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ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1988*

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* Organic Reactions of Selected π-Complexes, Annual Survey Covering the Year 1987, see J. Organomet. Chem., 357 (1988) 319.

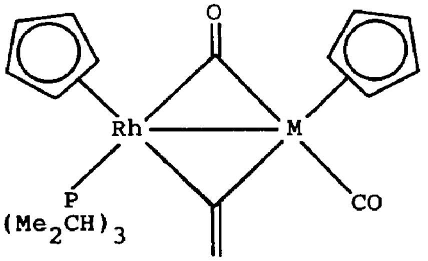
1. REVIEWS

Green, Qin and O'Hare have reviewed organometallic solid state chemistry. This review included a discussion of ferrocene, ruthenocene and bis(η-arene)chromium charge transfer complexes [1]. The importance of symmetry in the decomposition of bis(η-benzene)chromium has been reviewed by Domrachev [2]. The use of methylcymantrene as an octane improver in gasoline has been surveyed [3]. Herrmann and Okuda have reviewed the synthesis, structure and reactivity of trioxo(η-pentamethylcyclopentadienyl) rhenium(VIII) and related compounds [4]. A related review on the chemistry of the same system has been published [5].

Moriarty, Gill and Ku have produced a review on $(\eta^6$-arene)-$(\eta^5$-cyclopentadienyl)ruthenium complexes and related systems. The synthesis, chemical reactivity and photochemistry of these compounds were discussed [6]. Rybinskaya, Kreindlin and Fadeeva have considered the problem of stabilization of α-carbocationic centres in metallocenes. This discussion centred on the related interconversions of permethylated α-metallocenylcarbocations and metallocenium cation-radicals of iron, ruthenium and osmium [7]. Complexes of ruthenium and osmium containing cyclopentadienyl and dienyl ligands have been reviewed [8].

2. GENERAL RESULTS

Ligand configurational parameters have been calculated using molecular mechanics procedures and were found to be in good agreement with experimental values [9]. The electrochemical reduction of acetylferrocene, acetylcymantrene and acetylbenchrotrene in acetonitrile gave cyanoalkyl derivatives and was proposed as a method to lengthen the side chain by two carbon atoms [10]. Salts formed between TCNQ and metallocenes and which contained metallocene stacks have been evaluated by IR spectroscopy [11]. The photochemistry of ferrocene, cobaltocene and nickelocene in the presence of 2,2,2-trichloroethanol using near-UV and argon laser radiation has been studied. Cobaltocene, nickelocene and the trichloroethanol complexes of these metallocenes underwent photolysis. Equilibrium constants and molar extinction coefficients for the complexes were determined as were quantum yields in the photoreactions [12]. Rotation of the arene ring in (η-arene)transition metal complexes has been examined by ^{1}H and ^{13}C NMR spectroscopy. Restricted rotation was found to be limited to cases where the ring was prevented from tilting by bulky groups on both the metal and the arene ring [13]. Cymantrene, benchrotrene and tricarbonyl(η-cyclopentadienyl)-rhenium formed complexes with Lewis acids such as aluminium(III) bromide, gallium(III) chloride and mercury(II) trifluoroacetate. Heats of formation, dipole moments and IR spectra were measured and interpreted [14]. IR spectroscopy has been used to study complex formation at low temperatures between methane and organometallic compounds. High yields were obtained with $(\eta\text{-}C_5Me_5)_2Mn$ and $(\eta\text{-}C_5Me_5)_2Ni$. Yields with other compounds were found to be



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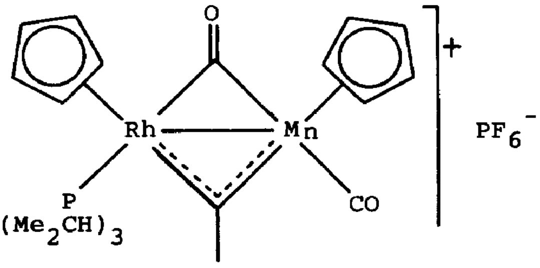

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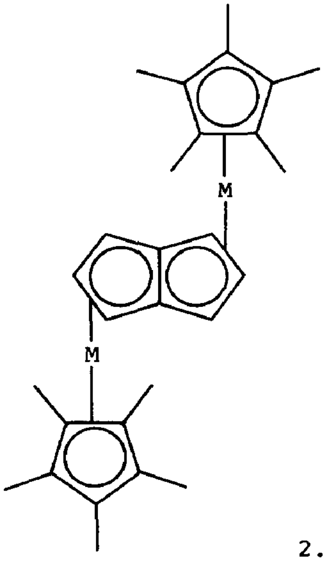
in the order:
$(\eta\text{-PhEt})W(CO)_3 > (\eta\text{-PhEt})Mo(CO)_3 > (\eta\text{-PhEt})Cr(CO)_3 > (\eta\text{-}C_5H_5)_2Ni >$
$(\eta\text{-}C_5H_5)_2Co$ [15].

Ferrocene, cobaltocene and nickelocene dications, generated by electron impact ionization in the gas phase, underwent charge separation reactions by two pathways. The first led to the formation of (η-cyclopentadienyl) metal cations and the second to demetalation:

$$[(\eta\text{-}C_5H_5)_2M]^{2+} \longrightarrow [(C_5H_5)M]^+ + (C_5H_5)^+$$
$$[(\eta\text{-}C_5H_5)_2M]^{2+} \longrightarrow (C_{10}H_{10})^{+\bullet} + M^+ \quad M = Fe, Co, Ni.$$

Intercharge distances in the transition structures have been calculated and correspond to 5.0Å for the first process and 6.2Å for the second [16]. Reaction of the vinylidene rhodium complex $(\eta\text{-}C_5H_5)Rh(=C=CH_2)P(CHMe_2)_3$ with (η-benzene)tricarbonylchromium or dicarbonyl(η-cyclopentadienyl)tetrahydrofuranmanganese produced the corresponding heterometallic compounds (2.1; M = Cr, Mn). Treatment of the manganese complex with HBF_4 gave, after exchange of the anion with NH_4PF_6 the salt (2.2) [17].

A series of organometallic compounds, including cymantrene and some (η-arene)tricarbonylchromium complexes, were embedded in polystyrene, poly(methyl methacrylate) and polystrene-polyacrylonitrile copolymer films. The FT-IR spectra of these films



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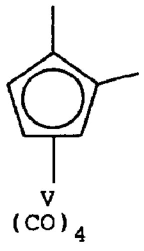
was recorded at room temperature. The ν(CO) vibrational band positions were approximately the same as when these compounds were dissolved in common organic solvents. Several of the films were irradiated with ultraviolet light and the photodegradation products were identified [18]. Extended Hueckel calculations have been carried out on the triple decker sandwich compounds $[(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_5)]^+$, $(\eta\text{-}C_5H_5)Co(\eta\text{-}C_6H_6)\text{-}Co(\eta\text{-}C_5H_5)$, $(\eta\text{-}C_5H_5)V(\eta\text{-}C_6H_6)V(\eta\text{-}C_5H_5)$, $(\eta\text{-}C_6H_6)Cr(\eta\text{-}C_6H_6)Cr\text{-}(\eta\text{-}C_6H_6)$, $(\eta\text{-}C_5H_5)Mo(P_6)Mo(\eta\text{-}C_5H_5)$, $(\eta\text{-}C_5H_5)Cr(P_5)Cr(\eta\text{-}C_5H_5)$ and $(\eta\text{-}C_5H_5)Mo(As_5)Mo(\eta\text{-}C_5H_5)$ to find the relationship between the stability of the metal-ring combination and the number of valence electrons. The number of electrons available varied from 26 to 34 depending on the magnitude of the interactions. In the vanadium complex the e_2^* interaction was large and with the P_5, P_6 and As_5 ligands the a_2'' interaction was strong [19]. Addition of lithium pentamethylcyclopentadienide to $M(\text{acetyl acetonate})_2$, where M = Fe, Co, Ni, followed by the addition of dilithium pentalenide produced the corresponding binculear metallocenes (2.3). X-ray analysis indicated that in the complex (2.3; M = Fe) the two iron atoms were in a trans configuration, each sandwiched between an η-pentamethylcyclopentadienyl ligand and one five-membered ring of the pentalene ligand [20].

The addition of nitrogen to the metallocenes Cp_2M, where Cp = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$ and M = V, Cr, Mn, Fe, Co, Ni, has been investigated via infrared spectroscopy at 16-18 and 80K. At 16-18K monodentate complexes $Cp_2M.N_2$ were formed and at 80K polymeric complexes were produced [21]. The microdetermination of molybdenum in organometallic compounds by molecular emission and atomic absorption spectrometry has been reported. Several organomolybdenum compounds were analyzed by both methods and by an alternative spectrophotometric method. Good agreement between the methods was obtained [22].

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

The reaction of alkylcyclopentadienes and annulated cyclopentadienes with $V(CO)_6$ has produced the corresponding (η-cyclopentadienyl($V(CO)_4$ complexes, for example compounds (3.1 and 3.2). Friedel-Crafts acylation of tetracarbonyl(η-cyclopentadienyl)-vanadium produced the acetyl derivative (3.3). The structure



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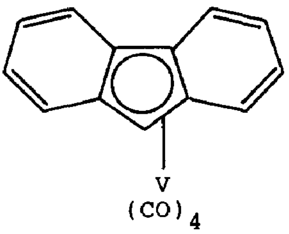

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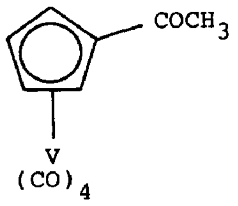

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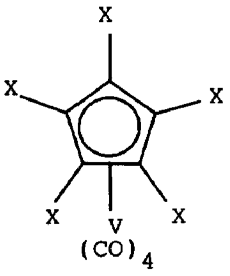
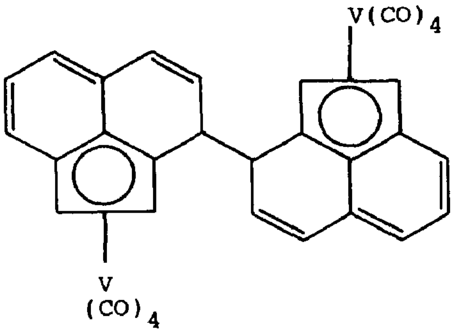


3.4

of this complex together with that of tetracarbonyl(η-cyclopentadienyl)vanadium was determined by X-ray analysis [23]. Hexacarbonylvanadium has been treated with hexachloro- and hexabromo cyclopentadienes to form the (η-perhalocyclopentadienyl)vanadium complexes (3.4; X = Cl,Br). The bromo complex (3.4; X = Br) was characterized by X-ray crystallography [24]. Hexacarbonylvanadium combined with acenaphthylene to give the binuclear complex (3.5) as two meso forms, the exo-exo-form was characterized by X-ray crystallography [25]. Tetracarbonyl(η-cyclopentadienyl)vanadium has been irradiated in the presence of tetrahydrothiophene (THT) to give the intermediate (3.6; L = THT) which combined with nitrogen ligands, such as pyrrolidine, to give the complex (3.6; L = pyrrolidine). The species (3.6; L = THT) has been characterized by X-ray crystallography [26].



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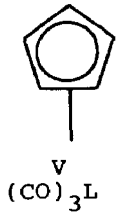

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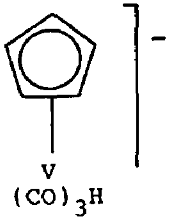
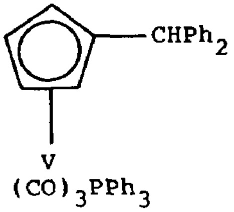
Treatment of tetracarbonyl(η-cyclopentadienyl)vanadium with sodium hydroxide, benzene and tetrabutylammonium hydrogen sulphate produced the hydrido-vanadate anion (3.7). This anion was used under phase transfer conditions for the reduction of halides, the reduction of sterically encumbered nitro compounds, the cyclodehydration of α,β-unsaturated ketones and the reduction of the double bond of cyclic ketones [27]. The complexes (η-Cp)V(CO)$_3$ (hydrazine), where Cp = C_5H_5, C_5Me_5, 1,2- and 1,3- C_5H_3(Me)-





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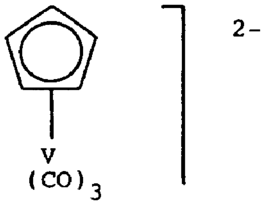
3.8

($C_{16}H_{33}$), indenyl and hydrazine = N_2H_4, N_2H_3Me, H_2NNMe_2, H(Me)NN(Me)H and N_2H_3Ph have been prepared from (η-Cp)$V(CO)_3$ (tetrahydrofuran) and the correponding hydrazine. The stuctures of these complexes were investigated via infrared, ^1H and ^{51}V NMR spectroscopy [28]. The cyclopentadienylization of pentafulvenes with stannyl- and nitrosyl- carbonylvanadium complexes has been investigated. The complexes $R_3SnV(CO)_5PPh_3$ and $R_3SnV(CO)_6$, where R = Ph, Et, n-Bu, CH_2Ph, underwent reaction with pentafulvenes $C_5H_4CZ_2$, where for example $Z_2 = Ph_2$, Me_2, $(CH_2)_4$, $(CH_2)_5$, $(NMe_2)_2$, to give ring-substituted cyclopentadienyl or fulvene complexes with the stannyl ligand being lost or retained. For example, the reaction of $Ph_3SnV(CO)_5PPh_3$ with 6,6'-diphenylfulvene, proceeded with elimination of the stannyl group to give the vanadium complex (3.8) [29].

The (η-cyclopentadienyl)vanadium dianion (3.9) combined with 2,4,6-Bu^t_3-$C_6H_2.PCl_2$ to form the phosphinidene complex, $V_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}P.C_6H_2Bu^t_3\text{-}2,4,6)$ [30]. The (η-methylcyclopentadienyl)vanadium complex (3.10) oxidized tetramethyltetrathiofulvalene (TTF) to give the magnetic charge-transfer salt $[TTF]^+[(\eta\text{-}MeC_5H_4)VCl_3]^-$ which was characterized by X-ray crystallography [31].



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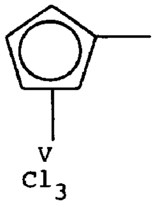

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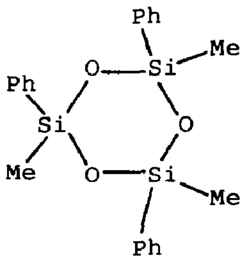
4. $(\eta\text{-}C_6H_6)Cr(CO)_3$

(i) Formation

Tricarbonylchromium complexes of phenyl-substituted cyclosiloxanes, for example, the *cis*- and *trans*- isomers of the siloxane (4.1) have been prepared by the reaction of the siloxane with hexacarbonylchromium [32]. The tricarbonylchromium complexes of pentaphenylethanes (4.2 and 4.3) have been prepared and characterized by X-ray crystallography [33]. Substituted methyl and ethyl benzoates have been treated with hexacarbonylchromium in dibutyl ether and THF to give the corresponding benchrotrenes such as the esters (4.4; R^1 = Me, Et; R^2 = H, Me, NHMe; R^3 = H, Me, OEt, NHMe, NH_2) [34]. Reaction of trinitrotoluene with tricarbonyl tri(methyl cyanide)chromium afforded the chromium complexes (4.5 and 4.6) [35]. The η-collidine-chromium complexes (4.7; L = CO, PPh_3) have been prepared from the



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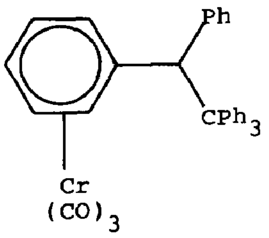

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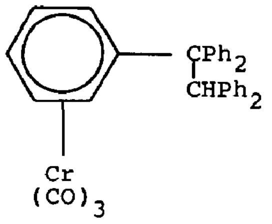

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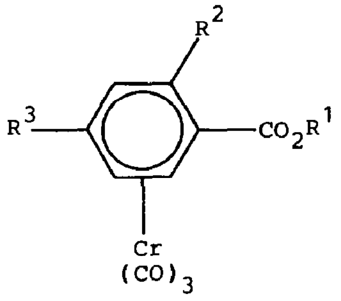

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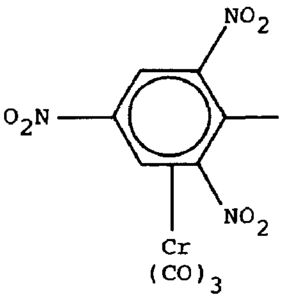

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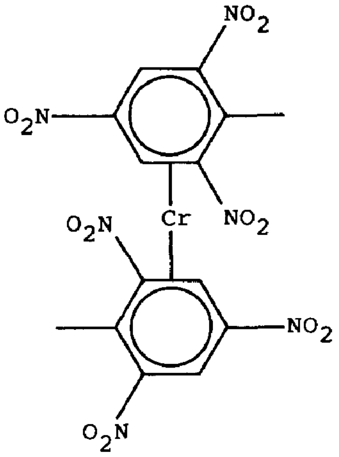
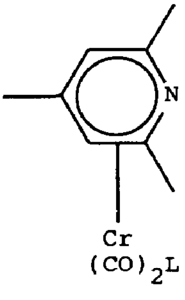


4.6

corresponding η-benzene-chromium compounds. Reaction of the η-collidine complexes (4.7; L = CO, PPh_3) with $Et_2O.BF_3$ afforded the corresponding boron trifluoride complexes (4.8) [36].

Benchrotrene complexes have been prepared by treatment of hexacarbonylchromium with substituted anilines such as N,N,2,4,6-pentamethylaniline and 2,5-di-t-butylaniline and with fluorobenzenes such as 1,2 -difluorobenzene. The characterization of eleven compounds has been described [37]. A range of (η-arene)



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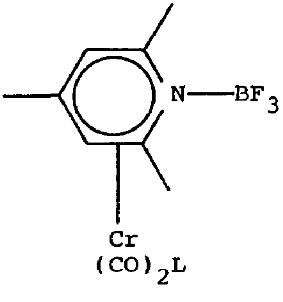

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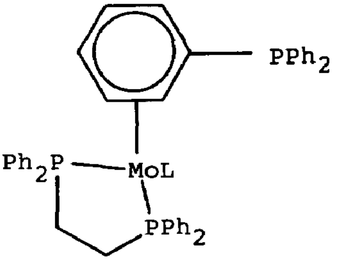

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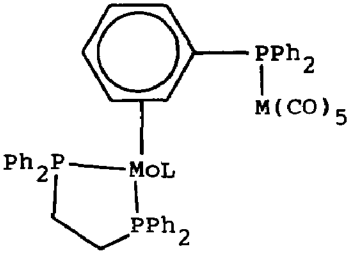
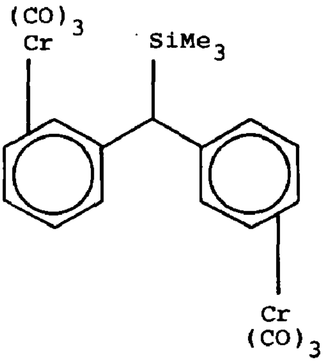


4.10

molybdenum complexes with chromium-, molybdenum- and tungsten-pentacarbonyl and -tetracarbonyl substituents have been prepared. Thus the (η-arene)molybdenum complexes (4.9; L = CO, PMe_3) were irradiated with the appropriate metal hexacarbonyl to give the products (4.10; M = Cr, Mo, W; L = CO, PMe_3). The complexes were evaluated by IR and NMR spectroscopy and by electrochemical oxidation [38]. The bis(tricarbonyl)chromium complex (4.11) has been prepared from hexacarbonylchromium and the free ligand. X-ray crystallography confirmed that one tricarbonylchromium



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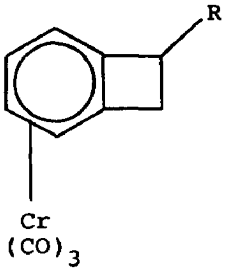

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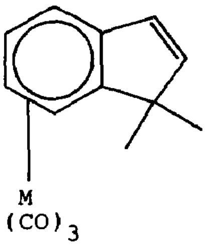

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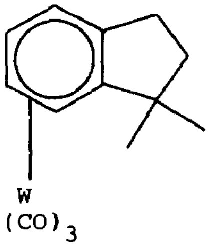
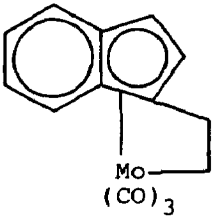


4.14

group was located between the two phenyl rings while the other was between a phenyl and the trimethylsilyl group [39]. A series of (η-cyclobutabenzene)$Cr(CO)_3$ complexes, for example [4.12; R = H, D, Cl, CH_3, $(CH_2)_3CH_3$, $(CH_2)_2CH{=}CH_2$, $Si(CH_3)_3$, $Sn(CH_3)_3$] have been prepared by reaction of the substituted cyclobutabenzenes with triammine(tricarbonyl)chromium [40].

1,1-Dimethylindene has been treated with $M(CO)_3(pyridine)_3$, where M = Cr, Mo, W, to give the (η^6-arene) metal complexes (4.13; M = Cr, Mo, W). However in the case of M = W the



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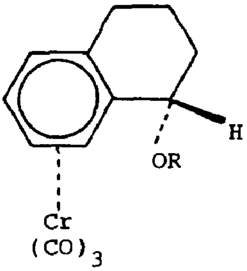

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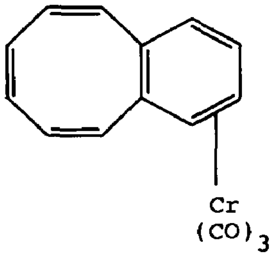
hydrogenated complex (4.14) was also formed and was the dominant product. Similar products were obtained from spirocyclopropane-1,1-indene and spirocyclopropane-9,9-fluorene although chelated σ,π-complexes such as the molybdenum complex (4.15) were formed as competing products [41]. Thermolysis of hexacarbonylchromium with 1-tetralol and 1-methoxytetralin gave the corresponding syn-tricarbonylchromium complexes (4.16; R = H, Me) by way of an oxygen chelation controlled mechanism. However complexation of the t-butyldimethylsilyl protected 1-tetralol gave a mixture of the syn-complex (4.16; R = t-BuMe$_2$Si) together with the corresponding anti-isomer. This was interpreted in terms of competition between the steric effect of the O-silyl group and the chelation effect [42]. Benzocyclooctatetraene has been treated with hexacarbonylchromium or $(NH_3)_3Cr(CO)_3$ to give the two tricarbonylchromium complexes (4.17 and 4.18). The structures in solution were investigated by ^{1}H and ^{13}C NMR spectroscopy and confirmed in the solid state by X-ray crystallography. Migration of the tricarbonylchromium group from the eight-membered to the six-membered ring has been investigated kinetically to give rate and activation parameters [43].

The reaction of methyl O-methylpodocarpate with hexacarbonylchromium produced the diastereomeric complexes (4.19 and 4.20)



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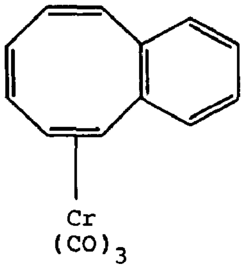

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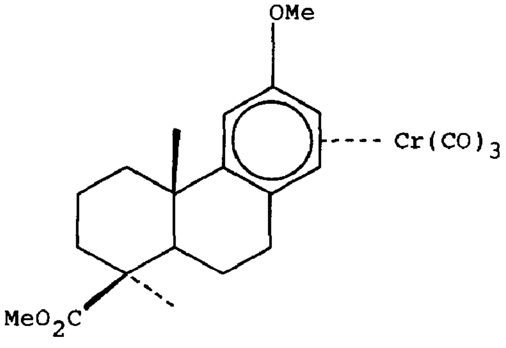

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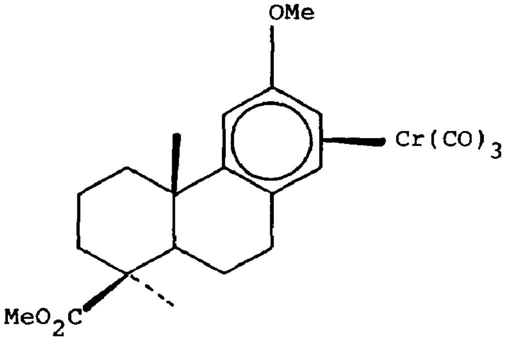

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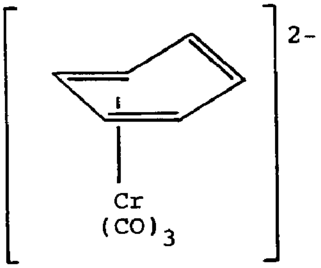
where the Cr(CO)$_3$ group was bound to either the α- or the β- face of the aromatic ring of the diterpenoid. These isomers were separated and the ^{1}H and ^{13}C NMR spectra were recorded. By the use of ^{1}H-^{1}H COSY and ^{1}H-^{13}C shift correlated two dimensional spectra, all the protons and carbons were assigned [44]. The treatment of Cr(II), Co(II), Co(III), Ni(II), Cu(II) and Zn(II) complexes of Schiff bases, formed from salicylaldehyde, with hexacarbonylchromium gave the corresponding (η-arene)Cr(CO)$_3$ compounds [45]. The η^4-benzene complex (4.21) exchanged with naphthalene at room temperature to give the corresponding η^4--naphthalene complex (4.22). In an atmosphere of oxygen this latter complex was rapidly oxidized to the η^6-naphthalene complex (4.23) and in the presence of water protonation occurred to give the η^5-cyclohexadienyl compound (4.24) [46]. The tetrahydropyridylcarbene complex, $(OC)_5Cr{=}C(Me)NC_5H_8$, combined with diphenylacetylene to give arene chromium complexes of unsaturated lactams by ring contraction (4.25) and ring expansion (4.26). The two products (4.25, 4.26) were characterized by X-ray analysis and the mechanism of the reaction was discussed [47].

The bis-carbene complexes (4.27; M = Cr, W) combined with diphenylacetylene to give complexes of naphthol derivatives when M = Cr (4.28) and indene derivatives (4.29) when M = W [48]. Reaction of the carbenes (4.30; R = Me, Et) with the phosphaalkyne, P≡CCMe$_3$, produced the corresponding tricarbonylchromium



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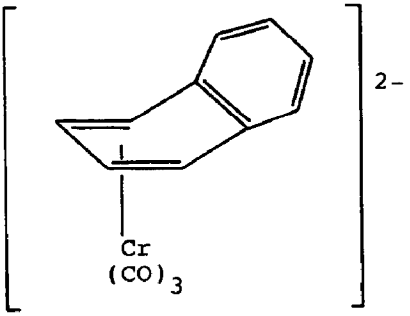

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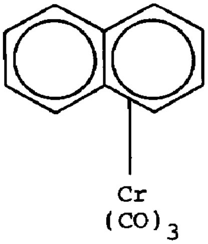

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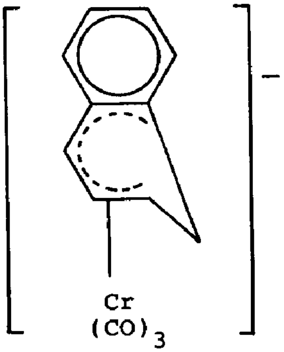

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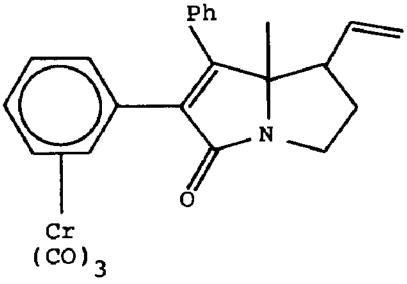

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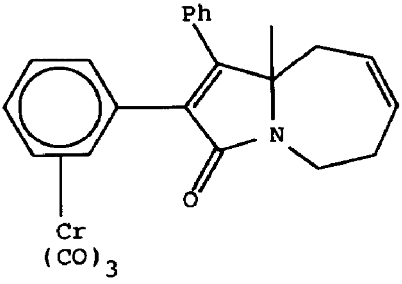

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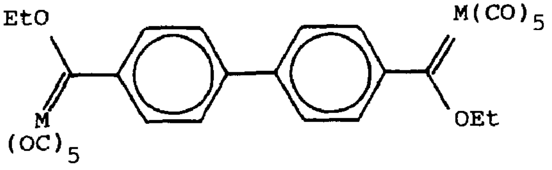

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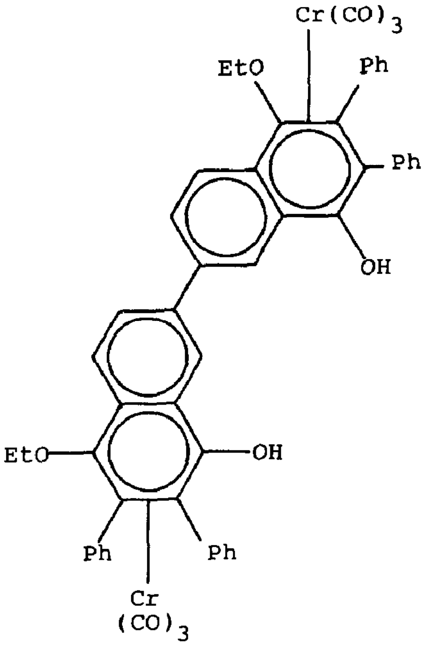

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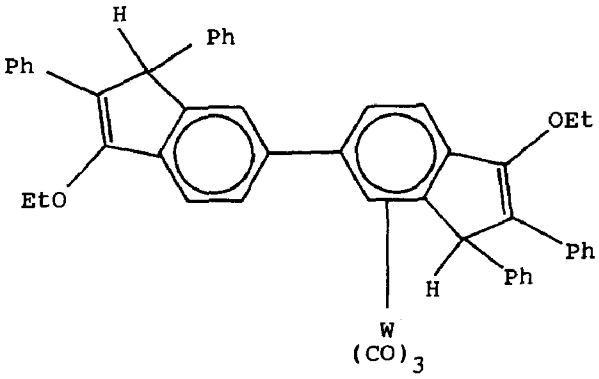
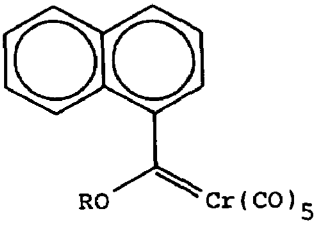


4.29

complexes (4.31) [49]. The bent terphenylene ligand (4.32) with appreciable double bond localization in the central arene ring, has been converted to the corresponding tricarbonylchromium complex (4.33). Variable temperature ^{13}C NMR spectroscopy has



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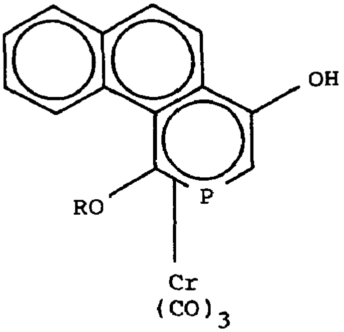
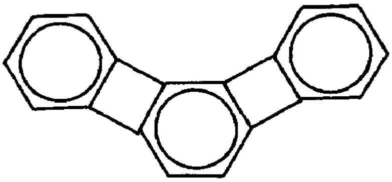


4.31

been used to investigate the barrier to rotation about the metal--arene bond, a value of 10.3 kcal/mole was obtained [50]. Methyl podocarpa-8,11,13-trien-19-oate has been treated with hexacarbonylchromium to give mixture of the α- and β-diasterioisomers of the tricarbonylchromium complex (4.34) [51]. The antitumour antibiotic 11-deoxydaunomycinone has been synthesized by way of the intermediate tricarbonylchromium complex (4.35) which was formed by addition of a chromium carbene complex to an acetylene [52].



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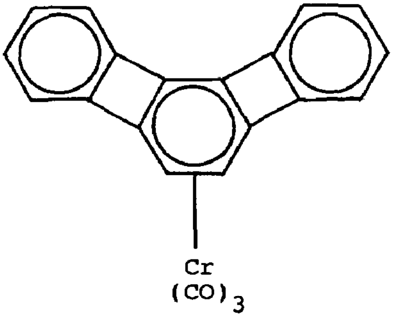

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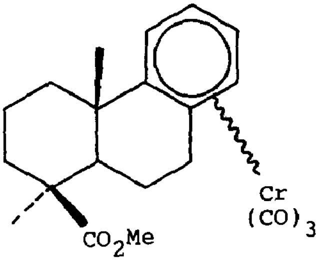

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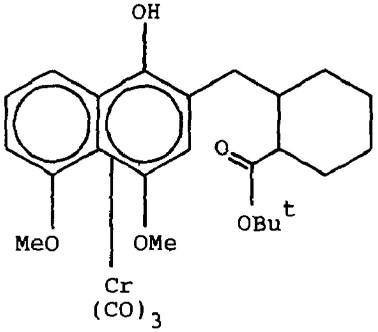

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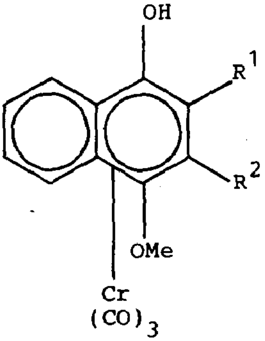
The insertion reactions of chromium-carbene complexes with organic nitriles have been examined. The products were imino-carbene complexes rather than the (η-naphthol)chromium complexes (4.36) obtained by insertion with acetylenes [53]. Treatment of the tricarbonylchromium complex (4.37) with K_4Sn_9 followed by the addition of excess 4,7,13,16,21,24-hexaoxa-1,10-diazatricyclo-[8.8.8]hexacosane (crypt) gave the tetrapotassium cryptate salt $(K\cdot crypt)_4Sn_9Cr(CO)_3$. X-ray analysis indicated a virtually undistorted bicapped square antiprismatic cluster which was isoelectronic and isostructural with $B_{10}H_{10}^{2-}$ and $[(\eta-C_5H_5)NiB_9H_9]^-$ [54].



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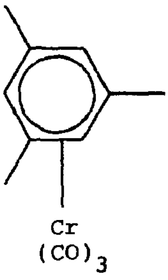
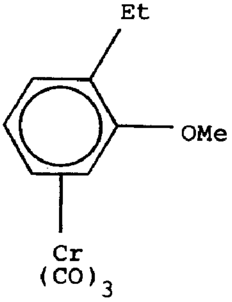


4.37

(ii) Spectroscopic and Physico-chemical Studies

Total geometry optimizations have been reported for (η-benzene)tricarbonylchromium, bis(η-benzene)chromium, cymantrene, ferrocene and other organometallic compounds. Different basis sets were considered, and based on the results a compact and accurate basis set was proposed. Metal-carbonyl, metal-benzene and metal-cyclopentadienyl bond distances were calculated and these were in close agreement with the experimentally determined values [55]. The structure of the tricarbonylchromium complex (4.38) has been determined by X-ray analysis. The aromatic ring was approximately planar and the methyl part of the ethyl substituent was located away from the methoxy group [56]. The stereochemistry and stereodynamics of the tricarbonylchromium complex (4.39) have been investigated. Empirical force field calculations indicated that the lowest energy up-down stereoisomer was that with D_{3d} symmetry and the barrier to topomerization of the n-propyl group was 57.7 kJ mol^{-1}. X-ray analysis showed that in the complex the ground-state stereoisomer of the uncomplexed arene was retained [57]. The structure of the tricarbonylchromium complex (4.40)has been determined by X-ray analysis [58]. The tricarbonylchromium complex (4.41) and the tricarbonylmanganese salt (4.42) have been prepared and characterized by X-ray crystallography [59]. Stopped-flow techniques have been used to investigate the kinetics of ionization of the bis(tricarbonylchromium) complex (4.43) by carboxylate ions, primary amines and piperidine-morpholine in aqueous dimethylsulphoxide [60]. The effect of the metal atom on the kinetic properties of photophysical processes in the complexes $(\eta\text{-}C_6H_6)M(CO)_3$, where M = Cr, Mo, W, has been investigated. The quantum photolysis yield was related to an increase in the spin-orbital interaction on going from chromium to tungsten [61]. Electrochemical oxidation of the (η-arene)-$Cr(CO)_3$ complexes, where arene = C_6H_6, C_6H_5Cl, dimethylaniline, thiophene or 3-methylthiophene, in methylcyanide led to a rapid follow-up reaction in which the cation $[Cr(CO)_3(MeCN)_3]^+$ was detected by cyclic voltammetry [62]. Arenes have been activated towards cathodic reduction by complexation with the tricarbonylchromium group. Thus stilbene underwent hydrodimerization and phenanthrene was hydrogenated at potentials ~0.6V less than the corresponding arenes [63]. Emission spectra have been recorded



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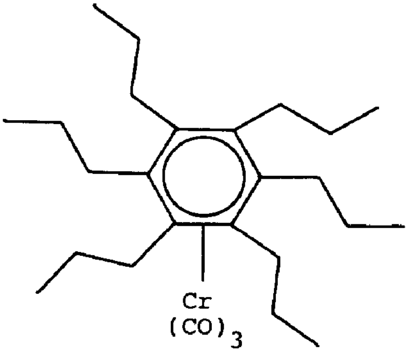

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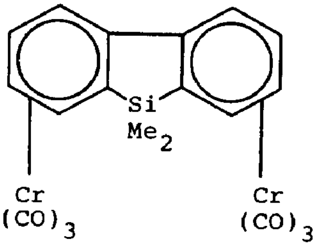

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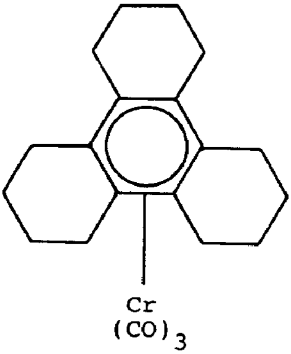

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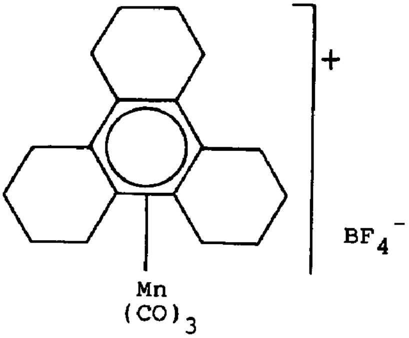

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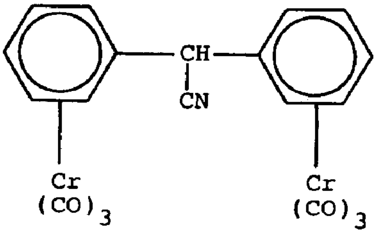
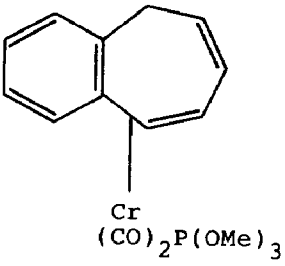


4.43

of helium plasma containing organometallic compounds. The dissociation of (η-benzene)tricarbonylchromium produced a chromium atom, three molecules of carbon monoxide and benzene [64]. Irradiation of pentacarbonyltrimethylphosphite-chromium with 5H-benzocycloheptene produced the chromium complex (4.44). The structure of this complex was determined by X-ray analysis. The Cr-C distances indicated that there was a weaker interaction between the chromium and the two carbon atoms which were common to both rings [65]. Chemical-ionization (NH_3) and electron--impact mass spectrometry have been used to examine the gas-phase structure of the complexes (η-arene)$Cr(CO)_3$ where arene = stilbene, $Ph(CH_2)_nPh$, n = 0-4, naphthalene and fluorene. Increasing alkane chain length in the diphenylalkane ligands led to an increase in the interaction between chromium and the uncoordinated phenyl ring [66]. The tricarbonylchromium complex (4.45) has been used to determine steroid receptors using FT-IR spectroscopy [67]. High-performance liquid chromatography has been used to analyse the products from the decomposition of benchrotrene complexes of bismuth [68]. Chiral benchrotrenes underwent the Darzens reaction enantioselectively to give epoxides. Thus the benchrotrene (4.46) combined with chloroalkanes, $ClCH_2R$, to give the products (4.47; R = CN, COPh, CO_2Bu^t) with enantiomeric excesses in the range 40-88% [69]. Deprotonation of the tricarbonylchromium complex (4.48) and hydroxylation gave the 2--hydroxy derivative with good regioselectivity [70]. The addition of α-nitrile carbanions to the bis(tricarbonylchromium) complex (4.49) was stereospecific and regiospecific. Subsequent decomplexation gave the corresponding substituted biphenyls or after treatment with trifluoroacetic acid the corresponding phenyl conjugated dienes. Thus proprionitrile gave the cyclohexadiene (4.50) [71]. Inter-ring haptotropic rearrangements in (η-naphthalene)chromium complexes (4.51 and 4.52; R = Me, $SiMe_3$, $SnMe_3$, n = 1; R = Me, n = 2) have been the subject of a kinetic investigation. An intramolecular reaction mechanism was indicated [72].

The benchrotrene complexes (4.53 and4.54; R = Br, $SnMe_3$) underwent metallotropic rearrangement on heating in dibutyl ether and decane . (η-2-Phenyltoluene) chromium tricarbonyl did not undergo rearrangement under these conditions [73]. Water vapour was found to be an effective catalyst for promoting



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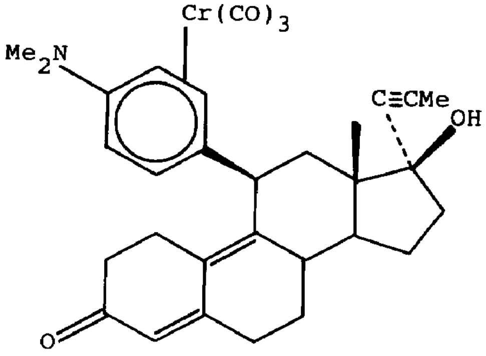

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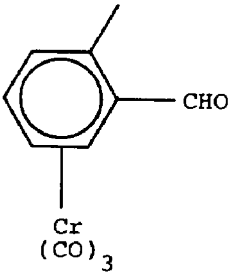

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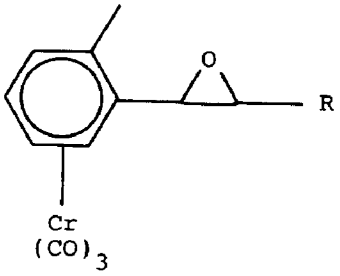

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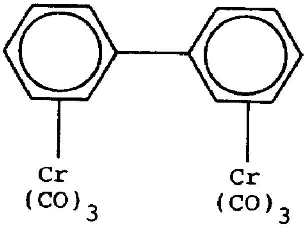

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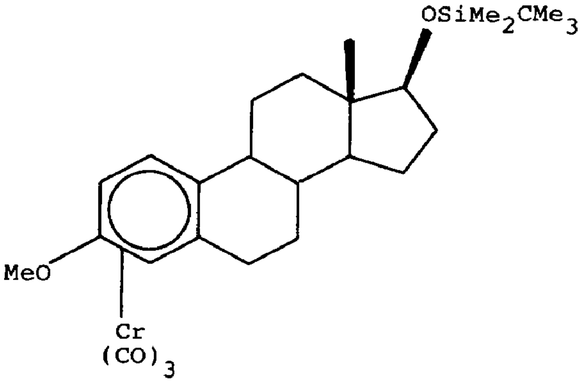

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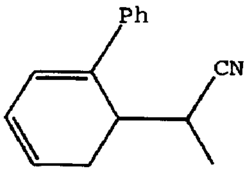

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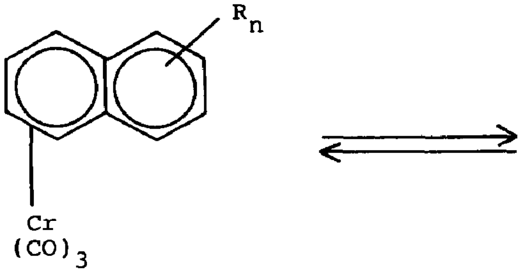
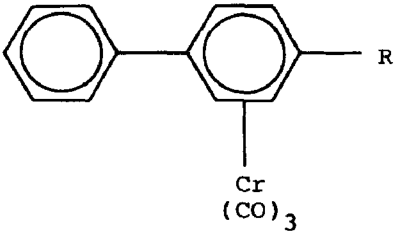


4.51 4.52

the formation of the binuclear ion $[(C_6H_6)_2Cr_2(CO)_3]^+$ from the ion molecule reaction of $(\eta\text{-}C_6H_6)Cr(CO)_3$ [74].



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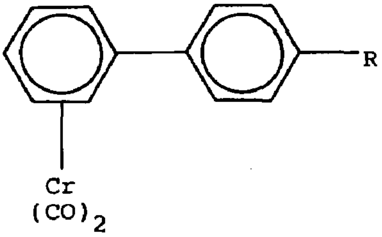
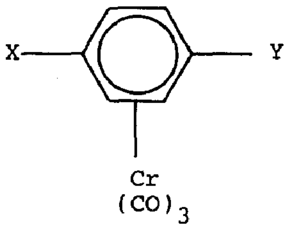


4.54

(iii) General Chemistry

The dichlorobenchrotrene (4.55; X = Y = Cl) underwent nucleophilic displacement on one chlorine by phenoxide to give the intermediate (4.55; X = Cl, Y = OPh) which was treated with sodium methoxide to displace the second chlorine and form the diether (4.55; X = OMe, Y = OPh) [75]. The benchrotrene complexes (4.56; X = H, CO_2Me; L = CS, CSe) underwent arene



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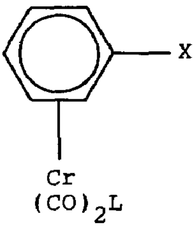

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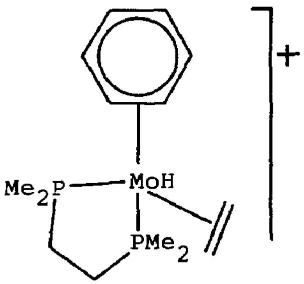

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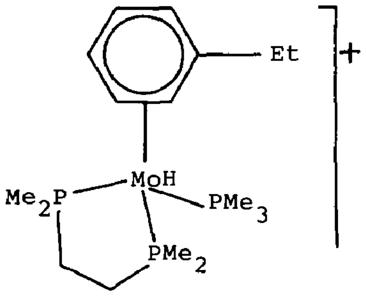
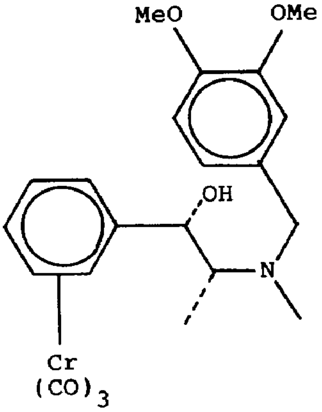


4.58

ligand displacement with phosphites and triphosphine reagents to give products such as the phosphites, $Cr(CO)_2L(Phos)_3$, where L = CS, CSe and Phos = $P(OMe)_3$, $P(OEt)_3$ [76]. The cis ethylene hydride complex (4.57) combined with trimethylphosphine to give the cationic (η-ethylbenzene)molybdenum complex (4.58). A detailed kinetic and spectroscopic study of the mechanism indicated an (η-cyclohexadienyl)molybdenum intermediate [77].

Cyclization of the tricarbonylchromium complex of (-)-N-(3,4-dimethoxybenzyl)ephedrine (4.59) with sulphuric and trifluoroacetic acid took place with high stereoselectivity to give the cis-tetrahydroisoquinoline complex (4.60) while cyclization of the free ligand gave the complementary trans-product [78]. Irradiation of the complexes (η-arene)$Cr(CO)_3$, where arene = C_6H_6, 1,3,5-Me_3-C_6H_3, and C_6Me_6, with ethyne produced the corresponding η-ethyne



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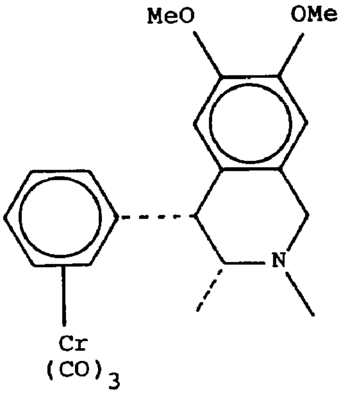

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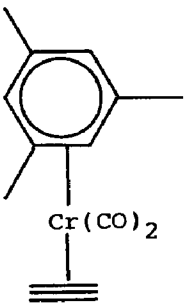

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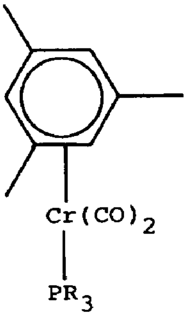

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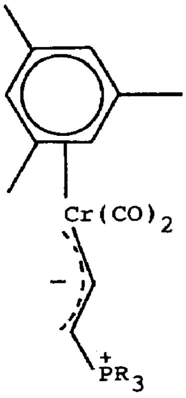

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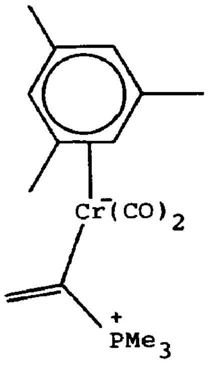
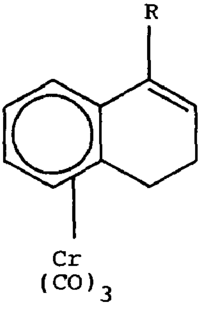


4.64

complexes (η-arene)$Cr(CO)_2C_2H_2$. Treatment of the η-mesitylene complex (4.61) with the phosphines PR_3, R = Me, Et, n-Bu, afforded three products (4.62; R = Me, Et, n-Bu, 4.63; R = Et, n-Bu and 4.64). Some reactions of these complexes were investigated [79]. Voltammetry has been used to investigate the oxidation of benchrotrene and tricarbonyl(η-mesitylene)chromium in non-aqueous solvents. A reversible one-electron oxidation was observed in dichloromethane or benzene while a two-electron process occurred in more nucleophilic solvents such as acetone or acetonitrile. Rates of reaction were measured [80]. Friedel-Crafts acylation of the tricarbonylchromium complexes (4.65; R = H, CH_3) produced the corresponding acetyl derivatives (4.66). Treatment of these complexes with aluminium chloride followed by aniline produced the imines (4.67) [81].



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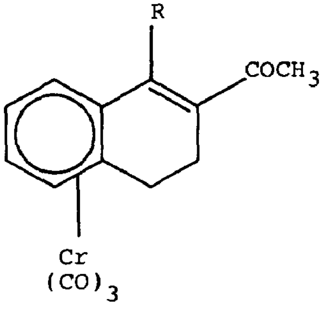

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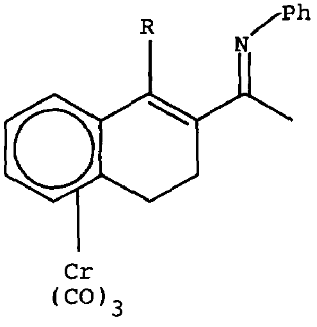

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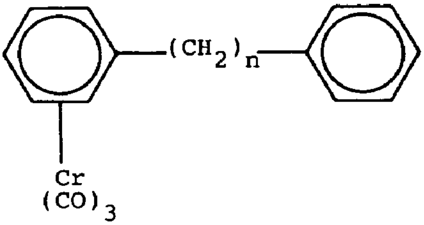
The tricarbonylchromium group deactivated the bound arene ring in (η-arene)chromium complexes (4.68; n = 0–4; 4.69) towards Friedel-Crafts acetylation. However in one case (4.68; n = 1) almost equal activity was shown by the two rings [82]. Tricarbonyl(η-chloroarene)chromium complexes have been shown to undergo palladium catalysed carbonylation under mild conditions to give the corresponding free or tricarbonylchromium coordinated esters, aldehydes, amides or α-oxo amides. The results suggested that the electron withdrawing tricarbonylchromium group promoted palladium insertion into the C-Cl bond [83]. Alkylation of the η-thiophene complexes (4.70; R = H, Me) with ethyl bromide,



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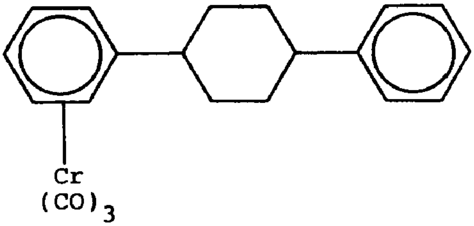
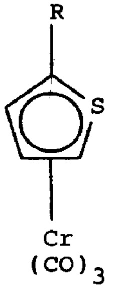


4.69

butyl bromide, butyl chloride or t-butyl bromide was studied in the presence of potassium hydroxide-18-crown-6. Alkylation of the thiophene ring occurred with ethyl and butyl bromide but there was no reaction with butyl chloride and t-butyl bromide [84].

Halobenchrotrenes have been converted to the corresponding O-aryloxime complexes and then decomplexed and cyclized to form benzofuran derivatives. Thus the chlorobenchrotrene (4.71; X = Cl) was converted to the oxime (4.71; X = ON=CMe_2) with Me_2C=NOH and then to the benzofuran (4.72) [85]. Propenylcodeine was obtained by the stereoselective alkylation of the



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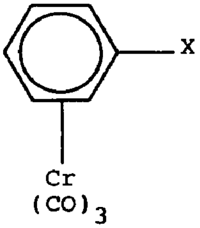

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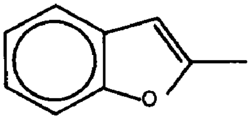

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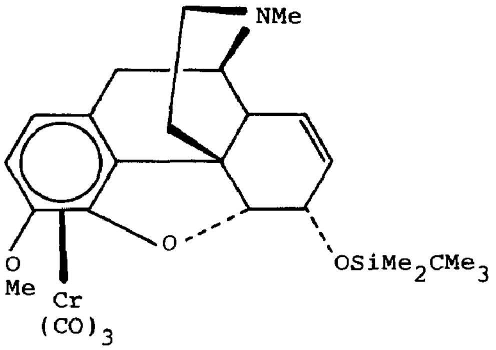

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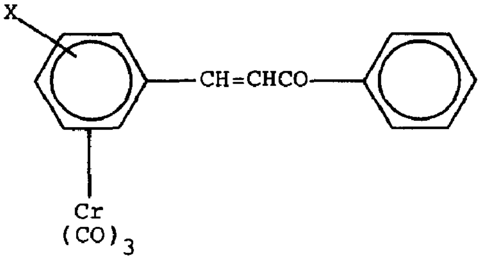
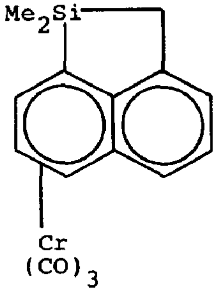


4.74

(η-codeine)chromium complex (4.73) followed by decomplexation and desilylation [86]. Several benchrotrene analogues of chalcone (4.74; X = H, 2-, 3-Me, 2-, 3-OMe, 2-, 3-Cl) have been prepared from the corresponding benchrotrenyl aldehydes and acetophenone. The products underwent Michael addition with dimethyl malonate [87]. Photolysis of benchrotrene complexes with diphenylsilane at low temperatures gave unstable hydrosilyl complexes, (η-arene)$Cr(CO)_2$-(H)$SiHPh_2$, where arene = 1,2-xylene, dimethylaminomethylbenzene, benzylmethyl ether and dimethyl terephthalic acid. A three-centre two-electron bond Cr-H-Si was indicated by ^{29}Si NMR spectroscopy [88]. The hydrosilylation of 2,3-dimethyl-1,3-butadiene with $HSiPh_2Me$ was catalysed by (η-arene)tricarbonylchromium complexes. The most efficient catalyst was the η-naphthalene complex (4.75) [89].

The 3-O-(3-hydroxypropyl)-17β-estradiol-chromium complexes (4.76 ; R = H, ^2H, ^3H) have been prepared by reduction of the corresponding estrone with $NaBH_4$, $NaBD_4$ or $NaB(^3H)_4$ respectively. The complex (4.76; R = ^3H) was claimed to be the first radioactive transition metal carbonyl steroid hormone and this compound was used in hormone receptor binding studies [90]. The tricarbonylchromium complexes (4.77; R = Me, Et, 4.78 and 4.79) have been reduced by baker's yeast to the corresponding alcohols. In some instances the presence of the tricarbonylchromium group increased the rate of reduction, increased enantiomeric excess and allowed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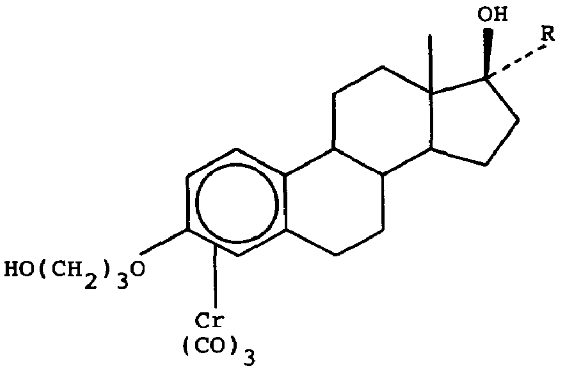
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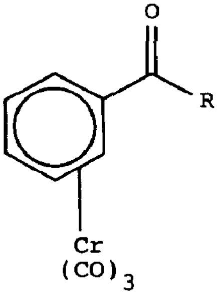
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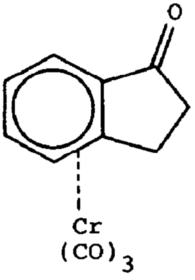
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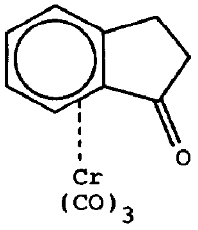
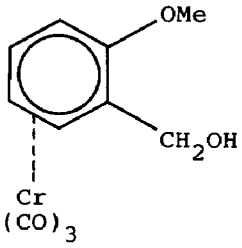

4.79

kinetic resolution of planar chiral complexes. For example, the η-acetophenone complex (4.77; R = Me) was completely reduced in 24h and after decomplexation the enantiomeric excess of the (S)-1-phenylethanol was greater than 99% [91]. In a related communication the reduction of racemic tricarbonyl(η-2-methoxybenzaldehyde)chromium by baker's yeast in the presence of D-glucose afforded (+)-(1R)-tricarbonyl(η-2-methoxybenzyl alcohol-chromium (4.80) in 66% enantiomeric excess and the optically active unchanged (+)-(1S)-enantiomer (4.81) of the starting aldehyde in 81% enantiomeric excess [92].

Metallation of the η-fluorene complex (4.82) with potassium hydride afforded the corresponding anion. Infrared spectroscopy indicated that the anion existed in solution as a solvent separated ion pair. Detailed analysis of the NMR spectra indicated that on ionization the two tricarbonylchromium groups



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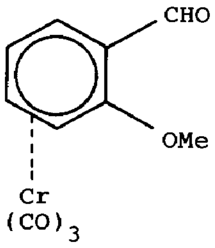

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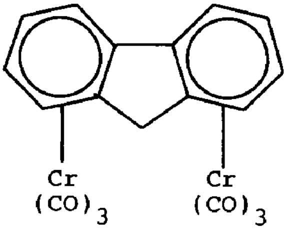

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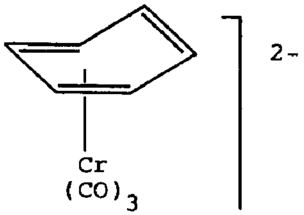

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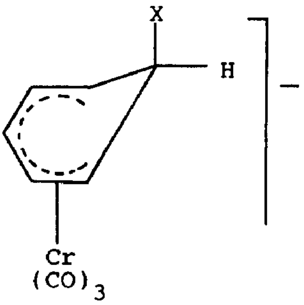

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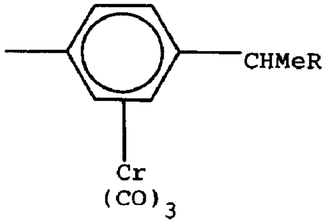
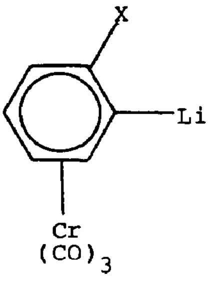


4.85

moved towards the five-membered ring [93]. Benchrotrene has been reduced by potassium naphthalenide to give the dianion (4.83) which was active towards electrophilic addition. Thus protonation and treatment with benzyl chloride gave the (η-cyclohexadienyl)chromium anionic complexes (4.84; X = H, $PhCH_2$) [94]. The benchrotrene complex (4.85; R = H) has been metallated with sodamide and treated with $BrCH_2CO_2Na$ to give the derivative (4.85; R = CH_2CO_2H). Oxidative decomplexation gave the free ligand and provided a convenient synthesis of arylpropionic acids [95].



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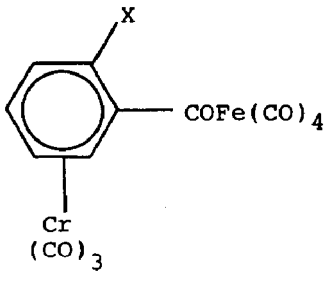

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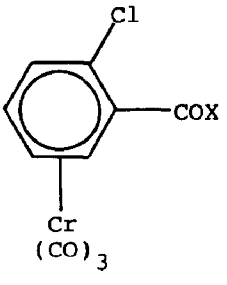
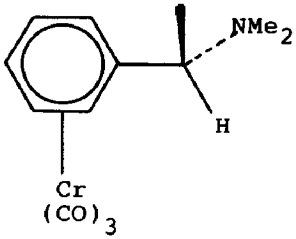


4.88

The lithiobenchrotrenes (4.86; X = H, Fe, Cl, OMe) combined with pentacarbonyliron to give the iron acyl substituted species (4.87; X = H, F, Cl, OMe). The tetracarbonyliron moiety was displaced from the chlorobenchrotrene (4.87; X = Cl) by trifluoroacetic anhydride, tetrafluoroboric acid, methyliodide and cyanoiodomethane to give the trifluoroacetyl, carbaldehyde, acetyl and cyanoacetyl derivatives (4.88; X = CF_3, H, Me, CH_2CN) respectively [96]. Lithiation of the tricarbonylchromium complex (4.89) with t-BuLi followed by the addition of methyl iodide gave a single diastereoisomer (4.90) in good yield. The structure of the complex (4.90) was confirmed by X-ray analysis. Regioselective metallation of the complexes (4.91 and 4.92) was also reported [97]. Treatment of tricarbonyl(η-hexamethylbenzene)chromium with n-butyllithium produced the lithio-intermediate (4.93) which was converted to the dilithio-intermediate



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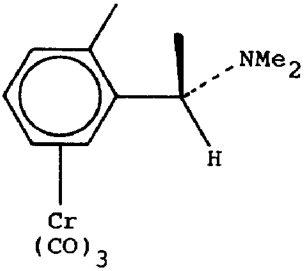

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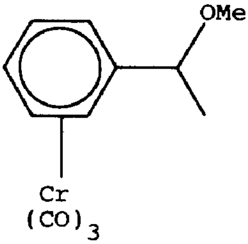

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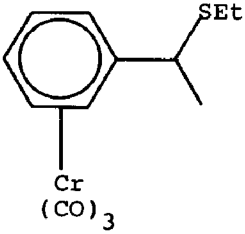

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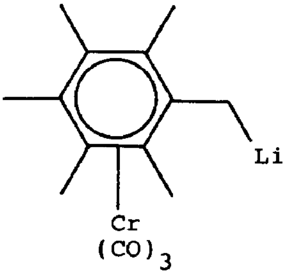

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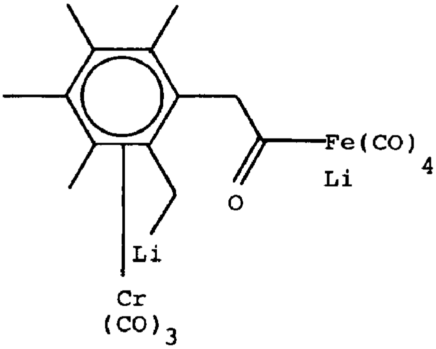

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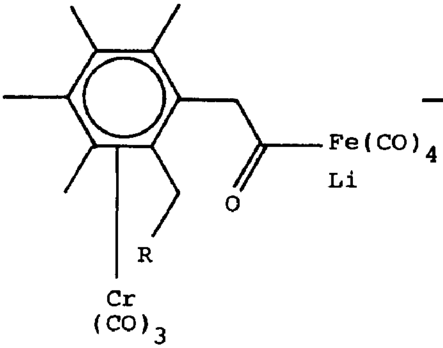

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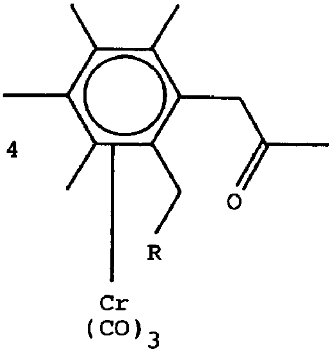

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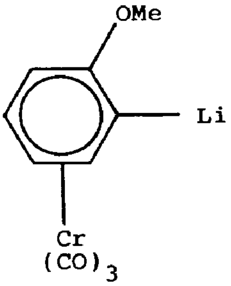

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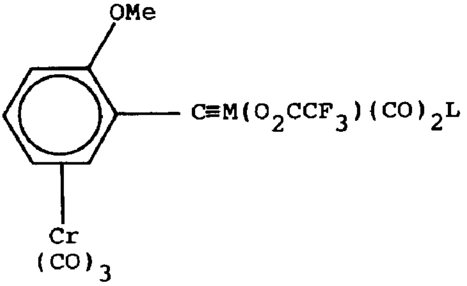

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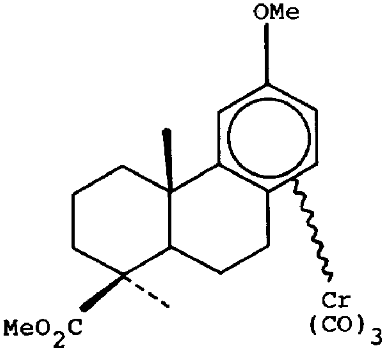

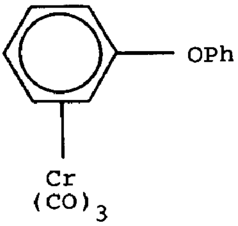

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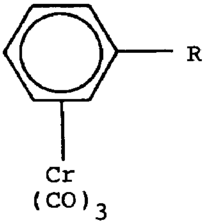

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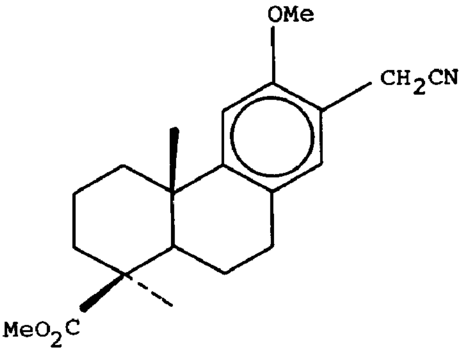

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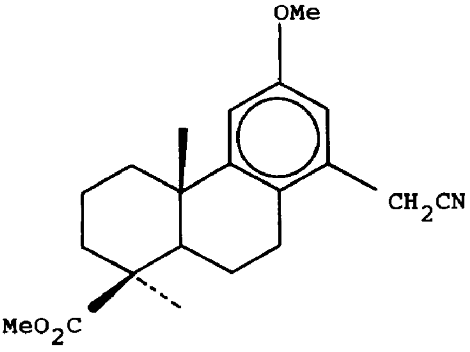
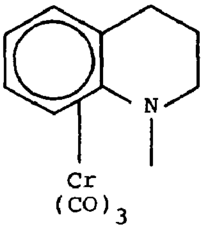


4.103

(4.94) by reaction with $Fe(CO)_5$ followed by more n-butyllithium. Addition of an electrophile RX resulted in alkylation of the more reactive benzylic position to give the intermediate (4.95; R = Me, CH_3CO, $CH_2CH{=}CH_2$, CO_2Me). Further alkylation with methyl iodide afforded the acyl complex (4.96) [98].

When the organolithium reagent (4.97) was added to a suspension of the carbonyls $M(CO)_6$, M = Mo or W, and the resultant solution was treated with $(CF_3CO)_2O$ followed by tetramethylethanediamine (TMEDA) or 2,2 '-bipyridine (bipy), the alkylidyne-metal complexes (4.98; M = Mo, L = TMEDA, bipy; M = W, L = TMEDA, bipy) were obtained. The reactions of these complexes



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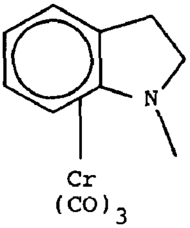

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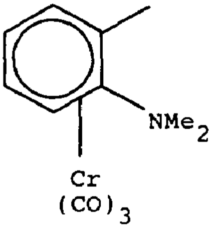

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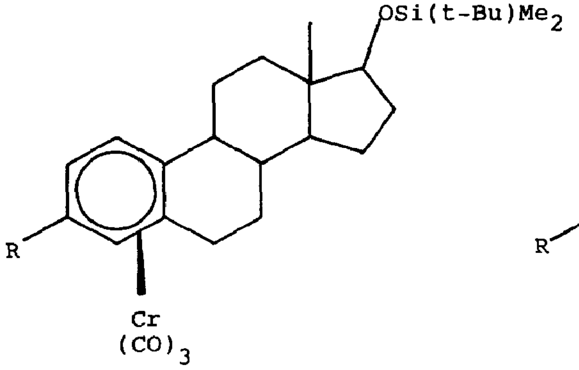

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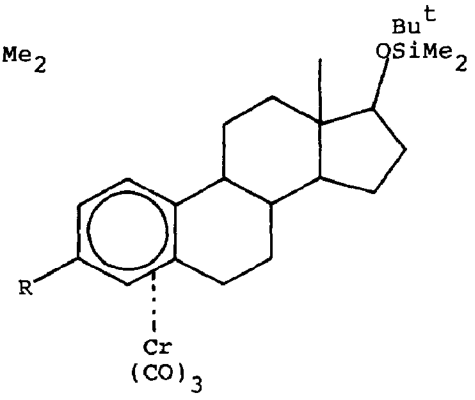
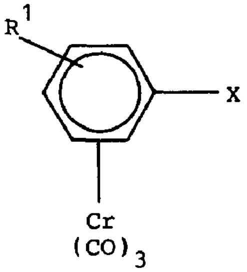


4.108

were investigated [99]. Nucleophilic substitution of the tricarbonylchromium complex (4.99) by the alkyllithiums RLi, where R = CH_2CN, $CH(CH_3)CN$ and $C(CH_3)_2CN$, proceeded by displacement of the phenoxy group to give the corresponding cyanoalkyl substituted products (4.100). This reaction was carried out with several substituted diphenylethers and it was concluded that it was proceeded by a regioselective <u>meta</u> substitution of the phenoxy group by the nucleophile [100]. The reactions of the tricarbonylchromium complex (4.101) with a variety of organolithium reagents have been investigated. For example, reaction with $LiCH_2CN$, followed by removal of the $Cr(CO)_3$ group, gave a 1:3 mixture



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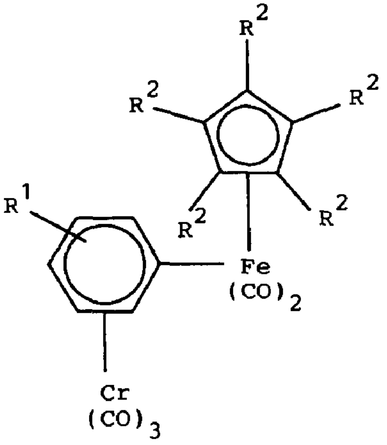

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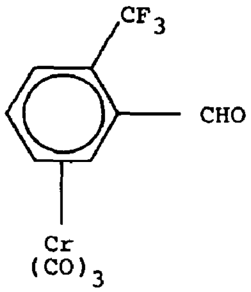

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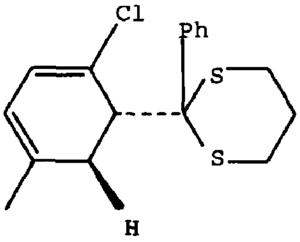


4.112

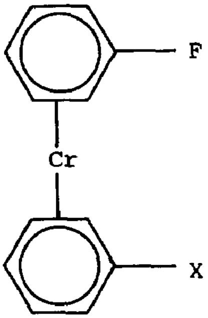
of the ortho- and meta-isomers (4.102 and 4.103) [101].

Nucleophilic addition-oxidation of the tricarbonylchromium complexes (4.104, 4.105 and 4.106) with 2-lithio-2-methyl-propionitrile, 2-lithioacetonitrile and 2-lithio-2-methyl-1,3-dithiane has been investigated. The additions were reversible as indicated by crossover experiments with (η-benzene)tricarbonylchromium [102]. Treatment of the diastereoisomers (4.107 and 4.108; R = OMe) with an excess of the lithium anion of acetonitrile gave the corresponding products of nucleophilic attack (4.107 and 4.108; R = CH_2CN) [103]. Nucleophilic substitution of the η-arene complexes (4.109; X = Cl, R^1 = m-, p-CF_3, p-MeO_2C, m-, p-Cl, p-CH_3, p-CH_3O, H; X = F, R^1 = p-F, H) by the metal carbonyl anions $[(\eta\text{-}C_5H_5)Fe(CO)_2]^-$ and $[(\eta\text{-}C_5Me_5)Fe(CO)_2]^-$ produced the corresponding bimetallic η-arene complexes (4.110; R^2 = H, Me) [104].

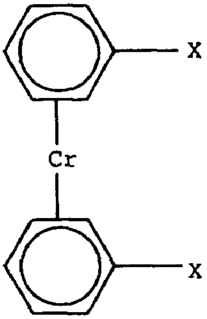
The η-arene complex (4.111) was resolved and nucleophilic addition of perfluoroalkyllithiums occurred in high yields with 90-95% asymmetric induction. Removal of the $Cr(CO)_3$ group gave the corresponding optically active alcohols o-$F_3CC_6H_4CH(OH)R$, where R = CF_2CF_3, $CF(CF_3)_2$ [105]. The reaction of tricarbonyl-(η-1-chloro-4-methylbenzene)chromium with 2-lithio-2-phenyl-1,3-dithiane gave, after treatment with trifluoroacetic acid, 1-methyl-4-chloro-5(2'-phenyl-1',3-dithiane)-1,3-cyclohexadiene (4.112). This was the only isomer of cyclohexadiene isolated and the structure was confirmed by X-ray analysis [106].

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

The elementary steps in the synthesis and decomposition of bis(η-arene)chromium have been modelled using semiempirical potential energy surface calculations. The activation barriers to formation of the complexes from chromium and arenes, exchange of ligands in complexes and chromium recombination into atomic clusters were found to be very low. Applications to the decomposition of organometallics to give metallic films have been discussed [107]. Cocondensation of fluorobenzene with chromium atoms and monosubstituted benzenes gave the heterodisubstituted complexes (5.1; X = H, Et, NMe_2, OMe, Cl, CF_3) together with bis(η-fluorobenzene)chromium and the homodisubstituted complexes (5.2; X = H, Et, NMe_2, OMe, Cl, CF_3). The ^{19}F NMR chemical shifts for the complexes (5.1) have been found to correlate with the substituent constants σ_m^+ and σ_m^n [108]. Cocondensation of pyridine, benzene and chromium atoms at liquid air temperatures gave the (η^6-pyridine)chromium complex (5.3). The bis(η^6-pyridine)chromium compound was obtained by cocondensation of 2,6-bis(trimethylsilyl)pyridine with chromium followed by desilylation. The pyridine ligand in the complex (5.3) was



5.1



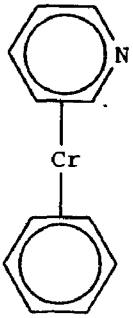
5.2

protonated at nitrogen and was found to be more basic then pyridine [109].

Chromium atoms have been cocondensed with [2_3]paracyclophane at liquid air temperatures to give the bis(exo) sandwich complex (5.4) in low yield. Hexacarbonylchromium in dibutyl ether combined with the same ligand to form the mono- di- and tri--nuclear complexes (5.5, 5.6 and 5.7) respectively. Weak inter-annular interactions in the half-sandwich complexes (5.5, 5.6 and 5.7) were indicated by IR, UV and ^{1}H NMR spectroscopy. The reversible redox processes:

$$(5.5) \rightleftharpoons (5.5)^+$$
$$(5.6) \rightleftharpoons (5.6)^+ \rightleftharpoons (5.6)^{2+}$$
$$(5.7) \rightleftharpoons (5.7)^+ \rightleftharpoons (5.7)^{2+} \rightleftharpoons (5.7)^{3+}$$

were evidenced by cyclic voltammetry [110]. The chromium complexes (5.8 and 5.9) have been prepared by metal-atom liqand-vapour cocondensation. These η^6-biphenylene complexes were inert to substitution. The structures were determined by X-ray analysis and in the complex (5.8) the ligands adopted the <u>syn</u>-conformation [111]. The double sandwich mixed chromium-nickel



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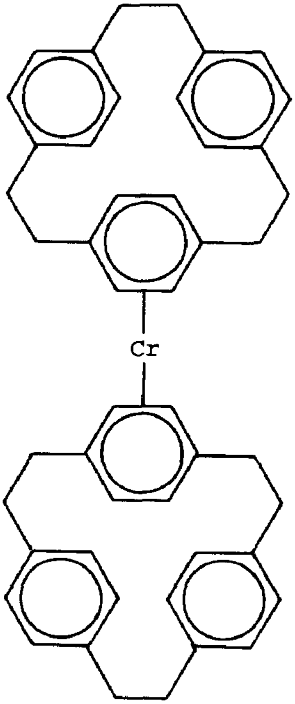

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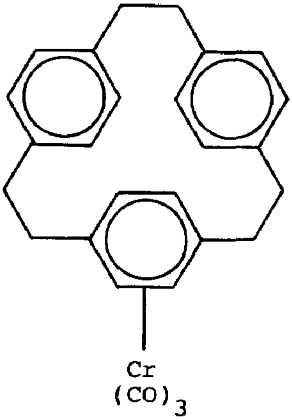

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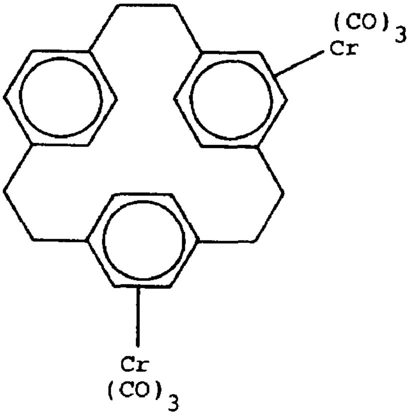

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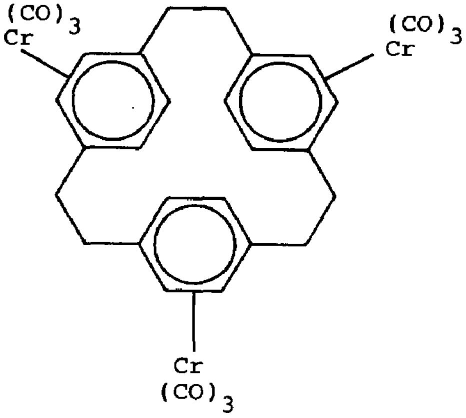

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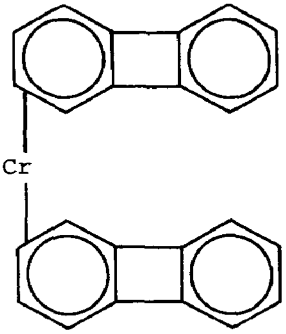

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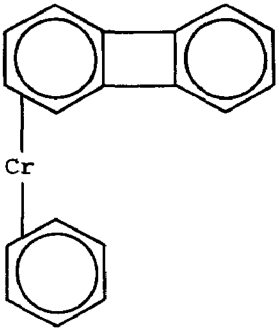

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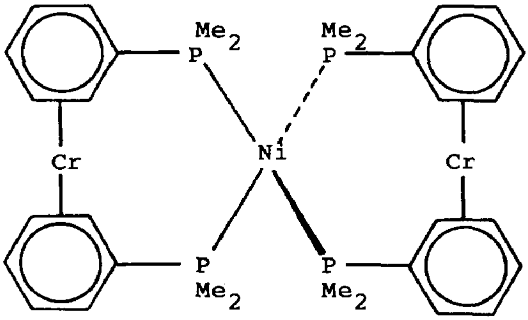
complex (5.10) has been prepared and examined by ESR spectroscopy of the corresponding double radical-double cation [112]. Reaction of bis(η-polyarene)chromium complexes with (MeCN)$_3$Cr(CO)$_3$ produced the corresponding tricarbonylchromium complexes [5.11 and 5.12; X = *trans*-CH=CH and (CH$_2$)$_n$ where n = 0, 1 and 2] [113].

The electronic absorption spectra of bis(η-benzene)chromium complexes have been studied and compared with the corresponding cations. The effects of substituents and conjugation were interpreted and discussed[114]. The electronic spectra of several bis(η-benzene)chromium complexes (5.13; R = H, Me, Et, CHMe$_2$) have been measured and shown to form a Rydberg series [115].



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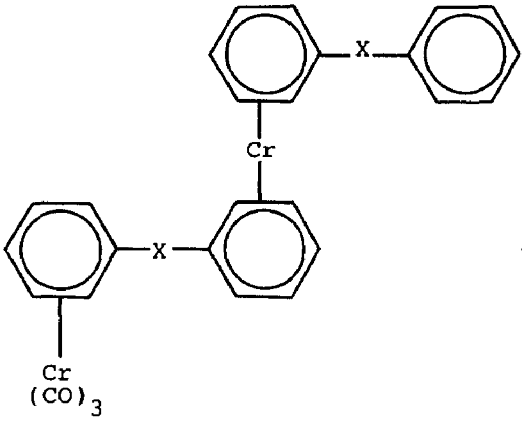

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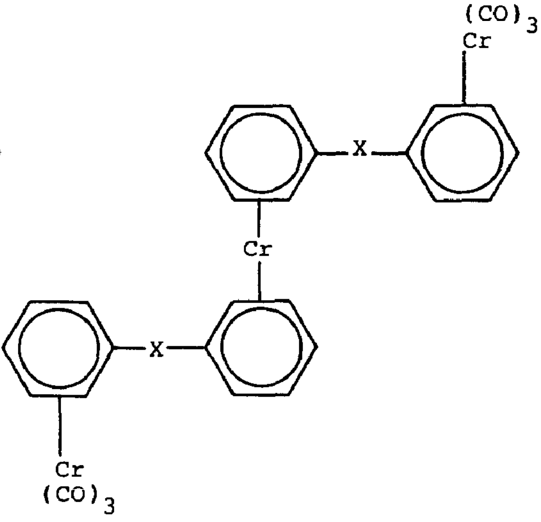

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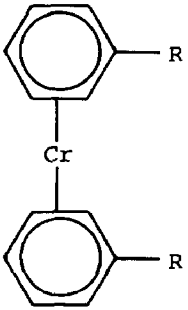
The reaction entropy for the electroreduction of bis(η-biphenyl)chromium has been measured in a series of solvents using a non-isothermal cell arrangement [116]. The effects of the substituent X on the rate of methoxydechlorination of the chromium complexes (5.14; A = PF_6, BPh_4) and on the dissociation constants of the acids (5.15; n = 0, 1) have been investigated. The effect of X was defined by the linear correlation equations using σ_p, σ^0 and σ_R constants [117]. Cyclization of the chromium



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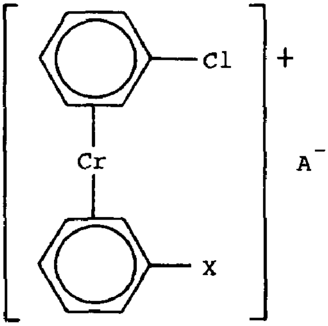

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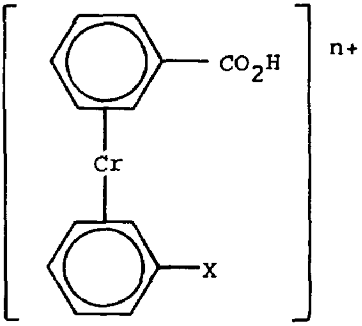

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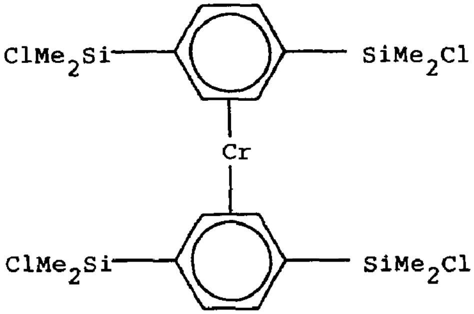
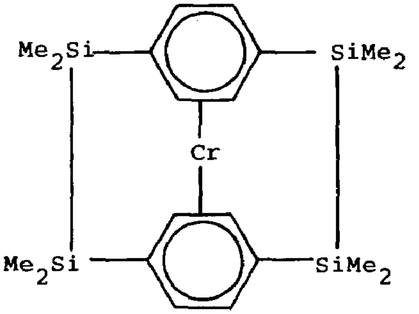


5.16

complex (5.16) with lithium-naphthalene afforded the paracyclophane (5.17). The structure of the paracyclophane was determined by X-ray analysis [118].

Poly(μ-η^6,η^6-naphthalene)chromium (5.18) was deposited from a solution of bis(η^6-naphthalene)chromium in tetrahydrofuran kept for one week at room temperature. Physical data indicated that the polymer had an eclipsed configuration [119]. The decomposition of substituted bis(η-benzene)chromium complexes on chromium coated quartz has been the subject of a kinetic and absorption study. The rate-determining step was decomposition of the absorbed complex [120]. The reduction of bis(η-arene)



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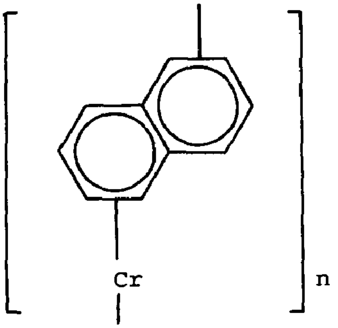


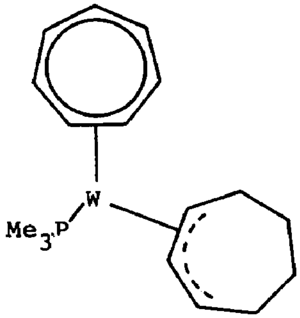
5.18

transition metal complexes has been used to produce catalysts for the aromatization of hydrocarbons. For example, when 1,4-cyclohexadiene was treated with a mixture of di(η-benzene)-chromium and potassium the diolefin was converted to benzene at room temperature and pressure. η-Arene-molybdenum and -iron complexes also behaved as catalysts under the same conditions [121].

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

Treatment of $[W(PMe_3)_3H_6]$ with cycloheptatriene gave two products (6.1 and 6.2). Reaction of the bis(trimethylphosphine) complex (6.2) with carbon monoxide produced the fluxional molecule (6.3) [122]. The crystal and molecular structure of pentacarbonyl(η-cycloheptatrienyl)(η-cyclopentadienyl)dimolybdenum (Mo-Mo) has been determined by X-ray crystallography. The molecule consisited of $Mo(\eta\text{-}C_7H_7)(CO)_2$ and $Mo(\eta\text{-}C_5H_5)(CO)_3$ moieties [123]. The crystal and molecular structure of the dinuclear (η-azulene)molybdenum complex (6.4) has been determined by X-ray crystallography. The related iron complex (6.5) has been characterized in the same way [124]. Variable temperature ^1H two-dimensional NMR exchange spectroscopy has been used to determine the rates and associated activation parameters for metal migration in the complexes (6.6; M = Cr, W). For the complex (6.6; M = W), 1,2 and 1,3 shifts were equally favoured whereas with the complex (6.6; M = Cr) the 1,3-migration pathway was just preferred [125].

Reaction of the η-cycloheptatrienyl complexes (6.7; M = Mo, W) with silver tetrafluoroborate in methyl cyanide produced the corresponding *trihapto*-cycloheptatrienyl complexes (6.8). In dichloromethane these complexes were converted into the η^7-cycloheptatrienyl complexes (6.9). The reactions of these and related complexes with phosphorus electron donor ligands were investigated [126]. Tricarbonyl(η-cycloheptatriene)-molybdenum and -chromium have been treated with aryllithium compounds at -60°C and then with $Et_3O.BF_4$ to give the corresponding ethoxyarylcarbene complexes (6.10; M = Cr, R = 4-CF_3; M = Mo, R = H, 2-, 4-Me, 4-CF_3). The crystal and molecular structure of one complex (6.10; M = Mo, R = 4-CF_3) has been determined by X-ray crystallography[127].



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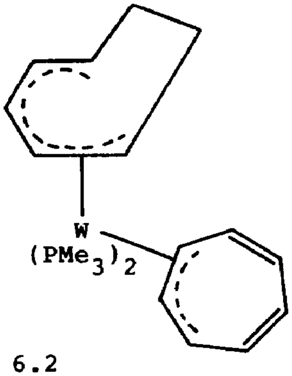

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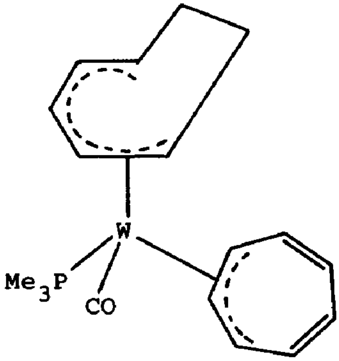

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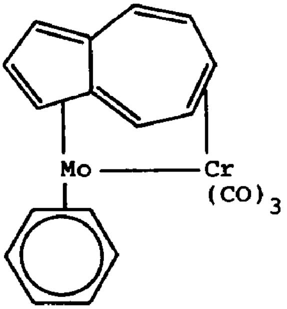

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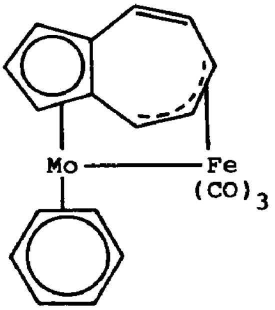

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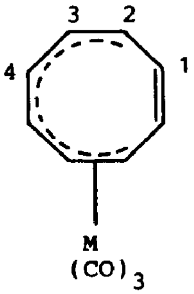

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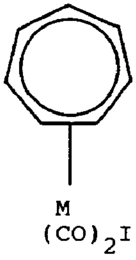

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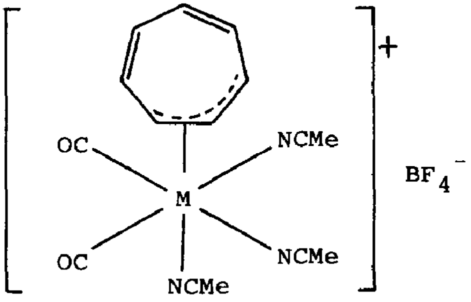

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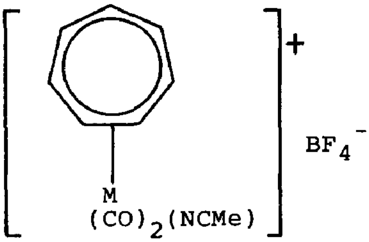

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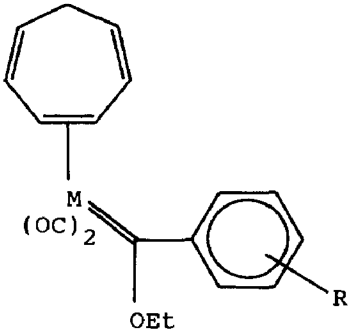
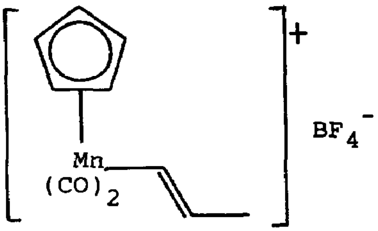


6.10

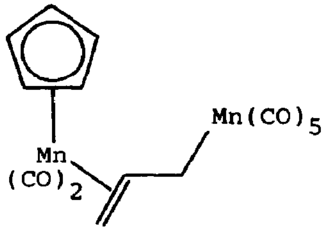
7. $(\eta\text{-}C_5H_5)Mn(CO)_3$

(i) Formation

Reaction of the cationic allyl complex (7.1) with $Na[Mn(CO)_5]$ produced the binuclear compound (7.2). Reduction of the complex (7.1) with $Na[(\eta\text{-}C_5H_5)Fe(CO)_2]$ afforded the alkene derivative (7.3) [128]. Chalcones have been prepared with ferrocenyl, ruthenocenyl and cymantrenyl substituents. The products of methyl malonate addition were examined by NMR spectroscopy [129]. Reduction of $(\eta^3\text{-}C_4H_7)Mn(CO)_4$ with sodium dihydridobis(2-methoxyethoxy)aluminate(III) (Red-Al) in the presence of 1,3-cycloheptadiene,1,3-cyclooctadiene,1,3,5-cycloheptatriene or 1,3,5,7-cyclooctatetraene produced the corresponding tricarbonylmanganese complexes (7.4, 7.5, 7.6 and 7.7) Protonation of these anionic



7.1



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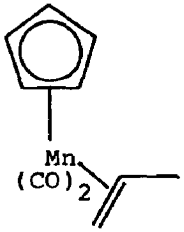

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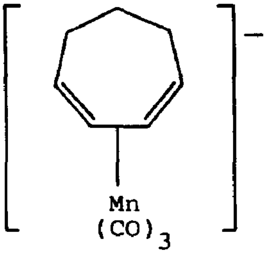

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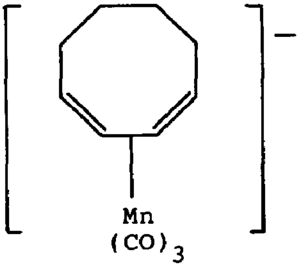

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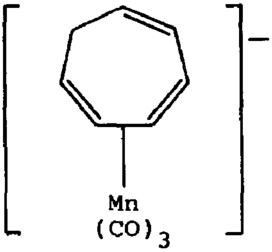

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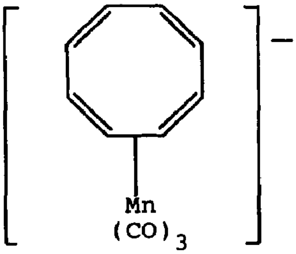
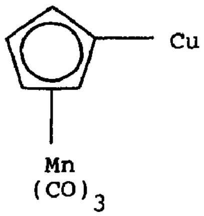


7.7

complexes was investigated [130].

(ii) Spectroscopic and Physico-chemical Studies

The cymantrenylcopper complex (7.8) has been characterized by X-ray crystallography together with thirteen related complexes [131]. The EPR spectrum of tricarbonyl(η-cyclopentadienyl)-chromium in a single crystal of cymantrene has been recorded at temperatures below 25K. The results indicated that the single unpaired electron in the chromium complex occupied an $\underline{a}'$ orbital (in $\underline{C}_s$ symmetry) which was composed of $d_{x^2-y^2}$ and d_{yz} chromium atomic orbitals [132]. The ESR spectrum of dicarbonyl(η-cyclopentadienyl)(triphenylphosphine)chromium has been recorded in toluene and in crystals of the manganese analogue (7.9). The species in the crystal appeared to reflect four different conformers [133]. A range of cyclic imides has been prepared including those containing cymantrene and methylcymantrene groups. The IR and NMR spectra were measured and reactions at the coordinated imidate ligands were investigated [134].



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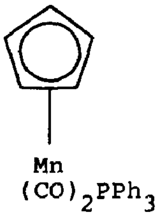
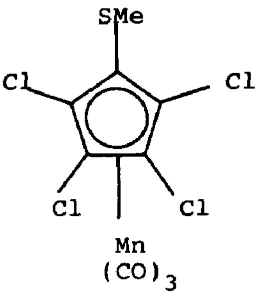


7.9

(iii) General Chemistry

Lithiation of the tricarbonylmanganese complex (7.10) with n-butyllithium followed by treatment with MeSSMe produced the η-methylthiocyclopentadienyl complexes (7.11; R^2 = SMe, $R^1 = R^3 = R^4$ = Cl; $R^2 = R^3$ = SMe, $R^1 = R^4$ = Cl, $R^1 = R^2 = R^3$ = SMe, R^4 = Cl and $R^1 = R^2 = R^3 = R^4$ = SMe). The crystal and molecular structure of the pentamethylthio complex (7.11;



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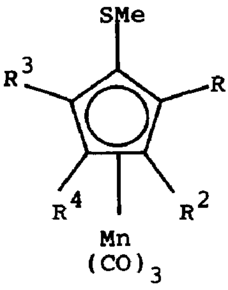

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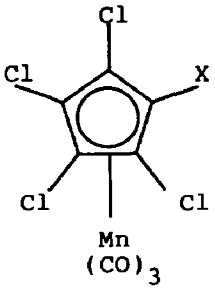

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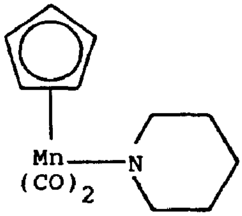

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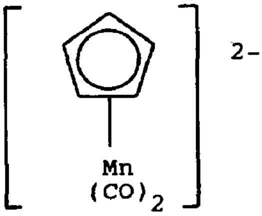

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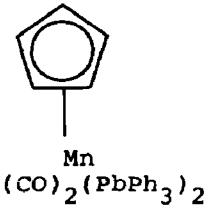

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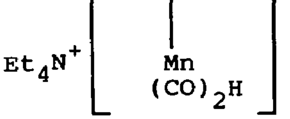

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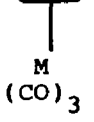

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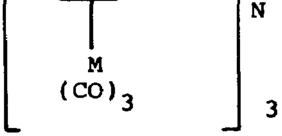
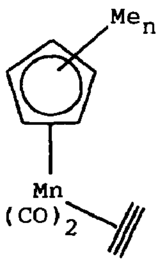


7.18

$R^1 = R^2 = R^3 = R^4 = = SMe$) was determined by X-ray analysis [135]. Metallation of the perhalogenated cymantrene (7.12; X = Br) with n-butyllithium gave the lithio species (7.12; X = Li) which was treated with electrophiles to give products such as (7.12; X = H, Me, $SiMe_3$, CO_2H, SMe) [136]. Reduction of the pyridine-manganese complex (7.13) with sodium naphthalenide produced the anion (7.14). Addition of Ph_3PbCl to the anion afforded the diadduct (7.15) and the addition of water gave the corresponding hydride which was isolated as the tetraethylammonium salt (7.16) [137]. The cymantrene and (η-cyclopentadienyl)-rhenium Grignard reagents, (7.17; M = Mn, Re) combined with $N(CH_2Cl)_3$ to give the trinuclear complexes (7.18; M = Mn, Re) which showed good thermal and photochemical stability [138].



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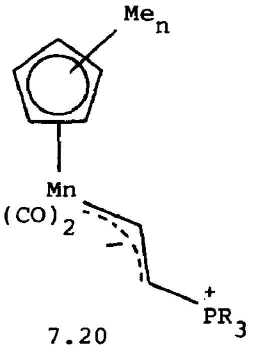

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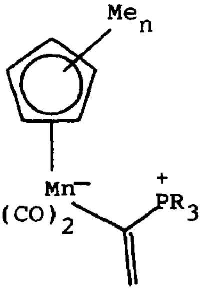
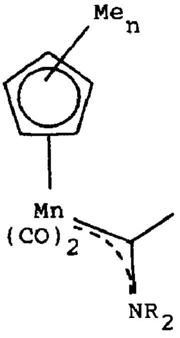


7.21

Phosphido-bridged heterobimetallic complexes have been prepared by treatment of (η-C_5H_5)$(OC)_2FeP(Si(Me_3)_2$ with organometallic compounds. Thus (η-C_5H_4R)$Mn(CO)_2THF$, where R = H, Me, gave the phosphido-derivatives (η-C_5H_5)$(OC)_2Fe[\mu$-$P(SiMe_3)_2]$-$Mn(\eta$-$C_5H_4R)(CO)_2$ which underwent photochemical decarbonylation to form the phosphido-bridged bimetallic species [139]. The cymantrenylacetylenes(7.19; n = 0, 1, 5) combined with tertiary phosphines to give the adducts (7.20 and 7.21; n = 0, 1, 5; R = Me, Et) [140], while with ammonia and primary or secondary amines they gave aminocarbene complexes (7.22; n = 0, 1, 5) [141]. The acetylenes (7.19) underwent addition with bromine and hydrogen chloride to form the ethylene complexes (7.23; X = Y = Br; X = H, Y = Cl) [142]. The manganese complex (7.24)



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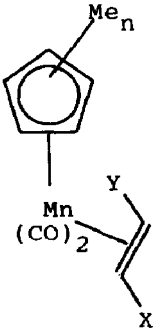

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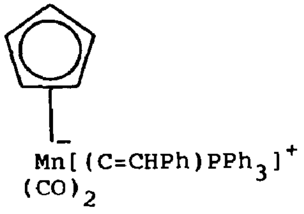

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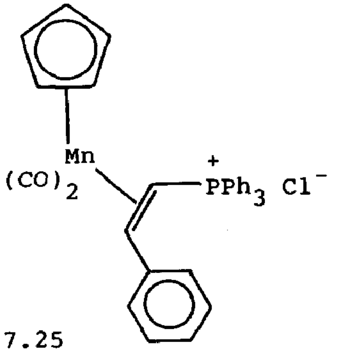

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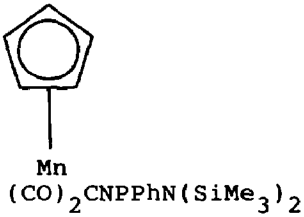
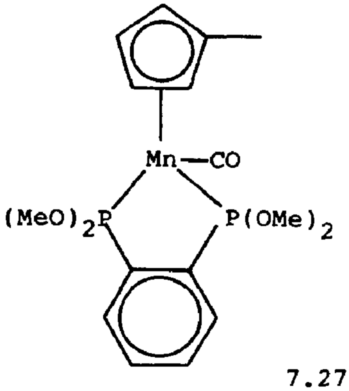


7.26

underwent a σ-π rearrangement in the presence of HCl to give the η^2-olefin complex (7.25). The crystal and molecular structure of this latter complex was determined by X-ray analysis [143]. The isocyanophosphine complex (7.26) underwent slow evolution of carbon monoxide to give a coordinatively unsaturated species which dimerized by linking the manganese atom on one molecule to the phosphorus atom on the second molecule [144].

Photolysis of methylcymantrene in the presence of the phosphorus derivatives $\underline{o}$-$C_6H_4(PR_2)_2$, where R = OMe, OEt; $\underline{m}$-$C_6H_4[P(NMe_2)_2]_2$ and $\underline{p}$-$C_6H_4(PR_2)_2$ where R = OMe, NMe_2 gave a series of new (η-methylcyclopentadienyl)-manganese complexes. For example, irradiation of methylcymantrene and $\underline{o}$-$C_6H_4[P(OMe)_2]_2$ afforded the manganese complex (7.27) [145]. The kinetics of photosubstitution of carbon monoxide and triphenylphosphine in



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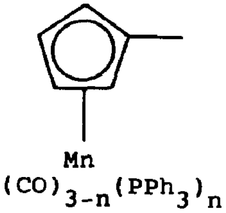

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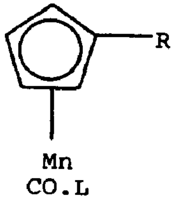

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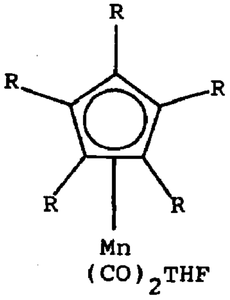

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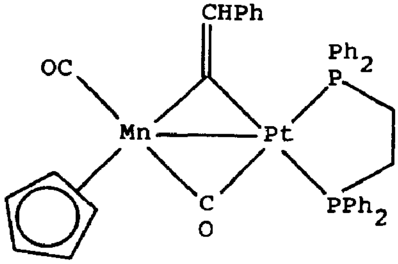

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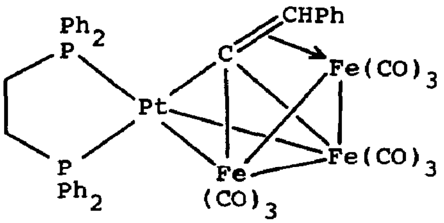

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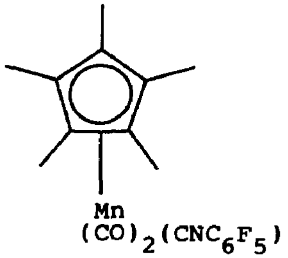


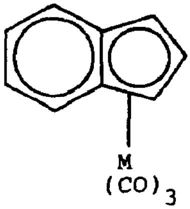
7.33

the methylcymantrene complexes (7.28; n = 0, 1, 2) have been investigated. The results indicated that on irradiation of methylcymantrene in the presence of triphenylphosphine the following reactions took place:

$$\mathrm{Mn(\eta\text{-}MeC_5H_4)(CO)_3 + PPh_3 \xrightarrow{h\nu} Mn(\eta\text{-}MeC_5H_4)(CO)_2PPh_3 + CO}$$
$$\mathrm{Mn(\eta\text{-}MeC_5H_4)(CO)_2PPh_3 + PPh_3 \rightleftharpoons Mn(\eta\text{-}MeC_5H_4)(CO)(PPh_3)_2 + CO}$$

[146].

Protonation of the cymantrene derivatives (7.29; R = H, Et, Me_3C, Ph_2CH; L = $Ph_2PCH_2CH_2PPh_2$) in dichloromethane-trifluoroacetic acid mixtures produced the corresponding [cis-(η-C_5H_4R)-Mn(CO)($Ph_2PCH_2CH_2PPh_2$)H]$^+$ compounds whereas protonation of the cymantrene derivatives {7.29; R = H, Ph_2CH; L = $Ph_2P(CH_2)_3PPh_2$, $(PPh_2Me)_2$, $[P(OEt)_3]_2$} gave the corresponding [trans-(η-RC_5H_4)Mn(CO)LH]$^+$ compounds [147]. Treatment of the THF complexes (7.30; R = H, Me) with 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide gave the corresponding disulphur monoxide complexes [148].



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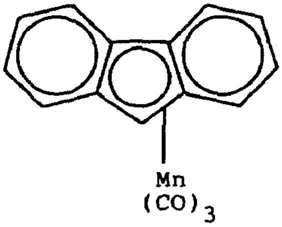

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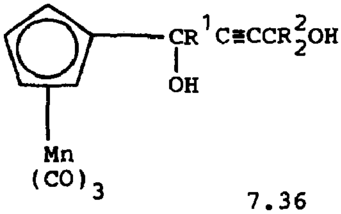

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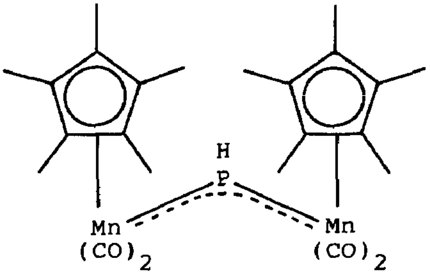
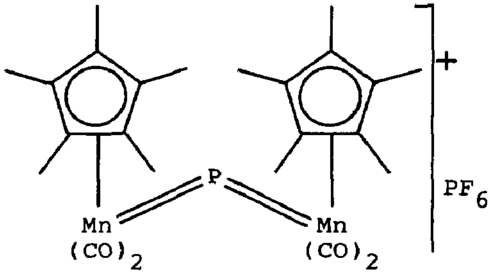
Reaction of the manganese complex (7.31) with $Fe_2(CO)_9$ produced the heterometallic μ_4-vinylidene cluster (7.32) [149]. Reaction of dicarbonyl(η-pentamethylcyclopentadienyl)tetrahydrofuranmanganese with pentafluorophenyl isocyanide produced the complex (7.33). The isocyanide group was stabilized by coordination with manganese and the structure of the complex (7.33) was confirmed by X-ray analysis [150]. Acetylation and deuteration of the η^5-indenyl complex (7.34; M = Mn) occurred at the 5- and 6-positions of the indenyl ring. Acetylation of the rhenium compound (7.34; M = Re) and the η^5-fluorenyl complex (7.35) occurred only at the 6-positions. Competitive acetylation indicated that the η^5-indenyl complex (7.34; M = Mn) was more reactive than cymantrene [151]. The cymantrenyl alcohols (7.36; R^1 = Me, Ph; R^2 = H, Pr) have been used to prevent the growth of actinomycetes and phytopathogenic bacteria [152].

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

Hydride abstraction from the manganese complex (8.1) with Ph_3CBF_4 gave the phosphacumulene (8.2) [153]. The structure of the bimetallic compound (8.3) has been determined by X-ray analysis. Both the iron and manganese atoms had piano stool structures [154]. The cymantrene complex (8.4) combined with (η-C_5H_5)M(CS)PMe_3, where M = Co, Rh, to give the mixed metal complexes (8.5; M = Co, Rh). Cationic and neutral derivatives of the products (8.5) were prepared [155]. Reaction of the



8.1



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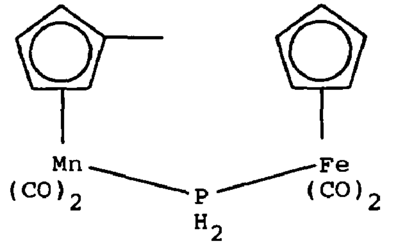

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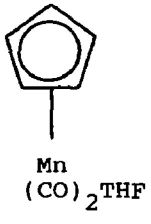

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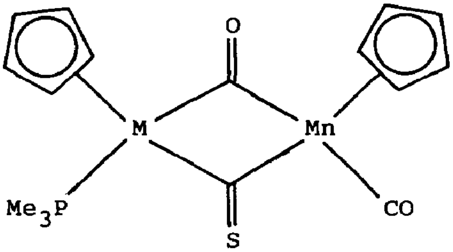
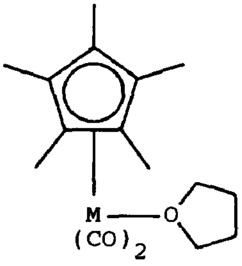


8.5

manganese and rhenium complexes (8.6; M = Mn, Re) with cyclo-octasulphur, S_8, afforded a series of products (8.7 and 8.8; M = Mn, Re; 8.9 and 8.10). These reactions were interpreted in terms of degradation of S_8 by the nucleophilic 16-electron fragments $[(\eta\text{-}C_5Me_5)M(CO)_2]$. Analogous reactions were observed with the corresponding unsubstituted cyclopentadienyl complexes [156].

Treatment of the radical complex (8.11) with $AgPF_6$ afforded the sulphur analogue (8.12) of a phosphindiyl complex. The crystal structure of the complex (8.12) was determined [157]. The cymantrene complex (8.13) has been prepared and characterized by X-ray crystallography [158]. The 2,7-dimethyl-as-indacene dianion has been treated with bis(pyridine)manganesetricarbonyl bromide to give a mixture of the cis and trans isomers of the bis(manganese tricarbonyl) complex (8.14). The cis complex (8.14) was characterized by X-ray crystallography and showed considerable bending of the as-indacene ligand because of steric



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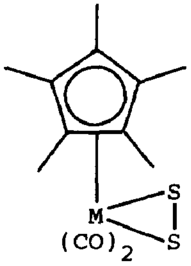

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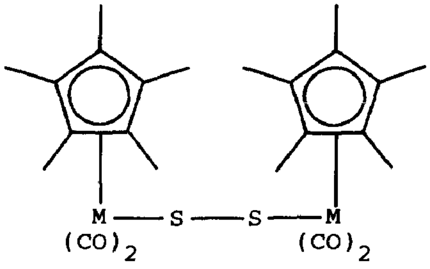

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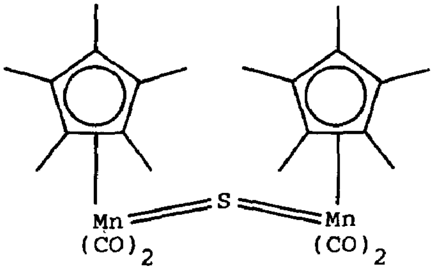

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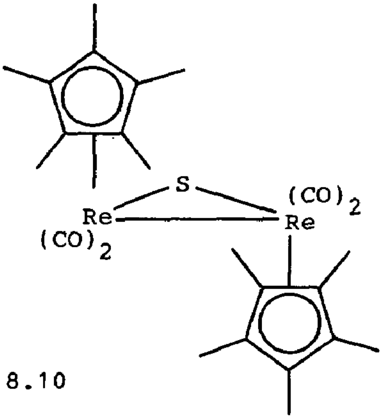
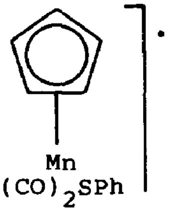


8.10

interaction between the two tricarbonylmanganese groups [159]. The isocyanide complex $[Cr(CO)_5NC(PPh_3)_2]Cl$, combined with the cymantrenyl salt $Na[(\eta-C_5H_5)Mn(CO)_2CN]$ to form the derivative $Cr(CO)_5C(N=CCl_2)[NCMn(\eta-C_5H_5)(CO)_2]$ which was characterized by X-ray crystallography [160].

The manganese-carbene complex (8.15) combined stepwise with two equivalents of isocyanide RNC, where R = Me, cyclohexyl, Ph. In the first step the corresponding ketenimine complexes (8.16) are obtained. Reaction of the ketenimine (8.16; R = cyclohexyl) with cyclohexyl isocyanide results in removal of N-cyclohexyl ketenimine. In contrast the ketenimine complexes (8.16; R = Me, Ph) combined with methyl or phenyl isocyanide to give the corresponding isomeric 3-imino-2-azetidinylidene compounds (8.17 and 8.18; R = Me, Ph) [161]. Reaction of the 1-propyn-3-ol or 1-butyn-3-ol complexes (8.19; R = H, Me) with phenyllithium, hydrochloric acid or acetic acid afforded the corresponding olefin complexes (8.20). Treatment with diethylamine produced the corresponding carbenes (8.21) [162].

Reaction of the carbyne complexes (8.22; R = Ph, $C_6H_4CH_3$) with nitrite ion gave the corresponding α-ketoacyl complexes (8.23). These latter complexes were also prepared by reaction of the 17-electron complexes (8.24) with NO gas. This reaction proceeded by insertion of CO into the metal-acyl bond [163]. The silylcymantrene, $[(\eta\text{-}C_5H_4Me)Mn(CO)_2SiMePh_2]^-$ has been treated with 3,3-dichloro-1,2-diphenylcyclopropene to give the cyclopropenylidene complex (8.25) which was characterized by X-ray crystallography [164]. The cymantrene vinylidene complex (8.26) has been treated with phosphites, $P(OR)_3$ where R = Me, $CHMe_2$, Bu, and $PhP(OEt)_2$ to give cymantrenes with the ligands $PhCH{=}CHP(O)(OR)_2$ and $PhCH{=}CHP(O)Ph(OEt)$ which were used to form styrylphosphonates [165].



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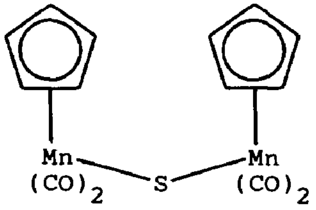

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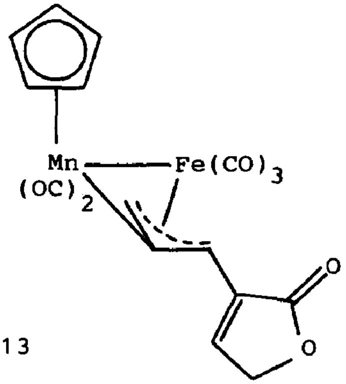

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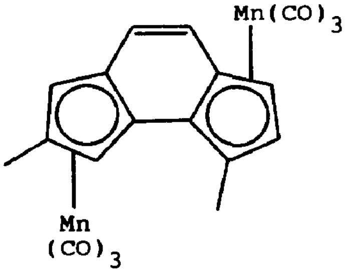

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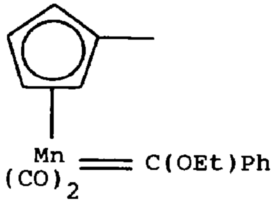

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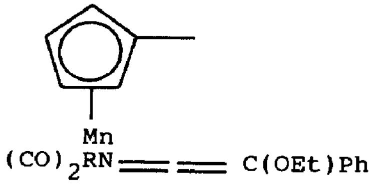

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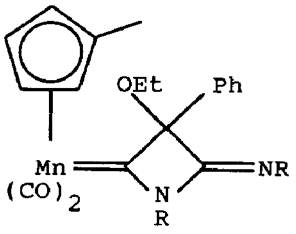

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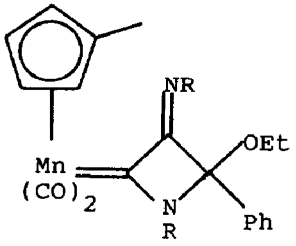

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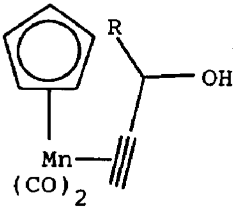

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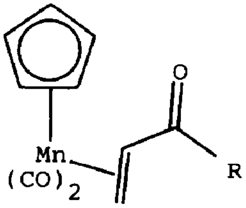

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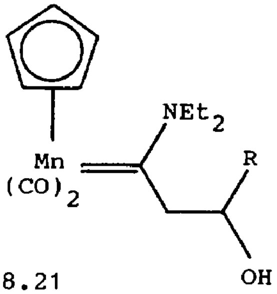

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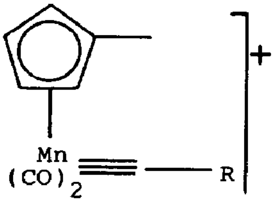

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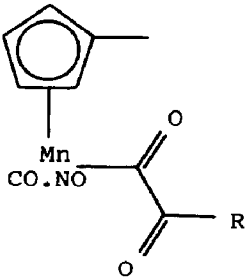

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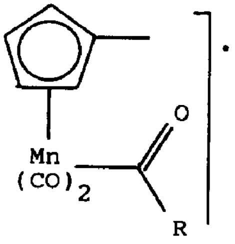

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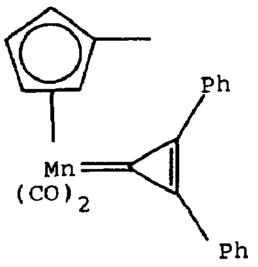

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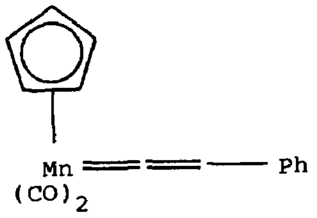
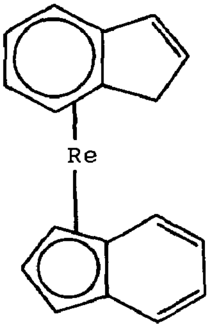


8.26

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

The cocondensation of rhenium atoms with indene produced $(\eta^6$-indene$)(\eta^5$-indenyl$)$rhenium (9.1) together with a minor product (9.2). The complex (9.1) was deprotonated with potassium hydride and then treated with $[Rh(\eta^4\text{-}C_8H_{12})Cl]_2$ to give the rhenium complex (9.3) which contained an $\eta^3{:}\eta^6$-indenyl ligand [166]. The crystal and molecular structure of the trioxo(cyclopentadienyl)rhenium(VII) complex (9.4) has been determined by



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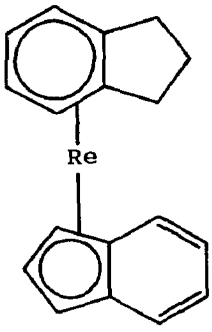

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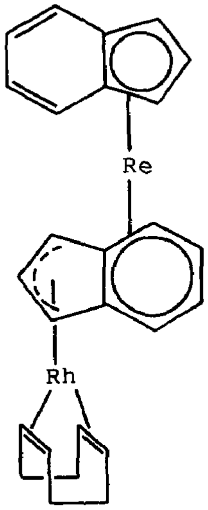

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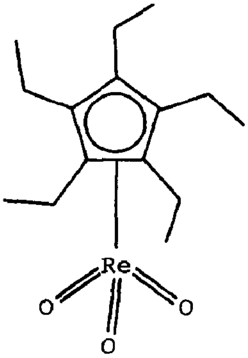

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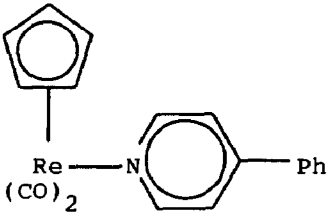
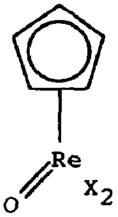


9.5

X-ray crystallography. Rhenium-oxygen double bonds were indicated while the rhenium-cyclopentadienyl distance was unusually long [167]. Treatment of (η-C_5Me_5)Re(CO)$_2$THF with MeSSMe gave the corresponding diamagnetic sulphur complex (η-C_5Me_5)Re(CO)$_2$(SMe)$_2$ which was characterized by X-ray crystallography [168]. The absorption spectrum of the complex (9.5) exhibited two intense Re(d_π)$\rightarrow$(π^*)L metal to ligand charge-transfer transitions which arose by degeneracy removal of the filled t_{2g} orbitals to yield levels of $\underline{b}_2$ and $\underline{e}$ symmetry. The luminescence spectrum exhibited three distinct maxima. The two strongest emissions were both solvent and temperature dependent and were associated with the metal-ligand charge transfer transitions [169].

The ^{17}O NMR spectra of the rhenium complexes (9.6; X = F, Cl, Br, I, alkyl, aryl) indicated that the chemical shift of the terminal oxygen was dependent on the σ-donor effectiveness of the ligand X. This correlated roughly with the electron density at rhenium [170]. The formation of the (η-cyclopentadiene)rhenium hydride (9.7) and its conversion to the corresponding (η-cyclopentadienyl)rhenium species has been reported. Variable temperature ^{1}H NMR spectroscopy of the (η-cyclopentadiene)rhenium complex (9.7) indicated three distinct fluxional processes including endo-cyclopentadiene hydrogen-hydride exchange [171]. Lithiation of the hydride (9.8) with n-butyl lithium-tetramethylenediamine (TMEDA) at -78°C gave the lithio-intermediate (9.9) which formed the methyl derivative (9.10) with $CH_3OSO_2CF_3$. The lithio-intermediate (9.9) rearranged at -32°C to the salt (9.11).



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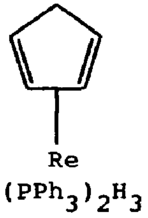

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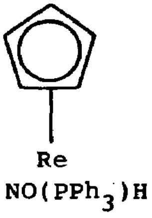

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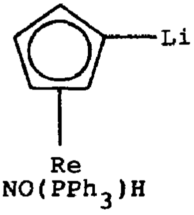

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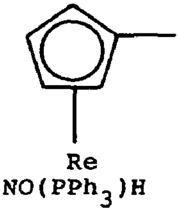

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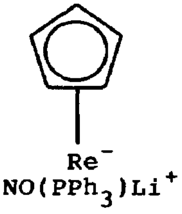

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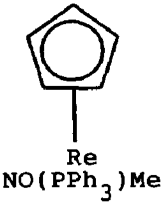

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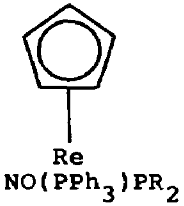
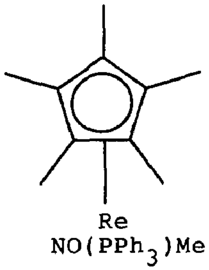


9.13

Treatment of this salt with methyl iodide produced the complex (9.12) [172].

The (η-cyclopentadienyl)rhenium phosphido complexes (9.13; R = Et, t-Bu, Ph, 4-Me.C_6H_4) have been prepared by proton abstraction from the corresponding cationic secondary phosphine complexes. ^{13}C and ^{1}H NMR spectroscopy were used to determine the PR_2 phosphorus inversion barriers, low values in the range 12.6-14.9 kcal/mol were obtained [173]. Reaction of the rhenium complex (9.14) with $HBF_4.OEt_2$ in dichloromethane at -78°C produced the dichloromethane complex (9.15) which converted to the oxidative addition product (9.16) at -35°C. The reaction of the complex (9.15) with halide nucleophiles was investigated [174]. The (η-cyclopentadienyl)rhenium halides (9.17; R = H; X = Cl, Br, I) underwent ring metalation with n-butyllithium-TMEDA



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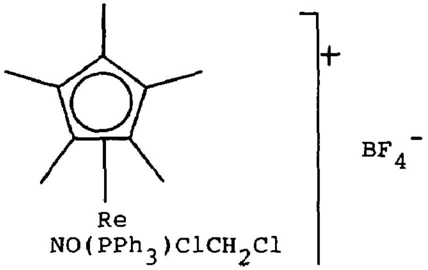

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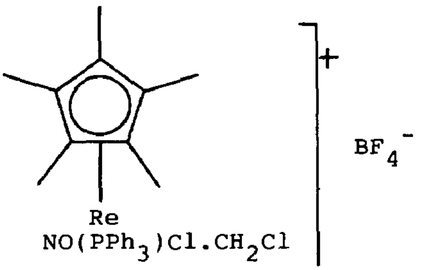

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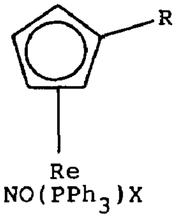

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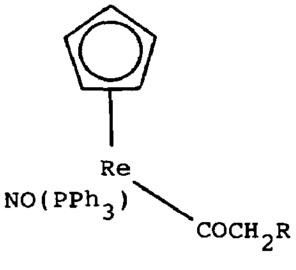

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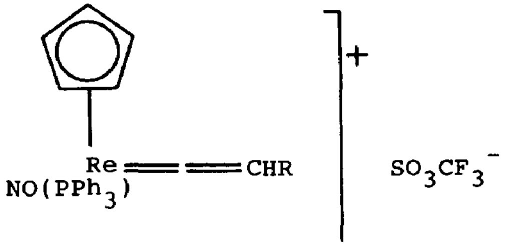

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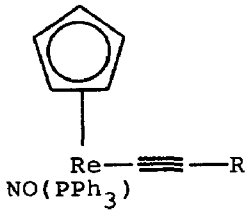

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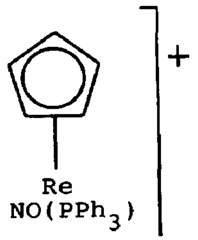
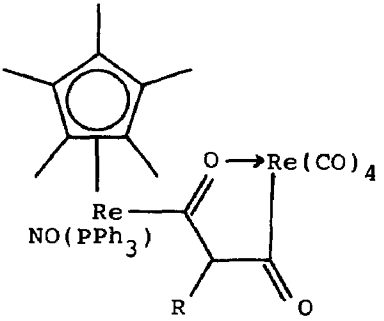


9.21

at -78°C to give the lithio species (9.17; R = Li; X = Cl, Br, I) which were characterized by NMR spectroscopy and by alkylation to the methyl derivatives (9.17; R = Me, X = Cl, Br, I) [175].

The sequential treatment of the acyl complexes (9.18; R = H, Me, Ph, 1-naphthyl) with $(CF_3SO_2)_2O$, base and then $(CF_3SO_2)_2O$ produced the corresponding vinylidene complexes (9.19). The complexes (9.19; R = Me, Ph, 1-naphthyl) existed as mixtures of geometric isomers. Treatment of these compounds (9.19) with base gave the corresponding acetylide complexes (9.20) [176]. The chiral (η-cyclopentadienyl)rhenium Lewis acid cation (9.21) underwent selective binding to one enantioface of monosubstituted olefins such as propene and allylbenzene. Equilibrium ratios of up to 50:1 for the two isomers were observed [177]. The same cation (9.21) combined with one methyl ketone enantioface to



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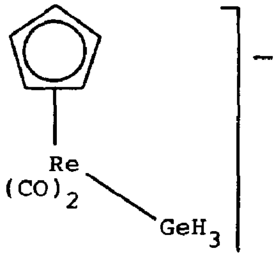

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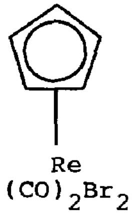

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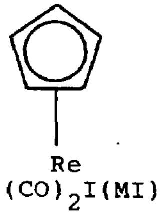

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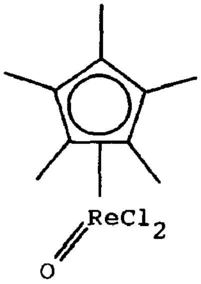

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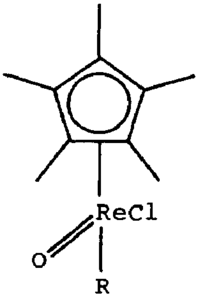

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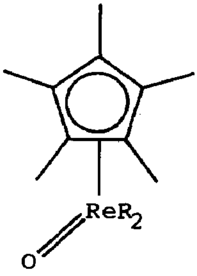

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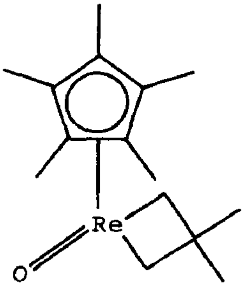
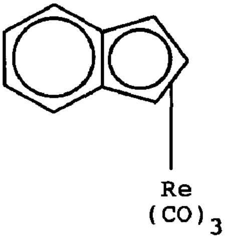


9.29

give the corresponding syn-methyl ketone complexes. The acetophenone complex was characterized by X-ray crystallography [178].

Alkylation of the (η-cyclopentadienyl)rhenium complex (9.22; R = H) by deprotonation and treatment with methyliodide gave the product (9.22; R = Me). This complex existed in equilibrium with the enol form, it was found that enolization did not lead to epimerization at the chiral carbon atom [179]. Reaction of tricarbonyl(η-cyclopentadienyl)rhenium with $KGeH_3$ afforded the carbonyl substitution product (9.23) [180]. A series of phosphine and phosphite derivatives of tricarbonyl(η-cyclopentadienyl)rhenium has been prepared [181]. Bromination of tricarbonyl(η-cyclopentadienyl)rhenium afforded the dicarbonyl-rhenium complex (9.24) [182]. Reaction of the $(\eta\text{-}C_5H_5)Re(CO)_2I_2$ with samarium and ytterbium amalgams gave the corresponding divalent lanthanide derivatives (9.25; M = Sm Yb) [183].



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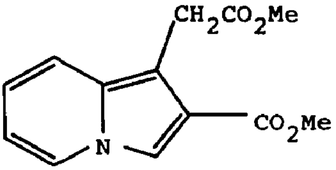
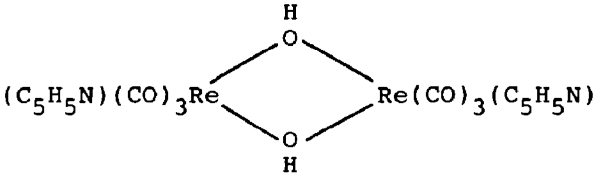


9.31

Treatment of the dichloro-rhenium complex (9.26) with Grignard reagents gave the corresponding mono- and di-alkyl derivatives [9.27; R = Ph, $CH_2Si(CH_3)_3$ and 9.28; R = CH_3, CD_3, C_2H_5, n-C_4H_9, CH_2Ph, Ph, $CH_2Si(CH_3)_3$]. Several of these complexes were characterized by single crystal X-ray diffraction studies. Reaction of the complex (9.26) with $(CH_3)_2C(CH_2MgBr)_2$ produced the stable rhenacyclobutane (9.29) [184]. Condensation of pyridine with methyl propiolate in the presence of the η-indenyl complex (9.30) produced the indolizine (9.31) [185]. Reaction of tricarbonyl(η^5-indenyl)rhenium with pyridine afforded the di-μ-hydroxy complex (9.32) [186]. Reaction of the carbyne



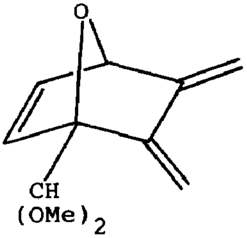
9.32

complex $[(\eta\text{-}C_5H_5)(CO)_2ReCCC_6H_5]BBr_4$ with 1,2-dilithiocarborane produced the 1-carboranyl complex $[(\eta\text{-}C_5H_5)(CO)_2ReC(C_2HB_{10}H_{10})(C_6H_5)]$ and the 1-carboranylformacyl complex $[(\eta\text{-}C_5H_5)(CO)(OCC_2HB_{10}H_{10})ReCC_6H_5]$. These products were identical with those obtained from the reaction with 1-lithiocarborane [187].

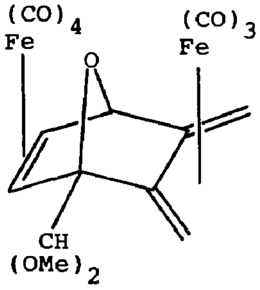
10. (Acyclic-η-diene)$Fe(CO)_3$

Reaction of the olefin (10.1) with $Fe_2(CO)_9$ gave the tricarbonyliron complex (10.2). Deoxygenation of this complex on heating afforded the η-dimethylidenecyclohexadiene complex (10.3; R = H). The same reaction in methanol gave the ester (10.3; R = CO_2Me). Oxidation of these complexes (10.3; R = H, CO_2Me) followed by decomplexation produced the corresponding indanone derivatives (10.4) [188]. Condensation of aniline with benzylideneacetone in the presence of zinc chloride gave a mixture of two stereoisomeric imines (10.5). Treatment of this mixture with $Fe_2(CO)_9$ produced the tricarbonyliron complex (10.6). Reaction of this complex with methyllithium followed by t-butyl bromide gave the pyrrole (10.7) [189]. The aldehyde (10.8) has been prepared by reaction of the uncomplexed ligand with pentacarbonyliron. The phosphoric acid ester (10.9) was prepared in good overall yield from the aldehyde (10.8). Treatment of the ester (10.9) with sodium hydride followed by an aldehyde RCHO produced the corresponding (E)-ene tricarbonyliron complexes [10.10; R = Ph, p-$CH_3OC_6H_4$, o-$CH_3OC_6H_4$, $CH_3(CH_2)_2CH{=}CH$, $CH_3(CH_2)_3CH{=}CHCH{=}CH$, $CH_3(CH_2)_4$] [190].

The dienealdehydes, $OCHCH{=}CHCH{=}CHC_nH_{2n+1}$, combined with enneacarbonyldiiron to give, after borohydride reduction and protonation the cationic (η-dienyl)iron complexes (10.11;



10.1



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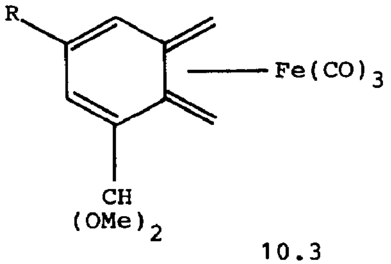

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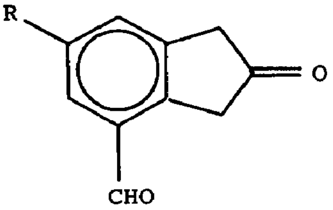
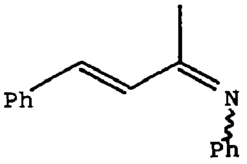


10.4

n = 1-7) [191]. Enneacarbonyldiiron combined with a substituted diphosphabutadiene to give the (η-diphosphabutadiene)iron complex (10.12) [192]. The tricarbonyliron complexes (10.13, 10.14 and 10.15) have been prepared and the structure of the complex (10.15)



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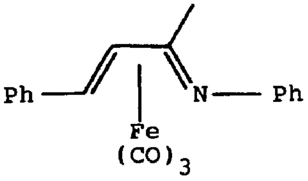

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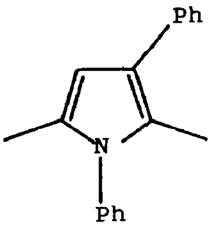

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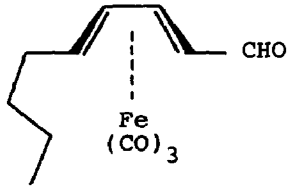

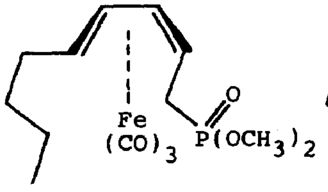

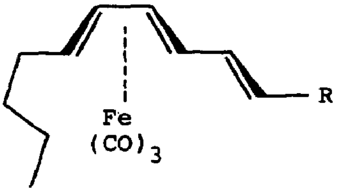

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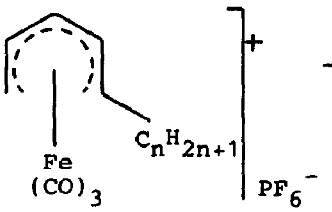
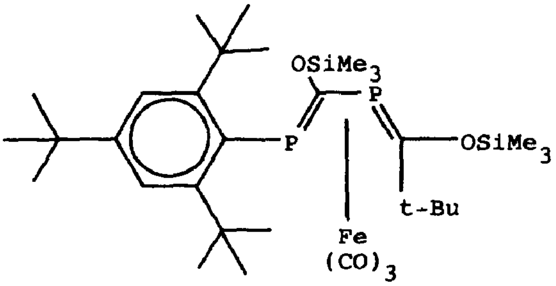
was determined by X-ray analysis. ^{13}C NMR spectroscopy indicated that one of the *exo*-Fe(CO)$_3$ groups in the complex (10.14) rotated three times faster than the other at 40°C [193]. The crystal and molecular structure of tricarbonyl(η-cyclobutadiene)iron has been determined at -45°C by X-ray crystallography. Temperature dependent ^{1}H NMR spectra of the complex have been reinterpreted to give a barrier to ring rotation of 22.6 kJ/mol in the solid state [194]. X-ray crystallography has been used to determine the crystal and molecular structure of tricarbonyl-(η^4-1,4-dibenzoyloxy-1,3-butadiene)iron. A diphenyl ester-vinyl moiety was bonded to iron [195].





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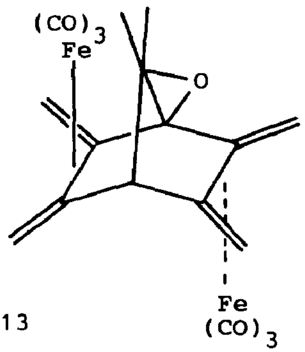

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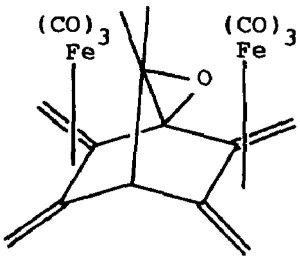

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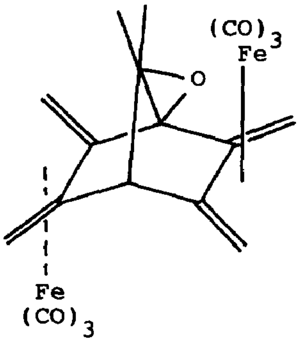
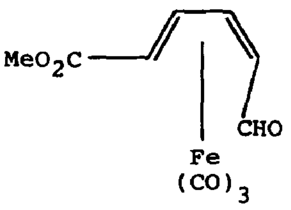


10.15

Electron transmission spectroscopy has been used to determine the attachment energies of low energy electrons to $Fe(CO)_5$ and the complexes (η^4-1,3-butadiene)-,(η^4-1,3-cyclohexadiene)-, (η^4-cyclooctatetraene)- and (η^4-cyclobutadiene)-$Fe(CO)_3$ [196].



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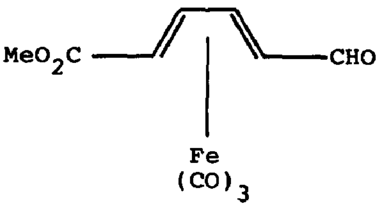
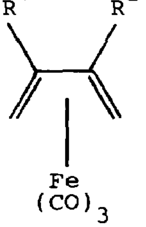


10.17

The ^{57}Fe spin-lattice relaxation times have been determined at two widely different fields for a range of organometallic complexes including (η-butadiene)tricarbonyliron derivatives. The results were used to separate the contributions of different relaxation mechanisms to the longitudinal relaxation rate [197]. Thermal rearrangement of the (E,Z-butadiene)iron complex (10.16) to the isomer (10.17) required an activation energy of 120 ± 2 kJ mol^{-1} as determined by ^1H NMR spectroscopy. The two complexes (10.16 and 10.17) were characterized by X-ray crystallography [198].



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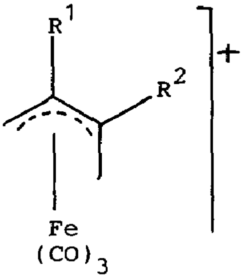
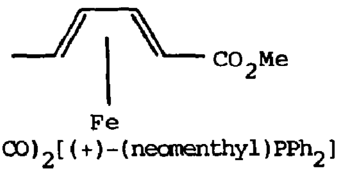


10.19

Replacement of a carbonyl ligand by triphenylphosphine in the (η-diene)iron complexes (10.18; R^1, R^2 = H, Me) changed the regiospecificity of electrophilic attack and allowed easier access to the (η-allyl)iron cations (10.19). In the same way substitution of triphenylphosphine for carbonyl in (η-dienyl)-irontricarbonyl cations resulted in decreased reactivity towards nucleophiles [199]. Displacement of a carbonyl ligand by a chiral phosphine in tricarbonyl(η-butadiene)iron complexes has been used to facilitate diastereomer separation. Thus the phosphine derivative (10.20) was prepared and separated quantitatively into the two diastereomers by preparative TLC. The absolute configuration of 1S,4R-(10.20) was established by X-ray crystallography [200]. Carbon nucleophiles combined with diastereoisomeric (η-trans-pentadienol)iron complexes to give regio- and stereo-specific products. Thus the diastereomer (10.21; R^1 = H, Me, Et; R^2 = OAc) gave the products (10.21; R^1 = H, Me, Et; R^2 = $CH_2CH=CH_2$, Me, Et, CH_2OPh) [201]. The stereoselective



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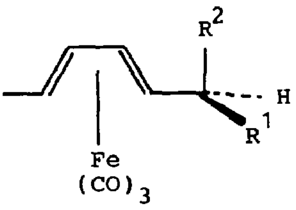

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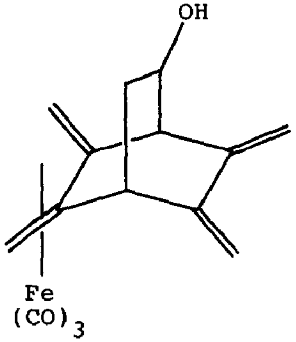

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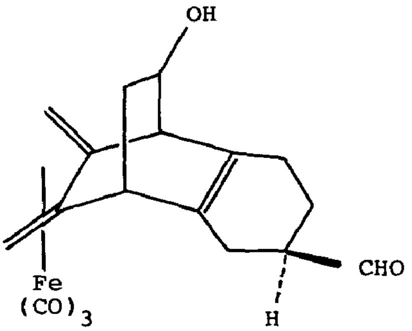

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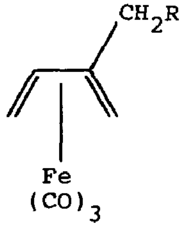
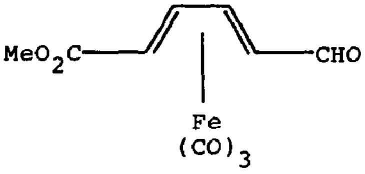


10.24

syntheses of the η-diene-Fe$(CO)_3$ complex (10.22) and its tosylate and benzoate derivatives have been reported. The large size of the endo-substitutent and the benzoate groups ensured that the ester underwent highly para regioselective Diels-Alder additions with methyl propynoate, butynone and 1-cyanovinylacetate. Addition of the complex (10.22) to methylvinyl ketone in the presence of BF_3-Et_2O was stereo- and para-regioselective to give the adduct (10.23) [202].

Tricarbonyl(η-2-ethoxycarbonylbuta-1,3-diene)iron has been resolved by enantioselective hydrolysis using pig liver esterase to form the enantiomers of the corresponding acid in good optical purity [203]. Tricarbonyl(η-isoprene)iron has been deprotonated with $LiN(CHMe_2)_2$ to give an anion which combined with aldehydes, ketones and other electrophilic reagents to give the appropriate derivatives. Thus benzyl bromide and Me_2C=CHCHO gave the products [10.24; R = CH_2Ph and $CH(OH)CH{=}CMe_2$]. Oxidative decomplexation afforded the free ligands which were sex pheromones of the bark beetle [204]. The (η-butadiene)iron complex (10.25) has been treated with CH_2ClI and n-butyl-lithium to give the complexed *exo*- and *endo*-chlorohydrins (10.26 and 10.27) which decomplexed and converted to the corresponding epoxides [205].

Treatment of (η^4-PhCH=CHCH=NPh)$Fe(CO)_3$ with aryllithium reagents followed by alkylation with Et_3OBF_4 gave the dicarbonyliron complexes (10.28; R = H, *m*-Me, *p*-CF_3). These products (10.28) combined with Lewis bases to give η^2-olefin carbene complexes [206]. Treatment of the η-limonene complex (10.29) with aryllithium reagents RLi, where R = C_6H_5, *o*-, *p*-MeC_6H_4, *p*-$MeOC_6H_4$ and *p*-$CF_3C_6H_4$, afforded acylmetallate intermediates. Alkylation of these intermediates with Et_3OBF_4 produced the carbene complex (10.30) or the rearranged products (10.31; R = H, Me, OMe, CF_3) [207]. The Friedel-Crafts acetylation of



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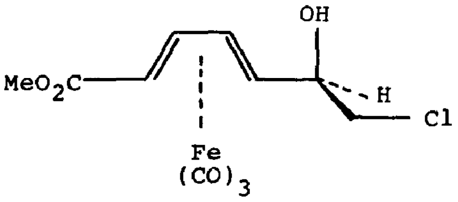

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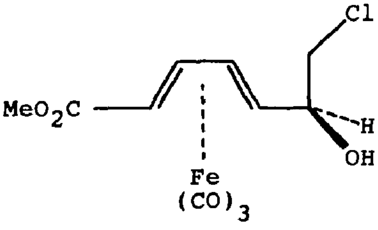

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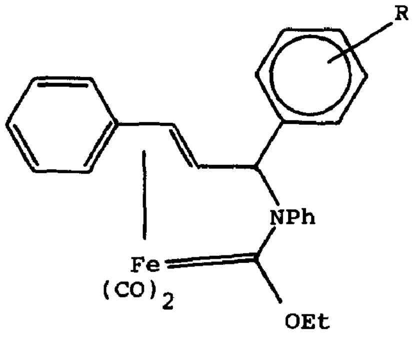

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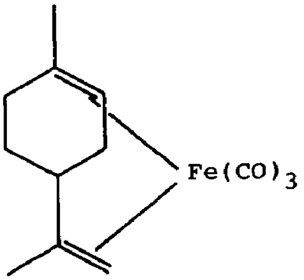

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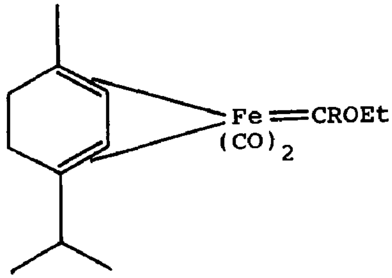

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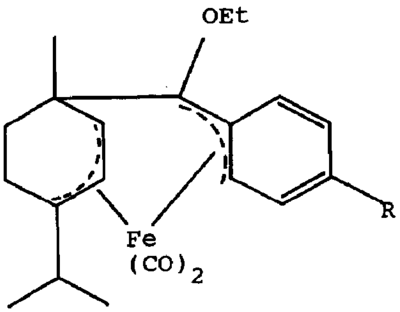

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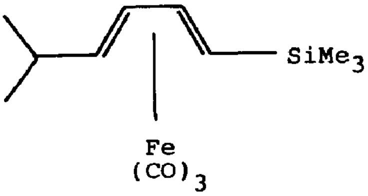

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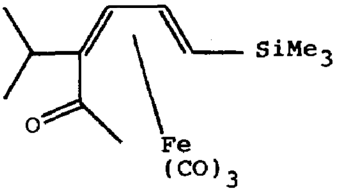

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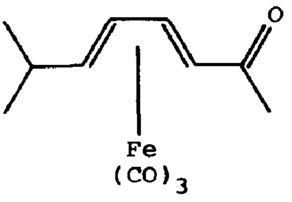

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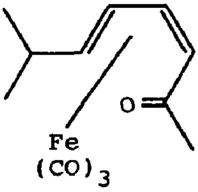
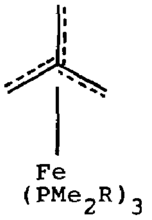


10.35

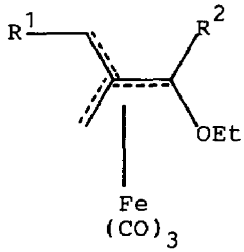
1-silylated and 1,4-disubstituted tricarbonyl(η-butadiene)iron complexes has been examined. Terminal acylation was observed in the presence of a 1-trimethylsilyl group. When the second terminal position was also substituted then acetyldesilylation was observed. Thus the 1,4-disubstituted complex (10.32) gave the principal products (10.33, 10.34 and 10.35) on acetylation [208]. The thermal decomposition of a butadiene-styrene block copolymer with an iron tricarbonyl complex gave, initially, iron(O) species bonded to two polymer chains. Further heating gave iron(II) species associated with organic anions [209].

11. (η-Trimethylenemethane)Fe(CO)$_3$ and (η-C_4H_4)Fe(CO)$_3$ complexes

(η-Trimethylenemethane)iron complexes (11.1; R = Me, Ph) have been prepared from $CH_2{=}C(CH_2Cl)_2$ and $FeCl_2(PMe_2R)_2$. The phosphine ligands enhanced the transfer of electron density from the iron atom to the η-trimethylenemethane group. Oxidation of these complexes (11.1) has been investigated by cyclic voltammetry. The cation obtained from the trimethylphosphine complex (11.1; R = Me) has been characterized by X-ray crystallography.



11.1



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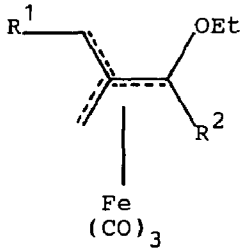
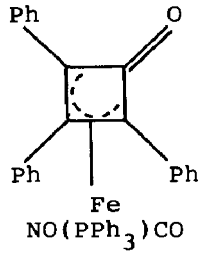


11.3

(η^4-o-Xylylene)iron phosphine complexes have been prepared and studied by electrochemistry [210]. The methylenation of the allenes $H_2C{=}C{=}CHR^1$ (R^1 = H, Ph, OMe) by the carbene-iron complexes $(CO)_4Fe{=}C(OEt)R^2$ (R^2 = Ph, Me) afforded the corresponding η-trimethylenemethane complexes (11.2 and 11.3) [211]. Reaction of the η^3-oxocyclobutenyl complex (11.4) with $[Me_3O][BF_4]$ afforded the η^4-cyclobutadiene complex (11.5). The structure of this



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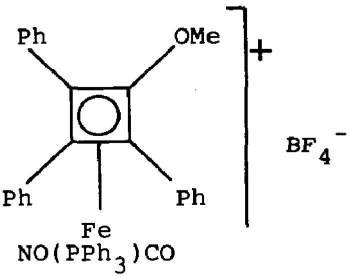

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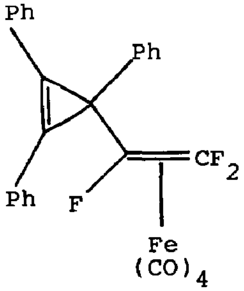

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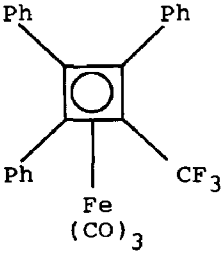


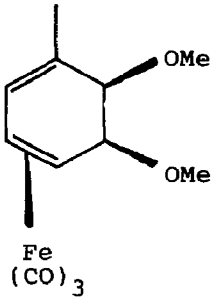
11.7

latter complex was confirmed by X-ray analysis [212]. The (η-vinylcyclopropene)iron complex (11.6) underwent ring expansion on irradiation to give the (η-cyclobutadiene)iron complex (11.7) [213].

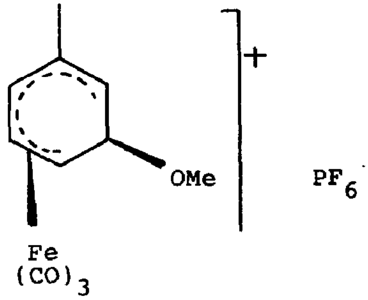
12. (Cyclic-η-diene)Fe(CO)$_3$

(i) Formation

Reaction of the dimethyl ether of 1-methylcyclohexa-1, 3-diene-5,6-diol with $Fe_2(CO)_9$ produced the corresponding tricarbonyliron complex (12.1) as a single stereoisomer. Treatment of this complex with Ph_3CBF_4 preferentially removed the less hindered OMe group to give a 5:1 mixture of the complexes (12.2 and 12.3) together with the dienone complex (12.4) [214]. Nonacarbonyldiiron combined with di-tert-butoxyethyne to give [η-tetra(tert-butoxy)cyclopentadienone]tricarbonyliron which has been characterized by X-ray diffraction. Hydrolysis of the complex with trifluoroacetic acid formed [η-(tetrahydroxy)cyclopentadienone]tricarbonyliron [215]. Three moles of ethyne and



12.1



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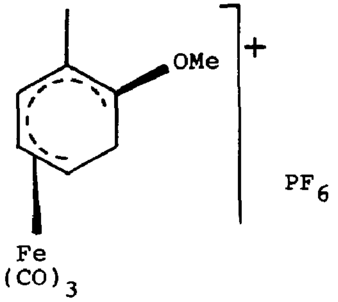

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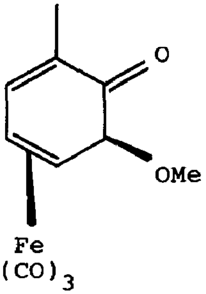

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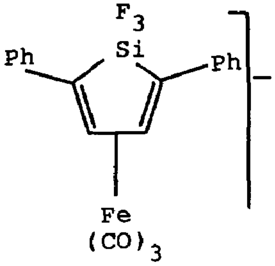
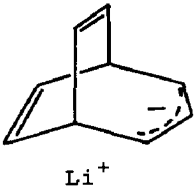


12.5

one of carbon monoxide combined together at a di-iron centre to give tropone as a di-iron complex [216]. Diazadiene derivatives of (η^6-cycloheptatriene)ruthenium have been prepared and characterized. The complexes were used as stereospecific catalysts for alkene isomerization [217].

The anionic (η-silacyclopentadiene)iron complex (12.5) has been prepared and characterized by X-ray crystallography as the potassium 18-crown-6 salt. The complex (12.5) was shown to be fluxional by ^{1}H and ^{19}F NMR spectroscopy [218]. Bis-(acetonitrile)dichloro(cycloocta-1,5-diene)ruthenium(II) monohydrate has been prepared and the structure was determined by X-ray analysis. The coordination geometry was irregular octahedral with the acetonitrile ligands trans to each other [219]. 1,3-Cyclohexadiene has been used in the preparation of η^4-diene, η^5-dienyl and η^6-arene complexes of ruthenium, osmium and iridium. For example, treatment of 1,3-cyclohexadiene with Na_2OsCl_6 in the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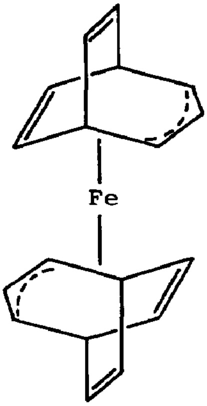
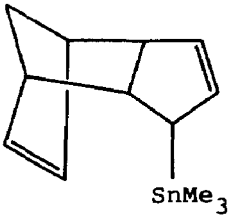

12.7

presence of tin(II) chloride produced (η^4-cyclohexadiene)(η^5-cyclohexadienyl)(trichlorostannyl)osmium [220].

Reaction of the lithium salt (12.6) with iron(II) chloride produced the iron complex (12.7) which was a ferrocene analogue with separated allyl and olefin systems. X-Ray analysis indicated that the complex (12.7) was centrosymmetric which implied opposite orientation of the two η^5-bicyclo[3.2.2]nona-2,6,8-trien-4-yl ligands to each other. The complex was less thermally stable than ferrocene and decomposed above 50°C [221]. Treatment of trimethyl(dicyclopentadiene)tin (12.8) with methyllithium produced lithium cyclopentadienide and dicyclopentadiene. When the same reaction was carried out in the presence of iron(II) chloride the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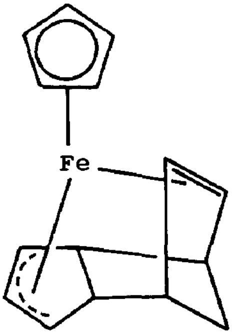
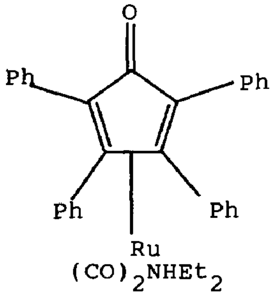

12.9

iron complex (12.9) was isolated. The crystal structure of this latter complex was determined and the electrochemical properties were investigated via cyclic voltammetry [222]. The η^4-tetraphenylcyclopentadienone complex (12.10) was prepared by the reaction of tricarbonyl(η^4-tetraphenylcyclopentadienone)ruthenium with diethylamine. The structure of the complex (12.10) was determined by X-ray analysis and the ruthenium atom possessed pseudotetrahedral geometry [223].



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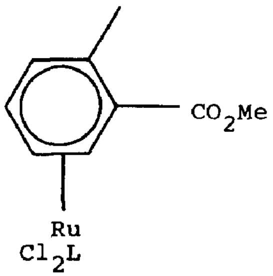
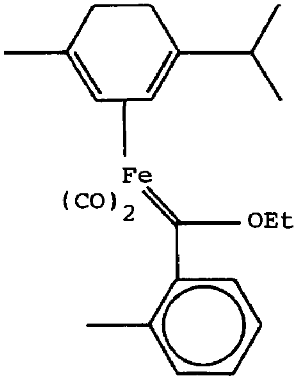


12.11

The dinuclear arene complex [RuCl$_2$(η-*o*-MeC$_6$H$_4$CO$_2$Me)]$_2$, has been prepared and has shown planar chirality with respect to the face of the coordinated arene. With coordinating solvents the complex gave the mononuclear species (12.11; L = MeCN, Me$_2$SO) which were racemic mixtures of enantiomers [224].

(ii) Spectroscopic and Physico-chemical Studies

An INDO MO approach has been used in a theoretical study of the cation $[(\eta\text{-}C_8H_{13})Fe(PH_3)_3]^+$ as a simplified model for the phosphite $\{(\eta\text{-}C_8H_{13})Fe[P(OMe)_3]_3\}^+$. Iron was found to be in oxidation state 2+ and the C_8H_{13} ring behaved as an η^4-ligand with three π-conjugated carbon atoms [225]. Tricarbonyl(η-limonene)iron has been treated with aryllithium reagents, such as *o*-tolyllithium, to give the (η-cyclohexadiene)iron carbene complex (12.12). Iron complexes with cyclohexenyl ligands were also obtained. The carbene complex (12.12) was characterized by X-ray crystallography [207, 226]. The mixed iridium iron complexes (12.13; X = CO,PPh$_3$) have been prepared and characterized. ^{13}C NMR spectroscopy was used to demonstrate the fluxional behaviour of the complexes [227]. Kinetic studies have been carried out on the addition of phosphine and phosphite nucleophiles to the



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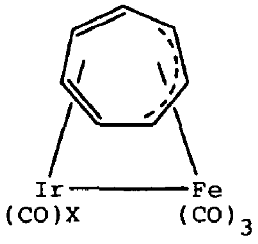
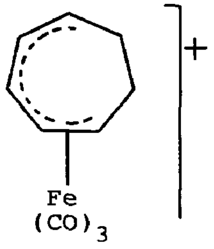


12.13

cation (12.14) to give exo-phosphonium adducts [12.15; PR_3 = $P(2\text{-}MeOC_6H_4)_3$, $P(4\text{-}MeC_6H_4)_3$,$P(4\text{-}MeC_6H_4)Ph_2$, PPh_3, $P(2\text{-}CNC_2H_4)Ph_2$, $P(2\text{-}CNC_2H_4)_3$, $P(OBu)_3$]. The results obtained were combined with those obtained earlier with amine and anionic nucleophiles to give a nucleophilic order for attack upon the cation (12.14) [228].

An extensive nucleophilicity scale has been developed for the addition of above 40 nucleophiles to the (η-cyclohexadienyl)-iron cation (12.16). The factors influencing nucleophilicity have been discussed [229]. Kinetic studies on the reversible addition of pyridines to the cation (12.17) to give the η^4-diene



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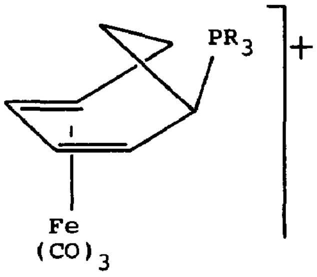

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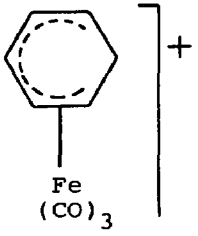

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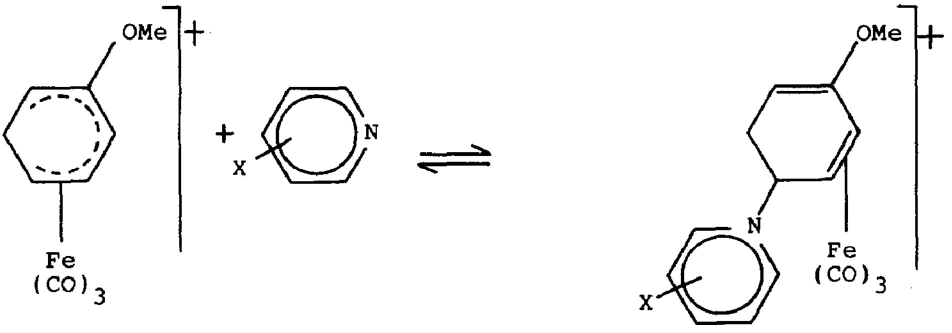
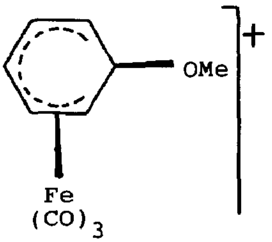


12.17

12.18

complexes (12.18; X = H, 2-Me, 3-Me, 4-Me, 4-Ph, 2-Cl, 3-CN, 2-CHO, 4-$COCH_3$, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-Me_2 and 2,4,6-Me_3) have been carried out. The results indicated that the rate of the reaction was dependent on the steric and electronic nature of the attacking nucleophile [230]. Benzene underwent microbial oxidation to cyclohexa-1,3-diene-5,6-diol and this was converted to the dimethyl ether and then to the (η-cyclohexadienylium)iron cation (12.19) by complexation and demethoxylation. The stereochemistry of the cation (12.19) was confirmed by relating it to the endo, exo-dimethoxy complex (12.20) [231]. Pyridines under-



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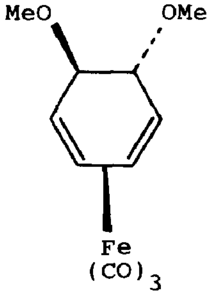

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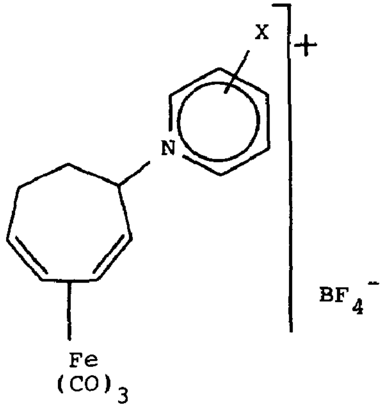
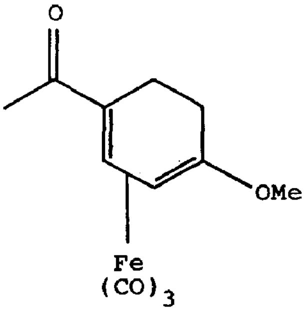


12.21

went reversible addition to the tricarbonyl(η-cycloheptadienyl)-iron cation to give the (η-cycloheptadiene)iron complexes (12.21; X = 2-Me, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-Me_2, 2-CHO, 4-Ac). Rate constants were measured and rate dependence on amine basicity was observed [232].

(iii) General Chemistry

Reaction of the (η-cyclohexadiene)$Fe(CO)_3$ complex (12.22) with Ph_3CBF_4 or $Tl(CF_3CO_2)_3$ afforded the corresponding cation (12.23). Reaction with $NaBH_4$ in methanol followed by $Tl(CF_3CO_2)_3$ gave the alcohol (12.24) [233]. The cation (12.25) has been used as a protecting group in peptide synthesis. Treatment with equimolar amounts of glycine ethyl ester and diisopropylamine gave the N-protected ester (12.26). This was coupled with N-t--butoxy-alanine in the presence of dicyclohexyl carbodiimide to give the full protected peptide (12.27) in good yield. The



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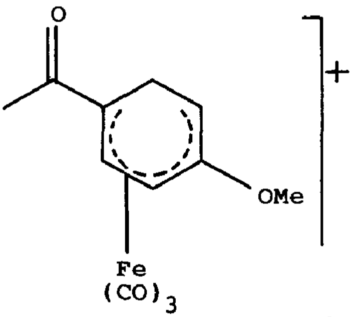

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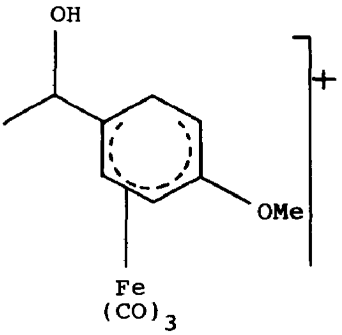

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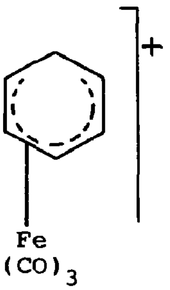

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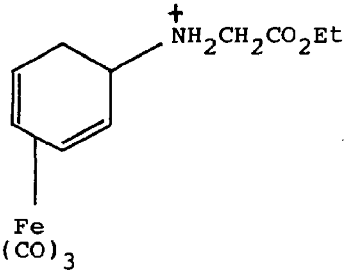

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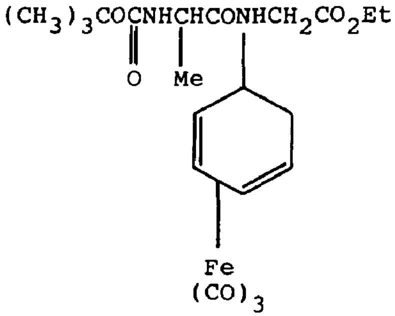
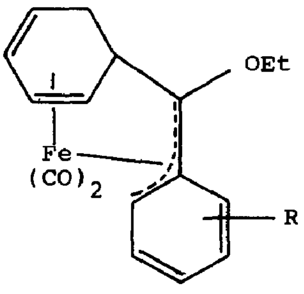


12.27

$[Fe(CO)_3(C_6H_7)]^+$ protecting group was easily removed and recovered by room temperature treatment of the peptide (12.27) with trifluoroacetic acid [234]. Aryllithium reagents combined with tricarbonyl(η-cyclohexadiene)iron in diethyl ether at -60°C to give, after alkylation with $Et_3O.BF_4$, the ethoxy-arylcarbene iron complexes (12.28; R = H, 3-, 4-Me, 4-MeO, 4-CF_3). The crystal and molecular structure of one complex (12.28; R = H) was determined by X-ray crystallography [207, 226, 235].

Optically pure tricarbonyl(η-2,4-cycloheptadienonium)iron (12.29) has been prepared from tricarbonyl(η-tropone)iron by way of the l-menthoxy derivatives [236]. Reaction of the bis(tricarbonyliron) complex (12.30) with $Me_3NO.2H_2O$ afforded the corres-



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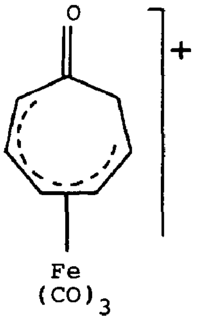

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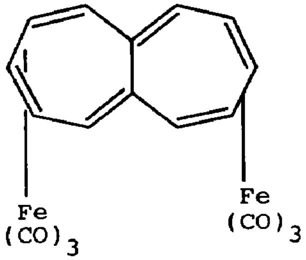

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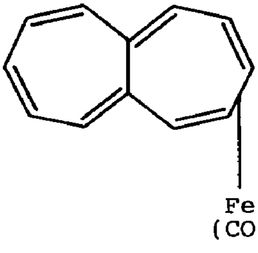

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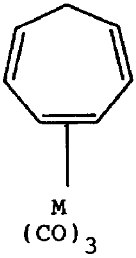

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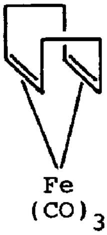

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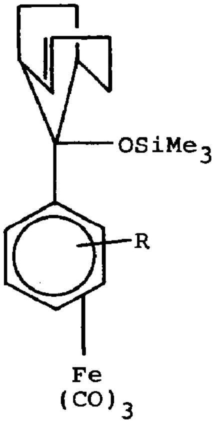

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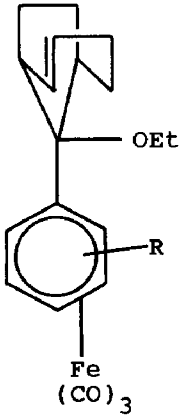

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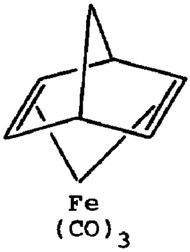
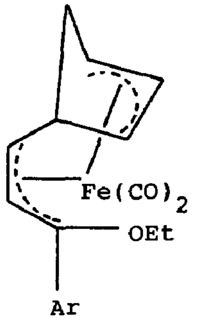


12.36

ponding tricarbonyliron complex (12.31). The structure of this latter compound was determined by X-ray analysis. NMR spectroscopy showed that the complexes (12.30 and 12.31) underwent isodynamic 1,2-migration of the $Fe(CO)_3$ groups together with carbonyl scrambling [237]. The (η-cycloheptatriene)metal complexes (12.32; M = Cr, Mo, W) have been used as reagents for the preparation of dimethyl(trimethylsiloxymethyl)phosphine complexes [238]. Deprotonation of tricarbonyl(η^4-cycloheptatriene)ruthenium gave the tricarbonyl(η^3-cycloheptatrienyl)ruthenium anion which combined with triphenyltin chloride to form a fluxional triphenyltin derivative [239].

Treatment of the η-cycloocta-1,5-diene complex (12.33) with aryllithium reagents LiC_6H_4R, R = H, m-Me, p-Me, p-Ph, followed by alkylation with Me_3SiCl or Et_3OBF_4 gave the corresponding η^6-arene complexes (12.34; R = H, m-Me, p-Me, p-Ph and 12.35; R = H, p-Me). The structure of the complex (12.34; R = p-Me) was determined by X-ray analysis [240]. Treatment of tricarbonyl-(η-norbornadiene)iron (12.36) with ArLi, where Ar = $p\text{-}CH_3C_6H_4$, $o\text{-}CH_3C_6H_4$, $p\text{-}CF_3C_6H_4$, followed by alkylation of the intermediate acylmetallates with Et_3OBF_4 gave the corresponding ring-opened diallyl complexes (12.37). When the complex (12.37; Ar = $p\text{-}CF_3C_6H_4$) was heated in a sealed tube the acyclic 1,3-diene-$Fe(CO)_3$ complex (12.38) was obtained [241]. Reaction of tricarbonyl(η^4-1,5-cyclooctadiene)iron with RC_6H_4Li, where R = H, 3- and 4-Me, 4-Ph, followed by treatment with Me_3SiCl or Et_3OBF_4 produced the



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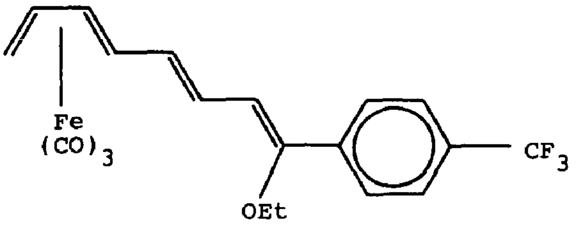

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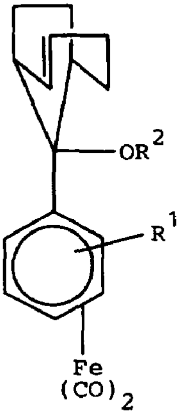

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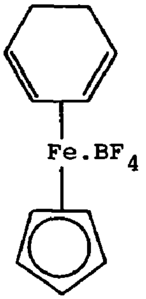
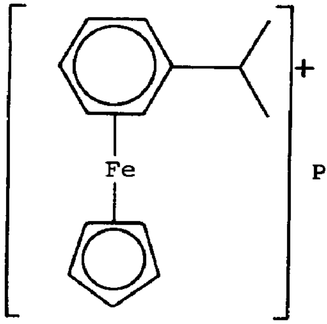


12.40

corresponding η^6-arene complexes (12.39; R^1 = H, 3- and 4-Me, 4-Ph; R^2 = $SiMe_3$, Et). Removal of the dicarbonyliron group from the η^6-arene ligand was effected with ammonium hexanitratocerate(IV) [242]. Treatment of (η-cyclohexadienyl)(η-cyclopentadienyl)iron with fluoroboric acid gave the (η-cyclohexadiene)-iron complex (12.40) which was characterized by ^{19}F NMR spectroscopy. The BF_4^- and cyclohexadiene ligands underwent stepwise displacement by Me_2S, Me_2Se and Me_2Te [243].

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

A process for the preparation of [(η^6-arene)(η^5-cyclopentadienyl)iron]PF_6 complexes has been reported. For example, the reaction of ferrocene with cumene in the presence of aluminium, aluminium chloride and titanium(IV) chloride gave $(\eta\text{-}C_5H_5)_2TiCl_2$ and the complex (13.1) after treatment with potassium hexafluorophosphate [244]. Intramolecular ligand exchange in the dichlorides (13.2; M = Rh, Ir) or the corresponding dicarbonylcobalt complex produced the bridged cations (13.3; M = Rh, Ir, Co). An analogous bridged dimethylpropane-ruthenium complex was also prepared [245]. Several reactions of the chlorine bridged complex $[(\eta\text{-}C_5Me_5)RuCl]_2$ have been explored, treatment with hexamethylbenzene and then ammonium hexafluorophosphate gave the (η-hexamethylbenzene)ruthenium cation (13.4) [246]. Reduction of $[(\eta\text{-}C_5Me_5)RuCl_2]_n$ which combined with arenes to give the sandwich complexes $[(\eta\text{-}C_5Me_5)Ru(\eta\text{-arene})]^+$, where arene = benzene, pyridine, 2,6-lutidene, 3,5-lutidene, 3-methylthiophene, furan [247].



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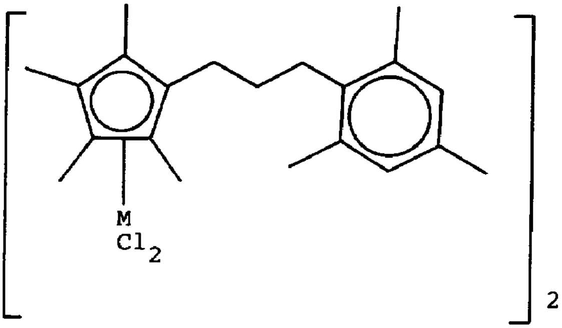

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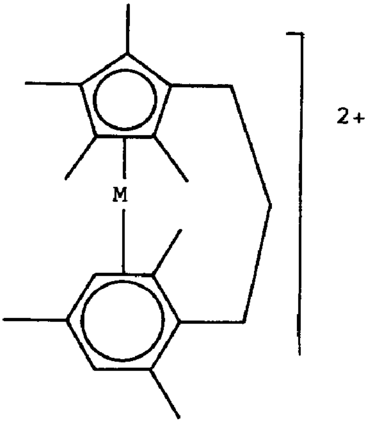

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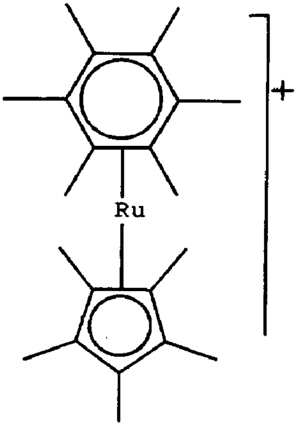

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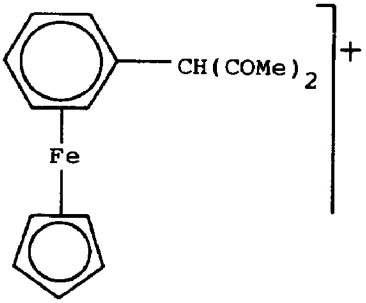

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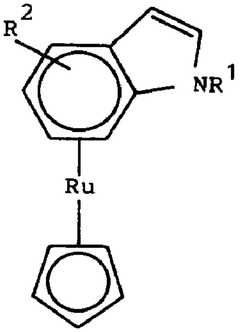

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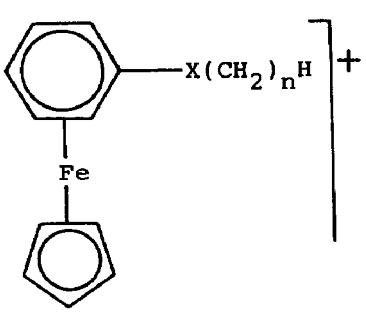

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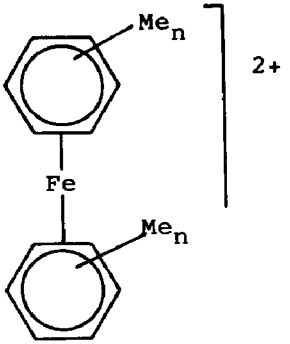

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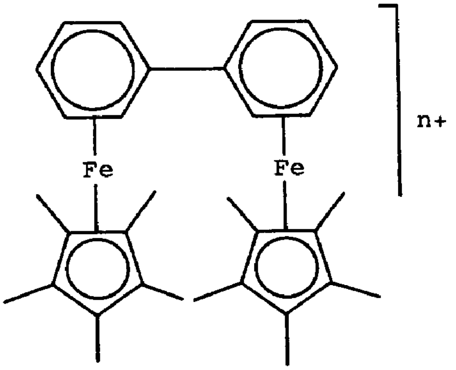

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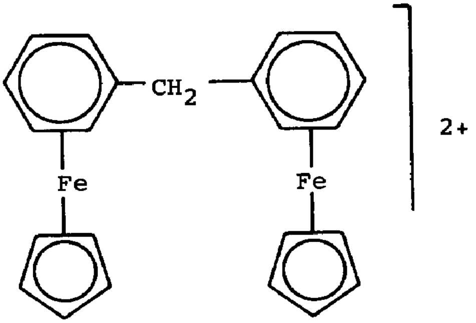

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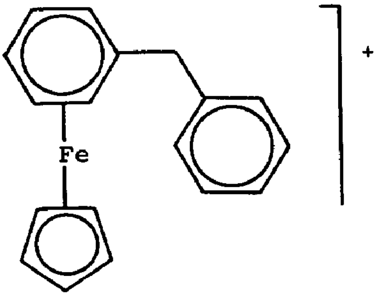

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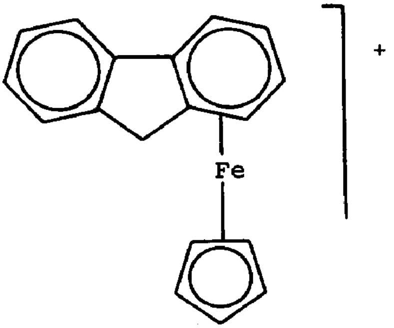
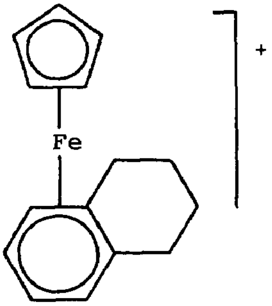


13.12

The binuclear ruthenium complex $[Ru(\eta-C_6Me_6)Cl_2]_2$ combined with closo-$B_{10}H_{10}^{2-}$ to give the closo-metallaborane $1-(\eta-C_6Me_6)-1-RuB_{10}H_{10}$ [248].

β-Diketones, such as 2,4-pentadione, underwent arylation with (η-arene)(η-cyclopentadienyl)iron cations to give products such as the (η-arene)iron cation (13.5) [249]. Sandwich complexes have been formed from toluene, thermally generated iron atoms and thiaboranes [250]. The indole ruthenium complexes (13.6; R^1 = H, Me; R^2 = H, 4-, 5-Cl, 5-Br) have been prepared from $[(\eta-C_5H_5)Ru(NCMe)_3]PF_6$ by substitution with the appropriate indole. The complexes (13.6; R^1 = Me; R^2 = 4-, 5-Cl) underwent displacement of chloride by the anions of $CH_2(CO_2R)_2$, $HSCH_2CO_2H$ and $PhCH_2OH$ [251,252]. Several different procedures have been used to prepare long-chain alkyl substituted (η-benzene)iron cations such as the complexes (13.7; X = CO_2, n = 8; X = CONH, n = 12) which were surface active [253]. Tetracyanoquinodimethane salts $[(\eta-C_5H_5)Fe(\eta-arene)]^+(TCNQ)_2^-$, where arene = 2,4,6-$C_6H_3Me_3$, C_6Me_6 and C_6Et_6, have been prepared and characterized. The complexes contained 1-dimensional stacks of organometallic cations and TCNQ anions. Electric transport properties were determined [254].

The (η-benzo[b]thiophene)(η-cyclopentadienyl)ruthenium cation has been prepared and used as a model for the adsorption of thiophenes on hydrodesulphurization catalysts. The tetrafluoroborate salt of the cation has been characterized by X-ray crystallography



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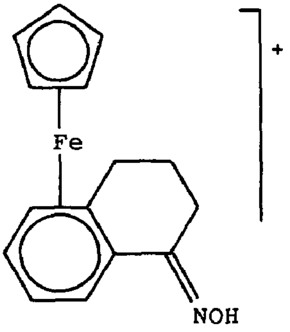

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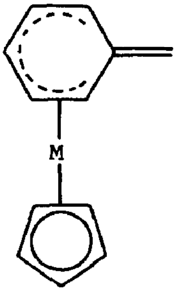
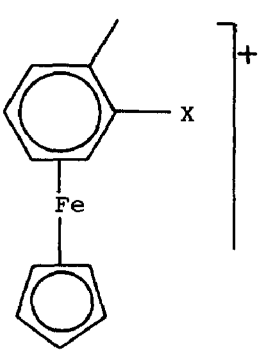


13.15

[255]. The bis(η-arene)iron dications (13.8; n = 3, 5, 6) underwent ethylation with triethylaluminium to give the corresponding (η-cyclohexadienyl)iron cations. Increased substitution of the arene ring facilitated the alkylation. Two of the products were characterized by X-ray crystallography [256]. Organo-iron complexes containing polyaromatic bridging ligands, for example, the complex (13.9; n = 0-2) have been studied in the solid state by Moessbauer spectroscopy. The complexes where n=0, with formally 38 electrons in the coordination spheres of the iron atoms, had temperature independent quadrupole splitting and isomer shift values. The two additional electrons available to the iron atoms were mostly located on the polyaromatic bridge [257]. Eight bis(η-arene)iron(II) compounds have been investigated by Moessbauer spectroscopy. The results indicated that these complexes were covalently paramagnetic [258].

The electronic spectrum of the binuclear dication (13.10) showed a large bathochromic shift by comparison with the mononuclear cation (13.11). The shift was rationalised in terms of redistribution of charge in the ligand and structural changes [259]. Variable temperature cross polarization ^{13}C NMR spectroscopy has been used to demonstrate phase transitions between three different crystal forms of the (η-benzene)(η-cyclopentadienyl)iron cation [260]. Fast cyclic voltammetry has been used to study the electron transfer kinetics in the electrochemical reduction of forty nine (η-arene)- and (η-heterocycle)-iron(η-cyclopentadienyl) complexes. Rate constants obtained indicated that the second of the two reduction steps was relatively fast and this was ascribed to extensive electron delocalization in the twenty-electron complexes [261]. The electric and magnetic properties of the salts $[(\eta-C_5H_5)FeAr]^+[(\text{tetracyanoquinodimethane})_2]^-$, where Ar = 2,4,6-$C_6H_3Me_3$, C_6Me_6, C_6Et_6, have been investigated. The salts exhibited quasi-semiconducting properties and the magnetic properties were determined by the non-paired electrons of the tetracyanoquinodimethane [262].

Mono- and di-nuclear (η^5-cyclopentadienyl)(η^6-thianthrene)iron cations have been the subject of an electrochemical study. The effect of solvent on the reduction process was explored [263]. The (η-arene)iron complexes $(\eta-C_6R^1_6)Fe(\eta-C_5R^2_5)$, with one to six alkyl groups on the arene ligand, have been used to investigate the activation of benzylic C-H bonds by O_2 in organic solvents.



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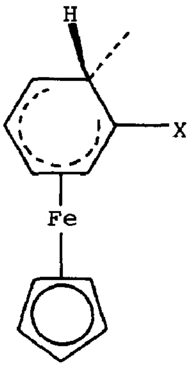

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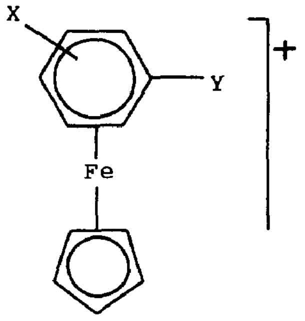

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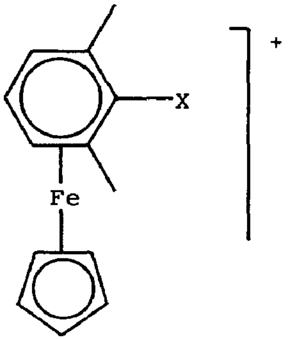

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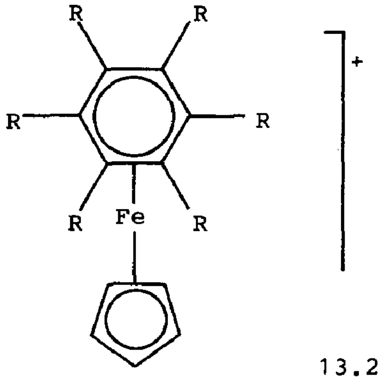
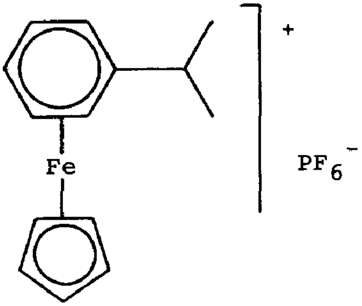


13.20

The superoxide anion $O_2^{\cdot-}$ was generated under these conditions and its reactivity was examined [264]. Classical polarography and electrolysis at a controlled potential have been used to study the cation (13.12). Three cathodic waves were obtained on the polarogram of the tetrafluoroborate salt of complex (13.12). The product of reduction was (η^6-fluorene)(η^5-cyclopentadienyl)iron. An electrolysis at the potential of the limiting current of the first wave, (η^6-fluorenyl)(η^5-cyclopentadienyl)iron was obtained and when this was heated it converted to (η^5-fluorenyl)(η^5-cyclopentadienyl)iron [265].

The photochemical removal of the arene ligand has been studied in the complexes $[(\eta^6\text{-arene})M(\eta^5\text{-}C_5H_5)]^+$ where M = Fe and arene = p-dichlorobenzene, benzene, toluene, p-xylene, mesitylene, durene, pentamethylbenzene, hexamethylbenzene, hexaethylbenzene and tri-*t*-butylbenzene; and M=Ru, arene = a similar range of substituted benzenes. The quantum yields were determined and the photoactive state was the a^3E_1 ligand field excited state [266]. Deprotonation of the cation (13.13) with potassium t-butoxide followed by treatment with menthyl nitrite produced the optically active oxime (13.14). Hydrolysis of the oxime group afforded the corresponding chiral ketone. The stereoselectivity of the cathodic reductions of the oxime (13.14) and the corresponding ketone to give the optically active *endo*-amine and optically active *endo*-alcohol respectively were studied [267].

Deprotonation of the iron and ruthenium cationic complexes $[(\eta\text{-}C_6H_5Me)M(\eta\text{-}C_5H_5)]^+$, where M = Fe, Ru, gave the corresponding (η-cyclohexadienyl)metal complex (13.15; M = Fe, Ru) which was attacked by alkyl halides [268]. The (η-arene)iron cations (13.16; X = Cl, CN, NO_2, $SO_2C_6H_4Me$) have been reduced with sodium borohydride to give the C2,3,4,5 or 6 *exo*-adducts, such



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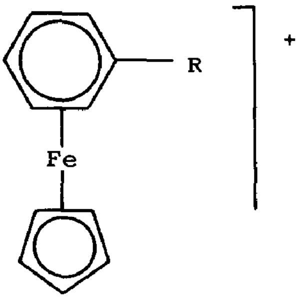


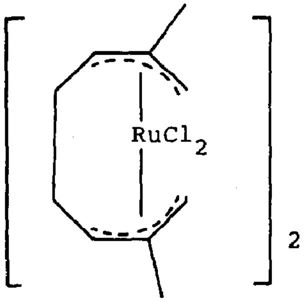
13.22

as the C2 adducts (13.17; X = Cl, CN, NO_2, $SO_2C_6H_4Me$). The cyanide and acetonyl anions also underwent addition to give only *ortho*-products indicating steric hindrance by the 2-methyl group [269]. The (η-arene)iron cations (13.18; X = *p*-Me, *o*-, *m*-, *p*-Cl; Y = Cl) underwent nucleophilic substitution with carbanion nucleophiles to give the products [13.18; X = *p*-Me, *o*-, *m*-, *p*-Cl; Y = $CH(CO_2Et)_2$, $CH(CO_2Ph)_2$, $CH(COMe)CO_2Et$, CH_2COMe]. The sterically hindered (η-arene)iron cations (13.18; X = Cl, NO_2) were attacked by nitrogen, oxygen and carbon nucleophiles to give products such as the cations [13.19; X = NH_2, $NHMe_2$, OPh, $CH(COMe)CO_2Et$] [270].

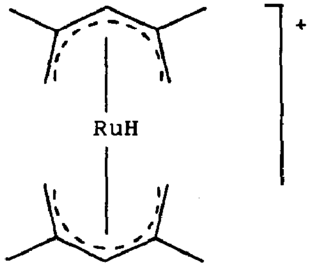
The cationic (η-arene)iron complex (13.20; R = Me) has been alkylated with allyl bromide to form the hexaallyl derivative (13.20; R = $CH_2CH_2CH{=}CH_2$) which was degraded to the free arene ligand and subjected to hydrosilylation and hydroboration at the allyl groups [271]. The reactivity of diphosphaferrocenes towards aluminium(III) chloride in aromatic solvents has been explored. When a 2-acyl group was present then (η-arene)-(η-phosphacyclopentadienyl)iron cations were formed [272]. The η-cumene complex (13.21) has been used as one of the components in photohardenable material suitable for the production of images after exposure to a negative [273]. The (η-benzene)iron cation (13.22; R = H, Me, Cl) has been used as a catalyst for the photooxidation for furfural to methyl-2-furoate. The reaction was quantitative in the presence of methanol and hydrogen peroxide [274].

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

Treatment of the η^3: η^3-$C_{10}H_{16}$-ruthenium complex (14.1) with cyclopentadiene in the presence of $AgBF_4$ produced ruthenocene in moderate yield. When the same reaction was carried out with 2,4-dimethylpenta-1,3-diene the protonated open metallocene (14.2) was obtained [275]. Treatment of dichloro(η-pentamethylcyclo-

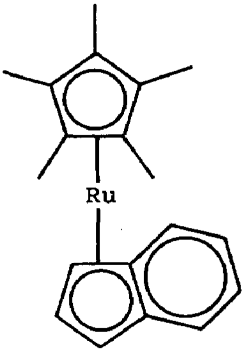


14.1

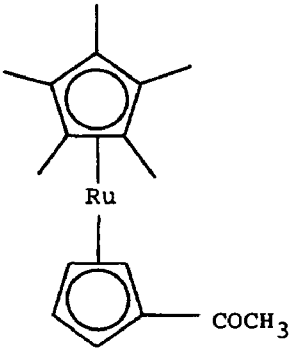


14.2

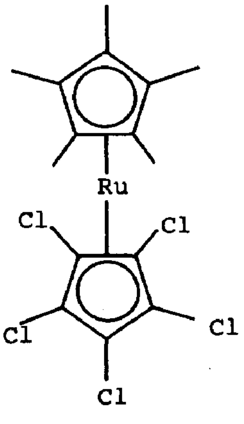
pentadienyl)ruthenium(III) oligomer with alkali metal salts of a series of cyclopentadienyl derivatives produced the unsymmetrical ruthenocenes (14.3, 14.4, 14.5 and 14.6). The electronic effects of the different ligands were studied electrochemically and by electron spectroscopy. The order of decreasing electron donating power was fluorenyl > pentamethylcyclopentadienyl > indenyl > cyclopentadienyl > acetylcyclopentadienyl > pentachlorocyclopentadienyl [276]. Reaction of some ferrocene amphetamine



14.3



14.4



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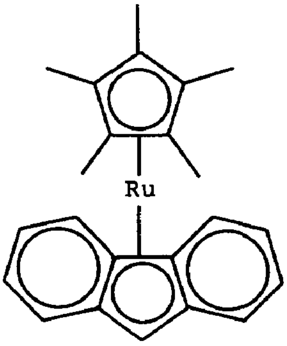
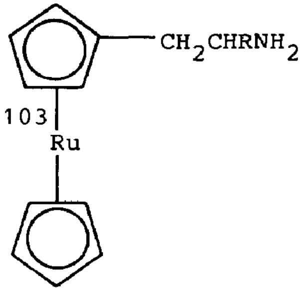


14.6

analogues with $^{103}RuCl_3$ gave the corresponding ruthenocene compounds (14.7; R = H, Me, Et) labelled with ^{103}Ru [277]. Reaction of the tetrabutylammonium salt $(Bu_4N)_2OsCl_6$ with cyclopentadiene or methylcyclopentadiene and zinc produced the osmocenes (14.8; R = H, Me) respectively. Treatment of the same salt or the oligomer $[(\eta\text{-}C_5Me_5)RuCl_2]_n$ with $Me_2C{=}CHCMe{=}CH_2$ afforded the corresponding open sandwich complexes (14.9 and 14.10) [278].



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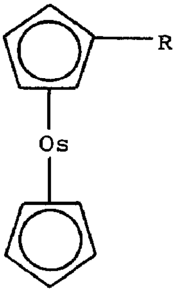

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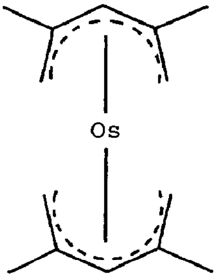

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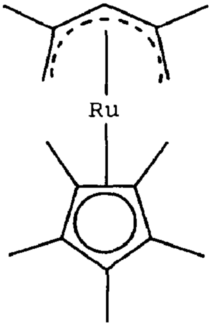
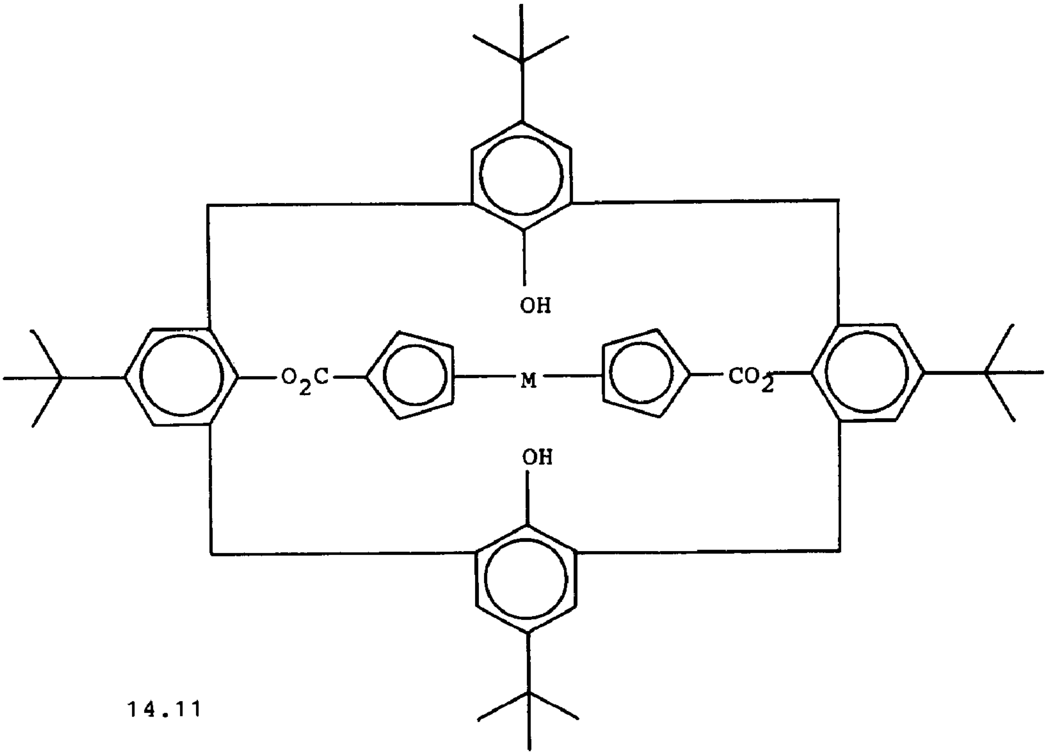


14.10

The condensation of 1,1'-bis(chlorocarbonyl)-ferrocene or -ruthenocene with p-tert-butylcalix[4]arene afforded the corresponding metallocene calix[4]arenes (14.11; M = Fe, Ru) [279]. The30-electron triple-decker complexes (14.12; M = Ru, Os) have been prepared and characterized [280]. X-ray analysis of the ruthenium complex (14.13) indicated that the molecule had a ruthenium hydride structure. Ring exchange reactions with the complex (14.13) were used to prepare the η-cyclopentadienyl complexes (14.14; R = H, Me). ^1H and ^{13}C NMR spectroscopy indicated an agostic interaction for the hydrogen atom in these molecules [281]. The ruthenocene adducts with Lewis acids such as iodine, mercury(II) chloride and tin(IV) chloride have been studied by Moessbauer spectroscopy and ^{13}C CP-MAS NMR spectroscopy. Chemical bonding between ruthenium and the Lewis acid was indicated [282].

Treatment of the alcohol (14.15) with acid HX, where X =



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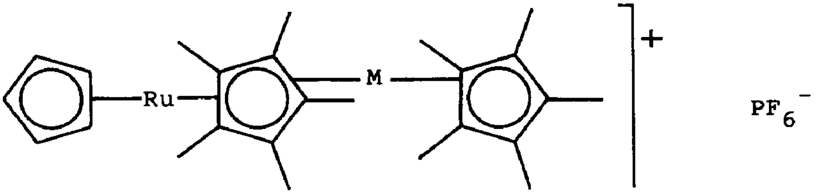

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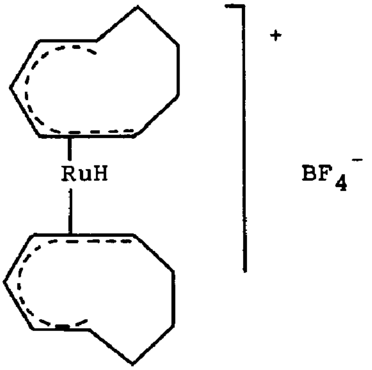

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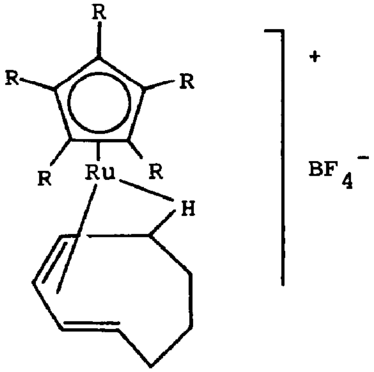
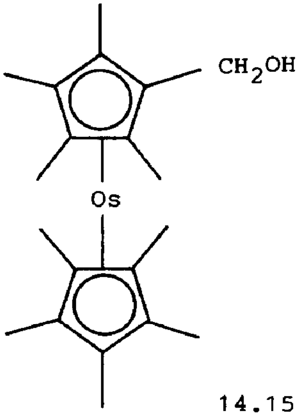
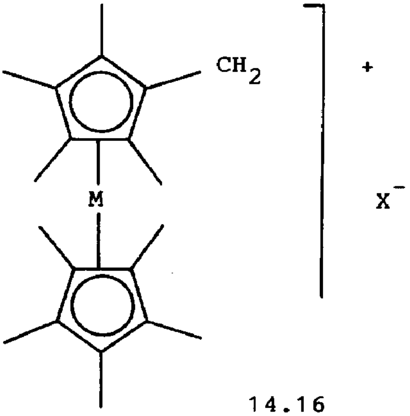


14.14

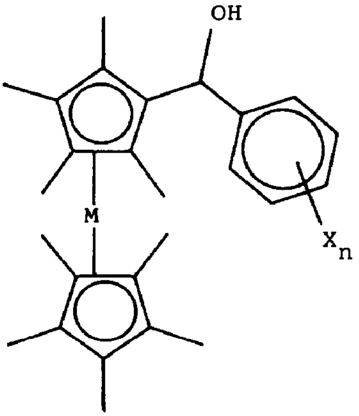


14.15

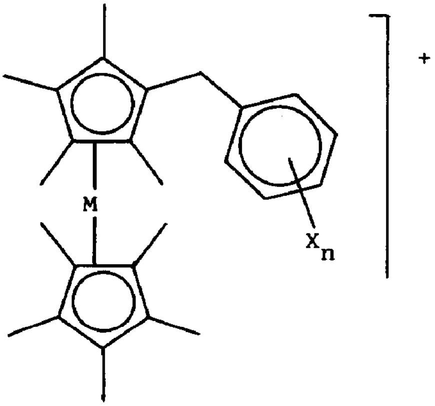


14.16

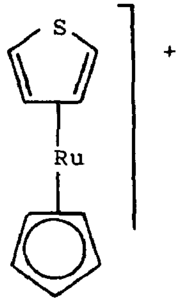
CF_3CO_2, BF_4or PF_6, gave the corresponding carbenium ion salts (14.16; M = Os). The stability of the cations (14.16; M = Fe, Ru, Os) increased in the order Fe < Ru < Os [283]. Treatment of the permethylated-ruthenocene and -osmocene carbinols (14.17; X_n = H_5, Me_3, F_5; M = Ru, Os) with trifluoroacetic acid and other strong acids gave the air stable carbocations (14.18; X_n = H_5, Me_3, F_5; M = Ru, Os). ^{1}H and ^{13}C NMR spectroscopy indicated that shielding by the carbenium centre increased in the order M = Fe < Ru < Os [284]. Reduction of the η^5-thiophene complex (14.19) with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ ("Red Al") gave the C-S cleaved butadiene-thiolate product (14.20). The reactions of this latter compound were investigated [285]. The organ distribution



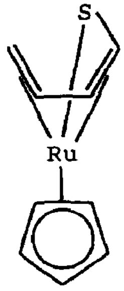
14.17



14.18



14.19



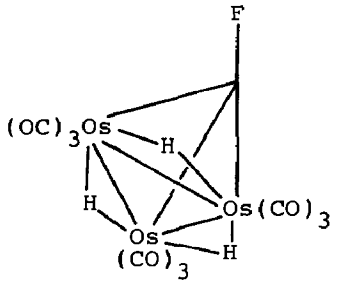
14.20

of the tropanol esters of metallocenylcarboxylic acids has been studied. The metallocenes examined were ferrocene, ^{103}Ru-ruthenocene and ^{103m}Rh-rhodocenium. The ruthenocene ester showed a high heart/blood ratio [286].

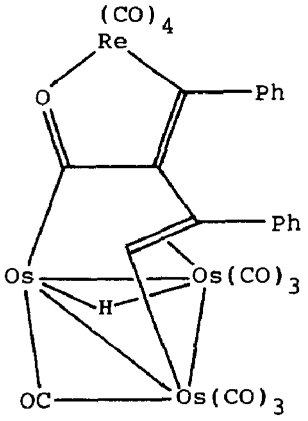
15. Iron-, Ruthenium- and Osmium-carbon Cluster Compounds

The mixed-metal ketenylidene cluster complex [bis(triphenylphosphine)nitrogen(1+)][$Fe_2Co(CO)_9CCO$] has been prepared and characterized by X-ray crystallography. It showed reactivity similar to that of the cationic cluster $[Co_3(CO)_9(CCO)]^+$ and underwent protonation at the α-carbon atom. Nucleophilic reagents attacked the β-carbon atom to give dinegatively charged species. Thus methyllithium gave the product $[Fe_2Co(CO)_9\{CC(O)Me\}]^{2-}$ [287]. The fluoroalkylidynetriosmium cluster complex (15.1) has been prepared and the ^{13}C and ^{19}F spectra of alkylidyne-triosmium, -tricobalt and -triiron complexes have been compared. There was evidence for low delocalization at the apical carbon in the osmium clusters by comparison with the cobalt clusters [288]. Photolysis of a mixture of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ and $Re_2(CO)_{10}$ generated the radical $H_3Os_3(CO)_9(\mu_3\text{-}C^{\bullet})$ which abstracted hydrogen from the cyclohexane solvent to give the cluster compound $H_3Os_3(CO)_9(\mu_3\text{-}CH)$. In cyclohexane-$\underline{d}_{12}$ the corresponding deuterated complex $H_3Os_3(CO)_9(\mu_3CD)$ was formed together with the diketone $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$ [289].

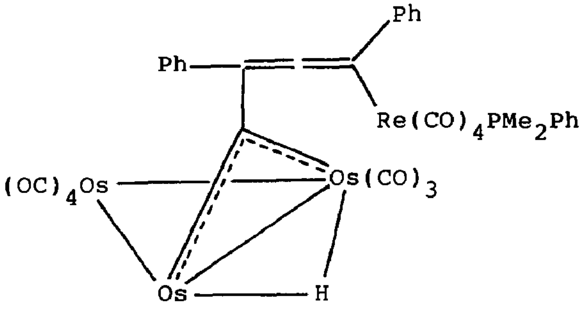
Diethylaminopropyne, $MeC{\equiv}CNEt_2$, combined with enneacarbonyldiiron at room temperature to give a di-μ_3-carbyne cluster in



15.1



15.2

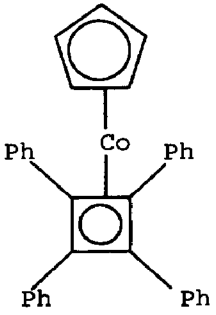


15.3

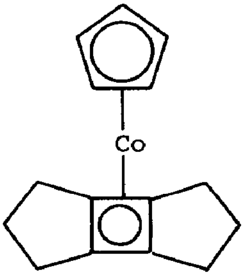
which the alkyne had been split into two fragments, μ_3-CMe and μ_3-C=NEt$_3$ [290]. Treatment of the osmium complex (15.2) with phenyldimethylphosphine produced the cluster compound (15.3) [291]. The dicarbonyl(η-methylcyclopentadienyl)manganese fragment has been incorporated into a carbyne-ethylidene cluster containing two iron atoms [292]. Ligand transformations on several 50-electron phosphido-bridged triruthenium clusters, such as the cluster complex $Ru_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C{\equiv}CR](\mu\text{-}PPh_2)$. have been reported. Thus the ligand $\mu_3\text{-}\eta^2\text{-}C{\equiv}CCHMe_2$ was attacked by CH_2N_2 to give the ligand $\mu_3\text{-}\eta^3\text{-}CH_2{=}C{=}CCHMe_2$, further reaction with CH_2N_2 gave a μ-CH_2 μ_3-diene cluster complex [293]. Isomerization of the triruthenium cluster complex containing the ligand $\mu_3\text{-}\eta^3\text{-}CH_2{=}C{=}CCHMe_2$ gave the ligand $\mu_3\text{-}\eta^4\text{-}CH{=}C(CHMe_2)C{=}CH_2$ while treatment with triphenylphosphine gave a phosphine cluster containing the ligand $\mu_3\text{-}\eta^4\text{-}CH_2{=}C(CHMe_2)C{=}CH_2$ [294]. The allenyl cluster $Ru_3(CO)_8[\mu_3\text{-}\eta^3\text{-}CH_2C{=}C(CHMe_2)](\mu\text{-}PPh_2)$ was converted by hydrogen at room temperature to a cluster containing the μ_3-η^2-MeC=CCHMe$_2$ ligand [295].

16. (η-C_4H_4)Co(η-C_5H_5)

Electrolysis of cyclopentadiene and tolan at a cobalt anode has been used to prepare the (η-tetraphenylcyclobutadiene)cobalt complex (16.1). Yields of 80% were obtained [296]. Cyclodeca-1,6-diyne combined with tricarbonyl(η-cyclopentadienyl)-cobalt and (η-cyclopentadienyl)(η-1,5-cyclooctadiene)cobalt to form binuclear and mononuclear (16.2) (η-cyclobutadiene)cobalt complexes [297]. Several (η-phosphacyclobutadiene)cobalt complexes have been prepared including the species (16.3 and 16.4; R = Me_3C, Me_2CH) [298]. The optically active η^4-2-formylnorbornadiene-rhodium complex (16.5) was resolved via fractional crystallization of the corresponding L-valine salts (16.6). The configuration of one of the enantiomers was determined by X-ray analysis [299]. Cerium(IV) oxidation of the cobalt complex (16.7) produced the diene (16.8). The chemistry of the diene (16.8) was investigated [300].



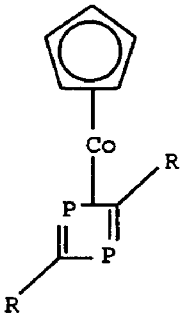
16.1



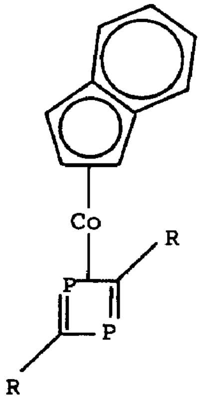
16.2

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

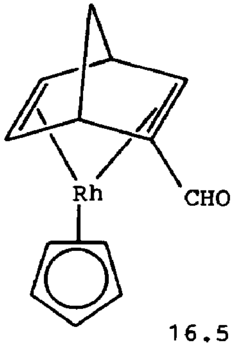
The bis(η-isodicyclopentadienyl)-cobalt and -nickel complexes have been prepared from isodicyclopentadienylthallium and the metal dihalide [301]. The cobaltocenium salts (17.1 and 17.2) have been prepared and characterized [302]. The cobaltocenium



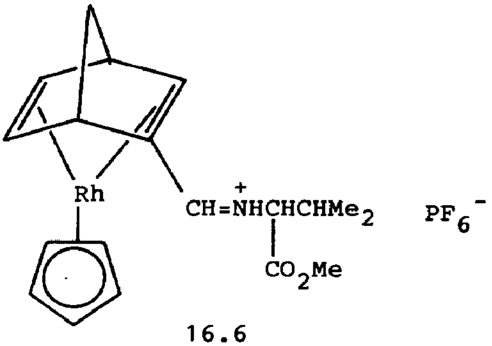
16.3



16.4



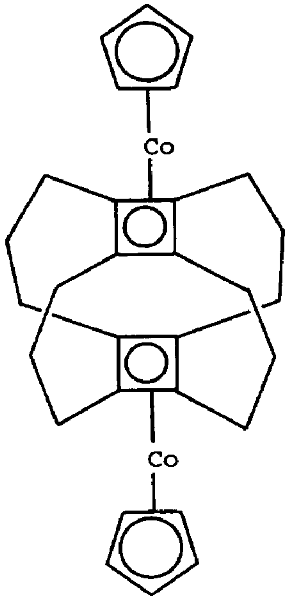
16.5



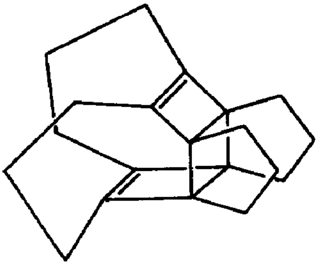
16.6

salts $[(\eta\text{-}C_5H_5)_2Co][(\eta\text{-}MeC_5H_4)MCl_3]$, where M = Ti, V, have been prepared and characterized. Strong oxidizing properties were demonstrated [303]. The tetrahydropentalenyl complex of cobalt (17.3) has been prepared from $(\eta^5\text{-}C_5Me_5)Co(\eta^4\text{-}C_8H_8)$ and $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-}CH_2CMeCH_2)]^+$. The structure of the complex (17.3) has been confirmed as a substituted cobaltocenium cation [304].

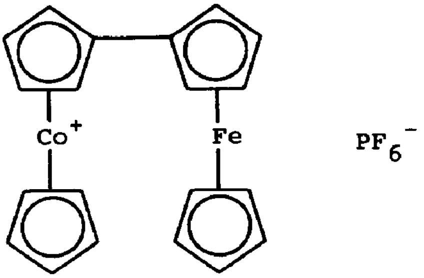
The solvated ions of $[(\eta\text{-}C_5H_5)Co]^{2+}$, $[(\eta\text{-}C_5Me_5)Co]^{2+}$ and $[(\eta\text{-}C_5Me_5)Co]^+$ were generated from $[(\eta\text{-}C_5Me_5)CoCl_2]_2$ and treated with $[2_n]$cyclophanes. In this way the complexes {17.4; M = $[(\eta\text{-}C_5H_5)Co]^{2+}$, $[(\eta\text{-}C_5Me_5)Co]^+$, $[(\eta\text{-}C_5Me_5)Co]^{2+}$} were prepared with, for example, $[2_2]$(1,4)cyclophane and $[2_4]$(1,2,4,5)cyclophane. The complexes containing two cobalt moieties (17.5) were prepared with $[2_2]$(1,4)cyclophane; 4,5,7,8-tetramethyl-



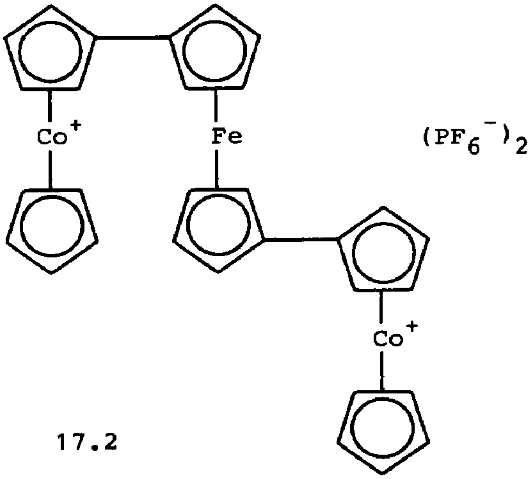
16.7



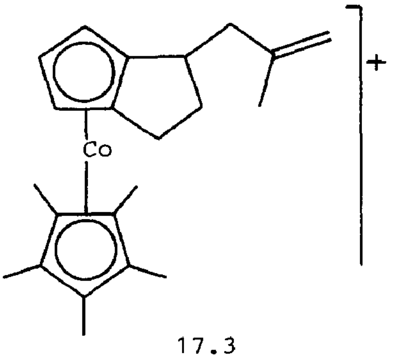
16.8



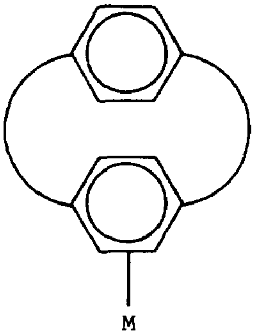
17.1



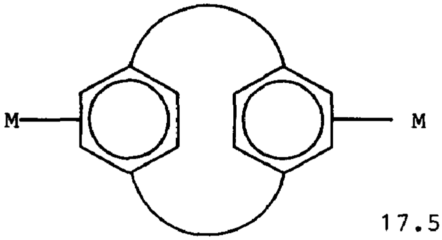
17.2



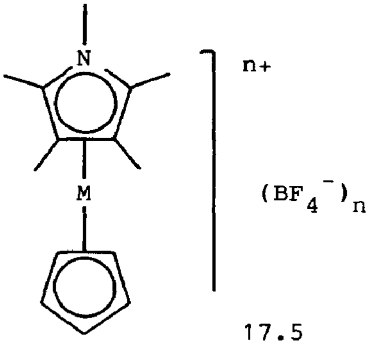
17.3



17.4



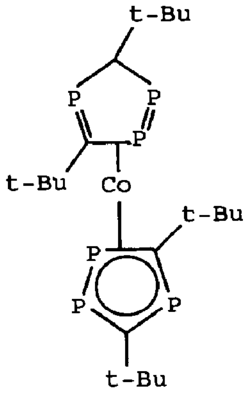
17.5



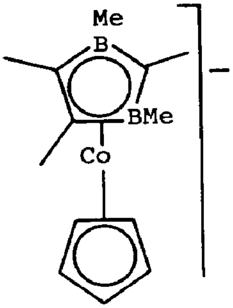
17.5

$[2_2](1,4)$cyclophane and 5,8,12,15-tetramethyl-$[2_2](1,4)$ cyclophane. Similar rhodium and iridium complexes were made [305]. Reaction of the η-cyclopentadienyl complexes $[(\eta\text{-}C_5H_5)Fe(SMe_2)_3]BF_4$ or $[(\eta\text{-}C_5H_5)Co(SMe_2)_3](BF_4)_2$ with pentamethylpyrrole afforded the corresponding sandwich complexes (17.6; M = Fe, n = 1; M = Co, n = 2) [306]. Cobalt(II) chloride combined with $Li(C_2t\text{-}Bu_2P_3)$ to give the mixed sandwich complex (17.7) which was shown by X-ray crystallography to contain the 1,2,4-triphosphabuta-1,3-diene ligand [307].

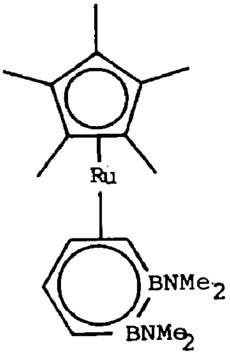
2,3-Dihydro-1,3-diboroles have been used to prepare the mixed ligand cobalt anionic complex (17.8) [308]. Reaction of the 1,2-diborabenzene derivative $Li_2[C_4H_4B_2(NMe_2)_2]$ with various transition metal compounds produced a series of sandwich and triple-decker complexes, for example (17.9 and 17.10). Reaction of the rhodium complex (17.9) with BCl_3 afforded the 1,2-dichloro compound (17.11). The structure of this latter complex was



17.7



17.8



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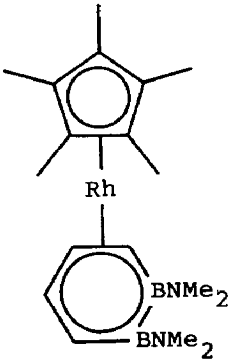

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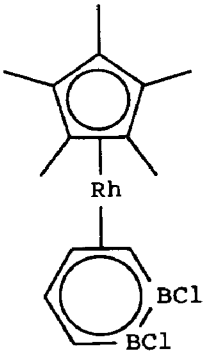

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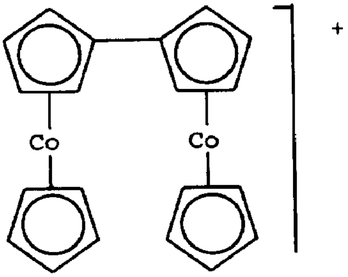

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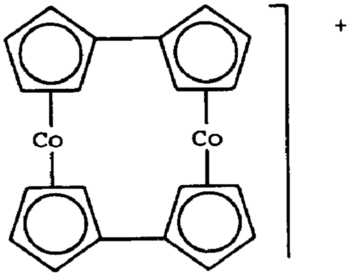
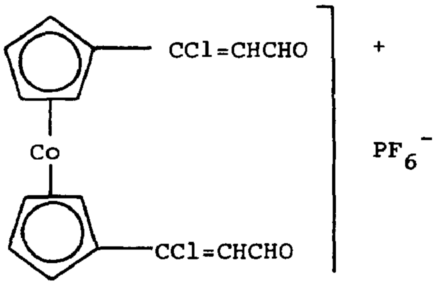


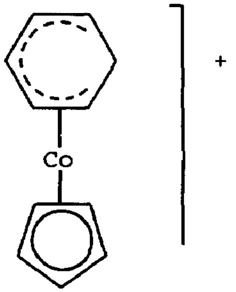
17.13

determined by X-ray analysis [309]. The cobaltocenium ion has been incorporated into a monocarbon carborane complex [310]. Cobaltocene has been determined spectroscopically as a solution in hexane-diethylamine mixtures [311]. Intervalence electron transfer in the bicobaltocene cation (17.12) and the bicobaltocenylene cation (17.13) have been studied by spectroscopy and cyclic voltammetry. The high rate of self exchange observed was interpreted in terms of electronic coupling effects. Comparisons were made with the corresponding biferrocene and biferrocenylene cations [312].

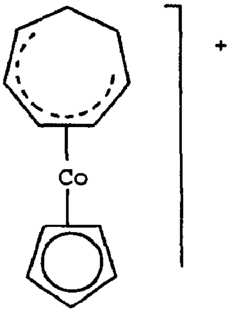
The electron self-exchange in cobaltocenium-cobaltocene, and decamethylcobaltocenium-decamethylcobaltocene has been studied by an NMR line-broadening technique and rate constants, k_{ex}, determined. These have been compared with the values for the ferrocenium-ferrocene, decamethylferrocenium-decamethylferrocene and bis(η-benzene)chromium(1)-(0) couples. The k_{ex} values for



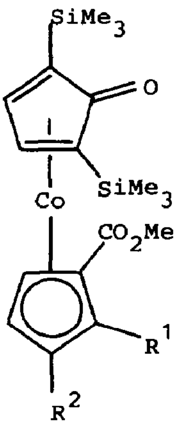
17.14



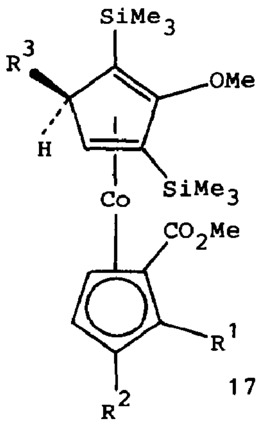
17.15



17.16

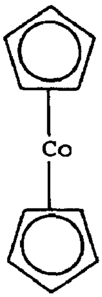


17.17

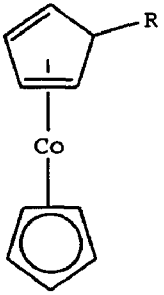


17.18

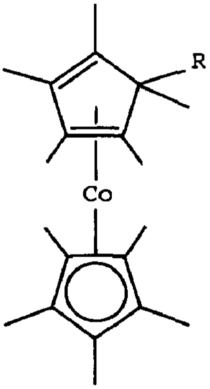
cobaltocene were ten times greater than for ferrocene and the decamethyl derivatives had k_{ex} values ten times greater than the unsubstituted parents. The results were interpreted in terms of donor-acceptor electronic coupling in outer-sphere redox species [313]. A chemical diode device has been constructed from a ferrocene polymer and the cobaltocenium salt (17.14) it was functional in the gas phase [314].



17.19

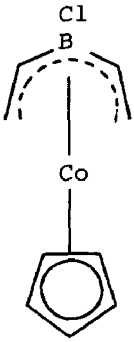


17.20



17.21

The rate of reduction of the proton to hydrogen by cobaltocene has been determined by pulse radiolysis in aqueous acid. The reaction was first order in cobaltocene and in protons, possible mechanisms were discussed [315]. The rate of addition of phosphines PBu^n_3 and $p(OBu^n)_3$ to the (η-dienyl)cobalt cations (17.15 and 17.16) has been determined (η-diene)cobalt cationic complexes were obtained [316]. The chiral cobalt complex (17.17; R^1, R^2 = H, Me) was methylated with dimethylsulphate to give an intermediate cobaltocenium salt which underwent, diastereoselectively, nucleophilic addition of an organo-lithium R^3Li, where R^3 = $Me_3SiC{\equiv}C$, 1-octynyl, $EtOC{\equiv}C$, to give the corresponding η-cyclopentadiene complex (17.18) [317]. Treatment of cobaltocene (17.19) with the organocadmium compounds R_2Cd, where R = Me, Pr, Ph, produced the corresponding η-diene complexes (17.20). The reaction of nickelocene and several other metallocenes with organocadmium compounds was also investigated [318]. Cobaltocene (17.19) has been attacked by organocadmium compounds R_2Cd to give the (η-cyclopentadienyl)(η-cyclopentadiene)cobalt products (17.20; R = Me, Et, n=Pr, Ph, $GeEt_3$, CH_2SiMe_3). The mass spectra of



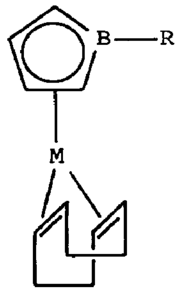
17.22

these complexes (17.2) revealed three pathways for degradation [319].

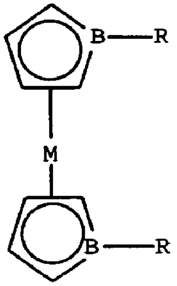
The decamethylcobaltocenium cation has been treated with alkyllithium compounds to give the (η-cyclopentadiene)cobalt complexes (17.21; R = Et, Pr, Me_2CH and Bu) [320]. Cobaltocene has been used for the two electron reduction of some η-thiophene-iridium complexes [321]. Cobaltocene has been used as a reducing agent in the preparation of some carbonyl-iron cluster complexes. The cobaltocenium salts of some cluster complexes were also prepared [322]. Cobaltocene has been treated with octacarbonyldicobalt followed by $BiCo_3(CO)_{12}$ to give the paramagnetic, 10-electron, bismuth complex $[(\eta\text{-}C_5H_5)_2Co][Bi\{Co(CO)_4\}_4]$ which was structurally characterized by X-ray crystallography [323]. The boron containing complex (17.22) readily underwent nucleophilic substitution with an amine or an alcohol in the presence of base to give the corresponding (η^5-aminodivinylborane)- or (η^5-alkoxydivinylborane)-(η^5-cyclopentadienyl)cobalt complexes. Other nucleophilic substitutions were investigated [324]. Cobaltocene and nickelocene have been used in the preparation of magnetic thin films on glass substrates [323].

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

Reaction of the ammonia adducts $C_4H_4BR.NH_3$ (R = Me, Ph) with (η- 1,5-cyclooctadiene)$_2$M (M = Ni, Pd, Pt) afforded the corresponding mixed-ligand complexes (18.1). Thermolysis of these complexes afforded the sandwich complexes (18.2) together with free

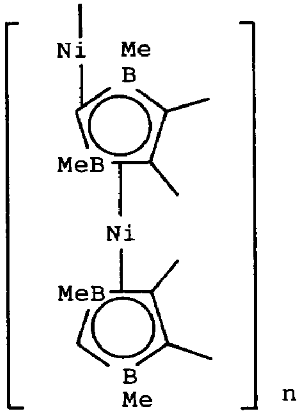


18.1

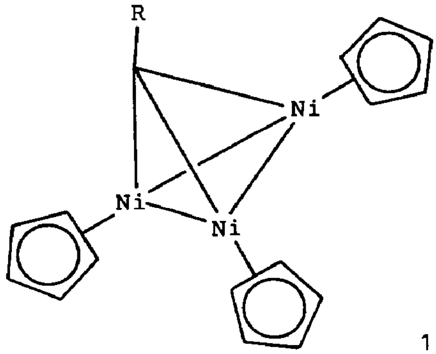


18.2

cyclooctadiene and elemental metal [326]. The polymeric (η-dihydrodiborolyl)nickel complex (18.3) has been prepared and its physical properties determined. The conductivity of the complex (18.3) was similar to that of highly doped polyacetylene [327]. 2,5--Dihydro-1,2,5-thiasilaborole ligands combined with (η-cyclodecatriene)nickel to give the corresponding sandwich complexes [328].



18.3



18.4

Decamethylnickelocene, together with other decamethylmetallocenes, has been investigated by mass spectrometry. There were five major dissociative pathways: sequential removal of the methyl groups from the molecular ion, removal of hydrogen atoms from the molecular ion, sequential loss of hydrogen molecules from the molecular ion, elimination of C_5Me_5H molecules and removal of the η-C_5Me_5 ligand from the molecular ion [329].

Patterned deposits of nickel on silica were obtained by photoassisted decomposition of nickelocene. Good resolution of patterns on the 1μm scale was observed [330]. The magnetic properties of nickelocene have been reinvestigated by magnetic susceptibility and inelastic neutron scattering. The molecule showed ferromagnetic coupling to its nearest neighbours [331]. The CNDO method has been used to calculate the electronic structures of nickelocene and $[(\eta\text{-}C_5H_5)_3Ni_2]^+$ and to characterize the metal-ligand bonding [332]. Reaction of nickelocene with methyllithium or vinyllithium, with MeCH=CHMgBr or with Me_2C=CHMgBr produced the trinickel cluster compounds (18.4; R = Me, Et and $CHMe_2$) respectively. X-Ray analysis showed that the complex (18.4; R = Me) possessed a tetrahedral $Ni_3\text{-}(\mu_3\text{-}C)$ core [333].

The oxidation of a series of metallocenes, including nickelocene and ferrocene, by hydroperoxides ROOH, where R = H, $C(CH_3)_3$, has been investigated [334]. Nickelocene has been used as a catalyst component for the oligomerization of olefins to give high-linearity products [335].

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