ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1983*

GEORGE MARR and BERNARD W. ROCKETT
Department of Physical Sciences, The Polytechnic,
Wolverhampton WV1 1LY (Great Britain)

CONTENTS

---

* Organic Reactions of Selected π-Complexes; Annual Survey covering the year 1982, B. W. Rockett and G. Marr, J. Organometal. Chem., 257 (1983) 275.

1. Reviews

The proceedings of the China-Japan-United States Trilateral Seminar on Organometallic Chemistry held in Peking have been published. Details of the twenty-eight plenary lectures and the poster sessions were given. Many of the articles contained material relevant to this annual survey [1].

Rybinskaya and Krivykh have reviewed new organometallic chelates with η-arene and η-cyclopentadienyl ligands [2].

Organometallic intramolecular-coordination compounds containing a diene donor ligand have been the subject of an extensive review by Omae [3].

The application to organic synthesis of transition metal diene complexes has been reviewed [4]. Kerber has reviewed the interaction of organometallic moieties with carbanions and other electron-rich centres. Literature data was cited that suggested organometallic groups provided effective stabilization of β-carbanions by interactions of the type:

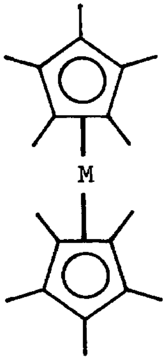
$$L_nM-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^{-} \longleftrightarrow L_nM^{-}\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}$$ [5].

Mono- and di-nuclear complexes analogous to cymantrene have been included in a more general review of methylene-bridged organometallic complexes [6].

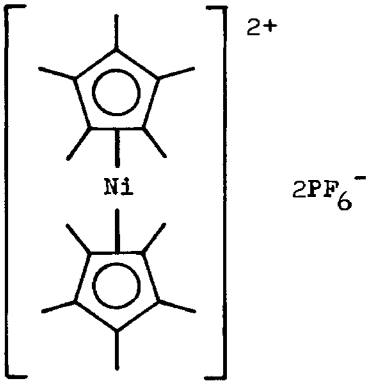
Watts has discussed the effect of metal π-complexation on the properties of organic molecules and ions [7].

2. General Results

Several decamethylmetallocenes (2.1; M = Mg, V, Cr, Co, Ni) have been synthesized. Spectroscopic, magnetic susceptibility and X-ray crystallographic evidence indicated that the metallocenes (2.1) were D_{5d} or D_{5h} species with low spin electronic configurations. Decamethylmanganocene was inert to ring loss and hydrolysis but underwent one-electron oxidation and reduction to give isolable low spin 16 and 18 electron complexes $[(\eta\text{-}Me_5C_5)_2Mn]PF_6$ and $Na[(\eta\text{-}Me_5C_5)_2Mn]$ respectively. The dicationic nickelocene (2.2) was also prepared [8].



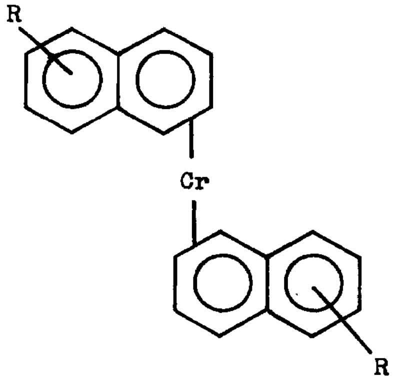
2.1



2.2

Intercalates of MPS_3 (M = Zn, Cd, Mn, Fe, Co, Ni) with $[(\eta\text{-}C_5H_5)_2Co]^+$ and $[(\eta\text{-}C_6H_6)_2Cr]^+$ have been studied by ultraviolet-visible, infrared and Raman spectroscopy. The vibrational spectra of MPS_3 were interpreted in terms of normal modes of flat PS_3 pyramids weakly coupled through P-P interactions, and in terms of translations of metallic ions in distorted octahedral environments [9].

Transition metal chlorides in THF have been reduced by condensing potassium atoms into the solution at -110°C. The reduced transition metal species combined with benzene, naphthalene and their methyl derivatives to form bis(η-arene) complexes of titanium, vanadium, chromium and molybdenum. Typical products were the (η-naphthalene)chromium complexes (2.3; R = H, Me) [10].

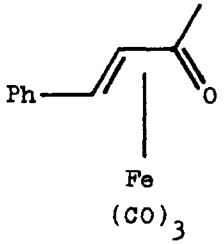


2.3

The ligands η^5-pentamethylcyclopentadienyl and $B_9C_2H_{11}^{2-}$ exhibit similar electronic and steric properties in the formation of transition metal complexes [11].

Solid phase synthesis has been used to prepare enkephalin substance P (EP) and bradykinin (BN) analogues in which ferrocenylalanine, tricarbonyl(η-cyclobutadiene-alanine)iron and cymantrenylalanine were substituted for phenylalanine. The metallocenyl group in the ferrocenyl substituted peptides did not interact with the aryl receptors of EP and BN. The cymantrenyl substituted peptide was the only one of the three that was hydrolyzed by chymotrypsin [12].

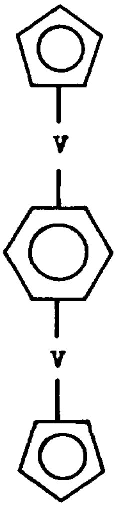
Cyclic trimeric phosphazenes have been used as models for poly(aryloxyphosphazines) in a study of phosphine-transition metal complex interaction. Complexes such as cymantrene and



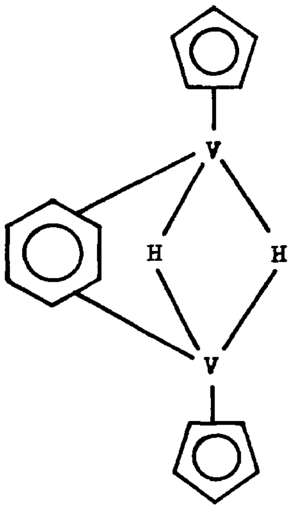
2.4

the (η-enone)iron complex (2.4) combined with phosphazenes such as $[NP(OPh)_2]_3$ to give species resembling triphenylphosphine-metal complexes without interference from skeletal nitrogen atoms [13].

The triple-decker sandwich complex (2.5) has been prepared by reaction of $(\eta\text{-}C_5H_5)V(\eta\text{-}C_3H_5)_2$ with an excess of 1,3-cyclohexadiene. The complex (2.5) underwent arene ligand exchange with toluene or mesitylene and the triple-decker sandwich structure was retained [14].



2.5

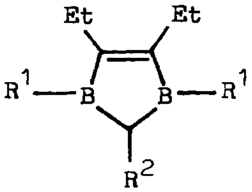


2.6

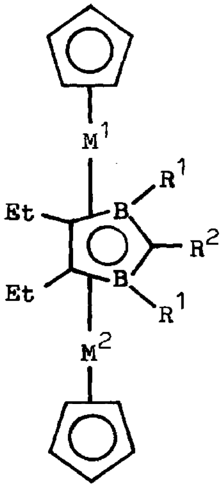
In related work, Jonas and co-workers prepared the binuclear hydridovanadium complex (2.6). The two $\eta\text{-}C_5H_5\text{-}V$ units were bridged by a nonplanar benzene ring as well as two hydrogen atoms. When this complex was treated with carbon monoxide tetracarbonyl-(η-cyclopentadienyl)vanadium was produced [15].

The synthesis, structure and properties of several homonuclear and heteronuclear triple-decker sandwich complexes have been studied. Methyltetraethyl and dimethyldiethyl derivatives of the Δ^4-1,3-diborolene ligand (2.7; R^1 = Et, R^2 = Me; R^1 = Me, R^2 = H) have been used to prepare the complexes (2.8; M^1 = Fe, M^2 = Co, "FeCo"; M^1 = M^2 = Co, "CoCo"; M^1 = Co, M^2 = Ni, "CoNi"; M^1 = M^2 = Ni, "NiNi"; R^1 = Et, R^2 = Me; R^1 = Me, R^2 = H). The crystal and molecular structures of the FeCo, NiCo and NiNi complexes were determined by X-ray crystallography and found to be isomorphous, with each complex having a planar μ-1,3-diborolenyl ligand. Chemical or electrochemical oxidation or reduction of the complexes (2.8) gave the corresponding charged species. The FeCo, CoCo$^+$ and NiNi$^-$ complexes were diamagnetic while the FeCo$^+$, CoCo, NiCo$^+$ and NiNi species were paramagnetic with one unpaired electron. The NiCo and NiNi$^+$ species had two unpaired electrons. The electronic structures of the complexes (2.8) were determined by employing semiempirical INDO MO calculations and the results obtained compared with some of the experimantal observations. Moessbauer measurements on the FeCo and FeCo$^+$ species indicated parallels with the ferrocene-ferrocenium couple. Polarography, cyclic voltammetry and controlled potential coulometry were used to show that each of the complexes (2.8) was oxidized or reduced in more than one reversible electron-transfer process. The CoCo complex underwent three reversible electron-transfer reactions (2+/+/0/-) and one irreversible reaction (-/2-). Several carbonyl-bridged complexes were derived from the complexes (2.8) and the NiNi species was converted into a quadruple-decker complex [16].

The structure of the triple-decker sandwich molecule $[Ni_2(\eta\text{-}C_5H_5)_3]BF_4$ has been determined by X-ray analysis. The three η-C_5H_5 groups were coplanar to within 3.97° [17].



2.7



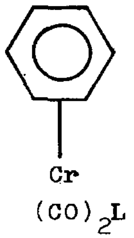
2.8

A neutron scattering study has been carried out on the reorientational motions in (η-benzene)tricarbonylchromium and tricarbonyl(η-cyclopentadienyl)manganese. The aromatic rings were involved in a reorientational process characterized by an activation energy of approximately 16 kJ mol^{-1} and correlation times of 2 x 10^{-11}s and 5 x 10^{-11}s at 300 K for the η-C_6H_6 and η-C_5H_5 ligands respectively. The $M(CO)_3$ groups were fixed during the reorientational process [18].

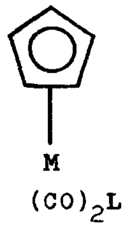
Several metallocenes and half-sandwich complexes including ferrocene, nickelocene, benchrotrene and cymantrene have been examined as crystalline solids by vibrational spectroscopy, quasielastic neutron scattering and calorimetry in order to classify the order-disorder phase transitions. The three techniques were synergistic in elucidating activation energies, residence times and geometries for reorientational motion of the hydrocarbon ligands [19].

Electron transmission spectroscopy has been used to determine the energies of low-lying, unstable negative ion states for the metallocenes, vanadocene, chromocene, manganocene, ferrocene, cobaltocene and nickelocene. Calculations for ferrocene, cobaltocene and nickelocene using the multiple scattering X_α procedure have allowed the observed states to be assigned to electron capture into metal $3\underline{d}$, $4e_{1g}$ orbitals or into cyclopentadienyl π^* orbitals [20].

Mass spectrometric fragmentation patterns have been recorded and interpreted for the complexes (2.9; L = CO, CS, CSe) and (2.10; M = Mn, Re, L = CO, CS, CSe) [21].



2.9



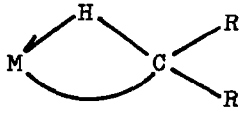
2.10

The intercalation compounds formed between $ZnPS_3$ and the cobaltocenium ion and the bis(η-benzene)chromium cation have been examined by IR and Raman spectroscopy. The spectra were assigned and the guest metallocene species were intercalated as the cations. Interactions between them and the host lattice were weak and the guest cations showed dynamic disorder at room temperature [22].

Qualitative molecular orbital theory, based upon Extended Hueckel calculations has been used in a study of the coordinatively unsaturated sixteen-electron fragments d^8 (η-C_5H_5)ML with respect to their geometric and electronic features [23].

The electronic structures of benchrotrene, cymantrene, tricarbonyl(η-cyclobutadiene)iron, (η-butadiene)tricarbonyliron and tricarbonyl(η-trimethylenemethane)iron in the ground state and in the cationic hole states have been the subject of a semiempirical INDO MO study based on the Green's function formalism. The sequence of ionization potentials calculated for the chromium and manganese complexes corresponded to the energy levels of the ground state molecular orbitals. However, the HOMO's for the three iron complexes had principally ligand character while the ionization potentials were associated with molecular orbitals of mainly metal 3_d_ character [24].

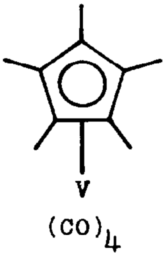
Brookhart and Green have collected together and discussed evidence that carbon-hydrogen bonds may act as ligands to transition metal centres to form covalent C-H—M systems in which, formally, the C-H group donates two electrons to the metal. They have used the term "agostic" to discuss the various manifestations of covalent interactions of this type in organometallic compounds. The agostic C-H→M interaction may be represented by the complex (2.11) where M = titanium, tantalum, molybdenum, tungsten, manganese, iron, ruthenium, osmium and palladium. Crystal structure, NMR and IR results were important in providing evidence for the interaction proposed [25].



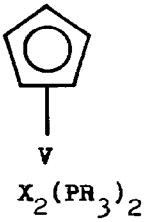
2.11

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

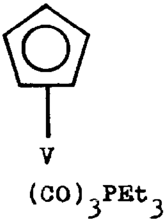
Pentamethylcyclopentadiene has been treated with hexacarbonylvanadium to form the (η-pentamethylcyclopentadienyl)-vanadium complex (3.1) which underwent photolysis to give a binuclear complex $(\eta\text{-}C_5Me_5)_2V_2(CO)_5$ [26].



3.1



3.2



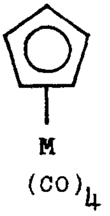
3.3

Reaction of $VX_3(PR_3)_2$, (R = Me, Et; X = Cl, Br) with C_5H_5M [M = Na, Tl, $(n\text{-}Bu)_3Sn$, 1/2Mg] produced the corresponding η-cyclopentadienyl-vanadium complexes (3.2). Reduction of the chloro complex (3.2; R = Et, X = Cl) with zinc or aluminium in an atmosphere of carbon monoxide produced the tricarbonyl compound (3.3) [27].

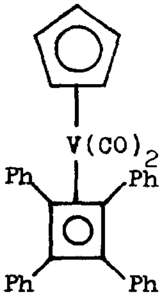
The ^{93}Nb and ^{51}V NMR spectra of the tetracarbonylmetal complexes (3.4; M = Nb, V) have been recorded in nematic liquid crystal matrixes and in the polycrystalline state. The quadrupole coupling constants for the two complexes were approximately the same [28].

The reactions of $(\eta\text{-}C_5H_5)_2V_2(CO)_5$ and $(\eta\text{-}C_5H_5)V(CO)_4$ with alkynes have been investigated. Photolysis of the dimer with large electron-poor alkynes, for example diphenylacetylene, produced the corresponding η-cyclobutadiene complexes (3.5). Smaller, more basic alkynes $RC\equiv CR$ (R = H, Me) produced simple monomeric adducts (3.6; R = H, Me). The adducts (3.6; R = H, Me, Ph) were formed on photolysis of $(\eta\text{-}C_5H_5)V(CO)_4$ with the corresponding alkynes [29].

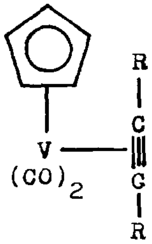
The binuclear vanadium complex (3.7) has been obtained as a brown diamagnetic solid by treatment of $VCl_2.2THF$ with



3.4

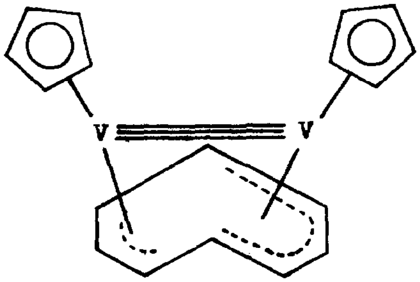


3.5



3.6

sodium cyclopentadienide and $K_2C_8H_8$. The crystal and molecular structure of the complex (3.7) has been determined by X-ray analysis. The η-C_8H_8 ligand consisted of two planar moieties inclined at an angle of 124°. The complex may be regarded as two semiopen vanadocene sandwich complexes which share the two terminal carbon atoms of their pentadienyl ligands [30].

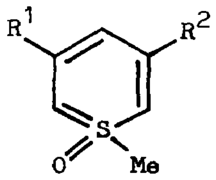


3.7

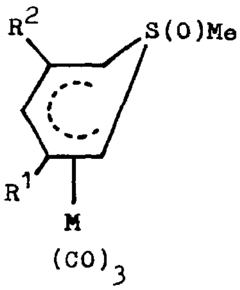
4. (η-C_6H_6)Cr(CO)$_3$

(i) Formation

Treatment of the methylcyanide complexes $(MeCN)_3M(CO)_3$, where M = Cr, Mo, W, with the thiabenzene oxides (4.1; R^1,



4.1



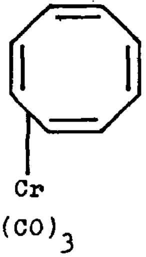
4.2

R^2 = Ph, Me; Me, Me,; Ph, Me_3C; Me_3C, Me_3C) produced the corresponding tricarbonylmetal complexes (4.2). The chromium complex (4.2; R^1, R^2 = CMe_3, M = Cr) was obtained only as the *anti*- isomer while the corresponding molybdenum and tungsten compounds were produced in both the *syn*-and *anti*- forms [31].

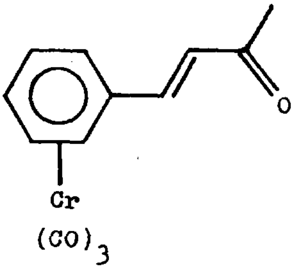
Removal of the oxygen atom from the *anti*-thiabenzene oxide complexes (4.2; R^1, R^2 = Ph, Me and Ph, CMe_3, M = Cr; R^1, R^2 = CMe_3, M = Mo, W) with $Na[(MeOCH_2CH_2O)_2AlH_2]$ produced the corresponding thiabenzene complexes. It was concluded that the thiabenzene ligands were stronger electron donors than the thiabenzene oxides [32].

The reaction of tricarbonyl(η-cyclooctatetraene)chromium (4.3) with acetylchloride and aluminium chloride at 0 °C lead to a product derived by ring contraction (4.4) [33].

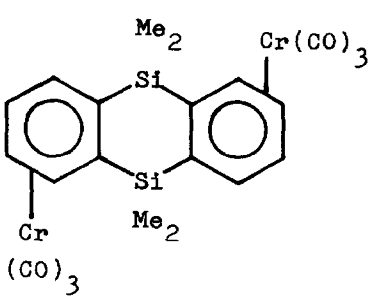
The *endo,exo*- (4.5) and *exo,exo*-bis(tricarbonylchromium) complexes together with the corresponding tricarbonylchromium



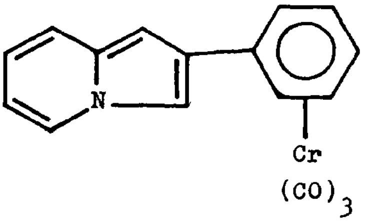
4.3



4.4



4.5



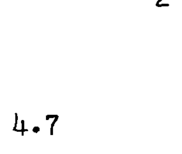
4.6

complex have been obtained by heating the free ligand with hexacarbonylchromium [34].

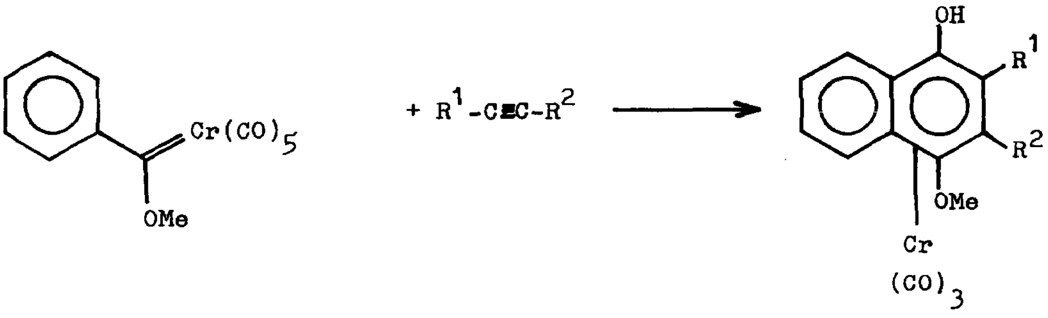
The tricarbonylchromium complex (4.6) has been prepared by the reaction of 2-phenylindolizine with hexacarbonylchromium [35].

Tricarbonylchromium groups have been introduced into siloxane oligomers containing methyl and phenyl groups to form organometallic catalysts for the hydrogenation of dienes to alkenes [36].

A series of η^6-biphenyl complexes (4.7; X = H, m-F, p-F, L = CO, PPh_3, $AsPh_3$) has been prepared and the spectral and physical properties recorded. The Taft substituent constants were calculated and discussed [37].



4.7

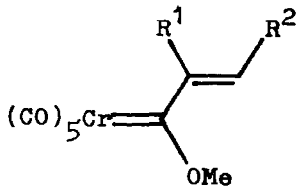


4.8

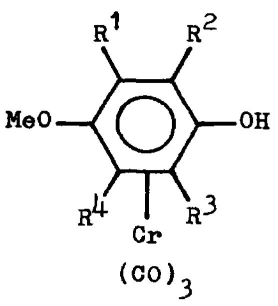
4.9

Pentacarbonyl(methoxyphenylcarbene)chromium (4.8) combined with alkynes to give tricarbonyl(η-4-methoxy-1-naphthol)-chromium complexes (4.9; R^1 = H, alkyl, Ph; R^2 = H, alkyl, Ph). Aliphatic n-1-alkynes gave 2-alkylnaphthol complexes regiospecifically while 2-alkynes gave mixtures of 2,3-dialkylnaphthol complexes. The reaction with diarylalkynes showed very little selectivity [38].

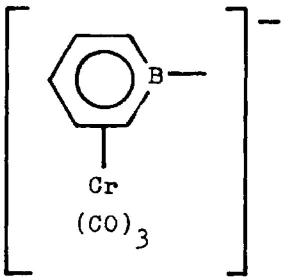
Treatment of the pentacarbonyl[alkenyl(methoxy)carbene]-chromium complexes (4.10; R^1 = H, Me, R^2 = H, Me, Ph) with the alkynes R^3-C≡C-R^4 (R^3 = Me, Pr, Ph; R^4 = H, Me, Pr, Ph) produced the corresponding tricarbonylchromium complexes (4.11) [39].



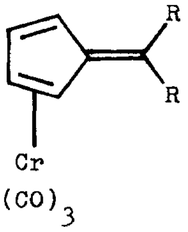
4.10



4.11



4.12



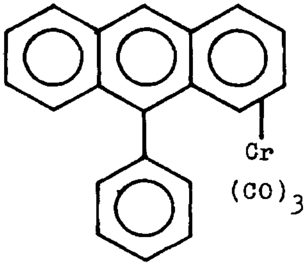
4.13

Tricarbonylchromium complexes of some benzylferrocene derivatives have been prepared [40].

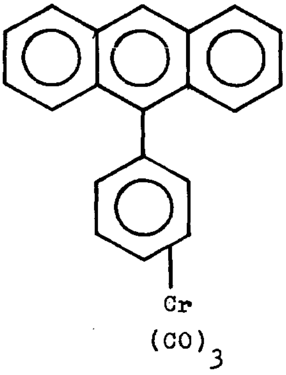
The reaction of Na[$C_5H_5BCH_3$] with $Cr(CO)_3(NH_3)_3$ provided a good route to derivatives of the anion (4.12) [41].

Thirteen 6,6-disubstituted fulvene complexes, including the complexes (4.13; R = H, Me, MeS, Et, Ph; RR = SCH_2CH_2S, SCH=CHS) have been prepared by treating the appropriate fulvene with $(MeCN)_3Cr(CO)_3$ in THF. The crystal and molecular structures of four complexes (4.13; R = MeS, cyclopropyl; RR = SCH_2CH_2S, SCH=CHS) were determined by X-ray crystallography [42].

The reaction of o-$RCB_{10}H_{10}CLi$ (R = Ph, Me) with tricarbonyl(η-chlorobenzene)chromium gave (η-o-$RCB_{10}H_{10}CPh)Cr(CO)_3$ in good yield [43].



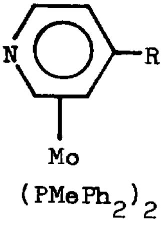
4.14



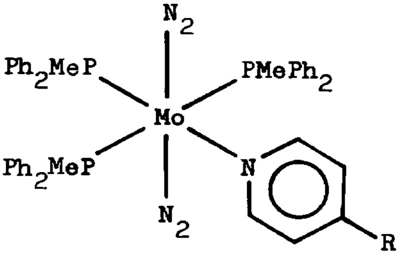
4.15

The tricarbonylchromium group in 9-phenylanthracene migrated between two sites under the appropriate conditions. Thus 9-phenylanthracene was heated with hexacarbonylchromium in di-n-butyl ether to give a purple solution which on low temperature chromatography yielded the purple (4.14) and yellow (4.15) complexes as well as a binuclear complex. A dioxan solution of the freshly prepared complex was purple but turned yellow on standing overnight and gave the solid product (4.15). A dioxan solution of the complex (4.15) turned dark brown on heating and presumably contained a mixture of the isomers (4.14 and 4.15) [44].

The first stable η^6-pyridine complexes of molybdenum (4.16; R = H, Me) have been prepared by keeping solutions of the corresponding dinitrogen complexes (4.17; R = H, Me) under vacuum when nitrogen was evolved and a σ to π rearrangement of the pyridine ligand occurred [45].



4.16

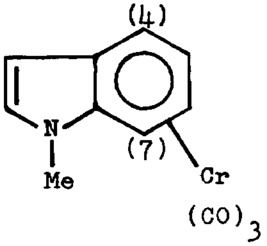


4.17

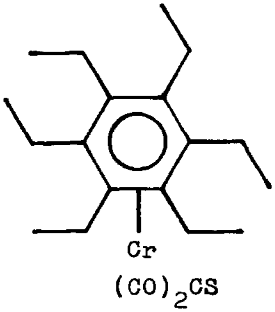
4. (ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structure of the benchrotrene complex, $[(\eta-C_6H_5)Cr(CO)_3]_2Hg$, has been determined by X-ray crystallography [46].

The structure of tricarbonyl(η-N-methylindole)chromium (4.18) has been determined by X-ray analysis. The projection of the chromium atom on the N-methylindole plane did not coincide with the centre of symmetry of the benzene ring. The carbonyl group tripod was distorted and the overall conformation of the complex was gauche. These results were used to explain



4.18

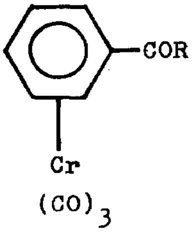


4.19

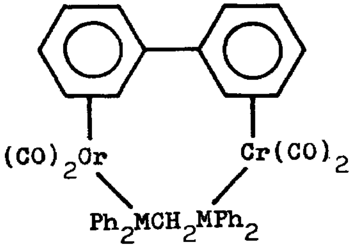
why nucleophilic attack occurred at carbon atoms 4 and 7 in the complex (4.18) [47].

The X-ray crystal structure and low temperature ^{13}NMR spectroscopy for the benchrotrene complex (4.19) indicated C_s symmetry and provided evidence for the cessation of tripodal rotation at low temperatures [48].

The negative-ion chemical-ionization mass spectra of several benchrotrene complexes including the ketones (4.20; R = Me, Et, Pr, t-Bu) have been measured using methane and ammonia as the reagent gases. The complexes (4.20) showed abundant $[M]^{-}$ ions while complexes without the PhCO group showed $[M-H]^{-}$ as the base peak. The results confirmed the electron withdrawing character of the tricarbonylchromium group [49].



4.20



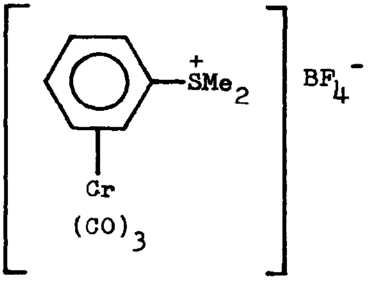
4.21

The π-donor ability of the arylacetylenes p-$R^1C_6H_4C{\equiv}CR^2$ (R^1 = H, Me, OMe, Br, Cl; R^2 = H, Me, Ph) with tetracyanoethylene and a series of (η-arene)tricarbonylchromium complexes have been studied by an electron spectroscopic method. In the molecular complexes formed with diphenylacetylene the chromium complexes behaved as electron acceptors [50].

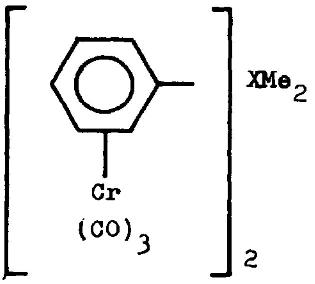
Ultraviolet irradiation of (η-biphenyl)bis(tricarbonylchromium) in the presence of bis(diphenylphosphido)methane or bis(diphenylarsino)methane produced the corresponding dicarbonylchromium complexes (4.21; M = P,As). Addition of strong acid to these dinuclear compounds caused a rapid evolution of hydrogen gas and the decomposition of the oxidized chromium complexes. It was suggested that both metal centres were protonated in an oxidative addition step and this was followed by reductive elimination of dihydrogen from the two metal centres [51].

The mechanism of the electrochemical reduction of the tricarbonylchromium complex (4.22) in dimethyl sulphoxide has been investigated. On changing the reduction potential and the protonating power of the medium the number of electrons transferred varied together with the nature of the products. It was suggested that an intermediate sulphonium ylid was formed by a two electron process and this was followed by an acid-base reaction [52].

Cyclic voltammetry and coulometry have been used to investigate the electrochemistry of several (η-arene)bis(tricarbonylchromium) complexes with arene ligands containing



4.22

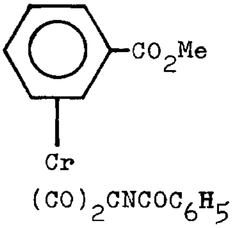


4.23

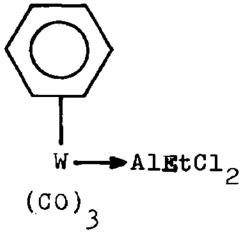
two conjugated benzene rings. Examples were biphenyl, cis- and trans-stilbene and 9,10-dihydrophenanthrene. The complexes underwent two-electron reduction to give persistent dianions [53].

Several binuclear tricarbonylchromium complexes (4.23; X = C, Si, Ge, Sn, Pb) have been examined by cyclic voltammetry and found to give dications on oxidation. The two (η-arene)-tricarbonylchromium groups did not interact. However when the Me_2X group was absent then interaction was observed and mixed valence character was indicated [54].

The IR and Raman spectra of the benchrotrene complex (4.24) have been recorded and assigned. The effect of metal coordination on the aromatic ring modes has been discussed [55].



4.24

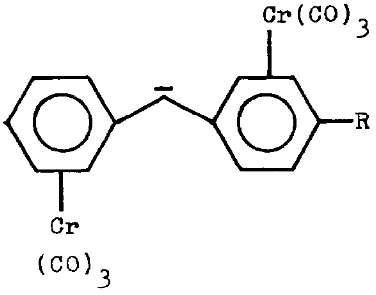


4.25

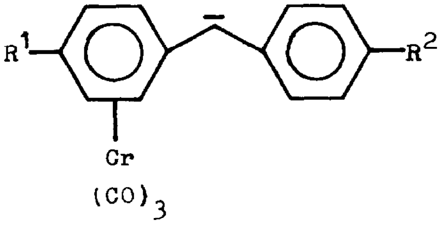
The photolysis of benchrotrene and related complexes has been studied by IR, UV and NMR spectroscopy. Evidence was obtained for the formation of an intermediate trinuclear complex which underwent photodecay to hexacarbonylchromium [56].

Aspects of the mechanism of catalysis of linear olefin metathesis by (η-arene)tricarbonylmolybdenum have been studied by IR and ^1H NMR spectroscopy. $EtAlCl_2$ formed tungsten (4.25) and carbonyl coordinated adducts with the (η-arene)molybdenum complex. Oxygen promoted dissociation of the arene ligand [57].

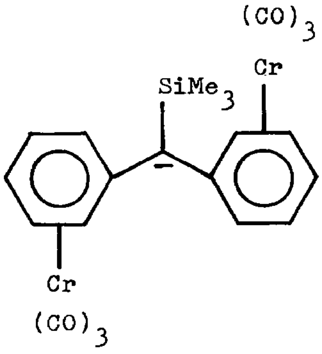
The anions (4.26; R = H, $SiMe_3$; 4.27; R^1 = H, R^2 = $SiMe_3$; R^1 = $SiMe_3$, R^2 = H and 4.28) have been prepared and studied by variable temperature and ^{13}C NMR which allowed the evaluation of the barriers to phenyl rotation. It was concluded that the $Cr(CO)_3$ group stabilized the negative charge much more efficiently



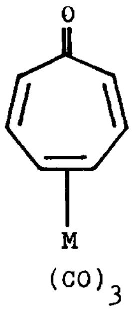
4.26



4.27



4.28



4.29

than a *p*-$SiMe_3$ group. When the $SiMe_3$ group was bound directly to the α-carbon atom, the charge preferentially resided on the silicon and this allowed the $[\eta\text{-}C_6H_5\text{-}Cr(CO)_3]$ to rotate unhindered [58].

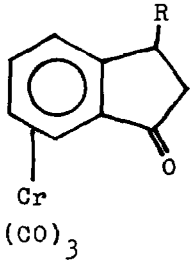
The heats of iodination of tricarbonylchromium complexes of benzene, toluene, mesitylene and cycloheptatriene have been determined by solution calorimetry in THF at 25 °C. The order of Cr-ligand bond strength was:

mesitylene > cycloheptatriene > toluene > benzene

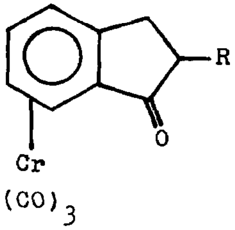
and it differed from that determined by high temperature decomposition and iodination [59].

The relative base strengths of the $Cr(CO)_3$, $Mo(CO)_3$ and $W(CO)_3$ complexes of tropone (4.29; M = Cr, Mo, W) have been determined. The ketonic base strength in water increased by approximately 2 pK units with only a small metal dependence in the sequence Mo ≈ W > Cr [60].

The borohydride reduction of the exo-substituted (η-indanone)chromium complexes (4.30; R = Me, Et, i-Pr; 4.31; R = Me, Et, i-Pr) has been the subject of a kinetic investigation. The enthalpy of activation decreased and the entropy of activation increased with an increase in the size of the alkyl group R. The results were explained in terms of the displacement of the transition state by the steric effect of the alkyl substituent [61, 62].



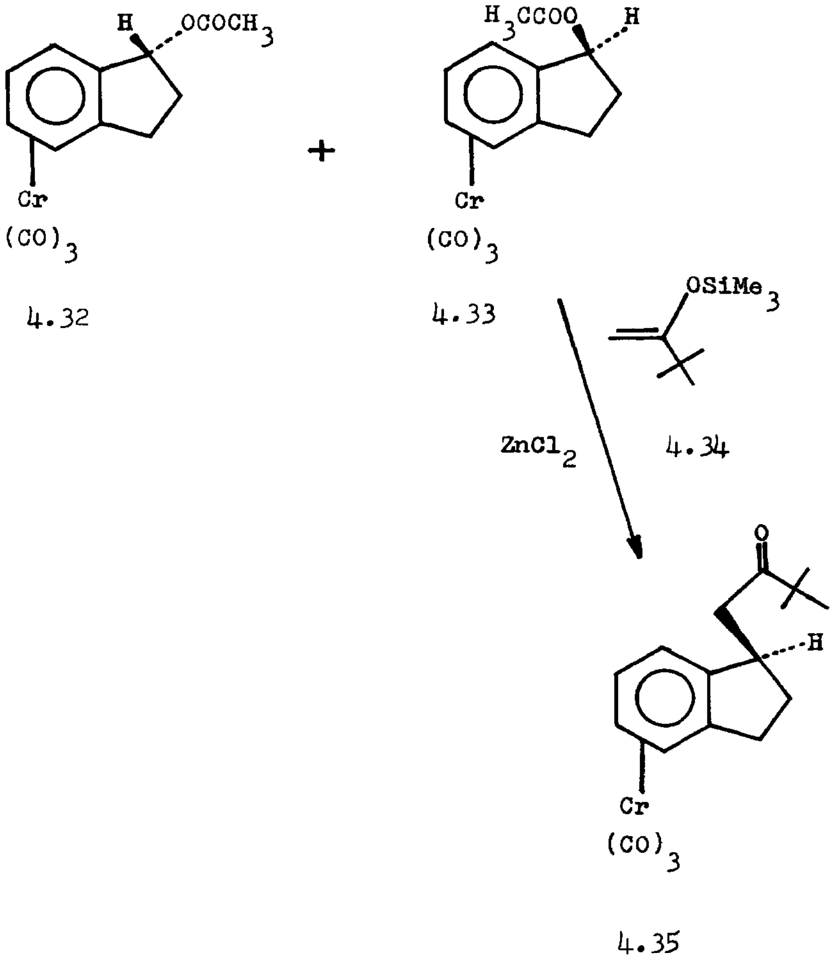
4.30



4.31

The nucleophilic addition of carbanions to alkylbenchrotrene complexes has been the subject of a stereochemical investigation. The reaction was regioselective and the selectivity was sensitive to both the size of the alkyl substituent on the benzene ring and the reactivity of the carbanion. The observed results were correlated with theoretical predictions based on Hueckel theory calculations involving a balance of charge control and orbital control [63].

Reetz and Sauerwald have shown that tricarbonylchromium complexes of secondary benzyl acetates react 100% stereoselectively with silyl enol ethers in the presence of zinc chloride. For example, treatment of a mixture of the diastereoisomers (4.32 and 4.33) with the ether (4.34) produced only the anti- adduct (4.35) [64].

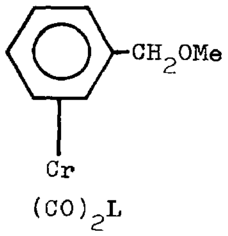


4. (iii) General Chemistry

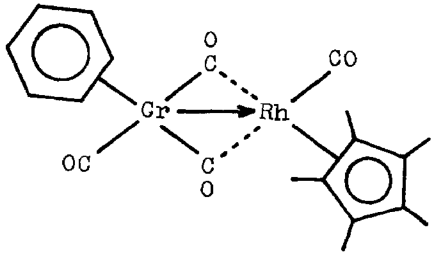
The benchrotrene complex (4.36; L = CO) has been irradiated with cyclooctene and then treated with silica containing 3-isocyanopropyl functional groups. The benchrotrene was incorporated into the macromolecule as the isonitrile complex [4.36; L = $(CH_2)_3NC$][65].

Benchrotrene and methylsubstituted benchrotrenes have been irradiated with dicarbonyl(η-pentamethylcyclopentadienyl)-rhodium in THF to form binuclear heterometallic complexes. The crystal and molecular structure of one of these complexes (4.37) has been determined by X-ray crystallography [66].

Benchrotrene and substituted benchrotrenes have been attacked by isocyanides in boiling heptane in the presence of



4.36

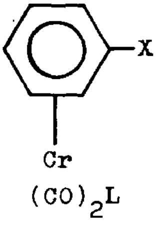


4.37

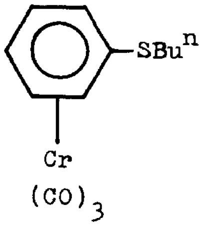
$[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ and PdO to give isocyanide derivatives. The benchrotrenes (4.38; X = H, Me, CO_2Me, Cl; L = CO) combined with Me_3CNC to form the derivatives (4.38; X = H, Me, CO_2Me, Cl; L = $CNCMe_3$). The crystal and molecular structure of one of the complexes (4.38; X = CO_2Me; L = $CNCMe_3$) has been determined by X-ray crystallography. The $Cr(CO)_2CNCMe_3$ group was staggered with respect to the carbon atoms of the benzene ring and the CNC bond angle of the isocyanide was 166.8 ° [67].

Trifluoroacetic acid has been shown to be an effective solvent for the stabilization of cations obtained by the electrolytic one-electron oxidation of benchrotrene and several of its derivatives [68].

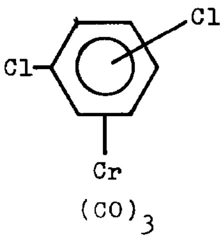
Halogen substituted benchrotrenes underwent nucleophilic substitution with thiolates using solid-liquid and liquid-liquid



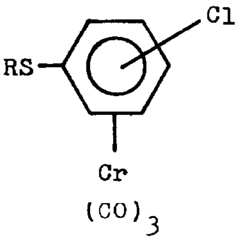
4.38



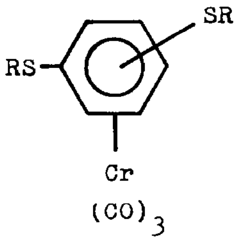
4.39



4.40



4.41

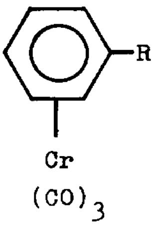


4.42

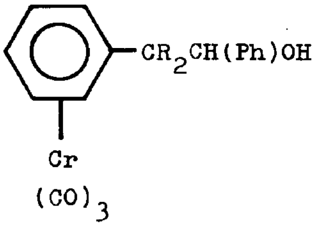
phase transfer conditions with quaternary ammonium salts. Thus fluoro- and chloro-benchrotrene were stirred in benzene with n-butanethiolate and 10-50% aqueous sodium hydroxide to form the butyl sulphide (4.39) which was characterized after decomposition with iodine [69].

The η-dichlorobenzene complexes (4.40; 1,2-Cl_2, 1,3-Cl_2, 1,4-Cl_2) underwent nucleophilic substitution with the thiolates RS^- (R = Me, Bu, Me_3C) under phase transfer conditions or in dimethylsulphoxide to give the corresponding sulphides (4.41 and 4.42). The presence of the tricarbonylchromium moiety strongly activated the chloride atoms towards nucleophilic substitution [70].

The alkylbenchrotrene complexes (4.43; R = Me, Et, i-Pr) were attacked at the α-carbon atom with benzaldehyde in the presence of potassium t-butoxide to form the alcohols (4.44;



4.43



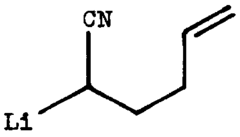
4.44

R = H, Me). Similar reactions were carried out with formaldehyde although polycondensation products were also obtained [71].

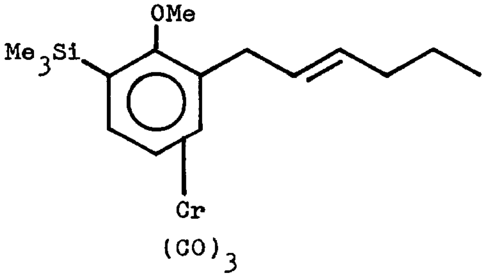
Benzaldehyde underwent base-catalyzed condensation with benchrotrene to form, after oxidative decomplexation, 1,2-diphenylethanol and stilbene [72].

Addition of the cyano-stabilized anion (4.45) to the trisubstituted benchrotrene (4.46) to form the tetrasubstituted benchrotrene (4.47) was a key step in the synthesis of the racemic natural quinone antibiotic frenolicin [73].

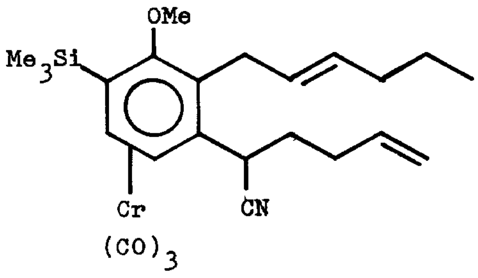
η-Di- and tri-phenylmethane-tricarbonylchromium complexes have been converted into the corresponding anions by α-hydrogen abstraction with potassium hydride. ^{1}H NMR data for the anions suggested that the negative charge density was substantially withdrawn from the uncoordinated rings and delocalized into the complexed moiety to give a planar η^5-cyclohexadienyl structure



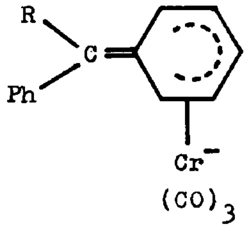
4.45



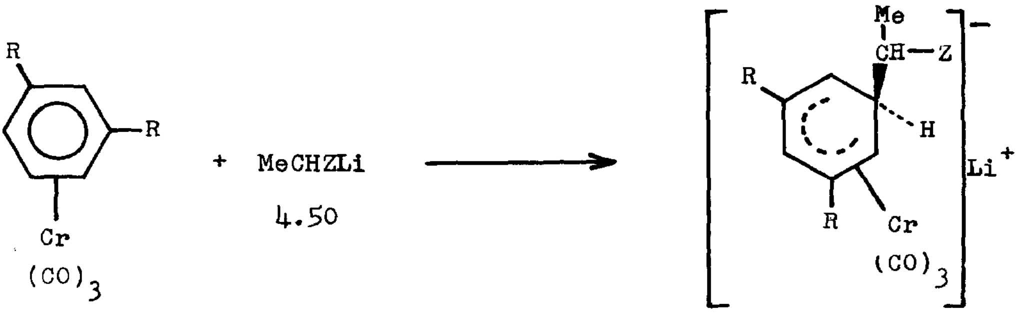
4.46



4.47



4.48



4.49

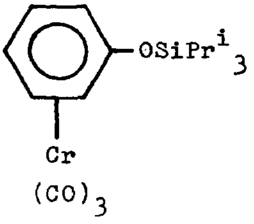
4.51

(4.48; R = H, Ph) containing an exocyclic double bond [74].

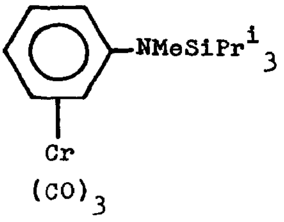
Treatment of the tricarbonylchromium complexes (4.49; R = H, $CHMe_2$) with the lithium salts (4.50; Z = CN, CO_2CMe_3) produced the adducts (4.51). Treatment of these adducts with trifluoroacetic acid under carbon monoxide produced the corresponding substituted cyclohexadienes and hexacarbonylchromium in good yield. There was substantial recovery of the metal carbonyl, thus allowing a cyclic process [75].

Lithiation of the triisopropylsilyl derivatives of the phenol- and aniline-tricarbonylchromium complexes (4.52 and 4.53) occurred predominantly meta to the heteroatom and subsequent reaction with electrophiles produced overall meta-electrophilic substitution of phenols and anilines [76].

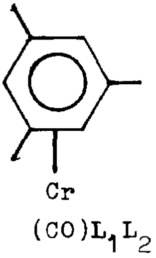
Electrochemical oxidation of the η-arene complex (4.54;



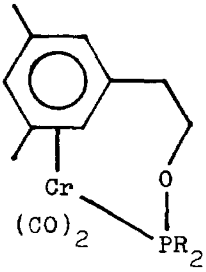
4.52



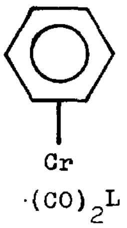
4.53



4.54



4.55

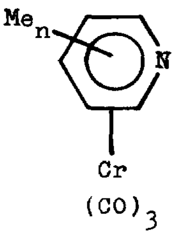


4.56

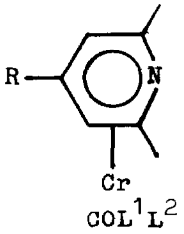
$L_1 = L_2 = CO$) in the presence of triethylphosphite followed by electrochemical reduction produced a mixture of the phosphite complexes, [4.54; $L_1 = CO$, $L_2 = P(OEt)_3$; $L_1 = L_2 = P(OEt)_3$]. Under similar conditions (η^6-arene)$Cr(CO)_3$, where arene = 3,5-$Me_2C_6H_3(CH_2)_2OPR_2$ (R = OEt, OPh, F), gave the corresponding arenephosphite chelate complexes (4.55) [77].

One carbonyl ligand in benchrotrene has been displaced by cis-cyclooctene to form the intermediate (4.56; L = cis-cyclooctene) which was treated with CSe_2 to give the seleno-carbonyl complex (4.56; L = CSe) in 43% yield. Carbon monoxide converted this complex to $Cr(CO)_5(CSe)$ in 48% yield [78].

The trimethylphosphine and trimethylphosphite ligands have been introduced into the di- and tri-methylpyridine chromium complexes (4.57; n = 2, 3) by photochemical substitution of the carbonyl group to give the products [4.58; R = H; $L^1 = L^2 = CO$,



4.57

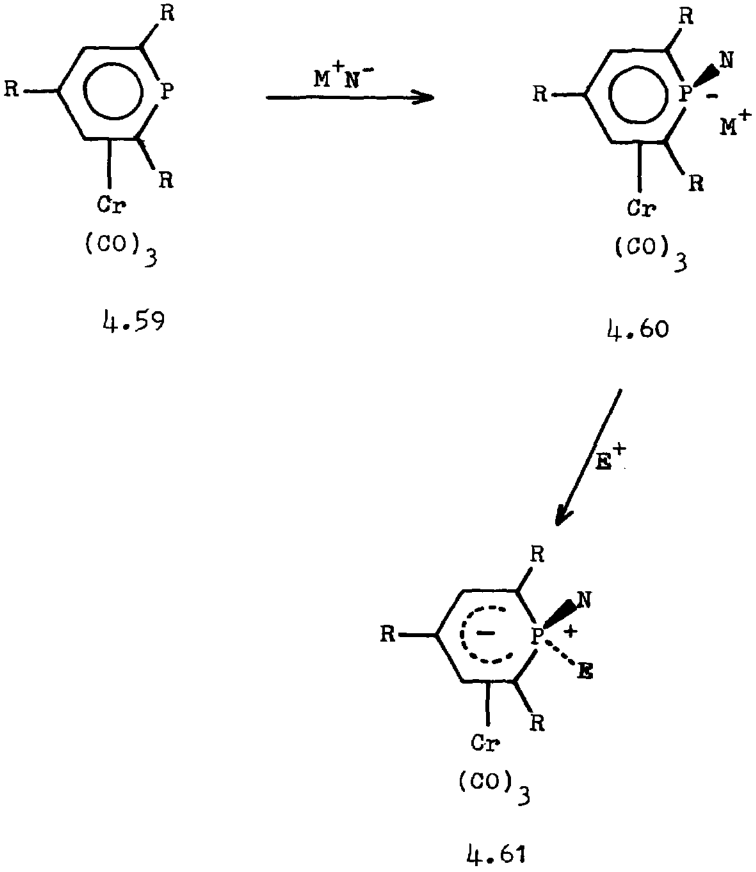


4.58

P(OMe)$_3$; L^1 = CO, L^2 = PPh$_3$, P(OMe)$_3$; R = Me, L^1 = CO, L^2 = PPh$_3$]. The phosphine complexes (4.58) exhibited better thermal stability than the tricarbonyl analogues and were resistant to arene exchange reactions [79].

The tricarbonyl(η-λ^3-phosphorin)chromium complexes (4.59; R = Bu^t, Ph) underwent regio- and stereo-specific addition to the phosphorus atom in the exo-position to form the λ^4-phosphorin anion complexes (4.60; R = Bu^t, Ph) which then added electrophiles in the endo-position to give the η-λ^5-phosphorin ylide complexes (4.61; R = Bu^t, Ph). Nucleophiles included methyllithium and electrophiles included methyl iodide [80].

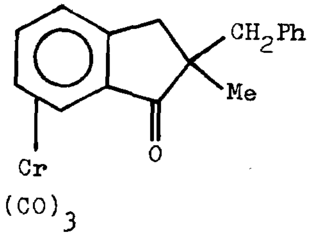
Indanone has been converted to the tricarbonylchromium complex and alkylated to form the (η-indanone)chromium complex (4.62) which was hydrogenated and cyclodehydrated to give the tetracyclic derivative (4.63). Subsequent decomplexation of the derivative (4.63) gave the free tetracyclic ligand (4.64) [81].



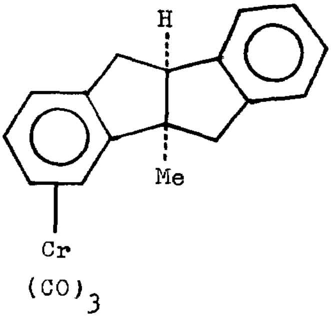
4.59

4.60

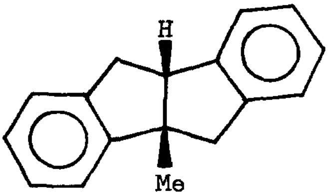
4.61



4.62

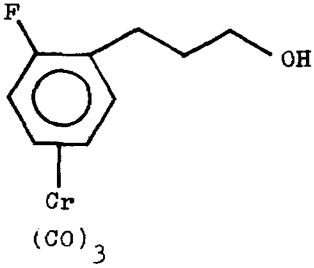


4.63

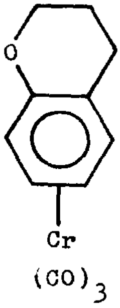


4.64

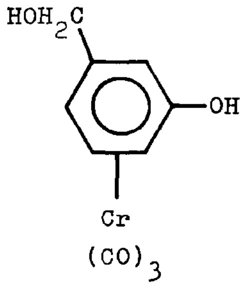
When the tricarbonylchromium complex (4.65) was treated with potassium t-butoxide, rapid intramolecular nucleophilic substitution occurred to give the corresponding complex of chroman (4.66). Oxidation of this complex with iodine produced chroman in quantitative yield [82].



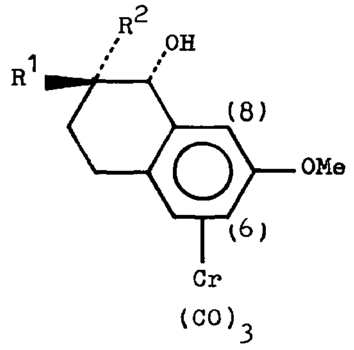
4.65



4.66



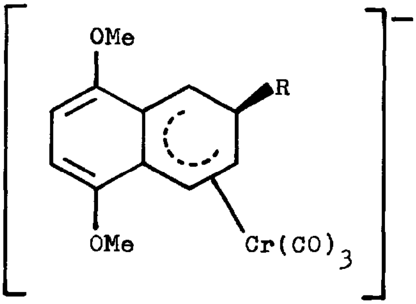
4.67

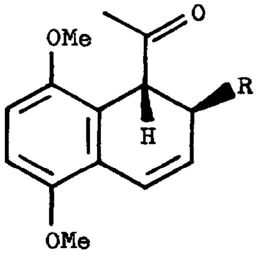


4.68

The tricarbonyl chromium complexes (4.67) and (4.68; $R^1 = R^2$ = H, Me; R^1 = Me, CHMeOH, R^2 = H) were selectively lithiated at the 4 and 6 positions respectively by treatment with n-butyllithium-tetramethylethylenediamine. An increase in bulk of the butyllithium reagent improved the regioselectivity of the lithiation. The influence of the tricarbonylchromium moiety on the lithiation was discussed. Lithiation of the tricarbonylchromium complexes of benzylmethyl ether and ethylene-acetals of benzaldehydes occurred preferentially at the 2-position [83].

Treatment of tricarbonyl(η-1,4-dimethoxynaphthalene-chromium with the organolithium reagents RLi [R = $\overline{\text{C(H)S(CH}_2\text{)}_3\text{S}}$, $\overline{\text{C(Me)S(CH}_2\text{)}_3\text{S}}$] produced the corresponding η-cyclohexadienyl complexes (4.69). Addition of methyl iodide followed by removal





4.69

4.70

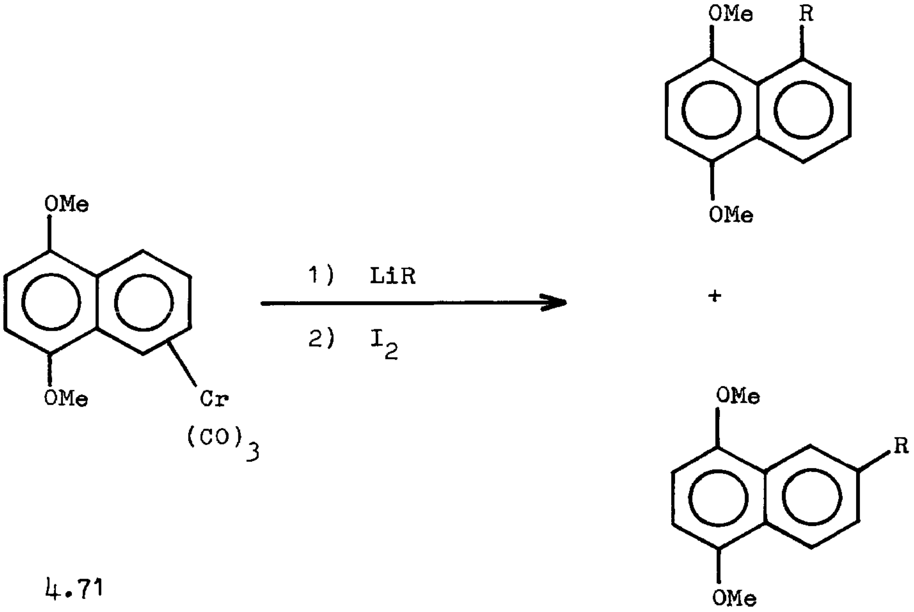
of the Cr(CO)$_3$ moiety produced the acetyl dienes (4.70). Incorporation of CO occurred in the absence of external CO but a higher yield was obtained in a CO atmosphere [84].

Regioselectivity in the addition of carbanions to tricarbonyl(η-1,4-dimethoxynaphthalene)chromium (4.71) has been investigated. The small nucleophile 2-lithioacetonitrile yielded predominantly the α-substitution product (4.72; R = CH$_2$CN) whereas the sterically more demanding 2-lithio-2-methylpropionitrile gave predominantly the product of β addition (4.73; R = CMe$_2$CN) together with some of the α-substitution product (4.72; R = CMe$_2$CN). The addition of t-BuOOCCH$_2$Li and 2-lithio-2-methyl-1,3-dithiane to the tricarbonylchromium complex (4.71) was also investigated [85].

Treatment of the dianion (4.74) with water produced the η^5-cyclohexadienyl complex (4.75) [86].

The regioselective lithiation of the (η-arene)tricarbonylchromium complexes (4.76 and 4.77) at the 6-position has been used in the preparation of (±)-3-deoxyrabelomycin (4.78) and the linear anthraquinone (4.79) [87].

Reaction of the cations (4.80; R^1 = Ph, Me, R^2 = Ph, Me,

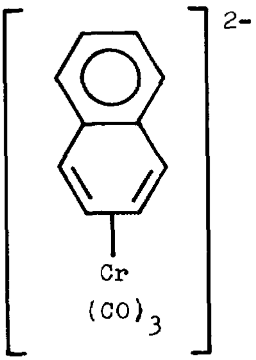


4.71

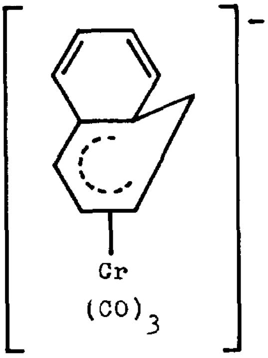
4.72

4.73

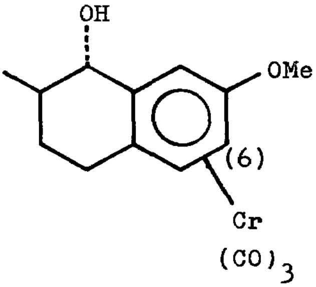
t-Bu) with $LiBHEt_3$ resulted in endo-addition of hydride ion to give the neutral complexes (4.81) [88].



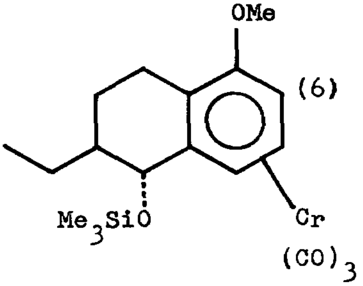
4.74



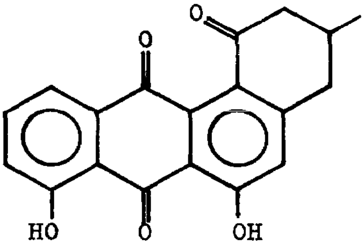
4.75



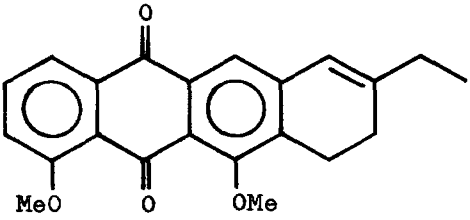
4.76



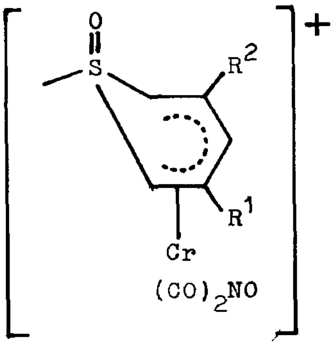
4.77



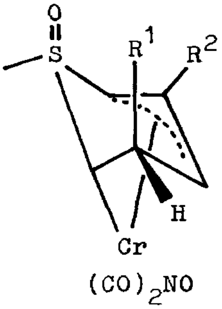
4.78



4.79



4.80

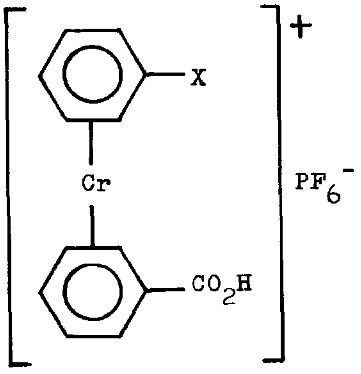


4.81

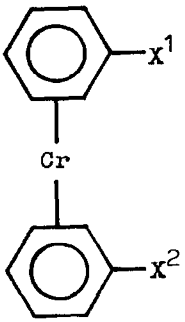
5. $(\eta\text{-}C_6H_6)_2Cr$

The cocondensation of chromium atoms with a mixture of two substituted benzenes at low temperatures and pressures gave unsymmetrical bis(η-arene)chromium complexes which were characterised as the hexafluorophosphates (5.1; X = H, Me, Cl, CF_3, CO_2Me). Several related symmetrical and unsymmetrical complexes were also prepared [89].

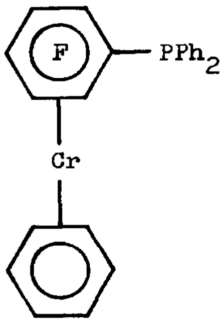
The relative rates of formation of bis(η-arene)molybdenum complexes from molybdenum atoms and toluene, t-butylbenzene, o-xylene, benzotrifluoride, N,N-dimethylaniline, fluorobenzene, methyl benzoate and anisole at -170 °C have been measured and



5.1



5.2



5.3

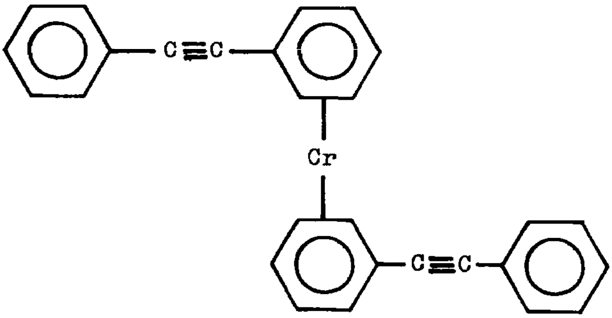
found to cover a range of 3.7. Silica gel has been used to catalyze the exchange of toluene with bis(η-methyl benzoate)-molybdenum to form both bis(η-toluene)molybdenum and the mixed complex (η-methyl benzoate)(η-toluene)molybdenum [90].

Bis(η-2-chloro-1,4-dimethylbenzene)chromium, bis(η-4-chloro-1,2-dimethylbenzene)chromium, bis(η-2,4-dichloro-1-methylbenzene)chromium, bis(η-2,6-dichloro-1-methylbenzene)-chromium and bis(η-1,4-dichlorobenzene)chromium have been prepared by cocondensation of chromium vapour with the corresponding organic ligand at 77 K [91].

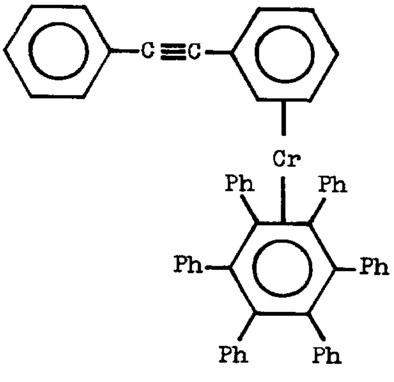
Chromium atoms have been cocondensed with mixtures of benzonitrile and either benzene or chlorobenzene to give both the unsymmetrical bis(η-arene)chromium complexes (5.2; X^1 = CN, X^2 = H, Cl) and the symmetrical complexes (5.2; $X^1 = X^2$ = CN, H, Cl) [92].

Metal-atom synthesis has been used to prepare (η-benzene)-(η-pentafluorobenzene)chromium which was subsequently lithiated and treated with chlorodiphenylphosphine to form the (η-triphenylphosphine)chromium complex (5.3). The crystal and molecular structure of this complex has been determined by X-ray crystallography [93].

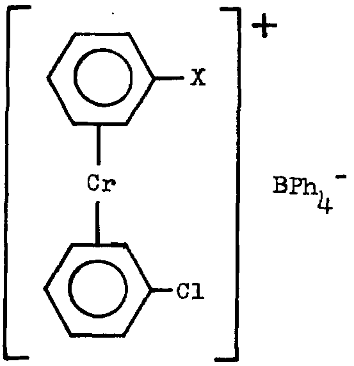
Diphenylacetylene has been cocondensed with chromium atoms at low temperatures to give bis(η-arene)chromium complexes containing diphenylacetylene (5.4) and its cyclotrimer as ligands. The unsymmetrical complex (η-diphenylacetylene)(η-hexaphenylbenzene)chromium (5.5) was also obtained [94].



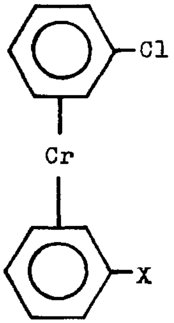
5.4



5.5



5.6



5.7

Nucleophilic displacement of chloride from bis(η-chlorobenzene)chromium by amines and alcoholates and subsequent treatment with sodium tetraphenylborate gave the bis(η-arene)-chromium complexes (5.6; X = OMe, OEt, OBu, $OCHMe_2$, piperidino, cyclohexylamino, morpholino). Disubstitution products were also obtained [95].

A kinetic study of the nucleophilic displacement of chloride from the complex (5.7) by methoxide gave the following order for the effect of the transannular substituents on the rate:

5.7; $X = NMe_2 < OCHMe_2 < OBu < OMe < CO_2Na < H < Cl < CO_2Me < CF_3$ [96].

Bis(η-benzene)chromium displaced thallium from the complex $[(C_6F_5)_3Ge]_3HgTl.1.5$dimethoxyethane to give the product $\{[(C_6F_5)_3Ge]_4Hg\}[(\eta-C_6H_6)_2Cr]_2$ in which the bis(η-benzene)-chromium moiety was present as the cation [97].

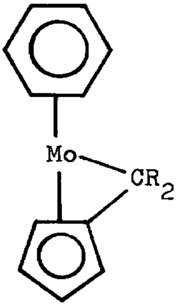
The ionization of ferrocene and bis(η-arene)chromium complexes on the surface of tungsten oxide has been investigated. Bis(η-benzene)chromium gave a stable molecular ion and at temperatures above 1100 ^{o}K degradation occurred to give the $[C_6H_6Cr]^+$ and $[Cr]^+$ ions. (η-Benzene)(η-ethylbenzene)chromium behaved in the same way and at higher temperatures benzene rather than ethylbenzene was lost [98].

Conditions controlling the deposition of pyrolytic chromium from the thermal decomposition of bis(η-arene)chromium complexes have been investigated. Temperature, the proportions of gaseous reactants and the flow rate were shown to be important [99].

The mechanism of thermal degradation of the metal-ligand bond in bis(η-arene) complexes of chromium, molybdenum and vanadium has been investigated [100].

Several bis(η-arene)-molybdenum and -tungsten complexes have been prepared by the metal vapour method and their electronic structures were examined by electron spin resonance and photoelectron spectroscopy. The spectra of W(η-arene)$_2$, (arene = C_6H_6, PhMe, mesitylene) were consistent with a $^2A_1$ ground state for the cation, with ionization energies of 5.2-5.4 eV, and a $^2E_{5/2}/^2E_{3/2}$ doublet appearing at approximately 1.2 eV higher energy [101].

Bis(η-benzene)molybdenum underwent ligand displacement with the fulvenes $C_5H_4{=}CR_2$ to form the fulvene complexes (5.8; R = Me, Ph) which were characterized by X-ray crystallography. The analogous tungsten complexes were reported and characterized in the same way [102].



5.8

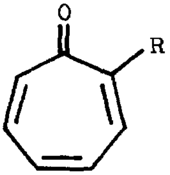
6. [(η-C_7H_7)Cr(CO)$_3$]$^+$ and (C_7H_8)Cr(CO)$_3$

Tricarbonyl(η-cycloheptatriene)tungsten has been prepared from cycloheptatriene and the easily obtained trinitrile complexes W(CO)$_3$(NCR)$_3$, where R = Et, Pr [103].

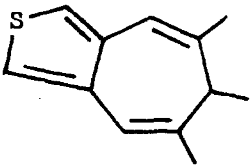
π-Complexation of tropone (6.1; R = H) and the 2-methoxy (6.1; R = OMe) and ethoxy (6.1; R = OEt) derivatives with the Cr(CO)$_3$ group increased the ketonic base strength by approximately 1.7 p*K* units [104].

Treatment of the thiophenotropylidenes (6.2 and 6.3) with hexacarbonylchromium produced the tricarbonylchromium complex (6.4). Reaction of the thiophenotropylidene (6.5) and two of its isomers with hexacarbonylchromium produced in each case the same complex (6.6) [105].

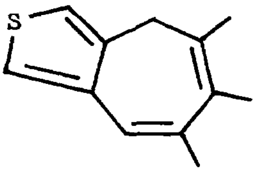
Photolysis of tricarbonyl(η^6-cyclooctatetraene)chromium with 6,6-disubstituted fulvenes gave chromium complexes with bicyclononatriene and cycloheptatrienylidene ligands [106].



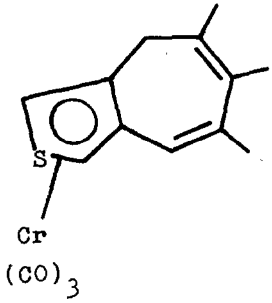
6.1



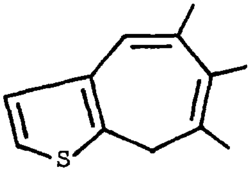
6.2



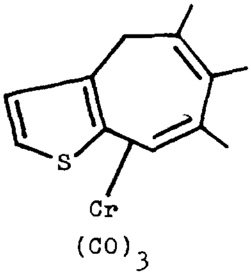
6.3



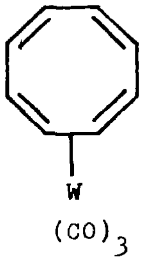
6.4



6.5

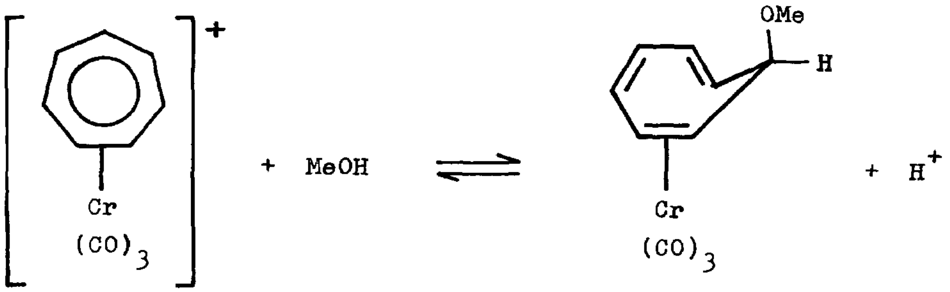


6.6



6.7

Irradiation of cyclooctatetraene with hexacarbonyltungsten produced initially tetracarbonyl(η^4-cyclooctatetraene)tungsten. Prolonged irradiation gave the corresponding tricarbonyltungsten derivative (6.7) [107].

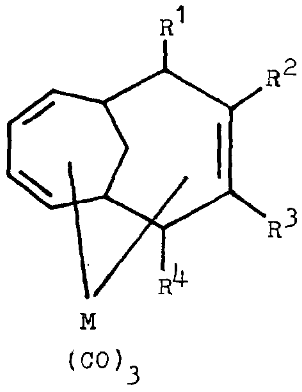


6.8

6.9

A comparison has been carried out on the stability and reactivity in solution of the tropylium cation (Tr$^+$) and its tricarbonylchromium complex (6.8). This complex was approximately 2 x 10^3 times less reactive than Tr$^+$ towards addition of methanol. The complex (6.9) was approximately 20 times more reactive than TrOMe towards acid heterolysis in methanol [108].

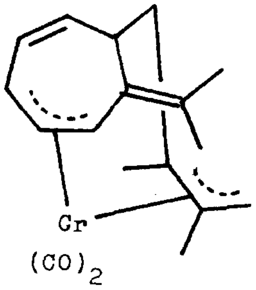
Photolysis of tricarbonyl(η^6-1,3,5-cycloheptatriene)-chromium with $R^1CH{=}CR^2CR^3{=}CHR^4$ (R^1 = H, Me, $CH{=}CH_2$; $R^2 = R^3$ = H; R^4 = H, Me, CO_2Me) gave the corresponding triene complexes (6.10; M = Cr). The tricarbonylmolybdenum complexes (6.10;



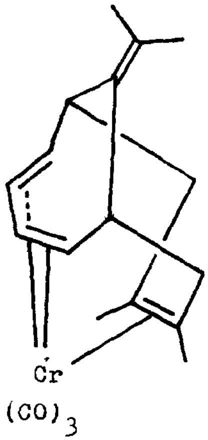
6.10

M = Mo, $R^1 = R^2 = R^3 = R^4 = H$; $R^1 = R^4 = Me$, $R^2 = R^3 = H$) were also prepared [109].

Ultraviolet irradiation of tricarbonyl(η^6-8,8-dimethylheptafulvene)chromium with 2,3-dimethyl-1,3-butadiene produced the dicarbonylchromium complex (6.11). Treatment of this latter complex with carbon monoxide at atmospheric pressure yielded the corresponding substituted tricarbonyl(η^6-bicyclo[4.4.1]-undeca-2,4,8-triene)chromium complex (6.12) [110].



6.11

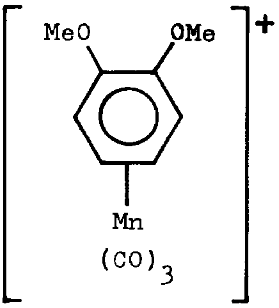


6.12

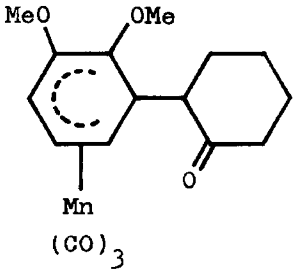
7. (η-C_5H_5)Mn(CO)$_3$

(i) Formation

Reaction of pentacarbonylmanganese tetrafluoroborate with 1,2-dimethoxybenzene produced the η^6-arene complex (7.1). This complex underwent highly regiospecific reaction with the lithium enolate of cyclohexanone, ortho to the MeO substituent, to give the (η-dienyl)manganese complex (7.2) [111].

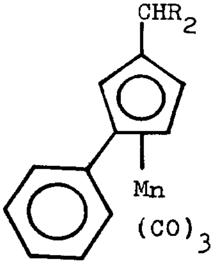


7.1



7.2

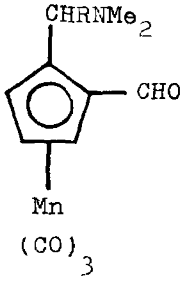
Ultraviolet irradiation of pentacarbonylphenylmanganese in the presence of 6,6-dimethyl- or 6,6-diphenyl-fulvene produced the corresponding $C_6H_5(CO)_4Mn(\eta^2\text{-fulvene})$ complexes. These rearranged thermally by insertion of the two ring double bonds of the fulvenes into the $Mn\text{-}C_6H_5$ bond to give 1,2- and 1,3-substituted $(CO)_4Mn(\eta^3\text{-3-cyclopenten-5-yl})$ complexes. The 1,3-substituted isomers readily lost one molecule of carbon monoxide at room temperature and rearranged further to give the 1,3-disubstituted cymantrene complexes (7.3; R = Me, Ph) [112].



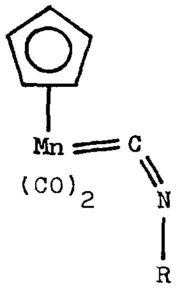
7.3

7. (ii) Spectroscopic and Physicochemical Studies

X-ray crystallography has been used to determine the crystal and molecular structure and the absolute configuration of $(-)_{578}$-1-[α-(N,N-dimethylamino)ethyl]-2-formylcymantrene (7.4; R = Me) and thereby elucidate the orientation and stereo-



7.4



7.5

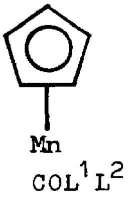
chemistry of the metalation of [α-(N,N-dimethylamino)ethyl]-cymantrene with n-butyllithium. The CD and UV spectra of the disubstituted cymantrenes (7.4; R = H, Me) have been examined in both aprotic and acidic solvents. The results indicated that the optical properties of these compounds were determined by molecular conformations rather than by absolute configurations [113].

The dicarbonyl-manganese complexes (7.5; R = t-Bu, $PhCH_2$, C_6H_{11}, 2,6-$Me_2C_6H_3$) have been prepared by the palladium(II) oxide catalysed thermal reaction between cymantrene and the appropriate isonitrile RNC. X-ray analysis showed that the isonitrile ligand was bent away from the ring with a C-N-C angle of approximately 172 ° [114].

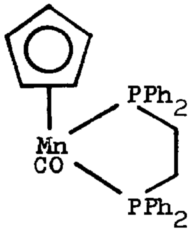
The crystal and molecular structures of (cymantrenoyl-methyl)- and (ferrocenoylmethyl)-cyclopentadienyldicarbonyliron have been determined by X-ray analysis [115].

The electronic structure of cymantrene, the phosphine complexes (7.6; L^1 = CO, L^2 = PPh_3 and 7.7) and the nitrosyl complexes (7.8; L^1 = L^2 = CO; L^1 = CO, L^2 = PPh_3 and 7.9) has been investigated by X-ray and XPS spectroscopy. Variation in the number of carbonyl ligands caused significant changes in the cyclopentadienyl-manganese interaction. A 4*p* orbital participated in the donor-acceptor interactions and played an important part in ligand interactions [116, 117].

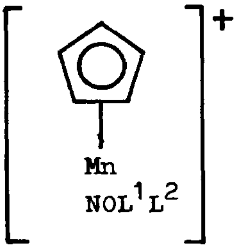
Cymantrene has been used for comparative purposes in a study of electron addition to various carbonyl(η-cyclopentadienyl)metal halides via electron spin resonance. Irradiation



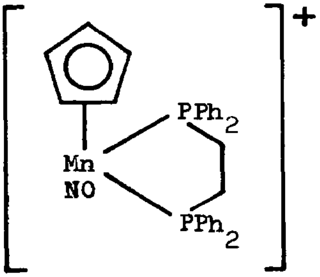
7.6



7.7



7.8



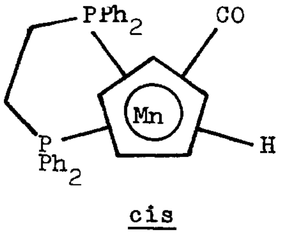
7.9

of cymantrene with ^{60}Co γ-rays gave the anion $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]^-$ [118].

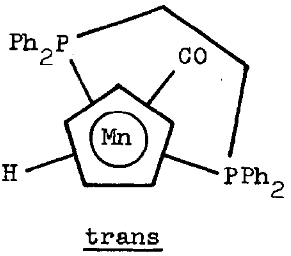
Ion cyclotron resonance spectroscopy has been used to examine the formation of the non-classical cation $[(C_5H_5)C]^+$ from the ionization of cymantrene and tetrachloromethane in the gas phase [119].

Infrared spectroscopy has been used to investigate the formation of the cis- and trans-isomers (7.10a and 7.10b) obtained during the protonation of $(\eta\text{-}C_5H_5)Mn(CO)Ph_2P(CH_2)_2PPh_2$ in trifluoroacetic acid. The results indicated that the conversion of the initially formed cis-isomer into the thermodynamically favoured trans-isomer involved an intermolecular rather than an intramolecular mechanism [120].

On treatment of tricarbonyl(η-cyclopentadienyl)-manganese and -rhenium and (η-benzene)tricarbonyl-chromium, -molybdenum and -tungsten with mercury(II) acetate or trifluoroacetate,



7.10a

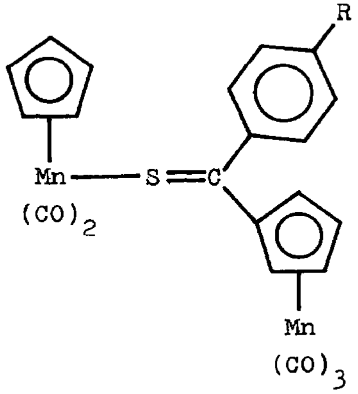


7.10b

coordination occurred at the metal atom. This was accompanied by an increase in the frequency and a change in the intensity of the carbonyl stretching frequency in the infrared [121].

The temperature dependence of the ^{1}H NMR spectra of the cymantrenyl aryl thioketones (7.11; R = H, Me) has been used to study rotation about the C=S bond. Rotation was found to be restricted [122].

Spin-lattice relaxation-time methods have been used to measure the barriers to η-cyclopentadienyl ring rotation for (η-C_5H_5)Mn(CO)$_3$ (7.24 kJ mol^{-1}), (η-C_5H_5)Re(CO)$_3$ (7.15 kJ mol^{-1})

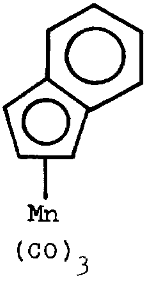


7.11

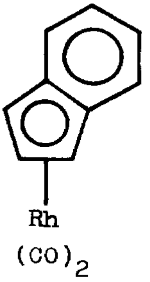
and $(\eta\text{-}C_5H_5)V(CO)_4$ (7.07 kJ mol^{-1}). Nonbonded atom-atom potential calculations of the barriers to rotation in the manganese and rhenium complexes showed that the molecular conformation was determined by crystal-packing forces and that concerted ring motions were possible [123].

Adiabatic calorimetry has been used to measure the heat capacities of cymantrene and tricarbonyl(η-pyrrolyl)manganese in the temperature range 10-300 K. Thermodynamic functions were calculated and comparisons were made with other (η-arene)-metalcarbonyl complexes [124].

Substitution of one of the carbonyl groups by triphenylphosphine in the η-indenyl compounds (7.12 and 7.13) has been studied. The reaction proceeded by a second order rate law which was first order in both the complex and triphenylphosphine. For both compounds the rates of substitution were much greater than for the corresponding η-cyclopentadienyl complexes [125].



7.12

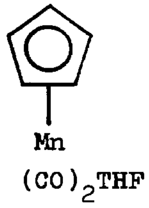


7.13

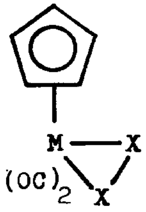
7. (iii) General Chemistry

The cymantrenyl complex (7.14) has been treated with selenium to form the diselenium derivative (7.15; M = Mn, X = Se). The rhenium disulphur complex (7.15; M = Re, X = S) was prepared by a similar reaction and in this case binuclear products were also obtained [126].

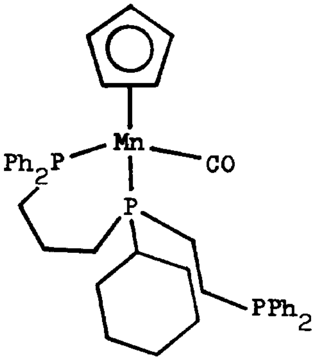
The trifunctional phosphine, $Ph_2PCH_2CH_2P(C_6H_{11})CH_2CH_2PPh_2$ combined photochemically with cymantrene to form the diphosphine (7.16) and triphosphine (7.17) derivatives together with the binuclear phosphine bridged complex (7.18). Further reactions



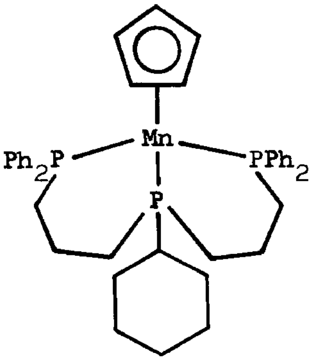
7.14



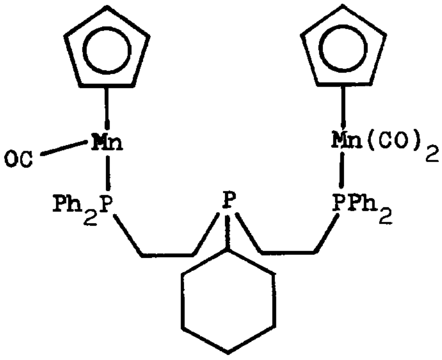
7.15



7.16



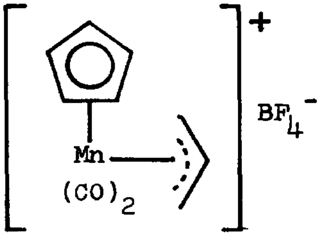
7.17



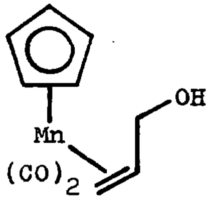
7.18

of the diphosphine (7.16) were reported, it formed homodinuclear and heterodinuclear complexes containing vanadium, chromium, molybdenum, tungsten and cobalt [127].

The ultraviolet irradiation of cymantrene with $H_2C{=}CHCH_2OH$ and HBF_4 produced the η-allyl complex (7.19). Treatment of this complex with potassium hydroxide gave the olefin complex (7.20) [128].



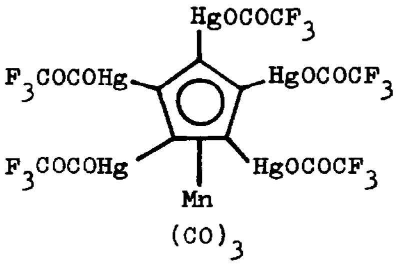
7.19



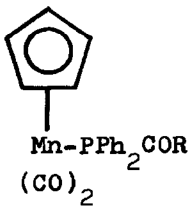
7.20

Reaction of cymantrene with excess mercury trifluoroacetate produced the pentamercurated complex (7.21). The complex $(\eta\text{-}C_5H_5)Mn(CO)_2PPh_3$ where the basicity of the manganese was considerably higher formed the adduct $[(\eta\text{-}C_5H_5)Mn(CO)_2PPh_3 - Hg(OCOCF_3)_2]_2$ with the same reagent. The structure of the adduct was determined by X-ray analysis [129].

Ligand substitution reactions of $(\eta\text{-}C_5H_5)Mn(CO)_2THF$ with the air sensitive aroyl- and acyl-diphenylphosphines $RCOPPh_2$



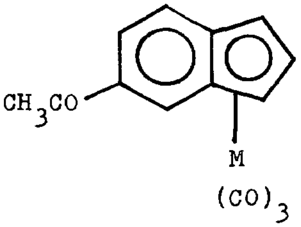
7.21

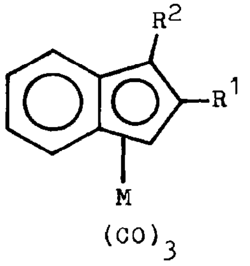


7.22

[R = p-ClC_6H_4, o-$ClCH_2C_6H_4$, p-anisyl, n-nonyl, n-undecyl, $H_2C{=}CH(CH_2)_8$] produced the corresponding stable manganese complexes (7.22) [130].

The acetylation of tricarbonyl(η^5-indenyl)-manganese and -rhenium under Friedel-Crafts conditions gave the acetyl derivatives (7.23; M = Mn, Re). The manganese complex also gave a product acetylated in the cyclopentadienyl ring and a diacetylated complex [131].





7.23

7.24

Lithiation of tricarbonyl(η-cyclopentadienyl)-manganese and -rhenium, followed by carboxylation with carbon dioxide gave the corresponding acids (7.24; M = Mn, Re; R^1 = H, R^2 = CO_2H R^1 = CO_2H, R^2 = H) [132].

Sodium borohydride treatment of the η-cyclohexadienyl-manganese complex (7.25) resulted in hydride addition at C-1 and C-5 in a ratio of 1.5:1 to give the η-diene complexes (7.26 and 7.27). X-ray analysis of the complex (7.26) showed that the hydrogen was positioned endo to the metal and it was concluded that hydride addition occurred in a stereospecific endo manner [133].

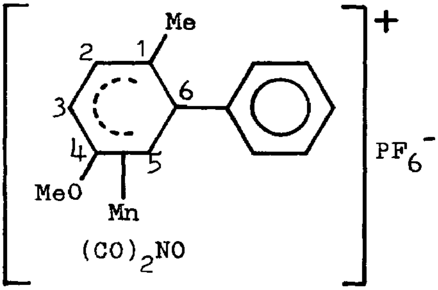
The first stage in the electrochemical reduction of the manganese and rhenium complexes (7.28; R = Ph, Me_3C, M = Mn; R = Me_3C, M = Re) gave radicals without any metal-carbon bond cleavage. Electrochemical oxidation of the complexes (7.29; M = Mn, L = PPh_3; M = Re, L = CO) proceeded via cation radicals [134].

Treatment of $[(\eta\text{-}C_5H_4R)Mn(CO)(NO)]_2$ with two equivalents of $HBF_4.OMe_2$ gave a complex mixture of products which included

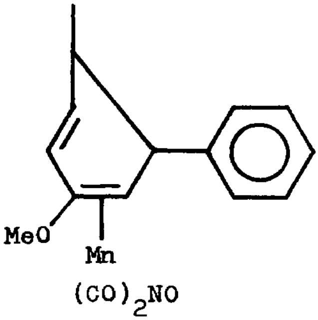
$[(\eta\text{-}C_5H_4R)Mn(CO)_2NO]^+$, $[(\eta\text{-}C_5H_4R)_3Mn_3(NO)_3NH]^+$ and $[(\eta\text{-}C_5H_4R)_2Mn_2(NO)_2(CO)(NH_2)]^+$ [135].

The effects of the i.p. administration of methylcymantrene on the lungs of rats and mice has been investigated. The animals suffered acute lung injury. Fibrosis in mice was significantly enhanced when the animals were exposed to 80% oxygen immediately after treatment with methylcymantrene. This effect was not shown in rats [136].

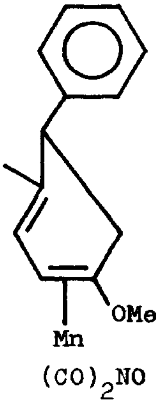
Substance P acylated at the α-amino group by cymantreneacetic acid, 1-methyl-3-cymantrene-1-carboxylic acid or ferrocenecarboxylic acid has been prepared by solid-phase synthesis.



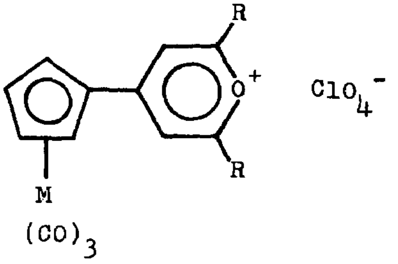
7.25



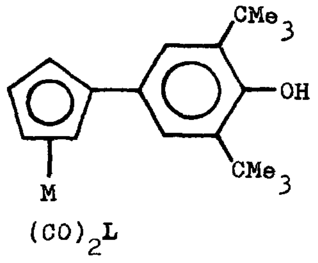
7.26



7.27



7.28



7.29

The protected peptides were cleaved from the resin by hydrogen fluoride in anisole. The metallocene protected analogues of substance P retained their spasmogenic potency in the guinea pig ileum assay [137].

The effects of tricarbonyl(η-methylcyclopentadienyl)-manganese on the energy metabolism in rat liver mitochondria has been investigated. The complex at concentrations >0.2 mM specifically promoted the state 4 respiration but it had no effect on the respiration at other states. The release of potassium ion from the mitochondria was enhanced which indicated damage to the mitochondrial membrane [138].

Tricarbonyl(η-methylcyclopentadienyl)manganese was added to a fuel based on propane for use in an oxyfuel torch for cutting mild steel plates. The cutting speed and general performance were improved in the presence of the additive [139].

Cymantrene and substituted ferrocenes have been used to increase the heat and radiation resistance of silicon rubber vulcanizates [140].

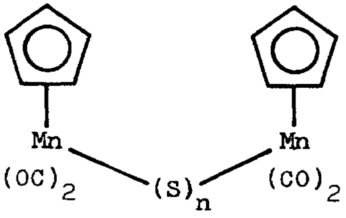
A mixture of the 1,2- and 1,3-isomers of methylvinyl-cymantrene has been copolymerized with styrene crosslinked with 1,4-divinylbenzene. A dinitrogen complex was formed from the copolymer in the form of a membrane and nitrogen by UV irradiation at room temperature. The same complex was obtained from the THF derivative of the copolymer and nitrogen under mild conditions. Polymer-supported dinitrogen complexes were found to be more stable than the low molecular-weight analogues [141].

Inductively coupled plasma emission spectrometry has been used for the determination of manganese in methylcymantrene.

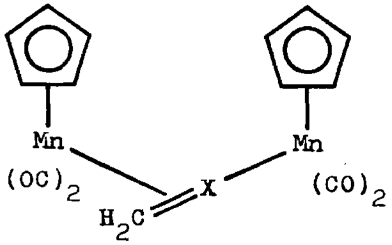
The sample was dissolved in toluene and a water emulsion of this solution was introduced directly into the plasma. Manganese was detected down to a limit of 7μg l^{-1} [142].

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

Cymantrene combined with sulphur under photolytic conditions to give the sulphur bridged complexes (8.1; n = 1, 2) which were attacked by diazomethane to form the thioformaldehyde complex (8.2; X = S). The corresponding selenium and tellurium complexes (8.2; X = Se, Te) were formed in the same way [143].

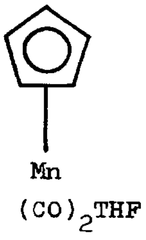


8.1

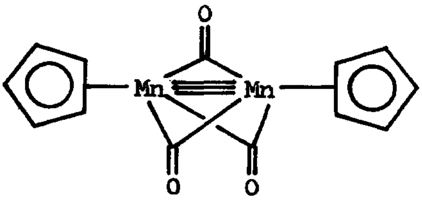


8.2

The (η-cyclopentadienyl)manganese THF complex (8.3) underwent spontaneous elimination of carbon monoxide in 20 h to give the binuclear complex (8.4) with a manganese-manganese triple bond [144].



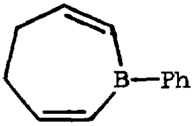
8.3



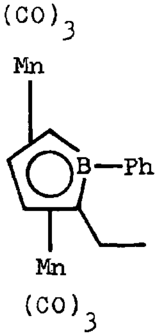
8.4

The thermal reaction between manganese carbonyl and 1-phenyl-4,5-dihydroborepin (8.5) produced the triple-decker (η-2-ethyl-1-phenylborole)manganese complex (8.6). In the same way the (η-cyclopentadienyl)iron complexes (8.7 and 8.8) were prepared [145].

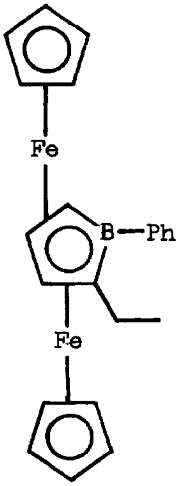
The cymantrene phosphorus tribromide complex (8.9) has been treated with nonacarbonyldiiron to form the tetranuclear heterometallic complex (8.10) which was characterized by X-ray crystallography [146].



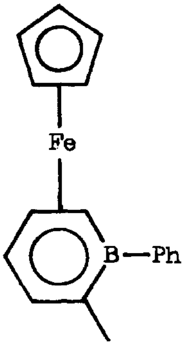
8.5



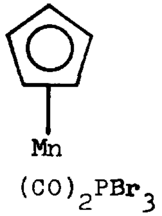
8.6



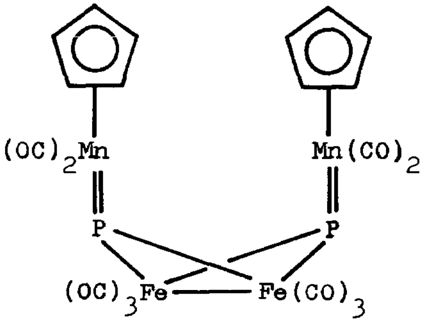
8.7



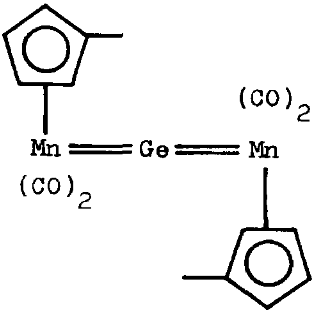
8.8



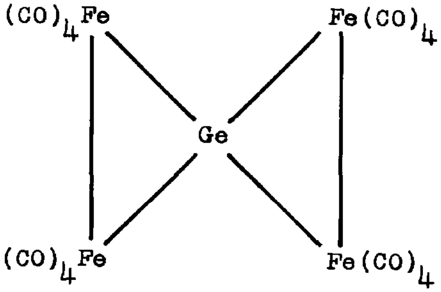
8.9



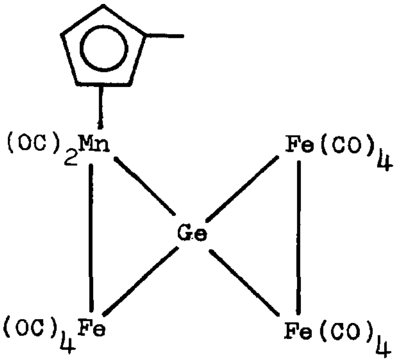
8.10



8.11



8.12



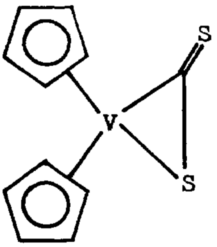
8.13

Reaction of the dicarbonylmanganese complex (8.11) with $Fe_2(CO)_9$ produced the germanium containing complexes (8.12 and 8.13). The structures of the latter two complexes were determined by X-ray analysis [147].

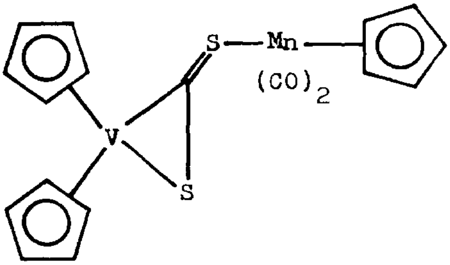
The bis(η-cyclopentadienyl)vanadium complex (8.14) formed coordination complexes with organometallic species that behaved as Lewis acids. Thus the (η-cyclopentadienyl)manganese THF complex (8.3) gave the paramagnetic heterobimetallic complex (8.15) [148].

Several borole complexes, including the dimanganese complex (8.16) have been prepared by treatment of 1-phenyl-2,5-dihydroborole with metal carbonyls and organometallic compounds [149].

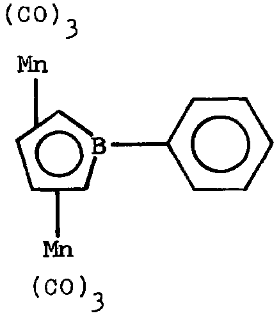
The cymantrene complex (8.3) has been treated with the titanocene derivative (8.17) to form the heterobimetallic



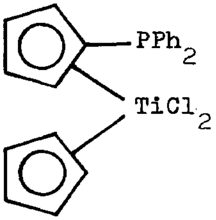
8.14



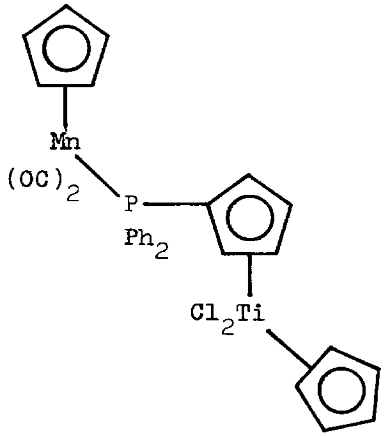
8.15



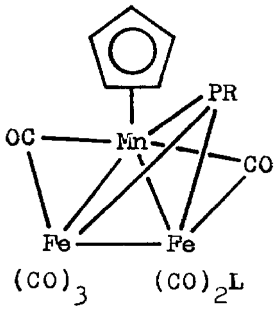
8.16



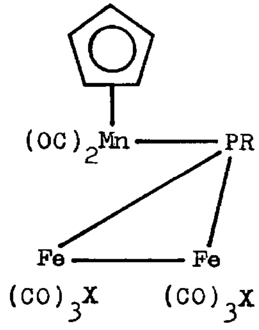
8.17



8.18



8.19



8.20

complex (8.18) which has been characterized by X-ray crystallography. Some reactions of the complex (8.18) were reported [150].

The crystal and molecular structure of dicarbonyl(η-cyclopentadienyl)-μ_3-(phenylphosphinidene)[(tricarbonyltriphenylphosphine)(tricarbonyl)diiron]manganese-(Fe-Fe) has been determined by X-ray crystallography. The structure showed similarities to the structure of the cymantrene complex $(\eta^5\text{-}C_5H_5)(CO)_2MnFe_2(CO)_7(\mu_3\text{-}PPh)$ [151].

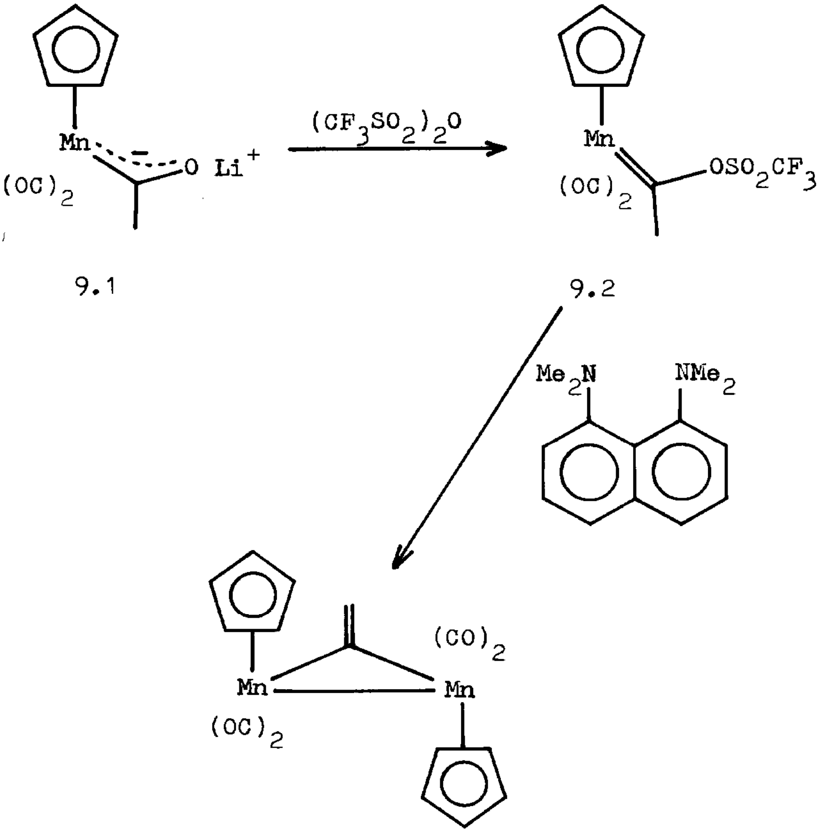
Group V ligands attacked the mixed manganese-iron cluster complexes (8.19; R = Me, Et, Bu, Ph; L = CO) at iron to form R_3P, R_3As and R_3Sb adducts with the cleavage of an Fe-Mn bond. Under thermal conditions, the reactions were reversible, however, UV irradiation enhanced the uptake of ligand and caused elimination of carbon monoxide to form the products (8.19; R = Me, Et, Bu, Ph; L = R_3P, R_3As, R_3Sb). Trialkylphosphines and phosphites (X) underwent the same reaction but gave the di-adduct (8.20) with cleavage of both Fe-Mn bonds [152].

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

The anionic manganese acyl complex (9.1) has been attacked by trifluoromethane sulphonic anhydride to form the intermediate carbene complex (9.2) which was treated in situ with 1,8-bis(dimethylamino)naphthalene to give the μ-vinylidene complex (9.3). Several related (η-cyclopentadienyl)iron complexes were reported [153].

The nucleophilic addition of halide ions, as the tetrabutylammonium salts, to the cationic complexes (9.4; M = Mn, Re) produced the corresponding carbene derivatives (9.5; M = Mn, Re; X = F, Cl, Br, I) [154].

Nucleophilic cleavage of the fluorine-carbon bond occurred in the carbene complex (9.5; X = F) on treatment with n-butyllithium or ethanol to give the complexes (9.5; X = Bu and OEt) respectively [155].



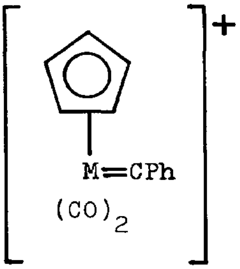
9.1

9.2

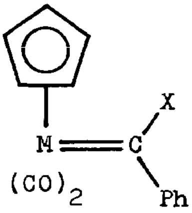
9.3

Aziridine, oxirane and thiirane underwent ring expansion with carbonyl and thiocarbonyl ligands in (η-cyclopentadienyl)-manganese, -iron and -ruthenium complexes to form cyclic carbene complexes. Thus the cation (9.6) combined with oxirane to form the carbene derivative (9.7) [156].

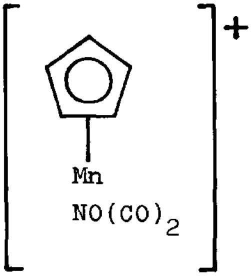
Cymantrene and methylcymantrene have been treated with $Me_3P{=}CH_2$ to form the anionic manganeseacyl-phosphorus ylides (9. 8; R = H, Me). These, and related ylides, were converted to the corresponding neutral ylide and "ylide-carbene" complexes such as the complex (9.9). The crystal and molecular



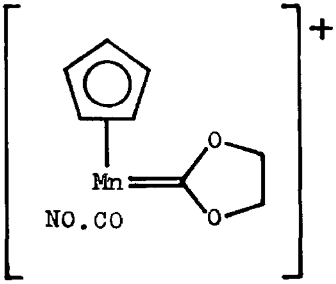
9.4



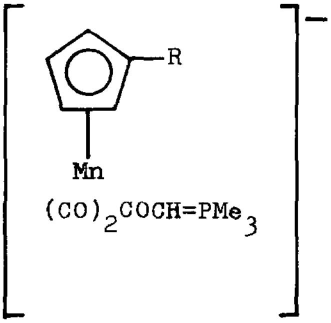
9.5



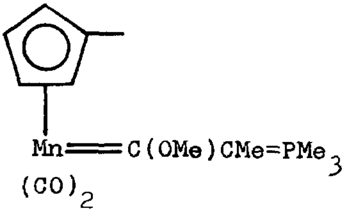
9.6



9.7



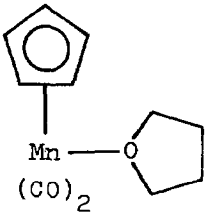
9.8



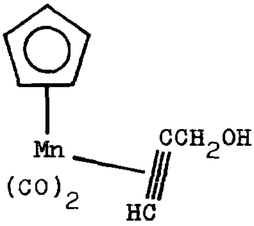
9.9

structure of this complex has been determined by X-ray crystallography [157].

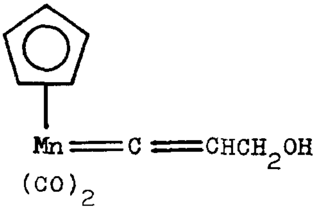
UV irradiation of cymantrene or the THF derivative (9.10) with 2-propyn-1-ol gave the acetylene complex (9.11) which was



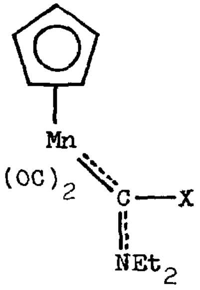
9.10



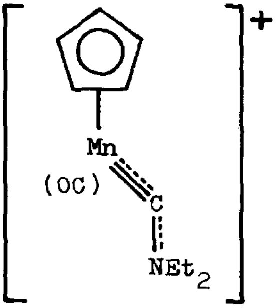
9.11



9.12



9.13



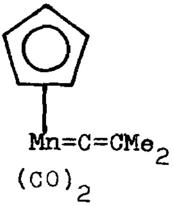
9.14

converted to the carbene (9.12) with phenyllithium [158].

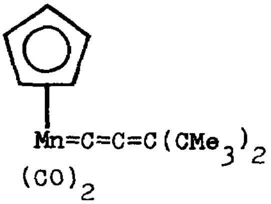
Methylcymantrene has been treated with $LiNEt_2$ and then alkylated with $(Et_3O)BF_4$ to form the carbene complex (9.13; X = OEt) which was in turn converted to the cationic carbyne complex (9.14) by reaction with borontrihalides. Fluoride addition to the carbyne (9.14) using $[(C_4H_9)_4N]F$ gave the fluorocarbene complex (9.13; X = F) [159].

The electronic structures of the dicarbonylmanganese complexes (9.15 and 9.16) have been investigated by He(I) photoelectron spectroscopy. The results indicated that there was considerable mixing of transition metal and ligand orbitals [160].

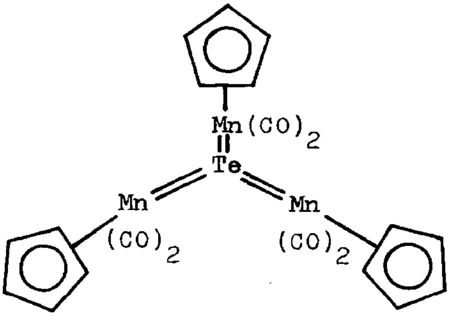
The cymantrene complex (9.10) combined with Al_2Te_3 to give a polynuclear complex (9.17) in which tellurium behaved as a six-electron donor. The crystal and molecular structure of the



9.15



9.16



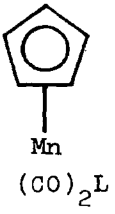
9.17

complex (9.17) was determined by X-ray crystallography. The complex $Te_2[Mn(CO)_2(\eta\text{-}C_5H_5)]_3$ was also obtained [161].

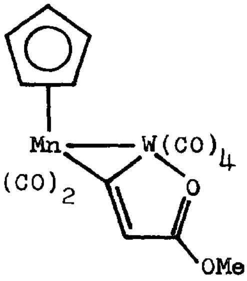
Treatment of the η-acetylene and the η-vinylidene complexes (9.18; L = $HC{\equiv}CCO_2Me$, $=C{=}CHCO_2Me$) respectively with pentacarbonyltetrahydrofuran-molybdenum or -chromium gave the corresponding tetracarbonylmetal complexes (9.19) [162].

Protonation of the allenylidene complexes (9.20; R = Ph, CMe_3) with HCl and CF_3CO_2H has given the manganese carbyne complex cations (9.21; R = Ph, CMe_3) [163].

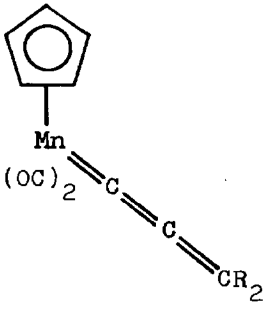
The acetylene complexes (9.22; R = Me, Ph) have been treated with alkyllithium and alkoxide reagents to form the manganese



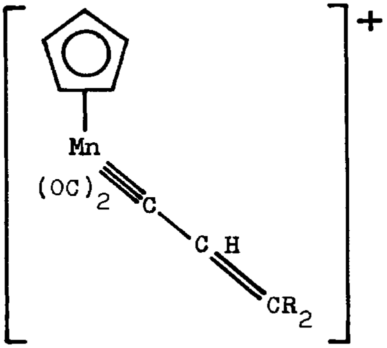
9.18



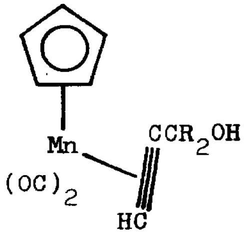
9.19



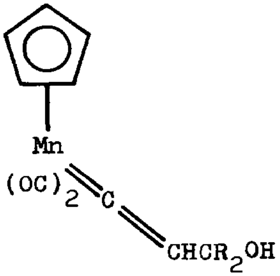
9.20



9.21



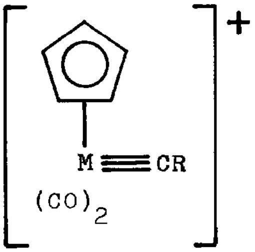
9.22



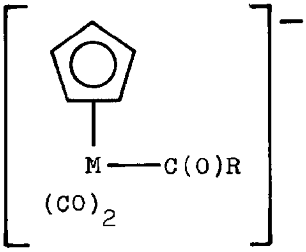
9.23

carbene complexes (9.23; R = Me, Ph) which were subsequently dehydrated with alumina, silica or mineral acids to form the manganese allenylidene derivatives (9.20; R = Me, Ph) [164].

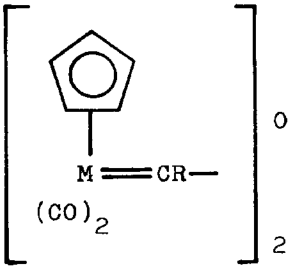
The cationic carbyne complexes (9.24; M = Mn, Re; R = Ph, 4-$CF_3.C_6H_4$) combined with the corresponding acylate anions (9.25; M = Mn, Re; R = Ph, 4-$CF_3.C_6H_4$) to form the symmetrical anhydrides (9.26; M = Mn, Re; R = Ph, 4-$CF_3.C_6H_4$) of hydroxycarbene complexes. The manganese complex (9.26; M = Mn, R = Ph) was characterized by X-ray crystallography [165].



9.24



9.25

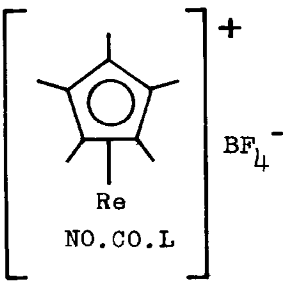


9.26

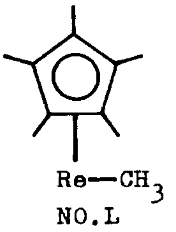
10. $(\eta\text{-}C_5H_5)Re(CO)_3$

Tricarbonyl(η-pentamethylcyclopentadienyl)rhenium has been prepared from $Re_2(CO)_{10}$ and pentamethylcyclopentadiene. Treatment of this compound with $NOBF_4$ produced the complex cation (10.1; L = CO) which in the presence of $C_6H_5I^+\text{-}O^-/MeCN$ gave the methyl cyanide complex (10.1; L = CH_3CN). Reaction of the latter complex with PPh_3 or $P(OPh)_3$ produced the corresponding phosphorus derivatives [10.1; L = PPh_3, $P(OPh)_3$] which were reduced to give the methyl compounds [10.2; L = PPh_3, $P(OPh)_3$]. When these complexes were treated with Ph_3CPF_6 the stable methylidene compounds [10.3; L = PPh_3, $P(OPh)_3$] were formed [166].

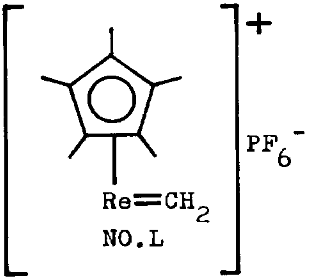
Decacarbonyldirhenium combines with acyclic and cyclic olefins containing one to four C=C bonds under photochemical conditions. The main products were octacarbonyl-μ-hydrido-μ-



10.1



10.2



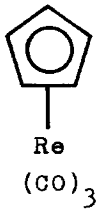
10.3

olefinyldirhenium complexes. Tricarbonyl(η-cyclopentadienyl)-rhenium and its pentacarbonylrhenium derivative were among the products obtained when the olefin was cyclopentadiene [167].

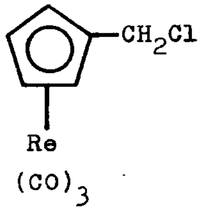
The photolysis of tricarbonyl(η-cyclopentadienyl)rhenium (10.4) in an argon matrix at low temperatures led to the reversible formation of dicarbonyl(η-cyclopentadienyl)rhenium. When a nitrogen matrix was used then $Re(\eta\text{-}C_5H_5)(CO)_2N_2$ was the irreversible product [168].

Tricarbonyl(η-cyclopentadienyl)rhenium has been attacked by trimethylphosphine to give <u>fac</u>-$(\eta^1\text{-}C_5H_5)Re(CO)_3(PMe_3)_2$ in equilibrium with the starting materials. The equilibrium mixture slowly formed the dicarbonyl complex, $(\eta^5\text{-}C_5H_5)Re(CO)_2PMe_3$. The crystal and molecular structure of the first formed product has been confirmed by X-ray crystallography [169].

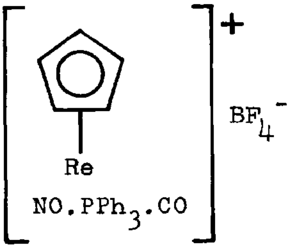
Treatment of tricarbonyl(η-cyclopentadienyl)rhenium with $MeOCH_2Cl$ in the presence of $AlCl_3$ produced the chloromethyl derivative (10.5) [170].



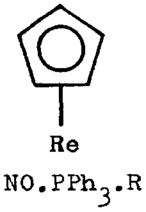
10.4



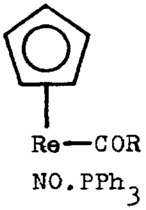
10.5



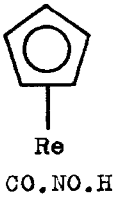
10.6



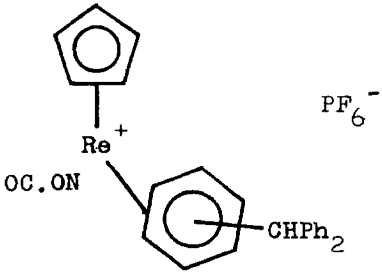
10.7



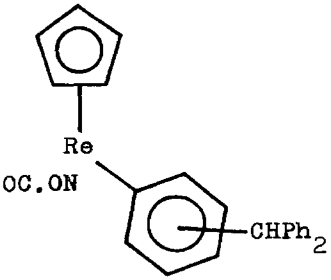
10.8



10.9



10.10



10.11

The organorhenium cation (10.6) has been resolved and used to prepare the optically active complexes [10.7; R = COOMe, Me, CH_2Ph, Et, COPh, COMe, $COCH_2CH_2Ph$, CD_3, CD_2Ph, $CH(CH_3)Ph$, $CH(CH_2CH_3)Ph$, $CH(CH_2Ph)Ph$, $CH(CH_2CH_2CH_3)Ph$, $CD(CH_2CH_2CH_3)Ph$, $=CH_2^+$, $=CHPh^+$, $=CHCH_3^+$]. The structure of the complex (10.7; R = Et) was determined by X-ray analysis and used to establish the absolute configuration of these molecules [171].

The chiral rhenium acyls (10.8; R = Me, Et, n-nonyl, Ph, CH_2Ph, CH_2CH_2Ph, vinyl, allyl) have been prepared in good yields by reaction of the Grignard reagents RMgX with $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)OCOCH_3$. The methylation and protonation of the rhenium acyls was investigated [172].

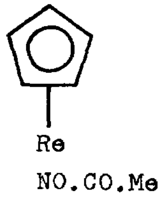
The (η-cyclopentadienyl)rhenium complex (10.9) has been treated with $Ph_3C^+PF_6^-$ in dichloromethane at -78 °C to form the (η^2-arene)rhenium complex (10.10) which was a solid, stable at room temperature for limited periods. The complex underwent deprotonation with triethylamine at -78 °C to form the (σ-arene)-rhenium complex (10.11) as the m- and p-isomers. Migration of rhenium about the benzene ring took place by way of intermediate (η^1-arenium)rhenium species which were analogous to those formed in electrophilic aromatic substitution [173].

The (η^5-cyclopentadienyl)rhenium complex (10.12) underwent addition of triphenylphosphine at high concentrations to form the (η^1-cyclopentadiene)rhenium complex (10.13) which was converted to the cyclopentadienylidene ketone complex (10.14) [174].

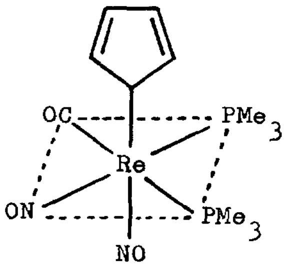
Treatment of the aryldiazenido complexes (10.15; R = Me, OMe, NEt_2) with aqueous sodium hydroxide produced the air-stable hydroxycarbonyl complexes (10.16; L = COOH) and reaction with excess aqueous potassium hydroxide gave the corresponding hydrides (10.16; L = H) [175].

The reaction of $(\eta\text{-}C_5H_5)Mo(CO)_2(p\text{-}N_2C_6H_4Me)$ with $(\eta\text{-}C_5H_5)Re(CO)_2THF$ produced the bimetallic aryldiazenido complex (10.17). The structure of this complex was determined by X-ray analysis and the MoNN skeleton was essentially linear [176].

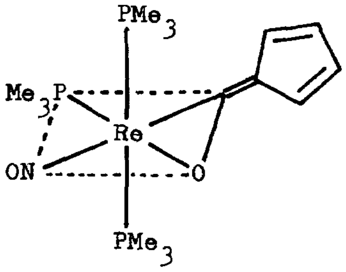
Treatment of the alkylidenes (10.18; R = H, Me, n-Pr) with potassium t-butoxide gave the corresponding vinyl complexes (10.19). The propenyl and pentenyl compounds (10.19; R = Me, n-Pr) crystallized as 97:3 mixtures of E/Z geometric isomers. Reaction of the vinyl complexes (10.19) with CF_3SO_3H produced the alkylidenes (10.18). The chiral vinyl-rhenium complexes underwent electrophilic attack with appreciable 1,3-asymmetric



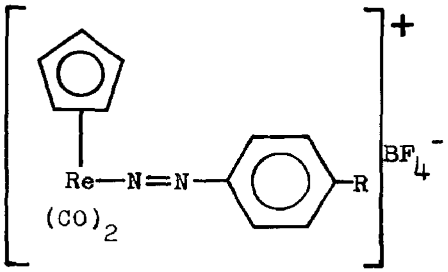
10.12



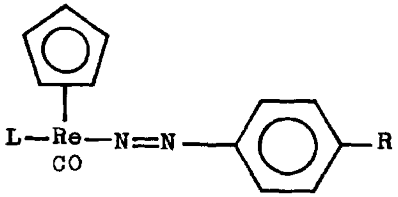
10.13



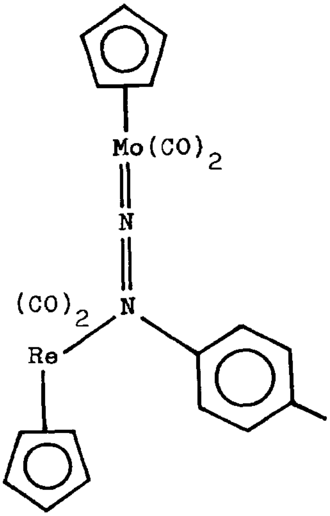
10.14



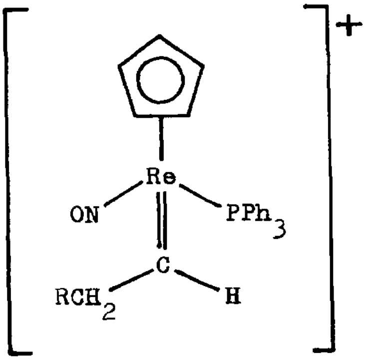
10.15



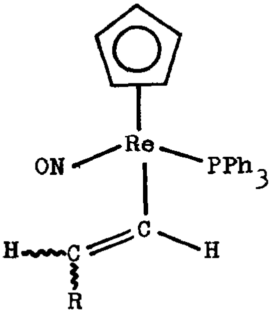
10.16



10.17



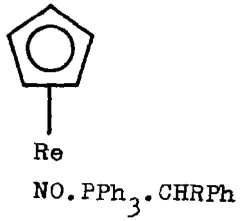
10.18



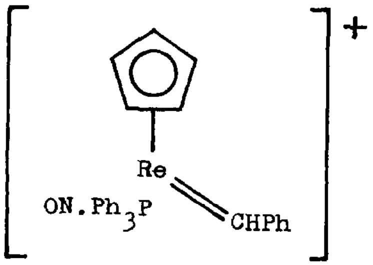
10.19

induction [177].

Hydride ion abstraction from the (η-cyclopentadienyl)rhenium complex (10.20; R = H) with trityl hexafluorophosphate afforded the benzylidene cation (10.21) which underwent stereoselective attack by nucleophiles such as methyllithium, ethylmagnesium bromide and benzylmagnesium chloride to form the adducts (10.20; R = Me, Et, PhCH$_2$) respectively. A number of related reactions were reported [178].



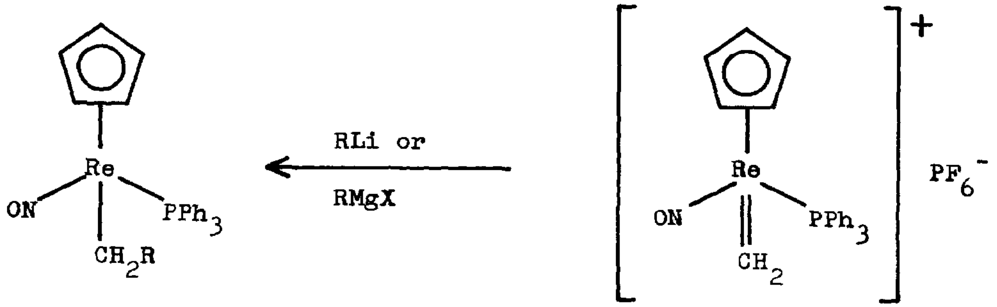
10.20



10.21

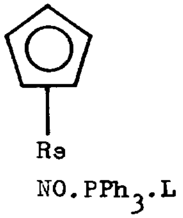
Primary rhenium alkyls (10.22; R = Me, Et, n-Bu, i-Pr, t-Bu) have been prepared by attack of Grignard or alkyllithium reagents on the methylidene complex (10.23). Secondary rhenium alkyls were prepared by a similar reaction. The rhenium alkyls were treated with Ph_3CBF_4 to give methylidene complexes and the regiochemistry and stereochemistry of hydride abstraction were examined. Detailed transition-state models for α- and β-hydride abstraction were proposed [179].

The (η-cyclopentadienyl)rhenium formate (10.24; L = OCHO) has been prepared by treatment of the rhenium methyl complex (10.24; L = Me) with 88% formic acid and the mechanism of decarboxylation to the rhenium hydride (10.24; L = H) investigated. Decarboxylation of the optically active and deuterium labelled complex (10.24; L = OCHO) indicated that carbon dioxide was lost by an intramolecular process [180].



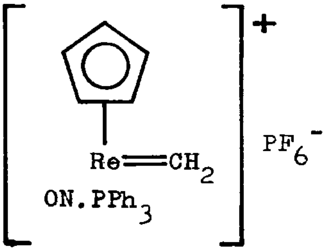
10.22

10.23

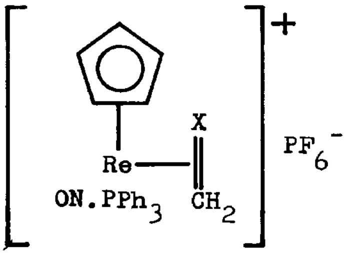


10.24

The η^2-$CH_2C{=}O$ rhenium complex (10.26; X = O) has been prepared by treatment of the methylidene complex (10.25) with PhI^{+}—O^{-}. The thioformaldehyde complex (10.26; X = S)has also been obtained from the same starting material (10.25). The crystal and molecular structures of the complexes (10.26; X = O, S) have been determined by X-ray crystallography. Several reactions of the coordinated formaldehyde and thioformaldehyde ligands were reported [181].



10.25

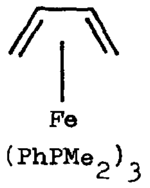


10.26

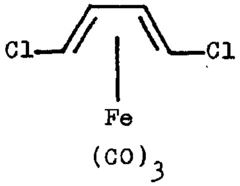
11. (Acyclic-η-diene)Fe(CO)$_3$ and (η-trimethylenemethane)Fe(CO)$_3$

The reaction of tris(2,4-pentanedionato)iron(III) with diethylaluminium ethoxide in the presence of dimethylphenylphosphine gave bis(η-ethylene)tris(dimethylphenylphosphine)iron(0). The coordinated ethylene was displaced easily by 1,3-butadiene to give the η-butadiene complex (11.1) [182].

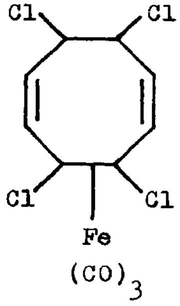
Thermal and photochemical reactions of trans-dichlorobutadiene with pentacarbonyliron produced the tricarbonyliron



11.1



11.2

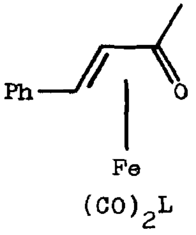


11.3

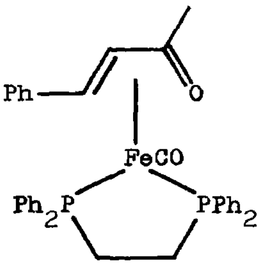
complex (11.2), as the major product, together with a minor product (11.3) [183].

Irradiation of tetracarbonylphosphineiron and tricarbonyldiphosphineiron complexes in the presence of benzylideneacetone produced the corresponding dicarbonyl (11.4; L = PEt_3, $PPhMe_2$, PPh_2Me) and monocarbonyl complexes (11.5). The structures of the complexes (11.4; L = PEt_3, $PPhMe_2$) were determined by X-ray analysis. The iron atom adopted a distorted octahedral coordinated geometry in which three of the sites were occupied by the benzylideneacetone ligand [184].

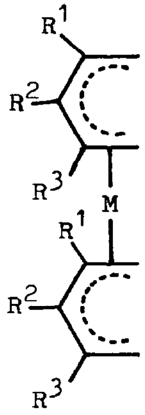
The bis(η-pentadienyl)iron compounds (11.6; M = Fe, R^1, R^2, R^3 = H, Me) have been prepared. These complexes were red and air-stable with similar properties to those of their cyclic ferrocene counterparts. X-ray analysis of the complex (11.6;



11.4



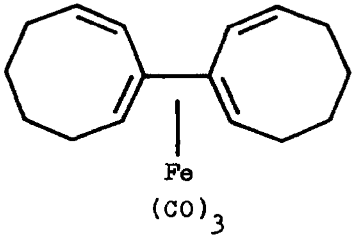
11.5



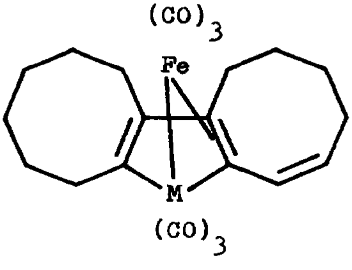
11.6

M = Fe, $R^1 = R^3$ = Me, R^2 = H) showed a gauche-eclipsed ligand conformation with carbon-iron bond distances that were slightly greater than those in ferrocene [185]. The corresponding ruthenium complexes (11.6; M = Ru, $R^1 = R^2 = R^3$ = Me; $R^1 = R^3$ = Me, R^2 = H) have also been prepared and shown to have similar structures to the corresponding iron compounds [186]. The reaction of pentacarbonyliron with cis-polybutadiene produced poly(1,3-octadieneirontricarbonyl) [187].

Bi-2,7-cyclooctadienyl has been attacked by dodecacarbonyltriiron to form the tricarbonyliron complex (11.7) which underwent further reaction with either the same reagent or with dodecacarbonyltriruthenium to form the bimetallic complexes (11.8; M = Fe, Ru) respectively. Formation of the binuclear complexes involved dehydrogenative metallacyclization followed by intramolecular transfer of the abstracted hydrogen atoms. The crystal and



11.7



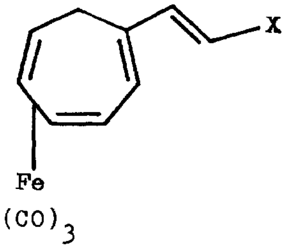
11.8

molecular structure of the heteronuclear bimetallic complex (11. 8; M = Ru) was determined by X-ray crystallography [188].

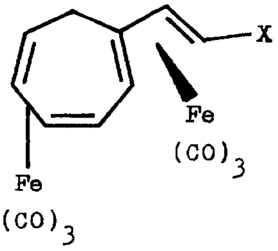
When the complexes (11.9; X = CO_2Me, p-COC_6H_4Me) were heated in toluene the corresponding bis(tricarbonyliron) compounds (11.10) were isolated. In a similar reaction the complex (11.9; X = Ph) produced the metal-hydrogen shift isomer (11.11) as the major product. The anti configuration of the binuclear complexes was was established by X-ray crystallography [189].

Reaction of dehydro-β-ionone with $Fe_2(CO)_9$ and $Fe(CO)_5$ produced the tricarbonyliron complexes (11.12, and 11.13) together with the dicarbonyliron compound (11.14) [190]. Treatment of the complex (11.12) with alkaline hydrogen peroxide in methanol gave dehydro-β-ionone in 95% yield [191].

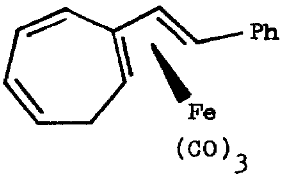
Condensation of ruthenium vapour with a mixture of buta-1,3-diene and pentane at -196 °C, followed by warming to -40 °C and treatment with PF_3, CO or Me_3CNC produced the corresponding complex $[RuL(\eta^4-C_4H_6)_2]$ in good yield [192].



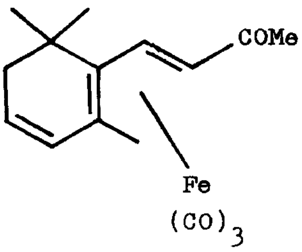
11.9



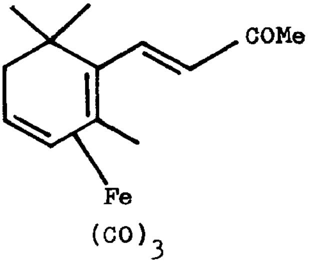
11.10



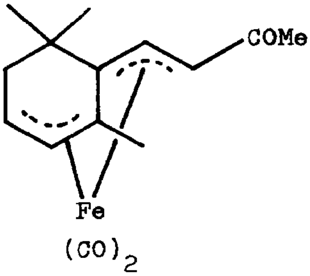
11.11



11.12



11.13

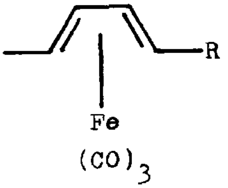


11.14

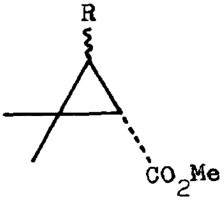
Raman and infrared spectra of solid, liquid and solution phases of (η-butadiene)tricarbonyliron have been recorded and interpreted [193].

Tricarbonyl[(1,2,3,6-η)-2-methylenecyclopentane-1,3-diyl]iron has been prepared and the barrier to internal rotation 15.2 kcal mol^{-1}, was determined via NMR spectroscopy. The oxidative decomposition of this complex with trimethylamine-N-oxide in the presence of diethyl fumarate was investigated [194].

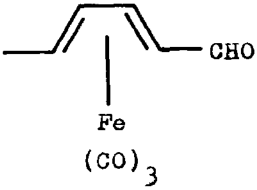
The [η-(E,E)-butadiene]iron complex (11.15; R = CHO) has been used as the starting material for the synthesis of cis- and trans-hemicaronic acid esters (11.16; R = β-CHO, α-CHO) respectively. The synthetic route involved stereospecific cycloaddition of $Me_2C=N_2$ to the cis- and trans-esters (11.15; R = CH=CH∿CO_2Me) [195].



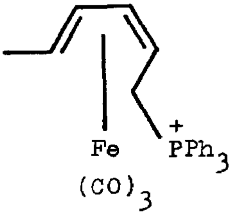
11.15



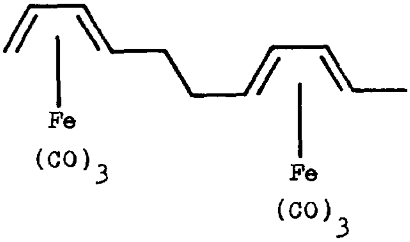
11.16



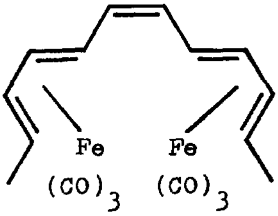
11.17



11.18

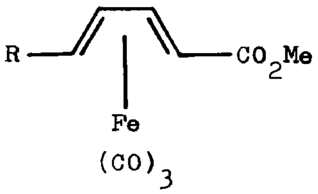


11.19

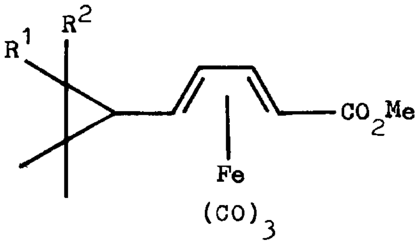


11.20

Reaction of the tricarbonyliron complex (11.17) with sodium tetrahydridoborate and hydrogen tetrafluoroborate followed by triphenylphosphine produced the phosphonium compound (11.18). This latter compound was deprotonated with n-butyllithium to



11.21

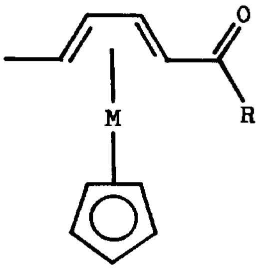


11.22

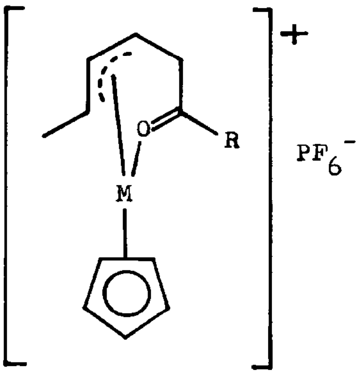
give the corresponding ylide which underwent a Wittig reaction with the η-diene complex (11.17) to give the bis(tricarbonyliron) complexes (11.19 and 11.20). The crystal structure of the complex (11.19) was determined by X-ray analysis [196].

The (+)-(η-butadiene)iron complex (11.21; R = CHO) has been converted to the intermediate (+)-triene complex (11.21; R = $CH{=}CMe_2$) using the Wittig reaction and then cyclized to the isomeric (+)-cyclopropane complexes (11.22; $R^1 = \alpha$-H, $R^2 = \beta$-CO_2Me; $R^1 = \alpha$-CO_2Me, $R^2 = \beta$-H) with diazoacetic ester. The isomeric mixture (11.22) was used as a convenient source of (+)-1R,3R-hemicaronaldehyde and its (+)-cis-isomer which were intermediates in pyrethroid synthesis [197].

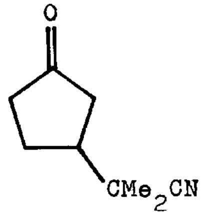
The dienone complexes (11.23; M = Rh, Ir; R = Me, OMe) were converted to the corresponding allyl complexes (11.24;



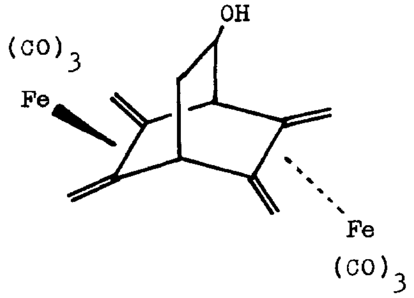
11.23



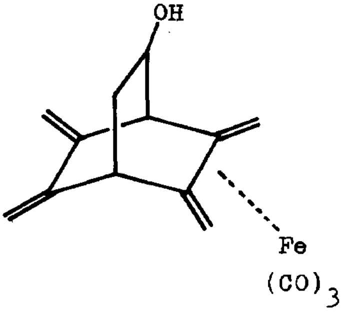
11.24



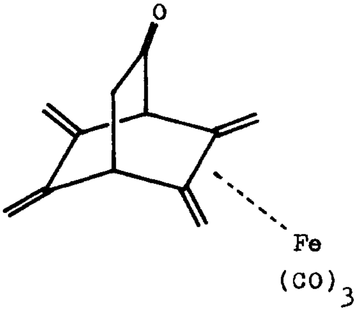
11.25



11.26



11.27



11.28

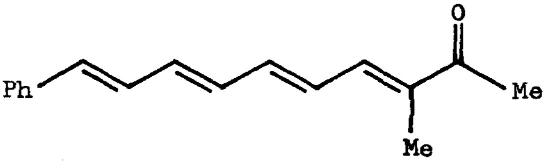
M = Rh, Ir; R = Me, OMe) on treatment with hexafluorophosphoric acid. The esters (11.23; M = Rh, Ir; R = OMe) underwent base catalyzed hydrolysis to afford the corresponding dienoic acids [198].

The addition of carbon nucleophiles to tricarbonyl(η-1,3-diene)iron complexes gave (η-homoallyl)tricarbonyliron anionic complexes which then incorporated carbon monoxide to produce acyliron anionic complexes. With most of the open-chain 1,3-diene ligands further cyclization occurred to give cyclopentanone derivatives with the anionic substituent in the three position. For example, the reaction of (1,3-butadiene)-tricarbonyliron with $LiCMe_2CN$ followed by carbon monoxide produced the cyclopentanone (11.25) [199].

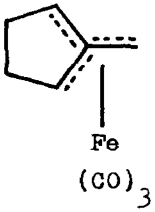
Oxidation of the bis(tricarbonyliron) complex (11.26) with chromium(VI) oxide produced the corresponding ketone. The syn-Fe(CO)$_3$ groups of the alcohol and the ketone were selectively oxidatively removed by treatment with Me$_3$NO to give the corresponding complexes (11.27 and 11.28) containing one tricarbonyliron moiety [200].

A dicarbonyl(η-2,3-dimethylbutadiene)iron species has been invoked as the intermediate in the photolytic isomerization of tricarbonyl(η-allyl)iron complexes [201].

3-Methyl navenone-B (11.29) has been prepared and the stereochemistry of the 3-methyl ene-one moiety was established unambiguously via an Fe(CO)$_3$ complex [202].



11.29



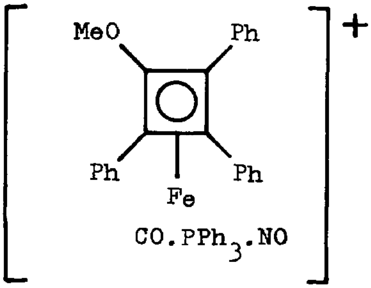
11.30

In an attempt to elucidate the primary processes involved in the reactions of acetylenes, cyclobutenes and methylenecyclopropanes with transition metal complexes, the critical intermediates involved in these reactions have been investigated. For example, the reactions of different cyclobutenes with Fe$_2$(CO)$_9$ were investigated. "The Induced Kinetic Isotope Effect" was used to distinguish between two different reaction mechanisms in the formation of tricarbonyl(η-trimethylenemethane)iron [203].

Oxidative degradation of the (η-trimethylenemethane)iron complex (11.30) under various conditions indicated a sequential mechanism with the liberation of a metal-free trimethylenemethane species in its ground triplet spin state [204].

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

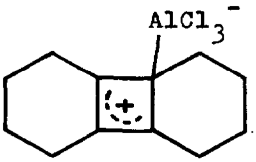
Alkylation of the keto group in the ring of the complex $(\eta^3\text{-}C_3Ph_3CO)Fe(CO)(PPh_3)NO$ produced the cation (12.1). The structure of the cation was determined by X-ray analysis [205].



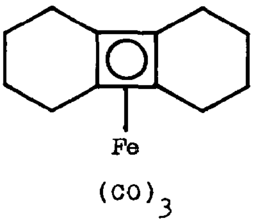
12.1

The zwitterion (12.2) has been treated with thionyl chloride to give an intermediate dihalocyclobutene which was converted to the (η-cyclobutadiene)iron complex (12.3) with enneacarbonyldiiron. Tricarbonyl(η-tetramethylcyclobutadiene)iron was prepared in the same way [206].

The ^1H NMR spectra of tricarbonyl(η-cyclobutadiene)iron and the corresponding monoiodo derivative together with the ^1H and ^2H NMR spectra of the monodeuterated compounds oriented in various liquid crystals have been recorded and interpreted. The direct coupling constants obtained deviated from the values expected for a square. This was explained in terms of a slight



12.2



12.3

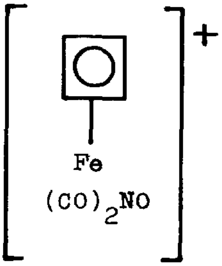
fluxional rhombic deformation caused by interaction with the solvent and averaged by ring rotation in a plane with degrees of order of the opposite sign. This model was also used to explain the observed quadrupole splitting assuming two different field gradients at the corners of the rhombus. The time averaged structure of the η-cyclobutadiene ring was square [207].

Generalized molecular orbital calculations have been carried out on $(\eta\text{-}C_4H_4)Fe(CO)_3$ and several of its low-lying ionic states. The results suggested rather strong polarization of the six electrons in the cyclobutadiene-metal bond towards cyclobutadiene. Differential electron correlation was shown to be important in determining the order of the low-lying ionic states [208].

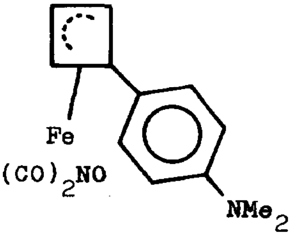
As part of a study of the acetylene metathesis reaction, bonding in the metallacyclobutadiene, $[W(C_3H_3)]$ has been compared with bonding in the η-cyclobutadiene ligand [209].

The (η-cyclobutadiene)iron cation (12.4) underwent nucleophilic addition with N,N-dimethylaniline to give the (η^3-cyclobutenyl)iron complex (12.5) with the p-$C_6H_4NMe_2$ group exo to the cyclobutenyl ring. The second order reaction involved π-complexation followed by rate-determining conversion to a σ-complex [210].

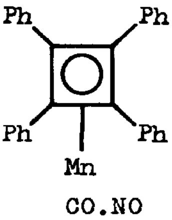
The (η^4-cyclobutadiene)manganese complex (12.6) has been prepared by the thermal reaction of diphenylacetylene with tetracarbonylnitrosylmanganese [211].



12.4



12.5

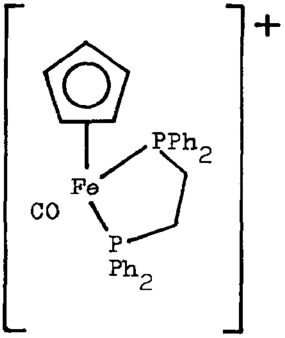


12.6

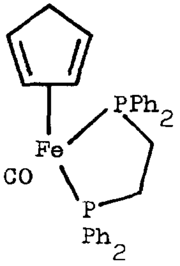
13. (Cyclic-η-diene)Fe(CO)$_3$

(i) Formation

Reduction of the (η-cyclopentadienyl)iron cation (13.1) with $LiAlH_4$ at 70 °C gave the (η-cyclopentadiene)iron complex (13.2) together with a (η-cyclopentadienyl)iron reduction product [212].

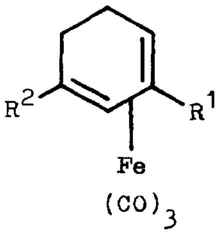


13.1

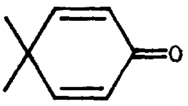


13.2

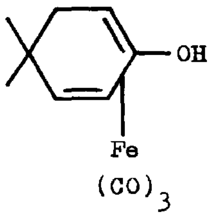
1,3-Dimethylcyclohex-2-enol and 1-butylcyclohex-2-enol were treated with pentacarbonyliron and the corresponding tricarbonyliron complexes (13.3; $R^1 = R^2 = Me$; $R^1 = H$, $R^2 = Bu$) were obtained in good yields. Treatment of these complexes with triphenylmethyl tetrafluoroborate followed by cerium(IV) ammonium nitrate produced <u>meta</u>-xylene and n-butylbenzene respectively [213].



13.3



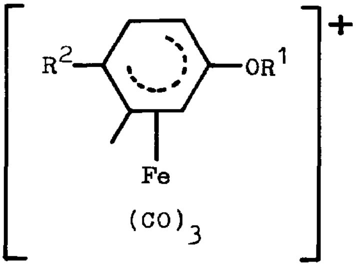
13.4



13.5

The cross-conjugated cyclohexadienone (13.4) was selectively monohydrogenated with enneacarbonyldiiron and water to form the corresponding cyclohexadienol which was trapped as the tricarbonyliron complex (13.5) and thus protected from further hydrogenation. The mechanism and stereochemistry of the reaction was discussed [214].

The 1,2-disubstituted-4-alkoxycyclohexadienylium complexes [13.6; R^1 = Me, $CHMe_2$, R^2 = Me, $(CH_2)_2CO_2Me$] have been prepared from the corresponding dienes and pentacarbonyliron in syntheses that involved several steps. The cation (13.6; R^1 = $CHMe_2$, R^2 = Me) underwent reaction regioselectively with stable enolate nucleophiles to give 3,4,4-trisubstituted cyclohexenones [215].

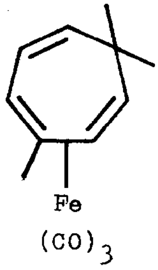


13.6

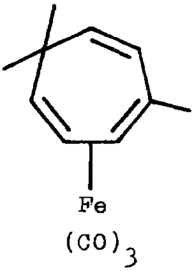
Tricarbonyl[(1-4η)-3,7,7-trimethylcycloheptatriene]iron (13.7) has been prepared by direct reaction of 3,7,7-trimethylcycloheptatriene with $Fe_2(CO)_9$. An attempt was made to prepare the isomer (13.8) by dehydration of the alcohol (13.9) but only the η-cycloheptatriene complex (13.7) was isolated. Treatment of the complex (13.7) with tetracyanoethylene produced a mixture of the 1,3- and 1,6-cycloadducts in a 4:1 ratio [216].

Heterodimetallic complexes of seven-membered cycloolefins have been prepared and characterized for example the iron-rhodium complex (13.10). Cisoid, dimetallic coordination was ascribed for the cycloheptatrienyl ligand [217].

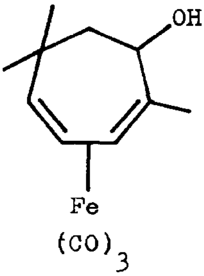
Tricarbonyl(η-tropone)iron (13.11) together with a small proportion of the binuclear complex (13.12) have been formed from enneacarbonyldiiron and tropone. The (η-heptafulvalene)-iron complex (13.13) was obtained by treatment of the (η-tropone)-iron complex (13.11) with 8-oxoheptafulvene [218].



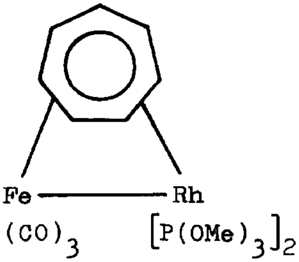
13.7



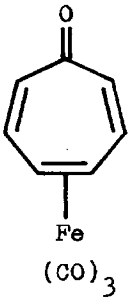
13.8



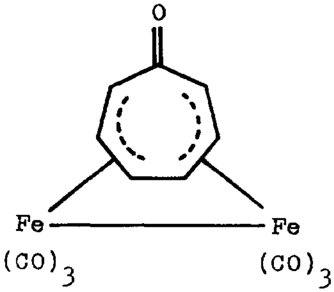
13.9



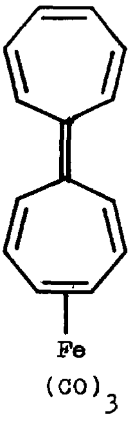
13.10



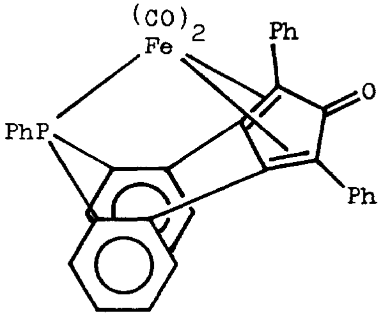
13.11



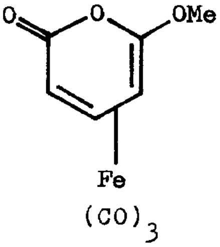
13.12



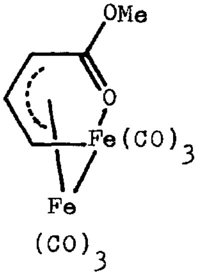
13.13



13.14



13.15



13.16

The reactions of $PhP(C_6H_4C{\equiv}CPh\text{-}\underline{o})_2$ with $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ have been investigated. Cyclicdiene-Fe complexes, for example (13.14), were isolated from these reactions [219].

The reaction of the cyclooctatetraenide dianion with iron(II) chloride and the carborane anion $Et_2C_2B_4H_5^-$ produced the 1,3,5-cyclooctatriene complex $(\eta^6\text{-}C_8H_{10})Fe[Et_2C_2B_4H_4]$ as the major product. In this complex the six metal-coordinated carbon atoms were almost coplanar and the two methylene carbon atoms were bent out of the plane away from the iron atom. NMR data indicated that the structure was nonfluxional [220].

The treatment of 2-methoxyfuran with nonacarbonyldiiron gave the 2-pyrone derivative (13.15) and the α,β-unsaturated alkylidene complex (13.16) [221].

13. (ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structure of dicarbonyl-η^4-cyclooctatetraene)triphenylphosphineiron has been determined by X-ray analysis. The geometry around the iron atom was irregular and in the η^4-cyclooctatetraene ligand the carbon-carbon bond distances for the carbon atoms coordinated to the iron atom were nearly equivalent and approximately equal to C-C single bond distances. The C5-C6 and C7-C8 bond distances were consistent with C-C double bonds [222].

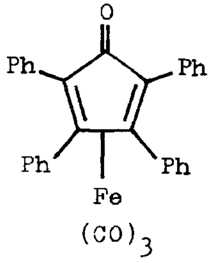
Nonparameterized molecular orbital calculations on the borabenzene anion and the sandwich complexes $(\eta\text{-}C_5H_6B)_2Fe$ and $(\eta\text{-}C_5H_6B)_2Co$ indicated that the π-electrons in the ligand were delocalized. The main bonding interactions between the transition metal and $(C_5H_6B)^-$ were similar to those in metallocenes and bis(η-arene)metal complexes, that is π-electron donation from the ring to the metal atom and δ back donation from the metal to the ring. X-Ray studies showed that in the η-borabenzene complexes the transition metal was closer to the p-carbon atom than to the boron atom. This slippage appears to maximize the π and δ overlaps and to minimize the total energy of the occupied molecular orbitals that are significantly delocalized over the metal atom and the rings [223].

Helium(I) and helium(II) photoelectron spectra of the substituted η-cycloheptatriene complexes $(\eta^4\text{-exo-7-}RC_7H_7)Fe(CO)_3$, where R = H, $SiMe_3$, $GeMe_3$, have been recorded and interpreted. The spectra indicated a rupture in conjugation between the free double bond and the coordinated butadiene moiety and a stronger iron-diene interaction in the substituted compounds relative to the unsubstituted molecule [224].

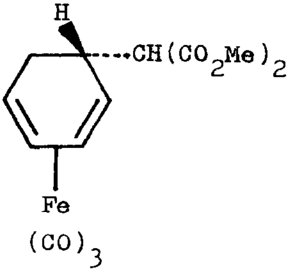
Field-desorption and electron-impact mass spectrometry have been used to investigate ferracyclic complexes of the type $Fe_x(CO)_y(C_4R_4)$, where x = 1, 2, 3 and y = 6, 8. Detailed fragmentation schemes were derived [225].

Electron-impact and field-desorption mass spectrometry has been used to obtain intense molecular ion peaks for several thermally labile ferracyclic complexes and for the (η-cyclopentadienone)iron complex (13.17) [226].

The racemic (η-cyclohexadiene)iron complex (13.18) and several ring substituted derivatives formed chelate complexes with tris[trifluoroacetyl-(+)-camphorato]europium(III). The



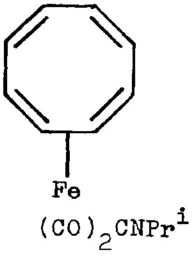
13.17



13.18

^1H NMR spectra of these complexes resolved the methoxy resonances of the two epimers. The method may be applied more generally to measurement of the enantiomeric excess in tricarbonyliron complexes [227].

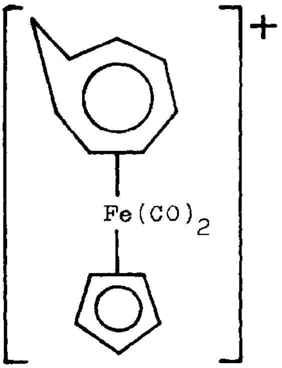
A mechanistic study on the fluxionality of the (η^4-cyclooctatetraene)iron complex (13.19) using ^{13}C NMR magnetization transfer has provided results that were consistent with the Woodward-Hoffmann mechanism but inconsistent with the least motion mechanism [228].



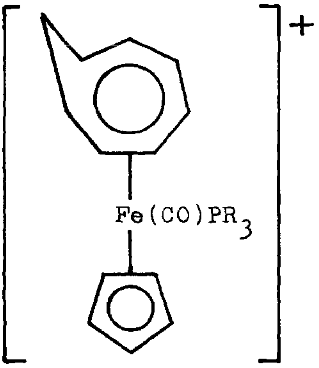
13.19

Some ^1H-^{31}P long range coupling constants have been used as criteria for the assignment of the stereochemistry of 5-substituted η^4-cyclopentadiene-iron and -ruthenium complexes [229].

The homocycloheptatrienylidene complexes (13.20 and 13.21, R = Bu, Ph) have been prepared by protonation of the corresponding η-cyclooctatetraene complexes. The ^1H and ^{13}C NMR spectra of



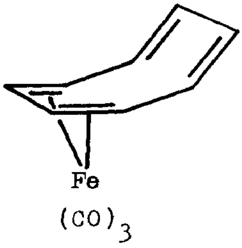
13.20



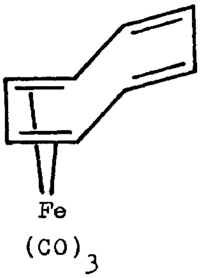
13.21

of the homocycloheptatrienylidene complexes were discussed [230].

Fourier-transform infrared spectroscopy including ^{13}CO labelling and energy-factored CO force-field fitting has been used to show that photolysis of [(tub-η^4-C_8H_8)Fe$(CO)_3$](13.22) in a methane matric at 12K gives [(chair-η^4-C_8H_8)Fe$(CO)_3$] (13.23) via an η^2-C_8H_8 intermediate [231].



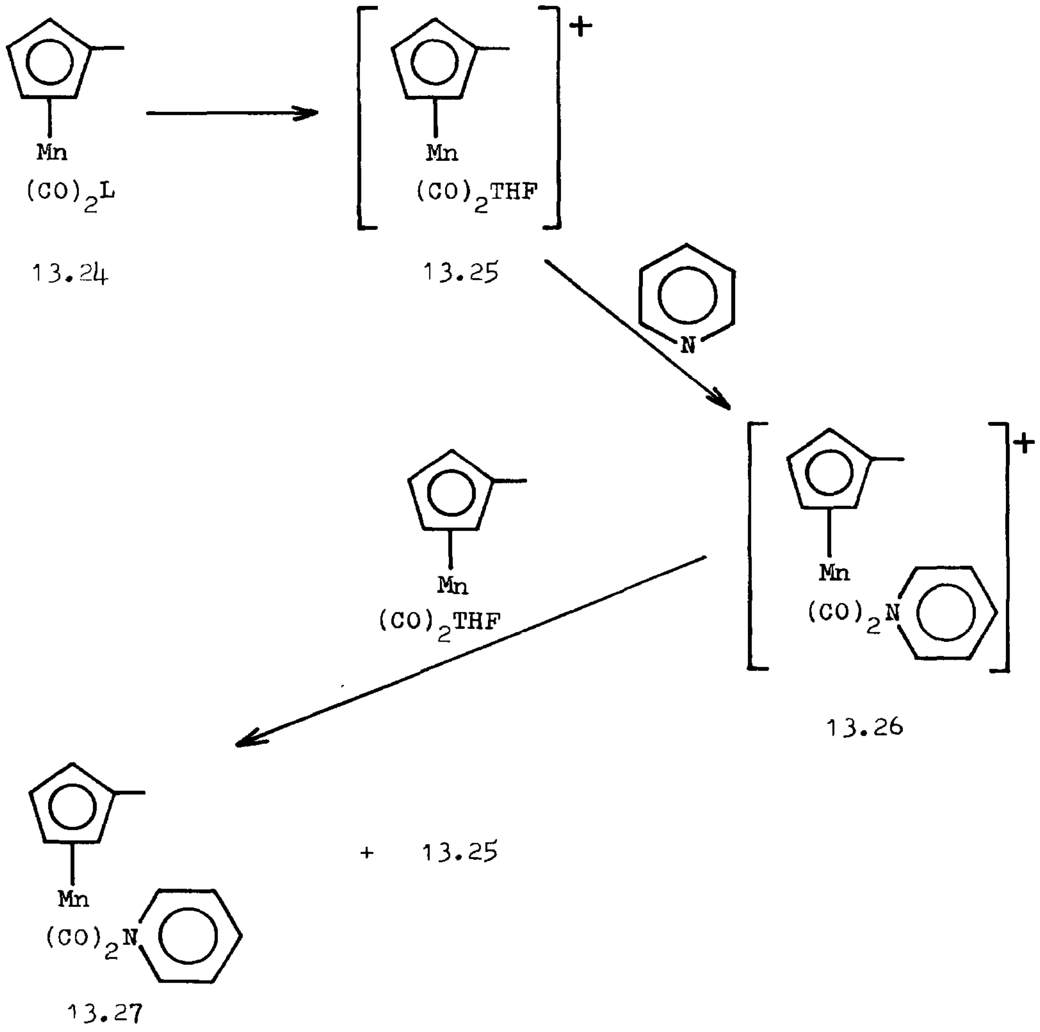
13.22



13.23

Metal carbonyl derivatives of manganese, rhenium, molybdenum and tungsten including the methylcymantrene analogues (13.24; L = THF, MeCN, pyridine) underwent facile ligand substitution by an electrode mediated process. The mechanism of the exchange has been investigated by cyclic voltammetry. Substitutions by phosphines, pyridine and isocyanides were shown to be chain reactions. The process involved, with for example the THF complex (13.24; L = THF) and pyridine, initial formation of the radical cation (13.25) which underwent rapid exchange with pyridine to give the substituted species (13.26). This was followed by electron transfer with the reactant (13.24; L = THF) to yield the product (13.27) and regenerate the radical cation (13.25) [232].

Ligand effects on the redox potentials of the complexes (13.24; L = alkyl and aromatic amines, alkyl cyanides and isocyanides, alkenes, alkyl and aryl phosphines and phosphites) have been investigated. The relationship of the redox potentials with the carbonyl force constants was evaluated [233].



The electronic structure of tricarbonyl(η-norbornadiene)-iron in the ground state and in the cationic hole-states has been investigated by a semiempirical INDO MO approach. Bonding characteristics and vertical ionizations potentials of the outer valence electrons have been determined. The correlation between calculated reorganisation energies and localization properties of the orbital wave function was in violation of Koopmans' theorem [234].

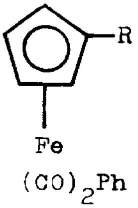
A molecular orbital study has been carried out on the cations $[\eta\text{-LFe(CO)}_3]^+$, where L = C_5H_5, C_6H_7 and C_7H_9 [235].

13. (iii) General Chemistry

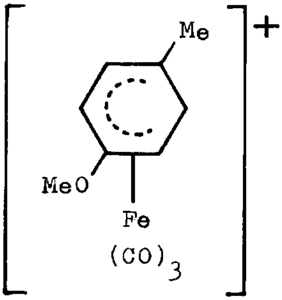
Alkyllithium reagents attacked tricarbonyl(η-cyclohexadiene)iron to form intermediates which were protonated with trifluoroacetic acid to yield 1-, 2-, or 3-substituted cyclohexenes, or mixtures of these isomers as the products. Typical substituents introduced were: CMe_2CN, CHMeCN, CMe_2CO_2Et, $CHMeCO_2Bu^t$, CH_2COCMe_2, $CHPh_2$ and CH_2SPh [236].

The η-cyclopentadienyl ligands in the complexes $(\eta\text{-}C_5H_5)\text{Fe(CO)}_2\text{Ph}$, $(\eta\text{-}C_5H_5)\text{Fe(CO)}_2\text{CH}_2\text{Ph}$ and $[(\eta\text{-}C_5H_5)\text{Fe(CO)}_2]_2$ have been metallated by n-butyllithium. For example, lithiation of $(\eta\text{-}C_5H_5)\text{Fe(CO)}_2\text{Ph}$ followed by condensation with electrophiles produced the substituted-cyclopentadienyl complexes (13.28; R = $SiMe_3$, $SnMe_3$, Me, Et) [237].

Methods for controlling the regioselectivity of carbanion addition to (η-cyclohexadienyl)iron cations such as the cation (13.29) have been examined. Attention was focussed on the effects of changing the nature of the 4-alkoxy substituent and



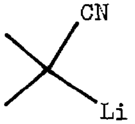
13.28



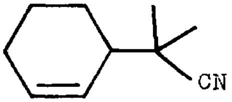
13.29

on the effect of enolate-cation association in the reagent. Several factors were identified in the control of the addition [238].

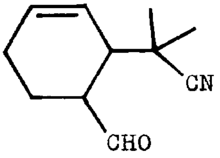
The incorporation of carbon monoxide during the addition of reactive carbanions to tricarbonyl(η-cyclohexadiene)iron complexes has been studied. When the organolithium (13.30) attacked tricarbonyl(η-cyclohexadiene)iron under argon and carbon monoxide was subsequently introduced then only the nitrile (13.31) and its isomer were isolated as the organic products. However, when carbon monoxide was present throughout the reaction then the aldehyde (13.32) was the product [239].



13.30



13.31

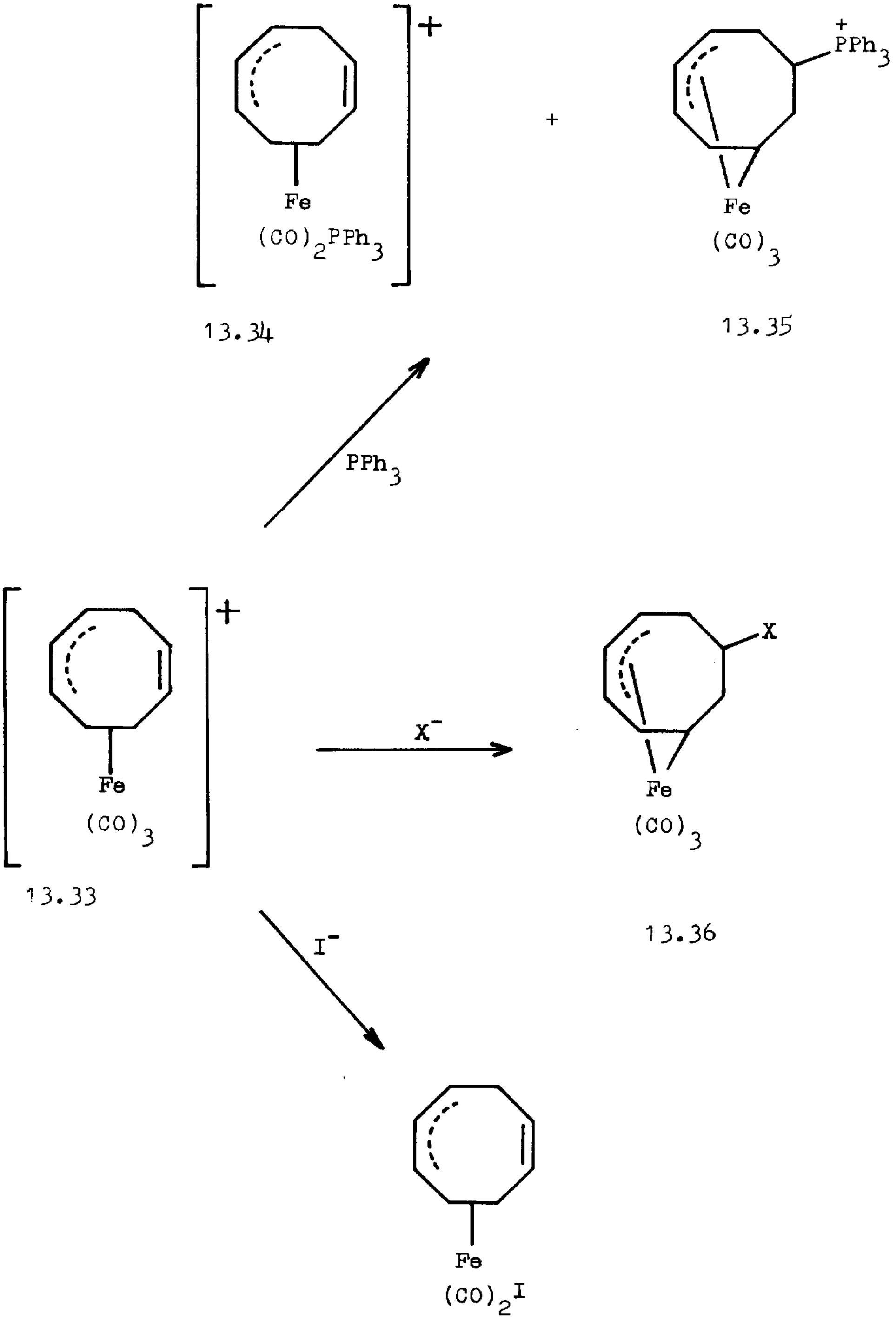


13.32

The tricarbonyl(η^5-cyclooctadienylium)iron cation (13.33) underwent attack by nucleophiles at either the organic ligand or at the metal atom. Thus triphenylphosphine gave the cations (13.34 and 13.35) while cyanide ion, methoxide ion and azide ion gave the products of ring addition (13.36; X = CN, OMe, N_3) respectively. Iodide ion afforded the product of attack at the iron atom (13.37) although evidence for ring addition was also obtained [240].

The nucleophilic attack by imidazole and pyridine on tricarbonyl(η-cyclohexadienyl)iron cations has been the subject of a kinetic investigation. Imidazole was more reactive than pyridine when the reactant was the $(C_6H_7)^+$ ion but this order was reversed when the reactant was the $[(\eta\text{-}C_6H_6OMe)Fe(CO)_3]^+$ ion [241].

The (η-cycloheptadienyl)iron cation (13.38) underwent addition with nucleophiles including lithium dimethylcuprate, dimethyl sodiomalonate, methyl sodioacetoacetate and methyl phenylsulphonyl sodioacetate to give the products of terminal addition [13.39; R = Me, $CH(CO_2Me)_2$, $CH(COMe)CO_2Me$, $CH(SO_2Ph)CO_2Me$] respectively. When methyllithium was the



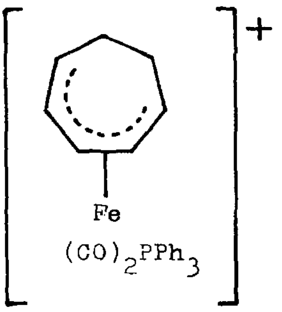
13.34

13.35

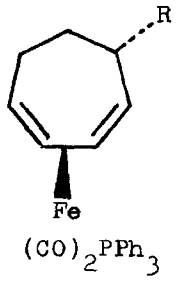
13.33

13.36

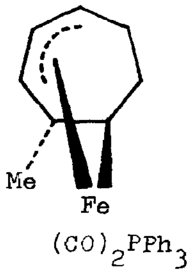
13.37



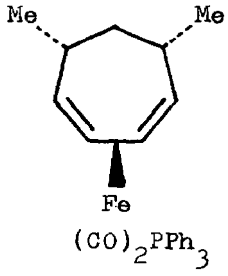
13.38



13.39



13.40

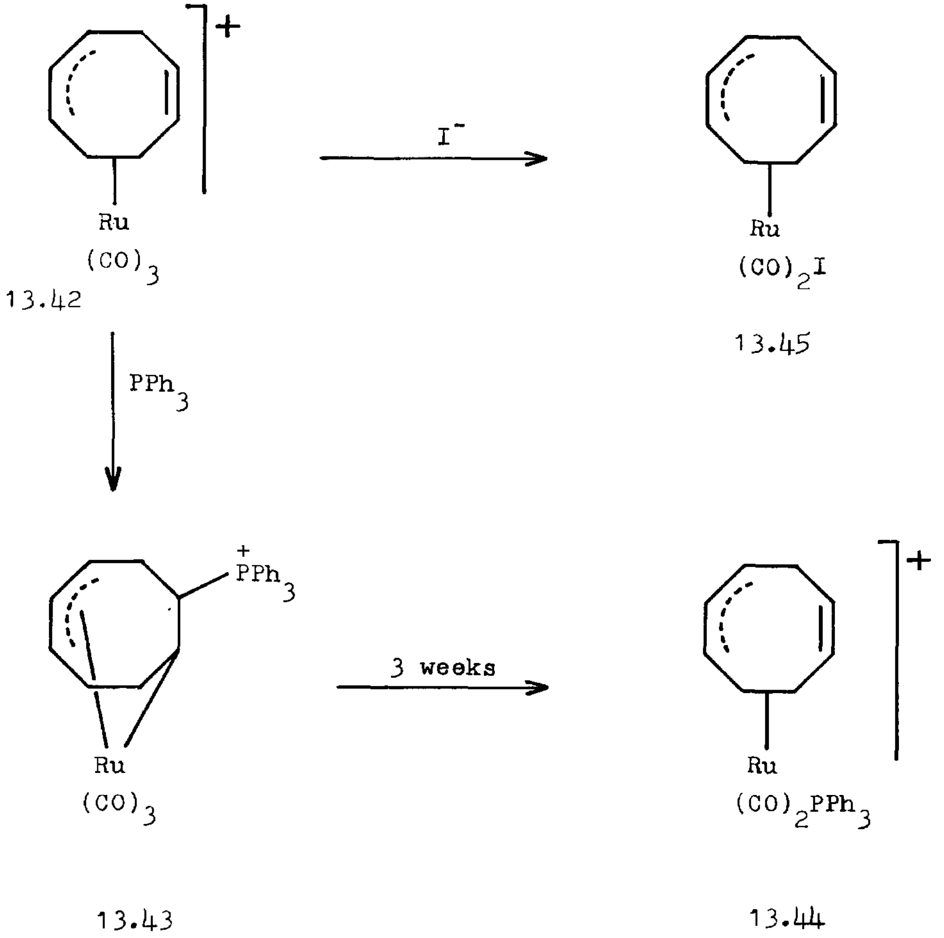


13.41

nucleophile then addition at C-2 of the dienyl ligand was observed to give the product (13.40). Hydride abstraction from the (η-methylcycloheptadiene)iron complex (13.39; R = Me) and treatment of the resulting (η-methylcycloheptadienyl)iron cation with lithium dimethylcuprate gave the symmetrical dimethyl complex (13.41). Several related reactions were reported [242].

The (η-cyclooctadienylium)ruthenium cation (13.42) underwent attack by nucleophiles at both the metal atom and the hydrocarbon ligand. Thus triphenylphosphime gave the phosphonium ion (13.43) which slowly isomerized to the cation (13.44) while iodide ion gave the dicarbonylruthenium iodide (13.45). Further transformations of these products were reported [243].

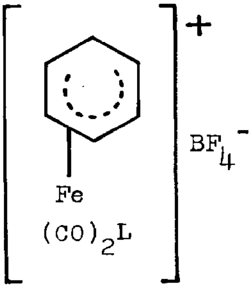
Methods for the resolution of tricarbonyl(1-5-η-cyclohexadienyl)iron salts have been reported that involve the



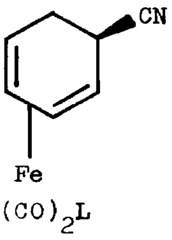
separation of diastereomeric pairs obtained by nucleophilic attack with chiral phosphines, alkoxides and amines. Nucleophilic attack by cyanide ion on the η-cyclohexadienyl salt [13.46; L = (+)-neomenthyldiphenylphosphine] gave the corresponding 5-exo-cyanocyclohexadiene complex (13.47) with significant asymmetric induction at the chiral carbon atom [244].

A kinetic study of the reaction between the tricarbonyl-(η-cyclohexadienyl)iron cation and hydroxide ion to form the (η-cyclohexadiene)iron complex (13.48) indicated that the reaction involved the carboxylic acid intermediate (13.49) [245].

Direct carbomethoxymethylation of the organoiron (13.50; R = H, OMe, X = PF_6) and organomanganese (13.51) complexes was achieved with the Reformatskii reagent, $BrZnCH_2CO_2Me$, to give the complexes (13.52 and 13.53) respectively [246].

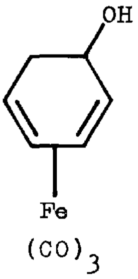


13.46

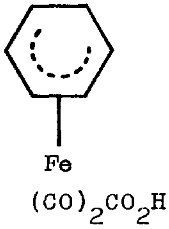


13.47

Treatment of the salts (13.50; R = OMe, X = PF_6, BF_4) with HXR [R = (-)-menthyl], followed by Huenig's base gave a diastereomeric mixture of ethers which was separated by medium pressure liquid chromatography. The ethers were converted into the diastereoisomeric salt by treatment with HBF_4 or HPF_6 [247].



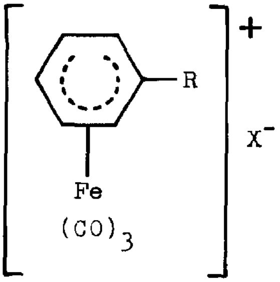
13.48



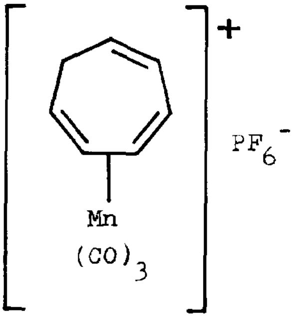
13.49

Synthetic and mechanistic studies have been carried out on the electrophilic attack of the cation (13.54) on the aryltrimethyl-silanes, -germane, -stannanes and -plumbane (13.55) M = Si, X = 4-MeO, 4-Me_2N; M = Ge, X = 4-MeO; M = Sn, X = H, 4-MeO, 4-Me_2N, 4-Me, 4-SMe, 4-F, 4-Br, 4-Cl, 3-F, 3-CF_3, M = Pb, X = H) to give the corresponding substituted dienes (13.56). The related reactions between the cation (13.54) and 2-trimethylsilylfuran, 2-trimethylsilylthiophen and CH_2=$CHCH_2SnMe_3$ were investigated [248].

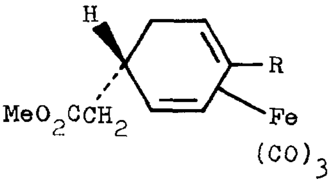
The arenediazonium salt $[N_2C_6H_4NO_2$-p$]^+BF_4^-$, attacked tricarbonyl(η-cyclooctatetraene)iron (13.57; n = 0) to form



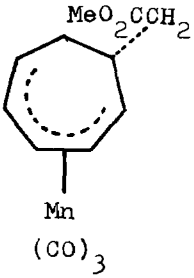
13.50



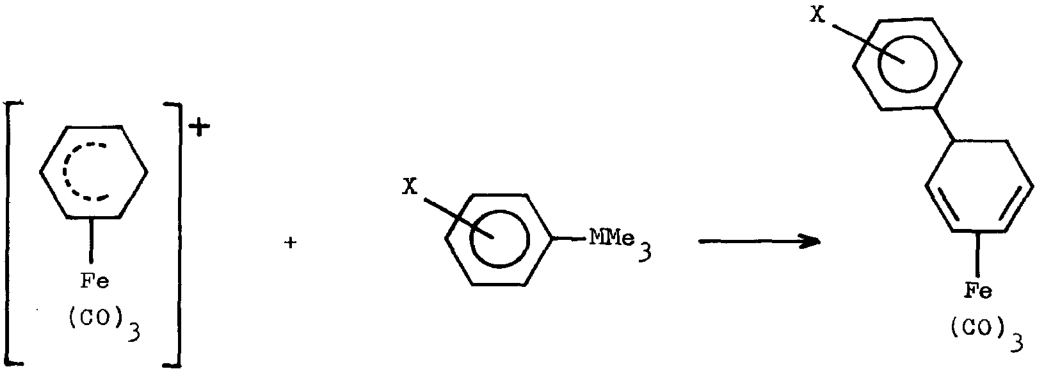
13.51



13.52



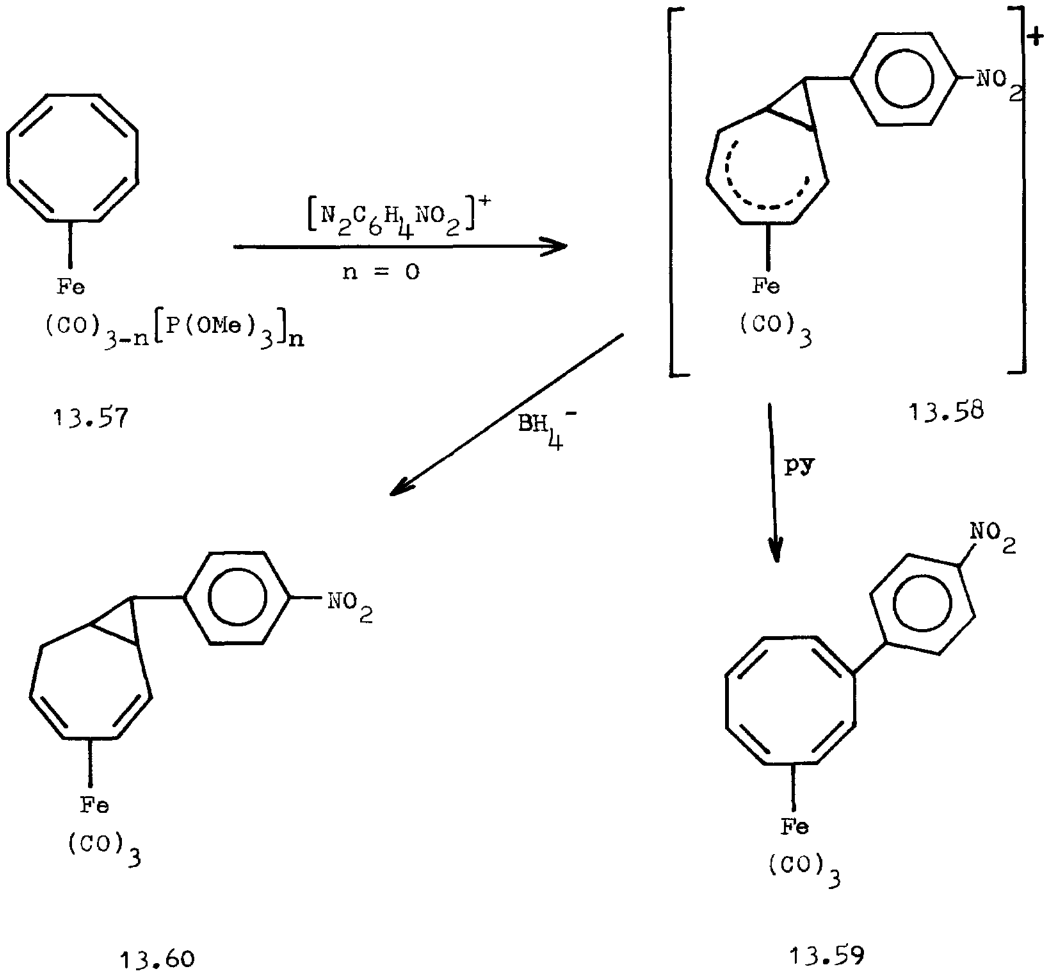
13.53



13.54

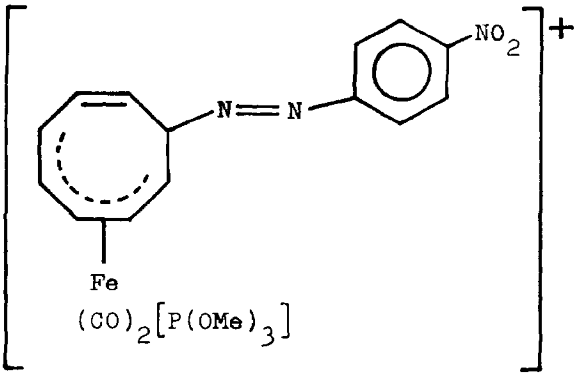
13.55

13.56

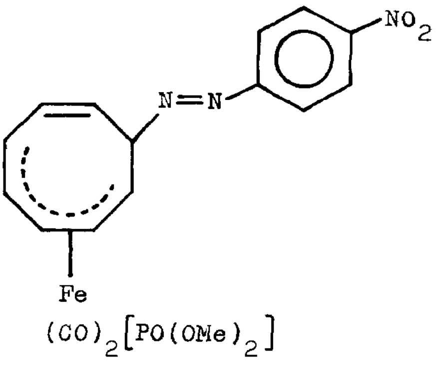


the (η-bicyclooctadienyl)iron complex (13.58) which was deprotonated to the fluxional (η-cyclooctatetraene)iron complex (13.59) with pyridine and reduced to the (η-bicyclooctadiene)-iron complex (13.60) with sodium borohydride. The complexes (13.57; n = 1, 2) were attacked by arenediazonium salts to form azo-coupled (η-cyclooctatrienyl)iron complexes which were deprotonated to give the corresponding (η-cyclooctatetraene)-iron complexes [249].

In a related study the (η-cyclooctatrienyl)iron complex (13.61) has been shown to undergo methyl halide elimination with halide ions to form the phosphonate complex (13.62). However the corresponding (η-bicyclo[5.1.0]octadienyl)iron complex underwent ring opening with halide ions to form an



13.61



13.62

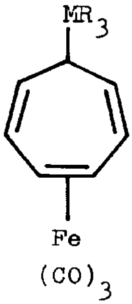
(η^3-cyclooctatrienyl)iron complex [250].

The 7-substituted (η-cycloheptatriene)iron complexes (13.63; MR_3 = $SiMe_3$, $GeMe_3$, $GePh_3$) have been prepared by treatment of the tricarbonyl(η-cycloheptatrienyl)iron with the appropriate electrophile. The exo-orientation of the 7-substituent was confirmed by X-ray crystallographic analysis of the germanium complex (13.63; MR_3 = $GePh_3$). The complexes (13.63) were fluxional and low temperature ^1H and ^{13}C NMR spectroscopy has been used to determine the energy barrier to oscillation of the tricarbonyliron group for the three complexes [251].

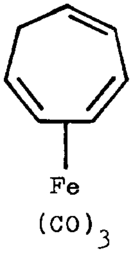
Reaction of the η^4-cycloheptatriene complex (13.64) with the diazonium salt $(p\text{-}O_2NC_6H_4N_2)^+ BF_4^-$ produced the unstable compound (13.65) which was deprotonated on alumina to give syn- and anti-isomers of the hydrazone complex (13.66) [252].

The (η-cyclohexadienyl)iron cation (13.67) has been attacked by O-silylated enolates and allyltrialkylsilanes to form (η-cyclohexadiene)iron complexes. Thus the allyl silane CH_2=$CHCH_2SiMe_3$ gave the allyl derivative (13.68). Analogies with simple (η-cyclohexadienyl)iron cations were drawn [253].

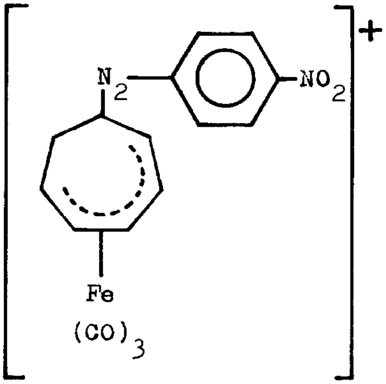
The selective, homogeneous hydrogenation of 1,3- and 1,5-cyclooctadiene to cyclooctene took place in the presence of (η^4-cycloocta-1,5-diene)(η^6-cycloocta-1,3,5-triene)ruthenium as catalyst. Isomerisation of the 1,5- to the 1,3-diene was considered to occur before hydrogenation [254].



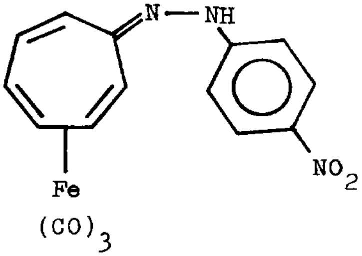
13.63



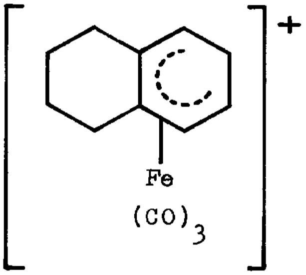
13.64



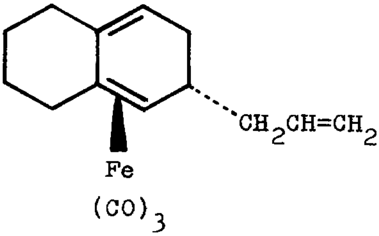
13.65



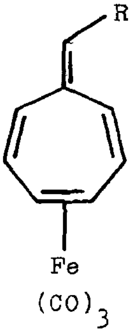
13.66



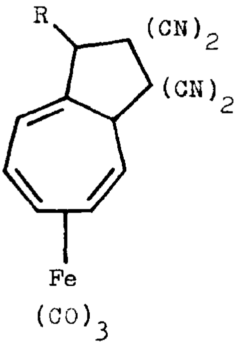
13.67



13.68



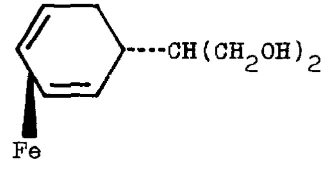
13.69



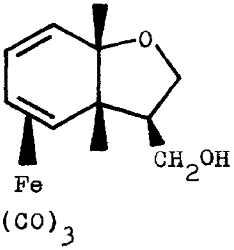
13.70

Tetracyanoethylene underwent addition to (η-7-methylenecycloheptatriene)iron complexes (13.69; R = H, OMe, Ph, 4-Me.C$_6$H$_4$) to give the 1,8-addition products (13.70; R = H, OMe, Ph, 4-Me.C$_6$H$_4$). In two cases, 1,3-addition products were implicated as intermediates [255].

Thallium(III) was effective in promoting the oxidative cyclization of suitably substituted tricarbonyl(η-cyclohexa-1,3-diene)iron complexes to form the corresponding benzofuran complexes. A 5-substituent with a β-hydroxy group was necessary for the reaction to take place. Thus the diol complex (13.71) was treated with $(CF_3CO_2)_3Tl$ in ethanol at -10 °C to form the benzofuran complex (13.72) in 54% yield. The benzofuran complexes obtained were demetalated to give the free ligands and



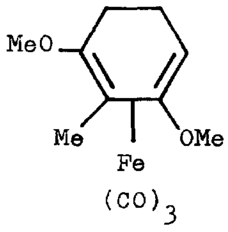
13.71



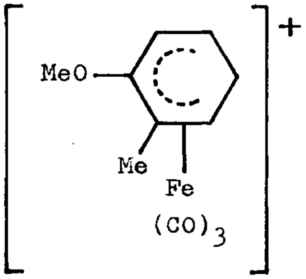
13.72

were also treated with HBF_4 in Ac_2O to give the corresponding 6-exo-substituted(η-cyclohexadienylium)iron complexes [256].

The (η-cyclohexadiene)iron complex (13.73) underwent elimination of methanol with acid to form the (η-cyclohexadienyl)iron cation (13.74) which underwent alkylation with



13.73

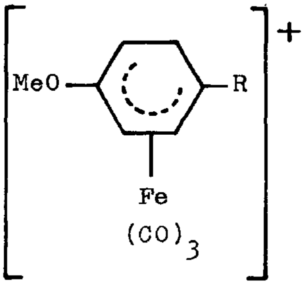


13.74

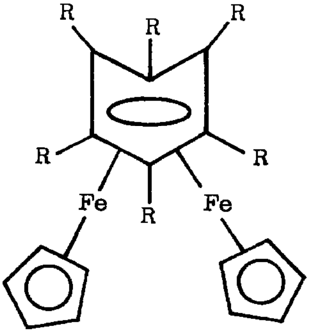
bis(1-methylethenyl)cadmium to give a mixture of two isomeric alkylation products. The regioselectivity of several related alkylations was examined and these provided stages in the synthesis of carvone, cryptomerion and bilobanone [257].

The Wittig reaction has been used to convert the optically active (η-cyclohexadienyl)iron cation (13.75; R = H) into the enantiomerically pure methyl derivative (13.75; R = Me) [258].

Reaction of (η-1,5-cyclooctadiene)(η-cyclopentadienyl)iron with 2-butyne or 3-hexyne gave the corresponding η^6-alkylbenzene



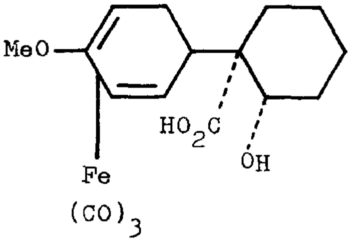
13.75



13.76

complexes (13.76; R = Me, Et) which were fluxional and displayed antiferromagnetic behaviour [259].

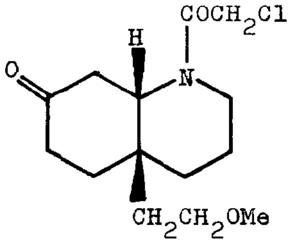
Tricarbonyliron complexes have been used as intermediates in the synthesis of steroid and aphidicolane precursors. Thus the (η-cyclohexadiene)iron complex (13.77) has been converted



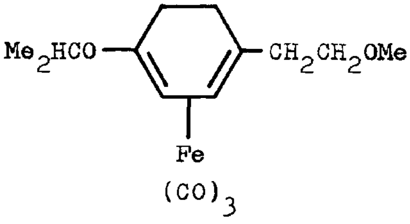
13.77

to a precursor of the tetracyclic diterpene aphidicolin in a nine-stage process [260].

The (±)-limaspermine precursor (13.78) was prepared from $4\text{-HOC}_6H_4CH_2CO_2H$ in several stages via the tricarbonyliron complex (13.79) [261].



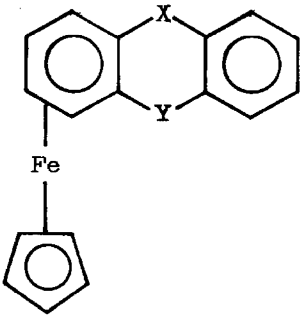
13.78



13.79

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

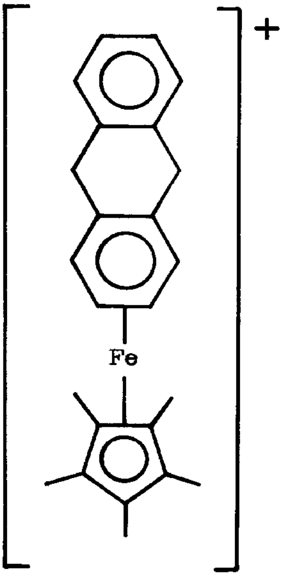
Ferrocene underwent ligand exchange with dibenzodioxin, phenoxathiin, thianthrene and phenoxazine to give (η^6-heterocycle)(η^5-cyclopentadienyl)iron cations (14.1; X = O, S, Y = O, S; X = NH, Y = O). The corresponding binuclear cations were obtained in some cases [262].



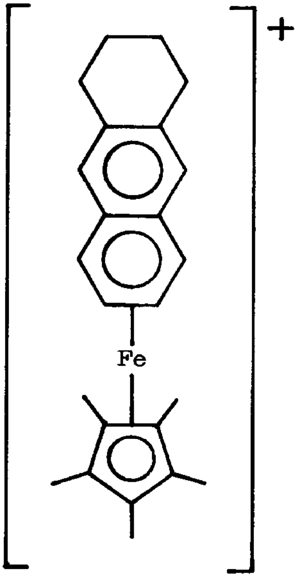
14.1

Ferrocene underwent ligand exchange with benzene, diphenyl, naphthalene and anthracene in the presence of aluminium and aluminium chloride to form the (η-arene)(η-cyclopentadienyl)iron cations which were isolated as the I_3^- and BPh_4^- salts [263].

The reaction of anthracene or 9,10-dihydroanthracene with (η-C_5Me_5)Fe(CO)$_2$Br and aluminium chloride produced a mixture (60:40) of the (η^6-9,10-dihydroanthracene) (14.2) and (η^6-1,2,3,4-tetrahydroanthracene) (14.3) complexes. Under identical reaction



14.2



14.3

conditions (η-C_5H_5)Fe(CO)$_2$Cl produced only the cation [(η-C_5H_5)-Fe(η^6-9,10-dihydroanthracene)]$^+$ [264].

The syntheses and reactions of carbenium ions stabilized with η-cyclopentadienyl-η-(3)-1,2-dicarbollyliron have been investigated [265].

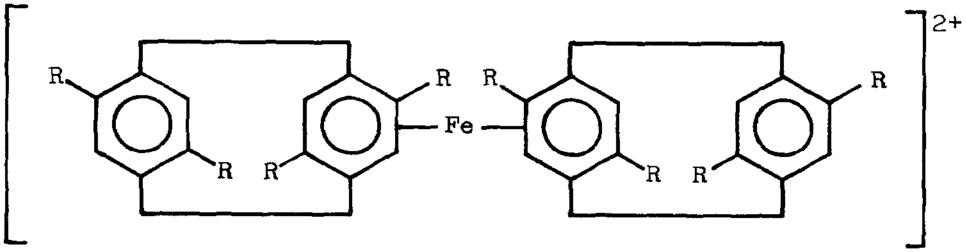
The η-[2.2]paracyclophane-iron complexes (14.4; R = H, Me) and (14.5; R = Me, H) have been prepared via a modification of Fischer-Hafner synthesis. The electron spectra of the latter complexes showed an absorption at 400-600 nm which was assigned to charge-transfer interactions between the complexed and noncomplexed aromatic rings of the paracyclophane ligands [266].

N-(Benzylidene)aniline combined with dodecacarbonyltriiron to form the $\sigma,\pi(\eta^1,\eta^6)$arene triiron complex (14.6) which was characterized by X-ray crystallography [267].

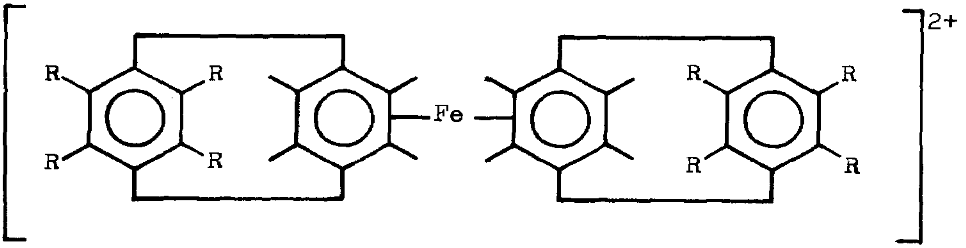
The crystal and molecular structure of [η^6-bis(2',5'-dimethyl-3',4'-cyclobutabenzo)-1,5-cyclooctadienyl](η^5-cyclopentadienyl)iron(II) hexafluorophosphate has been determined by X-ray crystallography [268].

The crystal and molecular structure of {η^6-[2_5](1,2,3,4,5)-cyclophane}(η^5-cyclopentadienyl)iron(II) hexafluorophosphate has been determined by X-ray crystallography [269].

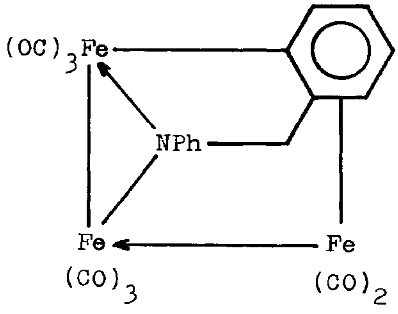
The He(I) and He(II) photoelectron spectra of the (η-arene)iron complexes (14.7; R^1 = Me, Et, R^2 = H, n = 6;



14.4

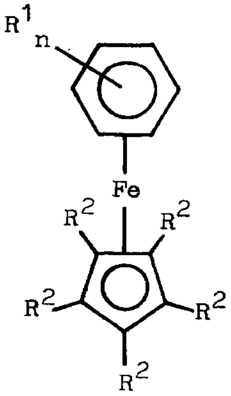


14.5

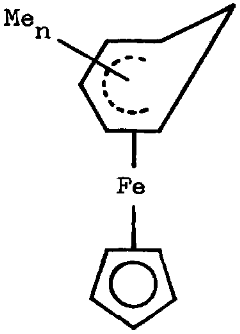


14.6

$R^1 = CMe_3$, $R^2 = H$, $n = 3$; $R^1 = R^2 = Me$, $n = 6$) have been recorded and assigned. The spectra resembled those of the corresponding isoelectronic cobaltocenes. The complex (14.7; $R^1 = R^2 = Me$, $n = 6$) had a low molecular ionization potential at 4.21 eV. The spectra of the complexes (14.7) were consistent with the optical spectra of the corresponding (η-arene)(η-cyclopentadienyl)iron cations only if a substantial origin shift was assumed. The photoelectron spectra of the (η-cyclohexadienyl)-iron complexes (14.8; n = 0, 5, 6) were recorded and assigned, they were typical of d^6 species and showed high first ionization energies [270].



14.7



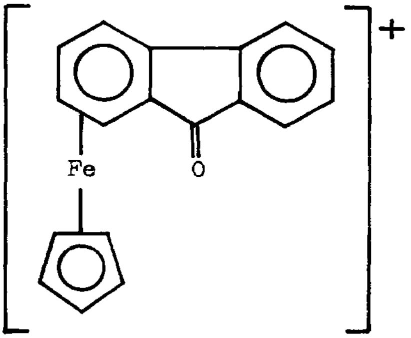
14.8

The effects of substitution of an η-arene ring for one of the η-cyclopentadienyl rings in ferrocene have been investigated. There was a reduction in the e_1(antibonding) interaction and an increase in the back-bonding e_2(weakly bonding) interaction [271].

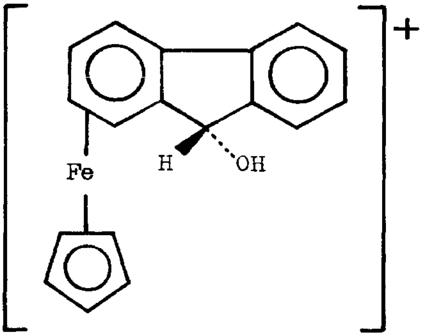
The oxidation of (η-arene)(η-cyclopentadienyl)iron cations with potassium permanganate has given (η-ketoarene)(η-cyclopentadienyl)iron cations. The methylene groups α to the complexed aromatic ring were the centres of attack by the oxidizing agent. The ketoarene complexes were reduced by sodium borohydride to give the corresponding endo-alcohols. Thus the (η-cyclopentadienyl)(η-fluorene)iron cation gave the (η-ketoarene)iron complex (14.9) which was reduced to the alcohol complex (14.10). Other ketoarene complexes prepared contained the ligands benzophenone and anthraquinone [272].

Replacement of the arene group in the complexes $[Fe(\eta^5-C_5H_5)(\eta^6-C_6H_{6-n}Me_n)]^+$ (n≤4) by three $P(OMe)_3$ ligands has been carried out under mild conditions by reductive electron transfer catalysis to produce the free arene and $\{(\eta^5-C_5H_5)Fe-[P(OMe)_3]_3\}^+$ in good yields [273].

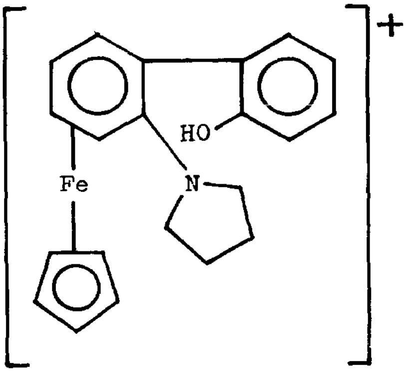
The ring opening reactions of some (η^6-heterocyclo)(η^5-cyclopentadienyl)iron hexafluorophosphates have been studied. The heterocyclic ligands investigated included those related to fluorene with an O, S or NH at C(9) and those related to 9,10-dihydroanthracene with O, S or NH at the C(9) or C(10)



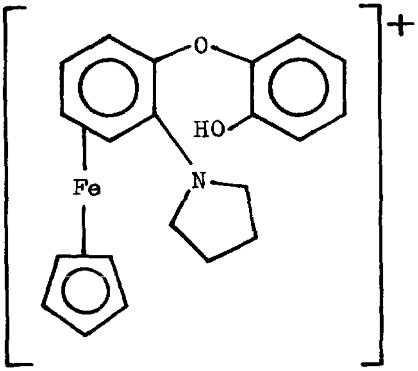
14.9



14.10



14.11

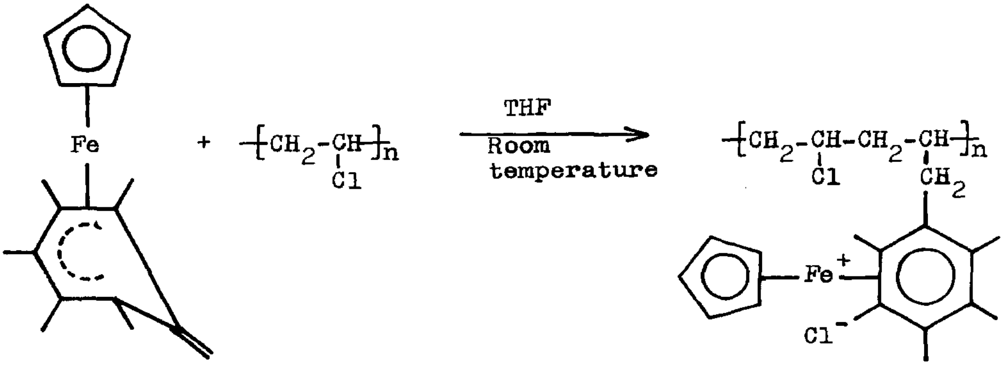


14.12

positions. For example, the reaction of pyrrolidine with the η-cyclopentadienyliron complex of dibenzofuran or dibenzodioxin gave, respectively, the η-cyclopentadienyliron of *o*-*N*-pyrrolidinyl-*o*$'$-hydroxybiphenyl (14.11) or *o*-*N*-pyrrolidinyl-*o*$'$-hydroxydiphenylether (14.12) [274].

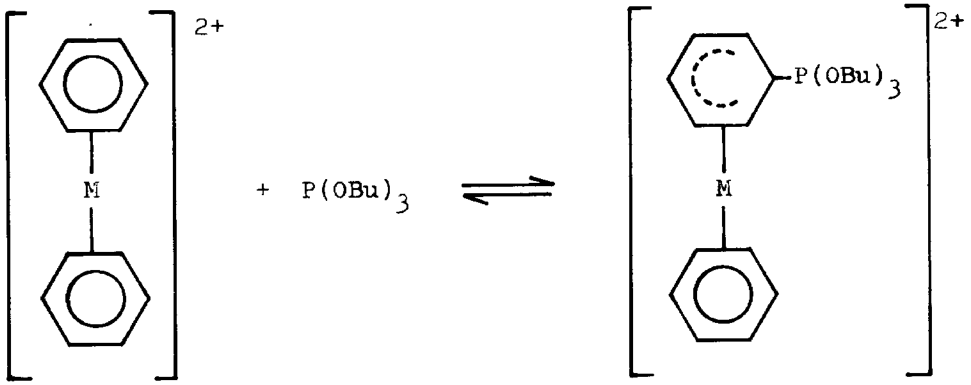
Treatment of poly(vinylchloride) with the iron complex (14.13) produced a polymer (14.14) with pendant $[(\eta^5\text{-}C_5H_5)Fe\text{-}(\eta^6\text{-}C_6Me_5CH_2\text{-})]^+Cl^-$ groups [275].

The reactions of tri-n-butylphosphite with the cations (14.15; M = Fe, Ru, Os) and tributylphosphine with the cations (14.16; R = H, Me, M = Mn, Re) to give the products of nucleophilic addition (14.17 and 14.18) respectively have been

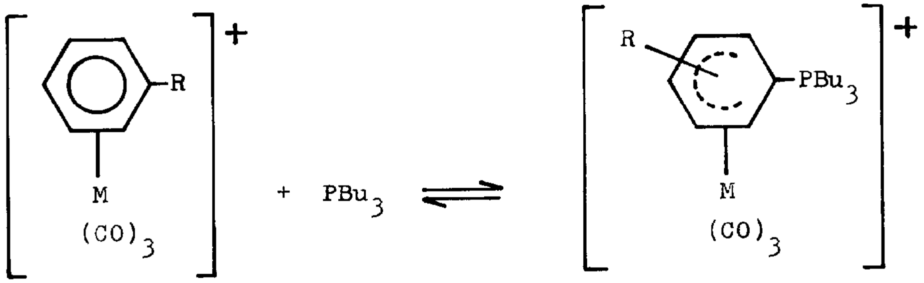


14.13

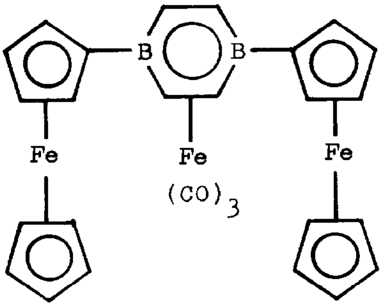
14.14



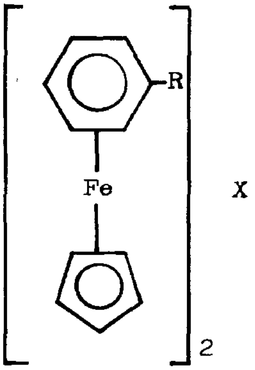
14.15 14.17



14.16 14.18



14.19



14.20

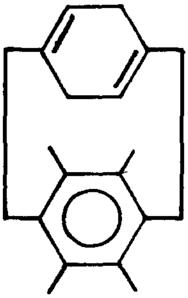
studied. The kinetic data obtained suggested that π-bonding was important in determining the dependence of the coordinated ring electrophilicity on the metal within a given triad. It was shown that phosphites as compared to phosphines were more reactive towards a metal centred electrophile than towards a carbon electrophile [276].

Iron atoms have been cocondensed with toluene and the carborane 2,3-$Et_2C_2B_4H_6$ at low temperatures to form the (η-arene)-ferracarborane complex (η^6-PhMe)Fe-2,3-$Et_2C_2B_4H_4$. The crystal and molecular structure of this complex has been determined by X-ray crystallography and the expected sandwich structure confirmed [277].

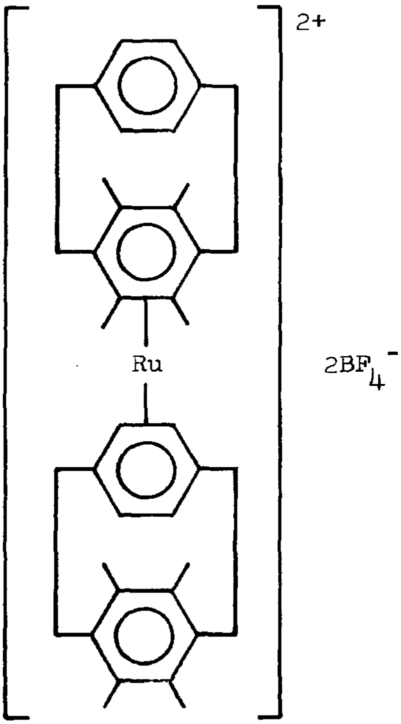
The (η^6-cyclooctatriene)ferracarborane complex, (η-C_8H_{10})-Fe($Et_2C_2B_4H_4$), underwent ligand exchange with benzene and other arenes in the presence of aluminium chloride to form the corresponding complexes, (η^6-arene)Fe($Et_2C_2B_4H_4$) where arene = benzene, 1,3,5-trimethylbenzene and hexamethylbenzene. The products were air-stable crystalline solids [278].

Six (η-1,4-dibora-2,5-cyclohexadiene) transition metal complexes including the tricarbonyliron complex (14.19) have been prepared and characterized. The 1,4-diborabenzene moiety behaved as a strongly back-bonding ligand in each case [279].

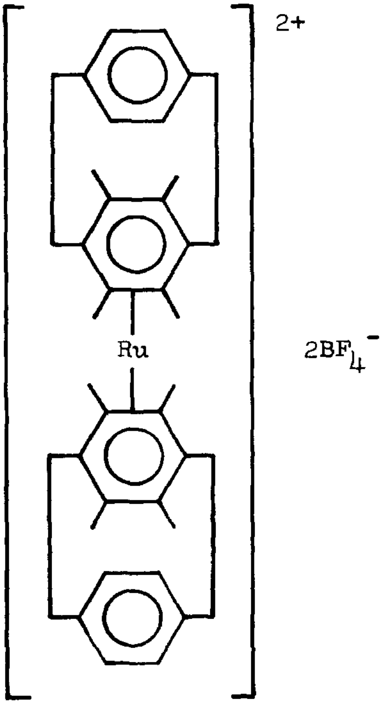
Salts have been formed by treatment of (η-arene)(η-cyclopentadienyl)iron cations with borane anions. Among the derivatives prepared were the salts (14.20; R = H, Me, Et, Pr, $CHMe_2$, CMe_3; X = $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$). The thermal stabilities



14.21



14.22

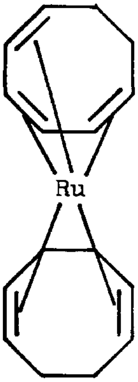


14.23

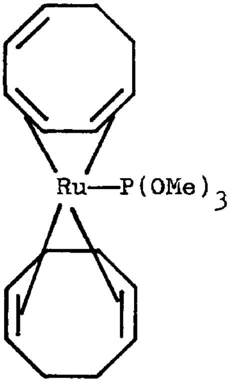
of the salts (14.20) were examined by differential thermogravimetric analysis and were found to depend on the nature of the substituent R and the borane anion [280].

The Bennett procedure has been used to convert the dihydroarene (14.21) into the ruthenium complexes (14.22 and 14.23) [281].

Treatment of the ruthenium complex (14.24) with trimethylphosphite produced (1—2:5—6-η-cycloocta-1,5-diene)(1—4-η-cycloocta-1,3,5-triene)(trimethylphosphite)ruthenium (14.25). The structure of this latter complex was determined by X-ray analysis [282].



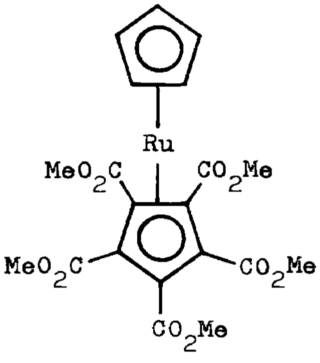
14.24



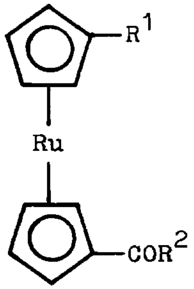
14.25

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

Reaction of the salt $Tl[C_5(CO_2Me)_5]$ with $[RuCl(PPh_3)_2\text{-}(\eta\text{-}C_5H_5)]$ in air afforded the substituted ruthenocene (15.1). The structure of this latter complex was determined by X-ray analysis and it was shown to be an eclipsed sandwich molecule. The $C_5(CO_2Me)_5$ ligand was displaced by tertiary phosphines and



15.1



15.2

this reaction formed the basis of a process for the oxidation of triphenylphosphine catalysed by the metallocene [283].

A force field study of ferrocene, ruthenocene and the corresponding metallocene dimers has enabled the intermolecular strain energy in the crystalline solids to be calculated as a function of the relative orientation of cyclopentadienyl rings in individual molecules. Strain energy minima corresponded to observed conformations when it was assumed that the relative orientation in neighbouring molecules changed with that of the reference molecule [284].

The crystal and molecular structure of diruthenocene has been determined by X-ray crystallography. The mutual orientation of cyclopentadienyl rings within a ruthenocenyl group depended on intermolecular interactions and was not conformationally important [285].

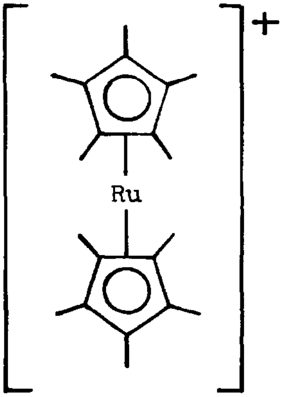
The mass spectra of the ruthenocene derivatives (15.2; R^1 = H, R^2 = Me, Ph; R^1 = COMe, R^2 = Me) have been recorded and compared with those of the ferrocene analogues. The higher metal-ligand bond strengths in the ruthenocene compounds was reflected in more extensive fragmentation of the metal-bound ligands as compared with the corresponding ferrocene compounds [286].

^{99}Ru NMR spectroscopy has been evaluated as a structural and analytical technique. Ruthenocene was included among the compounds discussed [287].

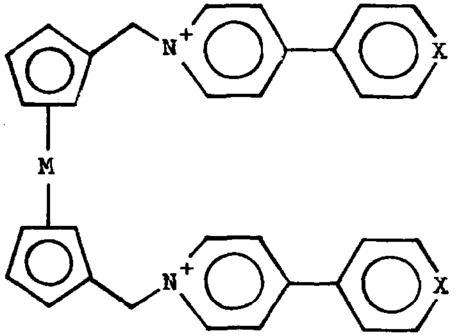
Proton spin-lattice relaxation time and DTA measurements have confirmed a low temperature phase for azaferrocene stable below 281 ^{o}K. A phase transition at 392 ^{o}K has been identified for ruthenocene [288].

The infinite-dilution molar Kerr constants, field-gradient birefringence constants and Cotton-Mouton constants have been measured for ferrocene and ruthenocene dissolved in cyclohexane. These observations produced the effective polarizability anisotropy, the electric quadrupole moment and the magnetic anisotropy of each molecule. It was concluded that ferrocene and ruthenocene were more polarizable in directions parallel, rather than perpendicular, to the ligand-metal-ligand axes. The molecular quadrupole moments were negative in sign and this established that, relative to the free atoms, the bonding results in transfer of electronic charge from the metal atom toward and onto the η-cyclopentadienyl rings. In the same paper a high yield preparation of ruthenocene was reported in which dichlorotetrakis(dimethylsulphoxide)ruthenium(II) was treated with sodium cyclopentadienide [289].

The electrochemical oxidation of decamethylruthenocene has been investigated by cyclic voltammetry, differential pulse polarography and ESR spectroscopy. Oxidation to the monocation (15.3) was observed [290].



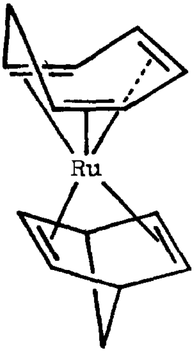
15.3



15.4

Viologen-metallocenes (15.4; X = N, N^+Me; M = Fe, Ru) have been prepared by treatment of the 1,1'-bis(chloromethyl)-metallocene with the appropriate 4,4'-bipyridine [291].

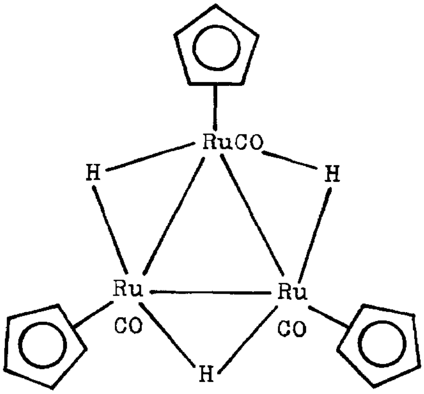
Reduction of dichloro(η^4-norbornadiene)dipyridineruthenium (II) followed by the addition of 1,3,5-cycloheptatriene produced



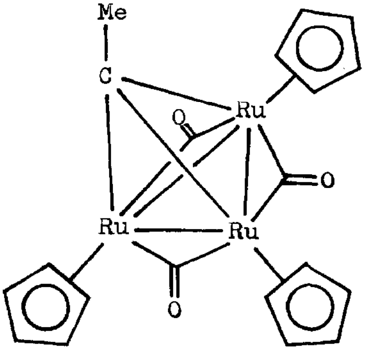
15.5

the ruthenium(0) complex (15.5). The latter complex underwent reaction with acetylene to give (η^{6}-bicyclo[4.2.1]nona-2,4,7-triene)(η^{4}-norbornadiene)ruthenium(0) by formal $[\pi 6_{s} + \pi 2_{s}]$-cycloaddition [292].

The blue, air-stable, fluxional triruthenium cluster complex (15.6) has been characterized by X-ray spectroscopy. It underwent addition with unsaturated hydrocarbons. Thus with ethylene the ethylidyne complex (15.7) was obtained which could provide an entry into the organic chemistry of triruthenium clusters [293].



15.6

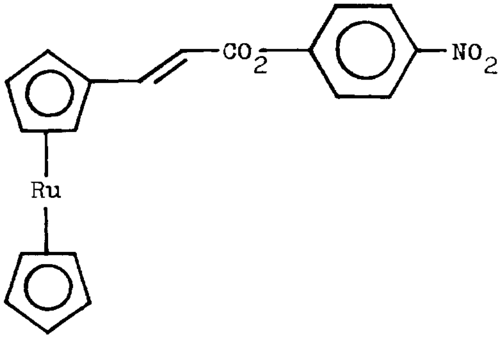


15.7

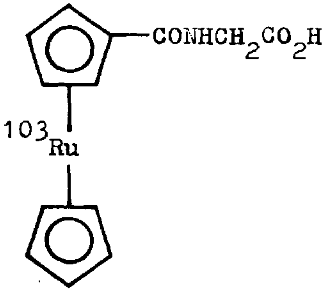
The p-nitrophenyl ester of (E)-ruthenoceneacrylic acid (15.8) has been used to acylate β-cyclodextrin, it was found to be less efficient than the corresponding ferrocene [294].

The organ distribution in rats and mice of ruthenocenoylglycine(15.9) labelled with ^{103}Ru has been investigated. High kidney accumulation was observed followed by rapid renal excretion [295].

The tissue distribution of pharmaceuticals and radiopharmaceuticals was altered appreciably by the addition of steroid hormones. Thus the tendency of acetylruthenocene to concentrate in the adrenal of female mice and the kidney in male rate was altered by the addition of testosterone or estradiol [296].

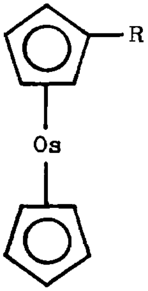


15.8



15.9

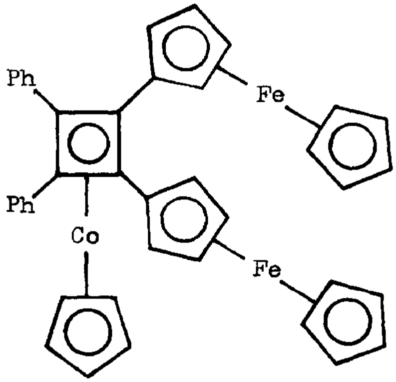
Several labelled osmocenes (15.10; R = H, COMe, CO_2Et, $CONH_2$, COCH=CHPh, CH=CHCOPh) have been obtained by ligand exchange between $^{191}OsCl_4$ and the appropriate ferrocene in the presence of HCl. The labelled osmocenes were injected into mice and the organ distributions compared with those of labelled ruthenocenes, $^{103}RuCl_3$ and $^{191}OsCl_4$ [297].



15.10

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

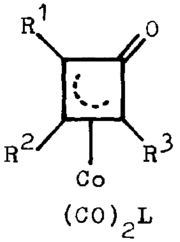
The cis- (16.1) and trans-(η-cyclobutadiene)cobalt complexes underwent two successive electrochemical oxidations at very similar potentials in the range 0.30-0.55 V. These corresponded to the Fe(II)-Fe(III) couple in the ferrocenyl group.



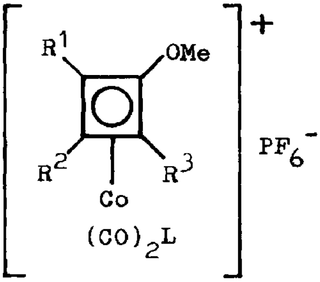
16.1

The mono- and di-cations of each isomer showed a band in the near IR spectrum assigned to intervalent transfer of class II mixed-valence ions. The spectra were interpreted in terms of Fe(II)-Fe(III) interaction for the monocations and in terms of Co(I)-Fe(III) interaction for the dications [298].

The η^3-cyclobutenonyl compounds (16.2; $R^1 = R^2 = Ph$, $R^3 = H$, L = CO, PPh_3, PPh_2Me, $PPhMe_2$, PEt_3; $R^1 = R^2 = Et$, $R^3 = H$, L = CO, PPh_3; $R^1 = Me$, $R^2 = Ph$, $R^3 = H$, L = CO; $R^1 = Ph$, $R^2 = Me$, $R^3 = H$, L = CO, PPh_3; $R^1 = Ph$, $R^2 = H$, $R^3 = Me$, L = CO; R^1 = t-Bu, $R^2 = R^3 = H$, L = CO, PPh_3; $R^1 = R^3 = H$, R^2 = t-Bu, L = $PPhMe_2$; R^1 = n-Bu, $R^2 = R^3 = H$, L = CO) were quantitively transformed into the corresponding cationic η^4-cyclobutadiene complexes (16.3) by treatment with Me_3OPF_6. The structure of the complex (16.3; $R^1 = Ph$, $R^2 = Me$, $R^3 = H$, L = CO) was determined by X-ray



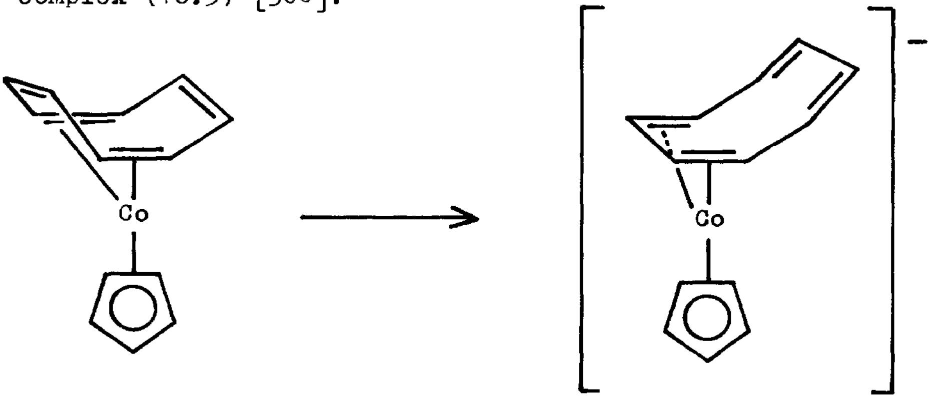
16.2



16.3

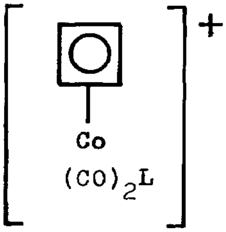
analysis. The η-cyclobutadiene ring was planar, and the substituent atoms on the ring were pointing away from the metal. The carbon-carbon bond distances within the ring were unequal as were the cobalt-carbon distances [299].

The (η^4-1,5-cyclooctatetraene)cobalt complex (16.4) has been shown by fast Fourier transform faradaic admittance measurements to undergo isomerization followed by electron transfer in the fast irreversible reduction to the isomerized complex (16.5) [300].



16.4 16.5

Oxidation of the cobalt cyclobutadiene complex, (η-C_4H_4)-$Co_2(CO)_6$, with triphenylmethyl tetrafluoroborate gave the mononuclear (η-cyclobutadiene)cobalt cation (16.6; L = CO). The triphenylphosphine derivative (16.6; L = PPh_3) was obtained by treatment of the iodide, (η-C_4H_4)Co(CO)$_2$I, with silver



16.6

hexafluorophosphate and triphenylphosphine. The (η-tetramethylcyclobutadiene)cobalt complex, $[(\eta\text{-}Me_4C_4)Co(CO)_3]^+$, has been formed by direct reaction between the appropriate cyclobutenyl ligand with octacarbonyldicobalt [301].

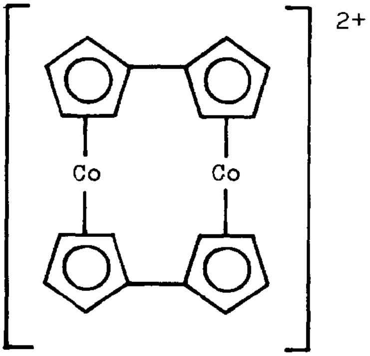
17. $(\eta\text{-}C_5H_5)_2Co$ and $[(\eta\text{-}C_5H_5)_2Co]^+$

Sheats and coworkers have reviewed the chemistry and properties of the cobaltocenium ion [302].

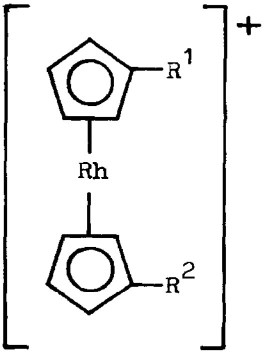
A mixture of magnesium powder and anthracene has been used to catalyze the complexation of dienes with transition metals. Cobaltocene and ferrocene were among the thirty-five complexes prepared and some of these products were used as cyclization catalysts [303].

The 1,1'-bicobaltocenium dication (17.1) has been used to prepare the 1,1'-bicobaltocenium salts of tetracyano-p-quinodimethane (TCNQ), tetrabromoquinone and tetrabromodiphenoquinone. The structure of [1,1'-bicobaltocenium]$[TCNQ]_3$ was determined by X-ray analysis. The bicobaltocenium salts were diamagnetic and the electrical conductivities of pressed pellet samples ranged from 3.0×10^{-2} to 3.0×10^{-4} ohm^{-1} cm^{-1} [304].

Methylrhodocenium and 1,1'-dimethylrhodocenium salts have been prepared by the reaction of cyclopentadienylthallium and methylcyclopentadienylthallium with rhodium(III) chloride. Oxidation of these methylrhodocenium salts with potassium permanganate produced the corresponding carboxylic acids (17.2; $R^1 = H$, $R^2 = CO_2H$; $R^1 = R^2 = CO_2H$). The 1,1'-dicarboxylic acid was converted to the corresponding acid chloride and this was



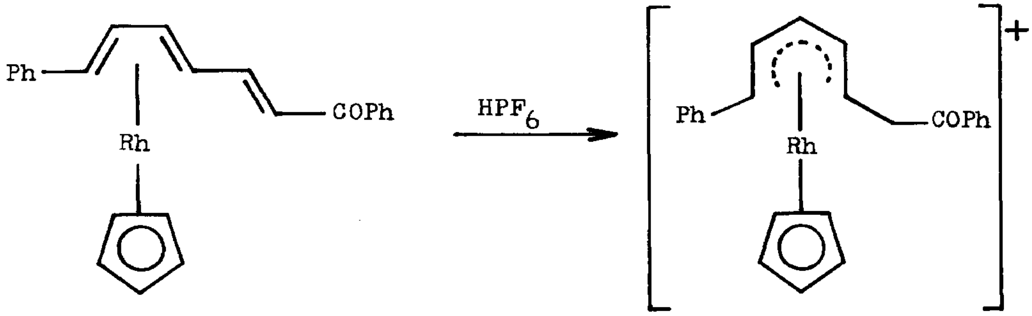
17.1



17.2

used to prepare the ester (17.2; $R^1 = R^2 = CO_2Me$) and the amine (17.2; $R^1 = R^2 = NH_2$) [305].

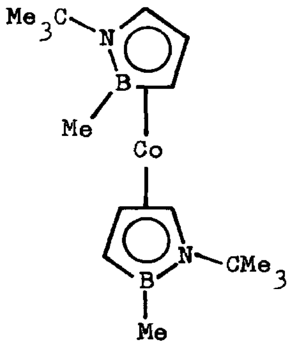
The (η-cyclopentadienyl)rhodium complex (17.3) has been protonated with HPF_6 to form the (η-cyclopentadienyl)(η-pentadienyl)rhodium cation (17.4) [306].



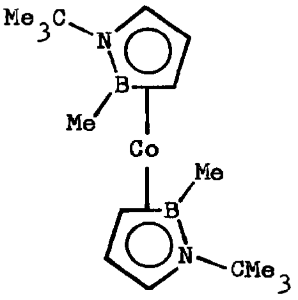
17.3 17.4

The reaction of cobaltocene with cyclopentadiene and air produced (η-cyclopentadienyl)[1-4-η-(5-*exo*-cyclopentadienyl-1,3-cyclopentadiene)]cobalt(I). The structure of this complex was determined by X-ray analysis [307].

The crystal and molecular structures of two isomers of bis(1-t-butyl-2-methyl-η-1,2-azaborolinyl)cobalt (17.5 and 17.6) have been determined by X-ray analysis. Isomer (17.5) showed a



17.5



17.6

clockwise and isomer (17.6) an anti-clockwise conformation of the azäborolinyl rings. In both compounds the rings were staggered with opposite positions of the CMe_3 groups. The rings were tilted so that the three ring carbon atoms were closer to the Co than the BN groups [308].

Michalowicz and co-workers have carried out an EXAFS study of the disorder effect induced in layered manganese phosphide sulphide ($MnPS_3$) by intercalation of the cobaltocenium ion and other cations [309].

The infrared and Raman spectra of the lamellar MPS_3 or $M_2P_2S_6$ compounds, where M = Fe, Co, Ni, $In_{2/3}$, and their intercalates with the cobaltocenium cation have been recorded and interpreted [310].

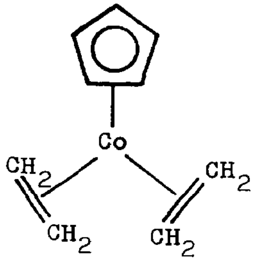
The magnetic susceptibilities of 1,1',2,2'-tetramethylcobaltocene and 1,1'-diethylcobaltocene have been studied at 0.99-296 K. Similar data was produced by a calculation of the dynamic Jahn-Teller effect for the $^2E_{1g}(a_{1g}{}^2e_{2g}{}^4e_{1g})$ ground state of D_{5d} symmetry [311].

Vanadium pentoxide gels have been used for the intercalation of several compounds including cobaltocene. The intercalation compounds were investigated by electron microscopy and X-ray diffraction methods [312].

The vaporization of cobaltocene and vanadocene has been studied by a static method using a membrane zero-manometer [313].

The treatment of cobaltocene with potassium and ethylene produced the bis(η-ethylene)complex (17.7) [314].

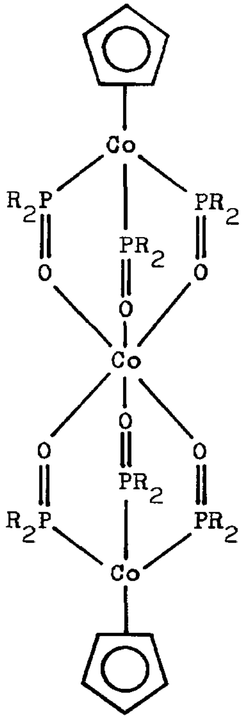
Treatment of cobaltocene and nickelocene with secondary phosphine oxides produced the corresponding phosphinito complexes (17.8; R = Et, CH_2Ph, Ph, p-ClC_6H_4) and (17.9; R = Et, CH_2Ph)



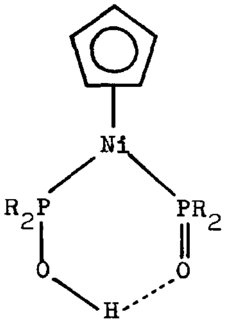
17.7

respectively. The dimeric nickel compounds (17.10; R = Me, cyclo-C_6H_{11}, Ph, OMe) were produced as the primary products in the reaction of nickelocene with the corresponding phosphine sulphides $HP(S)R_2$ [315].

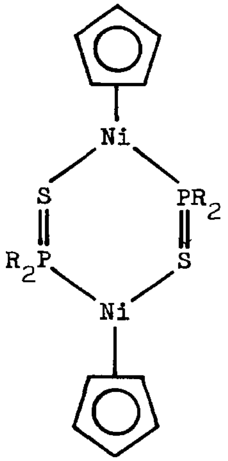
Oligophenylenes were prepared by the copolycyclotrimerization of diethynyl compounds in the presence of cobaltocene as the catalyst [316].



17.8



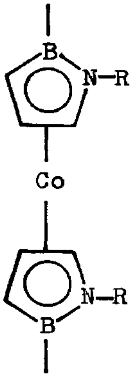
17.9



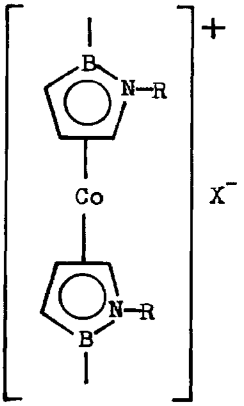
17.10

The role of η-cyclopentadienyl-transition metal compounds in reducing smoke and other volatile materials evolved in the combustion of poly(vinyl chloride) has been investigated. Nickelocene and dichlorobis(η-cyclopentadienyl)titanium were more effective than ferrocene while cobaltocenium sulphate was ineffective [317].

Oxidation of the paramagnetic cobalt complexes (17.11; R = $SiMe_3$, Me, CMe_3) with iodine vapour produced the corresponding diamagnetic cobaltocenium analogues (17.12; $X^- = I_3^-$, I_5^-). Oxidation with ferrocenium hexafluorophosphate produced the salts (17.12; $X^- = PF_6^-$, R = Me, CMe_3). The structure of the complex (17.11; R = Me) was determined by X-ray analysis [318].



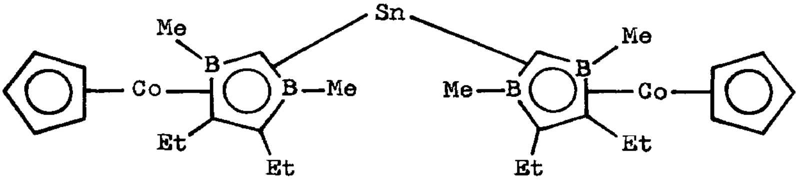
17.11



17.12

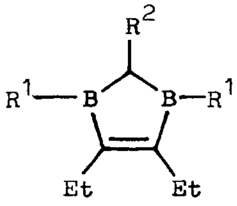
Reaction of the anion [(η-cyclopentadienyl)(η-4,5-diethyl-1,3-dimethyl-1,3-diborolenyl)cobalt] with tin(II) chloride produced the first tetradecker sandwich complex (17.13) containing a non-transition metal [319].

Reaction of the cobalt complex (η-C_5H_5)Co$(CH_2{=}CH_2)_2$ with the cyclic boranes (17.14; R^1 = Et, R^2 = Me; R^1 = Me, R^2 = H)

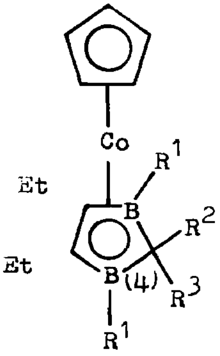


17.13

produced the corresponding diborolene complexes (17.15; R^3 = H). The crystal structure of the complex (17.15; R^1 = Et, R^2 = Me, R^3 = H) was determined by X-ray analysis. The sandwich structure was confirmed and carbon(4) was pentacoordinate [320].



17.14

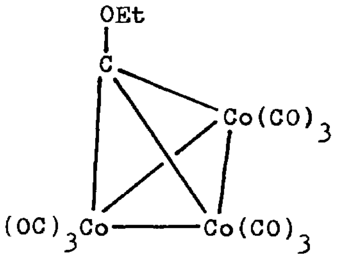


17.15

18. Cobalt-carbon Cluster Compounds

The ethoxy substituted cobalt cluster complex (18.1) has been prepared by attack of phenyllithium on octacarbonyldicobalt and subsequent treatment with Et_3OBF_4. The crystal and molecular structure of the cluster complex (18.1) has been determined by X-ray crystallography [321].

The bridged vinyl complex $FeCo(CO)_7(\mu\text{-}CHCH_2)$ underwent redistribution on heating in boiling hexane to give three



18.1

trinuclear cluster complexes including methylmethylidynetricobaltnonacarbonyl [322].

The cluster compounds $RCCo_2M(\eta\text{-}C_5H_5)(CO)_8$ (R = Me, Ph, H, M = Cr, Mo, W) and $RCCo_2Fe(\eta\text{-}C_5H_5)(CO)_7$ have been prepared by electron transfer reactions between metal carbonyl clusters and metal centred electrophiles. For example, the reaction of $PhCCo_3(CO)_9$ with $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ rapidly produced $PhCCo_2Mo(\eta\text{-}C_5H_5)(CO)_8$ in good yield [323].

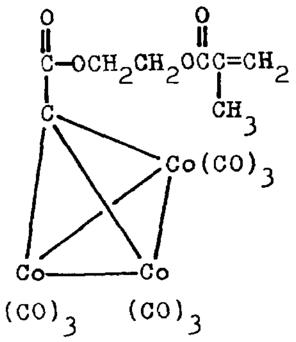
The ferrocene-tricobalt cluster compounds $(\eta\text{-}C_5H_4R)Fe[\eta\text{-}C_5H_4CCo_3(CO)_{9-n}L_n]$, where R = H, n = 0, 1, L = PPh_3, $P(C_6H_{11})_3$, $P(OMe)_3$, $P(OPh)_3$ and n = 2, L = $P(OMe)_3$, $P(OPh)_3$; R = $COCH_3$, n = 0, and $(\eta\text{-}C_5H_4R)Fe[\eta\text{-}C_5H_4COCCo_3(CO)_9]$ where R = H, Me have been studied by electrochemical and spectroscopic techniques. The data suggested that there was a weak interaction between the redox sites in the molecules with the cluster behaving as an electron withdrawing substituent and the cyclopentadienyl ring acting as a π-electron donor to the cluster [324].

In a similar study, the electron transfer and mixed-valence properties of the clusters $(\eta\text{-}C_5H_5)Fe[\eta\text{-}C_5H_4CCo_3(CO)_6L_3]$, where L = $P(OMe)_3$ and $P(OPh)_3$, were investigated. Both the clusters formed a redox series $[\text{cluster}]^{2+/+/0/-}$ with discrete redox potentials, but only the cationic derivatives were stable on the electrochemical and chemical time scale. In the dications both the ferrocenyl group and the Co_3C moiety functioned as redox sites [325].

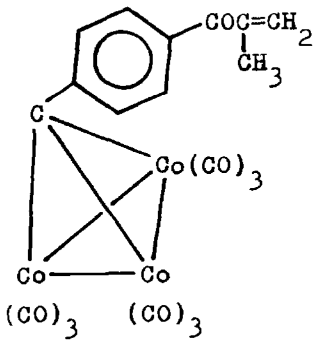
The reactions between methyl iodide and the metal cluster radical anions $YCCo_3(CO)_9^{-\bullet}$, (Y = Ph, Me, Et), $(CF_3)_2C_2Co_2(CO)_6^{-\bullet}$, $(CF_3)_6C_6Co_2(CO)_4^{-\bullet}$ and $SFeCo_2(CO)_9^{-\bullet}$ have been investigated. In each case the neutral parent cluster was produced in good yield together with methyl radicals and iodide ion. It was concluded that these were dissociative electron attachment reactions analogous to those of organic radical anions [326].

The polymerizable nonacarbonyl complexes (18.2, 18.3 and 18.4) have been prepared and the derived polymers and copolymers were evaluated as hydroformylation catalysts. In the hydroformylation partial decomposition of the cluster occurred and it was suggested that the mono- and/or di-nuclear cobalt carbonyl species formed were the catalysts [327].

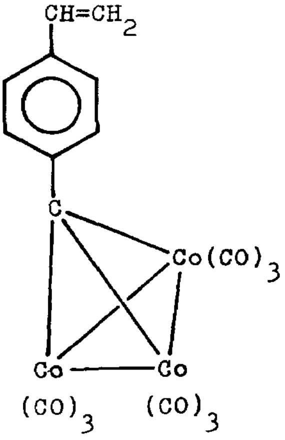
Reaction of the chiral clusters [18.5; LX = μ^2-1, 1-η^2-CMeN-cyclohexyl, μ^2-1,2-η^2-S=CNMe$_2$, μ^2-1,3-η^2-S=CPhNH; M = $Co(CO)_3$] with $[(\eta\text{-}C_5H_5)Mo(CO)_3]^-$ gave the products of either



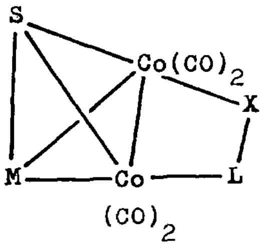
18.2



18.3



18.4



18.5

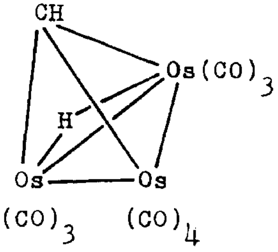
ligand exchange or removal of a $Co(CO)_3$ moiety. For example, the cluster [18.5; LX = μ^2-1,2-η^2-S=CNMe$_2$; M = $Co(CO)_3$]gave the complex (η-C_5H_5)Mo(CO)$_2$-1,2-S=CNMe$_2$ whereas the cluster [18.5; μ^2-1,1-η^2-CMe$_2$N-cyclohexyl; M = $Co(CO)_3$] produced the heteronuclear compound [18.5; LX = μ^2-1,2-η^2-CMe$_2$N-cyclohexyl, M = (η-C_5H_5)Mo(CO)$_2$] [328].

The osmium-methylidyne cluster complex (18.7) has been formed by hydride addition and then protonation of the methoxymethylidyne complex (18.6):

$$HOs_3(CO)_{10}(COMe) \xrightarrow{H^-} [HOs_3(CO)_{10}(CHOMe)]^- \xrightarrow{H^+} HOs_3(CO)_{10}(CH)$$

18.6 18.7

The crystal and molecular structure of the complex (18.7) has been determined by X-ray crystallography confirming that the triply bridging methylidyne ligand interacted more strongly with two of the osmium atoms than with the third. The electrophilic character of the methylidyne group was confirmed by facile reactions with nucleophiles such as pyridine and $LiBEt_3H$ which led to the opening of one side of the cluster nucleus [329].



18.7

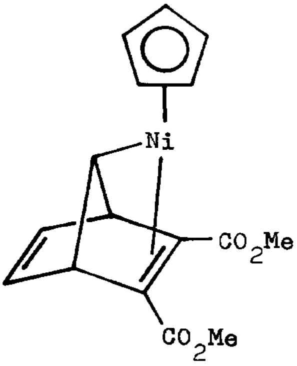
19. $(\eta-C_5H_5)_2Ni$

Reorientational processes in nickelocene have been studied by incoherent quasielastic neutron scattering. The cyclopentadienyl ring exhibited a $2\pi/5$ reorientational jump both below and above the diffuse phase transition at ~200 °K. A proton correlation time was estimated as 4×10^{12}s at 300 °K with an activation energy of 6.3 kj mol^{-1} which was in agreement with literature values [330].

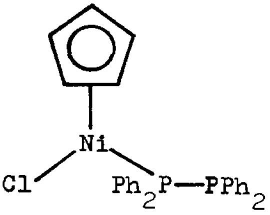
The reduction of nickelocene with sodium naphthalenide in tetrahydrofuran produced several η-cyclopentadienyl clusters including $Ni_2(\eta^5-C_5H_5)_2(\mu_2-C_5H_6)$, $Ni_3(\eta^5-C_5H_5)_3CR$, (R = Me, Et) and $Ni_4(\eta^5-C_5H_5)_4H_n$ (n = 2, 3). The reaction of nickelocene with $Na_3[Co(CO)_3]$ produced the air-stable complex $[Na(NCMe)]^+$-$[CoNi_2(\eta^5-C_5H_5)(\mu_3-CO)_2]^-$ [331].

$(\eta^2$-1,3-Alkadiene$)(\eta^5$-cyclopentadienyl)methylnickel complexes (alkadiene = butadiene, isoprene, 2,3-dimethylbutadiene) have been prepared by treating nickelocene with methyllithium and the alkadiene [332].

Nickelocene underwent addition to dimethyl acetylenedicarboxylate to form the (η-cyclcpentadienyl)nickel complex (19.1) which was used as a precursor for 7-substituted norbornadienes [333].



19.1

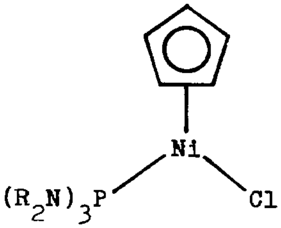


19.2

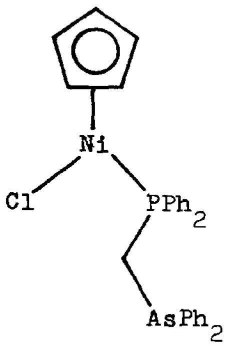
The reaction of nickelocene with tetraphenyldiphosphane in the presence of hydrogen chloride produced the nickel complex (19.2) where the diphosphane behaved as a monodentate ligand [334].

Reaction of nickelocene with nickel(II) chloride or bromide and $P(NR_2)_3$ (R = Me, Et) produced the corresponding η-cyclopentadienylnickel complexes (19.3) [335].

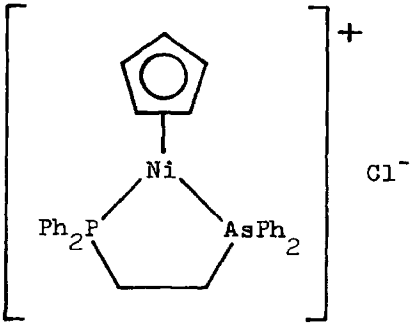
Nickelocene combined with the bidentate, mixed phosphorus, arsenic ligands $Ph_2PCH_2AsPh_2$ and $Ph_2PCH_2CH_2AsPh_2$ in carbon



19.3



19.4



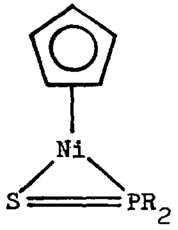
19.5

tetrachloride to form the (η-cyclopentadienyl)nickel complexes (19.4 and 19.5) respectively [336]. Similar reactions were achieved with cyclodiphosphazene ligands [337].

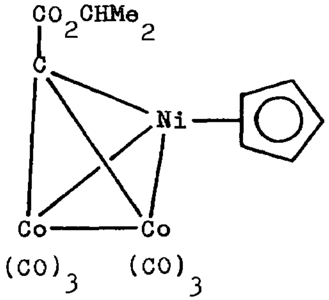
Nickelocene combined with the ligands Me_2HPS and Ph_2HPS to form the (η-cyclopentadienyl)nickel complex (19.6; R = Me, Ph) with a reactive three-membered heterometallic ring [338].

The reactions of the (η-cyclopentadienyl)tricarbonylmolybdenum cation with nickelocene and cobaltocene have been investigated. Redox reactions were observed, for example, with cobaltocene the cobaltocenium salts $[(\eta\text{-}C_5H_5)_2Co]^+X^-$, where $X = BF_4^-$ and $[(\eta\text{-}C_5H_5)Mo(CO)_3]^-$, were isolated [339].

Nickelocene has been converted by fluoroboric acid in



19.6



19.7

chloroform at -40 °C to the (η-cyclopentadiene)(η-cyclopentadienyl)nickel cation in 89% yield [340].

At room temperature the reaction of nickelocene with $Co_3(CO)_9CCO_2CHMe_2$ resulted in replacement of a $Co(CO)_3$ group by η-C_5H_5Ni to give the complex (19.7). The same reagents in refluxing tetrahydrofuran gave the products $(\eta\text{-}C_5H_5)_3Co_3(CO)(H)\text{-}CCO_2CHMe_2$ and $(\eta\text{-}C_5H_5)_3Co_2Ni(CO)CCO_2CHMe_2$ in which carbonyl groups had been replaced by η-cyclopentadienyl ligands [341].

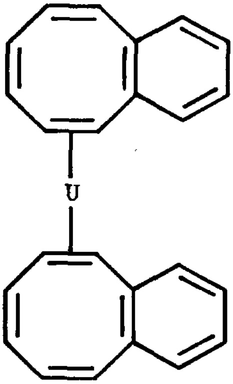
Tetrahedral Ni_2C_2 cluster complexes have been prepared by treatment of nickelocene with the acetylene (-)-(R)-PhC≡CCO-NHCHMePh. Substituted nickelocenes underwent the same reaction [342].

The treatment of nickelocene with $4\text{-}CB_8H_{13}Na$ gave the carborane $6\text{-}\eta^5\text{-}C_5H_5Ni\text{-}\eta^5\text{-}1\text{-}CB_8H_9$ which rearranged to the ten-vertex closo metallacarborane $10\text{-}\eta^5\text{-}C_5H_5Ni\text{-}\eta^4\text{-}1\text{-}CB_8H_9$ [343].

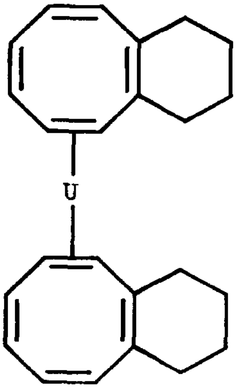
Nickel coatings have been deposited on ceramics, glass and quartz by hydrogenation of nickelocene at 180-300 °C. Films 0.3μ thick on palladium activated quartz were formed in 5 min. at 220 °C and had an adherence of 27 kg cm^{-2} [344].

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

Streitwieser and co-workers have prepared dibenzouranocene (20.1) by the reaction of the benzocyclooctatetraene dianion with uranium(IV) chloride. Catalytic hydrogenation produced the corresponding octahydro derivative (20.2). The NMR spectrum of the uranocene (20.1) indicated a spin density distribution



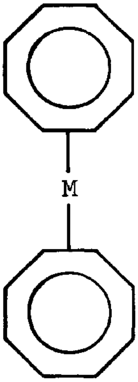
20.1



20.2

closely related to that in the radical anion of benzocyclooctatetraene [345].

Quasirelativistic SCF-X_α scattered-wave calculations have been carried out for uranocene (20.3; M = U) thorocene (20.3; M = Th) and cerocene (20.3; M = Ce). The calculations confirmed that the $f_{\pm 2}$ orbitals of the central metal atom contribute to the covalent ring-metal bonding and they also emphasised the importance of the 6d orbitals in this bonding [346].



20.3

REFERENCES

1. Fundamental Research in Organometallic Chemistry, Edited by M. Tsutsui, Y. Ishii and H. Yaozeng, Van Nostrand Reinhold (New York) and Science Press (Beijing), 1982.
2. M. I. Rybinskaya and V. V. Krivykh, Koord Khim., 9 (1983) 435.
3. I. Omae, Coord. Chem. Rev., 51 (1983) 1.
4. A. Nakamura, H. Yasuda, K. Tatsumi, I. Noda, K. Mashima, M. Akito and K. Nagasuna, Organomet. Compd: Synth., Struct., Theory, Proc. Symp. Ind.-Univ. Coop Chem. Program Dep. Chem., Tex. A & M Univ., (1983) 29, Ed. by B. L. Shapiro; Chem. Abstr., 100 (1984) 6580.
5. R. C. Kerber, J. Organometal. Chem., 254 (1983) 131 .
6. W. A. Herrmann, J. Organometal. Chem., 250 (1983) 319.
7. W. E. Watts, Indian J. Phys., B, 57B (1983) 4A.
8. J. L. Robbins, Diss. Abstr. Int. B, 43 (1982) 1843.

9. C. Sourisseau and Y. Mathey, Raman Spectrosc., Proc. Int. Conf., 8th, (1982) 641; Edited by J. Lascombe and P. V. Huong.
10. P. N. Hawker and P. L. Timms, J. Chem. Soc., Dalton Trans., (1983) 1123.
11. T. P. Hanusa, Polyhedron, 1 (1982) 663.
12. J. C. Brunet, E. Cuingnet, M. Dautrevaux, A. Demarly, H. Gras, P. Marcincal, C. Sergheraert, A. Tartar, J. C. Vanvoorde and M. Vanpoucke, Pept., Proc. Eur. Pept. Symp., 16th 1980 (Pub. 1981), 603; Chem. Abstr., 98 (1983) 89864.
13. H. R. Allcock, K. D. Lavin, N. M. Tollefson and T. L. Evans, Organometallics, 2 (1983) 267.
14. A. W. Duff and K. Jonas, J. Am. Chem. Soc., 105 (1983) 5479.
15. K. Jonas, V. Wiskamp, Y.-H. Tsay and C. Kruger, J. Am. Chem. Soc., 105 (1983) 5480.
16. J. Edwin, M. Bochmann, M. C. Boem, D. E. Brennan, W. E. Geiger, C. Kruger, J. Pebler, H. Pritzkow, W. Siebert, W. Swiridoff, H. Wadepohl, J. Weiss and U. Zenneck, J. Amer. Chem. Soc., 105 (1983) 2582.
17. E. Dubler, M. Textor, H. R. Oswald and G. B. Jameson, Acta Crystallogr., Sect. B: Struct. Sci., B39 (1983) 607.
18. G. Lucazeau, K. Chhor, C. Sourisseau and A. J. Dianoux, Chem. Phys., 76 (1983) 307.
19. G. Lucazeau, K. Chhor and C. Pommier, Spectrosc.: Int. J., 2 (1983) 79.
20. J. C. Giordan, J. H. Moore, J. A. Tossell and J. Weber, J. Am. Chem. Soc., 105 (1983) 3431.
21. D. Cozak and I. S. Butler, Can. J. Spectrosc., 27 (1982) 141.
22. C. Sourisseau, J. P. Forgerit and Y. Mathey, J. Phys. Chem. Solids, 44 (1983) 119; Chem. Abstr., 98 (1983) 206745.
23. P. Hofmann and M. Padmanabhan, Organometallics, 2 (1983) 1273.
24. M. C. Boehm, Theochem., 9 (1983) 73.
25. M. Brookhart and M. L. H. Green, J. Organometal. Chem., 250 (1983) 395.
26. W. A. Herrmann and W. Kalcher, Chem. Ber., 115 (1982) 3886.

27. J. Nieman, J. H. Teuben, J. C. Huffman and K. G. Caulton, J. Organometal. Chem., 255 (1983) 193.
28. D. Rehder, K. Paulsen and W. Basler, J. Magn. Reson., 53 (1983) 500.
29. L. N. Lewis and K. G. Caulton, J. Organometal. Chem., 252 (1983) 57.
30. Ch. Elschenbroich, J. Heck, W. Massa, E. Nun and R. Schmidt, J. Am. Chem. Soc., 105 (1983) 2905.
31. L. Weber and D. Wewers, Chem. Ber., 116 (1983) 1327.
32. L. Weber, Chem. Ber., 116 (1983) 2022.
33. P. Hackett, B. F. G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1982) 603.
34. O. B. Afanasova, N. G. Komalenkova, Yu. E. Zubarev, V. M. Nosova, A. V. Kisin, V. A. Sharapov, A. I. Gusev, N. V. Alekseev, N. I. Kirillova and E. A. Chernyshev, Zh. Obshch. Khim., 52 (1982) 2137.
35. G. M. Bogdanov, K. A. Paseshnichenko, Yu. G. Bundel, S. P. Gromov and V. N. Torocheshnikov, Khim. Geterotsikl. Soedin., (1983) 948.
36. L. M. Antipin, V. V. Fedoseevskii, V. N. Mochalov, A. S. Frenkel, G. K. Magomedov and M. F. Shostakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 642.
37. T. E. Bitterwolf, Polyhedron, 2 (1983) 675.
38. K. H. Dotz, J. Mulhlemeier, U. Schubert and O. Orama, J. Organometal. Chem., 247 (1983) 187.
39. K. H. Dotz and W. Kuhn, J. Organometal. Chem., 252 (1983) C 78.
40. M. J. Golightly, Report 1982, USNA-TSPR-116; Order No. AD-A124405, Avail NTIS. From Gov. Rep. Announce. Index (US), 83 (1983) 2606; Chem. Abstr., 99 (1983) 88334.
41. G. E. Herberich and D. Sohnen, J. Organometal. Chem., 254 (1983) 143.
42. B. Lubke, F. Edelmann and U. Behrens, Chem. Ber., 116 (1983) 11.
43. L. I. Zakharkin and G. G. Zhigareva, Zh. Obshch. Khim., 53 (1983) 953.
44. S. D. Cunningham, K. Ofele and B. W. Willeford, J. Am. Chem. Soc., 105 (1983) 3724.
45. R. H. Morris and J. M. Ressner, J. Chem. Soc., Chem. Commun., (1983) 909.

46. L. G. Kuz'mina and Yu. T. Struchkov, Koord. Khim., 8 (1982) 1542.

47. J.-C. Boutonnet, J. Levisalles, E. Rose, G. Precigoux, C. Courseille and N. Platzer, J. Organometal. Chem., 255 (1983) 317.

48. M. J. McGlinchey, J. L. Fletcher, B. G. Sayer, P. Bougeard, R. Faggiani, C. J. L. Lock, A. D. Bain, C. Rodger, E. P. Kundig, D. Astruc, J.-R. Hamon, P. Le Maux, S. Top and G. Jaouen, J. Chem. Soc., Chem. Commun., (1983) 634.

49. G. A. Vaglio, P. Volpe and L. Operti, Org. Mass Spectrom., 17 (1982) 617.

50. A. A. Tumanov, P. G. Sennikov, A. N. Egorochkin, M. V. Panicheva, G. V. Belysheva and N. I. Sirotkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 1634.

51. T. E. Bitterwolf, J. Organometal. Chem., 252 (1983) 305.

52. A. Ceccon, A. Gambaro, A. M. Romanin and A. Venzo, J. Organometal. Chem., 254 (1983) 207.

53. S. N. Milligan and R. D. Rieke, Organometallics, 2 (1983) 171.

54. S. N. Milligan, Diss. Abstr. Int. B, 43 (1983) 2560.

55. P. Caillet and P. Le Maux, J. Organometal. Chem., 243 (1983) 51.

56. E. A. Domogatskaya, V. N. Setkina, N. K. Baranetskaya, V. N. Trembovler, B. M. Yavorskii, A. Ya. Shteinshneider and P. V. Petrovskii, J. Organometal. Chem., 248 (1983) 161.

57. A. Korda and R. Giezynski, Pol. J. Chem., 56 (1982) 849.

58. S. Top, G. Jaouen, B. G. Sayer and M. J. McGlinchey, J. Am. Chem. Soc., 105 (1983) 6426.

59. C. D. Hoff, J. Organometal. Chem., 246 (1983) C53.

60. K. Lal, N. T. Leckey and W. E. Watts, J. Organometal. Chem., 258 (1983) 205.

61. B. Caro and G. Jaouen, Tetrahedron, 39 (1983) 83.

62. B. Caro and G. Jaouen, Tetrahedron, 39 (1983) 93.

63. M. F. Semmelhack, J. L. Garcia, D. Cortes, R. Farina, R. Hong and B. K. Carpenter, Organometallics, 2 (1983) 467.

64. M. T. Reetz and M. Sauerwald, Tetrahedron Lett., 24 (1983) 2837.

65. C. Andersson, R. Larsson and B. Yom-Tov, Inorg. Chim. Acta, 76 (1983) L 185.

66. R. D. Barr, M. Green, K. Marsden, F. G. A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1983) 507.

67. G. W. Harris, M. O. Albers, Jan C. A. Boeyens and N. J. Coville, Organometallics, 2 (1983) 609.

68. S. N. Milligan, I. Tucker and R. D. Rieke, Inorg. Chem., 22 (1983) 987.

69. A. Alemagna, P. Del Buttero, C. Gorini, D. Landini, E. Licandro and S. Maiorana, J. Org. Chem., 48 (1983) 605.

70. A. Alemagna, P. Cremonesi, P. Del Buttero, E. Licandro and S. Maiorana, J. Org. Chem., 48 (1983) 3114.

71. J. Lebibi, J. Brocard and D. Couturier, Bull. Soc. Chim. Fr., (1982) 357.

72. S. I. Rosca, S. Rosca, R. Patrascu and M. Avram, Bul. Inst. Politeh. "Gheorghe Gheorghiu-Dej" Bucuresti, Ser. Chim.-Metal., 43 (1981) 59; Chem. Abstr., 98 (1983) 54117.

73. M. F. Semmelhack and A. Zask, J. Am. Chem. Soc., 105 (1983) 2034.

74. A. Ceccon, A. Gambaro and A. M. Romanin, J. Organometal. Chem., 254 (1983) 199.

75. J.-C. Boutonnet, J. Levisalles, J.-M. Normant and E. Rose, J. Organometal. Chem., 255 (1983) C21.

76. N. F. Masters and D. A. Widdowson, J. Chem. Soc., Chem. Commun., (1983) 955.

77. M. G. Peterleitner, M. V. Tolstaya, V. V. Krivykh, L. I. Denisovitch and M. I. Rybinskaya, J. Organometal. Chem., 254 (1983) 313.

78. I. S. Butler, A. M. English and K. R. Plowman, Inorg. Synth., 21 (1982) 1.

79. H. W. Choi and M. S. Sollberger, J. Organometal. Chem., 243 (1983) C39.

80. K. Dimroth and H. Kaletsch, J. Organometal. Chem., 247 (1983) 271.

81. J. M. Lamarche and B. Laude, Bull. Soc. Chim. Fr., (1982) 97.

82. R. P. Houghton, M. Voyle and R. Price, J. Organometal. Chem., 259 (1983) 183.

83. M. Uemura, N. Nishikawa, K. Take, M. Ohnishi, K. Hirotsu, T. Higuchi and Y. Hayashi, J. Org. Chem., 48 (1983) 2349.

84. E. P. Kundig and D. P. Simmons, J. Chem. Soc., Chem. Commun., (1983) 1320.

85. E. P. Kundig, V. Desobry and D. P. Simmons, J. Am. Chem. Soc., 105 (1983) 6962.

86. W. P. Henry and R. D. Rieke, J. Am. Chem. Soc., 105 (1983) 6314.

87. M. Uemura, K. Take and Y. Hayashi, J. Chem. Soc., Chem. Commun., (1983) 858.

88. L. Weber and R. Boese, Angew. Chem., 95 (1983) 510.

89. V. V. Litvak, P. P. Kun and V. D. Shteingarts, Zh. Org. Khim., 18 (1982) 2153.

90. B. E. Wilburn, Diss. Abstr. Int. B, 43 (1983) 2216.

91. P. Lumme, P. Von Bagh, J. Kahima and H. Karrus, Inorg. Chim. Acta, 71 (1983) 209.

92. A. Yu. Vasil'kov, N. V. Zakurin, I. A. Uralets, N. N. Zaitseva, N. I. Vasyukova, A. G. Makarovskaya and L. P. Yur'eva, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2144.

93. R. Faggiani, N. Hao, C. J. L. Lock, B. G. Sayer and M. J. McGlinchey, Organometallics, 2 (1983) 96.

94. L. P. Yur'eva, N. N. Zaitseva, N. Y. Zakurin, A. Yu. Vasil'kov and N. I. Vasyukova, J. Organometal. Chem., 247 (1983) 287.

95. V. V. Litvak, P. P. Kun and V. D. Shteingarts, Zh. Org. Khim., 18 (1982) 1966.

96. V. V. Litvak, P. P. Kun and V. D. Shteingarts, Zh. Org. Chim., 19 (1983) 1784.

97. G. A. Razuvaev, M. N. Bochkarev and L. V. Pankratov, J. Organometal. Chem., 250 (1983) 135.

98. V. I. Paleev, Teor. Eksp. Khim., 19 (1983) 59; Chem. Abstr., 98 (1983) 198401.

99. L. M. Dyagileva, E. I. Tsyganova, V. G. Rabinovich, V. P. Popov and Yu. A. Aleksandrov, Zh. Prikl. Khim. (Leningrad), 56 (1983) 16; Chem. Abstr., 98 (1983) 198379.

100. V. V. Dodorov, V. K. Vanchagova, V. A. Umilin and A. D. Zorin, Khimiya Elementoorgan, Soedin., Gor'kii, (1982) 71; From Ref. Zh. Khim. 1983, Abstr. No. 12V147.

101. F. G. N. Cloke, A. N. Dix, J. C. Green, R. N. Perutz and E. A. Seddon, Organometallics, 2 (1983) 1150.

102. M. L. H. Green, A. Izquierdo, J. J. Martin-Polo, V. S. B. Mtetwa and K. Prout, J. Chem. Soc., Chem. Commun., (1983) 538.

103. G. J. Kubas, Inorg. Chem., 22 (1983) 692.

104. K. Lal, N. T. Leckey and W. E. Watts, J. Organometal. Chem., 254 (1983) 193.

105. M. El Borai, A. Akelah and M. A. Hassen, Egypt J. Chem., 24 (1981) 91; Chem. Abstr., 99 (1983) 53912.

106. C. G. Kreiter and H. Kurz, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 38B (1983) 841.

107. S. Oezkar and C. G. Kreiter, Z. Anorg. Allg. Chem., 502 (1983) 215.

108. C. A. Bunton, M. M. Mhala, J. R. Moffatt and W. E. Watts, J. Organometal. Chem., 253 (1983) C 33.

109. C. G. Kreiter and H. Kurz, Chem. Ber., 116 (1983) 1494.

110. E. Michels and C. G. Kreiter, J. Organometal. Chem., 252 (1983) C 1.

111. A. J. Pearson and I. C. Richards, J. Organometal. Chem., 258 (1983) C 41.

112. C. G. Kreiter and W. Lipps, J. Organometal. Chem., 253 (1983) 339.

113. N. M. Loim, M. V. Laryukova, V. G. Andrianov, V. A. Tsiryapkin, Z. N. Parnes and Yu. T. Struchkov, J. Organometal. Chem., 248 (1983) 73.

114. G. W. Harris, J. C. A. Boeyens and N. J. Coville, J. Organometal. Chem., 255 (1983) 87.

115. V. B. Rybakov, L. A. Aslanov, V. M. Ionov and S. A. Eremin, Zh. Strukt. Khim., 24 (1983) 74.

116. A. G. Kochur, A. T. Shuvaev, M. A. Tyzykhov, A. G. Ginzburg, Yu. A. Teterin and A. S. Baev, Deposited Doc. (1981) VINITI 4220; Chem. Abstr., 98 (1983) 72354.

117. A. T. Shuvaev, A. G. Kochur, Yu. A. Teterin and A. S. Baev, Dokl. Akad. Nauk SSSR, 266 (1982) 924.

118. M. C. R. Symons, S. W. Bratt and J. L. Wyatt, J. Chem. Soc., Dalton Trans., (1983) 1377.

119. R. Pikver, E. Suurmaa, E. Lippmaa, Yu. S. Nekrasov, D. V. Zagorevskii and V. F. Sizoi, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 1670.

120. B. V. Lokshin and M. G. Yezernitskaya, J. Organometal. Chem., 256 (1983) 89.

121. A. G. Ginzburg, V. N. Setkina and D. N. Kursanov, Akad. Nauk SSSR, Ser. Khim., (1983) 1155.

122. V. I. Bakhmutov, P. V. Petrovskii, S. P. Dolgova, V. N. Setkina, E. I. Fedin and D. N. Kursanov, J. Organometal. Chem., 246 (1983) 177.

123. D. F. R. Gibson, G. Gomez, I. S. Butler and P. J. Fitzpatrick, Can. J. Chem., 61 (1983) 737.

124. K. Chhor, C. Pommier and M. Diot, Mol. Cryst. Liq. Cryst., 100 (1983) 193.

125. M. E. Rerek, L.-N. Ji and F. Basolo, J. Chem. Soc., Chem. Commun., (1983) 1208.

126. M. Herberhold, D. Reiner and U. Thewalt, Angew. Chem., 95 (1983) 1028.

127. A. Kececi, D. Rehder, W. Roose and R. Talay, Chem. Ber., 115 (1982) 3257.

128. V. V. Krivykh, O. V. Gusev and M. I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 644.

129. L. G. Kuzmina, A. G. Ginzburg, Yu. T. Struchkov and D. N. Kursanov, J. Organometal. Chem., 253 (1983) 329.

130. E. Lindner and D. Huebner, Chem. Ber., 116 (1983) 2574.

131. I. A. Lobanova, V. I. Zdanovich and N. E. Kolobova, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2606.

132. I. A. Lobanova, V. I. Zdanovich, N. E. Kolobova and P. V. Petrovskii, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 684.

133. Y. K. Chung, E. D. Honig, W. T. Robinson, D. A. Sweigart, N. G. Connelly and S. D. Ittel, Organometallics, 2 (1983) 1479.

134. A. A. Bumber, A. G. Milaev and O. Yu. Okhlobystin, Zh. Obshch. Khim., 53 (1983) 606.

135. P. Legzdins, D. T. Martin, C. R. Nurse and B. Wassink, Organometallics, 2 (1983) 1238.

136. P. J. Hakkinen, C. C. Morse, F. M. Martin, W. E. Dalbey, W. M. Haschek and H. R. Witschi, Toxicol. Appl. Pharmacol., 67 (1983) 55.

137. P. Hublau, C. Sergheraert, L. Ballester and M. Dautrevaux, Eur. J. Med. Chem.-Chim. Ther., 18 (1983) 131.

138. K. Morida, T. Inoue, R. Ishida and M. Ogata, Okayama-ken Kankyo Hoken Senta Nenpo, 5 (1981) 250; Chem. Abstr., 99 (1983) 65497.

139. S. Adel, E. Yanir and I. Ron, (Paz Oil Co. Ltd; Pazgas Marketing Co. Ltd.), Israeli Pat. IL 57342, Aug. 31, 1982;

Chem. Abstr., 99 (1983) 25279.

140. M. D. Reshetova, V. I. Ivanov, V. E. Mikhlin, S. A. Eremin and E. G. Perevalova, Prom-st. Sint. Kauch., (1982) 19; Chem. Abstr., 98 (1983) 127455.

141. Y. Kurimura, F. Ohta, J. Gohda, H. Nishide and E. Tsuchida, Makromol. Chem., 183 (1982) 2889.

142. M. De la Guardia-Cirugeda, G. Legrand, M. Druon and J. L. Louvrier, Analusis, 10 (1982) 476.

143. M. Herberhold, W. Ehrenreich and W. Buehlmeyer, Angew. Chem., 95 (1983) 332.

144. W. A. Herrmann, R. Serrano and J. Weichmann, J. Organometal. Chem., 246 (1983) C 57.

145. G. E. Herberich, J. Hengesbach, G. Huttner, A. Frank and U. Schubert, J. Organometal. Chem., 246 (1983) 141.

146. H. Lang, L. Zsolnai and G. Huttner, Angew. Chem., 95 (1983) 1016.

147. D. Melzer and E. Weiss, J. Organometal. Chem., 255 (1983) 335.

148. C. Moise, J. Organometal. Chem., 247 (1983) 27.

149. G. E. Herberich, B. Hessner, W. Boveleth, H. Luethe, R. Saive and L. Zelenka, Angew. Chem., 395 (1983) 1024.

150. M. D. Rausch, B. H. Edwards, R. D. Rogers and J. L. Attwood, J. Am. Chem. Soc., 105 (1983) 3882.

151. J. Schneider, L. Zsolnai and G. Huttner, Cryst. Struct. Commun., 11 (1982) 943.

152. J. Schneider and G. Huttner, Chem. Ber., 116 (1983) 917.

153. B. E. Boland-Lussier, M. R. Churchill, R. P. Hughes and A. L. Rheingold, 1 (1982) 628.

154. E. O. Fischer, J. Chen and K. Scherzer, J. Organometal. Chem., 253 (1983) 231.

155. E. O. Fischer and J. Chen, Z. Naturforsch, B: Anorg. Chem., Org. Chem., 38B (1983) 580.

156. M. M. Singh and R. J. Angelici, Angew. Chem., 95 (1983) 160.

157. W. Malisch, H. Blau and U. Schubert, Chem. Ber., 116 (1983) 690.

158. N. E. Kolobova, L. L. Ivanov, Yu. A. Chernykh and V. V. Derunov, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 1395.

159. E. O. Fischer, W. Kleine, W. Schambeck and U. Schubert, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 36B (1981) 1575.

160. M. C. Boehm, R. Gleiter and H. Berke, J. Electron Spectrosc. Relat. Phenom., 31 (1983) 261.

161. M. Herberhold, D. Reiner and D. Neugebauer, Angew. Chem., 95 (1983) 46.

162. N. E. Kolobova, L. L. Ivanov and O. S. Zhvanko, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 956.

163. N. E. Kolobova, L. L. Ivanov, O. S. Zhvanko, A. S. Batsanov and Yu. T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2632.

164. N. E. Kolobova, L. L. Ivanov, O. S. Zhvanko, V. V. Derunov and I. N. Chechulina, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2633.

165. E. O. Fischer, J. Chen and U. Schubert, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 37B (1982) 1284.

166. A. T. Patton, C. E. Strouse, C. B. Knobler and J. A. Gladysz, J. Am. Chem. Soc., 105 (1983) 5804.

167. K. H. Franzreb and C. R. Kreiter, J. Organometal. Chem., 246 (1983) 189.

168. J. Chetwynd-Talbot, P. Grebenik, R. N. Perutz and M. H. A. Powell, Inorg. Chem., 22 (1983) 1675.

169. C. P. Casey, J. M. O'Connor, W. D. Jones and K. J. Haller, Organometallics., 2 (1983) 535.

170. Z. P. Valueva, M. Ya. Solodova and N. E. Kolobova, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 1863.

171. J. H. Merrifield, Diss. Abstr. Int. B, 44 (1983) 171.

172. W. E. Buhro, A. Wong, J. H. Merrifield, G. Y. Lin, A. C. Constable and J. A. Gladysz, Organometallics, 2 (1983) 1852.

173. J. R. Sweet and W. A. G. Graham, Organometallics, 2 (1983) 135.

174. C. P. Casey and J. M. O'Connor, J. Am. Chem. Soc., 105 (1983) 2919.

175. C. F. Barrientos-Penna, A. B. Gilchrist and D. Sutton, Organometallics, 2 (1983) 1265.

176. C. F. Barrientos-penna, F. W. B. Einstein, T. Jones and D. Sutton, Inorg. Chem., 22 (1983) 2614.

177. W. G. Hatton and J. A. Gladysz, J. Am. Chem. Soc., 105 (1983) 6157.

178. W. A. Kiel, Diss. Abstr., Int. B, 43 (1983) 2558.

179. W. A. Kiel, G.-Y. Lin, G. S. Bodner and J. A. Gladysz, J. Am. Chem. Soc., 105 (1983) 4958.

180. J. H. Merrifield and J. A. Gladysz, Organometallics, 2 (1983) 782.

181. W. E. Buhro, A. T. Patton, C. E. Strouse, J. A. Gladysz, F. B. McCormick and M. C. Etter, J. Am. Chem. Soc., 105 (1983) 1056.

182. S. Komiya, H. Minato, T. Ikariya, T. Yamamoto and A. Yamamoto, J. Organometal. Chem., 254 (1983) 83.

183. S. S. Ullah, S. E. Kabir, M. K. Begum and M. Mohibullah, J. Bangladesh Acad. Sci., 6 (1982) 53.

184. E. J. S. Vichi, P. R. Raithby and McPartlin, J. Organometal. Chem., 256 (1983) 111.

185. D. R. Wilson, R. D. Ernst and T. H. Cymbaluk, Organometallics, 2 (1983) 1220.

186. L. Stahl and R. D. Ernst, Organometallics, 2 (1983) 1229.

187. T. W. Smith and D. J. Luca, Org. Coat. Appl. Polym. Sci. Proc., 46 (1981) 358.

188. I. Noda, H. Yasuda and A. Nakamura, J. Organometal. Chem., 250 (1983) 447.

189. Z. Goldschmidt, Y. Bakal, D. Hoffer, A. Eisenstadt and P. F. Lindley, J. Organometal. Chem., 258 (1983) 53.

190. M. Franck-Neumann, M. P. Heitz, D. Martina and A. De Cian, Tetrahedron Lett., 24 (1983) 1611.

191. M. Franck-Neumann, M. P. Heitz and D. Martina, Tetrahedron Lett., 24 (1983) 1615.

192. D. Minniti and P. L. Timms, J. Organometal. Chem., 258 (1983) C12.

193. G. Davidson and G. E. Gadd, Raman Spectrosc., Proc. Int. Conf., 8th, (1982) 637.

194. J. A. Mondo, Diss. Abstr. Int. B, 44 (1983) 499.

195. M. Frank-Neumann, D. Martina and M. P. Heitz, Tetrahedron Lett., 23 (1982) 3493.

196. A. Hafner, J. H. Bieri, R. Prewo, W. Von Philipsborn and A. Salzer, Angew. Chem., 95 (1983) 736.

197. A. Monpert, J. Martelli, R. Gree and R. Carrie, Nouv. J. Chim., 7 (1983) 345.

198. P. Powell, J. Organometal. Chem., 243 (1983) 205.

199. M. F. Semmelhack, J. W. Herndon and J. K. Liu, Organometallics, 2 (1983) 1865.
200. R. Gabioud and P. Vogel, Helv. Chim. Acta, 66 (1983) 1134.
201. T. Akiyama, F. W. Grevels, J. G. A. Reuvers and P. Ritterskamp, Organometallics, 2 (1983) 157.
202. J. Clelland and G. R. Knox, J. Chem. Soc., Chem. Commun., (1983) 1219.
203. A. G. Samuelson, Diss. Abstr. Int. B, 43 (1983) 3989.
204. J. A. Mondo and J. A. Berson, J. Am. Chem. Soc., 105 (1983) 3340.
205. K. J. Jens, T. Valeri and E. Weiss, Chem. Ber., 116 (1983) 2872.
206. K. S. Fongers, H. Hogeveen and R. F. Kingma, Synthesis, (1982) 839.
207. P. Diehl, F. Moia, H. Boesiger and J. Wirz, J. Mol. Struct., 98 (1983) 297.
208. J. W. Chinn and M. B. Hall, Inorg. Chem., 22 (1983) 2759.
209. B. E. Bursten, J. Am. Chem. Soc., 105 (1983) 121.
210. J. C. Calabrese, S. D. Ittel, H. S. Choi, S. G. Davis and D. A. Sweigart, Organometallics, 2 (1983) 226.
211. B. H. Edwards, Diss. Abstr. Int. B, 43 (1983) 2554.
212. S. G. Davies, J. Hibberd and S. J. Simpson, J. Organometal. Chem., 246 (1983) C 16.
213. D. Farcasiu and G. Marino, J. Organometal. Chem., 253 (1983) 243.
214. P. Eilbracht and R. Jelitte, Chem. Ber., 116 (1983) 243.
215. A. J. Pearson, T. R. Perrior and D. A. Griffin, J. Chem. Soc., Perkin Trans. 1, (1983) 625.
216. Z. Goldschmidt and S. Antebi, J. Organometal. Chem., 259 (1983) 119.
217. A. Salzer, T. Egolf and W. Von Philipsborn, Helv. Chim., Acta, 65 (1982) 1145.
218. N. Morita and T. Asao, Chem. Lett., (1982) 1575.
219. E. Luppold and W. Winter, Chem. Ber., 116 (1983) 1923.
220. R. B. Maynard, R. G. Swisher and R. N. Grimes, Organometallics, 2 (1983) 500.
221. T. Mitsudo, Y. Ogino, Y. Komiya, H. Watanabe and Y. Watanabe, Organometallics, 2 (1983) 1202.
222. K. D. Karlin, M. D. Moisan, M. Kustyn, P. L. Dahlstrom, J. Zubieta and P. R. Raithby, Cryst. Struct. Commun., 11 (1982) 1945.

223. N. M. Kostic and R. F. Fenske, Organometallics, 2 (1983) 1319.

224. I. L. Fragala, J. Takats and M. A. Zerbo, Organometallics, 2 (1983) 1502.

225. N. Bild, E. R. F. Gesing, C. Quiquerez and A. Wehrli, J. Organometal. Chem., 248 (1983) 85.

226. N. Bild, E. R. F. Gesing, C. Quiquerez and A. Wehrli, J. Chem. Soc., Chem. Commun., (1983) 172.

227. G. R. Stephenson, Aust. J. Chem., 35 (1982) 1939.

228. M. J. Hails, B. E. Mann and C. M. Spencer, J. Chem. Soc., Chem. Commun., (1983) 120.

229. S. G. Davies, S. D. Moon, S. J. Simpson and S. E. Thomas, J. Chem. Soc., Dalton Trans., (1983) 1805.

230. M. D. Radcliffe and W. M. Jones, Organometallics, 2 (1983) 1053.

231. R. B. Hitam, R. Narayanaswamy and A. J. Rest, J. Chem. Soc., Dalton Trans., (1983) 1351.

232. J. W. Hershberger, C. Amatore and J. K. Kochi, J. Organometal. Chem., 250 (1983) 345.

233. J. W. Hershberger and J. K. Kochi, Polyhedron, 2 (1983) 929.

234. M. C. Boehm, Theochem, 6 (1982) 165; Chem. Abstr., 98 (1983) 54124.

235. D. A. Brown, J. P. Chester and N. J. Fitzpatrick, J. Indian Chem. Soc., 59 (1982) 1273.

236. M. F. Semmelhack and J. W. Herndon, Organometallics, 2 (1983) 363.

237. T. Yu. Orlova, V. N. Setkina, V. F. Sizoi and D. N. Kursanov, J. Organometal. Chem., 252 (1983) 201.

238. A. J. Pearson, P. Ham, C. W. Ong, T. R. Perrior and D. C. Rees, J. Chem. Soc., Perkin Trans. 1, (1982) 1527.

239. M. F. Semmelhack, J. W. Herndon and J. P. Springer, J. Am. Chem. Soc., 105 (1983) 2497.

240. G. Schiavon and C. Paradisi, J. Organometal. Chem., 243 (1983) 351.

241. D. J. Evans and L. A. P. Kane-Maguire, Inorg. Chim. Acta, 62 (1982) 109.

242. A. J. Pearson, S. L. Kole and B. Chen, J. Am. Chem. Soc., 105 (1983) 4483.

243. C. Paradisi and G. Schiavon, J. Organometal. Chem., 246 (1983) 197.

244. J. A. Howell and M. J. Thomas, J. Chem. Soc., Dalton Trans., (1983) 1401.

245. J. G. Atton and L. A. P. Kane-Maguire, J. Organometal. Chem., 246 (1983) C 23.

246. A. J. Pearson and I. C. Richards, Tetrahedron Lett., 24 (1983) 2465.

247. B. M. R. Bandara, A. J. Birch, L. F. Kelly and T. C. Khor, Tetrahedron Lett., 24 (1983) 2491.

248. G. R. John, L. A. P. Kane-Maguire, T. I Odiaka and C. Eaborn, J. Chem. Soc., Dalton Trans., (1983) 1721.

249. N. G. Connelly, A. R. Lucy and M. W. Whiteley, J. Chem. Soc., Dalton Trans., (1983) 111.

250. N. G. Connelly, A. R. Lucy and M. W. Whiteley, J. Chem. Soc., Dalton Trans., (1983) 117.

251. L. K. K. LiShingMan, J. G. A. Reuvers, J. Takats and G. Deganello, Organometallics, 2 (1983) 28.

252. N. G. Connelly, A. R. Lucy and J. B. Sheridan, J. Chem. Soc., Dalton Trans., (1983) 1465.

253. A. J. Birch, L. F. Kelly and A. S. Narula, Tetrahedron, 38 (1982) 1813.

254. M. Airoldi, G. Deganello, G. Dia and G. Gennaro, Inorg. Chim. Acta, 68 (1983) 179.

255. S. K. Chopra, M. J. Hynes, G. Moran, J. Simmie and P. McArdle, Inorg. Chim. Acta, 63 (1982) 177.

256. A. J. Pearson and M. Chandler, J. Chem. Soc., Perkin Trans., 1 (1982) 2641.

257. G. R. Stephenson, J. Chem. Soc., Perkin Trans., 1 (1982) 2449.

258. J. A. S. Howell and M. J. Thomas, J. Organometal. Chem., 247 (1983) C 21.

259. K. Jonas, G. Koepe, L. Schieferstein, R. Mynott, C. Krueger and Y. H. Tsay, Angew. Chem., 95 (1983) 637.

260. A. J. Pearson, G. C. Heywood and M. Chandler, J. Chem. Soc., Perkin Trans., 1 (1982) 2631.

261. A. J. Pearson, D. C. Rees and C. W. Thornber, J. Chem. Soc., Perkin Trans., 1 (1983) 619.

262. C. C. Lee, A. Piorko and R. G. Sutherland, J. Organometal. Chem., 248 (1983) 357.

263. H. Schumann, Chem.-Ztg., 106 (1982) 369; Chem. Abstr., 98 (1983) 54132.

264. V. Guerchais and D. Astruc, J. Chem. Soc., Chem. Commun., (1983) 1115.

265. L. I. Zakharkin, V. V. Kobak, A. I. Yanovsky and Yu. T. Struchkov, Tetrahedron, 38 (1982) 3515.

266. J. Elzinga and M. Rosenblum, Organometallics, 2 (1983) 1214.

267. N. S. Nametkin, V. D. Tyurin, A. I. Nekhaev, Yu. P. Sobolev, M. G. Kondrat'eva, A. S. Batsanov and Yu. T. Struchkov, J. Organometal. Chem., 243 (1983) 323.

268. A. W. Hanson, Cryst. Struct. Commun., 11 (1982) 937.

269. A. W. Hanson, Cryst. Struct. Commun., 11 (1982) 1395.

270. J. C. Green, M. R. Kelly, M. P. Payne, E. A. Seddon, D. Astruc, J. R. Hamon and P. Michaud, Organometallics, 2 (1983) 211.

271. I. Pavlik and J. Klikorka, Proc. Conf. Coord. Chem., 9 (1983) 327.

272. C. C. Lee, K. J. Demchuk, U. S. Gill and R. G. Sutherland, J. Organometal. Chem., 247 (1983) 71.

273. A. Darchen, J. Chem. Soc., Chem. Commun., (1983) 768.

274. C. C. Lee, A. Piorko, B. R. Steele, U. S. Gill and R. G. Sutherland, J. Organometal. Chem., 256 (1983) 303.

275. E. Roman, G. Valenzuela, L. Gargallo and D. Radic, J. Polym. Sci., Polym. Chem. Ed., 21 (1983) 2057.

276. Y. K. Chung, E. D. Honig and D. A. Sweigart, J. Organometal. Chem., 256 (1983) 277.

277. R. P. Micciche and L. G. Sneddon, Organometallics, 2 (1983) 674.

278. R. G. Swisher, E. Sinn and R. N. Grimes, Organometallics, 2 (1983) 506.

279. G. E. Herberich and M. M. Kucharska-Jansen, J. Organometal. Chem., 243 (1983) 45.

280. L. Zhang, P. Hu and G. Zhang, Youji Huaxue, (1983) 277; Chem. Abstr., 100 (1984) 51728.

281. W. D. Rohrbach and V. Boekelheide, J. Org. Chem., 48 (1983) 3673.

282. P. Pertici, G. Vitulli, W. Porzio, M. Zocchi, P. L. Barili and G. Deganello, J. Chem. Soc., Dalton Trans., (1983) 1553.

283. M. I. Bruce, R. C. Wallis, M. L. Williams, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans., (1983) 2183.
284. J. C. A. Boeyens and D. C. Levendis, S. Afr. J. Chem., 35 (1982) 144.
285. D. C. Lavendis, J. C. A. Boeyens and E. W. Neuse, J. Crystallogr. Spectrosc. Res., 12 (1982) 493.
286. R. Davis and D. J. O'Reardon, J. Indian Chem. Soc., 59 (1982) 1270.
287. C. Brevard and P. Granger, Inorg. Chem., 22 (1983) 532.
288. A. Kubo, R. Ikeda and Nakamura, Chem. Lett., (1982) 1487.
289. G. L. D. Ritchie, M. K. Cooper, R. L. Calvert, G. R. Dennis, L. Phillips and J. Vrbancich, J. Am. Chem. Soc., 105 (1983) 5215.
290. U. Koelle and A. Salzer, J. Organometal. Chem., 243 (1983) C 27.
291. A. Meyerhans, W. Pfau, R. Memming and P. Margaretha, Helv. Chim. Acta, 65 (1982) 2603.
292. H. Nagashima, H. Matsuda and K. Itoh, J. Organometal. Chem., 258 (1983) C 15.
293. N. J. Forrow, S. A. R. Knox, M. J. Morris and A. G. Orpen, J. Chem. Soc., Chem. Commun., (1983) 234.
294. R. Breslow, G. Trainor and A. Ueno, J. Am. Chem. Soc., 105 (1983) 2739.
295. M. Wenzel and G. Schachschneider, Z. Naturforsch., C; Biosci., 38 C (1983) 806.
296. M. Wenzel, Ger. Pat. DE 3132669, 1983, Feb. 24; Chem. Abstr., 98 (1983) 155639.
297. G. Schachschneider and M. Wenzel, J. Labelled Compd. Radiopharm., 19 (1982) 1071.
298. J. Kotz, G. Neyhart, W. J. Vining and M. D. Rausch, Organometallics, 2 (1983) 79.
299. W. A. Donaldson, R. P. Hughes, R. E. Davis and S. M. Gadol, Organometallics, 1 (1982) 812.
300. M. Grzeszczuk, D. E. Smith and W. E. Geiger, J. Am. Chem. Soc., 105 (1983) 1772.
301. P. Harter, P. L. Pauson and S. S. Ullah, J. Organometal. Chem., 247 (1983) C 27.
302. J. E. Sheats, G. Hlatky and S. M. De Oliveira, Quim. Nova, 6 (1983) 49.

303. H. Boennemann and B. Bogdanovic (Studiengesellschaft Kohle), Ger. Pat. DE 3205550, 1983, Aug. 25; Chem. Abstr., 100 (1984) 22805.

304. C. P. Lau, P. Singh, S. J. Cline, R. Seiders, M. Brookhart, W. E. Marsh, D. J. Hodgson and W. E. Hatfield, Mol. Cryst. Liq. Cryst., 86 (1982) 1871.

305. J. E. Sheats, W. C. Spink, R. A. Nabinger, D. Nicol and G. Hlatky, J. Organometal. Chem., 251 (1983) 93.

306. P. Powell, J. Organometal. Chem., 244 (1983) 393.

307. H. Boennemann, M. Radermacher, C. Krueger and H. J. Kraus, Helv. Chim. Acta, 66 (1983) 185; Chem. Abstr., 99 (1983) 5792.

308. G. Schmid and R. Boese, Z. Naturforsch., B; Anorg. Chem., Org. Chem., 38 B (1983) 485.

309. A. Michalowicz, G. Vlaic, R. Clement and Y. Mathey, Springer Ser. Chem. Phys., 27 (1983) 222; Chem. Abstr., 99 (1983) 149871.

310. C. Sourisseau, J. P. Forgerit and Y. Mathey, J. Solid State Chem., 49 (1983) 134.

311. E. Koenig, V. P. Desai, B. Kanellakopulos and F. H. Koehler, Chem. Phys., 80 (1983) 263.

312. P. Aldebert, N. Baffier, J. Legendre and J. Livage, Rev. Chim. Miner., 19 (1982) 485.

313. A. A. Barkatin, A. K. Baev, V. P. Nistratov and M. S. Sheiman, Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk, (1983) 49.

314. K. Jonas, E. Deffense and D. Habermann, Angew. Chem., 95 (1983) 729.

315. W. Klaui, W. Eberspach and R. Schwarz, J. Organometal. Chem., 252 (1983) 347.

316. V. V. Korshak, V. A. Sergeev, N. S. Kochetkova, Yu. A. Chernomordik, E. V. Leonova and A. S. Kurapov, USSR Pat., US 1002303, Mar. 7; 1983; From Otkrytiya, Izobret., Prom Obraztsy, Tovarnye Znaki, (1983) 79; Chem. Abstr., 99 (1983) 23104.

317. G. Ortaggi and V. Paolucci, Acqua Aria, (1982) 45; Chem. Abstr., 99 (1983) 6453.

318. G. Schmid, U. Hohner, D. Kampmann, D. Zaika and R. Boese, J. Organometal. Chem., 256 (1983) 225.

319. H. Wadepohl, H. Pritzkow and W. Siebert, Organometallics, 2 (1983) 1899.

320. J. Edwin, M. C. Boehm, N. Chester, D. M. Hoffman, R. Hoffman, H. Pritzkow, W. Siebert, K. Stumpf and H. Wadepohl, Organometallics, 2 (1983) 1666.

321. E. O. Fischer, J. Schneider and D. Neugebauer, Monatsh. Chem., 114 (1983) 851.

322. J. Ros and R. Mathieu, Organometallics, 2 (1983) 771.

323. S. Jensen, B. H. Robinson and J. Simpson, J. Chem. Soc., Chem. Commun., (1983) 1081.

324. S. B. Colbran, B. H. Robinson and J. Simpson, Organometallics, 2 (1983) 943.

325. S. B. Colbran, B. H. Robinson and J. Simpson, Organometallics., 2 (1983) 952.

326. C. M. Kirk, B. M. Peake, B. H. Robinson and J. Simpson, Aust. J. Chem., 36 (1983) 441.

327. H. P. Withers and D. Seyferth, Inorg. Chem., 22 (1983) 2931.

328. C. Mahe, H. Patin, J. Y. Le Marouille and A. Benoit, Organometallics, 2 (1983) 1051.

329. J. R. Shapley, M. E. Cree-Uchiyama and G. M. St. George, J. Am. Chem. Soc., 105 (1983) 140.

330. C. Sourisseau, G. Lucazeau, A. J. Dianoux and C. Poinsignon, Mol. Phys., 48 (1983) 367.

331. M. A. Murphy, Diss. Abstr. Int. B, 43 (1983) 3591.

332. H. Lehmkuhl, F. Danowski, R. Benn, A. Rufinska, G. Schroth and R, Mynott, J. Organometal. Chem., 254 (1983) C 11.

333. C. Bleasdale and D. W. Jones, J. Chem. Soc., Chem. Commun., (1983) 214.

334. N. Kuhn and M. Winter, J. Organometal. Chem., 254 (1983) C 15.

335. N. Kuhn and M. Winter, J. Organometal. Chem., 252 (1983) C 5.

336. N. Kuhn and M. Winter, J. Organometal. Chem., 243 (1983) C 42.

337. N. Kuhn and M. Winter, J. Organometal. Chem., 243 (1983) C 47.

338. E. Lindner, F. Bouachir and S. Hoehne, Chem. Ber., 116 (1983) 46.

339. K. Sunkel, U. Nagel and W. Beck, J. Organometal. Chem., 251 (1983) 227.

340. N. Kuhn and M. Winter, Chem.-Ztg., 107 (1983) 14.

341. M. Mlekuz, P. Bougeard and M. J. McGlinchey, J. Organometal. Chem., 253 (1983) 117.

342. H. Brunner and M. Muschiol, J. Organometal. Chem., 248 (1983) 233.

343. B. Stibr, Z. Janousek, K. Base, J. Dolansky, S. Hermanek, K. A. Solntsev, L. A. Butman, I. I. Kuznetsov and N. T. Kuznetsov, Polyhedron, 1 (1982) 833.

344. Yu. A. Kaplin, G. V. Belysheva, L. S. Chernyshova, M. K. Kuskov, S. F. Zhil'tsov and G. N. Bortnikov, Deposited Doc., 1982, VINITI, 1730; Chem. Abstr., 98 (1983) 183887.

345. A. Streitwieser, R. Q. Kluttz, K. A. Smith and W. D. Luke, Organometallics, 2 (1983) 1873.

346. N. Rosch and A. Streitwieser, J. Am. Chem. Soc., 105 (1983) 7237.