ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1987[*]

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

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1. REVIEWS

In a special issue of the Journal of Organometallic Chemistry entitled "Transition Metal Organometallics in Synthesis and Catalysis" Mitsudo and co-workers reviewed the catalytic activity of (η-cyclooctadiene)(η-cyclooctatriene)ruthenium and its derivatives. Special attention was paid to the catalysis of the codimerization of acetylenes with 1,3-dienes, the [2+2] cross cycloaddition of norbornenes with dimethyl acetylenedicarboxylate and the addition of carboxylic acids to acetylenes to give enol esters [1].

The stereospecific reduction of acetylenes and the 1,4-reduction of dienes in the presence of an (η-arene)tricarbonylchromium has been reviewed [2]. The photochemical ligand exchange of (η-cyclopentadienyl)iron complexes including the (η-benzene)-(η-pentamethylcyclopentadienyl)iron cation have been surveyed by Roman and Astruc. The emphasis was centred on the design of organometallic photochrome systems [3].

Manriquez and Astruc have reviewed the chemistry of η-pentamethylcyclopentadienyl-iron compounds [4]. The use of organo-iron electron-reservoir sandwich complexes as reducing agents for specific substrates has been surveyed [5]. The history, current status and perspectives of the non-platinum group metal antitumour agents have been reviewed. This is a good review and it demonstrates the potential of metallocenes as cytostatic agents [6].

Electron transfer reactions of polynuclear organotransition metal complexes have been reviewed, polydecker sandwich compounds were included [7]. Ring slippage or interconversion of η^5-, η^3-, η^1-cyclopentadienyl and η^5-, η^3-indenyl ligands in transition metal complexes has been surveyed by O'Connor and Casey [8].

2. GENERAL RESULTS

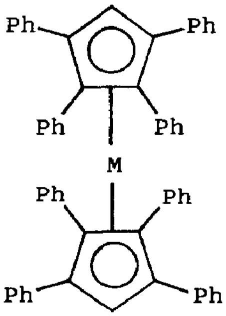
Ligand configurations have been calculated for several sandwich and half-sandwich organometallic complexes using a simplified form of the molecular dynamics method. The complexes studied included the metallocenes $(\eta\text{-}C_5H_5)_2M$, $(\eta\text{-}C_5Me_5)_2M$, $(\eta\text{-}C_5H_5)_2MX_2$, where X = H, Cl, CO and $(\eta\text{-}C_5H_5)_2MH_3$ together with the half-sandwich species $(\eta\text{-}C_5H_5)M(CO)_n$, where n = 3, 4 and $(\eta\text{-}C_4H_6)M(CO)_3$. Calculated ligand-metal-ligand angles were in agreement with experimental values [9].

Chemical doping of (η-diene)-, (η-cyclopentadienyl)- and (η-arene)-transition metal complexes in the form of compressed discs gave species with good electrical conductivity [10]. The structure rules for transition metal heterocarboranes have been applied to the electronic configurations of multi-decker sandwich complexes with the skeletons $Fe_2C_5(D_{5h})$, $Ni_2C_5(D_{5h})$, $V_2C_6(D_{6h})$, $Co_2C_6(D_{6h})$ and $Fe_2C_4(D_{4h})$. EHMO calculations indicated that the number of valence bonding orbitals varied with the distance between the metal atoms in the complexes. Species with 29-34 valence electrons were considered [11].

The indirect scalar spin-spin coupling constant $^1J(^{13}C, ^{13}C)$ has been determined for nineteen $(\eta^4$-diene)transition metal complexes containing Zr, Hf, Th, Mo, W, Fe and Co. The coupling constant $^1J(^{13}C, ^{13}C)$ was found to be a sensitive measure for metal-diene bonding. In planar η^4-s-cis-diene complexes with similar carbon bond lengths $^1J(^{13}C1, ^{13}C2) \sim {}^1J(^{13}C2, ^{13}C3)$ was found, while increasing participation of metallacyclopentene resonance hybrids, $^1J(^{13}C1, ^{13}C2) < {}^1J(^{13}C2, ^{13}C3)$ was observed [12].

A wide range of metallocenes in conjunction with titanium alkyls supported on inert inorganic materials have been used as heterogenous catalysts for the polymerization of α-olefins [13]. Reaction of transition metal halides with $K(C_5HPh_4)(THF)_{0.5}$ gave the paramagnetic metallocenes (2.1; M = V, Cr, Co, Ni). The crystal structures of these complexes were determined by X-ray analysis and they closely resembled those of the corresponding unsubstituted metallocenes. The reactivity of the metallocenes (2.1) was less than the corresponding unsubstituted compounds [14, 15].

The metallocenes (2.2; M = V, Cr, Co, Ni; E = C, Si, Ge, Sn) have been prepared from the anions $[Me_3EC_5H_4]^-$ and the metal salts in tetrahydrofuran. The ^1H and ^{13}C NMR spectra of the metallocenes (2.2) were recorded and interpreted. The results indicated that Me_3C was electron releasing and all the other



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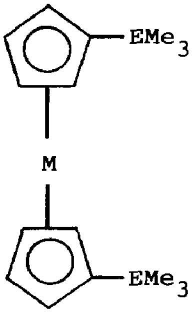

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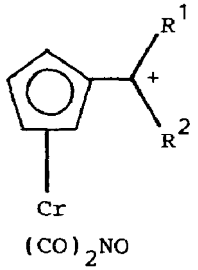
Me_3E groups were electron attracting, in the sequence Me_3Si > $Me_3Ge \gtrsim Me_3Sn$ [16]. Open-ring η-pentadienyl sandwich complexes of titanium, vanadium, chromium and iron have been examined by the EHMO method [17]. Bis(η-2,4-dimethylpentadienyl)vanadium and its adducts with Lewis bases were analysed in detail [18]. The electronic structures of some bis(η-cyclopentadienyl)-transition metal complexes were also examined [19].

The stabilization of ferromagnetic exchange in molecular solids has been the subject of a theoretical study. The McConnell model was used and considered coupling in linear chains of alternating radical cation donors and radical anion acceptors by means of interaction between the ground state and a virtual charge-transfer excited state. Several organometallic radicals were considered including $[(\eta\text{-}C_6H_6)_2Cr]^+$, $[(\eta\text{-}C_6R_6)_2Fe]^{\cdot+}$, $[(\eta\text{-}C_6R_6)_2Co]^+$, $[(\eta\text{-}C_5R_5)_2Co]^{\cdot}$, $[(\eta\text{-}C_5R_5)_2Ni]^{\cdot+}$ and $(\eta\text{-}C_5H_5)_2Ni$ [20].

Gas phase electron-transfer reactions of organometallic molecules and ions have been studied by Fourier transform ion cyclotron resonance. Rate constants for thermal self-exchange and cross reactions have been determined for metallocenes and metallocenium cations including manganocene, decamethylmanganocene, ferrocene, ruthenocene, cobaltocene and nickelocene [21].

The electronic effects of η-cyclopentadienyl ring substitution in a series of ferrocenes and ruthenocenes and titanocene, zirconocene and hafnocene dihalides has been investigated electrochemically and via ESCA spectroscopy. Trifluoromethylcyclopentadienylthallium was used to prepare the trifluoromethyl-substituted metallocenes [22].

The pK_{R^+} values for a series of dicarbonyl(η-cyclopentadienyl)nitrosylchromium "cynichrodenyl" carbinyl cations (2.3; R^1 = H, R^2 = phenyl, p-tolyl, p-anisyl; R^1 = Me, Ph, R^2 = Ph) have been determined and comparisons made with the efficiency of other organometallic moieties in the stabilization of α-carbocations. The order of efficiency was:
ferrocenyl > tricarbonyl(η-cyclobutadienyl)iron > cynichrodenyl > cymantrenyl > benchrotrenyl > benzyl [23].



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The mechanism of negative molecular ion formation by ferrocene, cobaltocene and nickelocene through dissociative electron capture has been discussed using the molecular orbitals of the appropriate neutral and negatively charged metallocenes [24]. The Franck-Condon barriers associated with self-exchange electron-transfer kinetics of ferrocene, cobaltocene and ruthenocene in the gas phase have been satisfactorily predicted [25].

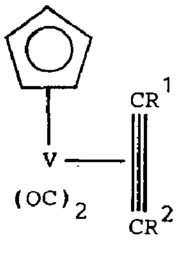
Ferrocene and nickelocene have been pyrolysed to give thin films of the free metals which were deposited on stainless steel and nickel. The gaseous decomposition of ferrocene, cobaltocene and nickelocene has been discussed in terms of Born-Haber cycles [26]. Benchrotrenyl and polyarene-iron derivatives of the carborane nido-2,3-dibenzyl-2,3-dicarbahexaborane(8) have been prepared and characterized [27] together with mono-, di- and tri-iron polyarene sandwich complexes of the carborane nido-2,3-$Et_2C_2B_4H_6$ [28] and (η-cyclopentadienyl)cobalt or tricarbonylchromium derivatives of nido-$(PhCH_2)_2C_2B_4H_6$ [29].

3. (η-C_5H_5)V(CO)$_4$

The dianion $[(\eta\text{-}C_5H_5)V(CO)_3]^{2-}$ combined with an aryldichlorophosphine to give the bridging phosphinidene complex $[(\eta\text{-}C_5H_5)V(CO)_2]_2\{\mu\text{-}P[2,4,6\text{-}(Me_3C)_3C_6H_2]\}$ which was shown by X-ray crystallography to contain vanadium-phosphorus multiple bonding [30]. Tetracarbonyl(η-cyclopentadienyl)vanadium underwent a photoinduced reaction with acetylenes to give the derivatives (3.1; R^1, R^2 = H, Me, Ph, $SiMe_3$) which were in turn converted into the products (3.2; R^1, R^2 = H, Me, Ph, $SiMe_3$; L = PMe_3, Me_3CNC) by treatment with the appropriate phosphine and isocyanide. NMR spectroscopy indicated that the acetylene ligand in the complex (3.2) was a four electron donor [31].

Oxidation of the tetracarbonylvanadium complex (3.3) in the presence of chlorine gave the vanadium(V) oxide derivative (3.4; L = Cl) which was converted to the diphenyl, dimethoxy and dibromo derivatives (3.4; L = Ph, OMe, Br) respectively with phenyl Grignard reagent sodium methoxide and boron tribromide. The same sequence of reactions was carried out with tetracarbonyl(η-pentamethylcyclopentadienyl)vanadium [32].

The preparation of the η^5-indenyl complex (3.5) has been reported. This compound was similar to the η^5-cyclopentadienyl



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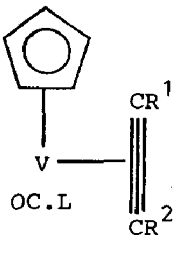
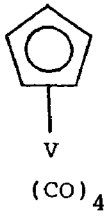


3.2

analogue and it underwent slow carbonyl substitution via a dissociative process [33].

The reaction of the phosphaalkyne P≡CCMe$_3$ with (η-pentamethylcyclopentadienyl)(η-naphthalene)vanadium produced the vanadium complex (3.6). Treatment of this complex with carbon monoxide afforded the carbonyl compound (3.7). The structures of the complexes (3.6 and 3.7) were confirmed by X-ray analysis [34].



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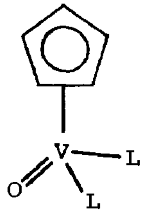

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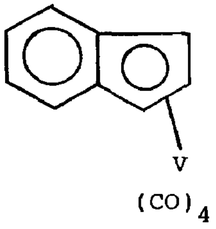

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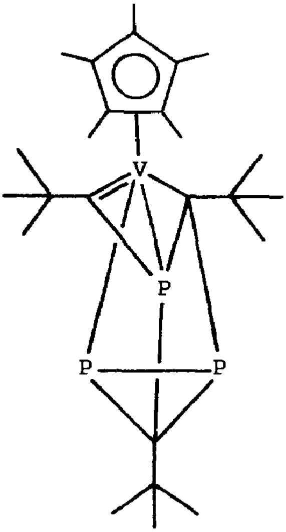

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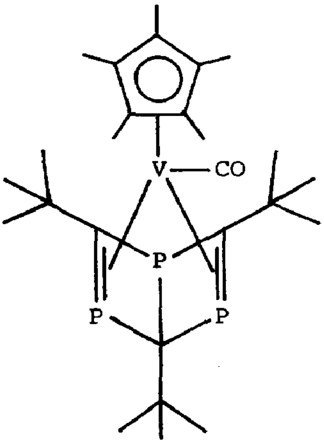

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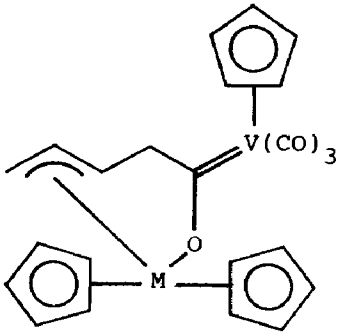

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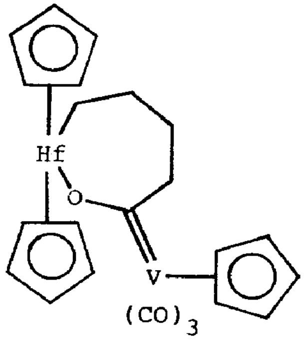

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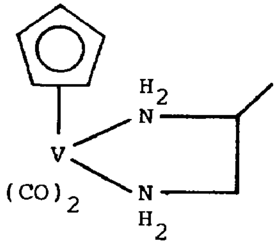

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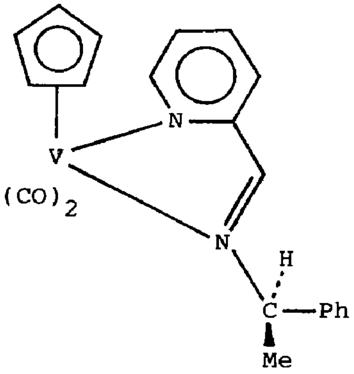

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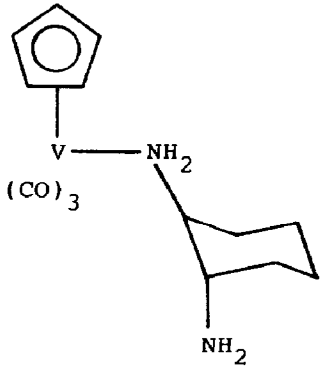

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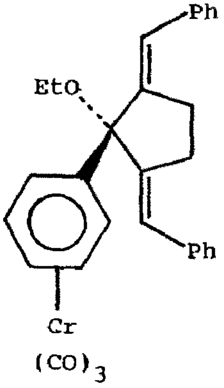
The treatment of (s-trans-η^4-butadiene)zirconocene or hafnocene with tetracarbonyl(η-cyclopentadienyl)vanadium produced the carbene complex (3.8; M = Zr) or a mixture of the complex (3.8; M = Hf) and an isomer (3.9). The structure of the carbene complex (3.8; M = Zr) was determined by X-ray analysis [35]. Photolysis of tetracarbonyl(η-cyclopentadienyl)vanadium with amines produced the corresponding amine-vanadium complexes (3.10, 3.11 and 3.12). The ^{51}V NMR spectra of these compounds indicated the presence of diastereomeric pairs of enantiomers [36].

4. (η-C_6H_6)Cr(CO)$_3$

(i) Formation

The cyclopentane benchrotrene complex (4.1) has been formed from phenylallene and an (η-trimethylenemethane)chromium complex [37]. Trimethylsilylmethoxybenzylalcohols have been treated with hexacarbonylchromium to give complexes such as the benchrotrene (4.2) and its enantiomer which were precursors for acorenone B and acorenone [38].

Reaction of the phosphite 3,5-$Me_2C_6H_3$ $(CH_2)_3P(O)(OEt)_2$ with hexacarbonylchromium produced the corresponding tricarbonylchromium complex (4.3). Treatment of this complex with lithium aluminium hydride and ultraviolet irradiation gave the bridged



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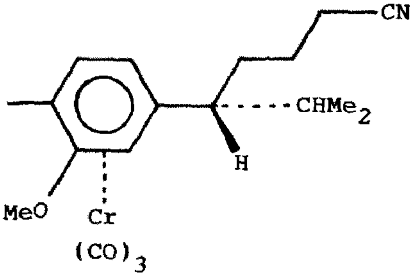

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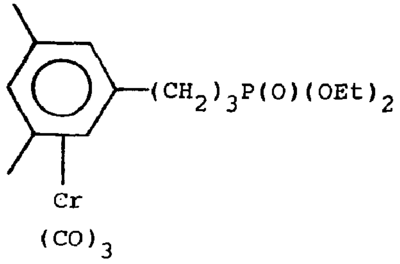

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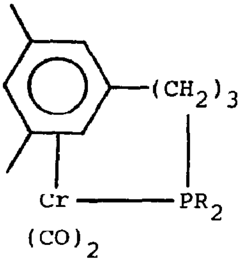
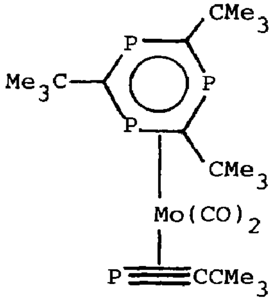


4.4

compound (4.4; R = H). The related complexes (4.4; R = OPh, OEt, $SiMe_3$) were also prepared [39]. Several (η-arene)$Cr(CO)_3$ complexes were isolated as secondary products from the reactions of chromium carbene complexes $(CO)_5Cr{=}C(OMe)R$ (R = Ph, *o*- and *p*-OMe and *o*-O-tBu-C_6H_4, 1-C_6H_9, 1-C_5H_7O) with a variety of acetylenes ($R^1C{\equiv}CR^2$, R^1, R^2 = H, Me, Et, n-Pr, Ph, $SiMe_3$) [40].



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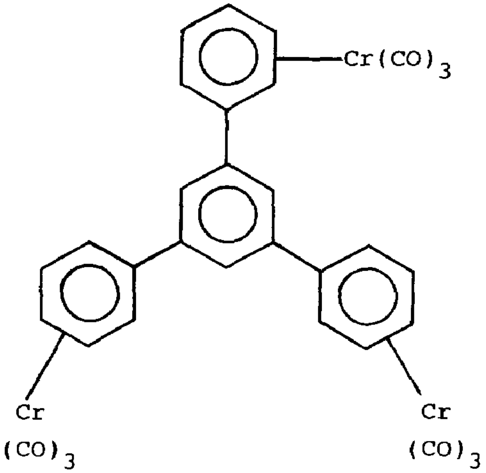

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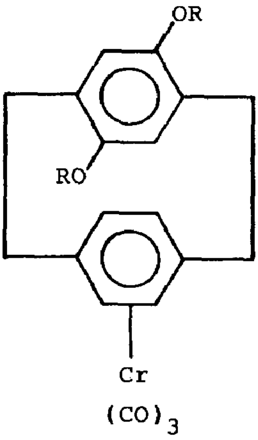
The cyclotrimerization of $\mathrm{Me_3CC{\equiv}P}$ in the presence of tricarbonyl(η-toluene)molybdenum produced the η-1,3,5-triphosphabenzene complex (4.5) [41]. A number of tricarbonylchromium complexes of pentaphenylethane have been prepared and their structures examined via X-ray diffraction [42].

The reaction of 1,3,5-triphenylbenzene with hexacarbonylchromium produced a series of products where the $\mathrm{Cr(CO)_3}$ group was bound to the central ring or to one, two or all three peripheral phenyl rings. The structure of the complex (4.6) was determined by X-ray analysis. The ^{1}H and ^{13}C NMR spectra of the complexes indicated that the peripheral rings did not exhibit restricted rotation even at low temperatures [43].

4,7-Dialkoxy[2.2]paracyclophanes and the corresponding 1,9-dienes underwent selective complexation with $\mathrm{(EtCN)_3Cr(CO)_3}$ to give the tricarbonylchromium complexes (4.7 and 4.8; R = H, Me, n-Bu) with the $\mathrm{Cr(CO)_3}$ moiety on the less substituted ring. Lithiation-trimethylsilylation of these and related complexes was investigated [44]. Reaction of bis(2,4-dimethyl-6-*t*-butylphenyl) ketone with hexacarbonylchromium produced a mixture of the stable torsional isomers (4.9 and 4.10) [45].



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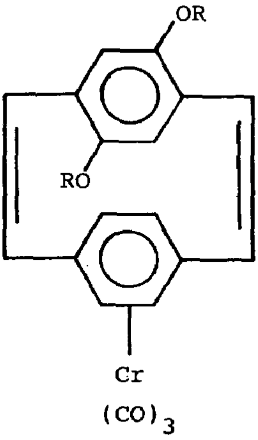

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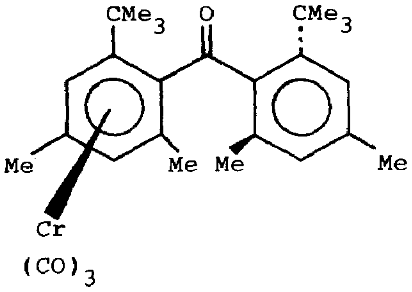

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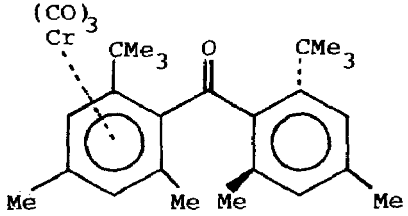

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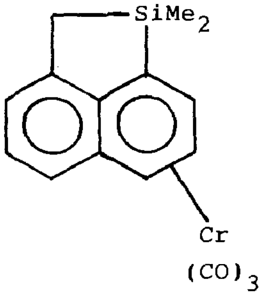
Reaction of 1,1-dimethyl-1-silaacenaphthene with $L_3Cr(CO)_3$, where L = NH_3 or pyridine, afforded a mixture of the tricarbonylchromium complexes (4.11 and 4.12). The inter-ring haptotropic rearrangement of the tricarbonylchromium group in the complex (4.12) was investigated [46]. Azulene combined with bis(η-benzene)molybdenum to give the (η-azulene)molybdenum complex (4.13) in which the azulene ligand was shown by X-ray analysis to be η^6-bonded. Treatment of this complex (4.13) with $(MeCN)_3$-$M(CO)_3$, where M = Cr, Mo, W, gave the binuclear complexes (4.14; M = Cr, Mo, W) with an η^6:η^4-azulene bridge in each case. One of the products (4.14; M = Cr) has been characterized by X-ray crystallography [47].



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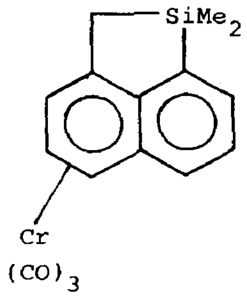

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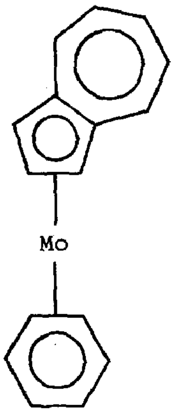

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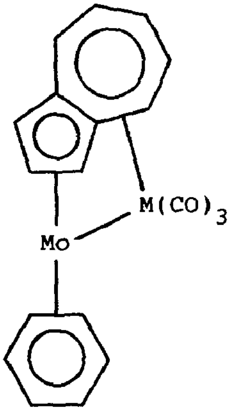

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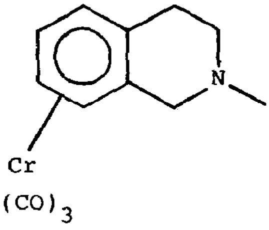
The treatment of hexacarbonylchromium with N-methyltetrahydroisoquinoline generated the tricarbonylchromium complex (4.15). The 4-*exo* proton in this complex was regio- and stereoselectively removed with n-butyllithium. Condensation of the lithio intermediate with a variety of electrophiles produced the corresponding 4-substituted products [4.16; R = D, Me, Et, CH_2Ph, $Me_2C(OH)$] with retention of configuration [48].

Seven planar and bent diarenes including fluorene and 9,10-dihydrophenanthrene have been treated with hexacarbonylchromium to give tricarbonylchromium and bis(tricarbonylchromium) derivatives. Bent arenes were attacked at either the convex (*syn*) or concave (*anti*) faces of the ligand. Reaction at the *anti*-face was favoured in the absence of other directing groups.



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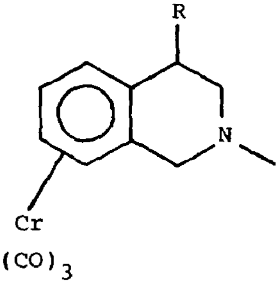
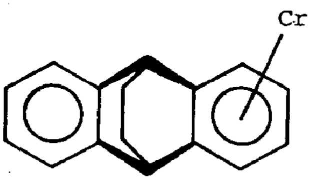


4.16

Dimetallation of planar diarenes gave exclusively trans-products while bent diarenes gave trans-products together with a small proportion of cis-syn-products. Thus 9,10-ethanoanthracene gave the mono-syn (4.17) mono-anti (4.18) and di-trans (4.19) products [49].

The complex (4.20) has been prepared by treating triammine-tricarbonylchromium(O) with 5,10-dihydroindene[2,1-a]indene. Deprotonation of the complex (4.20) produced the η^6-anion (4.21) which rearranged irreversibly into the η^5-anion (4.22). Alkylation of the anion (4.22) with benzyl iodide afforded the 5-exo-benzyl derivative (4.23) [50]. Reaction of the dianion (4.24) with diiodoethane produced the η^6-metallabenzene-



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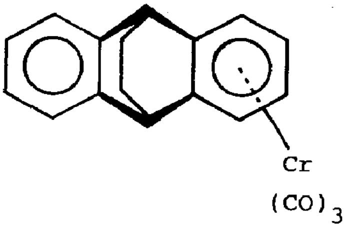

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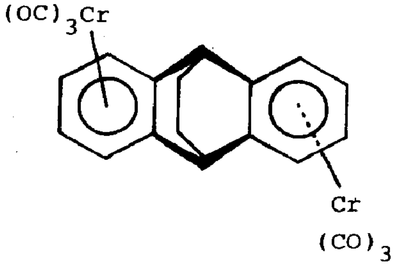

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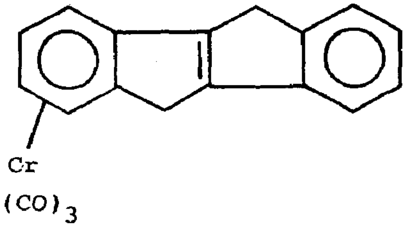

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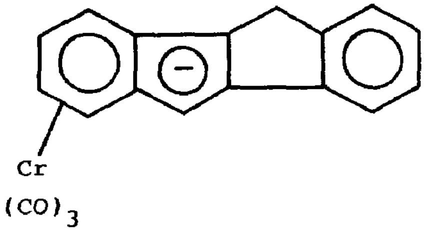

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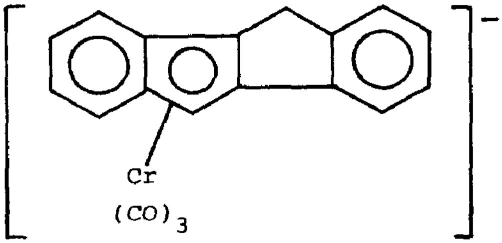

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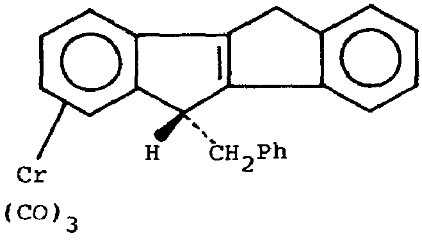

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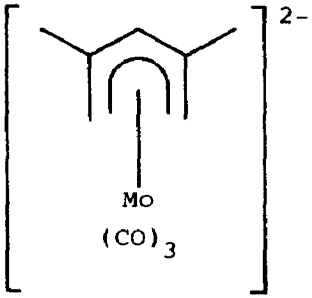

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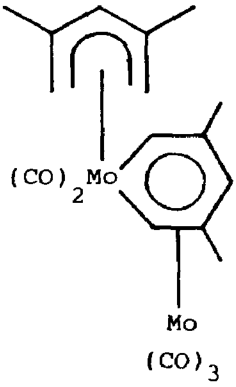


4.25

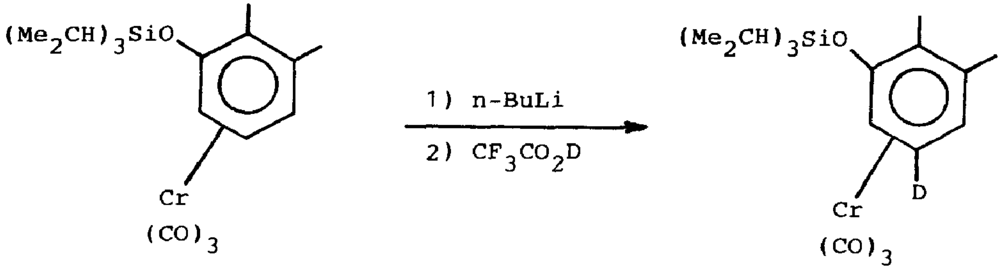
molybdenum complex (4.25). The structure of this latter complex was confirmed by X-ray analysis. Variable temperature ^1H NMR spectroscopy indicated hindered rotation of the η^5-dimethylpentadienyl ligand [51].

4. (ii) Spectroscopic and Physico-chemical Studies

A reinvestigation has been carried out of the X-ray crystal structure of tricarbonyl(η-hexamethylbenzene)chromium at low temperature. Carbon-carbon bond length alternation of 0.021 Å was found between the ring carbon atoms in the η-hexamethylbenzene ligand. All the C-CH_3 bond distances were essentially equal [52]. The structure of the tricarbonylchromium complex (4.26) has been determined by X-ray analysis. The complex adopted an eclipsed conformation with respect to the siloxy group. NMR spectroscopy indicated that in solution the major conformer had the same conformation. Lithiation, followed by deuteration produced the complex (4.27) [53].

The silylbenchrotrene complex (4.28) has been characterized by X-ray crystallography and contained a three-centre chromium-hydrogen-silicon two-electron bond. Structural and ^{29}Si NMR results indicated that the silicon-hydrogen interaction was stronger than in the analogous isoelectronic complex (η-C_5Me_5)-$(CO)_2Mn(H)SiHPh_2$. This difference was attributed to the larger size of the hexamethylbenzene ligand [54].

The complex formed between chromium and N,N'-diphenylpyromellitimide (4.29) using ultrahigh vacuum and clean surfaces



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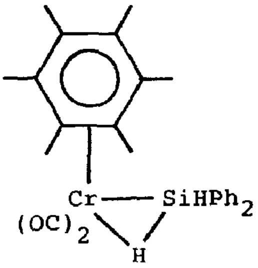

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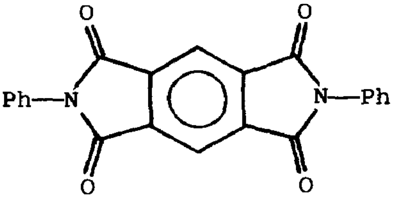


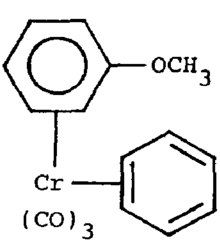
4.29

has been investigated by photoelectron spectroscopy. MO calculations have been made on the basis of a structure where the chromium atom is located over the face of the benzene ring. Reasonable agreement was obtained between the carbon 1s spectroscopic results and the calculated carbon 1s core levels [55].

Electron bombardment of mixtures of (η-benzene)tricarbonylchromium and ammonia produced $[Cr(NH_3)]^+$, $[Cr(NH_3)_2]^+$ and $[C_6H_6Cr(NH_3)]^+$ [56]. The electron deformation density in benchrotrene has been determined by the X-X method. Good agreement was obtained with a recent theoretical calculation of the deformation density [57]

A Fourier transform ion cyclotron resonance spectroscopic study has been carried out on the reactions of straight chain and cyclic alkenes and polyenes with the 13-electron radical anion $[Cr(CO)_3]^{\bar{\cdot}}$. Straight chain alkenes gave $[C_nH_{2n-2}Cr(CO)_3]^{\bar{\cdot}}$ as the main ionic product together with some $[C_nH_{2n-2}Cr(CO)_2]^{\bar{\cdot}}$, where n = 4 - 8. Similar reactions took place with cyclohexene and methylcyclohexene [58].

Laser flash photolysis has been used to investigate the transient species involved in the photochemical carbonyl substitution of $(\eta^6$-anisole$)Cr(CO)_3$. The results indicated the existence of an η^2-benzene intermediate (4.30) in benzene as the solvent. Similar types of transient intermediate were observed for fluorobenzene and mesitylene [59]. Gas-phase ultraviolet photoelectron spectra and parameter free Fenske-Hall molecular orbital calculations have been reported for the $(\eta$-$C_6H_6)$-,



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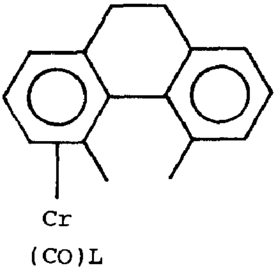
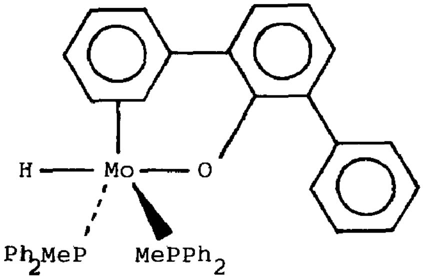


4.31

(η-1,3,5-$Me_3C_6H_3$) and (η-C_6Me_6)-$M(CO)_3$ complexes, where M = Cr, Mo or W. Data was obtained on the bonding interactions between the η-arene ligand and the $M(CO)_3$ fragment [60].

Photolysis of the (η-dimethyldihydrophenanthrene)chromium complex (4.31; L = CO) in the presence of CS and Ph_3P gave the derivatives (4.31; L = CS, Ph_3P) and these were each separated into four stereoisomers by chromatography. CD and ^1H NMR spectroscopy were used to make the configurational assignments. The exo and endo isomers of the complexes (4.31; L = CO, CS) were formed in equal proportions while the sterically crowded complex (4.31; L = Ph_3P) existed in an exo:endo ratio of 4:1 [61].



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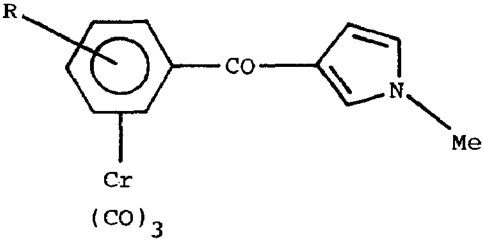


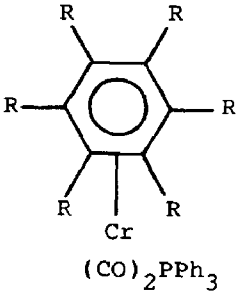
4.33

Extended thermolysis of the tetrahydrides $MH_4(PMePh_2)_4$ (M = Mo, W) with 2,6-diphenylphenol produced the corresponding phenoxides. The structure of the complex (4.32) was determined by X-ray analysis [62].

The radical anions of the tricarbonylchromium complexes (4.33; R = H, *o*-CH_3, *p*-CH_3) and the uncomplexed N-methyl-3-aroylpyrrole ligands were prepared by potassium reduction and the ESR spectra were recorded. The spectra indicated the withdrawal of unpaired electron density by the $Cr(CO)_3$ group. SCCC-MO calculations on the ligands showed that unpaired electron density was mainly on the benzene ring with a little on the CO and the pyrrole ring [63].

An *in situ* infrared transmission spectroelectrochemical study of tricarbonyl(η-mesitylene)chromium has been carried out in an optically transparent thin-layer electrochemical cell. The results indicated that the $[(\eta\text{-mesitylene})Cr(CO)_3]^+$ radical had a geometry similar to that of the neutral complex [64]. Three benchrotrene complexes and eight ferrocenes have been characterized by micro-Raman spectroscopy of the solids at room temperature. The use of microscope optics enabled low laser powers to be used and materials of low stability to be investigated [65].

Variable temperature ^{13}C NMR spectroscopy has been used to examine restricted rotation about the chromium-phosphorus bond in the benchrotrene complexes (4.34; R = H, Me, Et, n-Pr).



4.34

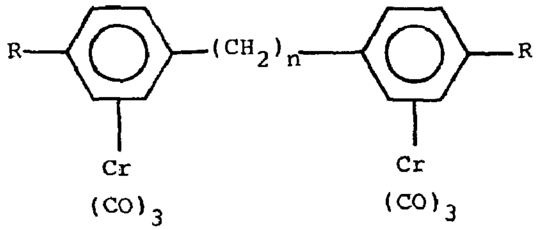
Restricted rotation was observed for the three hexaalkyl substituted benchrotrenes (4.34; R = Me, Et, n-Pr) with $\Delta G^{\neq} = 38$ kJ mol^{-1}. Intramolecular rotation in these complexes was discussed in terms of two cones with a common apex at the chromium atom. The structure of the complex (4.34; R = n-Pr) has been determined by X-ray crystallography, the hexa-n-propylbenzene ligand adopted an all-distal allkyl group conformation [66].

The variable-temperature cross polarization-magic angle spinning ^{13}C NMR spectra of crystalline $(\eta\text{-}C_6H_5CH_3)Cr(CO)_3$ and $(\eta\text{-}C_6H_5CH_3)Mo(CO)_3$ have been recorded and interpreted. The results suggested that the tricarbonyl groups rotated in the solid state and the η-arene rings were static [67]. Spin lattice relaxation times for the ^{96}Mo, ^{17}O and methine and carbonyl ^{13}C nuclei have been determined for a series of (η-arene)tricarbonylmolybdenum complexes, where arene = o-, p- and m-xylene, toluene and mesitylene. The results indicated that there was considerable dπ - pπ back bonding and a correlation between the carbonyl force constants and the ^{17}O quadrupole coupling constants was presented [68].

Linear correlations have been found between standard enthalpies of formation of crystalline inorganic and organometallic complexes MX_nL_m and enthalpies of formation of ligands L or LH in their standard reference state. This correlation was tested and found to be valid for $(\eta^6\text{-arene})Cr(CO)_3$ and $(\eta^6\text{-arene})_2Cr$ complexes [69]. The effect of ketones and ethers on the rates and mechanism of arene exchange reactions of the (η-diarylalkane)tricarbonylchromium complexes (4.35; n = 1, R = CH_3; n = 2, 3, R = H; 4.36, 4.37 and 4.38) have been investigated. The results suggested an intermediate chromium complex having three carbonyl groups, ketone and two η^2-bound arenes [70].

The kinetics of internal and external arene exchanges in hexadeuterobenzene have been determined for a series of (η-arene)-$Cr(CO)_3$ complexes, where arene = ditolylmethane, ditolylcyclopropane, dimesitylmethane and dibenzobicyclo[2.2.2]octadienes. The results indicated that the exchange was a stepwise process where the bonding in the displaced arene proceeded from η^6 to η^4 to η^2 [71].

The rates of internal and external exchange of (diarylalkane)tricarbonylchromium complexes have been measured.



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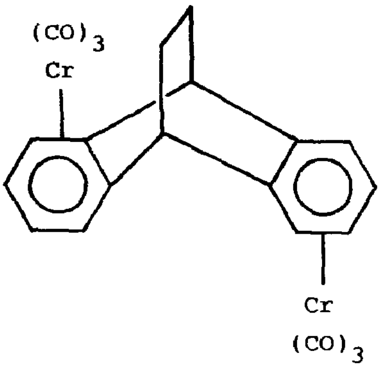

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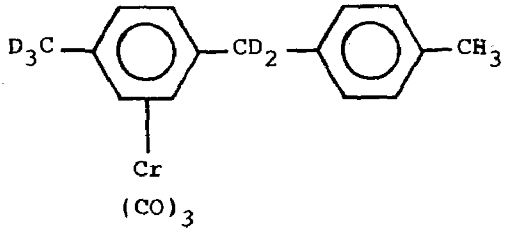

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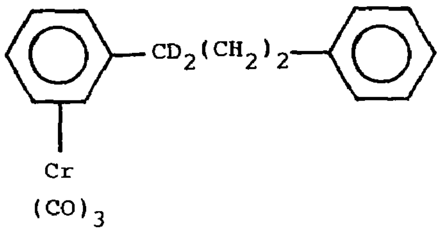
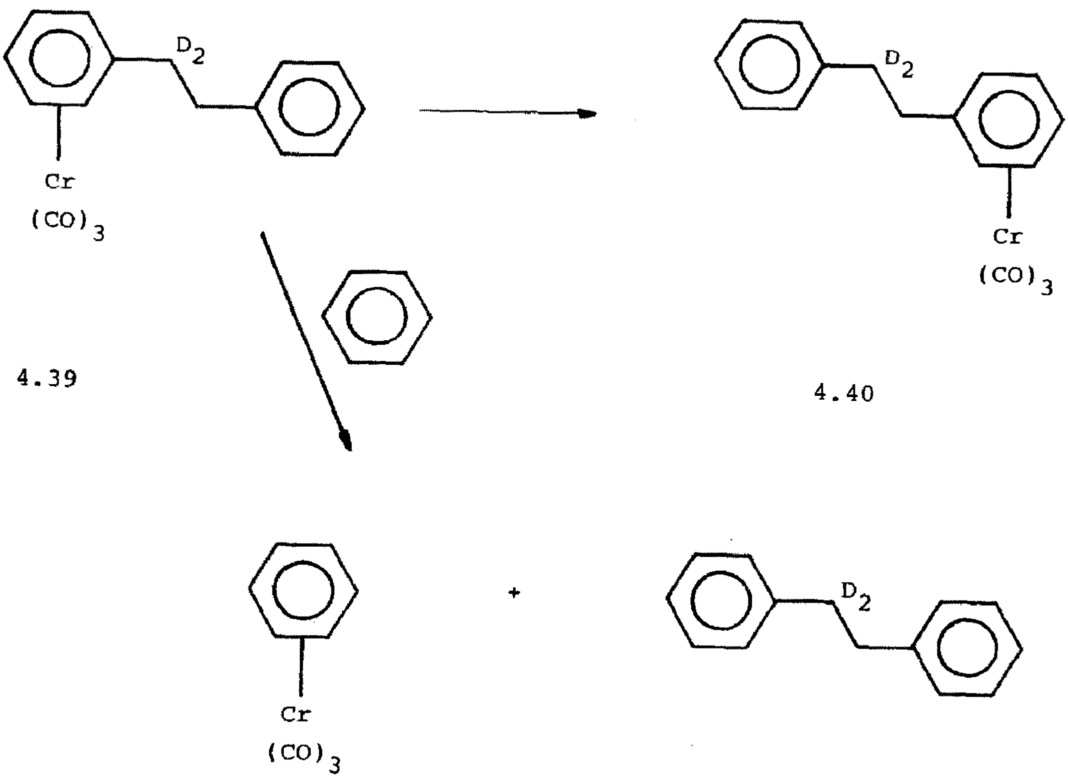


4.38

Classical neighbouring group participation was observed for the internal exchange reactions. Thus the benchrotrene (4.39) underwent internal exchange to give the isomer (4.40) and external exchange with benzene to form the products (4.41 and 4.42) [72].

The (η^6-fluorene)chromium complexes [4.43; L = CO, $P(OPh)_3$, PPh_3, $P(n\text{-}Bu)_3$] have been prepared and metallated with potassium hydride and THF at -20°C to form the corresponding (η^6-fluorene)-chromium anions. These underwent equilibration with the (η^5-fluorene)chromium anions (4.44). The $\eta^6 \rightleftharpoons \eta^5$ haptotropic equilibrium was markedly influenced by the nature of the ligand L. Thus the equilibrium ratios η^6/η^5 observed at 30°C were:

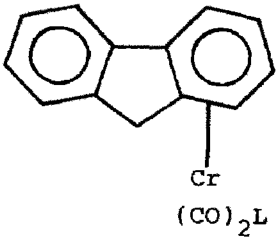


4.39

4.40

4.41

4.42



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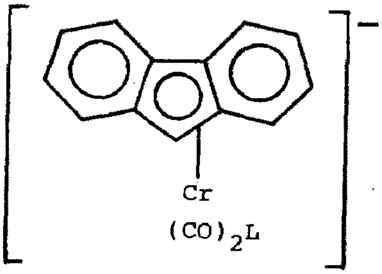
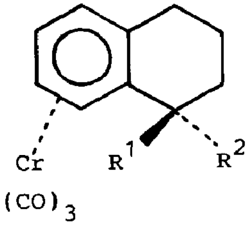


4.44

$$\begin{array}{ccccccc} L = CO & > & P(OPh)_3 & > & PPh_3 & > & P(n\text{-}Bu)_3 \\ 7 & & 0.25 & & 0.10 & & 0 \end{array}$$

The ^{13}C and ^{31}P NMR spectra, the reduction potentials and IR carbonyl stretching frequencies were dependent on the nature of L [73].

The (η-arene)chromium complexes (4.45; R^1 = H, Me; R^2 = OH, OAc) underwent stereoselective exo-substitution at the benzylic carbon atom with allyltrimethylsilane and propargyltrimethylsilane. Thus the complex (4.45; R^1 = H, R^2 = OAc) and allyltrimethylsilane gave the exo-allyl product (4.45; R^1 = $CH_2CH{=}CH_2$ R^2 = H) [74].

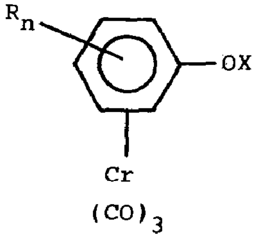


4.45

4. (iii) General Chemistry

Displacement of halide from the substituted benchrotrenes (4.46; R = alkyl, alkoxy, haloalkyl, amino; X = Cl, Br; n = 0-3) has been achieved by carbonylation with carbon monoxide in the presence of a palladium phosphine complex such as $PdCl_2(PPh_3)_2$. The products were the corresponding benzoic acids and benzoates [75]. Exchange reactions of a series of (η-diarylalkane)-tricarbonylchromium complexes with arenes and carbon monoxide have been studied. Neighbouring group participation in these exchange reactions was investigated [76].

The kinetics of the arene exchange reaction in (η-arene)-$Cr(CO)_3$ complexes with benzene has been investigated. The η-arene groups contained ketone, ether or nitrile groups as substituents and these groups catalyzed the exchange. All the

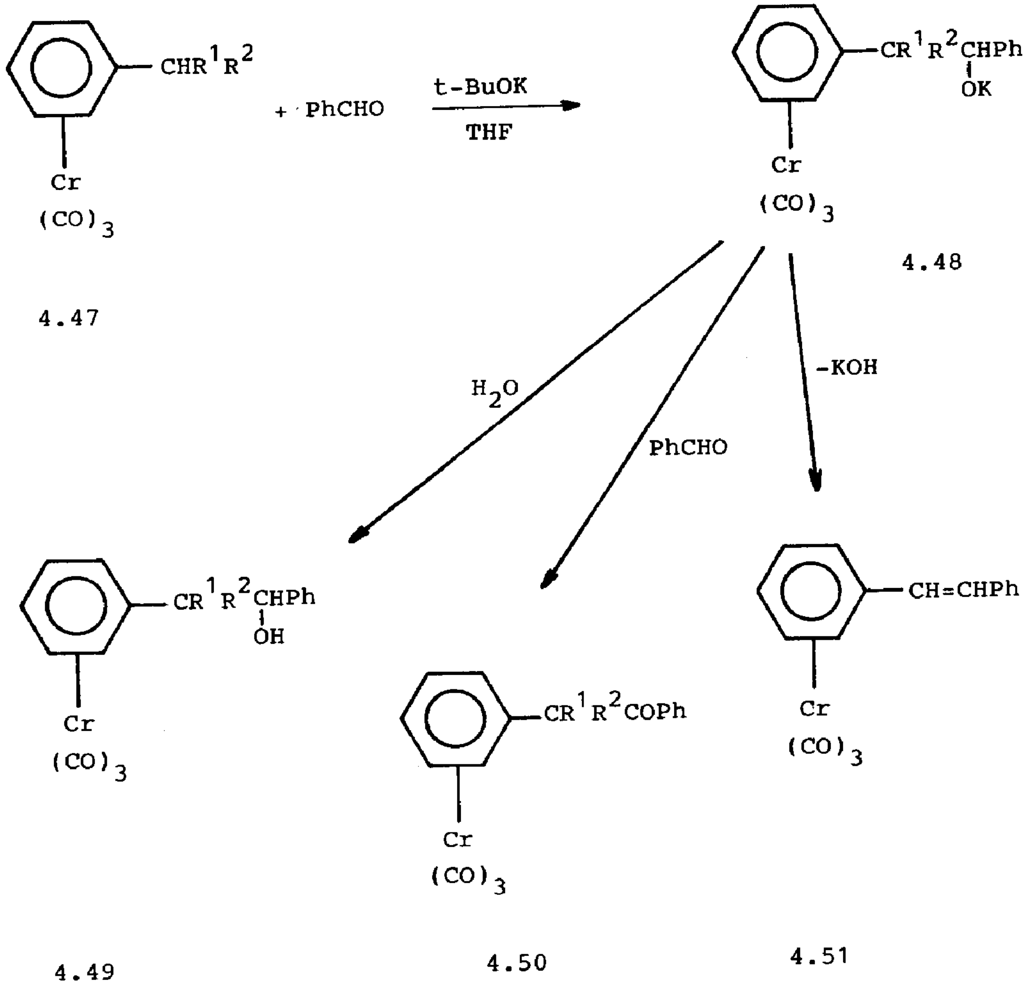


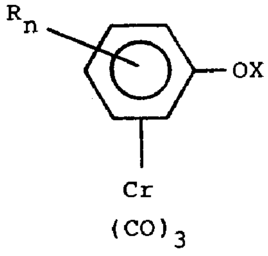
4.46

reactions were first order in the η-arene complex [77]. Benchrotrene complexes (4.47) underwent addition with benzaldehyde in the presence of potassium t-butoxide and THF to form the intermediates (4.48) which gave products determined by the nature of the substituents on the α-carbon atom. Where two substituents were present, the alcohols (4.49; R^1 = Me, R^2 = Me, OMe) were obtained, with one substituent the ketones (4.50; R^1 = H, R^2 = alkyl, OMe) were formed and the intermediate (4.48, R^1 = R^2 = H) gave the olefin (4.51) [78].

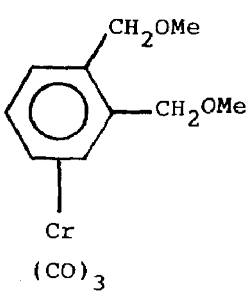
The nucleophilic substitution of the (η-fluoroarene)(Cr(CO)$_3$ complexes (4.46; X = F, R = 2,3-, 2,6-Me_2; 2-H_2N, 4-Me; o-, p-NH_2; o-, m-, p-Me; o-, m-, p-OMe; p-NHMe; 2-Me, 3-NH_2; 2-Me, 5-NH_2) with alkoxides gave the corresponding ethers (4.52; X = Me, Et, i-Pr). The $Cr(CO)_3$ group was removed from these latter complexes by photolysis [79].

α-Substitution of benzyl alkyl ethers and sulphides was achieved by complexation to the tricarbonylchromium group which suppressed Wittig and related rearrangements. For example, the reaction of 1,2-$(MeOCH_2)_2C_6H_4$ with hexacarbonylchromium afforded the complex (4.53). Treatment of the complex (4.53) with n-BuLi followed by methyl iodide produced the stereoselectively methylated derivative (4.54). When the same reaction was repeated with complex (4.54) the dimethylated product (4.55) was obtained stereoselectively [80]. The lithiation of the isomeric tricarbonylchromium complexes (4.56; X = o, m or p-F)


CHR^{1}R^2
+ PhCHO
t-BuOK
THF
CR^{1}R^{2}CHPh
OK
Cr
(CO)$_3$
4.47
4.48
H$_2$O
PhCHO
-KOH
CR^{1}R^{2}CHPh
OH
CR^{1}R^{2}COPh
CH=CHPh
4.49
4.50
4.51


R$_n$
OX
Cr
(CO)$_3$

4.52



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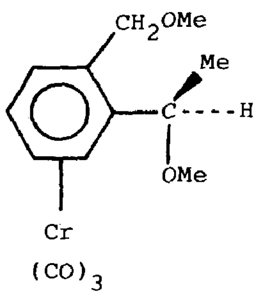

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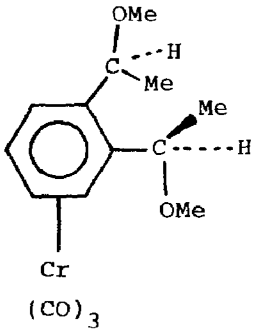
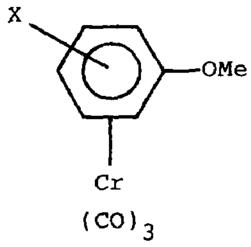


4.55

has been carried out. The lithio-intermediates were quenched with a series of electrophiles and nucleophilic substitution of the products was investigated [81].

Metallation of the tricarbonylchromium complexes (4.57, 4.58 and 4.59) with t-BuOK in tetrahydrofuran followed by condensation with a carbonyl compound gave exclusively the γ-adducts. For example, metallation of the η-allylbenzene complex (4.58) followed by reaction with benzaldehyde produced the γ-adduct (4.60) [82]. Lithiation of the η-benzo[b]thiophene complex (4.61; $R^1 = R^2 = H$) with an equimolar amount of n-butyllithium followed by methyl iodide gave the 2-substituted derivative (4.61; R^1 = Me, R^2 = H). Lithiation with a four fold molar



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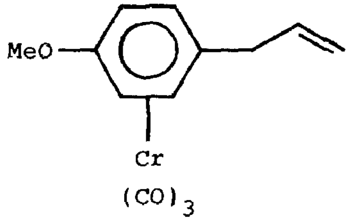

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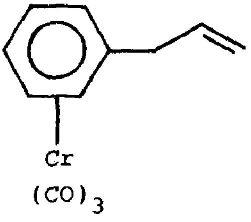

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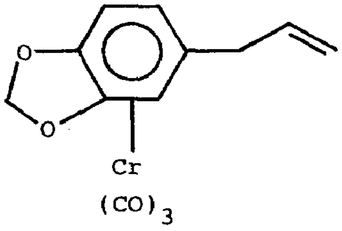

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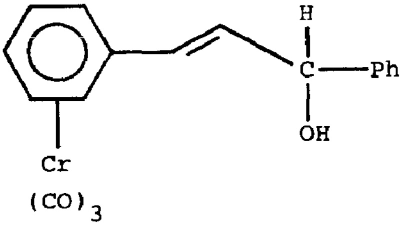
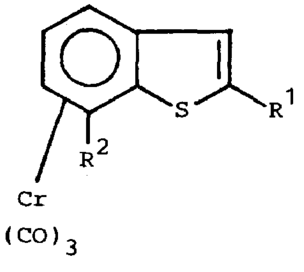


4.60

excess of n-butyllithium followed by methyl iodide gave mainly the 2,7-dimethyl substituted complex (4.61; $R^1 = R^2 = Me$) [83].

The tricarbonylchromium complexes of naphthalene and acenaphthylene have been prepared. The lithiation of these complexes was investigated [84]. The hydrocarbon ligand in (η-acenaphthylene)tricarbonylchromium was lithiated preferentially at C-3 and the lithio-intermediate was treated with deuterium oxide, iodomethane, chlorotrimethylsilane, 1,2-dibromoethane, acetaldehyde and benzaldehyde to give the corresponding 3-derivatives. The lithio derivatives $LiCMe_2CN$, $LiCMe_2CO_2Et$, $LiCMe_2CONEt_2$ and $LiCMe_3$ underwent addition of the carbanion moiety to the hydrocarbon ligand in (η-acenaphthylene)tricarbonyl-



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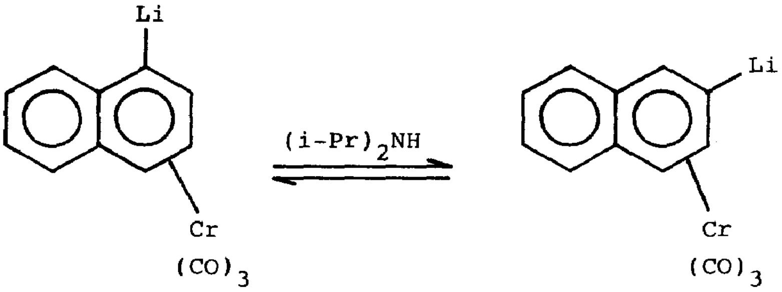
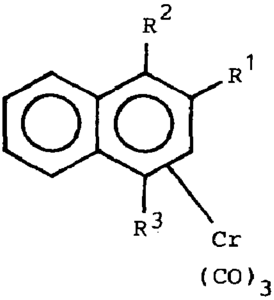


4.62 4.63

chromium to give, after oxidative cleavage with iodine the corresponding 3-substituted acenaphthylenes [85].

Lithiation of (η-naphthalene)tricarbonylchromium with n-butyllithium gave a 37/63 mixture of the 1- and 2-substituted products (4.62 and 4.63). Lithiation with tetramethylpiperidyllithium produced 96% of the 2-lithiated product (4.63). Addition of isopropylamine to this latter reaction mixture rendered the process reversible and a 1/1 equilibrium mixture of the 1- and 2-substituted products was formed [86].

Lithiation of tricarbonyl(η-naphthalene)chromium (4.64; $R^1 = R^2 = R^3 = H$) with (tetramethylpiperidinyl)lithium followed by treatment with an electrophile (D^+, Me_3SiCl, CO_2, MeI or



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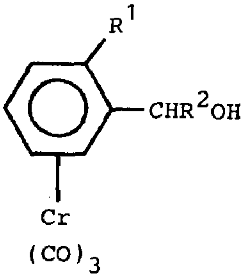
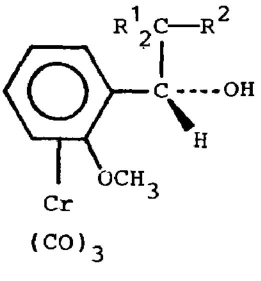


4.65

$EtOSO_2CF_3$) gave exclusively the corresponding substituted complex (4.64; R^1 = D, $SiMe_3$, CO_2H, Me, Et; $R^2 = R^3$ = H). When the same reaction was carried out with n-BuLi mixtures of products were obtained (4.64; R^1 = D, $SiMe_3$, Et; $R^2 = R^3$ = H) and (4.64; R^2 = D, $SiMe_3$, Et; $R^1 = R^3$ = H) in approximately 3:7 ratios [87].

The tricarbonylchromium complexes, (η-polyarene)$Cr(CO)_3$, where polyarene = naphthalene, 5-methoxynaphthalene, 2,6- and 2,7-dimethoxynaphthalene and phenanthrene, have been metallated at -78 to -95°C with $LiN(CHMe_2)_2$. The lithio intermediates decomposed rapidly but were trapped by reaction with deuterium oxide, iodomethane, chlorotrimethylsilane, acetaldehyde and benzaldehyde to give the corresponding derivatives. Kinetic evidence suggested that (η-naphthalene)$Cr(CO)_3$ underwent initial lithiation at C-1 followed by rearrangement to give the thermodynamically preferred C-2 lithiated species [88].

Benzylic alcohols have been treated with hexacarbonylchromium to give the benchrotrene complexes (4.65; R^1 = MeO, Me; R^2 = Me, $CHMe_2$) with a diastereoisomeric excess of 38-86%. The diastereoisomers showed different chemical reactivities; thus treatment with sulphuric acid and methanol gave the (RS,SR)-ether while the (RR,SS)-alcohol was unchanged [89].



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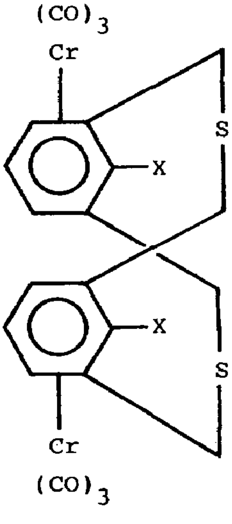

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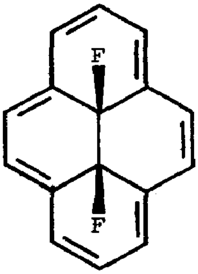
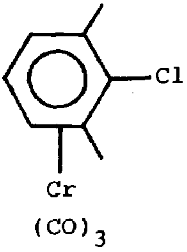


4.68

The addition of the 2-bromoesters or 2-bromonitriles $R^1_2C(Br)R^2$, where R^1 = H, Me, and R^2 = CO_2Me, CO_2-t-Bu, CN, CO_2Et, to tricarbonyl(η-o-methoxybenzaldehyde)chromium proceeded with complete asymmetric induction to give the corresponding optically active alcohols (4.66) [90]. Davies has briefly reviewed the role of the tricarbonylchromium group in stereoselective synthesis [91].

The (η-syn-dithia[3,3]metacyclophane)chromium complexes (4.67; X = H, F, Me) have been prepared from hexacarbonylchromium and the appropriate ligands. Methylation, Stevens rearrangement, Hofmann elimination and decomplexation gave the syn-[2,2]metacyclophanes. The difluoro compound was isomerized to cis-difluorodihydropyrene (4.68) [92]. The chlorobenchrotrene (4.69) underwent tele-nucleophilic substitution with high regioselectivity. Thus, treatment with 2-lithio-isobutyronitrile at -78°C and then with trifluoroacetic acid gave the derivative (4.70) in 89% yield. The mechanism involved stereospecific hydrogen migrations and HCl elimination [93].

The benchrotrene ketone (4.71) underwent diastereoselective addition with 2-butenylmagnesium chloride in the presence of trialkylaluminium to give predominantly the anti-adduct (4.72). The benzylic hydroxyl group in this product (4.72) was susceptible to stereospecific substitution with nucleophiles [94]. Reaction of the acetal (4,73) with hexacarbonylchromium gave an easily separable diastereomeric mixture of the S,R-complex (4.74) and the R,R-complex (4.75). Treatment of the acetal (4.73) with



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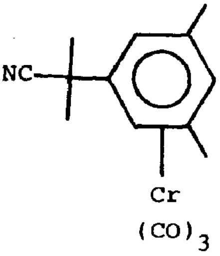

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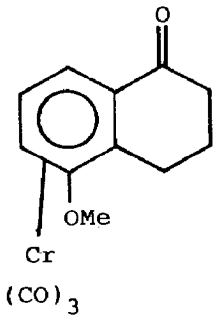

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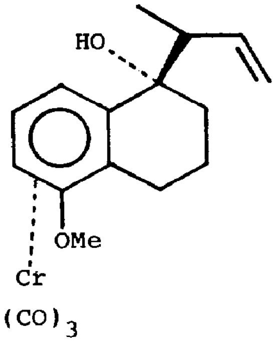

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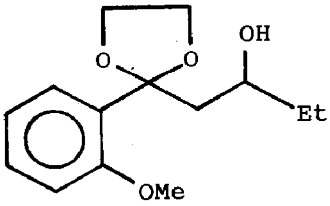

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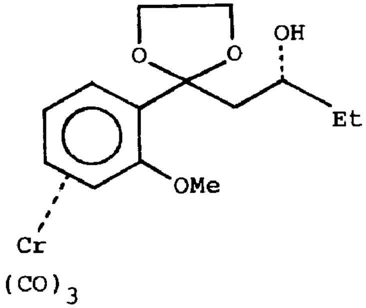

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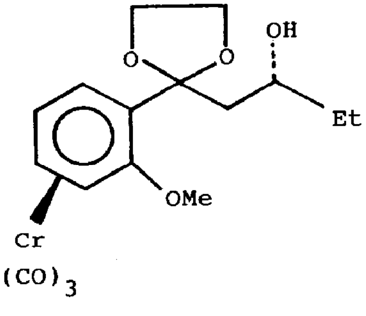

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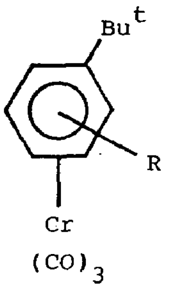

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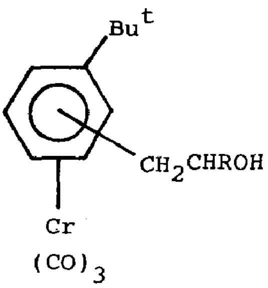
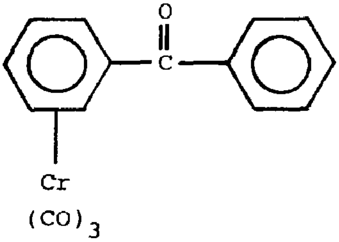


4.77

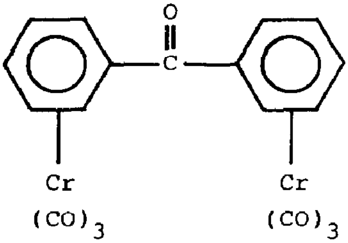
(η-naphthalene)tricarbonylchromium afforded predominantly the S,R-complex (4.74). The diastereoselectivity of this ligand exchange reaction was investigated [95].

Regiospecific attack on disubstituted benchrotrenes (4.76; R = 3-Me, 4-Me, 3,4-Me_2) by aldehydes in the presence of potassium t-butoxide was interpreted in terms of electronic effects rather than by preferential attack at the carbon atom eclipsed by the chromium-carbonyl bond. The products obtained were the secondary alcohols (4.77; R = H, Ph) [96].

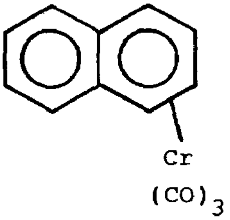
The electrochemical reduction of the η-benzophenone complexes (4.78 and 4.79) has been carried out in the presence of alkyl chlorides, which were more difficult to reduce. In the presence



4.78



4.79



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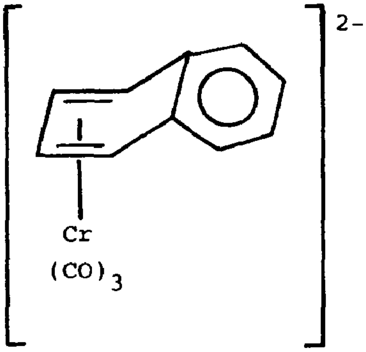
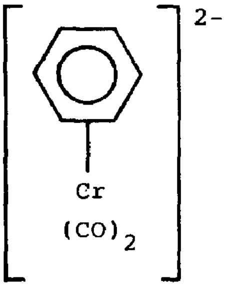


4.81

of methyl chloride and p-cyanobenzyl chloride complexed monoalkylated ethers were obtained. When the reductions were carried out in the presence of benzyl chloride or o,o',p-trimethylbenzyl chloride complexed alkylated alcohols were produced [97]. The electrochemical or chemical reduction of tricarbonyl(η-naphthalene)chromium (4.80) was a two stage ECE process to give a stable dianion. Haptotropic rearrangement gave the product as an (η^4-naphthalene)chromium complex (4.81). The mechanism of reduction was discussed and it was considered that an η^2,σ^2 canonical form was significant for the bonding in (4.81) [98].

Reduction of the chromium complex $[(\eta\text{-}C_6H_6)Cr(CO)_2\text{pyridine}]$ produced the dianion (4.82). Reaction of this anion with



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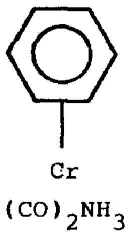
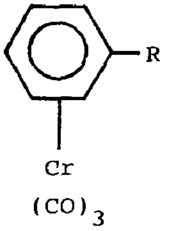


4.83

NH_4PF_6 afforded the ammonia complex (4.83) [99]. Benchrotrene compounds such as the phenyl derivatives (4.84; R = Ph, cis-, trans-CH=CHPh) and the binuclear species (4.85; Y = cis-, trans-CH=CH-) have been reduced electrochemically. The complexes (4.85) underwent a reversible two-electron reduction to give a stable dianion in each case with a half-life of more than an hour at room temperature. The benchrotrenes (4.84) were reduced in an irreversible two-electron reaction [100].



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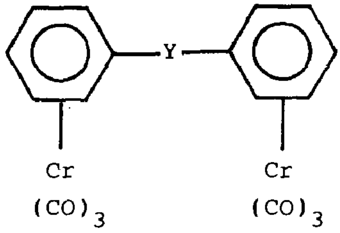
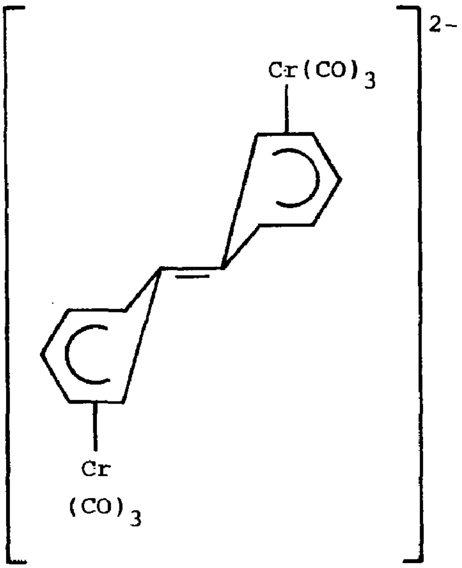


4.85

The reduction of (η^6:η^6-biphenyl)bis(tricarbonylchromium) produced the (η^5:η^5-biphenyl)$[Cr(CO)_3]_2$ dianion (4.86). The reactions of this dianion with H_2O, D_2O and methyl or 1-alkyl iodides and bromides were investigated. For example, reaction with bromoethane produced the anion (4.87) which was oxidized with iodine to give 2-ethylbiphenyl [101]. Photolysis of tricarbonyl(η-hexaethylbenzene)chromium in the presence of diphenylacetylene under nitrogen produced the dinitrogen complexes (4.88 and 4.89). The structure of the complex (4.89) was determined by X-ray analysis and the η-hexaethylbenzene group adopted a 1,3,5-distal-2,4,6-proximal methyl conformation [102].

Irradiation of the tricarbonylchromium complexes (4.90; R^1 = H, Me; R^2 = H, Me, OMe; n = 2, 3 and 4.91) with chlorodifluorophosphine in the presence of triethylamine produced the corresponding phosphite-chromium complexes (4.92 and 4.93) [103]. The electrochemical displacement of carbonyl by phosphites in substituted benchrotrenes has been examined using both free phosphites such as $P(OEt)_3$ and intramolecular phosphites as



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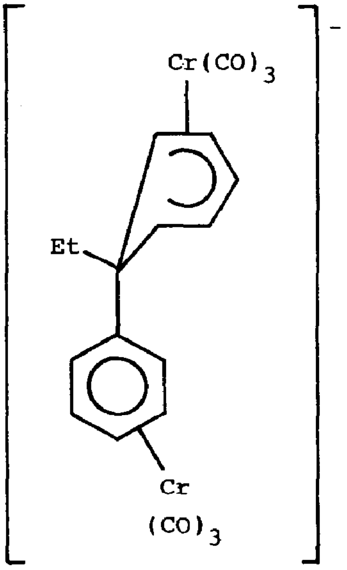

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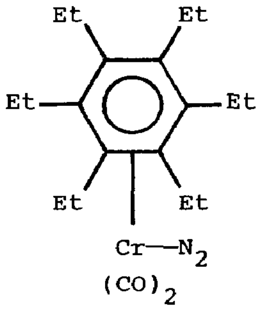

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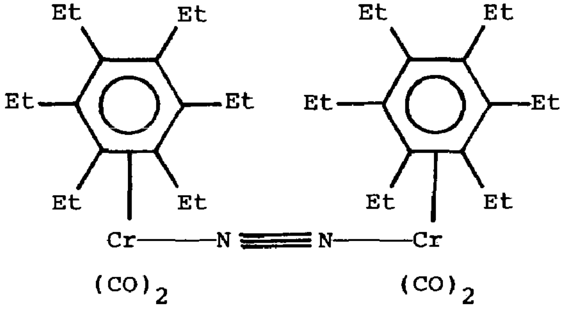
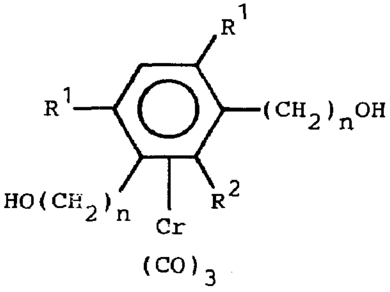
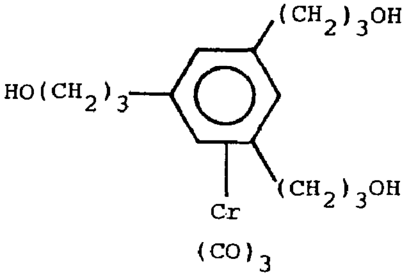


4.89

in the trisubstituted benchrotrene (4.94) [104]. The (η-arene)-tricarbonylchromium ions [4.95; X = OMe, R^1 = R^2 = H; R^1 = H, R^2 = Me; R^1 = R^2 = Me; X = R^1 = H, R^2 = Ph, X = R^1 = H, R^2 = $PhCr(CO)_3$] underwent reaction with n-butylmagnesium bromide to give a variety of products. Alkylation products were formed by nucleophilic attack and dimeric compounds were formed by



4.90



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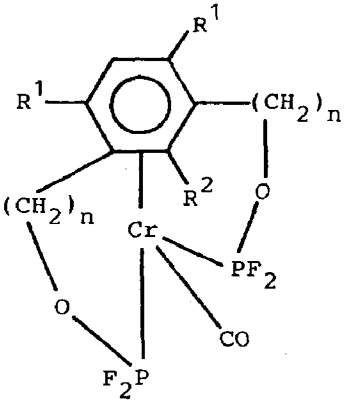

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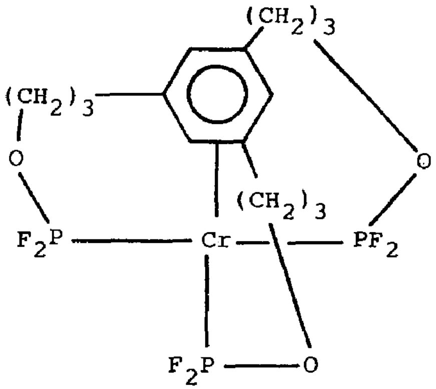

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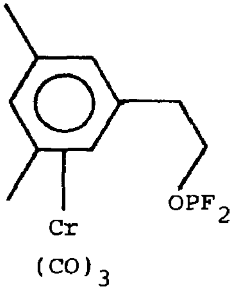

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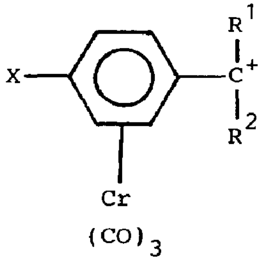
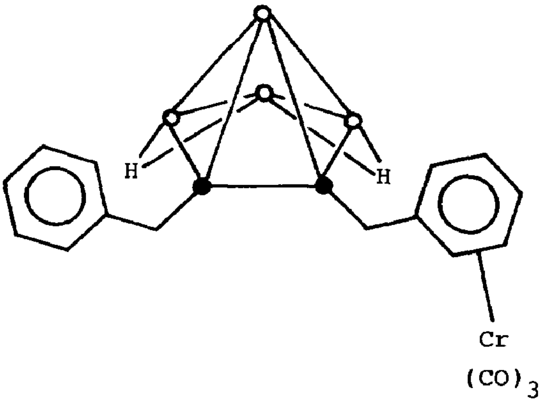


4.95

electron transfer [105]. The effect of the coordination of $Cr(CO)_3$ groups on the chemistry of C,C'-dibenzylcarborane *nido*-2,3-$(PhCH_2)_2C_2B_4H_6$ has been investigated. The tricarbonylchromium complex (4.96) was treated with sodium hydride when bridge (B—H—B) deprotonation occurred to give the corresponding anion. Reaction of this anion with iron(II) chloride followed by oxidation gave two isomers of $[(CO)_3Cr]_2(PhCH_2)_4C_4B_8H_8$ [106].



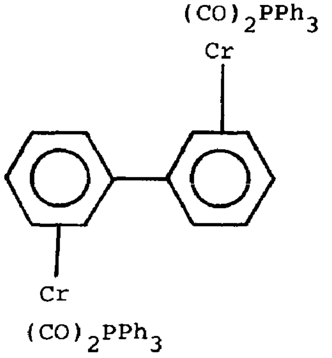
where ● = C, O = BH

4.96

The oxidation of a series of dinuclear chromium carbonyl complexes linked by a biphenyl ligand and/or a diphosphine or diarsine ligand, for example, the complexes (4.97, 4.98 and 4.99), have been studied electrochemically, by infrared and electron spin resonance spectroscopy and by X-ray crystallography. Each of the dinuclear complexes exhibited two successive one electron oxidations. The infrared and ESR data for the monocation derived from the complex (4.97) indicated a charge- and spin-localized mixed valence complex [107].

The tricarbonylchromium complexes of acetophenone, 1-indanone and 1-tetralone underwent hyperiodinative oxidation with $PhI(OAc)_2$ and methanolic potassium hydroxide to give the corresponding α-hydroxydimethylacetals. The oxidation was stereoselective for the benzocyclanone complexes, structure and stereochemistry were confirmed by X-ray crystallography [108].

The cationic benchrotrene complexes (4.100; R^1 = H, Me; R^2 = H, CH_2OH, CH_2CH_2OH) have been used as catalysts for the carboxylation of olefins $RCH{=}CH_2$, where R = Bu, n-hexyl, to the esters $RCHMeCO_2Et$ and $RCH_2CH_2CO_2Et$. High conversions were



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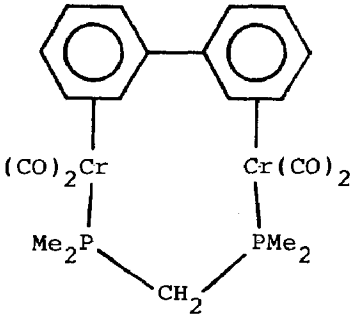

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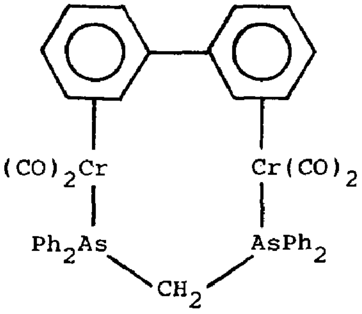

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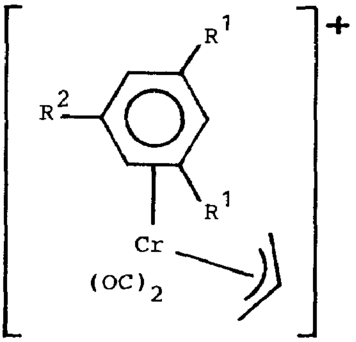
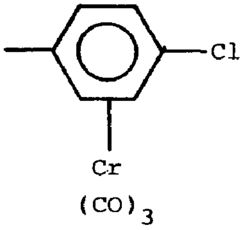


4.100

achieved relative to those obtained with octacarbonyldicobalt as a catalyst [109].

Scott has shown that (η-chloroaryl)Cr(CO)$_3$ complexes can undergo palladium catalysed coupling reactions with nucleophiles and palladium catalysed olefination with alkenes. For example, the treatment of tricarbonyl(η-*p*-chlorotoluene)chromium (4.101) with tetrabutyltin in the presence of tetrakis(triphenylphosphine)-palladium(0) gave *p*-butyltoluene (75%) after oxidative removal of the tricarbonylchromium group. Reaction of the complex (4.101) with methyl vinyl ketone in the presence of dichlorobis(triphenylphosphine)palladium(0)-triethylamine followed by treatment with iodine gave the ketone (4.102) [110].



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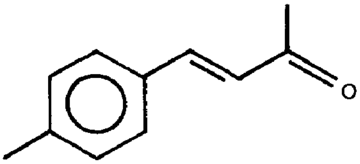
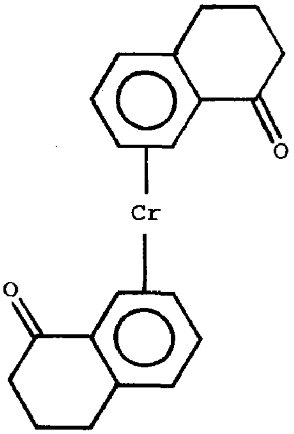


4.102

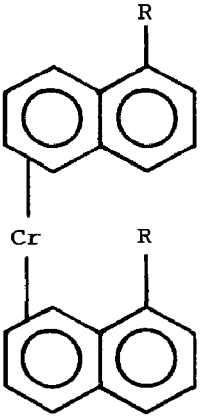
The adsorption of the $Mo(CO)_3$ group onto alumina has been investigated. (η-Benzene)tricarbonylmolybdenum lost benzene upon adsorption on partially dehydroxylated alumina to give $Mo(CO)_3$-Al_2O_3 which was identical to the material produced directly from molybdenum carbonyl and alumina [111].

5. (η-C_6H_6)$_2$Cr

The cocondensation of chromium with benzene, o-methylacetophenone, tetralone, methyl o-methylbenzoate, or menthyl o-methylbenzoate and mixtures of these arenes afforded a series of



5.1

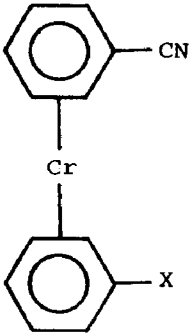


5.2

(η-arene)$_2$Cr compounds. Titration with iodine produced the corresponding chromium(I) complexes. The unsymmetrically 1,2-substituted arenes on cocondensation gave geometrical and optical isomers which were separated. Cis-bis(η-tetralone)-chromium (5.1) was characterized by X-ray analysis [112].

Cocondensation of phenylacetylene and chromium vapour gave 1,2,4- and 1,2,3-triphenyl substituted bis(η^6-arene)chromium complexes. The oxidation of these complexes was investigated [113]. The cocondensation of chromium vapour with naphthalene or 1-eicosylnaphthalene produced the corresponding chromium complexes (5.2; R = H, $C_{20}H_{41}$). Spectroscopic evidence suggested that these complexes adopted an eclipsed structure in solution. The interaction of iron vapour with benzene and naphthalene derivatives was also investigated. The iron-arene interaction varied as a function of temperature. With naphthalene, bis-(η^4-naphthalene)iron was thought to be formed initially and above 77°K, this decomposed to give bis(η^6-naphthalene)iron [114].

Cocondensation of benzonitrile and fluorobenzene or trifluoromethylbenzene with chromium atoms at liquid nitrogen temperatures gave the mixed ligand complexes (5.3; X = F, CF$_3$) in addition



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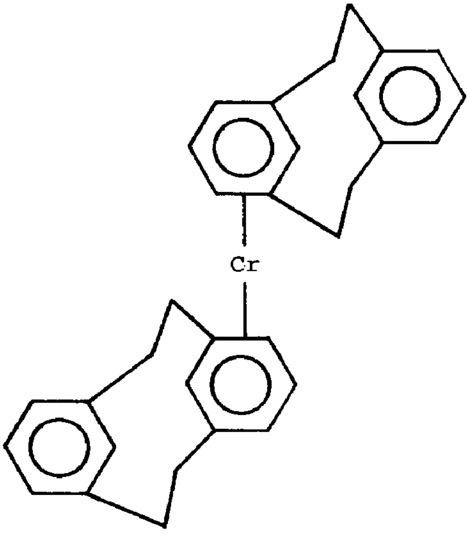
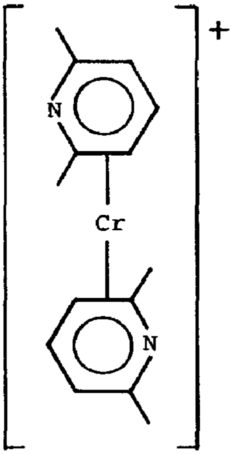


5.4

to the corresponding symmetrical complexes [115]. The cocondensation of chromium vapour with [2_2]metacyclophane produced the chromium complex (5.4). This complex was characterised by ^{1}H and ^{13}C NMR spectroscopy, ESR spectroscopy and cyclic voltammetry. The ^{1}H NMR spectra indicated a 25% reduction of the diamagnetic ring current in the uncomplexed arene rings [116].

The cocondensation of chromium, titanium, vanadium or molybdenum vapour with 2,6-dimethylpyridine produced the corresponding bis(η^6-2,6-dimethylpyridine)metal complexes. Oxidation of the chromium complex with silver tetrafluoroborate gave the salt (5.5). Spectral properties indicated that these complexes were structurally and electronically similar to the corresponding bis(η^6-benzene)metal compounds [117]. The structure of the salt (5.5) was determined by X-ray analysis [118].

The ligand exchange reaction of bis(η^6-naphthalene)chromium with fluorobenzene, benzene, toluene, 1,3,5-trimethylbenzene and hexamethylbenzene has been carried out to give a series of (η^6-arene)(η^6-naphthalene)chromium and (μ,η^6,η^6-naphthalene)-bis(η^6-arene)dichromium compounds. The structure of the slipped triple-decker complex (5.6) was determined by X-ray analysis [119].



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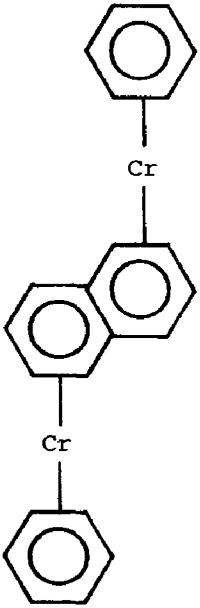
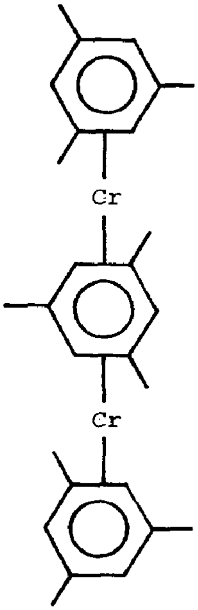


5.6

Qualitative group theory has been used to discuss the molecular orbital basis of dibenzenechromium [120]. Bis(η-benzene)chromium has been the subject of an MO study using the SCF-X_α-DV method. A ligand-field discussion of bonding used pseudooctahedral metal d orbitals. Electrons were donated from benzene ligand e_{1g} π orbitals into vacant metal $4e_{1g}$ orbitals and the filled chromium $3e_{2g}$ orbitals delocalized into empty benzene e_{2u} π^* orbitals. Bis(η-naphthalene)chromium in two alternative geometries, C_{2h} and C_{2v}, was examined in the same way, the HOMO in each case was a metal d_{xz} orbital that was directed towards the centre of the arene ring. The LUMO's were of naphthalene π^* character with some metal d character [121].

Calculation of potential energy surfaces has been used to investigate the stages involved in the synthesis and decomposition of bis(η-benzene)chromium and bis(η-toluene)chromium. Steric effects were found to be significant [122]. The structure of the triple-decker sandwich complex (5.7) has been determined by X-ray analysis. The aromatic rings were parallel and eclipsed when viewed down the three-fold chromium-chromium axis normal to the ring planes [123].



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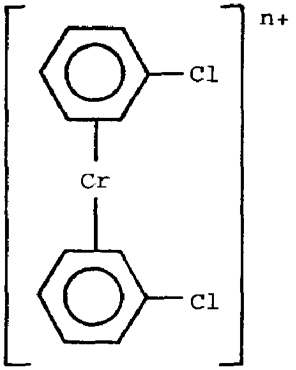

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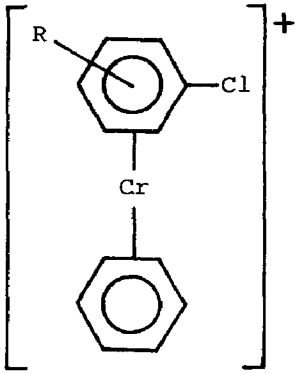
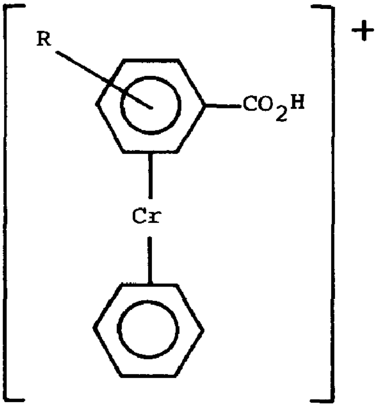


5.9

^{35}Cl NQR spectroscopy has been used to show that the chlorobenzene ligand was a more effective electron withdrawing group in the cationic complex (5.8; $n = 1$) than in the neutral species (5.8; $n = 0$) [124]. The electronic absorption spectra of the complexes (η-arene)$_2$Cr (arene = benzene, toluene, ethylbenzene, cumene, t-butylbenzene, mesitylene) in the vapour phase have been recorded and the bonds were assigned [125].

The reversible electrochemical oxidation of a series of bis(η-arene)chromium complexes has been studied in dimethylsulphoxide. The half-wave potentials correlated well with the <u>meta</u>-substituent constants and with the vertical ionization potentials of the complexes [126]. The rates of substitution of chlorine by methoxide has been studied in a series of chromium complexes (5.9). The rates increased in the following order $R = 4\text{-}Me_2N < 3\text{-}Me < 4\text{-}Me < 4\text{-}MeO \leq 3\text{-}MeO \leq 3\text{-}CO_2^- < H < 3\text{-}Cl < 4\text{-}Cl < 4\text{-}CO_2Me < CO_2Me$ [127].

Substituent effects on the pK_a values of a series of bis(η-benzene)chromium cations including the species (5.10; R = H, 4-Me, 3-, 4-Cl, 3-, 4-MeO) have been measured and the Hammett parameters determined. The pK_a values of the acids (5.11; R^1 = Me, R^2 = H; R^1 = CO$_2$Me, R^2 = Me) were consistent with additive transannular and intraligand effects [128].



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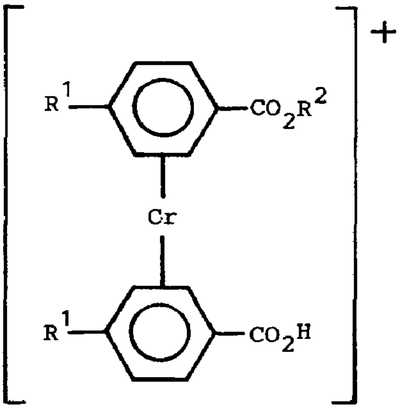
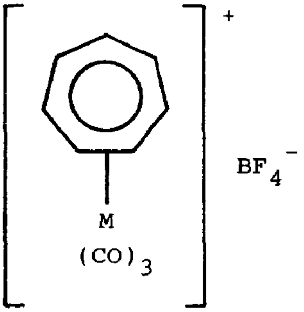


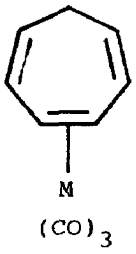
5.11

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

The crystal and molecular structure of (η-bicyclo[6.1.0]-nona-2,4,6-triene)tricarbonylmolybdenum and its *endo*-9-bromo derivative have been determined by X-ray crystallography. The cyclopropane ring is *syn* to the metal atom in each complex. Kinetic studies and deuterium labelling have been used to investigate the thermal rearrangement of the first complex [129]. Activation energies for arene ring rotation in the (η-tropylium)-metal complexes (6.1; M = Cr, Mo) have been determined by measurement of ^1H and ^{19}F spin-lattice relaxation times of the solids in the temperature range 93-296 K. Values of 12.8 and 13.6 kJ mol^{-1} were obtained for the complexes (6.1; M = Cr, Mo) respectively. Barriers to ring rotation arose from ring-carbonyl and ring-BF_4^- interactions [130].



6.1



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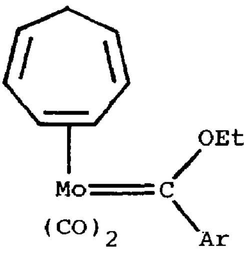
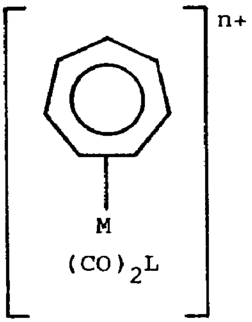


6.3

Treatment of the η-cycloheptatriene complex (6.2; M = Mo) with an aryllithium and subsequent alkylation of the intermediate acylmetallate with Et_3OBF_4 gave the corresponding carbene complexes (6.3; Ar = C_6H_5, *p*-MeC_6H_4, *o*-MeC_6H_4, *p*-$CF_3C_6H_4$). Reaction of the complex (6.2; M = Cr) with C_6H_5Li or *p*,*o*-MeC_6H_4Li resulted in deprotonation of the η-cycloheptatriene ligand but with *p*-$CF_3C_6H_4Li$ the intermediate acylmetallate was formed [131].

Treatment of the neutral tungsten iodide complex (6.4; M = W, L = I, n = 0) with $AgBF_4$ in acetonitrile gave the (η^3-cycloheptatrienyl)tungsten cation (6.5; M = W) which was converted to the (η^7-cycloheptatrienyl)tungsten cation (6.4; M = W, L = MeCN, n = 1) with dichloromethane. The corresponding



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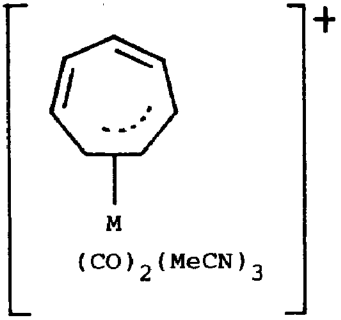

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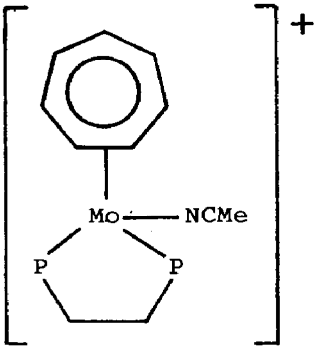

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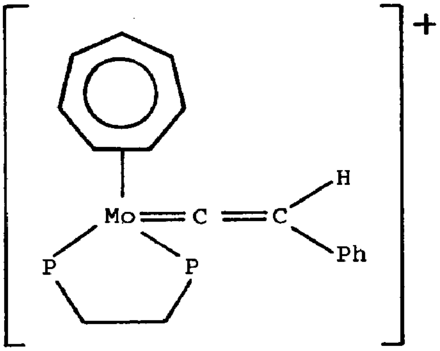

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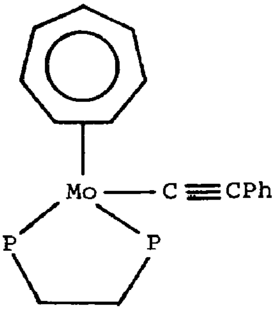

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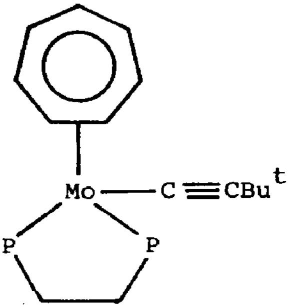
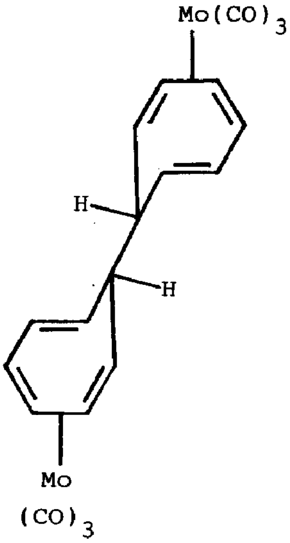


6.9

reaction with the molybdenum iodide (6.4; M = Mo, L = I, n = 0) gave a mixture of the products (6.5; M = Mo and 6.4: M = Mo, L = MeCN, n = 1) [132].

Reaction of the molybdenum complex (6.6) with phenylacetylene produced the cationic, phenylvinylidene complex (6.7) which was deprotonated to the neutral phenylalkynyl complex (6.8). The molybdenum complex (6.9) was prepared by a similar sequence of reactions. The electrochemistry and synthetic redox chemistry of the complexes (6.8 and 6.9) was investigated [133]. Reduction of $[(\eta\text{-}C_7H_7)Mo(CO)_3]^+BF_4^-$ with either sodium amalgam or sodium naphthalide resulted in dimerization to the ditropyl complex (6.10). This complex was characterized by X-ray crystallography. The reaction of hexacarbonylmolybdenum with ditropyl, $C_{14}H_{14}$, produced three isomers of $[Mo(CO)_3]_2(\eta^6,\eta'^6\text{-}C_{14}H_{14})$ [134].

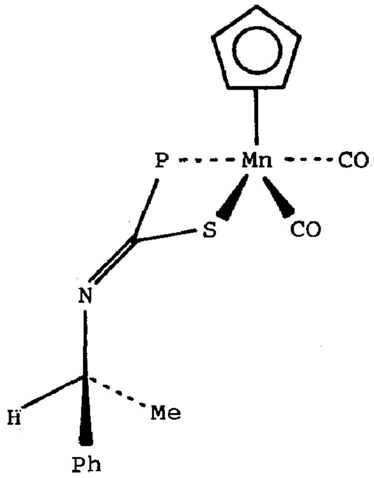


6.10

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

(i) Formation

Reaction of the chiral phosphinothioformamide (-)-S-Ph_2-PC(S)NHCHMePh with pentacarbonylchloromanganese produced the chelate complex (7.1) [135]. Condensation of manganese atoms



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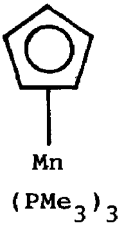

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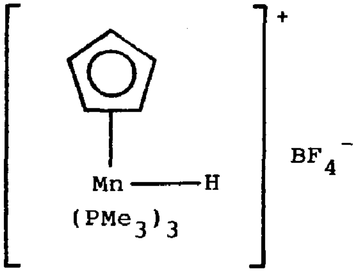

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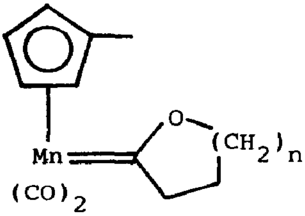

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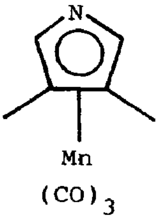

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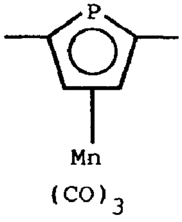

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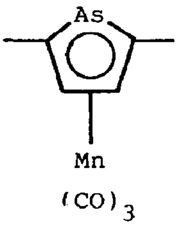


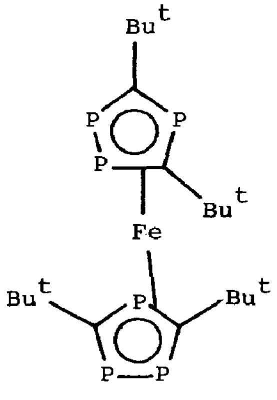
7.7

with a cyclopentadiene-trimethylphosphine mixture produced the tris(trimethylphosphine) complex (7.2) which was protonated by HBF_4 to give the salt (7.3) [136].

The 2-oxacycloalkylidene complexes (7.4; n = 1, 2) have been prepared in one step by cyclizing $HC{\equiv}CCH_2(CH_2)_nOH$ (n = 1, 2) with $(\eta\text{-}MeC_5H_4)Mn(CO)_2OEt_2$ [137]. The synthesis and characterization of some $(\eta^5\text{-heterocycle})Mn(CO)_3$ compounds, for example complexes (7.5, 7.6 and 7.7), have been reported. Only the N-heterocycle complexes underwent carbon monoxide substitution by phosphorus ligands. This was attributed to the greater electronegativity of nitrogen as compared with carbon, phosphorus and arsenic. The mechanism of carbon monoxide substitution in these compounds was discussed [138].

The reaction of iron(II) chloride and $[Li(1,2\text{-dimethoxyethane})_3][C_2(t\text{-}Bu)_2P_3]$ at room temperature afforded the hexaphosphorus complex (7.8) as the major product together with some of the penta-phosphorus complex (7.9). X-ray diffraction studies showed that the complexes (7.8 and 7.9) were the phosphorus analogues of ferrocene. They had sandwich structures with the two planar η^5-rings eclipsed and approximately parallel. A brief description of the preparation of the cymantrene analogue (7.10) was also reported [139, 140].

Reaction of $[\eta^6\text{-}C_6(CH_3)_6]Mn(CO)_2H$ with carbon monoxide at atmospheric pressure or under pressure produced the endo-complex (7.11). The structure of this complex was determined by X-ray analysis [141].



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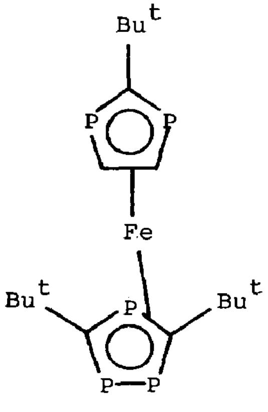

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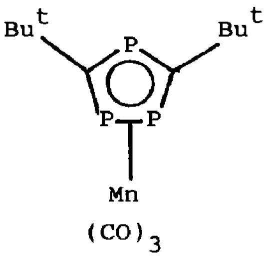

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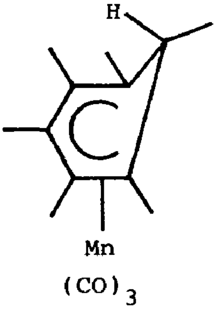


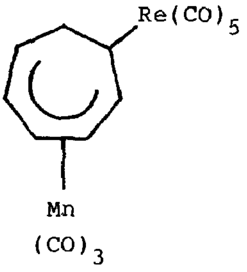
7.11

7.12

Sodiomanganesepentacarbonyl combined with <u>trans</u>-1-bromopenta-2,4-diene in THF at -78° to give (η^1-2,4-pentadienyl)-manganesepentacarbonyl which underwent an $\eta^1 \rightarrow$ <u>syn</u>-$\eta^3 \rightarrow \eta^5$ transformation to give (η^5-pentadienyl)manganesetricarbonyl (7.12) "open cymantrene" [142].

7. (ii) Spectroscopic and Physico-chemical Studies

The crystal structure of 1-ferrocenyl-1-(methylphenylcymantrenyl)silylethylene has been determined by X-ray analysis. The structure was as expected [143]. The pentacarbonylrhenium anion attacked the hydrocarbon ligand in the tricarbonyl(η-cycloheptatriene)manganese cation to give the neutral



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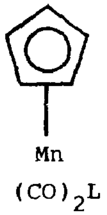

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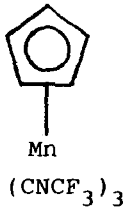
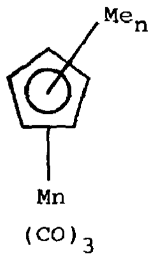


7.15

(η-cycloheptadienyl)manganese complex (7.13) which was characterized by X-ray crystallography [144].

The cymantrene derivatives (7.14; L = MeNC, CF_3NC and CS) and (7.15) have been prepared and examined by IR spectroscopy. The trifluoromethyl isocyanide ligand was shown to be a strong π-acceptor ligand and a more efficient acceptor than the thiocarbonyl ligand [145]. Transient species formed on flash photolysis of alkane solutions of cymantrene were characterized with ultraviolet-visible monitoring and time-resolved infrared spectroscopy. The transient species identified were $(\eta\text{-}C_5H_5)\text{-}Mn(CO)_2S$ (S = cyclohexane, n-heptane) and $(\eta\text{-}C_5H_5)_2Mn_2(CO)_5$ [146].



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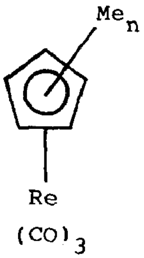
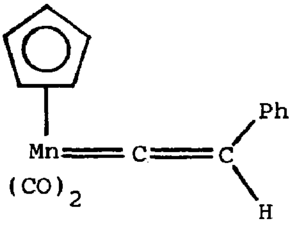


7.17

The mass spectra of the polymethylcyclopentadienyl metal complexes (7.16 and 7.17; n = 0 - 5) have been studied systematically. The most intense fragment ion was $(M\text{-}2CO)^+$ for (7.16; n = 0, 1) but was $(M\text{-}2CO\text{-}H_2)^+$ for (7.16; n = 2 - 5) [147]. Fragmentation of the complexes (7.17) followed a simpler pattern because the (η-cyclopentadienyl)-manganese and carbonyl-manganese bonds were weaker than in the corresponding rhenium complexes [148]. The ^1H and ^{13}C NMR spectra of the rhenium complexes (7.16; n = 0 - 5) showed upfield shifts with an increase in the number of methyl groups [149].

The electrochemical and spectroscopic properties of the (η-cyclopentadienyl)manganese complexes [7.18, 7.19 and 7.20;



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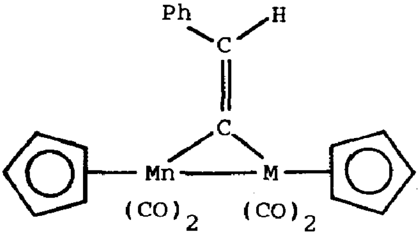

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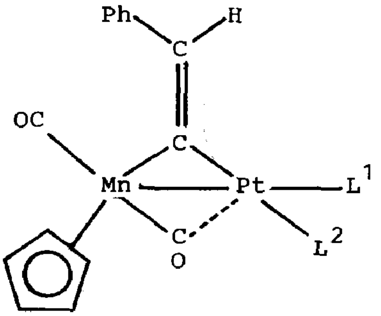
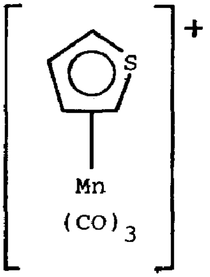


7.20

$L^1 = L^2 = PPh_3$, $P(OEt)_3$, $P(OPr^i)_3$, $P(OPh)_3$; $L^1 = P(OPr^i)_3$, $L^2 = PPh_3$; $L^1 = PPh_3$, $L^2 = CO$; $L^1 = P(OPr^i)_3$, $L^2 = CO$] have been investigated [150].

Hydride ion transfer from $[HFe(CO)_4]^-$ to the (η-thiophene)-manganese cation (7.21) has been studied as a model for surface hydride transfer to thiophene which was π-bound on a hydrodesulphurization (HDS) catalyst. The cation (7.21) underwent addition at C-2 of the thiophene ring and deuteration experiments indicated that addition occurred both endo and exo to the ring [151]. A molecular orbital analysis has been carried out on the MnSiH three centre interaction in the manganese complexes (7.22). Extended Hueckel calculations indicated the σ-H-Si bond was coordinated to the $(\eta\text{-}C_5H_5)MnL_2$ fragment and that it behaved as a two electron ligand [152].



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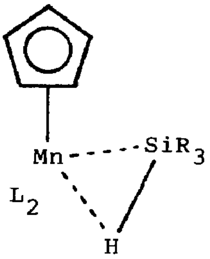


7.22

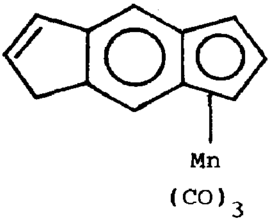
7. (iii) General Chemistry

Transmetallation of the mono- and bis-(trimethyltin) complexes of s-indacene with bromopentacarbonylmanganese gave the 5-hydro-s-indacene manganese complex (7.23) and the s-indacene dimanganese complex (7.24) respectively [153]. The cationic cymantrene complexes (7.25; L = CO, PPh_3, PEt_3) have been prepared from the corresponding diphenylmethanols and studied by cyclic voltammetry and polarography. Reduction gave metastable radicals which were analogous to the triphenylmethyl carbenium ion while oxidation gave stable cation and dication radicals [154]. The alkanoyl chloride, $PhCO(CH_2)_nCOCl$, where n = 4, 6, combined with cymantrene to give the corresponding unsymmetrical diketones [155].

The reaction of dicarbonyl(η-methylcyclopentadienyl)tetrahydrofuran manganese with 4-cyanopyridine produced three products (7.26, 7.27 and 7.28). In the same reaction with 2-cyano- and 3-cyano-pyridine single products (7.29 and 7.30) were isolated. Spectroscopic and electrochemical evidence indicated superior π back-bonding from the pyridine nitrogen atom and the isolation of the cyanide complexes was attributed to the kinetic stability of the CN-Mn bond [156].

Addition of dicarbonyl(tetrahydrofuran)(η-methylcyclopentadienyl)manganese to $Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}NO)_2$ gave the 48-electron ON-capped complex (7.31). The electrochemistry of this latter complex was investigated and the structure was determined by X-ray analysis [157]. Irradiation of the intermediate (7.32) with TCNE and TCNQ gave mixed valence manganese complexes with η^4-TCNE or η^4-TCNQ ligands [158]. Photolysis of the phosphine (7.33) in the presence or absence of triphenylphosphine produced $(\eta\text{-}C_5H_4PPh_2)Mn(CO)_2PPh_3$ and a mixture of the isomers (7.34 and 7.35) [159].

Photochemical reaction of methylcymantrene with 1,1'-bis-(diphenylphosphino)ferrocene produced the manganese complex (7.36)



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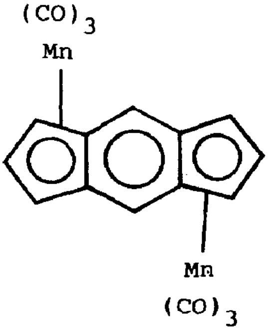

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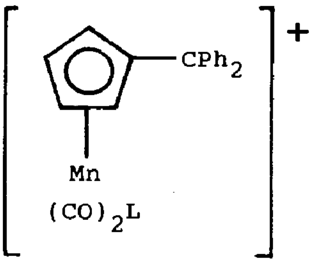

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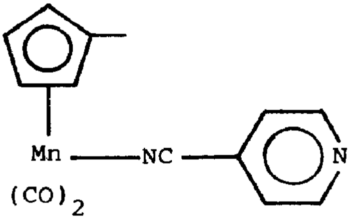

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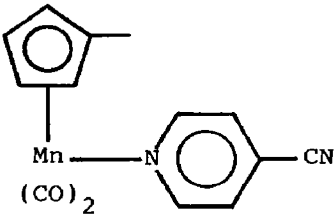

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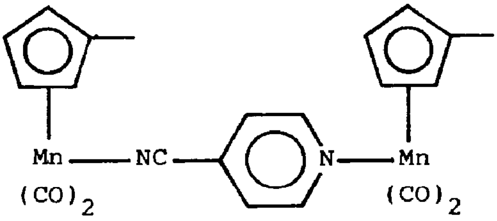

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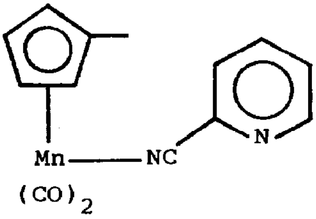

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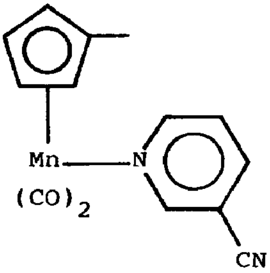

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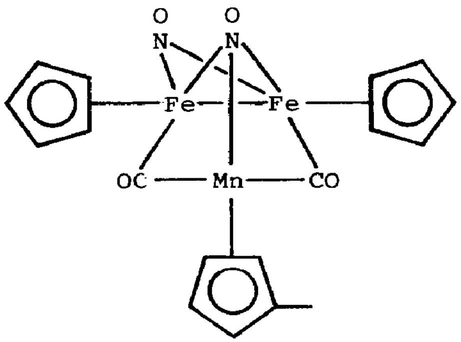

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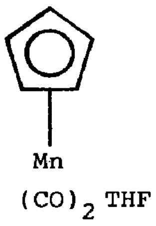


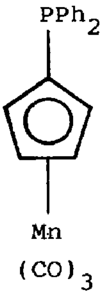
7.32

whose structure was determined by X-ray analysis [160].

Irradiation with visible light of polymer bound methylcymantrene in an atmosphere of acetylene produced polymer bound (η-C_5H_4Me)Mn(CO)$_2C_2H_2$. The reaction mechanism of the coordination and elimination of acetylene was investigated [161]. Photochemical reaction of methylcymantrene in tetrahydrofuran with $Ph_2C{=}C(Cl)$-$SiMe_3$ afforded the vinylidene complex (7.37; R = Ph). A similar reaction with $Me_2C{=}C(Cl)SiMe_3$ produced the η^2-butatriene complex (7.38) but when the photolysis was carried out in pentane the vinylidene complex (7.37; R = Me) was isolated [162].

A number of metallophosphines have been prepared including the cymantrene analogue (7.39) which was obtained from (η-C_5H_5)-Mn(CO)$_2$Na and PhPCNClN($SiMe_3$)$_2$ [163]. Several ytterbium derivatives of cymantrene have been prepared. Thus cymantrenyllithium combined with YbI_2.nTHF to give the dicymantrenyl complex (7.40) and the ytterbium iodide (7.41; X = I.nTHF) while iodomercuricymantrene gave the ytterbium iodide (7.41; X = I_2.3THF) [164].

The methylcymantrene reagent (7.42) has been treated with [M(COD)Cl]$_2$ in THF to give the heterobimetallic di-t-butylphosphido bridged complexes (7.43; M = Rh, Ir) which have been characterized



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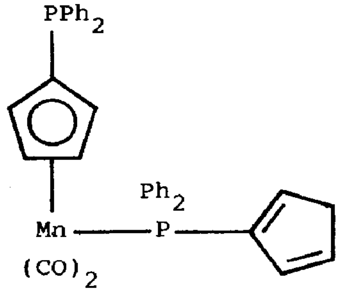

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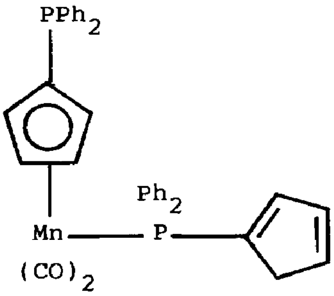

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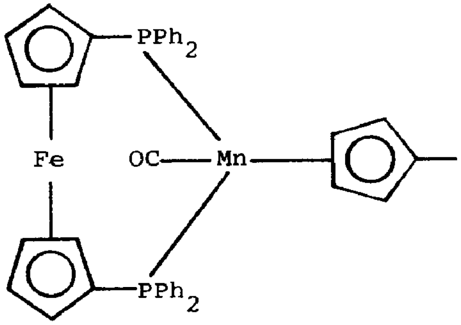

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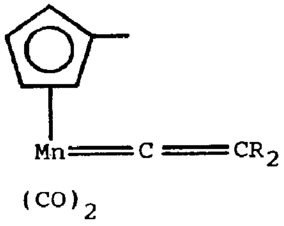

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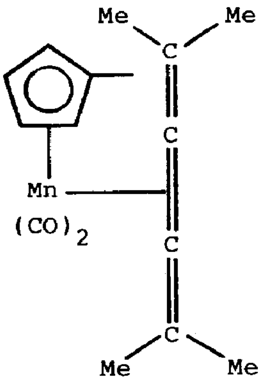

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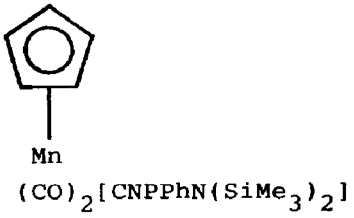

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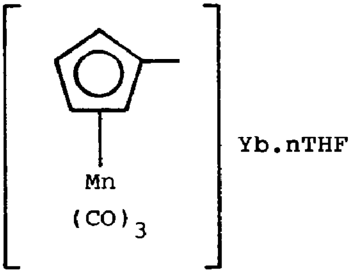

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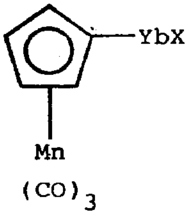

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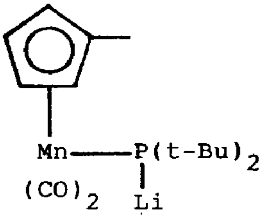

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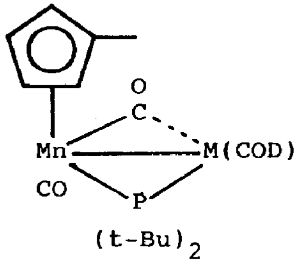
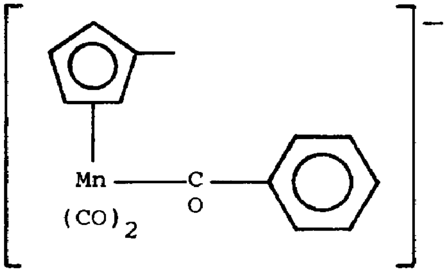


7.43

by X-ray crystallography [165]. The anionic acyl complex (7.44) combined with one equivalent of the chlorosilane $RSiMe_2Cl$ to give the siloxycarbene manganese complexes (7.45; R^2 = Me, $CH=CH_2$, $CH_2CH=CH_2$). Low temperature photolysis of one of these complexes (7.45; R = $CH=CH_2$) gave the chelated manganese siloxy-carbene-alkene complex (7.46) [166].

The manganese-allene complex (7.47) combined with the diphosphine $Ph_2PCH_2CH_2PPh_2$ to give the phosphoniovinyl complex (7.48) together with the corresponding dicymantrenyl species. The phosphorane, $Ph_3P=CHCO_2Et$, attacked the intermediate $(\eta-C_5H_5)-Mn(CO)_2.THF$ to form the zwitterionic cymantrene (7.49) which was converted to the cymantrenyl-carbene (7.50) by chromatography on alumina [167].



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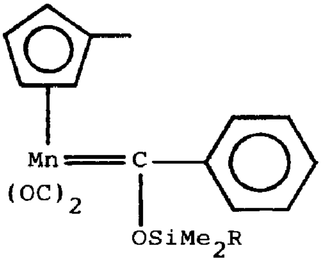

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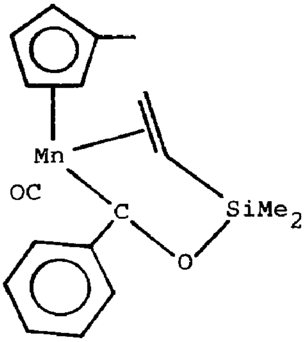

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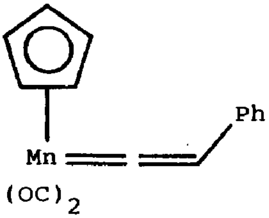

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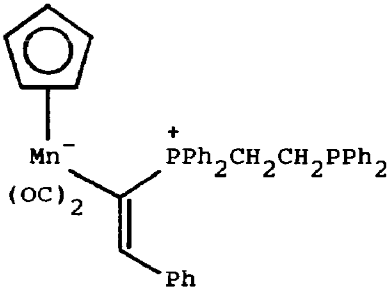

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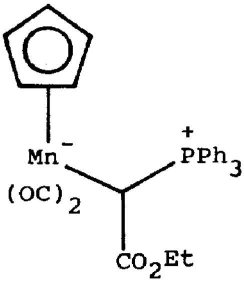

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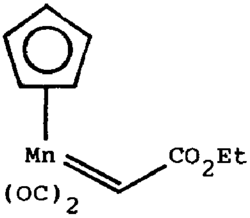

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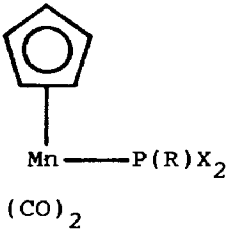

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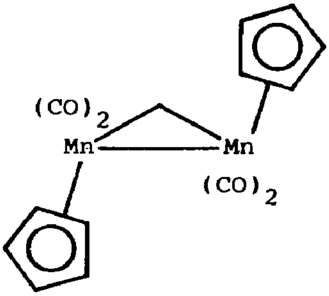
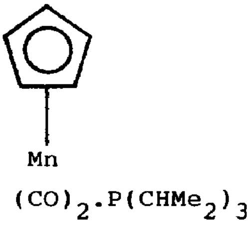


7.52

The dihalophosphines (7.51) have been converted into phosphinidene, diphosphene and diphosphine derivatives by treatment with metallating agents such as Me_3CLi-TMEDA [168]. The electrochemical oxidation and reduction of the methylene-bridged manganese complex (7.52) and related compounds has been investigated. Both oxidation and reduction weakened the Mn-C-Mn triangle [169]. A hydrogen bonded species (Mn-CO····HO-) was formed by the reaction of the manganese complex (7.53) with $(CF_3)_3COH$ in liquid xenon [170].

Methylcymantrene has been administered to rats by injection and the LD_{50} value was 12.1 mg/kg. Two major metabolites of methylcymantrene were much less toxic and at doses of 250mg/kg did not show acute toxicity [171]. The pneumotoxic properties of the fuel additive methylcymantrene have been investigated. The administration of methylcymantrene dissolved in polyethylene glycol to dogs and rats led to neurogenic pulmonary edema and death within ten minutes. Administration in corn oil resulted in a differenct toxicity profile. Severe pulmonary capillary congestion occurred accompanied by perivascular and alveolar edema [172].

The toxicity of tricarbonyl(η-methylcyclopentadienyl)-manganese in rats has been investigated. After injection at a dose of 4 mg/kg the blood, lung, liver and kidney manganese levels increased to a maximum after 3-6 h. The maximum accumulation of tricarbonyl(η-methylcyclopentadienyl)manganese occurred in the lung, liver and kidney. Maximum pulmonary toxicity occurred 24-48 h after injection [173].



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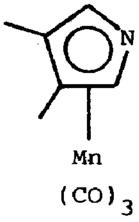

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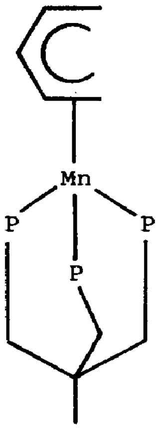
7.55

Mice treated with tricarbonyl(η-methylcyclopentadienyl)manganese (TMM) in propylene glycol or corn oil suffered seizures. The LD_{50} associated with seizure activity was lower in propylene glycol (152 mg kg^{-1}) than in corn oil (999 mg kg^{-1}). It was concluded that TMM or a closely related metabolite and not elemental manganese was responsible for the seizures [174]. The azacymantrene (7.54) underwent substitution of CO 100 times faster than the isomer (7.55). This indicated that $\eta^5 \rightarrow \eta^3$ ring slippage towards nitrogen to give a 2-azaallyl caused steric hindrance by the ortho-methyl groups in the complex (7.55). The crystal and molecular structure of the azacymantrene (7.54) confirmed that the tricarbonylmanganese group was displaced towards nitrogen [175].

The (η^5-pentadienyl)manganese complex (7.56) has been attacked by acids to give the cation (7.57) in which the added hydrogen occupied an agostic position between manganese and C-1 of the pentadienyl ligand. However, the corresponding rhenium cation (7.58) contained a normal terminal hydrogen. The crystal and molecular structure of this cation (7.58) has been determined by X-ray crystallography [176].



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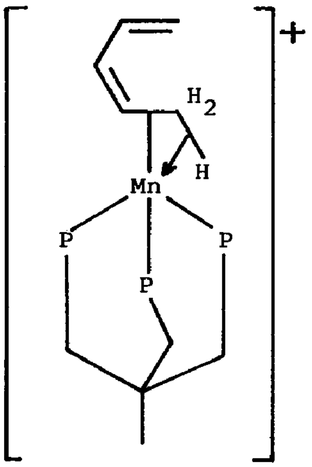

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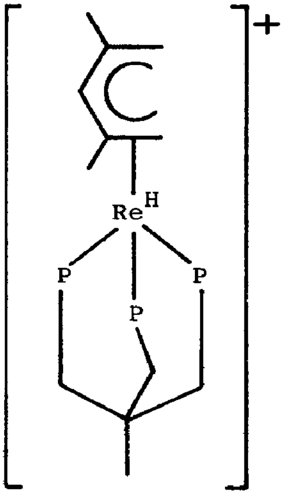
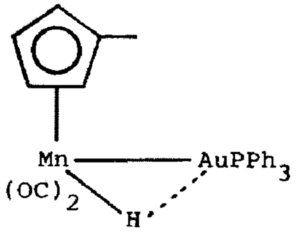
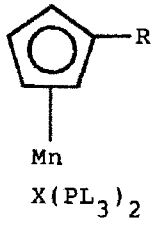


7.58

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



8.1



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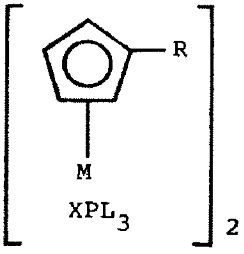
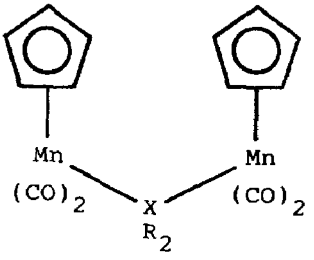


8.3

The sodium salt, Na[(η^5-MeC_5H_4)(CO)$_2$MnSiMePh$_2$] has been treated with Ph$_3$PAuCl in the presence of moist picoline to form the dinuclear hydrido complex (8.1). A heteronuclear hydrido platinum complex was prepared in the same way [177]. Several mono- and di-nuclear cymantrene complexes (8.2 and 8.3; R = H, Me; X = Cl, Br, I; L = alkyl) have been prepared and characterized. The dinuclear complexes (8.3) were favoured when small ligands with high electron donor capacity were present. In the case of the complexes (8.2 and 8.3; R = Me; X = I; L = Me) the two were present in equilibrium in solution. NMR spectroscopy and solid-state magnetic measurements were used to distinguish between the complexes (8.2 and 8.3) and to establish the presence of five unpaired electrons in each case [178].

The reaction of dicarbonyl(η-cyclopentadienyl)tetrahydrofuranmanganese with the sulphides, selenides and tellurides XR$_2$, where X = S, Se, Te; R = Me, R$_2$ = (CH$_2$)$_3$, (CH$_2$)$_4$, produced the corresponding bis(η-cyclopentadienyl)manganese complexes (8.4). The structure of the complex [8.4; X = S, R = (CH$_2$)$_3$] was determined by X-ray analysis [179]. The cymantrene complex (η-C_5H_5)-Mn(CO)$_2$THF combined with phosphino- or arsino-substituted sulphur diimides to give sulphur diimide bridged complexes (8.5; M = P, As). One of these complexes (8.5; M = P) has been characterized by X-ray crystallography [180].

Photolysis of dicymantrene (8.6; L^1 = L^2 = CO) with π-donor



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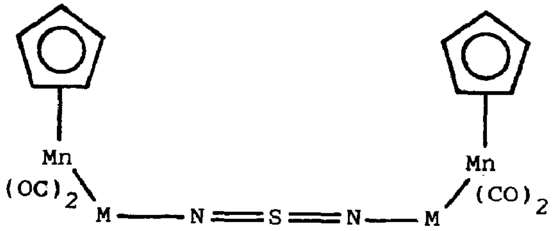
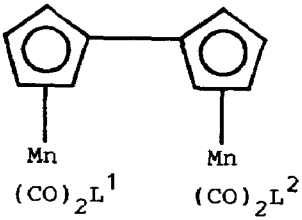


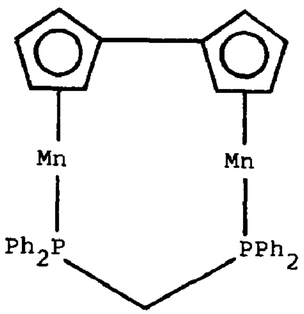
8.5

ligands gave monosubstituted derivatives such as the complexes (8.6; L^1 = ethylene, cyclooctene, 2-butyne, L^2 = CO) while σ-donor ligands gave disubstituted derivatives (8.6; L^1 = L^2 = triphenylphosphine, pyridine, THF). One product (8.7) was characterized by X-ray crystallography and exhibited a twisted fulvene residue [181].

Reaction of the (η-pentamethylcyclopentadienyl)manganese complex (8.8; L = tetrahydrofuran) with phosphine produced the corresponding phosphine complex (8.8; L = PH_3). The Mn-P bond length in this complex was very short being 219 pm. Deprotonation of the phosphine derivative (8.8; L = PH_3) with potassium hydride followed by condensation with dicarbonyl(η-cyclopentadienyl)-iron iodide afforded the dinuclear complex (8.9). X-ray analysis



8.6



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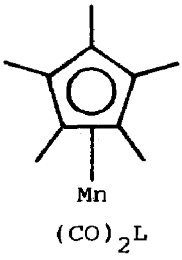

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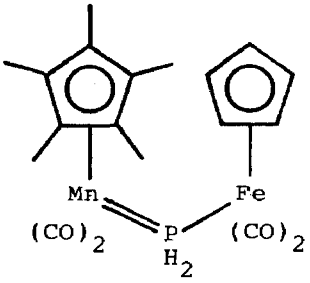
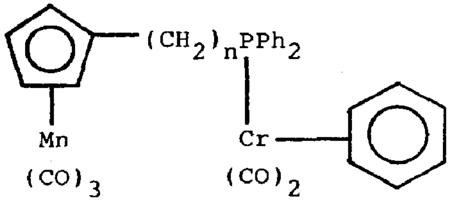


8.9

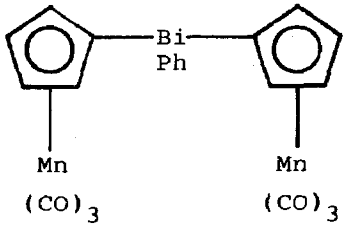
of this complex showed a short Mn-P bond length of 225 pm, a double bond, and a Fe-P bond length of 229 pm, a single bond [182].

Treatment of the cymantrene derivatives (η-$C_5H_4PPh_2$)- and (η-$C_5H_4CH_2PPh_2$)-$Mn(CO)_3$ with (η-benzene)tricarbonylchromium produced the corresponding phosphine complexes (8.10; n = 0, 1) [183]. Cymantrenyllithium combined with $PhBiCl_2$ to give dicymantrenylphenylbismuth (8.11) which combined with copper(II) chloride to give chlorocymantrene and chlorobenzene together with a small proportion of dicymantrenyl and diphenyl [184].

The UV irradiation of methylcymantrene in tetrahydrofuran followed by the addition of $Me_3CC{\equiv}P$ produced the bis(phosphavinyl)-ether complex (8.12). The structure of the complex (8.12) was



8.10



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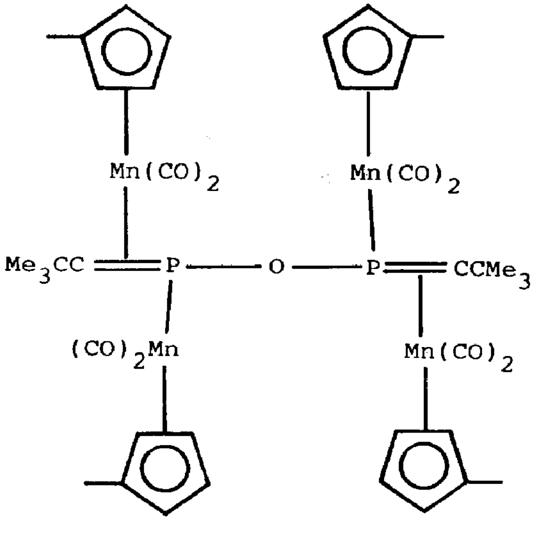
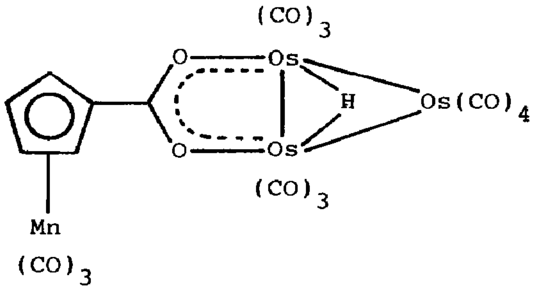


8.12

determined by X-ray analysis [185]. Cymantrenecarboxylic acid combined with $HOs_3(OH)(CO)_{10}$ to give the cluster complex (8.13) wich has been characterized by X-ray crystallography [186]. The tellurium atom in the complex (8.14) exhibited electrophilic reactivity when it was treated with methyllithium to give the anion (8.15). X-Ray analysis showed that the anion (8.15) was pyramidal with the tellurium atom above the plane defined by the



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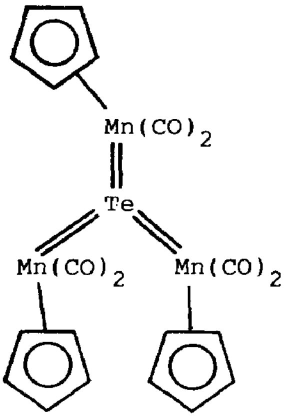

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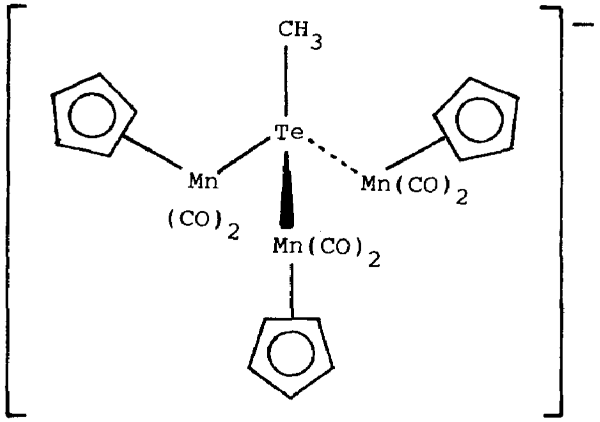

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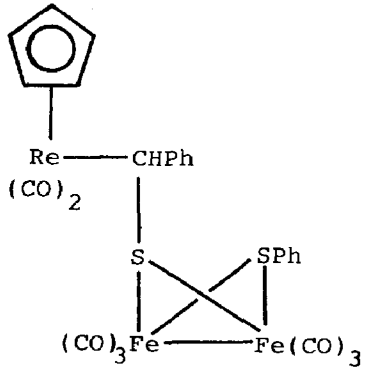
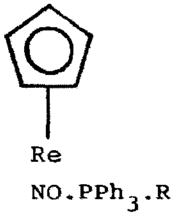


8.16

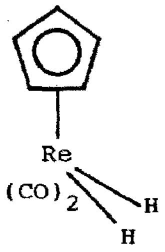
three manganese atoms [187]. Treatment of the carbyne complex $[(\eta\text{-}C_5H_5)Re(CO)_2(\equiv CPh)]BBr_4$ with the anion of $(\mu\text{-}PhS)(\mu\text{-}LiS)\text{-}Fe_2(CO)_6$ produced the complex (8.16) whose structure was confirmed by X-ray analysis [188].

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

The mechanism of hydride abstraction from the alkyl-rhenium complexes (9.1; R = CH_2Ph, CHMePh, CH_2CHMe_2) has been investigated by electrochemical and kinetic isotope effect techniques. It was concluded that hydride abstraction took place by initial electron transfer followed by hydrogen atom transfer [189]. The electrochemical oxidation of the rhenium alkyl complexes (9.1;



9.1



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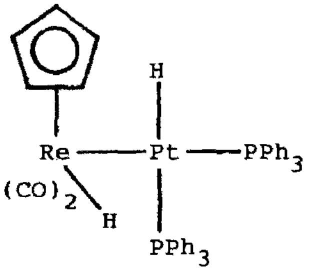
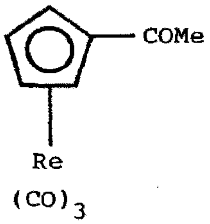


9.3

R = $PhCH_2$, Me_2CHCH_2, PhCHMe) has been investigated. The results indicated an initial one-electron oxidation to give the corresponding cation radicals [190].

The rhenium dihydride (9.2) has been used in the preparation of some iridium dihydrides. As part of this study the heterobimetallic dihydride (9.3) was prepared from the rhenium complex (9.2) and $(Ph_3P)_2Pt(CH_2{=}CH_2)$ [191]. The (η-cyclopentadienyl)-rhenium complex (9.4) has been attacked by trimethylphosphine to form the rhenium(I) enolate complex (9.5) which was characterised by X-ray crystallography [192].

Treatment of the reactive intermediate (9.6) with alkyl iodides produced the stable alkyl halide complexes [9.7; R = CH_3,



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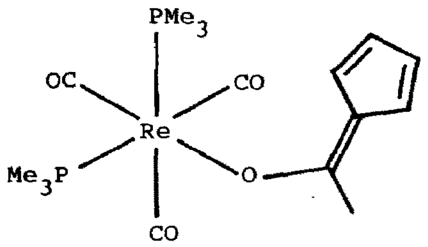

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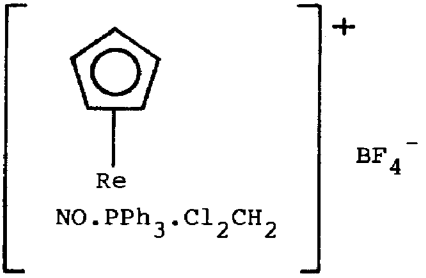

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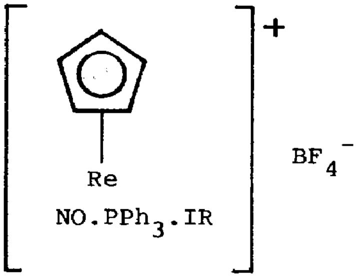

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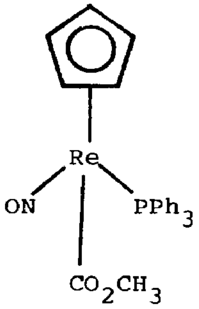

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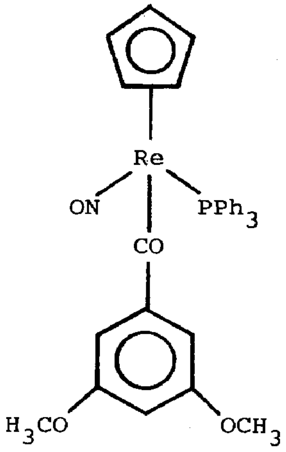

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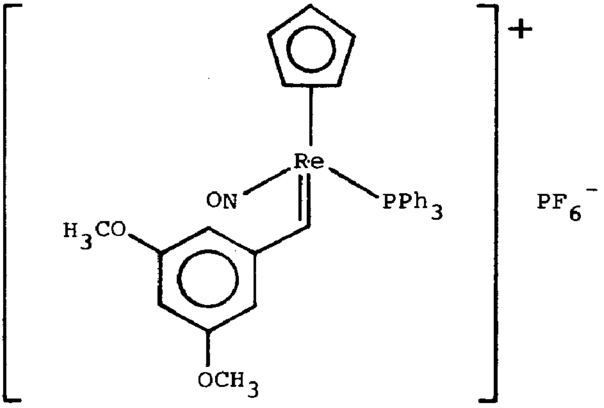
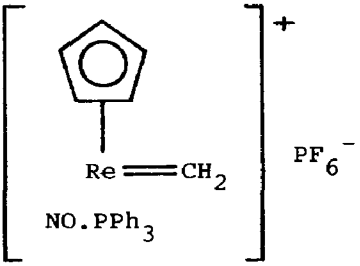


9.10

C_2H_5, C_3H_7, $CH_2Si(CH_3)_3$] [193]. Reaction of the methyl ester complex (9.8) with 3,5-dimethoxyphenylmagnesium iodide gave the 3,5-dimethoxybenzoyl complex (9.9) in almost quantitative yield. Reduction of the complex (9.9) with BH_3.THF produced the corresponding benzyl complex which on treatment with $Ph_3C^+PF_6^-$ gave the carbene complex (9.10). Rhenium-carbon bond cleavage in chiral complexes was also investigated [194].

Reaction of the η-cyclopentadienyl-rhenium salt (9.11) with triphenylphosphine sulphide produced a 1:1 mixture of the thioformaldehyde complex (9.12) and the ylide complex (9.13). The structure of the complex (9.12) was determined by X-ray analysis and its reactivity was compared with that of the corresponding formaldehyde complex [195].



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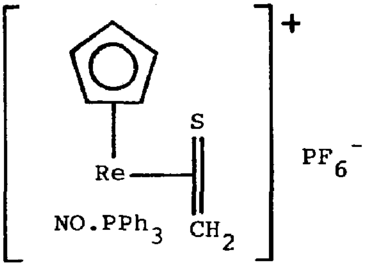

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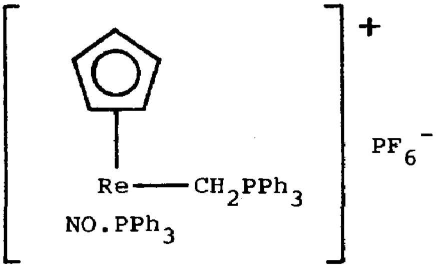

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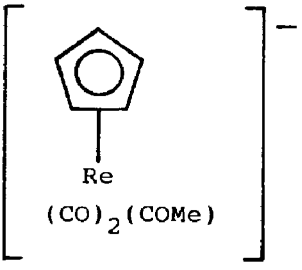
The (η-cyclopentadienyl)rhenium anion (9.14) underwent alkylation with the hard electrophile, Me_3OPF_6, to give the carbene complex (9.15) while alkylation with the soft electrophile, methyl iodide, gave the rhenium-methyl product (9.16) which was characterized by X-ray crystallography as a complex with trans-piano stool geometry. Thermal decomposition of this complex (9.16) in the presence of carbon monoxide gave tricarbonyl(η-cyclopentadienyl)rhenium and acetone while photolysis under carbon monoxide at 20 atmospheres gave tricarbonyl(η-cyclopentadienyl)rhenium and 2,3-butanedione [196].



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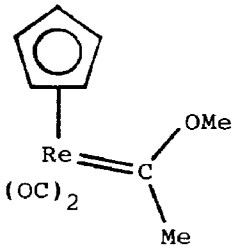

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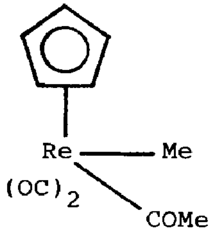
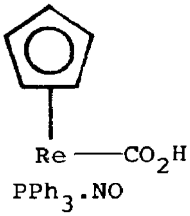


9.16

Reaction of the rhenium complex (9.17) with lithium hydride or potassium hydride followed by Ph_3SnCl, Me_3SnCl or Ph_3PbCl produced the corresponding carboxylates (9.18; R = Ph, Me; M = Sn, Pb). Decarboxylation of the triphenyl-tin and -lead derivatives gave the rhenium-tin and rhenium-lead compounds (9.19; M = Sn, Pb). The germanium complex (9.20) was prepared by a similar series of reactions [197]. Condensation of the rhenium complex (9.21) with silver sulphate or silver carbonate gave the metallacycles (9.22, X = CO, SO_2) respectively [198].

The Grignard reagent $Me_2C(CH_2MgBr)_2$ attacked (η-C_5Me_5)-$Re(O)Cl_2$ to give the rhenium metallacycle (9.23) [199]. The (η-pyrrolyl)rhenium complex (9.24) underwent N-methylation with methyl triflate to form the cation (9.25) while with acyl chlorides the corresponding N-acylpyrroles were formed directly [200]. The rhenium complex (9.26) was dechlorinated with



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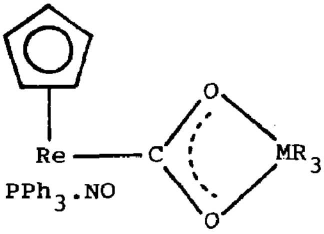

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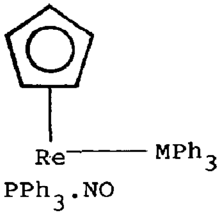

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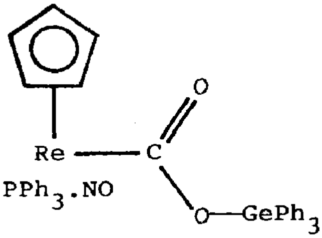

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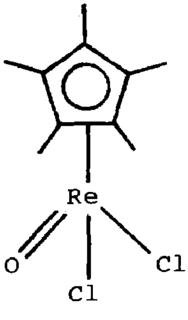

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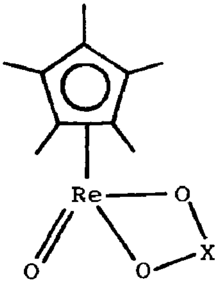

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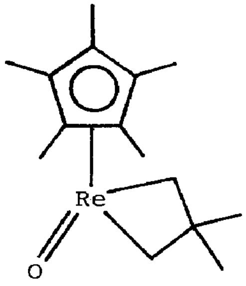

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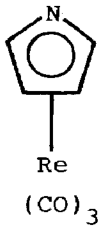

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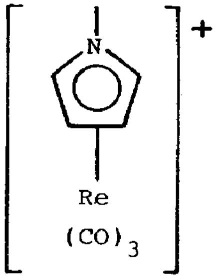

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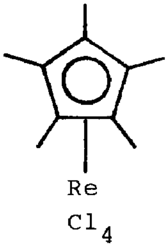

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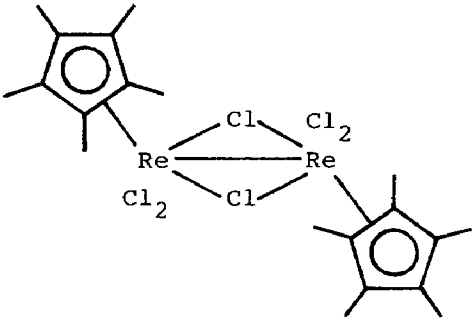

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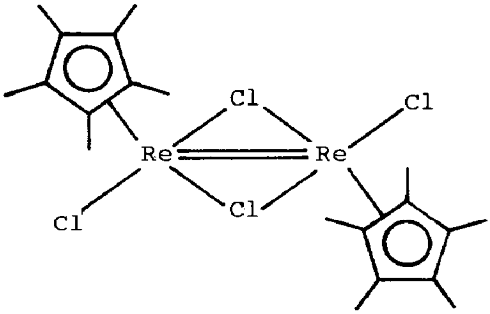

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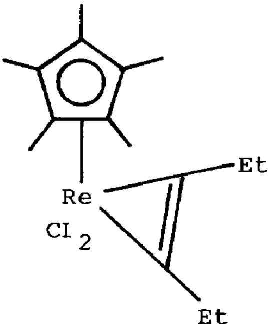


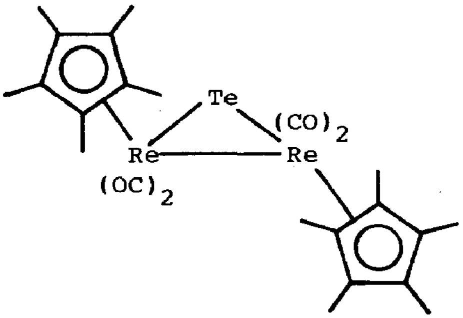
9.29

$HgCl_2$-activated alumina to give the dimers (9.27 and 9.28). Reduction of the complex (9.26) in the presence of hexyne produced the complex (9.29) which according to an X-ray study contained a four electron alkyne ligand [201].

Oxidative addition of hydrogen telluride to $(\eta\text{-}C_5Me_5)$-$Re(CO)_2(THF)$ in THF at 25°C gave several mixed rhenium-tellurium complexes including the hydride $(\eta\text{-}C_5Me_5)ReHTeH(CO)_2$, the trinuclear complex (9.30) and the tetranuclear complex (9.31). Further reaction of the hydride with $(\eta\text{-}C_5H_5)Mn(CO)_2(THF)$ gave a dimanganese-rhenium-ditellurium species [202]. The rhenium complex (9.32) has been used as a catalyst in the hydrogenation of enamides [203].

Treatment of the η^5-pentadienyl complex (9.33) with trimethyl- or triethyl-phosphine produced initially the corresponding η^1-cis-pentadienyl complex (9.34; R = Me, Et) which converted slowly to the trans-isomer (9.35) [204]. Gladysz and co-workers have reported the synthesis, structure and alkylation of the chiral vinylrhenium complexes (9.36; X = H, R = H, Me, n-Pr, benzyl; X = OCH_3, R = OCH_3, R = H, Me, benzyl, Ph). A mechanistic study of 1,3-asymmetric induction from the rhenium atom to carbon was carried out [205].

The structures of the formyl and acyl complexes (9.37 and 9.38) have been determined by X-ray analysis. E.H.M.O. calculations on model compounds predicted that the ON-Re-C-O torsion angle (Θ) should be 0° or 180° to give maximum overlap of the Re fragment HOMO with the carbonyl π^* orbital. In the complexes



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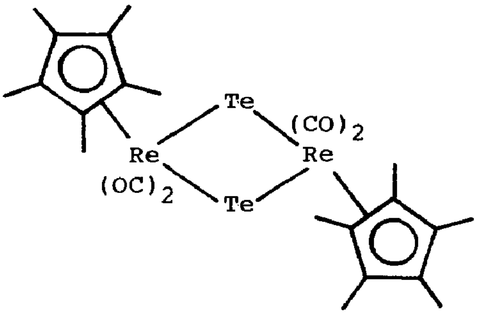

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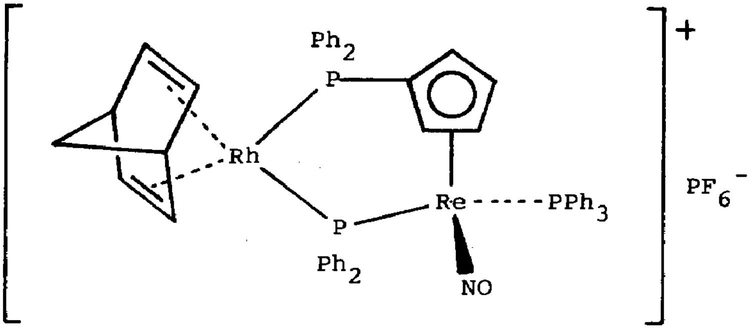

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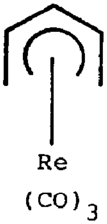

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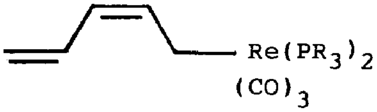

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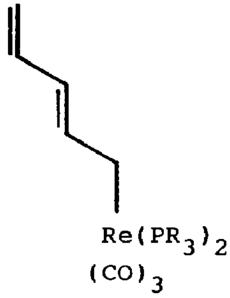

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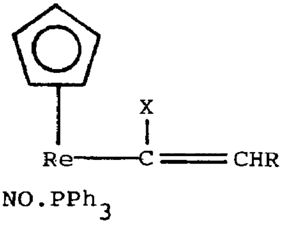

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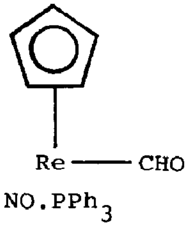

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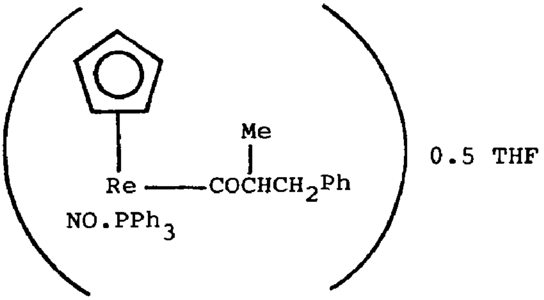
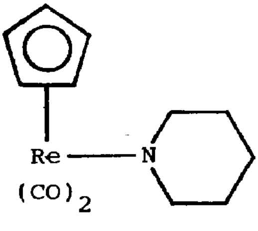


9.38

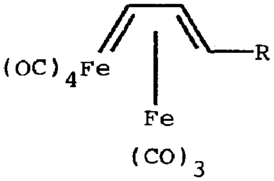
(9.37 and 9.38) Re-C conformations with Θ near to 180° were found [206]. The electronic structures of η-cyclopentadienyl complexes [η-$C_5H_5M(L)R_2$], where M = Re, W; L = O, NO; R = alkyl, have been investigated via Fenske-Hall molecular orbital calculations [207].

Room temperature ligand field luminescence has been observed for a number of rhenium compounds including the η-cyclopentadienyl complex (9.39). The results indicated that luminescence studies in solution could be informative for many transition metal organometallic compounds which exhibited low-lying ligand field excited states [208].



9.39

10. (Acyclic-η-diene)Fe(CO)$_3$



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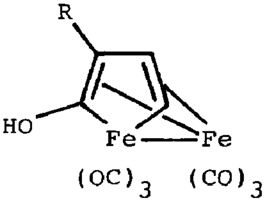

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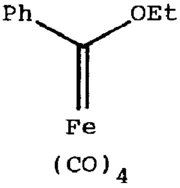
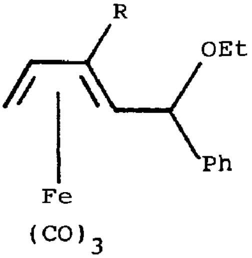


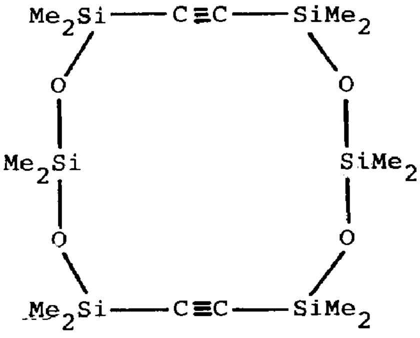
10.3

Allenes combined with iron carbonyls to give intermediate (η-allyl)iron complexes which isomerized at 60°C to form 1-ferra-1,3-diene complexes (10.1; R = H, Ph) and these rearranged at 130°C by regiospecific insertion of carbon monoxide to give the ferracyclopentadienes (10.2; R = H, Ph) [209]. The carbene complex (10.3) has been coupled with eight 1,3-dienes, mainly methyl- and dimethyl-butadienes, to give the corresponding (η-1,3-diene)iron complexes such as the complex (10.4; R = H, Me, OMe) as a mixture of two diastereomers. Some related reactions were reported [210].



10.4

UV irradiation of $Fe(CO)_2(NO)_2$ in liquid xenon doped with butadiene gave (trans-η^2-C_4H_6)$FeCO(NO)_2$, (trans-η^2-C_4H_6)$_2Fe(NO)_2$ and (cis-η^4-C_4H_6)$Fe(NO)_2$. The last complex was stable up to -35°C in liquid xenon [211]. Treatment of the diyne (10.5) with nonacarbonyldiiron generated the (η-methylenecyclopropene)-tricarbonyliron complex (10.6). The structure of this complex was established by X-ray diffraction. The C_3-C_4 double bond was bent towards the iron atom by 27.9° from the planar cyclo-



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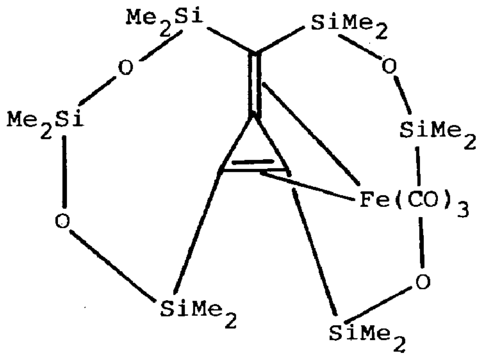

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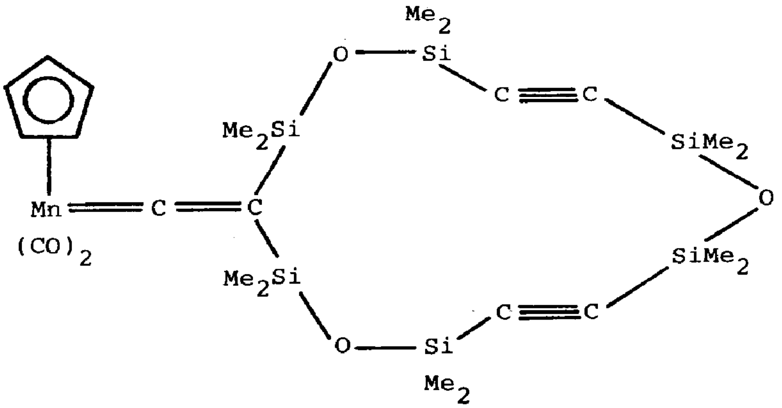


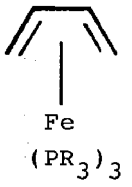
10.7

propene ring. The preparation of the vinylidene complex (10.7) was also reported [212].

Reduction of iron(II) chloride with activated magnesium in the presence of 1,3-dienes and trialkylphosphines gave the (η^4-diene)iron complexes (10.8; R = Me, Et, Pr^n). The bis(η^4-diene) complexes (10.9; R = Me, Et, Pr^n) were obtained in the same way. The crystal and molecular structure of one complex, (η^4-1,3-butadiene)(η^4-1,5-cyclooctadiene)triethylphosphineiron, was determined by X-ray crystallography and this confirmed the square-pyramidal geometry of these complexes [213].

Tricarbonyliron groups were introduced into polybutadiene and butadiene-styrene block copolymers. The changes in the structural transitions of these modified polymers were investigated [214, 215]. The crystal and molecular structure of the chiral (η-bicyclooctanone)iron complex (10.10) has been determined by X-ray crystallography. The CD spectra of the two chiral complexes (+)-(10.10) and (+)-(10.11) have been recorded and found to be solvent and temperature dependent. The octant rule was obeyed in each case [216].

The crystal and molecular structure of the (η-butadiene)iron complex (10.12) has been determined by X-ray crystallography [217]. The crystal and molecular structure of the two diethyl muconate-iron complexes (10.13; L = quinoline, pyrazine) have been determined by X-ray crystallography. When the structure was regarded as a tetragonal pyramid then the N-heterocycle occupied different positions in the two compounds [218].



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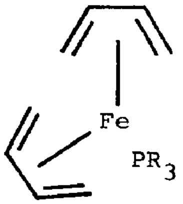

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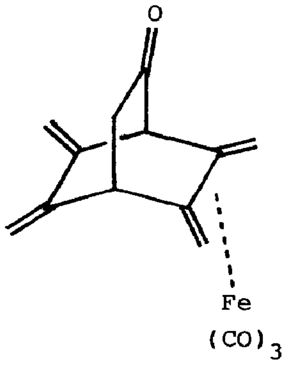

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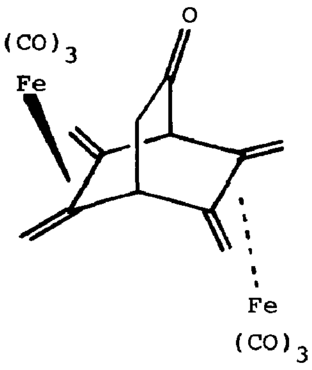

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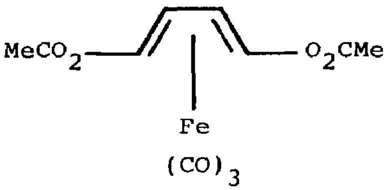

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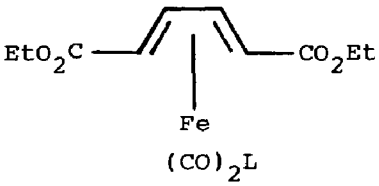
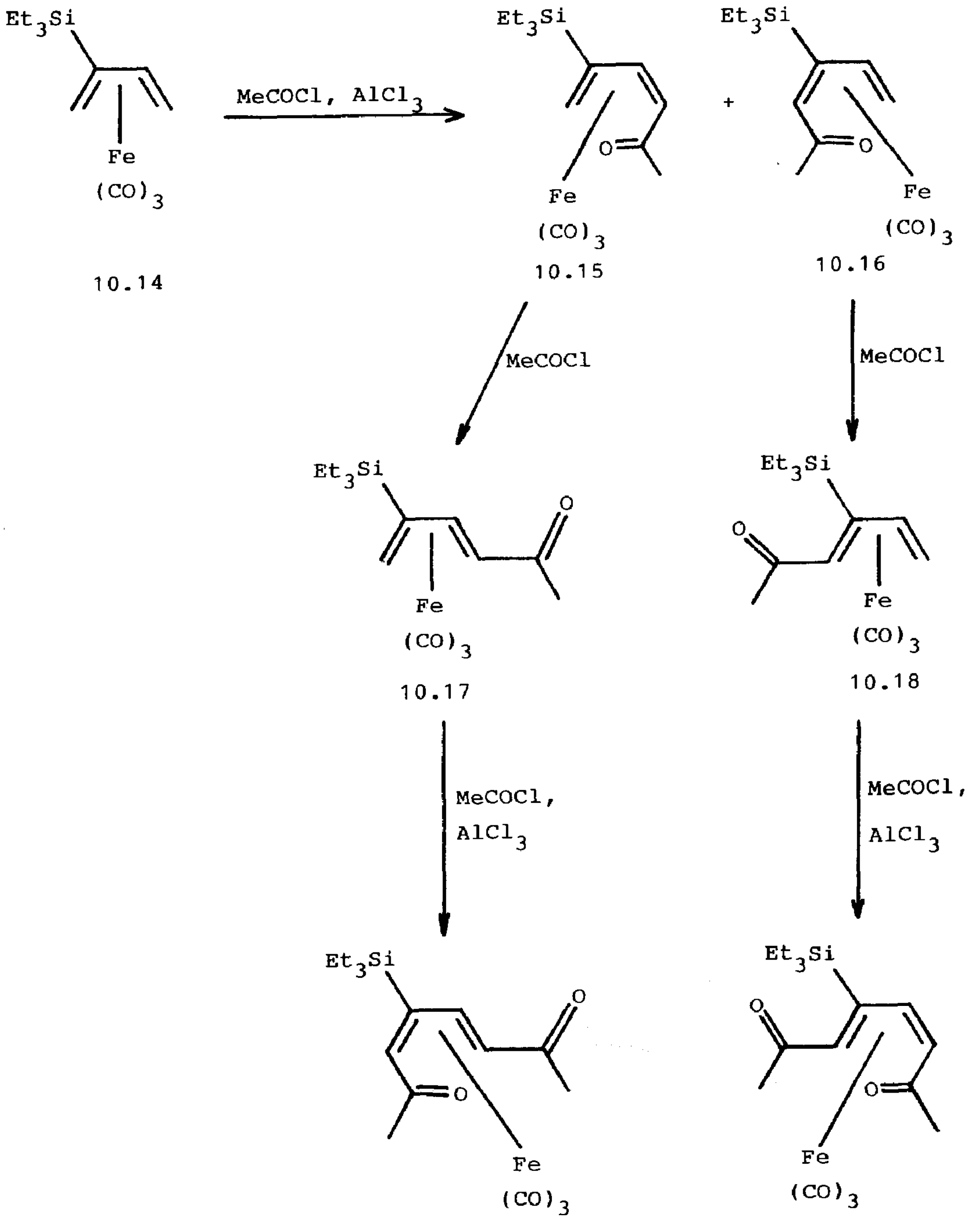


10.13

Friedel-Crafts acetylation of the 2-silylated (η-butadiene)-tricarbonyliron complex (10.14) gave only the terminal *cis*-dienone products (10.15 and 10.16). After *cis*-*trans* isomerization in the presence of acetyl chloride to give the rearranged species (10.17 and 10.18), a second *endo*-acetylation occurred at the unsubstituted terminal carbon atom to form the derivatives (10.19 and 10.20). The resultant 1,4-diacylation was achieved in the presence of several acylating agents [219].

In related work Friedel-Crafts acylation of the η-butadiene complexes (10.21; R^1 = Et, Me_2CH) with acetyl chloride-aluminium chloride produced the *endo*-substituted complexes (10.22). These complexes isomerized in the presence of acetyl chloride to give



10.14

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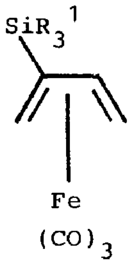
10.19

10.20

the corresponding exo-compounds (10.23). Acylation of these exo-complexes produced the diacylated derivatives [10.24; R^2 = Me, Me_2CH, Me_3C, Ph, $(CH_2)_7CO_2Me$] [220].

The (η-diene)iron complex (10.25) combined with carbon dioxide to give the (η-allyl)iron carboxylate (10.26) which underwent rearrangement and insertion of a further molecule of carbon dioxide to form, after acid hydrolysis, olefin dicarboxylates [221]. The tricarbonyliron complexes of α,β-unsaturated ketones (10.27; R = Me, n-Bu, i-Bu, t-Bu) combined with methyl lithium or methyl Grignard reagent to form, after treatment with t-butylbromide, the diketones (10.28; R = Me, n-Bu, i-Bu, t-Bu). The reaction appeared to take place by way of a metal acyl intermediate [222].



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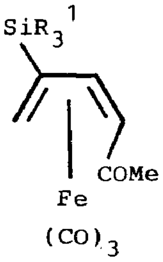

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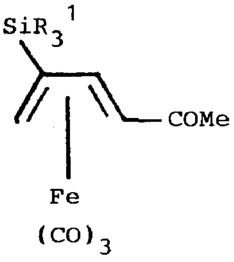

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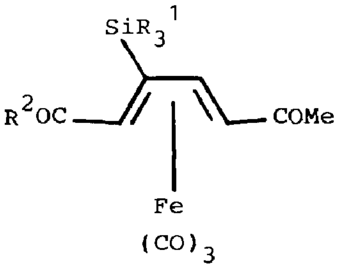

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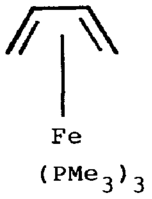

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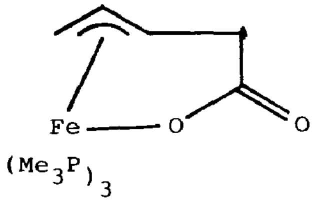

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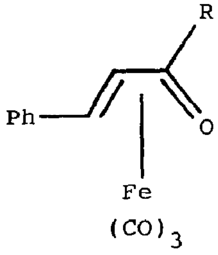

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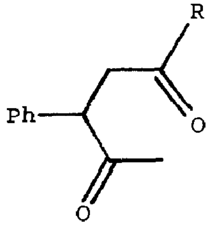

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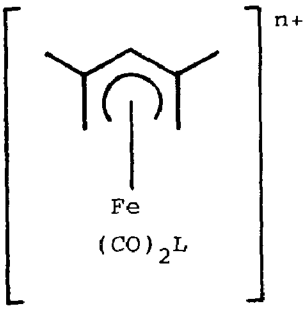
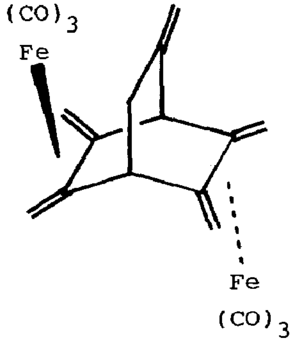


10.29

The (η-2,4-dimethylpentadienyl)iron cation (10.29; L = CO; n = 1) has been attacked by potassium iodide in acetone to give the iodide (10.29; L = I; n = 0) which underwent alkylation with methyl iodide to the derivative (10.29; L = Me; n = 0) and dimerization with sodium amalgam to give an ESR active product. The iodide (10.29; L = I; n = 0) was characterized by X-ray crystallography [223]. Several (η-tetramethylenebicyclo[2.2.2]-octane)diiron complexes such as the optically pure species (10.30) have been characterized in solution by measurements on the CD spectra. The complex (10.30) showed solvent- and concentration-



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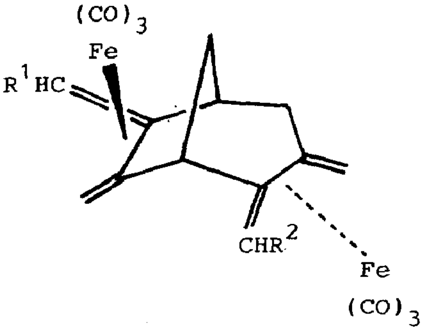
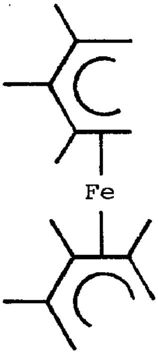


10.31

independent spectra but temperature dependence which was interpreted in terms of rapid interconversion between diastereoisomeric forms [224].

Friedel Crafts acylation of the tetramethylidenebicyclooctaneiron complex (10.31; $R^1 = R^2 = H$) gave the mono- and di-acetyl derivatives (10.31; $R^1 = H$, $R^2 = COMe$; $R^1 = R^2 = COMe$) respectively. The products were formed stereoselectively [225]. The chemistry of η-pentadienyl-transition metal compounds has been reviewed [226]. The bis(η-pentadienyl)-iron (10.32) and -osmium (10.33) complexes have been prepared. Variable temperature NMR spectroscopy and X-ray crystallography show that these complexes adopt a gauche-eclipsed conformation. Photoelectron spectra have been obtained and suggest that the radical cations of bis(η-pentadienyl)iron complexes differ markedly from the corresponding ruthenium and osmium species [227].

The solid state structure of bis(η-2,3,4-trimethylpentadienyl)iron (10.32) has been determined by X-ray crystallography. The complex existed in a distorted gauche-eclipsed structure [228].



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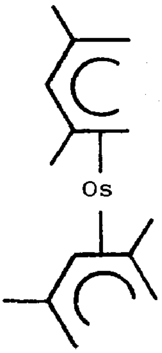
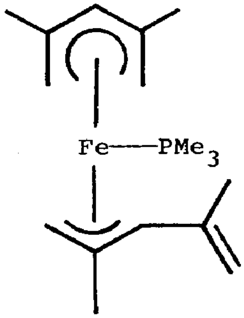


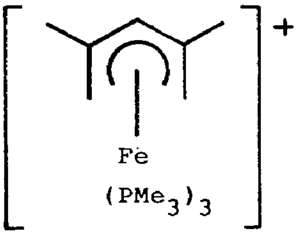
10.33

11. (η-Trimethylenemethane)Fe(CO)$_3$

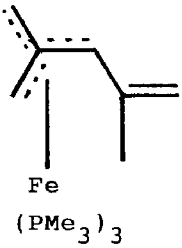
Potassium 2,4-dimethylpentadienide-THF combined with $FeCl_2(PMe_3)_2$ to give several products which were dependent on the proportions of the two reactants. When an excess of the hydrocarbon ligand was used then the (η^5-pentadienyl)iron complex (11.1) was formed while an excess of $FeCl_2(PMe_3)_2$ gave the cation (11.2). Equimolar proportions of the two reactants gave the



11.1



11.2

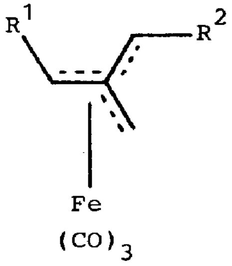


11.3

(η^4-trimethylenemethane)iron complex (11.3). The products (11.2 and 11.3) were characterized by X-ray crystallography [229].

Photolysis of aldehydes, R^{1}CHO, where R^1 = Me, Et, Ph, and allenes, R^{2}CH=C=CH$_2$, where R^2 = H, Me$_2$CH, Ph, PhCH$_2$, with pentacarbonyliron gave the (η-trimethylenemethane)iron complexes (11.4; R^1 = Me, Et, Ph; R^2 = H, Me$_2$CH, Ph, PhCH$_2$). The reaction mechanism involved an intermediate η-allyl-σ-complex which eliminated carbon dioxide to give the product with high stereospecificity. The trimethylenemethane ligand underwent thermal isomerization at 180°C without decomposition [230].

Three equivalent stretching bands of the tricarbonyliron complexes LFe(CO)$_3$, where L = 1,3-butadiene, norbornadiene,



11.4

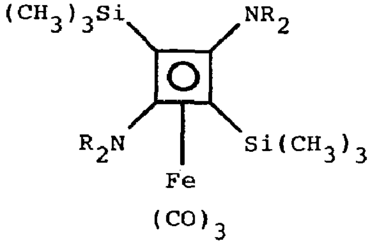
11.5

1,5-cyclooctadiene and trimethylenemethane were measured in the infrared time scale. At room temperature the infrared spectra of the complexes, L = trimethylmethane and 1,3-butadiene, showed three carbonyl stretching frequencies whereas the other two complexes only exhibited two such bands. At 10-12 K these latter two complexes, L = norbornadiene and 1,5-cyclooctadiene, showed three bands as would be expected for a square pyramidal structure, which was confirmed by X-ray analysis [231].

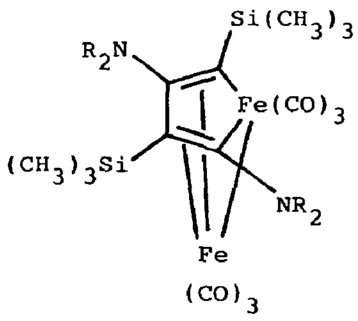
Tricarbonyl(η-trimethylenemethane)iron (11.5) has been compared with the isomeric (η-butadiene)tricarbonyliron by electron impact mass spectrometry. Ion-molecule gas-phase reactions of the two parent molecule negative ions have been examined. The butadiene ligand was more easily displaced than the trimethylenemethane ligand under a variety of conditions. In reactions of the two isomers with a range of reference acids the butadiene complex anion showed a lower proton affinity than trimethylenemethane species by 5 kcal mol^{-1} [232].

12. (η-C_4H_4)Fe$(CO)_3$

King and co-workers have reported the reactions of dialkylaminotrimethylsilylacetylenes, $(CH_3)_3SiC{\equiv}CNR_2$ (R = Me, Et or R_2N = piperidino), with pentacarbonyliron to give the corresponding η-cyclobutadiene derivatives (12.1) as the major product. In two of the reactions the tricarbonylferrole-iron tricarbonyl derivatives (12.2; R = Et or R_2N = piperidino) were also obtained in low yield. The structure of the complex (12.1; R_2N =



12.1



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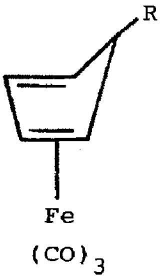

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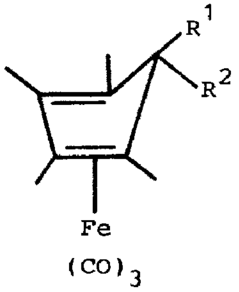
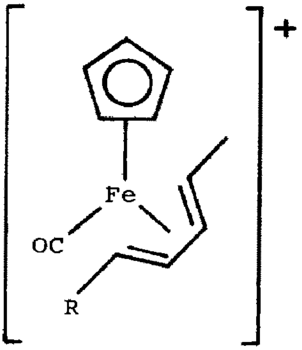


12.4

piperidino) was determined by X-ray analysis [233]. Ultraviolet irradiation of the η^4-cyclopentadiene-iron complexes (12.3; R = exo-H, exo-CH_2Ph and 12.4; R^1 = exo-Me, R^2 = endo-Me; R^1 = endo-Me, R^2 = exo-Me; R^1 = exo-CH_2Ph, R^2 = endo-Me) resulted in loss of a carbonyl group to give the corresponding iron dicarbonyls which were detected by infrared spectroscopy at low temperatures. Irradiation of these 16 electron species resulted in transfer of the 5-endo substituent to iron to form the corresponding (η^5-cyclopentadienyl)$Fe(CO)_2R$ products. The transfer of the 5-endo group was not very competitive with the back reaction with the carbonyl group to form the original (η^4-cyclopentadiene)$Fe(CO)_3$ starting material [234].



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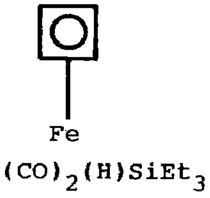


12.6

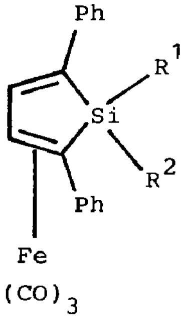
As part of a study of η-dienyl-iron complexes the cations (12.5; R = H, Me) were prepared. The structure of η^4-2,4-hexadiene complex (12.5; R = Me) was determined by X-ray analysis. The geometry around the iron atom was approximately tetrahedral with the carbonyl, the η-cyclopentadienyl group and the olefin occupying the four coordination sites [235].

Cymantrene, pentamethylcymantrene, tricarbonyl(η-cyclopentadienyl)rhenium, benchrotrene and tricarbonyl(η-butadiene)iron have each been irradiated in methylcyclohexane or Et_2CHMe at 85-157 K to form 16-electron dicarbonyl species in each case. These intermediates were characterized by IR spectroscopy and the rate of reaction with triethylsilane to form 18-electron adducts, such as the iron adduct (12.6), was determined for each species. The relative rates of reaction were: $(\eta\text{-}C_6H_6)Cr(CO)_3 > (\eta\text{-}C_5H_5)Mn(CO)_3 > (\eta\text{-}C_4H_4)Fe(CO)_3 > (\eta\text{-}C_5H_5)Re(CO)_3$ and $(\eta\text{-}C_5Me_5)Mn(CO)_3 > (\eta\text{-}C_5H_5)Mn(CO)_3$ [236].

13. (Cyclic-η-diene)Fe(CO)$_3$

(i) Formation

Treatment of 1,1-dimethoxy-2,5-diphenylsilacyclopentadiene with nonacarbonyldiiron gave the tricarbonyliron complex (13.1; $R^1 = R^2$ = OMe). Reduction with $(i\text{-}Bu)_2AlH$ gave the dihydro complex (13.1; $R^1 = R^2$ = H) and this was transformed into the fluoro, chloro, bromo and alkoxy derivatives (13.1; R^1 = F, Cl,



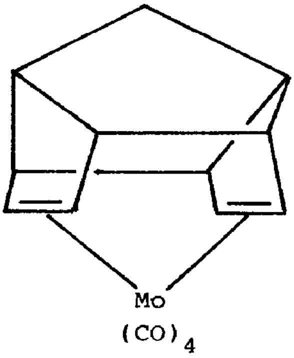
13.1

Br, OMe, p-C_6H_4.OMe) respectively [237]. When homohypostrophene was heated with hexacarbonylmolybdenum the tetracarbonyl derivative (13.2) was isolated as the major product together with a dicarbonylmolybdenum complex. Prolonged heating of these two compounds afforded the dicyclopentadienylmethane complex (13.3) [238].

The silacyclopentadienes and germacyclopentadiene (13.4; R = H, Me, M = Si; R = Me, M = Ge) respectively have been used as ligands with transition metals. For example, reactions with $Fe_2(CO)_9$ or $Ru_3(CO)_{12}$ produced the corresponding η^4-complexes (13.5; R = Me, M = Si, Ge; R = H, M = Si and 13.6). The (η^4-metallole)$Fe(CO)_3$ complexes (13.5; R = H, Me; M = Si) underwent carbonyl replacement with triphenylphosphine on ultraviolet irradiation [239].

(η-Dihydroacepentalene)hexacarbonyldiiron complexes have been formed from enneacarbonyldiiron and 1,4-dibromo-, 1,4,7-trichloro- and 1,4,7-tribromotriquinacene [240]. The cation $[(\eta\text{-}C_5Me_5)Fe(CO)_2THF]^+$ combined with 2-methyl-1,3-butadiene, 1,3-cyclohexadiene and substituted 1,3-cyclohexadienes, and 1,5-cyclooctadiene to give products such as the (η-diene)iron complex (13.7). The Bronstead plot derived from the rate of addition of amine nucleophiles to the complex (13.7) indicated an essentially "soft" nature for the complexed 1,3-diene [241].

The mechanism of the reaction of the 4-vinylcyclohexenes (13.8; R = H, CO_2Me, Ph, CN, CH_3) to give the corresponding



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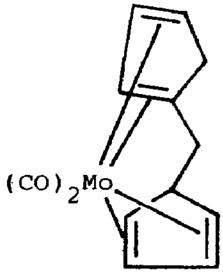

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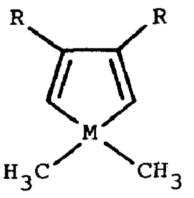

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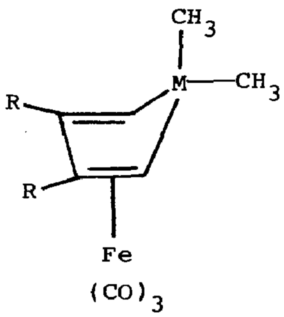

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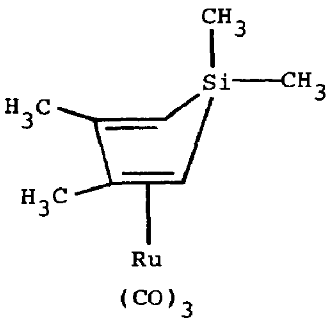
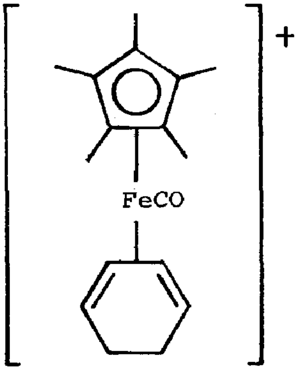


13.6

tricarbonyliron complexes (13.9, 13.10, 13.11 and 13.12) has been investigated [242].

The (η-silacyclohexadiene)iron complexes (13.13; R^1, R^2 = H, $SiMe_3$) have been obtained from pentacarbonyliron or enneacarbonyliron and the corresponding ligand. The isomerized products (13.14; R^1, R^2 = H, $SiMe_3$) were obtained in the same reaction [243]. Reaction of the tricyclooctene diester (13.15) with pentacarbonyliron produced the single organoiron product (13.16) together with a non-iron containing dimer. The synthesis of the starting ester (13.15) and related molecules was also reported [244].

Treatment of the metal salts $MCl_n(THF)_m$ with n equivalents of potassium 6,6-dimethylcyclohexadienide (KdmC) produced the



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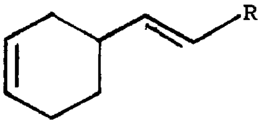

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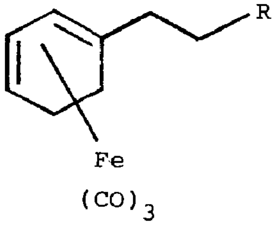

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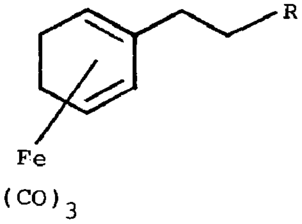

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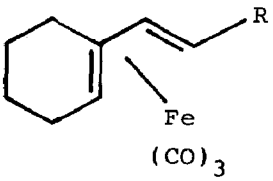

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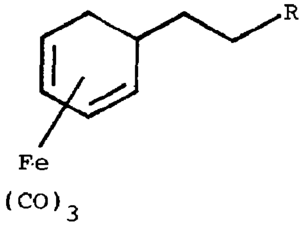

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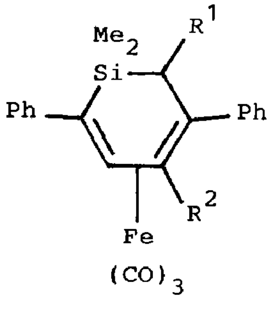

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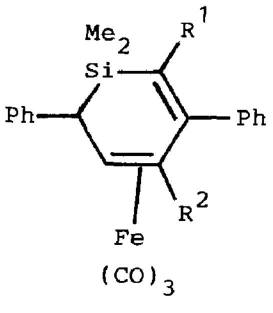

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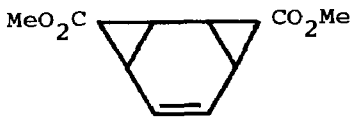

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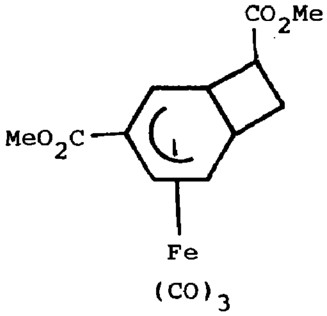

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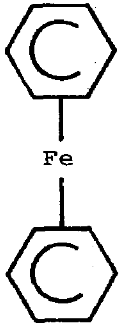

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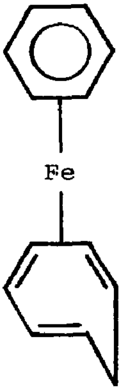

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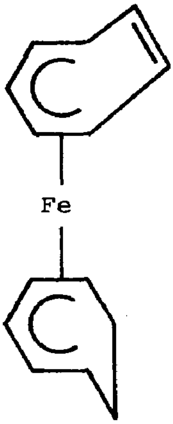

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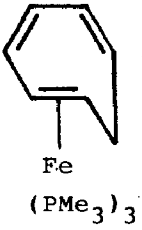

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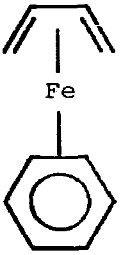

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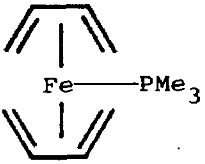
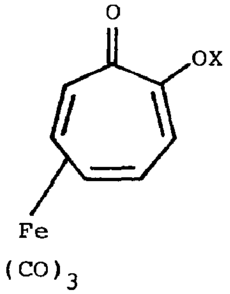


13.22

sandwich complexes (dmC)$_2$M, where M = Ti, V, Cr, Fe. The Ti and Fe complexes were diamagnetic and the V and Cr compounds were paramagnetic. In a related reaction bis(η^5-cyclohexadienyl)-iron (13.17) was prepared from lithium cyclohexadienide and iron(II) chloride [245].

(η-Benzene)bis(trimethylphosphine)iron has been used as a precursor for the preparation of polyene iron derivatives. For example, treatment with cycloheptatriene produced the iron complexes (13.18, 13.19 and 13.20) and treatment with buta-1,3-diene afforded the complexes (13.21 and 13.22) [246]. Irradiation of 2-acetoxytropone or 2-benzoyloxytropone with pentacarbonyliron generated a mixture of the isomeric tricarbonyliron complexes (13.23 and 13.24; X = COCH$_3$, COPh) respectively. The isomers (13.23 and 13.24) were separated by medium pressure liquid chromatography. The rearrangement of the isomers (13.23 and 13.24) in solution to their equilibrium mixtures was monitored by ^{1}H NMR spectroscopy [247].



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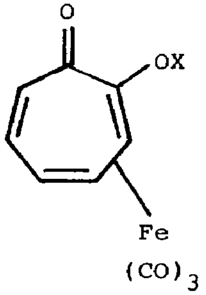
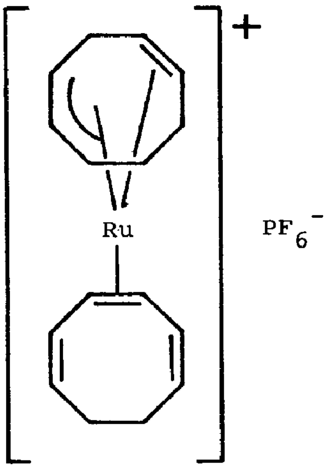
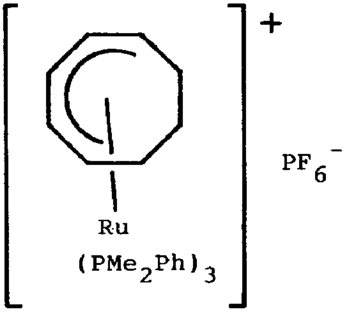


13.24

13. (ii) Spectroscopic and Physico-chemical studies

The crystal and molecular structure of tricarbonyl(*o*-xylylene)iron[tricarbonyl(1,1',2,2'-η^4-1,2-dimethylene-cyclohexa-3,5-diene)iron] has been determined by X-ray crystallography [248]. The structures of the ruthenium complexes (13.25 and 13.26) have been determined by X-ray analysis. The reactions of complex (13.25) with a variety of ligands have been investigated [249].

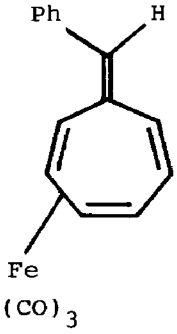




13.25

13.26

An ^1H NMR study has been carried out on the addition of tetracyanoethene to substituted (η^4-7-methylenecycloheptatriene)-$Fe(CO)_3$ complexes. The results indicated that the dominant initial reaction was 1,3-addition followed by isomerization to 1,6- or 1,8-adducts. The addition of tetracyanoethene to the η^4-7-phenylmethylenecycloheptatriene complex (13.27) produced the 1,8-adduct (13.28). The structure of the adduct (13.28) was confirmed by X-ray analysis [250].



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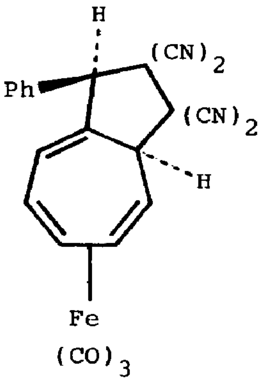
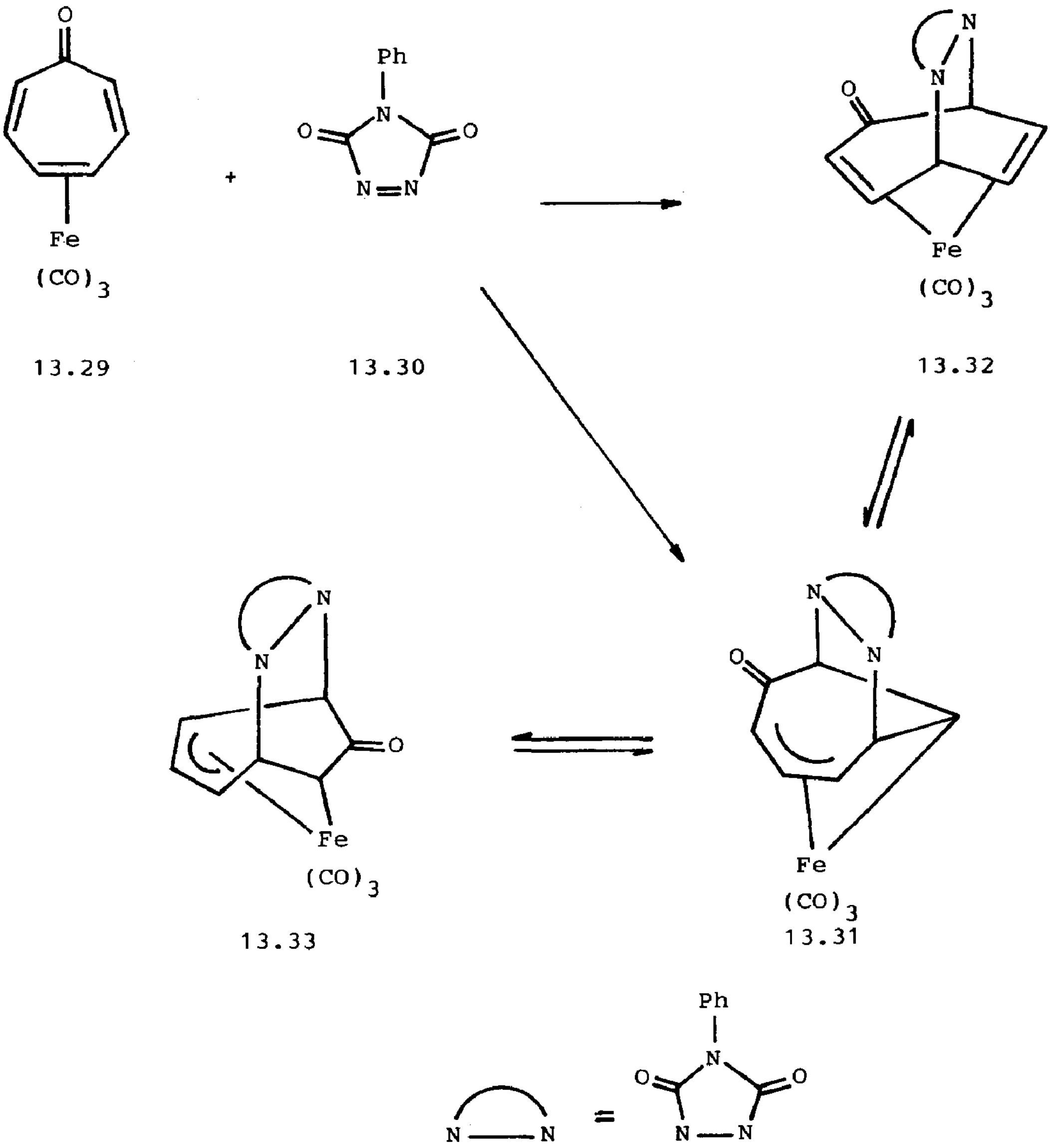


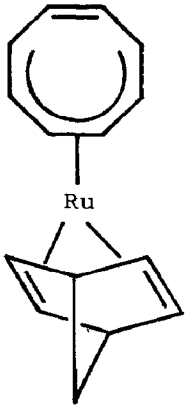
13.28

The reaction between (η^4-tropone)irontricarbonyl (13.29) and 4-phenyltriazoline-3,5-dione (13.30) gave the [3+2]- and [4+2]-cycloadducts (13.31 and 13.32) in the ratio 3:1 as the initial kinetic products. Slow rearrangement occurred to give the [5+2]-isomer (13.33) with a final equilibrium ratio (13.31: 13.32:13.33) of 2:1:39. The [3+2] and [4+2] adducts underwent equilibration by a [2,2]-sigmahaptotropic pathway while the [3+2]- and [5+2]-isomers equilibrated by a [3,3]-sigmahaptotropic mechanism [251].



13.29 13.30 13.32

13.33 13.31



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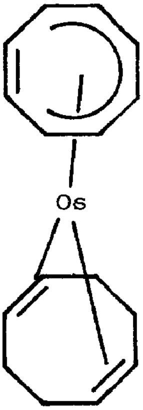
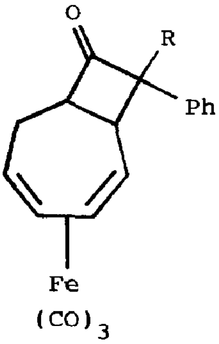


13.35

Magnetization transfer measurements have been used to reinvestigate the mechanism of fluxionality of the ruthenium complex (13.34) and to examine the osmium complex (13.35). The mechanism of cyclooctatetraene fluxionality for both complexes was a [1,5]-shift with [1,3]-shifts occurring at a slower rate. The osmium complex (13.35) also exhibited two lower energy processes consistent with a staggered relative arrangement of the two ligands [252]



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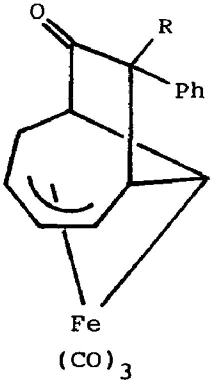


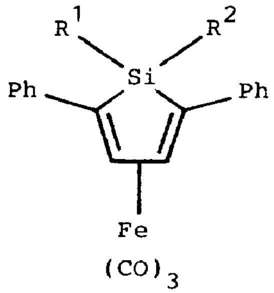
13.37

The kinetics and stereochemistry of the pericyclic [2,2]-sigmahaptotropic rearrangement of the cyclic-diene complex (13.36; R = Ph, CH_3) to the σ-π-allylic compound (13.37) has been studied by ^1H NMR spectroscopy. The reaction occurred in a single kinetic step of low activation with a negative entropy and a moderate solvent effect [253].

13. (iii) General Chemistry

Tricarbonyl(η-1-chloro-2,5-diphenylsilacyclopentadiene)iron complexes underwent nucleophilic displacement of chlorine with complete retention of configuration at both the exo- (13.38; R^1 = Cl, R^2 = Me) and the endo- (13.38; R^1 = Me, R^2 = Cl) positions. Substitution of exo-Cl was faster then endo-Cl and was discussed in terms of electronic factors [254]. Regiocontrol in the formation of tricarbonyl(η^5-cyclohexadienyl)iron cations from the corresponding tricarbonyl(η^4-cyclohexadiene)iron complexes has been investigated. Thus, the complex (13.39) gave the cation (13.40) in 72% yield on oxidation with thallium(III) while hydride abstraction with triphenylcarbenium hexafluorophosphate gave the cation (13.41) in 70% yield [255].

The kinetics of the reaction between the η-dienyl complexes (13.42; $R^1 = R^2 = R^3$ = H; $R^1 = R^3$ = H, R^2 = OMe; $R^1 = R^3$ = H, R^2 = Me; R^1 = OMe, $R^2 = R^3$ = H; R^1 = OMe, R^2 = H, R^3 = Me) and trimethylsilyl cyanide to give the corresponding η-diene complexes (13.43) have been studied. The reaction proceeded via the isocyanide isomer with a rate-limiting pre-equilibration of the trimethylsilyl cyanide [256].



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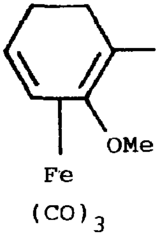

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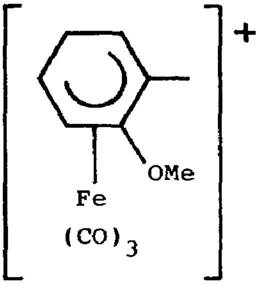

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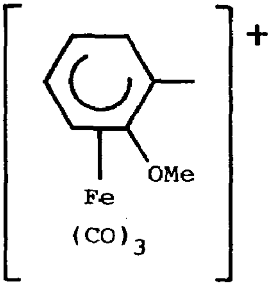

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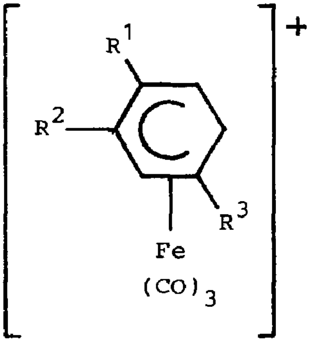

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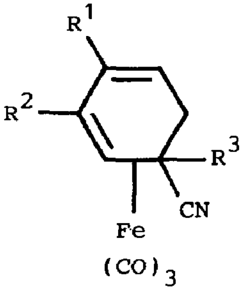

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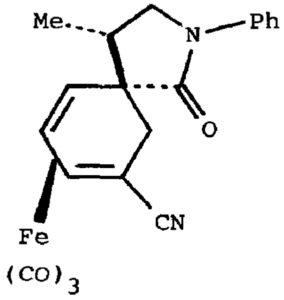

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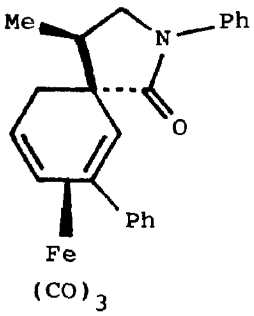
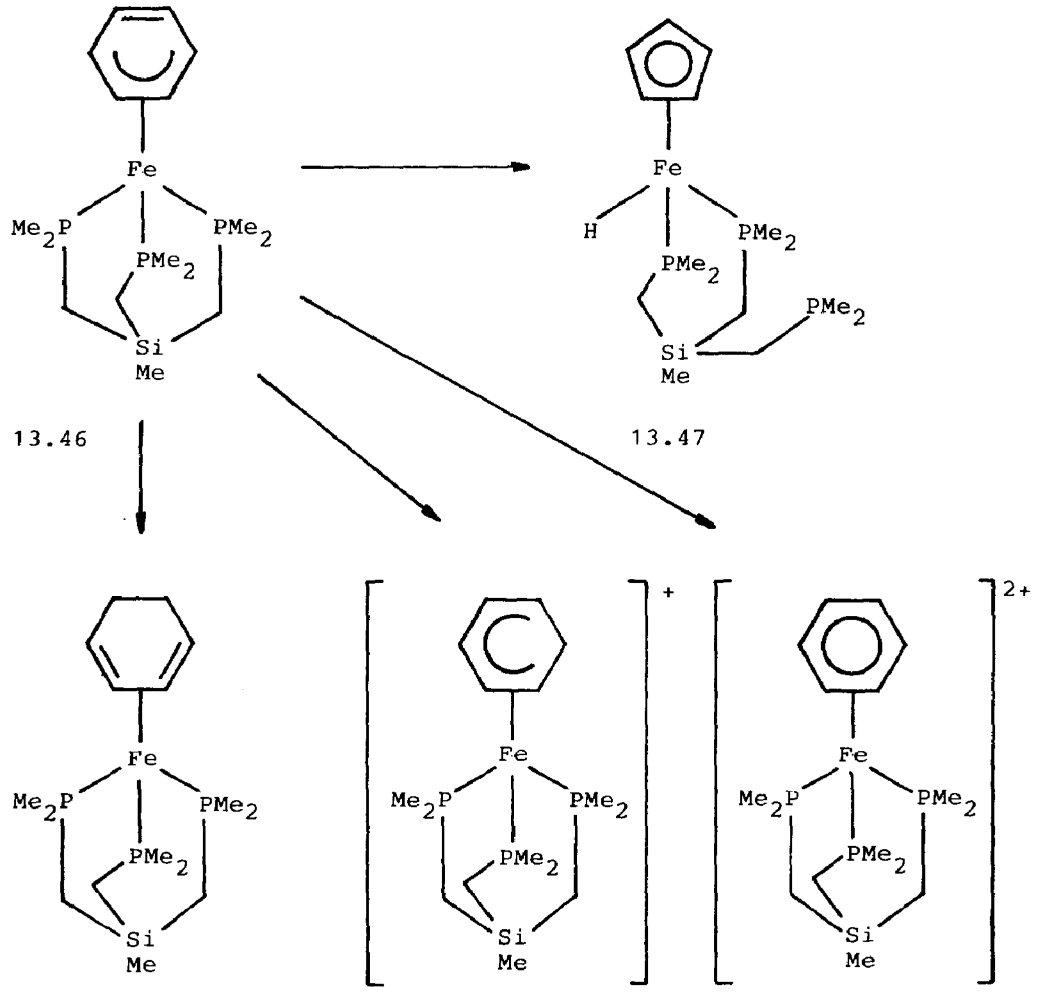


13.45

Pearson and Zettler have shown that intramolecular coupling between alkenic groups and an appropriately C(5)-substituted (η-cyclicdiene)Fe(CO)$_3$ complex proceeded with high stereoselectivity. The enantiomer produced was predetermined by having either an electron withdrawing or an electron donating substituent at C(5). The enantiomerically pure spirolactams (13.44 and 13.45) were prepared in high yields [257]. The tri-tertiary-phosphine, tris(dimethylphosphinomethyl)methylsilane (tmps)



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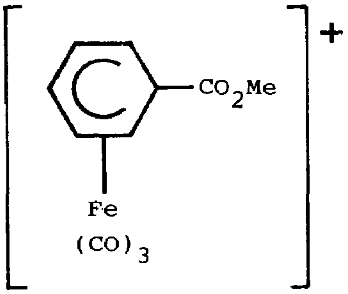
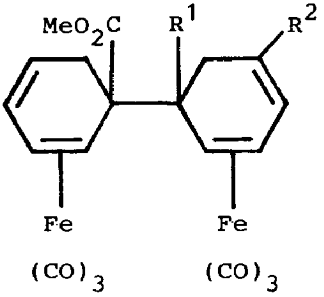


13.51

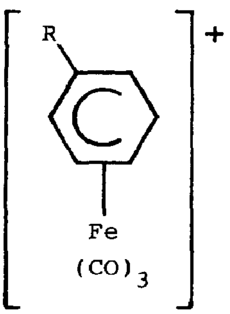


13.52

combined with (η-C_6H_6)Fe(PMe_3)$_2$ to give the complex (η^4-C_6H_6)-Fe(tmps) (13.46). The η^4-C_6H_6 ligand was displaced by carbon monoxide to give Fe(CO)$_2$(tmps), by cyclopentadiene to give the (η-cyclopentadienyl)iron complex (13.47) and by cyclohexa-1,3-diene to give the (η-cyclohexadiene)iron derivative (13.48). Treatment with NH_4PF_6 gave the (η-cyclohexadienyl)iron cation (13.49) while oxidation with $AgBF_4$ led to the (η-benzene)iron dication (13.50) [258].

Reductive dimerization of the (η-cyclohexadienyl)iron complex (13.51) using zinc dust or an electrochemical technique gave a mixture of two regioisomers (13.52; R^1 = H, R^2 = CO_2Me; R^1 = CO_2Me, R^2 = H) each of which consisted of two diastereomers. Electrochemical evidence was obtained for a free radical mechanism [259]. The (η-cyclohexadienyl)iron cation (13.53; R = H, OMe) was attacked by 4-chloroaniline in an equilibrium process with direct addition of the nucleophile to the dienyl ligand. Similar results were obtained for tricarbonyl(η-cycloheptadienylium)iron and the observed rate sequence for the three cations was: (η-C_6H_7) > (η-2-$MeOC_6H_6$) > (η-C_7H_9) [260].

The tricarbonyl(η^5-cyclohexadienyl)iron cation (13.54) underwent regioselective alkylation by (-)-1-phenylethylamine to form diastereomeric adducts (13.55; a, b) which were separated and converted back to (+)-(13.54) and (-)-(13.54) by trifluoroacetic acid. The resolved complex (13.54) had a planar chiral element which conferred stereochemical properties that prevented racemization when it was used in the synthesis of organic



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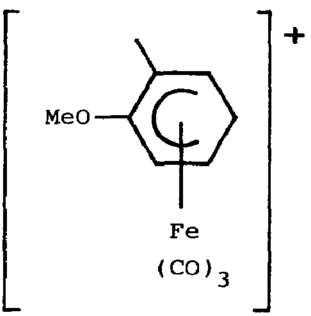
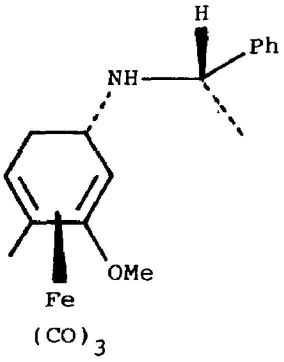


13.54

enantiomers. Similar reactions between the complex (13.54) and phosphoramide derivatives of carboxylic acid esters were examined [261].

Substitution of carbonyl by (+)-(neomenthyl)PPh_2 in the (η-tropone)iron and (η-isoprene)iron complexes (13.56 and 13.57; L = CO) gave diastereomeric products [13.56 and 13.57; L = (+)-(neomenthyl)PPh_2] that were separated by fractional crystallization. The absolute configuration of the complex [13.57; L = (+)-(neomenthyl)PPh_2] was determined by X-ray crystallography [262]. Pearson and O'Brien have described the



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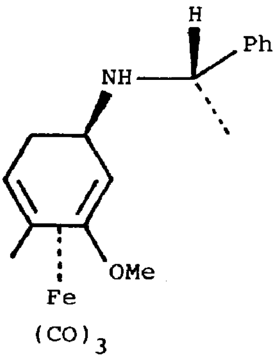
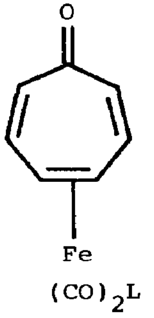


13.55b



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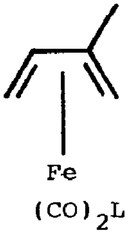


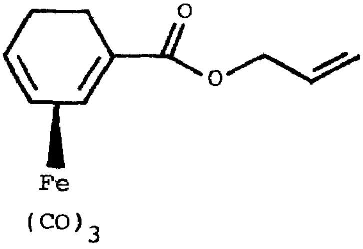
13.57

reactions of tin enolates with tricarbonyl(η-cyclohexadienylium)-iron cations to effect C-C bond formation in systems where lithium enolates and silyl enol ethers were useless. This new carbon-carbon bond forming reaction was used in a short diastereoselective synthesis of (±)-trichodiene [263].

Heating the allylic ester substituted diene-tricarbonyliron complex (13.58) gave the spirolactone (13.59) by way of intramolecular coupling of the pendant double bond with the diene group. An X-ray crystallographic structure determination on the product suggested that the mechanism involved coordination of the pendant double bond to iron. The allylic amide (13.60) underwent cyclization in the same way to give the spirolactam (13.61) [264].

Chloroformates, ClCO$_2$R, combined with (η-cycloheptatrienyl)-tricarbonylferrate(-1) (13.62) to give the corresponding 5- or 6-substituted ester complexes (13.63; R = Me, Et, Bu) together with the binuclear complex (13.64). Photochemical reaction of isomeric carbethoxycycloheptatrienes, principally the 7-substituted isomer, with pentacarbonyliron, gave the 5- or 6-substituted complexes (13.63; R = Et) but not the 7-substituted product. The reaction proceeded by way of deprotonation of a neutral (1-4-η-cycloheptatriene)iron complex with an anionic (η^3-cycloheptatrienyl)iron species followed by electrophilic attack [265].

The addition of P(OMe)$_3$ to the η-cycloheptadienyl complex (13.65) gave the phosphonate (13.66). The acyclic η-hexadienyl



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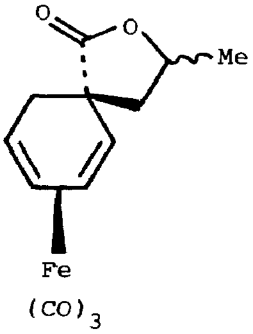

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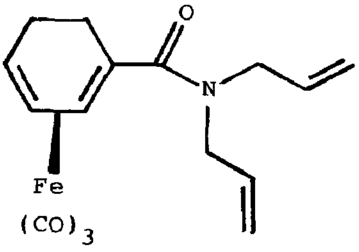

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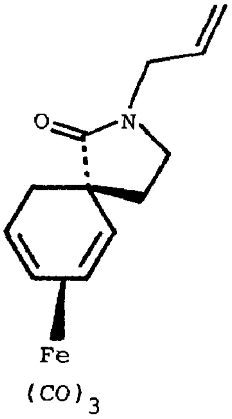

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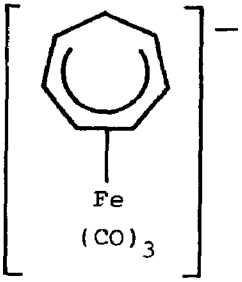

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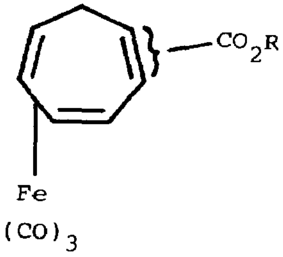

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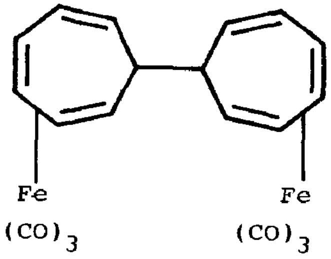
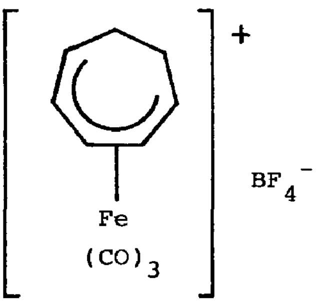


13.64

salt (13.67) produced the regioisomeric phosphonium salts {13.68; R^1 = Me, R^2 = $[CH_2P(OEt)_3]^+BF_4^-$ and R^1 = $[MeCHP(OEt)_3]^+BF_4^-$} on treatment with $P(OEt)_3$ [266].

Treatment of tricarbonyl(η-cycloheptatriene)iron with o-tolyllithium followed by Et_3OBF_4, in dichloromethane or in aqueous solution, produced the dicarbonyliron complexes (13.69 and 13.70) respectively. The structures of these complexes were determined by X-ray analysis [267]. The effect of pressure and solvent was investigated on the reaction of tricarbonyl-(η-cycloheptatrienone)iron with tetracyanoethene. The results supported a concerted cycloaddition mechanism for this reaction [268].



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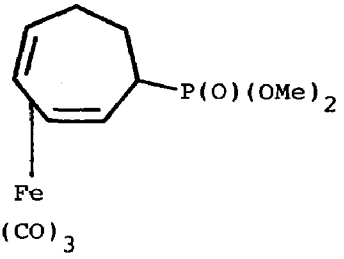

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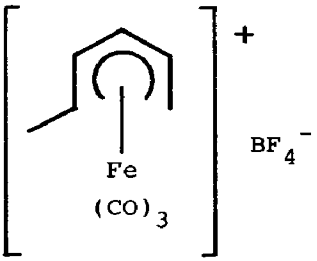

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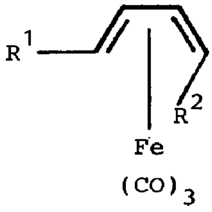

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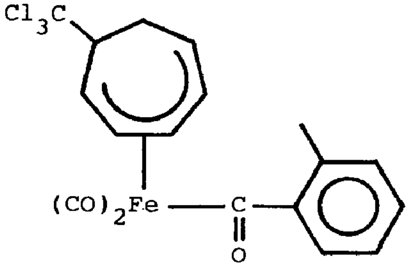

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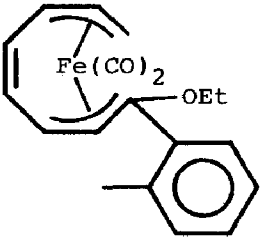
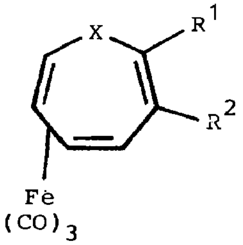


13.70

The rates of addition of tetracyanoethene to the azepines (13.71; X = CH_2, R^1 = R^2 = H; X = NCO_2Et, R^1 = R^2 = H; X = NH, R^1 = H, R^2 = COMe, X = NCO_2Et, R^1 = H, R^2 = COMe; X = CH_2, R^1 = CN, R^2 = H; X = CO, R^1 = R^2 = H) to give the corresponding 1:1 adducts (13.72) have been measured. The rate of addition of tetracyanoethene to 1-cyanocycloheptatriene was also measured. The results indicated a Diels-Alder type reaction and a concerted mechanism [269].

Tricarbonyl(η-cycloheptatriene)iron has been deprotonated and the resulting anion combined with acyl chlorides to give the exo-derivatives (13.73). Treatment with base caused isomerization to give C-5 acyl derivatives. The acyl complexes (13.73)



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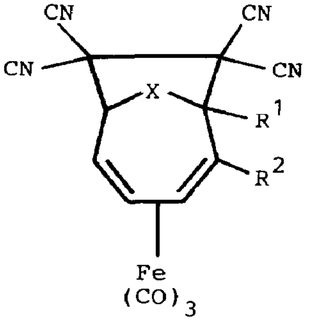

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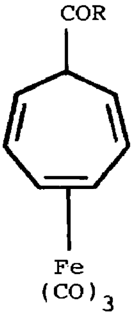
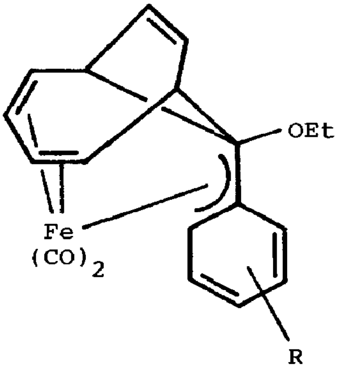


13.73

underwent deprotonation to give anions that were attacked at O by acyl chlorides and at C with methyl iodide [270].

Cis-keto-hydroazulenediiron complexes have been formed by the 3 + 2 cycloaddition of (η-oxotropylium)iron tricarbonyl cations to (η-allyl)(η-cyclopentadienyl)iron dicarbonyl. The effect of substituents on the reaction was examined [271]. Equimolar quantities of tricarbonyl(η^4-cyclooctatetraene)iron and an aryllithium ArLi, where Ar = Ph, *o*, *p* or *m*-MeC_6H_4, *p*-$CF_3C_6H_4$, C_6Cl_5, were mixed. The acylmetallate compounds produced were alkylated with Et_3OBF_4 to give complexes of the type (13.74) and/or (13.75) [272]. In a related paper Chen and



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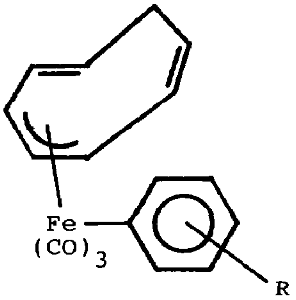

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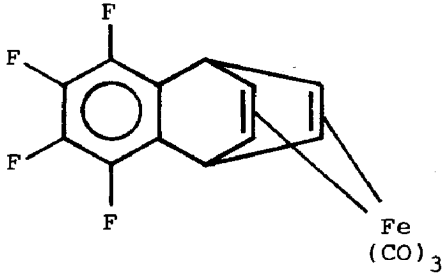

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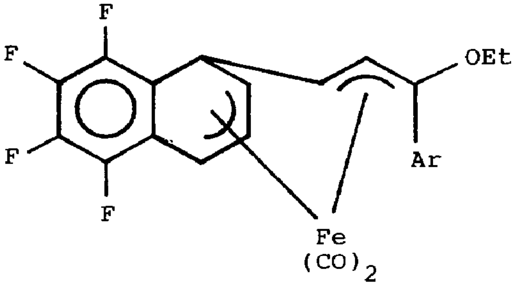
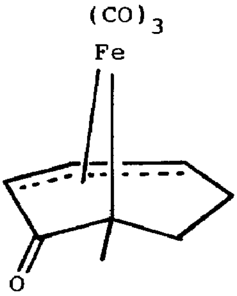


13.77

co-workers reported the reaction of the tricarbonyliron complex (13.76) with aryllithiums followed by Et_3OBF_4 to give the corresponding products (13.77; Ar = Ph, o, m and p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4) formed by ring opening. The structure of the complex (13.77; Ar = p-$CH_3C_6H_4$) was determined by X-ray analysis. The six membered ring containing the π-allyl ligand adopted a twisted boat conformation [273].

Ring enlargement of tricarbonyl(η-1-methyl-1,3-cyclohexadiene)iron with aluminium(III) chloride and carbon monoxide gave the (η-oxocycloheptenediyl)iron complex (13.78). Carbonylation of this species followed by decomplexation gave the bicyclooctene dione (13.79) [274].



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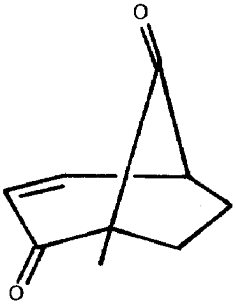


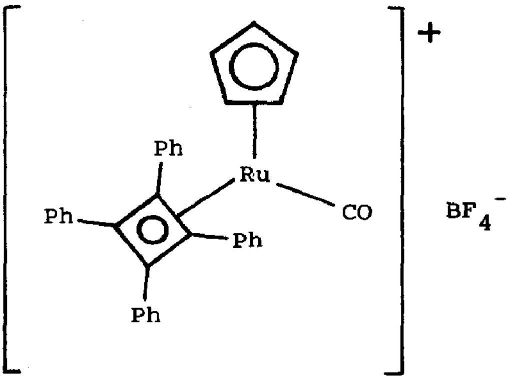
13.79

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

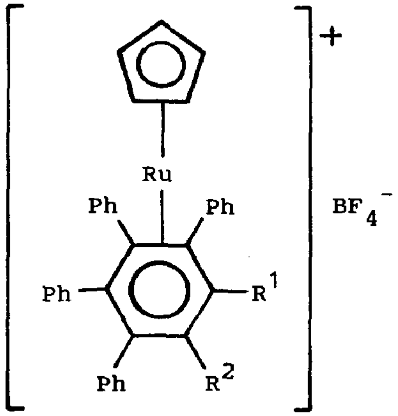
The cation $[(\eta\text{-mesitylene})_2Fe.THF]^{2+}$ has been treated with chromium(II) chloride to give the binuclear complex $(\eta\text{-mesitylene})_2CrFeCl_2(THF)_2$ [275]. The cationic complexes $[(\eta\text{-}C_5R_5)(\eta\text{-polyarene})Fe]^+$, where R = H, Me and polyarene = biphenyl, naphthalene, phenanthrene, triphenylene, pyrene, have been prepared in the melt at 120-140°. Under these conditions hydrogenation of the polyarene group was avoided. Measurement of the first reduction potentials by cyclic voltammetry demonstrated stabilization of the Fe(I) state by permethylation of the cyclopentadienyl ring [276].

The $(\eta^6$-arene)ferracarborane complexes closo-3-$(\eta^6\text{-}CH_3C_6H_5)$-3,1,2-$FeC_2B_9H_{11}$ and closo-3-$[\eta^6\text{-}1,4\text{-}(CH_3)_2C_6H_4]$-3,1,2-$FeC_2B_9H_{11}$ have been prepared directly by the reaction of K[nido-7,8-$C_2B_9H_{12}$], iron(III) chloride and triethylamine in either toluene or p-xylene. The structures of the complexes were determined by X-ray diffraction [277]. Ultraviolet irradiation of the ruthenium complex (14.1) in the presence of the alkynes $R^1C_2R^2$, where $R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = Me$; $R^1 = R^2 = Me$; $R^1 = R^2 = CO_2Me$, produced the corresponding η^6-arene complexes (14.2) [278].

The reaction of bis(η-ethene)(η-toluene)iron or (η-1-methylnaphthalene)(η-toluene)iron with t-butylphosphaacetylene produced the iron complexes (14.3, 14.4 and 14.5) [279]. The η-phenanthrene and η-9,10-dihydrophenanthrene complexes (14.6 and 14.7) have been prepared and studied electrochemically. The results indicated significant interaction between the two ruthenium atoms in the



14.1



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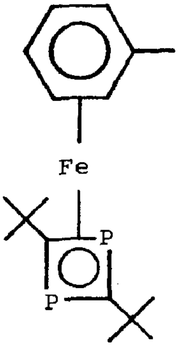

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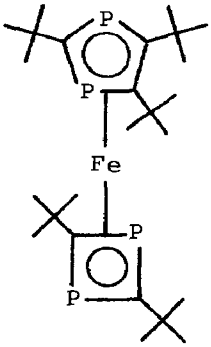

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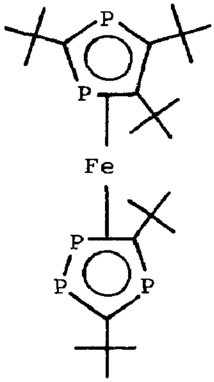
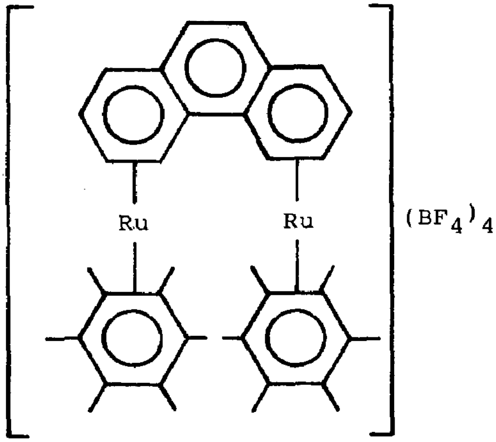


14.5

corresponding mixed valence complexes [280]. The phenanthrene complex (14.8) and the corresponding 9,10-dihydrophenanthrene complex have been prepared by the reaction of $(\eta\text{-C}_6\text{Me}_6)\text{Ru}(\text{BF}_4)_2$ with phenanthrene and 9,10-dihydrophenanthrene respectively [281].

The ligand transfer reactions of the substituted fulvene (14.9) with tris(acetonitrile)(η^5-cyclopentadienyl)ruthenium(II) hexafluorophosphate or (η^5-cyclopentadienyl)(η^6-*p*-xylene)iron(II) hexafluorophosphate produced the substituted ruthenocenes (14.10 and 14.11; M = Ru) and substituted ferrocenes (14.10 and 14.11;



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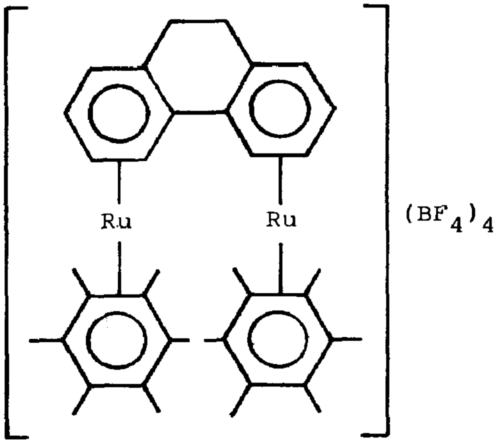

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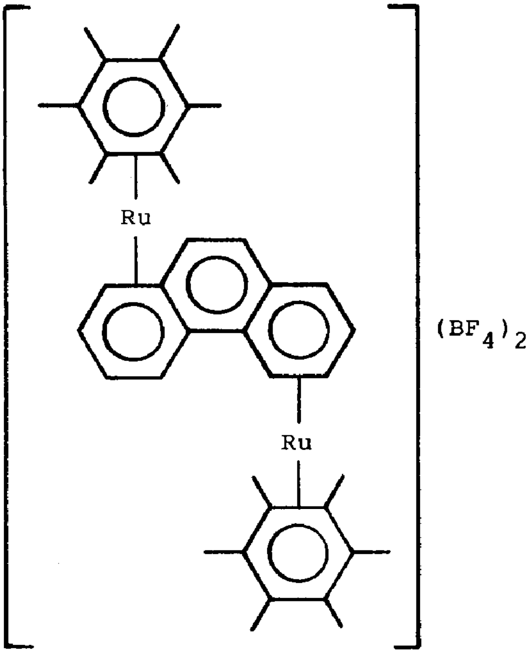

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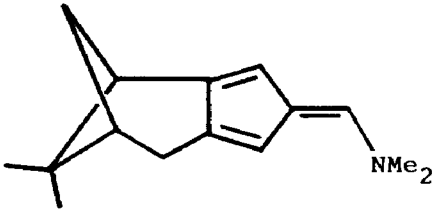

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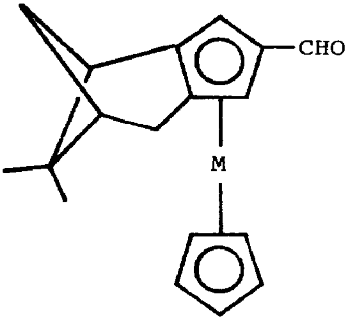

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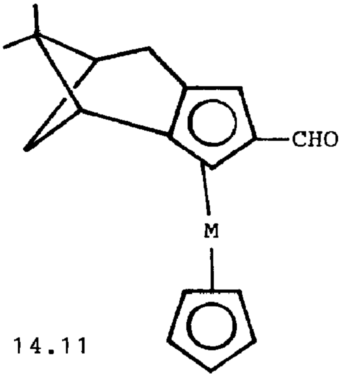
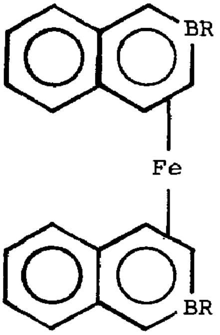


14.11

M = Fe) respectively as isomeric pairs. The aldehydes (14.10 and 14.11; M = Ru, Fe) were reduced with sodium borohydride to give the corresponding alcohols [282].

The (η-boratanaphthalene)iron complexes [14.12; R = Ph, $(Me_2CH)_2N$] have been obtained from the corresponding lithium boratanaphthalene species [283]. ^{13}C NMR spectroscopy has been used to investigate transition metal complexation effects in a series of (η^6-cyclophane)(η^6-benzene)ruthenium(II) bis(tetrafluoroborate) complexes, where the cyclophane moiety was [8]-[15]-paracyclophane, [2.2]paracyclophane or 5,13-dimethyl-[2.2]metacyclophane. The complexation shifts for the cyclophane-ring carbons were dependent on the degree and direction of ring



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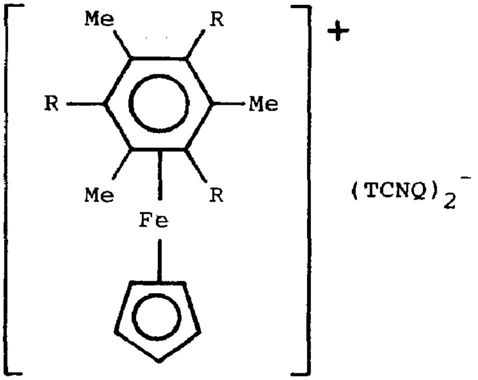
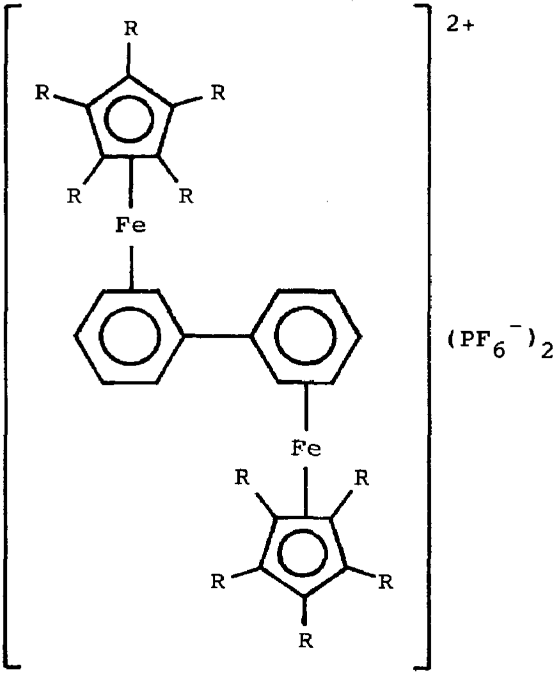


14.13

bending [284]. Several (η^6-biphenyl)(η^5-cyclopentadienyl)iron hexafluorophosphates have been prepared, in each case complexation involved the unsubstituted phenyl ring. Hammett resonance parameters σ_R have been determined by ^{13}C NMR spectroscopy and show that the $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6H_5)]^+$ group is an electron withdrawing substituent comparable in strength to the cyano group. ^{57}Fe Moessbauer results support the strong electron acceptor properties of the $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6H_5)]^+$ group [285].

The (η-arene)iron salts (14.13; R = H, Me) have been prepared and characterized by IR spectroscopy and dc conductivity. Both salts showed quasi-semiconducting behaviour with temperature dependent activation energy [286]. Astruc and co-workers have examined the electron transfer properties of the (η-biphenyl)-iron complexes (14.14; R = H, Me). These complexes could be reduced either in four single-electron steps or in a single two-electron step depending on the ligand present. The iron complex (14.15) containing the novel η-bicyclohexadienylidene ligand was characterised by X-ray analysis [287].

The crystal and molecular structure of the p-tosylate of the dication (14.16) has been determined by X-ray crystallography [288]. A large number of (η-arene)(η-cyclopentadienyl)iron cations have been examined by ^{57}Fe Moessbauer spectroscopy. Hammett plots of quadrupole splitting for arene ring substituents were sigmoidal suggesting limits to electron withdrawal and donation. The data were best fitted by use of σ_R^- constants. Comparisons with the corresponding ferrocenes indicated enhanced



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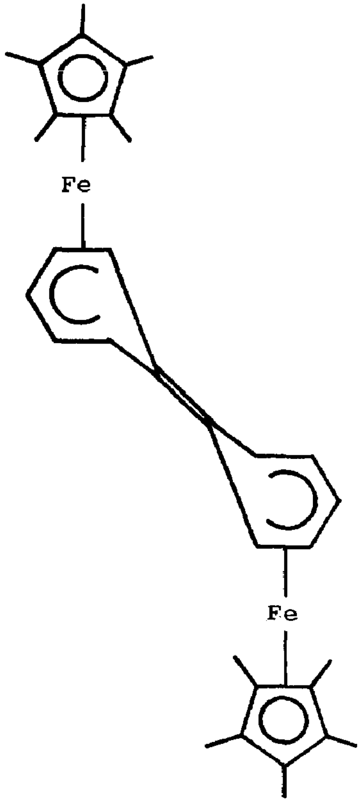

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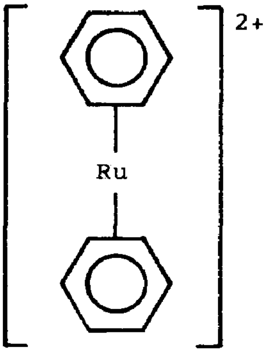


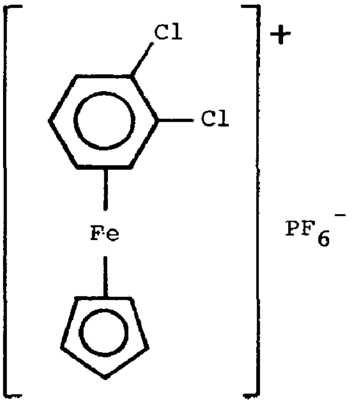
14.16

substituent effects in the (η-arene)(η-cyclopentadienyl)iron cations due to the positive charge on iron. Moessbauer parameters were presented for polysubstituted complexes, polycyclic species and phosphacyclopentadienyl complexes [289].

The chloro and nitro groups were displaced from (η-chloroarene)- and (η-nitroarene)-(η-cyclopentadienyl)iron cations by nucleophiles such as piperidine, piperazine and the anions derived from acetylacetone, diethyl malonate and ethyl acetoacetate. Pyrolytic decomplexation of the product gave synthetically useful substituted arenes [290].

Reaction of the salt (14.17) with nitroethane or nitromethane in the presence of excess potassium carbonate produced the corresponding nitroalkane substituted derivatives (14.18; R = Me, H) in good yields [291]. The carbanion formed from nitroethane displaced chloride from the (η-arene)iron cation (14.19; X = Cl) to give the (η-acetophenone)iron cation (14.19; X = COMe) [292].

The keto arene complex cations (14.20; R = Me, OEt, OH) have been obtained by deacetylation or decomplexation of



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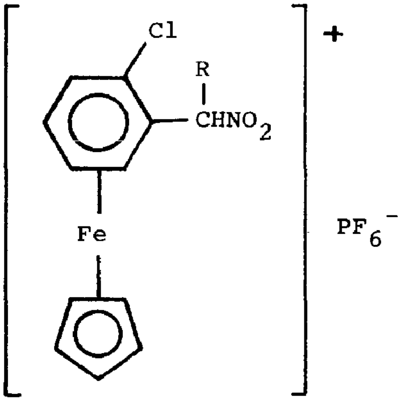

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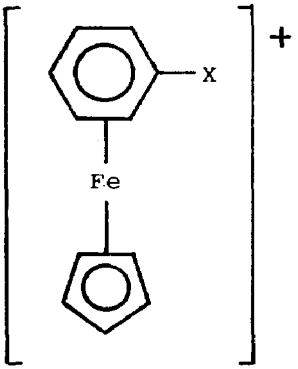

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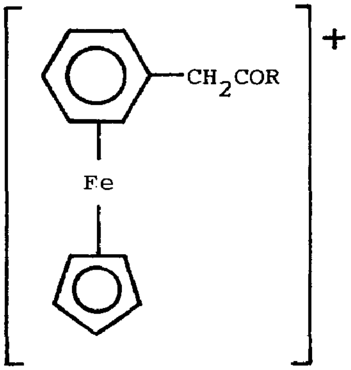
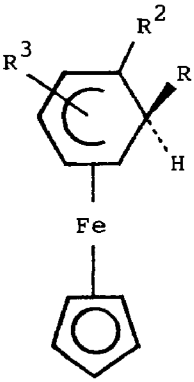


14.20

β-dicarbonyl complexes [293]. Phase transitions in the salt $[(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)Fe]^+(PF_6)^-$ have been studied by heat capacity measurements. Four phase transitions and two glass transitions were detected and the possible origins of the phase transitions were discussed [294].

The addition of hydride ion to the η-cyclopentadienyliron complexes [14.19; X = NMe_2, NO_2, PhO, CH_3O, *p*-$CH_3C_6H_4S$, $PhCH_2$, $(CH_3)_3C$, CH_3, CH_3CH_2, Ph, Cl, CO_2CH_3, PhCO, CN, *p*-$CH_3C_6H_4CH_2$] has been investigated by high resolution ^1H NMR spectroscopy. When X = NMe_2 only *m*- and *p*-hydride addition occurred and when X = NO_2 only *o*-addition occurred. With all the other substituents studied, *o*-, *m*- and *p*-hydride addition products were obtained together with minor amounts of *ipso*-products [295].

Oxidative demetallation of the η-cyclohexadienyl derivatives (14.21; R^1 = CH_2COCH_3, R^2,R^3 = 1,4-Cl_2; 1,2-Cl_2; 1-CN,H; 1-NO_2, 4-Me; R^1 = CD_2COCD_3, R^2,R^3 = 1-COPh,H; R^1 = CN, R^2,R^3 = 1-NO_2,H; 1-COPh, H) to give the corresponding aromatic compounds (14.22) in good yields has been effected with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone or 3,4,5,6-tetrachloro-1,2-benzoquinone [296]. The salt $[Bu_4N]_2[C_6(CN)_6]$ combined with the cations $[(\eta\text{-arene})_2\text{-}M]^{2+}$, where arene = mesitylene and hexamethylbenzene and M = Fe, Ru, to give the linear chain complexes $[(\eta\text{-arene})_2M][C_6(CN)_6]$. X-ray crystallography confirmed that the complexes contained mixed stacks of alternating cations and anions. Strong charge transfer absorptions suggested a superionic donor-acceptor (DA) structure with essentially a $(D^{2-}A^{2+})$ ground state and a (D^-A^+) excited state [297].



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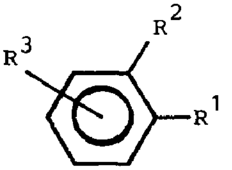
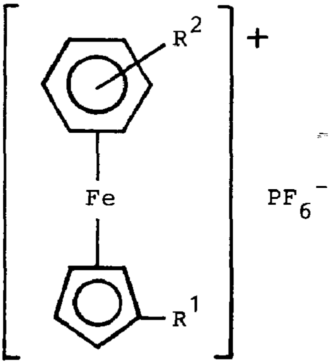


14.22

Treatment of the (η-arene)(η-cyclopentadienyl)iron cations (14.23; R^1 = COMe, COPh, $COCMe_3$, CO_2H, Me, CH_2NMe_2; R^2 = H, 1,3,5-Me_3) with phospholyl anions produced the corresponding 1'-substituted monophosphaferrocenes (14.24; R^3 = H, 3-Me, 3,4-Me_2, 2,3,4,5-Ph_4). Treatment of the (η-chlorobenzene)-(η-cyclopentadienyl)iron cation with the diphenylphospholyl cation produced the product of nucleophilic displacement (14.25) [298].

Organometallic conductors have been obtained by treatment of the cations [(η-arene)(η-cyclopentadienyl)iron]$^+$ and [(bis(η-arene)iron]$^{2+}$ with tetracyanoquinodimethane in neutral or anionic form [299]. Thermal isomerization of the complex (14.26)



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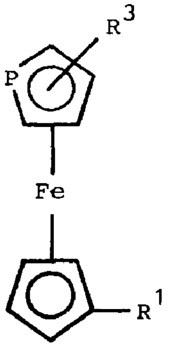

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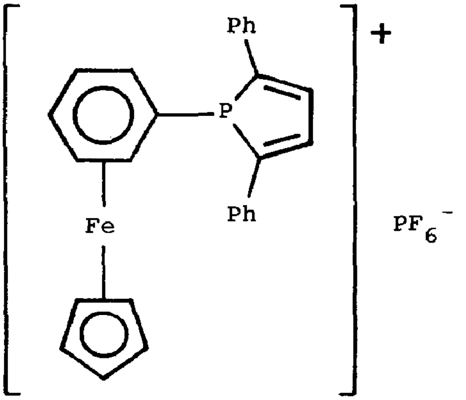

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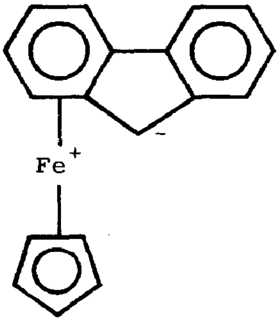

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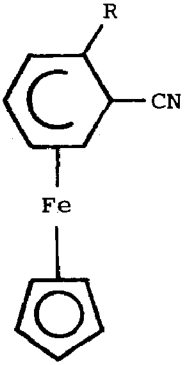

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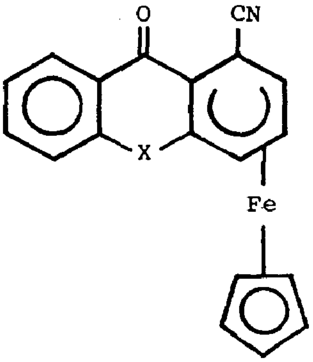
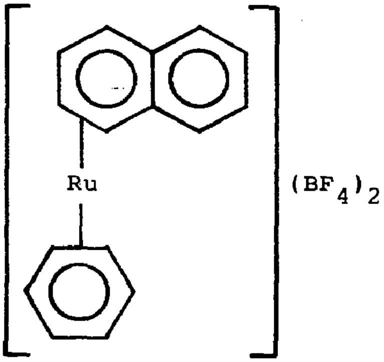


14.28

occurred on heating to 80° to give the η^5-isomer [300]. The cyanide ion attacked (η-arene)(η-cyclopentadienyl)iron cations bearing electron withdrawing substituents in the arene ring to give regiospecific ortho-addition to the arene group with the formation of (η-cyanocyclohexadienyl)iron complexes (14.27; R = COPh, NO_2, CO_2Me). In the same way η-anthraquinone, xanthone, thioxanthone and thioxanthone-10,10-dioxide complexes underwent addition solely at C-1, the position ortho to the keto substituent to give the products (14.28; X = CO, O, S, SO_2) respectively [301].

When the ruthenium salt (14.29) was heated with the substituted alkyl benzenes $Ph(CH_2)_nR$ [R = $CH=CH_2$, Br, OH, $Fe(CO)_2$-(η-C_5H_5); n = 1-3] in nitromethane the corresponding arene



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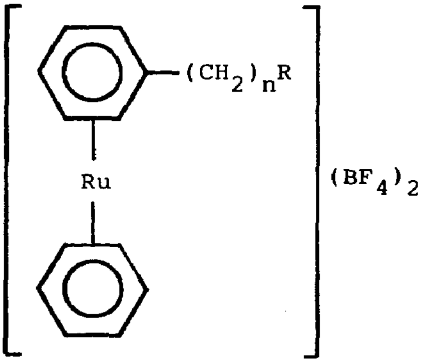
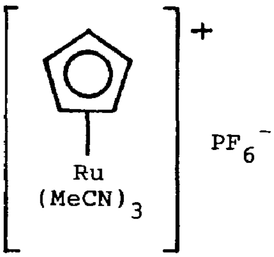
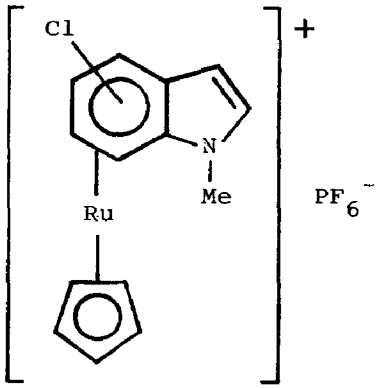


14.30

complexes (14.30) were formed [302]. Reaction of the ruthenium salt (14.31) with 4- or 5-chloroindole produced the corresponding η-chloroindole complex (14.32) in good yield. These complexes readily underwent nucleophilic displacement reactions with a range of oxygen, nitrogen, sulphur and carbon nucleophiles to give the corresponding 4- or 5-substituted indole complexes [303].



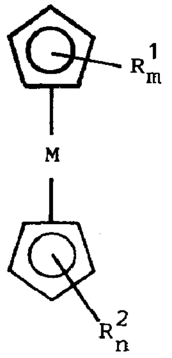
14.31



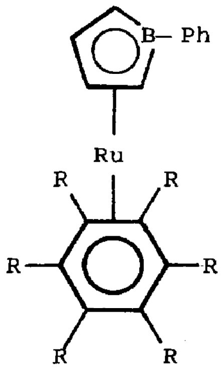
14.32

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

A series of radio-labelled ruthenocenes and osmocenes (15.1; M = labelled Ru, Os; R^1, R^2 = H, alkyl, CO_2Me; n,m = 1-4) has been prepared by reaction of the corresponding substituted ferrocene with either a ruthenium or osmium chloride [304].



15.1

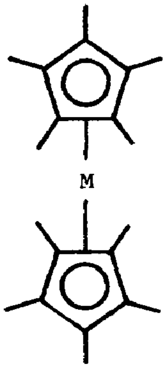


15.2

Dehydrogenation of borolenes in the presence of (η^6-arene)-ruthenium complexes gave the (η^5-borole)(η^6-benzene)ruthenium complexes (15.2; R = H, Me) [305].

Reaction of $[Fe(\eta-C_5H_5)(\eta-C_6H_6)]PF_6$ or $[Ru(\eta-C_5R_5)-(CH_3CN)_3]PF_6$ (R = H, Me) with the decamethylmetallocenes (15.3; M = Fe, Ru, Os) produced the first 30-electron triple-decker complexes of the iron group metals (15.4; M^1 = Fe, R = H, M^2 = Fe, Ru, Os; M^1 = Ru, R = H, Me, M^2 = Ru, Os). The structure was confirmed by NMR spectroscopy together with an X-ray diffraction study of the diruthenium complex (15.4; M^1 = M^2 = Ru, R = Me) [306].

The cationic metallocyclophanes (15.5 and 15.6; M = Co, Rh, Ir) have been prepared by ligand exchange in trifluoroacetic



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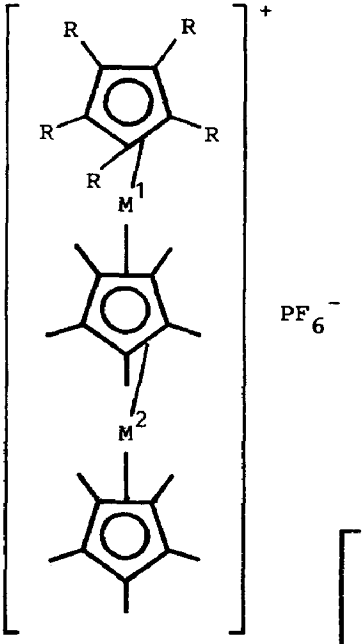

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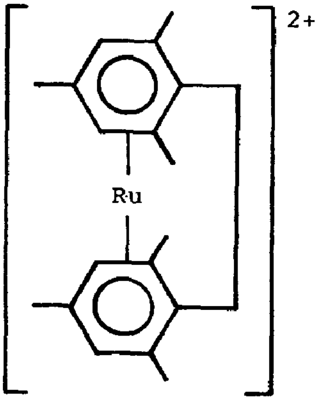

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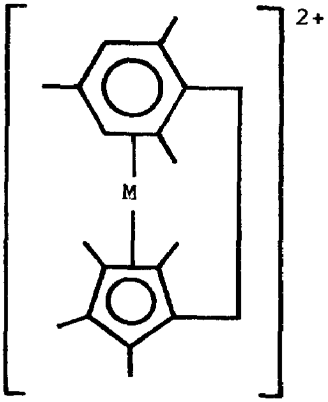

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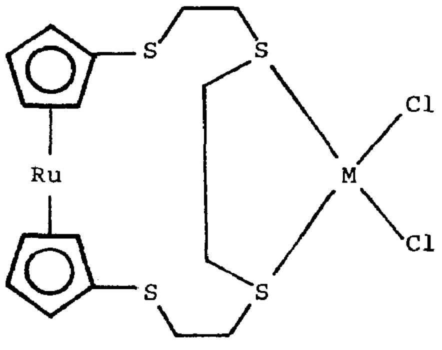

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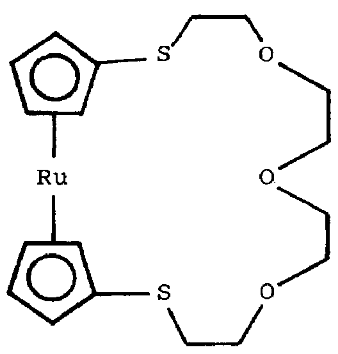
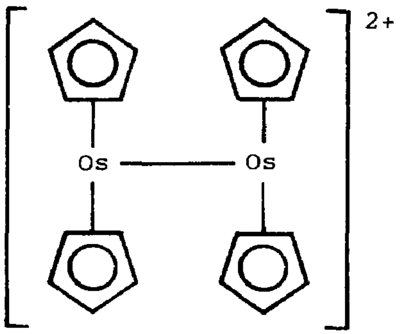


15.8

acid [307]. Reaction of 1,1'-bis(2-chloroethylthio)ruthenocene with disodium alkanedithiolates produced the corresponding polythia[n]-1,1'-ruthenocenophanes. These ruthenocenophanes readily formed 1:1 complexes with Pt(II) and Pd(II) chlorides. X-ray analysis of the complexes (15.7; M = Pt, Pd) showed that these metals adopted a slightly distorted cis square-planar configuration [308].

The structure of the ruthenocenophane (15.8) and its palladium(II) chloride complex have been determined by X-ray analysis. In the complex the palladium atom was bound to the sulphur atoms of the ligand [309]. Oxidation of osmocene with cerium(IV) gave the metal-metal-bonded osmocenium dimer (15.9)



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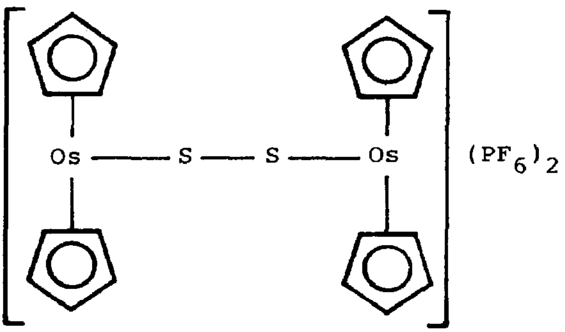


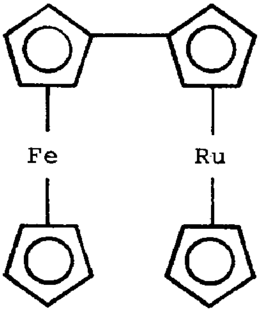
15.10

which was characterized by X-ray crystallography as the hexafluorophosphate salt. This dication (15.9) underwent disproportionation, substitution and radical reactions to give several Os(IV) metallocenes [310].

The reaction of osmocenium hexafluorophosphate with elemental sulphur produced the disulphur bridged complex (15.10). This complex was fully characterised including an X-ray diffraction structure determination. The results indicated two osmium(IV) metallocene groups linked by a disulphide (S_2^{2-}) bridge [311]. Biruthenocenyl and ferrocenylruthenocene (15.11) each combined with iodine to give coloured diamagnetic adducts. Direct interaction of ruthenium and iodine in these adducts was indicated by ^{1}H NMR and ^{57}Fe Moessbauer spectroscopy [312].

The stable mercury(II) chloride adducts of ferrocenylruthenocene (15.11) and biferrocene have been investigated via Moessbauer spectroscopy. The results indicated the presence of direct interaction between ruthenium and iron in ferrocenylruthenocene and the two iron atoms in biferrocene with the mercury [313]. Biruthenocene and ferrocenylruthenocene (15.11) formed adducts with tin(IV) chloride which were investigated via ^{119}Sn Moessbauer spectroscopy. Covalently bonded tin(IV) species were present and the results suggested bond formation between the ruthenium and tin atoms [314].

^{119}Sn Moessbauer spectroscopy has been used to study tin(IV) halide adducts with ruthenocene and [2]ferrocenophanes. The spectra indicated the presence of a Ru-Sn bond in the $SnCl_4$



15.11

adduct of ruthenocene [315]. The rates of halogen mediated electron transfer of the type:

$$[M(\eta\text{-}C_5H_5)_2X]^+ + M(\eta\text{-}C_5H_5)_2 = M(\eta\text{-}C_5H_5)_2 + [M(\eta\text{-}C_5H_5)_2X]^+$$

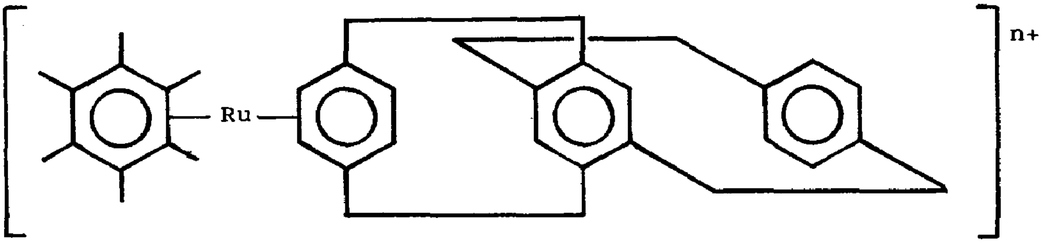
where M = Ru or Os and X = Cl, Br or I,
have been studied by NMR line broadening techniques. The rates of self-exchange increased along the series Cl > Br > I and was more rapid for ruthenocene than for osmocene [316].

Benzoyl-, 1,1'-dibenzoyl-, 1,1'-dimethyl- and 1,1'-diphenylruthenocene have been prepared and used to formulate Ru/ZSM-5 catalysts. ESCA and IR spectroscopic studies of pyridine adsorbed on the catalysts showed differences between those formulated with ruthenocene from those using substituted ruthenocenes. These differences were in surface segregation of ruthenium and in the cationic exchange of ruthenium with Broensted acid sites of the zeolite [317].

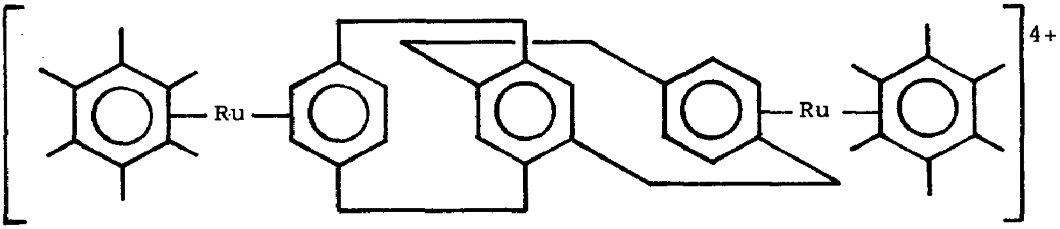
Structural phase transitions and molecular dynamics in the cyclopentadienyl rings of ruthenocene, ferrocene and azaferrocene have been studied by ^1H NMR spectroscopy. A second-order phase transition was observed for ruthenocene at 392 K. The cyclopentadienyl rings in each of the three metallocenes underwent in-plane C_5 or pseudo-C_5 reorientations with different activation energies. Phase transition mechanisms and the properties of each phase were discussed in terms of ring dynamics [318].

The triple-layered paracyclophane ruthenium complexes (15.12; n = 2 and 15.13) have been prepared and examined by cyclic voltammetry. The dication (15.12; n = 2) was reduced by a two-electron reversible wave to the neutral complex (15.12; n = 0) while the tetracation (15.13) was reduced in two overlapping, reversible two-electron waves. The extent of interaction between the two ruthenium centres in the mixed-valence ion (15.13) was small [319].

The reaction of 1,1'-dilithioruthenocene with selenium powder produced the ruthenocenophane (15.14). The energy barriers of the bridge inversion of the ruthenocenophane (15.14) and the corresponding sulphur compound were determined [320]. Reaction of the ruthenocenophane (15.15) with $Ni(PPh_3)_4$ produced the Ru-Ni metallocycle (15.16). Treatment of the sodium salts (15.17; M = Fe, Ru) with $Pd(PPh_3)_2Cl_2$ gave the corresponding metalloceno-



15.12

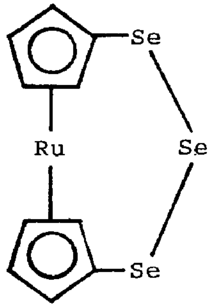


15.13

phanes (15.18). The structure of the metallocycle(15.16) was determined by X-ray analysis. ^{1}H MNR spectra suggested that Ru-Ni, Fe-Pd and Ru-Pd dative bonding occurred in the metallocenophanes (15.16 and 15.18; M = Fe, Ru) [321].

Labelled ruthenocenylamines have been prepared and used as radiodiagnostic agents. Thus ferrocenylisopropylamine has been heated with $^{103}RuCl_3$ and HCl in a sealed ampoule to give the labelled ruthenocene (15.19). This product was administered to rats and mice and showed rapid enrichment in the brain, heart, lungs, liver and kidney [322]. Ruthenocene labelled with ^{103}Ru underwent radioactive decay to give [^{103m}Rh]rhodocenium ions and the two were separated by extraction of a lipophilic solution of the ruthenocene with water. Rhodocenium amphetamine was taken up by the liver and kidneys more efficiently than ruthenocene amphetamine [323]

Reduction of the (η^7-tropylium)ruthenium dication (15.20) with zinc gave the (η^6-cycloheptatriene)ruthenium product (15.21). Electrochemical oxidation of this complex (15.21) indicated a ligand-centred reaction to form a tropylium cation while the dication (15.20) underwent metal centred reduction [324].



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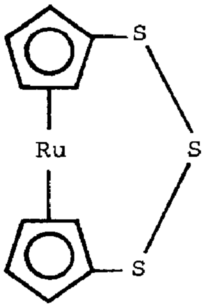

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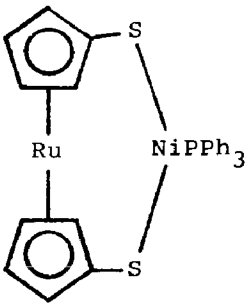

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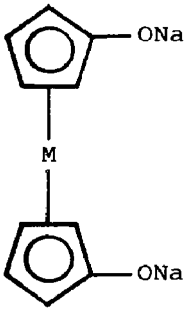

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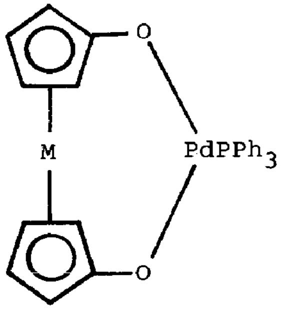

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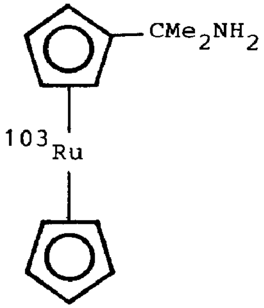

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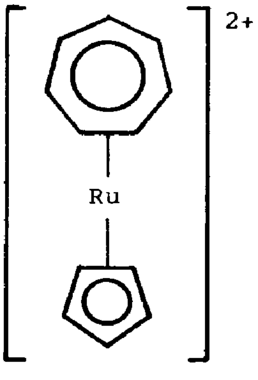

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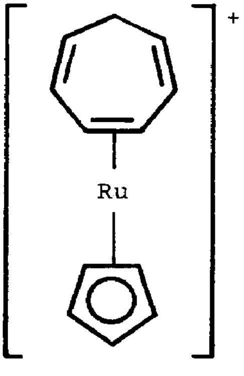


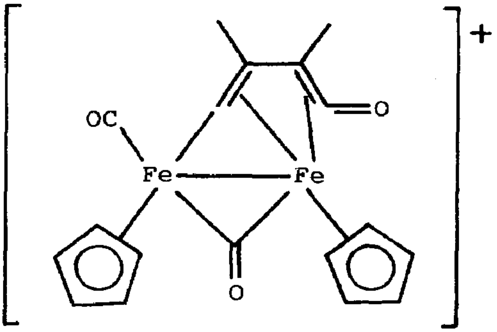
15.21

The organoruthenium and organoosmium species, $[(\eta\text{-}C_6Me_6)\text{-}MCl_2]_2$, where M = Ru, Os, have been used as organometallaborane synthons [325]. Mixed valence cations, $[(\eta^6\text{-arene})_2(\eta^{10}\text{-cyclophane})\text{ruthenium}]^{2+}$, have been prepared and evaluated as model monomers for 1-dimensional delocalized polymers of $[2_n]$cyclophane-transition metal complexes. Three-decker $[2_n]$-cyclophanes underwent simultaneous π-electron interaction, a feature which would be useful in 2-dimensional, network polymers [326].

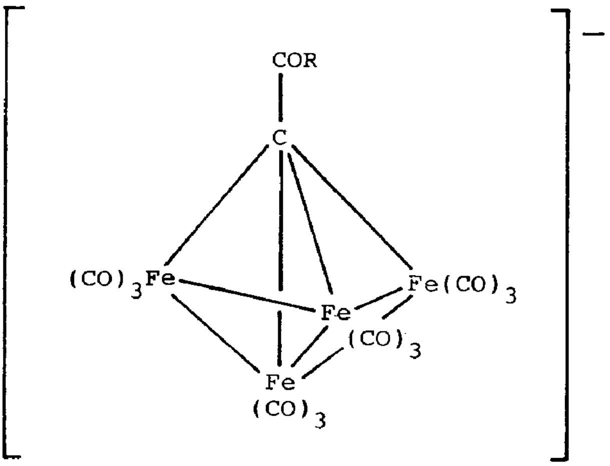
16. Iron-, Ruthenium- and Osmium Cluster Compounds

The cationic bridging methylidyne complex, $[(\eta\text{-}C_5H_5)COFe]_2\text{-}(\mu\text{-}CO)(\mu\text{-}CH)^+$, combined with 2-butyne to give the $(\eta^4$-butadiene)-diiron complex (16.1) which was characterized by X-ray crystallography. Similar reactions were carried out with phenylacetylene and t-butylacetylene [327]. The structures of the cluster complexes (16.2; R = OMe, Me) have been determined by X-ray analysis. The complexes had an open butterfly core with the organic groups situated in the plane defined by the two backbone iron atoms and the methylidyne carbon atom [328].

Several chiral organotransition metal complexes $PhC{\equiv}CCHMe_2\text{-}MM^1Fe(CO)_3$ where M^1 = $Ni(\eta\text{-}C_5H_5)$, $Co(CO)_3$, $MoCO(\eta\text{-}C_5H_5)$ have been shown by X-ray crystallography to adopt a square pyramidal geometry. Fluxional behaviour in these complexes has been characterized in terms of alkyne rotation relative to the triangle of metals [329].



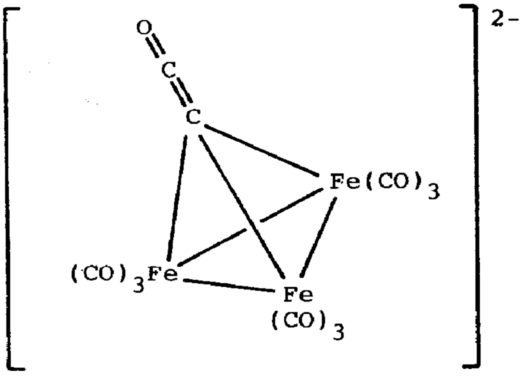
16.1



16.2

The structure and reactivity of some group VIII methylidyne cluster complexes has been examined [330]. Alkyne ligands in cationic molybdenum complexes have been converted to vinyl, carbyne and vinylidene ligands. Thus the cation $[Mo(\eta^2\text{-}PhC_2Br)\text{-}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$ with $[BHBu^s_3]^-$ gave the vinylidene complex $[Mo(C{=}CHPh)Br\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ together with the related carbyne complex [331].

The triosmium cluster complex $[Os_3(\mu_3,\eta^2\text{-}Et_2C_4)(\mu\text{-}CO)(CO)_9]$ containing the Et-C≡C-C≡C-Et moiety underwent decarbonylation at 120°C to give the hydrido complex $[Os_3H(\mu_3,\sigma,\eta^2,\eta^2\text{-}EtC{\equiv}C\text{-}C{=}C{=}CHMe)(CO)_9]$ [332]. When the ketenylidene cluster (16.3) was treated with acetyl chloride and trifluoromethanesulphonate the corresponding anionic acetylide clusters (16.4; R = $COCH_3$, C_2H_5) were formed. The reaction of the dianion (16.3) with trifluoromethane sulphonate generated the acetylide cluster (16.4; R = CH_3) and the alkylidyne (16.5) [333]. In related work Shriver and co-workers described the alkylations of a series of ruthenium ketenylidenes (16.6, 16,7 and 16.8) [334]. The acylation of $[Os_3(CO)_{11}]^{2-}$ with acetyl chloride followed by reductive cleavage with Na/Ph_2CO produced the osmium ketenylidene (16.9). The reactions of the CCO ligand in the complex (16.9) were dependent on the presence or absence of carbon monoxide. In the presence of carbon monoxide attack by $CH_3OSO_2CF_3$ generated the acetylene cluster (16.10) and in the absence of carbon



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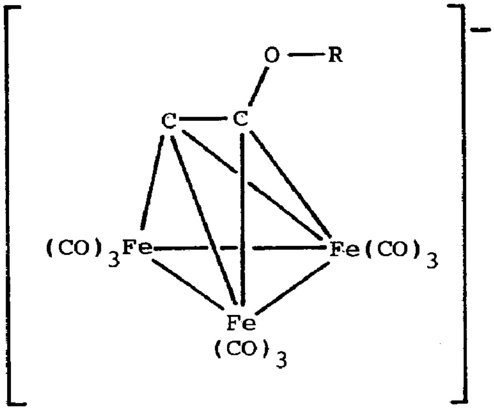

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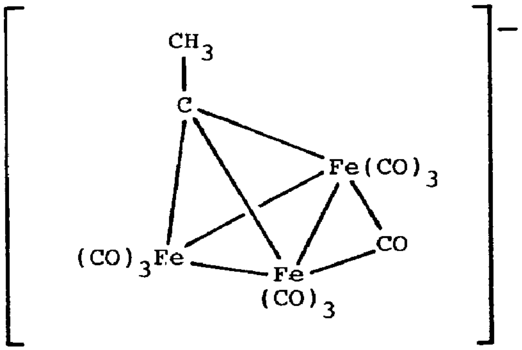

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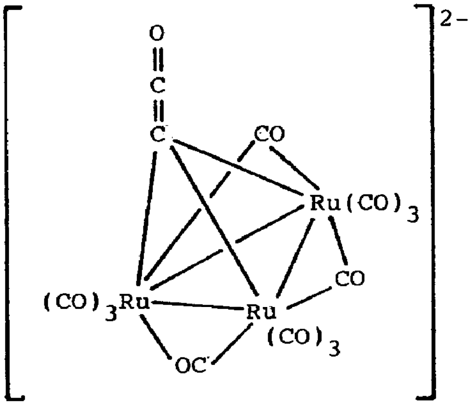

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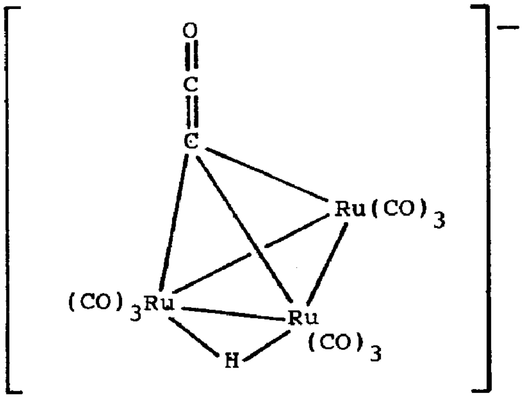

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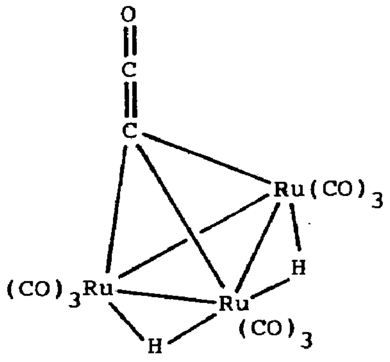

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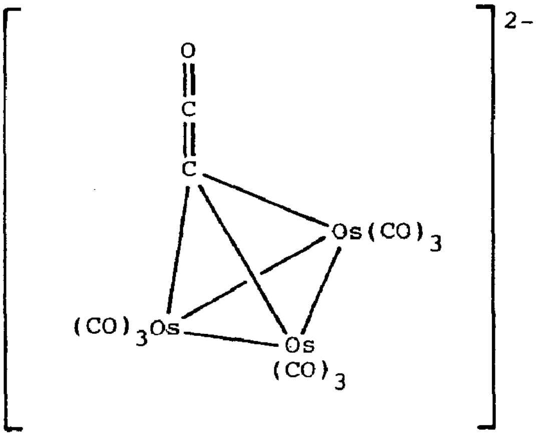

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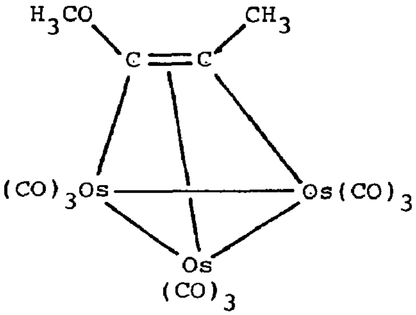

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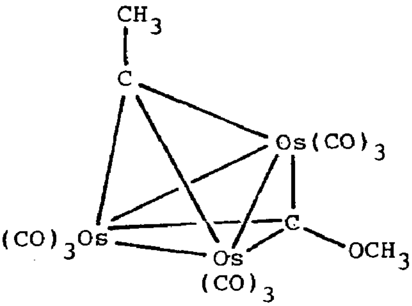

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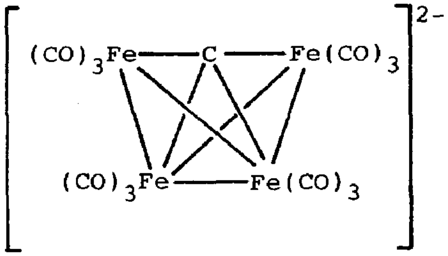

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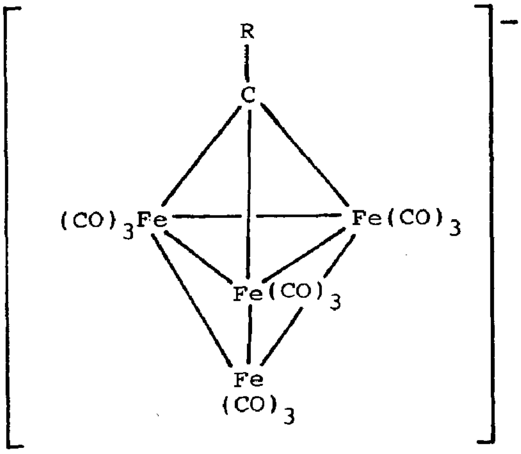

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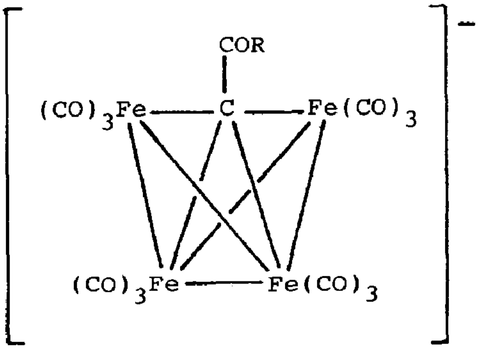


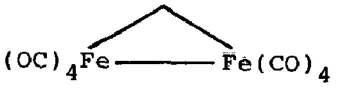
16.14

monoxide the alkylidene cluster (16.11) was the major product [335]. The reactions of the carbide cluster (16.12) with alkylating agents have been investigated. Direct electrophilic attack occurred with $EtSO_3CF_3$ and CF_3I to give the tetrahedral clusters (16.13; R = Et, CF_3) respectively. Reaction of methyl iodide or benzyl bromide occurred with carbon monoxide uptake to give the corresponding monoanionic cluster (16.14; R = Me, CH_2Ph) which had a butterfly-shaped framework [336].

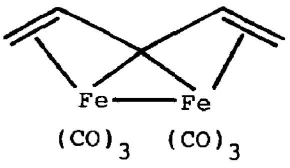
Acetylene underwent double insertion into the μ-methylene-iron complex (16.15) to give the μ(divinyl)carbene complex (16.16) which was characterized by X-ray crystallography [337]. The bridging thiolate ligand in the complex $Li[(\mu\text{-}RS)(\mu\text{-}CO)Fe_2(CO)_6]$, where R = Me_3C, Et, Ph has been expanded to a vinylthioketal bridge by treatment of the complex with acetylenes and then acid chlorides [338].

The oxidative addition of $CH_2{=}CHCH_2CH_2COMe$ to $Os_3(CO)_{10}(MeCN)_2$ to give $Os_3H(\mu\text{-}CH{=}CHCH_2CH_2COMe)(CO)_{10}$ involved C-H bond cleavage at the terminal 6-position. Thermolysis of the product gave the dinuclear compound $Os_2H(EtC{=}CHCOMe)(CO)_6$ transforming the γδ- to the αβ-unsaturated ketone [339]. Allene coupled to the alkyne ligand in the tetraosmium cluster complex, $Os_4(CO)_{11}(\mu_4\text{-}HC{\equiv}CCO_2Me)(\mu_4\text{-}S)$, to form the derivative $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}(CH_2)_2CCHC(CO_2Me)](\mu_3\text{-}S)$ the structure of which was confirmed by X-ray crystallography [340].

Carbon-carbon bond formation accompanied by hydrogen migration between carbon centres has been observed in the reaction of μ-alkylidyne iron-molybdenum cluster complexes and but-2-yne.



16.15

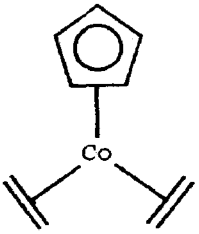


16.16

Thus the trinuclear complex $[MoFe_2(\mu_3\text{-}C.C_6H_4Me)(\mu\text{-}CO)(CO)_8\text{-}(\eta\text{-}C_5H_5)]$ combined with but-2-yne to give the dinuclear species $[FeMo\{\mu\text{-}C(C_6H_4.Me)\overline{C(CHMe)C}H_2CMeCMe\}(CO)_4(\eta\text{-}C_5H_5)]$ and the structure of this product was confirmed by X-ray crystallography [341].

The bridging alkene ligand in the dirhenium complex $[Re_2(\mu H)(\mu\text{-}CH{=}CHEt)(CO)_8]$ combined with 3,3-dimethylcyclopropane at room temperature to form the bridging allylidene ligand in the complex, $[Re_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_8]$ which was characterized by X-ray crystallography [342].

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



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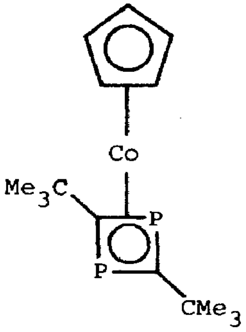

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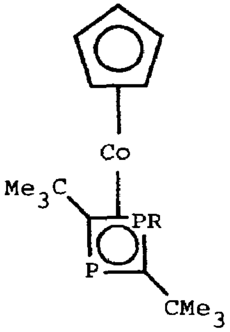

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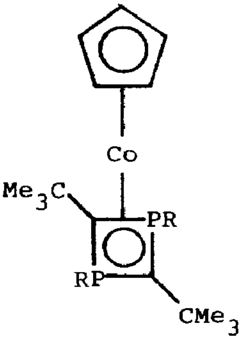

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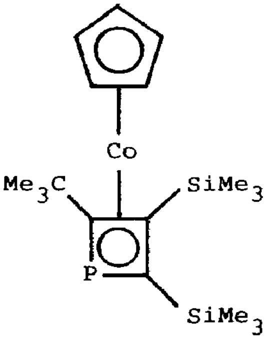
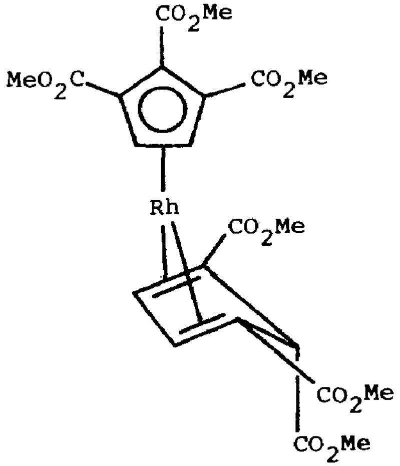


17.5

Reaction of the olefin complex (17.1) with $P{\equiv}CCMe_3$ produced the (η-1,3-diphosphacyclobutadiene)-cobalt compounds [17.2, 17.3 and 17.4; R = $(\eta^2\text{-}C_2H_4)(\eta^5\text{-}C_5H_5)Co\text{-}$] [343]. The (η-phosphacyclobutadiene) cobalt complex (17.5) has been obtained by codimerization of t-butylphosphaacetylene with bis(trimethylsilyl)-acetylene in the presence of (η-cyclopentadienyl)diethene cobalt [344].

Bruce and co-workers isolated the eighteen electron rhodium complex (17.6) as one of the products from the reaction of $Tl[C_5(CO_2Me)_5]$ with $[RhCl(CO)_2]_2$. The complex (17.6) was characterised by an X-ray crystal structure determination [345]. EHMO and ab initio calculations on the cobalt complex (17.7; X = CH) and the isolobal structure (17.8; X = CH) together with EHMO calculations on (17.7 and 17.8; X = BH^-) showed energy difference of < 2eV between each of the isolobal pairs [346].

(η-Pentamethylcyclopentadienyl)bis(η-ethene)cobalt has been treated with dimethyl acetylenedicarboxylate in boiling hexane to give the cobalt complexes (17.9 and 17.10). Reduction of $[(\eta\text{-}C_5Me_5)CoCl]_2$ with amalgam in the presence of bistrimethylsilylacetylene gave among other products the (η-cyclobutadiene)-cobalt complex (17.11) [347]. The electrochemistry of the Co(III) metallacycles (17.12; R^1 = Ph, Me, R^2 = Ph, Et) has been investigated. Reduction occurred by a one electron transfer to give a 19-electron complex which rapidly lost the phosphine



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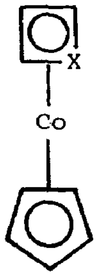

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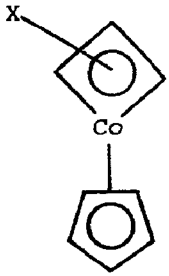

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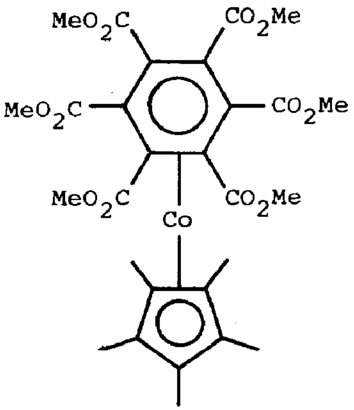

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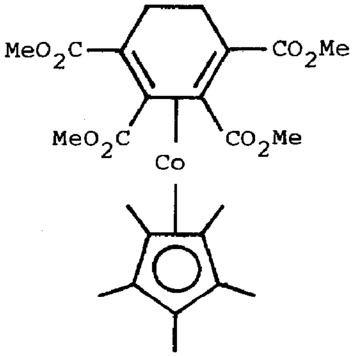

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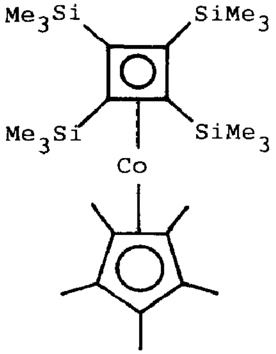

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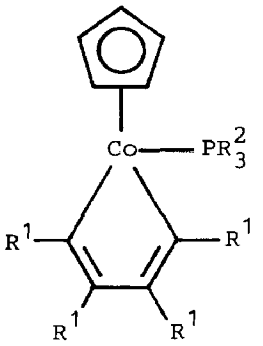

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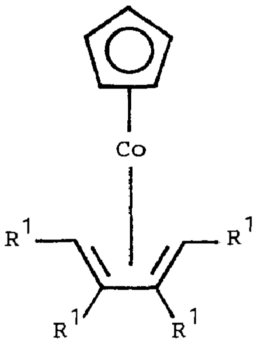
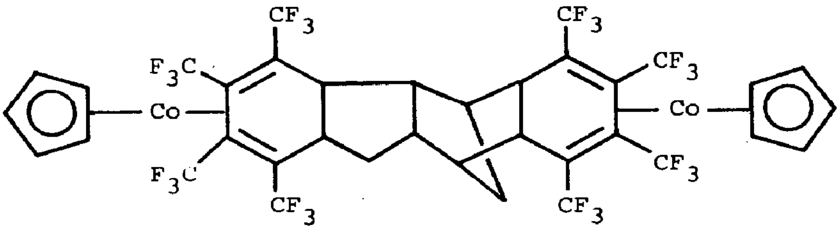


17.13

ligand to produce a transient 17-electron anion. In the absence of any added ligands this anion underwent protonation and reduction to give the corresponding η^4-butadiene complex (17.13) [348].

Unexpected carbon-carbon bond formation occurred in the reaction between dicarbonyl(η-cyclopentadienyl)cobalt and hexafluorobut-2-yne when the two cobalt complexes (17.14 and 17.15) were isolated. The structure of the dicobalt compound (17.14), the major product, was confirmed by X-ray analysis [349]. The structure of the cycloocta-1,5-diene complex (17.16; M = Rh) has been determined by X-ray analysis. The η-C_5H_5 ring was



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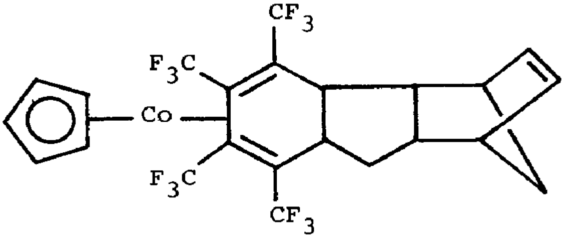

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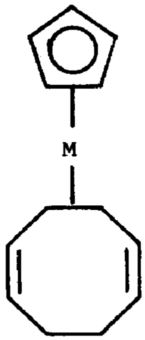
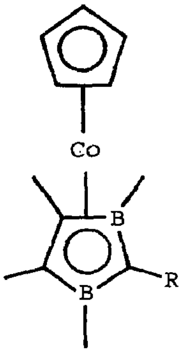


17.16

distorted in a manner consistent with a allyl-ene structure. ^{13}C and ^{103}Rh NMR spectroscopy were used to determine the activation energies for η-C_5H_5 rotation and molecular tumbling in the complexes (17.16; M = Rh, Ir) [350].

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

Treatment of diborole complexes (18.1 and 18.2; R = H) with potassium and then $ClAuPPh_3$ afforded the corresponding gold compounds (18.1 and 18.2; R = $AuPPh_3$) [351]. Helical metallocene oligomers, analogous to the cobaltocenium ion, have been prepared by treatment of the anionic helicene anion with cobalt(II) bromide followed by oxidation [352]. Treatment of the salt (18.3) with tetra-n-butylammonium iodide produced the halide (18.4). Reaction of this halide with the appropriate arene in the presence of aluminium chloride afforded the corresponding η^6-arene complexes [18.5; R = H, CH_3; 1,4-$(CH_3)_2$; 1,3,5-$(CH_3)_3$; 1,2,4,5-$(CH_3)_4$; $(CH_3)_6$; Cl, OCH_3, NH_2]. Some carbonyl substitutions of the salt (18.3) were also investigated [353].



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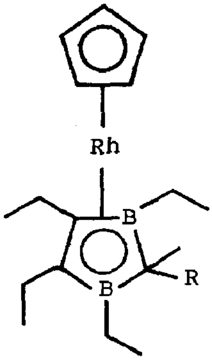

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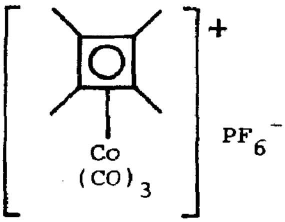

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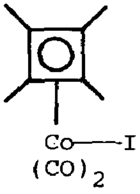

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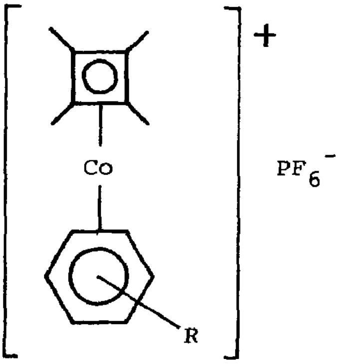
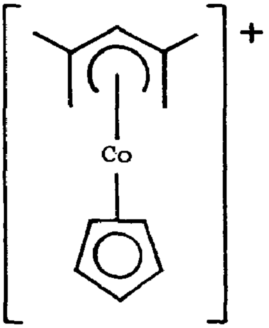


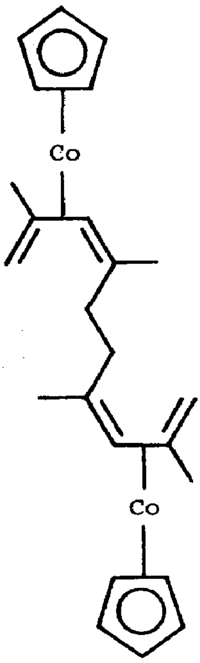
18.5

X-ray crystallography confirmed that the two ligands in the half-open sandwich complex (18.6) were eclipsed. Reduction of the cation (18.6) gave a binuclear complex containing η-cyclopentadienyl and η-decatetraene ligands (18.7) [354]. X-ray crystallography has been used to determine the crystal and molecular structure of the salt $[(\eta\text{-}C_5Me_5)_2Co]_2{}^+(DDQ)^{2-}$. The anion $(DDQ)^{2-}$ had a structure consistent with a localized electronic distribution [355].

An ab initio LCAO-MO SCF method has been used to calculate a potential energy curve for the $^1A_1$ state of cyclopentadienylcobalt [356]. Cobaltocene has been used as a one-electron reductant for titanium(IV), zirconium(IV) and hafnium(IV)



18.6

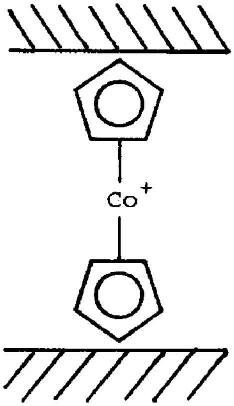


18.7

halogeno complexes such as $MCl_4(THF)_2$ where M = Zr, Hf [357]. The structure and dynamics of cobaltocene intercalated in tantalum disulphide has been investigated by NMR spectroscopy. It was concluded that the cobaltocenium ion could adopt two orientations, one with the metallocene parallel to (18.8) and the other perpendicular to (18.9) the interlamellar plane [358].

The reaction of cobaltocene with bis[tris(pentafluorophenyl)-germyl]mercury produced the ionic polynuclear complex (18.10) [359]. Decamethylcobaltocene combined with tetracyanoethylene (TCNE) to give 1:1 and 2:1 complexes. The crystal and molecular structure of the 2:1 species has been determined by X-ray crystallography. It contained two cobaltocenium cations and a dianion (18.11). Comparisons have been made with the corresponding ferrocenium complex and the electronic structures of the species $[TCNE]^n$, where n = 0, 1, 2, have been studied by IR, Raman and UV-visible spectroscopy [360].

Cobaltocene has been used as a catalyst for the preparation of α-methylene cyclic carbonates from α-ethnyl tertiary alcohols and carbon dioxide [361]. Electroreduction of the cobaltocenium salt (18.12) and related 1,1'-disubstituted ferrocenes led to



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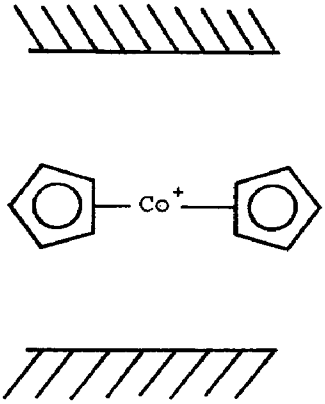

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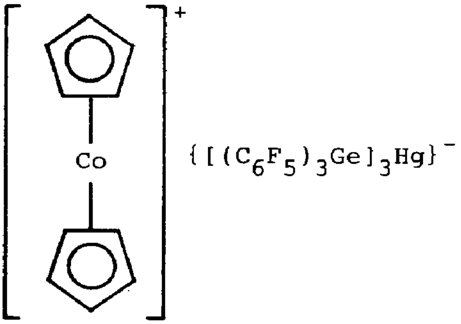
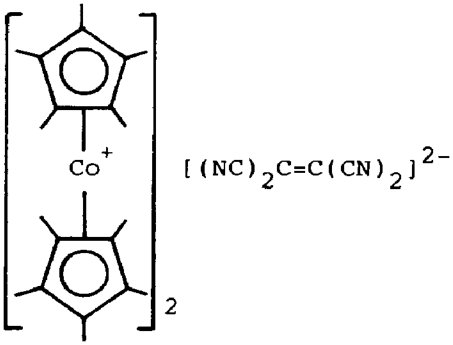


$\{[(C_6F_5)_3Ge]_3Hg\}^-$

18.10

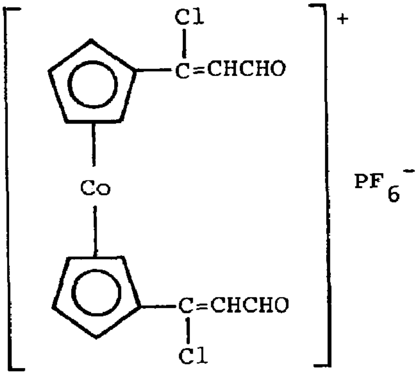


$[(NC)_2C=C(CN)_2]^{2-}$

18.11

the deposition of stable electroactive films on glassy-carbon and indium tin oxide coated glass electrodes. The spectral and electrochemical properties of these films were investigated [362].

The electrochemical reduction of the cobaltocenium ion and the oxidation of ferrocene have been studied in media of low ionic strength [363]. The cobaltocenium/cobaltocene system has been used as a standard in an investigation into the adsorption of quinones on a mercury electrode [364]. Reaction of cobaltocenium iodide with copper(I) iodide produced the



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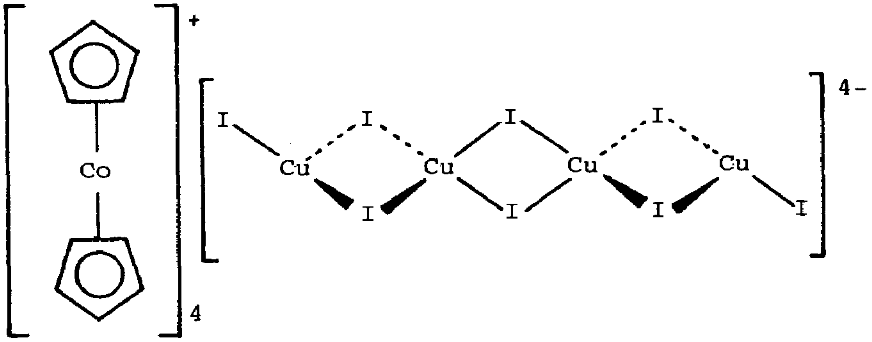

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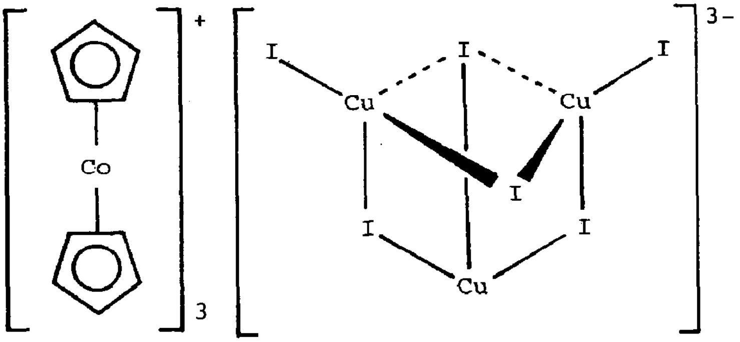


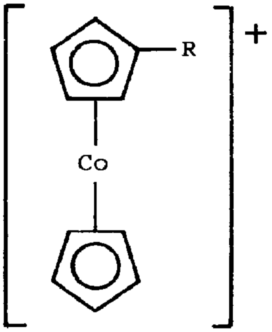
18.14

cobaltocenium iodo cuprates(I) (18.13 and 18.14). The structures of these complexes were determined by X-ray analysis [365].

Zeolite Y underwent ion-exchange with a bipyridyl complex, $[Ru(bipy)_3]^{2+}$ or $[Os(bipy)_3]^{2+}$ and a metallocenium ion $[(\eta\text{-}C_5H_4R)_2Fe]^+$ or $[(\eta\text{-}C_5H_4R)_2Co]^+$, where R = H, Me, CO_2Me, NH_2, CH_2NMe_2, and the resulting material used to modify an SnO_2 electrode. The presence of the bipyridyl complex caused a tenfold increase in the rate of charge transfer between the metallocene and the electrode. When the couples of the bipyridyl complex and the metallocene were matched then both oxidation and reduction of the metallocene was facilitated. This was explained in terms of a fast electron-transfer cross reaction between the complex and metallocene [366].

Several cobaltocenium ions (18.15; R = H, Me, Et, $CHMe_2$, CMe_3, cyclohexyl, CH_2Ph, Ph) have been examined by ^1H NMR spectroscopy. The chemical shift of protons in the unsubstituted cyclopentadienyl ring showed that the role of the substituent was dependent on the hyperconjugation effect. Chemical shift differences between the α- and β-protons of the substituted cyclopentadienyl ring became less with increasing size of the substituent R [367].

Reactions of the dication $[(\eta\text{-}C_5H_5)Co(SMe_2)_3]^{2+}$ have been investigated, with $Li[C_4H_4N]$ it formed the azacobaltocenium ion (18.16) [368].



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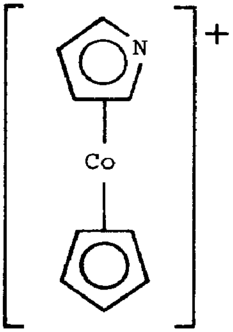


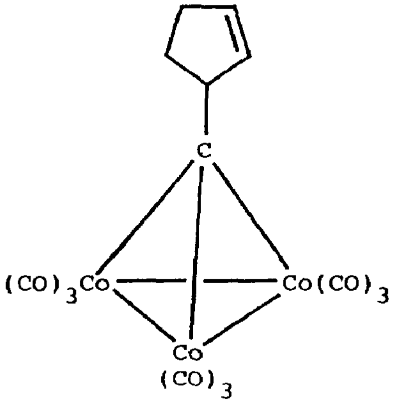
18.16

19. Cobalt-carbon Cluster Compounds

Radiolysis of benzene solutions of dicobalt octacarbonyl produced μ^2-(η^2-cyclohexyne)[$Co(CO)_3$]$_2$ and the alkylidynetricobalt complex (19.1) [369]. The crystal and molecular structures of the cobalt cluster complexes (19.2 and 19.3) have been determined by X-ray methods. In both structures the ferrocenyl group was tilted towards one cobalt atom of the cluster and this was attributed to the non-degeneracy of the carbyne p(π) orbitals which was caused by a cooperative π-interaction between the clusters and the ferrocenyl groups [370].

The methoxymethylidyne cluster complex $Co_3(\mu_3\text{-COMe})(CO)_9$ has been characterized by X-ray crystallography and shown to have a nearly ideal mirror symmetry. EHMO calculations have indicated that the observed conformations of the COMe group were close in energy with a low barrier to inversion or rotation. The COMe moiety had a similar bonding ability to CO and the alkylidyne ligand CR [371].

EXAFS results for the Co K-edges of cobalt carbonyl complexes, including $Co_3(CO)_9CH$, have been analyzed and structural parameters obtained. A spherical wave theory was used with ab initio phase shifts and multiple scattering to third order. The near-edge structure for cobalt K-edges was used as a fingerprint for specific cobalt environments [372]. Reduction of the phosphine-cobalt clusters (19.4; R = Me, Et) has been studied by cyclic



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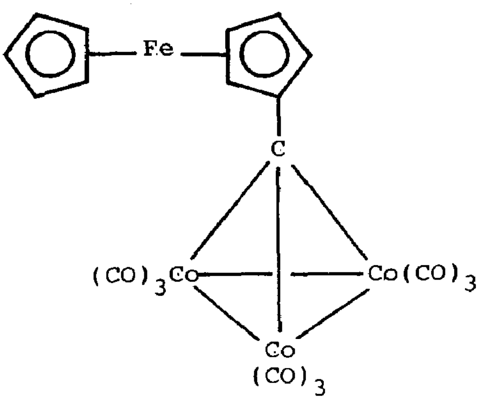

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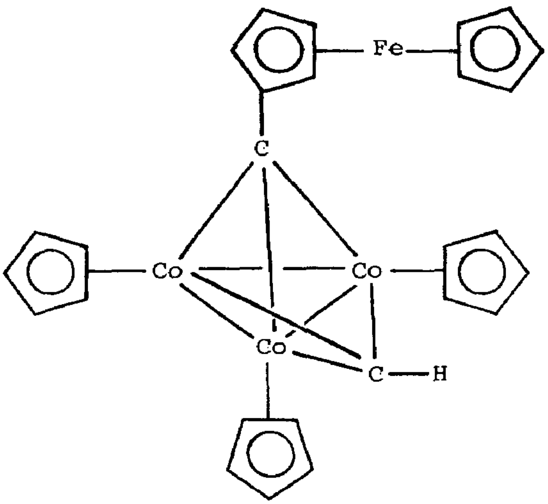
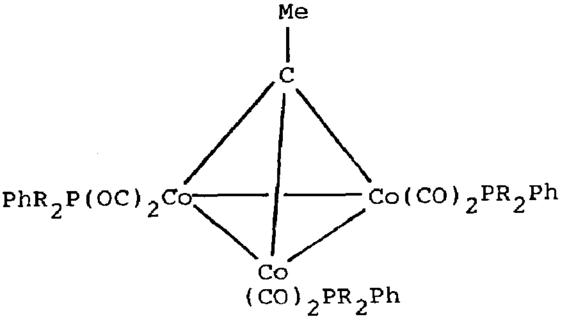


19.3

voltammetry. Evidence was obtained for electron-transfer-chain ligand substitution and a 17-electron intermediate was detected [373].

Reaction of the cation $[(Co_3(CO)_9CC{=}O]^+$ with the amines $(\eta\text{-}C_5H_4NH_2)Fe(\eta\text{-}C_5H_5)$ and $[\eta\text{-}C_5H_4CH_2CH(CO_2Me)NH_2]Fe(\eta\text{-}C_5H_5)$ produced the corresponding cluster compounds (19.5 and 19.6). The electrochemical behaviour and spectroscopic properties of these two complexes were investigated [374]. The alkylidynecobalt cluster (19.7) has been attacked by $Na_2[Fe(CO)_4]$ in THF to give the mixed metal hydride cluster $HFeCo_2(\mu_3CPh)(CO)_9$ (19.8). The two cluster complexes (19.7 and 19.8) were characterized by X-ray



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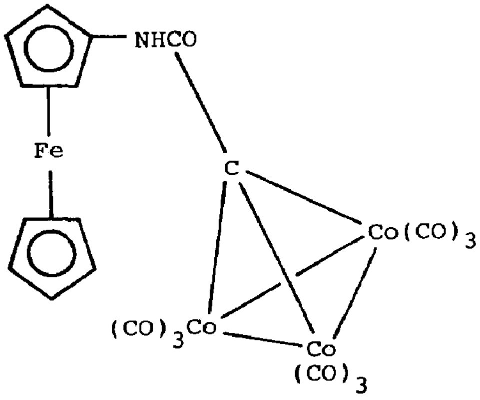
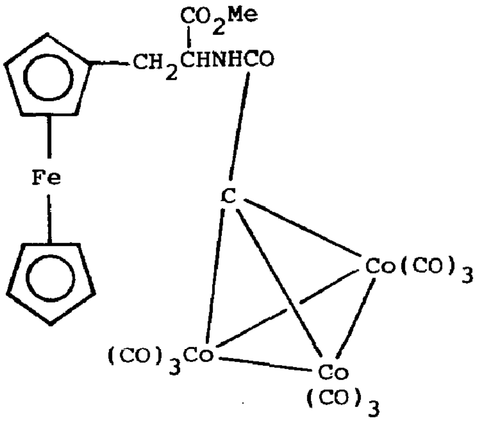


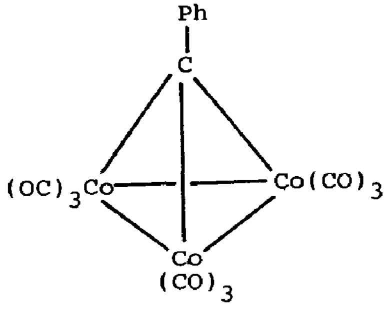
19.5



19.6

crystallography and were found to have similar structures. The position of the hydrogen ligand was not confirmed although it appeared to occupy an edge bridging position [375].

Treatment of the cluster complex (19.9; L = CO) with trimethylphosphine, methylphosphine or dimethylphenylphosphine gave the products of nucleophilic addition to the vinylidene ligand 9.10; L = PMe$_3$, MePh$_2$, Me$_2$PPh). When the complex (19.10; L = PMe$_3$) was heated the vinylidene cluster complex (19.10; L = PMe$_3$) was generated [376].



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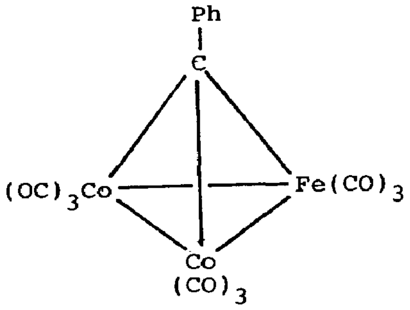

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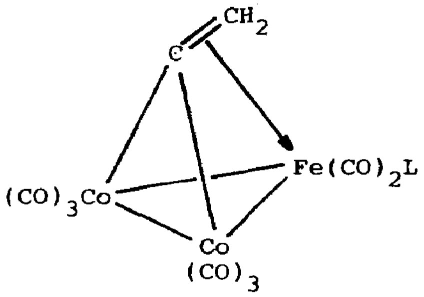

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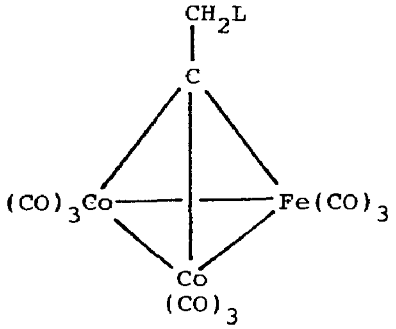
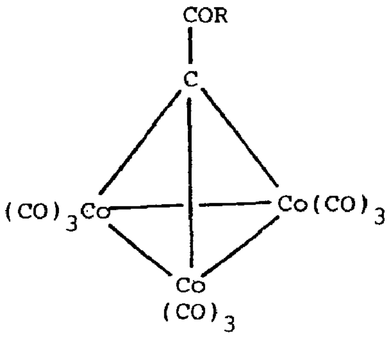


19.10

The methylidynetricobalt cluster complexes, $RCCo_3(CO)_9$, where R = Me, Ph, COPh, CO_2Me, CO_2Ph have been treated with metal exchange reagents such as $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$, $NaW(\eta\text{-}C_5H_5)\text{-}(CO)_3$, $(\eta\text{-}C_5H_5)Ni(CO)_2$ to give known clusters of the form Co_2Mo, Co_2W, Co_2Ni together with the new cluster complexes $RCCoM_2\text{-}(\eta\text{-}C_5H_5)_2(CO)_7$, where M = Mo, W and $RCCoNi_2(\eta\text{-}C_5H_5)_2(CO)_3$ [377]. The mechanism of decarbonylation of the ketone (9.11; R = 3-indolyl, $4\text{-}Me_2NC_6H_4$) to the corresponding cluster compound (19.12) has been investigated. ^{13}CO labelling experiments were carried out and ^{13}C NMR spectroscopy indicated that initial loss of CO



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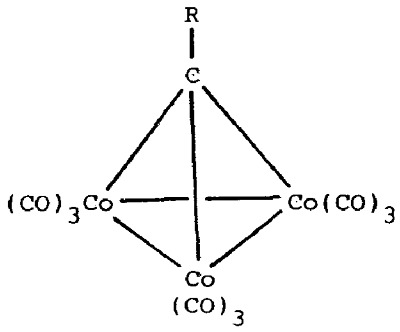
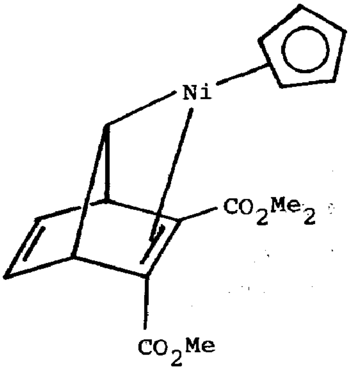


19.12

occurred at a $Co(CO)_3$ vertex and the complex (19.12) was formed via migration of the ketonic carbonyl to the vacant site on the cobalt atom [378].

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

A kinetic study of the quenching of singlet oxygen by nickelocene confirmed that it was an efficient quencher. The mechanism involved energy transfer and reversible charge transfer [379]. The reaction of nickelocene with dimethyl acetylenedicarboxylate produced the η-cyclopentadienylnickel compound (20.1) which was used as an intermediate in the synthesis of more complex polycyclic molecules [380].

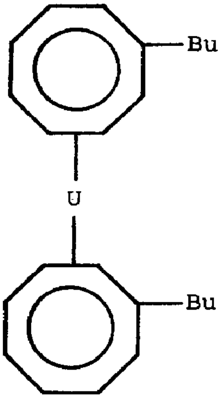


20.1

The decomposition of nickelocene over activated substrates in a hydrogen atmosphere has been investigated [381]. Nickelocene-lithium aluminium hydride mixtures in tetrahydrofuran have been shown to behave as homogeneous catalysts in hydrogenation. The catalytic behaviour was very similar to that of Raney nickel [382].

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

Some thermochemical parameters for 1,1'-dibutyluranocene (21.1) have been measured, the heat of formation was -32 kJ mol^{-1} in the condensed state and 115 kJ mol^{-1} in the gaseous state. The uranium-cyclooctatetraene ligand bond energy was determined as 417 kJ mol^{-1} [383].



21.1

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