ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1979*

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

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1. REVIEWS

The Organic Chemistry of Iron, Volume 1, edited by Koerner Von Gustorf, Grevels and Fischler contained several excellent surveys covering many different aspects of this field of chemistry. These included chapters on Structure and Bonding by Krueger, Barnett and Brauer; NMR Spectroscopy by Marks; Mass Spectra by Mueller; Moessbauer Spectroscopy by Parish; Optical Activity by Brunner; Monoolefin Iron Complexes, Allyl Iron Complexes and Diene Iron Complexes all three by King and Stabilizing of Unstable Species with Carbonyliron by Landesberg [1].

Arene exchange between a free arene and an arene-transition metal complex was reviewed briefly with respect to structure, thermodynamics, kinetics and reaction mechanism. The role of a catalyst in an arene exchange reaction was also considered. Experimental results were presented for arene exchange reactions with the complexes (η^6-arene)-1,5-cyclooctadieneruthenium, the cationic (η^6-arene)-1,5-cyclooctadieneiridium and (η^6-arene)-tricarbonylmolybdenum. The mechanisms of these reactions were discussed [2].

Wong has discussed the use of transition metal complexes with optically active phosphine residues as catalysts for asymmetric synthesis [3].

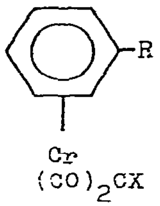
2. GENERAL RESULTS

Extended Hueckel calculations have been used in a theoretical study of bonding in M_3L_9 (Ligand) complexes. The frontier orbitals for an $M_3(CO)_9$ unit, where M = Fe, Ru, Os,Co,Rh, Ni, Pt were constructed from three $M(CO)_3$ pieces of by removal of three ligands from a D_{3h} symmetry $M_3(CO)_{12}$ molecule. The orbitals consisted of a low-lying Walsh -like set $1a_1$ + 1e and a higher cyclopropenium-like $2a_1$ + 2e set, the latter set was empty for a d^8 metal. The orbitals were used to analyze the electronic and geometrical structure of the M_3L_9 (Ligand) complexes where the ligand was CO, $(CO)_2$, S, S_2, CR, CCH_2^+, $CH_2{=}CH_2$, HC≡CH, polyene. In the case of $Co_3(CO)_9CCH_2^+$ the symmetrically topped structure was not a local energy minimum but contained three equivalent unsymmetrical structures of a complexed ethylidene type [4].

The electronic structure of the isoelectronic series: $(\eta\text{-}C_6H_6)Cr(CO)_3$, $(\eta\text{-}C_5H_5)Mn(CO)_3$, $(\eta\text{-}C_4H_4)Fe(CO)_3$, $[\eta\text{-}C(CH_2)_3]Fe(CO)_3$ has been compared with that of the corresponding dinitrogen complexes:
$(\eta\text{-}C_6H_6)Cr(CO)_2N_2$, $(\eta\text{-}C_5H_5)Mn(CO)_2N_2$, $(\eta\text{-}C_4H_4)Fe(CO)_2N_2$,
$[\eta\text{-}C(CH_2)_3]Fe(CO)_2N_2$,
by the application of the CNDO/2 method using both experimental and standard geometries. The calculated trends for the metal-CO and metal-N_2 bond strengths as measured by Wiberg indices, charge distributions, and orbital populations correlated well with the experimental CO and N_2 stretching frequencies and force constants. The following orders were obtained:
$Cr < Mn < Fe$ and $(\eta\text{-}C_nH_n)M(CO)_2 < (\eta\text{-}C_nH_n)M(CO)_2N_2 < (\eta\text{-}C_nH_n)M(CO)_3$.
The calculated total energies of the $(\eta\text{-}C_nH_n)M(CO)_2$ complexes indicated that a tilted geometry was preferred [5].

The ^{13}C NMR spectra of five series of (η-hydrocarbon)-transition metal complexes (2.1; R = H, CO_2Me; X = O, S, Se; 2.2; R = H, Me; X = O, S, Se; 2.3; X = O, S, Se) have been measured in the temperature range -30 to -50°C. The changes in chemical shift observed with changes in the nature of the chalcocarbonyl ligand indicated that the π-acceptor/σ-donor ratio of these ligands increased in the order $CO < CS < CSe$ [6].

A general theoretical analysis of the complexes (2.4; M = Mo, W, Mn, Fe; L = alkyl, carbene, ethylene, acetylene, imine, sulphur dioxide) has been carried out. The extended Hueckel method was



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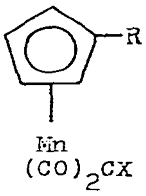

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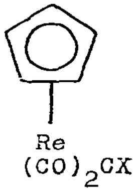
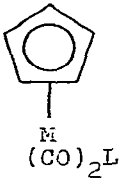


2.3

used, fragment orbitals of (η-C_5H_5)M$(CO)_2$ were constructed. This was then used as a basis for the discussion of the bonding with different ligands with the emphasis on conformational preferences and rotational barriers [7].

Metal binding energies for a number of bis(η-fulvalene)dimetal complexes have been determined by X-ray photoelectron spectroscopy. The values obtained for the diiron complex (2.5; M = Fe; n = 0), 708.5 eV, the dicobalt complexes (2.5; M = Co; n = 1, 2), 780.7 eV and 781.9 eV respectively and for the dinickel complexes (2.5; M = Ni; n = 0, 1), 854.9 eV and 856.7 eV respectively followed the trends expected. However the value for the neutral dicobalt complex (2.5; M = Co; n = 0) 779.5 eV, was lower than expected and suggested an electronic structure with Co(I) atoms. The low value, 856.2 eV, for the dinickel dication (2.5; M = Ni; n = 2) was explained in terms of an electronic structure with Ni(II) atoms and one pair of electrons removed from the two fulvalene ligands [8].



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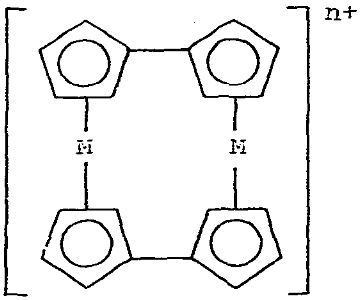

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An ab initio investigation of the structure of the $C_8H_8^{2+}$ cation has indicated that while the most stable form of the cation is a planar eight-membered ring, a structure related to "fly-over bridge" (η- hydrocarbon)transition metal carbonyl complexes was only 58 kcal mol^{-1} higher in energy [9].

The thermodynamics of the synthesis, hydrogenation and thermal decomposition of η-cyclopentadienyl-transition metal complexes was investigated [10].

The ^{17}O nuclear magnetic resonance spectra of a range of organometallic derivatives of metal carbonyls were recorded and interpreted. The ^{17}O shielding values for the terminal transition metal carbonyl oxygens were 300-400 ppm downfield from $^{17}OH_2$. The carbonyl ^{17}O chemical shift trends were opposite to those for the carbonyl ^{13}C chemical shifts and this was explained by metal π-backbonding to the carbonyl π^* orbitals [11].

The thermal decomposition of the bis(η-cyclopentadienyl) derivatives of vanadium, chromium, manganese, iron, cobalt and nickel in a vacuum has been investigated. Ferrocene was the most thermally stable and for the complexes which are to the left of iron in the Periodic Table the thermal stability decreased in the order: $(\eta\text{-}C_5H_5)_2V > (\eta\text{-}C_5H_5)_2Cr > (\eta\text{-}C_5H_5)_2Mn$. The thermodynamic dissociation characteristics of the ring-metal bond, that is, the average Gibbs free energy and the average dissociation energy decreased in the same order. The thermal stability of iron-triad metallocenes decreased in the order $(\eta\text{-}C_5H_5)_2Fe > (\eta\text{-}C_5H_5)_2Co > (\eta\text{-}C_5H_5)_2Ni$. It was concluded that the pyrolysis of metallocenes was a homogeneous-heterogeneous process that consisted of a series of consecutive, parallel and catalytic reactions [12].

The heats of formation were determined for the bis(η-cyclopentadienyl) derivatives of magnesium, vanadium, chromium, manganese, iron, cobalt and nickel and for tricarbonyl(η-cyclopentadienyl)manganese and dicarbonyl(η-cyclopentadienyl)cobalt by static-bomb calorimetry. The heats of formation were used to analyse the feasibility of the process $M(\eta\text{-}C_5H_5)_2 \rightarrow [M(\eta\text{-}C_5H_5)_2]^+ + e^-$. The feasibility order was determined as (M =) $V < Cr > Mn > Fe < Co > Ni$. It was shown also that bond energy additivity did not occur for the (η-cyclopentadienyl)metal carbonyls investigated [13].

Nickelocene, cobaltocene and ferrocene underwent ligand exchange with alkenes such as cyclooctadiene (COD) to form the corresponding diene complexes such as $Ni(COD)_2$. The complexes were metallated with lithium in THF to give the dilithio adducts such as $Ni(COD)_2Li_2(THF)_4$ [14].

Pyrolysis gas chromatography has been applied to the analysis of the thermal decomposition products of organometallic compounds containing the cyclopentadienyl ligand [15].

The homopolymerization and copolymerization of several (η-hydrocarbon)transition metal complexes has been investigated. Vinylcymantrene underwent anionic copolymerization with acrylonitrile and methyl methacrylate in the presence of butyllithium and sodium naphthalenide but it did not combine with styrene or undergo anionic homopolymerization. The failure of the last reaction was ascribed to resonance destabilization of the anionic intermediate by the electron-rich cyclopentadienyl group. (η-Benzyl acrylate)-tricarbonylchromium and (η-2,4-hexadienyl methacrylate)tricarbonyliron also failed to undergo anionic homopolymerization [16].

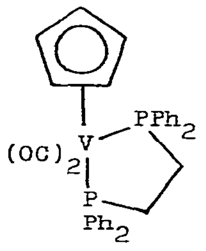
The mass spectra of four benchotrenyl- six cymantrenyl- and seven ferrocenyl- carbinols were recorded and interpreted. Elimination of water occurred via a 1,2- elimination mechanism and this involved hydroxyl transfer to the metal atom [17].

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

The crystal and molecular structure of the (η-cyclopentadienyl)vanadium complex (3.1) has been determined by X-ray crystallography. The vanadium-phosphorus distances were found to be relatively long while the phosphorus-vanadium-phosphorus angles were relatively small [18].

The infrared and Raman spectra of tetracarbonyl(η-cyclopentadienyl)niobium were recorded and interpreted [19].

Electrochemical reduction of carbonylbis(η-cyclopentadienyl)-vanadium took place by a one-electron process to give the corresponding anion $[(\eta\text{-}C_5H_5)_2VCO]^-$ which was further reduced to the cyclopentadienide ion, vanadium and carbon monoxide. The anion was unstable at room temperature decomposing to tetracarbonyl-(η-cyclopentadienyl)vanadium through the intermediate radicals $[(\eta\text{-}C_5H_5)VCO]^\cdot$ and $[(\eta\text{-}C_5H_5)V]^\cdot$ which combined with carbon monoxide.



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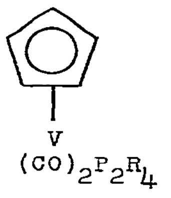

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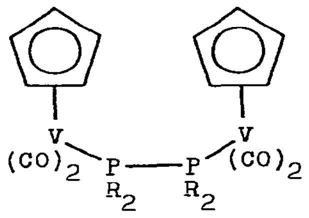

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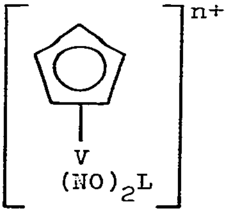
The reversible one-electron reduction of tetracarbonyl(η-cyclopentadienyl)vanadium gave the radical anion $[(\eta\text{-}C_5H_5)V(CO)_4]^{\dot{-}}$ which was decomposed by traces of water [20].

The electrochemical reduction of tetracarbonyl(η-cyclopentadienyl)vanadium and carbonylbis(η-cyclopentadienyl)vanadium has been investigated. Decomposition products of the former complex were identified while the latter complex gave the anion $[(\eta-C_5H_5)_2VCO]^-$ in a reversible process. The anion was not sufficiently stable to be used for synthetic purposes [21].

Tetracarbonyl(η-cyclopentadienyl)vanadium was irradiated in the presence of the diphosphine ligands, P_2R_4 (R = Me, cyclohexyl), to give the corresponding mononuclear complexes (3.2) and the dinuclear complexes (3.3). Similar reactions were carried out with diarsine and distibine ligands [22].

Tetracarbonyl(η-cyclopentadienyl)vanadium was reduced with sodium amalgam to form the tricarbonylvanadium salt $Na_2[(\eta-C_5H_5)V(CO)_3]$ which underwent carbonyl ligand exchange with p-Me.C_6H_4.SO_2NMeNO to give the dinitrosyl complex (3.4; L = CO; n = 0). Further reaction of this complex (3.4; L = CO; n = 0) with $NOPF_6$ in nitromethane at -25° gave the trinitrosyl complex (3.4; L = NO; n = 1) [23].

The photolysis of tetracarbonyl(η-cyclopentadienyl)vanadium using a falling-film photoreactor gave μ-dicarbonyl-tricarbonyl-bis[(η-cyclopentadienyl)vanadium] in 89% yield [24].



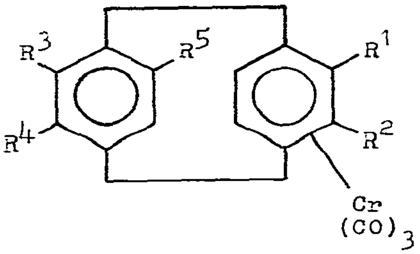
3.4

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

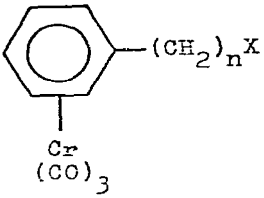
(i) Formation

A series of (η-arene)tricarbonylchromium complexes was prepared by the direct reaction of hexacarbonylchromium with the arene in a mixture of dibutylether and tetrahydrofuran (90/10 v/v). This method enabled (η-polyaromatic)tricarbonylchromium complexes to be prepared directly in good yields. The scope, limitations and advantages of this method were discussed [25].

The tricarbonylchromium complexes (4.1; $R^1 = R^4 = R^5 = H$, $R^2 = R^3 = Me$; $R^1 = R^2 = R^3 = R^4 = Me$, $R^5 = H$; $R^1R^5 = CH_2CH_2$, $R^2 = R^3 = R^4 = H$) were prepared by the reaction of hexacarbonylchromium with the corresponding cyclophane. The tricarbonyl-



4.1

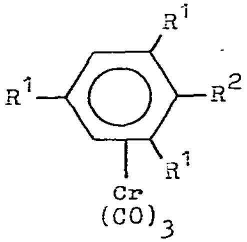


4.2

chromium group was displaced from the complex (4.1; $R^1 = R^2 = R^3 = R^4 = Me$, $R^5 = H$) by treatment with tetracyanoethylene [26].

The benchrotrene complexes [4.2; X = CO_2H, n = 0, 1, 2; X = Cl, Br, n = 2; 4.3; $R^1 = CH_2CH_2Br$, $R^2 = H$; $R^1 = Me$, $R^2 = (CH_2)_3CO_2H$, $(CH_2)_3OH$, $(CH_2)_4OH$, $(CH_2)_3Br$] have been prepared by treatment of the appropriate ligand with hexacarbonylchromium, $(NH_3)_3Cr(CO)_3$ or $(pyridine)_3Cr(CO)_3$ [27].

Substituted styrenes, indenes and related compounds combined with chromium hexacarbonyl to form the benchrotrene complexes



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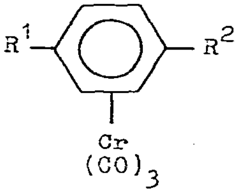

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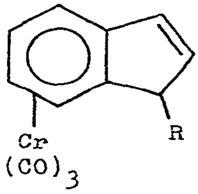
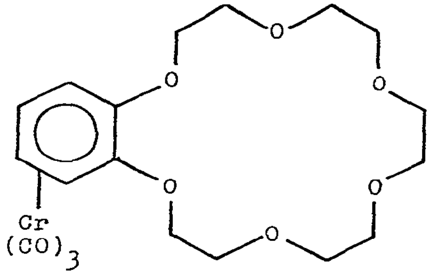


4.5

(4.4; R^1 = H, Me, OMe, F, Cl; $R^2 = CH{=}CH_2$, $OCH_2CH{=}CH_2$ and 4.5; R = H, Me). The reactions between these complexes and (η-phenylacetylene)hexacarbonyldicobalt have been examined. The aromatic ligand of the benchrotrene complexes underwent either addition or cycloaddition to form either butadiene or cyclopentenone complexes respectively. Thus the benchrotrene (4.4; R^1 = Me; $R^2 = CH{=}CH_2$) gave the diene complex [4.4; R^1 = Me; R^2 = E,E-$(CH{=}CH)_2Ph$] in 29% yield and the cyclopentenone complex (4.4; R^1 = Me; R^2 = 2-oxo-3-phenylcyclopent-3-en-1-yl) in 39% yield [28].

Prodedures have been described for the formation of (η-arene)-tricarbonylchromium complexes in 64-90% yield by treatment of the



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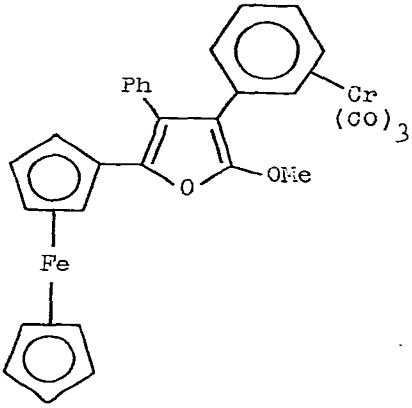

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appropriate ligand (arene = PhH, PhF, PhCl, PhOMe, PhNMe$_2$, PhCO$_2$Me) with chromium hexacarbonyl [29].

The reactions of benzo-crown ethers with transition metal carbonyls and transition metal organometallic compounds have been studied. Hexacarbonylchromium combined with benzo-18-crown-6 to give the tricarbonylchromium complex (4.6). Similar complexes have been formed also with benzo-15-crown-5 and methylbenzo-15-crown-5 [30].

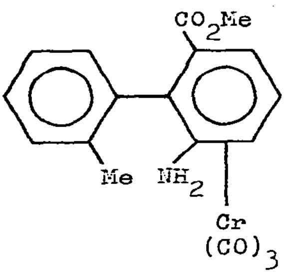
The treatment of pentacarbonyl[ferrocenyl(methoxy)carbene]-chromium with tolan in dibutyl ether gave the tricarbonylchromium complex (4.7) [31].

Reaction of methyl-2-amino-2-(o-tolyl)-benzoate with hexacarbonylchromium gave the isomeric tricarbonylchromium complexes (4.8 and 4.9). NMR spectroscopy showed that both the complexes (4.8 and 4.9) existed as two torsional isomers. The activation energy for the interconversion of the isomers of the major product (4.8) was approximately 91 kJ mol^{-1} [32].

Reaction of bis[tricarbonyl(η-phenyl)chromium]mercury with copper(II) chloride gave a mixture of benchrotrene and tricarbonyl-(η-chlorobenzene)chromium [33].

The η-thienyl (4.10) and η-benzofuryl (4.11) complexes were prepared by reaction of hexacarbonylchromium with the dicarbonyliron complexes (4.12; R = 2-thienyl, 2-benzofuryl) respectively [34].

Controlled reduction of N-methyl-3-ethylpyridinium iodide gave the corresponding 1,2-dihydropyridine which underwent reaction with tris(acetonitrile)tricarbonylchromium to give the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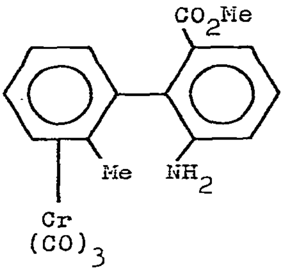
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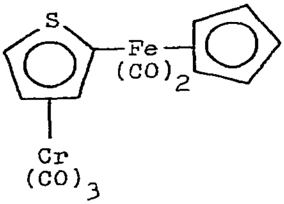
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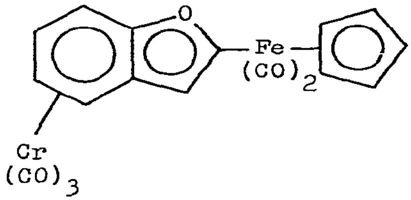
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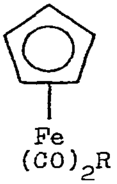
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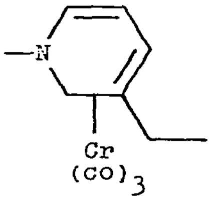
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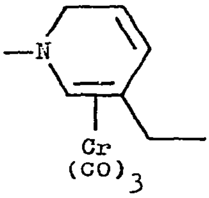
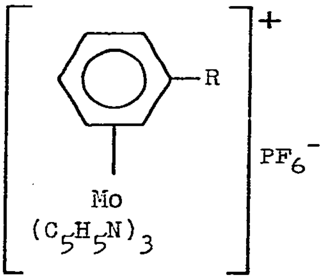

4.14

tricarbonylchromium derivatives (4.13 and 4.14). Analogous reactions were carried out with other dihydropyridine derivatives to give the corresponding tricarbonylchromium complexes [35].

The reaction of $[(\eta\text{-arene})_2Mo]PF_6$ (arene = benzene, toluene) with pyridine gave the corresponding paramagnetic molybdenum derivatives (4.15; R = H, Me). The three pyridine ligands were easily replaced by 1-methylimidazole (1-Me-Im) to give $[(\eta\text{-arene})Mo(1\text{-}Me\text{-}Im)_3]PF_6$. Treatment of the pyridine complexes (4.15; R = H, Me) with carbon monoxide gave the carbonyl complex <u>trans</u>-$[Mo(CO)_2(C_5H_5N)_4]PF_6$ [36].



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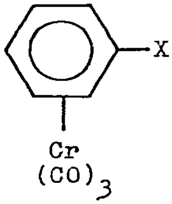
4. (ii) Spectroscopic and Physico-chemical Studies

Molecular orbital calculations were carried out for a series of tricarbonylchromium complexes (4.16; X = H, Me, NH_2, OH, F) in an attempt to rationalize substituent effects on the dipole moment and the infrared spectrum of (η-benzene)tricarbonylchromium [37].

The crystal and molecular structure of the (η-endo-7-phenylcycloheptatriene)chromium complex (4.17) has been determined by X-ray crystallography and the structure compared with the exo-7-phenyl isomer [38].



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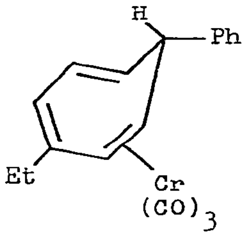

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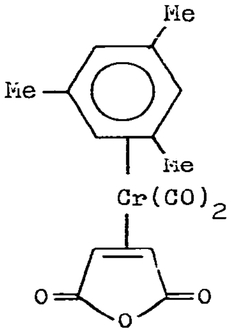

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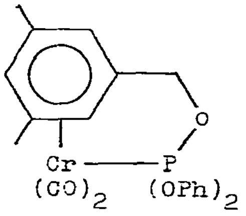
The crystal structure of dicarbonyl(η-maleic anhydride)-(η-mesitylene)chromium (4.18) was established by X-ray analysis. The maleic anhydride was symmetrically bonded to the chromium atom with the double bond almost parallel to the benzene ring plane. The double bond length (1.433 Å) was longer than its value in the non-coordinated molecule (1.303 Å). The maleic anhydride was almost planar, the oxygen atom deviated by 0.09 Å from the mean plane of the four carbon atoms. The hydrogen isotope exchange reaction of the complex (4.18) in deuterotrifluoroacetic acid was investigated. The presence of the electron accepting maleic anhydride ligand led to a twenty-fold decrease in the rate constant of this reaction [39].

The crystal and molecular structure of the bridged benchrotrene analogue (4.19) has been determined by X-ray diffraction. Distortions of the molecular structure were ascribed to strain inherent in the short benzene to chromium bridge. The chromium-phosphorus bond length was 2.201 Å, the shortest reported to date [40].

The crystal and molecular structure of the charge-transfer complex tricarbonyl(η-phenanthrene)chromium-1,3,5-trinitrobenzene was determined by X-ray analysis. In the solid state the phenanthrene and benzene rings were parallel to each other and the structure was composed of stacks of alternating donor and acceptor molecules [41].



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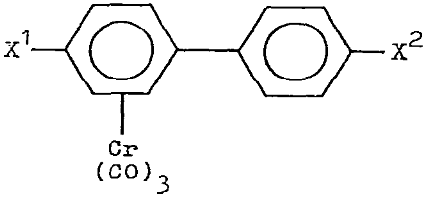


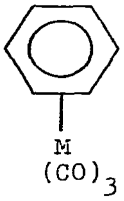
4.20

The crystal structures of $MoMe_2(\eta-C_6H_6)(PPhMe_2)_2$ and $MoMe_2(\eta-C_6H_5Me)(PPhMe_2)_2$ were determined by X-ray analysis. The Mo—C(π) bond distances, in the toluene derivative, ranged from 2.250 to 2.344 Å and varied in a pair-wise fashion such that the η-arene ligand showed a tendency to act as a diene [42].

The electric dipole moments and carbonyl stretching frequencies for tricarbonyl(η-diphenyl)chromium (4.20; $X^1 = X^2 = H$), tricarbonyl(η-fluorene)chromium and tricarbonyl(η-*cis*-stilbene)-chromium have been determined and indicate that the π-basicity of the arene ring bound to the metal is dominant over the π-basicity of the complete aromatic ligand. Substituent effects in the methyl and amino complexes (4.20; X^1 = Me, NH_2; X^2 = H; $X^1 = X^2 = NH_2$) were weaker than in the corresponding benchrotrene complexes. The amino complex (4.20; $X^1 = NH_2$; X^2 = H) was found to exist as two distinct conformers, one with the nitrogen lone pair electrons directed towards chromium, the other with the lone pair directed away. The tricarbonylchromium group was bound preferentially to the unsubstituted phenyl ring in the fluoro complex (4.20; X^1 = H, X^2 = F) [43].

The electronic absorption spectra of the η-benzene complexes (4.21; M = Cr, Mo, W) and (η-cyclopentadienyl)tricarbonylmanganese were recorded. The effect of substituents in the η-benzene ring of the chromium complexes was determined [44].

The IR and Raman spectra of (η-methylbenzoate)dicarbonylselenocarbonylchromium (4.22) have been measured and the vibrational modes assigned. A valence force field was determined and comparisons have been made with the corresponding thiocarbonyl complex. Donor-acceptor effects of the selenocarbonyl and thiocarbonyl ligands were discussed [45].



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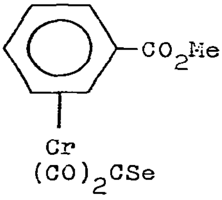


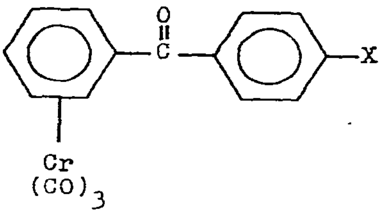
4.22

An investigation was carried out on the ring current contribution to the ^{1}H NMR chemical shifts of (η-benzene)tricarbonylchromium complexes. The results indicated that the ring current shielding in the complexes was considerably reduced above the ring plane [46].

^{13}C NMR spectra of a series of (η-arene)tricarbonylchromium complexes were recorded in trifluoroacetic acid. The signals for all the carbon nuclei in the η-arene ring were shifted 10 - 12 ppm in comparison to their positions in a neutral medium [47].

The ^{13}C NMR spectra of the (η-benzophenone)chromium complexes (4.23; X = F, Cl, OMe) indicated only a small substituent effect on the complexed benzene ring and on the Cr(CO)$_3$ carbon atoms. Self-consistent charge and configuration molecular orbital method calculations on the complexes (4.23) showed that σ-electron donation from chromium to the benzene ring outweighed π-electron donation from the benzene ligand to chromium which left the ring with a greater negative charge than before complexation. The chromium atom carried a greater positive charge than in benchrotrene and the calculated C—O bond orders showed the same trends as those determined by IR spectroscopy [48].

The ^{13}C NMR spectra of a series of (η-arene)carbonylchromium



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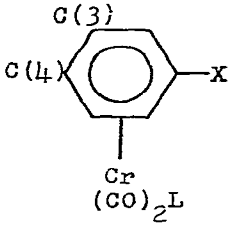

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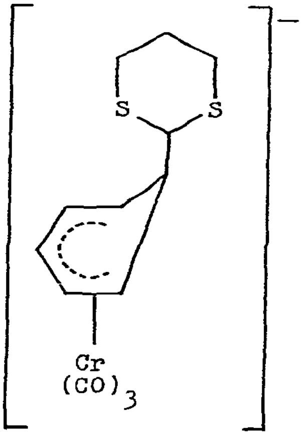
complexes (4.24; L = CO, PPh$_3$; X = aliphatic and aromatic substituents) were recorded and interpreted. It was found that correlations existed between $\delta(^{13}C)$ and σ_R (Taft's constant) in the tricarbonylchromium complexes for both the C(4) and C(3) nuclei, the difference being that the slopes of the corresponding curves were opposite [49].

Substituent effects in the attack of substituted benchrotrenes by carbanions have been investigated. The reaction proceeded by addition of the carbanion to the aromatic ligand to give an intermediate (η-cyclohexadienyl)chromium complex which was oxidized to an isomeric mixture of disubstituted benzenes. Thus the methylbenchrotrene (4.16; X = Me) was attacked by $LiCH_2CO_2R$ to give a mixture of the o- and m-substituted toluenes in the ratio 28:72. Similar reactions were carried out for the benchrotrenes (4.16; X = OMe, Cl, CF_3, $SiMe_3$, NMe_3, Et, Bu^t). Chloride and methyl substituents showed similar directing effects, ortho and meta, while CF_3 and $SiMe_3$ were para-directing. The results were discussed in terms of resonance effects and in terms of HOMO-LUMO interactions [50]. The crystal and molecular structure of one (η-cyclohexadienyl)chromium complex (4.25) was determined by X-ray crystallography [51].

A kinetic study was carried out on the replacement of halide by methoxide in a series of neutral and cationic complexes [4.26; L_nM = $Cr(CO)_3$, $Mo(CO)_3$, $Fe(\eta-C_5H_5)^+$, $Mn(CO)_3^+$] of fluoro- and chloro-benzene. The rate increased through the series $Cr(CO)_3 < Mo(CO)_3 \ll Fe(\eta-C_5H_5)^+ < Mn(CO)_3^+$, and the fluorobenzene complexes were more reactive than the chlorobenzene analogues [52].



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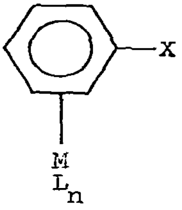

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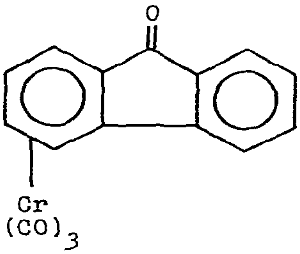

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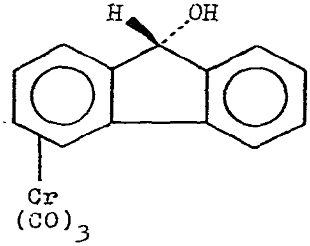

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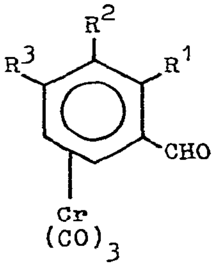
The racemic (η-fluorenone)chromium complex (4.27) was formed by treatment of fluorenone ethylene ketal with chromium hexacarbonyl and subsequent cleavage of the ketal. Asymmetric reduction of the racemate (4.27) gave the (-)-<u>endo</u>-alcohol (4.28) in 80% optical yield and the unreacted (+)-ketone (4.27) was recovered. The absolute chirality of this ketone was determined as S and attempts to racemize it were unsuccessful indicating that no



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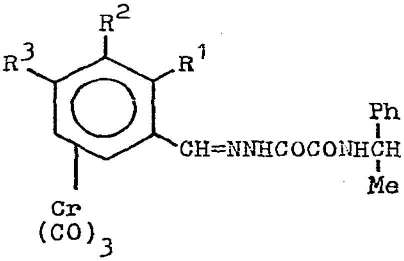

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transannular shift of the tricarbonylchromium group took place [53].

Resolution of the racemates of the aldehydes (4.29; R^1 = Me $R^2 = R^3$ = H; R^1 = OMe, $R^2 = R^3$ = H; $R^1 = R^2$ = OMe, R^3 = H; R^1 = H, $R^2 = R^3$ = OMe) was achieved by column chromatography of the corresponding semioxamazones (4.30) [54].

The exchange reaction (Equation 1) of (η-arene)tricarbonylchromium complexes with different arenes was studied:-

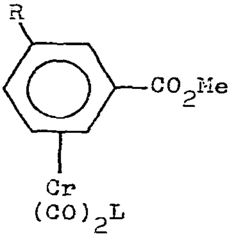
$$\eta\text{-ArYCr(CO)}_3 + \text{ArX} \rightleftharpoons \eta\text{-ArXCr(CO)}_3 + \text{ArY} \qquad (1)$$

The more firmly bound arenes tended to displace the more weakly held and the preferred order of displacement was $C_6Me_6 > C_6H_2Me_4 > C_6H_3Me_3 > PhNMe_2 \geqslant C_6H_4Me_2 > PhMe \backsim C_6H_6 > PhCOMe \backsim PhOMe > PhCO_2Me > PhCl \backsim PhF > C_{10}H_8$. The mechanism of the exchange reaction was discussed [55].

4. (iii) General Chemistry

Benchrotrene complexes, including the methyl esters (4.31; R = H, Me; L = CO) have been converted to the corresponding thiocarbonyl derivatives by photolysis with *cis*-cyclooctene to form the intermediates (4.31; R = H, Me; L = C_8H_{14}) which were treated with carbon disulphide and triphenylphosphine to give the products (4.31; R = H, Me; L = CS) in 84 - 90% yield [56].

Irradiation of (η-arene)tricarbonylchromium (arene = methyl benzoate, methyl *o*-methoxybenzoate, methyl *m*-methoxybenzoate,



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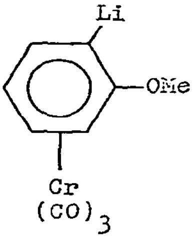

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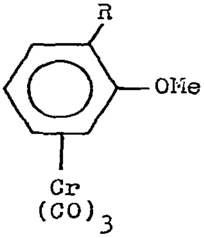

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benzene, hexamethylbenzene) in the presence of potassium cyanide, followed by the addition of benzoyl chloride, afforded the corresponding benzoyl isocyanide complexes (η-arene)Cr$(CO)_2$(CNCOPh). Spectroscopic evidence suggested that the N-benzoyl isocyanide group had electronic properties close to those of carbon monoxide. Photochemical substitution of carbon monoxide by triphenylphosphite to give (η-arene)Cr(CO)P$(OPh)_3$(CNCOPh) confirmed the strength of the Cr—CHCOPh bond and it also provided a route to chiral complexes [57].

Substituted benchrotrenes have been lithiated with n-butyllithium at -78°C in the presence of THF and tetramethylethylenediamine. The o-lithio species generated were quenched with electrophiles to form o-disubstituted benchrotrenes. Thus the (η-anisole)chromium complex (4.16; X = OMe) gave the lithio-intermediate (4.32) which was quenched with CO_2/CH_2N_2, $MeOSO_2F$, Me_2CO, PhCHO, Me_3SiCl to form the derivatives [4.33; R = CO_2Me, Me, $C(OH)Me_2$, CHOHPh, $SiMe_3$] respectively. Related reactions with benchrotrene and its fluoro and chloro derivatives (4.16; X = F, Cl) were reported and the stereochemistry of the reactions were studied [58].

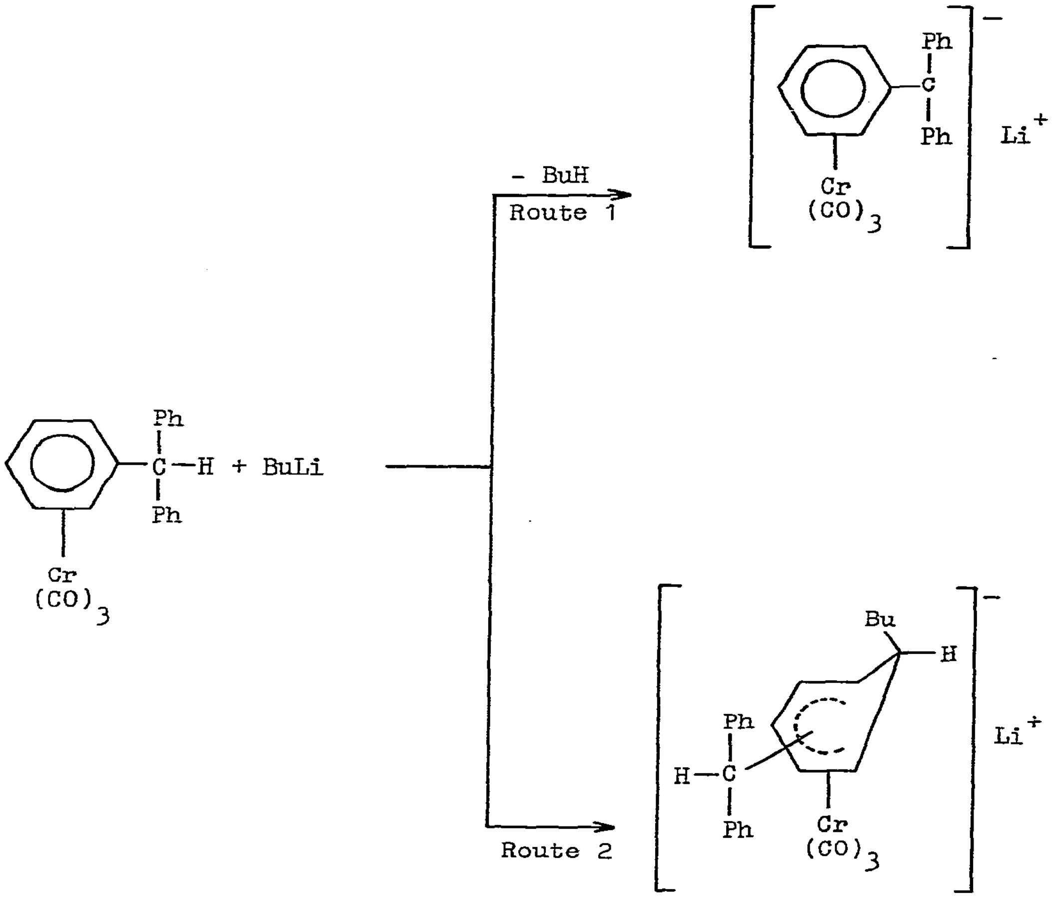
The metallation of the tricarbonylchromium derivatives of diphenylmethane and triphenylmethane was investigated. The preliminary results indicated that the coordination of an aryl ring with tricarbonylchromium greatly activated the ring towards carbon bases and that abstraction of an exocyclic hydrogen (Scheme 1; Route 1) was less important than alkylation (Scheme 1; Route 2) even with the triphenylmethane derivative whose pK_a was relatively high [59].

Reaction of (η-benzene)tricarbonylchromium with n-butyllithium in ether-tetrahydrofuran mixtures at -40° gave the lithio derivative (4.16; X = Li) in good yields. Reaction of the lithio derivative with trimethylchlorosilane or iodine gave the tricarbonylchromium derivatives (4.16; X = $SiMe_3$ and I) respectively [60].

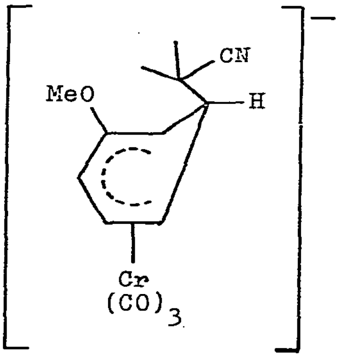
Treatment of tricarbonyl(η-methoxybenzene)chromium with 2-lithio-2-methylpropionitrile gave the anion (4.34). Reaction of the anion with trifluoroacetic acid followed by aqueous ammonium hydroxide produced the cyclohexadiene derivative (4.35) [61].

Grignard reagents attacked the benchrotrene aryl imine complexes (4.36; R^1 = H, Me, OMe, Cl; R^2 = H, Me, Et, Ph; R^3 = H, Me) to give the secondary amines (4.37; R^4 = Me, $PhCH_2$). The reaction proceeded with considerable asymmetric induction which was dependent on the position of the substituent in ring A. A large entering group favoured asymmetric induction and possible transition states for the reaction were discussed [62].

Treatment of (η-fluorobenzene)tricarbonylchromium with alcohols, RH, where R = MeO, Me_3CO, Me_3CS, cholesteryloxy and



Scheme 1



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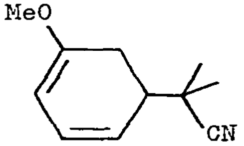
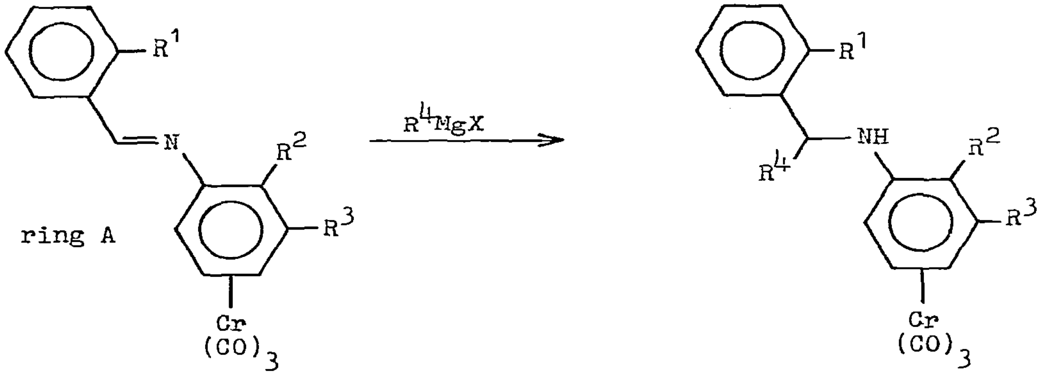


4.35

menth-1-en-8-yloxy and subsequent cleavage of the resulting complexes by air oxidation gave the ethers PhR in good yield [63].

Irradiation of the benchrotrene bisphosphite complexes (4.38; *o*, *m*, *p*, n = 2; *m*, n = 3) gave the corresponding di-bridged benchrotrene analogues (4.39; *o*, *m*, *p*, n = 2; *m*, n = 3) while the same reaction with the biphosphites (4.38; *o*, *m*, *p*, n = 1) gave the singly-bridged complexes (4.40; *o*, *m*, *p*). The failure of the second bridge to be formed in these cases was ascribed to steric hindrance. Irradiation of the symmetrical triphosphite complex (4.41) gave the di-bridged product (4.42) rather than a tri-bridged product [64].



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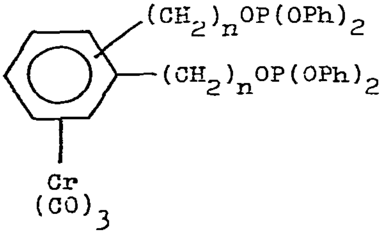

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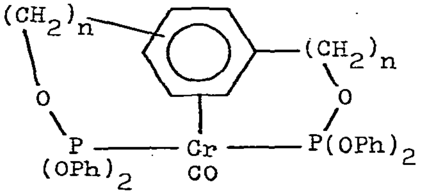

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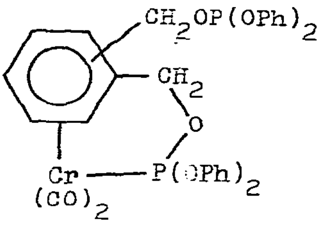
Difluorophosphite derivatives of benchrotrene were converted to the corresponding bridged complexes on UV irradiation in ether. Thus the tris(difluorophosphite) complex (4.43) gave the



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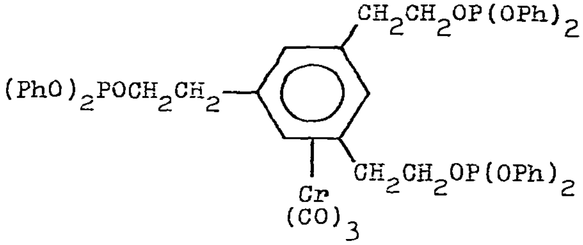

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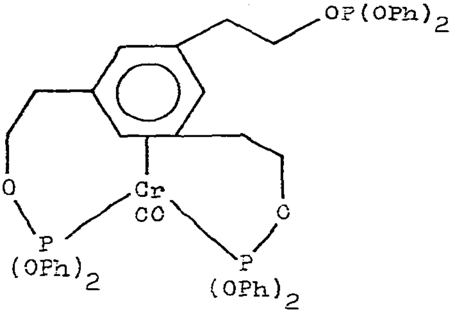

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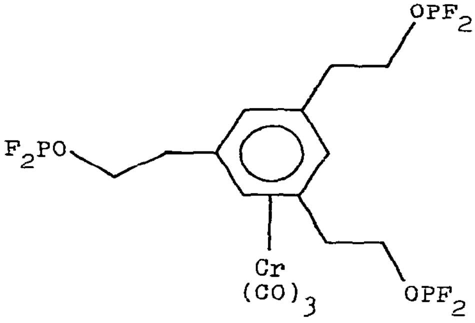

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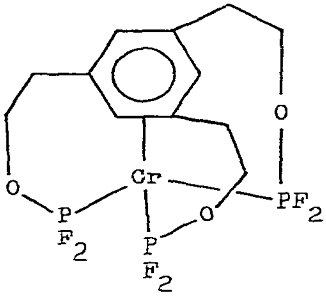

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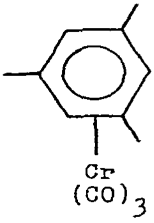

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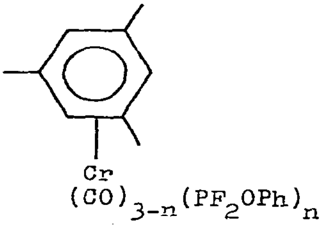
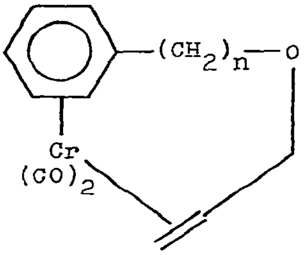


4.46

tri-bridged benchrotrene analogue (4.44), di-bridged and singly bridged complexes were formed in the same way. Irradiation of tricarbonyl(η-mesitylene)chromium (4.45) with phenyldifluorophosphite gave a mixture of mono-, di-, and tri-carbonyl displacement products (4.46; n = 1 - 3). The structure of the complex (4.44) was determined by X-ray analysis [65, 66].



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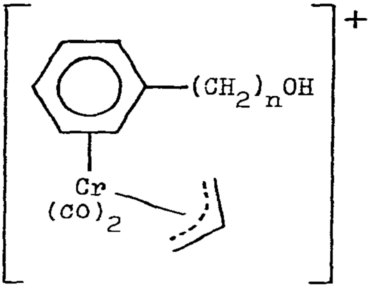

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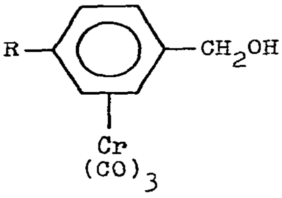
The bridged benchrotrene analogues (4,47; n = 0, 1) and methyl derivatives of these complexes were treated with aqueous tetrafluoroboric acid in ether to give the allyl benchrotrene analogues (4.48) with cleavage of the bridge [67].

The benchrotrenylcarbinols (4.49; R = Me, OMe) combined with acetonitrile and benzonitrile in the presence of sulphuric acid at -15°C to form the amide complexes (4.50; R^1 = Me, OMe; R^2 = Me, Ph). The reaction involved a carbenium ion intermediate stabilized by the α-benchrotrenyl group [68].

Tricarbonylchromiumphenyldimethylsulphonium, phenyldimethylsulphonium and 4-nitrophenyldimethylsulphonium tetrafluoroborates were treated with benzophenone in the presence of potassium t-butoxide. High yields of the oxirane (4.51) was obtained from the uncomplexed ylides but in the presence of the tricarbonylchromium group the olefin (4.52) was formed in high yield. The different reaction mechanisms were discussed and explained in terms of the strong electron withdrawing effect of the tricarbonylchromium group [69].



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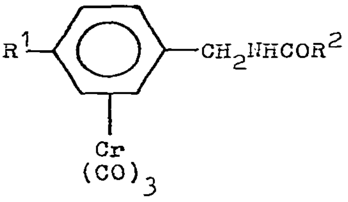

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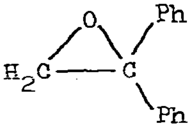

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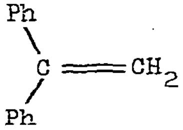
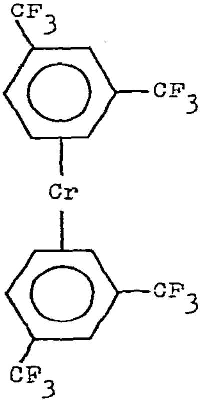


4.52

The reactivity of the formyl group was enhanced when salicylaldehyde was complexed with molybdenum in the compound (η-salicylaldehyde)tricarbonylmolybdenum. The effect was ascribed to the electron-withdrawing character of the metal atom which increased the carbonium ion character of the formyl carbon atom [70].

5. (η-C_6H_6)$_2$Cr

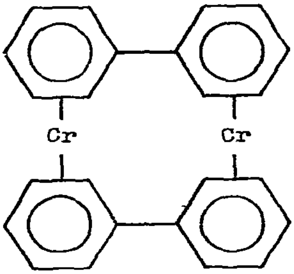
The reactions between metal atoms and ligands containing the cyclopropane group have been examined. Cyclopropylbenzene combined with chromium atoms to form bis(η-cyclopropylbenzene)chromium [71].



5.1

Chromium atoms and 1,3bis(trifluoromethyl)benzene vapour were cocondensed on a cold finger to give the bis(η-benzene)chromium complex (5.1) in 44% yield [72].

The η-biphenyl-chromium complexes (5.2, 5.3 and 5.4) were prepared by cocondensation of chromium atoms with biphenyl. The ^{1}H NMR spectra of the complexes were recorded and interpreted. The ESR spectra of the mono- and di-cations of the complexes (5.2 and 5.5) were recorded in solution and in glassy media. The ESR spectra were interpreted and compared to those of the ferrocene analogues [73].



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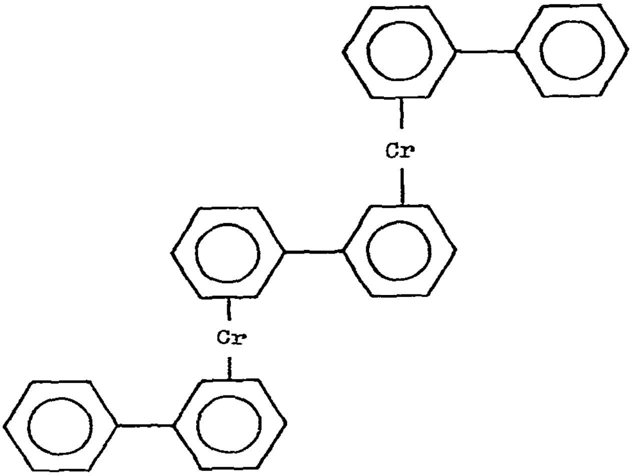

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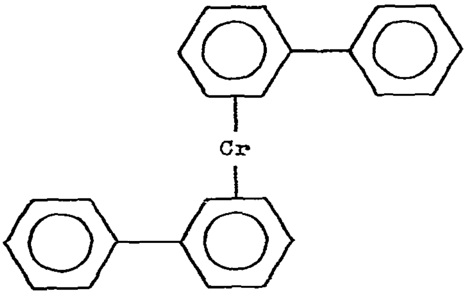

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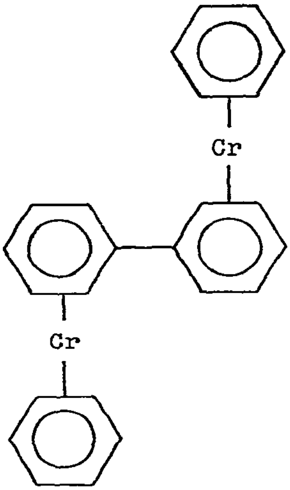

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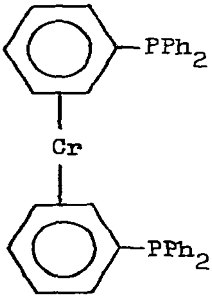

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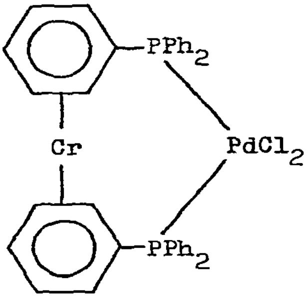
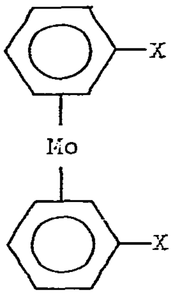


5.7

Reaction of chromium vapour with triphenylphosphine gave the chromium complex (5.6) in low yield. Treatment of the bis(triphenylphosphine) derivative (5.6) with bis(benzonitrile)-dichloropalladium gave the palladium complex (5.7) [74].

Cocondensation of molybdenum atoms and chlorobenzene or dimethylaniline vapour gave the corresponding bis(η-benzene)-molybdenum complexes (5.8; X = Cl, NMe_2) respectively in yields of up to 55% [75].

Various electrical properties, including the dielectric constant, the thermo emf and the temperature dependence of the a.c. conductivity, have been determined for bis(η-benzene)chromium chloride (5.9; R = H, X = Cl), bis(η-mesitylene)chromium phenolate (5.9 ; R = Me, X = OPh) and benchrotrene. The complexes (5.9) were n-type semiconductors while benchrotrene was a p-type semiconductor [76].



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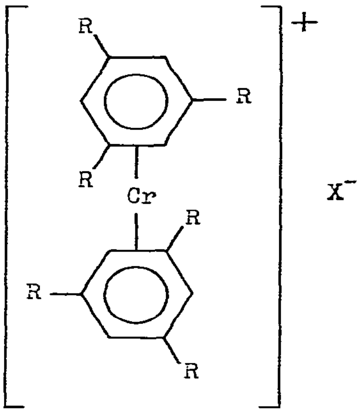


5.9

A series of bis(η-benzene)- and (η-olefin)-chromium complexes were oxidized and reduced electrochemically. The oxidations carried out in dichloromethane at a platinum electrode were chemically reversible [77].

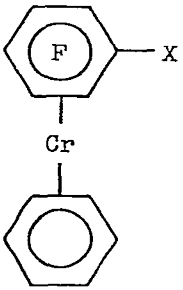
The heats of thermal decomposition and iodination were determined and used to calculate the standard enthalpies of formation of (η-1,3,5-$C_6H_3Me_3$)$_2$Cr, (η-C_6Me_6)$_2$Cr, (η-1,2,3,4,4a,8a-naphthalene)$_2$Cr and (η-1,2,3,4,4a,8a-naphthalene)Cr(CO)$_3$. A vacuum sublimation microcalorimetric technique was used to determine the enthalpies of sublimation of the same molecules. This data was used to evaluate the bond enthalpy contributions to the metal-ligand bond in the gaseous metal complexes, the values were: (η-C_6Me_6)-Cr (155 ± 7); (η-$C_6H_3Me_3$)-Cr (151 ± 6); (η-1,2,3,4,4a,8a-$C_{10}H_8$)-Cr (145 ± 6) k J mol^{-1} [78].

Bis(η-benzene)chromium has been pyrolyzed at 340-400°C and the first order rate constant determined [79].

The thermal decomposition of bis(η-benzene)chromium, bis(η-mesitylene)chromium and bis(η-ethylbenzene)chromium was studied in the presence of benzene, styrene, biphenyl and naphthalene [80].

(η-Benzene)(η-pentafluorobenzene)chromium has been lithiated and the lithio intermediate (5.10; X = Li) treated with acetylchloride, ethyl formate, ethyl chloroformate, furoyl chloride and acetaldehyde to give the organic derivatives (5.10; X = COMe, CHO, CO_2Et, CO.C_4H_3O, CHOHMe) respectively. The dilithio intermediate (5.11; X = Li), formed by lithiation of (η-benzene)-(η-1,2,3,4-tetrafluorobenzene)chromium (5.11; X = H), was condensed with ethyl chloroformate to give the corresponding diester (5.11; X = CO_2Et) [81].

As part of an investigation of the hydrogenation of (η-arene)-transition metal complexes, the hydrogenation of the dimer $[(\eta^6\text{-}C_6H_5Me)Mo(\eta^3\text{-}C_3H_5)Cl]_2$ has been examined. Hydrogenation occurred exclusively and irreversibly at the allyl ligand to form propylene [82].



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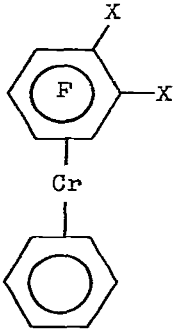
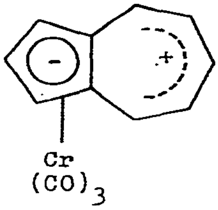


5.11

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

The structure of tricarbonyl(η-4,6,8-trimethylazulene)-chromium has been determined by ^{13}C NMR studies and by a single crystal X-ray analysis. It was confirmed that the chromium was bonded only to the five membered ring (6.1) and not to the seven membered ring (6.2) of the ligand [83].

The crystal and molecular structure of the methoxy bridged complex (η^3-cycloheptatrienyl)dicarbonylmolybdenumtris(μ-methoxo)-(η^7-cycloheptatrienyl)molybdenum (6.3) has been determined by



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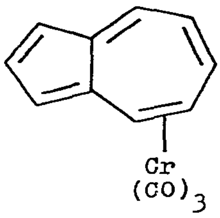

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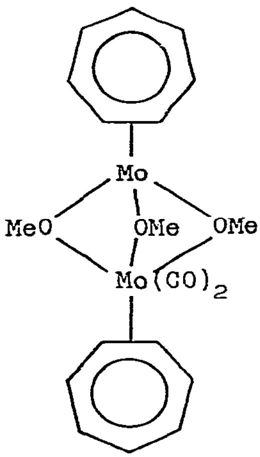

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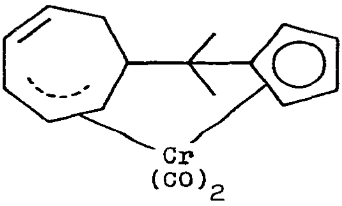


6.4

X-ray crystallography. The Mo—Mo distances indicate a single-bond but the Mo—O—Mo bond angles do not suggest a metal-metal interaction [84].

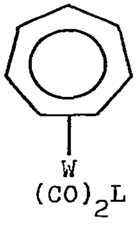
Mass spectrometric fragmentation of tricarbonyl(η-toluene)-chromium and tricarbonyl(η-cycloheptatriene)chromium gave the ion $[(C_7H_8)Cr]^{+\cdot}$. A deuterium labelling study indicated that the structure of the ion generated from the toluene complex was $[MeC_6H_4\text{-}CrH]^+$ while appearance-potential measurements and fragmentation patterns suggested that the ion generated from the cycloheptatriene complex did not have the same structure [85].

An investigation of the bonding in tricarbonyl(η-cycloheptatriene) complexes of the Group VIA metals has been carried out using He-I and He-II photoelectron spectra in conjunction with quantum-mechanical calculations. A general agreement between computed and measured ionization energies was found for molecular orbitals mainly ligand in character. Similar correlations did not hold for the highest energy orbitals which were mainly metal _d_ based [86].

The structures of the triply thiolato bridged complexes tricarbonylmolybdenum-tris(η^2-t-butylthio)(η^7-cycloheptatrienyl)-molybdenum and tricarbonylmolybdenum-tris(η^2-n-butylthio)-(η^7-cycloheptatrienyl)molybdenum were determined by X-ray analysis [87].

Irradiation of tricarbonyl(η-cycloheptatriene)chromium with 6,6-dimethylfulvene gave a mixed (η-cycloheptadienyl)(η-cyclopentadienyl)chromium complex (6.4) which was characterized by ^1H and ^{13}C NMR spectroscopy. A similar reaction was reported for 6,6-diphenylfulvene [88].

Reaction of the η-cycloheptatrienyl complexes (6.5; L = CO, Br) with triphenylphosphine and hydrazine gave the dicarbonyltungsten complexes (6.5, L = PPh_3 and N_2H_4) respectively. Similar reactions were carried out with triphenyl-arsine and -stibine. The binuclear complex $[(\eta\text{-}C_7H_7)W(CO)_3]_2$ was prepared electrochemically [89].



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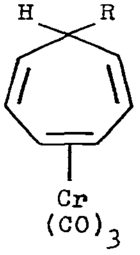

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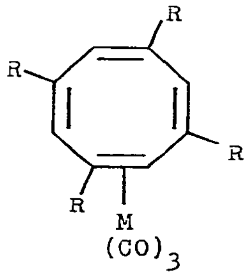


6.7

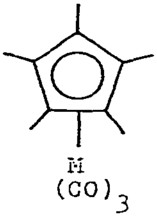
Reaction of tricarbonyl(η-cycloheptatrienyl)chromium tetrafluoroborate with a series of ketones in the presence of bases, such as hydroxide or fluoride ion, gave the tricarbonylchromium derivatives [6.6; R = CH_2COMe, CHMeCOMe, $CH(CHMe_2)COMe$]. These derivatives were formed by nucleophilic addition of the enolate ion to the η-cycloheptatrienyl ligand [90].

The mechanism of metal migration in the fluxional (η-cyclooctatetraene)-chromium and -molybdenum complexes (6.7; M = Cr, W; R = H, Me) has been reinvestigated by ^{13}C NMR spectroscopy using the Forsen-Hoffman spin-saturation method. It was concluded that metal migration proceeded by both 1,2- and 1,3-shifts [91].

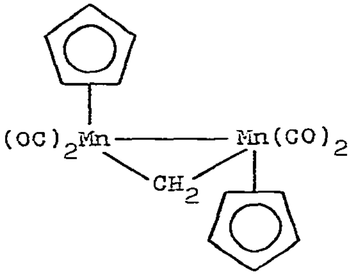
7. (η-C_5H_5)Mn$(CO)_3$

(i) Formation

An improved route to pentamethylcymantrene (7.1; M = Mn) and the corresponding rhenium compound (7.1; M = Re) has been reported. Pentamethylcyclopentadiene was heated with manganese carbonyl or methylmanganesepentacarbonyl in boiling n-decane to give the product (7.1; M = Mn) in 30% yield [92].



7.1



7.2

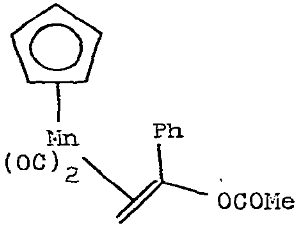
An improved preparation of cymantrene has been reported. Cyclopentadiene was treated with manganese(II) chloride and metallic manganese in THF in the presence of 0.01-5% by weight of titanium(IV) chloride or tetrabutoxytitanium and the intermediate formed was treated with carbon monoxide to give the product [93].

7. (ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structure of the binuclear manganese complex (7.2) has been determined by X-ray crystallography. It was found that ^{13}C NMR spectroscopy was a convenient technique for distinguishing between dimetallocyclopropanes of this type and Fischer-type carbenes as well as from μ-alkylidene complexes without metal-metal bonds [94].

The crystal and molecular structure of the cymantrene analogue (7.3) has been determined by X-ray crystallography [95].

The structure of the dimethylphosphine sulphides (7.4; n = 1,2) have been determined by X-ray crystallography. The manganese-phosphorus bonds were found to have appreciable π-character [96].



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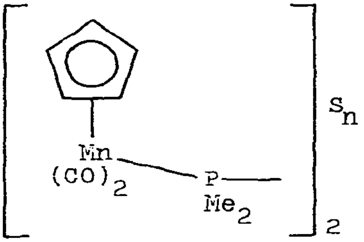
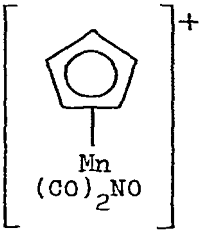


7.4

The nitrosyl cation (7.5) combined with liquid ammonia to give a neutral carbamoyl compound (7.6) the structure of which has been determined by X-ray crystallography [97].

Irradiation of tricarbonyl(η-methylcyclopentadienyl)manganese with hexa-2,5-diyne gave the dimeric dicarbonylmanganese complex (7.7). The structure of this complex (7.7) was determined by X-ray analysis. Structural and infrared data suggested that the alkyne ligand was a good σ-donor but a poor π-acceptor [98].

The mass spectrometric fragmentation of ferrocenyl- and cymantrenyl-chalcones (7.8 and 7.9) exhibited metal-ligand bond cleavage as the principal fragmentation process, the alternative



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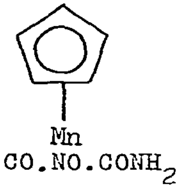
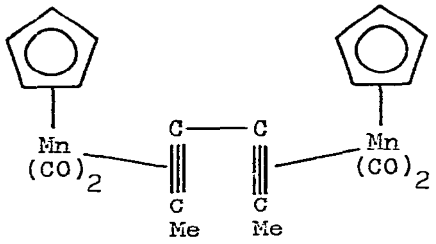


7.6

"chalcone" mode of fragmentation was weak because the positive charge was localised preferentially on the metal atom [99].



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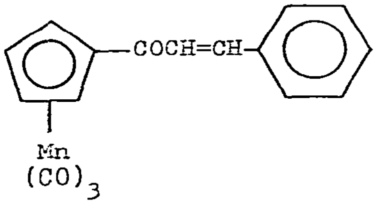

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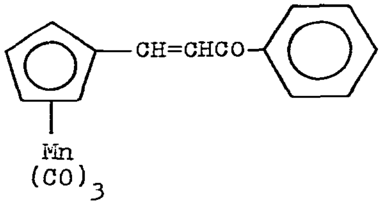

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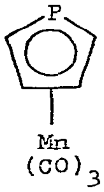

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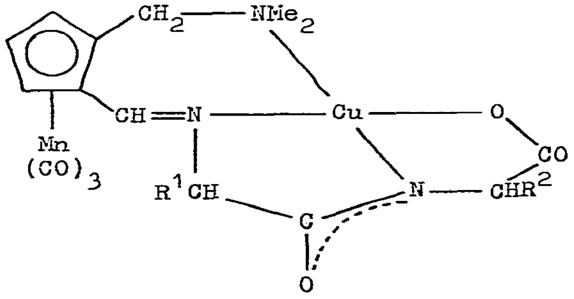


7.11

The ^{1}H NMR spectra of phosphacymantrene (7.10) orientated in the nematic phases of liquid crystals have been recorded and interpreted. The results indicated that the ring skeleton was essentially planar. The H–H and H–P direct dipolar coupling constants were used to determine the relative proton-proton and proton-phosphorus distances [100].

The optical isomers of 2-formyl(N,N-dimethylaminomethyl)-

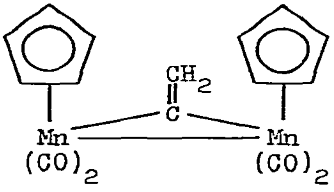
cymantrene were separated by liquid chromatography on silica gel of the Cu(II) chelates [7.11; $R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = H$, $R^2 = CHMe_2$] formed from the Schiff bases and a dipeptide. Hydrolysis of the chelates (7.11) gave optically pure enantiomers of 1,2-disubstituted cymantrene [101,102].

Tricarbonyl(η-cyclopentadienyl)manganese and dicarbonyl(η-cyclopentadienyl)(dinitrogen)manganese were separated on a preparative scale by high-pressure liquid chromatography at -15° [103].

7. (iii) General Chemistry

Some aspects of the chemistry of cymantrene have been compared with those of appropriate inorganic compounds [104].

Gas chromatography has been used to determine methylcymantrene at low levels in biological fluids and tissues. The samples were extracted into hexane containing biphenyl as internal standard. Flame ionization detection was used and this enabled ≤ 1-2 ppm of methylcymantrene in tissue to be determined easily. The procedure was used to show that the enzymic oxidation of methylcymantrene by rat liver microsomes was dependent on cytochrome P 450 [105].



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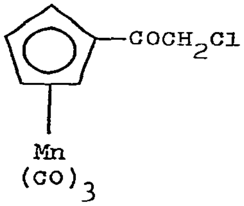

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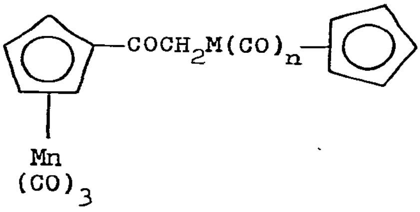
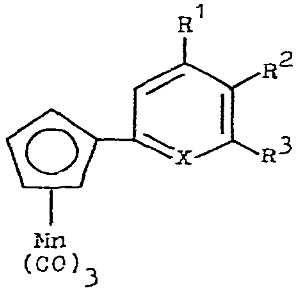


7.14

Dicarbonyl(η-cyclopentadienyl)tetrahydrofuranmanganese in tetrahydrofuran was irradiated in the presence of acetylene and hydroxide ion to give the bridged complex (7.12). The CCH_2 ligand symmetrically bridged the two manganese atoms and it had a carbon-carbon bond length of 1.31 Å, typical of a double bond. There was an 11° twist of the ligand about the double bond [106].

Cymantrenoylmethyl chloride (7.13) has been treated with the sodium salts $NaMo(CO)_3(\eta\text{-}C_5H_5)$, $NaW(CO)_3(\eta\text{-}C_5H_5)$ and $NaFe(CO)_2(\eta\text{-}C_5H_5)$ to give the mixed metal complexes (7.14; M = Mo, W, n = 3; M = Fe, n = 2) [107].



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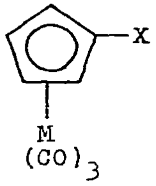
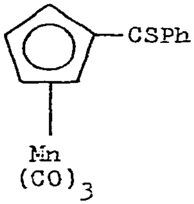


7.16

Acetylcymantrene has been cyclized with α,β-unsaturated ketones, $R^1CH = CR^2COR^3$, in acetic and perchloric acids to form the pyrylium complexes (7.15; R^1,R^3 = Ph, p-MeO.C_6H_4, R^2 = H; R^1 = H, R^2R^3 = CO.C_6H_4-o; X = $O^+ \cdot ClO_4^-$). Treatment of these complexes with ammonia and aniline gave the corresponding pyridines (7.15; X = N, NPh^+ ClO_4^-) [108].



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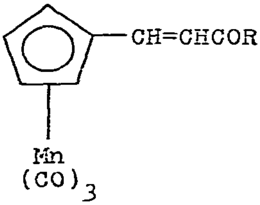

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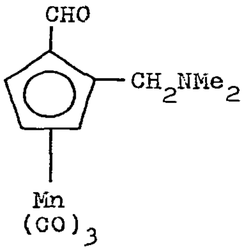


7.19

Treatment of the acid chlorides (7.16; X = COCl; M = Mn, Re) with $NaM(CO)_5$ (M = Mn, Re) gave the corresponding η-cyclopentadienyl derivatives [7.16; R = $COM(CO)_5$] which decarbonylated to give the octacarbonyls [7.16; X = $M(CO)_5$] [109].

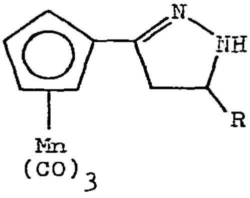
Reaction of benzoylcymantrene with phosphorus pentasulphide in carbon disulphide gave the thioketone (7.17) in good yield [110].

Treatment of formylcymantrene with a series of acetyl derivatives RCOMe [R = Ph, (η-C_5H_4)Mn$(CO)_3$, ferrocenyl, (η-CH=CHC_5H_4)Mn$(CO)_3$, (η-CH=CHC_5H_4)Fe(η-C_5H_5)] gave the corresponding olefins (7.18) [111].

1-(N,N-Dimethylaminomethyl)-2-formylcymantrene (7.19) was resolved into enantiomers and these isomers gave enantiomeric copper complexes with diglycine. The copper complexes were alkylated with acetaldehyde and then hydrolysed to give a mixture of dipeptides containing threonine and allo-threonine with an asymmetric yield of 92-98%. The enantiomeric copper complexes were used also to retroracemise the dipeptide (R,S)-alanine-R,S-(norvaline) [112].

Condensation of the pyrazolines (7.20; R = cymantrenyl, ferrocenyl) with benzaldehyde gave the corresponding 4-benzalpyrazolines (7.21) [113].

The reaction of (η-methylcyclopentadienyl)tricarbonylmanganese with bis(1,3-diphenyl-1,3-propane dionato)tin(II) in tetrahydrofuran gave bis(1,3-diphenyl-1,3-propanedionato)bis-(tetrahydrofuran)manganese(II) as one of the products. The



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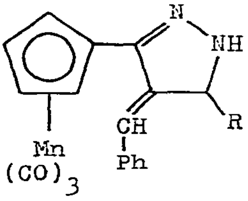

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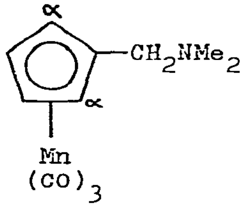

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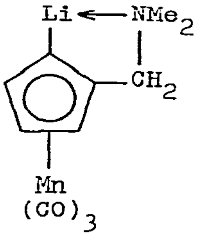

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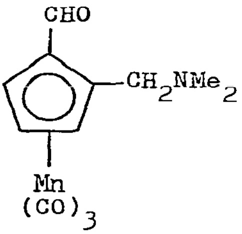

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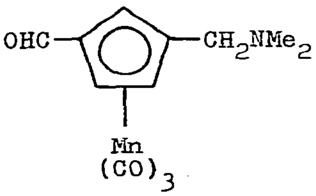

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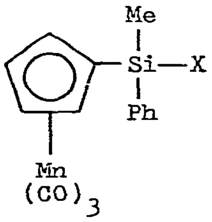


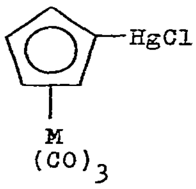
7.26

structure of this product was determined by X-ray analysis. The manganese atom was octahedrally coordinated by two chelating 1,3-diphenyl-1,3-propanedionato groups and two tetrahydrofuran molecules [114].

Lithiation of (N,N-dimethylamino)methylcymantrene (7.22) and treatment with N,N-dimethylformamide gave the 2-aldehyde (7.24). However when the lithio derivative (7.23) was quenched with deuterium oxide, converted again to the lithio intermediate, quenched again with deuterium oxide and then subjected to lithiation and treatment with N,N-dimethylformamide the predominant product was the 3-aldehyde (7.25) 70% yield. The 2-aldehyde (7.24) was a minor product, 30% yield. The exhaustive lithiation and deuteration had converted the α-hydrogen atoms in the original amine (7.22) to deuterium atoms which altered the course of a subsequent metallation [115].

The cymantrenylsilane (7.26; X = H) was chlorinated with palladium(II) chloride to form the chlorosilane (7.26; X = Cl) which was, in turn, treated with lithiated ferrocenylacetylene in THF to form the silylacetylene (7.26; X = C≡C.ferrocenyl) [116].

Mixed metal binuclear cymantrenes (7.28; M^1,M^2 = Mn, Re) were obtained by treatment of the mercurichloride (7.27; M = Mn, Re) with sodiorheniumpentacarbonyl or sodiomanganesepentacarbonyl [117].



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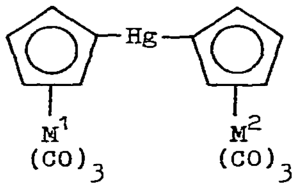
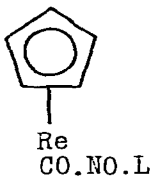


7.28

7. (iv) Analogues

The neutral formyl complex (7.29; L = CHO) underwent a Cannizzaro type reaction to give the binuclear ester (7.30) which was hydrolysed to the hydromethyl complex (7.29; L = CH_2OH) in the presence of methanol [118].

The manganese carbene cation (7.31) as the tetrachloroborate salt was treated with t-butylisocyanide at -50°C to give the adduct (7.32) characterized as the tetrachloroborate [119].



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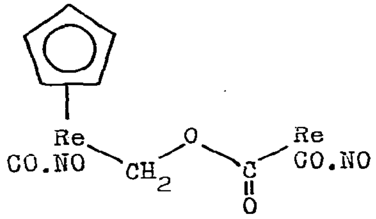

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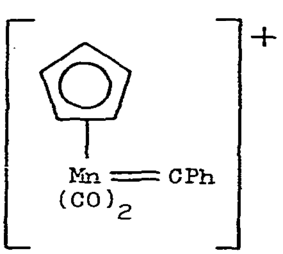
Reaction of di(carbonyl)(η-cyclopentadienyl)(tetrahydrofuran)rhenium with triphenylgermyl- and triphenylsilyl-phenylacetylene gave the rhenium complexes (7.33; M = Si, Ge, 7.34 and 7.35; X = CO, C=CHPh) [120].

The THF complex (7.36) derived from cymantrene combined with 9-diazoanthrone(10) to give a complex (7.37) containing the η^2-anthranylketone ligand. The crystal and molecular structure of the complex (7.37) was confirmed by X-ray crystallography [121].

Irradiation of phenalene with methylcymantrene gave the η^2-phenalene complex (7.38) [122].

Reaction of the (η-cyclopentadienyl)manganese complex (7.39) with the chlorophosphines, $ClPR_2$ (R = Ph, Et, OEt) and chlorodiphenylarsine gave the corresponding carbon-coordinated isocyano-



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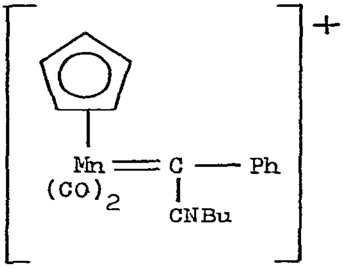

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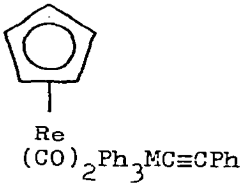

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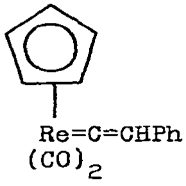

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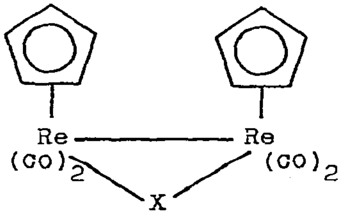

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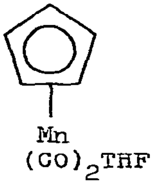

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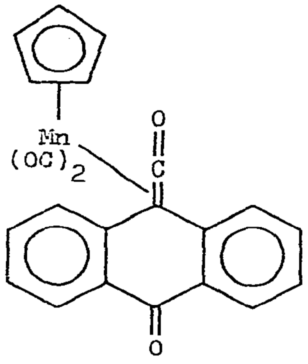

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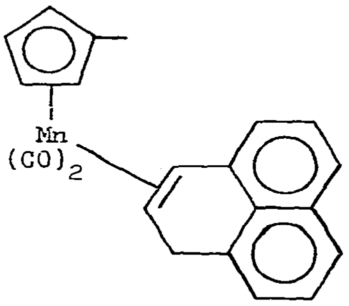

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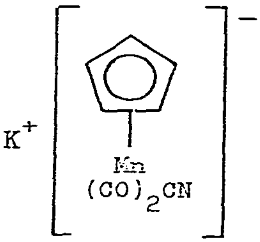

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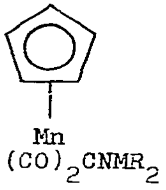

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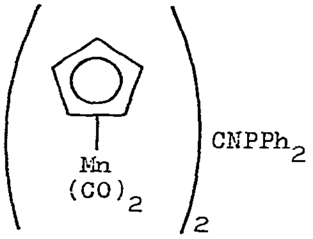


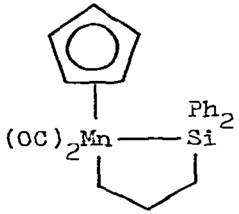
7.41

phosphines and arsine (7.40; M = P, R = Ph, Et, OEt and M = As, R = Ph) respectively. Treatment of the isocyanophosphine (7.40; M = P, R = Ph) with dicarbonyl(η-cyclopentadienyl)tetrahydrofuranmanganese gave a complex with an isocyanophosphine bridge (7.41) [123].

Cymantrene underwent a ligand exchange reaction on irradiation with diphenylsilacyclobutane to give the silane (7.42). The corresponding reaction with disilanes R_3SiSiR_3 gave the complex (7.43) [124].

Cymantrene has been irradiated with tin(II) chloride and THF to give the complex $(\eta\text{-}C_5H_5)Mn(CO)_2.SnCl_2.THF$ which on heating was converted to the tin complex (7.44; X = Cl), hydrolysis yielded the corresponding hydroxide (7.44; X = OH). Spectroscopic results suggested that these compounds contained a tin-manganese bond with carbenoid character [125].

Metallation of the cymantrene analogue (7.45; R = H) with an excess of n-butyllithium and subsequent treatment with methyl iodide and trimethylchlorosilane gave the phosphines (7.45; R = Me, $SiMe_3$). The trilithio species (7.45; R = Li) was invoked as the reaction intermediate [126].



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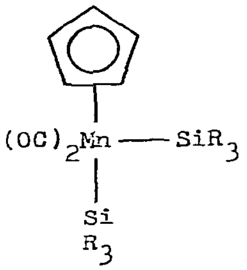

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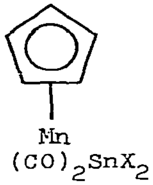

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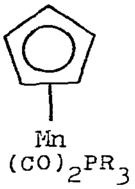

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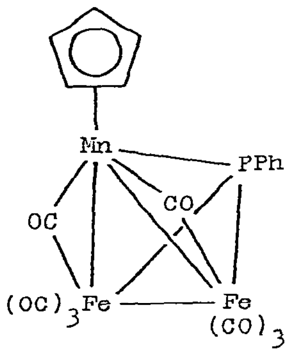

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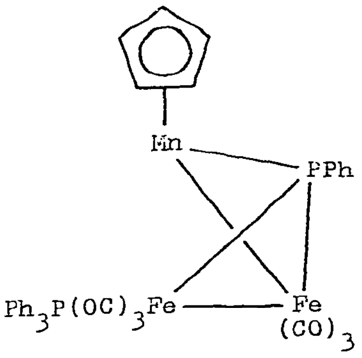

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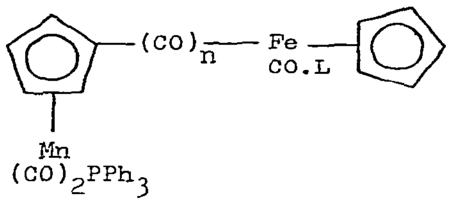

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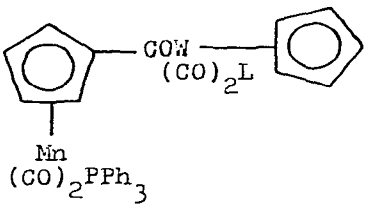
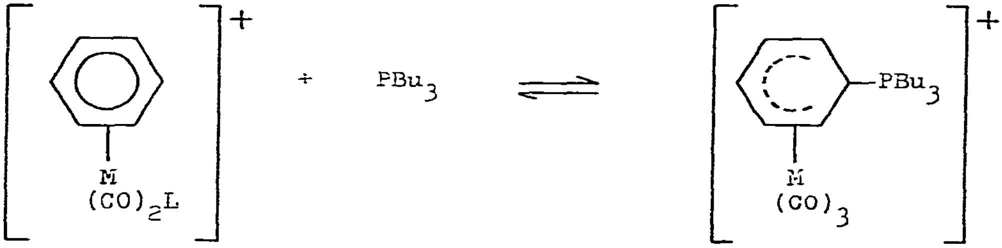


7.49

Attack on the trimetallic cluster complex (7.46) with triphenylphosphine led to cleavage of the iron-manganese bond and opening of the cluster to form the phosphine complex (7.47). The reaction was reversible allowing the original cluster complex to be reformed [127].

The mixed manganese-iron complexes (7.48; n = 0, 1; L = CO) underwent carbonyl ligand displacement on irradiation with triphenylphosphine to form the triphenylphosphine derivatives (7.48; n = 0, 1; L = PPh_3) [128].

Photolysis of the cymantrene analogue (7.49; L = CO) with triphenylphosphine gave the triphenylphosphine derivative (7.49; L = PPh_3) [129].



7.50

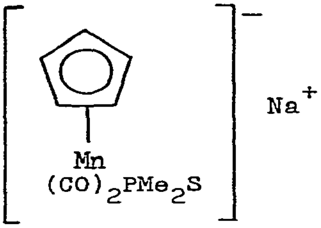
7.51

The nucleophilic addition of tributylphosphine to (η-arene)-manganese and -rhenium cationic complexes (7.50; M = Mn, Re; L = CO) to form (η-cyclohexadienyl)metal complexes (7.51; M = Mn, Re) has been the subject of a kinetic investigation. Activation parameters have been obtained for the forward and reverse reactions. The (η-cyclohexadienyl)manganese complex (7.51; M = Mn) was converted photochemically to the (η-arene)metal complex (7.50; M = Mn, L = PBu_3) [130].

Reaction of the (η-cyclopentadienyl)manganese derivative (7.52) with pentacarbonylchlororhenium gave the sulphur-rhenium bridged molecule (7.53). The structure of the bridged molecule (7.53) was confirmed by X-ray analysis [131].

Irradiation of cymantrenylcarbinols in the presence of diphosphines gave a series of thirteen diphosphine complexes (7.54; R^1, R^2 = H, Me, Et, Ph, CH_2Ph; n = 2, 3) which on treatment with trifluoroacetic acid formed the corresponding carbenium ions (7.55; R^1, R^2 = H, Me, Et, Ph, CH_2Ph; n = 2, 3). The ^{13}C and ^{31}P NMR spectra of the carbinols confirmed the equivalence of the two phosphorus atoms in the chelate diphosphine ligand while in the carbenium ions (7.55) they were non-equivalent. This effect was ascribed to changes in the geometry of the molecule on formation of the carbenium ions. Cymantrene carbinols with monofunctional phosphine ligands (7.56; R^1 = R^2 = Ph, R^1 = Me, R^2 = C_6H_4.Me-p; R^2 = Et, Ph, CH_2Ph) were protonated at manganese on treatment with trifluoroacetic acid [132].

Reaction of dicarbonyl(η-cyclopentadienyl)triphenylphosphine-rhenium with tin(IV) halides gave the 1:2 adducts (7.57; X = Cl, Br) [133].



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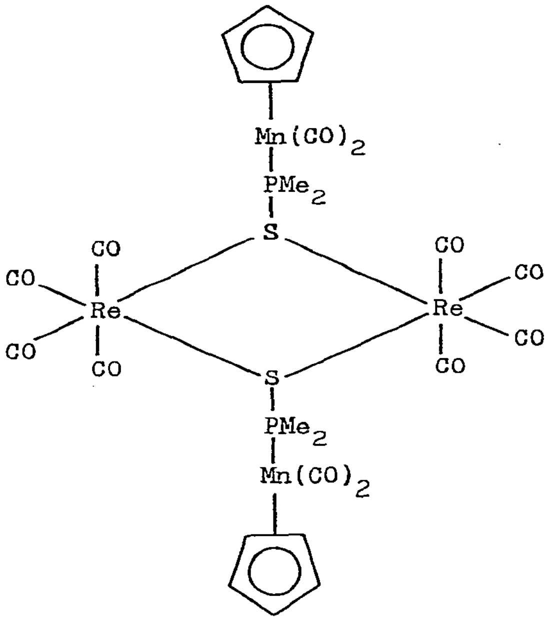

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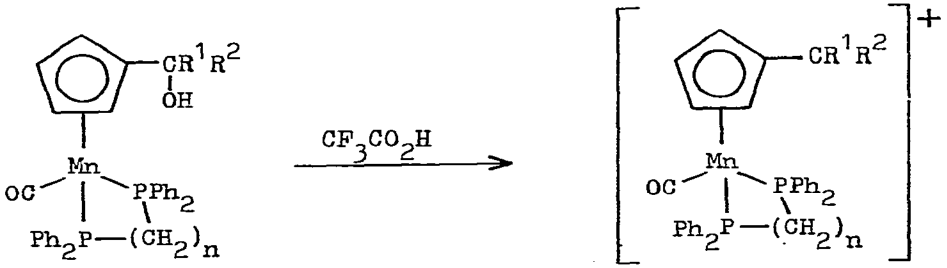

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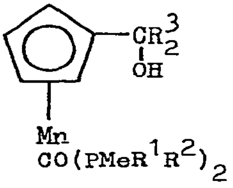

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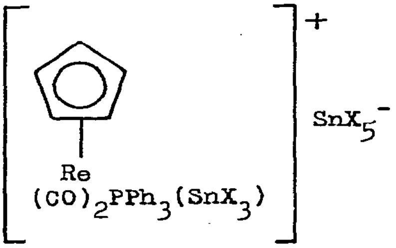

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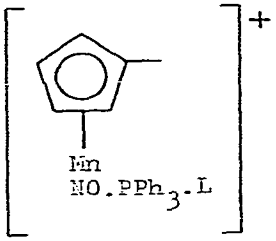

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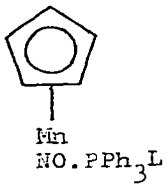

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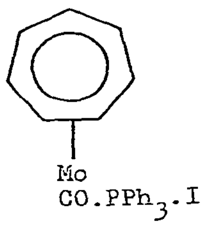

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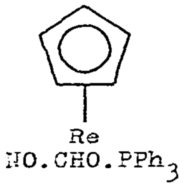

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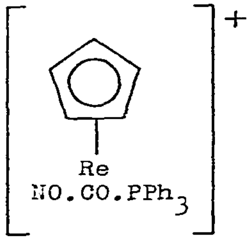

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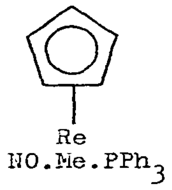


7.63

A number of ligand exchange reactions of the methylcymantrene analogue (7.58; L = CO) have been described. Cyanide, iodide, triphenylphosphine and triphenyltin ligands were involved and in a typical reaction sequence the cation (7.58; L = CO) was treated with sodium iodide to form the neutral iodide (7.59; L = I) and this was converted to the nitrile (7.59; L = CN) with sodium cyanide. The nitrile (7.59; L = CN) was in turn alkylated with $Et_3O^+BF_4^-$ to give the cation (7.58; L = CNEt). Some related reactions of the (η-cycloheptatrienyl)molybdenum complex (7.60) were described [134].

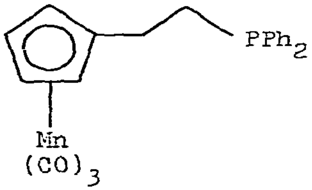
Treatment of the rhenium complex (7.61) with $MeSO_3F$ gave the carbonyl complex (7.62) and the methyl-rhenium derivative (7.63). Comparable results were obtained with other electrophiles. A mechanism was proposed for the formation of complex (7.63) via a cationic rhenium-carbene intermediate [135].

The rhenium formyl complex (7.61) has been characterized by X-ray crystallography. The formyl ligand was reduced to methyl with BH_3.THF and it underwent hydride loss with CF_3SO_3H to give the carbonyl ligand [136].

Irradiation of the cymantrenylethylphosphine (7.64) gave the bridged complex (7.65) by displacement of carbon monoxide [137].

Several metal carbonyl cations have been converted to the unstable neutral metal formyl complexes by treatment with LiEt$_3$BH at low temperatures. Thus the manganese and rhenium complex cations (7.66; M = Mn, Re) were converted quantitatively to the formyl complexes (7.67; M = Mn, Re). Reactions of the formyl complexes were investigated and were related to the mechanism of Fischer-Tropsch catalysis [138].

Ultraviolet irradiation of dicarbonyl(η-cyclopentadienyl)-triphenylphosphinemanganese and carbon disulphide gave the thiocarbonyl derivative (7.68) and irradiation with carbonyl sulphide gave a mixture of cymantrene and the thiocarbonyl compound (7.68). The effect of the carbonyl and thiocarbonyl ligands on the deuterium exchange properties of the η-cyclopentadienyl ring were investigated [139].



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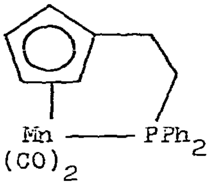

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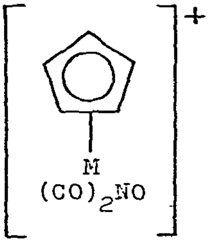

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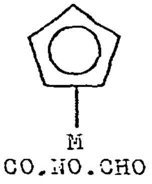

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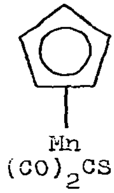
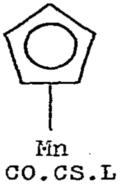


7.68

A procedure has been described for the conversion of the thiocarbonylcymantrene (7.69; L = CO) to the triphenylphosphine derivative (7.69; L = PPh$_3$) in 25% yield. A bidentate phosphine ligand was introduced in the same way [140].

Cymantrene has been irradiated in THF to form the intermediate (7.70 ; L = THF) which combined with carbon diselenide and triphenylphosphine to form the selenium and phosphorus derivatives (7.70; L = CSe, PPh_3) [141].

Direct iodination of the dimer $[(\eta\text{-}RC_5H_4)Mn(CO)NO]_2$, where R = H, Me, at room temperature gave the mixed carbonyl-nitrosyl-iodo complexes (7.71; R = H, Me; L = CO) as air sensitive solids. Triphenylphosphine smoothly displaced the carbonyl ligand to form the air stable derivatives (7.71; R = H, Me; L = PPh_3) [142].



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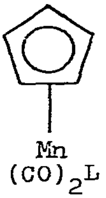

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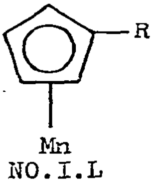

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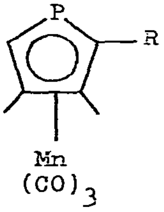
The acylation of 3,4-dimethylphosphacymantrene (7.72; R = H) with acyl chlorides in the presence of aluminium chloride gave the corresponding acyl complexes (7.73; R = Me, Pr^i, CH_2CMe_3, CH=CHMe, CH=CHPh, C_6H_4.p-F). The acetyl complex (7.73; R = Me) was reduced by lithium aluminium hydride and aluminium chloride to the ethyl derivative (7.72; R = Et) and by sodium borohydride to the 1-ethanol (7.72; R = CHOHMe). An iron tetracarbonyl complex (7.74) has been obtained by treatment of the phosphacymantrene (7.72; R = H) with $Fe(CO)_4THF$ [143].



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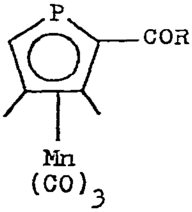

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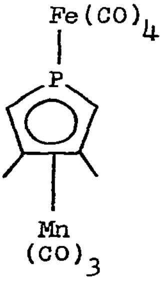


7.74

7. (v) Applications

The acute toxicity of methylcymantrene has been investigated. The LD_{50} values for mice were found to be 251.9 and 151.5 mg kg^{-1} for oral and i.p. administration respectively. Exposure of mice to methylcymantrene vapour at a level of 1 g m^{-3} for 1 hour caused 100% mortality. Organo-manganese compounds were found in the liver, kidney, lung and brain of these animals and the levels were dose-related. The two-week LC_{50} value was found to be 50.6 mg m^{-3} after a 4 hour exposure. Daily exposure of mice and rats , 6 or 22 hours per day, for 4 weeks at concentrations of 5-7 mg m^{-3} caused loss of weight and a high mortality [144].

The acute toxicity of methylcymantrene to small mammals has been investigated by dermal application of the complex to rabbits, rats and mice. The LD_{50} for rabbits was 140-795 mg kg^{-1}, moderate skin irritation was observed but eye irritation did not occur. Female rats were more sensitive than male rats or female mice to oral administration of the complex [145].

The use in gasoline of tricarbonyl(η-methylcyclopentadienyl)-manganese mixed with methylcyclopentadiene dimer or hydrogenated and alcohol derivatives of the same dimer were investigated. The addition of these mixtures at 0.125 g of manganese per gallon of gasoline improved the octane number [146].

The addition of tricarbonyl(η-methylcyclopentadienyl)manganese, a polyamine and paraffin oil to gasoline reduced the octane-requirement increase of the fuel [147].

Methylcymantrene and ferrocene showed a synergistic effect when used together as antiknock additives in gasoline. The research octane number of gasolines was increased to the same level by a mixture of the iron and manganese compounds as was achieved by the use of the more efficient manganese compound alone [148].

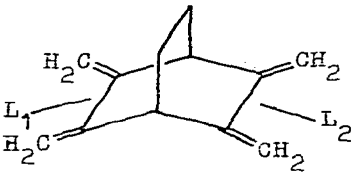
An investigation was carried out into how tricarbonyl(η-methylcyclopentadienyl)manganese caused the plugging of monolithic converters attached to automobile engines. It was concluded that the plugging was a physical rather than a chemical phenomenon and the manganese oxide was deposited primarily on the inlet edge of the converter [149].

8 (Acyclic-η-diene)Fe$(CO)_3$

Reaction of 2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]octane with nonacarbonyldiiron gave the tricarbonyliron complexes [exo-endo-, endo-exo- and exo-exo- 8.1; $L_1 = L_2 = Fe(CO)_3$] and (exo- and endo-8.2). The crystal structure of the complex (endo-8.2) was determined by X-ray analysis [150].

Complexes of the type Fe(η^4-diene)L_3 (L = phosphorus ligands), for example (8.3 and 8.4) were prepared from a variety of simple acyclic and cyclic dienes by metal atom evaporation techniques. Also, complexes of the type Fe(η^4-diene)$_2$L were prepared from acyclic dienes. The ^{31}P and ^{1}H NMR spectra of the complexes were recorded and discussed [151].

(η-Diene)tricarbonyliron complexes of the types (8.5, 8.6 and 8.7) were prepared by treating the dienes with pentacarbonyliron or enneacarbonyldiiron. The Moessbauer spectra of the complexes were recorded and discussed. The reaction of the



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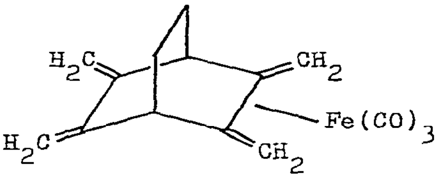

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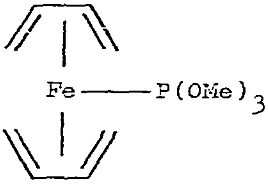

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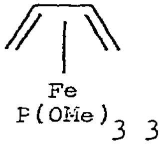

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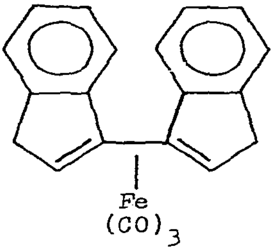

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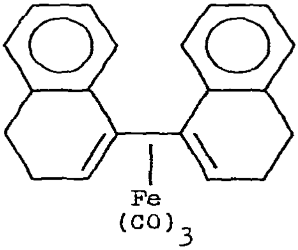

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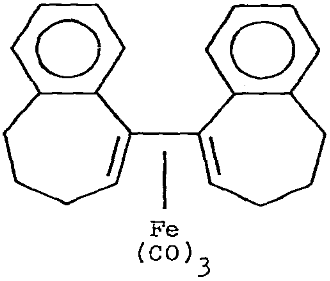

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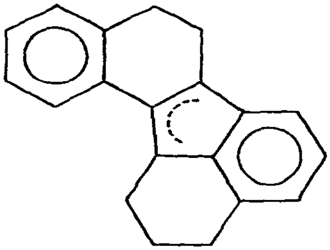


8.8

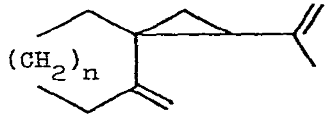
complexes with aluminium trichloride was investigated. For example, treatment of the complex (8.6) with aluminium trichloride gave the hydrocarbon (8.8) [152].

Photolysis of the methylenespiroalkanes (8.9; n = 0, 1, 2) with iron pentacarbonyl gave a mixture of the two (η-diene)iron complexes (8.10 and 8.11) together with a bis(η-allyl)diiron complex of a branched triene [153].

The mechanism of formation of α,β-unsaturated ketones in the reaction of allene and an alkyl bromide with disodium tetracarbonylferrate has been investigated. The reaction involved the insertion of allene into an iron-acyl bond and protonation of the resulting intermediate to form an (η-trimethylenemethane)-iron complex (8.12; R = H), which was characterized as the trimethylsilyl derivative (8.12; R = SiMe$_3$). The (η-trimethylene-methane)iron intermediate (8.12; R = H) rearranged by a sigmatropic shift to an (η-heterodiene)iron complex (8.13) which subsequently broke down to give the product [154].

Dienes and sulphur compounds were removed from a thermal cracking gasoline by treatment with triiron dodecacarbonyl [155].

The crystal and molecular structure of the (η-tetradeca-tetraene)diiron complex (8.14) has been determined by X -ray



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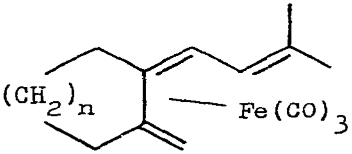

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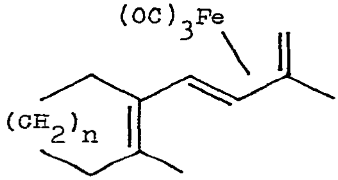

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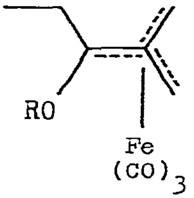

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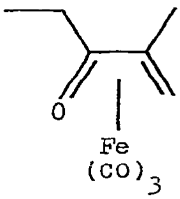

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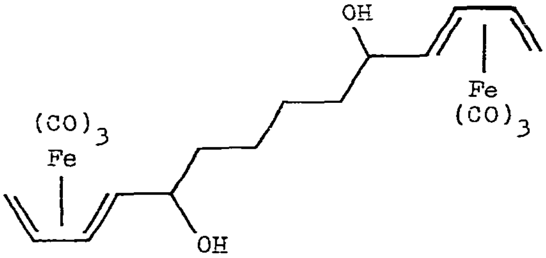


8.14

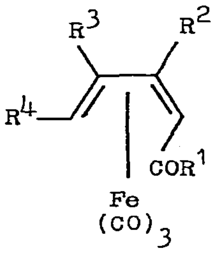
crystallography. The complex (8.14) contained two isolated (η-butadiene)iron groups [156].

(η-Benzylideneacetone)tricarbonyliron was heated with trans-1,3-pentadiene, trans,trans-2,4-hexadiene, 2,3-dimethylbutadiene and trans,trans-2,4-hexadienal to give the corresponding tricarbonyl(η-diene)iron complexes in yields of 54-96%. Cyclic dienes with planar diene units such as 1,3-cyclohexadiene, cycloheptatriene and cyclooctatetraene underwent the same reaction to give tricarbonyl(η-cyclodiene)iron products in 50% yield or better while cyclic dienes without a planar diene unit such as 1,4-cyclohexadiene, 1,3-cyclooctadiene and 1,5-cyclooctadiene were inert to (η-benzylideneacetone)tricarbonyliron. This difference was rationalized in terms of the high energy barrier to conversion of a dihapto-intermediate with a non-planar diene group to a tetrahapto-complex by twisting of the ligand [157].

The rates of isomerization of the tricarbonyliron derivative of the type (8.15; R^1 = Me or Ph; $R^2 = R^3 = R^4$ = H) which have *anti* acyl groups to the corresponding *syn* isomers (8.16) have been determined in the presence of strong acids and bases. In methanol the reactions were first order in methoxide or methyloxonium ion. Substitution of triphenylphosphine for carbonyl greatly reduced the rate of isomerization [158].

Relative partial rate factors have been obtained by a study of the competitive acetylation of tricarbonyl(η-diene)iron complexes with acetylchloride and aluminium chloride in dichloromethane. The factors are shown for the complexes (8.17 - 8.20) and the results indicated that substituent effects were small, that substituted carbon atoms were not acetylated and that acyl groups were strongly deactivating. The following sequence of relative reactivities was constructed: (η-*trans*-1-acetylbutadiene)tricarbonyliron < (η-1,4-dimethylbutadiene)tricarbonyliron < (η-cyclohexadiene)tricarbonyliron < (8.17) < [η-1-(*p*-acetylphenyl)butadiene]tricarbonyliron < (8.18) < (8.19) < (8.20) < (η-2-methoxybutadiene)tricarbonyliron < (η-bicycloheptadiene)-tricarbonyliron [159].

The photoelectron spectra of eight (η-butadiene)tricarbonyliron complexes, tricarbonyl(η-cyclobutadiene)iron and tricarbonyl-(η-trimethylenemethane)iron together with the spectra of the free butadiene ligands have been recorded. The perturbation energies of the π-orbitals introduced by the tricarbonyliron group have



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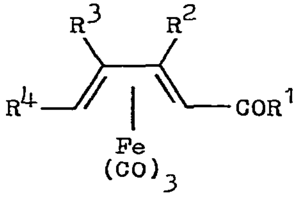

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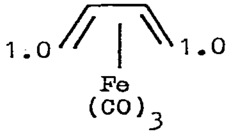

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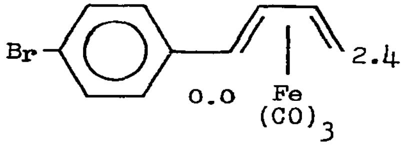

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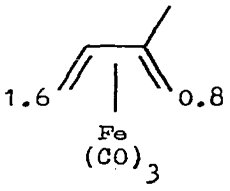

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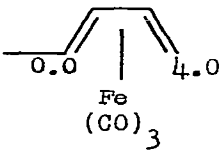

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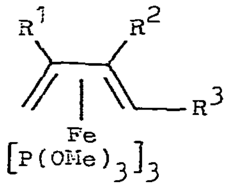

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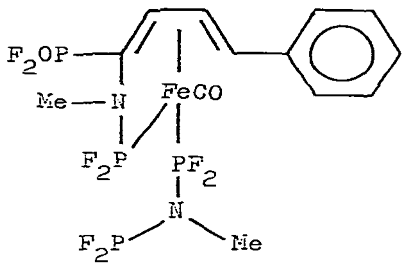
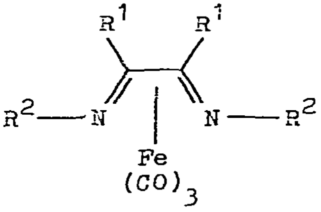


8.22

been determined as 0.89 and 0.22 eV for the first and second π-orbitals respectively. These perturbation energies were used together with the photoelectron spectra of the η-cyclobutadiene and the η-trimethylenemethane complexes to determine the π-ionization energies of the last two ligands as cyclobutadiene, 8.29 and 11.95 eV, trimethylenemethane, 8.36 and 11.79 eV [160].

The intramolecular exchange pathway in the fluxional (η-butadiene)iron complexes (8.21; $R^1 = R^2 = R^3 = H$, $R^1 = R^2 = Me$, $R^3 = H$, $R^1 = R^3 = Me$, $R^2 = H$) has been studied by ${}^{31}P\{^1H\}$ NMR spectroscopy. The results indicated a mechanism which involved cyclical exchange of the three phosphorus ligands and which may be described as diene rotation [161].

The reaction between (η-benzalacetone)tricarbonyliron and the ligand methylaminobis(difluorophosphine) gave a complex (8.22) containing a chelating ligand bonded to iron through both 1,3-diene and aminodifluorophosphine groups. The crystal and molecular structure of the complex (8.22) has been determined by X-ray diffraction analysis. The formation of the complex was explained by a mechanism involving an intramolecular Wittig-type reaction [162].



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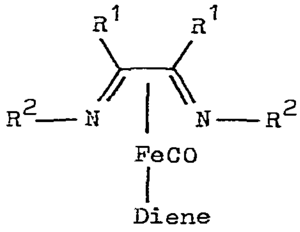

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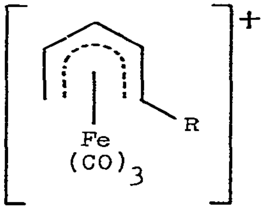

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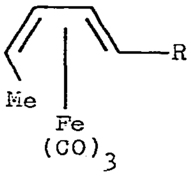

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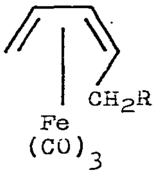

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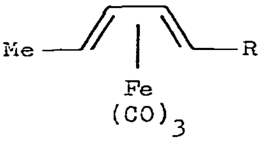

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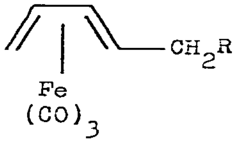

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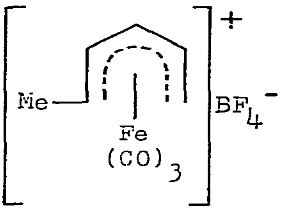


8.30

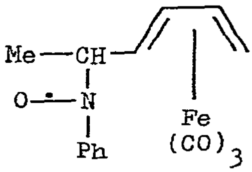
Photolysis of the tricarbonyl(1,4-diaza-1,3-diene)iron complexes [8.23; R^1 = H, R^2 = Me_2CH; R^1 = H, R^2 = C_6H_{11}; R^1 = Me, R^2 = C_6H_4OMe] in the presence of the dienes (butadiene, 2,3-dimethylbutadiene, 1,3-cyclohexadiene) gave the corresponding carbonyl(1,4-diaza-1,3-diene)(diene)iron complexes (8.24) [163].

A series of tricarbonyl(η-pentadienyl)iron fluoroborates [8.25; R = H, Me, Et, $CH(Me)_2$] was prepared and treated with the hydride donors sodium borohydride, sodium cyanoborohydride and lithium triethylborohydride. A series of products (8.26, 8.27, 8.28 and 8.29) was obtained but no products arising from attack at C(2), C(3) or C(4) of the pentadienyl ligand were isolated. Sodium cyanoborohydride gave products of retained configuration whereas lithium triethylborohydride gave tricarbonyl(η-diene)iron compounds of inverted configuration [164].

Treatment of (1-methylpentadienyl)tricarbonyliron tetrafluoroborate (8.30) with nitrosobenzene gave the nitroxide radical (8.31) which was examined by ESR spectroscopy. Reduction of nitroxide radical (8.31) with lithium aluminium hydride gave the corresponding amine (8.32)[165].

The treatment of 5-bromo-1,2-pentadiene with disodium tetracarbonylferrate gave, after protonation, 2-methylcyclopentenone in 30-40% yield. It was suggested that the intermediate in the reaction involved the delocalisation of electron density on to the organic ligand as an (η-tetramethylenemethane)iron species. This suggestion was confirmed by treatment of the reaction mixture with trimethylchlorosilane when the (η-trimethylenemethane)iron complex (8.33) was isolated [166].

Self consistent charge calculations were carried out on B_5H_9 and the 1- and 2-isomers of $[Fe(CO)_3B_4H_8]$ so that the contribution of the $Fe(CO)_3$ units to bonding in these species could be ascertained. It was concluded that the apical and basal $Fe(CO)_3$ units in the 1- and 2-isomers respectively have approximately one less electron involved in cluster bonding than the corresponding BH units [167].



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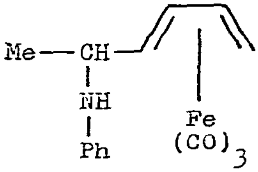

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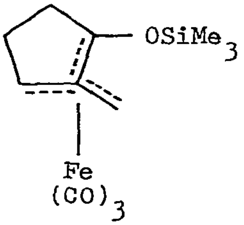


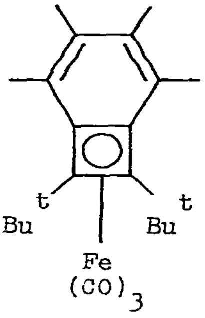
8.33

9. (η-C_4H_4)$Fe(CO)_3$

Nonempirical molecular orbital calculations were carried out on a variety of (η-cyclobutadiene) metal complexes. A detailed analysis of the frontier orbitals for tricarbonyl(η-cyclobutadiene)iron indicated that the molecule was best considered as an (η-C_4H_4)Fe fragment perturbed by the carbonyls rather than a tricarbonyliron moiety perturbed by the η-cyclobutadiene ring. For the η-cyclobutadieneiron fragment, when the total π system was considered there were six electrons in bonding metal-ring π-orbitals. It was concluded that the stabilization of the fragment and the π delocalization depended intimately upon the metal-ring bonding interactions and the phenomenon was referred to as "metalloaromaticity". The complexes (η-C_4H_4)$Cr(CO)_4$ and (η-C_4H_4)$Ni(CO)_2$ were considered and a comparison was made of η-C_4H_4 with η-C_5H_5 and η-C_6H_6 as ligands [168].

The character of the carbon-carbon bond in (η-butadiene)-tricarbonyliron has been investigated and the charge on manganese in cymantrene has been determined [169].

The crystal and molecular structure of the (η-benzocyclobutadiene)iron complex (9.1) has been determined by X-ray crystallography and compared with the structure of the free ligand. [170].



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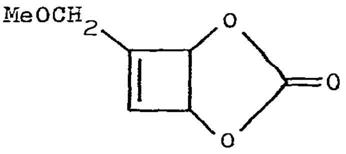

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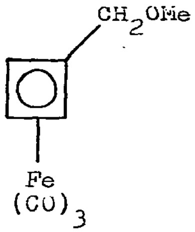


9.3

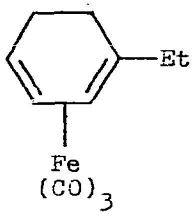
The tetracarbonyliron dianion combined with the bicycloheptenone ligand (9.2) to give the (η-cyclobutadiene)iron complex (9.3) [171].

10. (Cyclic-η-diene)Fe(CO)$_3$

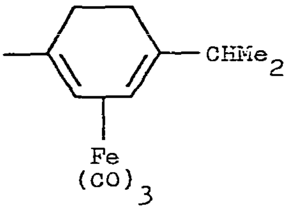
(i) Formation

The proportions of (η-cyclohexadiene)iron complexes obtained on thermal and photochemical isomerization of vinylcyclohexenes in the presence of iron pentacarbonyl have been compared. Under thermal conditions, 4-vinylcyclohexene gave the (η-1-ethylcyclohexadiene)iron complex (10.1) together with the 2-ethyl complex in the proportion 5:1. Under photochemical conditions the ratio of the same two products was 1:5. The thermal isomerization of α-phellandrene gave a mixture of the <u>endo</u> and <u>exo</u> forms of the (η-cyclohexadiene)iron complex (10.2) in the ratio 1:4, while the photochemical isomerization gave a ratio of 1:1 [172].

Bicyclo[4.2.1]nona-2,4,7-triene-9-one (10.3) formed several interesting chromium, molybdenum and iron complexes. Thus on heating with diiron nonacarbonyl in benzene at 60°C <u>exo</u>-tricarbonyliron complex (10.4) was obtained. Using methanol as solvent and a temperature of 30°C then the <u>endo</u>-tricarbonyliron complex (10.5; M = Fe) was formed. The ketone group in the bicyclic ligand of the complex (10.5; M = Fe) was reduced with borohydride to form the corresponding alcohol (10.6) which was further reduced by hydrogenation over palladium to the derivative (10.7). By contrast the <u>exo</u>-isomer (10.4) was inert to borohydride.



10.1



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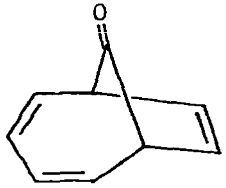

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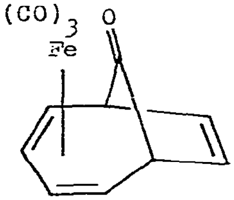

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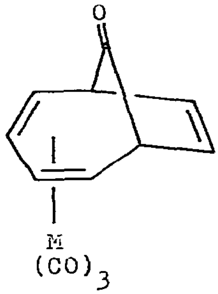

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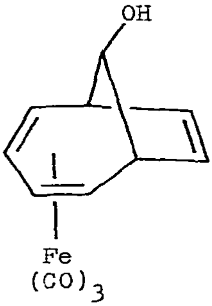

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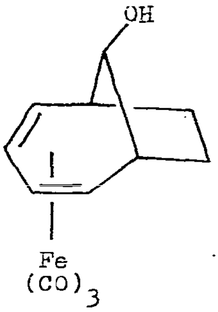

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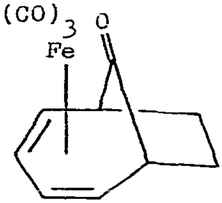

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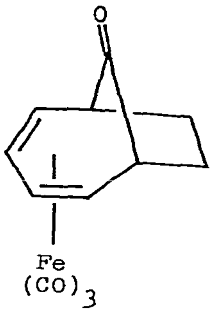


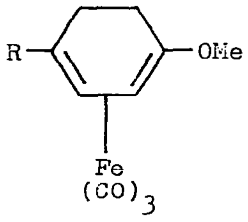
10.9

Both isomers (10.4 and 10.5; M = Fe) underwent hydrogenation over palladium to give the dienone complexes (10.8 and 10.9) respectively. Treatment of the original ligand (10.3) with $(MeCN)_3Cr(CO)_3$ gave the <u>endo</u>-tricarbonylchromium complex (10.5;

M = Cr). The corresponding molybdenum complex (10.5; M = Mo) was also prepared. A reaction between 9-methylenebicyclo-[4.2.1]nona-2,4,7-triene and $(MeCN)_3Cr(CO)_3$ gave the exo-tricarbonylchromium complex rather than the expected endo-isomer [173].

The tricarbonyliron complexes [10.10; R = $(CH_2)_2CO_2Me$, $(CH_2)_3CO_2Me$] were prepared by treatment of the parent diene with pentacarbonyliron. Treatment of the η-diene complexes with triphenylmethylium tetrafluoroborate gave the corresponding cationic complexes (10.11). Reaction of the tricarbonyliron derivatives (10.11) with sodio-dimethylmalonate gave the corresponding triester complexes (10.12) which on treatment with trimethylamine N-oxide removed the tricarbonyliron group [174].

The reaction of heptalene with benzylideneacetonetricarbonyliron gave the air-stable η-heptalene complex (10.13). Formylation of the complex (10.13) via the Vilsmeier method gave uncomplexed 1,6-heptalenedicarbaldehyde [175].



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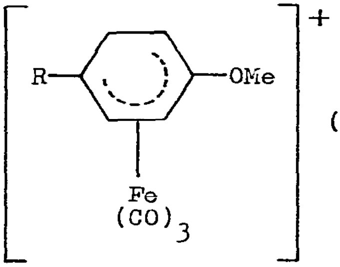

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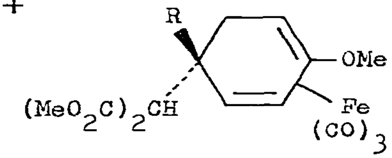

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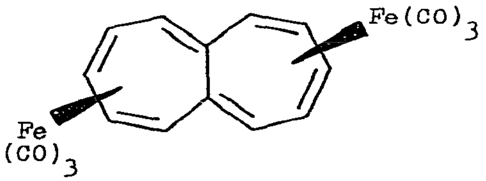

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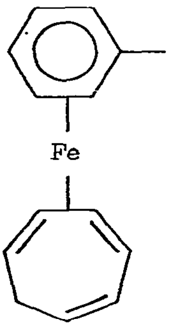

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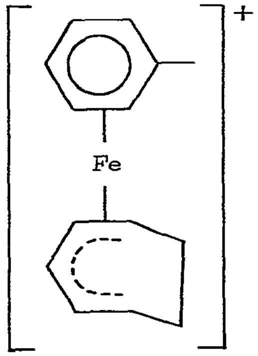

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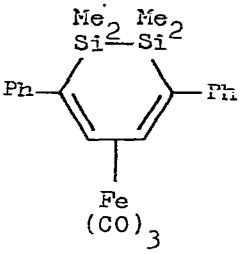

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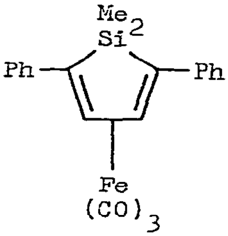

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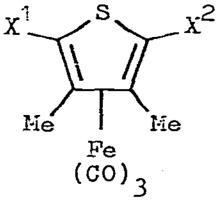

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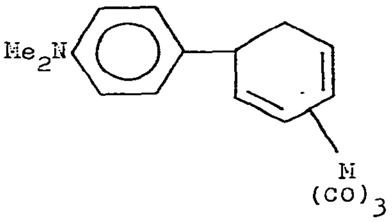

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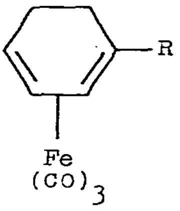

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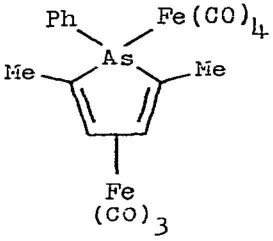


10.21

Cocondensation of iron atoms with toluene vapour at low temperatures and subsequent treatment with dienes such as 1,5-cyclooctadiene, cycloheptatriene and cyclooctatetraene gave the corresponding (η-arene)(η-diene)iron products of which the η-cycloheptatriene complex (10.14) was typical. Protonation of this complex gave the (η-cycloheptadienyl) cation (10.15) [176].

The (η-disilacyclohexadiene)iron complex (10.16) was obtained by heating the free ligand with iron pentacarbonyl in benzene, while the corresponding reaction in xylene at 160° gave a mixture of the cyclohexadiene complex (10.16) and the (η-silacyclopentadiene)iron complex (10.17). The cyclohexadiene complex (10.16) underwent ring contraction at 160° to form the cyclopentadiene complex (10.17) in separate experiments [177].

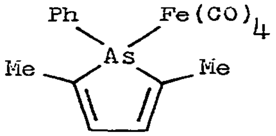
Irradiation of chloro- and bromo-thiophene-1,1-dioxides with iron pentacarbonyl gave initially the iron tricarbonyl complex of the ligand followed by stepwise reductive dehalogenation of the complexes. Thus 3,4-dibromo-2,5-dimethylthiophene-1,1-dioxide gave the iron tricarbonyl complex (10.18; $X^1 = X^2 = Br$), the mono-bromo complex (10.18; X^1 = Br, X^2 = H) and the dimethyl complex (10.18; $X^1 = X^2$ = H). The reaction involved insertion of irontricarbonyl into the carbon-bromine bond followed by displacement of the metal by a proton [178].

Direct reaction of the cationic complexes $[M(\eta-C_6H_7)(CO)_3]^+$, (M = Fe, Ru, Os), with N,N-dimethylaniline gave the corresponding η-diene complexes (10.19). A kinetic investigation indicated that the reactivity of the η-hexadienyl ligand, when coordinated to a metal, decreased in the order Fe>Os>Ru (41:3.6:1) [179].

Elimination reactions occurred on treatment of 3-bromocyclohexene, 3,4-dibromocyclohexene and 3,6-dibromocyclohexene with the iron carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, to give the tricarbonyliron complex (10.20; R = H). Similarly, the same reactions with 2-chloro-3-bromo-cyclohexene and 2,3-dichlorocyclohexene gave the tricarbonyliron complex (10.20; R = Cl) [180].

Reaction of 1-phenyl-2,5-dimethylarsole with triiron dodecacarbonyl in toluene gave the tricarbonyliron and tetracarbonyliron derivatives (10.21 and 10.22) respectively [181].

The cyclopentadienone complex (10.23) was prepared by the reaction of diiron nonacarbonyl with $PhC{\equiv}CCH(OEt)_2$ [182].



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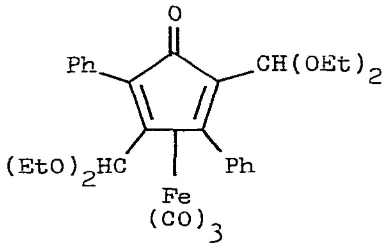
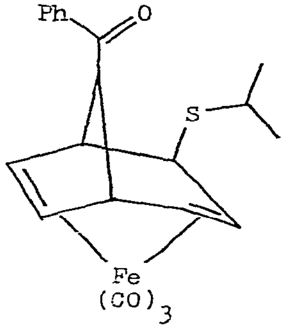


10.23

10. (ii) Spectroscopic and Physico-chemical Properties

The crystal structure of tricarbonyl[3-4:6-7-η-(2-isopropylthio-8-benzoylbicyclo[3.2.1]octadiene)]iron (10.24) was determined by X-ray analysis. The bicyclo-[3.2.1]octadiene ligand had M-exo stereochemistry at C(2) and it was coordinated to the iron atom *via* two π-alkene bonds [183].



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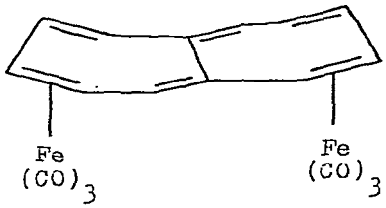
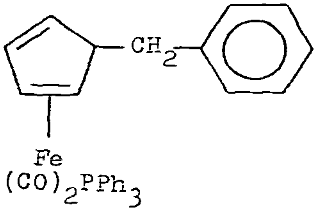


10.25

The crystal structure, molecular structure and conformation of bis-(η-heptalene)tricarbonyliron (10.25) has been determined by X-ray methods. The two outer butadiene moieties were *exo*-complexed with tricarbonyliron groups to form tetragonal pyramidal iron complexes. The seven-membered rings of the heptalene ligand have boat conformations with a flat central region [104].



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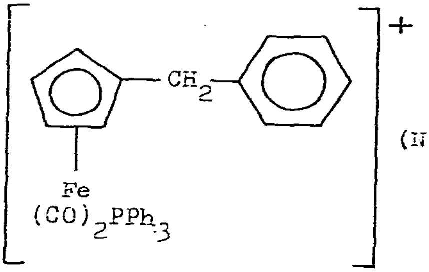
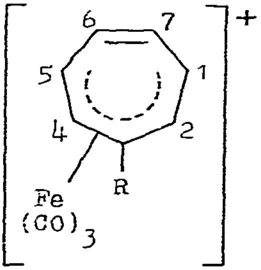


$(NC)_2C{=}C(CN){-}C(CN)_2^-$

10.27



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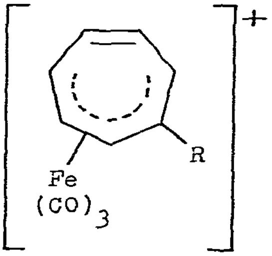

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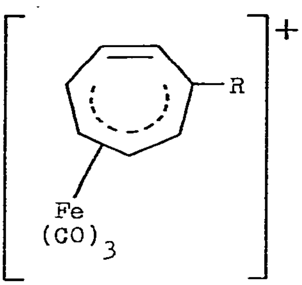

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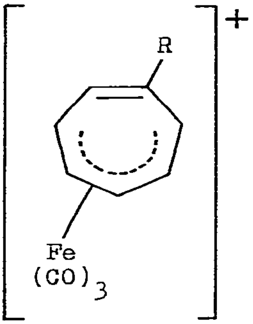


10.31

The (η-cyclopentadiene)iron complex (10.26) was attacked by tetracyanoethylene to form the (η-cyclopentadienyl)iron salt (10.27). The crystal and molecular structure of each of these complexes (10.26 and 10.27) has been determined by X-ray crystallography [165].

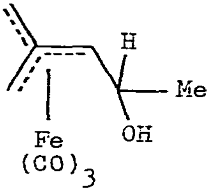
The negative ion mass spectra of η^4- and η^6-cycloheptatriene derivatives of iron, chromium, molybdenum and tungsten carbonyls exhibited molecular anions in high abundance and this was an apparent violation of the rare-gas rule. These mass spectra were explained and the fragmentation pathways were identified [166].

Infrared evidence indicated that in solution aluminium trihalides formed Lewis acid adducts at the iron atom in (η-cyclohexadiene)-, (η-cycloheptatriene)- and (η-cyclooctatetraene)-tricarbonyliron [167].

The fluxional behaviour and substituent site preferences in the cationic monosubstituted (η-tropylium)irontricarbonyl complexes (10.28; R = Me, Ph, cyclopropyl, Me_2CH) were studied by variable temperature ^{1}H and ^{13}C NMR spectroscopy. The relative stabilities of the four isomers (10.28-10.31) were determined. The substituent site preferences indicated that there was relatively little charge on the carbon atoms of the metal-complexed pentadienyl ring, but among the three different sites, the most positive charge resided at C_2 and C_4 [168].

Tricarbonyl(cross-conjugated dienyl)iron cations were generated from the precursor alcohols in strong acid solution and studied by ^{13}C and ^{1}H NMR spectroscopy. The 4-anti-methyl cation (10.33), generated from the alcohol (10.32), coordinated reversibly with fluorosulphonate ion to give the adduct (10.34). Other reactions of the cation (10.33) were also investigated [189].

Microcalorimetry has been used to determine several thermochemical parameters for tricarbonyl(η-cyclooctatetraene)iron and other complexes. The following values were obtained (kJ mol^{-1}) standard enthalpy of formation at 298°K, −237; enthalpy of sublimation at 298°K, 87; bond enthalpy for the gaseous metal complex [(η-C_8H_8)-Fe] 180 . The transferability of the enthalpy contributions between organoiron complexes was discussed [190]. The mechanisms of hydrogen shift in (η-cyclohexadiene)- and (η-cycloheptatriene)-irontricarbonyl were investigated [191].



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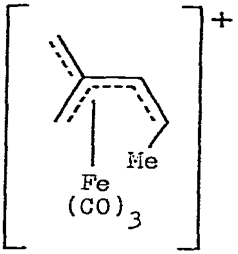

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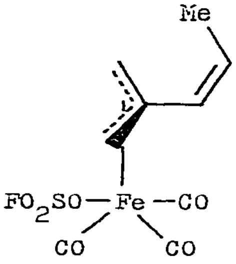
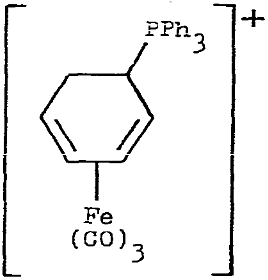
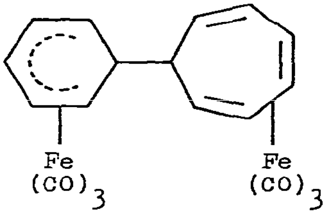


10.34

10. (iii) General Chemistry



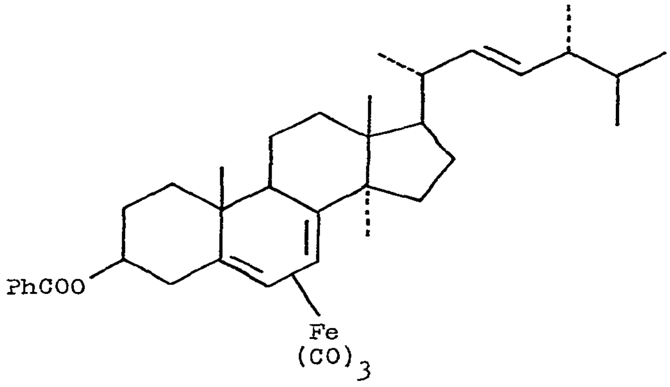
10.35



10.36

The tricarbonyl(η-cyclohexadienyl)iron cation was attacked by phosphines and phosphites to form (η-cyclohexadiene)iron cations, thus triphenylphosphine gave the product (10.35). Rate and activation parameters for the reaction indicated direct addition of the phosphine to the dienyl ring [192].

The (η-cyclohexadienyl)tricarbonyliron cation combined with the (η-cycloheptatrienyl)tricarbonyliron anion to form the neutral binuclear complex (10.36). Some related reactions were also described [193].



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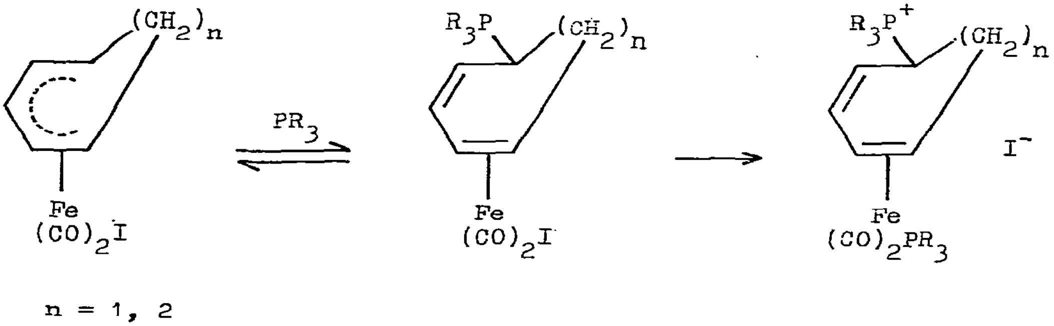
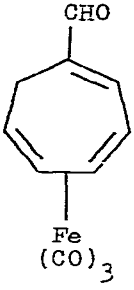


Scheme 10.1

Hydration of the tricarbonyliron complex (10.37) *via* hydroboration and removal of the tricarbonyliron moiety with iron(III) chloride or trimethylamine N-oxide gave a mixture of (22*R*)- and (22*S*)-3β-benzoyloxyergosta-5,7-dien-22-ol and (23*R*)-3β-benzoyloxyergosta-5,7-dien-23-ol [194].

The reaction of dicarbonyliron complexes [Fe(η-C_6H_7)$(CO)_2I$] and [Fe(η-C_7H_9)$(CO)_2I$] with tri-n-butylphosphine and triisopropylphosphine was shown to proceed stepwise (Scheme 10.1). A kinetic study of this reaction was carried out. It was concluded that



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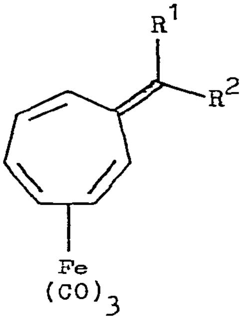

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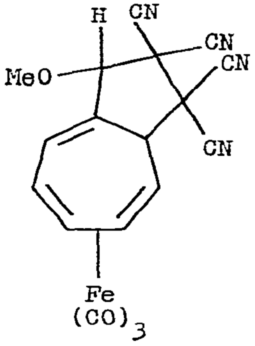

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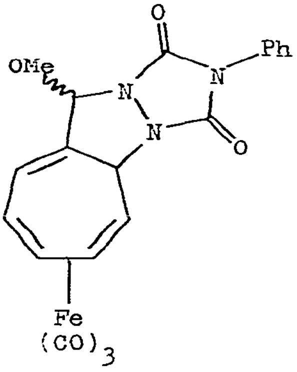
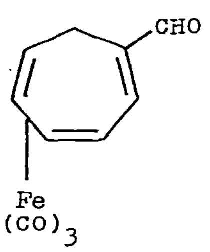


10.41

in this system, and in other related reactions, addition to the π-hydrocarbon ligand by a trialkylphosphine was kinetically favoured over attack at the metal [195].

Treatment of the aldehyde (10.38) with trimethylorthoformate in the presence of a catalytic amount of hydrogen chloride gave two isomers of the 8-methoxyheptafulvene derivative (10.39; R^1 = H, R^2 = OMe). The heptafulvene derivatives (10.39; R^1 = H R^2 = OEt; R^1 = OMe, R^2 = Ph) were prepared by similar reactions. Tetracyanoethylene and N-phenyltriazolinedione added to the complex (10.39; R^1 = H, R^2 = OMe) to give the tricarbonyliron derivatives (10.40 and 10.41) respectively [196].



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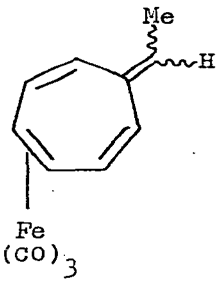

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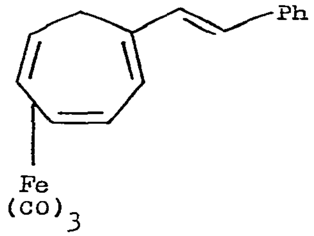

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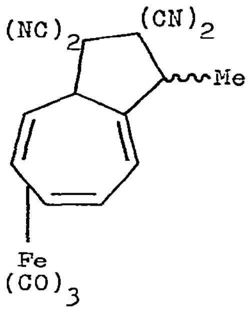

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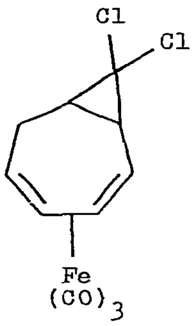

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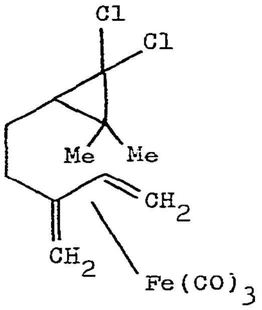
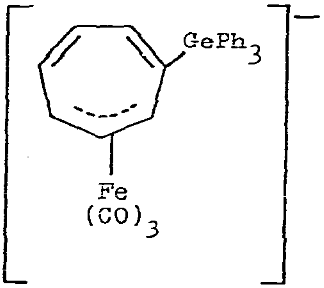


10.47

The Wittig reaction has been used to form tetraene-iron tricarbonyl complexes from the (η-cycloheptatriene)iron complex (10.42). The aldehyde (10.42) combined with triphenylmethylene-phosphorane to give a mixture of the two isomers of the (η-heptafulvene)iron complex (10.43). Triphenylbenzylidene phosphorane condensed with the same starting material to give the cis and trans isomers of the (η-cycloheptatrienylstyrene) iron complex (10.44). Similar reactions with the same aldehyde (10.42) gave the appropriate trans condensation products. Dienophiles such as tetracyanoethylene (TCNE) and N-phenyltriazolinedione underwent perioselective reaction at the free diene moiety of the Wittig reaction products. Thus the (η-heptafulvene)iron complex (10.43) combined with (TCNE) to give the 8 + 2 cycloadduct (10.45) [197].

Dichlorocarbene added to (η-cycloheptatriene)- and (η-myrcene)-tricarbonyliron to give the cyclopropyl derivatives (10.46 and 10.47) respectively. Treatment of the complex (10.47) with copper(II) liberated the ligand [198].

Addition of (η-7-$Ph_3GeC_7H_7$)Fe$(CO)_3$ to potassium t-butoxide resulted in endo-proton abstraction to give the anion (10.48). The anion (10.48) was fluxional and on treatment with DCl it produced exclusively the two isomers (10.49 and 10.50) [199].



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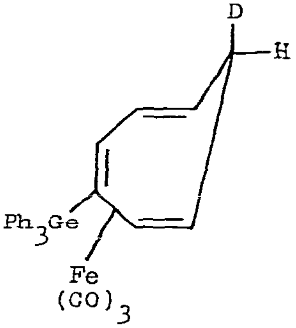

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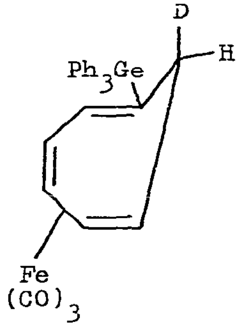
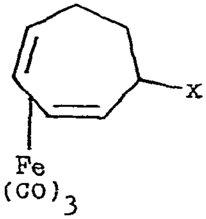


10.50

Tricarbonyl(η-cycloheptadienyl)iron fluoroborate has been treated with nucleophiles to give the substituted (η-cycloheptadiene)iron complexes (10.51; X = Me, OMe, OPh, SPh, NMe$_2$, NHCMe$_3$). These complexes were oxidized to liberate the corresponding substituted cycloheptadienes and thereby provide a convenient route to these compounds [200].

(η-Cyclohexadienyl)- and (η-cycloheptadienyl)-tricarbonyliron tetrafluoroborate were reduced in acetonitrile to give (η-1,3-cyclohexadiene)tricarbonyliron and 5,5'-di(η-1,3-cyclohexadiene)hexacarbonyldiiron, and di(η-cycloheptadienyl)tetracarbonyldiiron and 5,5'-di(η-1,3-cycloheptadiene)hexacarbonyldiiron respectively [201].



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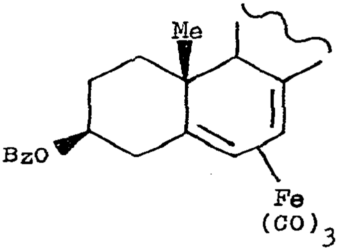

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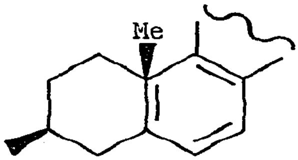
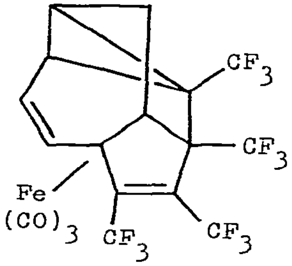


10.53

Pyrolysis of tricarbonyl(η-ergosteryl benzoate)iron (10.52) afforded neoergosteryl benzoate (10.53) together with ergosta-8(14)22-dienyl benzoate. The reaction proceeded by radical decomposition of the complex (10.52) to form an iron hydride species and bisergostatrienyl benzoate which subsequently decomposed to the product (10.53) [202].

The thermal decomposition of tricarbonyl(η-cycloheptatriene)iron was investigated [203].

Hexafluorobut-2-yne combined with tricarbonyl(η-cycloheptatriene)iron to give a quadricyclic complex (10.54) the structure of which was confirmed by X-ray crystallographic analysis of a phosphite analogue [204].



10.54

The hydrocarbon ligand was displaced from tricarbonyl(η-cyclooctatetraene)iron with bidentate phosphine ligands (L-L) to form the corresponding complexes, $Fe(CO)_3(L\text{-}L)$ [205].

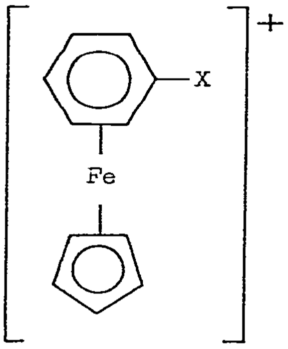
Diiron nonacarbonyl was active in the carbonylation of 2,3-homotropilidenes in the presence of rhodium complexes to give bicyclononadienones in high yields. The role of organometallic intermediates in the reaction was discussed [206].

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

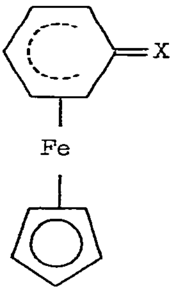
The hydrogenation of aromatic ligands during the synthesis of (η-arene)(η-cyclopentadienyl)iron mono- and di-cations was investigated. It was postulated that the hydrogenation was initiated by the abstraction of H^- by aluminium chloride to give a carbonium ion which was stabilized by a reversible intramolecular electron transfer. Successive abstractions of H by the iron atom and subsequent transfer to the ligand effect the hydrogenation [207].

The ligand exchange reaction between ferrocene and aniline in the presence of aluminium chloride gave the (η-aniline)-(η-cyclopentadienyl)iron cation (11.1; $X = NH_2$) which underwent nucleophilic displacement with NaOH and NaSH to form the (η-phenol)iron and (η-thiophenol)iron complexes (11.1; X = OH, SH) respectively. Deprotonation of these last two complexes gave the neutral (η-cyclohexadienyl)iron complexes (11.2; X = O, S) respectively [208].

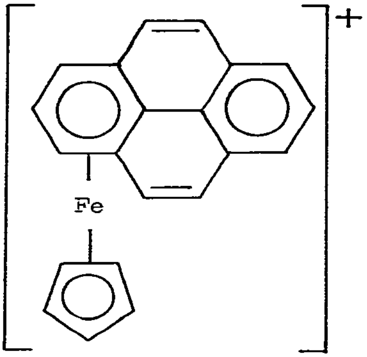
A series of (η-arene)(η-cyclopentadienyl)iron cations was prepared by ligand exchange between the arene, which possessed an α-carbon substituent containing one or more hydrogen atoms and ferrocene in the presence of aluminium-aluminium chloride. The cations were deprotonated with base to give the corresponding neutral zwitterionic species. These zwitterions behaved as nucleophiles with different substrates, such as methyl iodide, carbon disulphide and carbon dioxide, to give a wide range of products [209].



11.1

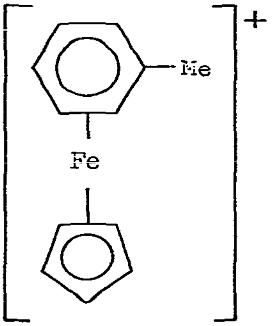


11.2



11.3

The ligand exchange reaction between ferrocene and pyrene was carried out in the presence of aluminium chloride-aluminium powder mixtures. Ligand exchange occurred to give the cation (11.3) together with the hydrogenated products (η-cyclopentadienyl)(η-4,5-dihydropyrene)iron cation, (η-cyclopentadienyl)-(η-4,5,9,10-tetrahydropyrene)iron cation, (η-pyrene)-trans-bis[(η-cyclopentadienyl)iron] dication and (η-4,5,9,10-tetrahydropyrene)-trans-bis[(η-cyclopentadienyl)iron] dication. The mechanism for partial hydrogenation of the pyrene ligand was discussed [210].



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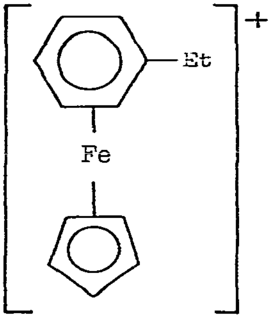
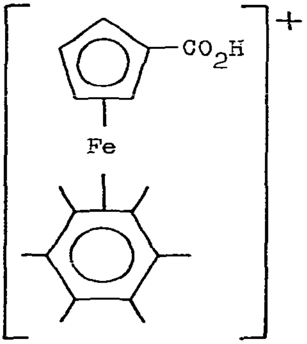


11.5

A series of (η-arene)(η-cyclopentadienyl)iron cations was prepared by ligand exchange between ferrocene and the arene. Deprotonation of the cations with potassium t-butoxide gave the corresponding zwitterions which then behaved as nucleophiles with alkyl halides, carbon dioxide and carbon disulphide. For example, treatment of the zwitterion, derived from the cation (11.4), with methyl iodide gave the ethylbenzene derivative (11.5) [211].



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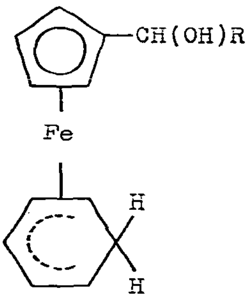

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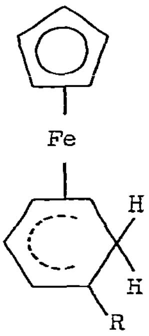
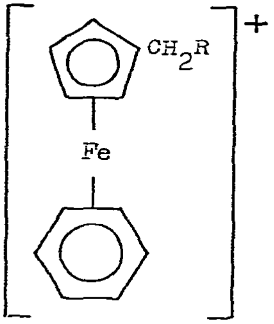


11.8

Reaction of ferrocene with hexamethylbenzene and aluminium chloride under an atmosphere of carbon dioxide resulted in carboxylation and ligand exchange to give the η-arene complex (11.6). When hexamethylbenzene was replaced by naphthalene or mesitylene the complexes $[(\eta\text{-naphthalene})Fe(\eta\text{-}C_5H_4CO_2H)]^+$ and $[(\eta\text{-mesitylene})Fe(\eta\text{-}C_5H_4CO_2H)]^+$ respectively were isolated [212].



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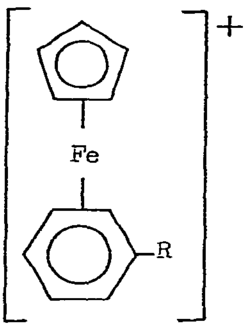

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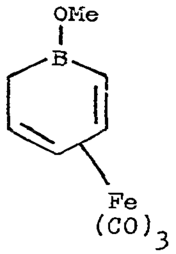


11.11

On dissolution of the (η-cyclohexadienyl)(η-cyclopentadienyl)-iron complexes (11.7; R = Me, Ph) and (11.8; R = CH_2OH, CMe_2OH) in trifluoroacetic acid the corresponding (η-arene)(η-cyclopentadienyl)iron cations (11.9 and 11.10) were formed by loss of the hydroxy group and hydride transfer. The mechanism of this reaction was studied by the use of deuterium-labelled substrates [213].

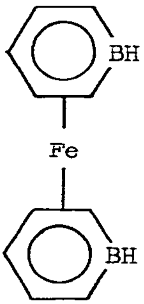
Addition of 1-bromo-1,4-dihydroborabenzene to dimethylether gave the corresponding methoxyborane which on treatment with $Fe_2(CO)_9$ gave the conjugated diene-tricarbonyliron complex (11.11). When the complex (11.11) was heated, bis(η-1-methoxyborabenzene)-iron was formed and this complex was reduced with lithium aluminium hydride to give bis(η-borabenzene)iron (11.12). Treatment of the iron complex (11.12) with butyllithium resulted in hydride displacement with the formation of bis(η-1-butylborabenzene)iron. Reaction of the complex (11.12) with trifluoroacetic acid-<u>d</u> resulted in the incorporation of up to four α-D atoms [214].

The theoretical model previously proposed by Bochvar and coworkers has been used to calculate charge distributions in the mixed sandwich compound (η-C_5H_5)Fe(η-C_6H_6) and the corresponding cation. Atomic charges obtained for the neutral complex were as follows; Fe +0.606, cyclopentadienyl C -0.092, benzene C -0.024 [215].

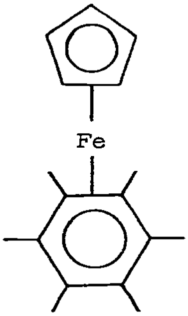
INDO Molecular orbital calculations were carried out for a series of cations $[(\eta\text{-}C_6H_5X)Fe(\eta\text{-}C_5H_5)]^+$ (X = H, Me, OMe, CO_2Me). An attempt was made to correlate the reactivity of the π-coordinated ligands with electronic parameters. It was concluded that the factors which determined the position of attack in a particular ring were neither charge controlled nor influenced by the lower energy unoccupied molecular orbitals in the complex [216].

ESR spectra of several electroneutral (η-arene)(η-cyclopentadienyl)iron complexes were measured at 77-300 K. The g-factors were slightly anisotropic and the values of the splitting of the e^{*}_{1g} energy levels were determined on the basis of g-factor anisotropy. An unusual temperature dependence of the ESR spectrum of (η-cyclopentadienyl)(η-naphthalene)iron was observed and this was discussed in terms of the Jahn-Teller effect [217].

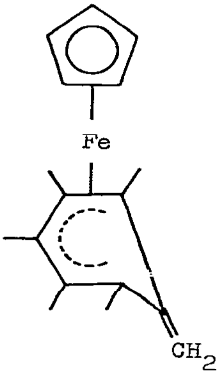
The 19-electron (η-hexamethylbenzene)iron complex (11.13) underwent hydrogen abstraction with molecular oxygen to form the (η-cyclohexadienyl)iron complex (11.14). Related (η-benzene)-(η-cyclopentadienyl)iron complexes where the benzene ligand had less than six methyls were dimerized by oxygen to give binuclear (η-cyclohexadienyl)iron complexes of which the dimer (11.15) was typical [218].



11.12



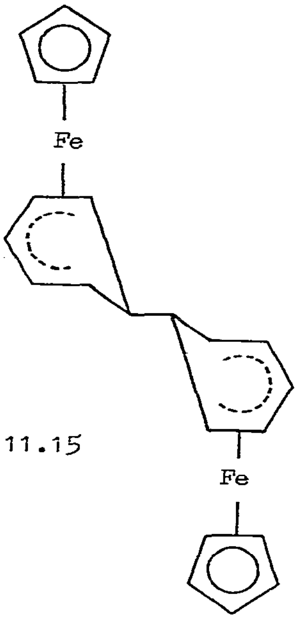
11.13



11.14

The η-arene-iron complexes (11.16) and (11.17; R^1 = Me, R^2 = Me, Et) were prepared by reduction of the parent cations. Reaction of the complex (11.16) with air followed by addition of excess methyl iodide, metathesis with HPF_6 and reduction with sodium amalgam gave the hexaethylbenzene derivative (11.17; R^1 = H, R^2 = Et). Treatment of the complexes (11.17; R^1 = H, R^2 = Et; R^1 = Me, R^2 = Et) with oxygen gave the corresponding $O_2^{-\cdot}$ salts. The crystal structure of the complex (11.16) showed that it was a 19-electron complex with both rings planar and parallel [219].

The neutral (η-arene)(η-cyclopentadienyl)iron complexes (arene = PhMe, PhPh, phenanthrene, fluorene, tetralin) were



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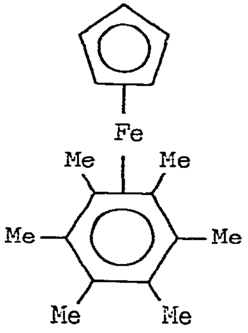
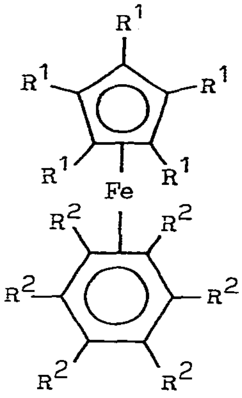


11.16



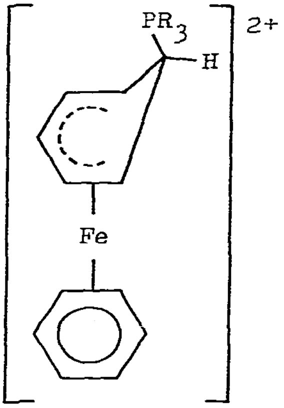
11.17

obtained by reduction of the corresponding cations with sodium amalgam in $MeOCH_2CH_2OMe$. Yields of 66-80% were obtained and the redox properties of the complexes were investigated [220].

Treatment of bis(η-benzene)iron(II) cation with tertiary phosphines gave the corresponding air-stable phosphonium cations (11.18; R = n-Bu, Ph, p-tolyl) [221].

The treatment of $[RuCl_2(\eta^6\text{-arene}^1)]_2$ in acetone successively with silver tetrafluoroborate or silver hexafluorophosphate, acid (trifluoroacetic acid, hydrogen tetrafluoroborate or hydrogen hexafluorophosphate) and arene^2 gave the ruthenium(II) salts $[Ru(\eta\text{-arene}^1)(\eta\text{-arene}^2)]X_2$ (arene^1 = benzene, mesitylene, hexamethylbenzene; arene^2 = a wide range of aromatic compounds; $X = BF_4$, PF_6) in good yields. Preliminary experiments indicated that these ruthenium(II) salts could be reduced by alkali metals to give zerovalent bis-arene-ruthenium(0) complexes of the type $[Ru(\eta^6\text{-arene}^1)(\eta^4\text{-arene}^2)]$ [222].

The 19-electron neutral complex (11.19) was used with the corresponding cation as a redox couple for the reduction of nitrate ion to ammonia at a mercury electrode [223].



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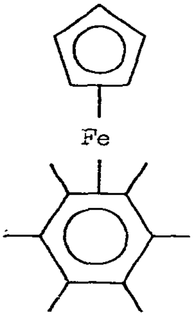


11.19

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

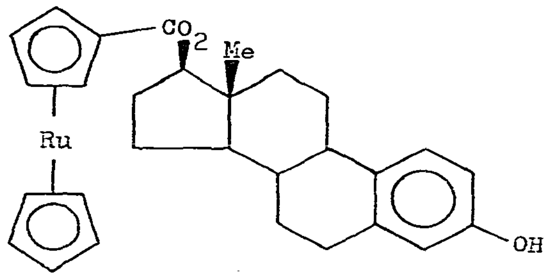
Ruthenocene was prepared in good yield by treating β-ruthenium(III) chloride with cyclopentadiene in ethanol [224].

The exchange of iron in ferrocenes with $^{103}RuCl_3$ gave a series of radioactive ruthenocenes. The reaction conditions were optimized to give the maximum yields of ^{103}Ru-ruthenocenes [225].

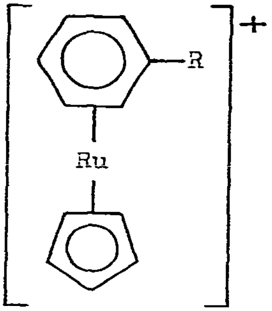
The application of thermal modulation spectroscopy to inorganic and organometallic compounds, including ruthenocene, was investigated. The thermal modulation method was useful for studying inorganic molecules and ions with (i) non-Boltzmann excited state populations, (ii) multiple levels responsible for the observed emission, (iii) vibronically allowed transitions [226].

Ruthenocene has been metallated with n-butyllithium in the presence of tetramethylethylenediamine to form lithio-, 1,1'-dilithio- and 1,3,1'-trilithio-ruthenocene. The metallated intermediates were treated with iodine to form iodo-, 1,1'-diiodo- and 1,3,1'-triiodo-ruthenocene. The relative yields of the iodoruthenocenes were dependent on the solvent mixture used and on the proportions of the reactants [227].

Estradiol-3-ruthenocene-^{103}Ru carboxylic acid ester (12.1) and -17-ruthenocene-^{103}Ru carboxylic acid ester were injected into three-day old rats. The radioactive label was concentrated to the greatest extent by the liver. With the C-17 ester the

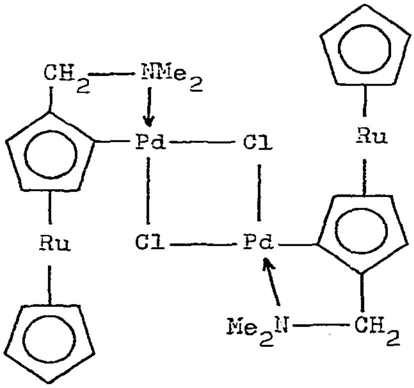


12.1



12.2

uterus and the ovary were also labelled and the kidney was labelled with the ruthenocene derivative (12.1). The greatest amount of labelling occurred with the C-17 ester [228].



12.3

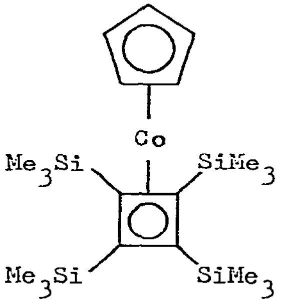
The reaction of ruthenocene with an arene in the presence of an aluminium halide and aluminium powder resulted in ligand exchange to give the corresponding η-arene complex (12.2; R =H , Me, Ph, Cl) in low yield. NMR spectroscopy indicated that these complexes had a sandwich structure with planar undisturbed cyclic ligands. It was concluded that the positive charge was delocalized onto the ligands to a lesser extent with $[(\eta\text{-arene})Ru(\eta\text{-}C_5H_5)]^+$ as compared with $[(\eta\text{-arene})Fe(\eta\text{-}C_5H_5)]^+$ [229].

(Dimethylamino)methylruthenocene combined with Li_2PdCl_4 to give the binuclear palladated ruthenocene (12.3). The structure of the complex was confirmed by IR spectroscopy and by reactions with triphenylphosphine, thallium(I)acetylacetonate and $LiAlD_4$. Some reactions of a related mononuclear palladated ruthenocene were described [230].

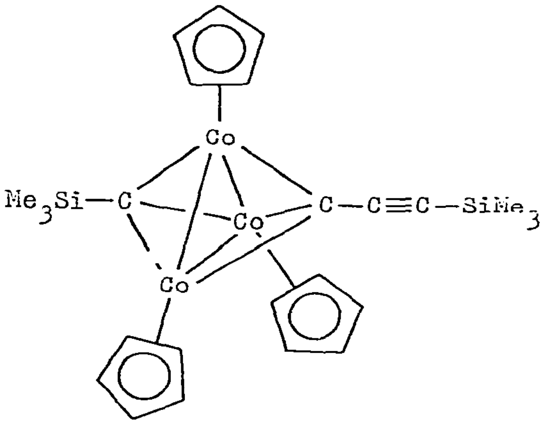
13. $(\eta\text{-}C_4H_4)Co(\eta\text{-}C_5H_5)$

Bis(trimethylsilyl)acetylene combined with dicarbonyl-(η-cyclopentadienyl)cobalt to give several products including the (η-cyclobutadiene)cobalt complex (13.1) and the trinuclear cluster complex (13.2) the structure of which was determined by X-ray crystallography. It was concluded that several mechanisms were operating concurrently to give the observed products [231].

Phenyl-1-naphthylacetylene combined with dicarbonyl-(η-cyclopentadienyl)cobalt to give two isomeric forms of the corresponding substituted (η-cyclobutadiene)(η-cyclopentadienyl)-cobalt complex. The crystal and molecular structure of one of these isomers (13.3) was confirmed by an X-ray crystallographic analysis [232].

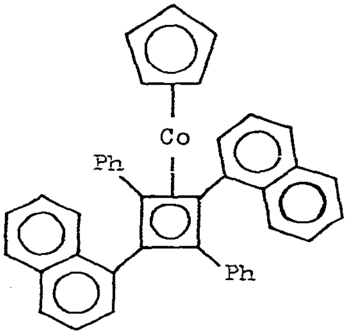


13.1



13.2

Reaction of the dienediyne (13.4) with dicarbonyl(η-cyclopentadienyl)cobalt gave the η-benzocyclobutadiene complex (13.5; R = $SiMe_3$). Desilylation of the complex (13.5; R = $SiMe_3$) with tetramethylammonium fluoride gave the parent complex (13.5;



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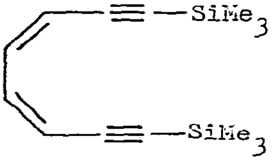

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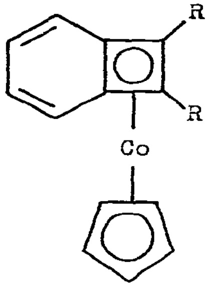
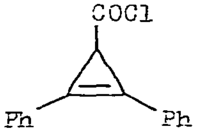
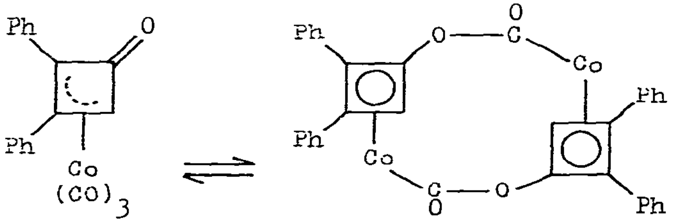


13.5

R = H) as an air stable solid. ^1H NMR spectroscopy provided evidence for diatropic character of the complexed as opposed to the free benzocyclobutadiene ligand [233].



13.6



13.7

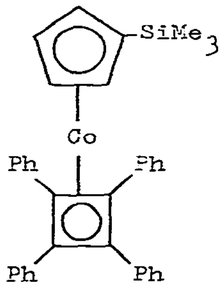
13.8

The 2-cyclopropene-1-carbonyl chloride (13.6) combined with the cobalt tetracarbonyl anion to give the (η-cyclobutenonyl)-cobalt complex (13.7) which was in a temperature dependent tautomeric equilibrium with the binuclear (η-cyclobutadiene)-cobalt complex (13.8). Several related reactions were reported [234].

The crystal and molecular structure of the cobalt complex (13.9) was determined by X-ray analysis. The perpendicular distances (η-$C_5H_4SiMe_3$)—Co and (η-C_4Ph_4)—Co were 1.688 and 1.699 Å respectively [235].

The flash vacuum pyrolysis of several substituted (η^4-cyclobutadiene)(η-cyclopentadienyl)cobalt complexes was studied. It was concluded that: (i) the η^4-cyclobutadiene complexes decomposed cleanly to regenerate their component acetylenes, (ii) the decompositions required intermediate bis(alkyne)cobalt complexes, (iii) rotation and reclosure of the complexed alkynes to cyclobutadiene rings competed with decomplexation; and (iv) migration of cobalt along the triple bonds of diyne ligands did not occur [236].

The reaction of dicarbonyl(η-cyclopentadienyl)cobalt and mesitylphenylacetylene gave the η-cyclobutadiene complex (13.10) and the η-cyclopentadienone complex (13.11). The structures of the complexes (13.10 and 13.11) were determined by X-ray analysis and the ^{1}H and ^{13}C NMR spectra were recorded and interpreted. Both the complexes (13.10 and 13.11) exhibited a high degree of intramolecular steric crowding [237].



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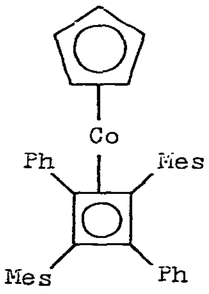

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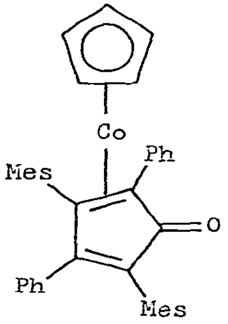

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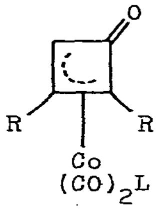
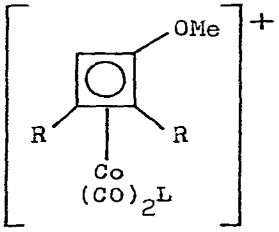
Mes = Mesityl



13.12



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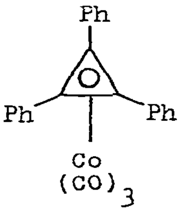


13.14

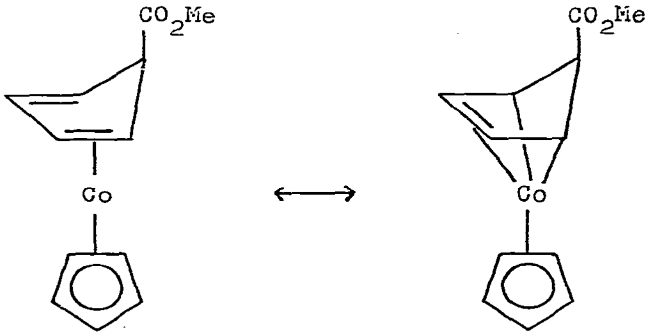
The (η-cyclobutenoyl)cobalt complexes (13.12; R = Et, Ph; L = CO, PPh_3, PEt_3, PMe_2Ph, $PMePh_2$) were converted to the cationic (η-cyclobutadiene)cobalt complexes (13.13; R = Et, Ph; L = CO, PPh_3, PEt_3, PMe_2Ph, $PMePh_2$) on treatment with $Me_3O^+PF_6^-$. The complex cations (13.13) were isolated as the tetrafluoroborate, hexafluorophosphate or hexafluoroantimonate salts. When the cation (13.13; R = Ph; L = CO) was warmed with benzene then all three carbonyl groups were displaced to give the corresponding (η-benzene)(η-cyclobutadiene)cobalt cation [238].

Octacarbonyldicobalt was attacked by triphenylcyclopropenium fluoroborate to form the (η-cyclopropenyl)cobalt complex (13.14), the complex was characterized by X-ray crystallography [239].

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

The chemistry of cobaltocene, cobaltocinium salts and other cobalt sandwich compounds was reviewed by Sheats. This is an exhaustive review of all the literature on cobaltocene and related compounds up to 1976 [240].

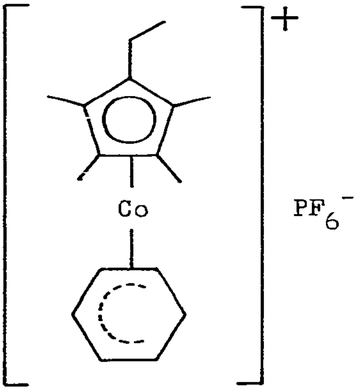
Electrochemical oxidation of the methyl ester (14.1) gave the corresponding cobaltocinium cation, the reaction was only partially reversible. The crystal and molecular structure of the complex (14.1) was determined by X-ray crystallography and this evidence together with that from ^1H and ^{13}C NMR spectroscopy suggested that the structure was better represented by the canonical form (14.2) rather than (14.1) [241].



14.1 14.2

Cobalt(II) chloride combined with tri-n-butyl(ethyltetramethylcyclopentadienyl)tin, Sn(etmcp)Bu^n_3, to form, after treatment with chlorine, the complexes $[Co(etmcp)Cl(\mu\text{-}Cl)]_2$ and $Co_3(etmcp)_2Cl_6$. These two complexes were used to prepare a range of (η-etmcp)Co complexes including the (η-cyclohexadienyl)cobalt derivative 14.3 the (η-butadiene)cobalt compound 14.4 and the carbonyl bridged binuclear complex 14.5 [242].

Cobalt chloride was treated with 5,6-bis(diisopropylamino)-calicene in THF and then with potassium perchlorate to form the cobaltocene complex (14.6) in 25% yield [243].



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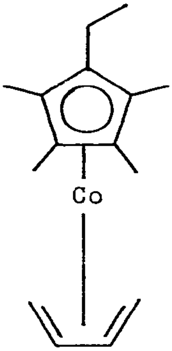

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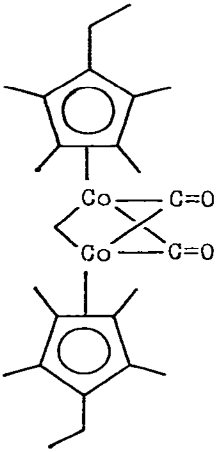
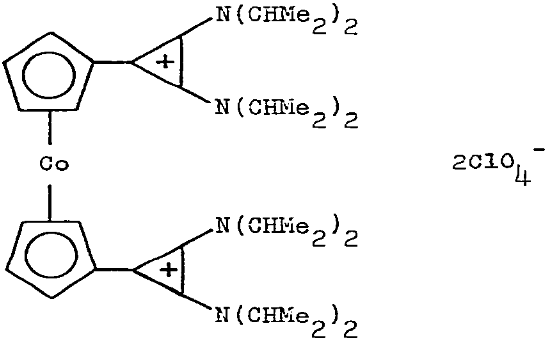


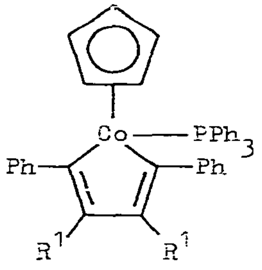
14.5



14.6

Treatment of the cobaltacyclopentadienes (14.7; R^1 = Ph, Me, CO_2Me) with the isocyanides R^2NC (R^2 = CMe_3, p-tolyl, 2,6-xylyl) gave the corresponding iminocyclopentadiene-cobalt complexes (14.8). Reaction of the cobalt complexes (14.8) with methyl iodide or hydrogen tetrafluoroborate gave the cobaltocinium salts (14.9; R^3 = Me, X = I and R^3 = H, X = BF_4) respectively [244].

The formation of (η-allyl)(η-cyclopentadienyl)cobalt derivatives has been investigated. In one case, the cobaltocinium ion was obtained from dicarbonyl(η-cyclopentadienyl)-cobalt and 2-methylallyl chloride [245].



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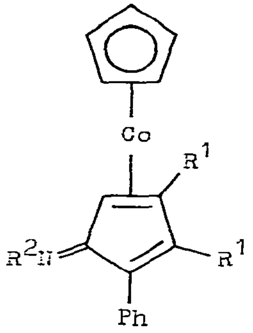

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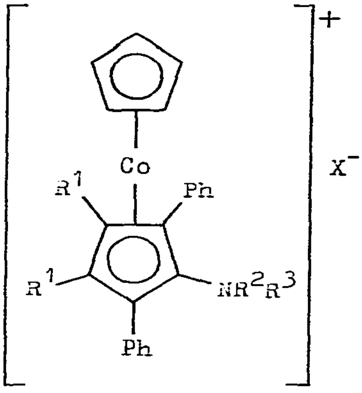


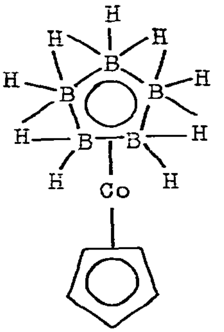
14.9

Treatment of $C_2B_9H_{11}K$ with cyclopentadiene in the presence of cobalt(II) chloride gave (η-C_5H_5)Co(η-$C_2B_9H_{11}$) in good yield. A similar route was used to prepare (η-C_5H_5)Ni(η-$C_2B_9H_{11}$), (η-C_5H_5)Co(η-$C_2B_8H_{10}$), (η-C_5H_5)Co(η-$C_2B_8H_{10}$)Ni(η-C_5H_5) and (η-C_5H_5)Co(η-$C_2B_6H_{10}$) [246].

The direct reaction between dicarbonyl(η-cyclopentadienyl)-cobalt and pentaborane(9) gave the cobaltaborane complex (14.10). The $B_5H_9^{2-}$ ring was formally isoelectronic with $C_5H_5^-$ and thus the complex (14.10) was isoelectronic with ferrocene [247].

Cyclic voltammetry and d.c. polarography have been used to investigate the electrochemical behaviour of the cobalt triple-decker sandwich complexes (14.11 and 14.12). The complexes were found to undergo a series of reversible one-electron oxidations and reductions in non aqueous solvents of the form:

$$(14.11)^{2+} \rightleftharpoons (14.11)^{+} \rightleftharpoons (14.11) \rightleftharpoons (14.11)^{-} \rightleftharpoons (14.11)^{2-}$$



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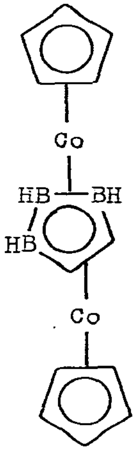

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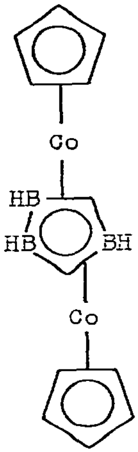
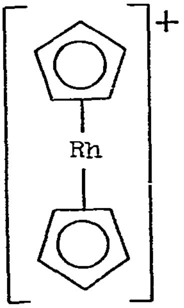


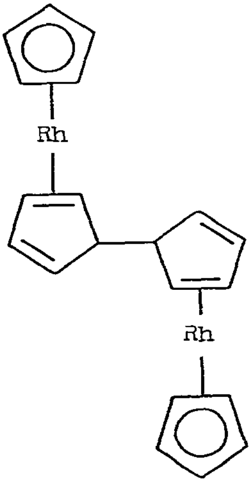
14.12

The results were discussed in terms of metal-metal interactions and delocalization of electron density [248].

The electrochemical reduction of the rhodocinium ion (14.13) has been investigated by polarography, cyclic voltammetry and controlled potential conlometry. The cation (14.13) was reduced in two successive, one-electron processes. Neutral rhodocene was highly reactive and dimerized to form the mixed (η-cyclopenta-



14.13



14.14

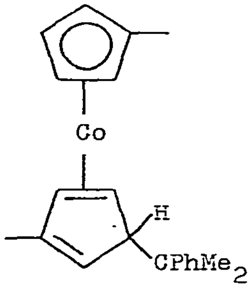
dienyl)(η-cyclopentadiene)rhodium complex (14.14) [249].

The reaction of the electrochemically generated cobaltocene anion with phenol was studied by polarography, cyclic voltammetry, differential pulse polarography and bulk electrolysis. It was established, via deuterium-labelling experiments, that protonation of the cobaltocene anion took place directly at the ligand and that a metal hydride intermediate was not involved [250].

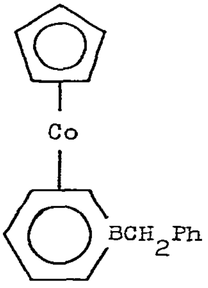
The magnetic susceptibilities of chromocene and cobaltocene have been studied over the temperature range 0.9-300°K and the results have been interpreted using complete ligand field theory in slighly distorted $C_{\infty v}$ symmetry [251].

^{59}Co Nuclear quadrupole resonance spectra were obtained for a series (η-cyclopentadienyl)-[η-(3)-1,2-dicarbollyl]cobalt derivatives. It was concluded that the electronic configurations of these molecules were similar to those of a metal [252].

The effect of substituents on the acidities of hydroxycobaltocinium and -rhodocinium salts was investigated. The acidity constants, K_a, were determined spectrophotometrically and the acidities increased with increasing electronegativity of the substituent but decreased when rhodium(III) replaced cobalt(III) or when five methyl groups were on the second η-cyclopentadienyl ring. An attempt was made to relate the acidities to Hammett's substituent constants [253].



14.15



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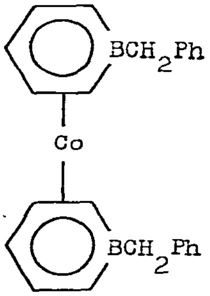
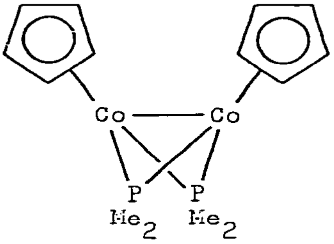


14.17

The alkylation of 1,1'-dimethylcobaltocene with 2-bromo-2-phenylpropane was stereospecific and afforded an *exo*-adduct (14.15) with 2,3-dimethyl-2,3-diphenylbutane as a minor product which suggested a radical mechanism for the addition. The reaction with 2-cyanoazopropane took place in the same way. Cobaltocene underwent ring expansion with benzyldibromoborane or dichloro(2,4,6-trimethylphenyl)borane to give several cobalt complexes containing borinato and boracyclohexa-2,4-diene ligands, typical products were the 1-benzylborinato cation (14.16) and the bis(1-benzylborinato) complex (14.17) [254].

Treatment of cobaltocene with tetraphenylcyclopentadienones, duroquinone and other dienes gave (η-cyclopentadienyl)(η-diene)-cobalt complexes in which the diene was activated. The preparation and reactivity of the corresponding rhodium and iridium complexes was described [255].



14.18

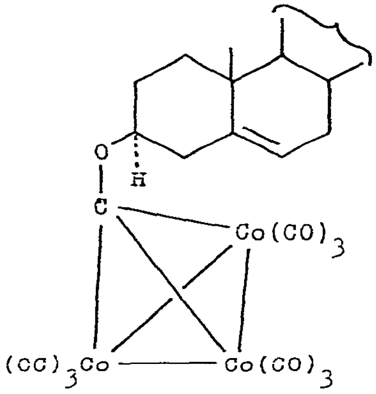
Cobaltocene was attacked by dimethylphosphine to give the diphosphine adduct (14.18) which in turn underwent protonation with trifluoroacetic acid in ammonium hexafluorophosphate. The proton occupied a bridging position between the two cobalt atoms [256].

The reduction of dichloro(1,5-cyclooctadiene)platinum with cobaltocene in the presence of excess 1,5-cyclooctadiene gave bis(1,5-cyclooctadiene)platinum [257].

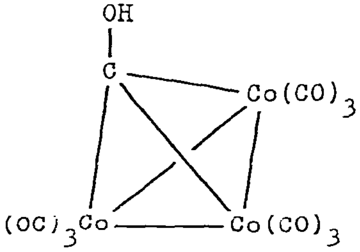
Cobaltocene in benzene has been used as a catalyst for the cycloaddition of acetylene to aminonitriles, $R_2N.CN$ where R = alkyl, aryl, $R_2 = (CH_2)_4$, $(CH_2)_5$ at 70 to 180°C under pressure to form the corresponding 2-aminopyridines [258].

15. Cobalt-carbon Cluster Compounds

The S-alkyl xanthates of α-cholestanol, cholestanol, cholesterol, adamantanethanol and menthol underwent desulphurization with dicobalt octacarbonyl to give the corresponding alkoxyalkylidynetricobaltnonacarbonyl cluster complexes. In a typical reaction the xanthate of cholesterol gave the cluster complex (15.1). The cluster complexes formed were optically active and were catalysts for the hydroformylation of linear and cyclic olefins but no asymmetric induction was detected [259].



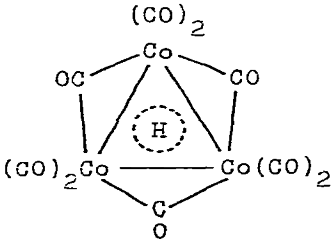
15.1



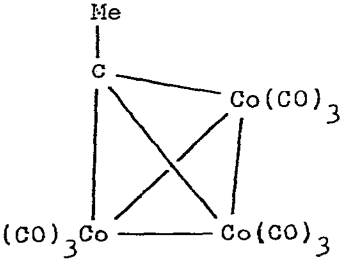
15.2

The heat, air and moisture sensitive cobalt cluster acid (15.2) was obtained by treatment of $Li[Co_3(CO)_{10}]$ with dry hydrogen chloride in hexane at $-20^\circ C$. The acid (15.2) decomposed quantitatively at $40^\circ C$ to form $HCo(CO)_4$ and $Co_4(CO)_{12}$, a reaction which involved migration of hydrogen from a carbonyl oxygen to cobalt [260].

The hydroxy-cluster compound, $Co_3(CO)_9C{-}OH$, (15.2) was shown to decompose at room temperature, via the hydrido cluster (15.3). Acetylene underwent reductive addition with the hydrido derivative (15.3) to give the cobalt complex (15.4) [261].



15.3

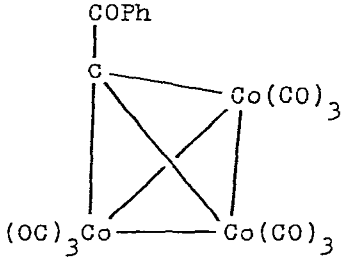


15.4

The crystal and molecular structure of benzoylmethylidynetricobaltnonacarbonyl (15.5) has been determined by single crystal X-ray crystallography. The molecule was found to have a regular and normal structure which did not help explain the chemical properties of these cluster complexes [262].

The X-band and Q-band ESR spectra of the tricobalt alkylidyne cluster, $PhCCo_3(CO)_9$ radical anion have been analyzed in order to examine the source of line broadening and line shape distortion in isotropic ESR spectra of organometallic radicals with two or more equivalent nuclei. Second-order hyperfine splittings were found to lead to asymmetric line shapes in both isotropic and frozen solution spectra [263].

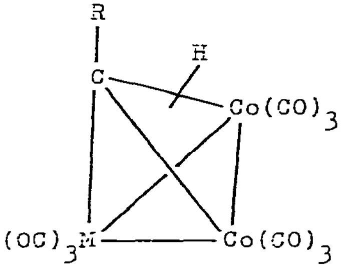
The redox behaviour of several tricobalt alkylidyne cluster complexes, $XCCo_3(CO)_{9-n}L_n$, where X = H, Me, Ph, F, L = PR_3, $P(OR)_3$, RNC and n = 1 - 3 has been studied by polarography and and cyclic voltammetry. For complexes with n = 1, reversible one-electron reduction was observed, while complexes with n = 2 showed irreversible oxidation. The complexes with n = 3 showed both reversible reduction and oxidation. In general, reduction was more difficult and oxidation easier as n increased. The frozen-solution ESR spectra of the complexes indicated that the a_2 antibonding orbital of the Co_3C cluster was only perturbed slightly by replacement of CO with a phosphorus ligand. The results were discussed in terms of the electronic structure of the complexes [264].



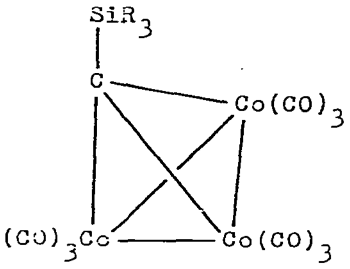
15.5

The tricobalt alkylidyne cluster complexes (15.6; M = Co; R = Me, Et, Ph) were attacked by $Na_2[Fe(CO)_4]$ in THF to form mixed metal alkylidyne clusters, $RCCo_2Fe(CO)_9H$, (15.6; M = Fe;

R = Me, Et, Ph). Spectroscopic evidence indicated that these complexes were similar in structure to the parent tricobalt clusters. The location of the hydride ligand was not confirmed [265].



15.6

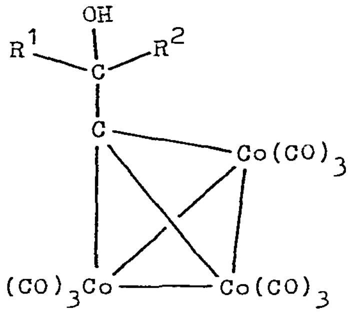


15.7

The reaction of bromomethylidynetricobalt nonacarbonyl or methylidynetricobalt nonacarbonyl with a series of silicon hydrides [Et_3SiH, Pr_3SiH, $Me_2(i\text{-}Pr)SiH$, Me_2PhSiH, $Me_2(OEt)SiH$, Me_2ClSiH] gave the corresponding silylmethylidynetricobalt nonacarbonyl complexes (15.7). The compounds $Me(HO)_2SiCCo_3(CO)_9$ and $(HO)_3SiCCo_3(CO)_9$ were prepared and incorporated into methylsilicone polymers [266].

Direct reaction of the methinyl tricobalt enneacarbonyls, $[Co_3(CR)(CO)_9]$ (R = Me, F), with tertiary phosphites, $P(OR)_3$ (R = Me, Ph), gave a series of mono-, di- and tri-substituted products. The crystal and molecular structure of the tri-substituted complex $[Co_3(CMe)(CO)_6\{P(OMe)_3\}_3]$ was determined by X-ray analysis. The carbonyl groups were all terminal and the three trimethylphosphite ligands occupied equatorial positions on the Co_3 triangle [267].

Treatment of the α-hydroxyalkylidynetricobalt nonacarbonyl complexes (15.8; R^1 = H, Me, Ph; R^2 = OH) with concentrated sulphuric acid, trifluoroacetic acid, or aqueous hexafluorophosphoric acid-propionic anhydride gave the corresponding carbenium ions (15.9). The hexafluorophosphate salts of the carbenium ions (15.9) were very stable and on treatment with alcohols, benzenethiol and aniline they gave the ethers (15.8; R^1 = H, Me, Ph; R^2 = OMe, OEt), the thioethers (15.8; R^1 = Me, Ph; R^2 = SPh) and the secondary amines (15.8; R^1 = H, Me, Ph; R^2 = PhNH) respectively. It was concluded from these reactions together with spectroscopic data that most of the positive charge generated at the carbon atom, at which C—O bond cleavage had occurred, was delocalized onto the cobalt atoms [268].



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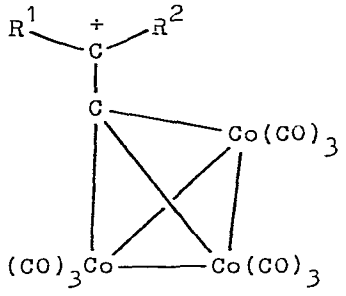
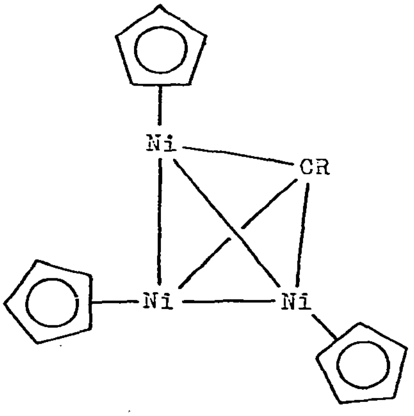


15.9

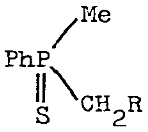
16. $(\eta\text{-}C_5H_5)_2Ni$

The electronic and magnetic circular dichroism spectra of cobaltocene and nickelocene, isolated in argon and nitrogen matrices, were recorded and interpreted [269].

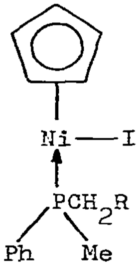
Reaction of excess nickelocene with the alkyllithiums, RCH_2Li ($R = Me_3Si$, Me_3C), gave the corresponding methylidyne trinickel cluster compounds (16.1). The cluster complexes (16.1; $R = Me_3Si$, Me_3C, Ph) were also prepared by treatment of the σ-allyl complexes $[(\eta\text{-}C_5H_5)Ni(CH_2R)(PPh_3)]$ ($R = Me_3Si$, Me_3C, Ph) with butyllithium in the presence of excess nickelocene [270].



16.1



16.2



16.3

Treatment of the phosphine sulphides [16.2; R = C(OH)Ph_2, COPh, CHO, CO_2Et] with nickelocene and allyl iodide gave the corresponding complexes (16.3). The phosphines were released from the nickel complexes (16.3) by treatment with trimethylphosphite. The optically active nickelocenes (16.4; R = CHPhMe, neomenthyl) were prepared by treatment of the corresponding lithiocyclopentadienyl derivative with tetrapyridinenickel(II) chloride [271].

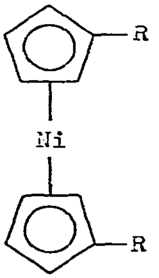
Reaction of α-bromophenylacetic acid with triphenylphosphine and nickelocene gave cyclopentadienylphenylacetic acid. The same reaction was used to prepare 2-cyclopentadienylpropionic acid and cyclopentadienylphenylmalonic acid [272].

Reaction of 1-phenyl-4-t-butylphosphorin-3-ene sulphide with nickelocene and allyl iodide gave the nickel complex (16.5) [273].

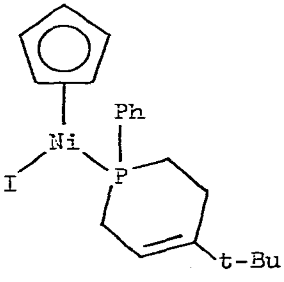
Reaction of excess methylenetriphenylphosphorane with nickelocene followed by treatment with sodium tetraphenylboron gave the cationic complex (16.6; X = BPh_4). The analogous PF_6^- salt (16.6; X = PF_6) was prepared by reaction of the ylide with nickelocene in the presence of ammonium hexafluorophosphate [274].

The bora-nickelocene complex (16.7) combined with carbonyl-(η-cyclopentadienyl)nickel dimer at 150° to give the triple-decker sandwich complex (16.8) in 96% yield [275].

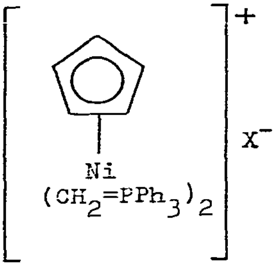
Bis carbonyl(η-cyclopentadienyl)nickel has been treated with the diboryl ligand (16.9) to form the (η-1,3-diborolenyl)-nickel complex (16.10). The crystal and molecular structure



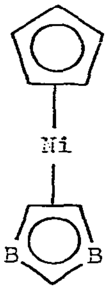
16.4



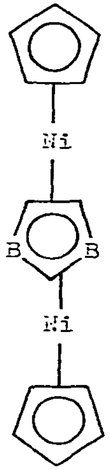
16.5



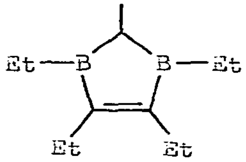
16.6



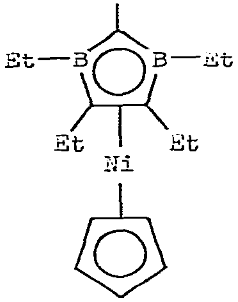
16.7



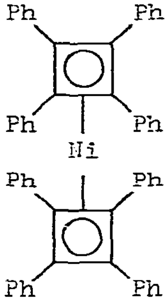
16.8



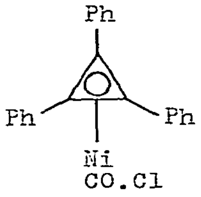
16.9



16.10



16.11



16.12

of this complex has been determined by X-ray crystallography [276].

A nickel film may be deposited by hydrogenation of nickelocene and its isopropyl- and isobutyl-derivatives in solution in benzene, toluene and ditolylmethane over a clay catalyst at 80-300°C [277].

The dimerization of 6,6-dimethylfulvene was promoted by nickel atoms and (η-cyclopentadiene)- and (η-cyclopentadienyl)-nickel complexes were invoked as intermediates in the reaction [278].

Bis(η-tetraphenylcyclobutadiene)nickel (16.11) has been synthesized by the treatment of (η-tetraphenylcyclobutadiene)-nickel dibromide with 1,2,3,4-tetraphenyl-1,4-dilithiumbutadiene (PhLiC=CPhCPh=CPhLi) in toluene at 20° [279].

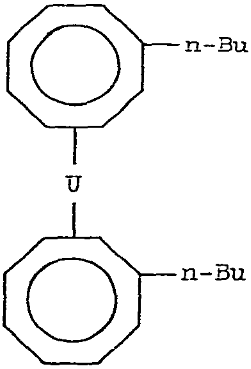
The isomerization of quadricyclane to norbornadiene was efficiently catalyzed by (η-triphenylcyclopropenyl)nickel complexes derived from the chloride (16.12) by loss of carbon monoxide. Reactions of the chloride (16.12) with nitrogen and phosphorus donor ligands were examined [280].

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

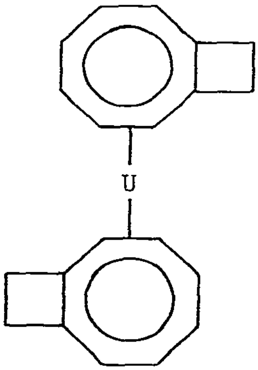
A convenient synthesis of 1,1'-di-n-butyluranocene (17.1) has been reported. Cyclooctatetraene was converted to the dianion of butylcyclooctatetraene with n-butyllithium and this dianion combined with uranium(IV) chloride to form the product (17.1) [281].

Streitwieser and coworkers have described a convenient preparation of bis(η-cyclooctatetraene)uranium(IV) from uranium(IV) chloride and the dipotassium salt of the cyclooctatetraene dianion. The yield obtained was 82% [282].

The crystal and molecular structure of the uranocene derivative (17.2) was determined by X-ray analysis. The molecule was a sandwich compound with the C_8 rings in an eclipsed configuration and the uranium atom was nearly equidistant from all the atoms of the C_8 ring. The cyclobuteno ring was planar and at an angle of 6.8° to the plane of the C_8 ring [283].



17.1



17.2

An electrochemical investigation of uranocene indicated that oxidation gave a dication which attacked a second molecule of uranocene to form a dimer dication. This species subsequently lost a molecule of the ligand and an electron to form a product with the stoichiometry $(\eta\text{-}C_8H_8)_3U^{3+}$ [284].

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