bu, Ph) has

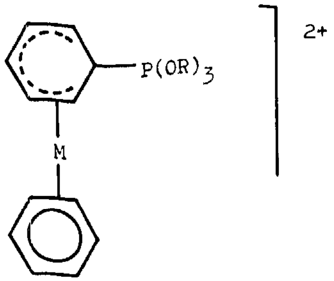


14.13

14.14

been studied via variable temperature ^{31}P and ^{1}H NMR spectroscopy. The electrophilic reactivity was very metal dependent: Fe ≫ Ru > Os (390:7:1). It was suggested that the metal→benzene π-backbonding in $[(\eta\text{-}C_6H_6)_2M]^{2+}$ followed the order Ru, Os ≫ Fe and this was used to account for the greater thermodynamic and kinetic electrophilic properties of the iron complex [239].

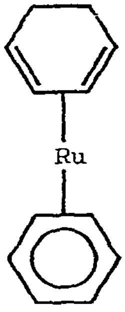
Reaction of bis(η-benzene)-iron (II) and -ruthenium (II) dications with trimethyl- and tri(η-butyl)-phosphite produced the corresponding phosphonium adducts (14.15; M = Fe, Ru; R = Me, Bu). The dications were good homogeneous catalysts for the conversion of $P(OR)_3$ into $HP(O)(OR)_2$, where R = Me, Bu [240]. Bis[(η-benzene)-osmium dichloride] has been obtained by treatment of 1,3-cyclohexadiene with an equimolar mixture of sodium hexachloroosmate and tin (II) chloride in alcohol at 40-80°C [241].



14.15

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

Theoretical calculations on the structures of ruthenocene and ferrocene in the solid state have shown that the eclipsed forms were more stable than the staggered forms. The principal contribution to the energy difference was the induction energy of the metal in the potential field of the rings. Direct ring-ring electrostatic energy also favours the eclipsed form [242]. The direct reaction of ruthenium (III) chloride trihydrate in the presence of metallic zinc with cyclohexa-1,3-diene and cycloocta-1,5-diene gave the ruthenium complexes (15.1 and 15.2) respectively. The analogous reaction with cycloocta-1,3-diene, cyclohepta-1,3-diene and cyclopentadiene gave the corresponding dienyl complexes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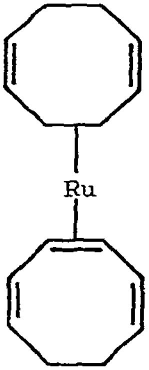
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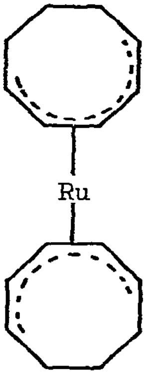
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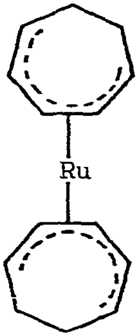
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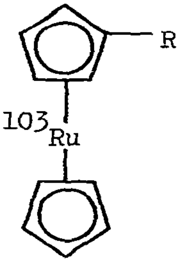
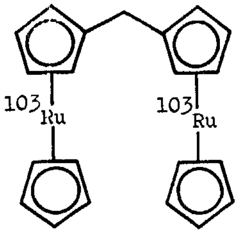

15.5

(15.3 and 15.4) and ruthenocene [243]. A series of ^{103}Ru labelled ruthenocene derivatives (15.5; R = Me, CH$_2$OH, CHO, CH$_2$OCH$_2$Ph, CH$_2$O$_2$CNHPh, 15.6 and 15.7) has been prepared by standard methods from labelled ruthenocene or by treatment of the corresponding ferrocene derivative with ^{103}RuCl$_3$. The tumor affinity of all the ruthenocene compounds was low [244].

The N-methyl-N-β-chloroethylhydrazone of ruthenocenecarbaldehyde has been synthesized using labelled ^{103}Ru. The hydrazone has been administered to rats and mice in order to investigate its metabolism and cytostatic effects. Measurements of organ distribution and excretion confirmed that one main metabolite was formed and was rapidly excreted in the bile, there was no indication of the formation of ruthenium ions. The hydrazone had a high affinity for lung tissue but only moderate amounts were found in the gut, kidney and liver. The cytostatic effects of the hydrazone were similar



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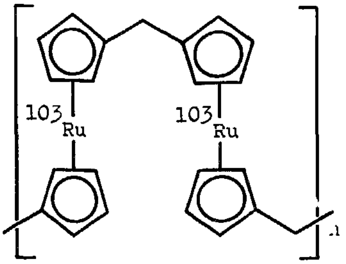
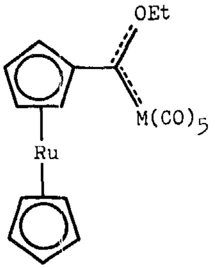


15.7

to those of the corresponding ferrocenecarbaldehyde and benzaldehyde hydrazones [245]. Lithioruthenocene was attacked by chromium-, molybdenum- and tungsten-hexacarbonyl to form, on subsequent alkylation with $[Et_3O][BF_4]$, the corresponding pentacarbonylethoxyruthenocenylcarbenes (15.8; M = Cr, Mo, W). The tungsten complex combined with boron and aluminium chloride and bromide at low temperature to give *trans*-halogenotetracarbonylruthenocenylcarbynes (15.9; X = Br, Cl). Some physicochemical properties of the carbynes were reported and the crystal and molecular structure of the carbene (15.8; M = W) has been determined by X-ray crystallography [246].



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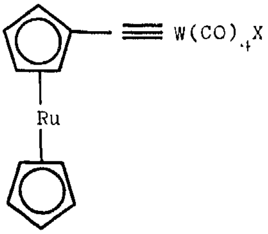
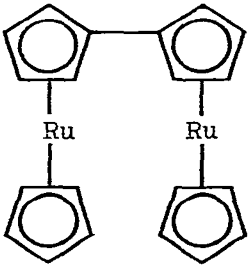


15.9

The coupling of 1,1'-diiodoruthenocene with the 1,1'-dilithioruthenocene-TMEDA complex in ether at 25-85°C gave a mixture of ruthenocene oligomers in an overall yield of 24%. Diruthenocene (15.10), 1,1'-terruthenocene (15.11; $n = 3$) and 1,1'-quaterruthenocene (15.11; $n = 4$) were separated from the mixture by chromatography. The low yield of coupled products, compared with the corresponding reaction of ferrocene, was explained in terms of low anion nucleophilicity of the lithioruthenocene. Electronic absorption spectra of the oligomers indicated little electronic interaction across the ruthenium atom of the metallocene group and thus no significant charge delocalization along the poly-1,1'-ruthenocene chain [247]. Ligand exchange in ruthenocene has been examined under various conditions. No exchange with benzene was observed at 80°C in contrast to the reaction of ferrocene under these conditions. Exchange with hexamethylbenzene at temperatures up to 250°C afforded only 10% yield of exchanged product whereas ferrocene gave yields of 60% under similar conditions. Exchange with mesitylene was facilitated by the addition of water to the reaction mixture [248].



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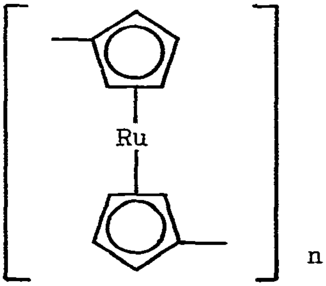
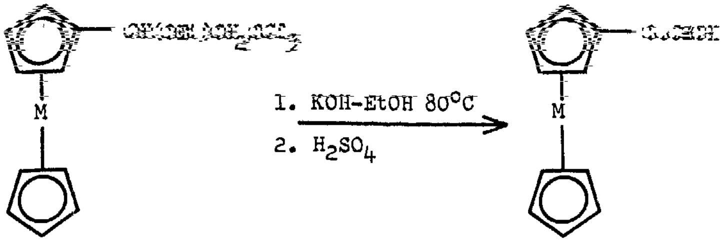


15.11

Treatment of the ruthenocenyl- and ferrocenyl-trichloropropanes (15.12; M = Ru, Fe) with potassium hydroxide in ethanol, followed by acidification, gave the corresponding ethynyl ketones (15.13) [249]. Mechanical spectroscopy, using the torsional pendulum and vibrating reed techniques, has been applied to the measurement of benzene and cyclopentadienyl ring rotation in organometallic complexes. Activation energies have been determined for several complexes and



15.12 15.13

found to fall in the range 4.9-6.2 k cal mole^{-1} compared with values for ferrocene, 2.0; ruthenocene, 4.5; bis(η-benzene)-chromium, 4.6 kcal mol^{-1} determined previously by NMR techniques [250].

The incubation of acetylruthenocene-^{103}Ru with rat liver homogenate, NADPH and UDP glucuronate gave hydroxyacetylruthenocene-^{103}Ru and its O-glucuronide. Conditions for the hydroxylation and glucuronidation in vitro were optimized. Hydroxyacetylruthenocene-^{103}Ru accumulated in the adrenal glands of mice after intravenous administration while the corresponding glucuronide did not [251]. Cholest-5-en-3-yl ruthenocenecarboxylate-^{103}Ru has been prepared by treatment of the corresponding ferrocene derivative with ^{103}RuCl$_3$. 17β-Hydroxy-1,3,5(10)-estratrien-3-yl- and 3-hydroxy-1,3,5(10)estratrien-17β-yl-ruthenocenecarboxylate-^{103}Ru were prepared by reaction of estradiol with ruthenocenecarbonyl chloride-^{103}Ru [252].

16. $(\eta\text{-}C_5H_5)_2Co$, $[(\eta\text{-}C_5H_5)_2Co]^+$ and $(\eta\text{-}C_4H_4)Co(\eta\text{-}C_5H_5)$

The intercalation compounds MOCl[Co(η-C$_5$H$_5$)$_2$]$_{0.16}$, where M = Ti, V have been prepared and examined by X-ray powder diffraction methods. The structures were found to be qualitatively similar to that reported previously for the compound FeOCl[Co(η-C$_5$H$_5$)$_2$]$_{0.16}$. Moessbauer spectroscopy and magnetic susceptibility measurements indicated that electron transfer from metallocene to host took place on intercalation [253]. Intercalation complexes of cobaltocene, nickelocene and ferrocene in iron oxychloride (FeOCl) have been investigated. From the Moessbauer spectra it was concluded that the high-spin Fe (III) state of the host lattice was retained on inclusion. Ferrocene was oxidized to the ferrocenium ion on intercalation and it was proposed that the intercalation compound contained free electrons. The conductivity of this latter intercalation complex was 10^4 times greater than that of FeOCl [254].

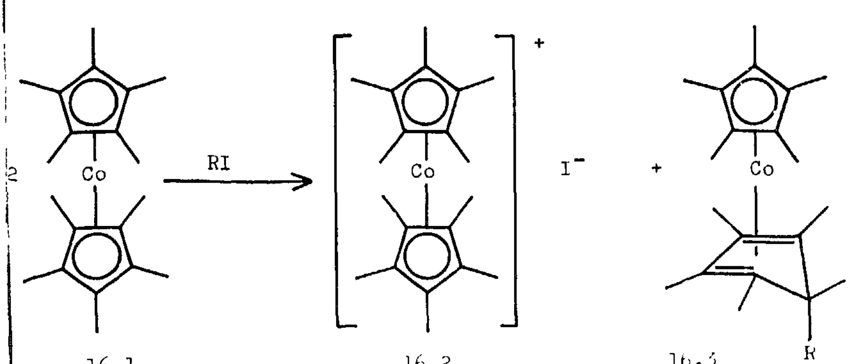
Cobaltocene and the cobaltocenium ion combined with the layer compound $CdPS_3$ to give intercalation compounds. Higher rates of intercalation were obtained using the metallocene cation. Physicochemical investigation of the intercalation products indicated that electron donation from metallocene to host took place and that the electrons gained by the host were probably paired and trapped in localized states [255]. The direct reaction of cobaltocene with zirconium hydrogen phosphate gave a cobaltocenium intercalation compound of zirconium hydrogen phosphate. The reaction was represented by the equation:

$$Zr(HPO_4)_2.H_2O + 0.5\ (\eta\text{-}C_5H_5)_2Co \longrightarrow Zr[(\eta\text{-}C_5H_5)_2Co]_{0.5}H_{1.5}(PO_4)_2 + 0.25H_2 + H_2O$$

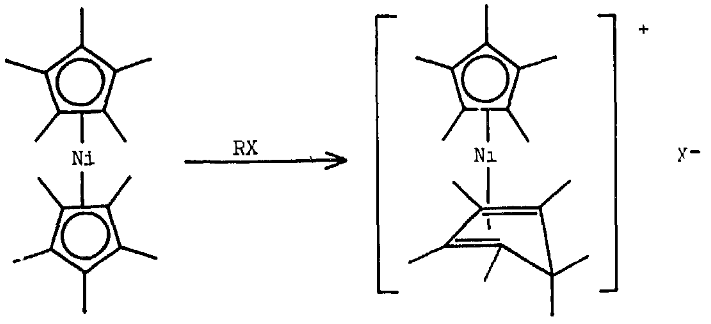
The same product was obtained by the ion exchange reaction of cobaltocenium solutions with zirconium hydrogen phosphate [256]. Raman (10-800 cm^{-1}) and infrared (10-4000 cm^{-1}) spectra of $MnPS_3$ and $CdPS_3$ intercalated with $[(\eta\text{-}C_5H_5)_2Co]^+$ and $[(\eta\text{-}C_6H_6)_2Cr]^+$ have been recorded in the 300-310°K temperature range. The chemical composition of the intercalated compounds was $M^1PS_3.0.33(\eta\text{-}L)M^2$, where M^1 = Mn, Cd; M^2 = Co, Cr; $\eta\text{-}L = (\eta\text{-}C_5H_5), (\eta\text{-}C_6H_6)$ and it was concluded that the sandwiches and intercalated molecules interacted weakly [257, 258].

The He (II) spectra of a series of metallocenes, including cobaltocene, nickelocene and ferrocene and the corresponding 1,1'-dimethylmetallocenes have been recorded. The He (I) and He (II) spectra of the corresponding decamethylmetallocenes were recorded. The photoelectron spectra were discussed and interpreted but overlap between the ligand and metal d band structures prevented complete assignment for cobaltocene and nickelocene [259]. The ^1H and ^{13}C NMR spectra of ethyl- and t-butyl-substituted cobaltocenes in acetone, benzene and toluene were strongly dependent on concentration and temperature. When the metallocene concentration increased and the temperature decreased all the ^1H and ^{13}C signals associated with the metallocene and the solvents shifted to higher field. A similar effect was found with substituted nickelocenes and vanadocenes in tetrahydrofuran or toluene. The effect was attributed to preferred mutual orientation of metallocene and solvent molecules which induced additional shifts in the metallocenes themselves and in the solvent. The effect was thought to originate from susceptibility shifts which were due to anisotropy and orientation of the molecules [260].

The ^{60}Co γ-radiolysis of the cobaltocenium cation in aqueous solution has been investigated. The radiation-chemical yield of decomposition products increased with a fall in pH and with an increase in the concentration of the substrate. It was proposed that the mechanism of radiolysis involved the solvated electron and a rate constant for the reaction was calculated [261]. Solutions of cobaltocene were neutron irradiated and the ^{60}Co yield,



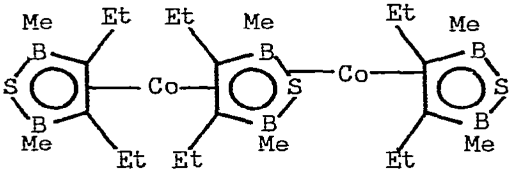
16.1 16.2 16.3



16.4 16.5

as cobaltocene-cobaltocenium ion, was concentration dependent and was increased by the addition of nickelocene [262]. Thermal decomposition of 1,1'-diethylcobaltocene in hydrogen at 240-400°C gave shiny coatings of cobalt on ceramics, glass, quartz, copper and on magnesium and aluminium alloys. Thus a solderable coating of thickness 0.1μ on glass-ceramic was formed in 20 min at 260°C [263].

The reaction of decamethylcobaltocene and decamethylnickelocene with electrophiles has been investigated. Decamethylcobaltocene (16.1) underwent oxidative addition on treatment with phenyl or methyliodide to form the cobaltocenium ion (16.2) and the cyclopentadiene complex (16.3). Treatment of decamethylnickelocene (16.4) with the electrophiles RX, where RX = CF_3CO_2H, CF_3SO_3Me, $PhCH_2Br$, CCl_4, PhCOCl, gave the salts (16.5) which were stable to air and water [264]. The charge transfer complexes cobaltocene-CCl_4 and



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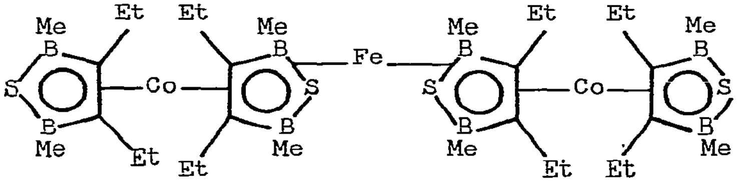

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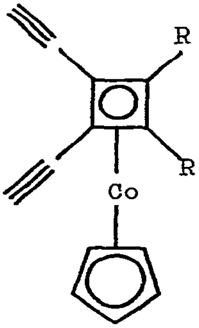
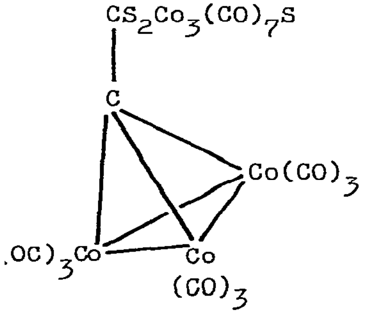


16.8

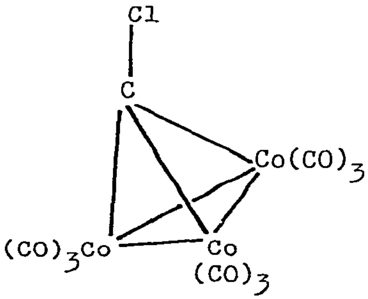
nickelocene-CCl_4 have been investigated photochemically in cyclohexane and ethanol. Equilibrium constants and molar extinction coefficients were obtained [265]. The three-layer sandwich thiaborelene (16.6) has been treated with sodium cyclopentadienide and iron (II) chloride to form the four-layer sandwich complex (16.7). The crystal and molecular structure of this trinuclear thiaborelene species has been determined by X-ray crystallography [266]. Potential mechanisms for the haptotropic rearrangement of (η-tetrasubstituted cyclobutadiene)cobalt complexes (16.8) have been theoretically evaluated using EHMO calculations [267].

17. Cobalt-carbon Cluster Compounds

Dicobalt octacarbonyl combined with carbon disulphide at room temperature to give a mixture of products from which the mixed cluster complex (17.1) has been isolated. The structure of the complex (17.1) was confirmed by an X-ray crystallographic analysis. The substituent group consisted of a Co_3S pyramid symmetrically linked to the Co_3C cluster by a CS_2 bridge [268]. A one-step synthesis of alkylidyne tricobalt nonacarbonyl complexes has been reported. Dithioesters RCS_2Me, where R = Me, Et, Me_2CH, $(CH_2)_3Me$, cyclohexyl, Ph, 4-Me.C_6H_4, 4-MeO.C_6H_4, 4-Me_2N.C_6H_4, 3,4-Me_2.C_6H_3, α-naphthyl, were attacked by dicobalt octacarbonyl in ethanol to give the cluster complexes, $RCCo_3(CO)_{12}$, in yields of up to 74%. The reaction mechanism involved desulphurization of the dithioester by radical pathways [269]. Octacarbonyldicobalt combined with the dichlorocarbene precursor $Hg(CCl_3)Ph$ in hexane at 60°C to give



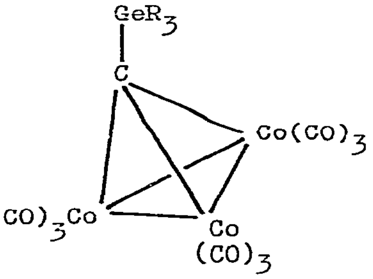
17.1



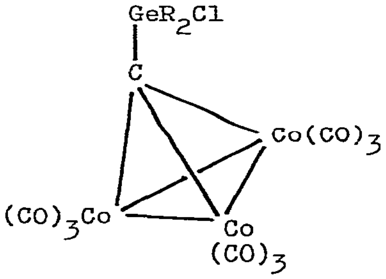
17.2

the chloro-substituted cluster complex (17.2). The mechanism of the reaction was investigated and the compounds $Co(CCl_3)(CO)_4$ and $Co(HgPh)(CO)_4$ were implicated as key intermediates [270]. The reactions of the double-bonded metal dimer, $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ with various photogenerated $M(CO)_x$ and $M(C_nR_n)(CO)_y$ species were investigated. Two electronically equivalent but structurally different series of triangular dicobalt-metal clusters, $MCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu_3\text{-}CO)$, where M = $Cr(\eta^6\text{-}C_6H_5Me)$, $Mn(\eta^5\text{-}C_5H_4Me)$, $Fe(\eta^4\text{-}C_4H_4)$, and $MCo_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2(\mu_3\text{-}CO)$, where M = $Fe(CO)_3$, $Co(\eta^5\text{-}C_5H_4Me)$, were characterised [271].

Methylidynetricobaltnonacarbonyl has been attacked by organogermanium hydrides in boiling benzene to form trialkylgermyl- (17.3; R = Et, Bu, Ph) and dialkylchlorogermyl-methylidynetricobaltnonacarbonyl complexes (17.4; R = Et, Ph, CH_2Ph) [272].



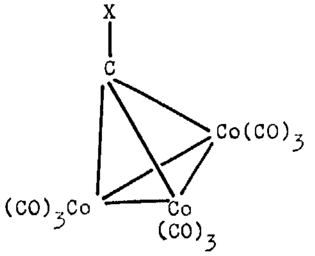
17.3



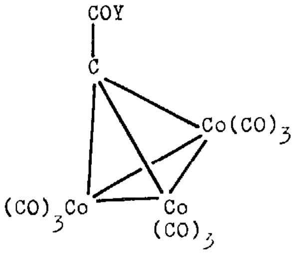
17.4

Bromo- and chloro-methylidynetricobalt nonacarbonyl (17.5; X = Br, Cl) combined with aliphatic alcohols, phenols, and secondary amines and anilines, in the presence of triethylamine, to form the derivatives (17.6; Y = RO, ArO, R^1R^2N, ArNH) respectively. In a typical reaction the bromo cluster complex (17.5; X = Br) was treated with diethylamine at room temperature to form the amide (17.6; Y = Et_2N) in 75% yield. The parent complex, methylidynetricobalt nonacarbonyl, combined with alcohols and amines to give similar products to those obtained from the halo cluster complexes but yields were poor. Several possible reaction mechanisms were considered [273]. Several mercapto-methylidynetricobaltnonacarbonyl complexes (17.7; R = Et, Pr, Pr^i, Bu^t, CH_2CO_2Me, Ph,

CH_2Ph, COPh, COMe) have been prepared in yields of 10-57% by heating the halides (17.5; X = Cl, Br) with the tin mercaptides $Me_2Sn(SR)_2$ in toluene [274].

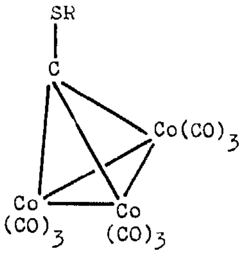


17.5

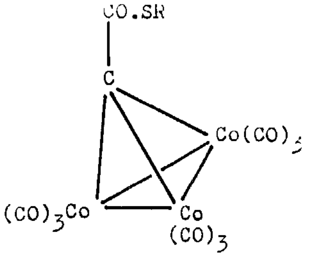


17.6

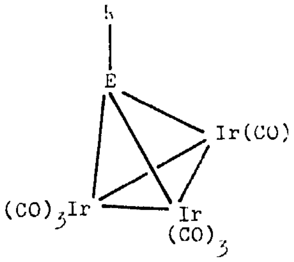
Bromomethylidynetricobalt nonacarbonyl combined with alkane thiols in the presence of triethylamine to form the thioesters (17.8; R = Me_2CH, Bu^n). Thioesters were also obtained from the same cluster complex and lithium alkane- and arene-thiolates. Arylthioethers (17.7; R = Ph, $Me.C_6H_4$) were formed when chloromethylidynetricobalt nonacarbonyl combined with arenethiols. The mechanism of the reaction was discussed [275]. Sodium tetracarbonyliridate was treated with Cl_3CR, where R = Me, Ph, Cl_3SiMe or Cl_3GeMe to form the corresponding cluster compounds (17.9;



17.7



17.8

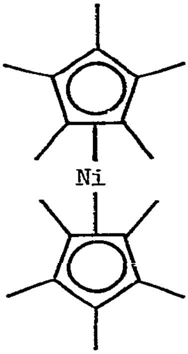


17.9

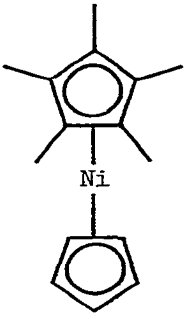
E-R = C-Me, C-Ph, Si-Me, Ge-Me). From infrared data it was suggested that these compounds had similar structures to those of the methylidyne clusters $(CO)_9Co_3CR$ [276].

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

Reaction of nickel (II) bromide with lithium pentamethylcyclopentadienide gave decamethylnickelocene (18.1) and pentamethylnickelocene (18.2) was prepared from chloro(η-pentamethylcyclopentadienyl)triphenylphosphinenickel and thallium cyclopentadienide. Treatment of the complexes (18.1 and 18.2) with hydrogen tetrafluoroborate gave the ring hydrides $[(\eta^5\text{-}C_5Me_5)Ni(\eta^4\text{-}C_5Me_5H)]^+BF_4^-$ and $[(\eta^5\text{-}C_5H_5)Ni(\eta^4\text{-}C_5Me_5H)]^+BF_4^-$. The reactions of the substituted nickelocenes with tetracarbonylnickel and triphenylphosphine were investigated [277]. The structure of nickelocene has been determined at room temperature and 101°K by X-ray analysis. At room temperature nickelocene was isostructural with monoclinic ferrocene but there was no phase change to a triclinic structure as occurred with ferrocene on cooling. When nickelocene was cooled there was an appreciable decrease in thermal motion and the η-cyclopentadienyl rings were staggered [278]. The electronic structure of nickelocene has been studied using calculations based on the all-electron self-consistent-field multiple scattering X_α method. Calculations were carried out both for nickelocene and the nickelocenium cation. The ionization energies calculated for nickelocene were in good agreement with data obtained by photoelectron spectroscopy. However, current interpretations of the UV-visible absorption spectra were questionable on the basis of the transition energy calculations



18.1

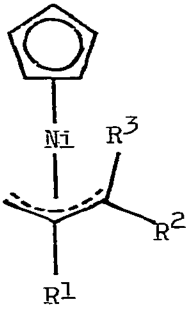


18.2

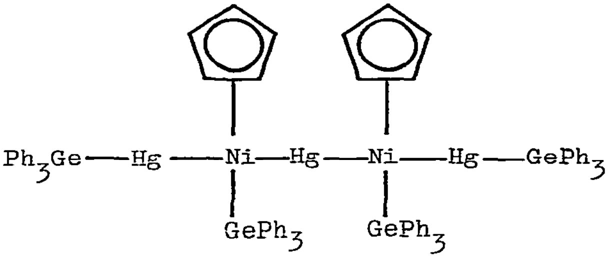
[279].

The multiphoton dissociation and ionization of nickelocene and ferrocene have been investigated with tuneable dye lasers. Excitation in the spectral range 3750-5200Å led to a collision-free multiphoton dissociation. The order and dynamics of this dissociation process were explored by determining its intensity dependence [280]. The ionization of a gas mixture containing nickelocene by an N_2-laser beam has been explored as a technique for testing and calibrating ionizing particle detectors [281]. The infrared spectra of nickelocene-HCl and ferrocene-HCl complexes in liquid xenon solutions indicated that the π-electrons of the metallocenes participated in complex formation. The enthalpies of complexation of hydrogen chloride with nickelocene and ferrocene were 2.4 and 1.1 kcal mol^{-1} respectively [282]. The mechanism of phase transitions in nickelocene and ferrocene has been investigated by analysis of the IR and Raman spectra of the polycrystalline solids in the temperature range 40-400°K. Ferrocene and nickelocene showed the same disorder at room temperature but the long-range order was found to be shorter for nickelocene than for ferrocene. The second-order phase transition mechanism was discussed [283].

^{13}C NMR spectra have been recorded for the following nickelocenes, $(\eta\text{-}C_5H_5)_2Ni$, $(\eta\text{-}C_5D_5)_2Ni$, $(\eta\text{-}MeC_5H_4)_2Ni$, $(\eta\text{-}EtC_5H_4)_2Ni$, $(\eta\text{-}\underline{n}\text{-}BuC_5H_4)_2Ni$ and $(\eta\text{-}\underline{t}\text{-}BuC_5H_4)_2Ni$. The spectra had individual signal halfwidths >5000 Hz with signal groups >20,000 Hz and they covered a range of >2200 ppm. It was concluded that nickelocenes were radicals with the two unpaired electrons in e_{1g} orbitals [284]. Hydrogenation of nickelocene at 200-300°C gave a mixture of cyclopentadiene, cyclopentene and cyclopentane. The yield of cyclopentadiene increased with increasing temperature while the yield of cyclopentane decreased. These results were consistent with the free energy of formation of cyclopentane at 200° and 350°C [285]. $(\eta^3$-Allyl)$(\eta^5$-cyclopentadienyl)nickel complexes (18.3; $R^1 = R^2 = R^3$ = H, Me) were prepared by the reaction of nickolocene with 2-alkenylmagnesium compounds or with dienes and alkylmagnesium halides. For example, the reaction of nickelocene with $Me_2C{=\!=}C(Me)CH_2MgCl$ gave the nickel complex (18.3; $R^1 = R^2 = R^3$ = Me) [286]. The reduction of nickelocene with sodium naphthalenide in tetrahydrofuran gave five different kinds of η-cyclopentadienyl-nickel clusters viz., $Ni_2(\eta\text{-}C_5H_5)_2(\mu\text{-}C_5H_6)$, $Ni_3(\eta\text{-}C_5H_5)_4$,



18.3



18.4

$Ni_4(\eta-C_5H_5)_4H_n$(n = 1, 3), $Ni_5(\eta-C_5H_5)_5H_3$ and $Ni_6(\eta-C_5H_5)_6$. Oxidation of the last complex with $AgPF_6$ produced $[Ni_6(\eta-C_5H_5)_6]^+$-PF_6^-. The structures of the complexes $Ni_6(\eta-C_5H_5)_6$ and $[Ni_6(\eta-C_5H_5)_6]^+$ were determined by X-ray analysis. They were both cluster compounds with the six nickel atoms located at the corners of an octahedron and a η^5-cyclopentadienyl ligand was coordinated to each nickel atom [287].

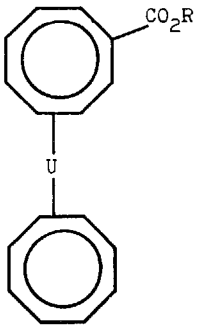
Nickelocene has been attacked by bis(triphenylgermyl)cadmium to form a polymetallic complex, $[Ph_3Ge.Cd.Ni(\eta-C_5H_5)(GePh_3)]_2Cd$, containing germanium-cadmium-nickel metal-metal bonds. The crystal and molecular structure of the complex was confirmed by X-ray crystallography [288]. The reaction of bis(triphenylgermyl)mercury with nickelocene gave the polymetallic molecule (18.4). The crystal structure of the monotoluene solvate of this latter molecule was determined by X-ray analysis [289]. The aging resistance of rubber was improved by the addition of nickelocene (3.2%) in the presence of a 'tellurium coupler' [290]. The hydrosilylation of styrene and octene with alkyldichlorosilanes in the presence of nickelocene and other nickel complexes has been investigated. The activating effect of triphenylphosphine in these systems was studied [291].

(η-Tetraphenylcyclobutadiene)nickeldibromide has been attacked by 1,5-cyclooctadiene (COD) and cyclooctatetraene (COT) to form the mixed sandwich complexes $(\eta-Ph_4C_4)Ni(COD)$ and $(\eta-Ph_4C_4)Ni(COT)$. In each case the complex underwent ligand exchange with bidentate nitrogen and phosphorus donors such as 2,2'-dipyridyl, 1,10-phenanthroline and $Ph_2PCH_2CH_2PPh_2(L_2)$ to give the products $(\eta-Ph_4C_4)$-

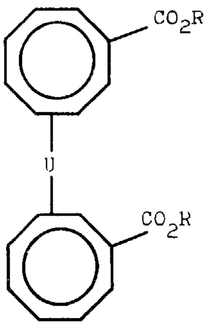
NiL_2 [292].

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

Deprotonation of 1,4-di-t-butylcyclooctatriene with potassium amide in liquid ammonia gave the corresponding dianion which was treated with uranium (IV) chloride to give 1,1',4,4'-tetra(t-butyl)uranocene. Thermal decomposition of the adduct of uranium (IV) chloride and n-butyllithium gave finely divided uranium which reacted with cyclooctatraene to form uranocene in good yield (69%). 1,1'-Di(n-butyl)uranocene was prepared by the same route [293]. Cyclooctatetraene dianion combined with alkyl halides to form bicyclooctatrienes which were deprotonated to the corresponding alkyl annulated cyclooctatetraene dianions and subsequently treated with uranium (IV) chloride to form the corresponding annulated uranocenes. The crystal and molecular structures of dicyclobuteno- and dicyclopenteno-uranocene have been determined by X-ray diffraction methods and the effects of annulation of the uranocene moiety were evaluated. The variable temperature ^1H NMR spectra of uranocene and seventeen substituted uranocenes have been obtained in the range -80°C to 70°C and energy barriers to ring rotation calculated [294]. The uranocenoic esters (19.1 and 19.2; R = Et, *t*-Bu and CH_2Ph) have been prepared from the corresponding cyclooctatetraene esters by reduction with potassium naphthalenide followed by reaction with uranium (IV) chloride. The esters were hydrolyzed immediately by hydroxylic solvents [295].



19.1



19.2

The bis(η^8-1,3,5,7-tetramethylcyclooctatetraene) complexes of protactinium, neptunium and plutonium were prepared by reaction of the corresponding actinide borohydride compounds $M(BH_4)_4$ with the tetramethylcyclooctatetraene dianion in tetrahydrofuran. From X-ray data it was concluded that these complexes had the same structure as the corresponding uranocene [296]. The electrochemical oxidation of uranocene in nonaqueous solvents has been investigated. Evidence was obtained that indicated the existence of the uranocene radical cation and dication intermediates [297].

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