

ORGANIC REACTIONS OF SELECTED  $\Pi$ -COMPLEXES  
 ANNUAL SURVEY COVERING THE YEAR 1984\*  
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\* Organic Reactions of Selected  $\pi$ -Complexes, Annual Survey  
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## 1. Reviews

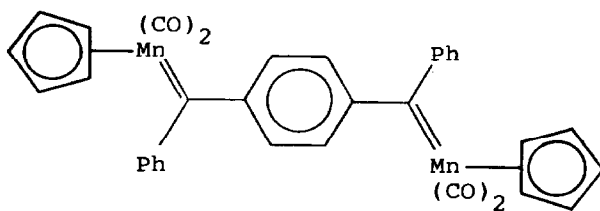
The application of organometallic compounds as electron, hydrogen-atom and hydride ion reservoirs, the reduction of iron sandwich complexes and the reduction of isolobal carbonyl complexes have been discussed by Michaud, Lapinte and Astruc [1]. The chemistry of vinylidene and propadienyldiene transition metal complexes has been surveyed by Bruce and Swincer [2]. The formation of reactive organometallic intermediates from metallocenes has been reviewed by Jonas [3]. Hegedus has provided a good review on the formation of carbon-carbon bonds via  $\pi$ -complexes of transition metals. This included a section on the alkylation of  $(\eta\text{-arene})\text{tricarbonylchromium}$  complexes [4]. Schumann has reviewed the syntheses, properties and reactions of  $(\eta\text{-arene})(\eta\text{-cyclopentadienyl})\text{-iron cations}$  [5]. The organometallic compounds of cobalt, rhodium, iridium and nickel have formed the 4th edition of volume 13, part 9B of Houben-Weyl, Methods of Organic Chemistry [6]. Dickson has reviewed the organometallic chemistry of rhodium and iridium [7].

## 2. General Results

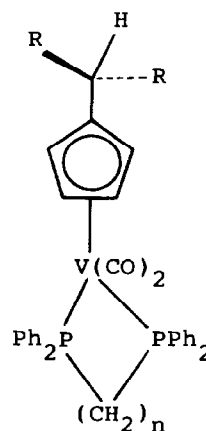
Borisov and Kritskaya have carried out a theoretical study of  $\pi$ -complexes of transition metals with aromatic ring fragments [8]. A semiempirical crystal-orbital approach using the INDO approximation has been used to predict the band structures of eleven one-dimensional polydecker sandwich complexes with manganese, iron, cobalt, nickel, copper and zinc as the metal centres. A range of  $\pi$ -bonding 5-membered ligand rings was examined from the cyclopentadienyl ring to the  $\text{B}_5\text{H}_5$  ring. The calculations allowed the prediction of possible conducting or semiconducting low dimensional materials

made up of metal-ligand fragments. The semiempirical tight-bonding approach indicated that forbidden gaps in the band structure were reduced as the number of boron atoms in the ligand increased. The  $\text{Mn}(\text{C}_5\text{H}_5)$  stack provided the only intrinsic conductor in the series studied, all of the others required charge carriers in the form of electrons or holes to be added. Synthetic approaches to these compounds were discussed [9].

Ab initio Hartree-Fock calculations have been carried out on a series of metallocenes  $(\eta\text{-C}_5\text{H}_5)_2\text{M}$ , where  $\text{M} = \text{V}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Mg}, \text{Ge}$ ,  $[(\eta\text{-C}_5\text{H}_5)_2\text{M}]^+$ , where  $\text{M} = \text{Fe}, \text{Co}$ ,  $(\eta\text{-C}_5\text{H}_5)\text{-NiNO}$  and  $(\eta\text{-C}_5\text{H}_5)\text{GeCl}$ . The results indicated that charge-transfer effects were important and more important than ring-ring dispersion forces [10]. Cyclic voltammetry has been used to measure the half-wave potentials for the individual redox-transitions of a series of bis( $\eta$ -cyclopentadienyl)metal complexes. An attempt was made to correlate these values with the ionization energies of the corresponding metals or metallocenes [11]. The transfer of carbene groups from aliphatic diazoalkanes to coordinatively unsaturated transition metal centres has been used as a general route to transition metal methylene complexes. Mononuclear organometallic substrates, metal-metal double bonds and metal-metal triple bonds underwent the reaction to form a range of mononuclear and dinuclear complexes. The cymantrene derivative (2.1) was a typical product [12].



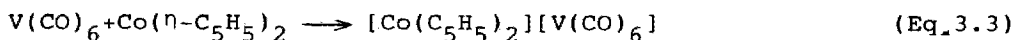
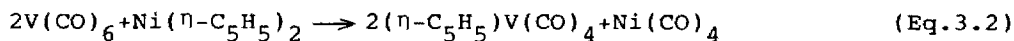
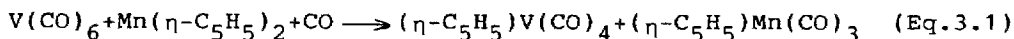
2.1



3.1

### 3. $(\eta\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$ and Related Compounds

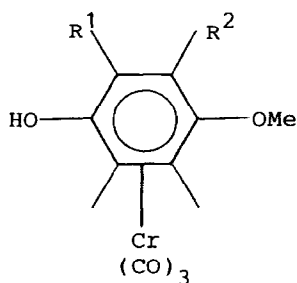
Wenke and Rehder have prepared the ring-substituted  $\eta$ -cyclopentadienylvanadium complexes (3.1; R = Me, Ph,  $p\text{-C}_6\text{H}_4\text{OMe}$ ,  $p\text{-C}_6\text{H}_4\text{NMe}_2$ ; n = 1, 2) by photochemical reaction of the corresponding fulvenes  $\text{C}_5\text{H}_4\text{CR}_2$  with the vanadium hydrides  $\text{VH}(\text{CO})_4\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ , where n = 1 and 2 [13]. As part of a study on the redox reactions of  $\text{V}(\text{CO})_6$ , manganocene and nickelocene were reduced (equations 3.1 and 3.2) and cobaltocene was oxidized (equation 3.3) [14].



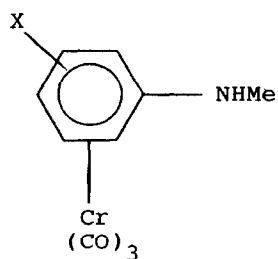
### 4. $(\eta\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$

#### (i) Formation

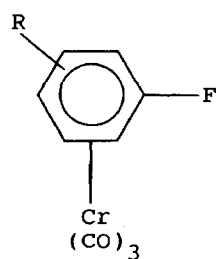
Reaction of hexacarbonylchromium with (E)-MeCLi=CHMe and  $\text{Me}_3\text{O}^+\text{BF}_4^-$  produced the carbene (Z)-(CO)<sub>5</sub>Cr=C(OMe)CMe=CHMe which cyclized with methylphytylacetylene to give a mixture of the tricarbonylchromium complexes [4.1; R<sup>1</sup> = Me, R<sup>2</sup> = (Z)-CH<sub>2</sub>-CH=CMe(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHMe)<sub>3</sub>Me and R<sup>1</sup> = (Z)-CH<sub>2</sub>CH=CMe(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHMe)<sub>3</sub>Me, R<sup>2</sup> = Me]. The tricarbonylchromium group was removed from the latter compound and the arene was brominated and cyclocondensed to give vitamin E in high yield [15]. Several (η-aniline)tricarbonylchromium complexes including the derivatives (4.2; X = 2-Et, 3-F, 4-CO<sub>2</sub>Et) have been prepared from the appropriate aniline and hexacarbonylchromium [16]. Several disubstituted benzotrene complexes including the fluoro complexes (4.3; R = 2-Me, 3-Me, 4-Me, 2-OMe, 3-OMe, 4-OMe, 2-NH<sub>2</sub>, 3-NH<sub>2</sub>, 4-NH<sub>2</sub>) have been prepared by direct reaction of hexacarbonylchromium and the ligand in the presence of THF [17]. Reaction of hexacarbonylchromium with pentaphenylcyclopentadiene produced the tricarbonylchromium complex (4.4) [18]. Treatment of hexacarbonylchromium with 2,4,6-tri-tert-butylpyridine and 2,6-di-tert-butylpyridine gave the corresponding tricarbonylchromium complexes (4.5; R = CMe<sub>3</sub>, H). The reactions of these complexes with methyl- and phenyl-



4.1



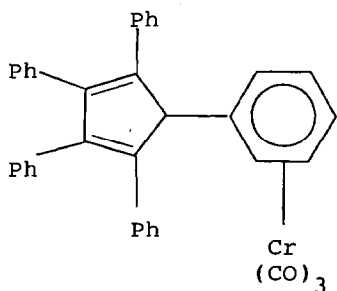
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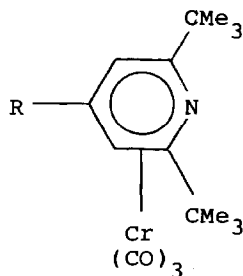
4.3

-lithium were investigated [19].

Direct reaction between hexacarbonylchromium and the ligand gave the ( $\eta$ -diaryldiphosphene)chromium complex (4.6) together with the corresponding binuclear complex [20].

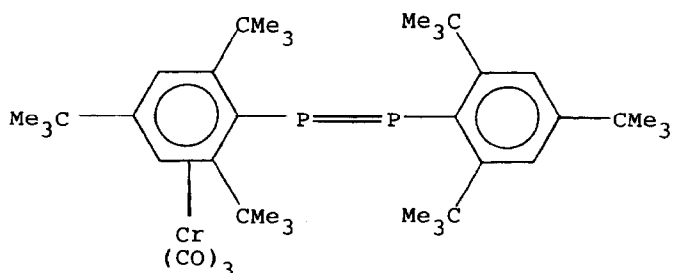


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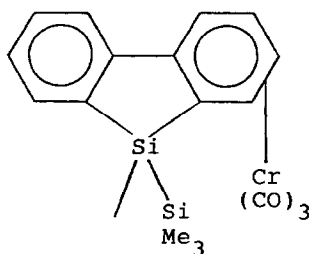
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The reaction of 1-methyl-1-(trimethylsilyl)dibenzosilole with hexacarbonylchromium produced the tricarbonylchromium complex (4.7). The treatment of this complex with methyllithium followed by iodine oxidation afforded 1,1-dimethyldibenzosilole (4.8) [21]. Methyl(3R,4R,6S)-1,3,4,6-tetrahydro-2-oxo-3,6-epoxy-2H-5,1-benzoxazocine-4-carboxylate, an optically active derivative of *o*-aminobenzaldehyde, was heated with hexacarbonylchromium to give the tricarbonylchromium complex

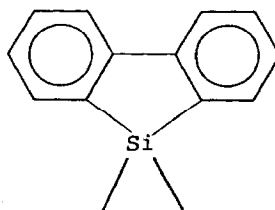


4.6

(4.9) with almost complete asymmetric induction. X-ray analysis indicated that complexation had occurred on the face of the aromatic that was syn to the 3,6-epoxy bridge [22]. Reaction of 10,10-dimethyl-10-sila-9-oxaphenanthrene with hexacarbonylchromium produced the tricarbonylchromium complex (4.10) whilst reaction with triaminetricarbonylchromium produced a mixture of isomers (4.10 and 4.11) [23].

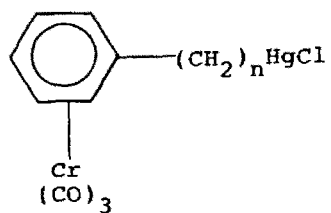
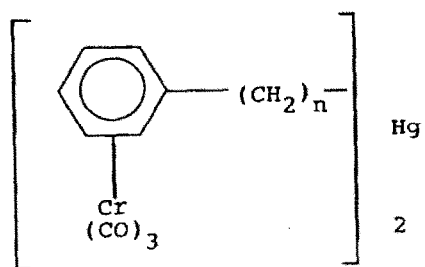
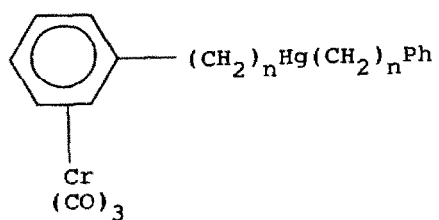
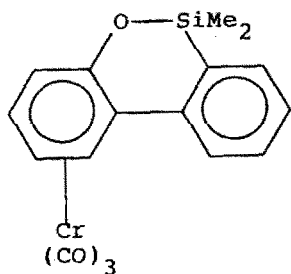
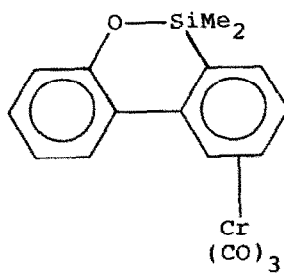
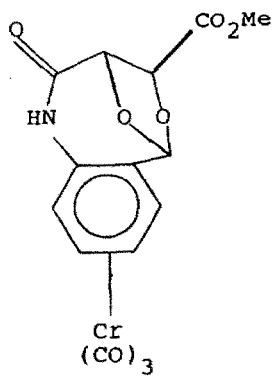


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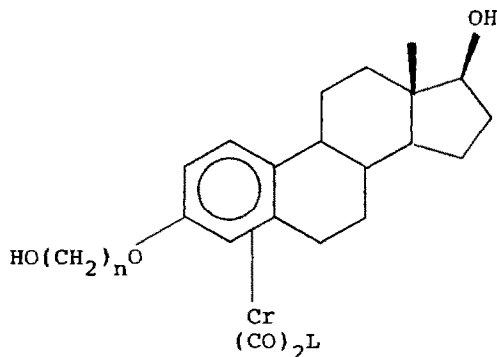


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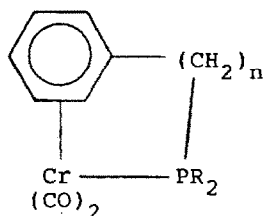
Mahaffy has reported the synthesis and characterization of the tricarbonylchromium complexes of dimethylaniline, dimethylanisole and related compounds [24]. The reaction of  $[\text{Ph}(\text{CH}_2)_n]_2\text{Hg}$ , where  $n = 3, 4$ , with triaminetricarbonyl-



chromium or hexacarbonylchromium produced the tricarbonylchromium complexes (4.12 and 4.13). Treatment of the complexes (4.13) with mercury(II) chloride produced the corresponding chloro-mercury complexes (4.14) [25]. The estradiol chromium complexes (4.15; L = CO, CS, CSe, n = 1-7) have been prepared. The complex (4.15; L = CO, n = 3) had a hormonal relative binding affinity of 28% compared to 3% for tamoxifen and 100% for estradiol [26]. A series of ( $\eta$ -arene)tricarbonylchromium compounds has been prepared where the arene ring was substituted



4.15

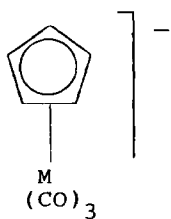


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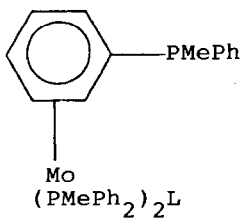
with a number of bulky groups such as *t*-butyl. The  $\text{Ph}_3\text{PCr}(\text{CO})_2$  and  $(\text{PhO})_3\text{PCr}(\text{CO})_2$  analogues of these compounds were prepared together with a number of bridged compounds of the type (4.16; R = OPh, Ph, n = 1, 2). The  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of these compounds were recorded and interpreted [27]. Iodine was effective as a catalyst for the exchange of benzene in benzotrene for toluene, mesitylene and *p*-xylene under mild conditions [28].

Salts of the anions (4.17; M = Cr, Mo, W) have been prepared by treatment of  $(\text{MeCN})_3\text{M}(\text{CO})_3$  complexes with sodium cyclopentadienide in THF [29]. Reduction of  $\text{Mo}_2\text{Cl}_{10}$  with magnesium in the presence of methyldiphenylphosphine gave the ( $\eta$ -arene)molybdenum complex (4.18; L =  $\text{PMePh}_2$ ) which underwent ligand exchange at  $25^\circ\text{C}$  to form the complexes [4.18; L =  $\text{P}(\text{OMe})_3$ ,  $\text{CNCMe}_3$ , CO] [30].

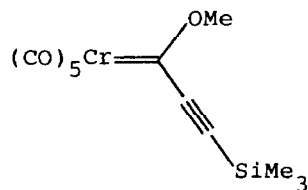




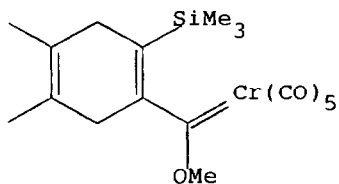
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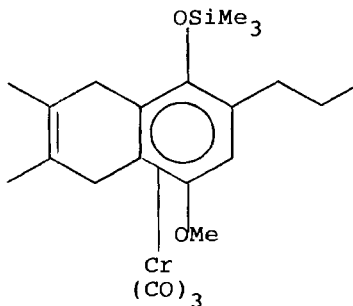
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4.19



4.20



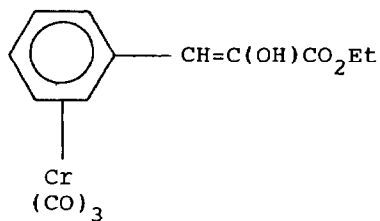
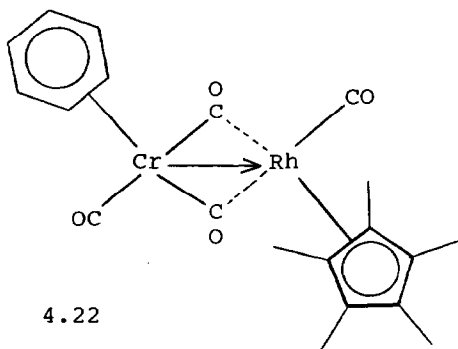
4.21

Chromium atoms have been condensed with cyclohexene and the resultant matrix has been treated with toluene. The organometallic derivatives in the product included ( $\eta$ -benzene)-( $\eta$ -toluene)chromium, di( $\eta$ -toluene)chromium and di( $\eta$ -benzene)-chromium. In a similar reaction, the condensation of chromium atoms with 4-methylcyclohex-1-ene followed by treatment with ethylbenzene produced di( $\eta$ -toluene)chromium, di( $\eta$ -ethylbenzene)chromium and ( $\eta$ -ethylbenzene)( $\eta$ -toluene)chromium. From the results it was concluded that the complexed alkene underwent isomerization and dehydrogenation [31]. The Diels-Alder reaction of  $\alpha,\beta$ -acetylenic chromium carbene complexes with a series of dienes has been studied and from some of these reactions tricarbonylchromium complexes were isolated. For example, the reaction of the trimethylsilylethynyl complex (4.19) with 2,3-dimethylbutadiene afforded the cycloadduct (4.20) which underwent reaction with 1-pentyne to produce the

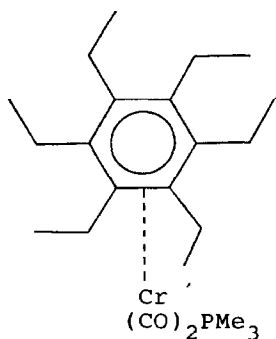
tricarbonylchromium complex (4.21) [32].

(ii) Spectroscopic and Physico-chemical Studies

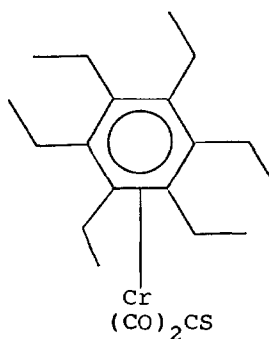
A theoretical study of the binuclear ( $\eta$ -benzene)chromium complex (4.22) has indicated that the ( $\eta$ -C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>3</sub> moiety was a good  $\pi$ -acid ligand for the electron rich ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Rh(CO) group. Bonding was ascribed principally to semi-bridging carbonyls with little metal-metal interaction [33]. Diethyl



oxalate combined with tricarbonyl( $\eta$ -toluene)chromium in the presence of potassium t-butoxide to give the tricarbonylchromium complex of ethylphenylpyruvate (4.23). This product was characterized by X-ray crystallography[34]. The crystal and molecular structure of the ( $\eta$ -hexaethylbenzene)chromium complex (4.24) has been determined by X-ray crystallography. The arene ligand adopted a 1,2,3,5-distal-4,6-proximal methyl conformation. The variable temperature <sup>31</sup>P and <sup>13</sup>C NMR spectra were rationalized in terms of slow ethyl group rotation which produced several coexisting stereoisomers in equilibrium but did not involve slow rotation about the chromium-arene bond [35]. A related <sup>13</sup>C NMR study of the ( $\eta$ -hexaethylbenzene)chromium complex (4.25) explained the low temperature spectra in the same way in terms of restricted ethyl group rotation [36]. Reconsideration of the recently reported conformational study of dicarbonyl( $\eta$ -hexaethyl-



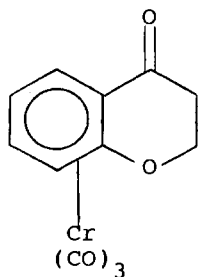
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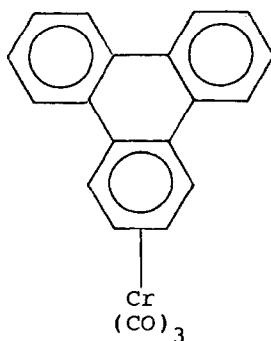
4.25

benzene)thiocarbonylchromium (4.25) using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy has shown that the only detectable isomer in both the solid state and in solution was the 1,3,5-distal-2,4,6-proximal form (4.25). The results indicated slowed tripodal rotation on the NMR time scale [37].

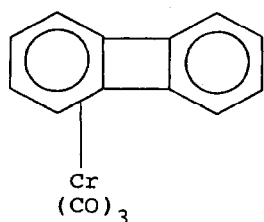
X-ray crystallography and  $^1\text{H}$  NMR spectroscopy have been used to show that the heterocyclic ring in the ( $\eta$ -chromanone)-chromium complex (4.26) adopted a "sofa" conformation in both the solid and solution phases [38]. The ( $\eta$ -triphenylene)-chromium complex (4.27) has been prepared by direct reaction between the ligand and hexacarbonylchromium or  $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$ . The crystal and molecular structures of the triphenylene (4.27) and biphenylene (4.28) complexes have been determined by X-ray crystallography. Conformational preferences in the two complexes were investigated by extended Hückel MO calculations. A strategy was developed for predicting the conformation of any bicyclic ( $\eta$ -polyene) $\text{ML}_3$  complex [39]. The crystal and molecular structures of the ( $\eta$ -arene)tricarbonylchromium complexes (4.29;  $\text{R} = \text{H}, \text{CO}_2\text{Me}$ ) have been determined by X-ray analysis. A noticeable feature in the structures of these complexes was the short Cr-S bond distances of 2.346 and 2.354 Å respectively [40]. The mass spectra of tricarbonylchromium complexes of a series of phenylmethylsilanes, for example compound (4.30), have been recorded and interpreted [41].



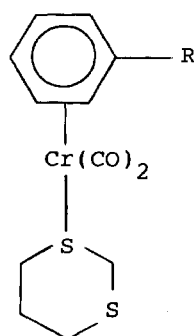
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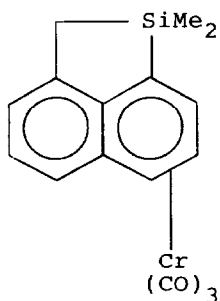


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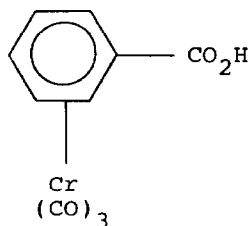


4.29

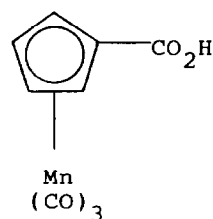
Complexes containing the benchrotrenyl and ferrocenyl groups in conjugation underwent an induced electrooxidation of the benchrotrenyl group in DMF. Chromium(I) species were implicated in the reaction which was facilitated by a decrease in the distance between the electroactive sites [42]. The electrooxidation of benchrotrene and substituted benchrotrenes has been studied in acetonitrile at a glassy carbon electrode. A two electron process was involved, with formation of chromium(II) species. Indirect and assisted electrooxidation in acetonitrile were inefficient by comparison with dimethylformamide [43]. The electrochemical oxidation of benchrotrene and substituted benchrotrenes containing one to six methyl groups has been studied. The complexes underwent reversible oxidation to the cation radicals at potentials in the range 493 to 281 mV vs.  $\text{Ag}/\text{Ag}^+$  and then irreversible oxidation to dication at



4.30



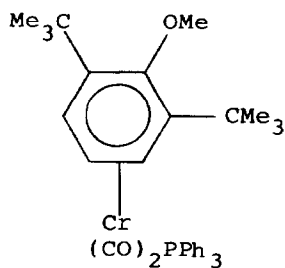
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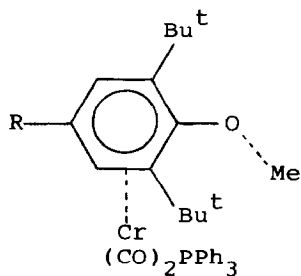
4.32

$\sim 1280$  mV. The intermediate cation radicals underwent first-order decomposition to the free arene ligands and carbon monoxide with rate constants in the range  $2500$  to  $0.046$   $\text{s}^{-1}$  at  $298\text{K}$  [44]. The standard oxidation potentials measured in trifluoroacetic acid correlated well with the vertical ionization potentials measured in the gas phase for an extensive series of alkyl substituted benzenes. The tricarbonylchromium complexes of these alkylbenzenes were prepared and the standard oxidation potentials were measured. These standard oxidation potentials showed a good correlation with the values obtained for the uncomplexed ligands [45].

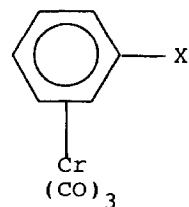
The tricarbonyl( $\eta$ -arene)chromium complexes, where arene = benzene, acetophenone, acenaphthene, have been adsorbed on to wet silica gel and suspended in cyclohexane. The electronic spectra of these suspensions showed shifts of both the carbonyl stretching absorptions and the metal-arene charge-transfer bands which were ascribed to chemisorptive interactions. Photolysis of the complexes under these conditions was sensitive to silica gel pore size. Large pore sizes gave larger quantum yields. The contributions of steric and electronic effects to photo-reactivity were discussed [46]. The inelastic electron tunnelling spectra of the chromium (4.31) and manganese (4.32) complexes have been recorded on Al-Al oxide-Pb junctions where they exhibited both infrared- and Raman-active vibrations [47].



4.33



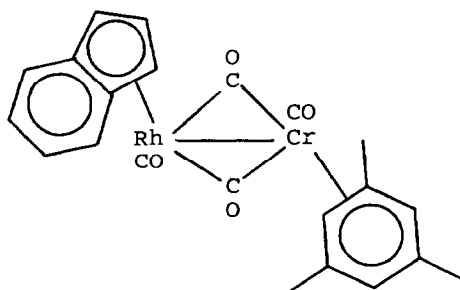
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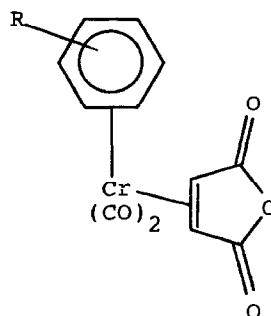
4.35

The interconversion of two forms of the benchrotrene complex (4.33) has been studied by  $^1\text{H}$  NMR spectroscopy. The two species differed in the orientation of the methoxy group towards the chromium atom and the interconversion had a free energy of activation of  $50 \text{ kJ mol}^{-1}$ . Restricted rotation about the benzene-chromium bond was not involved in the process [48]. The variable temperature  $^1\text{H}$  NMR spectra of the benchrotrene analogues (4.34;  $\text{R} = \text{H}, \text{D}, \text{Me}$ ) have been interpreted in terms of kinetic restriction of rotation about the arene-methoxy bond at low temperatures. The X-ray crystal structure of the complex (4.34;  $\text{R} = \text{H}$ ) has been determined and the syn-conformation of the methoxy group to the chromium has been confirmed [49].

The enthalpies of sublimation, thermal decomposition and bromination of hexacarbonylchromium and several benchrotrene complexes (4.35;  $\text{X} = \text{Me}, \text{OMe}, \text{NMe}_2, \text{COMe}, \text{CO}_2\text{Me}$ ) have been measured by microcalorimetry. The standard enthalpies of formation of the complexes (4.35) were determined [50]. Conformational analysis of some disubstituted ( $\eta$ -arene)tricarbonyl chromium complexes has been carried out by  $^1\text{H}$  NMR spectroscopy [51]. Variable temperature  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectroscopy for the mixed metal indenyl complex (4.36) confirmed the fluxional nature of the molecule and demonstrated hindered rotation of the  $\eta$ -indenyl ligand [52]. Isotopic hydrogen exchange in the maleic anhydride complexes (4.37;  $\text{R} = \text{H}, 1, 3, 5\text{-Me}_3$ )



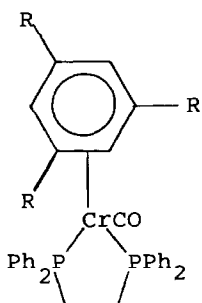
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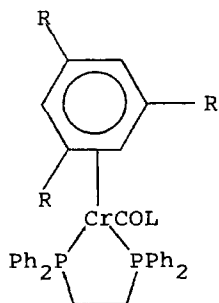
4.37

and ( $\eta$ -benzene)tricarbonylchromium has been studied in  $\text{CF}_3\text{CO}_2\text{D}$ . The replacement of a carbonyl group by maleic anhydride had little effect on the reaction properties of the  $\eta^6$ -arene ligands [53]. Protonation of the chromium complexes (4.38;  $\text{R} = \text{H}, \text{Me}$ ) in trifluoroacetic acid occurred at the chromium atom to give the cis and trans forms of the complex (4.39;  $\text{R} = \text{H}, \text{Me}$ ;  $\text{L} = \text{H}$ ). Isotopic hydrogen exchange in deuterated trifluoroacetic acid showed that the complex (4.39;  $\text{R} = \text{H}, \text{L} = \text{H}$ ) exchanged hydrogen for deuterium ten times slower than the complex (4.39;  $\text{R} = \text{Me}, \text{L} = \text{H}$ ) [54].

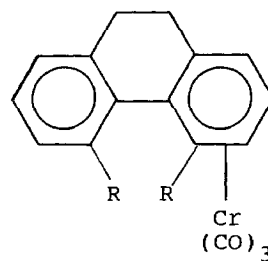
The bridged biphenyl chromium complexes (4.40, 4.41;  $\text{R} = \text{H}, \text{Me}$ ) have been prepared together with the corresponding bis(tricarbonylchromium) complexes. Exo-isomers were obtained for all four complexes together with endo-isomers in two cases. Exo-endo equilibrium was studied kinetically and the exo-isomers of the complexes (4.40, 4.41;  $\text{R} = \text{H}$ ) were resolved into enantiomers. The chiroptical properties of the complexes were discussed [55,56]. The kinetics of decomposition of the cation radicals (4.42;  $\text{R}^1 = \text{Me}, \text{R}^2 = \text{p-Me}_2\text{N}, \text{p-H}_2\text{N}, \text{p-MeO}, \text{p-COMe}$ ;  $\text{R}^1 = \text{MeO}, \text{R}^2 = \text{o-OMe}, \text{p-OMe}$ ) have been investigated. The first order rate constants for the decompositions ranged from  $3.5 \text{ s}^{-1}$  for the cation radical (4.42;  $\text{R}^1 = \text{Me}, \text{R}^2 = \text{p-NMe}_2$ ) to  $2000 \text{ s}^{-1}$  for the radical (4.42;  $\text{R}^1 = \text{Me}, \text{R}^2 = \text{p-COMe}$ ) [57]. The reversible oxidation potentials, the rate constants and the activation parameters have been determined for the formation and decomposition of the cation radicals derived from a series of (methyl-substituted benzene)-



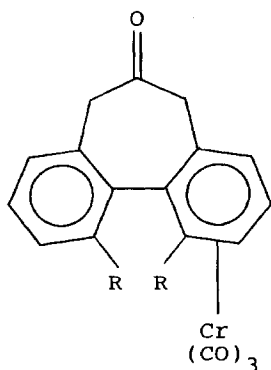
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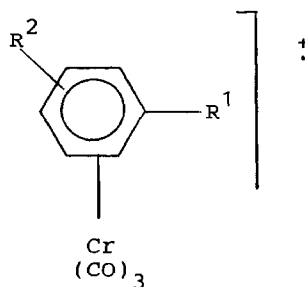
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4.41

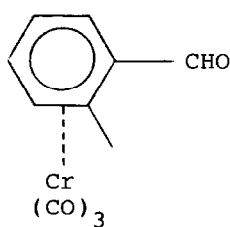


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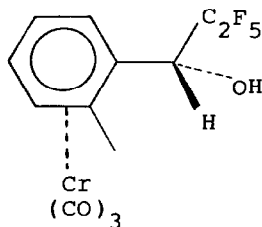
tricarbonylchromium compounds. The values obtained for the reversible potentials depended both on the number and position of the methyl substituents [58]. The effect of substituents R in the η-arene ligand of the complexes (4.3) on the rate of substitution of the fluorine atoms during the reaction with sodium methoxide in methanol has been investigated. The rate increased in the order: R = *p*-MeO < *o*-Me < *p*-Me < *m*-Me < H [59].

Traylor and co-workers have studied arene exchange reactions of (η-arene)tricarbonylchromium complexes. The uncatalysed exchange of arene for arene was first order in complex and first order in arene which indicated a displacement process. The reaction was catalysed by cyclohexanone and this process was first order in cyclohexanone and independent of arene concentration. A mechanism was proposed for these reactions that did not require the production of free tricarbonyl-

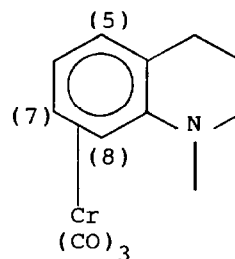




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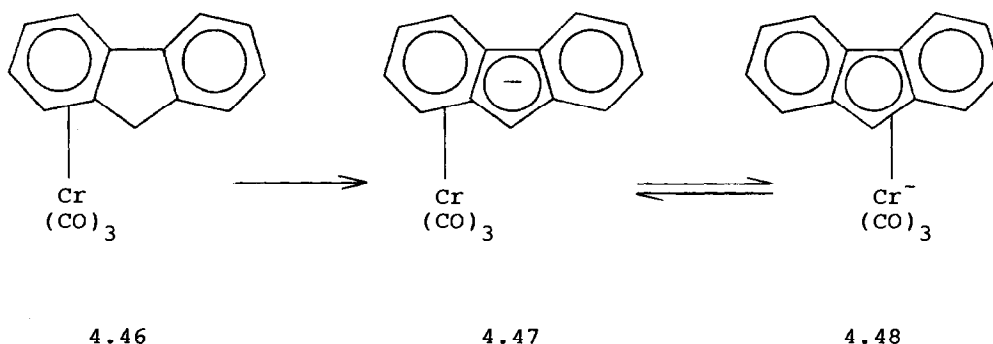


4.45

chromium [60]. Addition of perfluoroethyl lithium to the tricarbonylchromium complexes of the resolved aldehydes, for example complex (4.43), produced the corresponding alcohols (4.44) with 88% of diastereomeric excess. In a similar reaction with ethyl magnesium bromide the corresponding alcohols were obtained with 100% diastereomeric excess. These chiral alcohols were shown to be powerful inducers of chirality in Prelog-type asymmetric syntheses [61]. The resolution of torsional isomeric benzene compounds into enantiomers has been facilitated by conversion to the corresponding tricarbonylchromium complexes [62]. The regioselectivity of the reaction between 2-lithio-2-methylpropionitrile and the benchtrotrene complex (4.45) was found to be dependent on time and temperature. Reaction at  $-70^{\circ}\text{C}$  for 1 min gave the products of attack at C-5, C-7 and C-8 in the ratio 35 : 64 : 1. Reaction at the same temperature for 8.6h gave the ratio 2 : 97 : 1. Evidence was obtained to indicate that the initial addition of the carbanion was reversible [63].

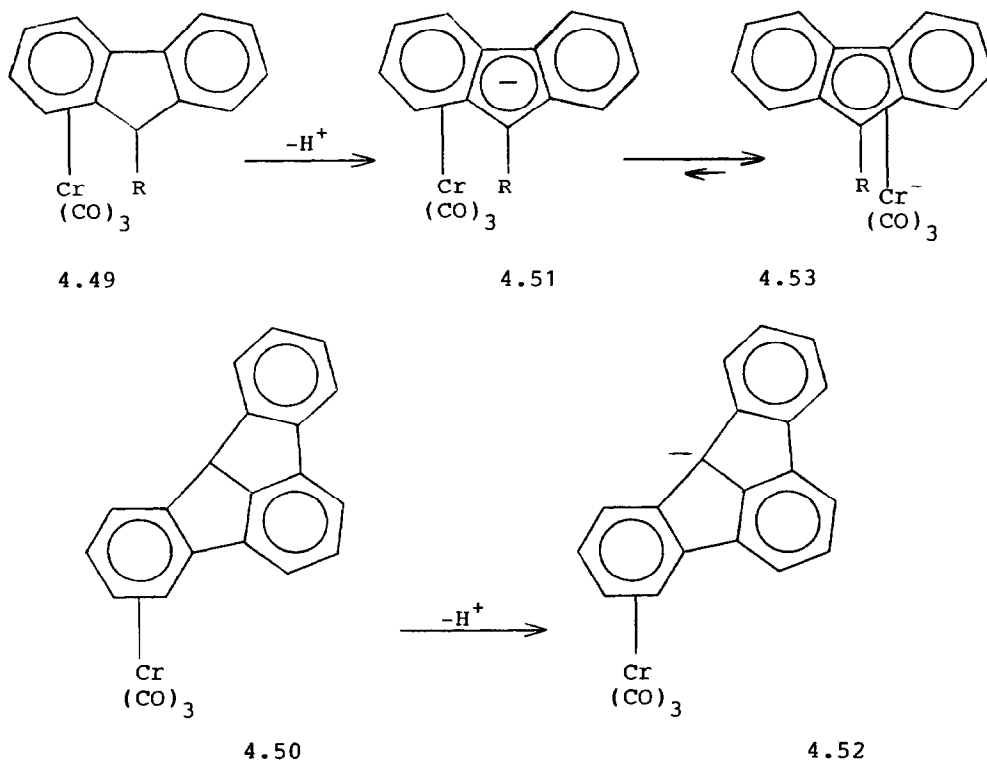
### (iii) General Chemistry

The photolysis of ( $\eta$ -benzene)tricarbonylchromium in carbon tetrachloride in the presence of  $\text{RNO}$ , where  $\text{R} = \text{CMe}_3$ , 2, 4, 6-( $\text{Me}_3\text{C}$ ) $_3\text{C}_6\text{H}_2$ , 2, 3, 5, 6- $\text{Me}_4\text{C}_6\text{H}$  and 2, 4, 6- $\text{Me}_3\text{C}_6\text{H}_2$ , has been studied by electron paramagnetic resonance [64]. Benzylic sites in ( $\eta$ -arene)chromiumtricarbonyl complexes were active to



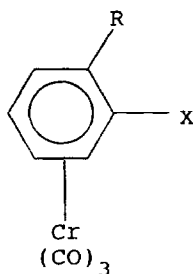
proton abstraction. The reactions were regiospecific and stereospecific and were applied to the synthesis of estradiol derivatives [65]. Deprotonation of the  $\eta^6$ -fluorene complex (4.46) with potassium in hexamethyltriimidophosphate produced an equilibrium mixture of the anions (4.47 and 4.48). Evidence for the intramolecular character of this equilibrium was provided by crossover experiments [66]. The tricarbonylchromium complexes (4.49; R = Me, t-Bu, Ph and 4.50) were deprotonated with BuOM (M = Na, K, Rb, Cs) at  $-78^\circ\text{C}$  to give the corresponding anions (4.51 and 4.52). Infrared evidence indicated that at temperatures above  $0^\circ\text{C}$  the  $\eta^6$ -benzene anions (4.51) isomerized to give the  $\eta^5$ -cyclopentadienyl forms (4.53) [67].

Lithiated benchrotrene (4.54; X = Li, R = H) underwent transmetalation with copper(I)bromide dimethyl sulphide to form the intermediate arylcopper dimethyl sulphide complex (4.54; X = CuSMe<sub>2</sub>, R = H) which underwent efficient attack by electrophiles such as MeCOCl, CH<sub>2</sub>=CHCOCl and Me<sub>2</sub>C=CHCH<sub>2</sub>Br to form the derivatives (4.54; X = COMe, COCH=CH<sub>2</sub>, CH<sub>2</sub>CH=CMe<sub>2</sub>, R = H) respectively. Substituted benchrotrenes were used to form reactive arylcopper intermediates such as the fluoro and methoxy complexes (4.54; X = CuSMe<sub>2</sub>, R = F, OMe) which underwent electrophilic substitution and palladium catalyzed cross coupling [68]. The metalation of a series of free and tricarbonylchromium complexed aromatic hydrocarbons by potassium hydride in tetrahydrofuran in the presence of

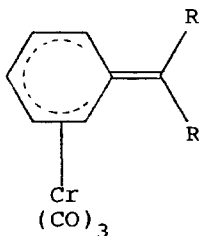


18-crown-6 ether has been carried out by following the evolution of hydrogen. The stable solutions of the complexed anions formed in the metalations were studied by  $^{13}\text{C}$  NMR spectroscopy. With the free ligands the kinetic acidity was largely structure dependent but in the corresponding tricarbonylchromium complexes the rates of metalation did not vary appreciably. The results suggested that the negative charge was situated in the phenyl-tricarbonyl moiety in which the tricarbonylchromium group was bound to the ring in a pentahapto manner (4.55) [69]. The bridged benchrotrene complex (4.56) has been reduced to the corresponding olefin (4.57) by treatment with sulphuric acid in ether at  $-10^{\circ}\text{C}$  and then sodium tetrahydroborate. Several reductions were reported [70].

Two electrochemical methods have been used to convert tricarbonyl( $\eta$ -fluorene)chromium (4.58) to the corresponding

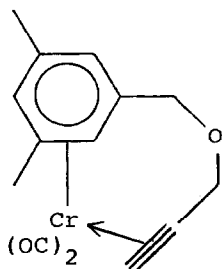


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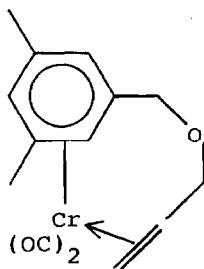


4.55

$\eta$ -fluorenone complex (4.59). The key step in these methods was the formation of the tricarbonyl( $\eta$ -fluorenyl)chromium anion which underwent further reaction with oxygen [71]. The

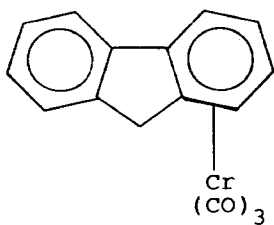


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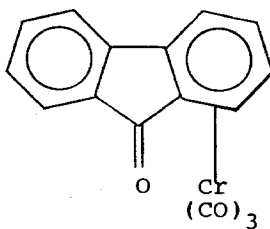


4.57

electrochemical oxidation of a series of ( $\eta^6$ -arene)tricarbonyl-chromium and -tungsten complexes has been investigated. The cation radical of tricarbonyl ( $\eta^6$ -hexaethylbenzene)chromium decayed slower than that of tricarbonyl(hexamethylbenzene)-chromium and it was suggested that steric effects were important as a means of stabilization. The presence of an alcohol group on the  $\eta$ -arene ligand destabilized the cation radical [72]. Addition of perfluoroalkyl iodides to the

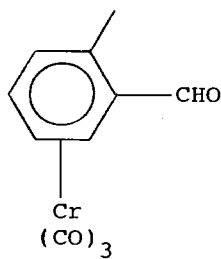


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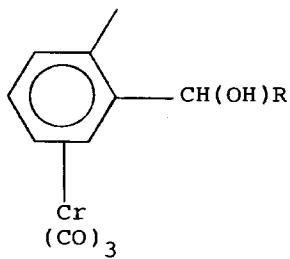


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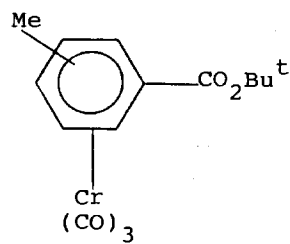
benzochromenylaldehyde (4.60) in the presence of ultrasonically dispersed zinc gave the enantiomeric benzochromenylcarbinols



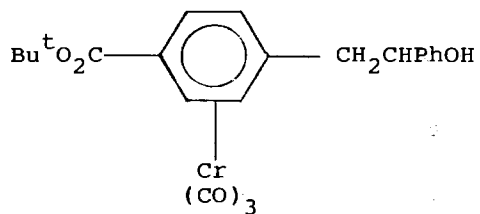
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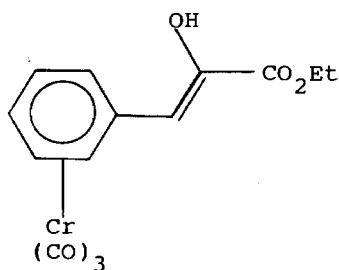
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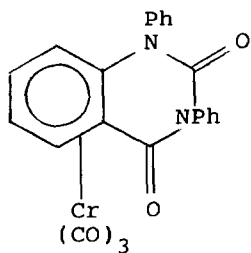


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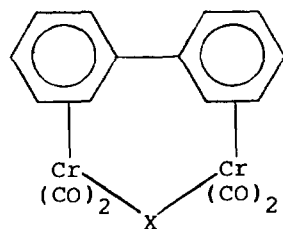
[4.61; R = C<sub>2</sub>F<sub>5</sub>, (CF<sub>3</sub>)<sub>2</sub>CF, n-C<sub>6</sub>F<sub>13</sub>] with 30-60% asymmetric induction [73]. Methyl groups in the para- and meta-positions to the CO<sub>2</sub>Bu<sup>t</sup> substituent in the benchtrorene complexes (4.62) were activated to attack by formaldehyde and benzaldehyde in the presence of Bu<sup>t</sup>OK. Thus benzaldehyde attacked the p-methyl complex to form the p-disubstituted benzene complex (4.63). When methyl groups were present in both the para- and meta-positions then attack took place exclusively on the para-methyl group [74]. Ethyl phenylpyruvate has been obtained in the enol form as the tricarbonylchromium complex (4.64) by treatment of tricarbonyl-( $\eta$ -toluene)chromium with potassium t-butoxide in the presence of ethyl oxalate in dimethyl sulphoxide [75].

Difunctional electrophilic reagents combined with tricarbonyl ( $\eta$ -1-lithio-2-trifluoromethylbenzene)chromium to form complexes of benzo-fused heterocycles. Thus phenylisocyanate gave the quinazolinone complex (4.65) in 90% yield [76]. The treatment of diphenyl with hexacarbonylchromium produced the bis(tricarbonylchromium) complex which underwent photochemical reaction with diarsines and diphosphines to give the bridged complexes [4.66; X = (Ph<sub>2</sub>P)<sub>2</sub>CH<sub>2</sub>, (Me<sub>2</sub>P)<sub>2</sub>CH<sub>2</sub>, Me<sub>2</sub>PPMe<sub>2</sub>, (Ph<sub>2</sub>As)<sub>2</sub>CH<sub>2</sub>]. The reaction of thallium phenylcyclopentadienide with bromopentacarbonylmanganese gave the tricarbonylmanganese complex (4.67) which was converted to the chromium complex (4.68) with triamminetricarbonylchromium [77]. Treatment of the ( $\eta$ -halobenzene)chromium complexes (4.69; X = F, Cl) with the alkoxides RONA, where R = Me, Et, Br, in the presence of tetrabutylammoniumbromide as the phase transfer catalyst afforded the products of nucleophilic substitution (4.69; X = OR). It was concluded that the presence of the Cr(CO)<sub>3</sub> group and the use of a phase transfer catalyst facilitated nucleophilic aromatic substitution [78]. Benzene replaced p-xylene in the complex ( $\eta$ -p-xylene)Cr(CO)<sub>3</sub> in the presence of ( $\eta$ -C<sub>6</sub>Me<sub>6</sub>)Cr(CO)<sub>3</sub> as a catalyst. The reaction was interpreted in terms of an ( $\eta$ <sup>4</sup>-p-xylene)Cr(CO)<sub>3</sub>( $\mu$ -CO)Cr(CO)<sub>2</sub>( $\eta$ -C<sub>6</sub>Me<sub>6</sub>) intermediate where a carbonyl group on ( $\eta$ -C<sub>6</sub>Me<sub>6</sub>)Cr(CO)<sub>3</sub> behaved as a nucleophilic catalyst [79].

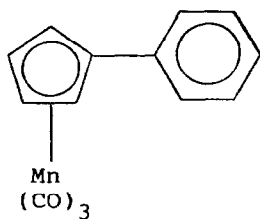
The addition of tetrachloromethane to oct-1-ene was catalysed by tricarbonyl( $\eta$ -naphthalene)chromium. Although free radical intermediates were implicated in the reaction mechanism a non-chain process was indicated by kinetic studies [80]. Tricarbonyl( $\eta$ -phenanthrene)chromium has been used as a



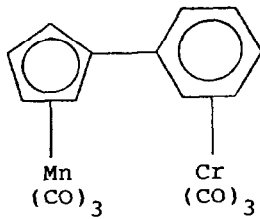
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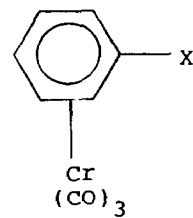
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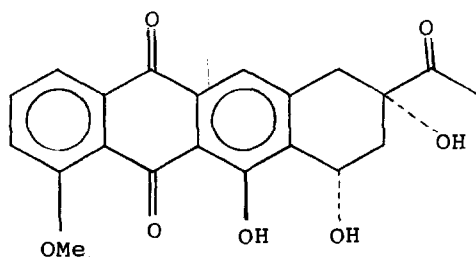


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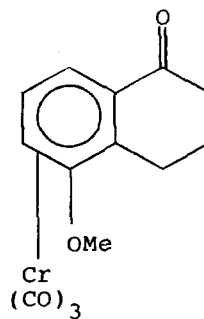


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catalyst for the hydrogenation of  $\alpha$ -terpinene and 2,3-dihydro-anisole in cyclohexane [81]. Aromatic steroids have been

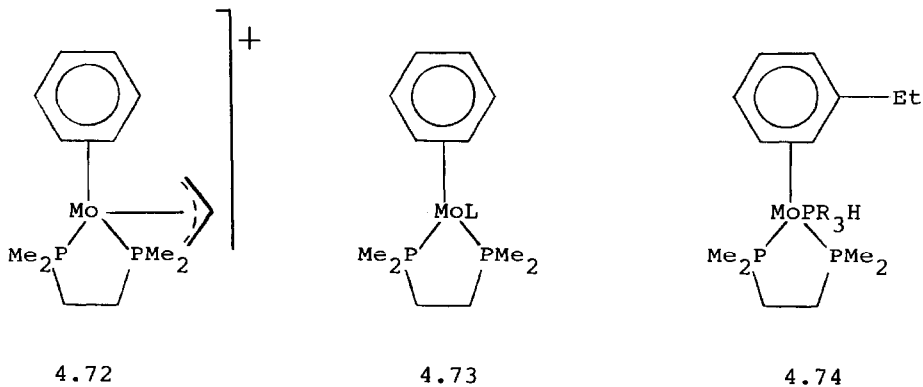


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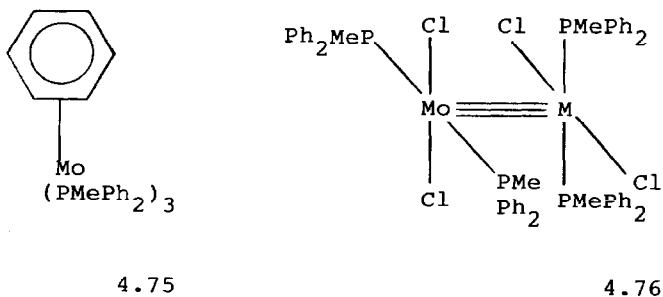


4.70

converted into tricarbonylchromium complexes in order to increase the kinetic acidity of benzylic hydrogens and thereby provide a route to 6-alkylated estradiol derivatives with specific stereochemistry [82]. Tricarbonyl(5-methoxy- $\alpha$ -tetralone)-

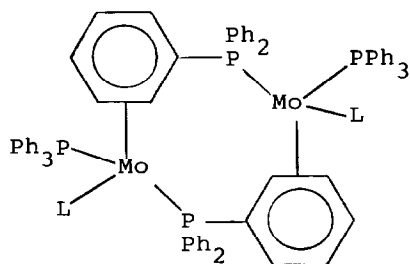


chromium (4.70) has been used as the starting material for the preparation of 11-deoxydaunomycinone (4.71) [83]. Reduction of the molybdenum complex (4.72) with sodium amalgam in the presence of an olefin afforded the corresponding  $\eta^2$ -olefin compounds (4.73; L = ethylene, propene, cyclopentene). The ethylene complex (4.73; L = ethylene) was protonated with

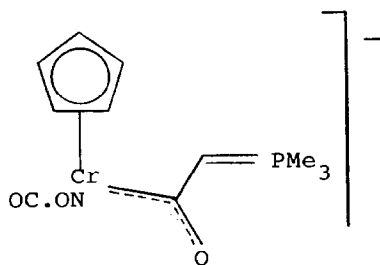




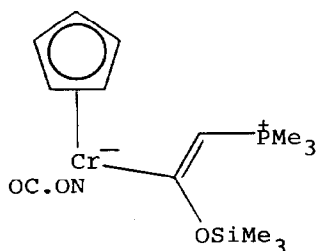
fluoroboric acid and then treated with a tertiary phosphine when it formed the corresponding  $\eta$ -ethylbenzene compounds (4.74;  $R_3 = \text{Me}_3$ ,  $\text{Me}_2\text{Ph}$ ) [84]. Reaction of the molybdenum complex (4.75) with  $\text{MoCl}_4(\text{THF})_2$  or  $\text{WCl}_4(\text{PPh}_3)_2$  produced the corresponding complexes (4.76;  $M = \text{Mo}, \text{W}$ ) which contained homonuclear quadruple Mo-Mo or Mo-W bonds [85].



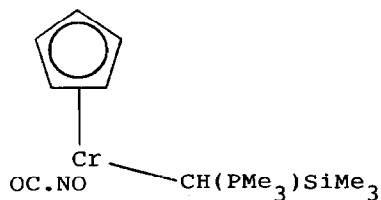
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4.78



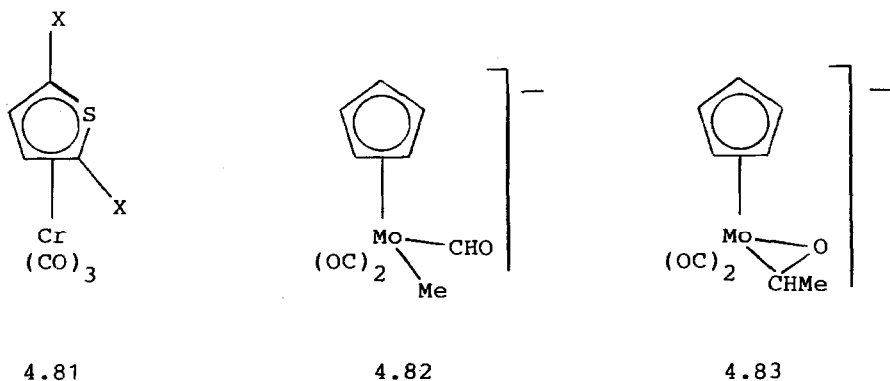
4.79



4.80

Reaction of tris(pentane-2,4-dionato)molybdenum with triphenylphosphine and triethylamine produced the dinitrogen complex (4.77;  $L = \text{N}_2$ ). The dinitrogen was removed by treatment with  $\text{RNC}$ , where  $R = \text{Bu}, \text{Me}_3\text{C}$ , to give the molybdenum complexes (4.77;  $L = \text{RNC}$ ) [86]. The zwitterionic vinylchromium complex (4.79) has been obtained from the chromium acylate (4.78) and  $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ . Carbon monoxide was lost from the complex (4.79) on photolysis to give the ylide complex (4.80) [87]. Treatment of ( $\eta$ -thiophene)chromium tricarbonyl (4.81;  $X = \text{H}$ ) with *n*-butyllithium in THF at  $-50^\circ\text{C}$

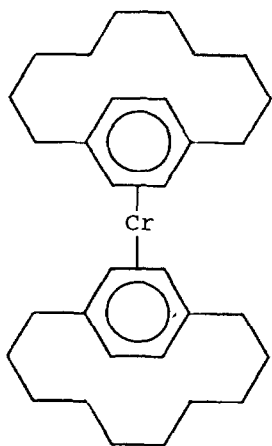
gave the dilithio intermediate (4.81; X = Li) which was converted to the dideutero and the bis(trimethylsilyl) derivatives (4.81; X = D, SiMe<sub>3</sub>) with D<sub>2</sub>O and trimethylsilylchloride respectively [88]. The reaction of (η-C<sub>5</sub>H<sub>5</sub>)MoMe(CO)<sub>3</sub> with LiEt<sub>3</sub>BH in THF afforded the anionic formyl intermediate (4.82)



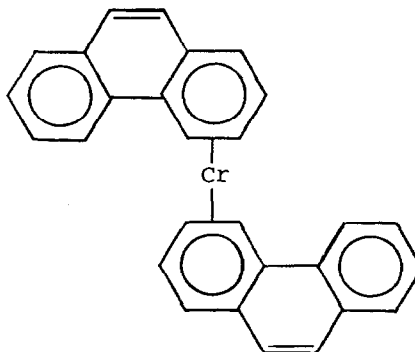
which rearranged to the anionic acetaldehyde complex (4.83). Treatment of this complex with benzylbromide liberated acetaldehyde [89].

### 5. $(\eta\text{-C}_6\text{H}_6)_2\text{Cr}$

Chromium atoms have been cocondensed with the appropriate ligand vapour at liquid nitrogen temperatures to give bis-(η-[10]paracyclophane)chromium (5.1). Coordination induced quenching of the aromatic ring current in arenes was investigated using the <sup>1</sup>H NMR spectra of this complex (5.1) which has twenty methylene groups on its periphery in well defined positions [90]. Phenanthrene vapour has been cocondensed with chromium atoms to give the bis(η-phenanthrene)chromium complex (5.2) which consisted of the rac- and meso-isomers in a 2:1 ratio. The four oxidation states 1<sup>-</sup>/0/1<sup>+</sup>/2<sup>+</sup> were characterized by cyclic voltammetry [91]. The cocondensation of anthracene vapour and chromium atoms produced the chromium complex (5.3) which was characterised as the radical cation

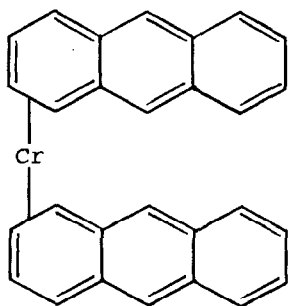


5.1

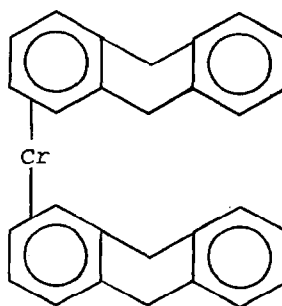


5.2

by ESR spectroscopy. In a similar reaction the cocondensation of chromium atoms with dihydroanthracene gave the chromium complex (5.4) [92]. Cocondensation of chromium vapour with the vapour of benzonitrile and one of the following ligands, toluene, anisole and acetophenone gave bis( $\eta$ -benzonitrile)-

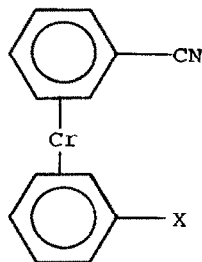


5.3

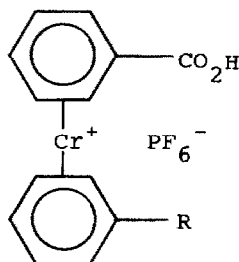


5.4

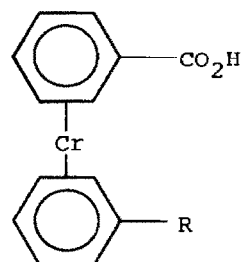
chromium and the corresponding mixed ligand complexes (5.5; X = OMe, COMe, Me). In the case of toluene, bis( $\eta$ -toluene)-chromium was also obtained [93]. The formation of molybdenum complexes by the cocondensation of molybdenum



5.5



5.6



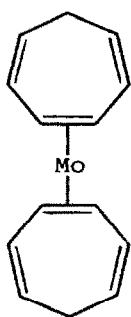
5.7

atoms with ligand vapour at low temperatures has been discussed in detail. Bis( $\eta$ -arene)molybdenum complexes were among the compounds prepared [94].

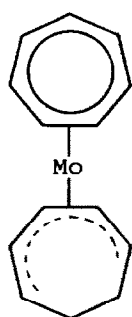
Reaction of di( $\eta$ -benzene)chromium with lamellar  $\text{FePS}_3$  in toluene at  $150^\circ\text{C}$  resulted in all the chromium compound being taken up provided the  $(\eta\text{-C}_6\text{H}_6)_2\text{Cr}:\text{FePS}_3$  ratio was kept below two. A series of semiconducting  $\text{FePS}_3\text{Cr}_x\text{C}_y$  materials ( $0.5 \leq x \leq 2$ ,  $x \simeq 2$ ) was prepared where the Cr(III) was bound to the sulphur atoms [95]. Pulsed gas chromatography has been used to study the kinetics of the gas phase thermal decomposition of ( $\eta$ -diethylbenzene)( $\eta$ -ethylbenzene)chromium and some substituted ferrocenes [96]. Pyrolysis of bis( $\eta$ -ethylbenzene)-chromium and bis( $\eta$ -isopropylbenzene)chromium gave chromium films containing hydrogen, carbon dioxide,  $\text{C}_1\text{-C}_3$  hydrocarbons, benzene and toluene [97]. The  $\text{pK}_a$  values of the carboxylic acids (5.6; R = H, alkoxy, Me, Cl,  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{Me}$ ,  $\text{CO}_2\text{Na}$ ,  $\text{CF}_3$ ) and (5.7; R = H, MeO,  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{Me}$ ,  $\text{CO}_2\text{Na}$ , Cl,  $\text{CF}_3$ ) have been determined and correlated with substituent constants. The best correlations for the cations (5.6) were obtained with the Swain-Lupton substituent parameters and with  $\sigma_{\text{R}}$  and  $\sigma_{\text{R}^+}$  constants. The values for the acids (5.7) correlated with the  $\sigma_{\text{R}^0}$  constants [98].



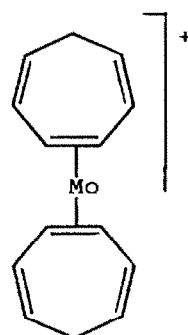
structures of the Ti, V and Cr complexes have been determined by X-ray crystallography [101]. Cocondensation of molybdenum atoms with cycloheptatriene produced initially the unstable compound (6.1) which isomerized quantitatively to the complex (6.2). In a similar reaction the cation (6.3) isomerized to the complex (6.4). It was proposed that these reactions proceeded via intramolecular hydrogen migration [102]. The ( $\eta$ -dimethylheptafulvene)chromium complex (6.5) has been attacked by 6-substituted pentafulvenes under photochemical conditions with displacement of a carbonyl group and formation of several ( $\eta$ -cyclopentadienyl)chromium complexes [103].



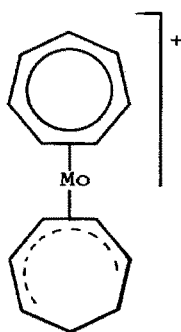
6.1



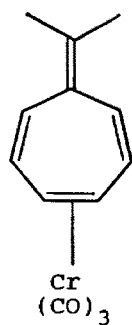
6.2



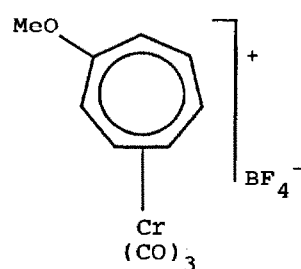
6.3



6.4



6.5



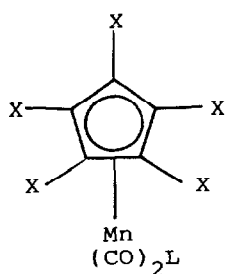
6.6

Brown and co-workers have described a method for computing the most favourable initial attacking site for a nucleophile on a transition metal complex. The method was applied to attack by methoxide ion on  $[(\eta^7\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3]^+$  cations, where M = Cr, Mo or W. Initial attack at the metal atom was predicted for the molybdenum and tungsten complexes and the results of extended Hückel calculations correlated well with the isolation of exo-ring addition products [104]. The same workers provided spectroscopic evidence for low temperature intermediates involving initial metal attack and carbonyl attack in the reaction of methoxide ion with  $[(\eta^7\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3]\text{BF}_4$  complexes, where M = Mo or W. No detectable intermediates were observed with the chromium analogue and only formation of the 7-exo ring product was found [105]. The structure of the  $\eta$ -methoxytropylium salt (6.6) has been determined by X-ray analysis. The seven membered ring was approximately planar and symmetrically bonded to the  $\text{Cr}(\text{CO})_3$  group. The C(1)-O(Me) bond distance was intermediate between the usual single and double bond values [106]. Dynamic  $^{13}\text{C}$  NMR spectroscopy has been used to determine rotational barriers in a series of 7-substituted- and 1-6-bridged- $(\eta\text{-cycloheptatriene})\text{chromiumtricarbonyl}$  complexes. Good agreement was obtained with previous theoretical predictions [107].

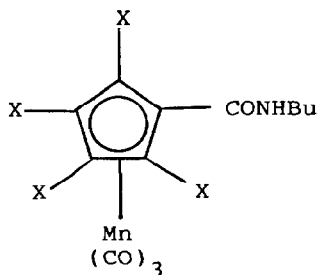
## 7. $(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$

### (i) Formation

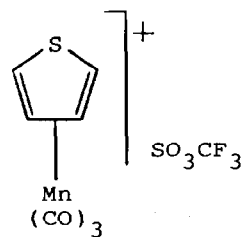
Bromopentacarbonylmanganese has been attacked by pentakis-(carbomethoxy)cyclopentadienide to form the pentasubstituted cymantrene (7.1; X =  $\text{CO}_2\text{Me}$ ; L = CO). This complex underwent reduction with lithium tetrahydroaluminate to give pentamethylcymantrene (7.1; X = Me; L = CO) and photochemical substitution with phosphines to give the derivatives [7.1; X =  $\text{CO}_2\text{Me}$ , L =  $\text{PPh}_3$ ,  $\text{PEt}_3$ ,  $\text{P}(\text{OEt})_3$ ]. One carbomethoxy group in the complex (7.1) was attacked by n-butylamine to afford the amide (7.2; X =  $\text{CO}_2\text{Me}$ ) [108]. Thiophene has been heated with  $\text{Mn}(\text{CO})_5\text{-OSO}_2\text{CF}_3$  to give the  $(\eta\text{-thiophene})\text{manganese}$  complex (7.3). Nucleophiles such as  $\text{CN}^-$  and  $\text{BH}_4^-$  attacked the complex (7.3) to form the neutral products (7.4; X = CN, H). The crystal and molecular structure of the nitrile (7.4; X = CN) has been



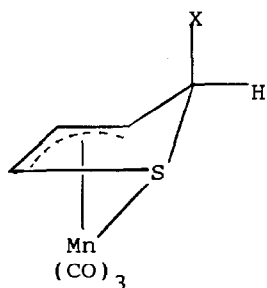
7.1



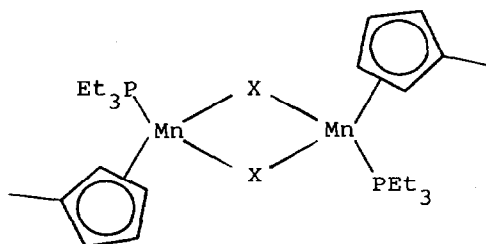
7.2



7.3



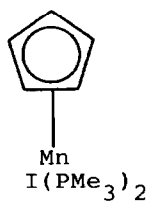
7.4



7.5

determined by X-ray crystallography [109]. The reaction of bis( $\eta$ -methylcyclopentadienyl)manganese with manganese(II) chloride, iodide or bromide in tetrahydrofuran produced the dimers  $[(\eta\text{-C}_5\text{H}_4\text{Me})\text{MnX}(\text{THF})]_2$ . Treatment of these dimers with triethylphosphine afforded the corresponding halo-bridged dimers (7.5; X = Cl, Br, I). The monomer (7.6) was produced from the dimer, when X = I, on reaction with trimethylphosphine [110]. Treatment of the  $\eta^5$ -pentadienyl complex (7.7) with strongly basic phosphines gave the corresponding  $\eta^3$ -allyl complexes (7.8; L =  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PBu}_3$ ). The structure of the complex (7.8; L =  $\text{PMe}_3$ ) was determined by X-ray analysis. It had an octahedral facial configuration with the  $\eta^3$ -allyl group bound unsymmetrically to the metal. Reaction of the complex (7.7) with the phosphines and phosphites L, where L =  $\text{PPh}_3$ ,  $\text{P}(\text{cyclohexyl})_3$ ,  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OEt})_3$ ,  $\text{P}(\text{OPh})_3$

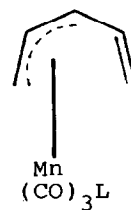




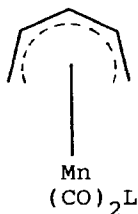
7.6



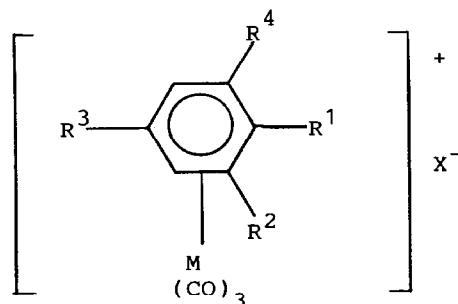
7.7



7.8

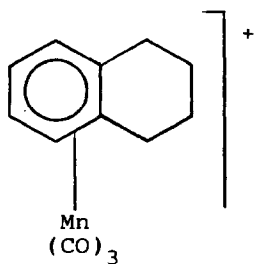


7.9

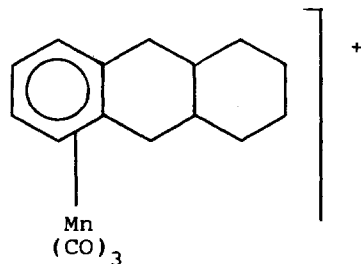


7.10

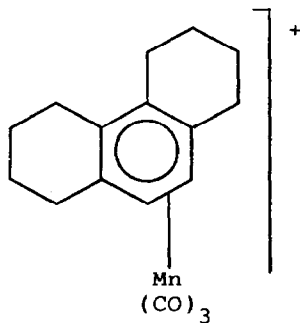
in cyclohexane gave the carbonyl substitution products (7.9) [111]. Treatment of  $\text{XM}(\text{CO})_5$ , where  $\text{X} = \text{Cl}, \text{Br}$  and  $\text{M} = \text{Mn}, \text{Re}$ , with an arene in trifluoroacetic acid followed by  $\text{NaBH}_4$ ,  $\text{NH}_4\text{PF}_6$  or  $\text{HBF}_4$  produced the corresponding  $\eta$ -arene complexes [7.10;  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$ ;  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Me}$ ,  $\text{R}^4 = (\text{CH}_2)_3\text{CO}_2\text{H}$  or  $(\text{CH}_2)_3\text{CO}_2\text{CF}_3$ ;  $\text{X} = \text{PF}_6, \text{BPh}_4, \text{BF}_4$ ] [112]. Reaction of bromopentacarbonylmanganese with naphthalene or anthracene in the presence of aluminium chloride afforded the complex cations (7.11 and 7.12) respectively. The complex (7.11) was obtained as the major product together with the  $\eta^6$ -octahydrophenanthrene complex (7.13) by treating  $\text{Mn}(\text{CO})_5\text{Br}$  with tetralin in the presence of aluminium chloride. Addition of methyl lithium to the cation (7.13) produced the complex (7.14) [113].



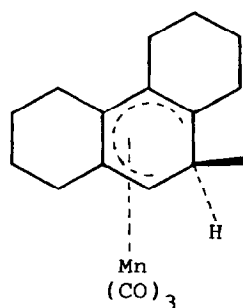
7.11



7.12



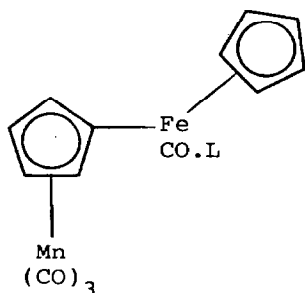
7.13



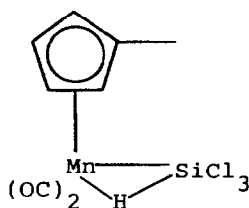
7.14

### (ii) Spectroscopic and Physico-chemical Studies

The cymantrene derivatives (7.15;  $L = \text{CO}, \text{PPh}_3$ ) have been characterized by X-ray crystallography. The  $\text{C}_5\text{H}_4$  moiety was an  $\eta^5$ -ligand for manganese and an  $\eta^1$ -ligand for iron [114]. The crystal and molecular structures of the two trichlorosilyl complexes (7.16 and 7.17) have been determined by X-ray crystallography. The Mn-Si bond was longer in the hydrido complex (7.16) than in (7.17) while the trichlorosilyl ligand was tilted relative to the Mn-Si vector in the complex (7.16) as a result of Mn-H-Si three-centre two-electron bonding [115]. The low-frequency IR ( $20\text{--}200\text{ cm}^{-1}$ ) and Raman spectra ( $5\text{--}200\text{ cm}^{-1}$ ) of cymantrene, cymantrene- $d_5$  and tricarbonyl( $\eta$ -cyclopentadienyl)-rhenium have been measured in the temperature range  $5\text{--}300\text{ K}$ . The low-frequency modes have been completely assigned and the temperature dependence discussed [116].

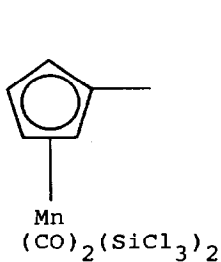


7.15

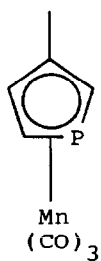


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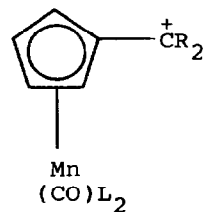
The  $^1\text{H}$  NMR spectrum of 3-methylphosphacyclopentadiene (7.18) in a nematic solvent, *N*-(*p*'-ethoxybenzylidene)-*p*-*n*-butylaniline, has been recorded and interpreted. The preferred conformation of the molecule appeared to be one where a C-H bond of the methyl group was perpendicular to the ring plane [117]. The  $^1\text{H}$  NMR



7.17



7.18



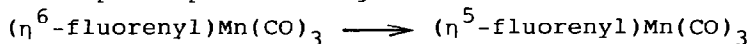
7.19

spectra of cyclopentadiene and tricarbonyl( $\eta$ -cyclopentadienyl)rhenium have been measured as oriented solutions in two different nematic liquid crystal solvents. The direct dipole coupling constants showed anomalous ratios. These ratios were temperature dependent in the solvents in which the complexes were parallel to the liquid crystal axis [118]. Protonation of the

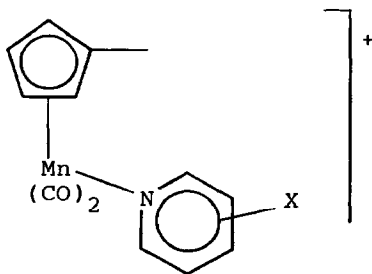
$\alpha,\beta$ -unsaturated carbonyl compounds  $R^1CH=CHCOR^2$ , where  $R^1$  = ferrocenyl, phenyl, cymantrenyl,  $R^2$  = methyl, phenyl, ferrocenyl, cymantrenyl, in trifluoroacetic acid has been studied via NMR spectroscopy [119]. The  $^{31}P$  NMR spectra of the carbenium ions [7.19,  $R = Me, Et, Ph$ ;  $L_2 = Ph_2P(CH_2)_n PPh_2$ ,  $n = 2, 3$ ;  $L = P(OMe)_3, P(OEt)_3$ ] have been recorded [120].

The gas-phase reactions of substituted cymantrenes with crown ethers (L) under electron impact have been studied. The complex cations  $[(\eta-XC_5H_4)MnL]^+$  were formed, where  $X = H, CN, CHO, COR, CH_2Ph, CO_2H, CH_2OH, CH_2NMe_2, CH(OH)R$ , and two mechanistic routes were implicated (i) by the addition of  $[(\eta-XC_5H_4)Mn]^+$  to the crown ether; (ii) by the exchange of carbonyl ligands in  $[(\eta-XC_5H_4)Mn(CO)_x]^+$  for the crown ether [121]. Steric and electronic effects in the nucleophilic substitution of the pyridine ligand in the cations (7.20;  $X = 3-F, 3-Cl, 4-Me, 4-MeO, 4-MeCO, 4-NO_2$ ) with a number of phosphines, has been the subject of a kinetic study. A unified free energy relationship was shown to accommodate all the rate data. The dependence of the initial rate constant on both steric and electronic effects in the pyridine ligand and in the phosphine nucleophile suggested an associative  $S_N2$  mechanism for the reaction [122].

The haptotropic rearrangement:



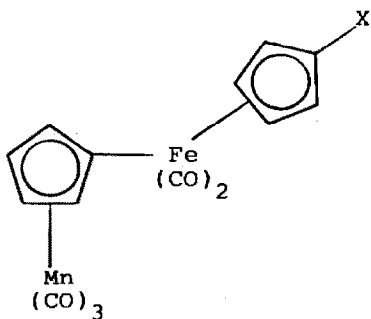
has been the subject of a kinetic investigation. Rate constants



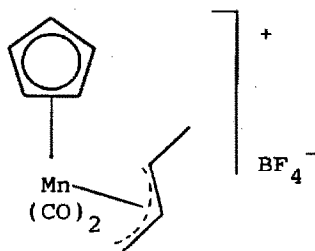
and activation energies were measured for the parent complex,  $(\eta^6\text{-fluorenyl})\text{Mn}(\text{CO})_3$ , and for the corresponding complexes with either a *t*-butyl substituent on the fluorenyl ligand or a tributylphosphine group bound to manganese. The three rearrangements gave  $\Delta H^\ddagger = 24\text{-}25 \text{ kcal mol}^{-1}$  in each case and the mechanism was considered to be intramolecular and involved an  $\eta^3$ -intermediate [123]. The manganese complexes  $(\eta^5\text{-C}_9\text{H}_7)\text{-Mn}(\text{CO})_3$  and  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$  underwent nucleophilic substitution with phosphines and phosphites in decalin. The reactions were first-order in metal complex and first-order in nucleophile while the reaction rates were sensitive to both the size and the basicity of the nucleophile. Monosubstitution products were usually obtained although disubstitution was observed with  $(\eta^5\text{-C}_{13}\text{H}_9)\text{Mn}(\text{CO})_3$  and tributylphosphine. These results contrasted with the inertness of cymantrene to thermal substitution and were interpreted in terms of differences between the indenyl and fluorenyl ligand vs. the cyclopentadienyl ligand [124]. The acidic vs. hydridic character of organometallic hydrides,  $(\eta^5\text{-C}_5\text{H}_5)\text{ML}_n\text{H}$ , including  $(\eta\text{-C}_5\text{H}_5)\text{MnCOQOH}$  has been examined using Fenske-Hall molecular orbital calculations [125].

### (iii) General Chemistry

Kursanov et al. have reviewed the chemistry of azacymantrene [126]. The cymantrenyl complex (7.21; X = H) was metallated by *n*-butyllithium at  $-78^\circ\text{C}$  to form the lithio inter-

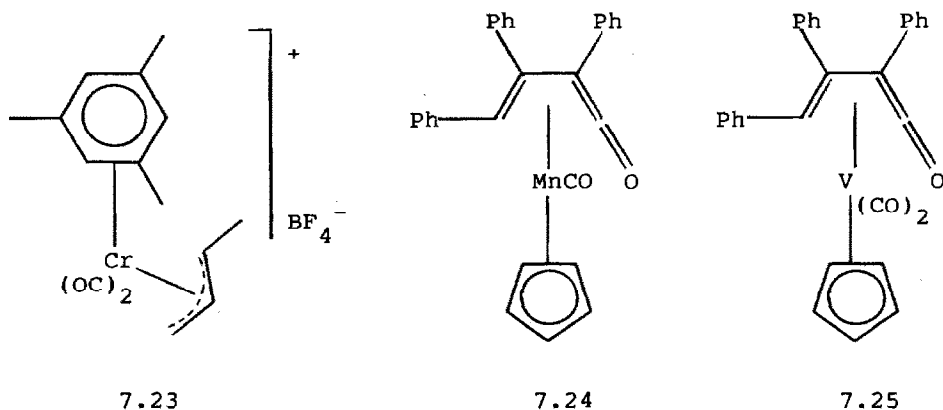


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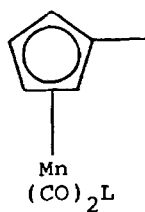
7.22

mediate (7.21; X = Li) which was converted to the carboxylic acid (7.21; X = CO<sub>2</sub>H) with carbon dioxide [127]. The vacuum pyrolysis of cymantrene at 380-400°C produced dicyclopentadiene, manganese and carbon monoxide [128]. Cymantrene has been irradiated with butadiene, methylbutadienes and cyclopentadiene in the presence of fluoroboric acid to form cationic allyl complexes such as the derivative (7.22). Tricarbonyl(1,3,5-trimethylbenzene)chromium underwent an analogous reaction to give products such as the complex (7.23) [129]. UV irradiation

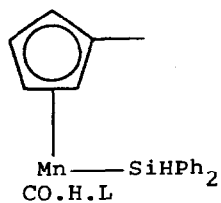


of acetylene with an ( $\eta$ -methylvinylcyclopentadienyl)manganese-tricarbonyl-styrene copolymer membrane gave a polymer-bound  $\eta^2$ -acetylene complex [130]. Irradiation of cymantrene with phenylacetylene followed by addition of hexamethylenetetramine produced dicarbonyl( $\eta$ -cyclopentadienyl)phenylvinylidenemanganese [131].

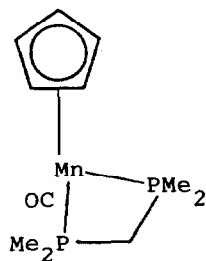
The reaction of cymantrene and tetracarbonyl( $\eta$ -cyclopentadienyl)vanadium with 1,2,3-triphenylcyclopropene produced the  $\eta^4$ -vinylketene complexes (7.24 and 7.25) respectively. Similar reactions were carried out with dicarbonyl( $\eta$ -cyclopentadienyl)cobalt and cobalt carbonyl [132]. Photochemical reaction of the manganese complexes [7.26; L = CO, P(OPh)<sub>3</sub>, P(OEt)<sub>3</sub>, PPh<sub>3</sub>, PBu<sub>3</sub>, PMe<sub>3</sub>] with diphenylsilane produced the chiral complexes (7.27). This reaction was controlled by steric, rather than electronic effects [133]. A number of



7.26

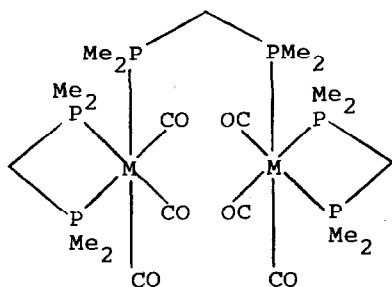


7.27

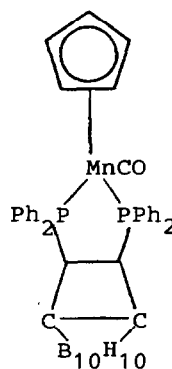


7.28

metal carbonyl complexes of the highly basic bidentate ligand bis(dimethylphosphino)methane have been prepared. Ultraviolet irradiation of cymantrene with this ligand produced the pyrophoric complex (7.28). The treatment of tricarbonyl( $\eta$ -cycloheptatriene)-chromium, -molybdenum or -tungsten with



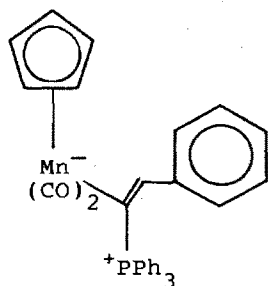
7.29



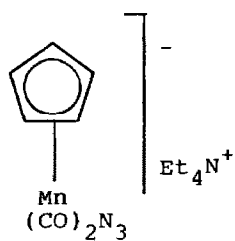
7.30

bis(dimethylphosphino)methane gave the corresponding binuclear complexes (7.29; M = Cr, Mo, W) [134].

A series of complexes of cymantrene with bidentate  $\sigma$ -carborane phosphine and arsine ligands has been prepared. For example, the photolysis of cymantrene with 1,2-bis(diphenyl-

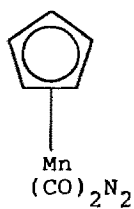


7.31

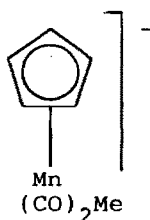


7.32

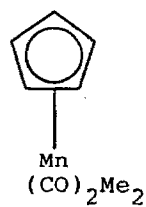
phosphino)-*o*-carborane produced the complex (7.30) [135].  
Kolobova and co-workers have studied phosphine group substitution



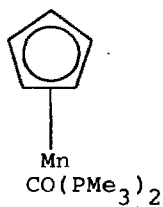
7.33



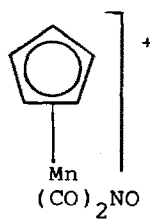
7.34



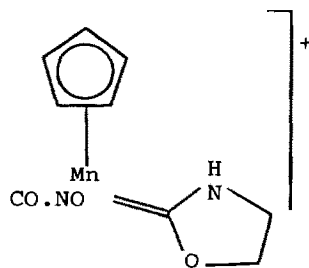
7.35



7.36



7.37

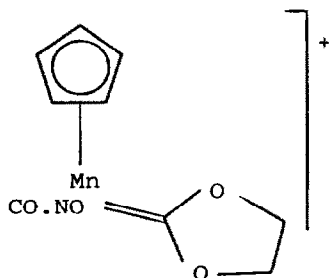


7.38

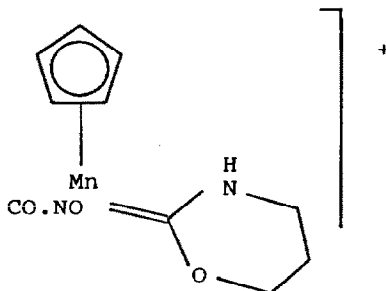


in the vinylphosphonium complex (7.31) [136]. The reaction of the cymantrene complex  $[(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{acetone}]$  with tetraethylammonium azide produced the salt (7.32) [137]. The manganese-nitrogen complex (7.33) has been attacked by methyllithium in THF at  $-20^\circ$  to  $+10^\circ\text{C}$  to form the anionic methyl derivative (7.34) which was alkylated with  $(\text{Me}_3\text{O})\text{BF}_4$  to give the thermolabile dimethyl complex (7.35). This complex (7.35) combined with trimethylphosphine to form acetone and the phosphine derivative (7.36) [138].

The 3-membered heterocycles aziridine and oxirane combined with a carbonyl group of the cation (7.37) in the presence of halide ion to form the corresponding 5-membered cyclic derivatives (7.38 and 7.39). Reaction of the cation (7.37) with  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{NH}_3\text{Br}^-$  and oxirane in the presence of bromide ion afforded the 6-membered aminooxycarbene complex (7.40) [139].

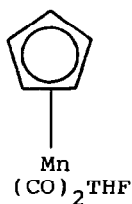


7.39

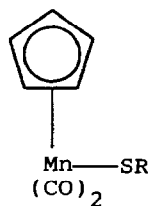


7.40

The THF complex (7.41) has been treated with mercaptans,  $\text{RSH}$ , to give the sulphides (7.42;  $\text{R} = \text{CMe}_3$ , 2-adamantyl). The crystal and molecular structure of one of these complexes (7.42;  $\text{R} = \text{CMe}_3$ ) has been determined by X-ray methods. The paramagnetic complexes (7.42) underwent reversible, one-electron reduction to the corresponding anion in acetonitrile [140]. The oxidative addition of (+)-1-naphthylSiHMePh to methylcymantrene to give the hydride (7.43) occurred with retention of configuration at the silicon atom. The germanium compound (7.44)

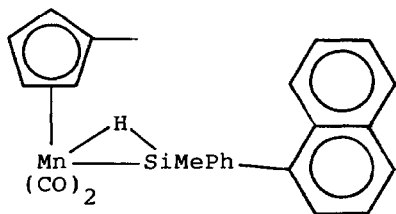


7.41

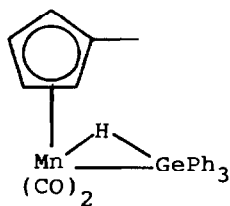


7.42

was prepared similarly and both these compounds underwent easy elimination of 1-naphthylSiHMePh or Ph<sub>3</sub>GeH when treated with triphenylphosphine. It was concluded that there was a 2-electron 3-centre bond between Mn, Si or Ge and H [141].



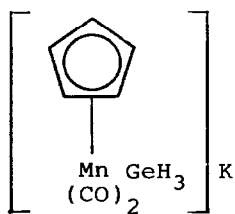
7.43



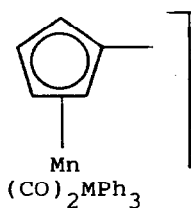
7.44

The reaction of cymantrene with KGeH<sub>3</sub> produced the germyl-substituted complex (7.45) [142].

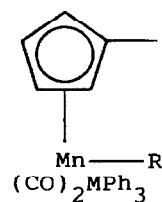
The cymantrenyl anions (7.46; M = Si, Ge), obtained by treatment of the corresponding neutral complexes with sodium hydride, combined with alkyl halides to form the neutral complexes (7.47; M = Si, Ge; R = Me, Et, CH<sub>2</sub>Ph, CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>). These complexes underwent deinsertion with triphenylphosphine to give the phosphine (7.48) together with the product of alkyl migration (7.49; R = Me, Et) [143]. Double hydride



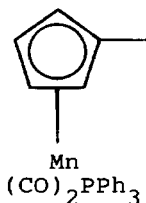
7.45



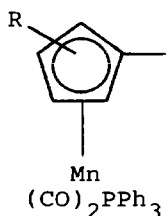
7.46



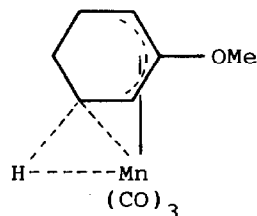
7.47



7.48

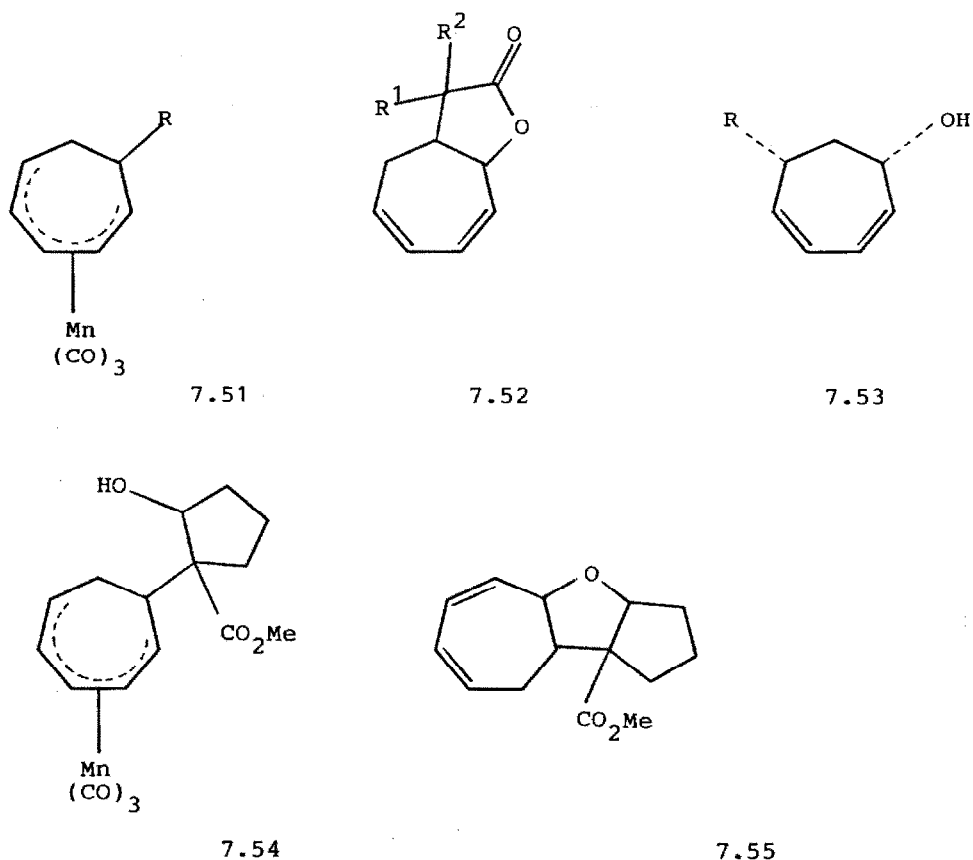


7.49



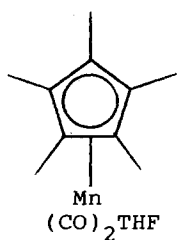
7.50

reduction of the cations  $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3]^+$  where arene = *o*-xylene, biphenyl and anisole, with excess potassium triisopropoxyborohydride followed by protonation gave the corresponding Mn-H-C bridged  $(\eta\text{-cyclohexenyl})\text{Mn}(\text{CO})_3$  compounds, for example complex (7.50). Treatment of these compounds with potassium hydride gave the corresponding substituted anions,  $[(\eta^4\text{-cyclohexadiene})\text{Mn}(\text{CO})_3]^-$ , which on oxidative cleavage gave the free substituted cyclohexa-1,3-dienes [144]. Alkylation of the tricarbonyl $(\eta\text{-cycloheptatriene})$ manganese cation with sodium enolate gave the manganese complexes [7.51;  $\text{R} = \text{CH}(\text{CO}_2\text{Me})_2$ ,  $\text{CMe}(\text{CO}_2\text{Me})_2$ ,  $\text{CH}(\text{SO}_2\text{Ph})\text{CO}_2\text{Me}$ ] which were subsequently demetallated with cerium(IV) to form the lactones (7.52;  $\text{R}^1 = \text{H}, \text{Me}$ ;  $\text{R}^2 = \text{CO}_2\text{Me}, \text{SO}_2\text{Ph}$ ) and the *cis*-hydroxy diesters [7.53;  $\text{R} = \text{CH}(\text{CO}_2\text{Me})_2$ ,  $\text{CMe}(\text{CO}_2\text{Me})_2$ ,  $\text{CH}(\text{SO}_2\text{Ph})\text{CO}_2\text{Me}$ ]. The  $(\eta\text{-cyclopentyl-cycloheptadienyl})$ manganese complex (7.54) was formed in the same way and demetallated to give the tricyclic compound (7.55) [145].

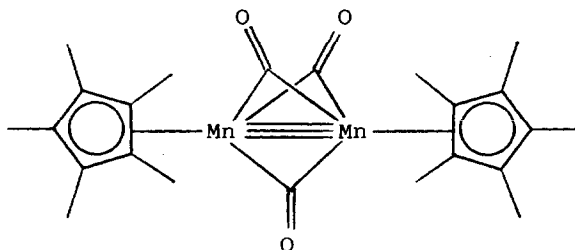


### 8. Polynuclear ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mn(CO)<sub>3</sub> Complexes

The THF complex (8.1), formed by photolysis of the parent complex in THF, was stable at temperatures below 0°C but underwent loss of carbon monoxide at room temperatures to form the dinuclear complex (8.2) with an Mn-Mn triple bond. The structure of this complex was confirmed by X-ray crystallography [146]. Treatment of tricarbonyl( $\eta$ -lithiocyclopentadienyl)-manganese and -rhenium with cadmium iodide produced a mixture of the monomer (8.3; M = Mn, Re) and the dimer (8.4; M = Mn, Re) which existed as a mixture of cis- and trans-isomers [147]. Dicymantrenylmercury has been treated with ytterbium in THF to form dicymantrenylytterbium (8.5). A similar reaction with cymantrenyliodide gave cymantrenylytterbium iodide [148]. Reaction of bis(cymantrenyl)mercury with samarium, europium or



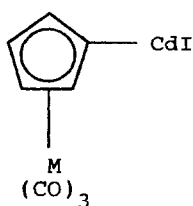
8.1



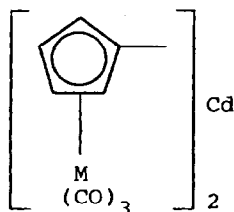
8.2

ytterbium in tetrahydrofuran produced the corresponding lanthanide derivative  $[(\eta\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3]_2\text{M}(\text{THF})_n$  where  $\text{M} = \text{Sm}$ ,  $\text{Eu}$  or  $\text{Yb}$  and  $n = 0, 1$ . Similar products were obtained for bis(ferrocenyl)mercury [149].

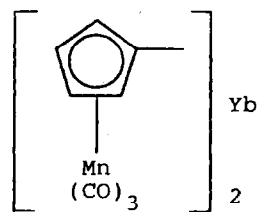
The crystal and molecular structure of the mixed cymantrene-ferrocene complex (8.6) has been determined by X-ray crystallography. The iron and manganese atoms were found to be on the same side of the  $\text{SiCH}=\text{CHC}$  plane [150]. The pyrazine derivatives (8.7;  $\text{R}^1 = \text{R}^2 = \text{H}, \text{Me}$ ;  $\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}$ ) have been prepared by reaction of the appropriate  $(\eta\text{-cyclopentadienyl})\text{dicarbonyl-tetrahydrofuranmanganese}$  complex with pyrazine. These complexes



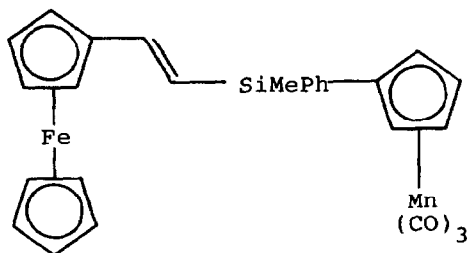
8.3



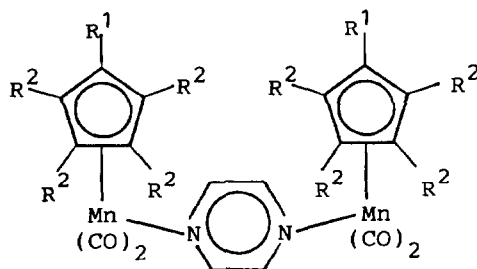
8.4



8.5



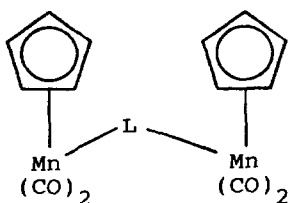
8.6



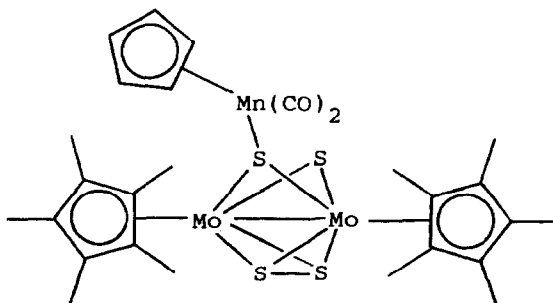
8.7

were studied electrochemically and via ESR spectroscopy. The results indicated that there was considerable  $\pi$ -back bonding between the manganese and the pyrazine ligand [151]. Reaction of  $(\eta\text{-MeC}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{THF}$  with the bidentate ligands L, where L = 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethylene and 1,2-bis(4-pyridyl)ethane, produced the corresponding binuclear derivatives (8.8) [152].

The complex  $(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{THF}$  has been treated with  $(\eta\text{-C}_5\text{Me}_5)_2\text{Mo}_2\text{S}_4$  to give the trinuclear complex (8.9). However treatment with  $(\eta\text{-C}_5\text{Me}_5)_2\text{Cr}_2\text{S}_5$  did not give mixed chromium-

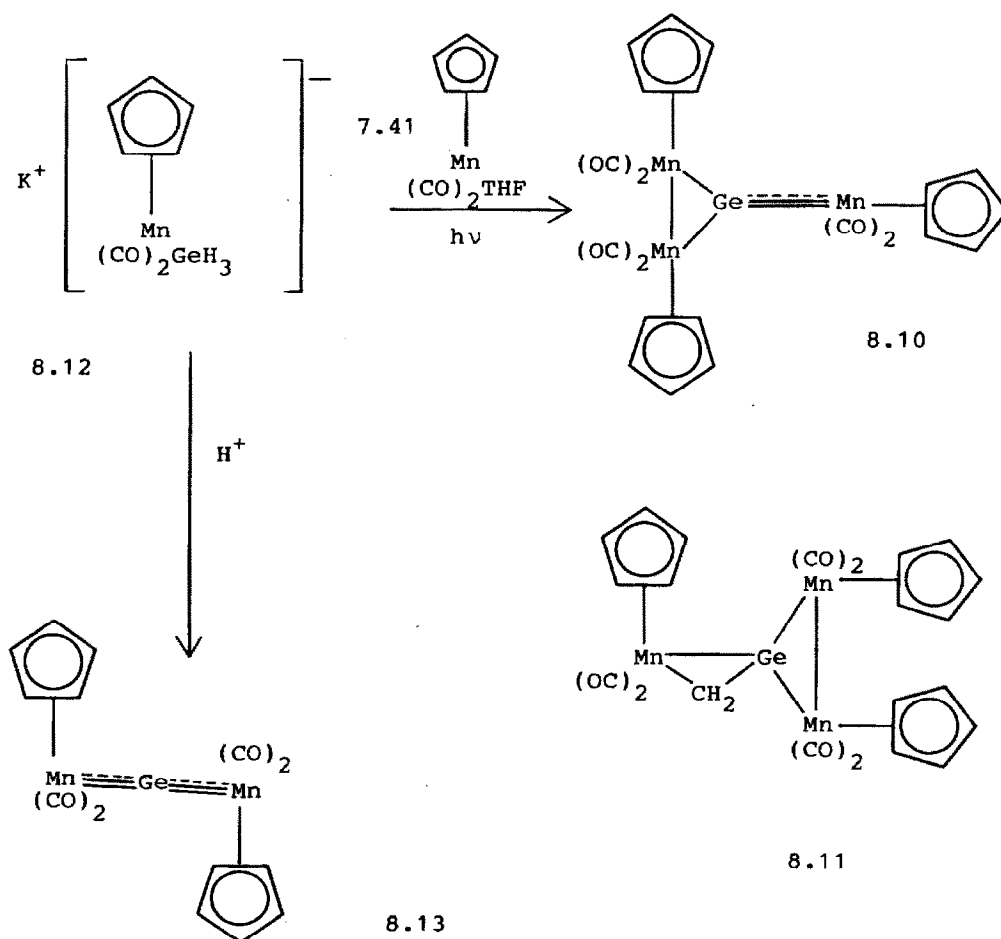


8.8



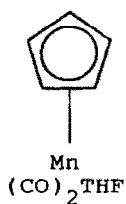
8.9

-manganese complexes [153]. The cymantrene complex (7.41) has been treated with germanium hydride in THF to form the tetranuclear complex (8.10) in 70% yield. Diazomethane combined with this product to give the adduct (8.11) which was a fluxional molecule [154]. The anionic germanium hydride complex (8.12) was attacked by acid to form the red dimanganese germanium complex (8.13) with a linear Mn-Ge-Mn arrangement. Photolysis of this product (8.13) with the THF complex (7.41) afforded the trimanganese germanium complex (8.10) which contained both Ge-Mn multiple and single bonds and which was characterized by X-ray crystallography [155].

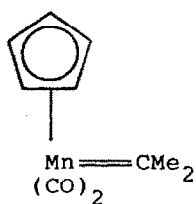


### 9. Carbene and Carbyne ( $\eta\text{-C}_5\text{H}_5$ )Mn(CO)<sub>3</sub> Complexes

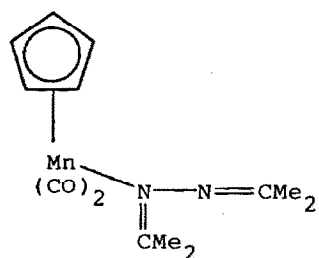
Diazopropane attacked the cymantrene complex (7.41) at 0°C to form the dimethylcarbene (9.1) and acetone azine (9.2) complexes. The crystal and molecular structure of this complex (9.2) was confirmed by X-ray crystallography. The N-N bond length, 2.063Å, was longer than the corresponding bond in analogous complexes [156]. The chromium complex (9.3) has been prepared and the structure of this compound has been compared with that of the isoelectronic manganese complex (9.4). In



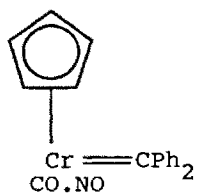
7.41



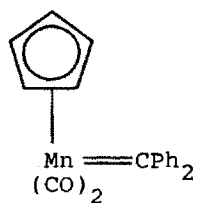
9.1



9.2



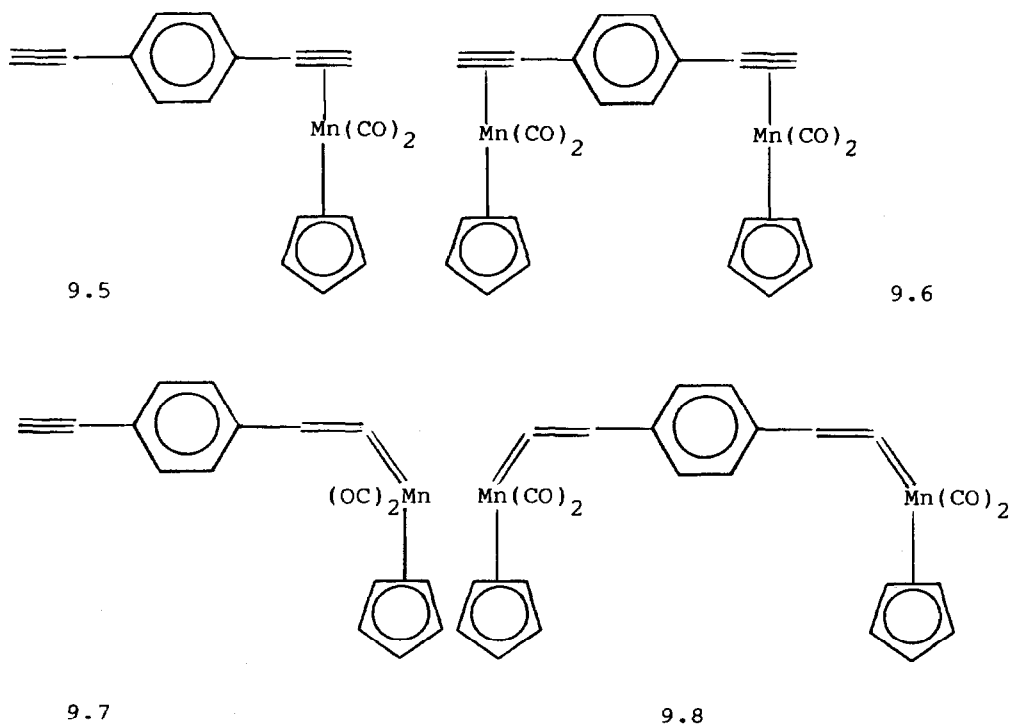
9.3



9.4

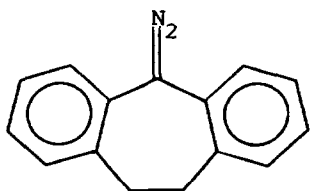
the manganese complex the carbene plane was coincident with the mirror plane of the ( $\eta\text{-C}_5\text{H}_5$ )Mn(CO)<sub>2</sub> fragment. NMR spectra of the complexes showed that the chromium-carbene conformation was locked whereas rotation about the manganese-carbene bond was rapid [157]. Reaction of dicarbonyl( $\eta$ -cyclopentadienyl)-tetrahydrofuranmanganese with  $p\text{-(HC}\equiv\text{C)}_2\text{C}_6\text{H}_4$  produced the



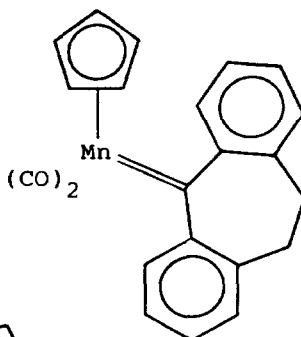


manganese complexes (9.5 and 9.6). Treatment of these compounds with phenyllithium produced the corresponding vinylidene complexes (9.7 and 9.8) [158].

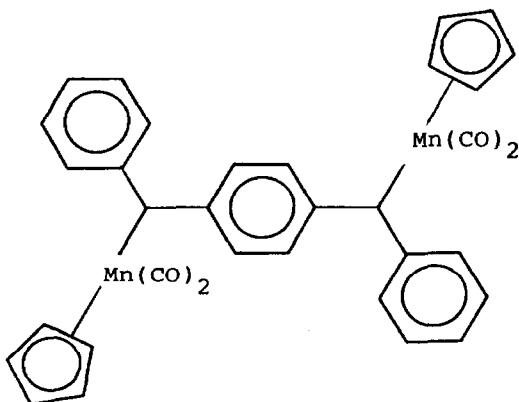
Diarylcarbene ligands have been incorporated into the complex  $(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{THF}$  using the diazoalkane route. Thus, diazosuberone (9.9) gave the carbocyclic carbene complex (9.10) the structure of which was established by X-ray crystallography. The same synthetic approach was used to form the dinuclear complex (9.11) from 1,4-bis(diazobenzyl)benzene. High pressure carbonylation of the carbene complex (9.10) was employed to give the  $\eta^2$ -ketene complex (9.12). Several related reactions and structural determinations were reported [159]. The manganese vinylidene complex (9.13) has been attacked by trialkylphosphites,  $\text{P}(\text{OR})_3$  where  $\text{R} = \text{Et}, \text{Ph}$ , to form the manganese



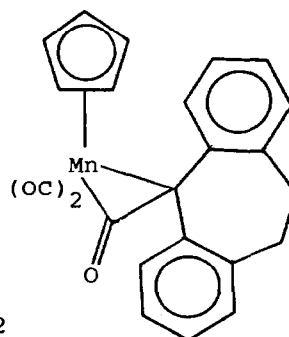
9.9



9.10



9.11

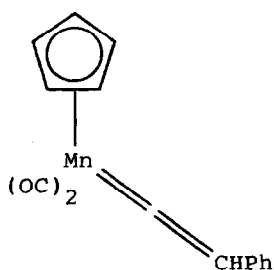


9.12

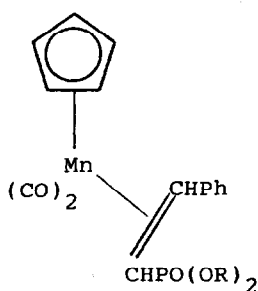
olefin complexes (9.14; R = Et, Ph) under mild conditions. One of the complexes (9.14; R = Et) has been characterized by X-ray crystallography [160]. Treatment of the cymantrene derivative (9.13) with  $\text{H}_2\text{Os}_3(\text{CO})_9$  afforded  $(\eta\text{-C}_5\text{H}_5)\text{MnOs}(\text{H})(\mu\text{-CH=CHPh})(\text{CO})_{12}$  as the major product together with the cluster compounds (9.15 and 9.16) [161]. The vinylidene complex (9.13) combined with  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  to give a tetranuclear cluster complex  $(\eta\text{-C}_5\text{H}_5)\text{MnOs}_3(\mu_2\text{-CH=CHPh})(\mu\text{-H})(\mu\text{-CO})(\text{CO})_{11}$  which was characterized by X-ray crystallography. The manganese atom was linked to one of the vertices of the osmium triangle and the Mn-Os bond was bridged by CO and CH=CHPh groups. The cluster complex readily eliminated the  $(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$  moiety in solution [162].

Several unsaturated carbene complexes (9.17 and 9.18) underwent addition at the  $\alpha$ -carbon of the cumulidene ligand with phosphines to give the phosphonium ylide complexes [9.19;

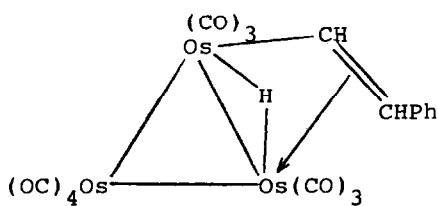
$R^1 = \text{Me, Ph}$ ;  $R^2 = \text{Ph, CO}_2\text{Me, C(OH)Bu}^t_2$  and 9.20;  $R = \text{Bu}^t, \text{Ph}$ ]. The crystal and molecular structure of one of these complexes (9.20;  $R = \text{Ph}$ ) has been determined by X-ray crystallography [163]. The allenylidene complexes (9.18;  $R = \text{Ph, Bu}^t$ ) have been protonated with  $\text{HCl}$ ,  $\text{HBF}_4$  and  $\text{CF}_3\text{CO}_2\text{H}$  to give the cationic vinylcarbene complexes (9.21;  $R = \text{Ph, Bu}^t$ ). One of these (9.21;  $R = \text{Ph}$ ) have been characterized by X-ray crystallography. The binuclear  $\mu$ -vinylidene complexes (9.22;  $R = \text{Ph, CO}_2\text{Me}$ ) were protonated in the same way at the  $\beta$ -carbon of the vinylidene ligand [164].



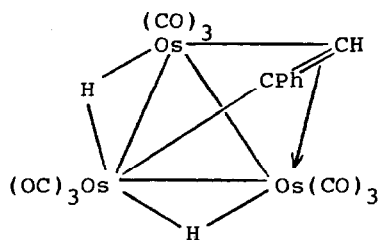
9.13



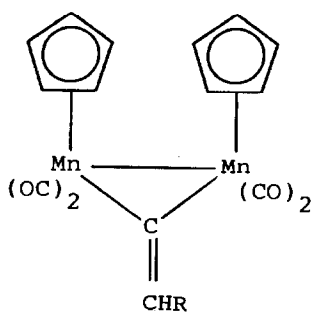
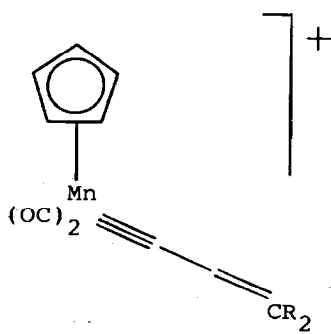
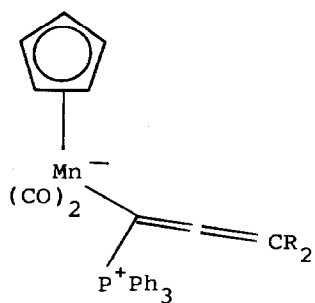
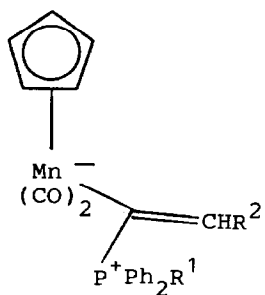
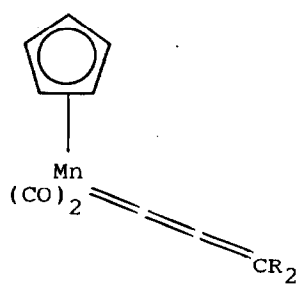
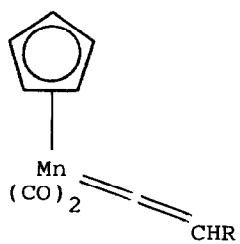
9.14



9.15

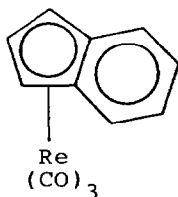


9.16

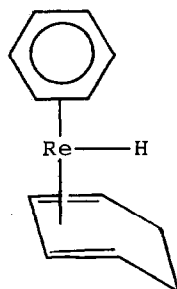


10.  $(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ 

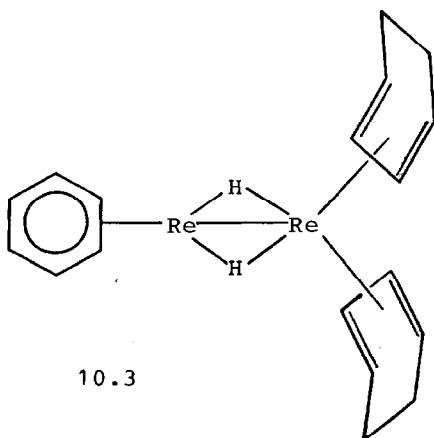
The direct reaction of indene with  $\text{Re}_2(\text{CO})_{10}$  produced the rhenium complex (10.1) in good yield [165]. The cocondensation



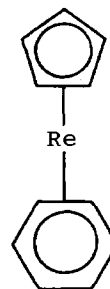
10.1



10.2

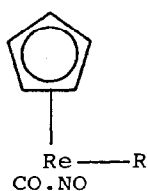


10.3

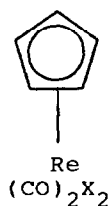


10.4

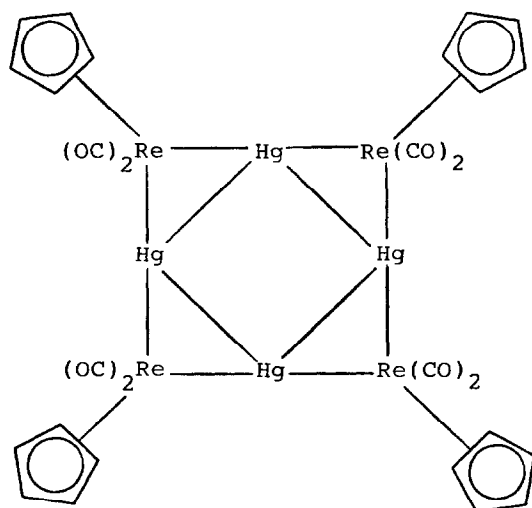
of rhenium atoms with a 1:1 mixture of benzene-cyclohexene produced a mixture of the complexes (10.2 and 10.3). In a similar reaction with a 1:1 mixture of benzene-cyclopentadiene,  $(\eta\text{-benzene})(\eta\text{-cyclopentadienyl})\text{rhenium}$  (10.4) was produced [166]. Lithiation of the rhenium complex (10.5;  $\text{R} = \text{H}$ ) with *n*-butyllithium occurred at the rhenium atom to give the lithio-derivative (10.5;  $\text{R} = \text{Li}$ ) which on treatment with chlorotrimethylsilane produced the silane (10.5;  $\text{R} = \text{SiMe}_3$ ) [167]. Reaction of the rhenium complex (10.6;  $\text{X} = \text{Br}, \text{I}$ ) with sodium-mercury amalgam in benzene gave a mixture of the tetramercuri complex (10.7) and the same complex containing one third of a molecule of benzene. The structure of the



10.5



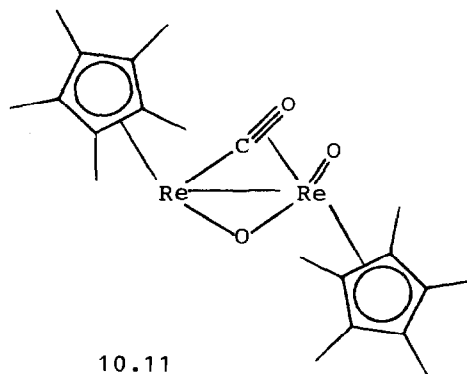
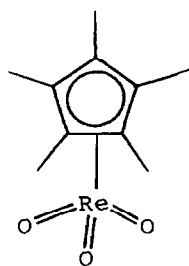
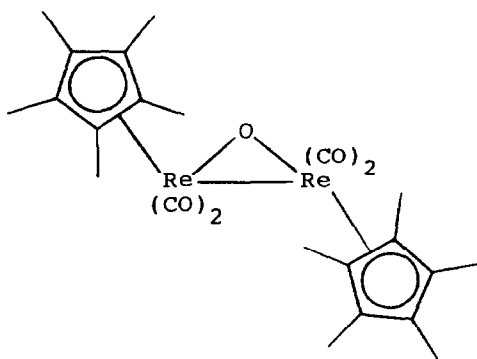
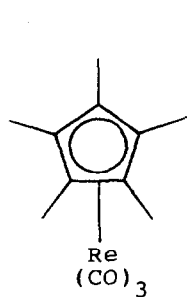
10.6



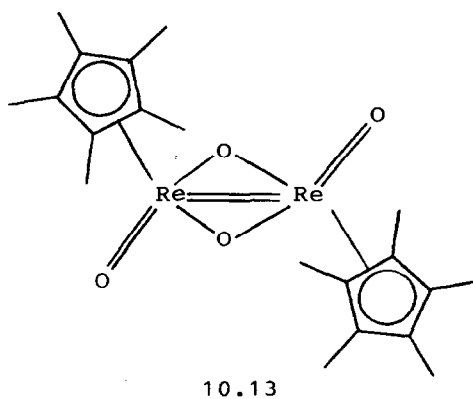
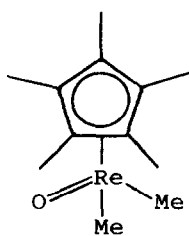
10.7

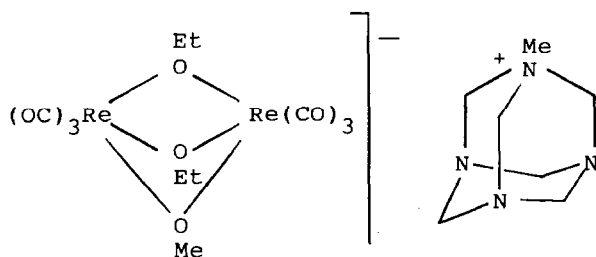
complex (10.7) was determined by X-ray analysis [168]. Short wavelength photolysis of tricarbonyl( $\eta$ -pentamethylcyclopentadienyl)rhenium (10.8) produced the organorhenium compounds (10.9, 10.10 and 10.11). The structure of the complex (10.9) was determined by X-ray analysis. The molecular structure of this compound centred around an isosceles  $\text{Re}_2\text{O}$  triangle where the metal centres exhibited a strongly distorted square-pyramidal geometry [169, 170]. Klahn-Oliva and Sutton also reported the preparation of the trioxorhenium complex (10.10) from dicarbonyl( $\eta$ -pentamethylcyclopentadienyl)tetrahydrofuran-rhenium and oxygen under pressure [171].

Some reactions of the trioxo complex (10.10) have been investigated. For example, treatment with trimethylaluminium produced the dimethyl compound (10.12) and treatment with tri-



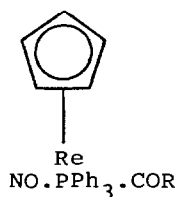
phenylphosphine afforded the readily oxidizable dinuclear rhenium derivative (10.13) [172]. Reaction of tricarbonyl-



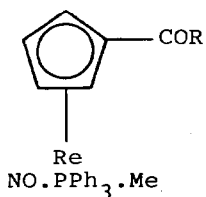


10.14

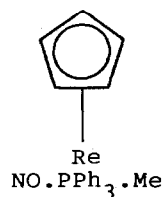
( $\eta^5$ -indenyl)rhenium with urotropin in ethanol produced the salt (10.14) [173]. Reaction of the acyl complexes (10.15; R = Me, Ph,  $\text{CH}_2\text{Ph}$ ) with  $\text{LiN}(i\text{-Pr})_2$  followed by methyl iodide produced the corresponding Me-Re derivatives (10.16). Treatment of the methyl complex (10.17) with n-butyllithium-tetramethylethylenediamine followed by acetic anhydride afforded the acetyl derivative (10.16; R = Me) [174].



10.15



10.16

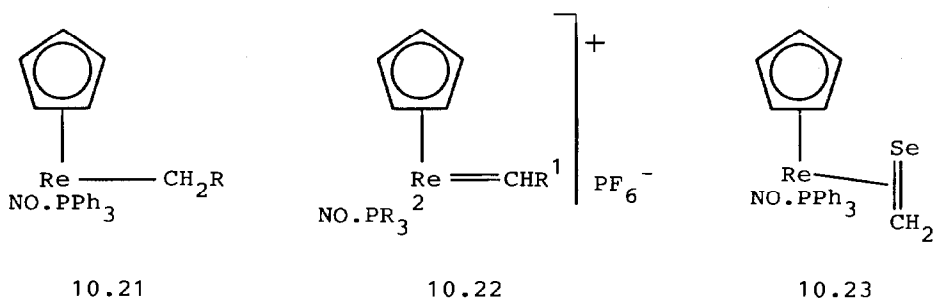
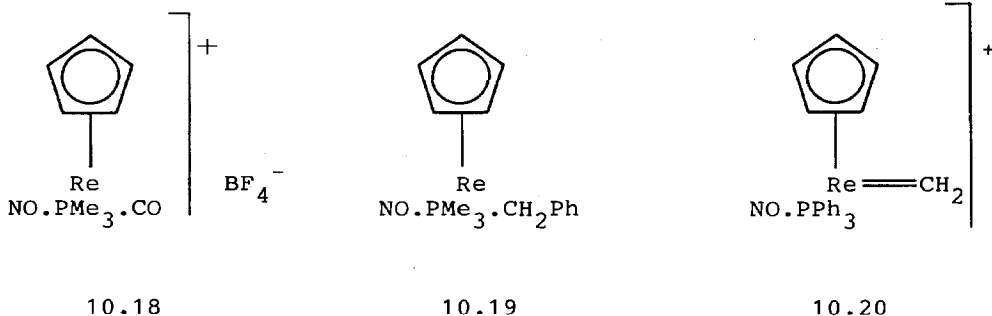


10.17

Sequential treatment of the salt (10.18) with sodium methoxide, phenylmagnesium bromide and diborane produced the benzylrhenium complex (10.19). Reaction of the cationic carbene complex (10.20) with a Grignard reagent  $\text{RMgBr}$ , where R =



2-MeC<sub>6</sub>H<sub>4</sub>, mesityl, produced the corresponding benzyl complexes (10.21). The complexes (10.19 and 10.21; R = mesityl) underwent exclusive pro-SH<sub>α</sub> abstraction to give the corresponding carbene complexes (10.22; R<sup>1</sup> = Ph, mesityl; R<sup>2</sup> = Ph, Me) [175].

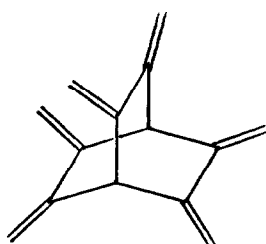


Several transformations of the ( $\eta$ -cyclopentadienyl)rhenium cation (10.20) have been reported, thus with Ph<sub>3</sub>P=Se the selenoformaldehyde derivative (10.23) was obtained and was characterized by X-ray crystallography [176].

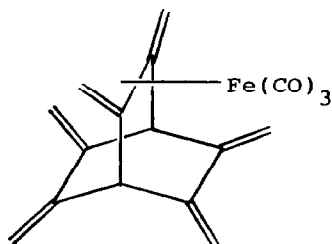
#### 11. (Acyclic- $\eta$ -diene)Fe(CO)<sub>3</sub> and ( $\eta$ -Trimethylenemethane)Fe(CO)<sub>3</sub>

Mononuclear (11.2), dinuclear (11.3, 11.4) and trinuclear (11.5) complexes have been formed by the reaction of [2.2.2]hericene (11.1) with nonacarbonyldiiron in hexane. The rates of Diels-Alder addition of tetracyanoethylene and dimethyl

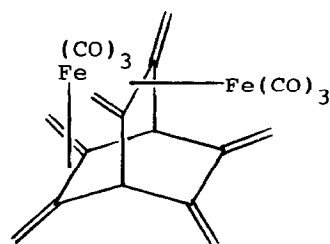
acetylenedicarboxylate to the uncomplexed diene residues in the dinuclear complexes (11.3, 11.4) were low by comparison with the rate of addition to the free ligand. A valence-bond model was used to discuss the origin of this effect [177]. Oxidative hydroboration of the exo- and endo-complexes (11.6 and 11.7) produced the corresponding alcohols which were oxidized to the ketones (11.8 and 11.9). These ketones underwent base catalysed hydrogen-deuterium exchange to give the dideuterated exo-complex and the monodeuterated endo-complex respectively. Similar reactions were also carried out with the exo- and endo-tricarbonyliron complexes of 5,6-dimethylidenebicyclo [2.2.1]hept-2-ene [178]. The endo-(-)- and exo-(-)-trimethyl- enenorbornane iron complexes (11.10 and 11.11) respectively were



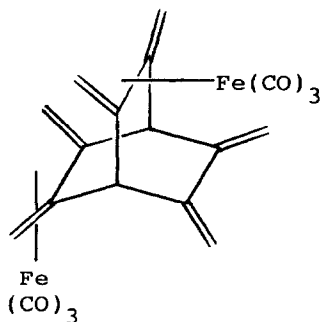
11.1



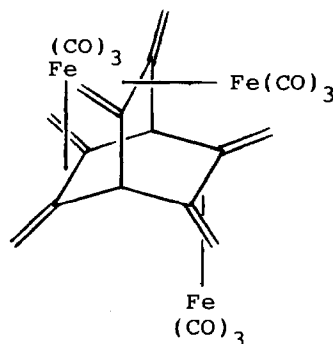
11.2



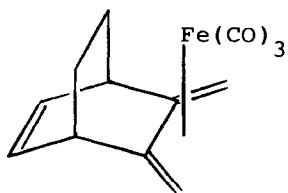
11.3



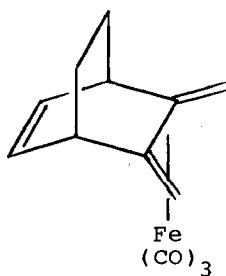
11.4



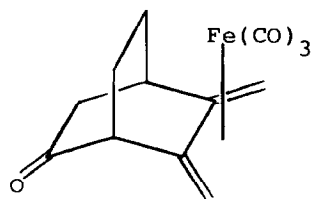
11.5



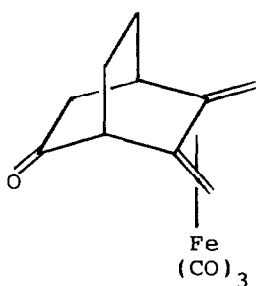
11.6



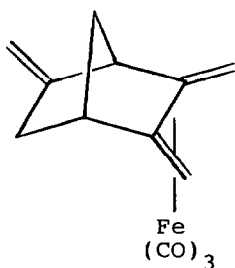
11.7



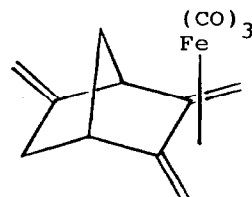
11.8



11.9



11.10



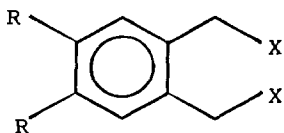
11.11

prepared from the (-)-trimethylenenorbornane ligand and enneacarbonyldiiron. The temperature dependence of the CD spectra of these and some related complexes suggested that equilibration occurred as rapidly interconverting pairs of diastereomers [179].

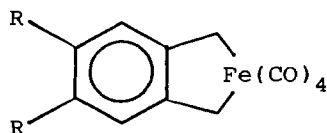
Reaction of the xylene dihalides (11.2; R = H, Me; X = Cl, Br) with sodium tetracarbonylferrate(II) produced the bis-( $\sigma$ -methylene)iron complexes (11.13). These complexes underwent both thermal and photochemical rearrangement to give the corresponding  $\pi$ -bonded complexes (11.14) [180]. The reaction of 2,3-bis(carbomethoxy)-9,10-dichlorobicyclo[6.2.0]deca-2,5-diene with nonacarbonyldiiron produced the tricarbonyliron complex (11.15) [181]. Pentacarbonyliron attacked cis-polybutadiene in

xylylene solution to form poly(1,3-octadieneirontricarbonyl) an alternating copolymer containing ( $\eta$ -butadiene)irontricarbonyl groups with trans-trans- and trans-cis-tetramethylene moieties [182]. Photolysis of pentacarbonyliron with cis-cyclooctene at  $-40^\circ\text{C}$  gave tricarbonylbis( $\eta^2$ -cis-cyclooctene)iron (11.16) which has been used as a tricarbonyliron transfer reagent under mild conditions. A number of ( $\eta$ -diene)irontricarbonyl complexes were prepared by treatment of the diene ligand with the reagent (11.6) [183].

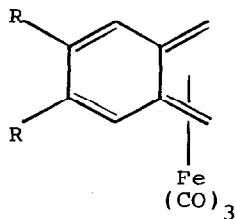
Tricarbonyliron complexes with  $\eta$ -allyl and  $\eta$ -diene ligands have been formed in the synthesis of the  $\beta$ -lactam antibiotic (+)-thienamycin [184]. Ruthenium atoms have been cocondensed with excess 2,3-dimethylbutadiene and 1,3- or 1,4-cyclohexadiene. When the condensates were warmed under an atmosphere of carbon



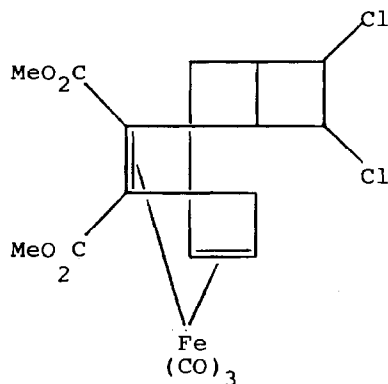
11.12



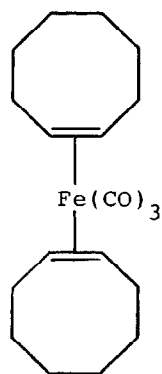
11.13



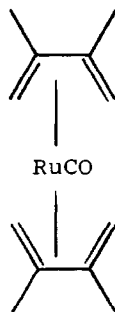
11.14



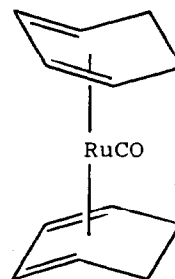
11.15



11.16

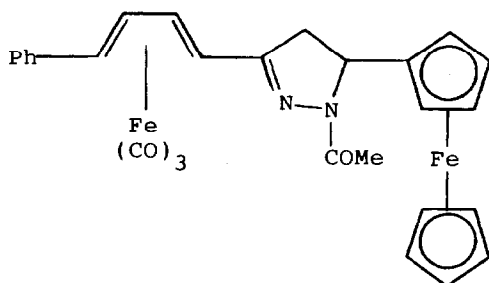


11.17

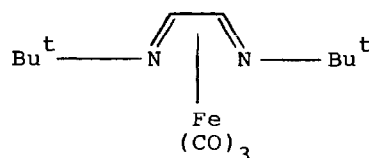


11.18

monoxide the complexes (11.17 and 11.18) were isolated [185]. Nucleophiles, such as  $\text{CHPh}_2^-$  and  $\text{CMe}_2\text{CN}^-$  attacked ( $\eta$ -diene)-irontricarbonyl complexes at  $-78^\circ\text{C}$  at an unsubstituted internal carbon atom. The reaction was subject to kinetic control and reversal of the initial reaction was also observed [186]. The synthesis of  $\beta$ -olefinic triphenylphosphonium salts has been described using ( $\eta$ -diene)irontricarbonyl complexes which were converted to ( $\eta$ -allyl)iron or ( $\eta$ -dienyl)iron intermediates and



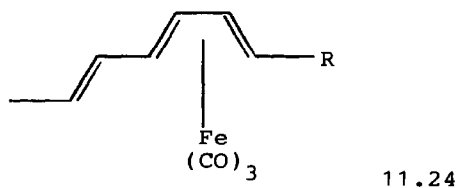
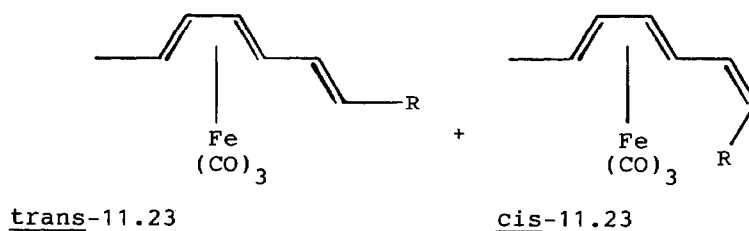
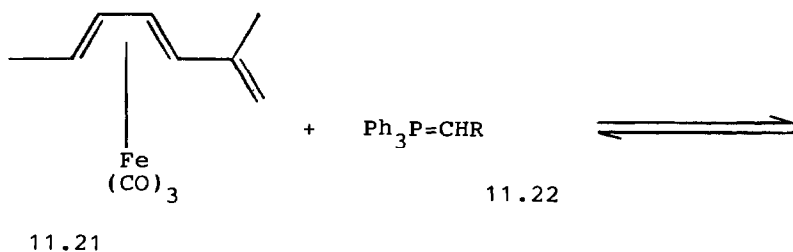
11.19



11.20

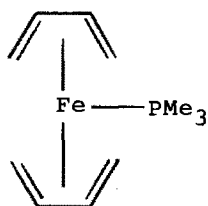
and then treated with triphenylphosphine [187]. Asymmetric induction in the synthesis of pyrazolines such as the complex (11.19) has been examined. Diastereomeric selectivity was shown to be high both by the induction of a chiral centre by a plane of chirality and vice versa. The crystal and molecular structure of two of the pyrazoline products was determined by X-ray crystallography [188].

Photolysis of tricarbonyl( $\alpha$ -di-imine)iron complexes in matrices at 10K caused intermediate formation of ( $\eta^4$ -di-imine)-iron complexes, such as the species (11.20), which decomposed to  $\sigma$ -complexes with the loss of carbon monoxide [189]. The reaction of tricarbonyl( $\eta^4$ -1,3-diene)iron complexes with carbon anions has been investigated. Carbon nucleophiles that were more reactive than ketone enolates and less reactive than phenyllithium

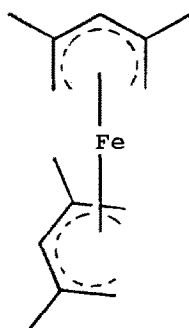


attacked the diene ligand to give substituted olefinic compounds after protonation [191]. The Wittig reaction of  $(\eta\text{-}2,4\text{-hexadienal})\text{Fe}(\text{CO})_3$  (11.21) with a phosphorane (11.22;  $\text{R} = \text{CO}_2\text{Me}$ ,  $\text{CO}_2\text{Et}$ ,  $\text{COPh}$ ,  $\text{CN}$ ) produced the corresponding tricarbonyliron complex (11.23) as a mixture of cis and trans isomers. At  $120^\circ\text{C}$  in toluene the isomeric esters and ketones underwent cis  $\rightarrow$  trans isomerization and metal shift tautomerization to give an equilibrium mixture of isomers containing mainly the trans-shift isomers (11.24;  $\text{R} = \text{CO}_2\text{Me}$ ,  $\text{CO}_2\text{Et}$ ,  $\text{COPh}$ ) [192].

The crystal structure of the  $\eta$ -butadieneiron complex (11.25) has been determined by X-ray analysis [193]. A series



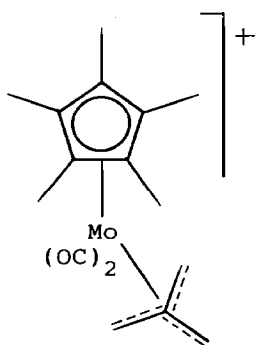
11.25



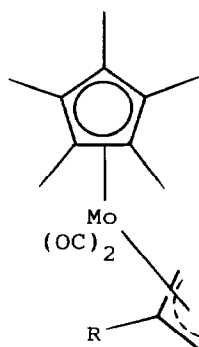
11.26

of methyl and dimethyl substituted bis( $\eta$ -pentadienyl)iron compounds has been prepared. X-ray analysis of the iron complex (11.26) showed that it had a gauche-eclipsed open sandwich structure with iron-carbon bond distances which were slightly longer than those of ferrocene [194]. The helium(1) photoelectron spectrum of bis( $\eta$ -pentadienyl)iron has been recorded and compared with the ferrocene spectrum [195]. A single crystal of  $(\eta\text{-C}_4\text{H}_6)_2\text{FePMe}_3$  has been doped with  $(\eta\text{-C}_4\text{H}_6)_2\text{MnPMe}_3$  and the ESR spectrum obtained of the manganese complex [196]. Optical spectroscopy has been used to study phasetransitions in two-dimensional physisorbed ( $\eta$ -butadiene)tricarbonyliron. The melting transitions and the melting phase diagram were obtained from the remission spectrum [197].

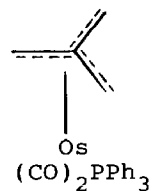
An  $^1\text{H}$  NMR study of ( $\eta$ -butatriene)hexacarbonyldiiron in three different liquid crystals has been used to determine the conformation of the molecule [198]. Fluxional isomerism in several enone complexes  $(\eta^4\text{-enone})\text{Fe}(\text{CO})_2\text{L}$ , where enone = benzylideneacetone, cinnamaldehyde and  $\text{L} = \text{PPh}_3, \text{PPh}_2\text{Me}, \text{PPhMe}_2, \text{P}(\text{OPh})_3$  has been investigated by NMR and IR spectroscopy. The complexes existed as interconverting isomeric mixtures in solution with the ligand  $\text{L}$  occupying either the axial or basal position of a square pyramid structure. The ratio of the isomers was dependent on the steric properties of both the enone group and the ligand  $\text{L}$  [199]. The electrical conductivities of poly{tricarbonyl-[3-(vinylloxy)ethyl]- $\eta^4$ -1,3-pentadieneiron} and the corresponding tricarbonylruthenium polymer



11.27



11.28



11.29

have been determined. The polymers were insulators but when they were doped with iodine the conductivity of polymer films increased markedly to approximately  $3.2 \times 10^{-3} \text{ s cm}^{-1}$  [200].

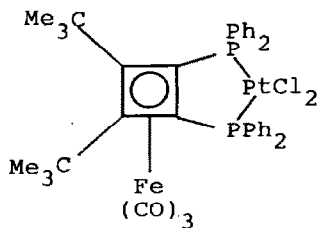
Methylenecyclopropane attacked  $\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{Me}_5)_2$  to form the cationic ( $\eta^4$ -trimethylenemethane)molybdenum complex (11.27). The crystal and molecular structure of the complex (11.27) has been determined by X-ray crystallography. The trimethylenemethane ligand was pyramidal and adopted a syn-orientation with respect to the OC-Mo-CO angle. Extended Hückel MO calculations indicated that the syn stereochemistry was electronically preferred. The cationic complex (11.27) was attacked by nucleophiles such as  $\text{BH}_4^-$ ,  $\text{OH}^-$  and  $\text{CuMe}_2^-$  at



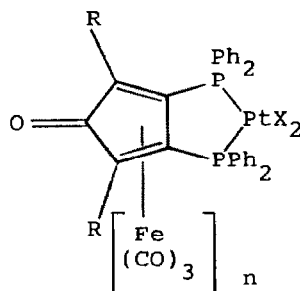
a peripheral carbon atom to form the  $\eta$ -allyl complexes (11.28; R = H, Oh, Me) respectively [201]. The ( $\eta^4$ -trimethylenemethane)-osmium complex (11.29) has been obtained by treatment of  $\text{Os}(\text{CO})_2(\text{PPh}_3)_3$  with  $\text{Me}_3\text{SiCH}_2\text{C}(=\text{CH}_2)\text{CH}_2\text{OAc}$  in boiling benzene. Evidence was offered for a staggered conformation [202].

## 12. $(\eta\text{-C}_4\text{H}_4)\text{Fe}(\text{CO})_3$

A method has been developed for the synthesis of heteroatom substituted cyclobutadienes and cyclopentadienones by metal carbonyl coupling of acetylenes held close to square-planar platinum (II). For example, the reaction of  $\text{cis-Cl}_2\text{Pt}(\text{Ph}_2\text{PC}\equiv\text{CCMe}_3)_2$  with  $\text{Fe}_2(\text{CO})_9$  produced the  $\eta$ -cyclobutadiene complex (12.1). Similarly, the treatment of  $\text{cis-X}_2\text{Pt}(\text{Ph}_2\text{PC}\equiv\text{CR})_2$ , where X = Cl, Br, I, Ph, 2-MeC<sub>6</sub>H<sub>4</sub>, CF<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>; 2X = 1,2-C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>, R = Ph, cyclohexyl, SiMe<sub>3</sub>, with  $\text{Fe}_2(\text{CO})_9$  produced the corresponding cyclopentadiene derivatives (12.2; n = 0, 1) [203]. Addition

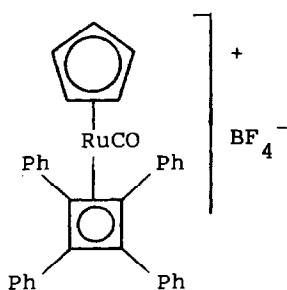


12.1

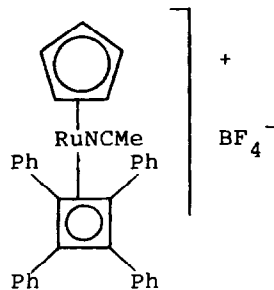


12.2

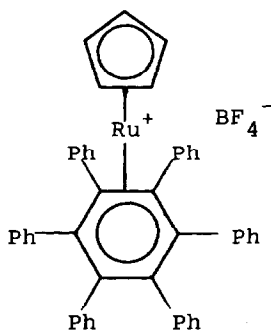
of silver tetrafluoroborate to a mixture of diphenylacetylene and  $[\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$  led to a mixture of products containing the salt (12.3). Ultraviolet irradiation of this salt in methyl cyanide produced the complex (12.4). The structure of this complex was determined by X-ray analysis. Irradiation of the complex (12.3) with diphenylacetylene afforded the  $\eta$ -hexaphenylbenzene complex (12.5). The same route was used to prepare other  $\eta$ -hexasubstituted benzene-ruthenium complexes [204].



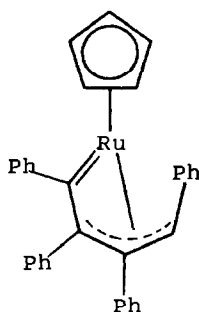
12.3



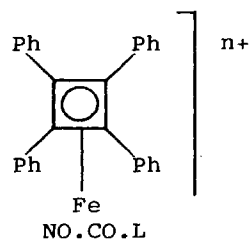
12.4



12.5



12.6



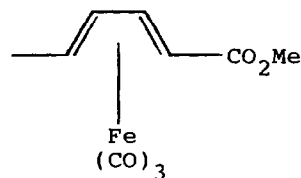
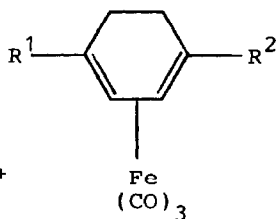
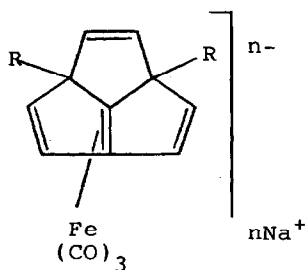
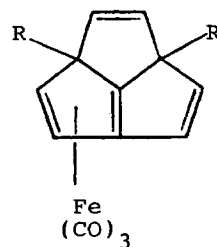
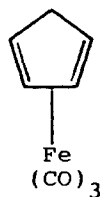
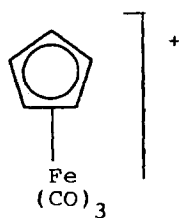
12.7

Addition of  $K[BHBU^S_3]$  to the methyl cyanide complex (12.4) produced the air-sensitive complex (12.6). The structure of this latter compound was determined by X-ray analysis [205]. Several reactions of the ( $\eta$ -tetraphenylcyclobutadiene)iron complexes (12.7;  $L = CO, PPh_3, n = 1$ ) with nucleophiles have been carried out. Thus the complex (12.7;  $L = CO, n = 1$ ) was attacked by chloride ion to give the product (12.7;  $L = Cl, n = 0$ ) [206].

### 13. (Cyclic- $\eta$ -diene)Fe(CO)<sub>3</sub>

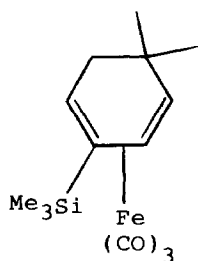
#### (i) Formation

Reduction of the ( $\eta$ -cyclopentadienyl)iron cation (13.1) with hydrides such as sodium tetrahydroborate gave several products including the ( $\eta$ -cyclopentadiene)iron complex (13.2) [207]. The  $\eta^4$ -dihydroacepentalene complexes (13.3;  $R = NEt_2$ ,

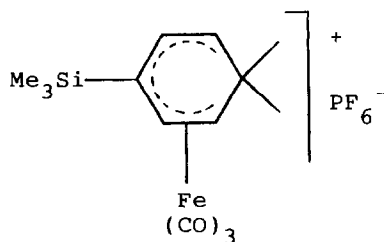


piperidino, 3,5-dimethylpiperidino, morpholino,  $\text{NMe}_2$ ) have been prepared by the reaction of  $\text{Fe}_2(\text{CO})_9$  with the corresponding dihydroacepentalene. Reduction of the complexes (13.3;  $\text{R} = \text{NEt}_2$ , piperidino) with sodium gave the corresponding anions (13.4;  $n = 1$ ) and these underwent further reduction to give the dianions (13.4;  $n = 2$ ) [208]. Optically active tricarbonyliron complexes (13.5;  $\text{R}^1 = \text{OMe}$ ,  $\text{R}^2 = \text{H}$ ,  $\text{Me}$ ;  $\text{R}^1 = \text{CHMe}_2$ ,  $\text{R}^2 = \text{Me}$  and 13.6) have been prepared by the transfer of chirality between a chiral donor complex and the unsymmetrical diene ligand. The chiral donor ligands used were (-)- $3\beta$ -(acetyloxy)-pregna,5,16-dien-20-one, (+)-pulegone, (+)-pinocarvone, (+)-3-benzylidenecamphor and (-)-cholest-4-ene-3,6-dione [209].

Direct reaction between pentacarbonyliron and the ligand has been used to prepare ( $\eta$ -2-trimethylsilyl-1,3-cyclohexadiene)-iron complexes such as the complex (13.7). Ligand rearrangement was not observed during the reaction and the complexes

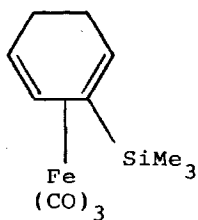


13.7

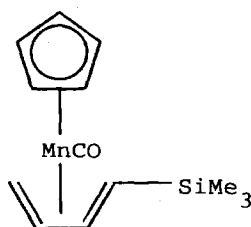


13.8

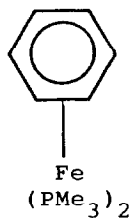
underwent regiospecific hydride abstraction with trityl tetrafluoroborate, thus the complex (13.7) gave the symmetrical ( $\eta$ -cyclohexadienyl)iron complex (13.8). Nucleophilic addition to the ( $\eta$ -cyclohexadienyl)iron complexes such as the complex (13.8) was regiospecific. Tandem photoelectron spectroscopy and INDO calculations were used to investigate the electronic structure and the chemical reactivity of the complexes. Electronic effects mainly within the HOMO were responsible for the regiospecific character of hydride abstraction [210]. Trimethylsilyl substituted butadienes and cyclohexadienes have



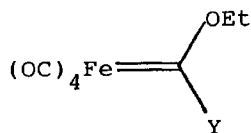
13.9



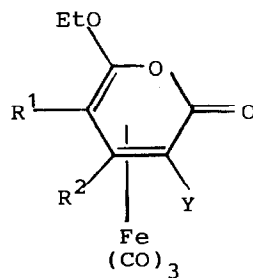
13.10



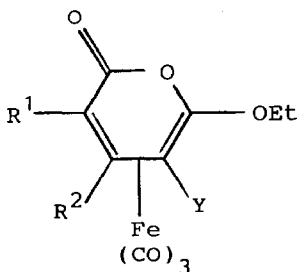
13.11



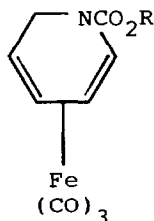
13.12



13.13



13.14

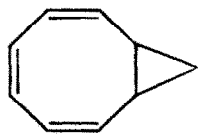


13.15

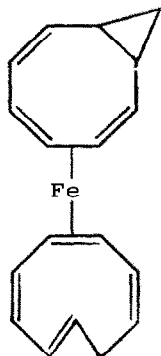
been attacked by iron carbonyls and by methylcymantrene to form ( $\eta^4$ -diene)metal complexes. Thus the complexes (13.9 and 13.10) were obtained by use of nonacarbonyldiiron and methylcymantrene respectively with the appropriate ligands [211]. Cocondensation of iron atoms with a mixture of benzene and trimethylphosphine afforded the  $\eta^6$ -benzene complex (13.11). This complex was used to prepare ( $\eta$ -C<sub>5</sub>R<sub>5</sub>)Fe(PMe<sub>3</sub>)<sub>2</sub>X, where R = H, Me, X = H, Cl, Me, Et, and other ( $\eta$ -C<sub>5</sub>R<sub>5</sub>)Fe(PMe<sub>3</sub>)<sub>2</sub> derivatives [212]. Reaction of the tetracarbonyliron complexes (13.12; Y = Ph, t-Bu, n-Bu) with the alkynes R<sup>1</sup>C≡CR<sup>2</sup> produced the corresponding 6-ethoxy- $\alpha$ -pyrone complexes (13.13; R<sup>1</sup> = R<sup>2</sup> = Me, Y = Ph; R<sup>1</sup> = Y = Ph, R<sup>2</sup> = H; R<sup>1</sup> = Et, R<sup>2</sup> = H, R<sup>3</sup> = Ph; R<sup>1</sup> = R<sup>2</sup> = Y = Ph; R<sup>1</sup> = CO<sub>2</sub>Me, R<sup>2</sup> = Me, Y = Ph; R<sup>1</sup> = R<sup>2</sup> = Me, Y = t-Bu; R<sup>1</sup> = Ph, R<sup>2</sup> = H, Y = t-Bu; R<sup>1</sup> = R<sup>2</sup> = Me, Y = n-Bu). The complexes (13.13; R<sup>1</sup> = R<sup>2</sup> = Me, Y = Ph; R<sup>1</sup> = Et, R<sup>2</sup> = H, Y = Ph) isomerized

slowly to the corresponding tricarbonyliron derivatives (13.14) [213].

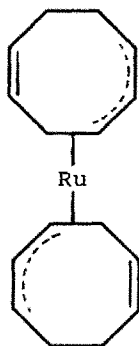
The  $\eta$ -N-alkoxycarbonyl-1,2-dihydropyridine complexes (13.15; R = Me, Et) were prepared in good yields by irradiation of the



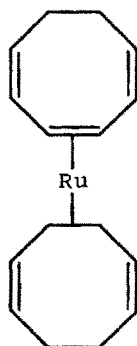
13.16



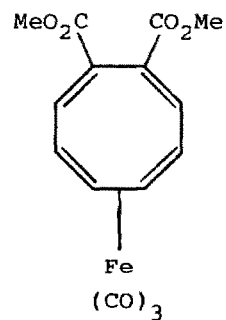
13.17



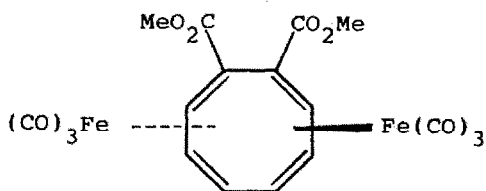
13.18



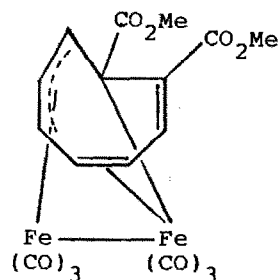
13.19



13.20



13.21

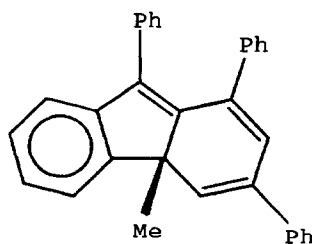
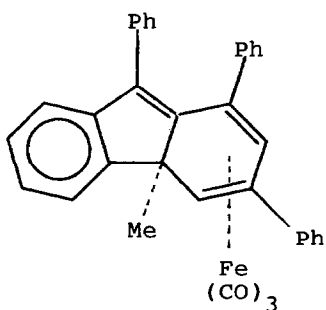


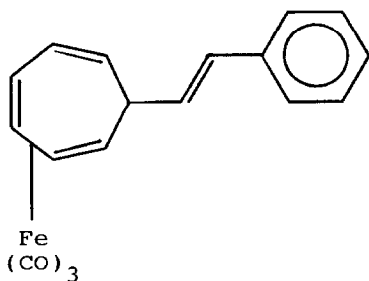
13.22

ligands in excess pentacarbonyliron in the absence of a solvent [214]. Bicyclononatriene (13.16) has been cocondensed with iron vapour at  $-120^{\circ}\text{C}$  to give the mixed sandwich complex (13.17). The same complex (13.17) was obtained in higher yield by treatment of bis( $\eta$ -1,5-cyclooctadiene)iron with the ligand (13.16) [215]. The reduction of ruthenium (III) chloride with zinc in the presence of 1,5-cyclooctadiene produced the complex (13.18). This compound isomerized to the ( $\eta^6$ - $\text{C}_8\text{H}_{10}$ ) ruthenium complex (13.19) at  $70^{\circ}\text{C}$  by migration of a hydrogen atom from one 1-3:5-6- $\eta$ - $\text{C}_8\text{H}_{11}$  ligand to the other [216]. Treatment of dimethyl cyclooctatetraene-1,8-dicarboxylate with iron carbonyls produced the tricarbonyliron complexes (13.20, 13.21 and 13.22) [217].

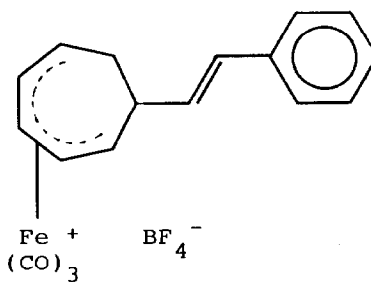
(ii) Spectroscopic and Physico-chemical Studies

The structure of the tricarbonyliron complex (13.23) has been determined by X-ray analysis. On complex formation the ligand (13.24) changed its conformation to allow iron co-ordination on the opposite site of the diene ring to the methyl group [218]. Tropylium tetrafluoroborate attacked tricarbonyl( $\eta$ -cyclooctatetraene)iron to form the ( $\eta$ -styrylcycloheptatriene)iron complex (13.25) the structure of which has been confirmed by X-ray crystallography. The cycloheptatrienyl ring adopted an envelope conformation with the  $\text{Fe}(\text{CO})_3$  group bonded to the convex face.





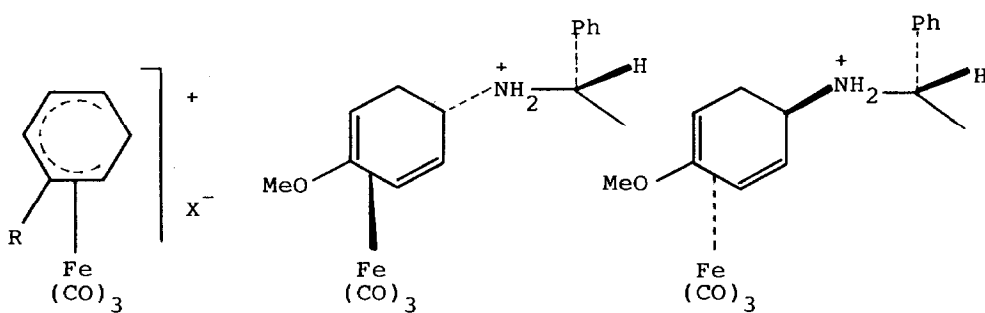
13.25



13.26

The mechanism of formation of the product (13.25) was discussed and the reaction of this complex (13.25) with tetrafluoroboric acid to give the ( $\eta$ -cycloheptadienyl)iron complex (13.26) was reported [219].

Mossbauer spectroscopy and  $^{13}\text{C}$  NMR spectroscopy have been used to indicate the presence of plastic phases in the solid state for ( $\eta$ -cyclohexadienyl)iron salts (13.27;  $\text{R} = \text{H}, \text{Me}, \text{OMe}$ ;  $\text{X} = \text{BF}_4, \text{PF}_6, \text{SnCl}_5$ ) through the effect of reorientational motion on the spectroscopic and crystallographic properties of the salts [220]. The barriers to tricarbonyliron rotation in substituted ( $\eta$ -cyclohexadienyl)iron cations have been determined by analysis of exchange-broadened line-shapes in  $^{13}\text{C}$  NMR spectroscopy. Values of 10.7, 11.4 and 12.6 kcal mol $^{-1}$  were

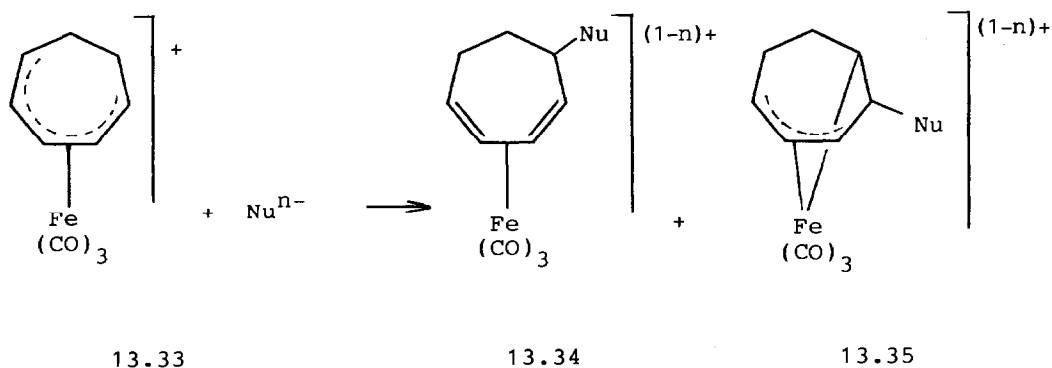
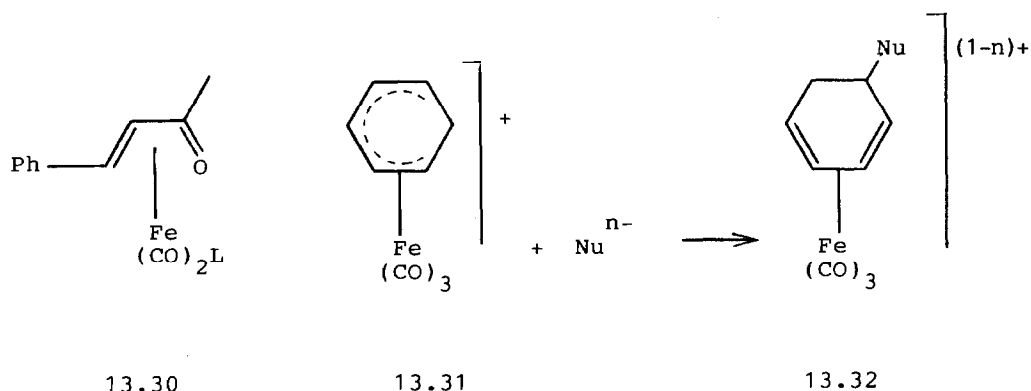


13.27

13.28

13.29





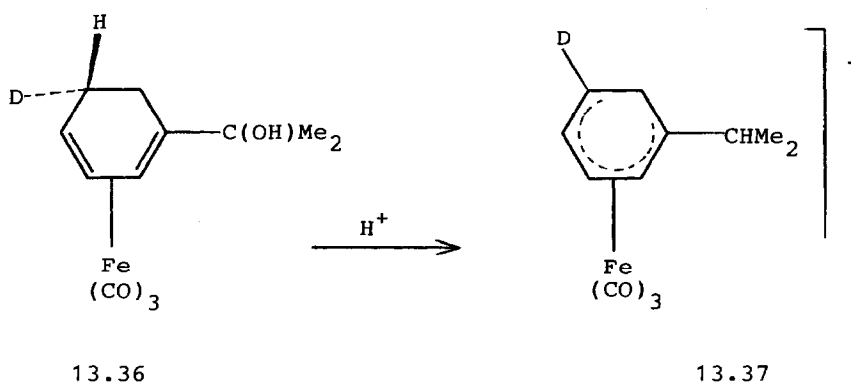
obtained for the complexes (13.27; R = H, OMe, Me) respectively [221]. The reaction of racemic (2R, 2S)-[(1-5-η-2-MeOC<sub>6</sub>H<sub>6</sub>)Fe(CO)<sub>3</sub>]<sup>+</sup> with (R)-(+)-1-phenylethylamine produced a mixture of the diastereoisomers (13.28 and 13.29). These isomers were easily separated by hplc and the addition of HBF<sub>4</sub> to each fraction quantitatively removed the amine substituents to give the enantiomers (2R)-(-)- and (2S)-(+)-[(1-5-η-2-MeOC<sub>6</sub>H<sub>6</sub>)Fe(CO)<sub>3</sub>]<sup>+</sup> with high optical purity. Circular dichroism was used to establish the optical purity of these compounds [222].

Ligand exchange of 1,3-cyclohexadiene with benzylidene in the complex [13.30; L = CO, PPh<sub>3</sub>, PPh<sub>2</sub>Me, PPhMe<sub>2</sub>, P(OPh)<sub>3</sub>] has been the subject of a kinetic study. The mechanism involved stepwise, competing D and I<sub>D</sub> opening of the ketonic M-CO π-bond. Both steric and electronic factors were important in the reaction.

Rates increased in the order:

$L = \text{CO} \gg \text{PPh}_3 \approx \text{P(OPh)}_3 > \text{PPh}_2\text{Me} \gg \text{PPhMe}_2$  [223].

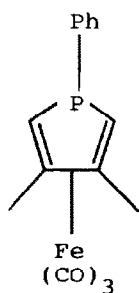
A kinetic comparison has been made of the addition of nucleophiles to ( $\eta$ -cyclohexadienyl)iron cations (13.31) and ( $\eta$ -cycloheptadienyl)iron cations (13.33) to form, in the first case, ( $\eta$ -cyclohexadiene)iron complexes (13.32) and in the second case a mixture of two products (13.34 and 13.35). The ( $\eta$ -cycloheptadienyl)iron complex (13.33) showed lower reactivities to phosphorus and nitrogen donor nucleophiles and this difference was explained in steric terms [224]. Proton elimination from the ( $\eta$ -cyclohexadiene)iron complex (13.36) occurred stereospecifically to



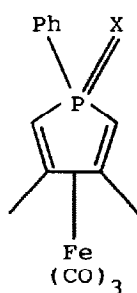
give only the ( $\eta$ -cyclohexadienyl)iron cation (13.37) [225].

### (iii) General Chemistry

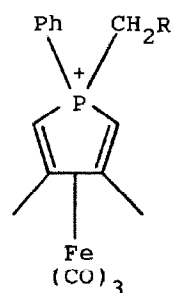
Nucleophilic substitution and addition reactions of the tricarbonyl( $\eta$ -cyclopentadienyl)-, tricarbonyl( $\eta$ -1,5-cyclohexadienyl)- and tricarbonyl( $\eta$ -1,5-cycloheptadienyl)-iron cations have been investigated. The six- and seven-membered ring cations were attacked by nitrite, cyanate, azide and dithiocarbamate ions to give the 5-exo ring adducts [226]. Several reactions of the ( $\eta$ -phosphole)iron complex (13.38) have been reported. Oxidation with hydrogen peroxide and treatment with sulphur gave the products (13.39; X = O, S) respectively while quaternization with benzylbromide and methyl iodide gave the salts (13.40; R = H, Ph). Ring expansion, dimerization



13.38



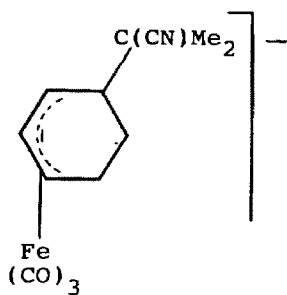
13.39



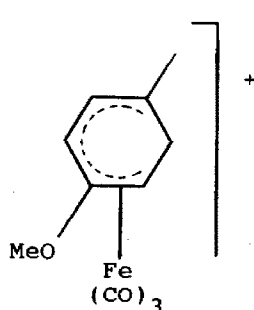
13.40

and complexation reactions were also described [227]. The addition of  $\text{LiCMe}_2\text{CN}$  to tricarbonyl( $\eta$ -cyclohexadiene)iron at  $-70^\circ\text{C}$  gave a homoallyl intermediate which on warming to  $0^\circ\text{C}$  gave the stable anionic allyl complex (13.41). Treatment of the homoallyl species with carbon monoxide followed by methylation gave an internally bound (alkene) (methoxy-alkylidene)tricarbonyliron complex [228].

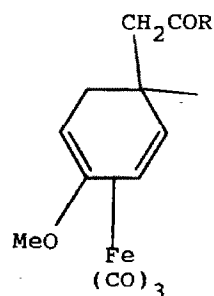
The ( $\eta$ -cyclohexadienyl)iron complex (13.42) underwent addition with the esters  $\text{RCH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{SiMe}_3$ , where  $\text{R} = \text{CH}_3\text{CO}$ ,  $\text{PhCO}$ , to form ( $\eta$ -cyclohexadiene)iron complexes which were



13.41

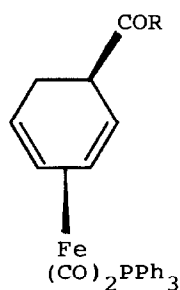


13.42

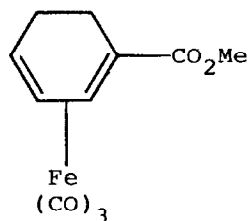


13.43

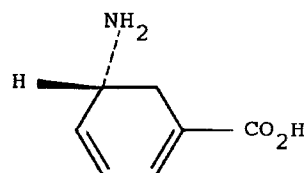
subsequently decarboxylated with tetrabutylammonium fluoride to form the products (13.43; R = Me, Ph) respectively [229].



13.44



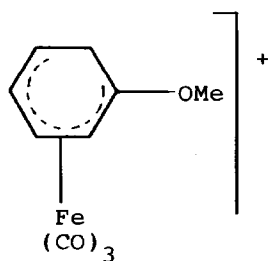
13.45



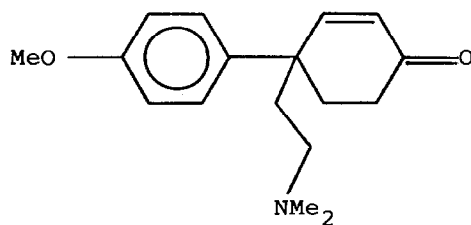
13.46

Friedel-Crafts acylation of dicarbonyl( $\eta$ -cyclohexadiene)triphenylphosphineiron with acetylchloride and benzoylchloride gave the ( $\eta$ -5-endo-acylcyclohexadiene)iron complexes (13.44; R = Me, Ph) [230]. The tricarbonyliron complex (13.45) has been used in the synthesis of (+)- and (-)- gabaculine (13.46). This is a naturally occurring amino acid which is an inhibitor of 4-aminobutyrate:2-oxoglutarate aminotransferase [231].

Pearson and co-workers have described the use of the 4-methoxycyclohexadienyl complex (13.47) as the synthetic equivalent of the *p*-anisyl cation for the synthesis of (+)-o-methyljouberti-

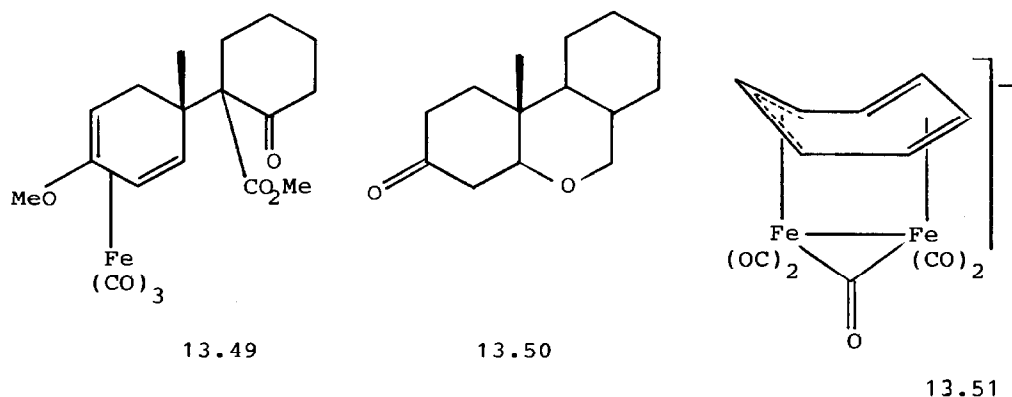


13.47



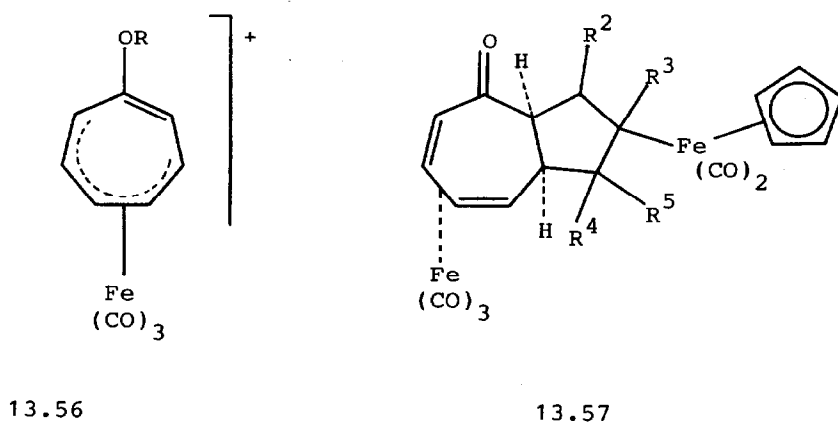
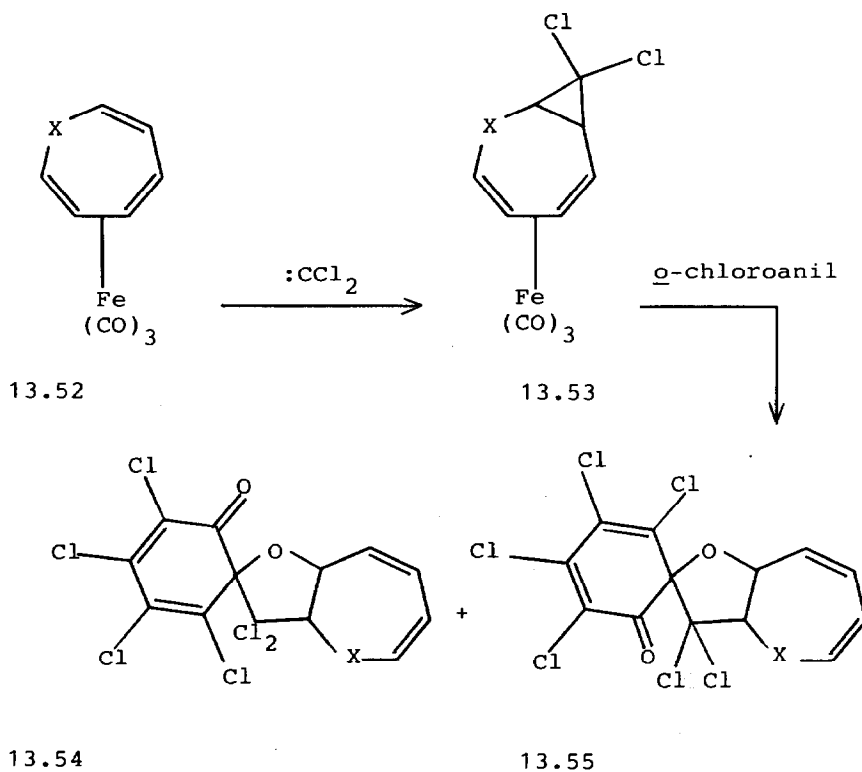
13.48

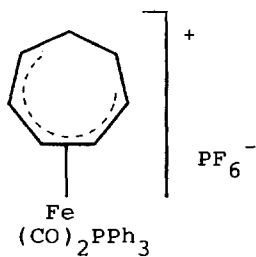
amine (13.48), a Sceletium alkaloid derivative [232]. The tricarbonyliron complex (13.49) has been used as the starting material in the preparation of the oxaperhydrophenanthrene (13.50) [233]. Deprotonation of the cycloheptatriene complex,  $(\eta\text{-C}_7\text{H}_8)\text{Fe}_2(\text{CO})_6$ , with  $\text{NaN}(\text{SiMe}_3)_2$  gave an unstable anionic complex,  $[(\eta\text{-C}_7\text{H}_7)\text{Fe}_2(\text{CO})_6]^-$  which decomposed with the loss of carbon monoxide to give the anionic complex (13.51). This species was



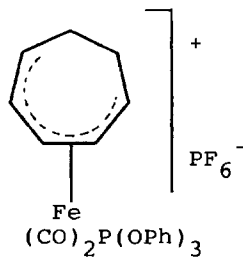
fluxional in solution and was characterized by X-ray crystallography [234]. Treatment of the tricarbonyliron complexes (13.52;  $\text{X} = \text{NCO}_2\text{Et}, \text{CH}_2$ ) with dichlorocarbene produced the corresponding addition products (13.53). These products underwent cycloaddition with *o*-chloroanil and removal of the tricarbonyliron moiety gave a mixture of the stereoisomers (13.54 and 13.55) [235].

Reaction of tricarbonyl( $\eta$ -tropone)iron with  $\text{RO}_2\text{CCF}_3$  gave the corresponding tropylium cations (13.56;  $\text{R} = \text{SiMe}_3, \text{BBu}_2$ ). Treatment of these cations with  $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}^1$ , where  $\text{R}^1 = \text{CH}_2\text{CH}=\text{CH}_2, \text{CH}_2\text{CH}=\text{CHMe}, \text{CH}_2\text{C}\equiv\text{CMe}, \text{CH}_2\text{C}\equiv\text{CSiMe}_3, \text{CH}=\text{C}=\text{CH}_2$ , produced the corresponding oxohydroazulene iron complexes (13.57;  $\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}, \text{R}^5 = \text{H}, \text{Me}; \text{R}^2 = \text{H}, \text{R}^3\text{R}^4 = \text{bond}, \text{R}^5 = \text{H}, \text{Me}; \text{R}^2\text{R}^3 = \text{bond}, \text{R}^4 = \text{R}^5 = \text{H}$ ) [236]. Pearson and co-workers have shown that the reactions of dicarbonyl(triphenylphosphine)-, (13.58) and dicarbonyl(triphenylphosphite)-( $\eta$ -cycloheptadienyl)iron salts (13.59) with nucleophiles give high yields

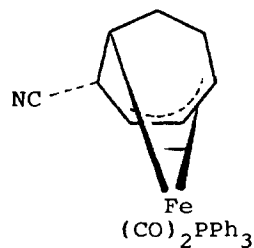




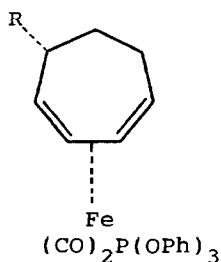
13.58



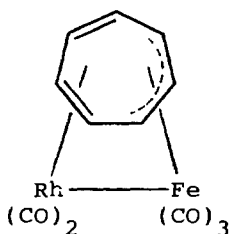
13.59



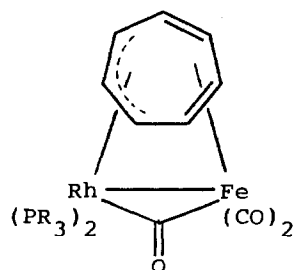
13.60



13.61



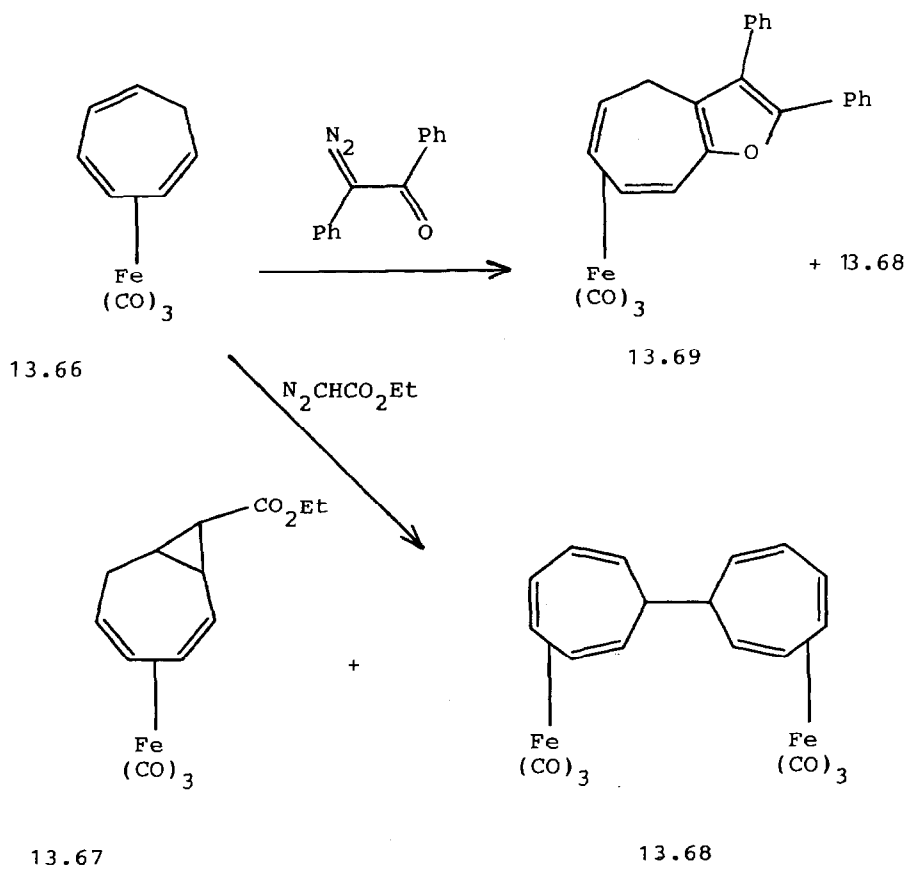
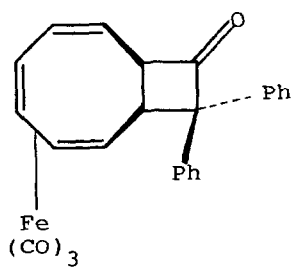
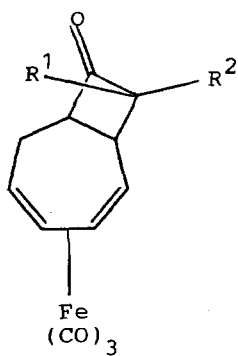
13.62



13.63

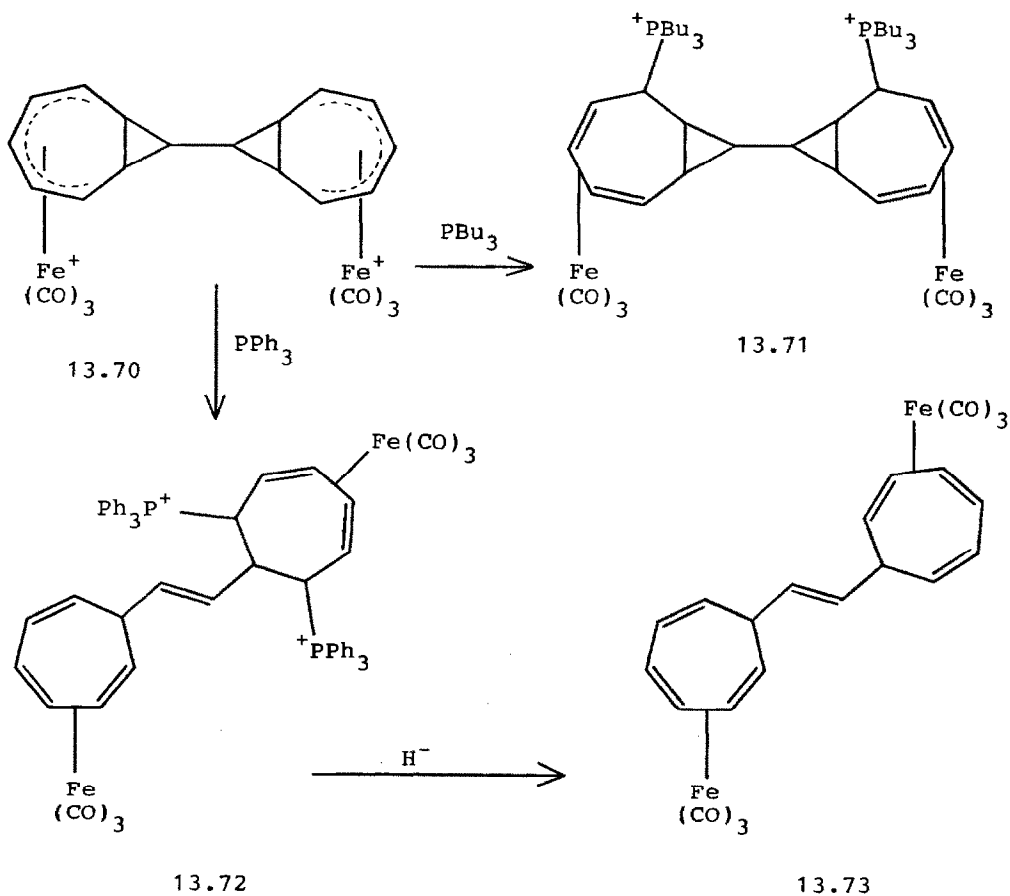
of single adducts. For example, cyanide ion, a "hard" nucleophile added to C(2) of the complex (13.58) to give the cyanide (13.60) whereas the "soft" nucleophiles thiophenoxide and *p*-nitrothiophenoxide added to the salt (13.59) to give the  $\eta$ -diene complexes (13.61; R = SPh, SC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*p*). Similar reactions with a range of nucleophiles were investigated [237].

Phosphine ligands displaced one or two carbonyl groups from the rhodium atom in the mixed metal complex (13.62). Thus PMe<sub>3</sub>, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> and Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> gave the product (13.63) in which the bonding mode had been reversed from  $\eta^4$ -Rh and  $\eta^3$ -Fe to  $\eta^3$ -Rh and  $\eta^4$ -Fe [238]. Cycloaddition of



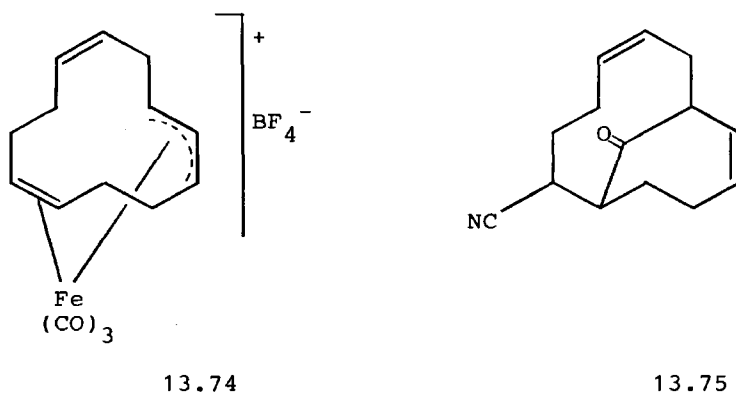


the ketenes  $R^1R^2C=C=O$  ( $R^1 = \text{Me}$ ,  $R^2 = \text{Ph}$ ;  $R^1 = R^2 = \text{Ph}$ ;  $R^1 = \text{Ph}$ ,  $R^2 = \text{p-tolyl}$ ) to tricarbonyl( $\eta^4$ -cycloheptatriene)iron gave regioselectively the corresponding cyclobutanones (13.64). Tricarbonyl( $\eta^4$ -cyclooctatetraene)iron underwent a similar reaction with diphenylketene to give the cyclobutanone (13.65). X-ray analysis of the complex (13.64;  $R^1 = \text{Ph}$ ,  $R^2 = \text{Me}$ ) confirmed the presence of the phenyl group at the endo position which provided stereochemical evidence for a concerted 2 + 2 mechanism [239]. Tricarbonyl( $\eta$ -cycloheptatriene)iron (13.66) combined with ethyl diazoacetate to form the expected 8-ethoxycarbonyl-homotropylidene complex (13.67) in addition to hexacarbonyl(bicycloheptatrienyl)diiron (13.68). However the corresponding reaction with azibenzil gave the oxidized adduct



(13.69) in addition to the dimer (13.68) [240].

The binuclear dication (13.70) combined with tributylphosphine to form the symmetrical diphosphonium adduct (13.71) while triphenylphosphine gave the unsymmetrical adduct (13.72) which was reduced with sodium borohydride to the neutral complex (13.73). The crystal and molecular structure of the adduct (13.72) was confirmed by X-ray crystallography [241]. The ruthenium complex,  $(\eta^4\text{-C}_8\text{H}_{12})\text{Ru}(\eta^6\text{-C}_8\text{H}_{10})$  was an effective catalyst for the homogeneous hydrogenation of 1,3- and 1,5-cyclooctadiene cyclooctene under mild conditions [242]. The photolysis of trans, trans, cis-1,5,9-cyclododecatriene with pentacarbonyliron

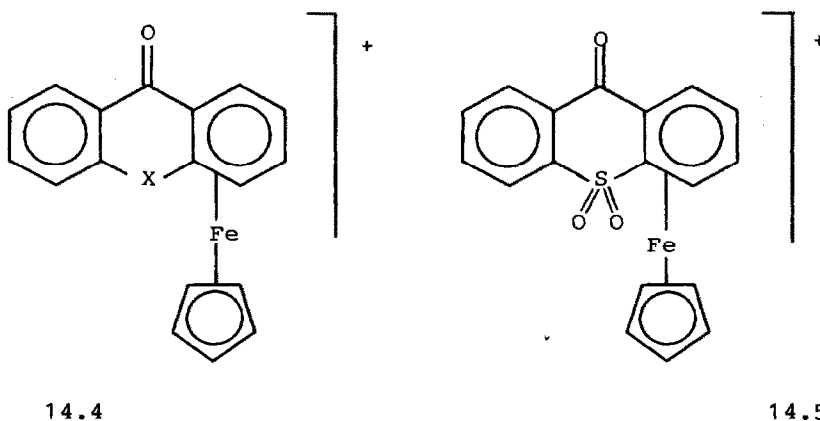
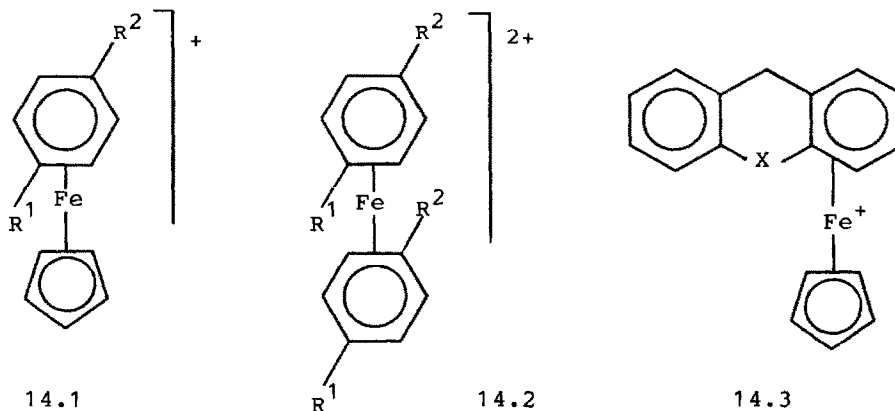


produced trans, trans, trans- and trans, trans, cis-1,5,9-cyclododecatrienetricarbonyliron. Reaction of the trans, trans, trans-product with  $\text{Ph}_3\text{CBF}_4$  afforded the trienyl salt (13.74) which on treatment with potassium cyanide gave the cyanoketone (13.75) [243].

#### 14. $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]^+$

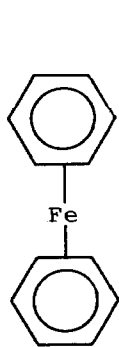
Ligand exchange between ferrocene and arenes in the presence of aluminium chloride gave the  $(\eta\text{-arene})$ iron cations (14.1;  $\text{R}^1 = \text{H}, \text{Me}$ ;  $\text{R}^2 = \text{Cl}, \text{F}, \text{MeO}$ ). At higher temperatures, the bis $(\eta\text{-arene})$ iron dications (14.2) were formed. The chloro group was displaced by nucleophiles, such as dimethylamine, morpholine, piperidine and azide, from the  $(\eta\text{-arene})$ iron

cation (14.1;  $R^1 = \text{H, Me, } R^2 = \text{Cl}$ ) [244]. The ( $\eta^6$ -xanthene)- and ( $\eta^6$ -thioxanthene)-iron complexes (14.3;  $X = \text{O, S}$ ) were prepared by ligand exchange between ferrocene and the appropriate heterocycle. The complexes (14.3) were oxidized with  $\text{KMnO}_4$  to form the ketones (14.4;  $X = \text{O, S}$ ), the thioxanthene complex

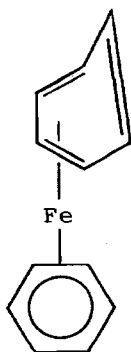


(14.3;  $X = \text{S}$ ) also gave the sulphone (14.5). Reduction and ring-opening reactions of the ketones (14.4) were described [245].

The products of cocondensation of iron atoms with benzene at both 7 and 77°K have been studied by Moessbauer spectroscopy. It was concluded that the 20-electron complex (14.6) and the 18-electron complex (14.7) were formed [246]. Iron, cobalt

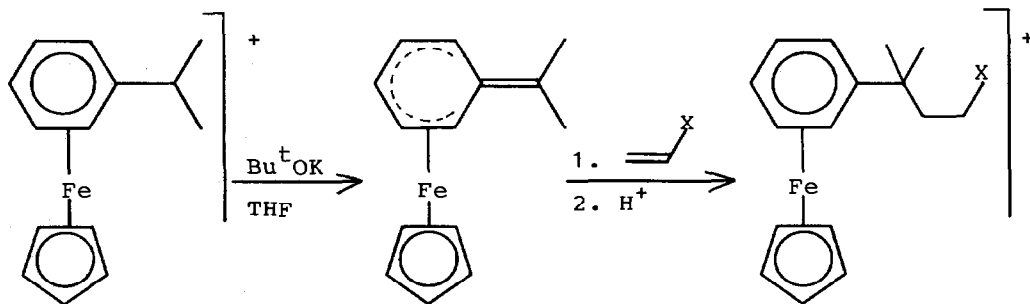


14.6



14.7

and nickel atoms have been condensed with benzene or toluene at liquid nitrogen temperatures to give unstable complexes with IR spectra analogous to the thermally stable bis( $\eta$ -arene)chromium complexes. The temperature dependence of the spectra suggested 1:1 complexes as precursors to more stable 1:2 complexes [247]. The reaction of iron atoms with decaborane(14) and either toluene or mesitylene under rotary metal atom conditions afforded 5- $[\eta^6\text{-C}_6\text{H}_5\text{CH}_3]\text{FeB}_9\text{H}_{13}$  and 5- $[\eta^6\text{-C}_6\text{Me}_3\text{H}_3]\text{FeB}_9\text{H}_{13}$  respectively. The structures of these compounds were confirmed by X-ray analysis [248].

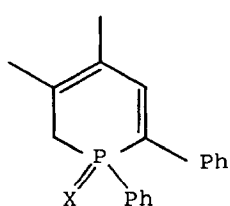


14.8

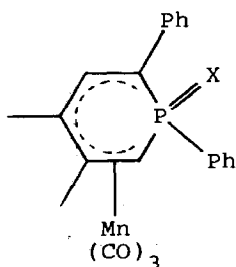
14.9

14.10

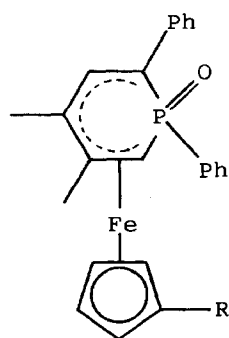
Neutral ( $\eta$ -cyclohexadienyl)iron complexes with exocyclic C=C or C=N bonds combined with Michael acceptors to give cationic adducts after protonation. Thus the ( $\eta$ -isopropylbenzene)iron complex (14.8) was deprotonated using potassium *t*-butoxide to give the neutral complex (14.9) which underwent addition with acrylonitrile and methyl acrylate to form the cationic products (14.10; X = CN, CO<sub>2</sub>Me) after hydrolysis [249].



14.11



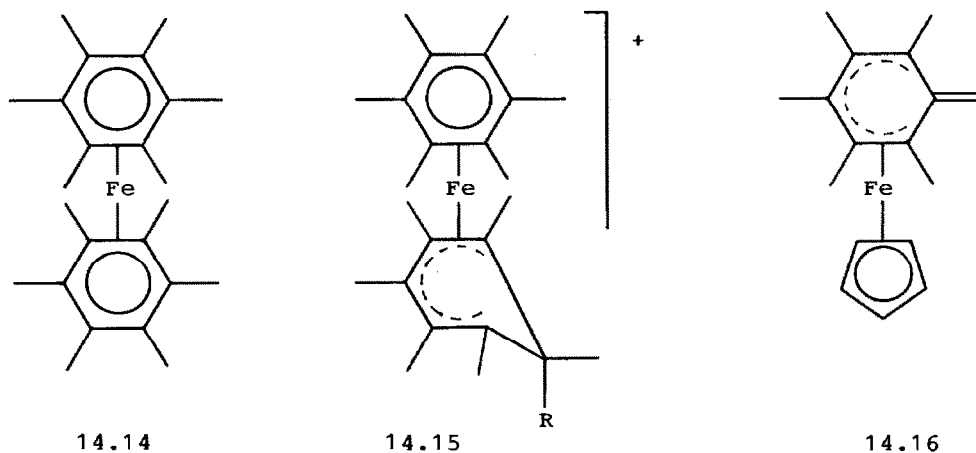
14.12



14.13

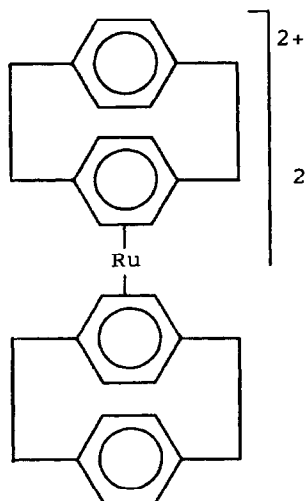
One of the products from the reaction of Mn<sub>2</sub>(CO)<sub>10</sub> with the phosphorin (14.11; X = S) was the tricarbonylmanganese complex (14.12; X = S). In a similar reaction the oxide (14.11; X = O) produced the complex (14.12; X = O). Reaction of the oxide (14.11; X = O) with [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>]<sub>2</sub> produced the iron complex (14.13; R = H). Treatment of this latter compound with *n*-butyllithium led to replacement of the P-Ph group by P-Bu and acylation with acetyl chloride-aluminium chloride gave the acetyl derivative (14.13; R = COCH<sub>3</sub>) [250].

Several reactions of the 20-electron bis( $\eta$ -arene)iron complex (14.14) have been reported. Organic halides, such as PhCH<sub>2</sub>Br, PhCOCl, BrCH<sub>2</sub>CO<sub>2</sub>Et, gave the cationic ( $\eta$ -cyclohexadienyl)iron complexes (14.15; R = CH<sub>2</sub>Ph, CPh, CH<sub>2</sub>CO<sub>2</sub>Et) respectively. Oxidation gave either a bis( $\eta$ -arene)iron cation or an ( $\eta$ -arene)( $\eta$ -cyclohexadiene)iron complex depending on the conditions used [251]. Poly(vinyl chloride) and chloromethylated polystyrene have been treated with the ( $\eta$ -cyclohexadienyl)iron complex (14.16) to form polymer supported redox catalysts.

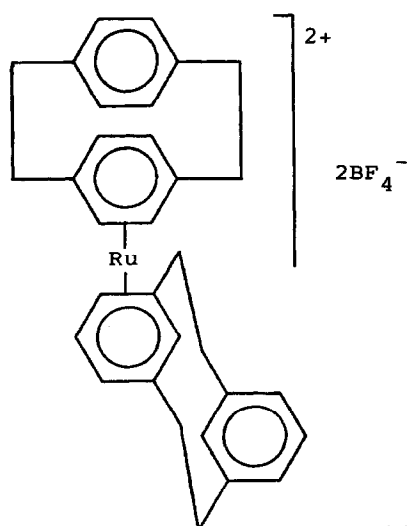


Some degradation of the polymer chain occurred during preparation and the viscosity of the polymer decreased linearly with an increase in the iron content [252]. Chloromethylated polystyrene and PVC have been treated with the ( $\eta$ -cyclohexadienyl)-iron complex (14.16) to give the corresponding polymer supported redox catalyst. The physical properties of the product were evaluated [252].

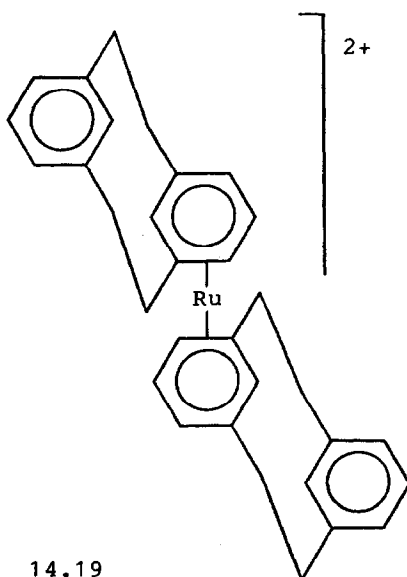
A general procedure has been reported for preparing bis-( $\eta^6$ -[2<sub>n</sub>]cyclophane)ruthenium(II) compounds via ruthenium(0) intermediates. The reduction of ( $\eta^6$ -benzene){ $\eta^6$ -[2<sub>2</sub>](1,4)cyclophane}ruthenium(II) afforded ( $\eta^4$ -1,3-cyclohexadiene){ $\eta^6$ -[2<sub>2</sub>](1,4)-cyclophane}ruthenium(0) which on treatment with hydrochloric acid produced the corresponding di- $\mu$ -chlororuthenium(II) species. Reaction of this latter compound with silver tetrafluoroborate in the presence of [2<sub>2</sub>](1,4-cyclophane) generated the  $\eta^6$ -[2<sub>2</sub>](1,4-cyclophane) complex (14.17). The  $\eta^6$ -cyclophane complexes (14.18 and 14.19) were prepared by similar routes [254]. Treatment of ( $\eta^4$ -cycloocta-1,5-diene){ $\eta^6$ -cycloocta-1,3,5-triene}ruthenium with naphthalene under hydrogen produced the  $\eta^6$ -naphthalene compounds (14.20) which underwent arene exchange reactions in the presence of methyl cyanide. For example, reaction of the complex (14.20) with chlorobenzene afforded the  $\eta^6$ -arene compound (14.21) [255]. The reaction of the  $\eta$ -arene-Ru complexes (14.22;  $\text{PR}_3 = \text{PMe}_3, \text{PMePh}_2$ ) with  $\text{AgPF}_6$  produced the dinuclear complexes (14.23).



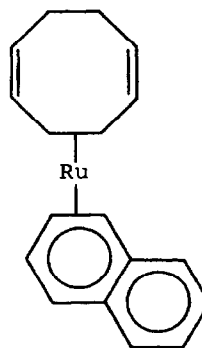
14.17



14.18

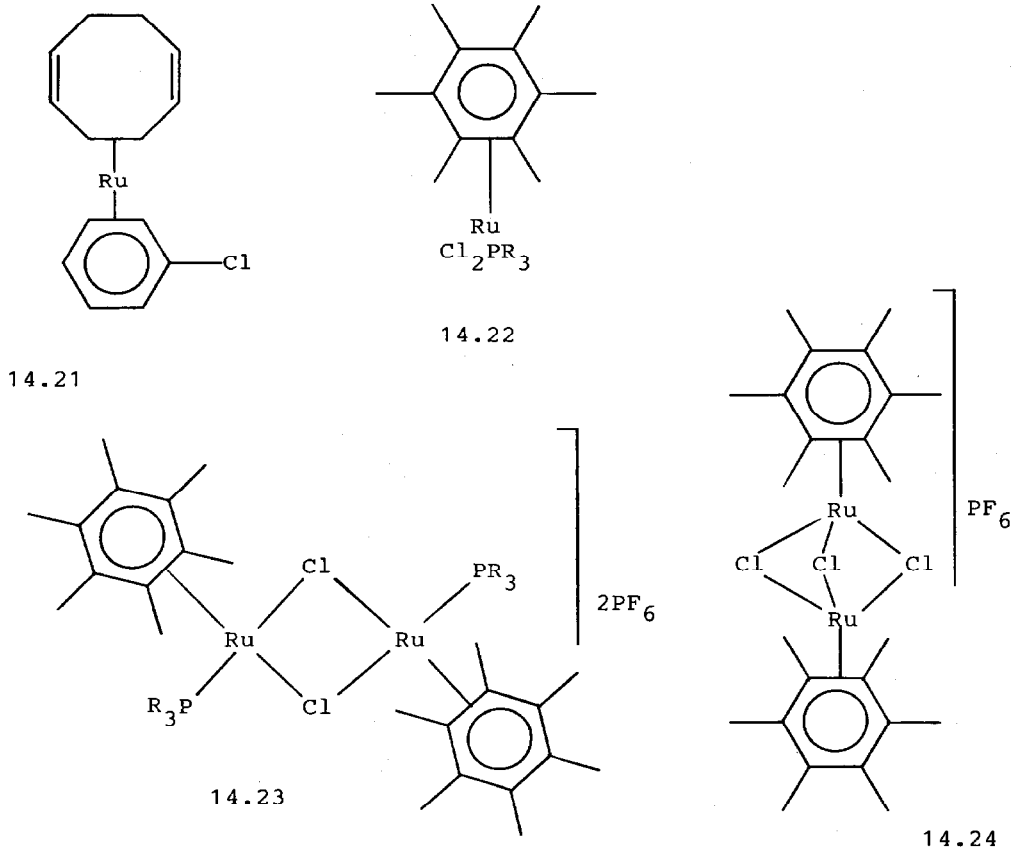


14.19



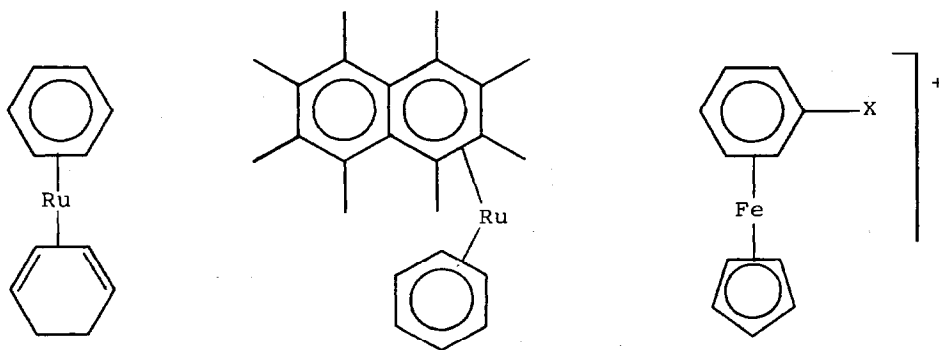
14.20

The dinuclear complex (14.24) was prepared by a similar route and the structure was determined by X-ray analysis [256]. The direct reaction of 1,3-cyclohexadiene with ruthenium(III) chloride in the presence of metallic zinc gave the ruthenium(0) complex (14.25). A similar route was used to prepare ( $\eta^4$ -1,5-cyclooctadiene)( $\eta^6$ -1,3,5-cyclooctatriene)-ruthenium(0), bis( $\eta^5$ -2,4-cycloheptadienyl) ruthenium(II) and ruthenocene [257].



Reaction of ( $\eta^4$ -1,5-cyclooctadiene)( $\eta^6$ -1,3,5-cyclooctatriene) ruthenium with chiral arenes produced the corresponding ( $\eta^6$ -arene)( $\eta^4$ -1,5-cyclooctadiene)ruthenium complexes where arene =  $C_6H_5OCHMeEt$ ,  $C_6H_5CHMeOEt$ , 4- $MeC_6H_4CHMeEt$ . The  $^1H$  NMR spectra of the latter two complexes, arene =  $C_6H_5CHMeOEt$  or 4- $MeC_6H_4CHMeEt$  and ( $\eta^6$ -PhCHMeEt)( $\eta^4$ -norbornadiene)ruthenium showed a large anisochronicity of the ortho and meta protons of the arene rings [258]. Octamethylnaphthalene ( $C_{10}Me_8$ ) combined with the ruthenium complexes,  $[(\eta\text{-arene})RuCl_2]_2$ , where arene = benzene, substituted benzene, to give bis-arene complexes,  $[(\eta^6\text{-}C_{10}Me_8)Ru(\eta^6\text{-arene})]^{2+}$ . These complexes were easily reduced with sodium amalgam to the neutral complexes  $(\eta^4\text{-}C_{10}Me_8)Ru(\eta^6\text{-arene})$ . The crystal and molecular structure of one complex (14.26) was confirmed by X-ray crystallography and this complex was

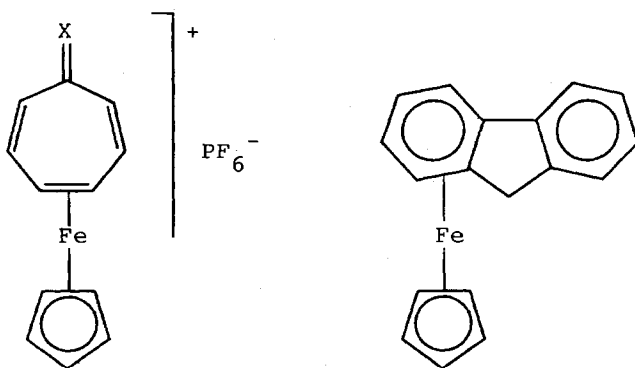




14.25

14.26

14.27

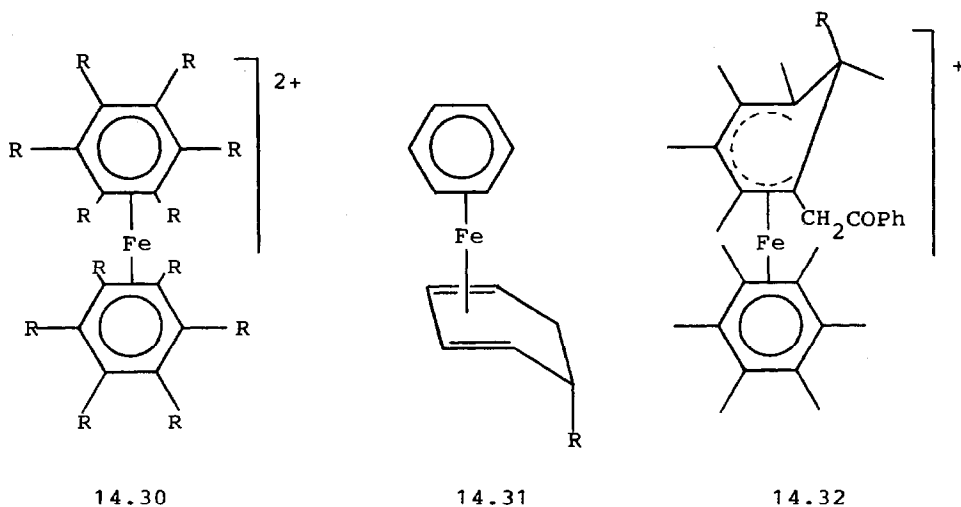


14.28

14.29

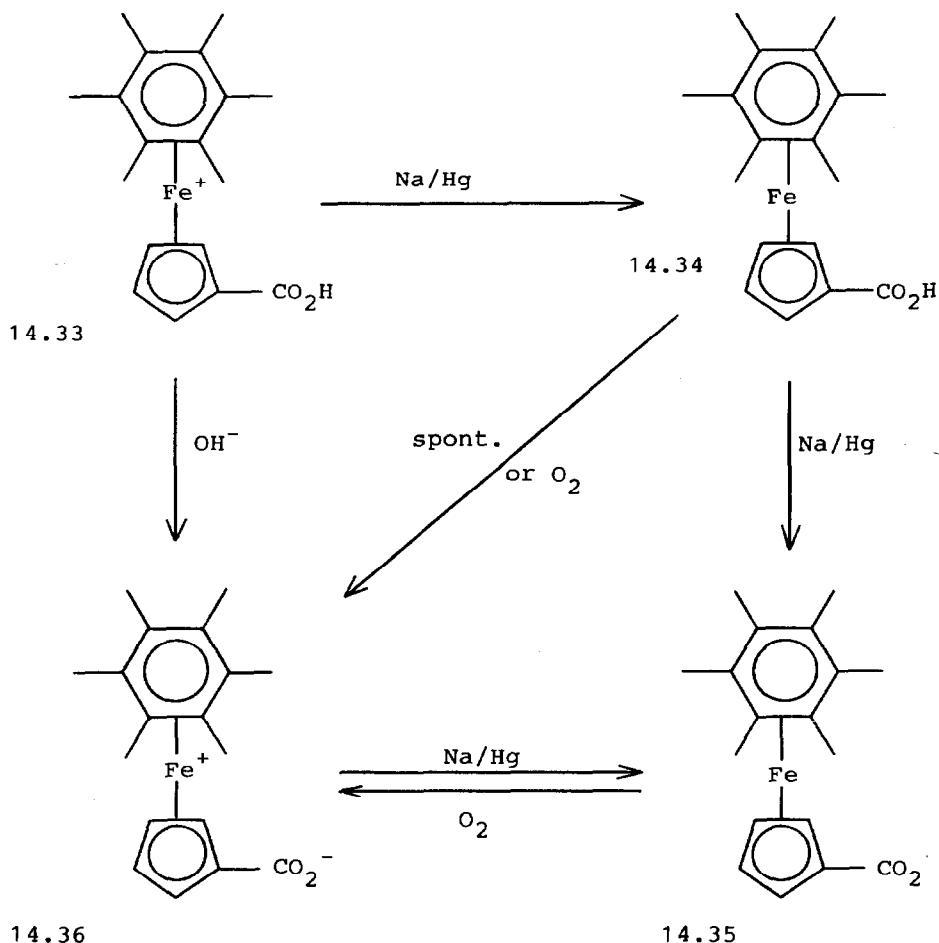
converted to a binuclear species,  $(\eta\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-C}_{10}\text{Me}_8)\text{Cr}(\text{CO})_3$  with  $\text{Cr}(\text{CO})_3(\text{MeCN})_3$  and to a cyclohexadienyl complex  $[(\eta\text{-C}_6\text{H}_6)\text{Ru}(\eta\text{-C}_{10}\text{Me}_8\text{H})]^+$  on protonation [259]. The ( $\eta$ -chlorobenzene)iron cation (14.27;  $\text{X} = \text{Cl}$ ) has been attacked by  $\text{NaOH}$  and  $\text{NaSH}$  to form the phenoxide and thiophenoxide complexes (14.27;  $\text{X} = \text{O}^-$ ,  $\text{S}^-$ ) which were treated with diazomethane to give the ring expansion products (14.28;  $\text{X} = \text{O}$ ,  $\text{S}$ ).  $^{13}\text{C}$  NMR spectroscopy suggested that the tropone- or trophione-iron bonding was different from that observed in  $(\eta^4\text{-tropone})\text{Fe}(\text{CO})_3$  [260].

The unstable 19-electron iron(I) complex (14.29) and the 9-exo- and endo-methyl derivatives have been prepared by reduction of the cationic precursors as  $\text{PF}_6^-$  salts on a sodium

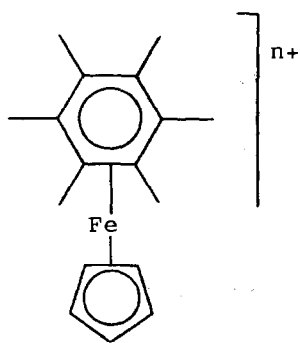


mirror. Addition of oxygen to these complexes caused C-H activation with the formation of zwitterions. From these results it was suggested that an outer-sphere electron transfer occurred from the iron(I) complex to oxygen forming ion pairs  $\{[(\eta\text{-C}_5\text{H}_5)(\eta\text{-arene})\text{Fe}(\text{II})]^+ \text{O}_2^-\}$  [261]. Functional groups have been introduced into a benzene ligand in the bis( $\eta$ -benzene)iron dication (14.30; R = H) by reduction with  $\text{NaBH}_4$  and then treatment of the cationic ( $\eta$ -cyclohexadienyl)iron intermediate with carbanions such as  $\text{CN}^-$ ,  $\text{CH}(\text{CO}_2\text{Et})_2^-$ ,  $\text{PhCH}_2^-$  to give the ( $\eta$ -arene)( $\eta$ -cyclohexadiene)iron complexes (14.31). A similar reaction sequence using the dication (14.30; R = Me) gave the difunctional ( $\eta$ -cyclohexadienyl)iron cations [14.32; R =  $\text{PhCH}_2$ ,  $\overline{\text{CHS}(\text{CH}_2)_3\text{S}}$ ] [262]. The dicationic complexes  $\{[(\eta^6\text{-C}_6\text{H}_6)\text{-M}(\text{C}_n\text{Me}_n)]\}^{2+}$ , where M = Ru, n = 6; M = Rh, Ir, n = 5, have been reduced with sodium tetrahydroborate to give the corresponding  $\eta^5$ -cyclohexadienyl complexes which were further reduced to the  $\eta^4$ -cyclohexadiene complexes  $\{[(\eta^4\text{-C}_6\text{H}_6)\text{M}(\text{C}_n\text{Me}_n)]\}$ . Treatment of these latter complexes with acid produced cyclohexene exclusively. The efficiency of the overall reduction of benzene to cyclohexene increased in the order  $\text{Ir} < \text{Ru} < \text{Rh}$  [263].

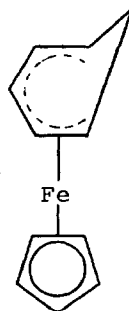
The interrelationships between some functional ( $\eta$ -benzene)-( $\eta$ -cyclopentadienyl)iron complexes have been investigated. Thus the cationic complex (14.33) has been reduced with sodium amalgam to the blue 19-electron complex (14.34) which was thermally labile and air sensitive. The complex (14.34) was



slowly converted under the same conditions to the purple, 19-electron, reactive, radical anion (14.35), the complex (14.34) also underwent spontaneous conversion to the yellow zwitterion (14.36). Both of the 19-electron complexes (14.34 and 14.35) were oxidized by oxygen to the product (14.36) [264]. The structure of ( $\eta^5$ -cyclopentadienyl)( $\eta^6$ -tetraphenylborato)iron has been determined by X-ray analysis. The iron atom was 1.66Å from the plane defined by the carbon atoms of the  $\eta^5$ -cyclopentadienyl ring and 1.54Å from the plane defined by the carbon atoms of the  $\eta^6$ -phenyl ring [265].

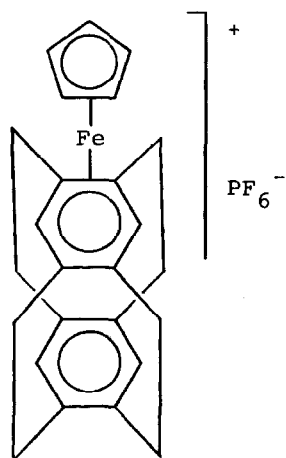


14.37

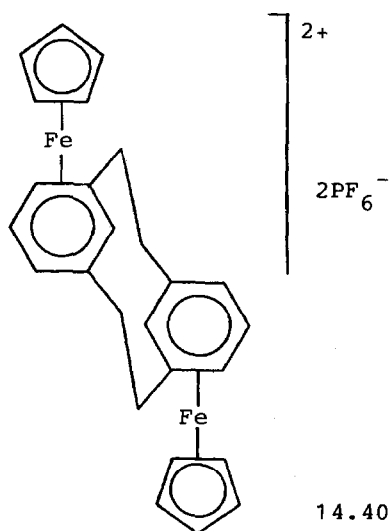


14.38

A theoretical study of the iron(I) and iron(II) complexes (14.37;  $n = 0, 1$ ) and related diamagnetic  $\eta$ -cyclohexadienyl-iron complexes such as (14.38) has been carried out using IEHMO calculations. Moessbauer spectroscopic and X-ray crystallographic results for the same complexes were obtained. It was concluded that negligible relaxation of the appropriate MO's occurred during reduction of iron(II) to iron(I). The iron(I)



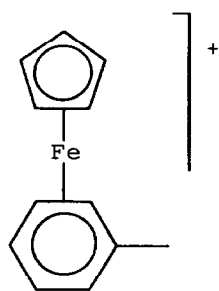
14.39



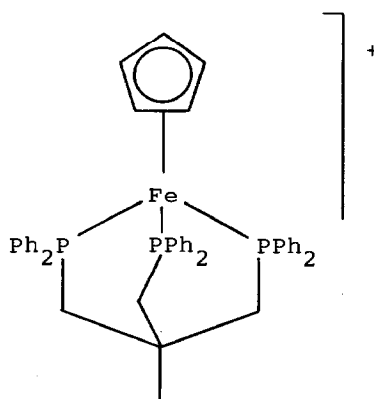
14.40

was best regarded as a combination of an iron(II) complex and an electron which occupied a doubly degenerate  $e^*_1$  orbital with 83% metallic character [266]. A Moessbauer study has been carried out on the twenty electron iron(0) complex (14.14). The results confirmed that the complex was paramagnetic and that it had  $D_{6h}$  symmetry [267]. The electrochemical reduction of six  $[(\eta-C_5H_5)Fe(\eta^6-cyclophane)]^+PF_6^-$  complexes, for example the cyclophane (14.39) and four  $\{[(\eta-C_5H_5)Fe]_2(cyclophane)\}^{2+}(PF_6)_2^{2-}$  complexes, for example the cyclophane (14.40) has been studied by cyclic voltammetry, polarography, chronoamperometry and coulometry. The complexes containing one iron atom were reduced in two one-electron steps (+/0/-) and those with two iron atoms also reduced in two one-electron steps (2+ / +/0). Decomposition of the reduced complexes proceeded via loss of the cyclophane followed by disproportionation of the  $(\eta-C_5H_5)Fe$  fragment to ferrocene and Fe(0) [268].

Electrochemical and physicochemical studies have been carried out on  $(\eta\text{-hexamethylbenzene})(\eta\text{-cyclophane})$ ruthenium complexes and a bis( $\eta\text{-hexamethylbenzeneruthenium}$ )cyclophane mixed-valance complex [269]. Photolysis of the cation (14.41) in the presence of the ligand  $CH_3C(CH_2PPh_2)_3$  produced the complex (14.42) in good yield [270]. Hexamethyl(Dewar benzene) has been shown to undergo photo-catalysed isomerization to hexamethylbenzene in the presence of the  $\eta\text{-arene-iron}$  complexes (14.43;

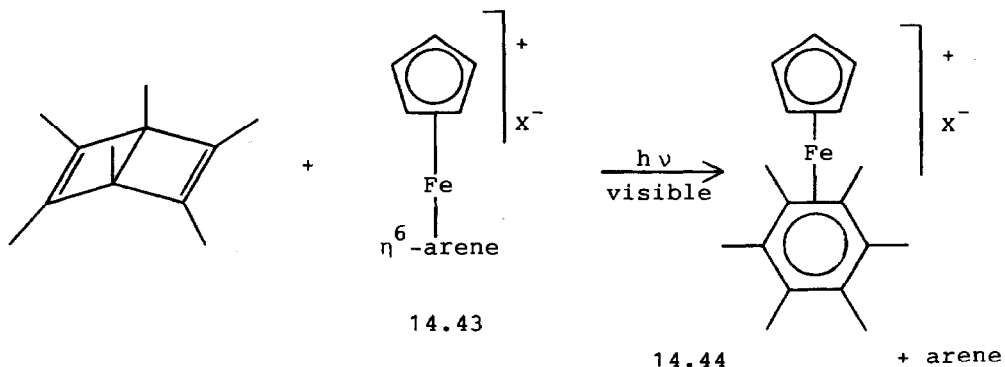


14.41



14.42

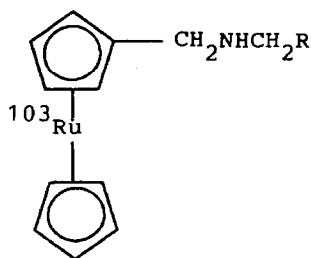
$\eta^6$ -arene = naphthalene, benzene, *p*-xylene, durene;  $X = \text{PF}_6^-$ ,  $\text{BF}_4^-$ ) to give the complex (14.44). Mixtures of hexamethyl- (Dewar benzene) and the arene complexes exhibited a luminescence band at 530–540 nm which was attributed to the formation of the corresponding exciplex [271].



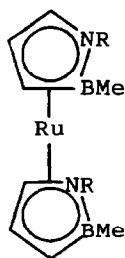
The photochemical removal of arenes from a series of iron and ruthenium complexes of the type  $[(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-arene})\text{M}]^+$  has been investigated. The photoactive state in these compounds was identified as the distorted  $a^3E_1$  ligand field excited state. In the presence of chloro- and methyl-substituted arenes a linear correlation existed between  $\log [\phi/(1-\phi)]$ , where  $\phi$  was the quantum yield, and the Hammett parameter  $\sigma_p$  [272]. ( $\eta^6$ -Arene)-( $\eta^4$ -cycloocta-1,5-diene)ruthenium complexes, where arene = benzene, *p*-xylene or mesitylene, have been found to be catalytic precursors for the homogeneous hydrogenation of  $\alpha$ -olefins and cycloolefins under mild conditions [273].

#### 15. $(\eta\text{-C}_5\text{H}_5)_2\text{Ru}$ and $(\eta\text{-C}_5\text{H}_5)_2\text{Os}$

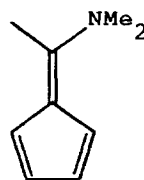
Ferrocene underwent ligand exchange with  $^{103}\text{RuCl}_3$  at  $180^\circ\text{C}$  to give labelled ruthenocene which was converted to the amines [15.1;  $\text{R} = \text{Ph}$ ,  $\text{PhCH}_2$ ,  $4\text{-HOC}_6\text{H}_4\text{CH}_2$ ,  $3,4\text{-(MeO)}_2\text{C}_6\text{H}_3\text{CH}_2$ ] by way of formylruthenocene [274]. The ruthenocenes (15.1) were injected into rats and the distribution of radioactivity determined [275]. Substituted 1,2-azaborolinyllithium compounds have been treated with ruthenium(II) chloride in THF at  $-70^\circ\text{C}$  to give the ( $\eta$ -1,2-azaborolinyllithium)ruthenium complexes (15.2;  $\text{R} = \text{CMe}_3$ ,  $\text{SiMe}_3$ ).



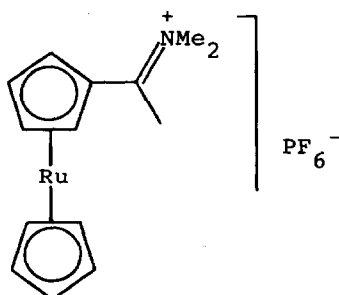
15.1



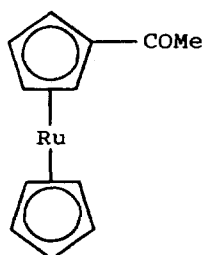
15.2



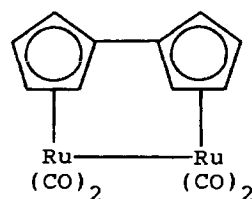
15.3



15.4



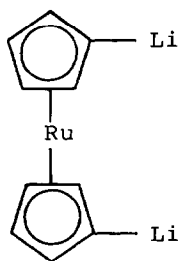
15.5



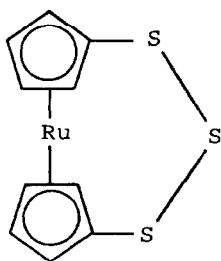
15.6

The azaborolanyl rings in each of the complexes (15.2) adopted clockwise or anticlockwise arrangements and thus gave two isomeric forms. The crystal and molecular structure of one complex (15.2;  $R = CMe_3$ ) was determined by X-ray crystallography [276]. The salt  $[(\eta-C_5H_5)Ru(MeCN)_3]^+ PF_6^-$  has been treated with 6-dimethylaminopentafulvenes to give the corresponding ruthenocenyl salts. Thus the fulvene (15.3) gave the ruthenocene (15.4) which was converted to the acetyl derivative (15.5) with ethanol and sodium hydroxide [277].

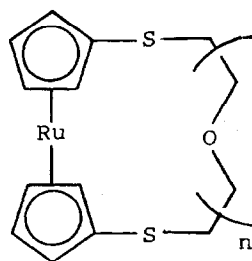
Dimetallafulvalene carbonyl complexes have been obtained by the addition of purified dihydrofulvalene to metal carbonyls. Among the complexes prepared was the diruthenium tetracarbonyl (15.6) which was derived from  $Ru_3(CO)_{12}$  [278]. The reaction of 1,1'-dilithioruthenocene (15.7) with sulphur produced the ruthenocenophane (15.8) which was reduced to give ruthenocene-1,-



15.7



15.8



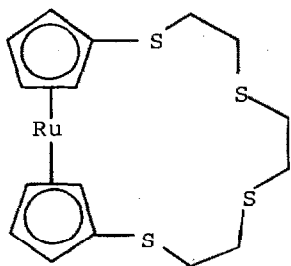
15.9

1'-dithiol. Treatment of the sodium salt of this dithiol with a series of dibromides afforded the corresponding ruthenocenophanes (15.9;  $n = 2, 3, 4$ ). The ability of these ruthenocenophanes to form complexes with transition metal ions was investigated [279]. Akabori and co-workers have reported the syntheses of a series of polythia[ $n$ ]ruthenocenophanes. The reaction of the disodium salt of 1,1'-diruthenocenedithiol with 1-bromo-2-chloroethane produced 1,1'-bis(3-chloropropyl-1-thia)ruthenocene which on treatment with disodium 1,2-ethanedithiolate produced the ruthenocenophane (15.10) as the major product together with trace amounts of the ruthenocenophanes (15.11, 15.12 and 15.13) [280]. The ruthenocenophanes (15.14 and 15.15) have been prepared via cyclization of the corresponding propionic acid derivatives with polyphosphoric acid or trifluoroacetic anhydride. Reduction of the ketones with  $\text{LiAlH}_4\text{-AlCl}_3$  produced the ruthenocenophanes (15.16 and 15.17) respectively. The spectra of these compounds were discussed and compared with those of monobridged ruthenocenes [281]. Ferrocene and ruthenocene diols have been condensed with dithiols to form hetero[ $n$ ](1,1')ferroceno- and ruthenoceno-phanes which were separated by partition thin-layer chromatography and high performance thin-layer chromatography [282]. Labelled [ $^{103,106}\text{Ru}$ ]ruthenocene has been converted to dimethylaminomethylruthenocene and then to the labelled ruthenocenylmalonate (15.18). Hydrolysis and decarboxylation of the malonate gave the labelled ruthenocenyl-alanine (15.19) which was examined as a pancreatic imaging

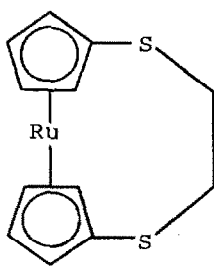


agent. Selective uptake by the pancreas was not observed in either rats or mice [283].

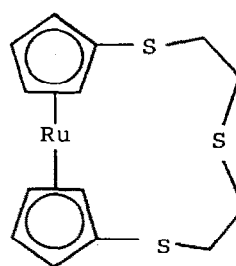
The ferrocene derivative of glycine (15.20) underwent metal exchange with  $^{103}\text{RuCl}_3$  to give the corresponding ruthenocene compound (15.21;  $\text{R} = \text{Et}$ ). The compound was saponified to produce the acid (15.21;  $\text{R} = \text{H}$ ) which was used as a radiopharmaceutical in rats and mice [284]. Treatment of  $(\eta^4\text{-hexamethylbenzene})(\eta^6\text{-hexamethylbenzene})\text{ruthenium}$  (15.22) with hydrochloric



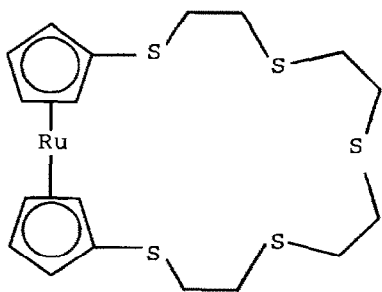
15.10



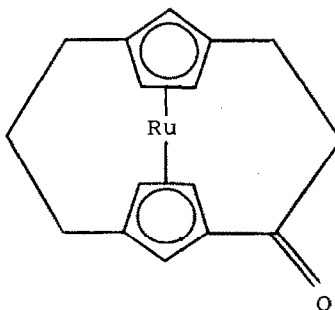
15.11



15.12

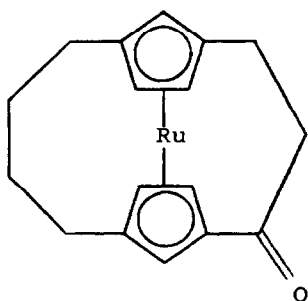


15.13

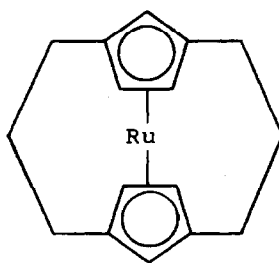


15.14

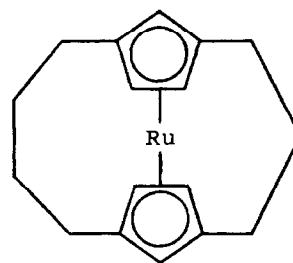
acid in acetone gave the  $(\eta\text{-cyclohexadienyl})\text{ruthenium}$  cation (15.23) which was reduced with sodium bis(2-methoxyethoxy)-aluminum hydride in THF to the bis $(\eta\text{-cyclohexadienyl})\text{ruthenium}$  complex (15.24) an analogue of ruthenocene [285]. Poly(vinylruthenocene) and the copolymers of vinylruthenocene with methyl-



15.15



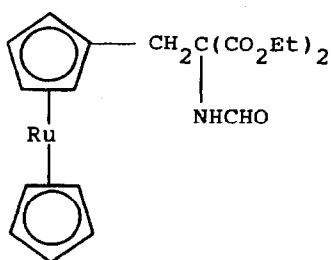
15.16



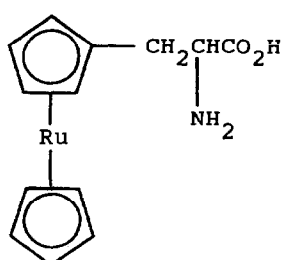
15.17

methacrylate, styrene and N-vinylpyrrolidinone have been prepared by free radical polymerization. The polymers were examined thermogravimetrically and they showed little weight loss up to 300°C but decomposed rapidly at temperatures >300°C [286].

Vinylsocene and vinylruthenocene have been homopolymerized and copolymerized with other organometallic monomers to give polymers for use in inertial fusion studies. The homopolymers had higher softening points and glass transition temperatures than the copolymers [287]. The ruthenium halide cations (15.25; X = Cl, Br) have been attacked by water to form ruthenocene and the ring-oxidation products (15.26; X = Cl, Br). The crystal and molecular structure of one of these products (15.25; X = Br)



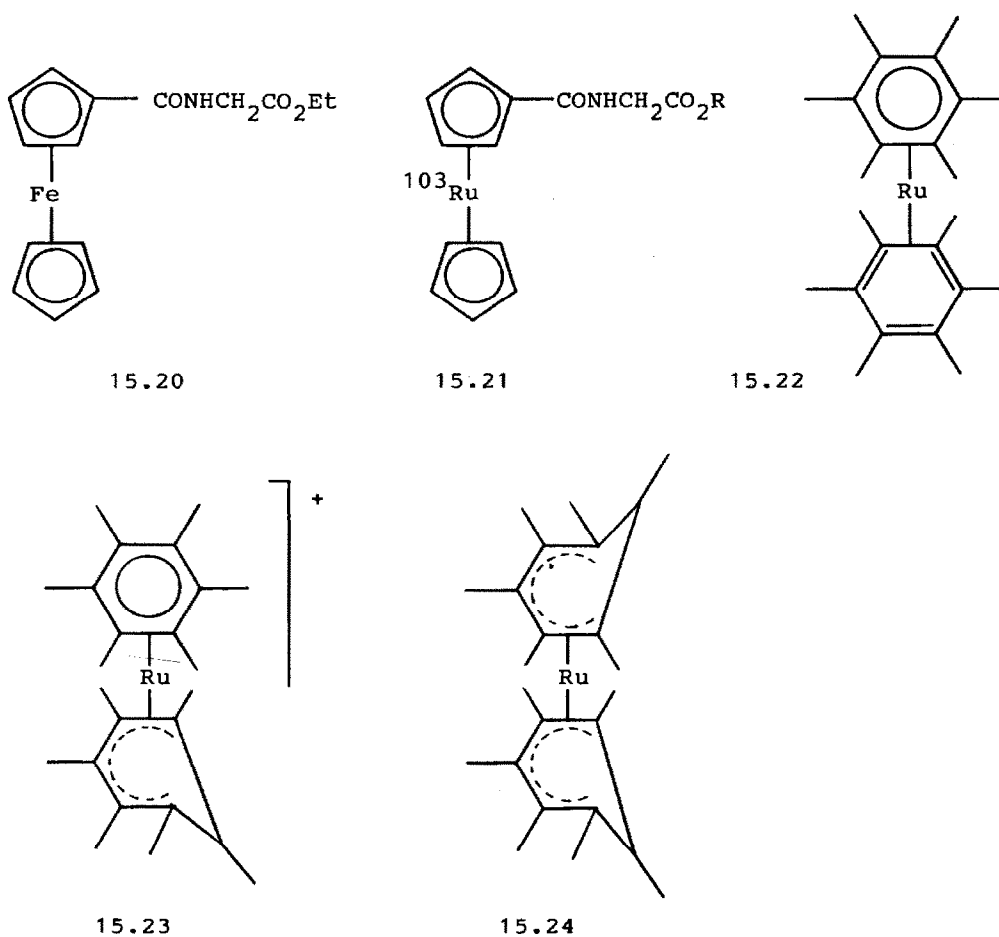
15.18

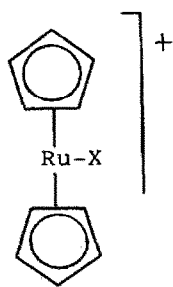


15.19

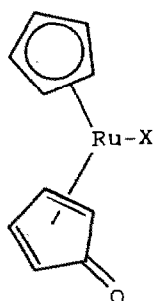
has been determined by X-ray crystallography. The five-membered rings adopted a staggered conformation and were inclined away from the bromine [288]. Assignment of the  $^{13}\text{C}$  NMR resonance signals in the cryptands (15.27;  $\text{M} = \text{Fe}, \text{Ru}$ ;  $m, n = 1, 2, 3$ ) has been carried out by the insensitive nuclear enhancement by polarization transfer and distortionless enhancement by polarization transfer techniques. A trans disposition of the carbonyl groups in the cryptands (15.27) was inferred [289].

Reaction of formyl-ruthenocene and -ferrocene with  $p\text{-FC}_6\text{H}_4\text{MgBr}$  produced the corresponding alcohols which in trifluoroacetic acid gave the carbenium ions (15.28;  $\text{M} = \text{Ru}, \text{Fe}$ ).  $^{19}\text{F}$  NMR spectroscopy indicated that the ruthenocenyl group was more effective

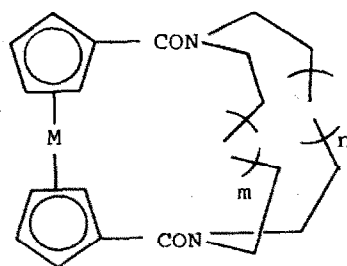




15.25



15.26

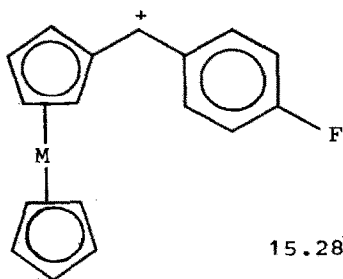


15.27

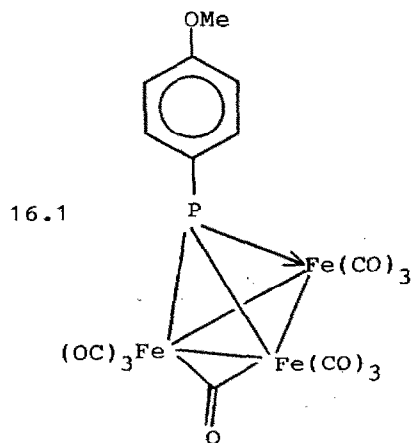
in charge delocalization than the ferrocenyl group [290]. The 280 nm continuous photolysis of ruthenocene in carbon tetrachloride gave initially  $[(\eta\text{-C}_5\text{H}_5)_2\text{RuCl}]^+$  and not the ruthenocenium ion as previously reported [291].

#### 16. Iron, Ruthenium and Osmium Cluster Compounds

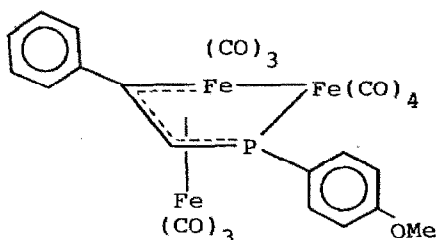
The triiron cluster complex (16.1) has been attacked by phenylacetylene to give the product of Fe-P bond insertion (16.2). The corresponding reaction with diphenylacetylene gave a diferra-



15.28

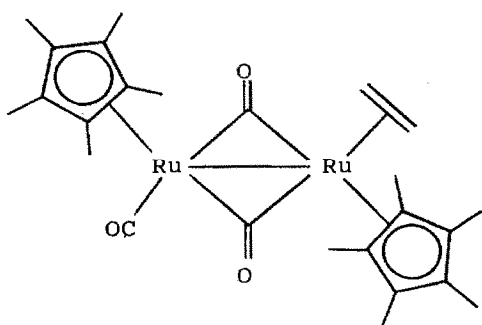


16.1

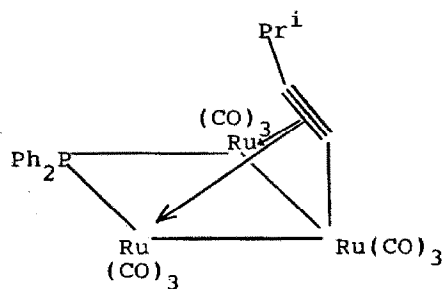


16.2

phosphacyclopentadienyl iron complex [292]. The cluster compounds  $(\mu\text{-H})(\mu\text{-CO})\text{Fe}_3(\text{CO})_9\text{BH}_2(\mu\text{-CO})\text{Fe}_3(\text{CO})_9\text{BH}_2^-$  and  $\text{Fe}_3(\text{CO})_9\text{BH}_4^-$  have been prepared and characterized. The  $^{11}\text{B}$  NMR spectra indicated that the capping B in  $\text{HFe}_3(\text{CO})_{10}\text{BH}_2$  was similar to the capping C in the isoelectronic cluster  $\text{HFe}_3(\text{CO})_{10}\text{CH}$  [293]. Carbon monoxide coupled with the ethylidene ligand in the complex  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-CMe})][\text{PPh}_4]$  during electrochemical one-electron reduction and afforded the propynolate complex  $[\text{Fe}_3(\text{CO})_9(\mu_3, \eta^2\text{-MeC}\equiv\text{CO})][\text{PPh}_4]_2$ . The structure of this product was confirmed by X-ray crystallography [294]. The ethylene ligand in the diruthenium complex (16.3) underwent isomerization to the ethylidene ligand on UV irradiation in toluene. Other ligand transformations were observed under similar conditions [295].



16.3

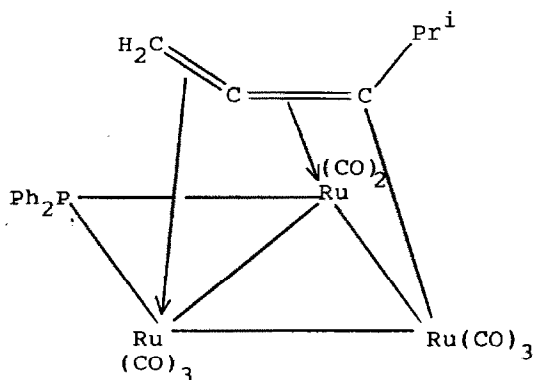


16.4

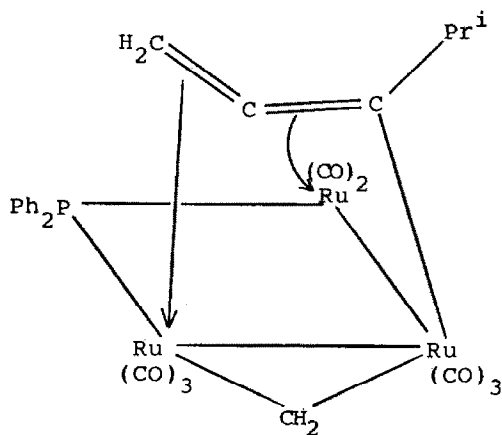
Acyl and Fischer-type carbene derivatives of triruthenium and triosmium cluster complexes have been prepared and characterized, in one case by X-ray crystallography. Several reactions of the cluster complexes were reported [296]. A  $\mu_3\text{-}\eta^2$ -acetylene ligand has been converted into a  $\mu_3\text{-}\eta^3$ -allenyl ligand and subsequently to a  $\mu_3\text{-}\eta^4$ -2,3-butadienylidene ligand by stepwise addition of methylene groups using diazomethane. Thus the triruthenium cluster complex (16.4) was treated with diazomethane at  $-5^\circ\text{C}$  to give a mixture of the three triruthenium cluster complexes (16.5, 16.6 and 16.7) which were isolated as crystalline solids and characterised by X-ray crystallography. The sequential interrelationships between the complexes (16.4-16.7)

were established in separate experiments [297].

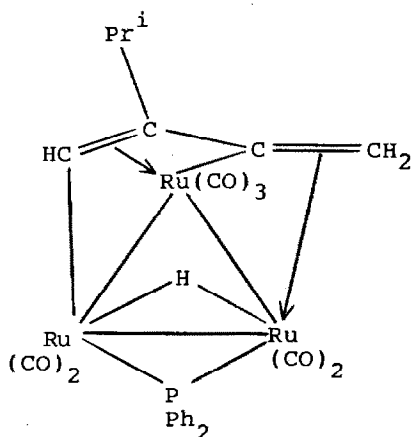
Hydroboration of the unsaturated triosmium cluster complex,  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ , in THF-dichloromethane afforded a boroxine nonaosmium cluster,  $[(\mu\text{-H})_3(\text{CO})_9\text{Os}_3(\equiv\text{CO})]_3(\text{B}_2\text{O}_3)$ , which was a convenient intermediate in the synthesis of the triosmium methylidyne cluster complexes (16.8;  $X = \text{Cl}, \text{Br}, \text{Ph}$ ) by using  $\text{BCl}_3$ ,  $\text{BBr}_3$  and benzene- $\text{BF}_3$  respectively as the reagents [298].  $^1\text{H}$  NMR spectroscopy has been used to demonstrate that the structure of the osmium cluster cation was tilted (16.9) rather than the upright carbenium ion alternative (16.10). The implications for the structure of the related cobalt cluster cations  $[\text{Co}_3(\text{CO})_9\text{CCR}_2]^+$  were discussed [299]. Heating the heterometallic tetranuclear cluster complex (16.11) which contained an activated C-O bond, caused acyl C-O bond scission with the formation of the



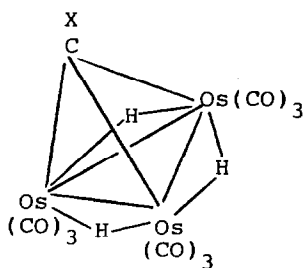
16.5



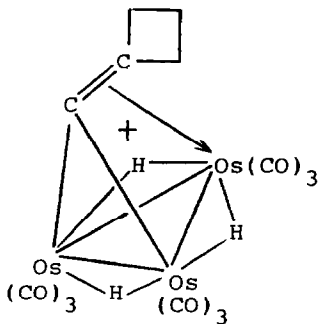
16.6



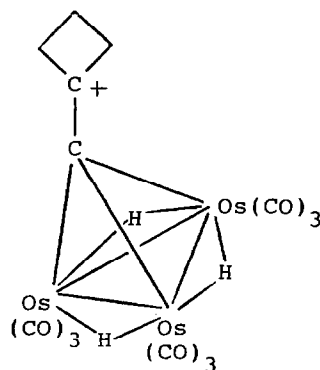
16.7



16.8



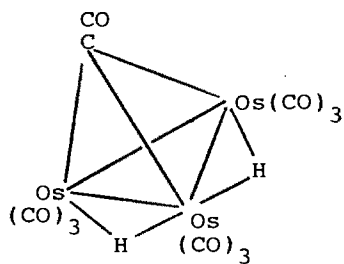
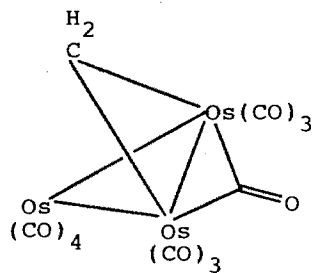
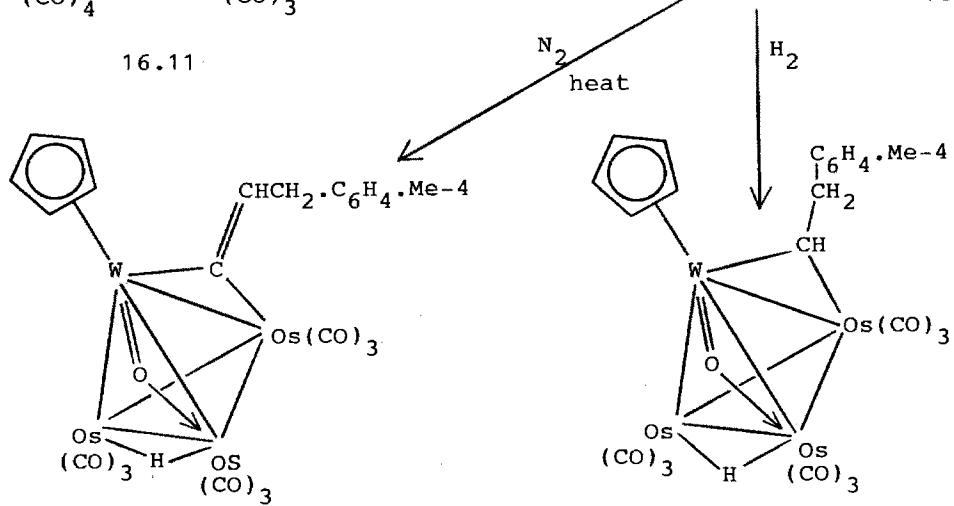
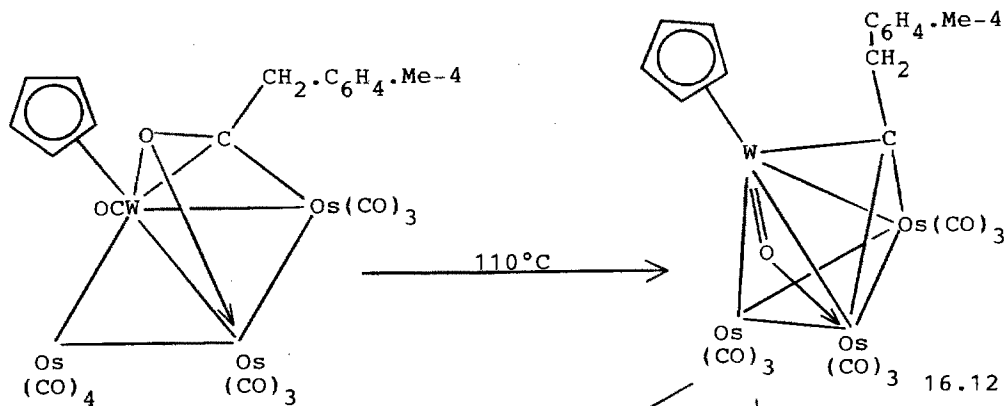
16.9



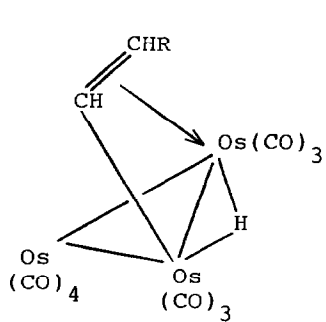
16.10

oxo-alkylidene complex (16.12). This complex was converted quantitatively to the alkylidene complex (16.13) with hydrogen and to the complex (16.14) on pyrolysis under nitrogen. The implications of the reactions in Fischer-Tropsch hydrocarbon synthesis were discussed [300].

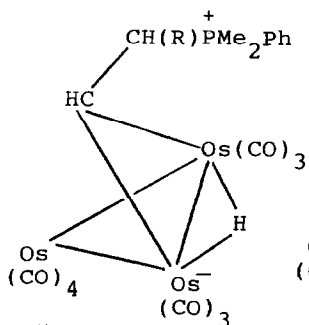
The trinuclear osmium carbonyl  $\text{Os}_3(\text{CO})_{12}$  has been treated with  $\text{K}[\text{BH}(\text{O}-i\text{-Pr})_3]$  at  $0^\circ\text{C}$  to give the unstable formyl cluster  $\text{K}[\text{Os}_3(\text{CO})_{11}\text{CHO}]$  which on acidification gave the methylene cluster (16.15). This complex gave methane on heating with hydrogen and the methinyl cluster (16.16) on heating in the absence of hydrogen [301]. The tetranuclear heterometallic cluster,  $(\eta\text{-C}_5\text{H}_5)\text{W}\text{Os}_3(\text{CO})_{12}\text{H}$ , has been attacked by  $\text{Me}_3\text{NO}$  and  $\text{C}_2\text{H}_2$  to form the complex  $(\eta\text{-C}_5\text{H}_5)\text{W}\text{Os}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-C}_2\text{H}_2)\text{H}$  which was further transformed with  $\text{Me}_3\text{N}$  to the species  $(\eta\text{-C}_5\text{H}_5)\text{W}\text{Os}_3(\text{CO})_8(\mu\text{-O})(\mu_3\text{-}\eta^2\text{-C}_2\text{H}_2)(\mu\text{-H})$ . This product has been characterized by X-ray crystallography and contained the  $\text{C}_2\text{H}_2$  ligand which bridged a W-Os-Os face and the O ligand which bridged a W-Os edge [302]. The bridging vinyl triosmium cluster complexes (16.17;  $\text{R} = \text{H}, n\text{-Bu}, \text{Ph}$ ) underwent addition with dimethylphenylphosphine to give the zwitterionic complexes (16.18;  $\text{R} = \text{H}, n\text{-Bu}, \text{Ph}$ ) which contained  $\mu$ -alkylidene ligands. The same reaction with cyanide ion gave the anionic clusters (16.19;  $\text{R} = \text{H}, n\text{-Bu}, \text{Ph}$ ) and the addition of methoxide ion was found



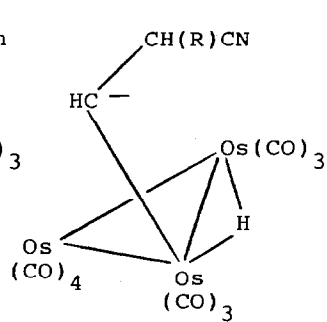




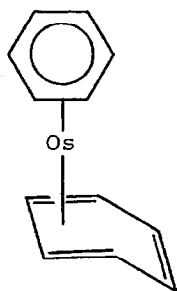
16.17



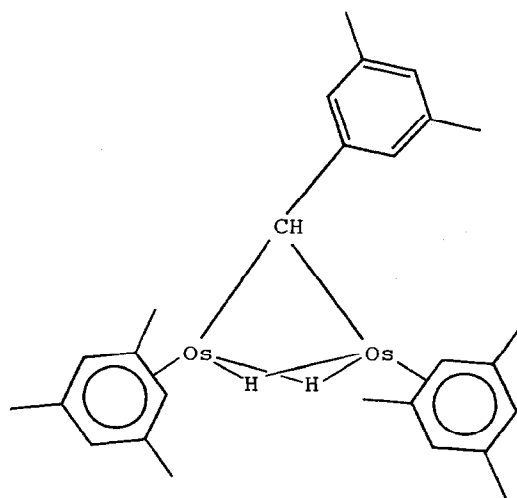
16.18



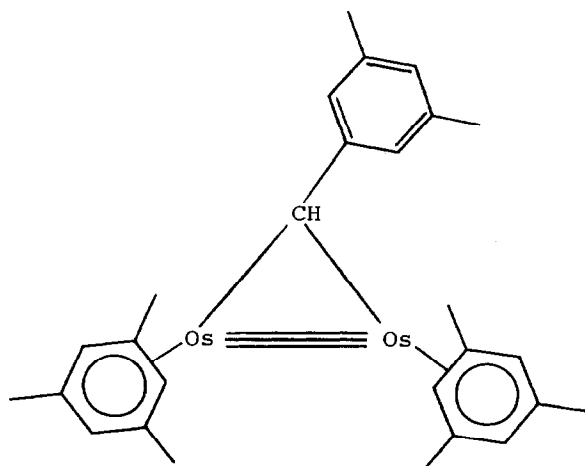
16.19



16.20



16.21

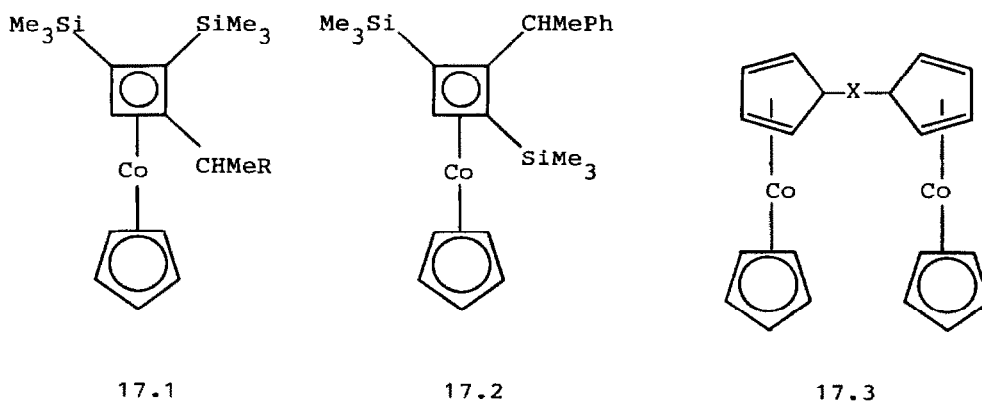


16.22

to be reversible [303]. Condensation of osmium atoms with excess benzene produced the  $\eta^6$ -,  $\eta^4$ -dibenzene complex (16.20). In a similar reaction with mesitylene the hydride (16.21) was formed as the major product together with a small quantity of the dimer (16.22) [304].

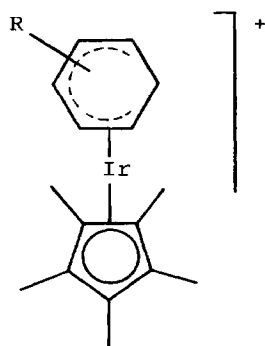
17.  $(\eta\text{-C}_4\text{H}_4)\text{Co}(\eta\text{-C}_5\text{H}_5)$

The chemistry of cyclobutadiene, cyclopentadienyl, cyclopentadienone and arene cobalt complexes has been discussed in an introductory survey by Sheats [305]. Cocyclization of  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ ,  $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$  and  $\text{HC}\equiv\text{CCHMeR}$  produced a series of

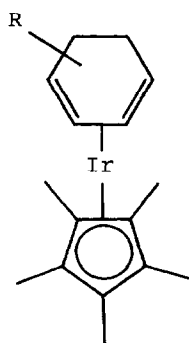


racemic diastereoisomers (17.1; R = OH, OSiMe<sub>3</sub>, OMe, Ph). Gas and solution phase pyrolyses of both diastereoisomers of the complex (17.1; R = Ph) showed that extensive mutual interconversion occurred. This reaction was shown to be unimolecular in character and studies on the complex (17.1; R = OH) indicated that the cobalt unit was the site of the diastereoisomerism as opposed to the chiral carbon atom. Gas phase pyrolysis of the complex (17.1; R = Ph) produced small amounts of the corresponding geometrical isomer (17.2) [306]. Several ( $\eta^4$ -ligand)-( $\eta^5$ -cyclopentadienyl)cobalt complexes have been obtained by reductive substitution of cobaltocene. The diene, such as duroquinone, 1,5-cyclooctadiene or 1-ethyl-1,4-cyclohexadiene, was heated with cobaltocene in a high boiling solvent or in the absence of solvent [307]. The cobalt complexes [17.3; X =

$\text{CH}(\text{CO}_2\text{Me})\text{CH}(\text{CO}_2\text{Me})$ ,  $\text{CH}(\text{CN})\text{CH}(\text{CN})$ ,  $\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)$ ], prepared by treatment of cobaltocene with the appropriately substituted acetylene, have been used as catalysts for the cyclization of acetylene with nitriles to form substituted pyridines [308].



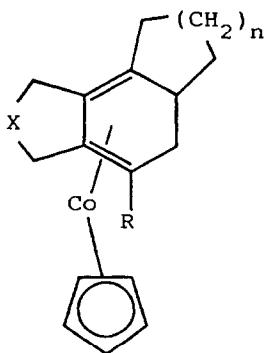
17.4



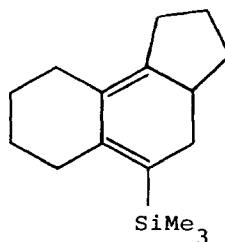
17.5

The complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^6\text{-arene})][\text{BF}_4]_2$ , where arene = toluene, toluene- $d_8$ , t-butylbenzene, methoxybenzene, chlorobenzene, *o*-xylene, *p*-xylene, tetralin and phenol, have been prepared and reduced with sodium borohydride to the corresponding  $\eta^5$ -cyclohexadienyl complexes (17.4). In these reductions attack was usually *exo* at the arene and never at the substituent. Further reduction occurred with strong hydride reducing agents to give mixtures of 1- and 2-substituted cyclohexa-1,3-diene complexes (17.5) [309]. Dicarbonyl( $\eta$ -cyclopentadienyl)cobalt combined with the linear enediyne,  $\text{CH}_2=\text{CH}(\text{CH}_2)_{n+2}\text{C}\equiv\text{CCH}_2\text{XCH}_2\text{C}\equiv\text{CR}$ , where  $\text{R} = \text{SiMe}_3$ ,  $n = 1$ ,  $\text{X} = \text{O}$ ,  $\text{CH}_2\text{CH}_2$ ;  $\text{R} = \text{H}$ ,  $n = 1, 2$ ,  $\text{X} = \text{CH}_2\text{CH}_2$ ;  $\text{R} = \text{SiMe}_3$ ,  $n = 2$ ,  $\text{X} = \text{CH}_2\text{CH}_2$ , to give the tricyclic diene complexes (17.6;  $\text{R} = \text{H}$ ,  $\text{SiMe}_3$ ,  $n = 1, 2$ ,  $\text{X} = \text{O}$ ,  $\text{CH}_2\text{CH}_2$ ). Oxidative demetallation of the complexes (17.6) gave the free ligands, such as the tricyclic diene (17.7). Several transformations of the ligands were reported. The mechanism of the intramolecular cobalt-mediated cycloaddition of the enediyne was discussed [310]. Several ( $\eta$ -borinato)( $\eta$ -cyclobutadiene)-cobalt complexes have been prepared by the reaction of ( $\eta$ -borinato)-( $\eta$ -cyclooctadiene)cobalt complexes with acetylenes. The ( $\eta$ -methylborinato)cobalt complex (17.8;  $\text{R} = \text{H}$ ) was more reactive

than ferrocene in electrophilic substitution. Friedel-Crafts acetylation with acetyl chloride and arsenic(III) chloride gave the 2-acetyl derivative (17.8;  $R = \text{COMe}$ ) together with the 2,4-diacetyl derivative and Vilsmeier formylation gave the



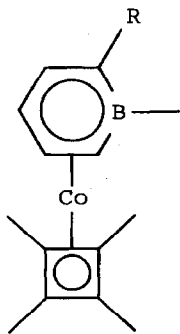
17.6



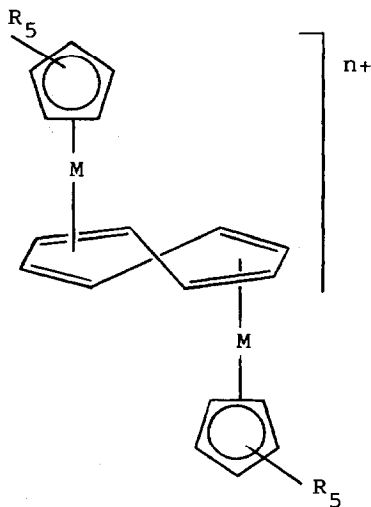
17.7

2-formyl derivative (17.8;  $R = \text{CHO}$ ) [311].

The bonding of tricarbonyliron and ( $\eta$ -cyclopentadienyl)-cobalt to cyclobutadiene and cyclopentadienone has been the subject of a theoretical investigation using MO and CI calculations. The ( $\eta$ - $\text{C}_5\text{H}_5$ )Co group formed a stronger bond to cyclo-



17.8

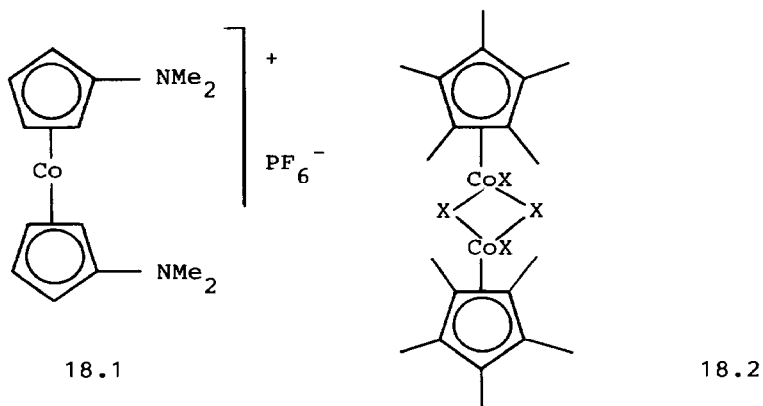


17.9

butadiene than to cyclopentadienone while the  $\text{Fe}(\text{CO})_3$  group showed the opposite effect. The two cobalt complexes showed higher covalent character in the diene-metal bond than did the iron complexes [312]. The structures of the cobaltaborane compounds  $1-[(\eta^5\text{-C}_5\text{R}_5)\text{Co}]\text{B}_4\text{H}_8$ , where  $\text{R} = \text{H}, \text{Me}$ , have been investigated. X-ray analysis of the  $\eta$ -cyclopentadienyl complex showed that it had a sandwich structure with a short Co-B bond distance ( $1.977\text{\AA}$ ) which was similar to the Co-C( $\text{C}_4\text{H}_4$ ) bond distance ( $1.965\text{\AA}$ ) in the analogous  $\eta^4$ -cyclobutadiene compound  $[(\eta^4\text{-C}_4\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{Co}]$  [313]. The  $^{59}\text{Co}$  NMR spectrum of  $(\eta^4\text{-cyclobutadiene})(\eta^5\text{-cyclopentadienyl})\text{-cobalt}$  was recorded as part of a study on the catalytic activity of organocobalt complexes in the synthesis of pyridine derivatives [314]. The electrochemistry and structure of the pseudo-triple-decker complexes (17.9;  $\text{M} = \text{Co}, \text{R} = \text{Me}; \text{M} = \text{Rh}, \text{R} = \text{H}; n = 0$ ) have been explored. Both complexes underwent chemically reversible two-electron oxidations and the structure of the dication (17.9;  $\text{M} = \text{Rh}, \text{R} = \text{H}, n = 2$ ) has been determined by X-ray crystallography. The two metal atoms were slipped to the side of the  $\text{C}_8$  ring which had two almost planar  $\text{C}_4$  fragments twisted by  $34.8^\circ$  [315].

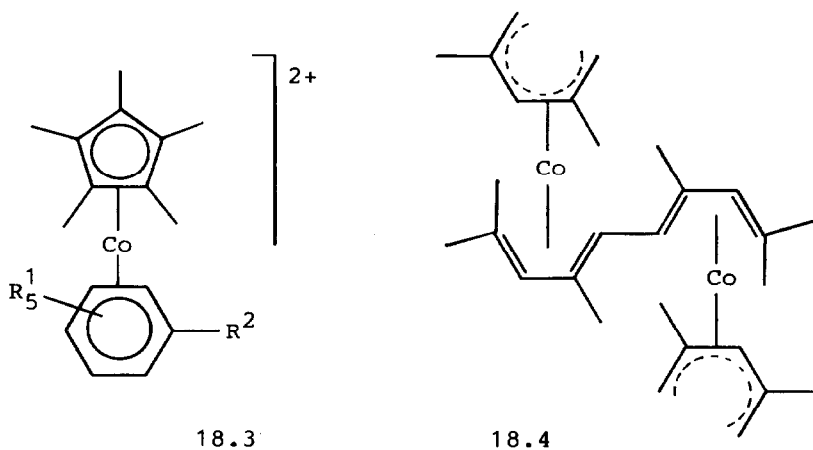
18.  $(\eta\text{-C}_5\text{H}_5)_2\text{Co}$  and  $[(\eta\text{-C}_5\text{H}_5)_2\text{Co}]^+$

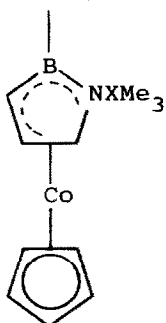
Boche and co-workers have described a general method for the preparation of 1,1'-bis-(N,N-dimethylamino)metallocenes. The reaction of N,N-dimethylaminocyclopentadienyllithium with cobalt(II) chloride followed by the addition of potassium hexafluorophosphate afforded the salt (18.1) [316]. The ferrocenyl-enecobaltocenyl cation, has been prepared as the chloride and hexafluorophosphate salts and found to be a paramagnetic valenced-averaged species [317]. Koelle and co-workers showed that aluminium chloride catalysed halogen/arene exchange reactions in the complex (18.2) gave the dications (18.3;  $\text{R}^1 = \text{R}^2 = \text{CH}_3$ ,  $\text{R}^1 = \text{H}, \text{R}^2 = \text{CH}_3$ ;  $\text{R}^1 = \text{R}^2 = \text{H}$ ). These complexes and the  $\eta$ -cyclopentadienyl complexes  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-arene})]^{2+}$ , where arene = benzene, mesitylene, pentamethylbenzene and hexamethylbenzene, were studied electrochemically. The corresponding paramagnetic  $d^7$  monocations were studied spectroscopically. The results indicated large static distortion and a high degree of covalency in the metal-ligand bonds [318]. Reaction of cobalt(II) chloride with  $\text{H}_2\text{C}(\text{CMe}=\text{CH}_2)_2$  gave bis( $\eta$ -2,4-dimethyl-



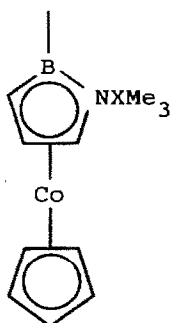
pentadienyl)cobalt which dimerized to produce the dicobalt deca-tetraene complex (18.4). The structure of this compound was determined by X-ray analysis [319].

The treatment of methyl cyanide with acetylene in a liquid phase at 120-150° and 15-20 atmospheres pressure in the presence of a catalyst produced 2-methylpyridine. The catalyst consisted of 1.7-3.2 wt.% diethylamine and 96.8-98.3 wt.% cobaltocene [320]. Cobaltocene-Cu(CH<sub>3</sub>COCH<sub>2</sub>CO<sub>2</sub>Et)<sub>2</sub> has been used as the initiator in the block copolymerization of methyl acrylate and (DL)- $\alpha$ -methylbenzylmethacrylate [321]. The azaboroline complexes





18.5



18.6

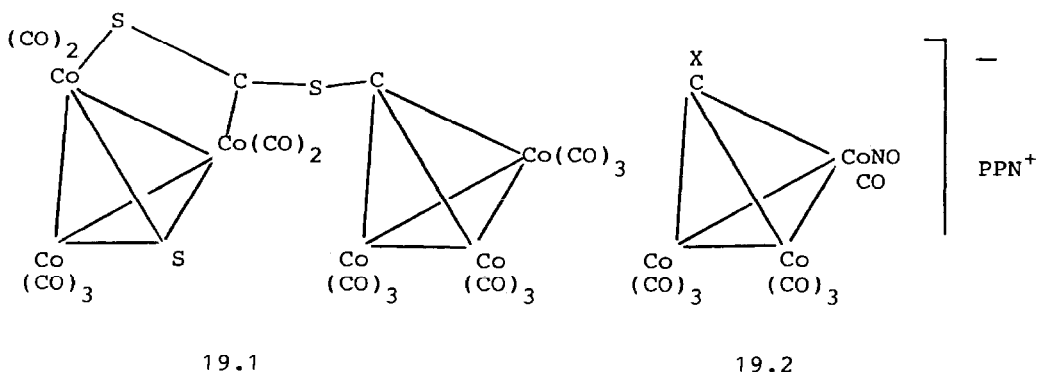
(18.5; X = C, Si) have been formed by treatment of  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_2\text{H}_4)_2$  with 1-*t*-butyl- and 1-trimethylsilyl-2-methyl- $\Delta^3$ -1,2-azaboroline. The four-electron azaboroline ligand in the complexes (18.5) was converted to a five-electron ligand by loss of a hydrogen atom to form the azaborolynyl complexes (18.6; X = C, Si) [322]. The electrochemical oxidation of bis(azaborolynyl)-cobalt and -iron complexes has been investigated by pulse and cyclic voltammetry. One-electron oxidations were observed which were reversible in some cases. The redox potentials were correlated with the structural and electronic characteristics of the complexes [323].

Inelastic neutron scattering has been used to determine the splitting of the two lowest orbitally degenerate Kramers doublets in  $d^5$  and  $d^7$  metallocenes. In cobaltocene the splitting was  $173\text{cm}^{-1}$  and in the ferrocenium salts  $\text{Fe}(\eta\text{-C}_5\text{D}_5)_2\text{X}$ , where X =  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$  and  $\text{I}_3^-$ , the separation was  $515\text{cm}^{-1}$  [324]. A low temperature single-crystal proton ENDOR study of a cobaltocene doped cymantrene crystal has been used to determine the spin density distribution in cobaltocene. Hyperfine tensors for the ten protons on the cyclopentadienyl rings were determined and the isotropic coupling was ascribed to polarization of the proton 1s orbitals [325].

### 19. Cobalt-carbon Cluster Compounds

Fragmentation of alkanes under  $\gamma$ -irradiation was reduced by the presence of metal carbonyls. When octacarbonyldicobalt

was used then the cluster complex  $\text{Co}_3(\text{CO})_9\text{CH}$  was obtained [326]. The treatment of  $\text{Co}_2(\text{CO})_8$  with carbon disulphide produced the hexanuclear cobalt carbonyl-sulphur complex (19.1). The structure of this complex was determined by X-ray analysis and this showed the presence of a four electron donor SCS ligand disymmetrically linked to two tricobalt clusters [327]. Nitrosyl derivatives of tricobaltcarbon clusters (19.2; X = Me, Ph,  $\text{CO}_2\text{H}$ , ferrocenyl) have been obtained by treatment of the substituted

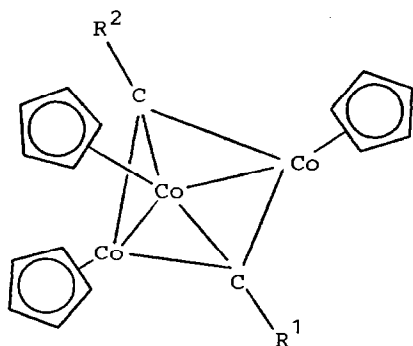


cluster complexes  $\text{XCo}_3(\text{CO})_9$  with bis(triphenylphosphine)nitrogen nitrite [PPN( $\text{NO}_2$ )]. Two carbonyl ligands on one cobalt atom were replaced by one linear terminal nitrosyl group. The nitrosyl complexes (19.2) were sensitive to oxidation [328]. The electronic structure of nonacarbonylalkylidynetrimer metal cluster complexes has been studied. The apical carbon atom was  $\text{sp}$  hybridized with a lone pair of electrons, it was not rehybridized on interaction with the metal orbitals and it was not an effective donor towards the metal atoms. The apical carbon  $2\text{p}$  and the  $\text{M}(\text{CO})_3 t_{2g}$  type orbitals were similar in energy and interacted strongly [329].

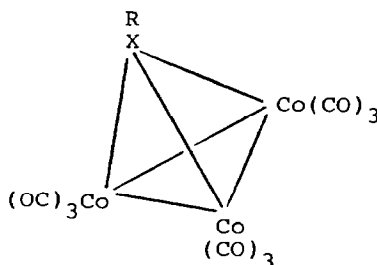
Reaction of ferrocenylacetylene and bis(ferrocenyl)acetylene with  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$  produced the ferrocenyl bis ( $\mu_3$ -carbyne) cluster (19.3;  $\text{R}^1 = \text{ferrocenyl}$ ,  $\text{R}^2 = \text{H}$ , ferrocenyl). The clusters (19.3;  $\text{R}^1 = \text{R}^2 = \text{Ph}$ ,  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{ferrocenyl}$ ,  $\text{SiMe}_3$ , Ph;  $\text{R}^1 = \text{I}$ ,  $\text{R}^2 = \text{SiMe}_3$ ) underwent an electrochemical and a chemical one-electron oxidation at 0.6V versus Ag/AgCl and an irreversible reduction at -1.55V at Pt. Spectral and electrochemical data indicated that  $\pi$  interactions between the carbyne and metal fragments were



particularly important in the redox chemistry of the bis(carbyne) molecules [330]. The redox chemistry of several capped tetrahedral cluster complexes including the cobalt clusters (19.4; R = Me, Ph, X = Ge, P) has been studied by electrochemical and spectroscopic techniques [331]. State correlation diagrams have been obtained for the photochemical metal-metal bond cleavage including ring opening of metal carbonyls and hydrocarbon metal carbonyls such as  $\text{Co}_3(\text{CO})_9\text{CH}$ . The mechanism of the reaction was discussed [332].



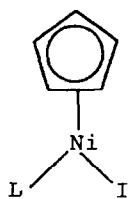
19.3



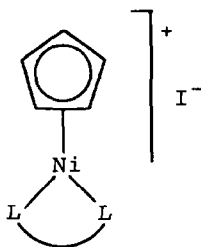
19.4

## 20. $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}$

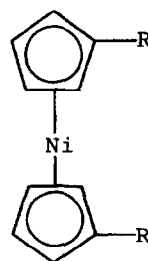
The reaction of nickelocene with anhydrous lithium iodide in the presence of ligands L gave the corresponding complexes [20.1; L = P(n-Bu)<sub>3</sub>, PPh<sub>3</sub>, AsPh<sub>3</sub>, SbMe<sub>3</sub>, Sb(n-Bu)<sub>3</sub>, SbPh<sub>3</sub> and 20.2; L<sub>2</sub> = (Ph<sub>2</sub>P)<sub>2</sub>, Ph<sub>2</sub>AsCH<sub>2</sub>AsPh<sub>2</sub>, Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, (Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>, (Ph<sub>2</sub>AsCH<sub>2</sub>)<sub>2</sub>] [333]. Nickelocene has been attacked by isopropylmagnesium chloride and five- to eight-membered 1,3-cycloalkadienes to give the corresponding ( $\eta^3$ -cycloalkenyl)( $\eta^5$ -cyclopentadienyl)-nickel complexes [334]. Nickelocene underwent reductive substitution on heating with tetracyclone under pressure to form bis( $\eta^4$ -tetracyclone)nickel and dihydrotetracyclone. An intermediate ( $\eta^3$ -hydrotetracyclone)nickel complex was isolated [335]. A nickelaborane anion has been prepared by the reaction of nickelocene with  $(\text{Bu}_4\text{N})_2\text{B}_6\text{H}_6$  [336]. Nickel films  $\ll 2\text{-}3\mu$  thick have



20.1



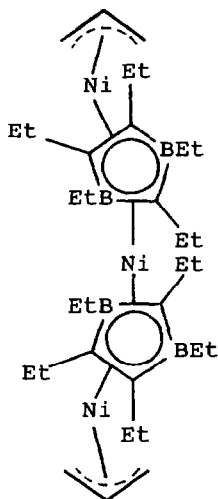
20.2



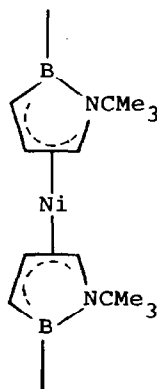
20.3

been formed by thermal decomposition of nickelocene in a hydrogen containing atmosphere [337].

The polymerization of vinyl monomers initiated by the binary systems of cobaltocene, nickelocene or ferrocene mixed with bis-(ethyl acetoacetato)copper(II) has been investigated. The presence of cobaltocene increased the rate of polymerization of methyl methacrylate. This polymerization was shown to proceed via a radical mechanism [338]. The structure and properties of the nickelocenes (20.3; R = H, Me, Et, Bu, PhCH<sub>2</sub>) have been



20.4



20.5

studied by mass spectrometry and  $^1\text{H}$  NMR spectroscopy [339]. Cyclic voltammetry and controlled potential electrolysis of nickelocene has been carried out under carbon monoxide gas. The results indicated that the initially generated nickelocene anion lost a cyclopentadienyl ligand and coordinated with CO to give  $[(\eta\text{-C}_5\text{H}_5)\text{NiCO}]^-$  which was reduced at the electrode to the corresponding anion. Under high carbon monoxide pressure  $[(\eta\text{-C}_5\text{H}_5)\text{NiCO}]^-$  lost the cyclopentadienyl group to give  $\text{Ni}(\text{CO})_4$  [340]. Alkyl-2,3-dihydro-1,3-diboroles have been treated with bis( $\eta$ -allyl)- or bis( $\eta$ -2-methylallyl)-nickel to form quadruple-decker sandwich complexes including the trinickel complex (20.4) [341]. The 1-t-butyl-2-methyl-1,2-azaborolanyl ligand in the ( $\eta$ -azaborolanyl)nickel complex (20.5) behaved as a three-electron donor rather than a five-electron donor as previously observed in transition metal complexes [342].

#### 21. $(\eta\text{-C}_8\text{H}_8)_2\text{U}$ and $(\eta\text{-C}_8\text{H}_8)_2\text{Th}$

Regiospecific syntheses have been used to prepare 1,3-, 1,4-, 1,5-di-t-butylcyclooctatetraenes and 1,4-, 1,5-diphenylcyclooctatetraenes which were converted to the appropriate tetra-substituted uranocenes by reduction to the dianion and treatment with uranium(IV) chloride. The rates of decomposition of these uranocenes were measured and found to be dependent on the nature of the substituents. Regiospecifically deuterated 1,1'-di-t-butyluranocenes were prepared and used to assign the  $^1\text{H}$  NMR spectrum of this complex [343]. Thorium(IV) chloride has been treated with  $\text{K}_2\text{C}_8\text{H}_8$  to form bis( $\eta^8$ -cyclooctatetraene)thorium, "thorocene". The saturated vapour pressure and thermal stability of the complex have been determined [344].

A comparison of non-relativistic and quasi-relativistic SCF- $X_\alpha$  calculations of uranocene, thorocene and cerocene has been carried out. The results were analyzed on the basis of selected orbital energies and charge distributions [345]. Thermogravimetry has been used to investigate the thermal decomposition of uranocene, 1,1'-dibutyluranocene and several other uranium complexes. Uranocene was found to have a higher thermal stability than 1,1'-dibutyluranocene [346].

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