SELECTED REACTIONS OF TRANSITION METAL π-COMPLEXES ANNUAL SURVEY COVERING THE YEAR 1986*

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*Annual Survey covering the year 1985, see J. Organomet. Chem., Library, 19 (1987) 403.

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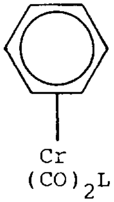
1. REVIEWS

The application of metallocenes, including ruthenocene and osmocene, in biochemistry, microbiology and medicine have been reviewed [1]. New editions of the Gmelin handbook, parts B10 and C7, have been published. These relate to mononuclear, binuclear and polynuclear complexes containing organoiron groups [2]. Eighteen retrospective reviews have been published in volume 300 of this Journal under the general title of "Additional Perspectives in Organometallic Chemistry". The contributions by Graham [3], Herrmann [4], Kochi [5] and Schlogl [6] are of especial relevance to this annual survey. Kundig has reviewed some recent advances in arene transformation reactions with the arene attached to the tricarbonylchromium moiety. The regioselectivity and reversibility in the addition of carbanions was discussed together with the addition of carbon electrophiles to (η-cyclohexadienyl)tricarbonylchromium anions [7].

Pittman and Rausch have reviewed the polymerization and copolymerization and η-vinylcyclopentadienyl and η-isoprenylcyclopentadienyl complexes of Co, Rh, Ir, W, Ti and Cu [8]. Sutherland, Iqbal and Piorko have surveyed the structure, characterization, properties and applications of (η-arene)-(η-cyclopentadienyl)iron cations and related species [9].

2. GENERAL

Bis(η^6-2,6-dimethylpyridine)metal complexes, where metal = Cr, Mo, Ti and V, have been prepared by metal vapour synthesis. These complexes were investigated by a wide range of physical methods and were found to be similar to the corresponding bis(η^6-benzene)metal complexes [10]. Photolysis of benchrotrene and cymantrene in the presence of phosphine ligands gave the derivatives (2.1 and 2.2; L = PPh_2Me, $Ph_2PCH_2PPh_2$). Proton-



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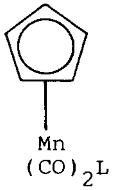

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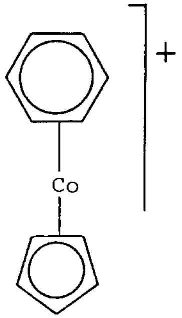

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ation of the two diphosphine complexes (2.1 and 2.2; L = $Ph_2PCH_2PPh_2$) occurred at the phosphorus atom not coordinated to the metal [11]. The metal-ligand bond strength in (η-cyclopentadienyl)- and (η-benzene)-transition metal complexes has been investigated. The average internal bond dissociation energies and the Wiberg parameters for a series of these complexes remained almost constant. This reflected a low ionic contribution to bond stability [12]. The ^{95}Mo and ^{13}C NMR spectra of a series of molybdenum sandwich complexes with a range of C_5, C_6 and C_7 rings as ligands have been recorded and interpreted on a ligand-field model by comparison with orbital ionization energies. The shielding decreased with increase in ring size and from closed to open π-systems [13].

Several (η-cyclopentadienyl)- and (η-arene)-metalcarborane complexes have been prepared by the reaction of cobalt, iron or nickel atoms with either cyclopentadiene, toluene or mesitylene and the nido-carborane 2,6-$C_2B_7H_{11}$. The structures of three of the metallacarborane clusters obtained were confirmed by X-ray crystallography [14]. Iron, cobalt and nickel complexes have been formed with 2,5-diphenylsilacyclopentadienes as η^4-silole ligands [15]. Manganocene, ferrocene, cobaltocene and nickelocene have been examined by doubly charged ion mass spectrometry. Molecular doubly charged ions were found to be the only metal containing species. The spectra for ferrocene and cobaltocene consisted of a single intense peak in each

case corresponding to $[(\eta\text{-}C_5H_5)M]^+$ formed from the doubly charged species $[(\eta\text{-}C_5H_5)_2M]^{2+}$ [16]. Electrochemical rate constants and activation parameters have been determined for the electron exchange of the metallocene couples $M(\eta\text{-}C_5R_5)_2$-$[M(\eta\text{-}C_5R_5)_2]^+$, where M = Fe, Co, Mn and R = H, Me, and $(\eta\text{-}C_6H_6)_2Cr(I)$ - $(\eta\text{-}C_6H_6)_2Cr(O)$ [17]. The electronic structure of mixed-sandwich cobalt complexes has been studied by EPR spectroscopy. Results for the 19-electron complex (2.3) and some ring methylated derivatives were consistent with a d^7 configuration for cobalt with an unpaired electron in the e_{1g} orbital with largely metal (d_{xz}, d_{yz}) character. Comparison of bonding parameters with those in analogous complexes gave the order of decreasing covalency as:
$[(\eta\text{-}C_5H_5)_2Ni]^+ > [(\eta\text{-}C_5Me_5)(\eta\text{-}C_6Me_6)Co]^+ > [(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Co]^+ > [(C_5H_5)_2Co]^+ > (\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Fe$ [18].

Procedures have been described for the growth of diamonds and diamond powders by plasma vapour deposition from hydrocarbon and hydrogen containing a transition metal organometallic compound as catalyst. Cyclopentadienyl complexes of iron, cobalt and nickel were effective catalysts [19, 20]. A series of silylmetallocenes has been prepared and these compounds were found to be useful as vulcanization accelerators [21]. Butadiene-, cyclobutadiene-, trimethylenemethane-, and p-quinodimethane-tricarbonyliron complexes have been the subject of a theoretical study. Molecular geometries and EHT total energies were calculated. EHT determinations for p-quinodimethane complexes were in agreement with X-ray results [22]. The mechanism of "ring whizzing" in d^{10} (η-cyclopolyene)ML_2 complexes, such as $(\eta^4\text{-}C_4H_4)Ni(PH_3)_2$. has been investigated by EHMO calculations. The process was analogous to the sigmatropic rearrangement of isolobal organic compounds and was under the control of topological and orbital overlap effects [23].

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

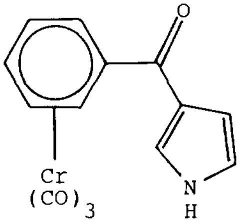
The effect of ^{13}CO, $C^{18}O$ and ^2H-ligand substitution on the ^{13}C and ^{51}V NMR spectra of $(\eta^5\text{-}C_5H_5)V(CO)_4$, $[(\eta^5\text{-}C_5H_5)V(CO)_3H]^-$ and $[V(CO)_6]^-$ has been investigated. The increase of ^{51}V shielding with ^{13}C

substitution was linear [24]. A series of ring substituted $(\eta^5\text{-}C_5H_5)V(CO)_4$ complexes $LV(CO)_4$, where L = indenyl, $C_5(\text{trityl})H_4$, C_5Me_5, $C_5(Et)Me_4$, $C_5Me(\text{cetyl})H_3$, $C_5Me(C_6H_{11})H_3$ and C_5MeH_4, have been prepared in good yields by the direct reaction of $V(CO)_6$ with the substituted cyclopentadiene. The ^{51}V NMR spectra of the complexes were recorded and discussed [25].

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

(i) Formation

Benchrotrene and its molybdenum and tungsten analogues have been prepared by heating the appropriate metal hexacarbonyl with benzene in the presence of pyridine [26].



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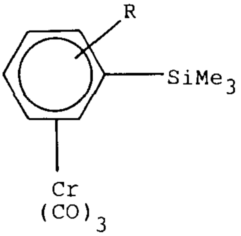

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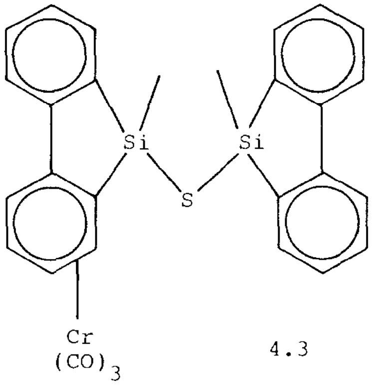
Several substituted benchrotrenes with fluoro, amino and alkyl groups have been prepared from hexacarbonylchromium and the free arene ligand in THF and dibutyl ether [27]. Hexacarbonylchromium combined with 3-benzoylpyrrole to give the benchrotrene derivative (4.1). This product contrasts with the previous report of the corresponding reaction of 2-benzoylpyrrole when the sole product was the σ-chelate complex tris(2-benzoylpyrrolato)-chromium(III). The differences were explained in terms of the stereochemistries of the ligands [28]. The trimethylsilylbenchrotrene complexes (4.2; R = 2-, 3-, 4-Me, -MeO, -Cl, $-Me_3Si$, $2\text{-}Me_3C$, $2,4,6\text{-}Me_3$) were formed by treatment of the appropriate trimethylarylsilanes with hexacarbonylchromium. The $SiMe_3$



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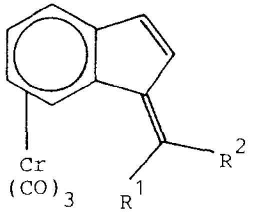

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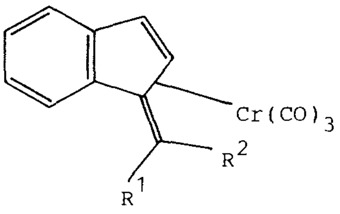

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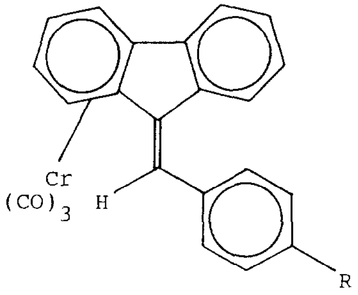

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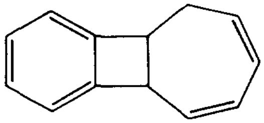
group in the complexes (4.2) was converted to CHPh($OSiMe_3$) on treatment with benzaldehyde [29]. Treatment of 1-methyldibenzosilole with elemental sulphur produced bis(1-methyldibenzosilole)-sulphide which formed the tricarbonylchromium complex (4.3) on reaction with hexacarbonylchromium [30].

The reaction of 1,2-benzofulvenes with $(CH_3CN)_3Cr(CO)_3$ afforded the corresponding η^6-1,2-benzofulvene complexes (4.4; $R^1 = R^2 =$ Me, $R^1 =$ H, $R^2 =$ Ph; $R^1 =$ H, $R^2 =$ p-$MeOC_6H_4$; $R^1 = R^2 =$ Ph). With 6-phenyl-1,2-benzofulvene a second product (4.5) was obtained. Similar reactions with 1,2,3,4-dibenzofulvenes produced the η^6-benzo-coordinated compounds (4.6; R = H, OMe) exclusively [31]. The bicyclononatriene (4.7) isomerized to benzo[7,8]bicyclo[4.2.1]nona-2,4,7-triene in the presence of $L_3M(CO)_3$, where L = CO, NH_3, MeCN and M = Cr, Mo, W. When $(MeCN)_3Cr(CO)_3$ was used in THF at 40°C then a small



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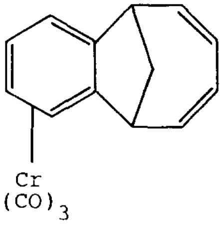

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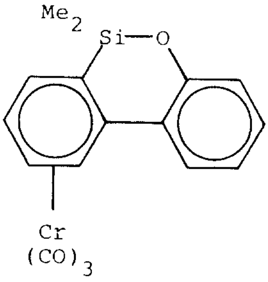
proportion of the product was obtained in the form of the tricarbonylchromium complex (4.8). At 129°C in n-butyl ether with $(NH_3)_3Cr(CO)_3$ this complex (4.8) was the main product, the crystal and molecular structure of which was determined by X-ray crystallography [32]. The reaction between 10,10--dimethyl-10-sila-9-oxa-9,10-dihydrophenanthrene and $Cr(CO)_3$-$(NH_3)_3$ gave two isomeric tricarbonylchromium complexes. In one case (4.9) the tricarbonylchromium group was bound to the silicon substituted arene ring and in the second case to the oxygen substituted arene. The two isomers were characterized by X-ray crystallography [33].

The reaction of 1- or 2-bromonaphthalene with tricarbonyltripyridinechromium in the presence of boron trifluoride etherate produced the corresponding tricarbonylchromium complexes (4.10; R = Br). Treatment of these complexes with n-butyllithium followed by R^1X, where R^1 = D, Me, $SiMe_3$, $SnMe_3$ and X = halogen, gave the corresponding complexes (4.10; R = R^1). When these complexes were heated in decane, equilibrium mixtures were obtained containing (4.10; R = R^1 and 4.11) [34]. Thermolysis of the carbene-chromium complex $(CO)_4\overline{CrC(OEt)CH(Ph)CH(Ph)C}(OEt)$ at 130° produced the diene (4.12) and the tricarbonylchromium complexes (4.13 and 4.14) [35]. The kinetics of migration of the tricarbonylchromium group from the eight- (4.15) to the six-membered ring (4.16) in benzocyclo-octatetraene have been investigated. The reaction was first order and low values for the entropy of activation were obtained. The results



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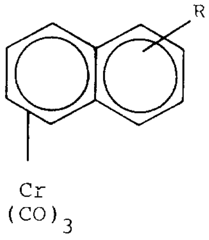

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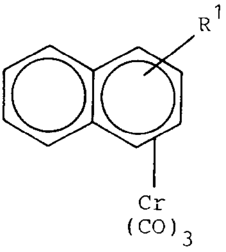

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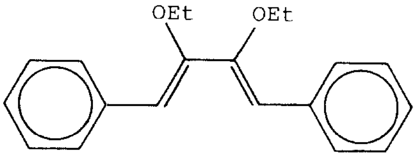

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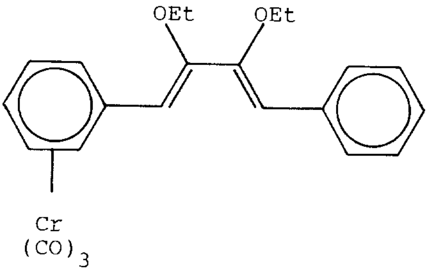

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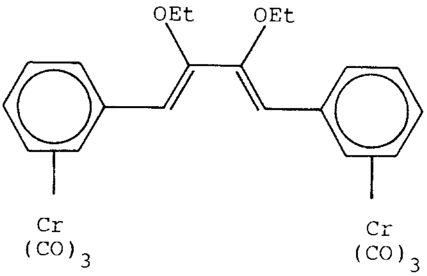

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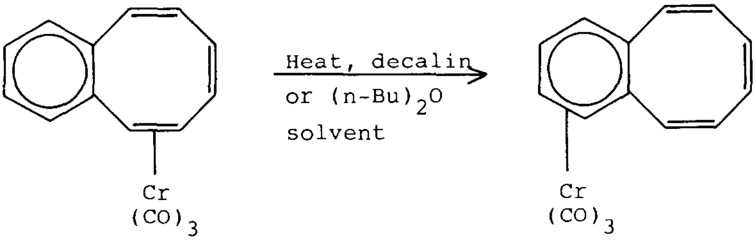
indicated that the reaction proceeded intramolecularly [36].



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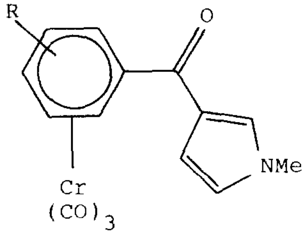
(ii) Spectroscopic and physico-chemical properties

The N-methyl-3-aroylpyrrole complexes (4.17; R = H, *p*-Me, *o*-Me, *p*-OMe, *p*-Cl) have been prepared. The infrared and ^{1}H NMR spectra were recorded and interpreted with the assistance of SCCC-MO calculations. The results indicated that there was little electron delocalization between the benzene and pyrrole rings [37]. Mahaffy has prepared and characterised a series of substituted aniline-tricarbonylchromium complexes [38]. The tricarbonylchromium complexes of *p*-dicyclohexylbenzene, N-cyclohexylaniline, 5-methoxy-1-tetralone, 6-methoxy-1-tetralone, 5,7-dimethyl-1-tetralone, 5-methoxy-1-indanone, 1-benzosuberone, 5-aminotetralin and 5-aminoindan have been prepared and characterised [39]. As part of a study of chiral perfluoroalkyl compounds tricarbonylchromium complexes, for example, the complex (4.18) was prepared [40].

The reactions of the anions (4.19, M = Cr, Mo, W) with electrophilic reagents have been investigated. Treatment with acyl halides RCOCl (R = CH_3, t-C_4H_9, C_6H_5, p-ClC_6H_4, OC_2H_5) afforded the corresponding (η^6-fulvene)Cr(CO)$_3$complexes (4.20) [41]. The η-bithiophene complexes (4.21; R^1-R^6 = H, Me, Br) have been prepared in good yields by the treatment of tricarbonyltris(γ-picoline)chromium with the appropriate 2,2'-bithiophene in the presence of boron trifluoride [42]. Treatment of (η^6-C_6H_5R)Cr(CO)$_2$CS, where R = H, Me, OMe, with Cr(CO)$_5$THF afforded the corresponding end-on-linked dinuclear complexes



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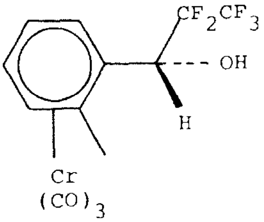

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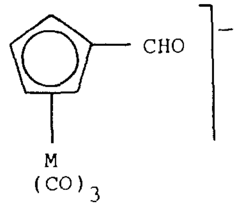

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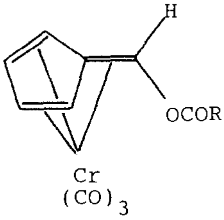

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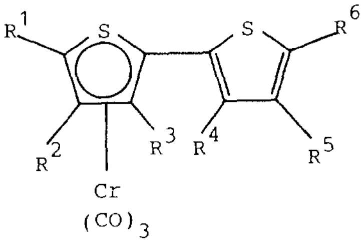

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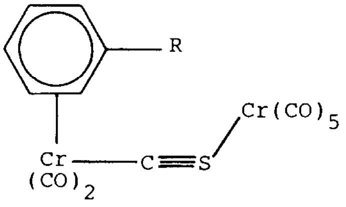
(4.22). The crystal and molecular structure of the complex (4.22, R = Me) was determined by X-ray analysis. The Cr-C-S linkage was linear but the C-S-Cr linkage deviated greatly from linearity. The very long S-Cr distance (2.486Å) was indicative of a weak bond [43]. The structure of the bis(tricarbonylchromium) complex (4.23) has been determined by X-ray analysis. The dihedral angle of the two η-arene rings was smaller than that in benzophenone [44]. Reduction of WCl_6 or $WCl_4(PR_2Ph)_2$, where R = Et, Pr^n, with magnesium in the presence of PR_2Ph under nitrogen in THF gave several dinitrogen complexes including the (η-arene)tungsten complexes (4.24; R = Et, Pr^n). The crystal and molecular structure of one of these complexes (4.24; R = Pr^n) has been determined by X-ray crystallography [45]. The photoelectron spectra of several benchrotrenes (4.25; X = H, F, Cl, I, $CH=CH_2$, CH_2OH, CO_2Me, NH_2) have been recorded and interpreted. Disruption of conjugation between the arene ring



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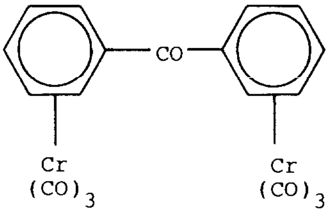

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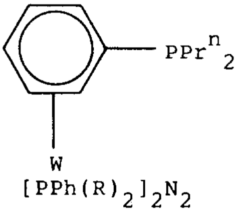
and the substituent X was indicated [46]. Photofragmentation processes of benzenetungsten and bis(η-benzene)tungsten in a molecular beam have been investigated. The results indicated that there was a rapid conversion of electronic to vibrational energy when these molecules were excited [47]. The positive chemical ionization mass spectra of the η-arene complexes (4.26; R = Me, Et, Pr, OMe, mesitylene, toluene) with propene, benzene and toluene as the reagent gases have been recorded. With all the complexes protonation, charge exchange, fragmentation and CO substitution occurred [48]. In the reaction of ^{13}CO-enriched (η-benzene)tricarbonylchromium with the deuterated complex



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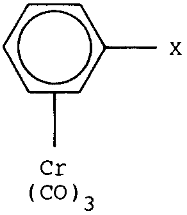

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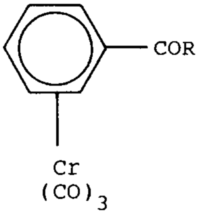

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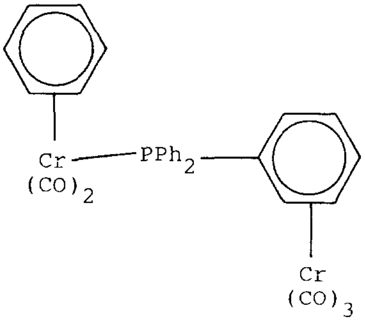
(η-C_6D_6)Cr(CO)$_3$ carbon monoxide redistribution occurred. Gaseous carbon monoxide did not participate in the redistribution process and it was thought that a bis(carbonyl)-bridged dimer was the intermediate in this reaction [49]. Photochemical substitution in benchrotrene and cymantrene has been used to prepare complexes of the types (4.27 and 4.28). Hydrogen isotope exchange in the complex (4.27) was measured kinetically, it took place only in the π-benzene rings. ^{13}C NMR spectroscopy was used to show that the central metal atom in the complexes (4.29; M = Cr, Mo, W) caused increased shielding of the carbonyl carbon atoms in the order $W \leqslant Mo < Cr$ [50]. The influence of tricarbonylmetal groups on ^{1}H NMR chemical shifts



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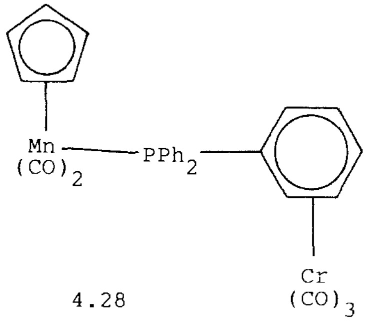

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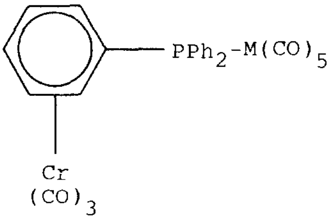

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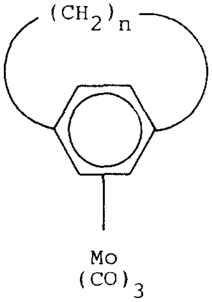
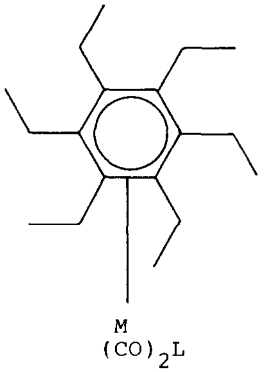


4.30

has been examined. The diamagnetic anisotropy of the carbonyl ligands in the $M(CO)_3$ groups, where M = Cr, Mo, W, has been evaluated using the McConnell relationship. The 500MHz ^1H NMR spectra of α- and β-$Cr(CO)_3$ estradiol complexes showed deshielding of protons proximate to the tricarbonylmetal group relative to protons in distal environments [51]. Arene and carbon monoxide exchange reactions in (η-arene)tricarbonylchromium complexes have been investigated. Kinetic studies using ^1H NMR spectroscopy showed that the arene exchange reaction proceeded by both direct attack of the free arene on the η-arene complex together with catalysis of arene exchange in one complex by another η-arene complex. Cyclohexanone was also shown to catalyze arene exchange in a bimolecular reaction with a complex. Carbon monoxide exchange was studied using ^{13}CO [52]. The ^{13}C NMR



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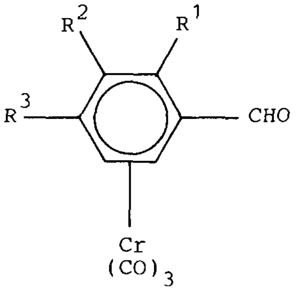

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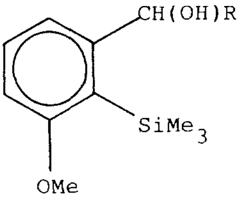
spectra of several tricarbonyl(η^6-cyclophane)molybdenum complexes, including the paracyclophanes (4.30; n = 8, 9, 11, 12, 15), have been recorded and interpreted. Complexation shifts for the complexed-ring carbons were found to be dependent on the degree and the direction of ring bending [53]. The stereochemistry of several (η-hexaethylbenzene)transition metal complexes [4.31; M = Cr, Mo, L = PEt_3, maleic anhydride; M = Cr, L = CS, PMe_3, $P(OPh)_3$] has been examined by variable temperature ^{13}C-{^1H}and ^{31}P-{^1H} NMR spectroscopy. In several cases, multiple hexaethylbenzene stereoisomers were found to coexist in equilibrium at low temperatures. Hindered rotation about the metal-arene bond was not invoked in the explanation of coalescence phenomena. Barriers to site exchange of ethyl groups were determined and the crystal and molecular structure of one complex (4.31; M = Mo, L = maleic anhydride) was obtained by X-ray analysis [54]. The racemic aldehyde-tricarbonylchromium complexes (4.32; R^1 = Me, OMe; R^2 = R^3 = H, OMe) have been treated with (S)(-)-PhCHMeNHCOCONHNH$_2$ to give diastereomeric mixtures which were separated by chromatography. Hydrolysis of the diastereoisomers produced the optically active forms of the complexes (4.32) [55]. Reaction of the 2-trimethylsilyl compounds (4.33; R = Me, Me$_2$CH) with hexacarbonylchromium followed by de-trimethylsilylation and acetylation afforded predominantly the S*, S* chromium complexes (4.34). In a similar series of reactions with the 6-trimethylsilyl compounds (4.35; R = Me, Me$_2$CH) the S*, R*- isomers (4.36) were isolated [56]. High performance liquid chromatography (HPLC) has been



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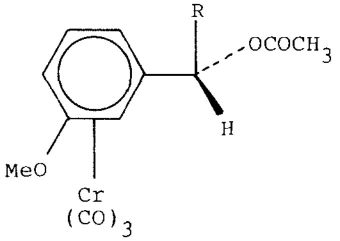

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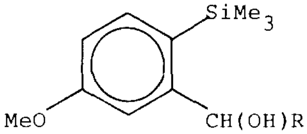

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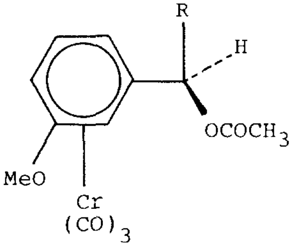

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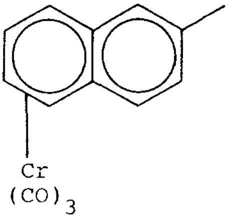

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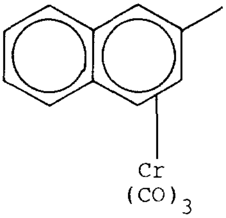

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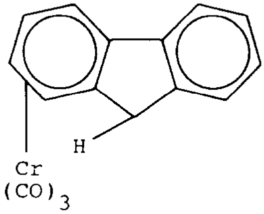

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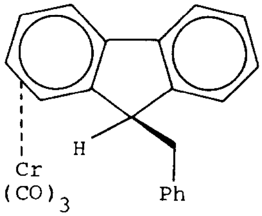

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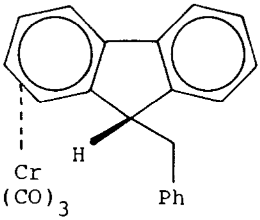

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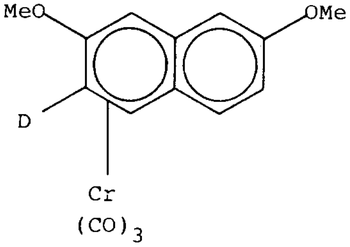

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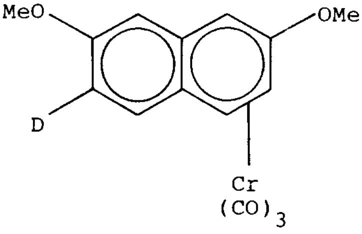
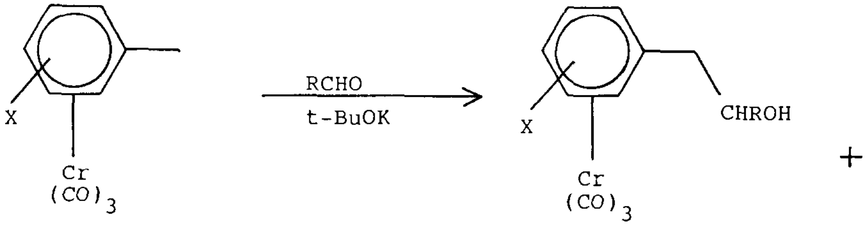


4.43

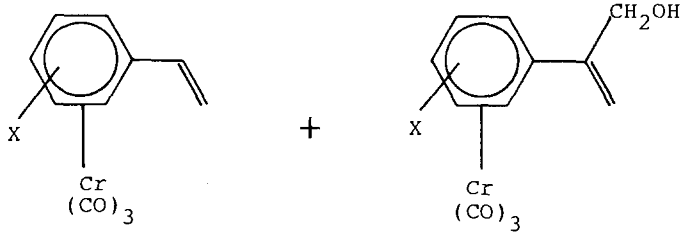
used to separate a series of (η^6-arene)Cr(CO)$_3$ complexes. The effects of solvent composition on the retention times was studied using amino, octadecylsilica, and β-cyclodextrin bonded phase columns in either a normal-phase or a reversed-phase mode [57]. Gas chromatographic separation of the isomers (4.37 and 4.38) of (η-2-methylnaphthalene)tricarbonylchromium has been achieved by direct injection onto a high-resolution capillary column. Interconversion of the isomers occurred on the column and the results suggested that the Cr(CO)$_3$ groups migrated intramolecularly [58]. The electrochemical reductive cleavage of (η^6-fluorene)Cr(CO)$_3$ produced the corresponding anion (4.39). Treatment of this anion with benzyl chloride during the electrolysis at 0° gave the exo- isomer (4.40) stereoselectively. At higher temperatures a mixture of the exo- (4.40) and endo- (4.41) isomers was obtained [59]. The effects of temperature and supporting electrolyte on the electrochemical oxidation of (η-benzene)tricarbonylchromium has been investigated. The oxidation was made chemically reversible in dichloromethane by using low temperatures or by using tetrabutylammonium hexafluorophosphate as the supporting electrolyte [60]. The acidities of the (η-arene)tricarbonylchromium complexes [4.25; X = H, OMe, Me, CON(i-Pr)$_2$] in tetrahydrofuran have been determined. The acidity data provided an estimate for the pK of benzene in tetrahydrofuran of 41.2 which was about 6.4 pK units greater than the value for the complex (4.25; X = H) [61]. Rate constants and activation energies have been determined for the haptotropic rearrangements of several methoxy- and methyl-substituted tricarbonyl(η-naphthalene)chromium complexes. Thus the activation energy for the conversion of the complex (4.42) to the isomer (4.43) was 27.2 Kcal mol^{-1} [62].

(iii) General

Benchrotrene and its derivatives formed 1:1 inclusion compounds with β- and γ-cyclodextrin. The reactions were selective and proceeded in high yield [63]. meta-Dialkylamino- and meta-chlorotoluenetricarbonylchromium complexes (4.44; X = NMe$_2$, Cl) were more reactive than the corresponding para-substituted complexes towards aldehydes, RCHO where R = H, Ph, in base to give the products (4.45, 4.46, 4.47; X = NMe$_2$, Cl;



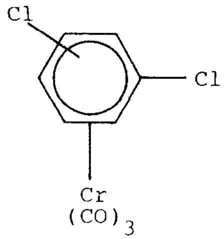
4.44 4.45



4.46 4.47

R = H, Ph). When the two potential sites of attack were present, that was the *meta* and *para* positions in the η^6-arene ring, then only *meta*-substituted hydroxymethyl products were obtained [64]. Treatment of the *o*- and *p*-dichlorobenzene complexes (4.48) with methanol or iso-propanol in the presence of potassium hydroxide under phase transfer conditions gave the correspoding monoalkoxy derivatives. The *meta*-isomer under similar reaction conditions afforded the corresponding disubstituted products. When the same reaction was carried out in dimethylsulphoxide all three isomers gave the dialkoxy products [65].

Benzylic functionalization of the chiral and prochiral tricarbonylchromium complexes (4.49; X = OMe, $OCHMe_2$, NMe_2, NEt_2) proceeded with high diastereoselectivity to give the disub-



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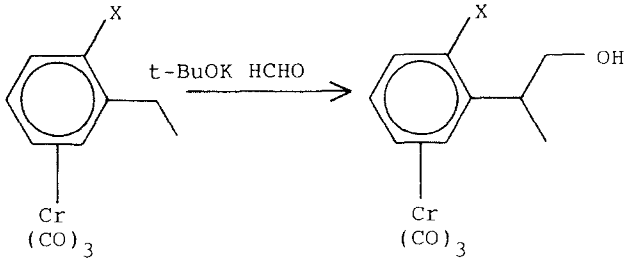
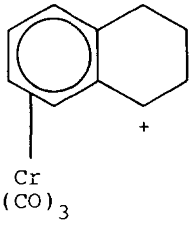


4.49 4.50

stituted benchrotrene products [4.50; X = OMe, $OCHMe_2$, NMe_2, NEt_2) [66]. Primary and secondary benzylic carbocations, stabilized by a tricarbonyl chromium group, were prepared from the corresponding alcohols and treated with aromatic or β-dicarbonyl compounds to give coupling products. Thus the carbocation (4.51) combined with anisole to give the product (4.52) [67]. Reductive acylation of the (η-benzophenone)-chromium complexes (4.53 and 4.23) has been carried out electrochemically in dimethylformamide to give benzhydryl esters such as the derivatives (4.54; R = Me, Ph) [68]. The 1,2-disubstituted benchrotrene (4.55; R = OPh) has been attacked by carbanions (Nuc^-) to give, after quenching with acid, the 1,4-disubstituted products (4.56). The reaction proceeded by regioselective meta substitution of the phenoxy group followed by a 1,3-hydride migration and elimination of phenol. At higher temperatures ortho-disubstituted products (4.55; R = Nuc) were obtained [69].

The molybdenum complexes $(\eta^6\text{-arene})Mo(CO)_3$, where arene = PhMe, $1,4\text{-}Me_2C_6H_4$ and $1,3,5\text{-}Me_3C_6H_3$, have been oxidized with iodine to give the corresponding iodine complexes $(\eta^6\text{-arene})Mo_3(CO)_9I_6$. The $[(\eta^6\text{-arene})Mo(CO)_3I]^+$ cation was always formed but the counterion varied depending on the reaction time and on the molar ratio of the reagents. The structures of the complexes $[(\eta^6\text{-}C_6H_3Me_3)Mo(CO)_3I][Mo_2I_5(CO)_6]$ and $[(\eta^6\text{-}C_6Me_6)Mo(CO)_3I][MoI_3(CO)_4]$ were determined by X-ray analysis [70].



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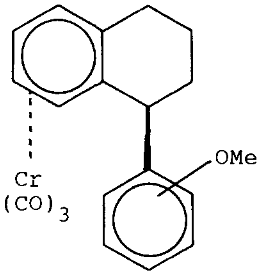

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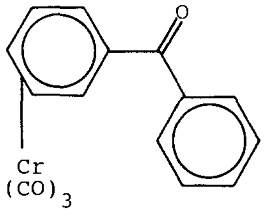

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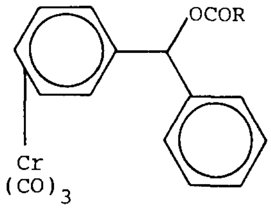

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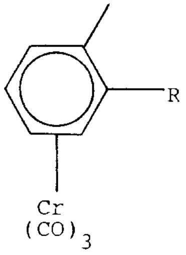
Reaction of the carbene complex (4.58) with diphenylacetylene produced a series of products which included the tricarbonylchromium complexes (4.57; $R^1 = H, R^2 = Ph$; $R^1 = Ph, R^2 = H$) [71]. Lithiation of tricarbonyl(η-fluorobenzene)chromium (4.59) followed by transmetalation with cuprous bromide-dimethyl sulphide and coupling with $Me_3SiOCH_2CBr{=}CH_2$ gave the 1,2-disubstituted benchrotrene (4.60). This product (4.60) underwent desilylation with Bu_4NF in THF to give the dihydrobenzofuran complex (4.61) [72]. The tricarbonylchromium complexes (4.62 and 4.63) have been lithiated at the 4- and 6- positions respectively by n-butyllithium-tetramethylethylenediamine. In the absence of the tricarbonylchromium group lithiation occurred at the 2- and 8- positions. The changes in the lithiation patterns were explained in terms of electrostatic factors and the relative configuration of the tricarbonylchromium moiety in the complex. The regioselective synthesis



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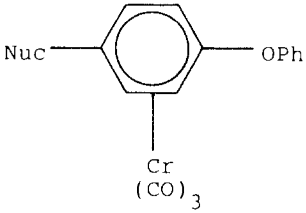

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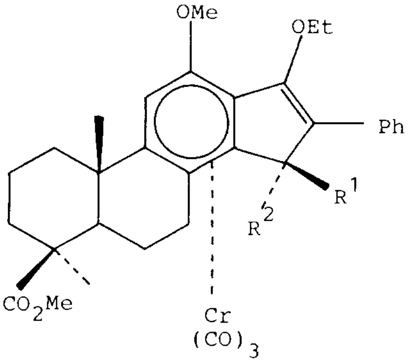

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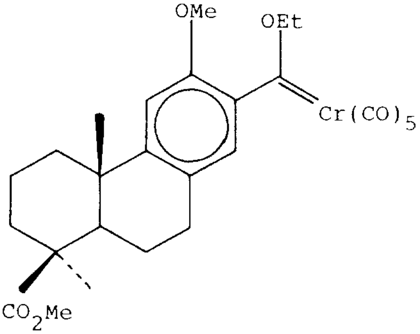

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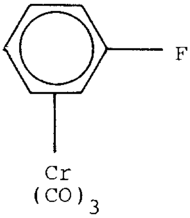

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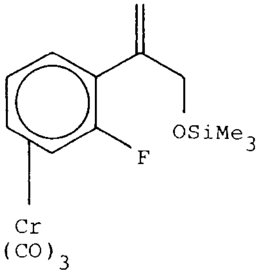

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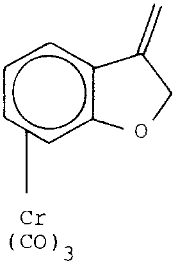

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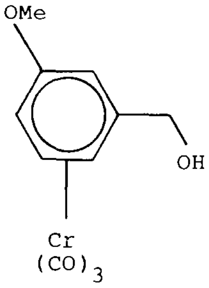
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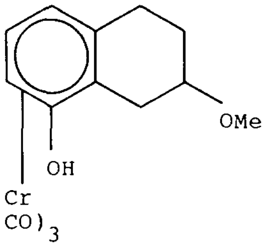
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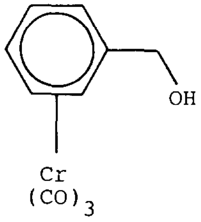
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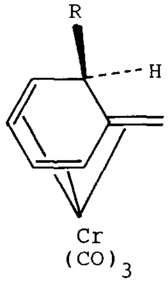
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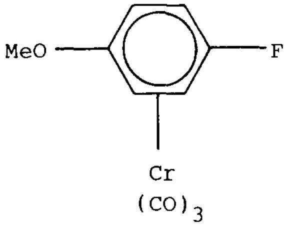
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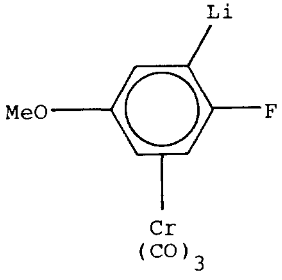
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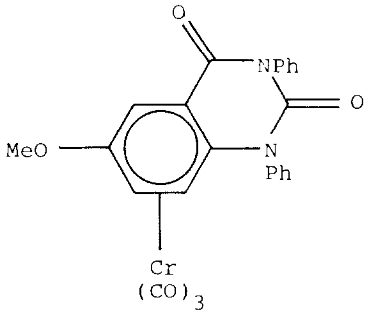
of some anthraquinones and calamenes were carried out via the lithiated complexes [73].

Reaction of the η^6-benzylalcohol complex (4.64) with two equivalents of an alkyllithium compound (t-BuLi, MeLi-tetramethylethylenediamine, n-BuLi, PhLi) regioselectively afforded the corresponding η^6-5-methylene-6-exo-alkylcyclohexa-1,3-diene complexes (4.65; R = t-Bu, Me, n-Bu, Ph). These complexes underwent proton catalysed isomerizations to produce the corresponding η^6-o-alkyltoluene complexes (4.55; t-Bu, Me, n-Bu, Ph). The structure of the complex (4.65; R = t-Bu) was determined by X-ray analysis [74]. Lithiation of the η-fluoroanisole complex (4.66) occurred exclusively ortho to the fluorine and not ortho to the oxygen as happens in the uncomplexed arene. Reaction of the lithio-intermediate (4.67) with phenyl isocyanate afforded the cyclic product (4.68). The lithiation of other η-fluoroanisole $Cr(CO)_3$ complexes was



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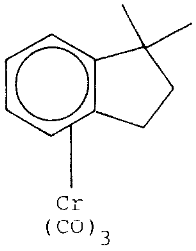

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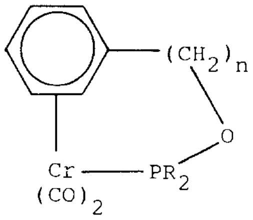

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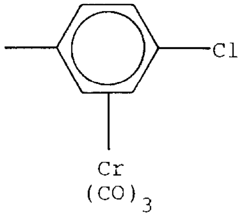

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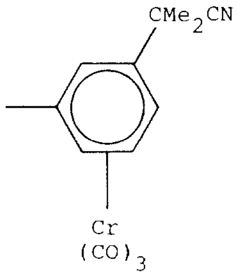

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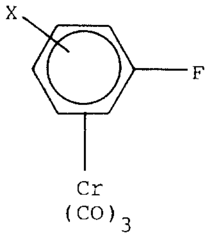

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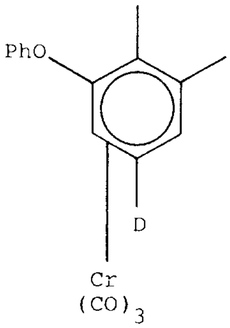

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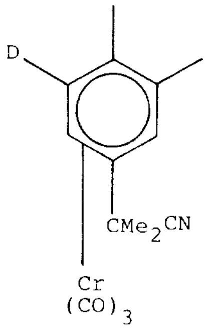
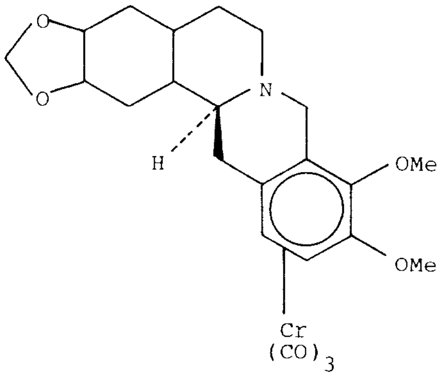


4.75

investigated [75]. Nucleophiles such as $LiCMe_2CN$ and LiCMe(CN)OCHMeOEt attacked arene carbon atoms eclipsed by a carbonyl chromium bond in the conformationally restricted benchrotrene compound (4.69). By contrast electrophiles, such as $AcAlCl_4$, attacked carbon atoms in staggered positions. The bridged benchrotrene compounds (4.70; R = Ph, OPh, n = 1-3) gave only poor yields of substitution products under the same conditions [76].

Reaction of the tricarbonylchromium complex (4.71) with 2-lithiosisobutyronitrile followed by CF_3CO_2H produced the η-m-2-cyanopropan-2-yltoluene complex (4.72) as the major product. The isolation of this product indicated that addition of the carbanion had occurred ortho to the chloro leaving group and meta to the methyl group, that was cine-substitution. A similar reaction was carried out between 2-lithio-2-phenyl-1,3-dithiane and the complex (4.71) [77]. Fluoride has been displaced by methoxide in the nucleophilic attack with sodium methoxide on the benchrotrene derivatives (4.73; X = Me, OMe, NH_2, F) [78]. The kinetics of η-arene substitution in the complexes (η-arene) $Cr(CO)_2CX$, where X = S, arene = PhH, PhMe, $PhCO_2Me$, $PhNMe_2$, o-$C_6H_4Me_2$, p-$C_6H_4Me_2$ m-$C_6H_4(CO_2Me)Me$, p-$C_6H_4(CO_2Me)_2$, p-$C_6H_4(OMe)_2$,1,3,5-$C_6H_3Me_3$; X = Se, arene = PhH, by a series of tertiary phosphites to give mer-$Cr(CO)_2(CX)$(tertiary phosphite)$_3$ have been investigated. The reactions were faster than those of the corresponding tricarbonyl complexes. This was attributed to the better π-acceptor properties of CS and CSe which reduced the bond strength between the chromium and the arene ligand [79]. Reaction of the deuterated-arene-tricarbonylchromium complex (4.74) with Me_2CLiCN followed by tri-fluoroacetic acid produced the tetrasubstituted-arene complex (4.75). Spectroscopic data for the product (4.75) showed that the deuterium atom in complex (4.74) migrated from the original C-5 carbon atom to the C-1 carbon atom which originally carried the phenoxy group [80].

Kinetic studies on the reaction of (η-trans-propenylbenzene)tricarbonylchromium with benzene indicated that the arene ligand exchange proceeded via intramolecular and intermolecular participation by the propenyl substituent. The mechanism suggested was supported by kinetic studies on related



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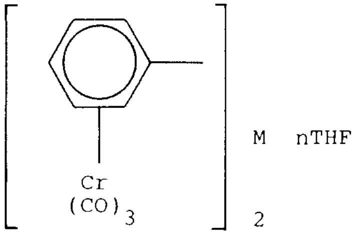

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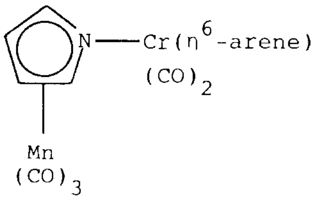

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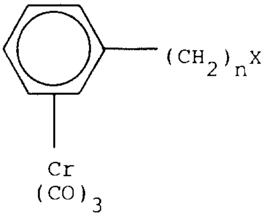

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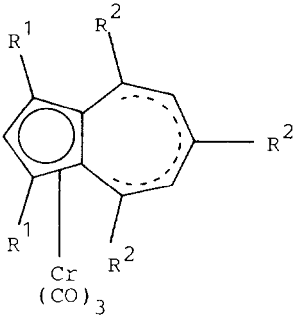

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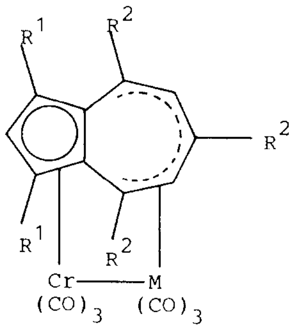


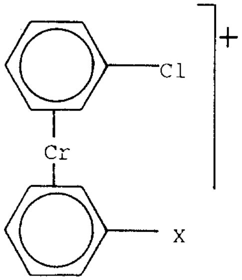
4.81

η-arenetricarbonylchromium complexes [81]. The mechanism of the rearrangement of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum to (bicyclo[4.2.1]nona-2,4,7-triene)tricarbonylmolybdenum has been investigated [82]. The alkaloid (-)-canadine underwent regiospecific attack by hexacarbonylchromium to give the complex (4.76) as a mixture of two diastereoisomers and this intermediate was used for the stereoselective synthesis of (-)-(8R)-methylcanadine [83]. The binuclear benchrotrene complex (4.77; M = Hg, n = o) was attacked by samarium, ytterbium and europium to give the bivalent lanthanide complexes (4.77; M = Sm, Yb, n = 2; M = Eu, n = 1) [84].

Azacymantrene combined with the photoproduct of THF and (η^6-arene)Cr(CO)$_3$ to form the mixed dinuclear product (4.78; arene = benzene, methyl benzoate, mesitylene) [85]. The benchrotrene complexes (4.79; n = 2,3; X = Br) combined with Na[Fe(CO)$_2$(η-C$_5$H$_5$)] to give the heteronuclear complexes [4.79; n = 2,3; X = Fe(CO)$_2$(η-C$_5$H$_5$)] and with sodium iodide in acetone to give the iodides (4.79; n = 2,3; X = I) [86]. Reaction of the η-azulene complexes (4.80) with (CH$_3$CN)$_3$M(CO)$_3$, (M = Cr, Mo) produced the corresponding dinuclear compounds (4.81; M = Cr, $R^1 = R^2$ = H, R^1 = H, R^2 = Me, R^1 = t-Bu, R^2 = H; M = Mo, $R^1 = R^2$ = H, R^1 = H, R^2 = Me). The structure of (μ-4,6,8-trimethylazulene)Cr$_2$(CO)$_6$ (4.81; M = Cr, R^1 = H, R^2 = Me) was determined by X-ray analysis and this complex had a long Cr-Cr bond of 3.26nm [87].

5. (η-C$_6$H$_6$)$_2$Cr

The formation of (η-arene)M$_2$ and (η-arene)$_2$M$_2$ complexes has been investigated by deposition of vanadium and chromium atoms into solutions of bis(η-toluene)-vanadium and -chromium respectively. Modes of bonding in metal-dimer arene molecules were discussed [88]. Bis(η^6-4-chloroanisole)chromium has been prepared by condensation of the arene ligand with chromium vapour [89]. Non-symmetrically substituted bis(η-arene)-chromium complexes (5.1-5.5; for example, X = H, CF$_3$, Cl,Me) have been prepared by the low-temperature condensation of chromium vapour with an arene or a mixture of arenes followed by modification of the substituents in the arene ligands [90]. The three isomeric bis(η-benzene)chromium complexes (5.6; X = o, m, p-Cl) were prepared by cocondensation of chromium



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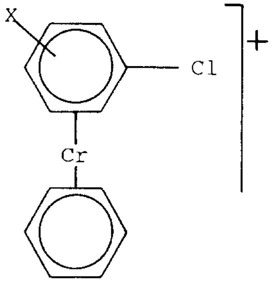

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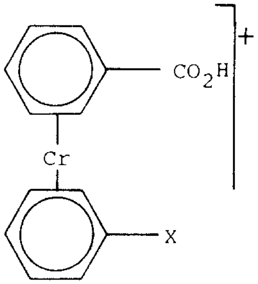

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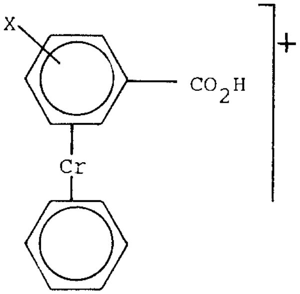

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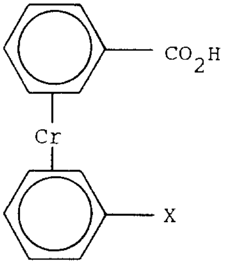

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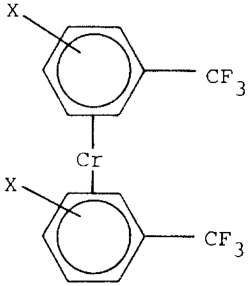

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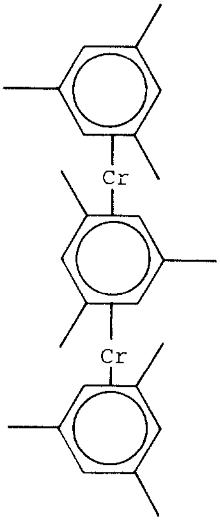

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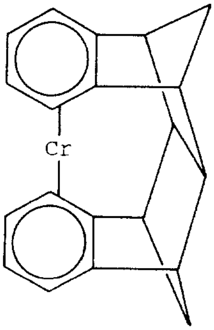
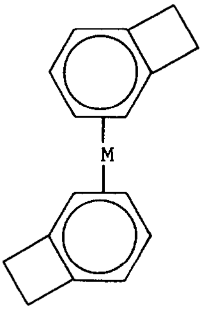


5.8

atoms with the appropriate ligand. The chlorine atom underwent nucleophilic dispacement by thiophenoxide to form the complexes (5.6; $\text{X} = \underline{o}, \underline{m}, \underline{p}\text{-S.C}_6\text{H}_5$). The displacements proceeded faster than with the free arenes and showed a different pattern of relative reactivities [91].

Cocondensation of mesitylene with chromium atoms at high metal to ligand ratios gave the triple-decker complex (5.7) in addition to the expected sandwich complex bis(η-mesitylene)-chromium [92]. The chromium complex (5.8) has been prepared by the cocondensation of chromium atoms with the ligand vapour. The ^{1}H NMR spectrum of the complex (5.8) was recorded and analysed together with the ESR spectrum of the corresponding radical cation [93]. The η^6-arene complexes (5.9; M = Cr, Mo, W and 5.10) have been prepared by metal atom, ligand vapour



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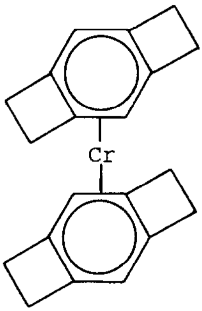

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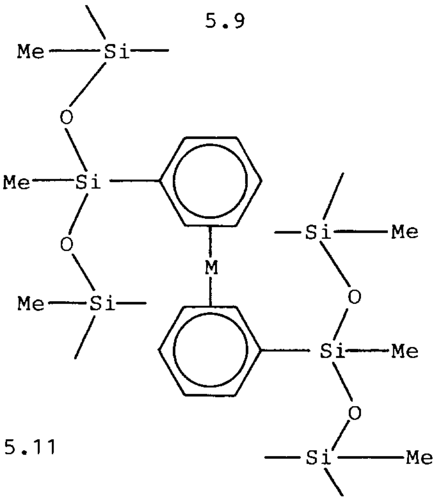

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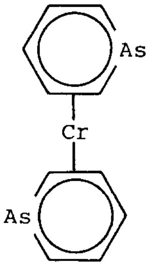
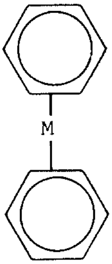


5.12

cocondensation techniques. The ^{1}H NMR spectra together with the ESR spectra of the corresponding radical cations were recorded and discussed [94]. The reactions of vanadium, chromium and molybdenum atoms with arene-functionalized liquid polysiloxanes to produce organometallic polymers (5.11; M = V, Cr, Mo) has been examined in detail [95].

Low molecular weight oligomers of poly(phenylmethylsilylene-*co*-dimethylsilylene) have been treated with molybdenum atoms to form oligosilastyrene-supported bis(η-arene)molybdenum complexes [96]. Cocondensation of chromium vapour with arsabenzene produced bis(η^6-arsabenzene)chromium (5.12). The structure of this complex was determined by X-ray analysis [97]. Bis(η-arene)-



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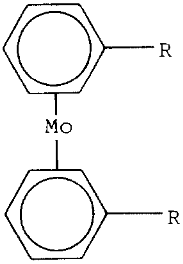

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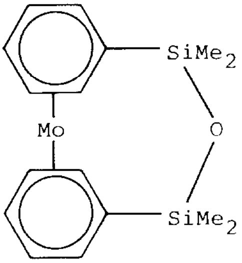

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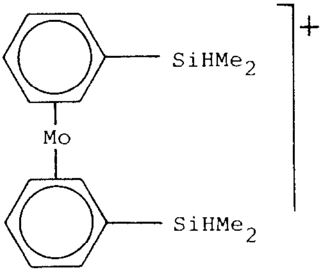
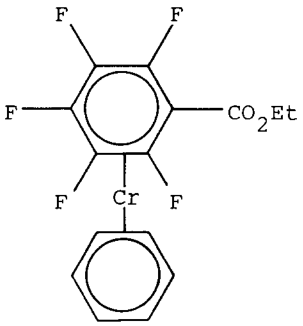


5.16

chromium(O) complexes combined with glycerin and ethylene glycol to give glycerates and glycolates of chromium(III) by way of the intermediate bis(η-arene)chromium(I) cations [98]. Two one-electron oxidation-reduction processes have been observed for bis(η-hexamethylbenzene)chromium(O) corresponding to the species 2+/1+/0 [99]. Charge separation in the complexes (5.13; M = Cr, Mo, W) has been studied by intensity analysis of the infrared spectra. It was concluded that the charges on the metals were higher than those in the corresponding bis(η-cyclopentadienyl) complexes [100].

The gas phase decomposition of bis(η-arene)chromium complexes proceeded by way of homogeneous and heterogeneous stages. Rate constants were determined for the process [101].



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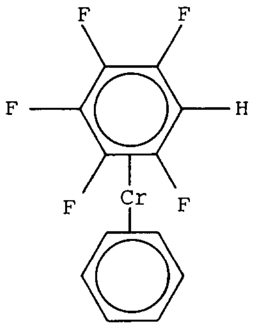

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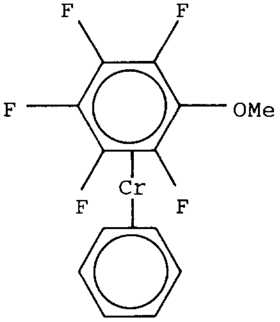

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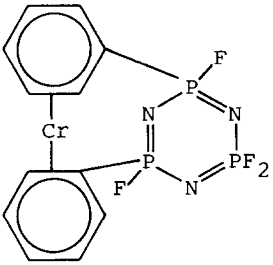


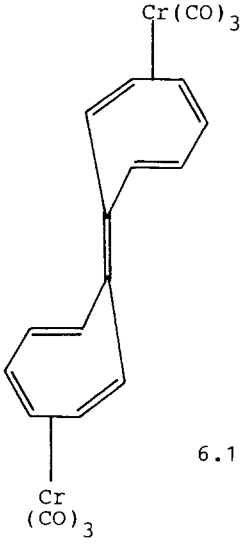
5.20

Interactions between benchrotrene or alkylbenchrotrenes and non-dipolar solvents such as cyclohexane, benzene and dioxane have been investigated by dipole moment, microwave dielectric absorption, electric birefringence, infrared and ^{1}H NMR spectroscopy. Atomic polarizations were found to be negligibly small while specific interactions took place between benzene or dioxane and the coordinated arene group which behaved as an electrophile [102]. The bis(η-benzene)molybdenum complexes with alkene substituents (5.14; R = $CH=CH_2$, 4-$C_6H_4CH=CH_2$, $CH_2CH=CH_2$) have been prepared and one of them (5.14; R = $CH_2CH=CH_2$) has been characterized by X-ray crystallography. The complexes (5.14) behaved as vinyl monomers and underwent polymerization in the presence of AIBN. Bis(η-benzene)molybdenum (5.14; R = H) has been dimetallated with n-butyllithium-tetramethylethylenediamine to give the intermediate (5.14; R = Li) which has then been treated with deuterium oxide, methyliodide and chlorotrimethylsilane to form the derivatives (5.14; R = D, Me, $SiMe_3$). The siloxane (5.15) has been prepared from the same intermediate (5.14; R = Li) while the cationic disilane (5.16) has been formed by cocondensation of molybdenum atoms with dimethylphenylsilane and acidification. Both of these products (5.15 and 5.16) have been characterized by X-ray crystallography [103].

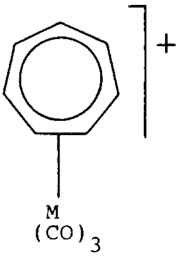
The attempted hydrolysis of the ester (5.17) did not give the expected acid but the product of decarboxylation (5.18) together with traces of the ether (5.19) [104]. The treatment 1,1'-dilithiobis(η-benzene)chromium with hexafluorocyclophosphazene afforded the bridged complex (5.20) [105]. Bis(η-benzene)chromium was an efficient catalyst for the cooligomerization of perfluoropropylene and perfluorobut-2-yne [106].

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

The thermal reaction of heptafulvalene with $[Cr(CO)_3(MeCN)_3]$ produced the bis(tricarbonylchromium) complex (6.1). Irradiation of this complex in the presence of 1,3-butadiene afforded tricarbonyl-η^6-11-(2,4,6-cycloheptatrien-1-ylidene)bicyclo[4.4.1]-undeca-2,4,8-triene-chromium and tricarbonyl-η^6-bi(bicyclo-[4.4.1]undeca-2,4,8-trien-11-ylidene)-chromium [107]. The electronic structure and reactivity of (η-cycloheptatrienyl)-metal complexes (6.2; M = Cr, Mo, W) have been the subject of a



6.1



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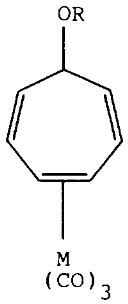
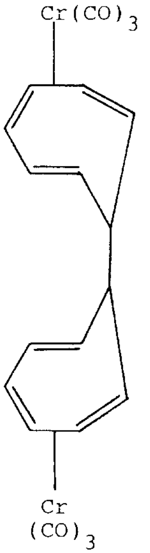


6.3

theoretical study using EHMO and interaction determinant reactivity methods. The attack by methoxide at metal and carbonyl sites of the complexes (6.2) has been interpreted in terms of charges, frontier charge densities and interaction energies. The formation of the 7-exo ring adduct as the thermodynamically preferred product was explained by extended Hueckel results [108]. The products obtained were the (η-cycloheptatriene)metal complexes (6.3; M = Cr, Mo, W; R = Me, Et) [109].

Ultraviolet irradiation of the bis(tricarbonylchromium) complex (6.4) in the presence of 1,3-butadiene gave preferentially the product of a twofold [4+6]-cycloaddition (6.5). Similar reactions were carried out between the complex (6.4) and E-1,3-pentadiene and EE-2,4-hexadiene. Further reactions of these complexes were investigated [110]. Methoxide ion attacked the (η-cycloheptatrienyl)metal cations (6.2; M = Cr, Mo, W) to give the carbomethoxy complex (6.6) in a fast, reversible reaction. A second slower process gave the products of addition to the η-cycloheptadienyl ring (6.3; M = Cr, R = Me). This latter reaction showed metal dependence with second order rate constants in the ratio 50:10:1 for Cr:Mo:W [111]. The formation and reactions of the (η-cycloheptatrienyl)molybdenum complexes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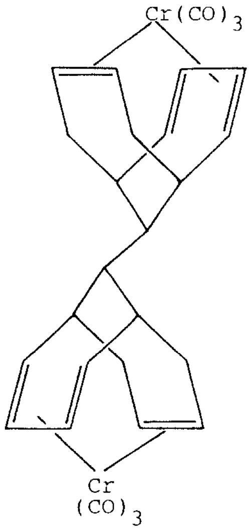
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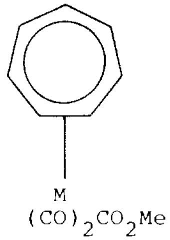
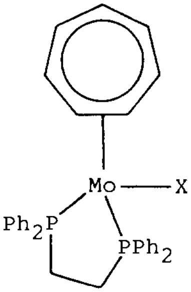

6.6

(6.7; X = Cl, I, Me, H) and the corresponding cations have been reported [112].

Reactions of the iodide (6.8) with bis(tertiaryphosphine) ligands have been studied and included the formation of the cationic complex (6.9) [113]. A kinetic study of the reaction of triphenylphosphine with the cation (6.2; M = W) indicated rapid formation of a π-complex followed by a rate-limiting attack of a further molecule of triphenylphosphine at the tungsten atom. Rapid displacement of the cycloheptatrienyl ring occurred on attack by a third molecule of triphenylphosphine to give tricarbonyltris(triphenylphosphine)tungsten [114]. The (η^3-cycloheptenyl)molybdenum complexes (6.10; R^1 = Me, $CH_2CH=CH_2$, 4-MeO.C_6H_4, R^2 = H) underwent hydride abstraction with Ph_3CPF_6 to give the (η^4-cycloheptadiene)molybdenum cations (6.11; R = Me, $CH_2CH=CH_2$, 4-MeO. C_6H_4) which then underwent regioselective and diastereoselective alkylation to form the (η^3-cycloheptenyl)molybdenum derivatives [6.10; R^1 = Me, $CH_2CH=CH_2$, 4-MeO.C_6H_4, R^2 = Me, CN, $CH(CO_2Me)_2$, $CH(CO_2Me)SO_2Ph$] and the regioisomers (6.12). Several of these products were decomplexed, thus the complex [6.10; R^1 = Me, R^2 = $CH(CO_2Me)$-SO_2Ph] was desulphonated, saponified and then decomplexed with



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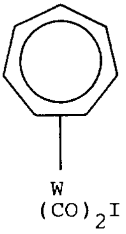

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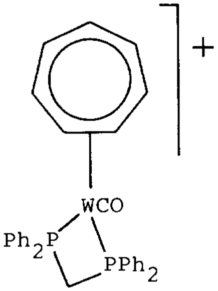

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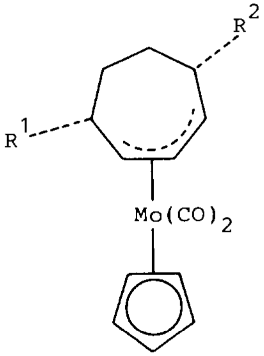

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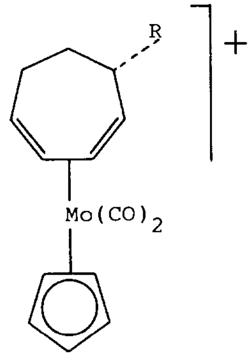

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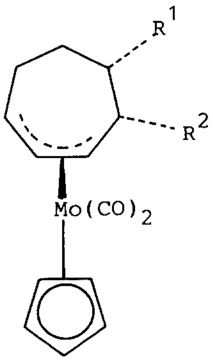

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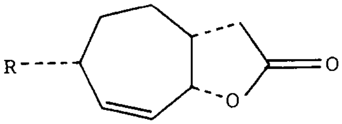


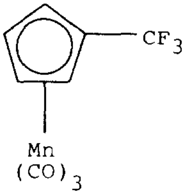
6.13

iodine or $NOPF_6$ to give the lactone (6.13) [115].

7. (η-C_5H_5)Mn(CO)$_3$

(i) Formation

The thermal reaction of neat pentamethylcyclopentadiene with $Mn_2(CO)_{10}$ produced a 77:23 mixture of the products (η-C_5Me_5)- and (η-C_5Me_4H)-Mn(CO)$_3$ produced by competitive activation of the doubly allylic C-H and C-Me bonds of the diene [116]. The reaction of thallium trifluoromethylcyclopentadienide with bromopentacarbonylmanganese produced the tricarbonylmanganese derivative (7.1) in good yield. Several other organometallic compounds containing the trifluoromethylcyclopentadienyl group were prepared including 1,1'-bis(trifluoromethyl)ferrocene where the trifluoromethylcyclopentadienyl group was shown to behave as a strong electron withdrawing ligand [117]. The reaction of 2-borolenes and 3-borolenes



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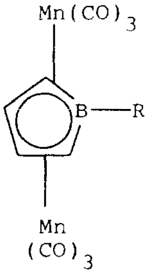

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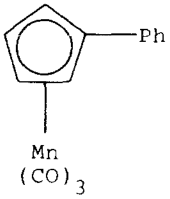

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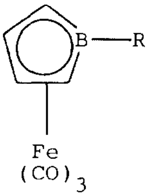

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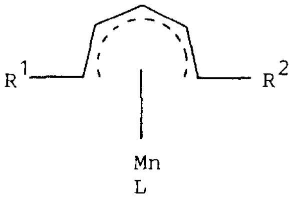

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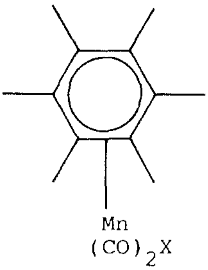

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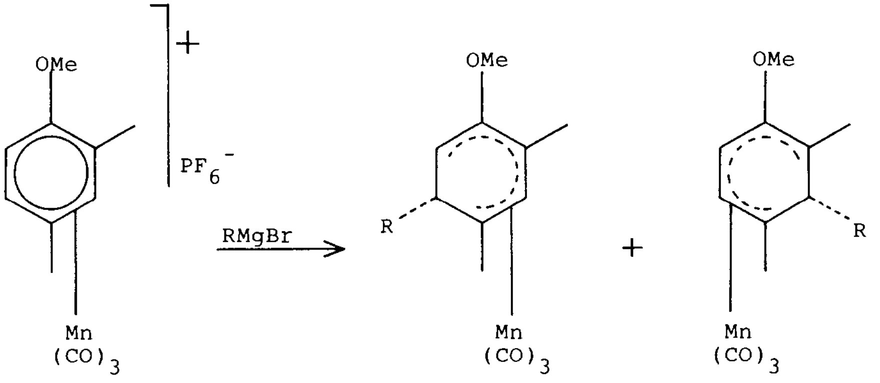

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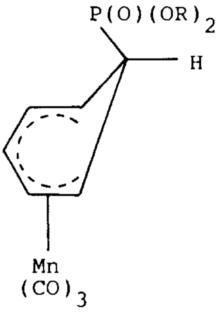

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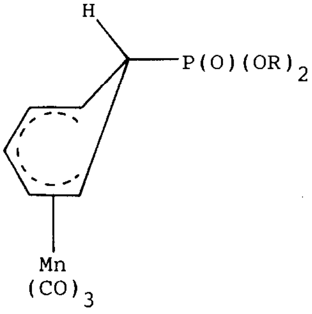

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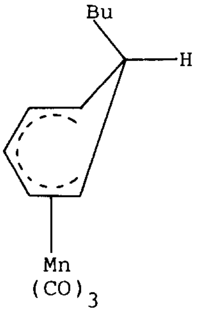

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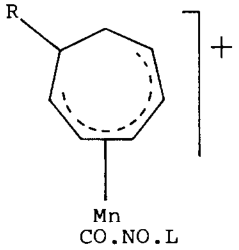

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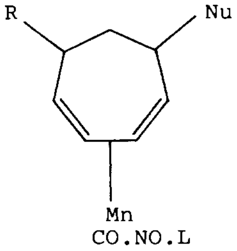


7.14

C_4H_6BR, where R = Ph, Me, C_6H_{11},OMe, with $Mn_2(CO)_{10}$, $Fe(CO)_5$ and $Co_2(CO)_8$ afforded the corresponding (η^5-borole)metal complexes. For example, $Mn_2(CO)_{10}$ gave the triple-decker complexes (7.2; R = Ph,OMe) together with some phenylcymantrene (7.3) and $Fe(CO)_5$ produced the half-sandwich complexes (7.4; R = Ph, Me, C_6H_{11}, OMe) [118].

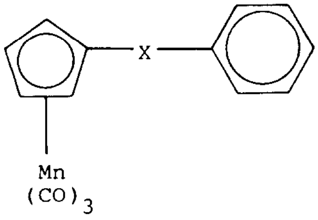
Treatment of potassium pentadienide or potassium 2,4-dimethylpentadienide with manganese(II) bromide in the presence of $(Me_2PCH_3)_3CMe$ or $(Et_2PCH_2CH_2)_2PPh$ produced the corresponding (η^5-pentadienyl)tris(phosphine)manganese complexes [7.5; L = $(Me_2PCH_2)_3CMe$, $(Et_2PCH_2CH_2)_2PPh$, R^1 = R^2 = H, Me]. The structures of two of the complexes were determined by X-ray analysis. The complexes had approximately octahedral geometries with C1, C3 and C5 of the η-pentadienyl ligands and the three phosphorus atoms of the phosphine ligands in the six coordination sites [119]. Photolysis of the cation $[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]^+$ in aqueous sodium halide solution produced the corresponding manganese-halogen compounds (7.6; X = Cl, Br, I). The reactions of these and related compounds were investigated. For example, treatment of the iodo-compound (7.6; X = I) with methyllithium gave the methyl derivative (7.6; X = Me). X-ray analysis indicated that the chloro-compound (7.6; X = Cl) had a "piano stool" type structure with the carbonyl and chloro groups staggered relative to the η-arene carbon atoms [120].

Reaction of the manganese complex (7.7) with vinylmagnesium bromide afforded a 4/1 mixture of the neutral complexes (7.8 and 7.9; R = $CH{=}CH_2$). When the alkylation was carried out with methylmagnesium bromide the reverse regioselectivity was observed and a 1/4 mixture of the neutral complexes (7.8 and 7.9; R = CH_3) was produced [121]. Reaction of $[(\eta^6\text{-benzene})Mn(CO)_3]$-$PF_6$ with an excess of sodium dialkylphosphate produced the exo-phosphonate complex (7.10; R = Me, Et). These complexes rearranged on treatment with n-butyllithium and water to give the corresponding endo- complexes (7.11) together with some of the butylated compound (7.12) [122]. In a related paper Honig and Sweigart investigated the electrophilic reactivity of the η-cycloheptadienyl ring in the manganese complexes (7.13; R = H, Ph; L = CO, PBu_3). Phosphorus and nitrogen donor nucleophiles (Nu) added to the ring to produce the corresponding cycloheptadiene complexes [7.14; Nu = for example, $P(OBu)_3$,

PPh_3, PBu_3, imidazole, 2-, 3- and 4-Me-pyridine]. A substituent on the C(6) carbon atom in the complexes (7.13) did not produce any detectable steric effect [123].

(ii) Spectroscopic and physicochemical properties

The electronic structures of cymantrene complexes (7.15; X = CO, CH_2, CH=CH) have been investigated using Self-Consistent Charge and Configuration calculations. The calculated charges and Mulliken populations correlated with the IR carbonyl frequencies. Delocalization was found to be important [124]. X-ray crystallography and ^{29}Si NMR spectroscopy have been used to characterize the cymantrene-silane complexes [7.16; L = CO, PR_3, $P(OR)_3$, CNR]. The complexes contained Mn, H, Si three-centre two-electron bonds which were strongly influenced by electronic and steric properties of both the metal containing moiety and the silyl group [125]. The η^5-ligand-metal bond strengths in the complexes $LM(CO)_3$, where L = cyclopentadienyl indenyl, fluorenyl; M = Mn, Re, have been determined by mass spectrometry. The bond strength decreased in the order cyclopentadienyl>indenyl>fluorenyl but the metal was more important than the η^5-ligand in determining bond strength [126].



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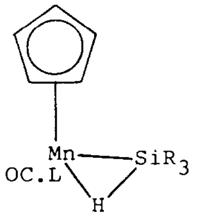

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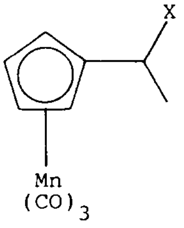

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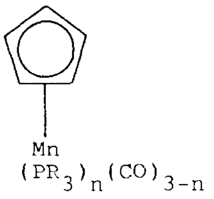
The chiroptical properties, as measured by CD, ORD and [α], have been determined for fourteen optically active monosubstituted cymantrenes, each with an chiral centre bonded directly to the cyclopentadienyl ring. Each of the (R)-enantiomers exhibited a negative Cotton effect for the metallocenyl transition in the



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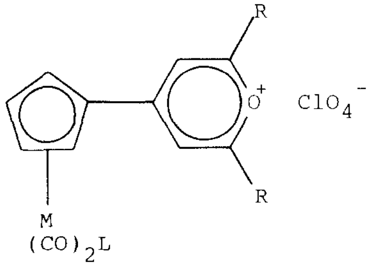

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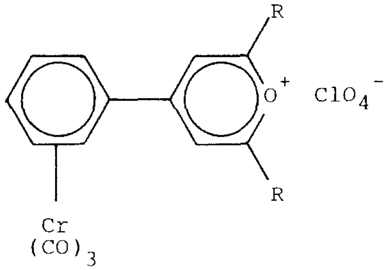

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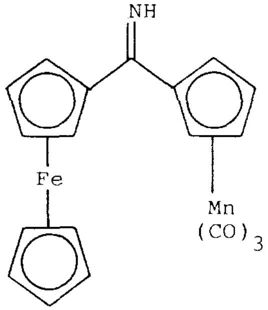

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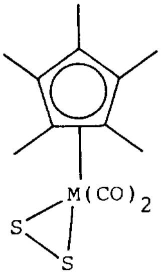
CD spectra in the range 310-360 mn which was independent of the nature of the substituent and the solvent. Among the complexes studied were the amines and amine derivatives (7.17; X = NH_2, NMe_2, $NHCH_2Ph$, NHMe, NMe_3I, N=CHPh, NHCHO) [127]. The ^{31}P NMR spectra of a series of (η-cyclopentadienyl)manganese complexes, for example, (7.18; n = 1,2) have been recorded. The coordination shifts $\Delta\delta$ decreased with decreasing Mn-P π-interaction as the steric requirement of the phosphine ligand increased [128]. Cymantrenyl-methanol has been used in an IR study of the acid-base properties of [2-(α-carbinol)norbornadiene]-(η-cyclopentadienyl)rhodium [129]. Carbonyl substitution in tricarbonyl(η^5-pyrrolyl)manganese by phosphines has been the subject of a kinetic study. Strongly basic ligands such as tributylphosphine gave disubstituted derivatives while weakly basic ligands such as triethylphosphite gave monosubstituted products [130].



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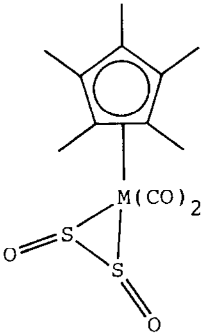

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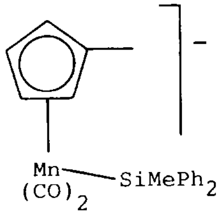

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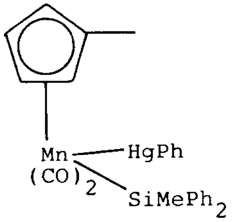

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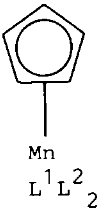

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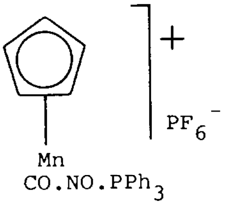


7.27

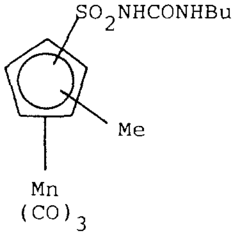
(iii) General

Cymantrenyllithium has been treated with pyrylium salts to give pyrans which were converted to the pyrylium derivatives (7.19; R = Ph, Me_3C; M = Mn; L = CO, PPh_3; M = Re, L = CO). The corresponding benchrotrene derivatives (7.20; R = Ph, Me_3C) were also prepared [131]. The reaction of lithiocymantrene with cyanoferrocene produced the ketimine (7.21). Some reactions of the ketimine were investigated [132]. Oxidation of the disulphur complexes (7.22; M = Mn, Re) with 3-chloro-perbenzoic acid afforded the corresponding disulphur monoxide complexes. Further oxidation produced the corresponding disulphur dioxide complexes (7.23). Infrared spectroscopy indicated that the sulphur containing ligands were stronger electron withdrawing groups than carbon monoxide and the acceptor capacity increased in the order $S_2<S_2O<S_2O_2$ [133]. The anionic silyl complex (7.24) combined with transition metal halide complexes to give hetero-

nuclear complexes. Thus phenylmercury bromide gave the very stable product (7.25) [134].

(η-Cyclopentadienyl)- and (η-methylcyclopentadienyl)-dicarbonyl(tetrahydrofuran)manganese have been treated with optically active chelating phosphine ligands. Mononuclear complexes containing the phosphines as unidentate or as bidentate ligands were obtained together with dinuclear complexes that contained the phosphines as bridging ligands. The complexes were used as enantioselective hydrogenation and hydrosilylation catalysts [135]. The (η-cyclopentadienyl)manganese complexes (7.26; $L^1 = L^2 = CO$; $L^1 = PPh_3$, $L^2 = CO$; $L^1 = CO$, $L_2^2 = Ph_2PCH_2CH_2PPh_2$ and 7.26) underwent hydrogenation over Pd/C to give cyclopentane together with a small amount of cyclopentene. Azaferrocene was also hydrogenated but tricarbonyl(η-cyclopentadienyl)rhenium was unaffected [136]. The cymantrene complexes $(\eta\text{-}C_5H_5)Mn(CO)_2PX_3$, where X = Cl, Br, have been treated with octacarbonyldicobalt to give the cluster complex $Co_3(CO)_9$-$[\mu\text{-}Mn(CO)_2(\eta\text{-}C_5H_5)]$. Carbonyl displacement reactions of the cluster were examined [137]. Styrene has been copolymerized with vinylmethylcymantrene to give a copolymer that underwent a light induced reaction with molecular nitrogen. Species containing the group $(\eta\text{-}MeC_5H_3)Mn(CO)_2N_2$ were identified [138].

The cymantrene derivative (7.28) has been compared with tolbutamide (7.29) in tests for hypoglycemic activity in streptozotocin-induced diabetic rats and formal fasted rabbits. The cymantrene compound (7.28) was less active than tolbutamide (7.29) [139]. Cymantrene has been used as a catalyst for the decompos-



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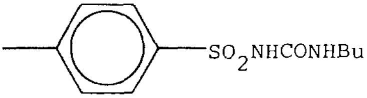

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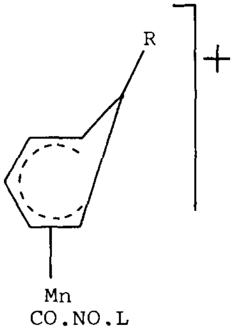

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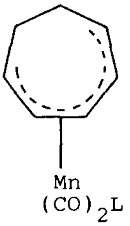

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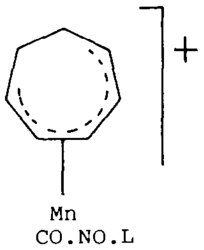

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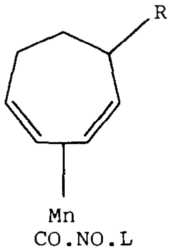
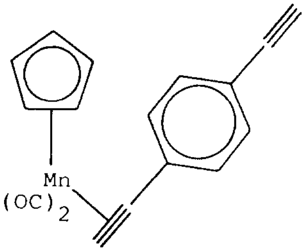


7.33

ition of dodecyl hydroperoxide [140]. A kinetic study has been carried out on the addition of phosphorus and nitrogen donor nucleophiles to the η-cyclohexadienyl ring in the manganese complexes (7.30; L = CO, PPh_3). From the result it was concluded that the $[Mn(CO)(NO)L]^+$ moiety was electronically equivalent to the $[Fe(CO)_2L]^+$ group for activating a η-cyclohexadienyl group. It was suggested that a substituent (R = Me, Ph, CN) at the C(6)-saturated carbon atom in the complexes (7.30) produced a steric retardation on the rate of nucleophilic addition [141]. The (η-cycloheptadienyl)manganese complexes (7.31; L = CO, PR_3) have been treated with $NOPF_6$ to generate the (η-cycloheptadienyl)manganese cations (7.32; L = CO, PR_3) which were susceptible to attack by nucleophiles such as MeLi and $NaCH(CO_2Et)_2$ to give the products [7.33; R = Me, $CH(CO_2Et)_2$ [142].



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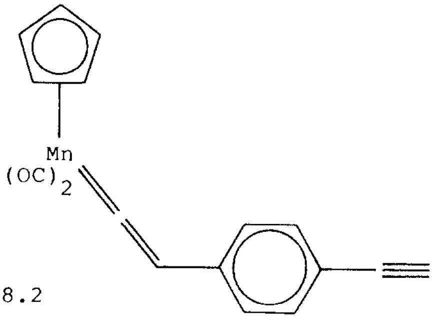

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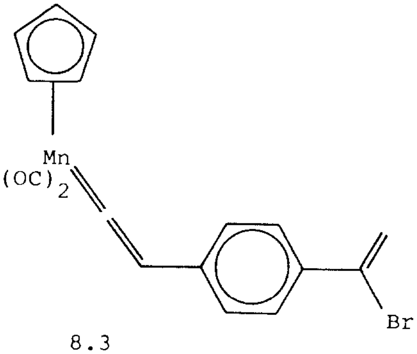

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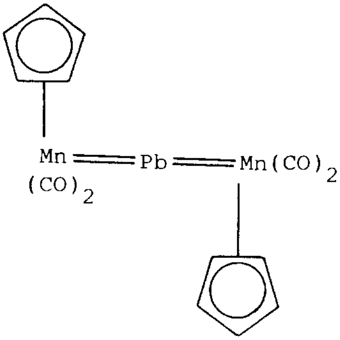

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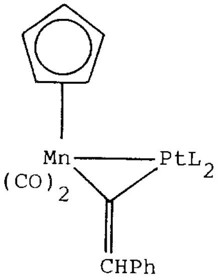

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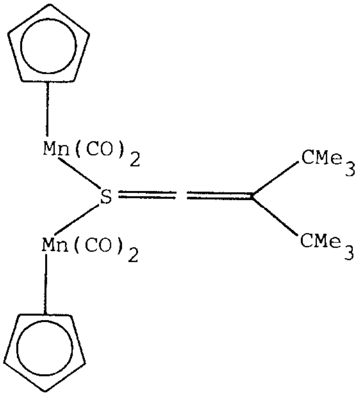
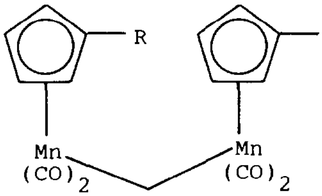


8.6

8. Polynuclear and carbene (η-C_5H_5)Mn(CO)$_3$ complexes

Diethynylbenzene combined with (η-C_5H_5)Mn(CO)$_2$. THF to give the η^2-acetylene complex (8.1) which isomerized in the presence of phenyllithium to give the allene (8.2) and this was in turn converted to the derivative (8.3) with lithium bromide. The crystal and molecular structure of this complex (8.3) has been confirmed by X-ray crystallography [143]. Cymantrene has been irradiated and then treated with lead(II) chloride to give the heteronuclear complex (8.4). X-ray crystallography confirmed that the Mn-Pb-Mn moiety was almost linear with Mn-Pb double bonds. The corresponding reaction with germanium(II) chloride gave (η-C_5H_5)Mn(CO)$_2$($GeCl_2$) [144]. The μ-vinylidene complexes [8.5; L = PPh_3, P($OCHMe_2$)$_3$] have been treated with nucleophilic molecules such as phosphines, phosphites and carbon monoxide. The dimetallacycle remained intact and products of substitution of the platinum bound terminal ligands were isolated [145].



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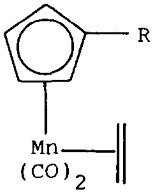

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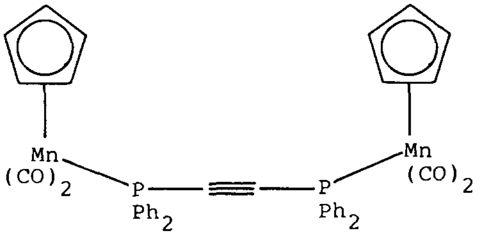

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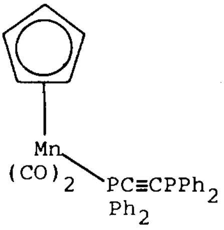

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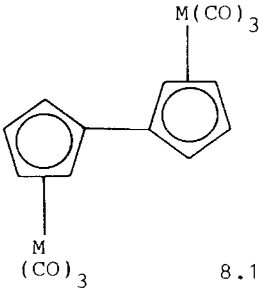
Treatment of di-t-butylthioketene $[(Me_3C)_2C{=}C{=}S]$ with dicarbonyl(η-cyclopentadienyl)tetrahydrofuranmanganese afforded the dinuclear complex (8.6) [146].

Reaction of dicarbonyl(η-cyclopentadienyl)tetrahydrofuranmanganese and the corresponding η-methylcyclopentadienyl complex with the sulphur ylides $(Me_2N)(R)S(O){:}CH_2$ (R = Me, Ph) afforded the μ-alkylidene complexes (8.7; R = H, Me) together with the



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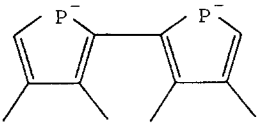

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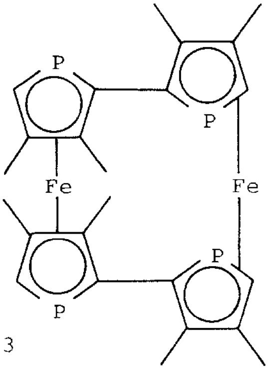

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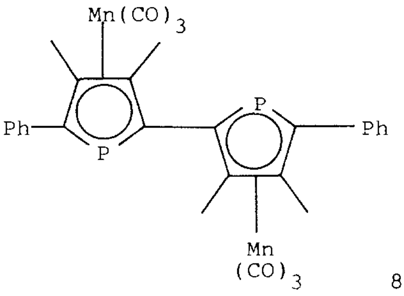
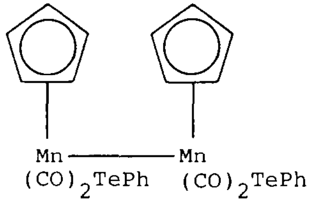


8.14

η-ethylene complexes (8.8; R = H, Me) [147]. The reaction of dicarbonyl(η-cyclopentadienyl)tetrahydrofuranmanganese with bis(diphenylphosphine)acetylene in a 2/1 molar ratio produced the binuclear diphosphine-bridged complex (8.9). When a 1/1 molar ratio of the reactants was used the mononuclear complex (8.10) was isolated [148]. The reaction of dihydrofulvalene with thallium ethoxide afforded fulvalenedithallium which was used to prepare the η-fulvalene complexes (8.11; M = Mn, Re) in high



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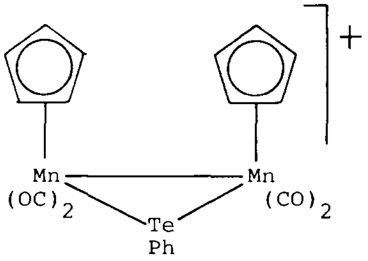

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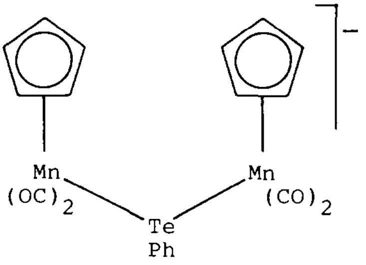

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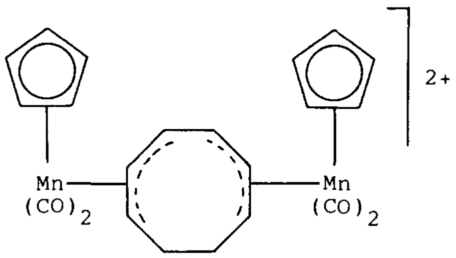
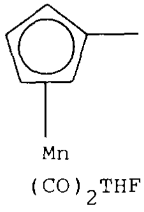


8.18

yields [149]. Reaction of the biphospholyl anion (8.12) with iron(II) chloride afforded the diiron complex (8.13) as a mixture of isomers. Treatment of 1,1'-diphenyl-3,3',4,4'-tetramethyl-2,2',5,5'-tetrahydro-2,2'-biphosphole with $Mn_2(CO)_{10}$ in a closed vessel under autogenous carbon monoxide pressure at 150° produced the dimanganese complex (8.14). This complex was formed via a [1,5]-sigmatropic shift of the two phenyl groups from phosphorus to carbon within the phosphole rings [150].

Oxidation of the binuclear cymantrene complex (8.15) with $AgPF_6$ gave the cation (8.16) with a long Mn-Mn bond while reduction with sodium tetrahydroborate gave the anion (8.17) with pseudotetrahedral coordination about tellurium [151]. The dimanganese cyclooctadienediyl cation (8.18) has been obtained from the corresponding cyclooctadiene complex by abstraction of hydride ions with trityl fluoroborate [152]. The cymantrene derivative (8.19) combined with $PhCH_2N_3$ to give



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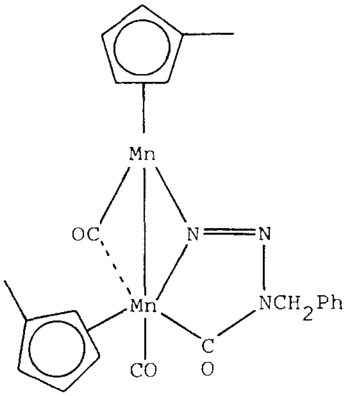

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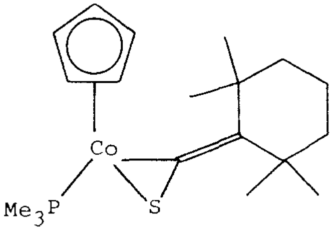

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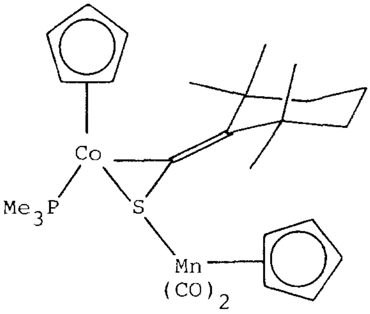
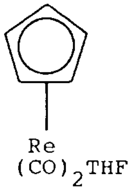


8.22

the binuclear complex (8.20) the structure of which was confirmed by X-ray crystallography. Photolysis of the complex (8.20) in methanol gave $PhCH_2NHCO_2Me$. Thus the reaction sequence achieved the carbonylation of benzylazide to benzyl isocyanate by way of an organometallic intermediate [153]. Reaction of the electrophile $[(\eta\text{-}C_5H_5)Mn(CO)_2THF]$ with the thioketene complex (8.21) produced the dinuclear thioketene derivative (8.22). The structure of this latter compound was determined by X-ray analysis [154].

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

The binuclear chalcogen-bridged rhenium complexes (9.2; X = S, Se, Te) have been prepared by treatment of the photochemical intermediate (9.1) with the appropriate chalcogen. The crystal and molecular structure of one of the complexes (9.2; X = Se) has been determined by X-ray crystallography [155].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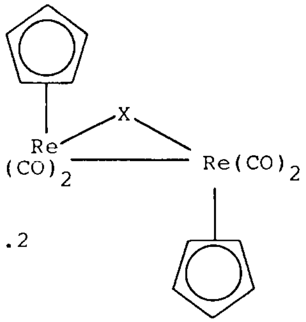
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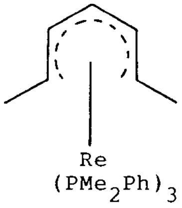
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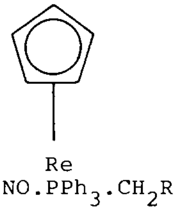
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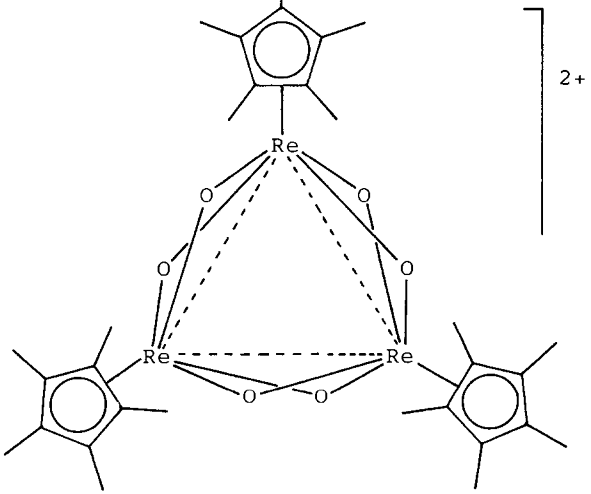
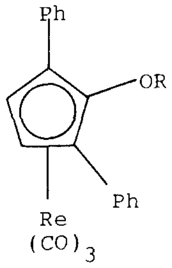

9.5

The η^5-pentadienyl complexes (9.3; R = H, Me) have been prepared by reaction of fac-$ReCl_3(PMe_2Ph)_3$ with an excess of the potassium salt of the appropriate pentadienide. The structure of the complex (9.3; R = Me) was determined by X-ray analysis. The five metal bound carbon atoms of the ligand were coplanar. NMR spectroscopy showed that the complexes were fluxional [156].

EHMO calculations have been used to determine the energy barrier to rotation about the Re-C(α) bond in the organorhenium complexes (9.4; R = Me, Ph) and in the corresponding cations. Values of 2.4 and 3.2kcal mol^{-1} respectively were obtained and these were used to analyze the energetics of α-hydride abstraction from the complexes (9.4) [157]. A theoretical analysis of the stepwise reduction of $[(\eta-C_5H_5)Re(NO)(CO)PPh_3]^+$ to $[(\eta-C_5H_5)Re$

(NO)(CH$_3$)PPh$_3$] has been carried out. The HOMOs of the complexes were predominantly metal d in character, while the LUMOs were apparently antibonding combinations of Re d orbitals and nitrosyl π^* orbitals [158]. Extended Hueckel and SCF Xα-SW calculations have been used to describe the bonding and structure of the cluster cation (9.5). The results indicated that the cation should possess two unpaired electrons resulting in paramagnetism and a triplet ground state [159].



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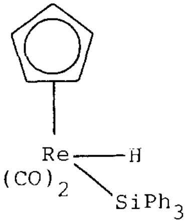

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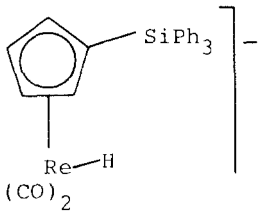

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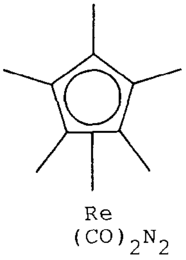

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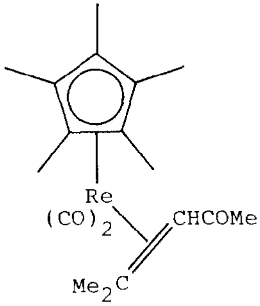

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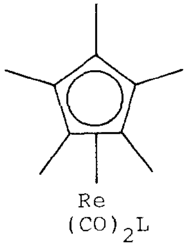
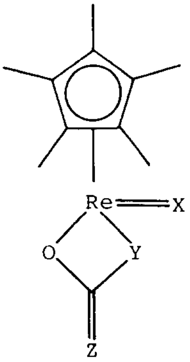


9.11

Desorption chemical ionization mass spectrometry has been used to analyze several rhenium complexes including the (η-cyclopentadienyl)rhenium derivatives (9.6; R = H, Me) [160]. Deprotonation of the (η-cyclopentdienyl)rhenium complex (9.7) with neopentyllithium at -78°C gave the anion (9.8) by way of initial deprotonation of the cyclopentadienyl ring followed by intramolecular silyl group migration. The anion (9.8) was protonated at rhenium to give the corresponding dihydride [161].



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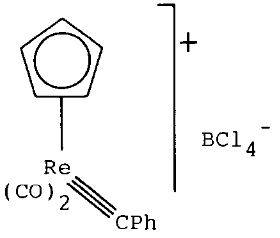

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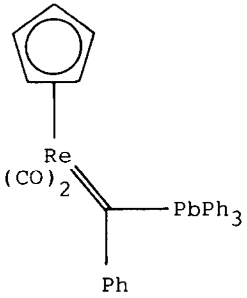

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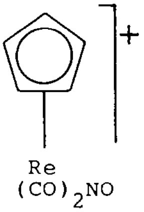

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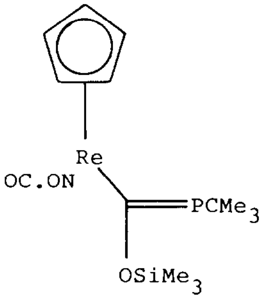
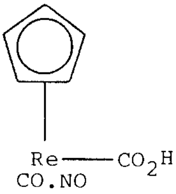


9.16

Reaction of the rhenium complex (9.9) with $[Me_3O]BF_4$ or $[Et_3O]BF_4$ in acetone produced the η-olefin complex (9.10)[162]. The (η-pentamethylcyclopentadienyl)rhenium complex (9.11; L = N_2) has been treated with hydrogen halides to give the *cis*-dihalides (9.11; L = 2Cl, 2Br, 2I) which isomerized to the *trans*-isomers on irradiation. The crystal and molecular structure of two complexes (*cis*-9.11; L = 2I and *trans*-9.11; L = 2Br) has been determined by X-ray crystallography [163]. Reductive carbonylation of the oxorhenium complexes (9.12; X = Y = O, Z = CPh_2; X = Z = O, Y = NPh) produced the corresponding rhenium dicarbonyls [9.12; X = $(CO)_2$, Y = CPh_2, Z = O; X = $(CO)_2$, Y = NPh, Z = O] [164]. The rhenium carbyne complex (9.13) has been converted to the triphenylplumbyl carbene (9.14) by treatment with $LiPbPh_3$ at -80°C [165].

The (η-cyclopentadienyl)rhenium cation (9.15) combined with $LiP(CMe_3)SiMe_3$ to form the phosphaalkenylrhenium complex (9.16)



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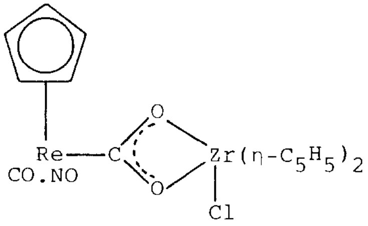

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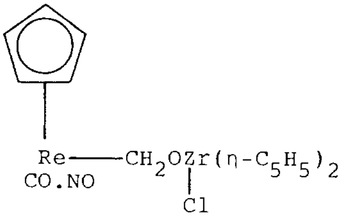

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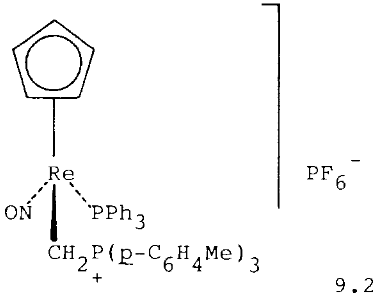

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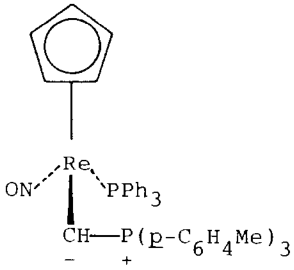

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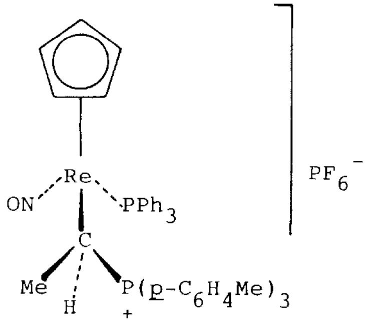
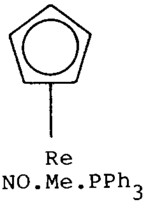


9.22

with a phosphorus-carbon double bond. The reaction mechanism involved nucleophilic addition of phosphide to a carbonyl ligand followed by 1,3-silyl migration from phosphorus to oxygen. The structure of the product (9.16) was confirmed by X-ray crystallography and several related complexes were reported [166]. Reaction of the metallo-carboxylic acid (9.17) with $(\eta\text{-}C_5H_5)_2(Cl)\text{-}Zr\text{-}CH_3$ afforded the μ-carboxylate complex (9.18). The addition of $HBF_4.OMe_2$ or $Et_3O^+PF_6^-$ to this complex immediately released the cation $[(\eta\text{-}C_5H_5)(NO)(CO)_2Re]^+$. The rhenium complex (9.19) was also prepared and investigated [167]. The salt (9.20) has been attacked by n-butyllithium-tetramethylethylenediamine to produce the ylide complex (9.21) which upon treatment with $MeOSO_2CF_3$ gave the (SS,RR)-complex (9.22) stereospecifically [168]. Reaction of the methyl complex (9.23) with $HBF_4.OEt_2$ or $HPF_6.OEt_2$ produced the corresponding salts (9.24; X = BF_4, PF_6)



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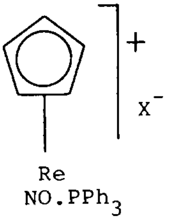

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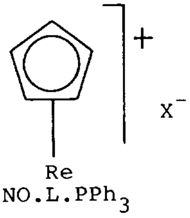

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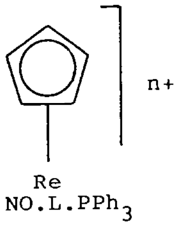

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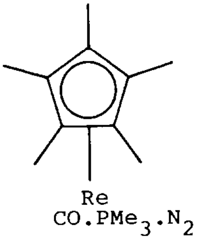

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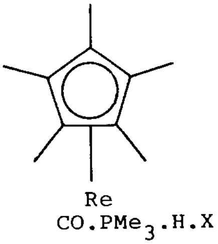
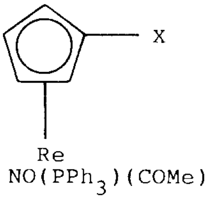


9.28

which formed derivatives (9.25; L = CO, C_2H_4, MeCN) with electron donor ligands. The syntheses of the salts (9.24; X = BF_4, PF_6) were carried out with the optically active methyl complex [(+)-(S)-9.23]. Further reactions showed that these salts (9.24; X = BF_4, PF_6) were chiral and configurationally stable [169].

The mechanism of reduction of the cation (9.26; L = CO, n = 1) has been investigated. An MO approach showed that the nitrosyl ligand was the preferred site for nucleophilic attack and formed the NHO ligand. This intermediate then rearranged to give the product (9.26; L = CHO, n = 0) [170]. The reactivity of the rhenium dinitrogen complex (9.27) has been investigated. The nitrogen ligand was displaced on brief photolysis with benzene to give the benzene C-H activation product (9.28; X = Ph) in quantitative yield. Thermal reaction with hydrogen bromide gave the bromine derivative (9.28; X = Br) [171].



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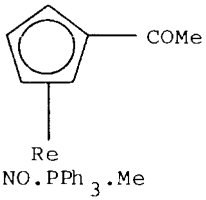

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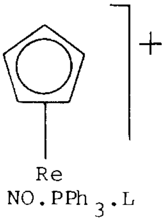

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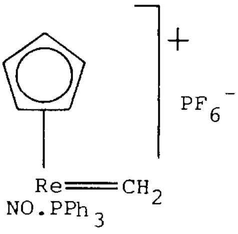

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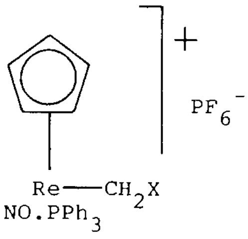
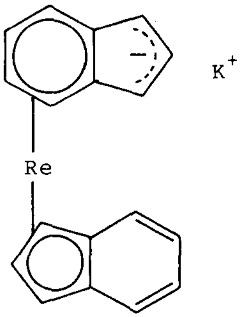


9.33

Lithiation of the (η-cyclopentadienyl)rhenium complex (9.29; X = H) at -78 °C gave the lithio-intermediate (9.29; X = Li) which underwent rapid intramolecular rearrangement to give, after methylation with iodomethane the ring-acetyl derivative (9.30). Factors determining the stereoselectivity and site of deprotonation in the reaction were investigated [172]. The complex (η-C_5H_5)Re(PPh_3)$_2$$H_2$ lost a triphenylphosphine group on photolysis to give an intermediate that was a catalyst for hydrogen-deuterium exchange between benzene, THF and alkanes [173]. The (η-cyclopentadienyl)rhenium cation (9.31; L = =CH_2) combined with $C_6H_5I^+O^-$ to give the formaldehyde complex (9.31; L = CH_2O) in 83% yield. X-ray crystallography indicated that the



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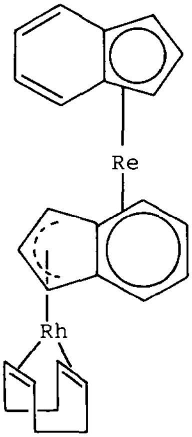

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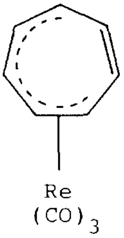
η^2-CH_2O ligand adopted a conformation that maximized overlap between the ligand π* orbital and the rhenium HOMO. The formaldehyde ligand was slowly displaced by deuterioacetonitrile to form the derivative (9.31; L = CD_3CN). Nucleophiles such as trialkylphosphines underwent addition to the complex (9.31; L = CH_2O) [174].

Reaction of the salt (9.32) with dimethylsulphide gave the sulphonium salt (9.33; X = SMe_2). Treatment of this salt with PPh_3 or pyridine produced the corresponding complexes (9.33; X = PPh_3, C_5H_5N). From these and related reactions it was concluded that the (η-C_5H_5)Re(NO)PPh_3 moiety enhanced the



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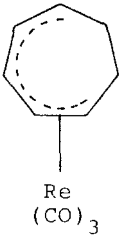

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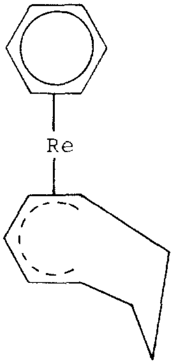

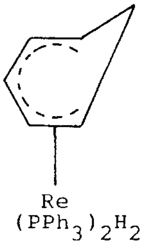

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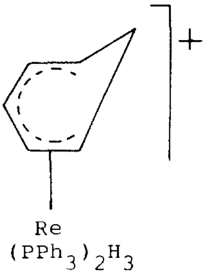

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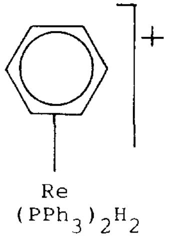


9.41

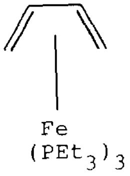
basicity of sulphide sulphur atoms that were β to it [175]. Cocondensation of rhenium atoms with indene produced (η^6-indene)-(η^5-indenyl)rhenium. Deprotonation of this complex with potassium hydride generated the salt (9.34) which underwent reaction with $[Rh(\eta\text{-}C_8H_{12})Cl]_2$ to form the complex (9.35) [176]. Photochemical reaction of rhenium carbonyl with 1,3,5-cycloheptatriene afforded two isomeric $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}\eta\text{-}C_7H_7)$ complexes together with the rheniumtricarbonyl complexes (9.36 and 9.37) [177].

Rhenium atoms have been cocondensed with benzene and either cycloocta-1,5-diene or cycloocta-1,3-diene to give the (η-benzene)-rhenium complex (9.38) [178]. Benzene, toluene and other arenes combined with the heptahydride $ReH_7(PPh_3)_2$ in the presence of 3,3,-dimethylbutene to give (η-cyclohexadienyl)rhenium complexes, such as the complex (9.39) which was converted to the cation (9.40) with acid. The complexes (9.39 and 9.40) were shown to be fluxional by ^{1}H NMR spectroscopy [179]. Hydride abstraction from the neutral (η-cyclohexadienyl)rhenium complex (9.39) with Ph_3CBF_4 gave the cationic (η-arene)rhenium product (9.41) which was reduced selectively with $LiAlH_4$ and $LiAlD_4$ to the corresponding (η-cyclohexadienyl)rhenium products (9.40) [180].

10. (Acyclic-η-diene)$Fe(CO)_3$

The (η-butadiene)iron complex (10.1) was formed from iron(II) chloride, triethylphosphine and magnesium-butadiene-2THF in THF at -10°C. Two triethylphosphine groups were readily displaced from the complex (10.1) to give products such as bis(η-butadiene)triethylphosphineiron [181]. The reaction of (η^4-butadiene)tris(trimethylphosphine)iron with carbon dioxide produced the iron complex (10.2) which was in equilibrium with the complexes (10.3 and 10.4). Treatment of the complex (10.2) with HCl-MeOH gave (Z)-$MeCH{=}CHCH_2CO_2H$ and $CH_2{=}CHCH_2CH_2CO_2H$ [182]. Treatment of trans-1-bromopenta-2,4-diene with $Fe_2(CO)_9$ produced (syn-η^3-C_5H_7)$Fe(CO)_3Br$ (10.5). Reduction of this complex afforded the tricarbonyliron complexes (10.6 and 10.7) [183]. The reaction of tetrabromodurene with $Fe_2(CO)_9$ produced the bis(tricarbonyliron) complex (10.8) [184]. Conjugated dienes combined with nonacarbonyldiiron at room temperature in reactions promoted by ultrasound to give tricarbonyl(η-diene)iron complexes in good yield. Thus the complexes (10.9; R = CO_2Me, H, OH) were obtained in yields of 100, 62 and 51% respectively. When 3-chloro-2-chloromethylprop-1-ene was the reagent then tricarbonyl(η-trimethylenemethane)iron (10.10) was obtained as the product in 90% yield [185].

Treatment of (η-C_5H_5)$Fe(CO)_2Na$ with trans-1-chloropenta-2,3-diene at -78° produced the complex (η-C_5H_5)$Fe(CO)_2$(η^1-2,4-pentadienyl). Irradiation of this complex at -20° gave a mixture of (η-C_5H_5)Fe(CO)(η^3-pentadienyl) and the η^5-pentadienyl complex (10.11). Spectroscopic evidence suggested that this molecule had a half-open-sandwich structure [186]. The (η^3,η^1-acylalkenyl)iron complexes (10.12; R = COPh, Et) underwent isomerization on thermolysis to give the (η^4-butadiene)iron complexes (10.13; R = COPh, Et) [187]. The He(1) photoelectronic spectra of tricarbonyl(η^4-α-methylstyrene)iron and tricarbonyl(η^4-1-vinylnaphthalene)iron have been recorded and the vertical ionization potentials were given [188]. The reduction of [(η-2,4-dimethylpentadienyl)$Fe(CO)_3$]$^+$ gave the



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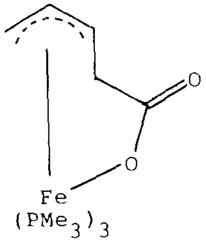

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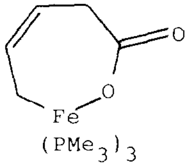

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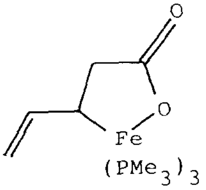

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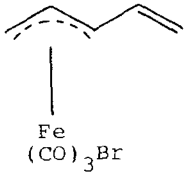

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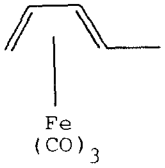

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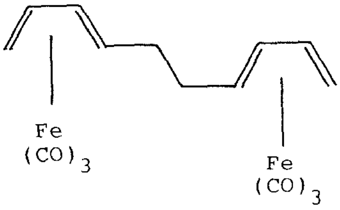

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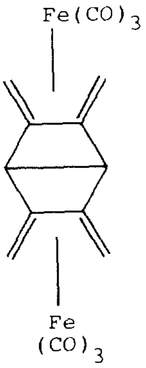

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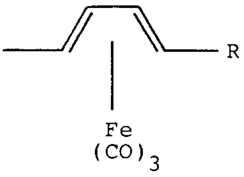

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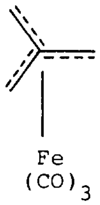

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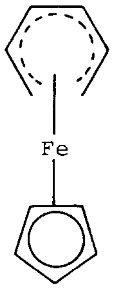
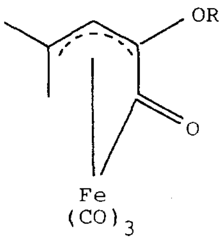


10.11

dimer ($\mu\eta^4,\eta^4$-2,4,7,9-tetramethyl-1,3,7,9-decatetraene diiron hexacarbonyl which was shown by X-ray analysis to be similar to other (η-diene)$Fe(CO)_3$ compounds [189]. Hydrocarbon-iron species have been formed by reaction between gas-phase $FeCO^+$ with dienes and alkynes in the high-pressure source of a tandem mass spectrometer. Rearrangements and structures of the species were investigated by way of the spectra of the product ions. Diene-iron adducts showed transfer of a hydrogen atom to C-1 of an η-allyl moiety to give a smaller diene ligand [190].

The molecular structures of the (η-butadiene)iron complexes (10.14; R = H, 2-Me-, 3-Me-, 4-Me-, 3-Cl-,4-Cl-, 4-MeO-, 4-CF_3-C_6H_4; 1-naphthyl, α-thienyl) have been examined by mass spectrometry [191]. ^{13}C and ^{31}P NMR spectroscopy has been used to show that (η-diene)$Fe(CO)_2PPh_3$ complexes existed as a mixture of isomers with the phosphine group in the axial (10.15) or basal (10.16 and 10.17) position of the square pyramidal structure. Methyl substitution at an internal diene carbon atom or trans- disubstitution at the terminal diene carbon atoms increased the concentration of the axial isomer. The concentration of the basal isomers was increased by cis- or trans- -monosubstitution or cis-disubstitution at the terminal carbons [192]. Matrix photolysis of the (η-azabutadiene)iron complexes (10.18; R = Pr^i, Bu^t, 4-MeC_6H_4, 4-ClC_6H_4) at 10K caused rupture of the iron-olefin bond with formation of a 16e species containing an iron-nitrogen σ bond. Photolysis in solution at 293K led to replacement of the azabutadiene ligand by PR_3 or by other azabutadiene ligands [193]. The (η-2-formylbutadiene)iron



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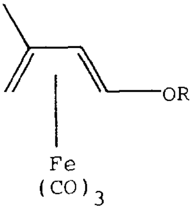

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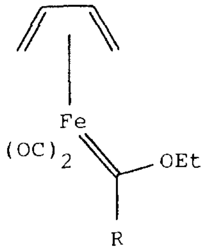

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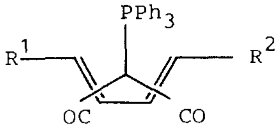

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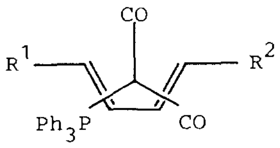

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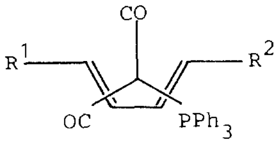

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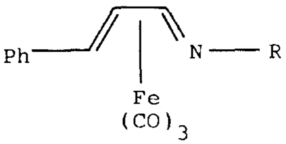

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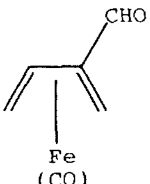

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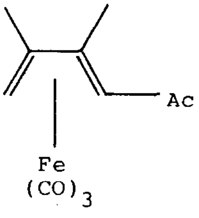

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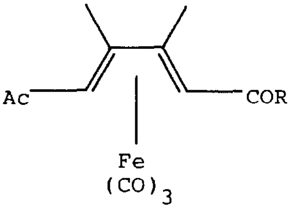

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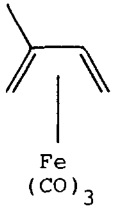
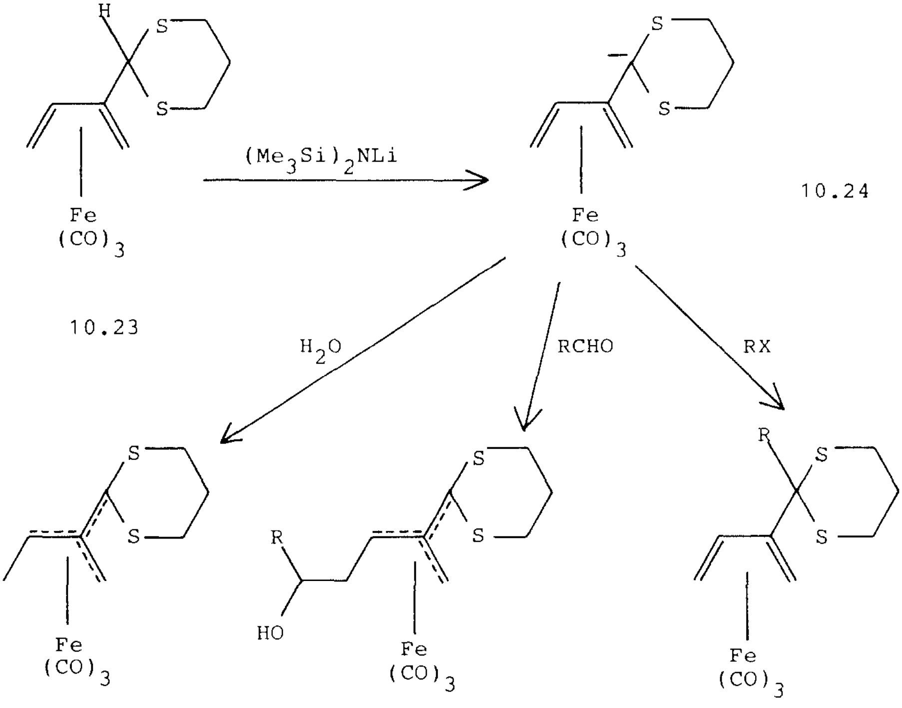


10.22

complex (10.19) has been prepared from the corresponding alcohol by treatment with oxalyl chloride. The complex (10.19) combined with Grignard reagents and alkyllithium compounds to give secondary alcohols that were decomplexed with iron(III) chloride to give stable diene alcohols. The reaction was diastereospecific with organolithium compounds and cuprates while Grignard reagents and organotitanium compounds gave mixtures of diastereoisomers. The formation of 1ps-type insect phenemones was explored by hydroboration of Wittig reagents derived from the formyl complex (10.19) [194].

The (η-butadiene)iron complex (10.20) underwent acylation with RCOCl in dichloromethane with aluminium chloride as catalyst to give the derivatives (10.21; R = Me, Et, Me_2CH). One of these products (10.21; R = Me) was isomerized with sodium methoxide and then demetallated with hydrogen peroxide to form (E,E)-AcCH=CMeCMe=CHAc in 82% yield [195]. The reaction of $Fe(CO)_3$(1—5-η-dienyl)]$^+$ cations (dienyl = C_6H_7, C_7H_9, 2-$MeOC_6H_6$) with diiodide ion has been investigated. Nucleophilic addition to a carbonyl ligand was found to compete with attack at the iron atom or the η-dienyl ring [196]. Reactive carbon nucleophiles add at an internal position of (η-1,3-diene)$Fe(CO)_3$ complexes at -78° to give the corresponding [(η-homoallyl)$Fe(CO)_3$]$^-$ ions. On warming to 0° reversal of the anion addition occurred with the anion adding again at the terminal position to form the (η-allyl)$Fe(CO)_3$ intermediate. The reaction between the η-isoprene complex (10.22) and Ph_2CHLi was studied in detail [197].



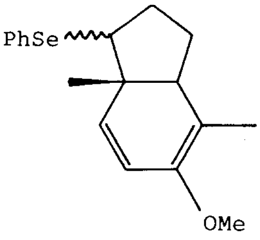
10.23 10.24 10.25 10.26 10.27

Lithiation of the tricarbonyliron complex (10.23) produced a dithiane stabilized carbanion (10.24). Treatment of this carbanion with electrophiles such as water, aldehydes and alkyl halides afforded a series of products (10.25; 10.26; R = Ph, $CHMe_2$, $CH=CMe_2$; 10.27; R = Me, $CH_2CH=CH_2$) [198]. Kinetic studies have been carried out on the reaction of the complexes $[Fe(CO)_3(\eta^5\text{-dienyl})]BF_4$, where dienyl = C_6H_7, 2-$MeOC_6H_6$ and C_7H_9, with 2-ethylpyridine in methyl cyanide. The second-order rate constants decreased in the order $C_6H_7 > 2\text{-}MeOC_6H_6 > C_7H_7$ which indicated direct addition of the 2-ethylpyridine to the dienyl rings [199]. Cationic polymerization of (3-allyl-1,4-η^4-pentadiene)tricarbonyliron gave a pale yellow powdery polymer, [3-(2-vinyloxyethyl)-1,3-pentadiene]tricarbonyl-iron and -ruthenium were also polymerized to linear polymers which were cast into thin, flexible films from dichloromethane solution. Doping of these and related polymers with iodine gave species with enhanced conductivity [200].

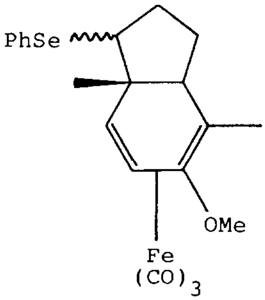
11. (Cyclic-η-diene)Fe(CO)$_3$

(i) Formation

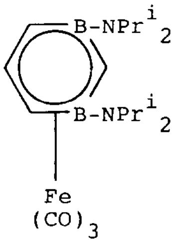
Treatment of the unstable trienol ether (11.1) with diiron nonacarbonyl produced the air sensitive tricarbonyliron derivative (11.2) [201]. Thermolysis of 2,6-bis(diisopropylamino)-2,6-diborabicyclo[3.1.0] hex-3-ene with pentacarbonyliron gave the 1,3-diborabenzene complex (11.3) [202]. Ferrocene has been treated with 2,4,6-triphenylphosphabenzene in the presence of aluminium chloride to give, after hydrolysis and reduction with HSiCl$_3$, a mixture of four isomeric (η^5-2,4,6,-triphenylhydrophosphabenzene)iron complexes one of which (11.4) has been characterized by X-ray crystallography [203]. Irradiation of 2-methyltropone with Fe(CO)$_5$ produced the tricarbonyliron complex (11.5). Similar reactions with Fe$_2$(CO)$_9$ afforded the diiron hexacarbonyl complexes (11.6; R = Me, Ph). 2-Dialkylaminotropones gave enamine type complexes, for example, 2-dimethylaminotropone produced the complex (11.7) [204].



11.1

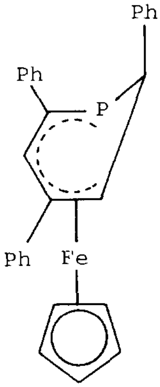


11.2



11.3

The cocondensation of ruthenium atoms with either 1,3- or 1,4-cyclohexadiene followed by the addition of carbon monoxide at -196° produced the ruthenium complex (11.8). This complex rearranged at room temperature to produce (η^4-C$_6$H$_8$)$_2$RuCO. When this latter complex was heated under carbon monoxide the



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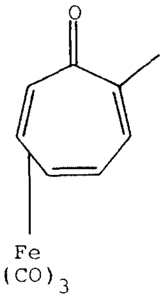

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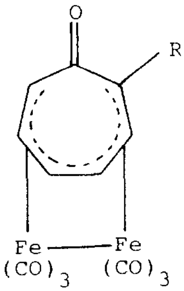

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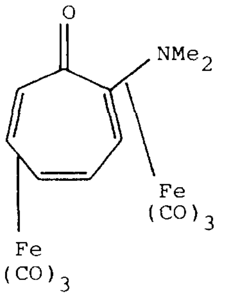

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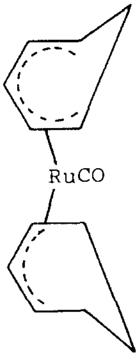

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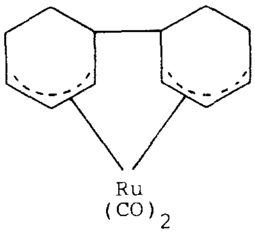
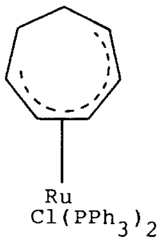


11.9

bis(η^3-allyl) complex (11.9) was formed [205]. Cycloheptatriene combined quantitatively with $RuHCl(PPh_3)_3$ in dichloromethane to form the (η^5-cycloheptadienyl)ruthenium complex (11.10) [206]. Cocondensation of osmium atoms with benzene produced the complex (11.11) which underwent hydrogenation at room temperature to give the cyclohexadiene complex $[(\eta^6-C_6H_6)(\eta^4-C_6H_8)Os]$. Cocondensation of osmium atoms and mesitylene afforded the hydride (11.12) the major product together with a minor product (11.13). The crystal structure of the binuclear complex (11.13) was determined. The metal-metal bond was short and consistent with an osmium--osmium triple bond [207].

(ii) Spectroscopic and physicochemical properties

Self-Consistent Charge and Configuration MO calculations have been used to investigate the electronic structures of the



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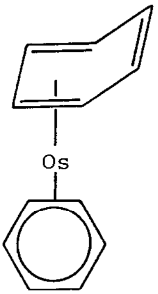

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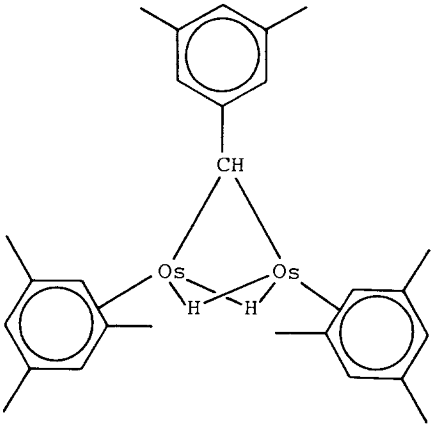

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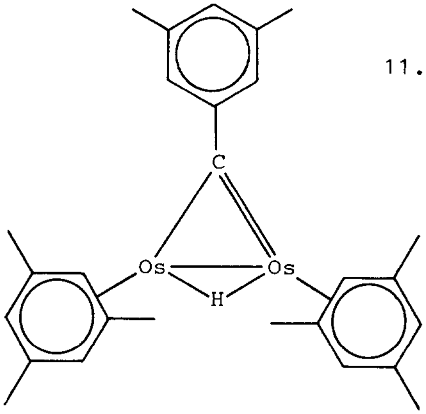
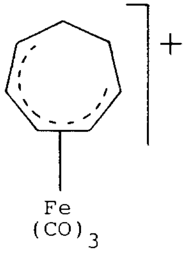
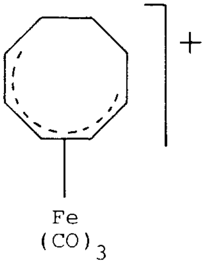


11.13

(η-cycloheptadienyl)iron and (η-cyclooctadienyl)iron complex cations (11.14 and 11.15) respectively. The geometrical conformations of the hydrocarbon ligands and the barriers to $Fe(CO)_3$ rotation have been calculated. Non-planar hydrocarbon ring geometries were preferred and these were influenced by distortions of the dienyl π molecular orbitals induced by the saturated part of the ring. The predictions made were in agreement with experimental determinations [208]. The structure of the cycloheptatrienyl-bridged heterobimetallic complex (11.16) has been determined by X-ray analysis [209]. The (η^5-cycloheptadienyl)iron complexes [11.17; L = CO, $P(OPh)_3$] have been prepared and one of them [11.17; L = $P(OPh)_3$] has been characterized by X-ray crystallography. The complex (11.17; L = CO) underwent insertion reactions with carbon monoxide and triphenyl



11.14



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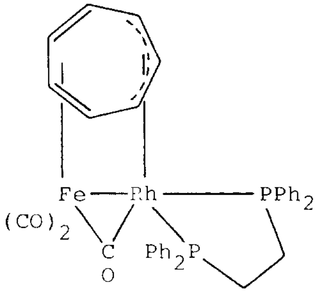


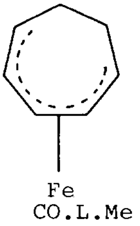
11.16

phosphite more readily than did the isoelectronic analogue (η^5-C_5H_5)Fe(CO)$_2$Me. Facile η^5-η^3 ring slip in (η^5-cycloheptadienyl)iron complexes was proposed to explain the difference in reactivity [210].

The He(I) and He(II) photoelectron spectra of tricarbonyl(η^3-cyclohexenyl)manganese have been recorded and interpreted. Comparisons were made with the electronic structure of methylcymantrene and tricarbonyl(η^4-cyclohexadiene)iron [211]. Proton spin-lattice relaxation, FT-IR and Raman spectroscopy have been used to determine the activation energy for ring rotation in tricarbonyl(η-cyclobutadiene)iron (11.18). Two inequivalent lattice sites were involved with values of 15.2 and 22.1kJ mol^{-1} [212]. Cyclic voltammetric studies have shown that the complexes (11.19; L = CO, PPh$_3$) undergo diffusion controlled irreversible one-electron oxidation. The reaction of ferrocenium hexafluorophosphate with the complex (11.19; L = PPh$_3$) afforded the dimeric dicationic salt (11.20) which was formed via C-C bond coupling of the radical cation [Ru(CO)$_2$PPh$_3$(C_8H_8)]† [213].

(iii) General

The (η-cyclopropenyl)iron complex (11.21) combined with tertiary phosphites, P(OMe)$_3$ and P(OPh)$_3$, to give the products of carbonyl substitution while with phosphines, PPh$_3$ and PMe$_2$Ph, it gave the products of carbonyl substitution together with



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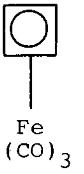

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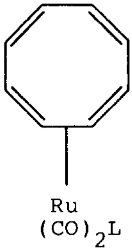

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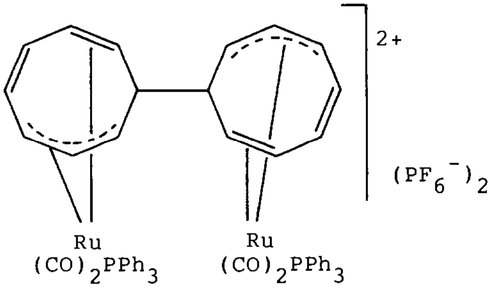

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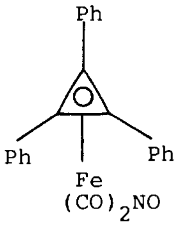
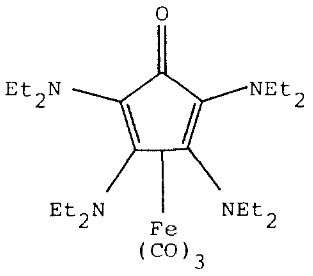


11.21

$(\eta^3$-oxocyclobutenyl)iron complexes by ring expansion [214]. Oxidation of the tricarbonyliron complex (11.22) electrochemically or with $NOPF_6$ produced the salt (11.23; $X = PF_6, ClO_4$). Oxidation with bromine afforded the aminodioxocyclobutenecarboxamide (11.24) [215]. Alkyllithium compounds and nitrogen- or oxygen-based nucleophiles combined with (η-cyclopentadienyl)iron-$(\eta^2$-alkyne) complexes to give ring-substituted and modified alkyne products. Thus, methyllithium attacked the (η-cyclopentadienyl)iron cation (11.25; R = H, L = η^2-MeC≡CMe, n = 1) to form the methyl substituted neutral complex (11.25; R = Me, L = η^1-(E)-CMe=CHMe, n = 0) while the iodide of the same cation combined with Et_2NLi to give the neutral iodide (11.25; R = Et_2N, L = I, n = 0) [216].



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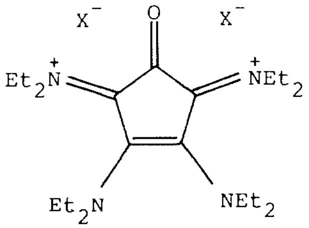

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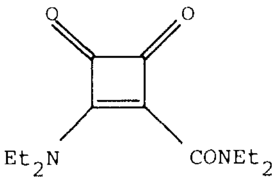
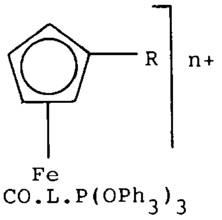


11.24

The (η-1,4-disubstituted cyclohexadienyl)iron cation (11.26) underwent nucleophilic addition with carbanions to give (η-cyclohexadiene)iron complexes such as the ester (11.27; R = CO_2Me, COMe) [217]. The tricarbonyliron complexes $[LFe(CO)_3]^+$, where L = 2,4-cyclohexadienyl, 4-methyl-2,4-cyclohexadienyl or $Me_2C{=}CHCMe{=}CH_2$, have been used to prepare a range of dienylacetic acid derivatives [218]. Oxidative cyclization of primary alcohol groups onto coordinated cyclicdienes has been used to prepare the cyclic ethers (11.28; R = Me, OMe and 11.29; R = H, CH_2OH, CH_2OCOCH_3). Treatment of these ethers with tetrafluoroboric acid in the presence of acetic anhydride resulted in ring opening and the formation of the corresponding stereospecifically substituted dienyl complexes (11.30 and 11.31). These latter complexes underwent nucleophilic addition stereo- and regiospecifically [219]. Nucleophilic addition to (η-cyclohexadienyl)-iron cations (11.32; L = PPh_3) showed better control than the corresponding reaction with the tricarbonyl cations (11.32; L = CO) [220].

Heterobifunctional cyclohexadienes have been obtained by sequential nucleophilic attack on (η-benzene)iron cations. Thus the (η-cyclohexadienyliron) complex (11.33) combined with benzylmagnesium bromide to give the (η-cyclohexadiene)iron complex (11.34) which underwent subsequent hydride ion abstraction to give the cation (11.35) and this in turn was attacked by cyanide ion to form the disubstituted (η-cyclohexadiene)iron complex (11.36). The crystal and molecular structure of this last complex (11.36)



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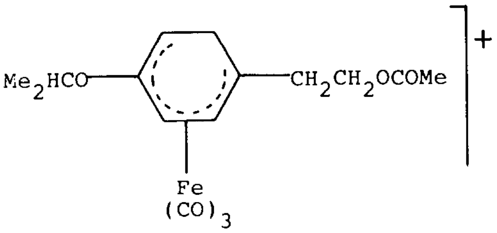

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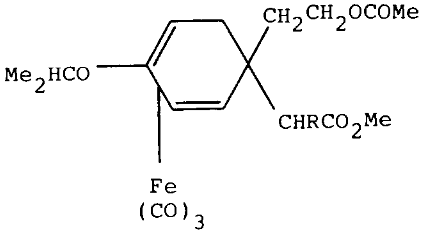

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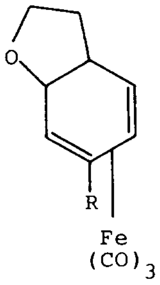

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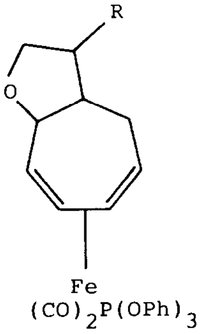

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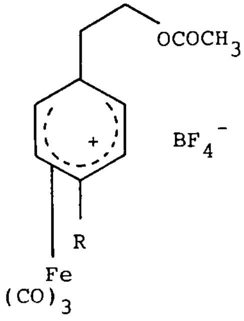

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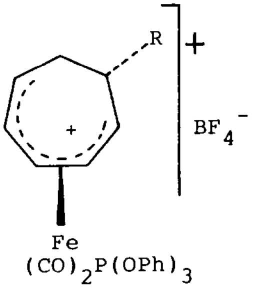

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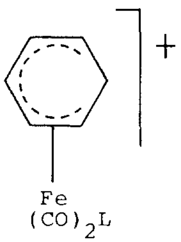

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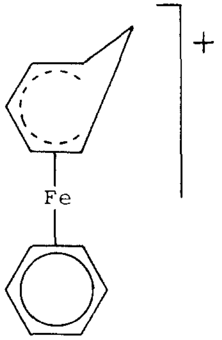

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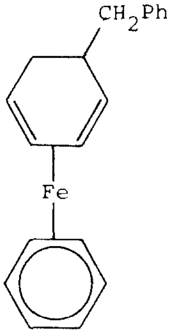

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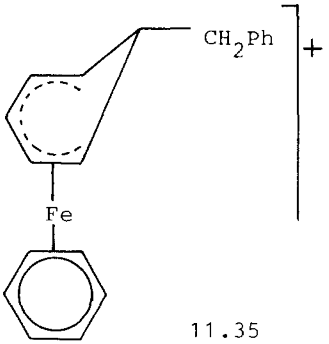

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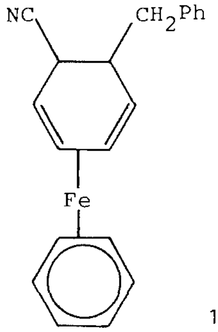
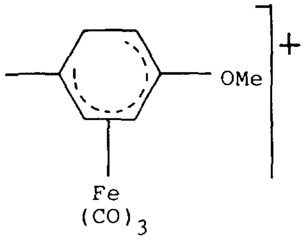


11.36

has been determined by X-ray crystallography [221]. Trimethylsilyl cyanide has been used as a reagent for the introduction of cyanide into (η^5-cyclohexadienyl)iron complexes. Thus the cation (11.37) gave the (η-cyclohexadiene)iron complex (11.38) in 95% yield [222]. Thermal energy electrons combined with tricarbonyl(η^4-cyclohexadiene)iron to form the radical anion (11.39) which was then attacked by hydrogen atoms to give fragmentation products together with a small proportion of $[(C_6H_8)Fe(CO)_2H]^-$ [223].

The (η-cyclohexadienyl)iron cation (11.40) was converted to the complex (11.41) by nucleophilic addition and this was used to derive the D-homosteroid (11.42) in an eight step sequence [224]. Tricarbonyl(η-cyclohexadienylium)iron tetrafluoroborate was converted by fluoride ion to the binuclear complex (11.43)



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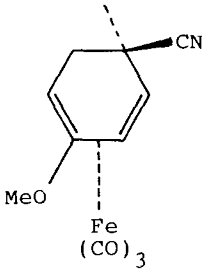

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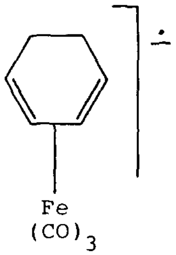
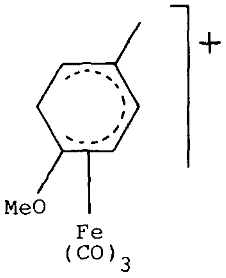


11.39

and not to tricarbonyl(η-fluorocyclohexadiene)iron as previously reported [225]. The (η-cyclohexadienyl)iron cation (11.44) coupled with the (η^4-cyclooctatetraene)ruthenium complex (11.45;



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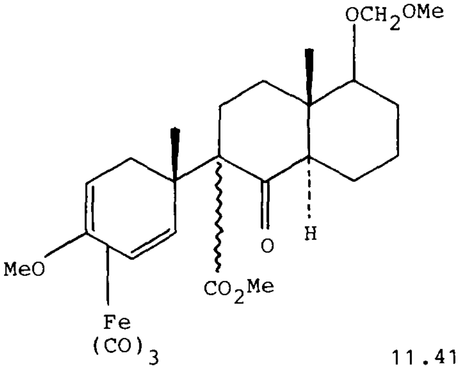

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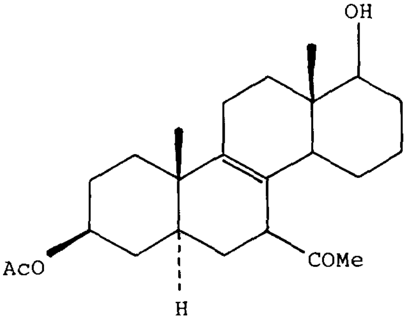

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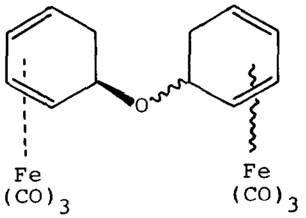

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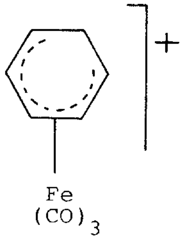

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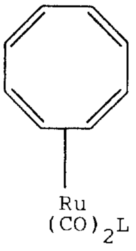

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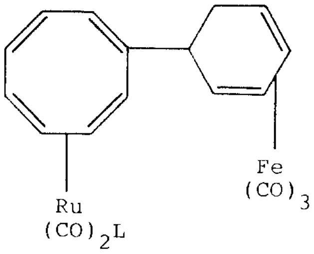

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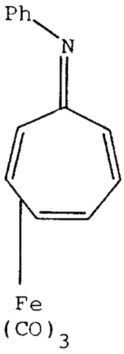

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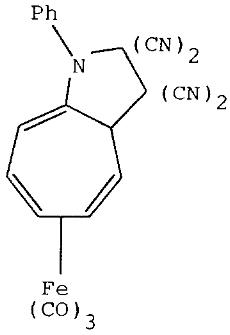

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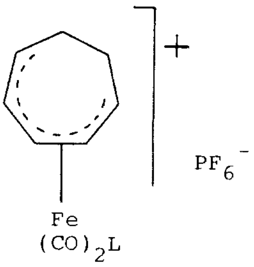

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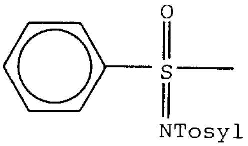

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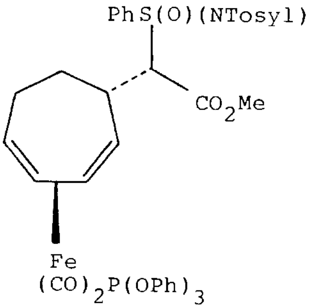

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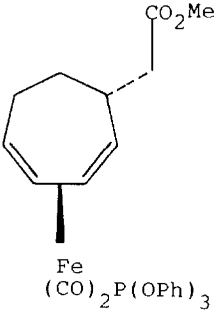
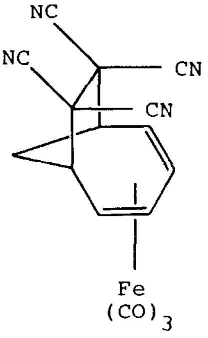


11.52

L = CO, PPh_3) to give, after treatment with triethylamine, the binuclear complex (11.46). Cobaltocene underwent an analogous reaction with the cation (11.44) [226]. Reaction of the tricarbonyliron complex (11.47) with tetracyanoethene (TCNE) produced the 1:1 adduct (11.48). A 1:2 adduct was observed in solution but this was not isolated. Kinetic studies were carried out and the rates of addition of both the TCNE molecules were determined [227].

Reaction of the dienyliron complex [11.49; L = $P(OPh)_3$] with the enolate anion obtained by treatment of the ester (11.50) with base produced the diene complex (11.51) as a mixture of diastereoisomers showing that chiral recognition had occurred. Some reactions of the complex (11.51) were examined, for example, reduction with Na/Hg amalgam gave the monoester (11.52) which was also optically active [228]. Treatment of the salt (11.49; L = CO) with organolithium, organocopper and stabilized enolate reagents afforded the corresponding substituted η^4-cycloheptadiene complex with the substituent *exo* to the iron atom [229, 230].



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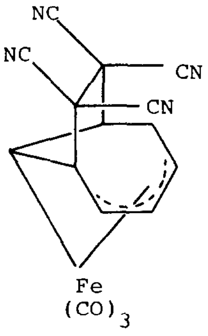

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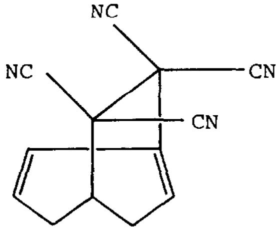
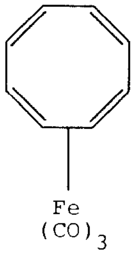


11.55

The cycloheptatriene-tetracyanoethylene adduct formed a tricarbonyliron complex (11.53) which underwent thermal rearrangement to give the diene-iron complex (11.54). Oxidation of the complex (11.54) with cerium(IV) gave the free tetracyanobicyclo[4.2.1]nona-2,4-diene ligand. The first-formed complex (11.53) was oxidised similarly to form the tetracyanobicyclononadiene (11.55) [231].



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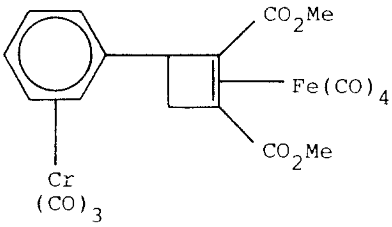

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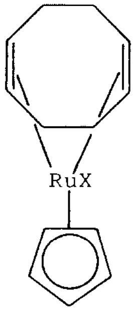

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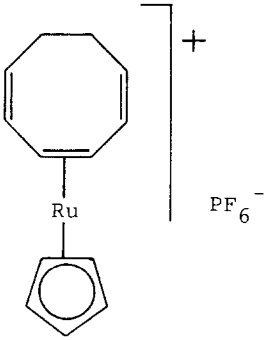

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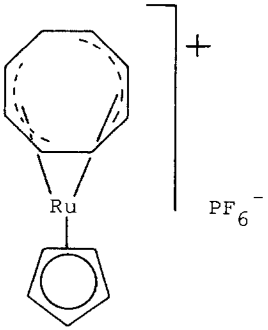

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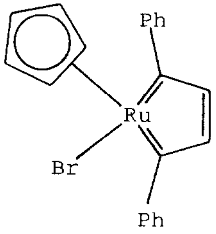


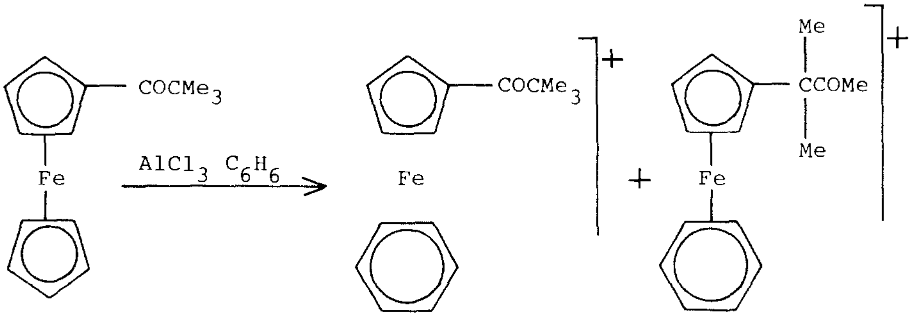
11.61

Tetracyanoethylene attacked tricarbonyl(η-cycloheptatriene)-iron to give the cycloadduct (11.54) which underwent thermal rearrangement to the isomer (11.53). A kinetic study of the rearrangement confirmed that it was a concerted, non-synchronous one-step process [232]. Triiron dodecacarbonyl, dimethylacetylene dicarboxylate and tricarbonyl(η^6-cyclooctatetraene)chromium were heated in boiling THF to give the metal exchange (η-cyclooctatetraene)iron product (11.56), 82%, together with the product of ring contraction (11.57), 10% [233]. The η^4-cyclooctadiene complex (11.58; X = Cl) underwent facile dehydrogenation in the presence of NH_4PF_6 to give an approximately 1:1 mixture of the complexes (11.59 and 11.60). The structure of the 1—3-η:5—7-η-cycloocta-1,5-dienediyl complex (11.60) was confirmed by X-ray analysis [234]. Reaction of the η^4-cyclooctadiene complex (11.58; X = Br) with phenylacetylene afforded the ruthenacyclopentatriene (11.61) which was characterized by X-ray analysis [235].

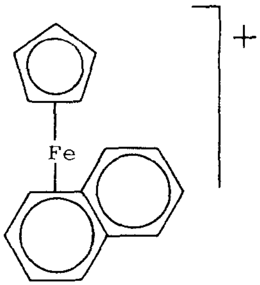
12. $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6H_6)]^+$

The reaction of the substituted ferrocene (12.1) with aluminium chloride in benzene produced two major products (12.2 and 12.3). The rearrangement of the substituent to give the product (12.3) was shown to occur after the cleavage of the unsubstituted η-cyclopentadienyl group and formation of the cation [236]. The mechanism of hydrogenation of polyaromatics during the ligand exchange with an η-cyclopentadienyl ring of ferrocene has been investigated via the reaction of ferrocene with naphthalene. The products were the naphthalene (12.4) and tetralin (12.5) cations which were formed at 80°C and 190°C respectively. The effect of temperature, aluminium powder, water and the quantity and quality of the aluminium chloride on this reaction were investigated. When ferrocene was replaced by $(\eta\text{-}C_5H_5)Fe(CO)_2Cl$ in the reaction with naphthalene the same products were obtained [237]. A series of cyclic halohydroborate salts of the η-benzene- and η-tetralin-η-cyclopentadienyliron cations have been prepared and investigated [238].

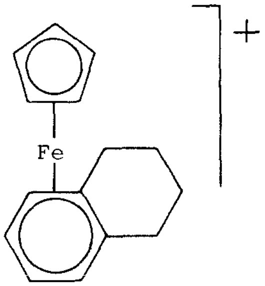
Ferrocene underwent ligand exchange with arenes in the presence of aluminium(III) chloride and carbon dioxide to give cations of the type $[(\eta^5\text{-}C_5H_4CO_2H)Fe(\eta^6\text{-arene})]^+$ where arene = benzene, mesitylene, hexamethylbenzene, naphthalene. For example, the cation (12.6) was prepared and deprotonated by base to give



12.1 12.2 12.3

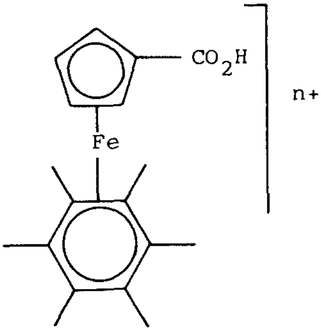


12.4

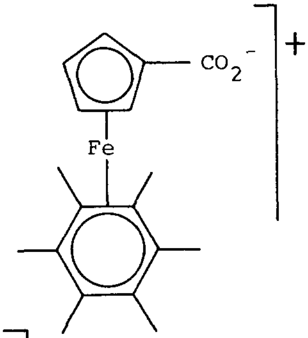


12.5

the water-soluble zwitterion (12.7). These two species (12.6; n = 1 and 12.7) were both reduced by Na/Hg in THF to give the acid (12.6; n = 0) and the radical anion (12.8) respectively. This product (12.8) was an active redox catalyst in basic media. Both (12.6; n = 0) and (12.8) were characterized by ESR and Moessbauer spectroscopy as d^7 Fe(I) complexes [239]. Bis(η5-cyclopentadienyl)iron complexed dications of 9,10-dihydroanthracene, xanthene, thioxanthene and diphenylmethane have been prepared by ligand exchange. These complexes were not isolated but they were oxidized in situ with potassium permanganate to give the dications (12.9, 12.10 and 12.12) respectively which were isolated as the dihexafluorophosphate salts. Some reactions of these salts were investigated [240]. Benzene and pentamethylcyclopentadiene were boiled with $RuCl_3.3H_2O$ in an alcoholic



12.6



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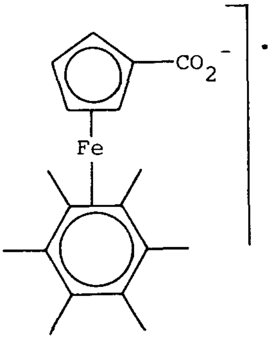

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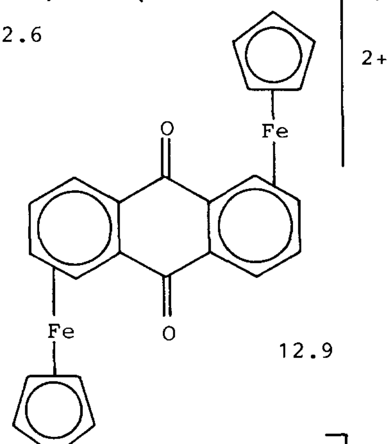

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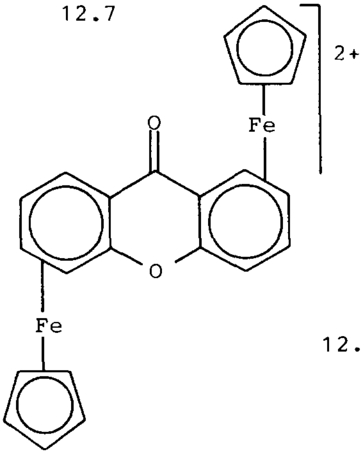

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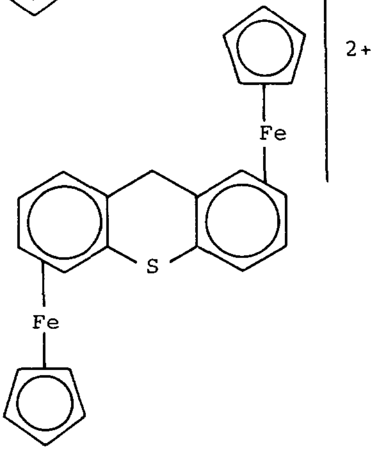

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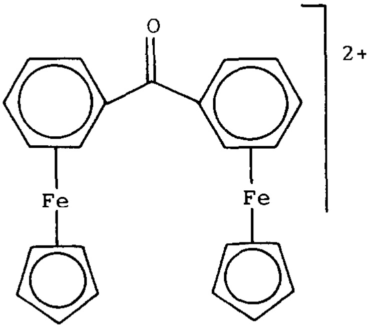
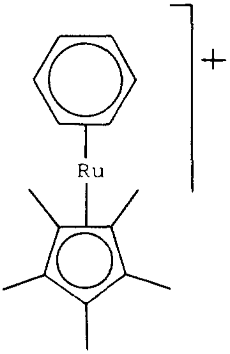


12.12

solvent to give the (η-arene)ruthenium cation (12.13). The same reaction was carried out using toluene or mesitylene in place of benzene [241].

The $[(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-arene})]PF_6$ and $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-arene})]PF_6$ complexes, where arene = naphthalene, anthracene, pyrene and chrysene, have been prepared by the reaction of $[(\eta^5\text{-}C_5H_5)Ru(MeCN)_3]PF_6$ and $[(\eta^5\text{-}C_5Me_5)Ru(MeCN)_3]PF_6$ with the appropriate



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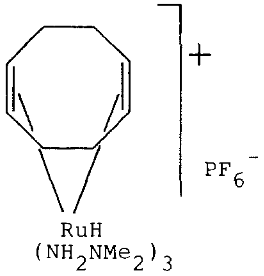

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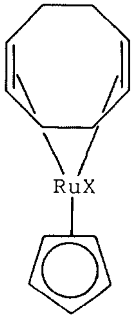

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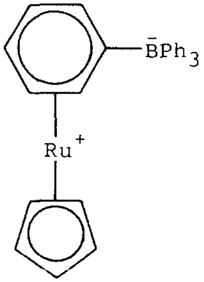

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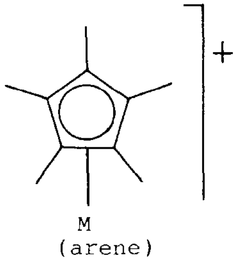
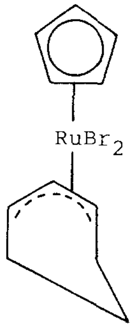


12.17

ligand. Kinetic studies of η-arene displacement by methyl cyanide were carried out and the rate constants for the compounds containing pyrene and chrysene were approximately 4x as large as those of the corresponding iron compounds. This difference was attributed to the large size of ruthenium which rendered it more susceptible to nucleophilic attack [242]. Reaction of the ruthenium complex (12.14) with $(C_5H_5)Tl$ produced the η-cyclopentadienyl complex (12.15; X = H). Treatment of this complex with CCl_4, CH_2Br_2 or CH_3I afforded the corresponding halogenated complexes (12.15; X = Cl, Br or I). Replacement of the η-cycloocta-1,5-diene and chloro ligands in the complex (12.14; X = Cl) was easily achieved with a range of ligands. For example, reaction with $NaBPh_4$ gave the zwitterionic complex (12.16) and treatment with cyclopentadienylsodium afforded ruthenocene [243].

The effect of arene methylation on the photochemical arene replacement reactions of the η-pentamethylcyclopentadienyl complexes (12.17; M = Fe, Ru; arene = benzene, mesitylene, hexamethylbenzene) have been studied. A decrease in the quantum yield was observed on permethylation of the η-cyclopentadienyl ligand, as compared with previous work [244], and there was also a decrease on methylation of the arene ligand. A very large decrease was observed for the complex (12.17; M = Fe; arene = hexamethylbenzene) and this was attributed to a steric blocking effect [245]. The reaction of $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]^+PF_6^-$ or $[(\eta\text{-}C_5Me_5)Ru(CH_3CN)_3]^+PF_6^-$ with a variety of arenes has been used to prepare the corresponding $(\eta\text{-}C_5H_5)$- and $(\eta\text{-}C_5Me_5)$-Ru(η-arene)$^+$ complexes [246]. The cation $[Ru(H_2O)_6]^{2+}$ combined with suitable arenes and dienes in ethanol to give yellow air-stable complexes $[(\eta^6\text{-arene})(\eta^5\text{-dienyl})Ru]^+$, where arene = benzene, mesitylene, hexamethylbenzene, p-toluenesulphonate and dienyl = pentamethylcyclopentadienyl, 2,4-dimethylpentadienyl and cyclooctadienyl. The crystal and molecular structure of one complex, (η-cyclooctadienyl)(η-p-toluenesulphonate)ruthenium(II), was determined by X-ray crystallography [247]. The $(\eta^3$-allyl)-ruthenium(IV) complex (12.18) underwent dehydrohalogenation and dehydrogenation at reflux temperature in ethanol to give the (η-benzene)ruthenium cation (12.19) in high yield [248].

The structures of the salts (12.20 and 12.21) have been determined by X-ray diffraction. In both complexes the heterocyclic groups were nearly planar. Asymmetric C-O bond lengths were found in complex (12.21) and this was attributed to the inductive effect of the coordinated $(\eta^5\text{-}C_5H_5)$Fe group [249]. The structure of bis[$(\eta^5$-cyclopentadienyl)$(\eta^5$-cyclohexadienyl)iron] has been determined by X-ray analysis. The two iron atoms were in pentagonal bipyramidal arrangements [250]. Complexation effects were shown to be related to the molecular geometry in chromium and iron complexes by ^{13}C NMR spectroscopy. Thus, the complexation shift for the aryl tertiary carbon in the



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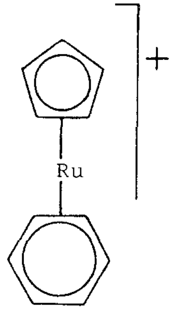

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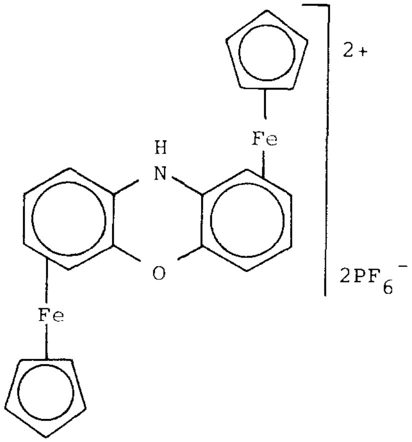

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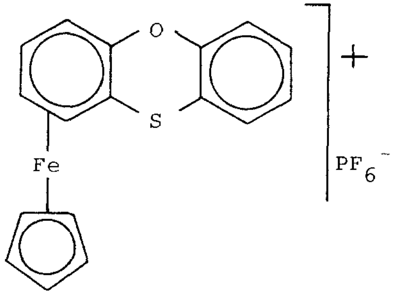

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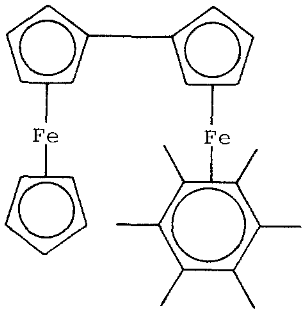

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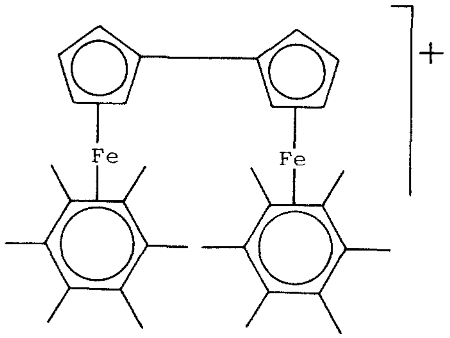

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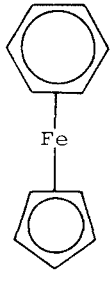

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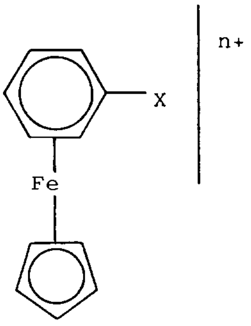

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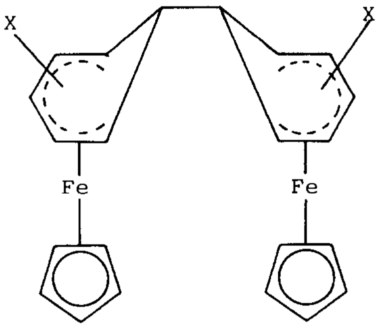
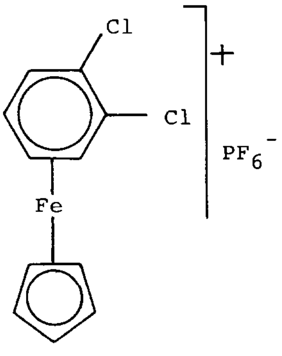


12.26

tricarbonyl(η^6-[n]paracyclophane)chromium complexes, where n = 8, 9, 11, 12, 15, increased with a decrease in the value of n. A similar pattern was observed for the (η^6-[n]paracyclophane)-(η^5-cyclopentadienyl)iron cations where n has the same values [251]. The mixed-valence Fe(II)Fe(I) complexes (12.22 and 12.23) have been investigated by Moessbauer spectroscopy in the temperature range 4.2-293K. The hexamethylbenzene complex (12.22) showed two types of iron atom and was confirmed as a localized mixed-valence species while the bis(hexamethylbenzene) cation (12.23) showed one type of iron atom and was a delocalized mixed-valence species. High magnetic field spectra demonstrated that this cation (12.23) had the valence electron delocalized on the two iron centres [252].



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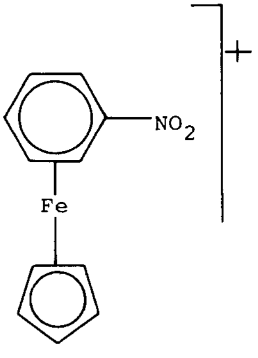

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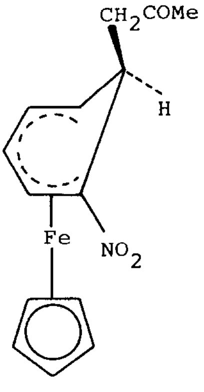
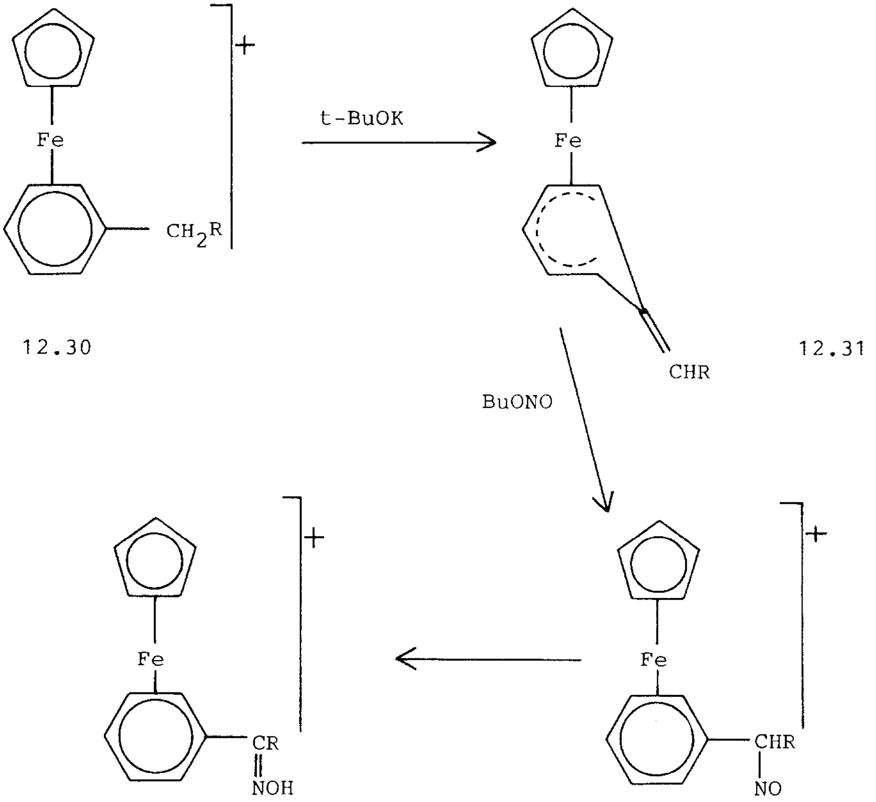


12.29

Cyclic voltammetry has been used to investigate the decomposition of the electrogenerated neutral (η-arene)iron(I) complex (12.24). In acetonitrile, the arene ligand is displaced by donor ligands such as $P(OMe)_3$, by way of a 17-electron intermediate, $(\eta^5\text{-}C_5H_5)Fe(I)(MeCN)_2$. In the absence of donor ligands, the product was ferrocene [253]. The (η-benzene)iron cations (12.25; X = F, Cl; n = 1) have been reduced by sodium amalgam in THF to give a mixture of the mononuclear (12.25; X = F, Cl; n = 0) and dinuclear (12.26; X = F, Cl) neutral complexes. Halide ions were not displaced from the complexes (12.25 and 12.26) by either sodium alkoxides or copper(II) acetate [254]. Reduction of the cations $[(\eta^6\text{-Ar})Fe(\eta^5\text{-}C_5H_5)]^+$, where Ar = naphthalene and phenanthrene, has been shown to take place in three stages [255].



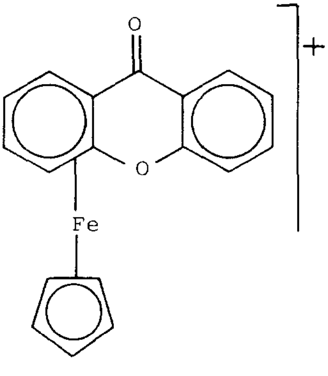
12.30 12.31

12.33 12.32

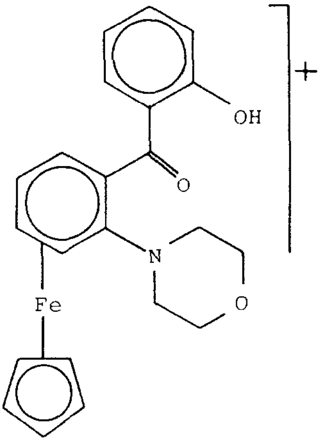
The (η-chlorobenzene)iron complex (12.25; X = Cl, n = 1) has been treated with Ph_3SnLi in THF to form the (η-triphenylstannylbenzene)iron complex (12.25; X = $SnPh_3$, n = 1) [256]. The nucleophilic substitution of η^6-dichlorobenzene complex (12.27) has been investigated. For example, reaction with an excess of phenol or p-thiocresol in the presence of potassium carbonate led to substitution of both the chloro groups. Under conditions of high dilution monosubstitution of one of the chloro groups was achieved [257].

The (η-chlorobenzene)iron complex (12.25; X = Cl; n = 1) combined with enolate anions to give the chloride displacement products. Thus, diethyl malonate, acetylacetone and phenylsulphonylacetone gave the derivatives [12.25; X = $CH(CO_2Et)_2$, $CH(COMe)_2$, $CH(SO_2C_6H_5)COMe$; n = 1]. Related reactions were carried out with the (η-o-dichlorobenzene)(η -cyclopentadienyl)iron cation [258]. The reactions between $[(\eta^6\text{-arene})(\eta^5\text{-}C_5H_5)Fe]^+$ cations and a carbanion derived from acetone, butanone or 3-pentanone have been investigated. For example, the reaction of the cation (12.28) with acetone in aqueous KOH gave the purple adduct (12.29) which was formed by exo addition of the acetonyl anion. Similar products were obtained from the reactions $(\eta\text{-}C_5H_5)Fe$ complexes of cyanobenzene, p-tolylsulphonylbenzene, benzoylbenzene, o-, p- or m-nitrotoluene and o-, p- or m-dichlorobenzene with acetone in aqueous KOH [259]. (η^6-Arene)(η^5-cyclopentadienyl)iron cations bearing methylene, methyl or methyne substituents on the arene have been deprotonated with t-BuOK and then treated with alkyl nitrites or $NOBF_4$. For example, with the complexes (12.30; R = Me, Ph), the corresponding oximes (12.33) were isolated by way of the intermediates (12.31 and 12.32). The oximes (12.33) underwent acidic hydrolysis to give the corresponding ketones and were reduced electrochemically to the primary amines [260].

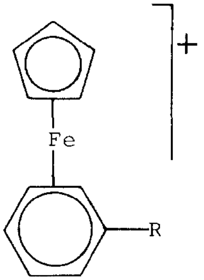
The (η^6-xanthone)iron cation (12.34) underwent ring opening with pyrrolidine in dichloromethane to form the (η-benzophenone)-iron cation (12.35). The substituted benzophenone ligand was liberated on irradiation of the cation (12.35) [261]. Benzene and toluene have been released on the photolysis of the (η-arene)-iron complexes (12.36; R = H, Me). The electronic absorption band at 650nm was identified with the lowest triplet excited state and sensitization experiments indicated that it was the photoactive state. A systematic study of solvent and counterion showed that



12.34



12.35

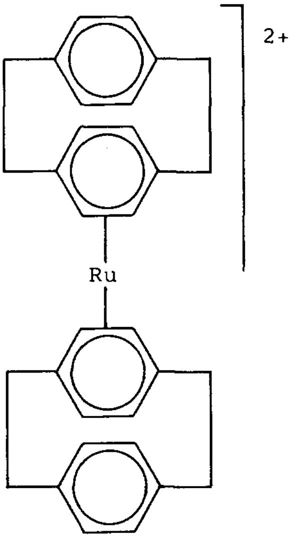


12.36

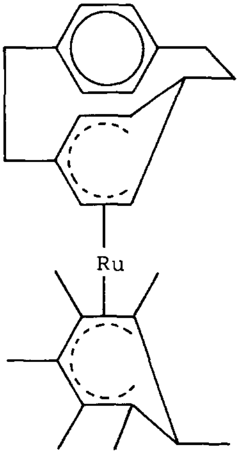
a media assisted pathway for arene release had operated [262]. Filled epoxy resin compositions curable by ultra-violet or visible radiation have been prepared. The resins were suitable for printed circuits and they contained η-arene metallocene salts, for example, (η-cyclopentadienyl)(η-2-methylnaphthalene)iron hexafluorophosphate [263].

13. $(\eta\text{-}C_6H_6)_2Fe$ and $[(\eta\text{-}C_6H_6)_2Fe]^{2+}$

Iron atoms have been co-condensed with benzene and infrared spectroscopy indicated the formation of $(\eta\text{-}C_6H_6)Fe$, $(\eta\text{-}C_6H_6)_2Fe$ and $(\eta\text{-}C_6H_6)Fe_2$ complexes. From the spectra it was not clear whether the compound $(\eta\text{-}C_6H_6)_2Fe$ was a $\eta^6\text{-}\eta^4$ or a $\eta^6\text{-}\eta^6$ coordination complex. When iron atoms were codeposited with 1,4-cyclohexadiene infrared spectroscopy indicated that the $(\eta\text{-}C_6H_8)Fe$ and $(\eta\text{-}C_6H_8)Fe_2$ adducts had been formed. Ultraviolet irradiation of $(\eta\text{-}C_6H_8)Fe$ led to the formation of FeH_2 and benzene [264]. Benzene, toluene, o-xylene and mesitylene combined with bis(η-1-t-butyl-2-methyl-1,2-azaborolinyl)iron in the presence of aluminium halides and aluminium to give the corresponding (η-1,2-azaborolinyl)(η-arene)iron cations. The products were characterized by ^1H, ^{11}B and ^{13}C NMR spectroscopy [265]. The bis(η-arene)iron(II) dodecahydrododecaborates and hexafluorophosphates, $(\eta\text{-arene})_2B_{12}H_{12}$ where arene = 1, 2, 3, 4-tetrahydro-



13.1



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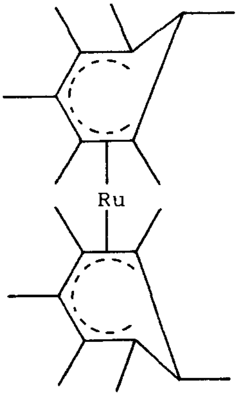
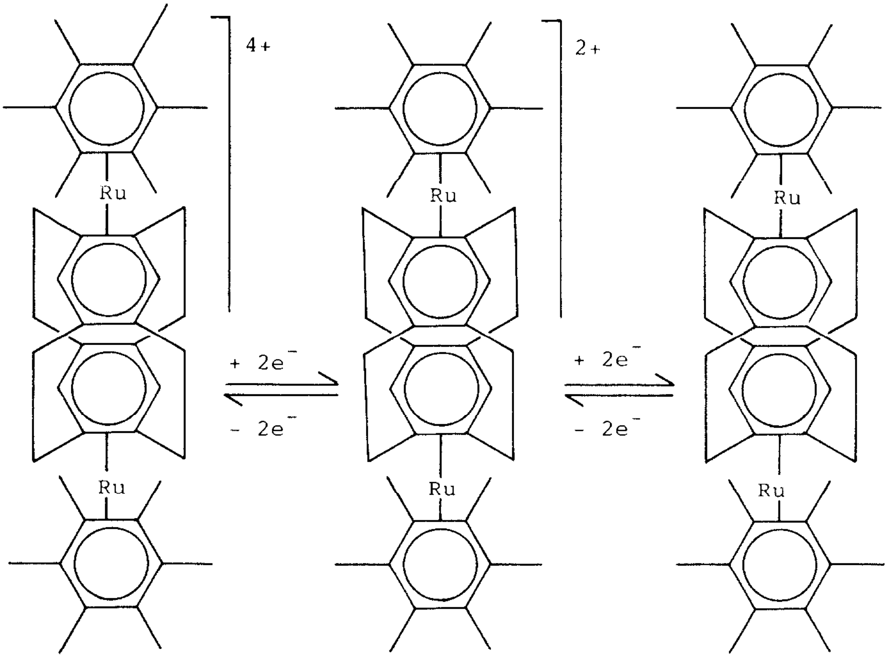


13.3

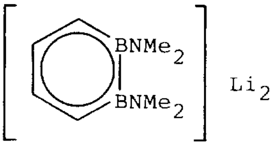
naphthalene, o-, p-$Me_2C_6H_4$, 1,2,4-$Me_3C_6H_3$, 1, 3,5-$Me_3C_6H_3$, 1,2,4,5-$Me_4C_6H_2$, RC_6H_5(R=H, Me, Et, Pr, $CHMe_2$) and (η-arene)$_2$Fe $(PF_6)_2$ where arene = p-$Me_2C_6H_4$, 1,2,3,4-tetrahydronaphthalene have been prepared by the treatment of iron-(II) or -(III) chloride with arenes in the presence of aluminium chloride followed by the addition of $H_2B_{12}H_{12}$ or NH_4PF_6 [266].

Bis(η-arene)ruthenium cations have been prepared by heating $[(\eta\text{-}C_6H_6)RuCl_2]_2$ with an arene, for example, mesitylene, anthracene, aniline and phenetole, in the presence of aluminium chloride [267]. A general method has been developed for the synthesis of bis(η^6-[2_n]cyclophane)ruthenium(II) dications and these were used to obtain oligomers with two or three ruthenium atoms in the chain. Thus (η^6-benzene) (η^6-[2_n]cyclophane)-ruthenium(II) dications were reduced to (η^4-cyclohexadiene)-(η^6-[2_n]cyclophane)ruthenium complexes and converted to (η^6-[2_n]cyclophane)ruthenium(II) solvate dications with trifluoroacetic acid and acetone and then coupled with another molecule of [2_n]cyclophane to give bis(η^6-[2_n]cyclophane)-ruthenium(II) dications such as the dication (13.1). Cyclophane (13.2) and cyclohexadienyl (13.3) analogues of ruthenocene were prepared in the same study [268]. The reaction of (η^6-hexamethylbenzene)ruthenium(II) tris(acetone) solvate with [2_4](1,2,4,5)-



13.4 13.5 13.6

cyclophane afforded the diruthenium cation (13.4). The two and four electron reduction of this complex to give the dication (13.5) and the neutral complex (13.6) were achieved by both chemical and electro-chemical means [269].



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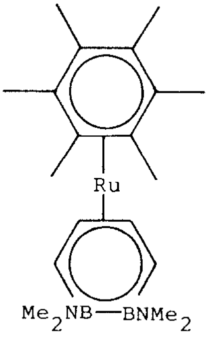

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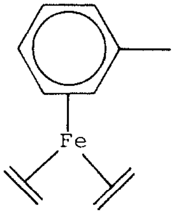
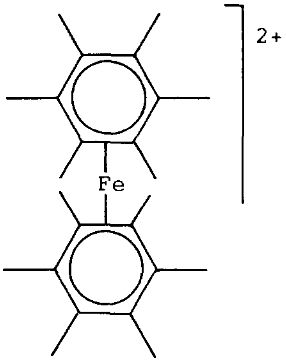


13.9

Reaction of the dilithio-borazabenzene derivative (13.7) with $[(\eta\text{-}C_6Me_6)RuCl_2]_2$ afforded the ruthenium complex (13.8) [270]. The treatment of bis(η^6-toluene)iron with ethene produced the bis(η^2-ethene) complex (13.9) [271]. Bis(η-arene)iron complexes, where arene = benzene, toluene, p-xylene, benzotrifluoride and



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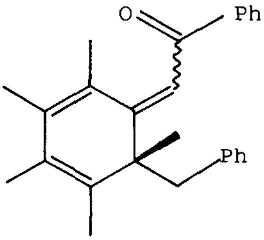
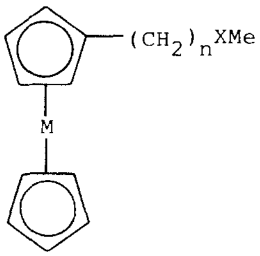


13.11

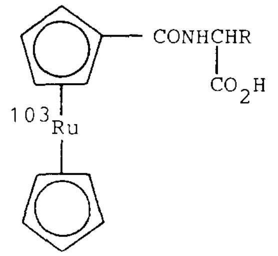
1,4-difluorobenzene, combined with 3,4-diethyl-2,5-dimethyl-2,5-dihydro-1,2,5-thiadiborole at -100° to give intermediates which were transformed at -30° to form (η^6-arene)(η^5-thiadiborolene)iron complexes [272]. The bis(η-hexamethylbenzene)iron dication (13.10) has been converted in a sequence of seven steps to give a regio- and stereo-specifically controlled product (13.11). Addition of hydride to the dication (13.10) gave an (η-cyclohexadienyl)iron cation; addition of a Grignard reagent then formed a bis(η-cyclohexadienyl)iron complex; hydride abstraction reformed an (η-cyclohexadienyl)iron cation; potassium t-butoxide gave a neutral (η-cyclohexadiene)iron species; attack by benzoyl chloride formed an (η-cyclohexadienyl)iron cation; potassium t-butoxide led to an (η-cyclohexadiene)iron complex and finally aluminium oxide and air gave the product (13.11) [273].

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

The reaction of (η^4-1,5-cyclooctadiene)$RuCl_2$ with thallium cyclopentadienyl or tributyltincyclopentadiene produced ruthenocene in high yields. A similar reaction with tributyltin(pentamethylcyclopentadiene) afforded decamethylruthenocene and treatment of (η^4-1,5-cyclooctadiene)$OsCl_2$ with tributyltincyclopentadiene



14.1



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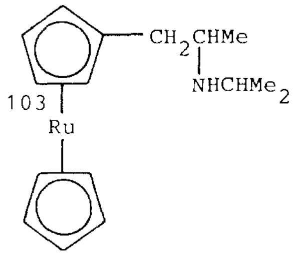
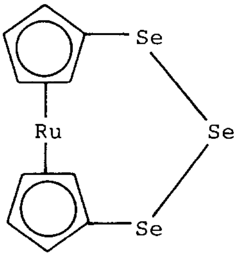


14.3

gave osmocene in high yield. Decamethylosmocene was obtained by the direct reaction of pentamethylcyclopentadiene with Na_2OsCl_6. The crystal and molecular structures of decamethyl-ruthenocene and -osmocene were determined by X-ray analysis [274]. The substituted ruthenocenes and osmocenes [14.1; M = labelled Ru, Os; X = NR, $CR(NR_2)$; R = H, Me, n = 0-2] have been prepared by ligand exchange between the corresponding substituted ferrocene and the labelled ruthenium or osmium halide. The labelled metallocenes were useful as radiopharmaceutical diagnostic agents [275]. The ^{103}Ru labelled ruthenocenes (14.2; R = H, CH_3, $CH_3SCH_2CH_2$), 1-methylruthenocenoylglycine and its methyl ester have been prepared from the corresponding amino-acids by exchange with ^{103}Ru. The use of these ^{103}Ru labelled compounds as radiopharmaceuticals was investigated and they were compared with ^{131}I-hippuren [276].

[^{103}Ru]Ruthenocenyl-tyramine, -histamine, -benzylamine, -phenethylamine and -homoveratylamine were fed to rats and the organ distribution was determined. The first three ruthenocene derivatives had a high affinity for the adrenals and the ovaries. The ruthenocene derivatives were compared with radioiodinated amphetamine analogues as diagnostic radiopharmaceuticals [277]. The [^{103}Ru]ruthenocene analogue of N-isopropyl-amphetamine (14.3) has been injected into rats and the organ distribution monitored. Organs with the highest concentrations were lung, adrenal, kidney and brain. Since the brain:blood radio for the ruthenocene (14.3) was similar to or higher than that for ^{123}I-labelled amphetamines then it could be used for brain imaging [278].



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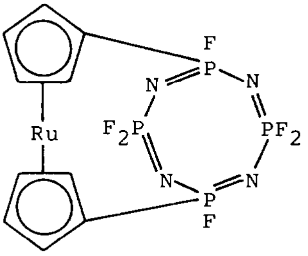

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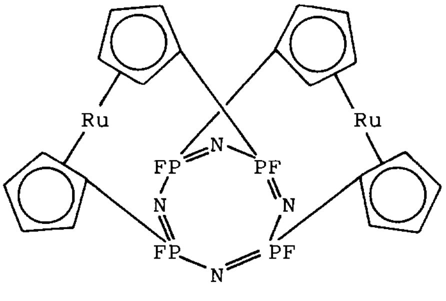

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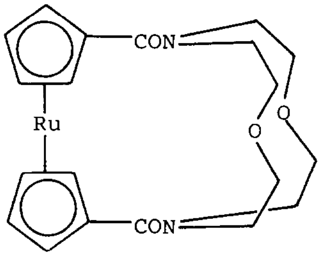

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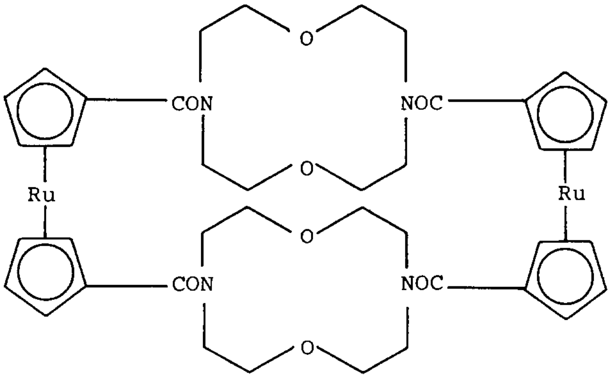

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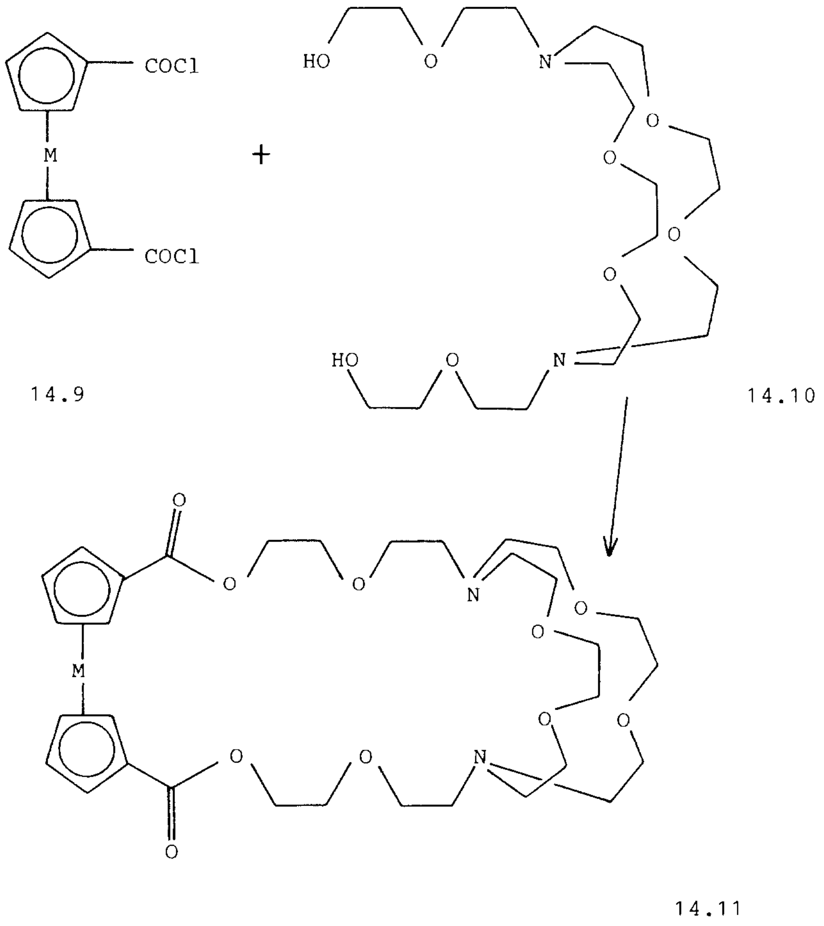
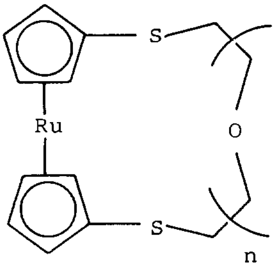
The crystal structure of osmocene has been determined by X-ray analysis. Osmocene was isomorphous with ruthenocene and had $\underline{D}_{5h}$ symmetry with a mean Os-C distance of 2.19A [279]. The reaction of 1,1'-dilithioruthenocene with selenium afforded the ruthenocenophane (14.4). The crystal structure of the complex (14.4) was determined by X-ray diffraction. The η-cyclopentadienyl rings were eclipsed and parallel and the two Se-Se bond lengths were identical [280]. Ruthenocene-mono- and di-carboxylic acids and ruthenocene boronic acid have been chromatographically separated and their chromatographic behaviour in the presence of alkali metal cations has been studied [281]. A cyclic voltammetric study has been carried out on [3](1,1')-ruthenocenophane, [4](1,1')-



-ruthenocenophane, [4](1,1')[3](3,3')-ruthenocenophane and [4](1,1')[4](3,3')-ruthenocenophane. The rates of heterogeneous electron transfer of oxidation in the ruthenocenophanes were less than those for the corresponding ferrocenophanes. An increase in the number of methylene groups in the ruthenocenophanes and the ferrocenophanes caused negative shifts of the oxidation peaks [282].

Dilithioruthenocene combined with the ruthenocenylene cyclophosphazene (14.5) to give the bis-transannular ruthenocenylene complex (14.6) the structure of which was determined by X-ray crystallography. The phosphazene ring was found to adopt a boat conformation [283]. The reactions of cyclotri- and cyclotetra-phosphazenes, that contained fluoro and ruthenocenyl or ferrocenyl substituents, with mono- and 1,1'-dilithio- ruthenocene or -ferrocene, methyllithium or phenyllithium have been investigated [284]. The ferrocene and ruthenocene (14.7 and 14.8) cryptands have been prepared and characterized by ^{1}H and ^{13}C NMR spectroscopy. The cryptands were fluxional and showed restricted rotation about the Ru-CO-N group [285]. Condensation of the 1,1'-bis(chlorocarbonyl)metallocenes (14.9; M = Fe, Ru) with the macrocyclic molecule (14.10) produced the corresponding cryptands (14.11). Both the cryptands (14.11; M = Fe, Ru) selectively complexed K^+ to the exclusion of Li^+, Na^+ and Cs^+ [286].



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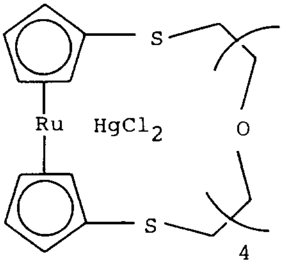
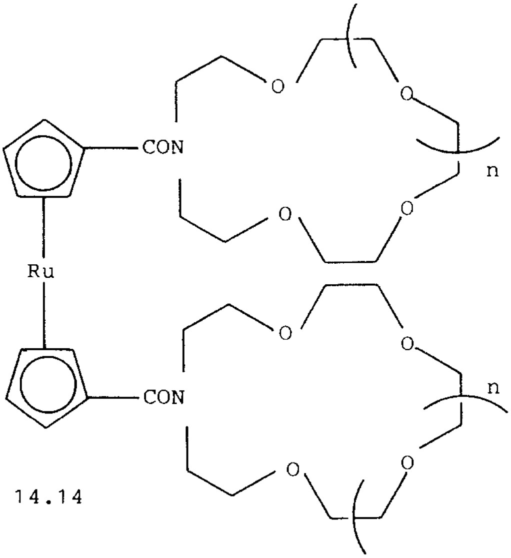
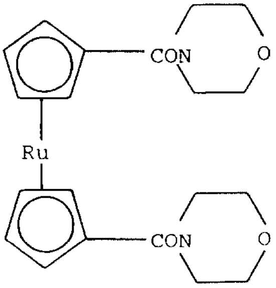


14.13

Polyoxa-1,n-dithia[n](1,1')ruthenocenophanes (14.12) have been prepared by reaction of 1,1'-ruthenocenedithiol with α,ω-dibromopolyethers. The ruthenocenophanes formed complexes with metal ions and the structure of the complex (14.13) was determined by



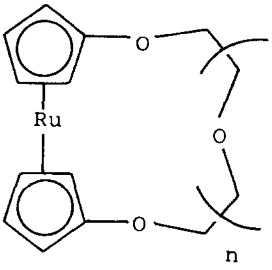
14.14



14.15

X-ray analysis. The mercury(II) chloride molecule was situated in the central cavity of the macrocyclic ring. The distance between the ruthenium and mercury atoms was too great for there to be any metal-metal interaction [287]. Polyoxa[n]- and 1,n-dioxathia[n]-ruthenocenophanes have been prepared and used as ligands to form complexes with transition metal cations. The silver(I) complex of 1,4,7,10,13,16-hexaoxa[16]ruthenocenophane showed electron-transfer interaction between the ruthenium atom and the silver(I) cation as evidenced by ^{1}H NMR and electronic spectroscopy [288].

Platinum(II) chloride and palladium(II) chloride formed complexes with 1,4,7,10-tetrathia[n]ruthenocenophanes, these were characterized by X-ray crystallography as cis-square planar complexes with the platinum or palladium bound to two of the four sulphur atoms [289]. The ruthenocene bis-crown ethers (14.14; n = 1,2 and 14.15) have been prepared from 1,1'-dichlorocarbonylruthenocene and the appropriate secondary amine. The complexes (14.14 and 14.15) were fluxional through rotation about the N-CO bond [290]. Polyoxa[n](1,1')ruthenocenophanes (14.16; n = 1-4) have been prepared by the reaction of 1,1'-diacetoxyruthenocene with the corresponding α-(2-bromoethyl)-ω-bromopoly(oxyethylene) in the presence of potassium hydroxide. The dioxa-ruthenocenophanes (14.17, 14.18 and 14.19) have been prepared by the reaction of 1,1'-bis(2-chloroethoxy)ruthenocene with the appropriate



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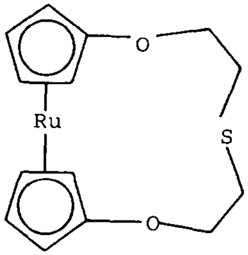

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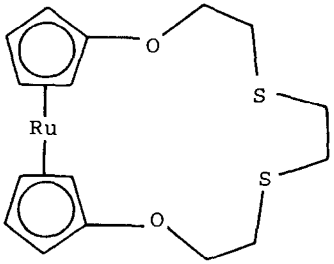

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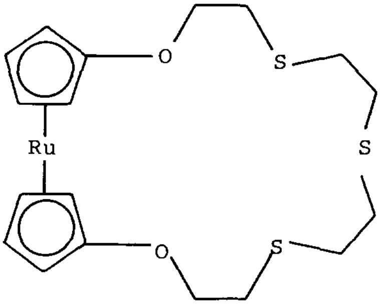

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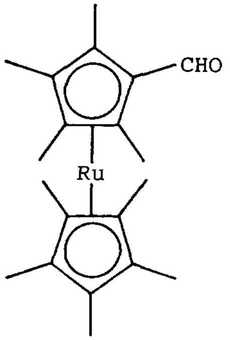

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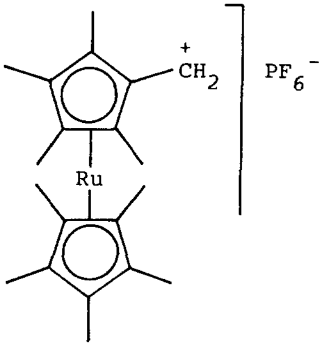

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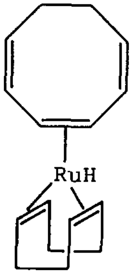


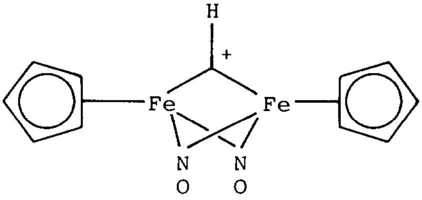
14.22

dithiolate in the presence of sodium hydroxide. The ruthenophanes formed 1:1 complexes with Hg(II) and Ag(I) ions. Spectral data indicated the presence of direct electronic interaction between these ions and the ruthenium atom of the ruthenocenophanes [291]. The structures of 1,10-(1,1'-ruthenocenediyl)-1,10-dioxa-dithiadecane (14.18) and its palladium(II) chloride complex have been determined by X-ray analysis. The conformations of the ruthenocene compound as the free ligand and complexed with the metal were different. In the complex the palladium was bonded to the two sulphur atoms and it had a cis square planar configuration [292].

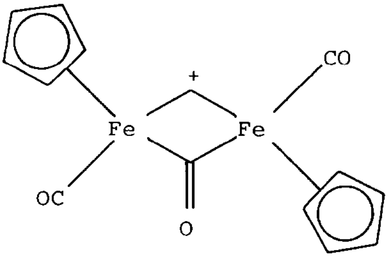
Oxidation of decamethylruthenocene with barium permanganate produced the aldehyde (14.20) which was reduced to the corresponding alcohol. Treatment of the alcohol with HPF_6 afforded the salt (14.21). The structure of the salt (14.21) was determined by X-ray analysis. The results indicated the presence of a direct Ru-$\overset{+}{C}$ interaction leading to a displacement of the Ru towards the exocyclic carbon atom together with a displacement of this carbon atom from the plane of the η-cyclopentadienyl ring towards the ruthenium atom [293]. Protonation of (η^4-cyclooctadiene)(η^6-cyclooctatriene)ruthenium by $HBF_4.Et_2O$ gave the cationic hydride (14.22) which underwent several ligand displacement and isomerization reactions. The complex (14.22) and related species were effective catalyst precursors for the isomerization and polymerization of olefins [294].

15. Iron, Ruthenium and Osmium Cluster Complexes

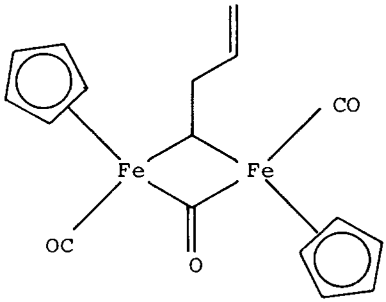
The μ-ethyne complex $Mo_2(CO)_3(PPh_3)(\mu\text{-}HC_2H)(\eta\text{-}C_5H_5)_2$, underwent isomerization in boiling octane to give the η^3-benzoylvinyl complex, $Mo_2(CO)_2(\mu\text{-}PPh_2)[\mu\text{-}HC_2(H)C(O)Ph](\eta\text{-}C_5H_5)_2$ which was characterized by X-ray crystallography. The reaction proceeded by phenyl migration from phosphorus to CO followed by benzoyl migration to the alkyne [295]. Treatment of the methylidene diiron complex, $[(\eta\text{-}C_5H_5)Fe(NO)]_2(\mu\text{-}CH_2)$, with the trityl cation at room temperature gave the methylidyne cation (15.1). With the same reagent at -78°C a bridging vinyl complex was obtained. The methylidyne cation (15.1) did not form stable 1:1 complexes with $KOCMe_3$, NMe_3 or PMe_3 and was inert to isobutylene, behaviour which contrasted with that of the corresponding carbonyl methylidyne complex [296]. The cationic methylidyne complex (15.2)



15.1



15.2



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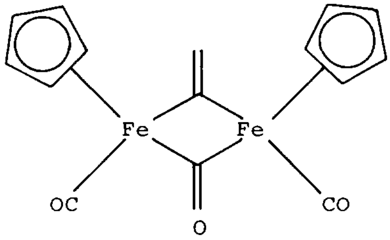

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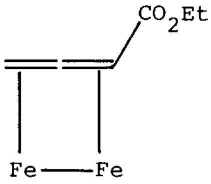

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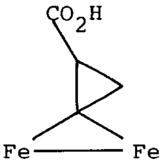
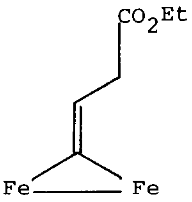


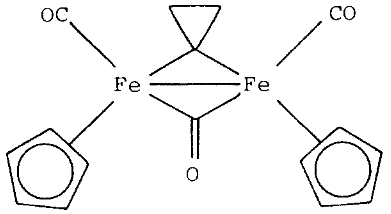
15.5



15.6

has been attacked by allylic reagents at the methylidyne bridge. Thus the silane $CH_2{=}CHCH_2SiMe_3$ gave the product (15.3) [297].

The μ-ethenylidene diiron complex (15.4) underwent addition of diazoacetic ester in the presence of CuI to give the cyclopropylidene complex (15.5) which was converted to the μ-ethenylidene derivative (15.6) by acid. The original complex (15.4) was photolyzed with diazoacetic ester to form the allene diiron complex (15.7), only reactive centres are shown in structures (15.5-15.7) [298]. The bridging cyclopropylidene ligand in the binuclear complex (15.8) underwent thermal rearrangement to a bridging allene ligand at temperatures above 100°. The complex



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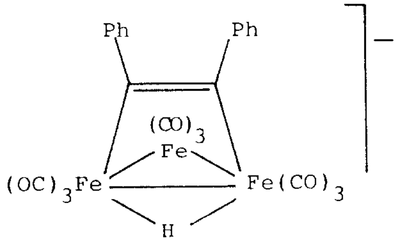
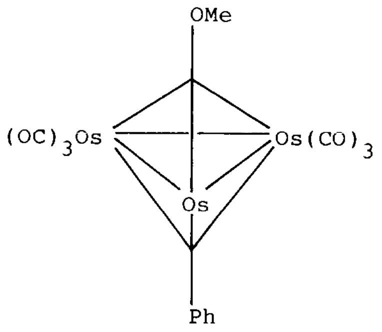


15.9

then broke down to liberate allene. The same ligand rearrangement took place under photochemical conditions, in each case the mechanism involved <u>cis-trans</u> equilibration of the carbonyl and cyclopentadienyl ligands before rearrangement [299]. The carbonyl-bridged diiron cation $[(\mu\text{-}CO)(\mu\text{-}RS)Fe_2(CO)_6]^+$ where R = Et, CMe_3, Ph underwent C-alkylation with alkyl HgX to form the neutral product $(\mu\text{-alkylCO})(\mu\text{-}RS)Fe_2(CO)_6$ while vinylic- and alkynyl-mercury reagents caused replacement of the bridging carbonyl by vinyl and alkynyl groups [300]. Ligand transformations have been reported in complex anions such as the trinuclear anion (15.9) derived from diphenylacetylene and iron carbonyls [301].

The bridging alkyne ligand in $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ underwent carbene addition with N_2CR_2, where R = H, Me, Ph, to form the allenyl ligand in $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}R_2C{=}C{=}CPh)(\mu\text{-}PPh_2)$ the structure of which was confirmed by X-ray crystallography. The



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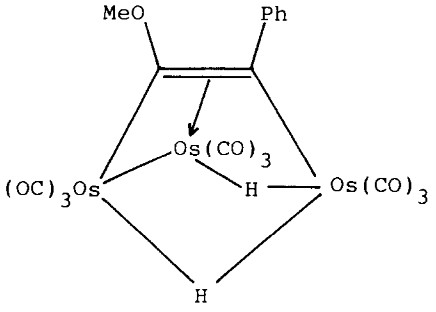

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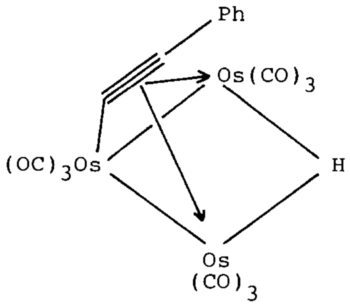


15.12

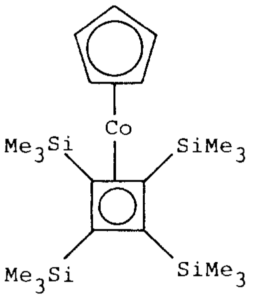
carbene reagent attacked at the α-carbon of the alkyne to give a σ,π-allenyl group [302]. The bridging ethynyl ligand in the cluster complex $Os_3H(\mu_3\text{-}C\equiv CH)(CO)_9$ was susceptible to attack by nucleophiles. Thus reaction with ethanol gave clusters containing the triply bridging ligands EtOCCH and CCHOEt while ammonia gave complexes with the ligand NH_2CCH. In the same way water attacked the cationic cluster $[Os_3H_2(\mu_3\text{-}C\equiv CH)(CO)_9]^+$ to give complexes containing the μ_3-CCHO and μ_3-CH ligands [303].

Phenylacetylene or allene underwent addition to the unsaturated ester ligand in the cluster $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC_2CO_2Me)$ to give the open cluster derivatives $Os_4(CO)_{11}(\mu\text{-}CPh{=}CH_2)(\mu_4\text{-}\eta^3\text{-}SCPh{=}CHC\equiv CCO_2Me)$ or $Os_4(CO)_{11}[\mu\text{-}C(CH_2)_2][\mu_3\text{-}\eta^5\text{-}(MeO_2C)C{=}CHC(CH_2)_2](\mu_3\text{-}S)$. These two products were characterized by X-ray crystallography [304].

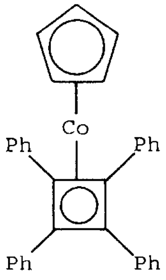
Hydrogenation of the cluster complex (15.10) resulted in alkylidyne-alkylidyne coupling and the alkyne complex (15.11) was produced. Reduction of the complex (15.10) with sodium benzophenone ketyl followed by protonation gave the phenylacetylide complex (15.12) [305].

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

The reaction of (dicarbonyl)(η-cyclopentadienyl)cobalt with bis(trimethylsilyl)ethyne produced tetrakis(trimethylsilyl)butatriene together with several complexes which included the η-tetrakis(trimethylsilyl)butadiene derivative (16.1) [306]. The electrolysis of cyclopentadiene and diphenylacetylene using a cobalt anode produced $(\eta^5$-cyclopentadienyl)$(\eta^4$-tetraphenylcyclobutadiene)cobalt (16.2) [307]. Displacement of ethylene from the complexes, $M(\eta\text{-}C_5H_5)(C_2H_4)_2$, where M = Co, Rh with $Bu^tC{\equiv}P$ gave the $(\eta^4$-diphosphacyclobutadiene)metal complexes (16.3; M = Cr, Rh) [308]. η-Cyclopentadienylcobalt compounds were effective catalysts for the preparation of pyridines from acetylenes and nitriles. The most active catalyst was (η-cyclooctatetraene)-(η-methoxycarbonylcyclopentadienyl)cobalt [309].



16.1



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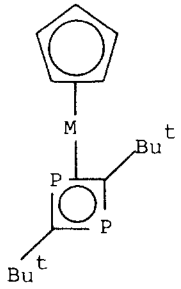
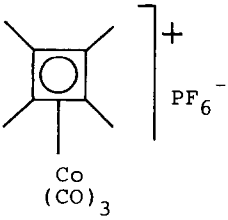


16.3

The reaction of the cobalt containing salt (16.4) with $Na[(\eta\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W) gave the corresponding binuclear complexes (16.5) which eliminated carbon monoxide to produce the tricarbonyl complexes (16.6) [310]. Dicarbonyl(η-cyclopentadienyl)cobalt has been effective in mediating the synthesis of highly crowded steroids through the formation of η-diene complexes



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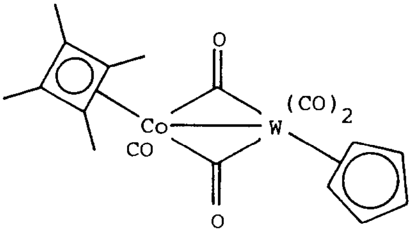
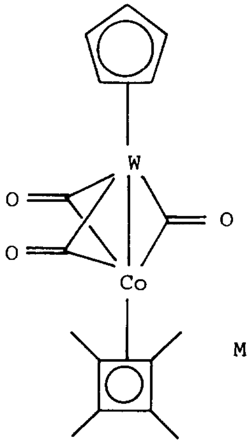


16.5



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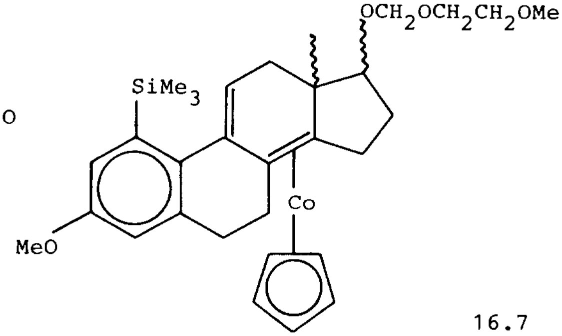
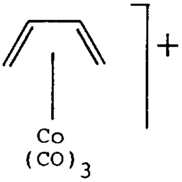


16.7

such as the steroid complex (16.7) [311]. The (η^4-butadiene)-cobalt cation (16.8) combined regiospecifically with nucleophiles such as the hydride ion and phenylmagnesium bromide to give the derivatives (16.9; R = H, Ph). Butadiene has been 1,4-difunctionalized regio- and stereo-specifically by double nucleophilic



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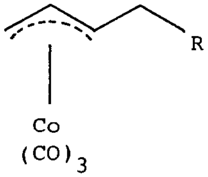
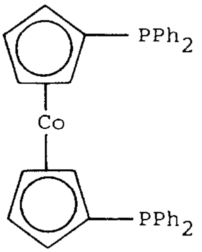


16.9

addition to the cation (16.8) [312].

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

The electrolysis of cyclopentadiene on a cobalt anode produced the cobaltocenium ion. The effect of the supporting electrolyte and the temperature on the product yield were investigated [313]. Flash-vacuum pyrolysis of (η-cyclopentadienyl)dicarbonylcobalt produced cobaltocene in 85% yield. Cobaltocene was produced in a bimolecular reaction between species from which the carbonyl ligands had been lost [314].



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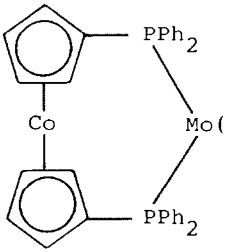

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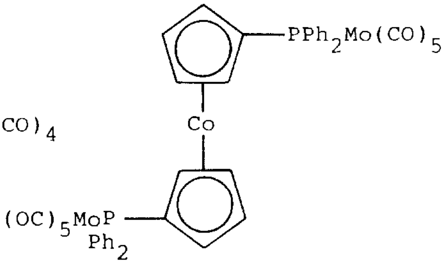
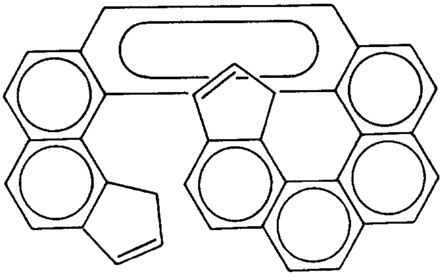


17.3

1,1'-Bis(diphenylphosphino)cobaltocene (17.1) has been prepared from $TlC_5H_4PPh_2$ and cobalt(II) chloride. The cobaltocene (17.1) formed two complexes (17.2 and 17.3) with molybdenum carbonyl. The structures of the complexes (17.2 and 17.3) were determined by X-ray analysis. The electrochemical properties of the cobaltocene (17.1) and its coordination complexes were compared with those of 1,1'-bis(diphenylphosphino)ferrocene [315]. Treatment of the helicene (17.4) with t-butyllithium in THF converted it to the dianion which then combined with cobalt(II) bromide to give the helical metallocene oligomer (17.5) in 64% yield [316]. Asymmetric synthesis has given the optically active helical metallocenes (17.6; $M = Fe, Co^+$) [317].

Reaction of the 2-hydroxypyridine (Hhp) complexes $Re_2(hp)_4X_2$, where X = Cl, Br, I, with cobaltocene produced the corresponding paramagnetic salts (17.7) [318]. The oxidation and reduction of the η-cyclopentadienyl-cobalt complexes (17.8, 17.9 and 17.10) have been studied electrochemically. The



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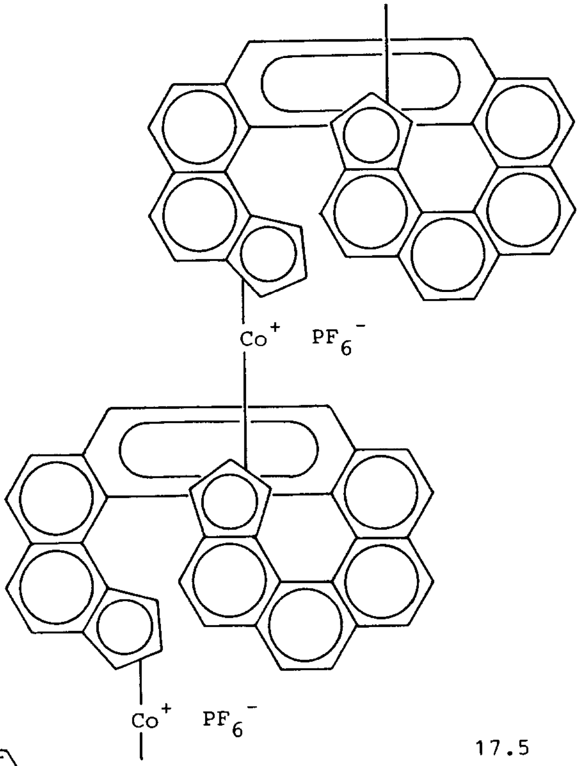

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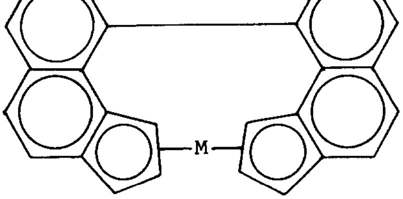

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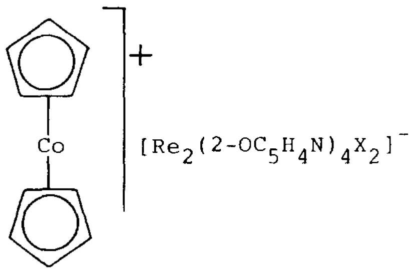

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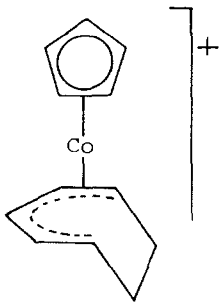

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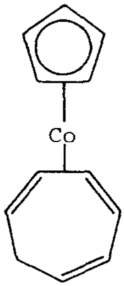

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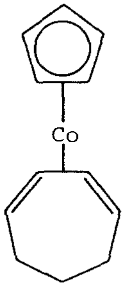
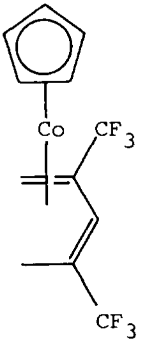


17.10

η^5-cycloheptadienyl complex (17.8) was reduced reversibly to a neutral radical which underwent slow dimerization. X-ray studies showed that this coupling occurred at the C_7 ligand [319]. Reaction of $Co(\eta\text{-}C_5H_5)(\eta\text{-}C_2H_4)_2$ with 2,4-bis(trifluoromethyl)-1,3-pentadiene led to the formation of the η^4-diene complex (17.11). An attempt to bring about hydride abstraction from this compound with the triphenylmethyl cation produced the complex (17.12) where the diene ligand had been replaced by the $[\eta^5\text{-}(C_6H_5)_3C]^+$ ligand [320]. Reaction of the borolenes C_4H_6BR (R = Me, Ph) with $[Rh(\eta^2\text{-}C_2H_4)_2Cl]_2$ afforded the triple decker complex (17.13). Treatment of the complex with sodium cyclopentadiene gave the corresponding η-cyclopentadienyl complexes (17.14) together with the salts (17.15). In $CD_2Cl_2\text{-}CF_3CO_2D$ the rhodium complex (17.14; R = Ph) underwent rapid deuterium exchange at the α-position to boron to give the dideutero complex (17.16) [321].



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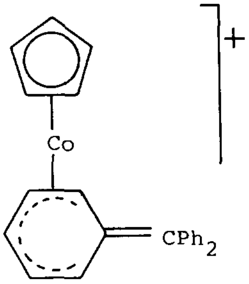

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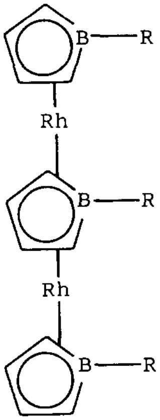

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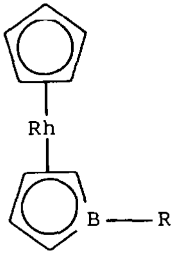

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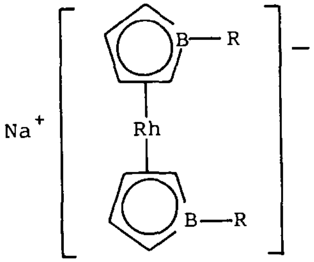

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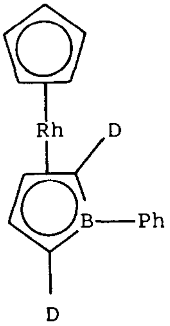

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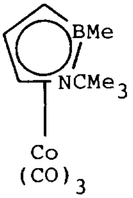

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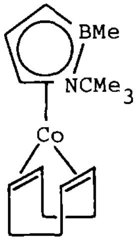

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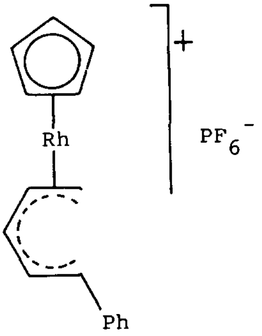
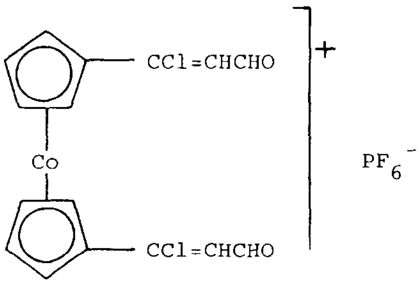


17.19

The reaction of cobalt carbonyl with 1-*t*-butyl-2,5-dihydro-2-methyl-1H-1,2-azaborole produced the complex (17.17). Irradiation of this complex with 1,5-cyclooctadiene gave (η^5-1-*t*-butyl-2,5-dihydro-2-methyl-H-1,2-azaborolyl)(η^4-1,5-cyclooctadiene)cobalt (17.18). The mobility of the ligands in this complex was studied by NMR spectroscopy [322]. The structure of the open-sandwich rhodium complex (17.19) has been determined by X-ray analysis. The structure contained discrete cations and PF_6^- anions. The η^5-cyclopentadienyl ring and the η^5-1-phenylpentadienyl group intersected at an angle of 9.6°. The phenyl ring was twisted out of the plane of the η^5-pentadienyl group [323].



17.20

An electron paramagnetic resonance study has been carried out on the electronic structure and the dynamic Jahn-Teller effect in decamethylcobaltocene and the isoelectronic decamethylnickelocenium cation. Covalency in these molecules, as compared with cobaltocene and the nickelocenium cation was unaffected by the presence of the methyl substituents [324].

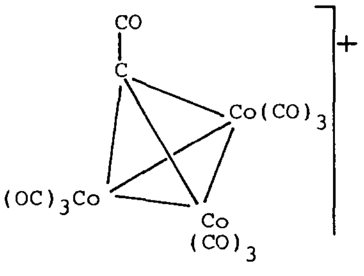
The salts formed from 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and cobaltocene or decamethylferrocene have been reinvestigated. On the basis of the UV-visible, infrared and Moessbauer spectra and electron spin resonance it was concluded that the anion formed was not the benzohydroquinone anion $[DDQH]^-$ as previously thought but the radical anion $[DDQ]^{\cdot -}$ [325]. Electron exchange in the cobaltocenium ion-cobaltocene and the tricarbonyl-(η^4-cyclooctatetraene)iron- the corresponding anion systems have been studied electrochemically in a series of organic solvents.

The rate constants obtained for the electron exchange processes in methanol, ethanol and propanol were anomalously high. The reasons for this behaviour were discussed [326]. Cobaltocene electrode films have been prepared by the electropolymerization of the salt (17.20). The films behaved as a one-way charge carrier for redox reactions in solution [327]. The reaction of crosslinked acetylated polystyrene with 1,1'-diacetylcobaltocenium hexafluorophosphate in the presence of triethylorthoformate was a good route for the preparation of polymers containing the cobaltocenium ion [328].

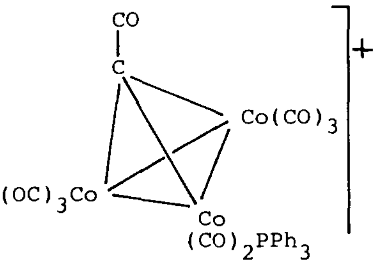
The polymer-supported moiety, $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_5)$, was heated at 150°C and 1 Torr to give the bound cobaltocenyl group which was in turn oxidized with bromine to the cobaltocenium ion. This cation was used as an ion-exchange medium [329]. Halogen containing polymers such as poly(cyanogen chloride) and iodomethylated styrene-divinylbenzene copolymer combined with cobaltocene to give polymers containing pendant cobaltocenyl groups. These polymers showed low thermal and oxidative stability but were effective as cyclotrimerization catalysts [330]. Cobaltocene has been used as a vulcanization accelerator in foamable silicone rubber that cured in air [331].

18. Cobalt-Carbon Cluster Compounds

The mixed metal cluster complex, $(\eta\text{-}C_5H_5)MoCo_2(CO)_8CCO_2CHMe_2$, which is formally related to the tricobalt cluster $Co_3(CO)_9CCO_2CHMe_2$ by replacement of a $Co(CO)_3$ vertex with an isolobal $(\eta\text{-}C_5H_5)Mo(CO)_2$



18.1



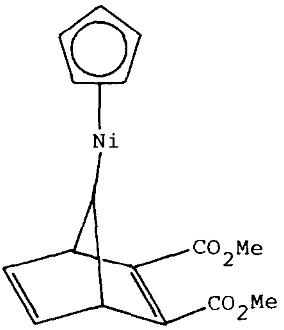
18.2

fragment; gave the mixed metal acylium salt $[(\eta\text{-}C_5H_5)MoCo_2(CO)_8\text{-}CCO]^+PF_6^-$ on treatment with HPF_6. The salt combined with methanol, diethylamine and dimethylaniline to give the products $(\eta\text{-}C_5H_5)MoCo_2(CO)_8CCO\text{-}OMe$, $\text{-}NEt_2$ and $\text{-}C_6H_4.NMe_2\text{-}4$ respectively [332]. The nonacarbonyltricobalt cluster complex, $(\mu_3\text{-}MeC)Co_3(CO)_9$, combined with the unsymmetrical diphosphine ligand $Ph_2PCH_2PMe_2$ to form the chiral cluster complex, $(\mu_3\text{-}MeC)\text{-}Co_3(CO)_7(\mu\text{-}Ph_2PCH_2PMe_2)$ which was isolated as a racemic mixture. Subsequent displacement of a further carbonyl ligand by an asymmetric phosphine gave a pair of diastereoisomers which were separable by chromatography. Catalytic applications of the complexes were explored [333].

Poly-dentate phosphorus and arsenic ligands such as $Ph_2PCH_2PPh_2$(DPPM), $Ph_2PCH_2CH_2PPh_2$(DPPE) and $MeC(CH_2PPh_2)_3$(TPME) underwent electron-transfer-catalyzed and thermal reactions with the cobalt cluster complexes $RCCo_3(CO)_9$, where R = Me, Ph, to give derivatives such as $[RCCo_3(CO)_8]_2(\mu\text{-DPPE})$, $RCCo_3(CO)_7(\mu\text{-DPPE})$, $RCCo_3(CO)_7(\mu\text{-DPPM})$, $RCCo_3(CO)_5(\mu\text{-DPPM})_2$ and $RCCo_3(CO)_6(\mu\text{-TPME})$. One of these complexes $[RCCo_3(CO)_8]_2(\mu\text{-DPPE})$ was characterized by X-ray crystallography [334]. An electrochemical study of the complexes indicated that the primary reduction step was a one-electron process in each case. Reversible oxidation was demonstrated in the series $[RCCo_3(CO)_5(\mu\text{-DPPM})_2]^{2/1/0/1-}$ and $RCCo_3(CO)_6(\mu\text{-TPME})^{1/0/1-}$ [335]. The mechanism of formation of the phosphorus complexes has been elucidated and the first order rate constant for the primary dissociation of $RCCo_3(CO)_9$ has been determined as 3.2 $mol^{-1}s^{-1}$ in dichloromethane [336]. A variable temperature ^{13}C NMR investigation on the cluster compounds (18.1 and 18.2) indicated a tilted geometry for the ketenylidene fragment rather than a perpendicular arrangement. This finding was supported by EHMO calcualtions [337]. Decomposition of the tricobalt alklidyne complex, $Co_3(CO)_9COAc$, in THF gave the anion $[Co(CO)_4]^-$ together with two tetranuclear complexes [338].

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

Nickelocene has been attacked by dimethylacetylene dicarboxylate to give a Diels-Alder adduct (19.1) which has been used as an intermediate in the synthesis of 7-substituted norbornadienes [339]. The halogen bridged binuclear nickel complexes $(\eta\text{-}C_5Ph_5)Ni(\mu\text{-}X)_2(\eta\text{-}C_5Ph_5)$, where X = Cl, Br, have been treated



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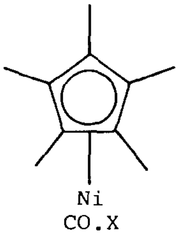

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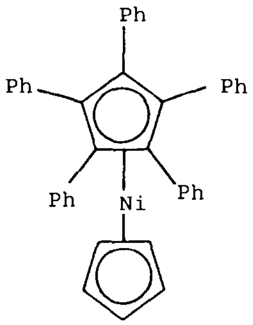
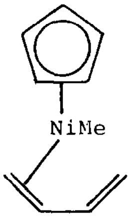


19.3

with carbon monoxide and THF to give the half-sandwich complex (19.2; X = Cl, Br) which combined with thallium(I) cyclopentadienide to form pentaphenylnickelocene (19.3) [340]. Treatment of nickelocene with methyllithium in the presence of 1-alkenes, olefins with internal double bonds, α,ω-alkadienes, cycloalkenes cycloalkapolyenes produced the corresponding (η^5-cyclopentadienyl)-methyl(η^2-olefin)nickel complex. For example, when the reaction was carried out in the presence of 1,3-butadiene the nickel complex (19.4) was isolated [341].



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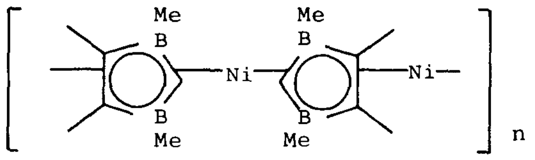


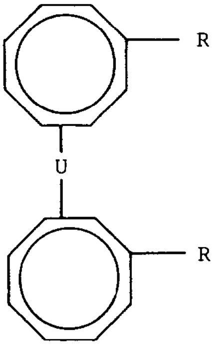
19.5

The reaction of nickelocene with pentacarbonylchlororhenium(I) produced the dimer $[ClRe(CO)_4]_2$ and the tris(η-cyclopentadienyl) complex $(\eta\text{-}C_5H_5)_3Ni_3(CO)_2$. The dimer $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ was obtained from the reaction of nickelocene with tris(acetonitrile)-tricarbonylmolybdenum [342]. Products from the hydrogenation of nickelocene during the nickel coating of quartz have been estimated by gas chromatography [343]. Pressure pyrolysis of a nickelocene--divinylbenzene polymer has been used to produce nickel-dispersed carbon particles. The morphology and magnetic properties of the particles were investigated [344]. The reaction of nickelocenium tetrafluoroborate with ferrocenium tetrafluoroborate produced polymeric material of composition $[(\eta\text{-}C_5H_5)_4FeNi](BF_4)_2$ for which a stacked structure was suggested [345].

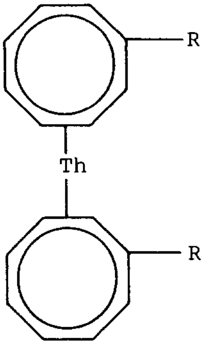
The multidecker (η^5-2,3-dihydro-1,3-diborolyl)nickel complex (19.5) has been prepared by pyrolysis of a triallyl (η-2,3-dihydro--1,3-diborolyl)dinickel precursor [346]. The crystal and molecular structure of bis(η^5-2,3,5-tricarbahexaboranyl)nickel has been determined by X-ray crystallography and shown to be a nickelocene analogue [347]. Nickelocene was an efficient catalyst in the cross-linking of the acetylene terminated monomer $(1,4\text{-}HC{\equiv}CCH_2\text{-}OC_6H_4)_2CMe_2$ [348]. Large EPR anisotropic g-shifts were observed for the $S = 1/2$ molecules, bis(η-benzene)vanadium and η-cycloheptatrienyl(η-cyclopentadienyl)vanadium, when they were doped into nickelocene [349]. In photochemical experiments nickelocene has been shown to be a good quencher of triplets in organic molecules in the energy range 0.9-3.2eV. This efficient quenching ability was explained in terms of a combination of energy and electron transfer. The results suggested the presence of a low-lying spin-forbidden transition in nickelocene [350].

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

The reaction of mesitylcyclooctatetraene or o-tolylcyclooctatetraene with uranium(IV) chloride and potassium afforded the corresponding uranocenes (20.1; R = $2,4,6\text{-}Me_3C_6H_2$, $o\text{-}MeC_6H_4$). ^1H NMR spectroscopy indicated that the mesityl and the cyclooctatetraenyl groups were not in the same plane and that the mesityl groups had different conformations at different temperatures [351]. The reaction of thorium(IV) chloride with a series of substituted cyclooctatetraenes and potassium in tetrahydrofuran

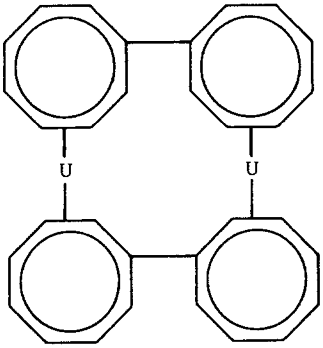


20.1



20.2

produced the corresponding thorocenes (20.2; R = 2,4,6-$Me_3C_6H_2$, o-MeC_6H_4, CMe_3). The NMR spectra of these compounds were recorded and interpreted [352]. 1,1'-Dibutyluranocene has been prepared by the treatment of uranium(III) iodide with $Li_2C_8H_7Bu$. The liquid to vapour equilibrium of this complex was investigated [353]. The reaction of butyllithium with cyclooctatetraene produced the dilithio salt of butylcyclooctatetraene which on



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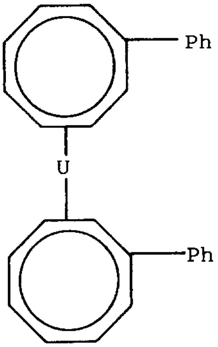

20.4

treatment with uranium(III) or (IV) iodide afforded 1,1'-dibutyluranocene in good yields [354]. Uranocene and its dibutyl and didecyl derivatives gave charge transfer complexes with nitrostilbenes in which cis-trans-isomerization of the stilbenes was observed [355]. Biuranocenylene (20.3) has been obtained by the treatment of 1,1'-dicyclooctatetraenyluranocene tetraanion with uranium(IV) chloride in THF under argon. Variable temperature ^{1}H NMR spectroscopy indicated that the two uranocenylene groups were twisted with respect to one another [356]. Ligand exchange in uranocene and in half-sandwich (η-cyclooctatetraene)uranium complexes has been studied. The ligands examined were dimethoxyethane, tetramethylethylenediamine, phenoxy and chloride [357]. The gas-phase X-ray photoelectron spectra of uranocene and related uranium compounds have been recorded and interpreted. Bonding in uranocene is essentially covalent with 5f electrons showing nonbonding character [358]. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been determined for the rotation of the phenyl group in 1,1'-diphenyluranocene (20.4) by line shape analysis of the ^{1}H NMR spectrum [359].

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