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ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1989*

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1. REVIEWS

As part of Polyhedron's Symposia-in-Print series, Chisholm has edited a collection of articles on the "Reactivity of Bridging Hydrocarbyl Ligands". The work contained many excellent articles on this important aspect of organometallic chemistry [1]. D'Agostino and McGlinchey have reviewed the use of high field NMR spectroscopy as a probe for structure and mechanism in mixed metal clusters containing carbyne or ketenylidene bridges. Included in this review was a discussion of cobalt-carbon cluster compounds [2].

2. GENERAL RESULTS

The modelling of nucleophilic and electrophilic additions to organometallic complexes using molecular graphics has been developed in the framework of the extended Hueckel method. The results obtained were in good agreement with those obtained experimentally with the site of attack being i) at the metal for the electrophilic substitution of ferrocene, $Fe(CO)_5$ and $M(\eta\text{-}C_5H_5)(CO)_2$, where M = Co, Rh; ii) on the $(\eta\text{-}C_5H_5)$ ligand for the nucleophilic substitution of $[(\eta\text{-}C_5H_5)_2M]^+$, where M = Co, Rh and iii) on the $(\eta\text{-}C_6H_6)$ ligand for the nucleophilic substitution of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$ [3].

CNDO-UHF molecular orbital calculations have suggested that formation of the unknown $(\eta^5$-thiophene)molybdenum complex (2.1) should be possible [4]. Linear relationships have been obtained between the redox potentials of a series of metallocenes and metallocarboranes and the ionization potentials of the constituent metal atoms [5]. The electronic structure and stability of transition metal triple-decker sandwich complexes has been the subject of a theoretical investigation. Electronic factors associated with the stability of complexes were identified and

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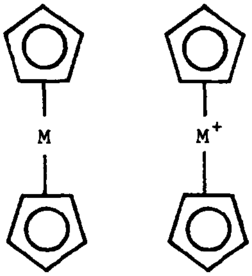

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correlated with eight types of complex [6]. The electronic structure of triple-decker sandwich complexes $(\eta\text{-}C_5H_5)M(\eta\text{-}L)\text{-}M(\eta\text{-}C_5H_5)$ where M = Cr, Mo and L = P_5, As_5, has been the subject of a theoretical investigation. Frontier orbitals of the $(\eta\text{-}C_5H_5)M$ and $(\eta\text{-}L)$ fragments were used in the analysis. The short metal-metal distances were responsible for the apparent electron deficiency in the complexes [7].

Channel inclusion complexes have been formed between $CS(NH_2)_2$ and tris-o-thymotide hosts and 27 organometallic guests such as benchrotrene, cymantrene, tricarbonyl(η-1,3-cyclohexadiene)iron and tricarbonyl(η-trimethylenemethane)iron. The inclusion complexes formed acentric crystals which caused 2nd-harmonic generation from 1.06 μm laser light [8]. Several η-diene, η-triene and η-polyene complexes of $Fe(CO)_3$, substituted ferrocenes, $(\eta\text{-arene})Cr(CO)_3$ complexes and $(\eta\text{-}C_4Ph_4)Co(\eta\text{-}C_5H_5)$ were doped with iodine and their electrical conductivities were measured in vacuo. Most of these compounds behaved as good semiconductors [9].

Chromocene, ferrocene and cobaltocene together with the redox pairs (2.2; M = Cr, Fe, Co) have been intercalated into a range of ion-exchanged Y and A zeolites. The kinetics of impregnation were investigated together with internal vs. external confinement of metallocene guests. Intrazeolite redox titrations, the homogeneity of metallocene impregnation and electron transfer were studied [10].

Cls core excitation spectra of $M(\eta\text{-}C_5H_5)_2$, where M = Fe, Co and Ni, have been derived from inelastic electron scattering spectra under conditions dominated by electric dipole transitions.

The spectra were quite different from that expected for the free cyclopentadienyl ligand. They showed a strong dependence of the near-edge π^* features on the nature of the metal atom. These spectra provided unambiguous experimental evidence for modification by metal bonding of the core excitation spectrum of a ligand [11].

The vibrational spectra of several organometallic compounds have been studied to probe intramolecular bonding. The infrared and low temperature Raman spectra of the manganese complexes $[(\eta\text{-arene})Mn(CO)_3]^+$, where arene = benzene, deuteriobenzene, toluene, mesitylene and hexamethylbenzene, were recorded and interpreted. The results indicated, 1) a stronger arene-manganese bond as compared to isoelectronic chromium compounds and 2) the arene ring coordinated to manganese was less aromatic than when it was coordinated to chromium. The Raman spectrum of $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ in liquid xenon was recorded. Improved spectral resolution led to reassignment of some of the vibrations [12].

The reaction of carbon monoxide with the complexes $(\eta\text{-}C_5H_5)_2M$ where M = V, Cr, Mn, Fe and Co; $(\eta\text{-}C_5Me_5)_2M$ where M = Mn and Ni, and $(\eta\text{-}C_6H_5Et)M(CO)_3$, where M = Cr, Mo and W, has been investigated at low temperatures via infrared spectroscopy [13]. Several mixed metal cluster compounds such as $R_2Sn[M^1(CO)_x]\text{-}[M^2(CO)_y(\eta\text{-}C_5H_5)]$, where M^1 and M^2 = Mo, Mn, Re, Fe, Co, have been prepared and investigated by ^{17}O NMR spectroscopy [14].

The reduction potentials of a number of metallocenes and metal complexes have been determined by cyclic voltammetry. It was suggested that electron transfer processes of complexes with potentials in the range +0.5 to -0.5 V were associated with antineoplastic properties [15]. A number of triple-decker sandwich complexes containing the carborane anion (cyclo-$Et_2B_3C_2H_3)^{4-}$ and the groups $(\eta\text{-}C_5H_5)Co$, $(\eta\text{-}C_5H_5)Fe$, $(\eta\text{-}Me.C_6H_4.\text{-}CHMe_2)Ru$, and $(\eta\text{-}C_5Me_5)Co$ have been prepared [16]. A related paper has described the use of fulvalene- and polyarene-transition metal-carborane complexes as building units for the construction of multilevel linked sandwich complexes [17].

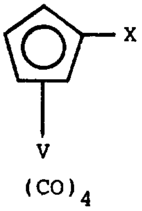
The ruthenium reagents $[(\eta\text{-}C_5Me_5)Ru(MeCN)_3]^+CF_3SO_3^-$ and $(\eta\text{-}C_5Me_5)Ru(\mu_3\text{-}Cl)$ have been prepared and treated with aromatic hydrocarbons to form polycationic complexes with specific shapes and geometries in respect of the positive charges [18,19].

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

Several Group IV derivatives of tetracarbonyl(η-cyclopentadienyl)vanadium (3.1; X = $SiMe_3$, $GeEt_3$, $SnEt_3$, $SnBu_3$) have been prepared by direct reaction between the ligand and hexacarbonylvanadium [20]. Reaction of vanadium hexacarbonyl with 1-phenyl-2,5-dihydro-1H-borole or with $[(\eta\text{-}C_5H_5)FeH(\eta\text{-}C_4H_4BPh)]$ gave the tetracarbonylvanadium complexes (3.2 and 3.3) respectively [21].

Bis(η-methylcyclopentadienyl)vanadium has been used in the synthesis of electron deficient tetrahedral clusters containing vanadium and chromium [22]. The bis(η-arene)vanadium complexes (3.4; R = H, Me, Et, $CHMe_2$, CMe_3) have been examined by UV spectroscopy and the ionization potentials calculated. Values in the range 5.63-6.16 eV were obtained [23]. Irradiation of the vanadium complex (3.5) at high dilution in frozen gas matrixes at 12 K has been studied by infrared spectroscopy using ^{13}CO labelling and energy-factored force-field fitting of terminal metal carbonyl stretching vibrations. Two types of reversible process occurred. One process was the ejection of carbon monoxide and the second involved a change in ring hapticity with the formation of species containing $\eta^3\text{-}C_5H_5$ [24].

Treatment of tetracarbonyl(η-cyclopentadienyl)vanadium with chlorine and oxygen afforded the vanadium oxodichloride (3.6) in good yield [25].



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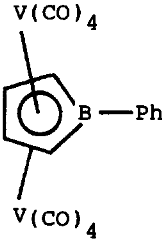

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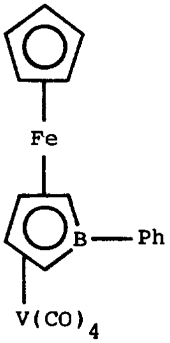

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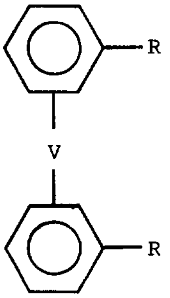

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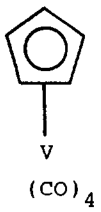

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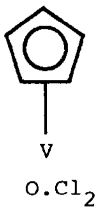

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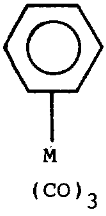
4. (η-C_6H_6)Cr$(CO)_3$

(i) Formation

The η^6-benzene complexes (4.1; M = Cr, Mo) have been prepared in 95 and 70% yields respectively by treating the metal carbonyl $M(CO)_6$ with benzene in the presence of pyridine as an initiator. The corresponding tungsten complex (4.1; M = W) was prepared in a similar manner in 80% yield using ammonium tetrafluoroborate as the initiator [26]. Eleven (η-anisole)tricarbonylchromium complexes, such as the (η-trimethoxytoluene)chromium species (4.2), have been prepared from the free ligand and hexacarbonylchromium [27].

Benchrotrenes have been prepared under mild conditions by irradiation of the arene and hexacarbonylchromium in THF. Ten complexes were prepared in this way [28]. The angiotensin II analogues (4.3; L = CO, PPh_3) have been prepared and shown to act as pure antagonists of angiotensin II on rabbit aorta strips [29].



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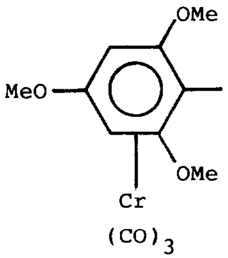

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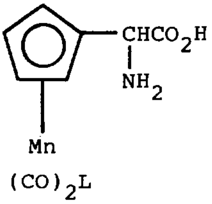

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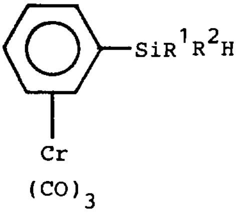
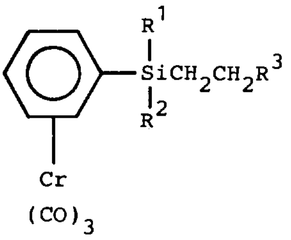
The tricarbonylchromium complexes (4.4; $R^1 = R^2$ = Ph, Me; R^1 = Ph, R^2 = Me) were formed by reaction of the corresponding silanes with hexacarbonylchromium. Treatment of the olefins $R^3CH=CH_2$ with the complexes (4.4; $R^1 = R^2$ = Ph, Me; R^1 = Ph, R^2 = Me) afforded the products of hydrosilylation (4.5; R^3 = Bu, $SiMe_3$) [30]. The 1,3- and 1,4-dilithiobenchrotrene complexes have been prepared from the corresponding bis(tributylstannyl)-benchrotrenes and treated with a variety of reagents to give several disubstituted benchrotrenes such as the 1,3-derivatives (4.6; X = Cl, Br, I, PPh_2) [31].

Reaction of hexacarbonylmolybdenum with trimesitylgallium (III) produced the η-mesityl-molybdenum complexes (4.7; n = 1, 2; M = Mo). Single crystal X-ray structural studies were used to characterize these complexes. Treatment of the complexes with hydrogen chloride demonstrated that the gallium-mesityl





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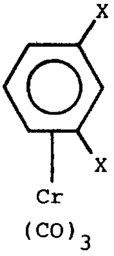

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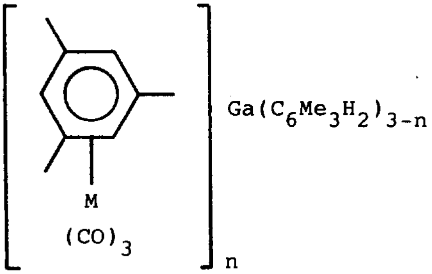

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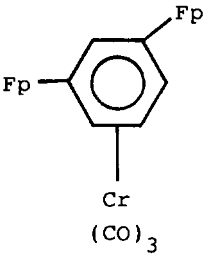
bond to the uncomplexed mesityl ring was preferentially cleaved. Reaction of hexacarbonylchromium with trimesitylgallium produced the chromium-complex (4.7; n = 1; M = Cr) [32].

Reaction of the phenylene-bridged complexes $C_6H_{6-n}(Fp)_n$, where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ and n = 2 or 3, with the metal carbonyls $M(CO)_6$, where M = Cr, Mo or W gave the complexes (4.8, 4.9; M = Cr, Mo, W and 4.10; M = Cr, Mo). Some related η^5-methylcyclopentadienyl-iron complexes were also prepared [33]. Benzoyl chlorides have been subjected to metathesis with $Na^+[(\eta\text{-}C_5H_5)Fe(CO)_2]^-$ to give phenylene bridged iron complexes which were treated with hexacarbonylchromium to give the corresponding benchrotrene complexes, such as the 1,3- and 1,4-substituted derivatives (4.11) [34].

Thermolysis of $Cr(CO)_6$ with 2,6-bis(trimethylsilyl)pyridine in dioxane followed by desilylation with aqueous Bu_4NF provided a good route to the η-pyridine complex (4.12). This complex



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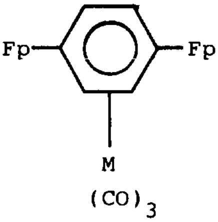

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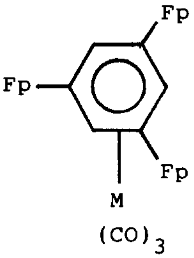

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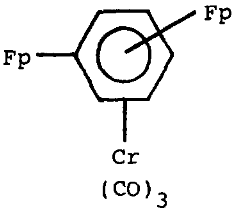

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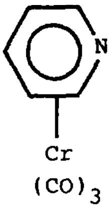

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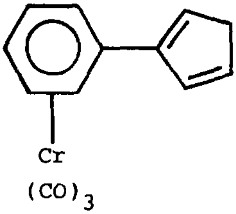

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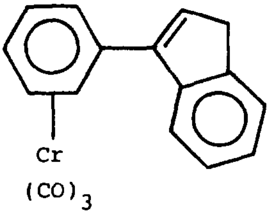

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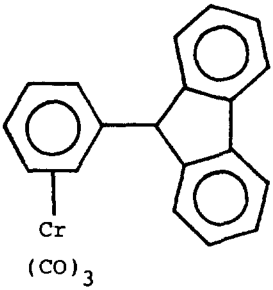

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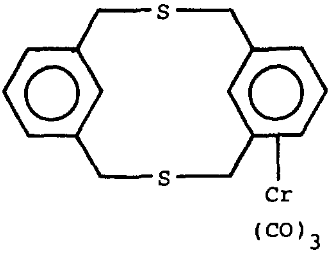

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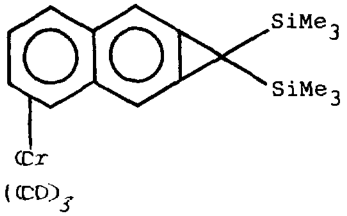
underwent regioselective lithiation and regio- and stereoselective nucleophilic additions at the 2-position [35].

Phenylation of several cyclic carbanions with fluorobenchrotrene gave benchrotrene derivatives of the reagents.

Thus the anions formed from cyclopentadiene, indene and fluorene gave the products (4.13, 4.14 and 4.15) respectively. Regio- and stereo-isomers obtained in the reactions were identified [36]. The (η-2,11-dithia[3,3]metacyclophane)chromium complex



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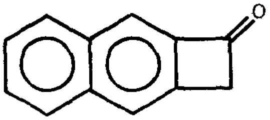

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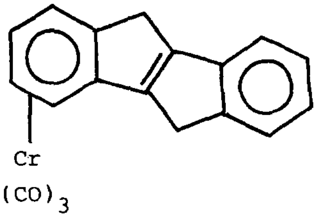

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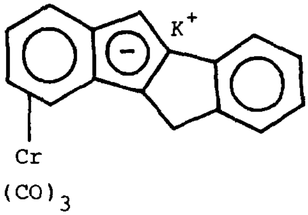

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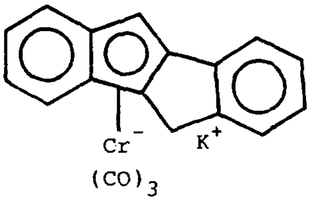

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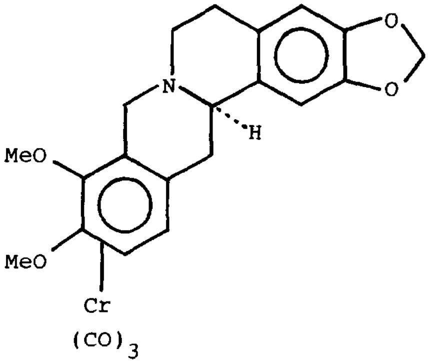
(4.16) and several of its derivatives have been prepared and characterized [37].

The tricarbonylchromium complex (4.17) was prepared by reaction of the free ligand with $Cr(MeCN)_3(CO)_3$. The presence of the trimethylsilyl groups was essential because when the reaction was carried out with unprotected cyclopropa[b]naphthalene, cyclobuta[b]naphthalen-1-one (4.18) was produced [38].

The (η-indenoindene)chromium complex (4.19) has been prepared by direct reaction between the ligand and $Cr(CO)_3(NH_3)_3$. Deprotonation of the complex (4.19) with the potassium salt of t-butanol in THF at -65°C gave the (η^6-arene)chromium anion (4.20) which isomerized to the (η^5-cyclopentadienyl)chromium anion (4.21) at 25°C. Some reactions of the anions (4.20 and 4.21) were examined [39].

Canadine underwent regioselective complexation with the tricarbonylchromium group to give the product (4.22) as a mixture



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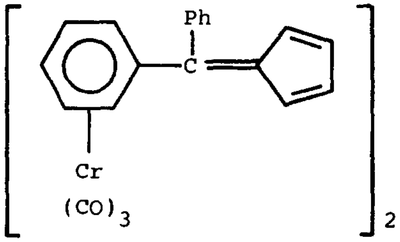

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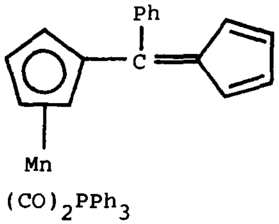

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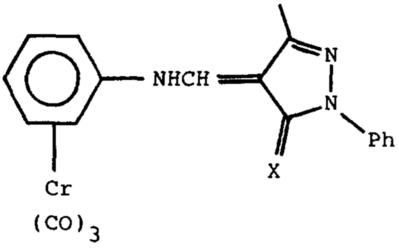
of two diastereoisomers which were separated by flash chromatography. The separated isomers were converted by several stages to enantiomerically pure (-)-(8R)- and (-)-(8S)-methylcanadine [40]. The pentafulvenes (4.23 and 4.24) have been prepared by condensing cyclopentadiene with (η^6-$C_6H_5CSPh)Cr(CO)_3$ and (η^5-$C_5H_4COPh)Mn(CO)_2PPh_3$ respectively [41].

(η^6-Aniline)tricarbonylchromium combined with 5-thiopyrazole and 5-selenopyrazole aldehydes to give the benchrotrene derivatives (4.25; X = S, Se). These derivatives (4.25) were used as chelating ligands towards transition metal cations, thus nickel(II) acetate in ethanol gave a dimeric chelate complex [42]. Treatment of $(OC)_4Cr{=}C(Me)NMe(\eta^2\text{-}CH_2CH{=}CH_2)$ with diphenylethyne gave the product of insertion and cyclopropanation (4.26). The phenyl-substituted carbene complex $(OC)_4Cr{=}C(Ph)NHCH_2CH{=}CH_2$ on reaction with alkynes produced the corresponding annulation products (4.27) and (4.28; $R^1 = R^2$ = Et; R^1 = Me, R^2 = Ph) [43].



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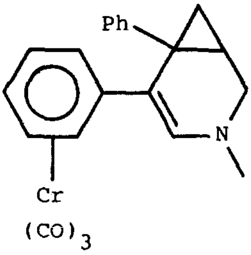

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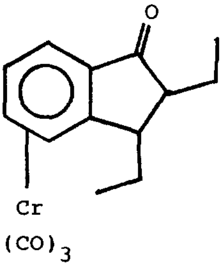

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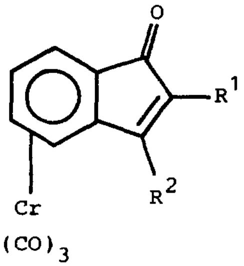

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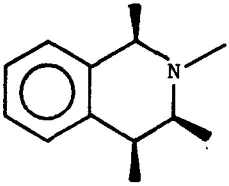

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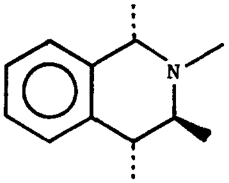
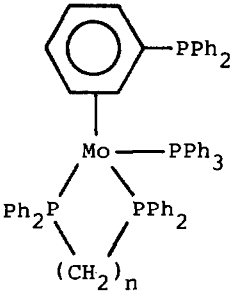


4.30

The tricarbonylchromium group coordinates preferentially to the least hindered face of (+)-(3S)-2,3-dimethyl-1,2,3,4-tetrahydroisoquinoline and the complexes formed undergo regio- and stereo-selective <u>exo</u>-1,4-dimethylation by sequential treatment with BuLi-MeI and Me_3CLi-MeI followed by oxidative decomplexation to give the products (4.29 and 4.30) [44].



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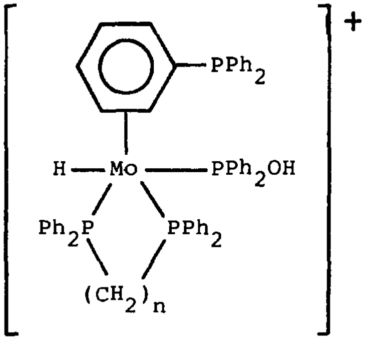

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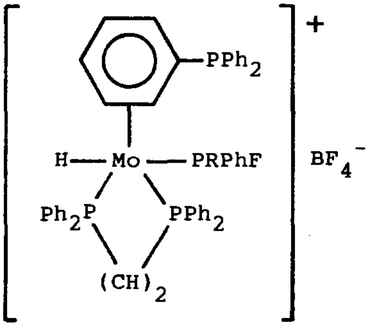

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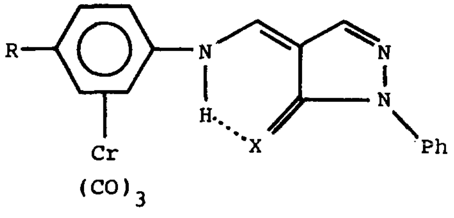
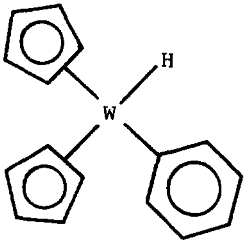


4.34

Reaction of the molybdenum complexes (4.31; n = 1-3) with aqueous HBF_4 or HF produced the corresponding fluxional cations (4.32) and $HPPh_3^+$. When the same reaction was carried out with anhydrous $HBF_4.OEt_2$ the fluorophosphine derivatives (4.33; R = Ph, Me) were isolated. The crystal and molecular structure of the salt (4.33; R = Ph) was determined by X-ray analysis [45]. Reaction of η-aniline- or η-toluidine-chromiumtricarbonyl complexes with pyrazolyl aldehydes gave the corresponding pyrazoles (4.34; R = H, Me; X = O, S, Se). Reaction of these pyrazoles with $M(OCOCH_3)_2$, where M = Ni, Zn, Cd, or Hg, produced the corresponding tetracoordinated bis[5-oxo(thio or seleno)pyrazolaldiminato]-metal chelates with an η-arenetricarbonylchromium moiety attached [46].

Treatment of the tungsten complex (4.35) with triammine-tricarbonylchromium gave the corresponding tricarbonylchromium complex (4.36; X = H). Reaction of this latter complex with CCl_4, $CHBr_3$ or MeI produced the halogenated derivatives (4.36; X = Cl, Br, I) [47].



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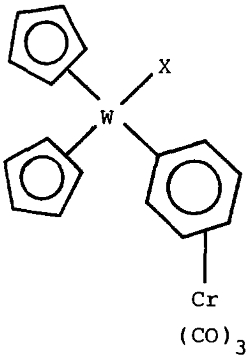
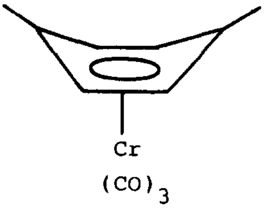


4.36

4. (ii) Spectroscopic and Physico-chemical studies

Ab initio SCF calculations have been used to predict the charge densities on the aryl carbons in the "boat" form of tricarbonyl(p-xylene)chromium (4.37). These predictions were found to be in agreement with the observed geometry-dependent ^{13}C NMR complexation shifts for Cr(η-paracyclophane)$(CO)_3$ complexes [48].



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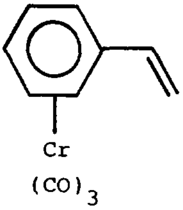
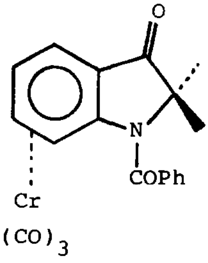


4.38

The structure of the tricarbonylchromium complex (4.38), a crystal active in second-harmonic generation, has been determined by X-ray analysis [49]. The crystal and molecular structures of four tricarbonylchromium complexes of [2.2]-paracyclophanes have been determined by X-ray crystallography. The interannular distances and widths across the two benzene decks varied with the substituents present and the number of tricarbonylchromium groups. Withdrawing π-electron density from the benzene decks caused them to move closer together [50].

Nucleophilic attack on the (η-indoxyl)chromium complex (4.39) occured at C-3 stereospecifically <u>anti</u> to the tricarbonylchromium moiety to give the hydroxyindoline complexes (4.40; R = H, Me, CH_2CN). The crystal and molecular structure of one complex (4.40; R = H) was determined by X-ray crystallography. The five-membered ring in the complexes (4.40) underwent ring opening by way of an intermediate carbanion [51].

The crystal and molecular structure of the bis(tricarbonyl-



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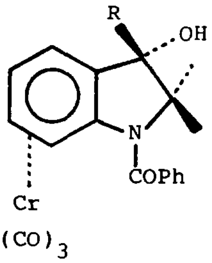

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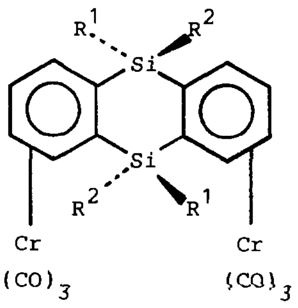

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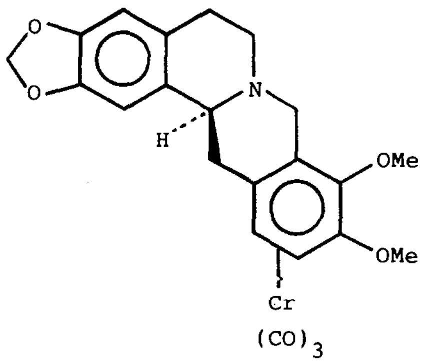
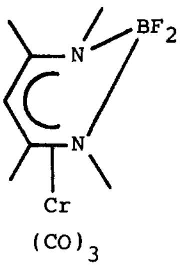


4.42

chromium) complexes (4.41; $R^1 = R^2 = OEt$; $R^1 = Me$, $R^2 = OCHMe_2$) have been determined by X-ray crystallography. The dihydroanthracene ligands in the complexes had boat and flattened chair conformations respectively [52]. The crystal and molecular structures of the endo- and exo-isomers of tricarbonyl(η-dibenzobicyclo[2.2.2]octadiene)chromium have been determined by X-ray crystallography. The exo-isomer showed deformations of Cr-C distances and Cr-C-O bond bending and tilting [53].

The structure of the tricarbonylchromium complex of the alkaloid (-)-canadine (4.42) has been determined by X-ray analysis. The molecule was almost planar with the two aromatic rings inclined at an angle of 150.1° to each other [54,40]. Reaction of $(CO)_3Cr(CH_3CN)_3$ with difluorodiazaborinane gave the tricarbonylchromium complex (4.43). X-Ray analysis showed the structure of this compound to be analogous to that of the isoelectronic complex (4.44) [55].

The X-ray photoelectron spectra of a series of benchrotrene complexes have been recorded and interpreted. The 2p electron binding energies indicated that the chromium atom was in a near zero oxidation state [56]. The valence photoelectron spectra of the cymantrene complex (4.45) and the ligand $HSiCl_3$ have been measured in an investigation of electronic structure factors that were involved in Mn to Si-H interaction. Fenske-Hall



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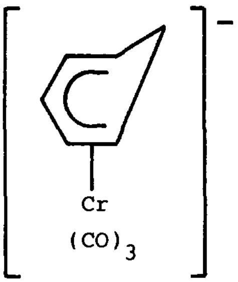
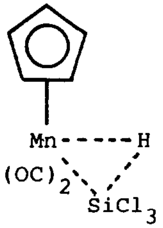


4.44

calculations showed that the metal d hybrid orbitals used for the Mn-Si and Mn-H bonds make an acute angle of 50° to 70° and bring about the close association of the silicon and hydrogen atoms [57].

Perbenzoyl-α- and -β-cyclodextrins have been treated with $(NH_3)_3Cr(CO)_3$ to give the corresponding benchrotrenylcyclodextrins. The CD spectra of these compounds showed a Cotton effect [58]. The IR spectra of a large number of benchrotrene compounds with various functional groups have been recorded and the carbonyl region interpreted to obtain the force constants for the carbonyl bond. The force constants were correlated with Hammett, Taft and Swain-Lupton parameters [59].

Cymantrene and methylcymantrene underwent infrared multiphoton decomposition with a carbon dioxide TEA laser. The manganese-cyclopentadienyl bond underwent homolytic cleavage in excited vibrational states to give the tricarbonylmanganese



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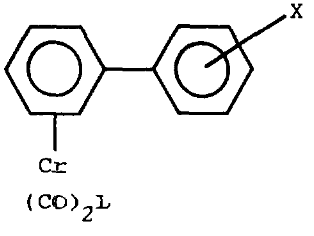

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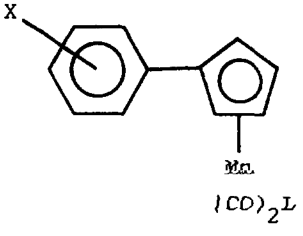
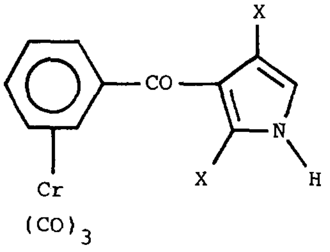


4.47

moiety and the cyclopentadienyl radical. The volatile organic products were carbon monoxide and cyclopentadiene or methylcyclopentadiene [60]. Several benchrotrene and cymantrene complexes (4.46 and 4.47; X = 3-F, 4-F; L = phosphine or phosphite) respectively, have been prepared and the IR and ^{19}F NMR spectra recorded. The carbonyl stretching frequencies and the ^{19}F chemical shifts have been used to calculate Taft substituent constants [61].

A series of monosubstituted (η-arene)chromium-tricarbonyl and -dicarbonyltriphenylphosphine complexes has been prepared and characterized via infrared and NMR spectroscopy. The carbonyl stretching force constants for all the compounds were calculated [62]. The tricarbonylchromium complexes of a series of substituted 3-benzoylpyrroles, for example, the complexes (4.48; X = Cl, I) have been prepared and studied by infrared and ^{1}H NMR spectroscopy. These spectra were compared with those



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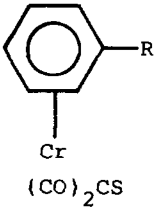

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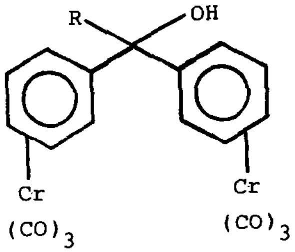

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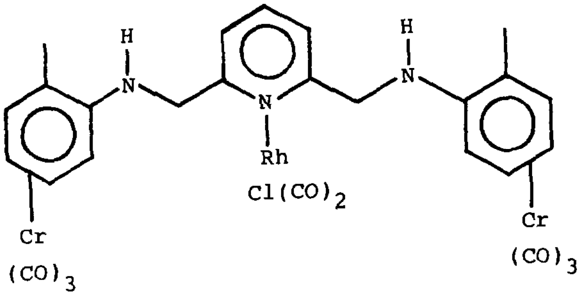

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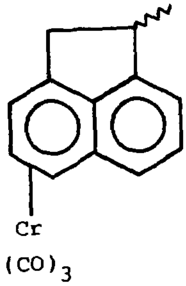

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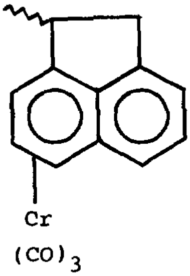


4.53

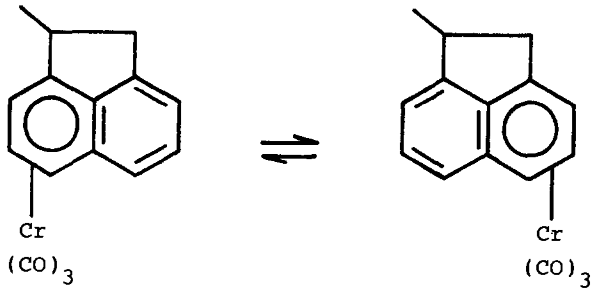
obtained in the absence of a tricarbonylchromium group [63]. The infrared stretching frequencies of the CO and CS ligands in the benchrotrene complexes (4.49; R = H, Me, Cl, CO_2Me) have been measured and interpreted. The intensities were dependent on the nature of the substituent R. A good correlation with the Hammett substituent parameter was obtained [64].

The tricarbonylchromium complexes [4.50; R = CH_3, $CH_3(CH_2)_n$ where n = 1, 2, 3, 4, 12, 14 and 16] have been prepared. The ^1H and ^{13}C NMR spectra of these complexes were consistent with the electron withdrawing properties of the tricarbonylchromium group [65]. Scalar ^{13}C, ^1H and ^{13}C, ^{19}F spin-spin coupling between carbonyl carbon atoms and aromatic protons or fluorine atoms has been observed in benchrotrene complexes. The coupling constants were dependent on the electron donating properties of the arene ligand [66].

Ten benchrotrene derivatives have been studied by thermal analysis and gas chromatography. Trends in the volatilities, thermal stabilities and gc retentions were interpreted in terms of chromium-ligand bond energies, polarity and steric effects [67]. The dynamics of the krypton fluoride laser multiphoton dissociation of a series of tricarbonylchromium complexes has been investigated in the gas phase using emission spectroscopy to detect the excited state photoproducts. For all the compounds electronically excited chromium atoms were formed via a two-channel dissociation mechanism. The lower energy excited states were formed by a sequential absorption and fragmentation process. The higher energy states were formed exclusively by a direct dissociation process [68, 69].

The heterotrimetallic complex (4.51) and the corresponding 1,10-phenanthroline complex have been synthesised and shown to undergo fast thermal and photochemical carbonyl exchange [70]. Treatment of 1-methylacenaphthene with $Cr(CO)_3(pyridine)_3$ gave the corresponding (η-arene)chromium complexes (4.52 and 4.53) each of which existed as two stereoisomers. The complexes (4.52 and 4.53) underwent haptotropic rearrangement by intramolecular transfer of the tricarbonylchromium group which preserved the stereochemistry [71].

Inter-ring haptotropic rearrangements in the η-acenaphthylene complex (4.54) and the η-biphenylene complexes (4.55; R = D, Me) have been studied by ^1H NMR spectroscopy [72]. The



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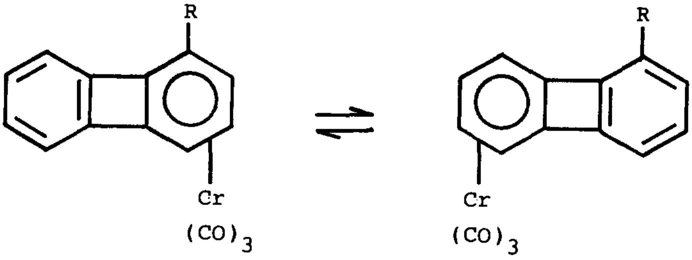
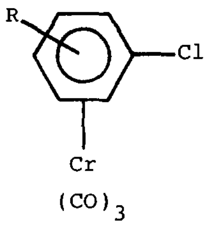


4.55

failure of highly electrophilic benchrotrenes to undergo nucleophilic substitution has been discussed [73].

The regioselectivity of the addition of nucleophiles to the benchrotrenes (4.56; R = 2-, 3-, 4-Me) has been studied under *cine* or *tele* S_NAr conditions. The results indicated that stabilized carbanions added predominantly to the carbon eclipsed by a Cr-CO bond of the most stable conformer [74]. Several diastereomeric *syn* and *anti* tricarbonylchromium complexes of 1-substituted indenes have been prepared and the regioselectivity of nucleophilic addition studied. Thus the *syn*-isomer (4.57) was attacked by $LiCMe_2CN$ to give the indanes (4.58 and 4.59) as the principal products while the *anti*- isomer (4.60) gave mainly the products (4.58 and 4.61) [75].

Diastereoselective tricarbonylchromium complexation has been used to achieve 1,5-remote diastereoselection in the alkylation of the benzylic position in the complex (4.62) [76].



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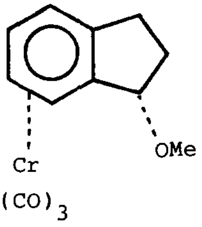

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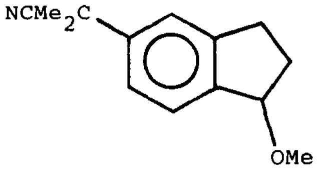

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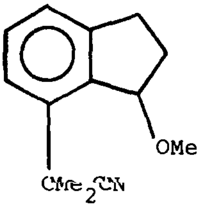

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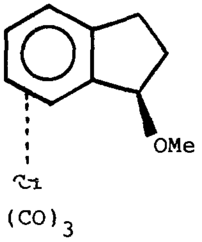

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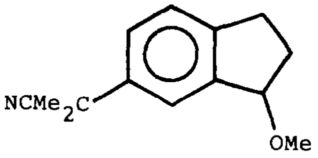

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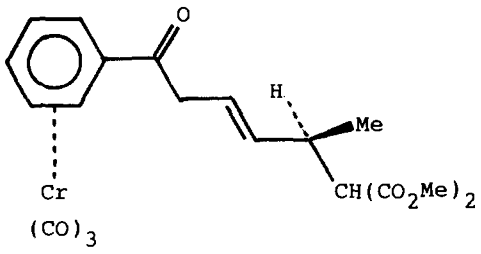

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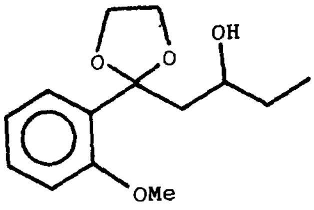
Diastereoselective tricarbonylchromium complexation of *o*-alkoxyphenyl ligands with a benzylic acetal and an allylic alcohol followed by chirality transfer of allyl group and then stereoselective conversion of the acetal to an alkyl group



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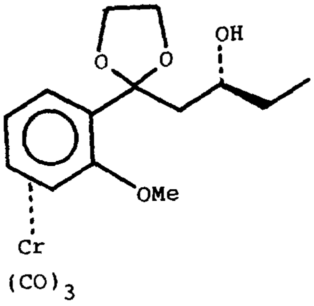

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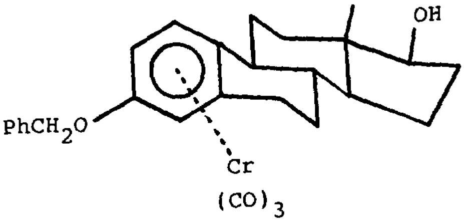

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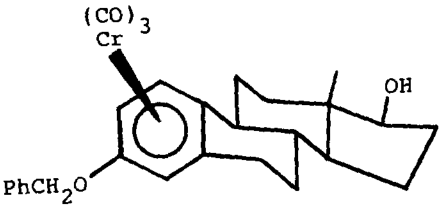

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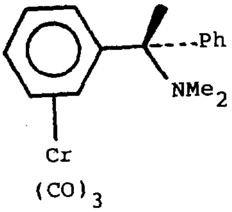


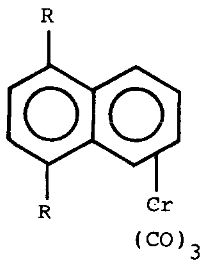
4.67

achieved 1,5-stereocontrol. Thus the ligand (4.63) gave predominantly one diastereomer of the tricarbonylchromium complex (4.64) [77].

The α- and β-diastereoisomers of the steroid hormone receptor marker [3-(benzyloxy)-17β-hydroxyestra-1,3,5(10)-triene]tricarbonylchromium (4.65 and 4.66) have been differentiated electrochemically. Voltammetry at both conventional (linear diffusion) and microsized (radial diffusion) platinum electrodes showed that the diastereoisomers exhibited oxidation processes which differed kinetically and thermodynamically. It was concluded that electrochemical techniques might provide a probe for ascertaining the bonding interactions in the hormone receptors known to be present in mammary tumours [78].

Benchrotrene complexes with chiral benzylic side chains, such as the tertiary amine (4.67), showed diastereotopic group selective deprotonation reactions. Product stereochemistry was determined by the side chain adopting a conformation which minimized steric contact with the tricarbonylchromium group [79]. The addition of carbanions to (η-arene)tricarbonylchromium has been found to show thermodynamic control of regioselectivity. Thus 2-lithio-2-methylpropionitrile underwent reversible addition to the naphthalene complexes (4.68; R = H, OMe), the anisole complex (4.69) and the t-butylbenzene complex (4.70). Rates of reaction and activation parameters were determined [80].

Cymantrene, pentaethylcymantrene, tricarbonyl(η-cyclopentadienyl)rhenium, trimethylbenchrotrene and related complexes formed hydrogen bonds to $(CF_3)_3COH$ through a carbonyl ligand. The interactions took place in liquid xenon at low temperatures



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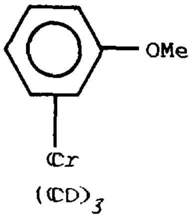

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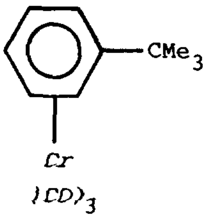
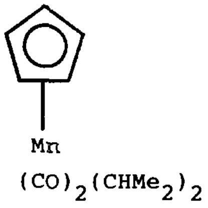


4.70

and tetrachloromethane at room temperature and were detected by IR spectroscopy [81].

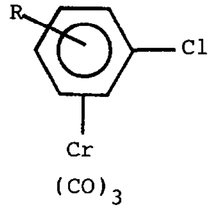
The cymantrene complex (4.71) underwent protonation with hydrogen chloride in liquid xenon, first at a carbonyl oxygen atom and then at manganese. Perfluoro-tert-butanol in tetrachloromethane formed hydrogen bonds with the carbonyl oxygen in related organometallic complexes [82].



4.71

4. (iii) General Chemistry

Fluoro- and chloro-benchrotrene underwent nucleophilic substitution with carbanions formed from $CH_2(CO_2Et)_2$, $CH_2(Ph)CN$ and $CH_2(CO_2Et)CN$ using phase-transfer conditions. Decomplexation with iodine gave the corresponding substituted benzene compounds [83]. Benchrotrene derivatives (4.72; R = H, 2-, 3-, 4-Cl, 3-OMe, 2-Me) underwent displacement of the chloride by Me_3CCO_2NHOH to give the O-arylhydroxylamines (4.73; R = H, 2-,



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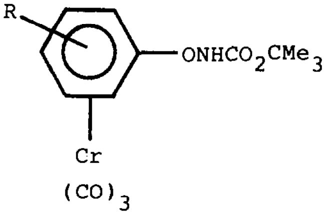

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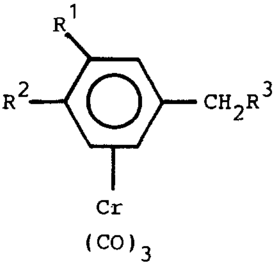

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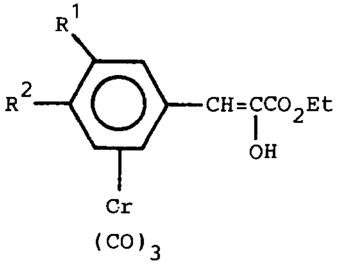

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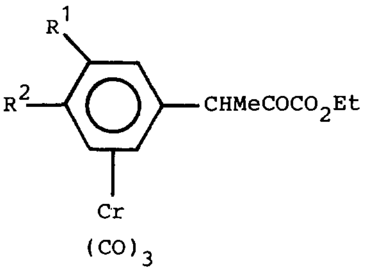
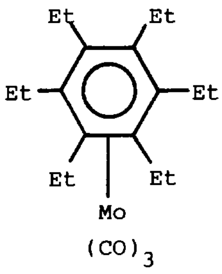


4.76

3-, 4-Cl, 3-OMe, 2-Me). These products (4.73) were decomplexed and then hydrolyzed with hydrogen chloride in diethyl ether to give the corresponding O-arylhydroxylamine hydrochlorides [84]. The benchrotrene complexes (4.74; R^1 = H, Me, R^2 = H,



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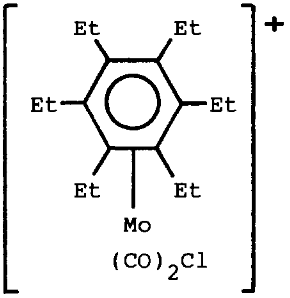
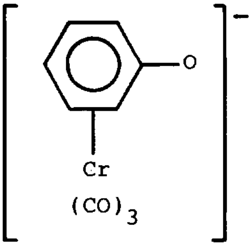


4.78

Me_3C, OMe, R^3 = H, Me, Et) were treated with EtO_2CCO_2Et in the presence of Me_3COK and Me_2SO gave the keto-esters (4.75 and 4.76; R^1 = H, Me, R^2 = H, Me_3C, OMe) as the enol and keto forms respectively. Increased conjugation favoured the enol form [85].

Chlorobenchrotrene underwent double carbonylation in the presence of diethylamine and the catalyst $(Ph_2PMe)_2PdCl_2$ to give the product $PhCOCONEt_2$ [86]. The (η-hexaethylbenzene)-molybdenum complex (4.77) has been oxidized with chlorine in tetrachloromethane to form the cation (4.78) [87]. Tricarbonyl-(η-phenol)chromium has been treated with aqueous base to give the (η-phenoxide)chromium complex (4.79) which on reaction with



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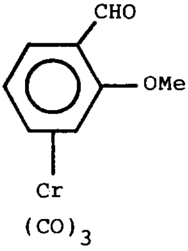

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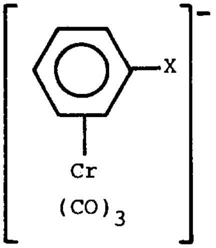


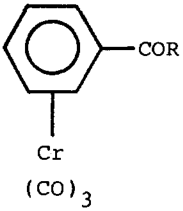
4.81

electrophiles, such as CF_3COCl, gave the corresponding derivatives. The zirconocene salt of the anion (4.79) has been characterized by X-ray crystallography. The O-arene bond showed some double bond character [88].

The homochiral [η-(+)-o-anisaldehyde]tricarbonylchromium complex (4.80) underwent stereoselective addition to give enantiomerically pure alcohols [89]. The metal carbonyl substituted benchrotrenes [4.81; X = $Fe(CO)_4$, $Cr(CO)_5$, $W(CO)_5$] have been prepared from fluoro- and chloro-benchrotrenes. X-ray crystallography has been used to confirm the η^6-arene structure as opposed to the possible η^5-cyclohexadienide carbene form [90]. Reduction of the benchrotrene ketones (4.82; R = Me, Et, $CHMe_2$) with bakers yeast gave alcohols (4.83) which in some cases showed a high enantiomeric excess [91].

Lithiation of the tricarbonylchromium complexes (4.84; R = H, CH_2OMe) followed by treatment with an electrophile produced the corresponding 4-substituted indole complexes (4.85; R^1 = H, R^2 = $SiMe_3$, CO_2Me, CO_2Et, $CH_2CH{=}CMe_2$, $SnMe_3$, I; R^1 = CH_2OMe, R^2 = $SiMe_3$, CO_2Me, $SnMe_3$, I). The tricarbonylchromium was removed almost quantitatively from these complexes by irradiation in air. Desilylation was carried out with tetrabutylammonium fluoride to give the corresponding 4-substituted indoles [92].

Tricarbonyl(η^6-indene)chromium (4.86) has been deprotonated with potassium hydride to give the anion (4.87) which has been trapped as a rhodium complex or converted on heating to the (η^5-indenyl)chromium complex (4.88) [93]. The bis(tricarbonylchromium complex (4.89) has been used to prepare substituted



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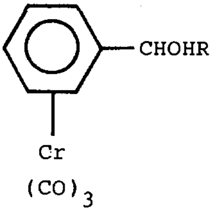

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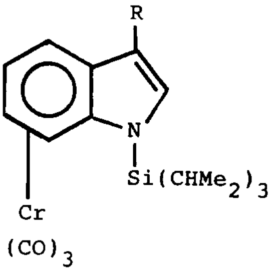

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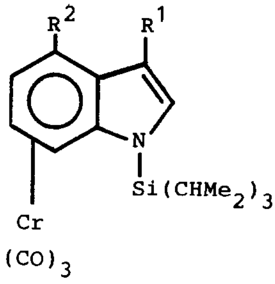

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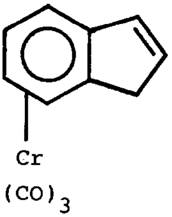

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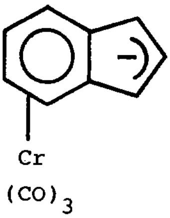

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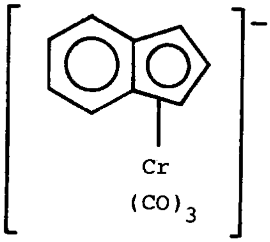

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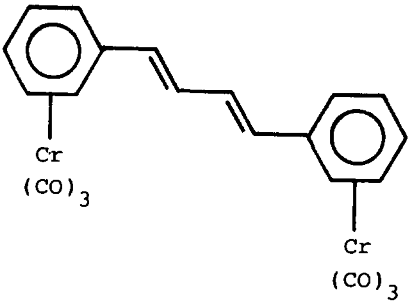
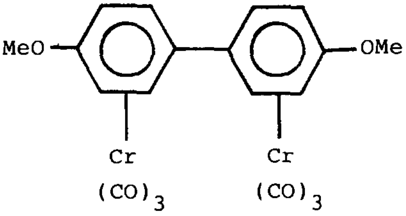


4.89

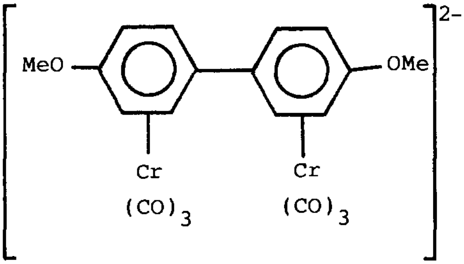
1,4-diphenyl-2-butenes [94]. The (E,E)-benchrotrene (4.89) has been reduced with lithium naphthalenide and then treated with acyl chlorides and alkyl halides to form, after oxidative decomplexation, diacylated and dialkylated 1,4-diphenylbutenes [95].

Reduction of the bis(tricarbonylchromium) complex (4.90) gave the dianion (4.91) which underwent reaction with the electrophiles methyl- or ethyl-trifluoromethanesulphonate or allyl tosylate followed by CF_3CO_2H and iodine to produce the corresponding 4-alkyl-4(4-methoxyphenyl)cyclohex-2-en-1-ones (4.92; R = Me, Et, allyl) [96].

The tricarbonylchromium steroid complex (4.93), as a mixture of α and β forms, underwent a nucleophilic addition-oxidation reaction with the lithium salt of 1,3-dithiane to form the C-1 substituted steroid (4.94) [97]. Photolysis of methylbenchrotrene with triphenyltin hydride gave the triphenyltin complex (4.95)



4.90



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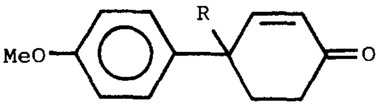

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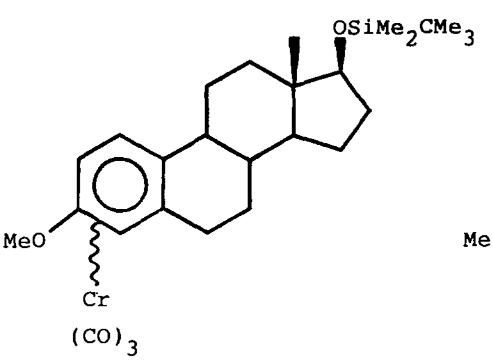

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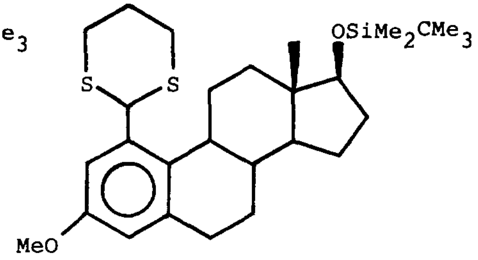
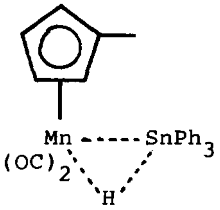


4.94

with an Mn, H, Sn three-centre bond. With an excess of triphenyltin hydride the complex (4.95) formed the bis-stannyl derivative (4.96) [98].

Benchrotrenes and related complexes (4.97; $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = R^2 = Me$; M = Cr, Mo, W) have been used as catalysts for the cleavage and benzoylation of dibutyl ether with benzoyl chloride. The reactivity of the catalysts varied with the metal in the order: Mo > W > Cr. Polymer-immobilised catalysts were also examined [99]. The tricarbonylchromium complexes (4.98 and 4.99; M = Cr) underwent metallotropic



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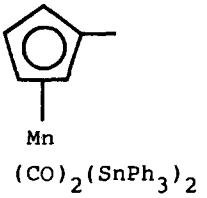

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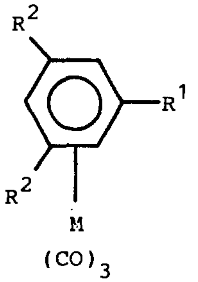

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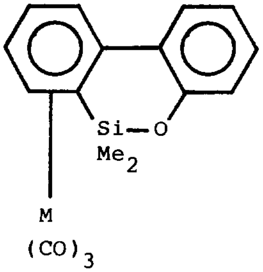

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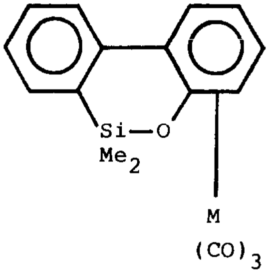
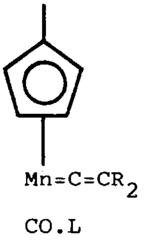


4.99

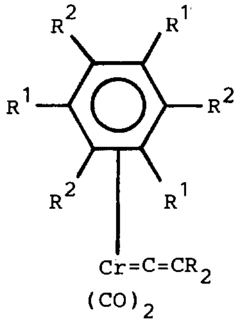
rearrangement on heating at >130° to give a mixture of the complexes. The tungsten analogues (4.98 and 4.99; M = W) behaved in a similar manner at lower temperatures [100].

The complexes (η^5-$C_5H_4CH_3$)MnCOL, where L = CO, $PMePh_2$, $P(OMe)_3$ and $P(OPh)_3$, and (η^6-$C_6R^1{}_3R^2{}_3$)$Cr(CO)_2$, where $R^1 = R^2$ = H, Me; R^1 = H, R^2 = 1, 3, 5-Me, were generated photochemically and when treated with (α-chlorovinyl)silanes gave the corresponding vinylidene complexes (4.100 and 4.101; R = Me, Ph). Reaction with an excess of the (α-chlorovinyl)silanes produced the corresponding butatriene derivatives, for example, the complexes (4.102) [101].

Benchrotrene compounds have been used to form inclusion complexes with β- and γ-cyclodextrin. When the arene ligand was benzene, toluene or o-xylene, 1:1 crystalline inclusion compounds were formed with β-cyclodextrin. However when mesitylene or hexamethylbenzene were ligands then no complex



4.100



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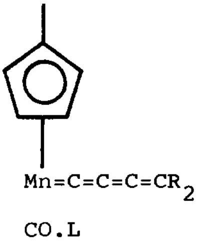
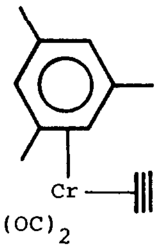


4.102



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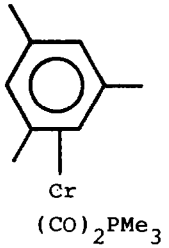

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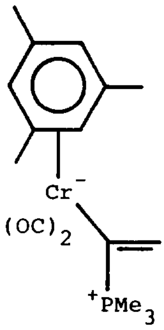
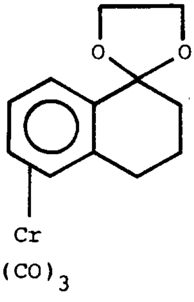


4.105

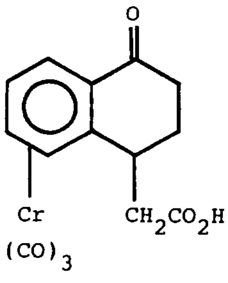
was formed. γ-Cyclodextrin formed complexes with all of the benchrotrenes used [102].

The benchrotrene complex (4.103) combined with trimethylphosphine to give the adduct (4.104) and the substitution product (4.105). Dimethylamine gave a dimethylaminocarbene derivative which was characterized by X-ray crystallography [103]. Reaction of the tricarbonylchromium complex (4.106) with sodium amide followed by $BrCH_2CO_2Na$ produced the keto-acid (4.107). This complex was used in the preparation of 6,7-benzomorphan [104].

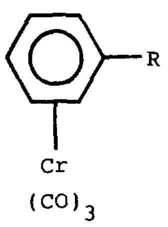
The gas phase reactions of several benchrotrene complexes (4.108; R = H, Me, CMe_3, F, Cl, Br, I) with ammonia have been studied by mass spectrometry. A proton added to the metal and then migrated to the arene ligand. An ammonia molecule then added to the protonated benchrotrene [105]. The effect of



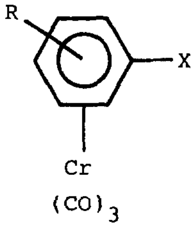
4.106



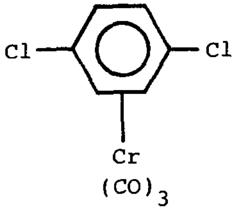
4.107



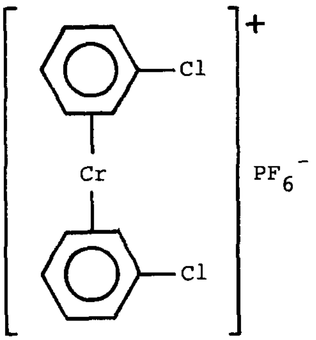
4.108



4.109



4.110



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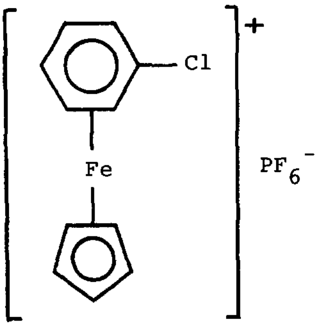
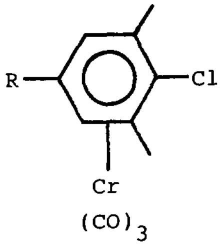


4.112

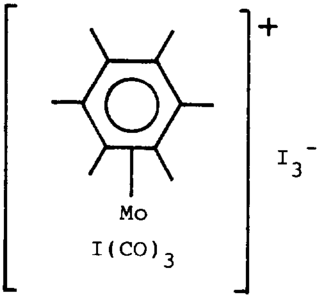


4.113

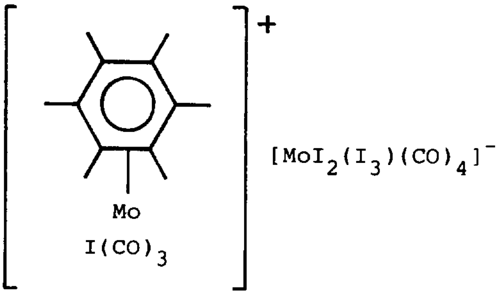
substituents on the rate of chlorine substitution by sodium methoxide in methanol has been investigated in the tricarbonylchromium complexes (4.109; X = Cl, R = 3- and 4-OMe, 2-, 3- and 4-Me, H, 2-, 3- and 4-Cl, 3- and 4-CO_2Me). The products of substitution (4.109; X = OMe, R as listed) were obtained in high yields [106].

The kinetics and mechanism of the substitution reactions of the complexes (4.110, 4.111 and 4.112) with piperidine in acetone have been investigated. The rate determining step for the complex (4.110) was the formation of an intermediate σ complex whereas with the other two complexes (4.111 and 4.112) it was the decomposition of the σ complex [107]. The chlorobenchrotrene complex (4.113; R = H) combined with 2-lithio-2-methylpropionitrile and 2-lithio-2-phenyl-1,3-dithiane to give, after treatment with trifluoroacetic acid the benchrotrene derivatives [4.113; R = CMe_2CN, $\overline{CPhS(CH_2)_3S}$] [108,109].

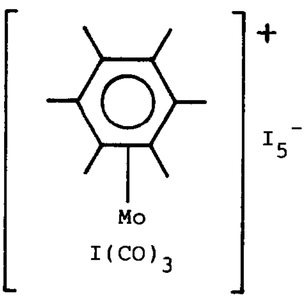
The carbonylation of (η^6-arene)$Mo(CO)_3$ complexes to $Mo(CO)_6$ was catalysed by iodine, $[MoI(CO)_3(\eta^6\text{-arene})][Mo_2I_5(CO)_6]$ or $Mo_2I_4(CO)_8$. The rate of carbonylation decreased with the introduction of methyl groups onto the η^6-arene ligand. In



4.114



4.115



4.116

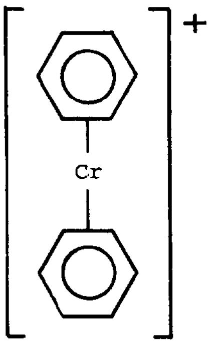
these reactions experimental evidence was obtained for an inner sphere electron transfer reaction between molybdenum(II) and molybdenum(O) [110]. In a related paper the reaction of $Mo_2I_4(CO)_8$ with the triiodide salt (4.114) to give the complex (4.115), containing a coordinated triiodide ligand, was reported. A small amount of the complex (4.116) was also isolated from this reaction. The structures of the molybdenum compounds (4.115 and 4.116) were determined by X-ray crystallography [111].

Reaction of the salts $[MoI(CO)_3(\eta^6\text{-arene})][Mo_2I_5(CO)_6]$, where arene = C_6H_5Me, $1,4\text{-}Me_2C_6H_4$ and $1,3,5\text{-}Me_3C_6H_3$, with carbon monoxide under pressure gave $Mo_2I_4(CO)_8$ in good yields [112].

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

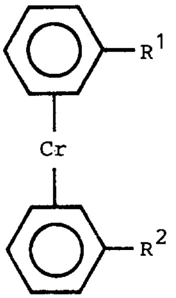
Bis(η-benzene)molybdenum has been formed from molybdenum atoms and benzene and used in the vapour phase deposition of a molybdenum film [113]. The crystal and molecular structure of the bis(η-benzene)chromium salt (5.1) has been determined by X-ray crystallography. The mercury atom was in triangular coordination [114]. Several bis(η-benzene)chromium complexes (5.2; R^1 = H, CN, R^2 = H, Me, OMe, Cl, F, CF_3, CN) have been studied by He-I photoelectron spectroscopy. Substituent parameters have been determined which permitted the calculation of the first and second ionization porentials [115].

A first ionization potential of 6.12 eV for the complex (5.3) has been determined from gas-phase electronic absorption spectral data [116]. Vapour-phase UV spectra of bis(η-arene)-chromium complexes have been recorded and compared with those of isoelectronic ferrocene and 1,1'-dimethylferrocene [117].

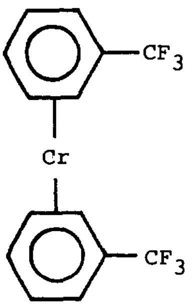


$[(C_6H_5)_3Ge]_2HgI^-$

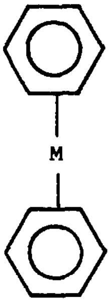
5.1



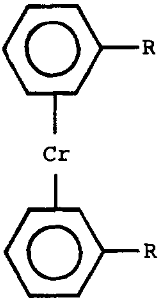
5.2



5.3



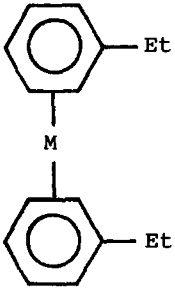
5.4



5.5

The vapour phase electronic spectra of bis(η-benzene)-molybdenum and bis(η-benzene)chromium (5.4; M = Mo, Cr) have been recorded and assigned. A Rydberg series was observed in the spectrum of (5.4; M = Mo) [118]. The near UV spectra of bis(η-arene)chromium complexes (5.5; R = H, Me, Et, $CHMe_2$, CMe_3) and polymethylarene complexes have been measured and assigned. Rydberg series corresponding to the ionization energy of the species were observed [119].

Infrared spectroscopy indicated that the complexes (5.6; M = Cr, Mo, V; 5.7 and 5.8) and 1,1'-diethylferrocene formed hydrogen bonds with phenol and t-butyl alcohol. The stability of the hydrogen bonds increased in the order Mo < V < Cr [120]. Reduction of bis(η-benzene)chromium complexes (5.9; X = H, Me, CF_3, OMe, COMe, F, Cl, CN) at a rotating disc cathode has been compared with the reactions of the free ligands. Two-electron waves were observed for the complexes while the ligands gave one-electron waves [121].



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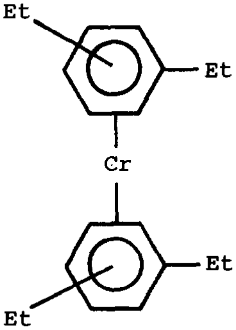

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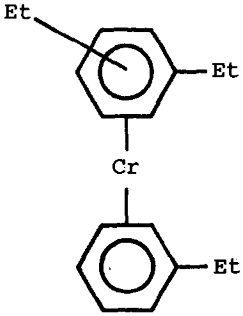

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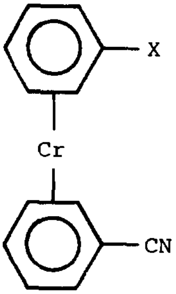

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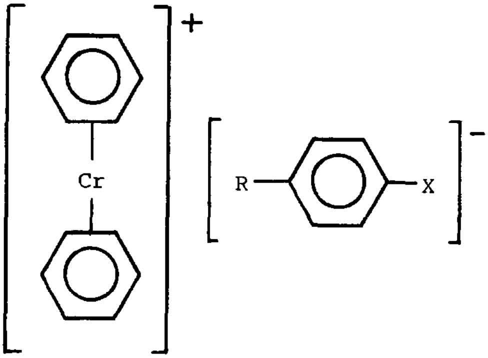
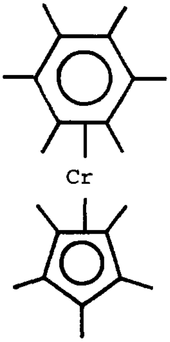


5.10

The voltammetric behaviour of bis(η-biphenyl)chromium in dimethylformamide at a glassy carbon electrode has been investigated. The voltammograms showed that the chromium complex was reduced in two one-electron steps and the first step was thermodynamically reversible [122]. Electron cyclotron resonance plasma chemical vapour deposition has been used to produce a chromium film from bis(η-benzene)chromium and an iron carbide film from ferrocene [123].

The salts (5.10; X = O, CO_2, S, NSO_2Ph; R = H, F, NO_2) were prepared by treating bis(η-benzene)chromium with the corresponding benzene derivative p-RC_6H_4XH [124]. The infrared and ultraviolet spectra of these bis(η-benzene)chromium phenolates, thiophenolates and N-phenylsulphonylanilides were recorded in the solid state and in solution. The results indicated that the salts (5.10) existed as ions rather than ion pairs [125].

The bridged complex $[(\eta^5\text{-}C_5Me_5)Cr(\mu\text{-}Cl)Me]_2$ underwent



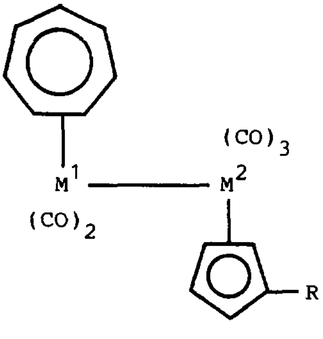
5.11

reaction with 2-butyne to give poly(2-butyne) and the 17-electron sandwich complex (5.11). This compound exhibited reversible oxidation and reduction [126]. Reaction of $(\eta\text{-}C_6Me_xH_{6-x})_2Cr(0)$, where x = 0, 3, 6, with tetracyanoethylene (TCNE) gave the corresponding 1:1 electron-transfer salts $[(\eta\text{-}C_6Me_xH_{6-x})_2Cr(I)]$-[TCNE]. The complexes where x = 0 or 3 were structurally characterized by X-ray analysis. In the solid state the complexes consisted of linear chains of dimers (D) and $[TCNE]_2^{2-}$ dimeric anions (A_2^{2-}) $\cdots\cdot D^{\cdot+}A_2^{2-}D^{\cdot+}D^{\cdot+}A_2^{2-}D^{\cdot+}\cdots\cdots$. The magnetic susceptibilities of the complexes were measured and discussed together with the electron paramagnetic resonance spectra [127].

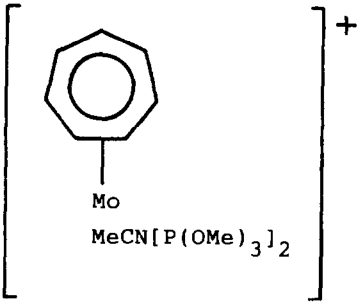
6. $[(\eta\text{-}C_7H_7)Cr(CO)_3]^+$ and $(\eta\text{-}C_7H_8)Cr(CO)_3$

Several metal-metal bonded η-cycloheptatriene complexes (6.1; $M^1 = M^2 = Mo$; R = H, Me; $M^1 = M^2 = W$; R = H; $M^1 = Mo$ $M^2 = W$; R = H) have been prepared and characterized by IR, UV and NMR spectroscopy [128]. Several reactions of the (η-cycloheptatrienyl)molybdenum cation (6.2) and the tungsten complex (6.3) have been reported. Reversible one-electron transfer processes were observed for several species by cyclic voltammetry [129].

The electrochemical behaviour of (η-cycloheptatriene) transition metal complexes (6.4; M = Cr, Mo, W) has been investigated in acetonitrile and dichloromethane. One electron



6.1



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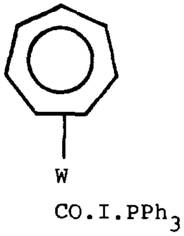


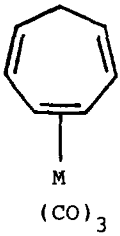
6.3

was transferred at the first oxidation peak of each of the three complexes [130]. The tricarbonylchromium complexes [6.5; $R^1 = R^2$ = Me, Et; R^1 = Me, R^2 = Et; R^1 = Et, R^2 = Me; R^1R^2 = $(CH_2)_2$, $(CH_2)_3$, $CH_2CH{=}CHCH_2$] underwent acid-catalyzed heterolysis in water to form the complex cations [6.6; R = Me, Et, $(CH_2)_2OH$, $(CH_2)_3OH$, $CH_2CH{=}CHCH_2OH$]. These cations were more stable thermodynamically than the corresponding uncomplexed alkoxytropylium cations [131].

Treatment of the (η^7-cycloheptatrienyl)molybdenum complex (6.7) with the ylide $Ph_3P{=}CH_2$ gave the triphenylphosphine complex (6.8) [132]. The tropylium cation abstracted a methoxide ion from Malachite Green methyl ether. Complexation of the cation with tricarbonylchromium to give the species (6.9) reduced this reactivity. The rate of transfer of alkoxide ion from the (η-7-exo-alkoxycycloheptatriene)chromium (6.10) to the tropylium ion decreased in the series:

MeO > EtO > iso-PrO > tert-BuO

The overall rate change was five-fold [133].



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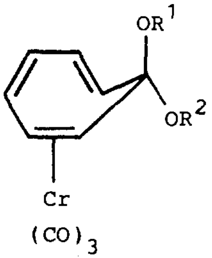

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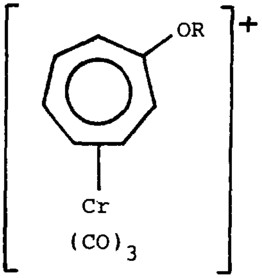

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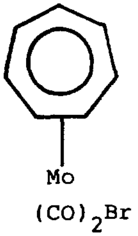

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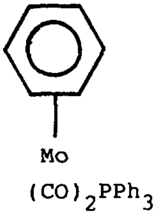

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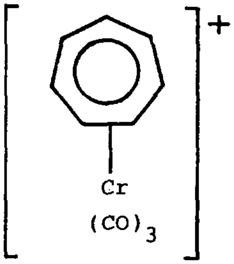

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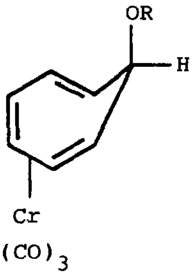

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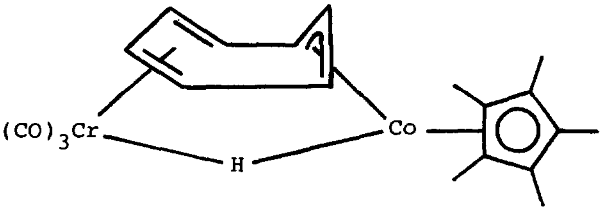
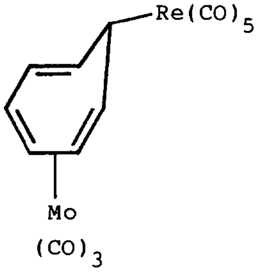


6.11

Reaction of $(\eta^6\text{-}C_7H_8)Cr(CO)_3$ with $(\eta\text{-}C_5Me_5)Co(\eta\text{-}C_2H_4)_2$ gave the binuclear hydride complex (6.11). The structure of this complex was determined by X-ray analysis [134]. Reaction of pentacarbonylrhenium anion with tricarbonyl(η^7-cycloheptatrienyl)-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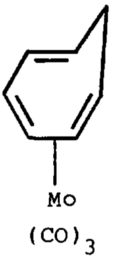

6.13

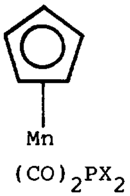
molybdenum cation produced the bimetallic complex (6.12) and the product of reduction (6.13) [135].

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

(i) Formation

Several cymantrene complexes (7.1; X = OEt, NEt_2, Cl) have been prepared by lithiation of cymantrene and treatment with phosphines $PClX_2$ [136]. Deprotonation of dihydro-1H-trindene with potassium hydride gave the corresponding trianion (7.2) which combined with $Mn(CO)_3(NC_5H_5)_2Br$ or $[Re(CO)_3(THF)Br]_2$ to give the corresponding trans-trimetallic complexes (7.3; M = Mn, Re). The crystal structure of the rhenium complex (7.3; M = Re) was determined. The mono- and di-rhenium complexes (7.4 and 7.5) were also prepared [137].

Reaction of the enolate derived from chiral N-acyloxazolidinone with the η^6-arene complexes (7.6; $R^1 = R^2 = H$, $X = PF_6$;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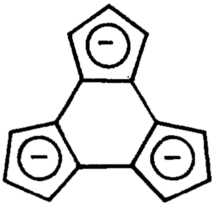

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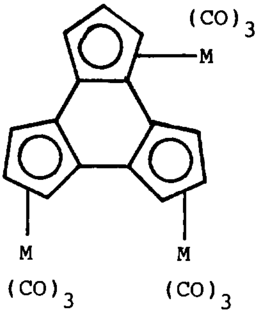

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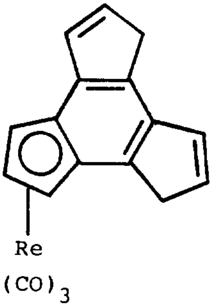

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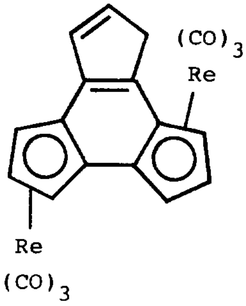

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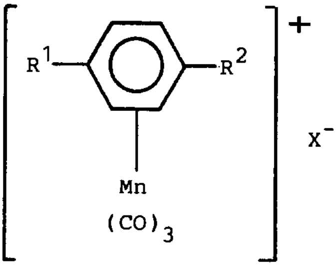

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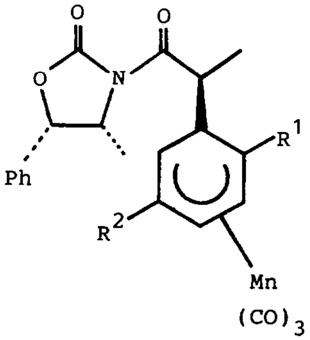
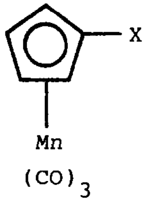


7.7

R^1 = H, R^2 = OMe, X = PF_6; R^1 = R^2 = OMe, X=BF_4; R^1 = H, R^2 = OPh, X = BF_4) gave the corresponding η^5-dienyl complexes (7.7). These complexes were converted into chiral 2-arylpropionic acids by cleavage of the chiral group and oxidation of the η^5-dienyl ligand [138].

Cymantrene has been treated with PhYbI to form the ytterbium iodide intermediate (7.8; X = YbI) which combined with electrophiles such as deuterium oxide, trimethylchlorosilane, acetyl chloride, triphenyltin chloride to give the derivatives (7.8; X = D, $SiMe_3$, COMe, $SnPh_3$). Tricarbonyl(η-cyclopentadienyl)-rhenium gave the corresponding ytterbium iodide with ytterbium amalgam [139].

Sodium 5-[(difluoroamino)difluoromethyl]tetrazolate combined with pentacarbonylmanganese bromide to form the η^5-complex (7.9) in solution. On removal of the solvent, reversible reorganisation of the ligands took place to give a binuclear complex with μ-2,3-η^2-ligands in the solid state [140]. The propargylamines,



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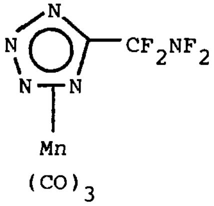

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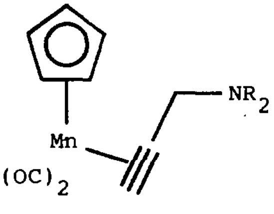

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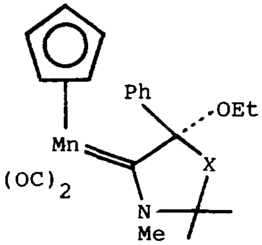


7.11

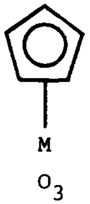
$R_2NCH_2C{\equiv}CH$, where R = Me, Et, Pr, Me_2CHCH_2, have been treated with the cymantrene derivative $(\eta\text{-}C_5H_5)Mn(CO)_2THF$ to give the complexes (7.10; R = Me, Et, Pr, Me_2CHCH_2) [141].

Aminocarbene derivatives of methylcymantrene (7.11; X = O, S, NMe) have been obtained from carbene and isocyanide reagents by three-component reactions. The mechanism involved an intermediate ketenimine manganese complex. The heterocyclic ligand was removed by potassium permanganate, elemental sulphur or selenium [142].

7.(ii) Spectroscopic and Physico-chemical Studies

Hartree-Fock molecular orbital calculations have been carried out on the trioxo complexes (7.12; M = Mn, Tc, Re) in an attempt to evaluate the stability of these molecules [143]. The structure of the manganese complex (7.13) has been determined by X-ray analysis. The dihedral angle between the two planar η^5-cyclopentadienyl groups was 99° [144]. The two cymantrene complexes (7.14 and 7.15) have been characterized by X-ray crystallography [145].

Pentabenzylcymantrene and the corresponding rhenium complex have each been prepared from the free ligand and the metal carbonyl $M_2(CO)_{10}$, where M = Mn, Re. The crystal and molecular structure of pentabenzylcymantrene has been determined by X-ray crystallography [146].



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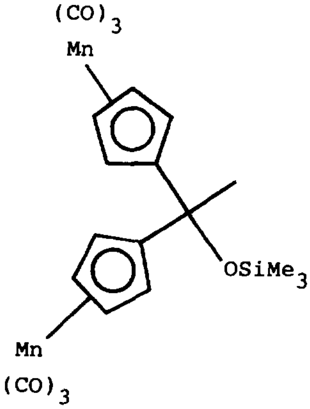

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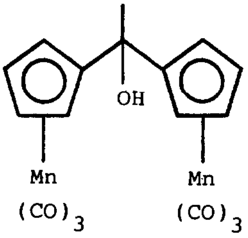

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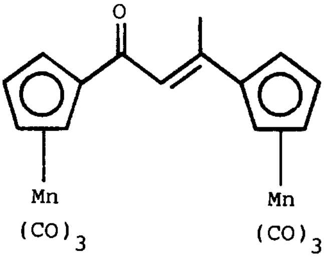
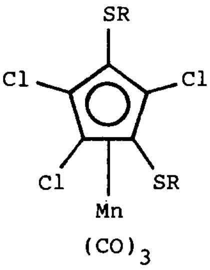


7.15

Alkylthio- and phenylthio-cymantrene complexes have been prepared and characterized by X-ray crystallography, including the phenylthio and methylthio derivatives (7.16; R = Ph, Me) respectively [147]. Gas phase and liquid phase CH-stretching overtone spectra have been recorded for methylcymantrene. A local mode model based on ab initio SCF MO calculations was used to interpret the spectra. Evidence was obtained for structurally non-equivalent CH bonds in the cyclopentadienyl ligand and for conformationally non-equivalent CH bonds in the methyl substituent [148].

^{55}Mn NQR spectra have been recorded for a series of substituted (η-cyclopentadienyl)Mn(CO)$_3$ complexes and the quadrupole coupling constants were correlated with the $\Sigma\sigma_I$ and $\Sigma\sigma_R$ substituent constants. The resonance component was more important than the inductive component [149].

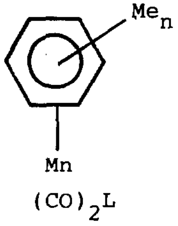


7.16

7. (iii) General Chemistry

The (η-arene)manganese cations (7.17; n = 3, 5, 6; L = CO) have been converted to the alkene complexes (7.17; n = 3, 5, 6; L = ethene, propene, norbornadiene) by way of the tetrahydrofuran species (7.17; L = THF) [150]. Reaction of lithiocymantrene with the aminofulvenes (7.18; R = H, RR = CH=CHCH=CH) produced the corresponding cymantrenyl derivatives (7.19). Lithiation of the derivative (7.19; R = H) with $Li[HB(C_2H_5)_3]$ followed by reaction with $ICo(CO)_4$ or $Mo(CO)_3(CH_3CN)_3$, then bromine, and with $(\eta\text{-}C_5H_5)TiCl_3$ afforded the complexes [7.20; M = $Co(CO)_2$, $Mo(CO)_3Br$ and 7.21] respectively [151].

The cymantrene derivative, $(\eta\text{-}C_5H_5)Mn(CO)_2THF$, combined with the phosphaferrocene, $(\eta\text{-}C_5Me_5)Fe(\eta\text{-}P_5)$ to give several cymantrenyl complexes, $(\eta\text{-}C_5Me_5)Fe\{\eta\text{-}P_5[Mn(CO)_2(\eta\text{-}C_5H_5)]_n\}$, where n = 1-4 [152]. The cymantrene phosphine complex (7.22; X = $SiMe_3$) has been desilylated to give the free phosphine species



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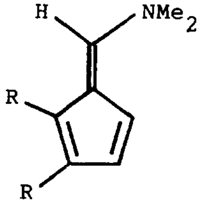

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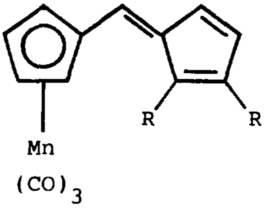

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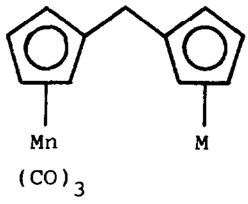

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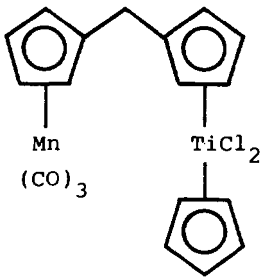

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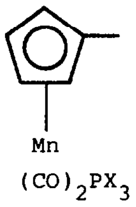

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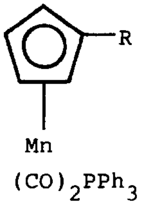

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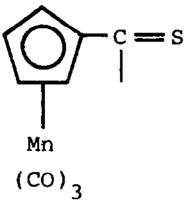
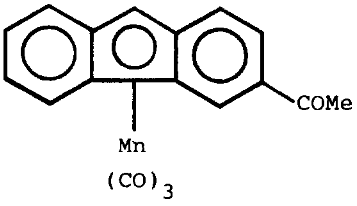


7.24

(7.22; X = H) which was used to prepare heterobimetallic complexes containing iron and manganese [153].

Friedel-Crafts acetylation of the cymantrene complex (7.23; R = H) gave the acetyl derivative (7.23; R = $COCH_3$) while lithiation and treatment with deuterium oxide, carbon dioxide and chlorodiphenylphosphine gave the products (7.23; R = D, CO_2H, PPh_2) respectively [154]. The thiocarbonyl cymantrene derivative (7.24) underwent a Diels-Alder addition to cyclopentadiene to give endo- and exo-thiabicycloheptene products. Benchrotrene, ferrocene and other organometallic species were used as substituents in the thiocarbonyl reagent [155].

The reaction of tricarbonyl(η^5-fluorenyl)manganese with acetyl chloride under Friedel-Crafts gave the 2-acetyl derivative (7.25) together with the dihydro complex (7.26) which has been characterized by X-ray crystallography [156]. Cymantrene has been irradiated with octafluorocyclooctatetraene to give the



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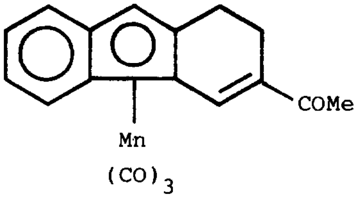

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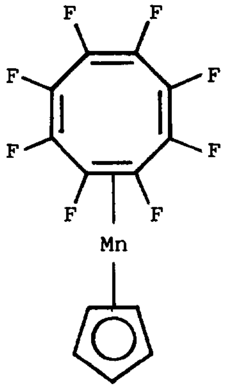

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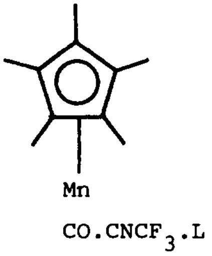
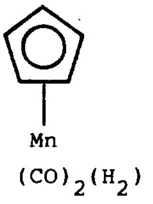


7.28

air stable sandwich complex (7.27). The analogous pentamethylcyclopentadienyl complex has been prepared in the same way and both have been characterized by X-ray crystallography [157].

Photolysis of the manganese complexes (7.28; L = CO) in the presence of <u>cis</u>-cyclooctene or THF afforded the corresponding carbon monoxide substitution products (7.28; L = η^2-C_8H_{14}, THF). Treatment of the complex (7.28; L = η^2-C_8H_{14}) with carbon disulphide in the presence of triphenylphosphine produced the complex (7.28; L = CS). Similar reactions were carried out with other ligands to give the products of substitution (7.28; L = PPh_3, PEt_3, PF_3, MeCN, PhCN, CF_3CN) [158].

Ultraviolet irradiation of cymantrene or the rhenium analogue at room temperature in supercritical xenon pressurized with hydrogen gave the 'non-classical' dihydrogen complex (7.29) and the dihydride (7.30) respectively [159]. Cymantrenylalanine (7.3; L = CO) underwent photochemical substitution with phosphine



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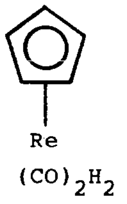

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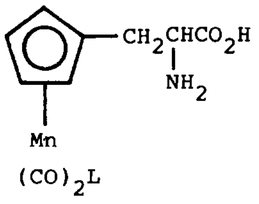


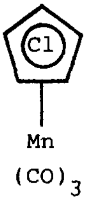
7.31

and phosphite ligands to give the products [7.31; L = PMe_3, PPh_3, $P(OEt)_3$, $P(C_{10}H_7)_3$] which had different hydrophobicity and steric requirements to the unsubstituted cymantrenylalanine [160].

Irradiation of pentachlorocymantrene (7.32) in alkane glasses caused loss of carbon monoxide and formation of 16-electron species. When triethylsilane was present, the adduct (7.33) was formed. The rate of reaction and the thermodynamic parameters for the process were determined [161]. Fluorescent layers of manganese doped zinc sulphide have been prepared by plasma enhanced decomposition of cymantrene in the presence of zinc sulphide [162].

Tricarbonyl(η-methylcyclopentadienyl)manganese has been used as a source of manganese in the preparation of metal films of the type $Cd_{1-x}Mn_xTe$, where $0 \leqslant x \leqslant 0.7$ [163]. The reaction of the α-ketoacyl complexes (7.34; L = CO, PPh_3) with a variety of electrophiles, nucleophiles and alkynes has been investigated. Protonation of the complex (7.34; L = PPh_3) at the α-carbonyl oxygen atom gave a hydroxy-carbene at low temperatures which rearranged on warming to give 4-methylbenzaldehyde and the cation (7.35). Oxidation of the complex (7.34; L = PPh_3) gave the same cation (7.35) together with a mixture of organic products. Photolysis of the complex (7.34; L = CO) in the presence of alkynes gave cyclic products, for example, the metallacycle (7.36). Demetallation of the metallacycles with HCl gave the corresponding vinyl α-diones [164].

The cymantrene carbyne complex (7.37) has been treated with the nitrite ion to give the ketoacyl complex (7.38) by



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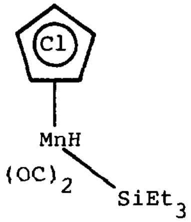

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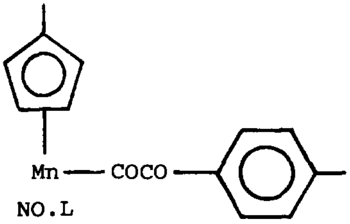

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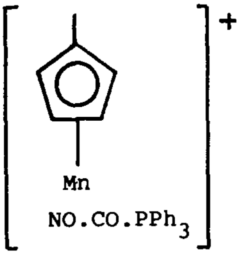

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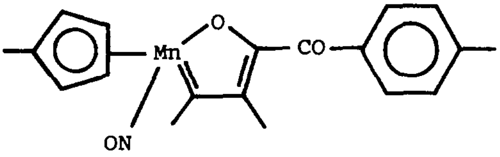

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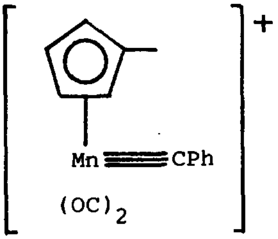

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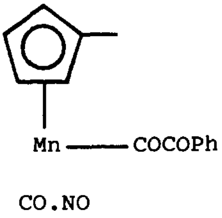
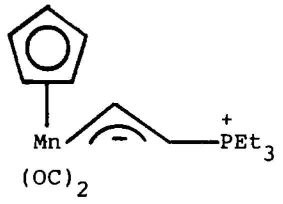


7.38

insertion of CO into the metal-acyl bond. The mechanism involved initial nitrosyl addition to manganese. The crystal and molecular structure of the complex (7.38) has been determined by X-ray crystallography, the ketoacyl ligand was η^1-bonded to manganese [165].



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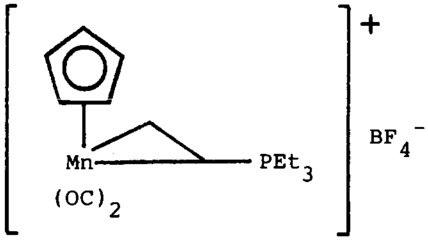
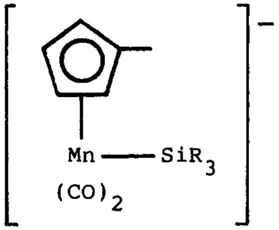


7.40

A membrane of the copolymer dicarbonyl(η-vinylmethylcyclopentadienyl)manganese and octyl methacrylate has been used in the spectroscopic determination of kinetic and equilibrium constants of nitrogen coordination to (η-cyclopentadienyl)-manganese. Nitrogen transport through the membrane was selectively assisted due to the rapid and reversible coordination of nitrogen to the pendant (η-cyclopentadienyl)manganese moiety [166].

The cymantrene ylide complex (7.39) has been protonated with HBF_4 to give the metallacyclopropane salt (7.40) which has been characterized by X-ray crystallography [167]. Reaction of the anionic manganese complexes (7.41; SiR_3 = $SiPh_2Me$, $SiPh_3$) with Me_3SnCl, Me_3PbCl, PPh_3AuCl, PhHgBr or $(\eta\text{-}C_5H_5)Fe(CO)_2I$ afforded the corresponding dinuclear products, for example, complex (7.42). Analogous germyl-substituted complexes were prepared together with hydrogen bridged compounds, for example the complex (7.43) [168].



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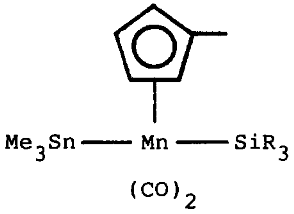
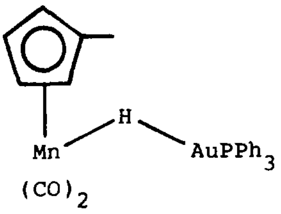


7.42



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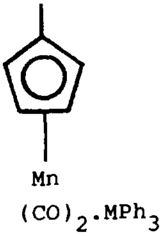

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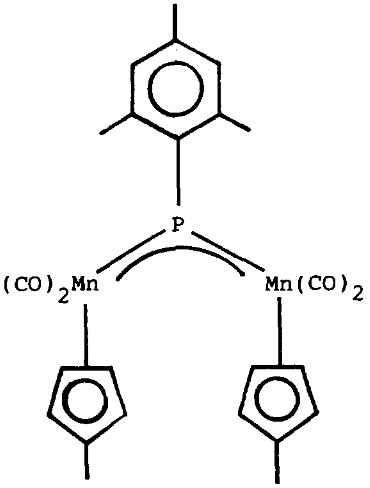
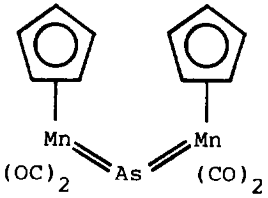


7.45

The methylcymantrene anion (7.41; $SiR_3 = SiMe_2Ph$) combined with equimolar proportions of zinc chloride, cadmium chloride or mercury(II) bromide to give the adducts $(\eta\text{-}MeC_5H_4)Mn(CO)_2$-$(SiMePh_2)MX$, where MX = ZnCl, CdCl, HgBr. These products combined with the original anions to give the symmetrical trinuclear complexes $[(\eta\text{-MeC}_5H_4)Mn(CO)_2(SiMePh_2)]_2M$, where M = Zn, Cd, Hg [169].

Reaction of the anion (7.41; SiR_3 = $SiMe_2Ph$) with Ph_3AsCl_2 or Ph_3SbBr_2 gave the corresponding arsenic and antimony derivatives (7.44; M = As, Sb). In a similar reaction with mesityldichlorophosphine the binuclear complex (7.45) was produced [170]. The dicymantrene complex (7.46) has been obtained by dechlorination of the corresponding arsenic chloride. X-ray crystallography was used to characterize the product (7.46) [171].

Reactions of the cationic (η-arene)manganese complex (7.47) have been described in which coupling with chiral glycine enolate species gave (η^5-dienyl)manganese products such as (7.48). These compounds were converted to arylglycine methyl esters without racemization [172].



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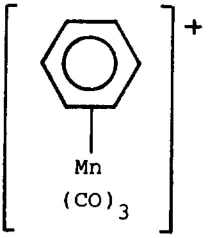

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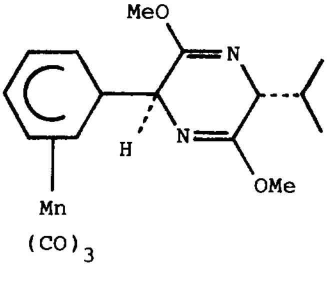
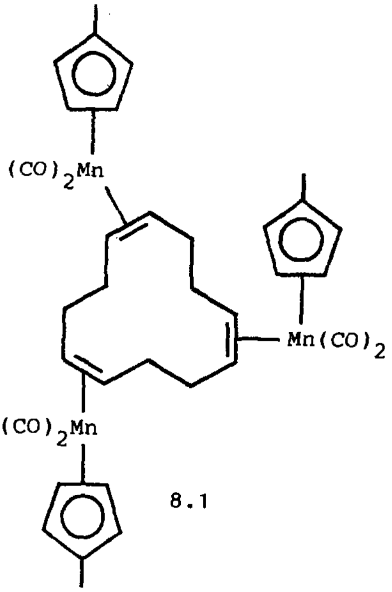
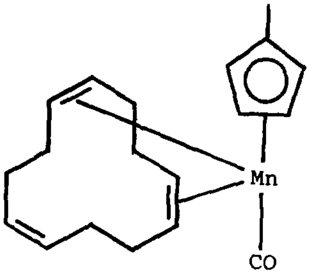


7.48

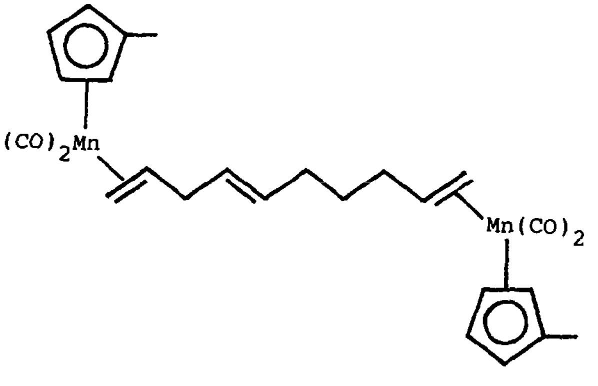
8. Polynuclear (η-C_5H_5)Mn(CO)$_3$



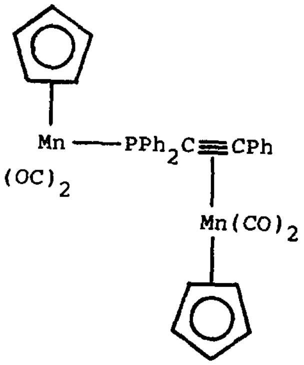
8.1



8.2



8.3

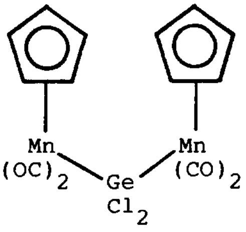


8.4

Photolysis of methylcymantrene with 1,5,9-cyclododecatriene afforded two products (8.1 and 8.2). The 1,4,9-decatriene derivative (8.3) was prepared in a similar manner [173]. The cymantrene complex $(\eta\text{-}C_5H_5)Mn(CO)_2THF$ combined with the alkyne $Ph_2PC{\equiv}CPh$ to give mononuclear and dinuclear (8.4) complexes [174]. Treatment of the cymantrene-THF complex, $(\eta\text{-}C_5H_5)Mn(CO)_2THF$, with germanium(II) chloride gave the trinuclear product (8.5) which was characterised by X-ray crystallography [175].

The cymantrene derivative $(\eta\text{-}C_5H_4Me)Mn(CO)_2(THF)$ was treated with tin(II) chloride and then zinc dust to give the polynuclear tin bridged species (8.6). In the same way, the pentamethylcyclopentadienyl analogue was prepared together with the dicymantrene complex (8.7). X-Ray crystallography showed that the complex (8.6) contained two manganese-tin single bonds and one manganese-tin double bond [176].

The tetrahydrofuran complexes $(\eta\text{-}C_5H_4R)Mn(CO)_2THF$, where R = H, Me, have been treated with lead(II) chloride to give



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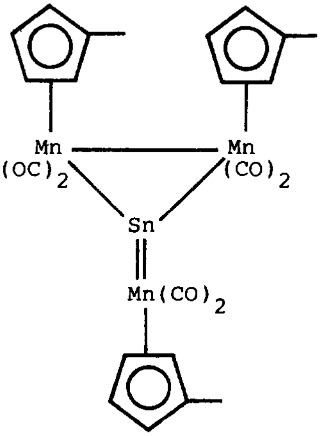
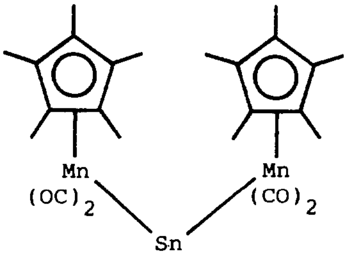
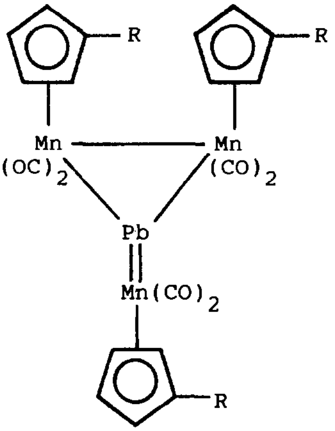


8.6



8.7



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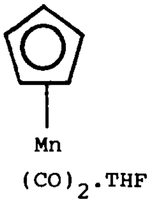

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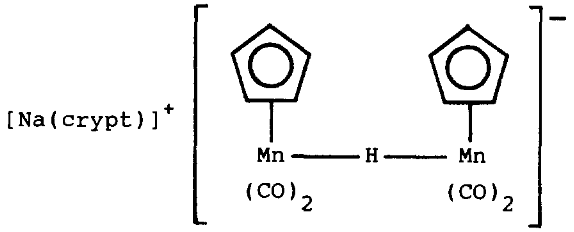

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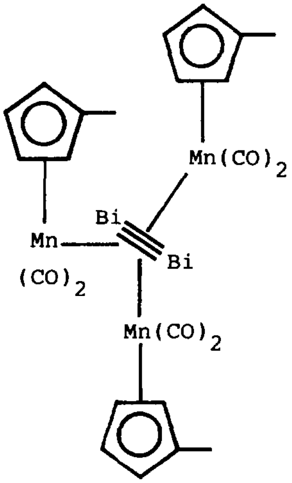
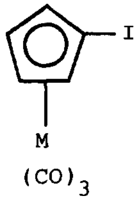


8.11

trinuclear and tetranuclear (8.8) cluster complexes. The structure of the tetranuclear species (8.8) was confirmed by X-ray crystallography [177].

Photochemical reaction of the tetrahydrofuran complex (8.9) with sodium tetrahydroborate followed by treatment with [2.2.2]cryptand produced the salt (8.10; crypt = [2.2.2]cryptate). Reaction of the corresponding η-methylcyclopentadienyl salt, in the absence of cryptate, with bismuth(III) chloride gave the complex (8.11). X-Ray analysis showed that the two bismuth atoms were side-on coordinated with the manganese atoms [178].



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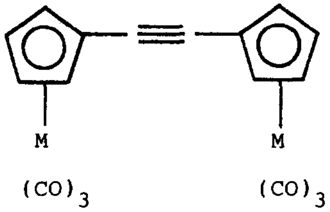
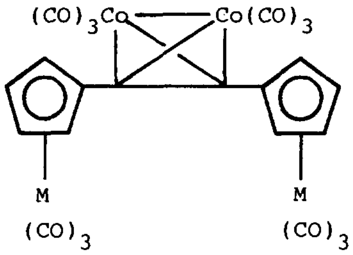


8.13



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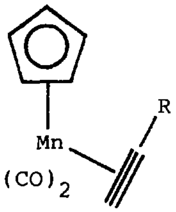
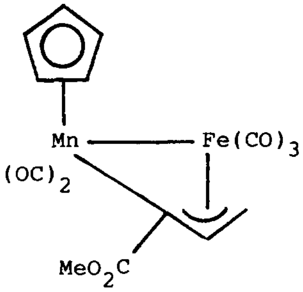


8.15



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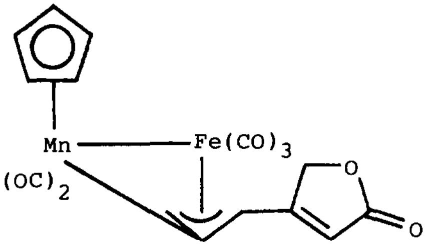


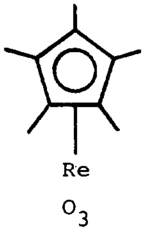
8.17

Palladium catalyzed coupling of the η-iodocyclopentadienyl compounds (8.12; M = Mn, Re) with $Bu_3SnC{\equiv}CSnBu_3$ afforded the corresponding bridged complexes (8.13). These complexes gave the dicobalt adducts (8.14) on treatment with $Co_2(CO)_8$ [179]. The cymantrene-alkyne complexes (8.15; R = Ph, CH_2OH, CH_2OMe) combined with enneacarbonyldiiron to give several tricarbonyliron-cymantrene products including the (η^3-allyl)iron complexes (8.16 and 8.17) [180].

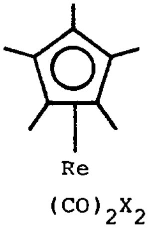
9. $(\eta\text{-}C_5H_5)Re(CO)_3$

The reactions of trioxo(η-pentamethylcyclopentadienyl)-rhenium(VII) have been discussed [181]. The oxide (9.1) was used as an example in a review about organometallic oxides and their role as models in catalysis [182]. An improved synthetic method has been described for the preparation of the dicarbonyl-rhenium complexes (9.2; X = Cl, Br, I). Treatment of tricarbonyl-(η-pentamethylcyclopentadienyl)rhenium with bromine or iodine in tetrahydrofuran produced a mixture of the cis- and trans-isomers of the dihalides (9.2; X = Br, I). Reaction of the salt (9.3) with water afforded the dichloro complex (9.2; X = Cl) [183].

Trindene has been converted to the trianion and treated with $[Re(CO)_3(THF)Br]_2$ to give the trinuclear half-sandwich complex (9.4) and the dinuclear complex (9.5) as a mixture of cis and trans isomers [184]. Several rhenium dinitrogen complexes (9.6; R = Me, Bu, cyclohexyl, Ph, OMe) have been prepared by treatment of the p-methoxyphenyldiazenido complexes with t-butyllithium. The products (9.6) were characterized by ^{14}N and ^{15}N NMR



9.1



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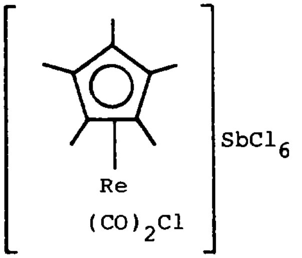

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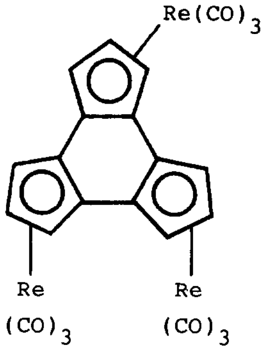

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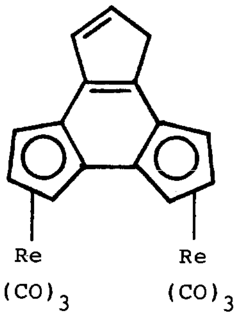
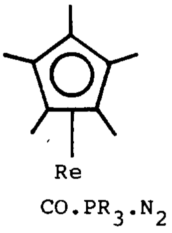


9.5

spectroscopy. The dinitrogen ligand in the trimethylphosphine complex (9.6; R = Me) was surprisingly inert, it was not displaced by triphenylphosphine at room temperature [185].

The formation of oxometal complexes by the oxidative decarbonylation of metal carbonyls with $ClC_6H_4CO_3H$ has been investigated. For example, the tricarbonylrhenium complex (9.7) was converted to the oxo-complex (9.8) [186]. Migration of the CHO group from the metal to the cyclopentadienyl ring in the nitrosylrhenium complex (9.9) has been the subject of a theoretical study. Total energy values for the possible stable molecules and intermediates in the process have been calculated and used to determine the pathway of lowest energy [187].



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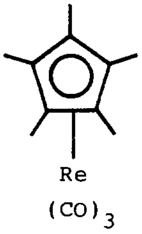

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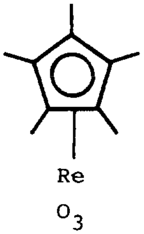

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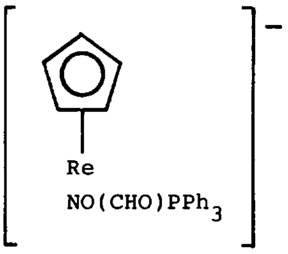

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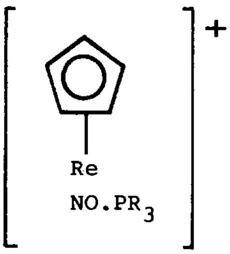
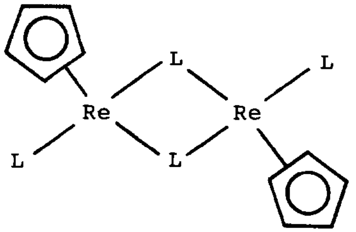


9.10

The electronic structure of the Lewis acid (9.10; R = Ph) and its coordination to the Lewis bases I^-, CH_3I and CH_2Cl_2 has been investigated via Fenske-Hall molecular orbital calculations on the prototype species (9.10; R = H). In each case electron density was transferred from the ligand to rhenium in a typical Lewis acid-base interaction. The alkyl halide ligands alkylate a range of nucleophiles and the reaction coordinate for these processes was also investigated. It was shown that extra virtual d orbitals had to be included in the basis set of the halogens to explain the reaction chemistry [188].

Fenske-Hall molecular orbital calculations have been applied to a series of bimetallic complexes and these included the rhenium compounds (9.11; L = O, S). The calculations on the oxygen containing complex (9.11; L = O) indicated the most stable configuration had an Re-Re distance of 0.314 nm [189].



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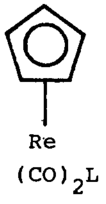


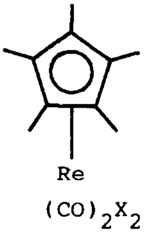
9.12

Treatment of (η^5-pentadienyl)Re(CO)$_3$ with Et$_2$PCH$_2$CH$_2$PEt$_2$(L) gave the complex (*cis*-η^1-pentadienyl)Re(CO)$_3$L. X-Ray analysis of this compound indicated that the rhenium atom was octahedrally coordinated with the carbonyl ligands in a facial arrangement. The cis-η^1-pentadienyl ligand was sickle-shaped and planar [190]. The luminescence spectra of the rhenium complexes (9.12; L = pyridine or 4-phenylpyridine) in room temperature solution exhibited three distinct maxima in the visible region. These spectra were discussed and interpreted [191].

The mechanism of the photochemical *cis-trans* isomerism of the rhenium complexes (9.13; X = Me, Cl, Br, I) have been investigated by FTIR at low temperatures. Photolysis of the *cis*-isomer resulted in extrusion of a carbonyl ligand and this then reattached itself to the rhenium to give only the *trans*-isomer [192].

The rate of linkage isomerization of coordinated dinitrogen in (η-C$_5$Me$_5$)Re(CO)$_2$(^{15}N≡^{14}N) to give (η-C$_5$Me$_5$)Re(CO)$_2$(^{14}N≡^{15}N) has been determined from ^{15}N NMR intensities. This end-to-end rotation process was shown to be intramolecular and non-dissociative [193]. Photolysis of the rhenium complex (9.14) with either supercritical xenon doped with nitrogen or in solid nitrogen matrices led to stepwise substitution of carbonyl groups to give the dinitrogen complexes (9.15; x = 1-3). The complex (9.15; x = 2) was stable at room temperature [194].

The methyl ligand in the neutral complex (9.16) has been replaced by alkyl- and aryl-iodides using HBF$_4$.OEt$_2$ and RI to give the salts [9.17; R = CH$_3$, CH$_3$CH$_2$, CH$_3$(CH$_2$)$_2$CH$_2$,



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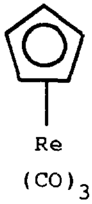

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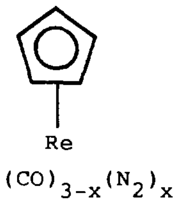

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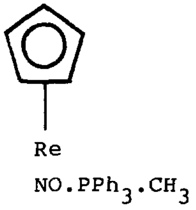

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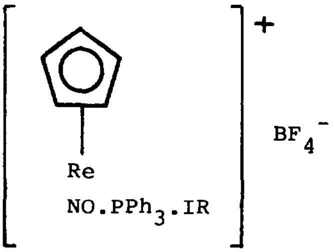

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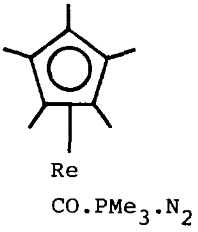

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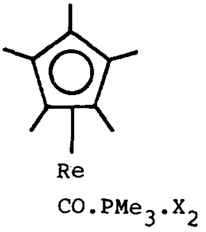

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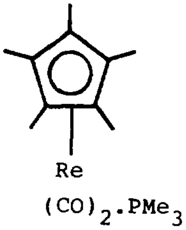

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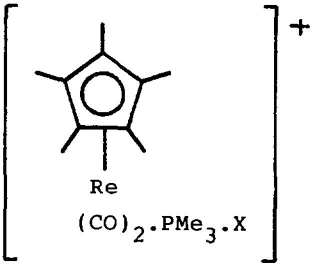

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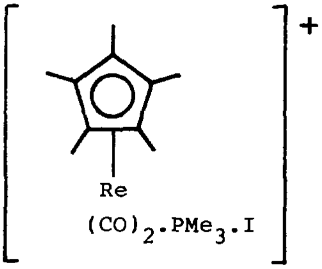

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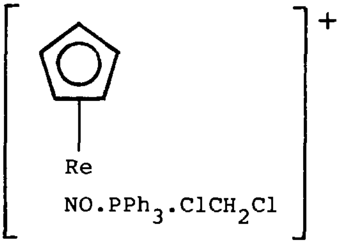
$CH_2Si(CH_3)_3$, $CH_2CH_2CH_2Cl$, CH_2Cl, C_6H_5, 4-$CH_3O.C_6H_4$]. The structure of one product [9.17; R = $CH_2Si(CH_3)_3$] was confirmed by X-ray crystallography and the chemical reactions of the compounds (9.17) were reported [195]. Reaction of the dinitrogen complex (9.18) with chlorine , bromine or iodine gave the corresponding cis-dihalide complexes (9.19; X = Cl, Br, I). Treatment of the trimethylphosphine complex (9.20) with halogens produced the trans-isomers (9.21; X = Cl, Br) and the cis-isomer (9.22) [196].

The (η-cyclopentadienyl)rhenium cation (9.23) has been formed as a reactive intermediate which combined with Lewis bases such as carbon monoxide, cyanide ion, triphenylphosphine oxide and ethene. The tetrafluoroborate salt of the cation (9.23) decomposed to give the binuclear cation (SS,RR)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+$ [197]. Reaction of the rhenium complex (9.24) with carbon tetrachloride at -98°C gave the labile chlorinated intermediate (9.25) which on treatment with methyl iodide gave the isolable salt (9.26). Further reactions of the labile intermediate (9.25) and related compounds were described [198].



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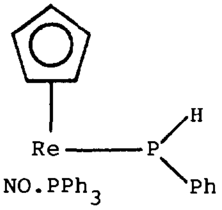

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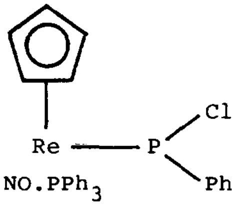

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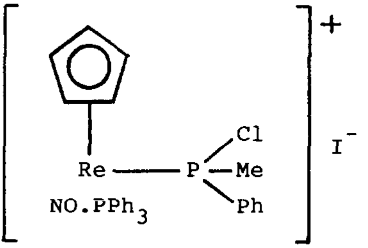

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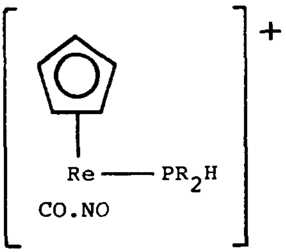

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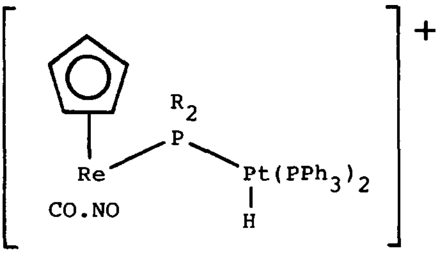

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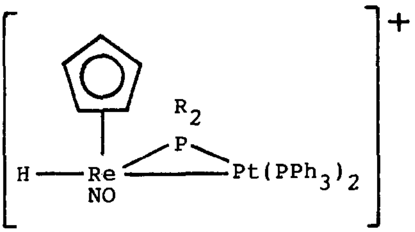

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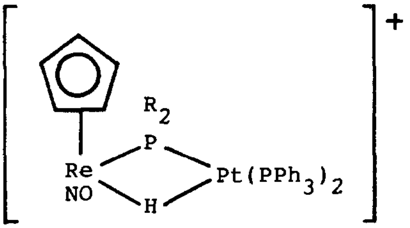
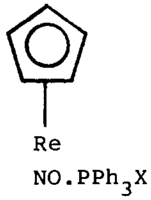


9.30

Oxidative addition of the rhenium complex (9.27; R = Ph, cyclohexyl, Pr) to Pt(η-C_2H_4)(PPh_3)$_2$ gave the bridged bimetallic compounds (9.28). These cations lost carbon monoxide in the presence of base to form the terminal rhenium hydride derivatives (9.29) which slowly transformed into the thermodynamically preferred bridging hydrido isomers (9.30) [199]. The iodo- and bromo-rhenium complexes (9.31; X = I, Br) have been treated with $AgBF_4$ in benzene to form the halogen bridged derivatives [(η-C_5H_5)Re(NO)(PPh_3)]$_2$$X^+BF_4^-$, where X = I, Br. The crystal and molecular structure of a solvate formed by the iodo bridged derivative was determined by X-ray crystallography [200].

Several reactions of the rhenium-germyl complexes (9.32; X = Cl, Ph) have been studied including the formation of labile triflate species (9.32; X = SO_2CF_3)[201]. Reaction of the rhenium complex (9.33; X = Me) with (η-C_5H_5)$TiCl_3$ gave the dichloride (9.34; X = Cl) which underwent reaction with methylmagnesium



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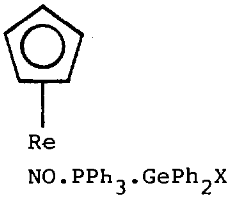
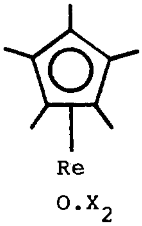


9.32

chloride to produce the trimethyl derivative (9.34; X = Me). Alkylation of the dichloride (9.33; X = Cl) with Me_3CCH_2MgI followed by reaction with $(\eta\text{-}C_5H_5)TiCl_3$ gave the rhenium complex (9.35; X = Cl). Halogen exchange with Me_3SiX produced the corresponding bromo and iodo complexes (9.35; X = Br, I) [202].

The dioxorhenium complex, $(\eta\text{-}C_5Me_5)_2\ Re_2O_4$, has been converted to the μ-sulphido complex, $(\eta\text{-}C_5Me_5)_2Re_2(\mu\text{-}S)_2O_2$, on treatment with carbon disulphide. X-Ray crystallography was used to confirm the bridging sulphur configuration [203]. Reaction of the rhenium complex (9.36) with RSLi, where R = Et, Ph or 2-pyridyl, gave the corresponding disubstituted products (9.37). Treatment of the dirhenium complex (9.38) with sodium cyclohexylxanthate or with LiS_2CNEt produced the corresponding xanthates (9.39; R = cyclohexyloxy, NEt_2) in good yields [204].

Stepwise dehalogenation of the organorhenium complexes (9.40; X = Cl, Br) was effected with $HgCl_2$-aluminium powder to



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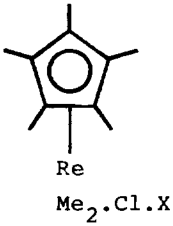

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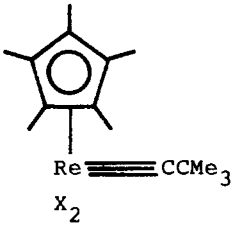

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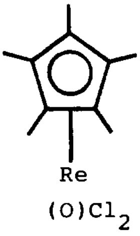

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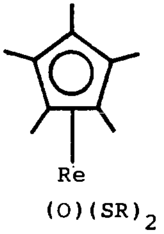

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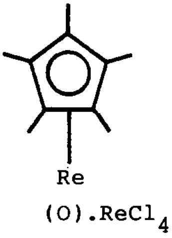

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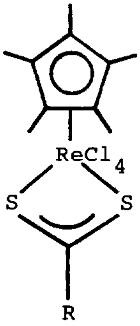

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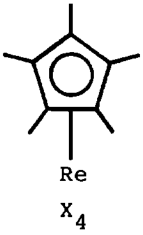

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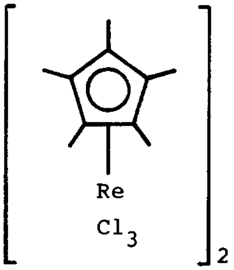

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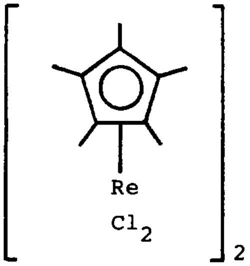

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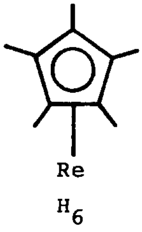
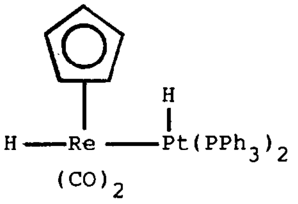


9.43

give the dimers (9.41 and 9.42). Some reactions of these complexes were investigated [205].

The (η-cyclopentadienyl)rhenium complex (9.43) has been shown to undergo a variety of thermal and photochemical reactions involving loss of some or all of the hydrogen ligands [206]. Reaction of trans-(η-C_5H_5)Re$(CO)_2H_2$ with $(CH_2{=}CH_2)Pt(PPh_3)_2$ gave the heterobimetallic dihydride complex (9.44). This compound acted as a catalyst for ethylene hydrogenation and it combined stoichiometrically with alkynes to produce rhenium-alkene complexes [207].

Reaction of the rhenium complex (9.45) with thiophene gave the stable sulphur bound thiophene complex (9.46). When this complex was treated with $Fe_2(CO)_9$ the thiophene bridged compound (9.47) was isolated. The structure of the bridged compound (9.47) was determined by X-ray analysis [208]. The lithium salt (9.48) has been used as the precursor of (η^1-allyl)rhenium



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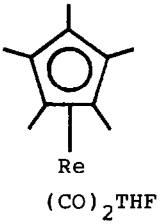

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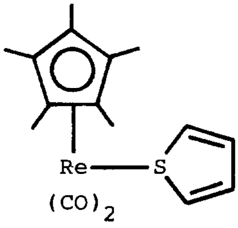

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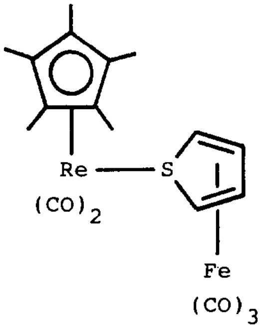

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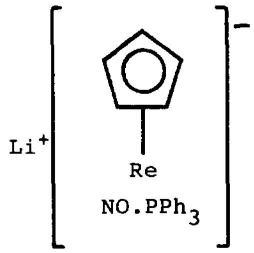

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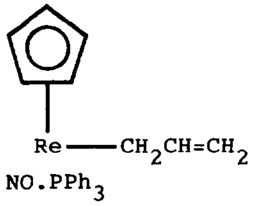
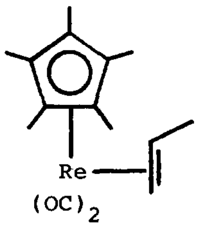


9.49

complexes such as the species (9.49) [209]. The (η^2-propene)-rhenium complex (9.50) underwent photochemical isomerisation to the (η^3-allyl)hydrido rhenium complex (9.51) [210].

The rhenium hydride complex anion (9.52) has been used to prepare rhenium carbene complexes such as the (η-cyclopentadienyl)rhenium species (9.53; R = H, CH_2CMe_3). The products (9.53) were sensitive to acids [211]. The rhenium complexes (9.54; MR_3 = $SiMe_3$, $GePh_3$, $SnPh_3$) were treated with n-BuLi or n-BuLi-$Me_2NCH_2CH_2NMe_2$ and only the $SiMe_3$ group migrated from the metal to the η-cyclopentadienyl ring. Treatment of the complex (9.54; MR_3 = $SiMe_3$) with n-BuLi and benzyl chloride produced the benzyl derivative (9.55) [212].

Addition of a Grignard reagent to [(η^6-arene)$Re(CO)_3$]PF_6 complexes, where arene = benzene, mesitylene, gave the corresponding (η^5-cyclohexadienyl)$Re(CO)_3$ compounds. When the dienyl carbon atoms in these molecules were substituted with methyl



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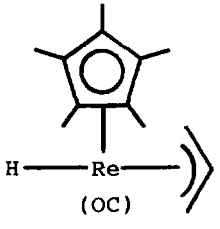

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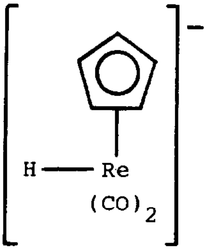

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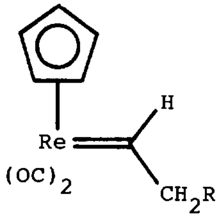

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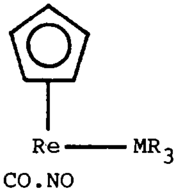

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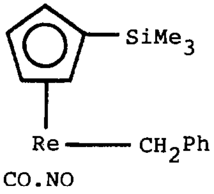

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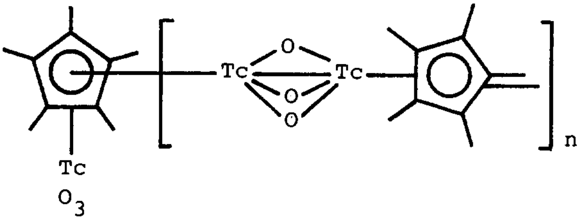


9.56

groups treatment with $NOPF_6$ produced the nitrosyl salts $[(\eta^5\text{-cyclohexadienyl})Re(CO)_2NO]PF_6$. The corresponding manganese complexes were prepared. Further reactions of these compounds were investigated [213]. The polymeric technetium compound

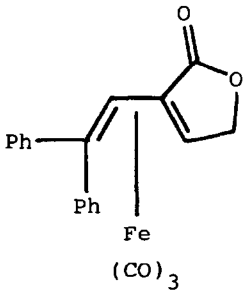
(9.56) has been prepared by oxidation of tricarbonyl(η-pentamethylcyclopentadienyl)technetium with hydrogen peroxide in benzene [214].

10. (Acyclic-η-diene)Fe$(CO)_3$

Irradiation of allenecarboxylates $Ph_2C=C=C(CO_2R)Me$, where R = Me, Et, with pentacarbonyliron gave binuclear and mononuclear (η^3-allyl)iron complexes together with the (η-diene)iron complexes (10.1 and 10.2). These two products (10.1 and 10.2) were characterized by X-ray crystallography and the mechanisms of the reactions were examined [215].

Several reactions of (η-vinyl)carbene iron complexes have been reported including the addition of CH_2 to give the (η-butadiene)iron derivative (10.3) [216]. Reaction of α,β-unsaturated ketimines with excess $Fe_2(CO)_9$ gave the η^4-complexes (10.4; R = H, Me) in good yield. Treatment of the complex (10.4; R = H) with $(Ph)_2CHLi$ or $Me_2(CN)CLi$ followed by acid produced the corresponding amines <u>trans</u>-PhCH=CHCH(R)NHPh, where R = $CHPh_2$ and CMe_2CN. When the latter reaction was carried out under an atmosphere of carbon monoxide followed by oxidation with $CuCl_2$ the carbamyl chloride <u>trans</u>-$PhCH=CH(CMe_2CN)NPhCOCl$ was isolated [217].

Nonacarbonyldiiron has been treated with 2,3,5-6-tetramethylidenebicyclo[2.2.1]heptan-7-one to give the binuclear complex (10.5). Mixed iron-rhodium and rhodium complexes of the same ligand have also been prepared [218]. Tetrabromodurene combined with disodium tetracarbonylferrate to give tetrakis-(σ-methylene)benzenediiron octacarbonyl (10.6) which was warmed



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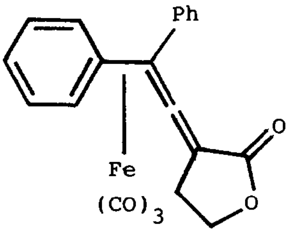

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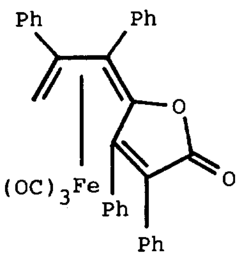

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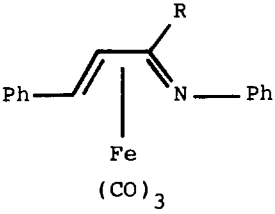

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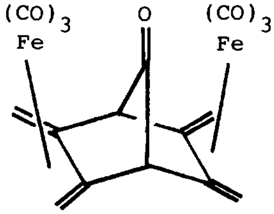

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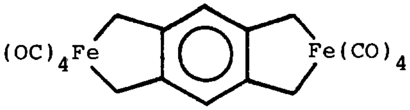

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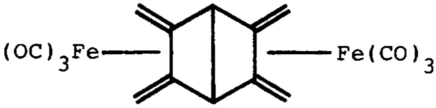

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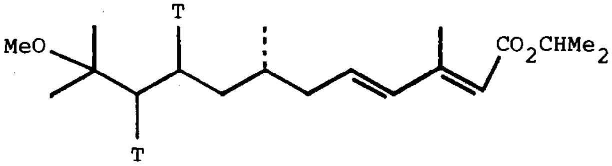


10.8

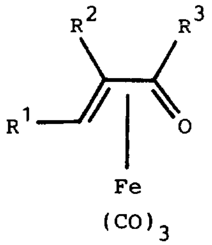
to 40°C to form the (η-tetramethylenebicyclo[2.2.0]hexane)diiron complex (10.7) by a σ to π rearrangement [219]. [8,9-$^3H_2$]-(7S)-Methoprene (10.8) a juvenile hormone analogue, was prepared in seven stages from (3S)-citronellol using the $Fe(CO)_3$ group to protect the dienoate moiety of iso-Pr(2E,4E)-3,7,11-trimethyl-

2,4,8-dodecatrienoate during titration of the remote double bond [220].

A series of mono- and bis-[η^4-diene)Fe(CO)$_3$] complexes with alkyl, CH_2OH, CHO, COMe, COOR and CN substituents on the 1,3-diene ligand have been prepared. The ^1H, ^{13}C and ^{57}Fe NMR spectra were recorded and interpreted [221]. The electrochemical oxidation of several (η-benzylideneacetone)tricarbonyliron complexes has been studied by cyclic voltammetry, controlled potential electrolysis and chronoamperometry [222].

Fast-atom-bombardment mass spectra of the tricarbonyliron complexes [10.9; R^1 = Ph, R^2 = H, R^3 = H, Me, $(CH_2)_3Me$, Me_2CH CMe_3; R^1 = Ph, R^2 = D, R^3 = CD_3] have been recorded and discussed [223]. The electron affinity of the η^4-1,3-butadiene complex (10.10) has been determined by pulsed high pressure mass spectrometry as -25.3 kcal mol^{-1} [224].

The (η-butadiene)iron complex (10.11) has been treated with VO(acetylacetonate)$_2$ and Me_3CO_2H to give the erythro-epoxide (10.12) together with the threo-isomer. X-ray crystallography has been used to characterize the erythro-complex (10.12) [225]. Reaction of 5,6-dimethylidenebicyclo[2.2.2]oct-2-ene with $Fe_2(CO)_9$ gave a 4:1 mixture of the tricarbonyliron complexes (10.13 and 10.14). Asymmetric hydroboration of this mixture with monoisopinocamphenylborane followed by oxidation gave the (+)-alcohol (10.15; R = H) in 16% enantiomeric excess. The camphanates derived from this alcohol were separated to give the (+)- and (-)-esters [10.15 and 10.16; R = (1S)-camphanoyl]. Saponification of these esters gave the (+)-alcohol (10.15; R = H) and the (-)-alcohol (10.16; R = H) with 99 and 95% enantiomeric excess



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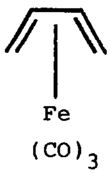

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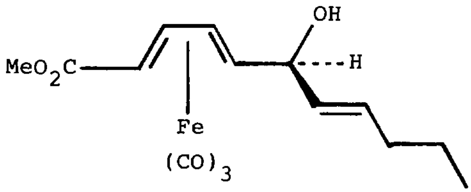

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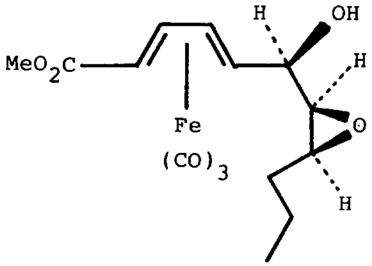

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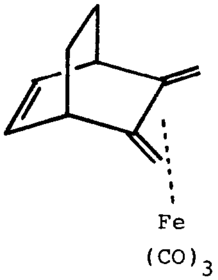

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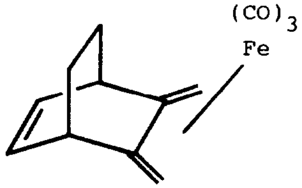

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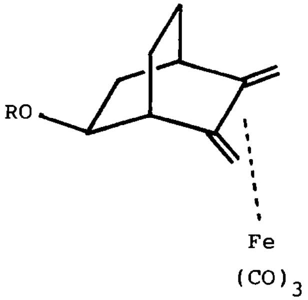

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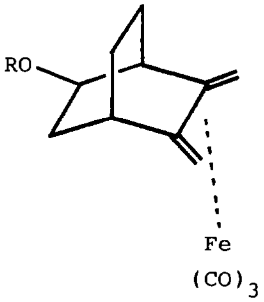

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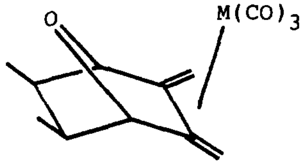

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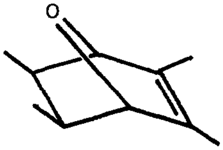

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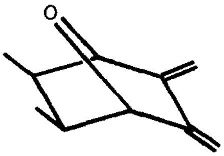

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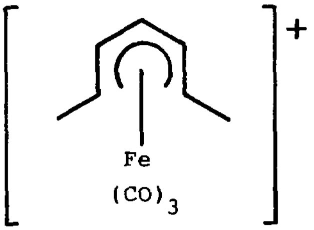

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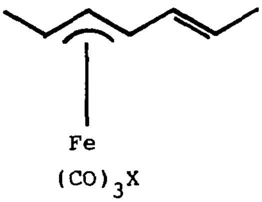

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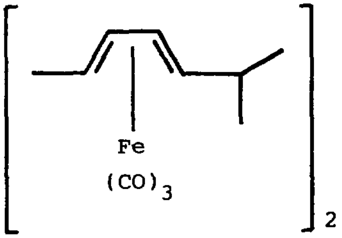

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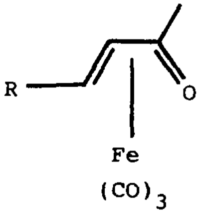


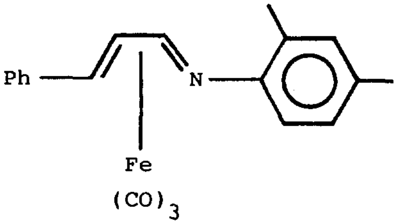
10.23

respectively. Esterification of the (+)-alcohol with p-bromobenzoyl chloride afforded the (+)-ester (10.15; R = 4-BrC_6H_4CO). The crystal structure and absolute configuration of the ester was determined by X-ray diffraction studies [226].

Under basic conditions water removed the tricarbonylmetal groups from the complexes (10.17; M = Fe, Ru) to give the bicyclic compounds (10.18 and 10.19) [227]. Treatment of the (η^5-1,5-dimethylpentadienyl)iron cation (10.20) with lithium halides in acetone gave the (η^3-pentadienyl)iron complexes (10.21; X = Cl, Br, I) together with the dimeric (η^4-butadiene)iron complex (10.22). The reaction mechanism was discussed [228].

Reaction of the tricarbonyliron complexes (10.23; R = H, Me, Ph) with organolithium and Grignard reagents produced the 1,4-diketones $R^1C(O)CHR^2CH_2C(O)Me$, where R^1 = Bu, CMe_3, hexyl, Ph, 4-$MeC_6H_4CH_2$, MeEtCH, $CH{=}CH_2$, R^2 = H, Me, Ph, in one step [229]. Lithiation of the tricarbonyliron complex (10.24) with phenyllithium or p-chlorophenyllithium followed by alkylation with $Et_3O^+BF_4^-$ gave the corresponding zwitterion (10.25; R = Ph, 4-ClC_6H_4) [230].

Irradiation of the (σ,σ-N,N'-diazabutadiene)iron complex (10.26) caused a change in coordination to the η^4-CN,C'N'-complex (19.27) when the substituent R was not too bulky, such as diisopropylphenyl and diisopropylmethyl [231].



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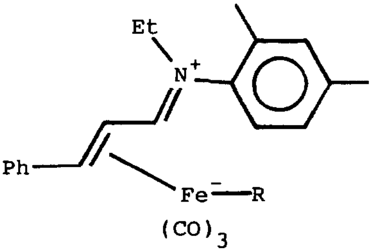

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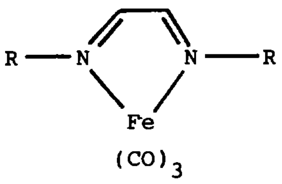

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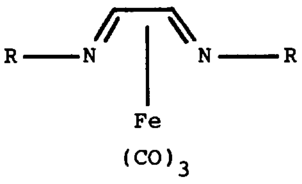
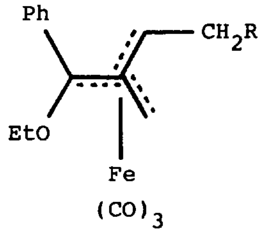


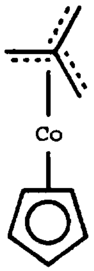
10.27

11. (η-Trimethylenemethane)Fe(CO)$_3$

Allenes have been treated with carbenemetal complexes to form (trimethylenemethane)metal complexes. Thus the carbene (CO)$_4$Fe=C(OEt)Ph combined with the allenes, $CH_2=C=CHCH_2R$, to give the products (11.1; R = CH_2OH, CO_2Et, OH) [232]. The neutral η-trimethylenemethane complex of cobalt (11.2) has been prepared by reaction of dilithioisobutylene with (η-cyclopentadienyl)triphenylphosphinecobalt diiodide. The trimethylenemethane complex (11.2) was characterised spectroscopically and by an X-ray structural analysis. Initial studies indicated that metallation via n-butyllithium occurred exclusively on the trimethylenemethane ligand [233].



11.1



11.2

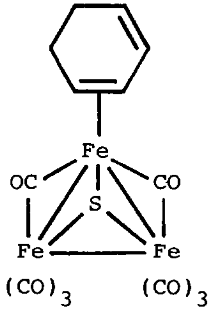
12. (Cyclic-η-diene)Fe(CO)$_3$

(i) Formation

The reaction of iron(I) with allenes in the gas phase has been investigated. Diene-iron complexes were formed and these were subject to isomerization. The position of the allene unit affected the extent of isomerization [234]. Treatment of $Fe_3(CO)_{12}$ with sulphur and 1,3-cyclohexadiene gave the cluster complex (12.1) [235].

Silyl ketene acetals undergo nucleophilic addition to (η-cyclohexadienyl)iron cations, such as the complex (12.2) to give the (η-cyclohexadiene)iron compound (12.3) with a quaternary carbon centre [236]. When a mixture of butylethyne and diethylamine was heated in an autoclave in the presence of (η-cyclooctadiene)(η-cyclooctatetraene)ruthenium, under an atmosphere of carbon dioxide, a mixture of (Z)- and (E)-$Et_2NCO_2CH{=}CHBu$ was obtained [237].

Hydride abstraction from the exo-substituted complexes $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_7R)$, where R = CH_2Ph, $\overline{CHS(CH_2)_3S}$, $CH(CO_2Et)_2$, CN and second addition of a nucleophile to the corresponding cations $[Fe(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_6R)]^+$ have been investigated with the aim of preparing heterobifunctional cis-1,2-cyclohexadienes from benzene. This route was used to prepare cis-1,2-$PhCH_2$-$(CN)C_6H_6$ from benzene in six steps (Scheme 12.1) [238].



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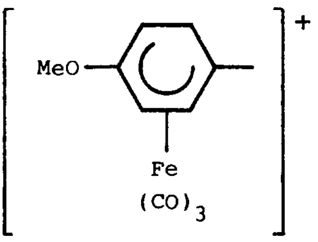
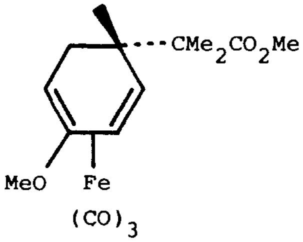


12.2



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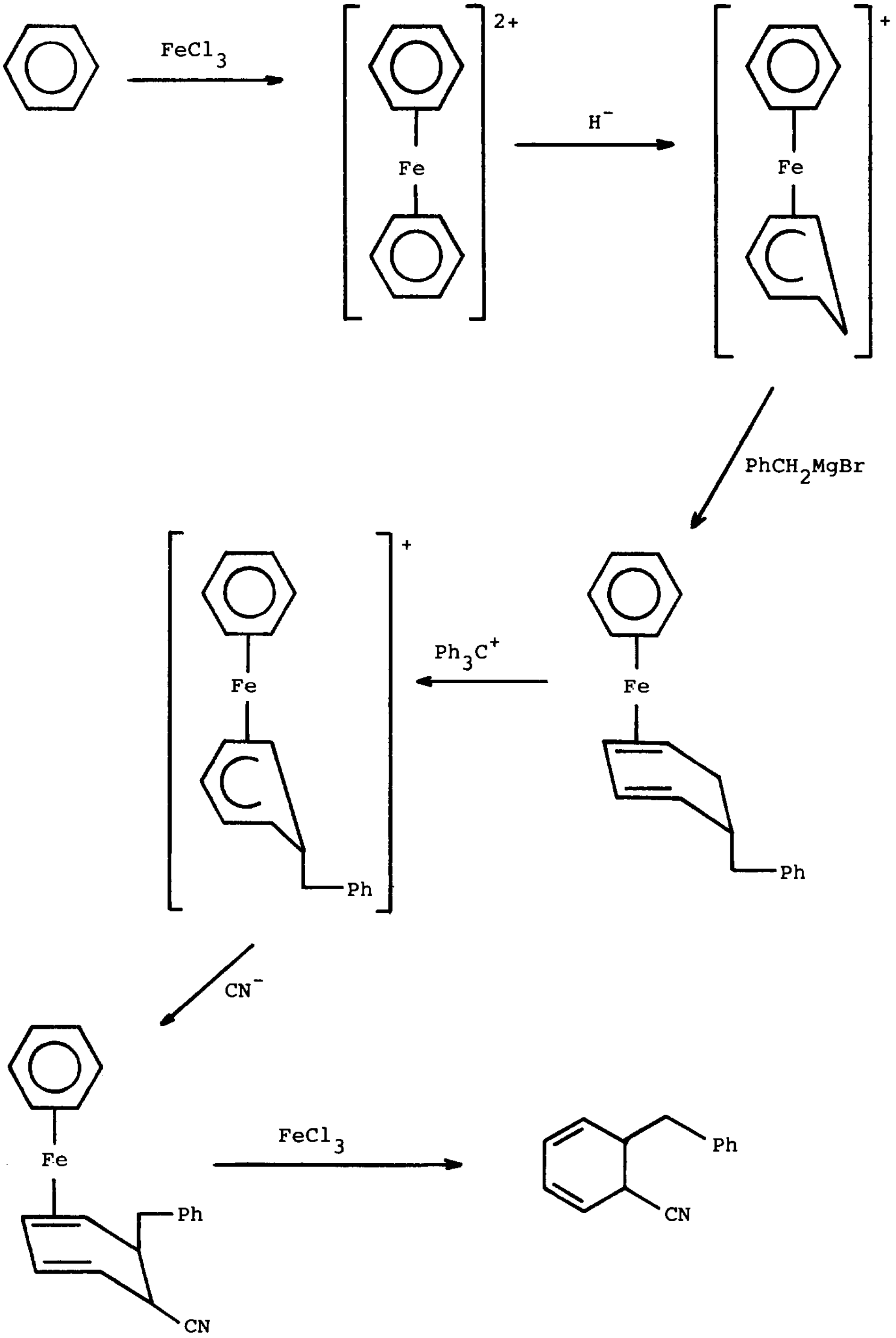
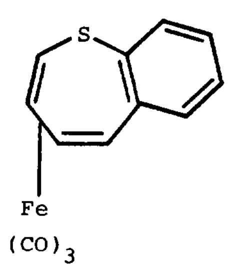


Scheme 12.1



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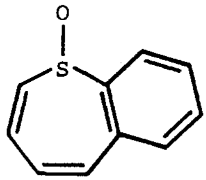
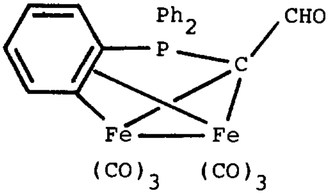


12.5

The (η-thiepin)iron complex (12.4) was obtained by direct reaction between the ligand and nonacarbonyldiiron. Oxidation of the product (12.4) with m-chloroperbenzoic acid gave the S-oxide (12.5) [239]. Ethylation of the complex (12.6) gave the ferrol-type compound (12.7). The structures of the complexes (12.6 and 12.7) were determined by X-ray analysis [240].

The (η-allyl)iron complex (12.8) combined with carbon monoxide to give the (η-5,6-dimethoxy-2-pyrone)iron complex (12.9) which was characterized by X-ray crystallography [241]. Reaction of 1,2,5-trimethylpyrrole with $[(\eta\text{-}C_5H_5)Fe(SMe_2)_3]BF_4$ gave the stable iron complex (12.10) [242]. Treatment of $H_3B.SMe_2$ with bis(tetramethylpyrrolyl)iron-tetramethylpyrrole adduct gave the sandwich complex (12.11). The structure of this complex was determined by X-ray analysis [243].



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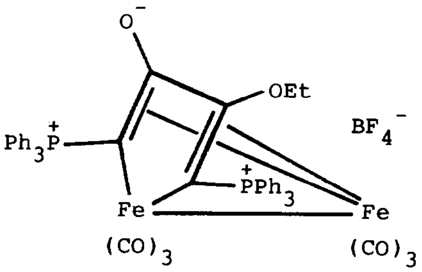

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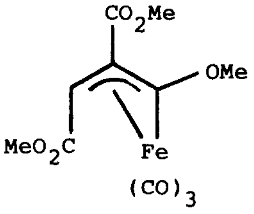

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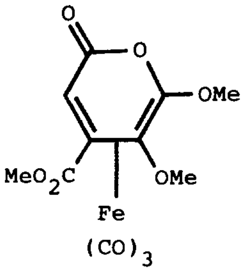

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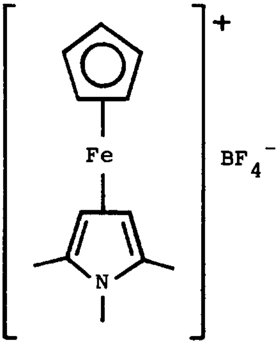

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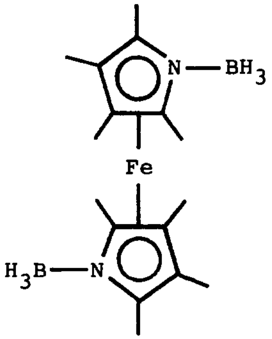

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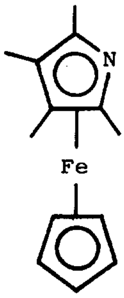

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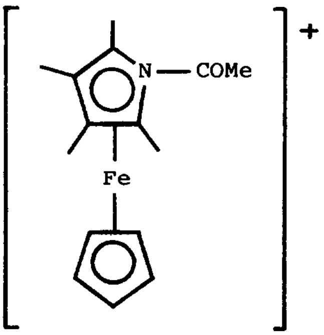
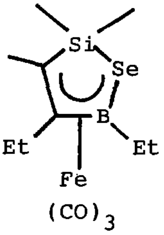
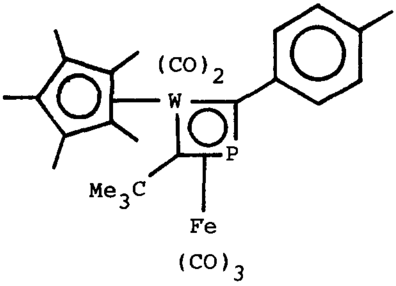


12.13

The azaferrocene (12.12) has been obtained by deprotonation of the corresponding pyrrole complex. The nitrogen basicity of (12.12) was similar to that of alkylpyridines, it combined with Lewis acids to give adducts such as the acetyl derivative





12.14

12.15

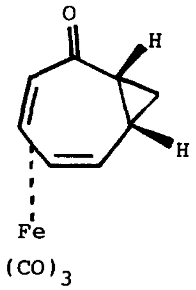
(12.13) [244]. Alkyl-2,5-dihydro-1,2,5-selenasilaboroles formed π-complexes with iron, ruthenium and nickel. Thus pentacarbonyliron combined with the ligand to give the (η-diene)iron complex (12.14) [245].

Electrochemical reduction of (η^6-arene)(η^5-cyclopentadienyl)-iron hexafluorophosphates, where arene = benzenophenone, o-chlorophenyldibenzoylmethane or diethyl ethylphenylmalonate, liberated the arenes in good yields without reduction of the keto or ester groups [246]. The (η-1-phospha-3-tungstacyclobutadiene)iron complex (12.15) has been prepared from (η-C_5Me_5)W($\equiv CC_6H_4$Me-p)-$(CO)_2Fe(CO)_3$ and $Me_3C\equiv P$ and characterized by X-ray crystallography [247].

12. (ii) Spectroscopic and Physico-chemical Studies

High performance liquid chromatography has been used to resolve homotropone and the corresponding exo- and endo-tricarbonyliron (12.16) complexes. The absolute configuration of the exo-isomer has been determined by X-ray crystallography [248]. HPLC has been used to achieve the optical resolution of (±)-tricarbonyl(η-2,3-dihydrotropone)iron. The crystal and molecular structure and the absolute configuration of the complex has been determined by X-ray crystallography and circular dichroism [249].

X-Ray diffraction studies on the iron complexes (12.17 and 12.18) indicated significant changes in molecular geometry as a result of one-electron oxidation. On going from complex



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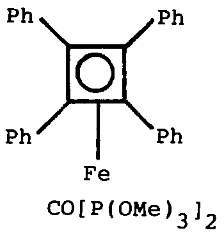

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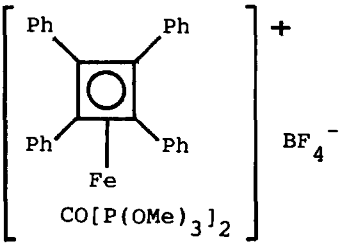

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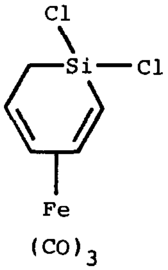
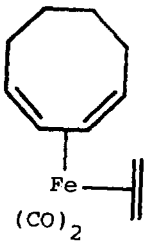


12.19

(12.17) to complex (12.18) the Fe-P distances increased by 0.0115 nm and the Fe-CO distance by 0.0075 nm together with a small increase in cyclobutadiene ring carbon-iron bond lengths. The Fe(CO)[P(OMe)$_3$]$_2$ fragment adopted a different conformation relative to the η^4-C_4Ph_4 moiety [250].

The crystal and molecular structures of (η^4-cyclohexa-1,3-diene)(2-t-butyl-1,1,4,4-tetrafluoro-1,4-disilabutene)-iron and -tungsten carbonyls have been determined by X-ray analysis [251]. The crystal and molecular structure of tricarbonyl-(η^4-1,1-dichloro-1-silacyclohexa-2,4-diene)iron (12.19) has been determined by X-ray crystallography. The structure was typical of tricarbonyl(η-diene)iron complexes [252].

Variable-pressure ^{1}H NMR spectroscopy has been used to investigate the fluxionality of the five-coordinate iron complex (12.20). The structure of this complex was determined by single crystal X-ray diffractometry. The complex had a tetragonal



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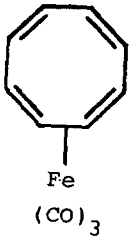

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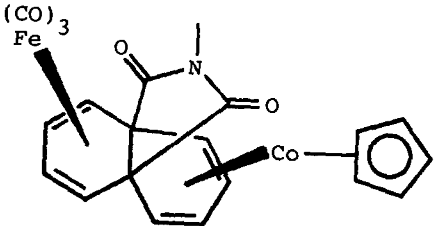

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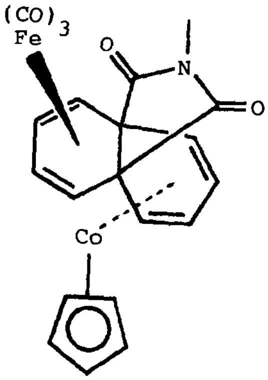

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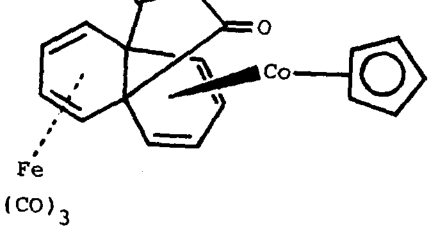


12.24

pyramidal structure with the endocyclic C=C bond and the triphenylphosphine ligand occupying basal sites [253].

FT-IR has been used to examine the electrochemical reduction of tricarbonyl(η^4-cyclooctatetraene)iron (12.21). In aprotic solvents the reduction was reversible and in protic solvents it was irreversible [254]. Fourier transform IR spectroscopy together with thin-layer electrochemistry have been used to study the reduction pathways of tricarbonyl(η-cyclooctatetraene)iron [255].

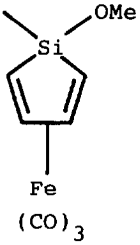
The ^{13}C NMR spectra of several tricarbonyl(η-cyclohexadiene)iron and tricarbonyl(η-vinylcyclohexene)iron complexes have been measured and interpreted. Chemical shift differences were used to distinguish between 1- and 2-substituted complexes [256]. The electron impact mass spectra of the stereoisomers (12.22, 12.23 and 12.24) have been recorded and interpreted. The spectra were interpreted in terms of steric interactions and metal-metal bond formation [257].

12. (iii) General Chemistry

The (η-silacyclopentadiene)iron complex (12.25) underwent nucleophilic substitution at silicon with Grignard reagents, lithium aluminium hydride, alcohols and water, the exo leaving group showed greater reactivity. Complete retention of configuration was observed with both exo- and endo-displacement [258].

Treatment of the η^6-benzene complex (12.26) with 6,6-diphenylfulvene gave the air-sensitive compound (12.27) which underwent a reversible reaction with methanol to form the cationic species (12.28). The tris(trimethylphosphine) complex (12.27) combined with carbon monoxide to give the air-stable compound (12.29) in good yield [259]. The dimeric (η-cyclopentadienone)ruthenium complex (12.30) has been characterized by X-ray crystallography. Catalytic properties were observed and discussed [260].

Photolysis of the binuclear complex (η-cyclohexadienyl)-$Fe_2(CO)_4$, in the presence of carbon monoxide or triphenylphosphine gave the (η-cyclohexadiene)iron complexes (12.31 and 12.32; L = CO, PPh_3) by way of a nineteen-electron (η-cyclohexadienyl)irondicarbonyl intermediate [261]. Aromatization of the tricarbonyliron complex (12.33) by iron(III) chloride to give the phenylcyclopentanol (12.34) was a key step in the preparation



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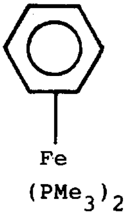

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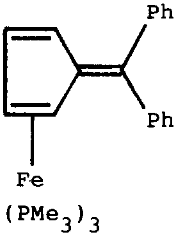

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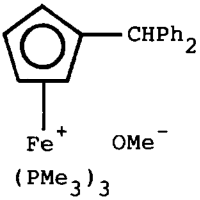

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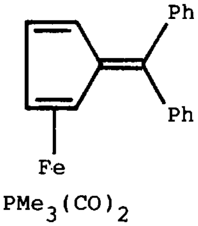
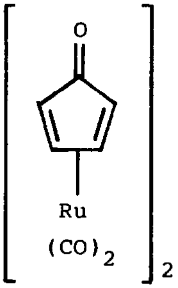


12.29

of pedicellanin methyl ether (12.35) and cuparene [262]. The isomerisation of 4-vinylcyclohexene compounds (12.36; R = Me, OMe, CH_2OMe, CO_2Me) in the presence of pentacarbonyliron into the corresponding cyclohexadiene compounds obtained as the complexes (12.37 and 12.38) has been studied. Thermal isomerisation occurred under thermodynamic control by way of η^2-complexes [263].

When the tricarbonyliron complexes (12.39; R^1 = Me, $CHMe_2$; R^2 = Me, Et, $CH_2CH_2OCOCH_3$) were treated with the organo-lithium reagents R^3Li, where R^3 = $CH(CO_2Me)_2$, $CH(CN)_2$, $CH(CO_2Me)COMe$, the products of C(1) and C(2) addition (12.40 and 12.41) were isolated [264]. Nitrosoarenes reacted with the (η-cyclohexadienyl)tricarbonyliron cation to give nitroxide radicals linked to the cyclohexadienyl ligand [265].

The (η-cyclohexadienyl)iron cation (12.42) has been alkylated at C-1 to give an (η-cyclohexadiene)iron adduct which was



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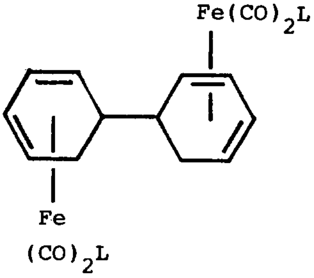

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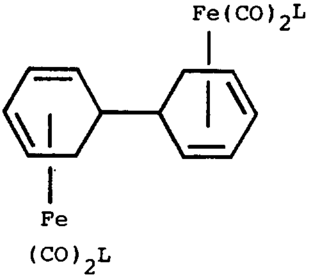

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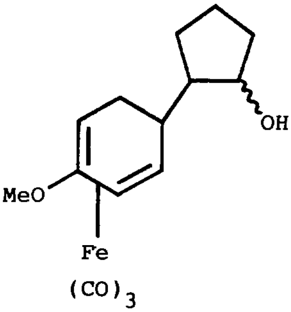

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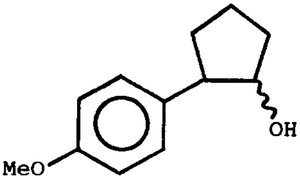

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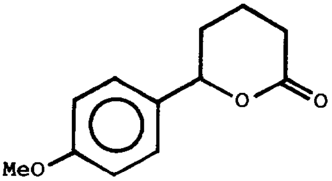

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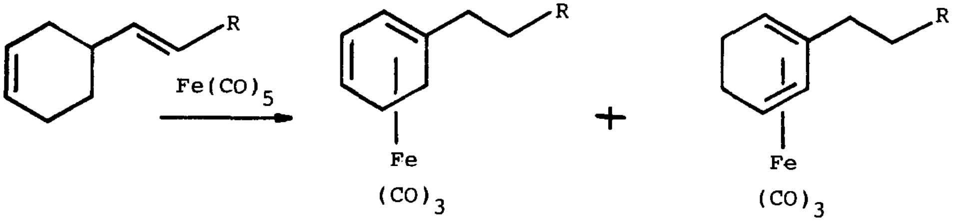

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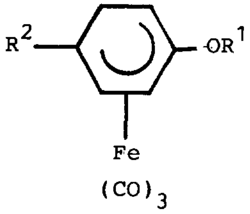

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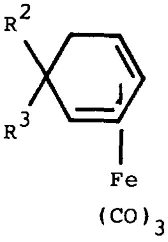

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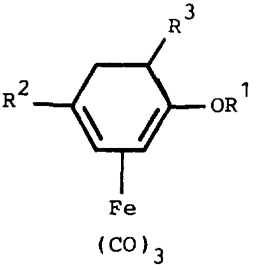

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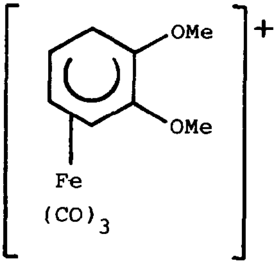

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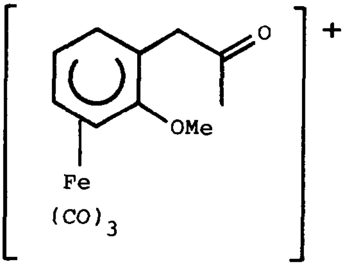

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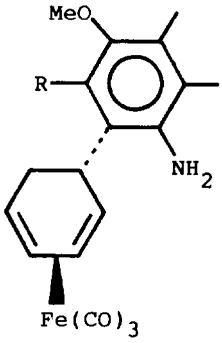

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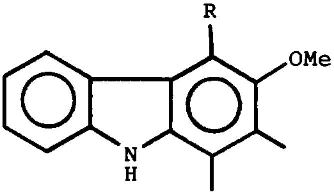

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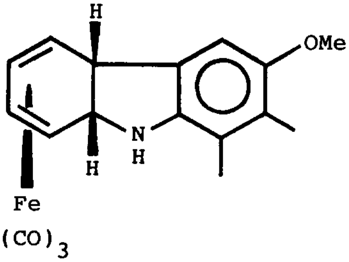


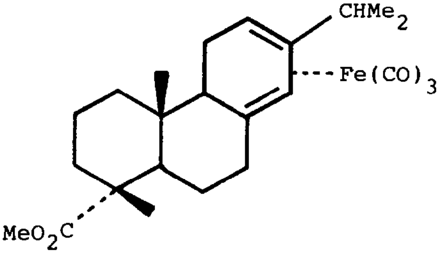
12.46

transformed into the carbomethoxymethyl derivative (12.43) in a regiocontrolled reaction sequence [266].

The (η-cyclohexadiene)iron complex (12.44; R = H) underwent oxidative cyclization with manganese (IV) oxide to give 4-deoxycarbazomycin B (12.45; R = H). The carbazole complex (12.46) was obtained from the starting material (12.44; R = H) and characterized by X-ray crystallography. Carbazomycin (12.45; R = MeO) was prepared from the complex (12.44; R = MeO) [267].

The tricarbonyliron complex (12.47) has been used in the stereoselective synthesis of the (+)-taxodione (12.48) [268]. The tricarbonyliron complex (12.49) has been used as an intermediate in the formation of 6-oxa- and 6-keto-6a-oxa-D-homo-aromatic steroids [269].

The kinetics and mechanism of the addition of 2,6-dimethylaniline to tricarbonyl(η-dienyl)iron cations has been studied. Thus the product (12.50) was obtained from the tricarbonyl-



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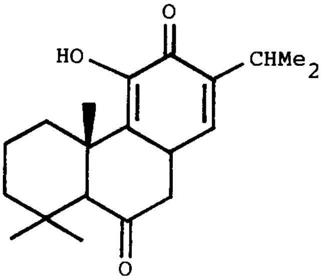

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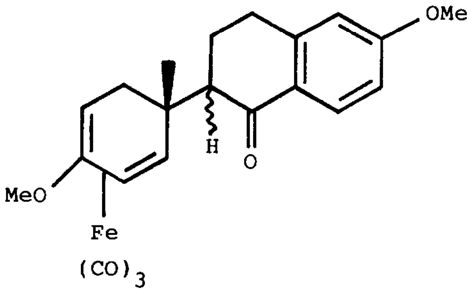
(η-cycloheptadienyl)iron cation. An equilibrium process was observed and the η-cyclohexadienyl complex was more reactive than the η-cycloheptadienyl complex [270].

The reaction of (η-tropone)iron tricarbonyl with diazomethane gave the reverse regioselective product (12.51) while (η-2-chlorotropone)iron tricarbonyl gave the normal regioselective product (12.52). The reactivity of the complex was dependent on the level of the LUMO of the free tropone ligand while the reaction was controlled by the HOMO of diazomethane [271]. Treatment of the η-azepine compound (12.53) with tropylium tetrafluoroborate produced the complex (12.54). Removal of the tricarbonyliron gave the isomerized ligand (12.55) [272].



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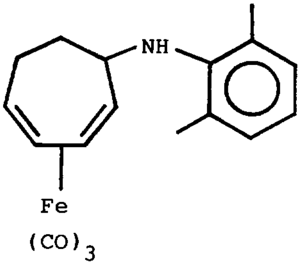

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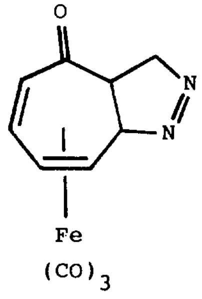

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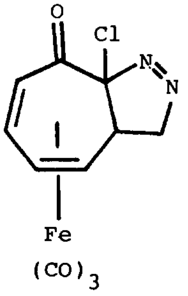

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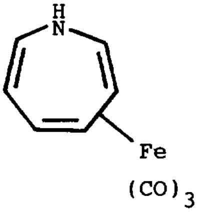

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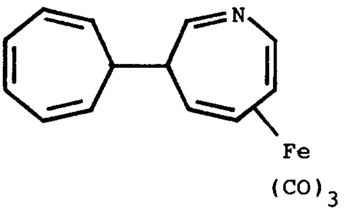

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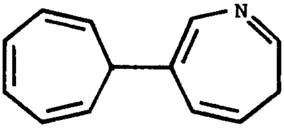

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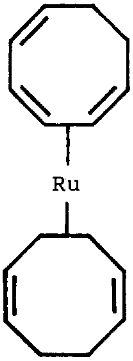


12.56

High levels of asymmetric induction have been observed in the reaction of enolates obtained from sulphoximinyl esters with (η-cyclohexadienyl)- and (η-cycloheptadienyl)-iron carbonyl complexes. The absolute stereochemistry of some products was established by X-ray crystallography and by Mosher's method [273].

The ruthenium complex (12.56) catalyzed the silylation of olefins to give allylsilanes in good yields with high selectivity [274].

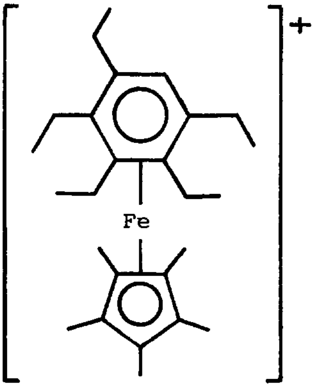
13. $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6H_6)]^+$

(i) Formation

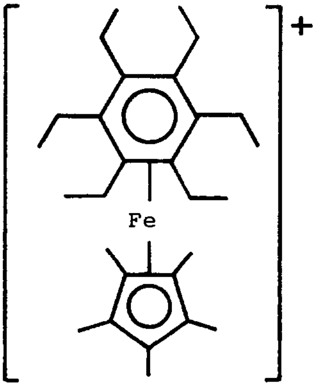
Reaction of $(\eta\text{-}C_5Me_5)Fe(CO)_2Br$ with hexaethylbenzene in the presence of aluminium chloride at < 100°C with the rigorous exclusion of water only the η-pentaethylbenzene derivative (13.1) was isolated. The same reaction carried out at 200°C gave a mixture of the corresponding tri-, tetra- and penta-ethylbenzene compounds. Deuterium labelling experiments indicated that the hydrogen atom replacing the ethyl group came from the reaction medium and not from the displaced ethyl group or from the $\eta\text{-}C_5Me_5$ ligand [275]. When the same reaction was repeated at < 100°C in the presence of protic impurities the cation (13.2) was formed. The structure of this cation was determined by X-ray analysis and all the ethyl substituents were distal [276].

In a related paper $(\eta\text{-}C_5Me_5)Fe(CO)_2Br$ was used to prepare a series of new $[(\eta^6\text{-polyaromatic})Fe(\eta^5\text{-}C_5Me_5)]^+PF_6^-$ complexes, where polyaromatic = biphenyl, phenanthrene, dihydrophenanthrene, triphenylene and pyrene. These compounds together with related complexes were reduced electrochemically and with $LiAlH_4$ and the electronic structures of the reduced species were investigated [277].

A series of $(\eta^6\text{-arene})(\eta^5\text{-cyclopentadienyl})$iron salts has been prepared by the reaction of a substituted ferrocene with an arene in the presence of a mixture of aluminium chloride



13.1

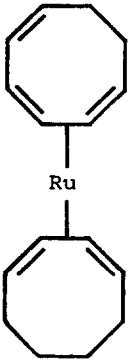


13.2

and zirconium or hafnium tetrahalide. The salts were shown to be useful as photoinitiators in cationic polymerization [278]. Ferrocene underwent ligand transfer with polynuclear arenes, such as biphenyl, diphenyl ether, diphenylmethane, phenanthrene, fluorene and triphenylmethane in decane containing aluminium and aluminium(III) chloride to give the dications {(η-arene)-[Fe(η-C_5H_5)]$_2$}$^{2+}$ and the monocations [(η-arene)Fe(η-C_5H_5)]$^+$. Phenanthrene and fluorene gave complexes containing only the trans-ligand [279].

Neutral mixed sandwich complexes such as closo-3-(η^6-MeC_6H_5)-3,1,2-$FeC_2B_9H_{11}$ have been prepared and characterized by X-ray crystallography [280]. The gas phase reaction of Fe^+-benzyne with small alkanes afforded a large number of (η^6-benzene)iron intermediates [281]. The η^6-cyclooctatriene complex (13.3) and the dimer (13.4) have been used as starting materials for chiral (η^6-arene)(η^4-diene)ruthenium complexes, where arene = PhCH(CMe_3)Me, 4-MeC_6H_4CH(Et)Me, PhCH(OEt)Me, PhOCH(Et)Me, diene = 1,5-cyclooctadiene; arene = PhCH(Et)Me, diene = norbornadiene. The ^{1}H NMR spectra of these complexes were discussed [282].

Protonation of [(η^5-C_5H_5)Ru(OMe)]$_2$ with CF_3SO_3H in the presence of methanol produced the complex [(η^5-C_5H_5)Ru(MeOH)$_3$]-(CF_3SO_3). Reaction of this complex with one or half an equivalent of diphenylacetylene, benzoic acid or phenol gave the complex cations (13.5, 13.6, 13.7 and 13.8) respectively [283].



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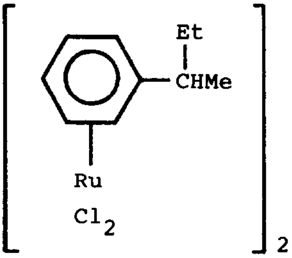

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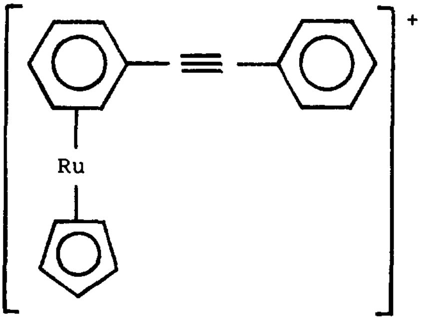

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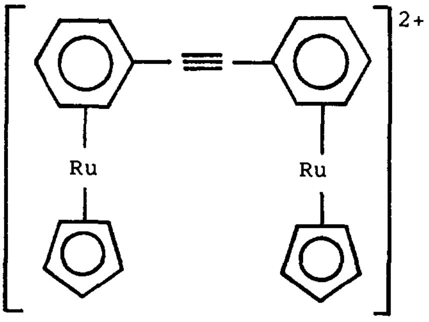

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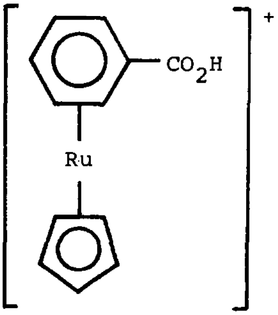

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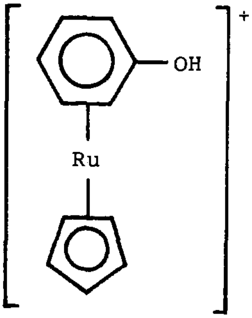
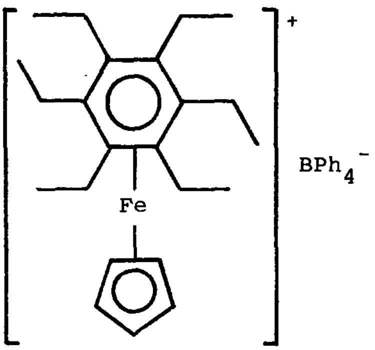


13.8

13. (ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structure of (η-hexaethylbenzene)-(η-cyclopentadienyl)iron tetraphenylborate (13.9) has been determined by X-ray crystallography. The arene ligand had five distal ethyl groups and one proximal group [284]. The cationic half-sandwich iron complex (13.10) has been prepared and characterized by X-ray crystallography. On heating with aluminium(III) chloride it was converted to the bis(η-arene)iron cation (13.11) [285].

Reaction of (η^4-1-methylnaphthalene)(η^6-toluene)iron with excess $Me_3CC{\equiv}P$ gave products of substitution together with four polycyclic phosphahydrocarbons. The crystal structures of these hydrocarbons were determined by X-ray analysis [286]. The mixed valence iron compound (13.12) has been prepared. The structure of the complex (13.12) was determined by X-ray analysis and confirmed the presence of a hexakis(isothiocyanato)ferrate



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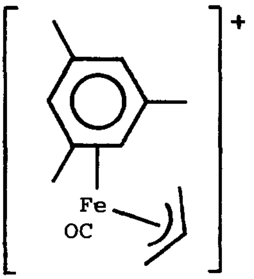

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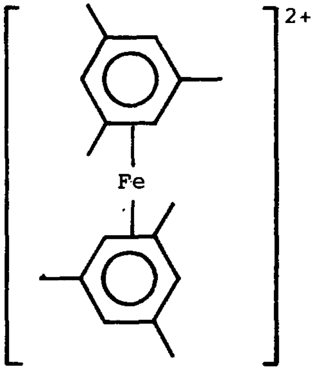

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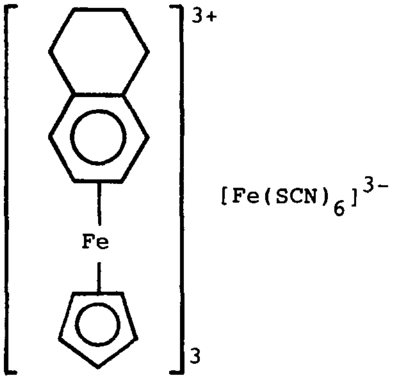
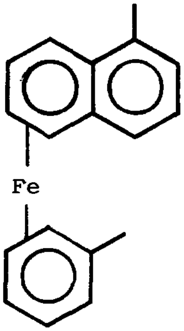


13.12

group [287]. Bis(η-toluene)iron underwent ligand exchange with 1-methylnaphthalene to give a mixture of the two isomeric complexes (13.13 and 13.14). (η-1,4-Dimethylnaphthalene)iron complexes were also prepared. X-Ray crystallography confirmed the η^4-bonding in both the 1-methyl- and 1,4-dimethyl-naphthalene ligands [288].

The 19-electron (η-hexaethylbenzene)iron(II) complex (13.15) has been studied by Moessbauer spectroscopy. The hyperfine data obtained were typical of a 19-electron system with one electron in the e_1^{o} orbital [289]. The binuclear sandwich complexes (13.16; R = H, Me) were prepared in modest yields from biferrocene and the corresponding aromatic compound. The cyclic voltammograms of these compounds showed four reversible waves at -35° corresponding to the 35 and 38 electron complexes. The 35, 36 and 37 electron complexes were isolated whereas the 38 electron form was only reversibly observed by cyclic



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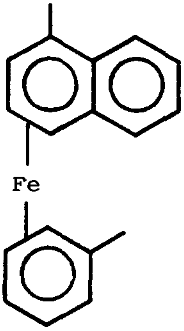

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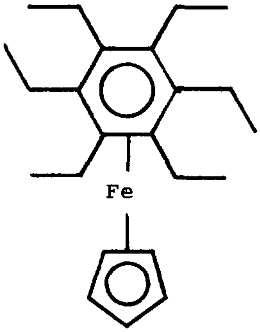


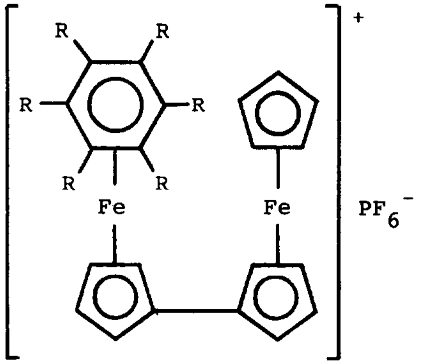
13.15

voltammetry. The Moessbauer and ESR spectra of the mixed valence complexes were recorded [290]. In a related paper Desbois and Astruc reported the preparation of the binuclear complex (13.17). Analogous salts containing other η^6-arenes, such as benzene, toluene, ethylbenzene and 1,3,5-trimethylbenzene, were prepared. The electrochemistry of these and related compounds was investigated [291].

Reduction of the dications (for example 13.18; R = H, Me, Et, 13.19; R = Me, Et) with Na/Hg gave the corresponding 37 electron Fe(I)/Fe(II) mixed valence complexes (13.20 and 13.21) in good yields. Moessbauer spectroscopy showed these monocations to be delocalized mixed valence Fe(I)/Fe(II) complexes with 42% spin density on each iron atom and no Jahn-Teller activity. Two electron reduction of the complexes (13.18 and 13.19) with Na/Hg in THF gave the corresponding Fe(I)/Fe(I) complexes which behaved as metal centred biradicals at room temperature with a Jahn-Teller activity comparable to that of monomeric Fe(I) complexes [292].

Several bis(η-arene)iron cations have been synthesised and contained ligands such as benzene, toluene, o-, m- and p-xylenes, mesitylene, tetramethylbenzene, pentamethylbenzene and hexamethylbenzene. Stability of the ions in solution was discussed and ^{13}C NMR chemical shifts were correlated with total charge density at the relevant carbon atom. ^{57}Fe Moessbauer quadrupole splittings increased with the number of methyl groups [293].

The redox couple $(\eta\text{-}C_6Me_6)_2Ru^{2+/0}$ has been used in a study of the splitting of a two-electron cyclic voltammetric wave



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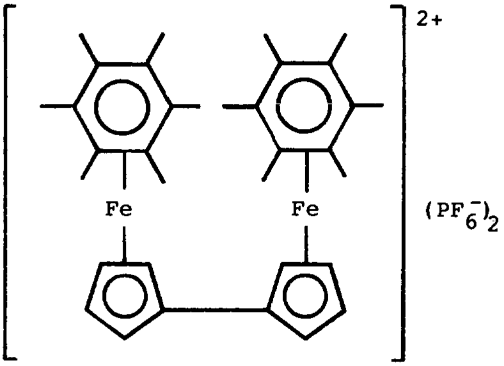

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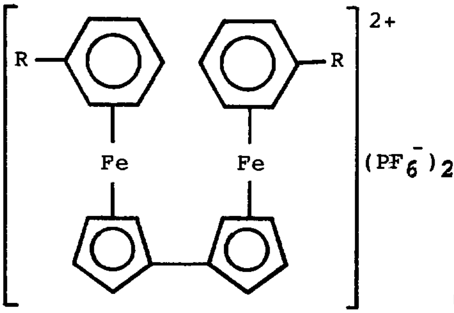

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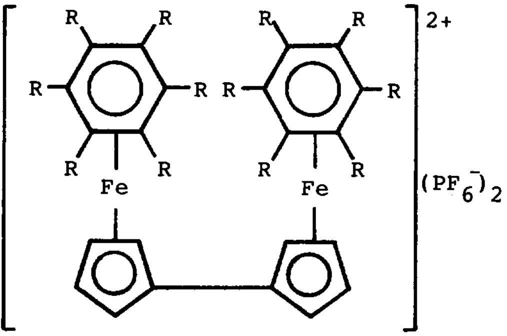

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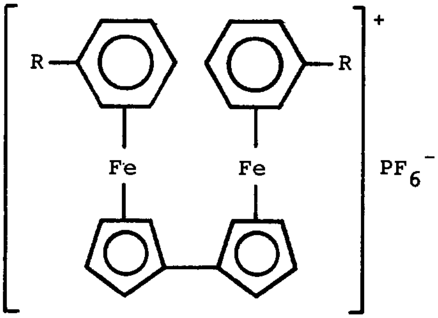

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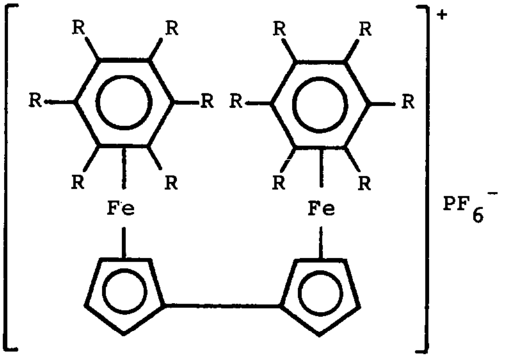
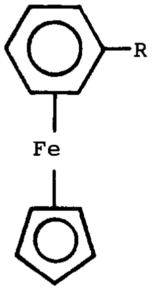


13.21

into its one-electron components [294]. 5,6,11,12-Tetra[(η-pentamethylcyclopentadienyl)ruthenium(η-phenyl)]naphthacene and decamethylferrocene have been used in an electrochemical study of electron-transfer reactions at solid platinum band electrodes of molecular widths [295].

The ESR spectra of the carboranyl-substituted compounds (13.22and 13.23; R = m or p-carboranyl) have been recorded and interpreted in terms of steric interactions [296]. The η-cyclopentadienyl complexes, (η-C_5H_5)Fe(η-arene), where the arene is diphenyl ether, triphenylmethane and 1,1,1-triphenylethane, show 3-axis anisotropy which appeared to be caused by steric interaction of an uncoordinated phenyl group with the (η-C_5H_5)Fe moiety [297].



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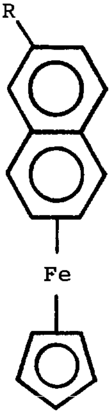
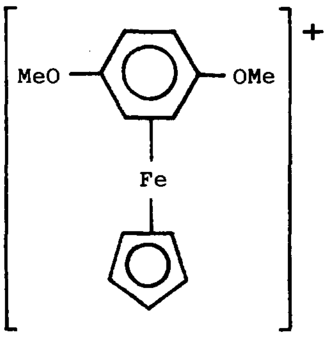


13.23

13. (iii) General Chemistry

Irradiation of (η-arene)iron cations such as the dimethoxyarene complex (13.24) at long wavelengths, showed a fluorescence band at 520 nm. The fluorescence yield was markedly dependent on the nature of the arene, the cation (13.24) gave a high yield while the cations (13.25; $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = R^2 = Me$) gave much lower yields [298]. Photopolymerizable compositions containing the (η-arene)iron salts (13.26; R = H, alkyl, aryl, alkoxy) have been used to prepare photoresists with high photosensitivity [299].

The mechanism of η-arene exchange by phosphines and phosphites in the 19-electron complex (13.27; R = H) and the



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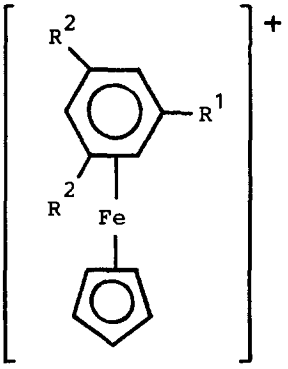

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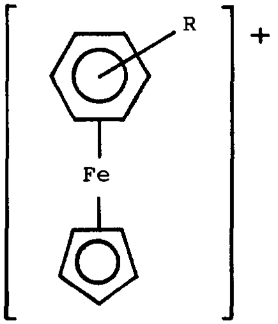
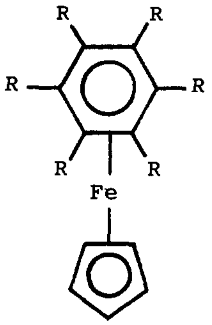


13.26

corresponding η-toluene compound was studied via visible spectroscopy. The results suggested an associative pathway in the rate limiting step together with a fast pre-equilibrium generating the 17-electron species (13.28) [300]. The 19-electron complexes (13.27; R = H, Me) underwent rapid reaction with CO_2 in tetrahydrofuran to give the corresponding salts (13.29). When the same reaction was carried out in the presence of trimethylphosphine and $NaPF_6$ the salt (13.30) was formed together with sodium carbonate, carbon monoxide and the complex (13.31) [301]. In a related communication the complex (13.27; R = H) underwent reaction with carbon monoxide to give the dicarbonyl compound (13.32). The presence of trimethylphosphine had no effect on this reaction. Treatment of the same complex (13.27; R = H) with trimethylphosphine in the presence of $NaPF_6$ resulted in disproportionation to give the salt (13.30) together with



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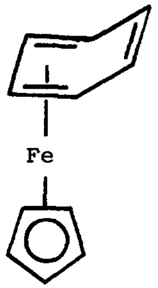

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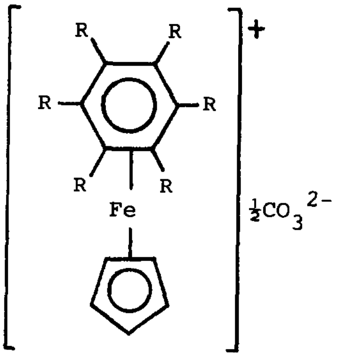

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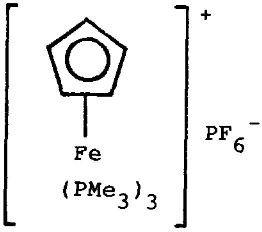

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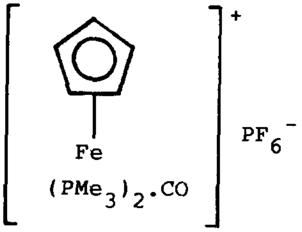

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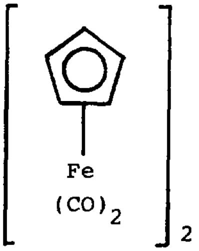

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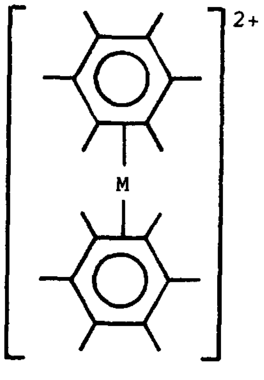

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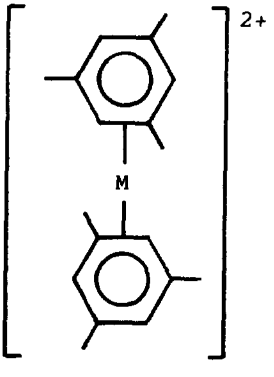
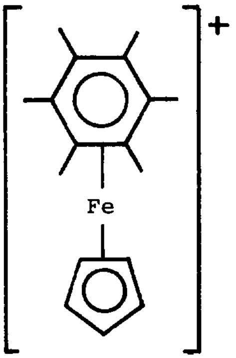


13.34

$(PMe_3)_3Fe(PMe_2CH_2)(H)$ [302]. The bis(η-arene)transition metal dications (13.33 and 13.34; M = Fe, Ru) combined with the dianion iso-$C_4(CN)_6^{2-}$(TCNE) to give donor-acceptor salts $[13.33]^{2+}$-$[TCNE]^{2-}MeNO_2$ and $[13.34]^{2+}[TCNE]^{2-}$. The donor-acceptor salts



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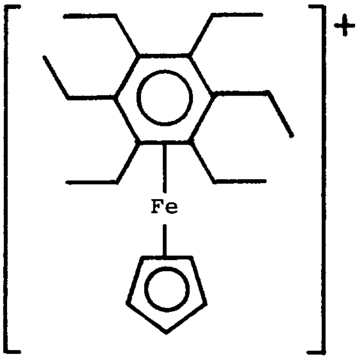
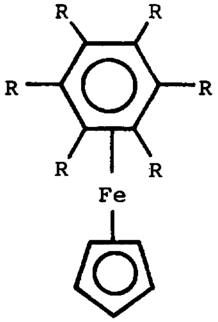


13.36

were characterized by X-ray crystallography and contained zigzag linear chains of closely spaced alternating cations and anions [303].

The cationic (η-arene)iron complex (13.35) underwent peralkylation with methyl iodide and potassium t-butoxide to give the hexaethyl derivative (13.36). The reaction was extended to allow peralkylation with CH_3CH_2I, n-$C_5H_{11}I$ and $MeO(CH_2)_6I$ using pseudo phase-transfer catalysis [304]. The 19-electron (η-arene)iron complexes (13.37; R = H, Me) combined with alkyl halides to give (η-alkylcyclopentadiene)iron complexes. When the alkyl group was chloromethyl the complexes underwent ring expansion to give (η-cyclohexadienyl)iron products [305].

Several arenebis[(η-cyclopentadienyl)iron] dications such as the biphenyl and phenanthrene complexes (13.38 and 13.39) respectively have been reduced on a sodium mirror and the ESR spectra recorded and discussed [306].



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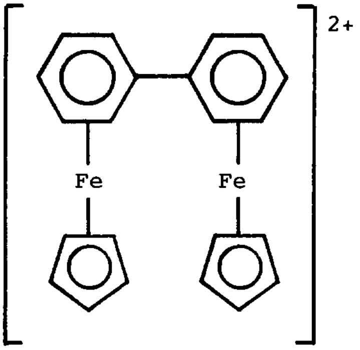

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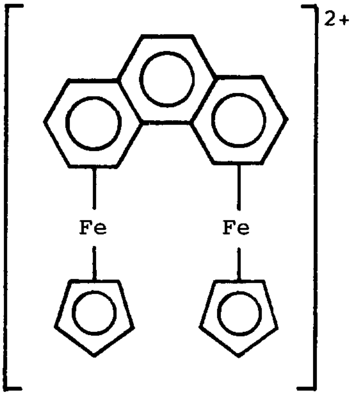

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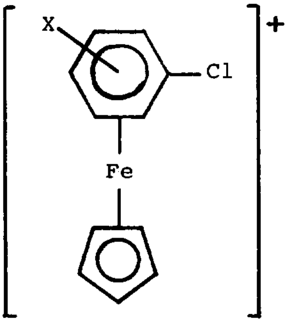

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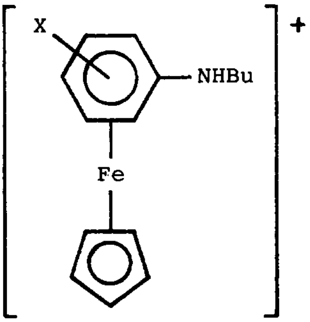
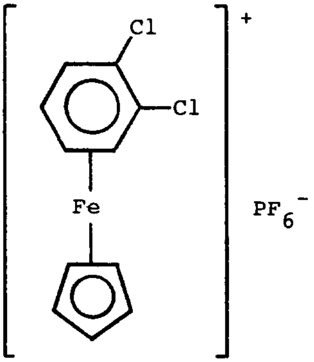


13.41

Treatment of the (η-chlorobenzene)iron cation (13.40; X = 2-, 3-, 4-Cl) with n-butylamine gave only the monosubstituted derivatives (13.41). However when acetic acid was added to the reaction mixture then both chlorine atoms were replaced [307]. The cations (13.40; X = 2-, 3-, 4-NO_2) underwent nucleophilic substitution with aniline, butylamine and pyrrolidine. Selective displacement of the nitro group was observed with aniline [308].

Treatment of the η-dichlorobenzene salt (13.42) with enolate anions gave the corresponding o-chlorophenylalkyl or alkylaryl ketone complexes. These complexes formed 3-mono- or 3,4-disubstituted-1,4-dihydrocinnoline complexes on reaction with hydrazine. When these complexes were treated with sodium amide aromatization and demetallation occurred to give the corresponding cinnolines. For example, the cinnolines (13.43; R^1 = Me, Ph, R^2 = H and R^1 = R^2 = Me) were prepared by this route [309].



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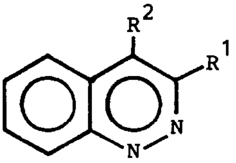
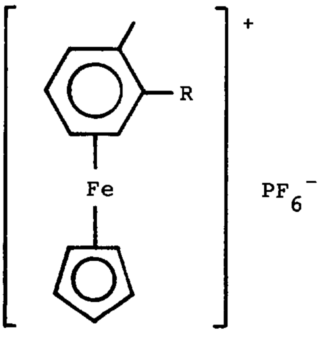


13.43

Nucleophilic substitution of the (η-chlorotoluene)iron compounds (13.44; R = Cl and 13.45; R^1 = R^2 =Cl) with the anions of K^+R^-, where R = SCH_2COMe, $CH(CO_2Et)_2$, $CH(CO_2Me)_2$, $CH(COMe)CO_2Me$, CH_2COMe, afforded the corresponding complexes [13.44; R = SCH_2COMe, $CH(CO_2Et)_2$, $CH(CO_2Me)_2$, $CH(COMe)CO_2Me$, CH_2COMe and 13.45; R^1 = R^2 =SCH_2COMe; R^1 = $CH(CO_2Et)_2$, $CH(CO_2Me)_2$, $CH(COMe)CO_2Me$, R^2 = Cl]. Further reactions of these compounds were investigated [310].

Reaction of (η^6-1,3-dichlorobenzene)(η^5-cyclopentadienyl)-iron hexafluorophosphate with the phenoxide from N-benzyloxy-carbonyl tyrosine methyl ester afforded the product of mono-substitution (13.46) or the product of disubstitution (13.47). Treatment of the monosubstituted product with dimethyl sodio-malonate afforded the complex (13.48). Related reactions of the ruthenium complex (13.49) were investigated [311].



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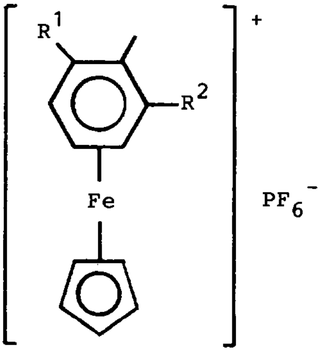

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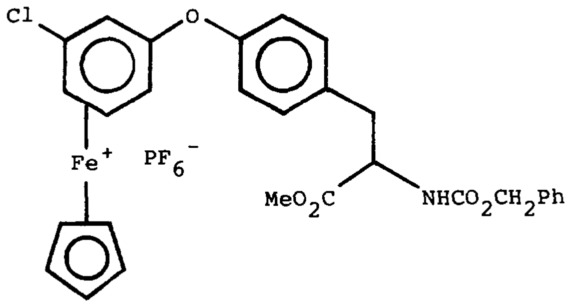

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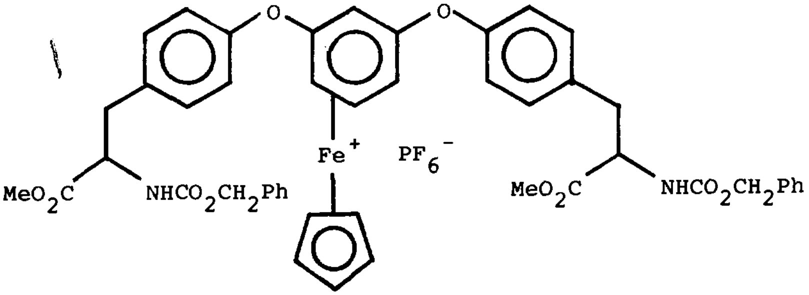

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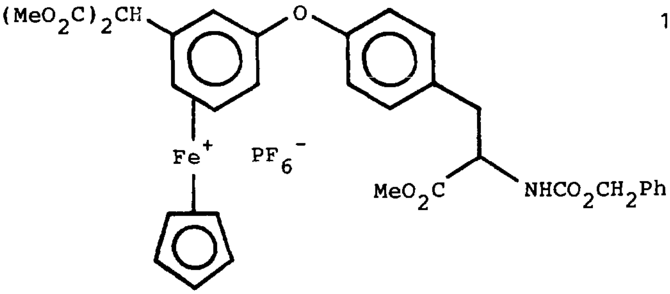

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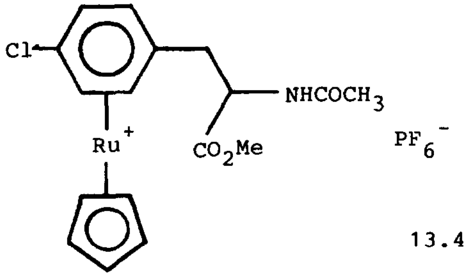
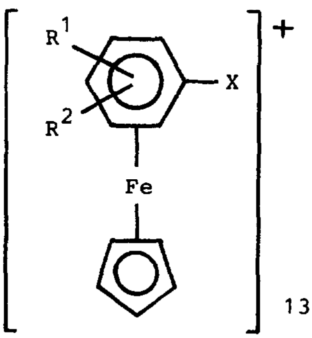


13.49

Displacement of chloride from the (η-arene)iron cations (13.50; R^1 = H, Me, R^2 = Me, Cl, X = Cl) by diethyl malonate gave the (η-phenylmalonate)iron cations [13.50; R^1 = H, Me, R^2 = Me, Cl, X = $CH(CO_2Et)_2$] which were subjected to pyrolytic sublimation to form the phenylmalonate esters (13.51; R^1 = H, Me,



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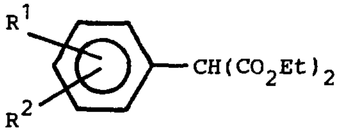

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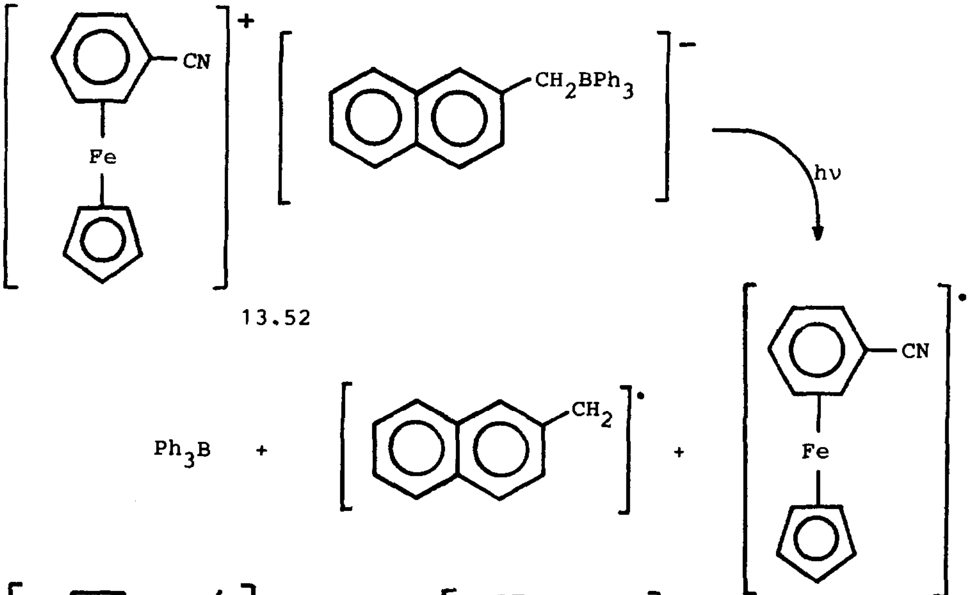

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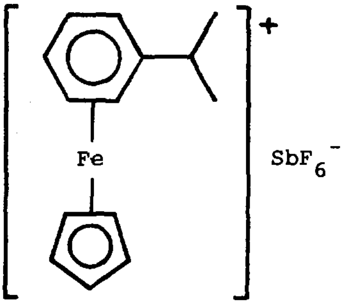

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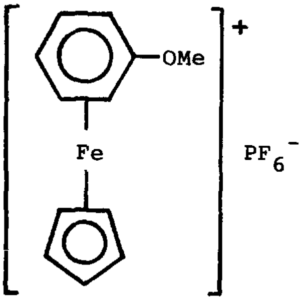


13.56

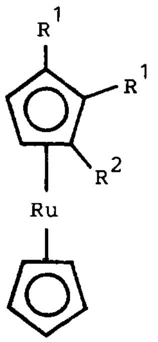
R^2 = Me, Cl) [312]. The photodissociation of the cationic complexes $[(\eta\text{-}C_5H_5)Fe(\eta^6\text{-arene})]^+X^-$ in the presence of nitriles led to the substitution of the η^6-arene ligand by three nitriles. The detection and characterization of the reactive intermediates in this photosubstitution was achieved via time-resolved laser spectroscopy [313]. Irradiation of the borate salt (13.52) in tetrahydrofuran initiated an intra-ion-pair electron-transfer reaction to give the neutral 19-electron complex (13.53) and the neutral boranyl (13.54). This radical was detected by laser flash photolysis and by chemical reactions in solution [314].

The iron complex (13.55) was one of the components of negative photoresists based on polyphenols and epoxide or vinyl ether compounds [315]. The iron complex (13.56) has been incorporated in positive-working photoresist compositions [316].

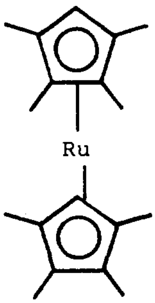
14. $(\eta\text{-}C_5H_5)_2Ru$ and $(\eta\text{-} C_5H_5)_2Os$

Substituted 3-vinyl-1-cyclopropenes combined with several (η-cyclopentadienyl)ruthenium complexes to give substituted ruthenocenes (14.1; $R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = H$; $R^1 = Ph$, $R^2 = Me$). The reaction involved ring expansion of the cyclopropene, no intermediates in the reaction were detected [317]. Reaction of tetramethylcyclopentadiene with ruthenium(III) chloride in the presence of zinc produced octamethylruthenocene (14.2). X-Ray analysis indicated that the $(\eta^5\text{-}C_5HMe_4)$ groups were eclipsed [318].

Indenyllithium has been treated with $[(\eta\text{-}C_5Me_5)Ru(MeCN)_3]^+ PF_6^-$ to give the ruthenocene (14.3) which gave the triple-decker complex (14.4) on further reaction with the same reagent [319]. The triple-decker complex (14.5) has been prepared from phenylborataferrocene and $BrRe(CH_3CN)_2(CO)_3$. The complexes (14.6 and 14.7) were prepared by ring ligand transfer reactions [320]. Reduction of ruthenium(III) chloride or Na_2OsCl_6 in the presence



14.1



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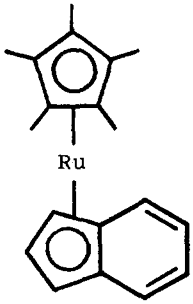

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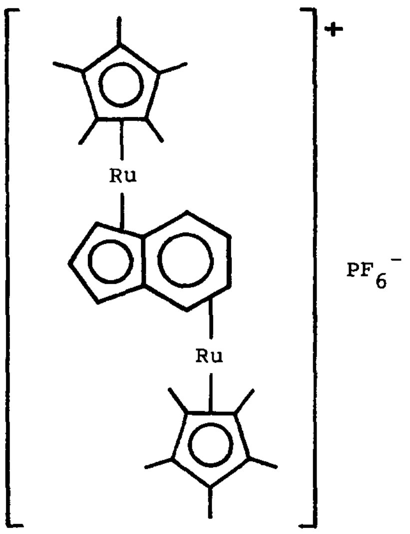

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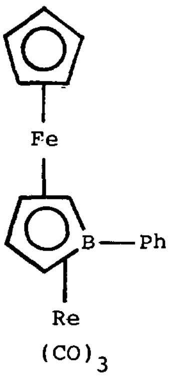

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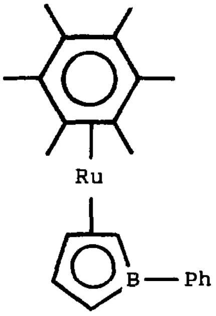

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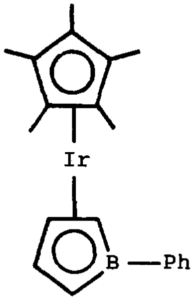
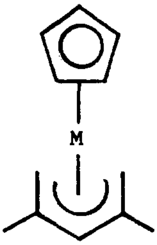


14.7

of cyclopentadiene and 2,4-dimethyl-1,3-pentadiene gave the "half-open" sandwich complexes (14.8; M = Ru, Os). The molecular structure of the complexes (14.8) has been confirmed by X-ray crystallography and the electronic structure has been explored by photoelectron spectroscopy and INDO MO calculations [321].



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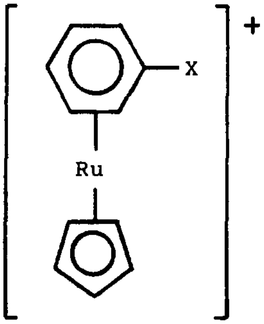
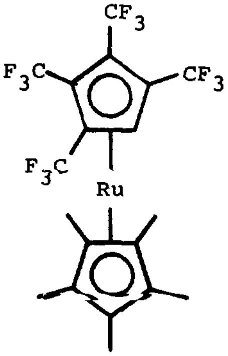


14.9

As part of a study of (η-cyclopentadienyl)ruthenium hydride complexes the (η-arene)ruthenium cations (14.9; X = PPh_2, BPh_3) were obtained [322]. Reaction of ammonium tetrakis(trifluoromethyl)cyclopentadienide with the solvated metal cation $[(\eta^5\text{-}C_5Me_5)Ru(MeCN)_3]^+O_3SCF_3^-$ gave the substituted ruthenocene (14.10). X-Ray analysis showed that the two rings in this complex were staggered and electrochemical oxidation potential measurements indicated that the tetrakis(trifluoromethyl)cyclopentadienyl ligand was strongly electron withdrawing [323].

Equilibrium constants have been determined for the displacement of thiophene by methylthiophenes from the complex (14.11). The values increased with an increasing number of methyl groups on the thiophene reagent. The analogy with Co-Mo/Al_2O_3HDS catalysts was discussed [324]. A kinetic study has been carried out on the reaction of the η^6-anthracene complex (14.12) with methyl cyanide which gave the tri(methylcyanide) compound (14.13).



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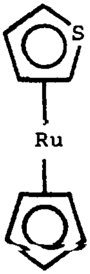

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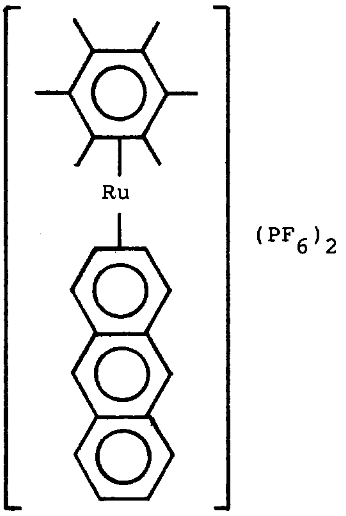

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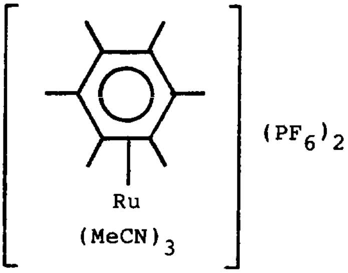


14.13

A mechanism for this reaction was proposed [325]. The effect of temperature and pressure on the ruthenocene-bromoruthenocene electron self-exchange in acetonitrile has been the subject of a kinetic study. Activation enthalpies and entropies were determined and the volume of activation was independent of temperature in the range 34-55°C [326].

ESR spectroscopy has been used to examine single crystals of the charge transfer complex salt bis[(η^5-pentamethylcyclopentadienyl)ruthenium{η^6,η^6-[2_2](1,4)cyclophane}$^{2+}$[(tetracyanoquinodimethane)$_4$]$^{2-}$. The anisotropic spectrum at 77-150 K was typical of an excitonic triplet species. This was attributed to electronic interactions within one of the TCNQ acceptor stacks [327].

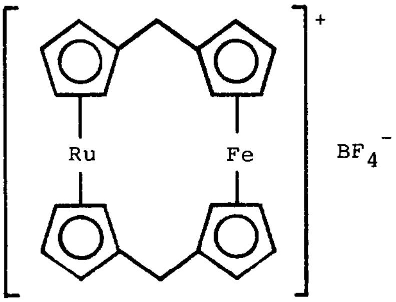
Ruthenocene and osmocene formed electron donor-acceptor complexes in chlorocarbon solvents such as CCl_4, $CHCl_3$, CH_2Cl_2 and C_2Cl_4. On irradiation in the presence of spin traps, nitroxide radical adducts of chlorocarbon radicals were detected and a photolysis mechanism was proposed [328]. Adducts of ferrocenylruthenocene, ferrocenylruthenocenylmethane and biruthenocene with the Lewis acids, iodine, $HgCl_2$ and $SnCl_4$ have been studied by ^{13}C-CPMAS NMR and ^{57}Fe- and ^{119}Sn-Moessbauer spectroscopy. The results suggested the presence of direct bonding between the metal atoms in the metallocenes with the Lewis acids [329].

The stoichiometry of charge transfer salts was determined by controlling the electrochemical potential during the crystallisation process. Bis[(η^5-pentamethylcyclopentadienyl)ruthenium-{η^6,η^6-[2_2](1,4)cyclophane}$^{2+}$[tetracyanoquinodimethane]$_x$$^{2-}$, where x = 2, 4 have been prepared in this way [330].

[1.1]Ferrocenylruthenocenophane has been prepared by the reduction of [1.1]ferrocenylruthenocenophane-1,12-dione. Reaction of these two ferrocenylruthenocenophanes with boron trifluoride etherate containing benzoquinone gave the black monocationic salts (14.14 and 14.15). Moessbauer spectroscopy indicated the presence of intramolecular electron transfer between the ruthenium and iron atoms [331].

Reaction of the osmocene (14.16) with sodium borohydride gave the cation (14.17) which was shown by X-ray crystallography to have an osmium-carbon covalent bond. This led to localisation of the positive charge on osmium. In nonamethylmetallocenylcarbenium ions the role of direct metal interaction in stabilizing the charge increases in the order Fe < Ru < Os [332].

Metallocenylphosphines (14.18; M = Ru, Os; R = alkyl, aryl) have been used as asymmetric hydrogenation catalysts for the preparation of optically active arylacetic acids [333]. Ruthenocene formed adducts with mercury(II) chloride, tin(IV) chloride and iodine, ferrocenylruthenocene (14.19) combined with mercury(II) chloride and iodine and ferrocenylruthenocenyl ketone (14.20) with mercury(II) chloride. A chemical bond between ruthenium and the adduct was indicated by ^{13}C-CP-MAS NMR spectroscopy and ^{57}Fe Moessbauer spectroscopy [334]. Lewis acids formed adducts with ferrocenylruthenocene (14.19) and biruthenocene



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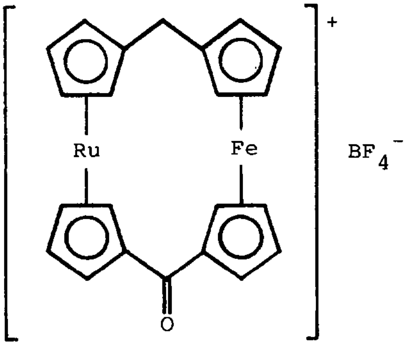

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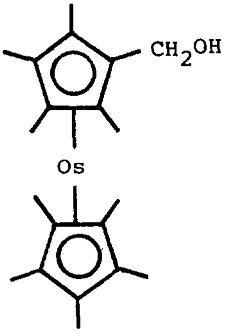

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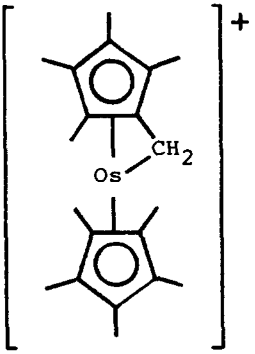

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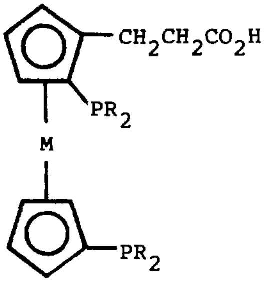

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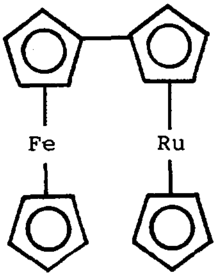

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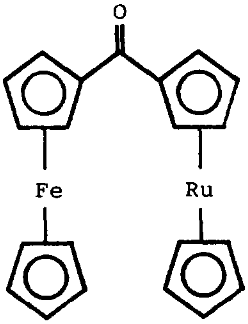

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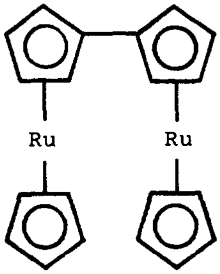

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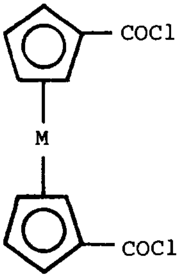

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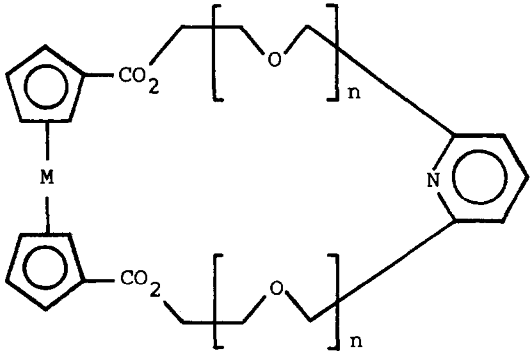

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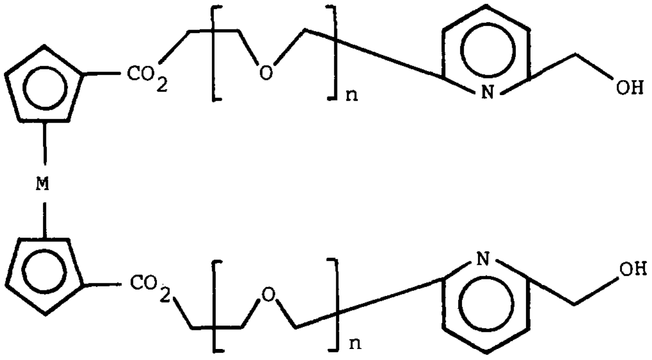

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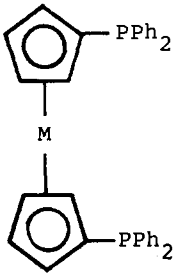

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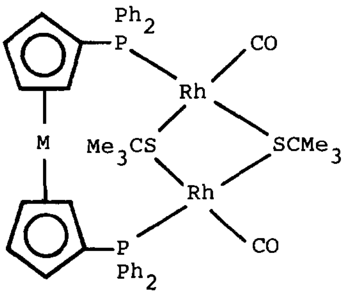
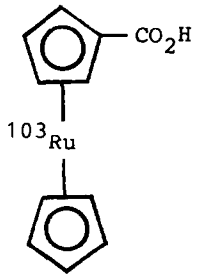


14.26

(14.21). Ruthenium-Lewis acid chemical bonding was investigated [335]. The metallocenyl acid chlorides (14.22; M = Fe, Ru) have been used to prepare the corresponding keto crown ethers (14.23, 14.24; n = 0-3). The complexing ability of these compounds was poor with alkali metal cations but good with Ag^+, In^{3+} and



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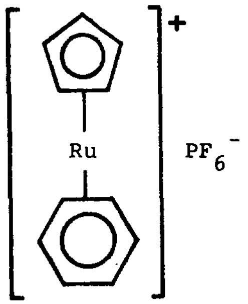

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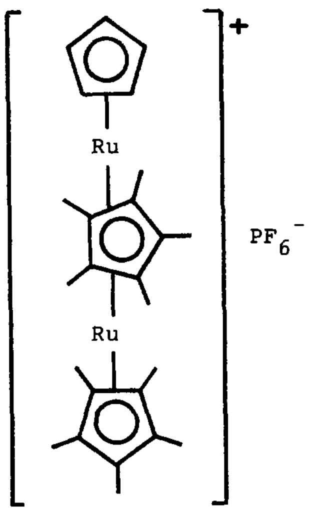
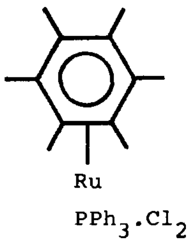


14.29

Zr^{4+} [336]. Chloroformylruthenocene has been converted to [1,1]ruthenocenophane [337].

The ruthenocenyl- and ferrocenyl-phosphines (14.25; M = Ru, Fe) have been used to prepare the rhodium complexes (14.26). The catalytic activity of these complexes for the hydroformylation of 1-hexene was investigated [338]. Radioactive ruthenocene-carboxylic acid (14.27) has been used to label a cytostatic platinum complex through a peptide linkage. Organ distribution experiments in mice showed that the complex accumulated in the liver and spleen [339].

The ruthenium complex (14.28) accelerated the hydrogenation of nitrobenzenes to anilines in the presence of the platinum(IV)



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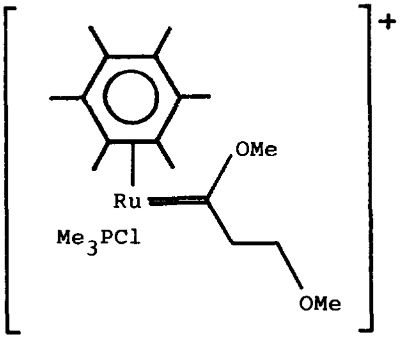


14.31

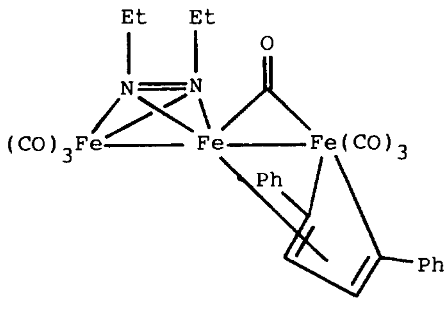
complex of alizarine red S as the catalyst. The same reaction was retarded by the presence of the complex (14.29) [340]. The carbene-metal complex (14.31) has been formed from the (η-hexamethylbenzene)ruthenium complex (14.30) and acetylenes; vinylcarbene complexes were also formed [341].

15. Iron-, Ruthenium- and Osmium-carbon Cluster Compounds

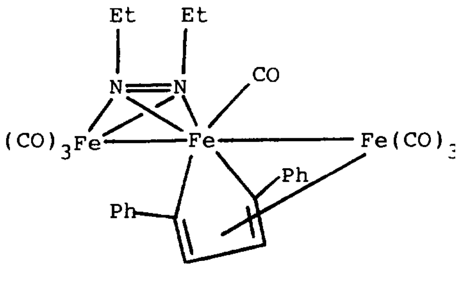
Reaction of the cluster complex $[Fe_3(CO)_9(N_2Et_2)]$ with phenylethyne gave a mixture of the isomeric butadienyliron compounds (15.1 and 15.2). These compounds were separated and their structures were determined by X-ray analysis. When either of the pure complexes (15.1 and 15.2) was heated a mixture of the isomers was obtained [342].

Addition of carbon monoxide to the μ_3-acetyl cluster (15.3) produced the acylketene cluster (15.4) and under moderate carbon monoxide pressures a mobile equilibrium was established between these two species. Treatment of the acetyl cluster (15.3) with triphenylphosphine gave the product of carbon monoxide substitution (15.5). This phosphine substituted cluster did not add carbon monoxide under the same conditions as the parent cluster (15.3) [343].

The hexacarbonyldiiron cluster complex $Fe_2(CO)_6[(Me_2CH)-NC(H)C(H)N(Me_2CH)C(H)CCO_2Me]$ has been heated to cause C-N bond breaking with loss of two carbonyl groups and the formation of a tetracarbonyldiiron complex containing an isomer of the initial ligand. The reaction was reversed on treatment of the product with carbon monoxide at 20°C [344]. Similar hexacarbonyldiiron cluster complexes underwent reversible metal-metal bond fission.



15.1



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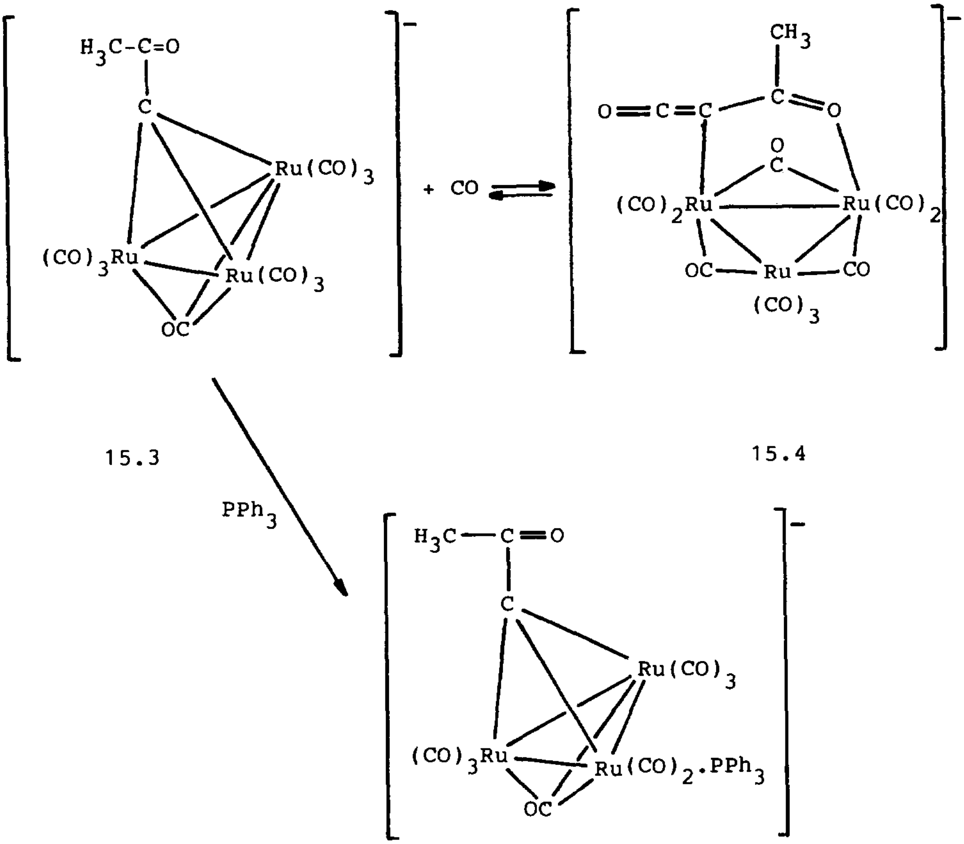


15.3

15.4

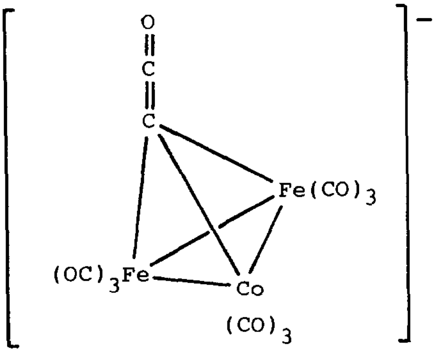
15.5

Key complexes were characterized by X-ray crystallography [345].

The proton affinity and site of protonation of the hydrocarbonyl-bridged dinuclear complex $[(\eta-C_5H_5)(CO)Fe]_2(\mu-CO)(\mu-C=CH_2)$ has been studied in the gas phase by Fourier transform mass spectrometry. Decomposition processes for the cation $\{[(\eta-C_5H_5)-(CO)Fe]_2(\mu-CO)(\mu-C=CH_2)H\}^+$ have been examined in the same way [346].

The kinetics and mechanism of phosphine substitution for carbonyl in the cluster complex (15.6) has been studied. The phosphine selectively attacks cobalt [347] and this is followed by migration of phosphine from metal to carbon [348]. Hydrogen-deuterium exchange between metal-hydride sites and the phenyl ortho-carbon-deuterium sites in the cluster complex (15.7) has been studied by ^1H NMR spectroscopy. The rate of exchange was not affected by the presence of carbon monoxide [349].

Pyrolysis of the triosmium cluster (15.8) gave the methyl-substituted benzyne complex (15.9). This process was shown to be reversible and it was investigated via deuterium labelling [350].



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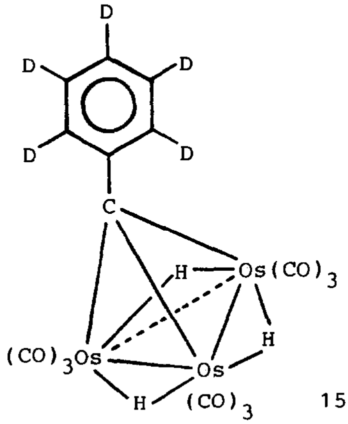

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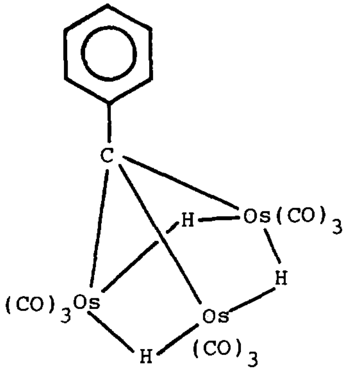

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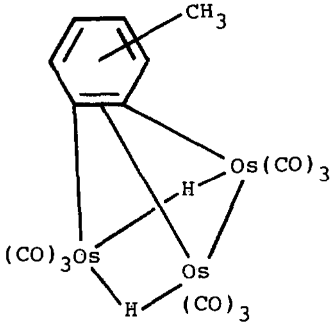
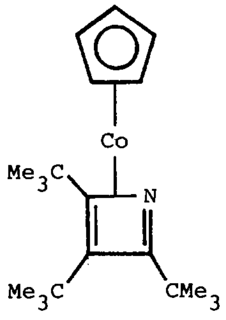


15.9

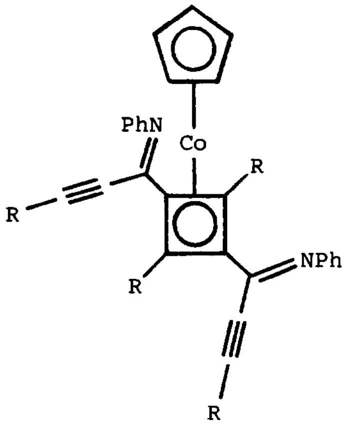
16. $(\eta\text{-}C_4H_4)Co(\eta\text{-}C_5H_5)$

The sandwich type compounds $(\eta\text{-}C_5H_5)CoL$ and the carbonyl complexes $(OC)_3FeL$, $(OC)_4CrL$, $(OC)_4MoL$ and $(OC)_4WL$, where the tetra-hapto diazadiboretidine ligands L = $(R^1BNR^2)_2$ (R^1 = Me, Et, Pr, Bu, R^2 = CMe_3; R^1 = R^2 = $CHMe_2$), have been prepared and characterised [351]. The free azete ligand combined with (η-cyclopentadienyl)bis(η-ethene)cobalt to give the (η-azete)-cobalt complex (16.1) which has been characterized by photoelectron spectroscopy and X-ray crystallography [352].

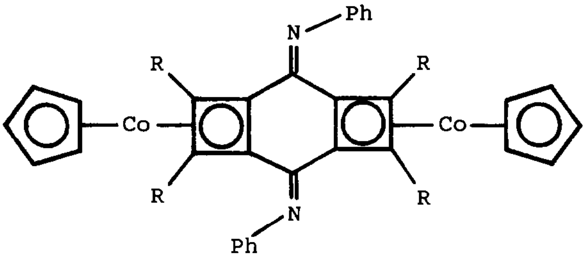
N-Substituted dialkynylimines combined with dicarbonyl-(η-cyclopentadienyl)cobalt to give (η-cyclobutadiene)cobalt



16.1



16.2



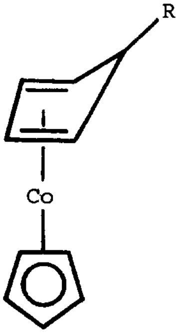
16.3

complexes such as the mononuclear and dinuclear species (16.2 and 16.3; R = H, Me_3Si, Ph) [353].

Thermolysis of the cobalt complexes (16.4; R = Et, CH_2Ph, Ph, 1-propenyl) gave the corresponding isomers (16.5) together with the products of elimination and disproportionation [354]. Metal-carboranyl triple-decker sandwich complexes containing the (η-cyclopentadienyl)cobalt group and (η-dihydroborolyl)iron residues have been synthesised [355].

Reaction of $K[Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})$ with $Bu^tC\equiv P$ and NEt_4Cl afforded the (η^4-1,3-diphosphacyclobutadiene)(η^5-1,2-dicarbaborane)rhodium salt $[NEt_4][Rh(\eta^4\text{-}P_2C_2Bu^t{}_2)(\eta^5\text{-}C_2B_9H_{11})]$. The crystal structure of this salt was determined and the reactivity was investigated [356].

The molecular structures of the rhodium complexes $[(\eta^4$-cycloocta-1,5-diene)$Rh(\eta^5\text{-}C_9H_7)]$, where R = H, Me, have been



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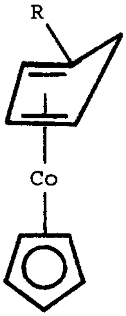
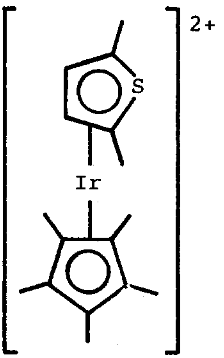


16.5

determined. The distinction between the η^5- and η^3-indenyl coordination modes was discussed [357].

Two electron reduction of η^5-2,5-dimethylthiophene complex (16.6) with cobaltocene gave the corresponding η^4-2,5-dimethylthiophene complex. X-Ray analysis showed that the η^4-ligand was only coordinated to the iridium via the four carbon atoms. The uncoordinated sulphur atom was sufficiently basic to form the sulphur adduct (16.7) with borane [358].

Treatment of the η^4-diene complex (16.8) with 4-methyl-3,5-dioxotriazolinedione resulted in the displacement of the (η^5-C_5H_5)Co group and the formation of the corresponding Diels-Alder adduct of the diene ligand [359]. Optimum reaction conditions for the preparation of the η-cyclobutadiene complexes (16.9 and 16.10) has been established. Reaction of the iodine derivative (16.11; X = I) with PPh_3 and CH_3MgI gave the products of substitution, (η^4-C_4H_4)$CoCOPPh_3I$) and (16.11; X = Me) respectively [360].



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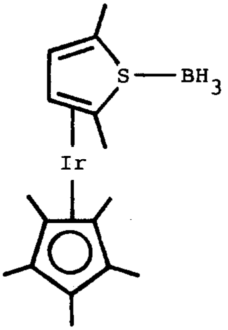

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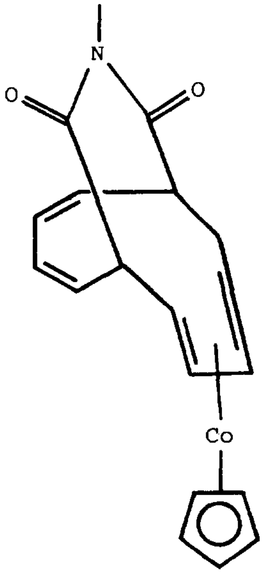

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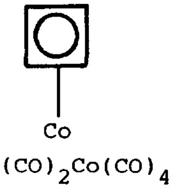

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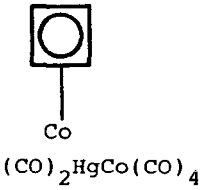

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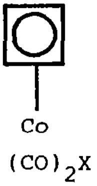


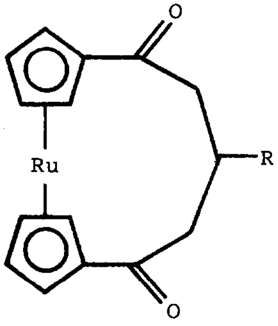
16.11

^{1}H NMR Studies on the rhodium(II) complex [(η^6-C_6Me_6)-Rh(η^5-C_5Me_5)]$^+$ indicated that the arene methyl groups were magnetically equivalent. These results suggested that the arene group was planar and not bent in this complex. The structures of other related complexes were considered and it was concluded that bent arene structures were more likely for electron-rich early transition metals than for their later transition metal counterparts [361].

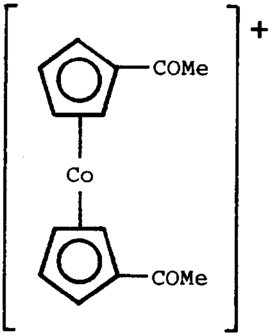
The tricarbonyliron or 2,4-pentanedionatorhodium groups have been linked to the ring B diene system of ergosteryl and 7-dehydrocholesteryl acetates in order to facilitate the ^{1}H and ^{13}C NMR analysis of these steroids [362].

17. (η-C_5H_5)$_2$Co and [(η-C_5H_5)$_2$Co]$^+$

The preparation of 3-aryl[5]ruthenocenophane-1,5-diones (17.1; R = Ph, ferrocenyl) has been reported, together with



17.1



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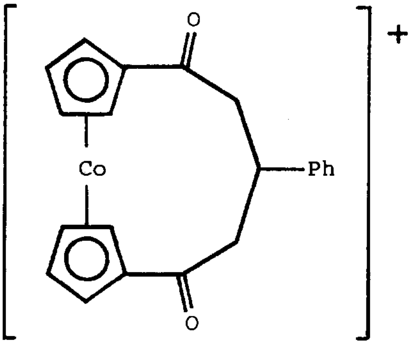

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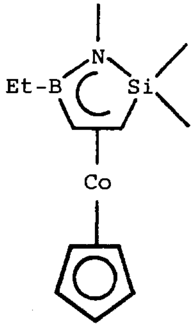
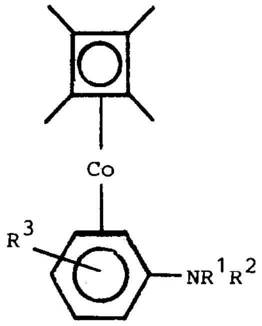


17.4

the formation of the analogous cobaltocenium ion (17.3) from the 1,1'-diacetylcobaltocenium cation (17.2) [363]. Reaction of the *nido*-$Et_2C_2B_4H_5^-$ anion with cobalt(II) chloride and dimethyl- or tetramethyl-pyrrolide ions followed by tetramethylethylenediamine produced the sandwich complexes $(\eta^5\text{-}NC_4Me_4R_2)$-$Co(Et_2C_2B_3H_5)$, where R = H or Me. These complexes were converted into the triple decker compounds $(\eta^5\text{-}NC_4Me_4)_2Co_2(\mu,\eta^5\text{-}Et_2C_2B_3H_3)$, $(\eta^5\text{-}NC_4Me_4R_2)Co(\mu,\eta^5\text{-}Et_2C_2B_3H_3)Co(\eta^5\text{-}C_5Me_5)$ and $(\eta^5\text{-}NC_4Me_2R_2)$-$Co(\mu,\eta^5\text{-}Et_2C_2B_3H_3)Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)$. All the triple decker complexes were air stable crystalline solids [364].

The cobaltocene analogue (17.4) containing the 2,5-dihydro-1,2,5-azasilaborole ligand has been prepared and characterized together with several alkyl derivatives [365].

Aromatic amines have been treated with tricarbonyl(tetramethylcyclobutadiene)cobalt(I) hexafluorophosphate and trimethylamine oxide to form the isometallocene complexes (17.5; R^1 or



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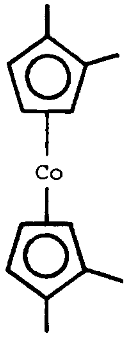

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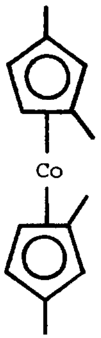


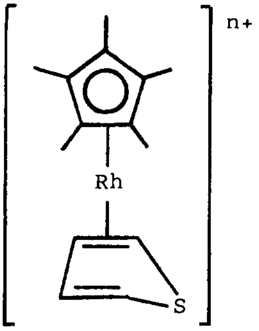
17.7

R^2 or R^3 = H, Me, Et, Me_3C). The complexes were deprotonated by bases [366].

Transannular interactions in complexes of the type $[(\eta^5-C_5Me_5)Rh(\eta^6$-dihydro-s-indacenophane)]$(SbF_6)_2$ have been investigated. The $(\eta^5-C_5Me_5)Rh$ group reduced electron density in both decks of the cyclophanes [367]. An ion cyclotron resonance study has been employed to evaluate the photoinduced reactivity of $RhC_5H_6^+$ with cyclopentane in the gas phase. The rhodocenium ions $[(\eta-C_5H_5)_2Rh]^+$ and $[(\eta-C_5H_5)Rh]^+$ were among product species identified [368].

Weaver and co-workers have evaluated electronic matrix coupling elements, $\underline{H}_{12}$, for metallocene electron-exchange reactions. Six metallocene couples based on cobaltocene and ferrocene were examined [369]. Cobaltocene and several methylated cobaltocenes including the tetramethyl compounds (17.6 and 17.7) have been examined by ^1H and ^{13}C NMR spectroscopy in order to determine the electronic structure and spin density distribution [370].

An absorption band was observed at approximately 500 nm, in the electron transport process of the chemical diode comprising a cobaltocenium-ferrocene bilayer film, and this was attributed to the charge-transfer complex formation at the film-film interface [371]. Cyclic voltammetry indicated that the complex (17.8; n = 2) underwent two reversible 1-electron reductions at low potentials. Cobaltocene was used to reduce this compound to the neutral product (17.8; n = 0). X-Ray analysis showed that the reduced complex (17.8; n = 0) contained a nonplanar η^4-thiophene ligand. Desulphurization of this complex occurred on



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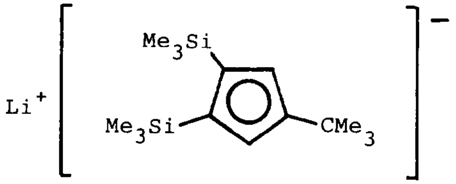

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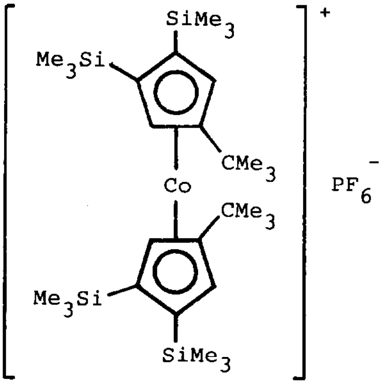

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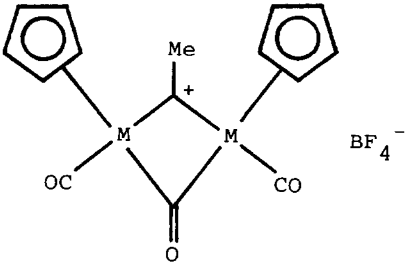
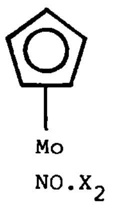


17.11

treatment with $Fe_3(CO)_{12}$[372]. 2-t-Butyl-5,5-bis(trimethylsilyl)-2,4-cyclopentadiene has been prepared from 1,1-dimethylfulvene and it was deprotonated with n-butyllithium to give the lithium salt (17.9). This salt was used to prepare the cobaltocenium salt (17.10). Variable-temperature ^1H NMR spectroscopy indicated that rotation of the trisubstituted η-cyclopentadienyl rings was hindered [373]. Cobaltocene has been used to reduce the complexes (17.11; M = Fe, Ru) [374]. It has also been used to reduce the molybdenum complexes (17.12; X = Cl, Br, I) and the resultant salts (17.13) were isolatable in good yields [375].

Reaction of cobaltocene with the secondary phosphine oxides $HP(O)R_2$, where R = n-Bu, s-Bu, cyclohexyl and 9H-9-phosphabicyclononane-9-oxide gave the corresponding cobalt(I) compounds (17.14) and hydrogen. Further reactions of these compounds were investigated [376]. Reaction of cobaltocenium hexafluorophosphate with the nucleophilic reagents RM, where R = organic



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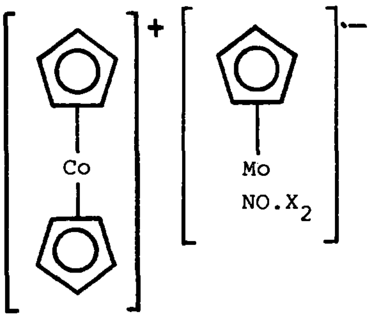

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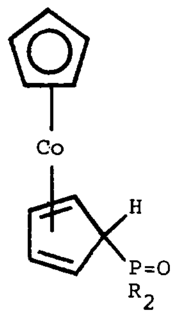

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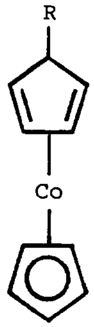

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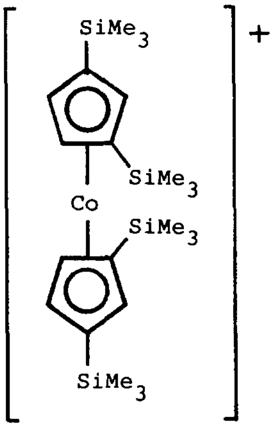


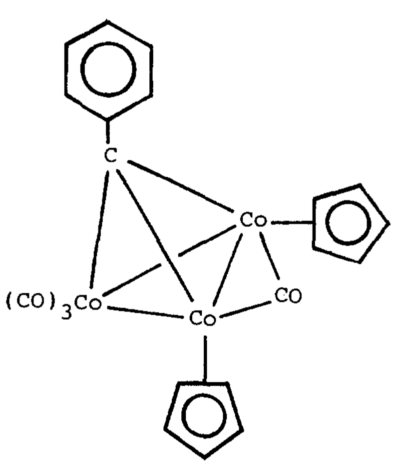
17.16

group, M = Li, Na or MgX and X = halogen, has been investigated. Soft nucleophiles with pk_a = 16 and hard nucleophiles with $pk_a > 20$ gave the corresponding π-complexes (17.15). Ambidentate nucleophiles with hard reaction centres added to the η-cyclopentadienyl ligand [377].

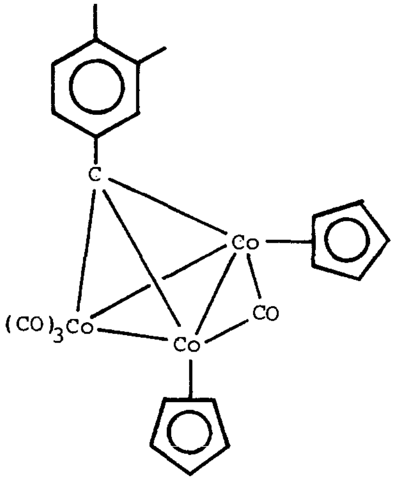
The tetrakis(trimethylsilyl)cobaltocenium ion (17.16) has been obtained by oxidation of the corresponding cobaltocene. The hexakis cation was formed in the same way [378].

18. Cobalt-carbon Cluster Compounds

The structure of the tetrahedral cluster complex (18.1) has been determined by X-ray analysis. The phenyl ring was in the plane containing the bridging carbonyl group. The barrier



18.1

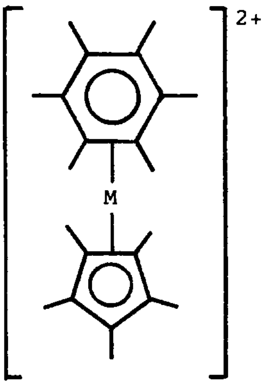


18.2

to phenyl ring rotation was too low to be observed by ^{13}C NMR spectroscopy. The corresponding xylyl complex (18.2) was prepared but even at -90° at a magnetic field of 11.7 T there was no evidence of restricted rotation of the aryl-carbynyl group [379].

Rate constants for the electron self-exchange of the cobaltocenium-cobaltocene and pentamethylcobaltocenium-pentamethylcobaltocene have been determined by an NMR line broadening technique. The rate constants obtained were compared with those for the corresponding ferrocene and bis(η-benzene)chromium couples. A relationship was obtained between the rate constants for the electron self-exchange and the nature of the donor and acceptor orbitals in the complexes [380]. In a related paper the effect of solvent on the rate constants was determined [381].

Rate constants for homogeneous self electron-exchange and electrochemical electron-exchange have been determined for the first and second reduction steps in the η^6-arene complexes (18.3; M = Co, Rh) in order to investigate the $\eta^6 \rightleftharpoons \eta^4$ hapticity change found upon formation of the Rh(I) two-electron reduction product. In the corresponding cobalt complex the arene ligand retained the η^6-configuration on reduction. The results indicated that the mechanism for Rh(II/I) was at least partly concerted in nature and the stabilization afforded to Rh(I) by the $\eta^6 \rightarrow \eta^4$ hapticity change was at least 6 kcal mol^{-1} [382]. The reaction of chloralose with $Co_2(CO)_8$ gave the tricobalt cluster complex



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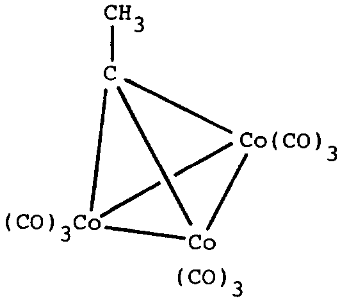


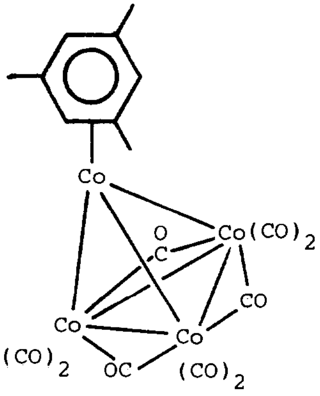
18.4

(18.4). The corresponding radical anion was generated electrochemically and the ESR spectrum was recorded and discussed [383].

The gas-phase photofragmentation of the cluster complex (18.4) in the visible and near-ultraviolet spectral regions has been investigated via laser photodissociation-multiphoton ionization techniques. The fragments observed were cobalt-carbon clusters free of terminal carbonyl ligands and the distribution of these fragments changed with wavelength [384].

The cobalt cluster complexes $MeCCo_3(CO)_{9-n}L_n$, where L = PMe_3, n = 1-3; L = PMe_2Ph, n = 1-3; L = $PMePh_2$, n = 1, 2; L = PPh_3, n = 1 and L = PEt_2Ph, n = 3, have been studied by cyclic voltammetry. The results showed the radical anion of the parent cluster $MeCCo_3(CO)_9$ to be of limited stability and it readily eliminated CO in a reversible reaction. In the phosphine-substituted clusters CO elimination became more difficult and PR_3 elimination competed with CO elimination [385].

γ-Cyclodextrin has been shown to form inclusion compounds with the cobalt complexes (18.5, 18.6 and 18.7) in high yields [386]. Treatment of the molybdenum dicobalt cluster (18.8) with lithiodiphenylphosphine produced the reactive anion (18.9; n = -1) which was readily oxidized to the stable 47 cluster valence electron radical (18.9; n = 0). The structure of this radical was determined by X-ray analysis. Low temperature protonation of the anion (18.9; n = -1) gave the μ-hydrido derivative (18.10) which slowly equilibrated with a new isomer (18.11) [387].



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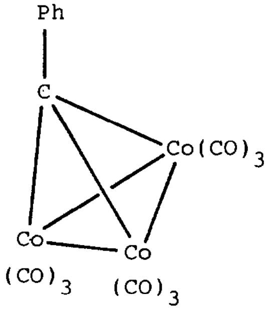

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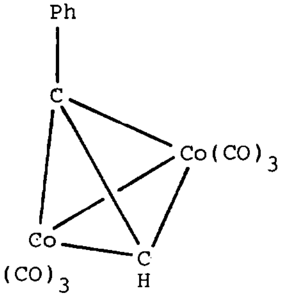

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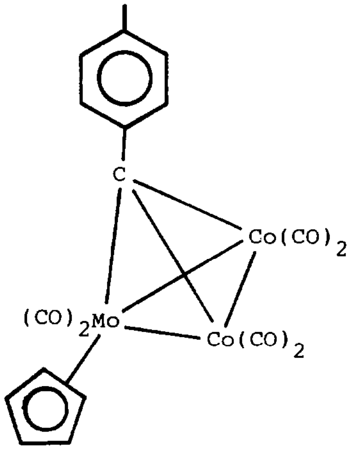

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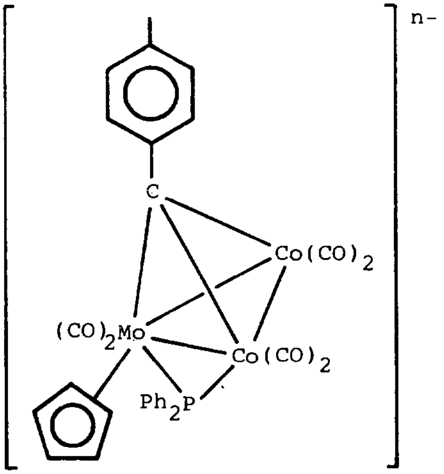

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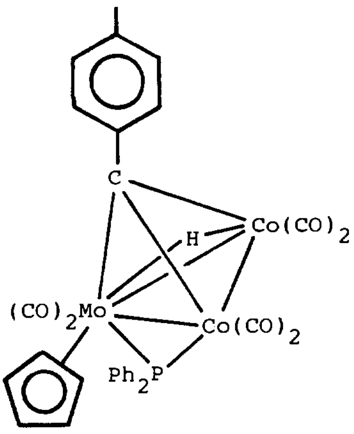

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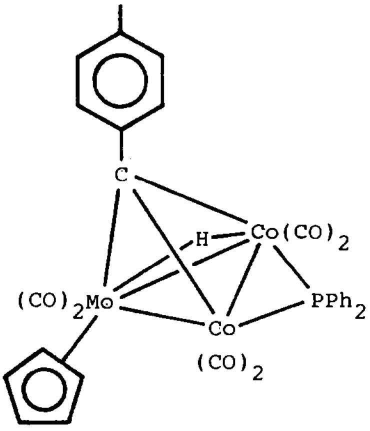
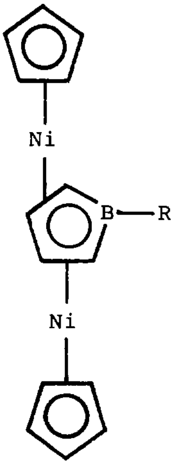


18.11

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

Nickelocene combined with borolenes to give the triple-decker nickel complexes (19.1; R = Me,Ph)[388]. Laser induced photolysis of nickelocene in the presence of palladium complexes has been used to give thin films containing Ni, Pd and Si [389].



9.1

Gas chromatography has been used to investigate the adsorption of diisopropylnickelocene on pyrolytic nickel. The enthalpy and entropy of adsorption have been determined as 77.3 kJ mol^{-1} and -167.2 J mol^{-1} K^{-1} respectively [390].

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

Ab initio procedures have been used to compute the wave functions and energy levels for uranocene. Details of bonding in the ground state have been obtained and the visible spectrum has been assigned. Mixing of ligand π-orbitals with uranium 6d and 5f orbitals was found, demonstrating considerable covalent bonding [391].

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