ORGANIC REACTIONS OF SELECTED π-COMPLEXES

ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

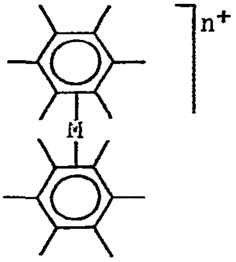
Organic reactions of selected π-complexes, covering the year 1973 see J. Organometal. Chem., 79(1975)347-443.

1. REVIEWS

The general development of π-organometallic chemistry has been discussed by Zeppezauer[1]. The bonding and properties of titanium, vanadium and chromium bis(η-cyclopentadienyl), di(η-benzene) and η-cycloheptatrienyl-η-cyclopentadienyl compounds have been discussed[2]. Bonding in other sandwich complexes was also reviewed[3]. Mawby has discussed the chemistry of η-cyclopentadienyl, η-arene and related π-complexes[4]. The π-organometallic research work of the Nobel prize winners Fischer and Wilkinson has been reviewed[5]. The chemistry of hydrocarbon-metal π-complexes has been surveyed by Bennett[6]. π-Organometallic complexes have been included in a more general review of transition metal chemistry by Braterman[7]. The organic chemistry and in particular substitution in π-hydrocarbon transition metal complexes has been summarized by Knox[8]. Deganello has reviewed the effect of metal carbonyls, especially those of iron and molybdenum, on the rearrangement of bicyclo [6.n.0] trienes[9]. The mass spectrometry of complexes of transition metals with aromatic, π-acceptor and σ-bonded ligands has been reviewed. The possibility of isotopic analysis of the elements in the form of π-complexes was discussed[10].

2. GENERAL RESULTS

Anderson has used wideline ^{1}H NMR spectroscopy to examine the structure and bonding in several η-benzene, η-cyclopentadienyl and η-cyclooctatetraene sandwich compounds (2.1; M = V, n = 0; M = Cr, n = 1; M = Fe, n = 1, 2; M = Co, n = 1,2; M = Ni, n = 2; 2.2; M = V, Cr, Fe, Co, Ni; 2.3). The spectra of the solid complexes were obtained in the temperature range 178-381°K, the second moments of the linewidths were determined and compared with the calculated values using the Van Vleck model. The results were in agreement with very low energy barriers to rotation about the principal molecular symmetry axes. Two distinct rotomers were probably present in uranocene (2.3). Metal-ring bonding in the η-benzene compounds (2.1) was found to be essentially the same as in the η-cyclopentadienyl compounds (2.2)[11].



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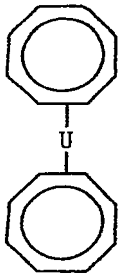

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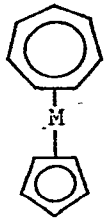
The principal ions formed in the mass spectrometic fragmentation of the η-cyclopentadienyl complexes (2.2; M = V, Cr, Fe and Ni) were confirmed as the molecular ion $(\eta\text{-}C_5H_5)_2M^+$, the η-cyclopentadienylmetal ion $(\eta\text{-}C_5H_5)M^+$ and the metal ion M^+. The average dissociation energies were determined as 91, 69, 72 and 69 kcal mol^{-1} for the complexes (2.2; M = V, Cr, Fe and Ni) respectively[12].

Metallation of the η-cyclopentadienyl-η-cycloheptadienyl complexes (2.4) has been studied. The titanium compound (2.4; M = Ti) is lithiated predominantly in the seven-membered ring (95%) rather than in the five-membered ring (5%). By contrast metallation of the vanadium and chromium compounds (2.4; M = V, Cr) occurred in the five-membered ring. The relative reactivities of these three compounds decreased in the order M = Ti > V > Cr. A qualitative MO approach was used to rationalize the results[13,14]. In a definitive paper, Warren has discussed the magnetic behaviour of metallocenes and bis-arene complexes with $\underline{d}^1$, $\underline{d}^2$, $\underline{d}^4$, $\underline{d}^5$, $\underline{d}^7$ and $\underline{d}^9$ configurations by use of a ligand field model. Possible ground states for each $\underline{d}^x$ configuration are discussed on the basis of axial $C_{\infty v}$ symmetry. Spin-orbital interactions and the matrix elements for the Zeeman operators in the ground state manifolds have been calculated. The temperature dependence and the magnetic moment anisotropies have also been evaluated. The calculated parameters have been compared with the experimental results for these complexes[15]. The same author has calculated the complete $\underline{d}^4$ strong-field electrostatic repulsion matrices in $C_{\infty v}$ symmetry and evaluated the Tanabe-Sugano diagram. These have been used to deduce the ground state of $(\eta\text{-}C_5H_5)_2M$, where M = V, Cr, Fe, Co, Ni.



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The calculated energy levels are compared with the experimental UV and photoelectron spectra[16].

Timms and coworkers have developed a technique for combining metal atoms with compounds in solution in inert solvents at temperatures up to 0°. The solution of the reactant was contained in a continuously evacuated flask rotated at 50-80 r.p.m. and the metal was vaporized upwards into the film of solution carried over on the top inside surface of the flask. The flask was rotated in a cooling bath maintained at a temperature at which the vapour pressure of the solution was less than 10^{-3} Torr, so that the vacuum in the flask permitted efficient vaporisation of the metal. This technique was used to prepare bis(η-cycloocta-1,5-diene)-iron(0)[17]. The structures of the biscyclooctatetraenyl compounds $(\eta\text{-}C_8H_8)_2M$, (M = U, Th, Ti and V) were inferred from the infrared spectra of these molecules. Assignments were made based on qualitative results from group theory, for the fundamental bands in the spectra. From the results obtained it was concluded for Ti and V, that rigorous $\underline{D_{8h}}$ symmetry did not exist but this type of structure was more probable for U and Th. The degree of electrostatic bonding between the metal and the C_8H_8 rings was greater for Ti and V than for U and Th[18]. The treatment of iron carbonyl complexes $(CO)_nFeL$ with trimethylamine oxide released the unsaturated hydrocarbon ligand L in good yield without any deterioration of the product.

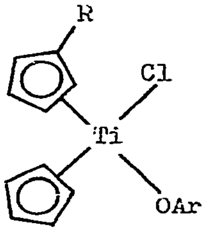
$$(CO)_nFeL + Me_3NO \longrightarrow L + R_3N + CO_2 + \text{"iron compounds"}$$

The advantages of this reaction are that only relatively low temperatures are required and aprotic solvents can be used. For example, 5-anilino-1,3-cyclohexadiene was obtained in good.

yield from the oxidation-sensitive complex tricarbonyl-(η-cyclohexadienylphenylamine)iron which indicated the mildness of this reaction[19]. A US Army report by Rosenblum on organometallic chemistry covered several related areas of organo-iron chemistry. Much of the work in this report has already been published by the author in the scientific literature[20].

3. $(\eta\text{-}C_5H_5)_2Ti$

The IR absorption frequencies have been determined for the CO_2 groups in a number of mono- and bis-(η-cyclopentadienyl)-titanium acetates with increasing numbers of methyl groups on the (η-cyclopentadienyl) ligands and with either CF_3 or CH_3 groups on the acetate ligand[21]. Treatment of the racemates (3.1; R = $CHMe_2$, $CHPh_2$) with optically active mandelic acid in benzene led to stereospecific degradation and the isolation of optically active starting material. The reaction was carried out also with complexes (3.2; R = C_6H_3.-3-Me-6-$CHMe_2$, C_6H_3.-2,6-Me_2) bearing a chiral cyclopentadienyl substituent[22].



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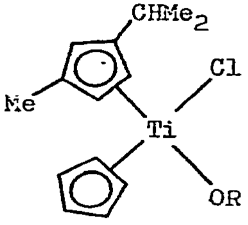

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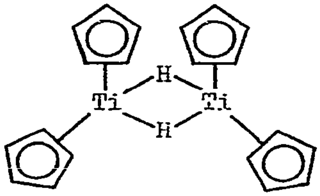
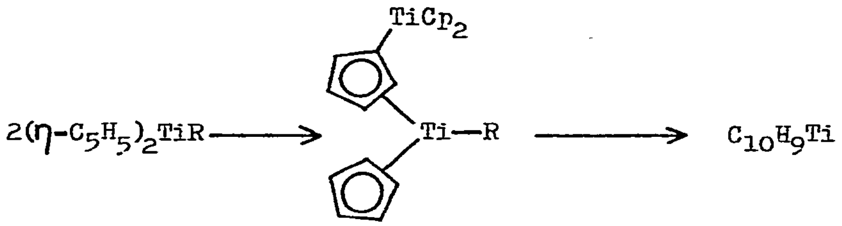


3.3

Teuben has investigated the thermal decomposition of the titanocene derivatives $(\eta\text{-}C_5H_5)_2TiR$ and their nitrogen complexes $[(\eta\text{-}C_5H_5)_2TiR]N_2$. The free titanocene derivatives lost RH by an intermolecular mechanism:



The compounds showed wide variations in thermal stability dependent on the R group in the sequence:

Ph ~ m-, p-MeC$_6$H$_4$ < CH$_2$Ph < o-MeC$_6$H$_4$ ~ C$_6$H$_5$

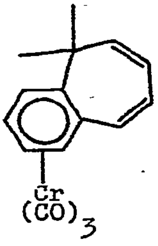
The complexes $[(\eta\text{-}C_5H_5)_2TiR]N_2$ lost nitrogen with the formation of $(\eta\text{-}C_5H_5)_2TiR$ in the order:

R = o-MeC$_6$H$_4$ < C$_6$F$_5$ < CH$_2$Ph < Ph ~ m-, p-C$_6$H$_4$[23]

The green dimeric form of titanocene has been shown by ^{13}C NMR spectroscopy to be a fulvalene dihydrido complex (3.3)[24].

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

Rausch has reported an improved synthesis of (η-benzene)-chromium tricarbonyl. Equimolar amounts of benzene and 2-picoline containing hexacarbonylchromium were heated under reflux to give a good yield (91%) of the product[25]. The reaction of benzocycloheptatriene with chromium carbonyl gave the chromium tricarbonyl complex (4.1) with the six membered ring π-bonded to the chromium[26]. The acids PhCH(CHMe$_2$)-CH$_2$CH$_2$CO$_2$H and PhCH$_2$CH(CHMe$_2$)CH$_2$CO$_2$H were cyclized to give the corresponding tetralones and these were treated with chromium carbonyl to give the complexes (4.2; R = α-Me$_2$CH, β-Me_2CH; 4.3; R = α-Me_2CH, β-Me_2CH)[27]. The benzene-



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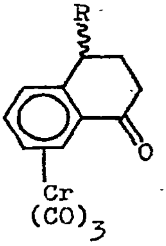

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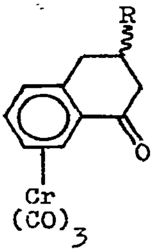

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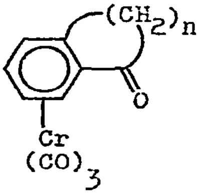
chromium tricarbonyl derivatives (4.4; n = 1 and 2) were prepared by cyclization of the corresponding propanoic and butanoic acids or by reaction of α-tetralone and α-indanone with chromium carbonyl[28].

The reaction of hexacarbonylchromium with benzocycloheptatriene gave (η-benzocycloheptatriene)chromium tricarbonyl (4.5)[29]. Heating o-$C_6H_4[CH(OEt)_2]_2$ with chromium carbonyl



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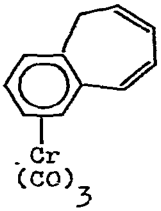

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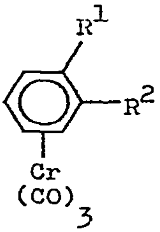

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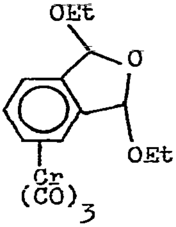
gave the complex [4.6; $R^1 = R^2 = CH(OEt_2)$] which on hydrolysis gave the corresponding dialdehyde (4.6; $R^1 = R^2 = CHO$) and the ether (4.7). Reaction of the dialdehyde with ketones gave the corresponding tropones (4.8)[30]. King and Nainan have



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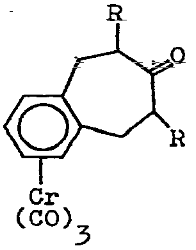

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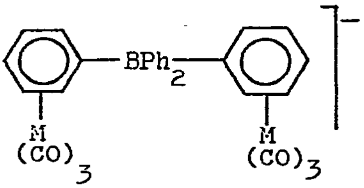

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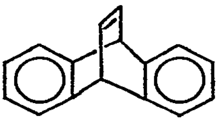
described the formation of the binuclear anions (4.9; M = Cr, W) from sodium tetraphenylborate and chromium or tungsten hexacarbonyl in boiling diglyme. The anions were isolated as their tetramethylammonium salts[31]. Neuse and Yannakou have reported the preparation of chromium tricarbonyl complexes of N-benzylideneaniline with metal carbonyl residues attached to either one or the other of the two benzene rings, or to both rings[32].

syn-(η-Dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium (4.11) was prepared from the arene (4.10) and triacetonitriletricarbonylchromium. Catalytic deuteration of the complex (4.11) over palladium on charcoal gave predominantly a deuterated product (4.12) with both the deuteriums on the ethane bridge anti to the tricarbonylchromium moiety. It was thought that this mode of addition occurred because the tricarbonylchromium moiety served as a blocking group to shield one face of the carbon to carbon double bond[33].



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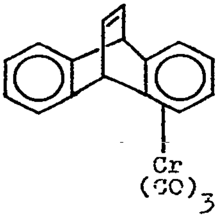

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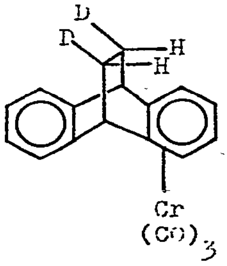

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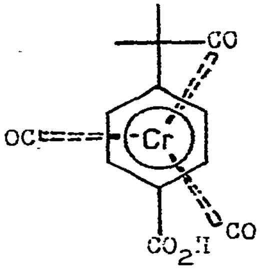
Triamminetricarbonylchromium was treated with thiophene, t-butylbenzene, phenyltrimethylsilane and iodobenzene to give the corresponding (η-arene)tricarbonylchromium complexes in yields, as good as or better than, similar reactions with hexacarbonylchromium. The use of $(NH_3)_3Cr(CO)_3$ was preferred in these reactions in that it did not sublime and it was more reactive in solution than the hexacarbonyl[34]. (η-Arene)-tricarbonylmolybdenum $ArMo(CO)_3$ [Ar = PhMe, mesitylene, PhBu, tetralin, $(p\text{-}Me_3C)_2C_6H_4$, PhOMe, $PhCH{=}CH_2$, $PhCH_2CH_2CH{=}CH_2$, $PhCH_2CH_2CH_2Br$, $PhCH_2CH_2OMe$, $PhCH_2CH_2COMe$, 2,4,6-$Me_3C_6H_2COMe$] were prepared by treating tricarbonyltris(pyridine)molybdenum with the aryl compound in ether containing boron trifluoride at 20°[35]. The compounds $[(\eta\text{-arene})Mo(PR_3)_3]$ (arene = benzene, R = Et; arene = mesitylene, R = Me) were prepared by reaction of $[(\eta\text{-arene})Mo(\eta\text{-}C_3H_5)Cl]_2$ with PR_3 followed by excess PR_3 and $NaBH_4$. The arene-molybdenum derivatives were protonated by dilute aqueous acid to give $[(\eta\text{-arene})Mo(PR_3)_3H]^+$ and diprotonated by concentrated acid to give $[(\eta\text{-arene})Mo(PR_3)_3H_2]^{2+}$[36].



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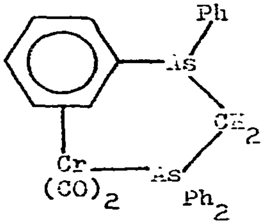

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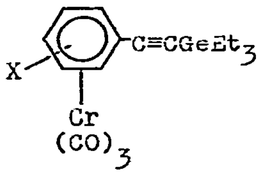
(ii) Structural and physico-chemical studies

In a theoretical study of benchrotrene, the complete electric dipole moment matrix was evaluated on the metal, carbon and oxygen centres employing an atomic orbital basis[37]. This study was followed by one on (η-$C_6H_5NH_2$)Cr(CO)$_3$ and (η-C_6H_5F)Cr(CO)$_3$ which allowed comparisons to be made of molecular orbitals derived from several approximation methods in common use. The empirical method of Basch, Viste and Gray gave the best values[38]. The molecular structure of the benzoic acid complex (4.13) was determined from three-dimensional X-ray data. The crystals were monoclinic, space group $\underline{P}2_1/\underline{C}$ with unit cell dimensions a = 12.23, b = 7.51, c = 18.1 Å and β = 117.9. The molecule (4.13) adopted a conformation which departed from perfect staggering by about seven degrees[39]. Three dimensional X-ray structure analysis has confirmed the bis(diphenylarsino)methane adduct of chromium hexacarbonyl as the bridged benchrotrene complex (4.14)[40]. Meyer has described the synthesis of several aldehyde, ketone, ketovinyl and hydroalkyl derivatives of benchrotrene by either direct reaction between the ligand and chromium hexacarbonyl or by secondary reactions of substituted benchrotrenes. The electron withdrawing character of the chromium tricarbonyl group was demonstrated by polarography of acylbenchrotrenes, the Hammett substituent constant was determined as $\sigma = 0.74$. Some aromatic and organometallic groups were arranged in order of electron withdrawing power; benchrotrenyl > 2-thienyl > cymantrenyl > phenyl > 2-pyrrolyl > ferrocenyl[41].

The rate of hydrogen-deuterium exchange in (η-C_6H_6)Cr(CO)$_2$PPh$_3$ was directly proportional to the acidity of the medium at $\underline{H}o$ + 1 to -2.5; at $\underline{H}o$ -2.5 to -7.1 the proportion was inverse[42]. Hydrogen-deuterium exchange rates were determined for a series of substituted arene-chromium complexes,

(η-RC_6H_5)$Cr(CO)_2PPh_3$(R = H, MeCO, MeO_2C), (η-C_6H_6)$Cr(CO)_3$ and (η-$Me_2NC_6H_5$)$Cr(CO)_3$. The acetyl and the protonated dimethylamino groups accelerated the rate of exchange[43]. The rates of deuterium and tritium exchange between (η-benzene)dicarbonyl-(triphenylphosphine)chromium, labelled in the benzene ligand with deuterium and tritium in CF_3CO_2H were determined. No isotope effect was observed and it was suggested that the rate determining step in the exchange might be the transfer of H^+ from chromium to the benzene ligand[44]. Substituent effects in benchrotrene derivates have been studied by measurement of rates of cleavage for C-MR_3 groups bound to the η-benzene ligand. The triethylgermane (4.15; X = H) was cleaved by aqueous-methanolic alkali sixteen times faster than the free ligand which gave a value for the $Cr(CO)_3$ substituent constant σ^-= +0.84. The relative rates of cleavage for the complexes (4.15; X = m-CF_3, m-Cl, m- and p-OMe, o- and m-Me, H) were found to correlate well with the relative rates for the free ligands although the substituents (X) had a smaller effect in the complexes (4.15) than in the uncomplexed arenes. Similar effects were observed in the basic cleavage of the aryl-$SiMe_3$ bond in a series of six silylbenchrotrene compounds (4.16; X = m-Cl, m- and p-OMe, m- and p-Me, H). The σ^- constant was determined as +1.12 for the $Cr(CO)_3$ group in the silicon complex (4.17)[45].



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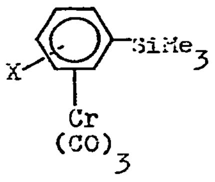

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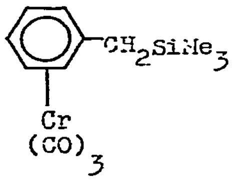

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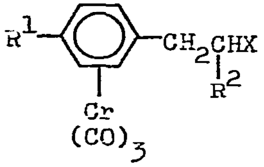
Ceccon and Catelani have compared the rates and products of elimination from the substituted benchrotrenes (4.18; $R^1 = H, NO_2, R^2 = H, Me, X = Br, OTs$), with those obtained from the free arenes. The eliminations were carried out with ethoxide in ethanol or t-butoxide in t-butanol. Higher rates of reaction were observed for the complexes than for the uncomplexed arenes. The percentage of olefin in the product mixture when substitution competed with elimination was greater for the complexed arene while the proportions of the olefin products were independent of complexation[46].



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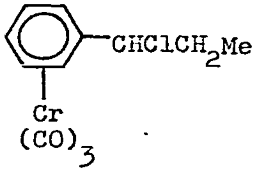

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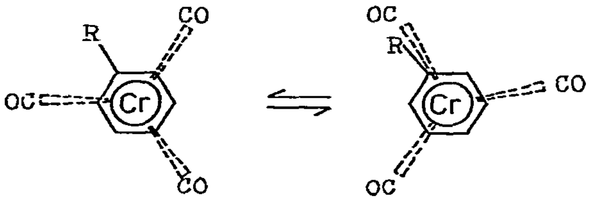
In a related study, the second-order elimination from the complexes (4.18; $R^1 = H, R^2 = Me, X = Br, OTs$ and 4.19) has been compared quantitatively with the same reaction in the free ligands. The reactions were induced by either tetrabutylammonium chloride or bromide in acetone. The rate of dehydrochlorination of 1-phenyl-1-chloropropane was almost unaffected when it was complexed as (4.19) but the rate and olefin yield from the 1-phenyl-2-propyl derivatives was decreased on formation of the complexes (4.18). An E2C transition state for the reaction was preferred over the alternative E2H transition state[47].

The kinetics of decomposition of several (η-arene)-chromium-tricarbonyl and -dicarbonyltriphenylphosphine complexes was studied spectrophotometrically under first order conditions. The complexes containing triphenylphosphine decomposed faster than the tricarbonyl compounds. Benchrotrene decomposed to give benzene and hexacarbonylchromium^{48}. The rapid exchange between the conformers (4.20 and 4.21) for some substituted benchrotrene complexes was studied by variable temperature ^{13}C NMR. An upfield shift for carbon atoms 2, 4 and 6 in the complexes (4.20; R = Me, Et, OMe) (R is electron releasing) with a decrease in temperature was interpreted in terms of an increased contribution from conformer (4.21). The opposite behaviour was observed for (4.20; R = COMe) (R is electron withdrawing). For the complex [4.20; R = $C(Me)_3$] no significant shift occurred and this was attributed to the existence of a single conformer (4.20)^{49}. Hindered rotation in (η-diarylmethane)chromium tricarbonyl compounds has been studied by ^1H NMR spectroscopy. The energy barriers to rotation of the uncomplexed rings in the complexes (4.22;



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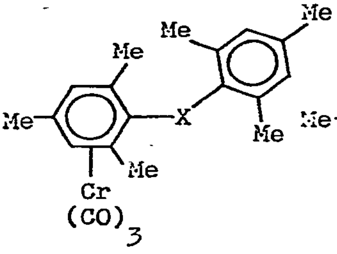
X = $>CH_2$, $>C{=}CH_2$, $>CHOH$) fell in the range 13.9-14.3 kcal mol^{-1} at 14-22° while the complexes (4.23; R = H, Me) had energy barriers of 19.4 and 19.6 kcal mol^{-1} at 115 and 118° respectively. The high barriers for the ketones (4.23) were ascribed to stabilisation of the ground-state conformations by carbonyl-uncomplexed ring conjugation[50]. Bodner and Todd



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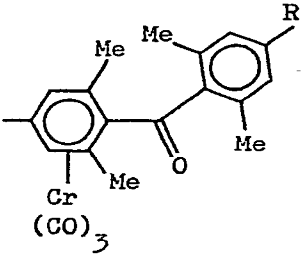

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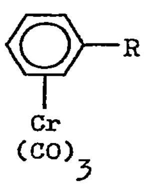
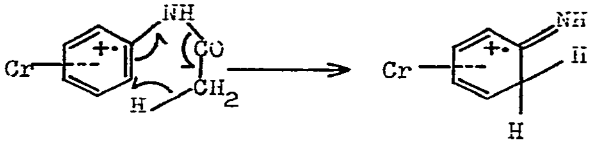


4.24

have used Fourier-transform ^{13}C NMR spectroscopy to study substituent effects when benzene and eight substituted benzenes were complexed with chromium carbonyl to give the benchrotrene derivatives (4.24; R = F, Cl, Me, OMe, OBu^n, CO_2Me, NH_2, NMe_2). No significant change in the transmission of resonance substituent effects was observed between the free and complexed ligands. The chromium tricarbonyl residue was effective in withdrawing electron density from the σ-skeleton of the arene ring[51].

Complete assignments of the vibrational spectra of the benchrotrenes (4.24; R = NH_2, OMe, CO_2Me) have been made on the basis of Raman polarization results. The need to use full factor-group analysis is emphasised and attention is called to the failure of the 'local' symmetry concept which has been used previously[52]. A single-crystal Raman study was made of the vibrations of the tricarbonylchromium unit in benchrotrene and tricarbonyl(1,3-dimethylbenzene)-chromium. In the 2000 cm^{-1} region a factor group analysis was appropriate. Also, low frequency bands, 400-700 cm^{-1}, were interpreted[53].

The chemical ionization mass spectra for the (η-arene)-chromium tricarbonyls (4.24; R = H, Me, F, Cl, CO_2Me) have been recorded and compared with the spectrum of (η-cycloheptatriene)chromium tricarbonyl. In each case the spectra were interpreted in terms of protonation at the metal atom. In the case of di(η-benzene)chromium the most abundant ion was the molecular ion formed by loss of a hydrogen atom from the protonated complex[54]. The dissociation and fragmentation of six alkyl- and halogeno-benchrotrenes has been examined by mass spectrometry. Appearance potentials were measured and dissociation energies obtained for the neutral molecular and the major fragment ions[55]. The mass spectra of (η-acetanilide)-tricarbonylchromium and the 2,4- and 2,6-dimethyl analogues indicated that ketene elimination from the ion $[(C_6H_5NHCOCH_3)Cr]^{+\bullet}$ occurred *via* a six membered transition state, Scheme 4.1[56].

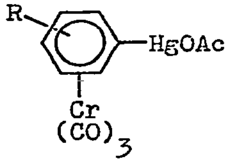


Scheme 4.1

In the mass spectrometer (η-methylbenzoate)tricarbonylchromium underwent secondary electron capture to give a molecular ion which suffered decarbonylation and further loss of three CO groups. Cr^- ions were also identified in the 70eV negative ion mass spectrum of this compound[57]. The use of mass spectroscopy for the analysis of mixtures of (η-benzene)-tricarbonylchromium complexes was investigated. Intense peaks were obtained for the molecular ions $[(\eta\text{-}C_6H_5X)Cr(CO)_3]^+$ (X = H, Me, Et, F and Cl) and $[(\eta\text{-}C_6H_5X)Cr]^+$. The ions $[(\eta\text{-}C_6H_5X)CrCO]^+$ $[(\eta\text{-}C_6H_5X)Cr(CO)_2]^+$ and $(C_6H_5X)^+$ were also useful in the identification of the (η-benzene)tricarbonylchromium derivatives[58].

(iii) General Chemistry.

Benchrotrene was mercurated with mercury (II) acetate to give the derivative (4.25; R = H) in 29% yield. Triethylsilylbenchrotrene was metallated in the same way to form the disubstituted compound (4.25; R = $SiEt_3$)[59]. The quantum yield for the photochemical decomposition of benchrotrene in cyclohexane was found to be proportional to the rate constant for decomposition and was inversely related to the intensity of the light used. A complex mechanism of decomposition was indicated with three competing reactions[60]. Jaouen and Dabard have cyclized the butyric acid (4.26) with polyphosphoric acid to give a mixture of the endo-cyclopentenone (4.27), 52% and the exo-isomer (4.28), 48%. When either the endo- or the exo-isomer was heated with sodium methoxide then an equilibrium mixture of the two isomers was obtained containing the same proportions as were formed in the initial cyclization. The equilibration presumably proceeded through the enol form (4.29) of the cyclopentenones. Cyclization of the butyric acid (4.30) also gave a pair of isomeric products[61].



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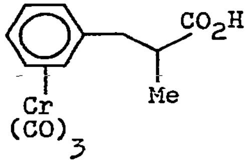

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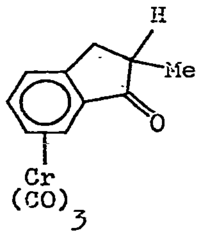

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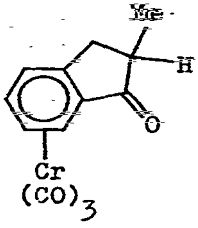

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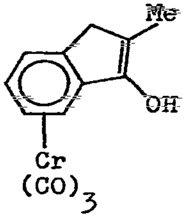

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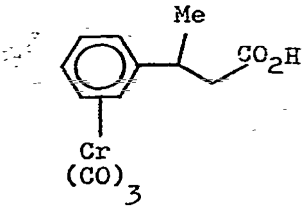

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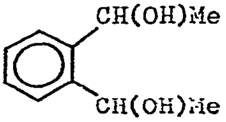
The reaction of methylmagnesium iodide with the dialdehyde (4.6; $R^1 = R^2 = CHO$) gave a mixture of two meso, pseudoasymmetric glycols and one racemic glycol [4.6; $R^1 = R^2 = CH(OH)Me$]. Photochemical removal of the ligands gave two diastereoisomeric alcohols (4.31). Oxidation of the alcohol [4.6; $R^1 = CH_2OH$, $R^2 = CH(OH)Me$] gave the cyclic hemiacetal (4.32; X = H, R = OH) and the phthalide (4.32; X = O, R = H)[62]. The benchrotrene monomer



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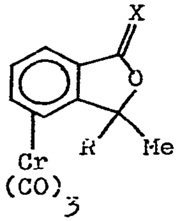
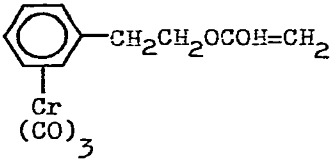


4.32

(4.33) was prepared from (η-2-phenylethanol)chromium tricarbonyl and acryloyl chloride in benzene. Approximate reactivity ratios were obtained for the copolymerization of the monomer (4.33) with styrene, methyl acrylate, acrylonitrile and 2-phenylethylacrylate in ethyl acetate with azobisisobutyronitrile as the initiator. High yields of the copolymers (4.34; R = Ph, CO_2Me, CN, $CO_2CH_2CH_2Ph$) were obtained at 70°

and all exhibited bimodal molecular weight distributions. The organometallic residues decomposed in sunlight and on UV irradiation in air or under nitrogen with the initial formation of Cr_2O_3[63]. The symmetrical benchrotrenyl mercury compounds



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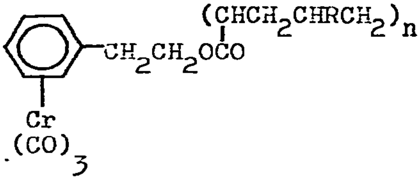
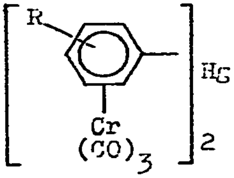


4.34

(4.35; R = H, Me, OMe, NMe_2) were cleaved with lithium aluminium hydride to give the substituted benchrotrenes (4.36; R^1 = H, Me, OMe, NMe_2, R^2 = H) in good yield. Cleavage with iodine at low temperature gave the iodo-benchrotrenes (4.36; R^1 = H, Me, OMe, NMe_2, R^2 = I)[64].



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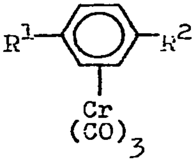
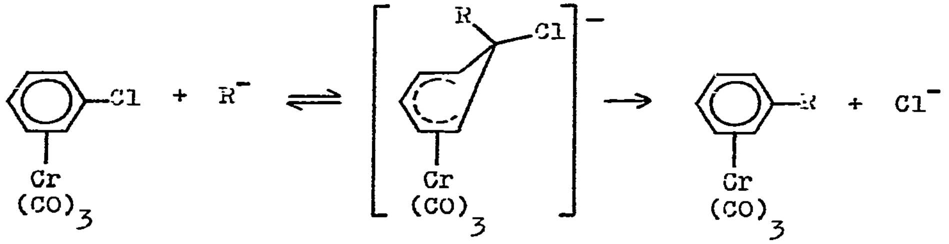


4.36

(η-Chlorobenzene)chromium tricarbonyl (4.37) was treated with the anion of isobutyronitrile to give the chromium tricarbonyl complex (4.39; R = CMe_2CN) which was readily cleaved with iodine in ether to give phenylisobutyronitrile. The large activating effect of the chromium tricarbonyl was apparent in that the reaction was complete within 20h whilst no reaction occurred with uncomplexed chlorobenzene over a similar period. Several other anions were used successfully in this reaction, however those generated from 1,3-dithiane, 2-methyl-1,3-dithiane, *tert*-butyl acetate, acetophenone, 5,6-dihydro-2,4,4,6-tetramethyl-4*H*-1,3-oxazine and acetonitrile failed[65]. The mechanism of the reaction of carbanions with (η-chlorobenzene)chromium tricarbonyl (4.37) was investigated. It was suggested that attack by the carbanion occurred to form a (η-alkylcyclohexadienyl)chromium tricarbonyl anion (4.38) followed by irreversible loss of halide anion to give the product (4.39). When an electrophile was added to the reaction system of (4.37) and the anion, followed immediately by addition of iodine, the following products were isolated; chlorobenzene, phenylisobutyronitrile, *o*- and *m*-chloro(2-cyano-2-propyl)benzene and a series of dihydro analogues of these last two products[66].

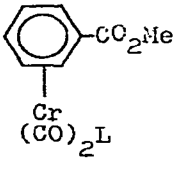


4.37 4.38 4.39

(η-Mesitylene)chromium tricarbonyl and other (η-arene)-chromium or molybdenum tricarbonyls have found application as catalysts for the polymerization of phenylacetylene[67]. (η-Phenanthrene)chromium tricarbonyl has been used to catalyse the selective hydrogenation of a propellatetraene to the corresponding propelladiene[68]. Phenylacetylene was polymerized rapidly and quantitatively in the presence of (η-toluene)-molybdenum tricarbonyl to give linear polymers with molecular weights up to 12,000. The polymerization proceeded *via* a ladder polymer intermediate which was isolated when (η-mesitylene)chromium tricarbonyl was used as the catalyst. The ladder polymer rapidly gave linear polyphenylacetylene in the presence of (η-toluene)molybdenum tricarbonyl and this reaction was thought to proceed *via* a free-radical mechanism[69].

(iv) Analogues

Jaouen and Dabard have converted monosubstituted benchrotrenes into chiral complexes by replacement of carbonyl groups by other ligands. Thus (η-methylbenzoate)chromium tricarbonyl was treated with cyclooctene to form the derivative (4.40; L = C_8H_{14}) and this intermediate was stirred with carbon disulphide and triphenylphosphine to give the thiocarbonyl complex (4.40; L = CS). Irradiation of the thiocarbonyl complex with triethyl phosphite led to the chiral phosphite (4.41). Several disubstituted benchrotrene derivatives [4.42; X = H, Bu^t, Me; R = H, Me, menthyl; L = CO, $P(OR)_3$, PPh_3] were described[70]. The photosubstitution of a carbonyl



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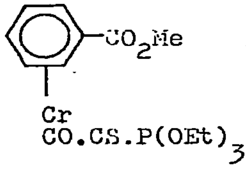

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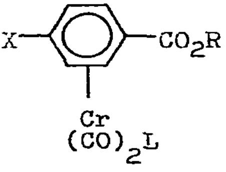
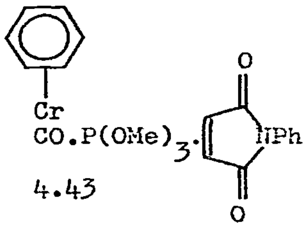


4.42

group in (η-ArH)Cr$(CO)_3$ by N-phenylmaleimide (NPhMI) gave

(η-ArH)Cr(CO)$_2$(NPhMI). Irradiation of complexes of this type in the presence of a phosphite gave the chromium complexes (4.43 and 4.44). These compounds are the first neutral asymmetric (η-benzene)chromium (0) complexes with the metal atom as the chiral centre. The vinylic protons of the N-phenylmaleimide ligand were diastereotopic and displayed a temperature dependant ^{1}H NMR spectrum[71]. Photolysis of η-LCr(CO)$_3$[L = hexamethylbenzene, mesitylene, *p*-RC$_6$H$_4$Me, (R = Me$_2$N, Me, MeO, F and CO$_2$Me), C$_6$H$_6$, and *p*-(MeO$_2$C)$_2$C$_6$H$_4$] in the presence of 2,3-diazobicyclo[2.2.1]hept-2-ene (L^1) gave η-LCr(CO)$_2$ L^1. The ligand L^1 was coordinated to chromium through the lone pair of electrons of one of the nitrogen atoms of the N=N double bond[72]. Connelly and Demedowicz have displaced carbonyl from (η-C$_6$Me$_6$)Cr(CO)$_3$ using the diazonium salts (*p*-RC$_6$H$_4$N$_2$)X (R = H, X = PF$_6$; R = OMe and NO$_2$, X = BF$_4$) to afford the complexes (η-C$_6$Me$_6$)-Cr(CO)$_2$(*p*-RC$_6$H$_4$N$_2$)$^+$X$^-$which were claimed to be the first examples of arylazochromium derivatives. Treatment of these derivatives with sodium borohydride gave the corresponding neutral cyclohexadienyl complexes (η-C$_6$Me$_6$H)Cr(CO)$_2$(*p*-RC$_6$H$_4$N$_2$). The reaction of (η-C$_6$Me$_6$)Cr(CO)$_2$PPh$_3$ with (*p*-RC$_6$H$_4$N$_2$)$^+$ gave the paramagnetic cation [η-C$_6$Me$_6$Cr(CO)$_2$(PPh$_3$)]$^+$ where the diazonium salt had behaved as an oxidizing agent.



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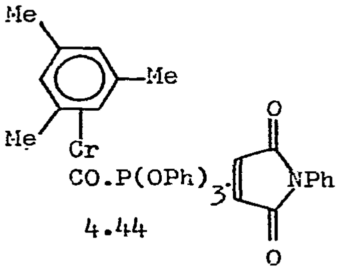
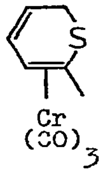


4.44

$(\eta\text{-}C_6Me_6)Mo(CO)_3$ was treated also with $(\underline{p}\text{-}RC_6H_4N_2)^+$ to give complexes that were apparently analogous to the chromium species but no stable products were isolated[73]. The reaction of $(\eta\text{-}C_6Me_{6-n}H_n)Cr(CO)_2PhC{\equiv}CPh$, n = 0 and 1, with either $NOPF_6$ or $AgPF_6$ gave the air stable salts $[(\eta\text{-}C_6Me_{6-n}H_n)Cr(CO)_2(PhC{\equiv}CPh)]PF_6$. The carbonyl stretching frequencies for the cations were 100-150 cm^{-1} higher than those of the neutral compounds. Cyclic voltammetry showed that the neutral acetylene complexes underwent a reversible one-electron oxidation[74].

6-Methyl-2$\underline{H}$-thiopyran was heated with $(MeCN)_3Cr(CO)_3$ in dibutyl ether to form the benchrotrene analogue (4.45) in which sulphur coordinates to the metal with nonbonding as well as olefinic electrons. The physical properties of the complex were compared with those of (η-thiophen)chromium tricarbonyl and the corresponding (η-1,2-dihydropyridine)chromium complex[75]. A series of (η-thiophen)chromium tricarbonyl complexes was



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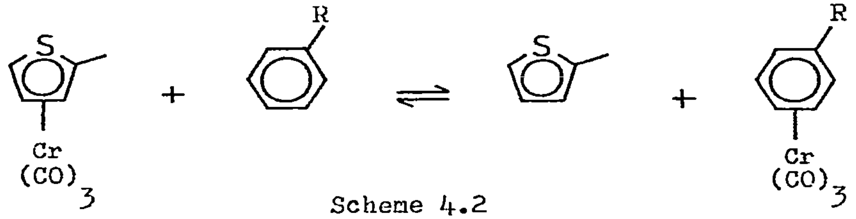


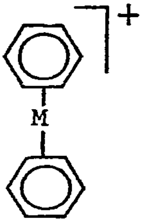
Scheme 4.2

prepared by reaction of the appropriate heterocycle with $(MeCN)_3Cr(CO)_3$. The yields in these reactions were higher than in preparations utilizing $Cr(CO)_6$. The separation and decomposition of the thiophene complexes was studied by gas-liquid chromatography. Treatment of the complexes with benzene resulted in ligand exchange (Scheme 4.2)[76]. The ^{1}HNMR spectra of the η-thiophene complexes were analysed[77]. The treatment of (η-$Me_3B_3N_3Me_3$)$Cr(CO)_3$ with $Me_3B_3N_3H_3$ brought about ligand exchange to give (η-$Me_3B_3N_3H_3$)$Cr(CO)_3$[78]. Scotti and Werner have attacked substituted borazines with $Cr(CO)_3$-$(MeCN)_3$ to give the chromium complexes (η-$R^1{}_3B_3N_3R^2{}_3$)$Cr(CO)_3$ (R^1 = Pr, R^2 = Me; R^1 = Me, R^2 = Pr; R^1 = *iso*-Pr, R^2 = Me; R^1 = Me, R^2 = *iso*-Pr). These compounds were more labile than the isomeric complex (η-$Et_3B_3N_3Et_3$)$Cr(CO)_3$ which was prepared from (η-$Et_3B_3N_3Me_3$)$Cr(CO)_3$ by ring ligand exchange[79].

5. (η-C_6H_6)$_2$Cr

The direct synthesis of bis(η-*m*-diisopropylbenzene)chromium, bis(η-cumene)chromium and (η-biphenyl)(η-*m*- dipropylbenzene)-chromium from chromium and the arenes has been reported[80]. Chromium atoms were cocondensed with benzene in an argon matrix, on a caesium iodide window at 14°K, to give di(η-benzene)-chromium which was characterized by infrared spectroscopy[81]. Nickel atoms were treated with hexafluorobenzene to give a highly reactive and explosive complex. In a similar manner hexafluorobenzene and benzene were allowed to react with chromium to give presumably bis(hexafluorobenzene)- and di(η-benzene)chromium respectively[82]. The formation of bis(η-arene)metal complexes has been achieved by condensation of metal atoms obtained by resistive heating with the arene at -196°. Arenes used were benzene, toluene, xylene, anisole and fluorobenzene and these were condensed with molybdenum and tungsten[83]. Bis(η-arene)molybdenum complexes have been separated from mixtures and purified by molecular distillation[84]. A series of bis(η-fluorobenzene)chromium complexes (η-$C_6H_4FX)_2Cr$ (X = H, F, Cl, CH_3, CF_3) were prepared by cocondensing chromium atoms and fluoroarenes. The ^{19}F NMR spectra of these complexes suggested that the overall electron-withdrawing effect of a π-bonded chromium atom on each ring was similar to that of four ring fluorine substituents[85].

The X-ray photoelectron (ESCA) spectra of fourteen bis(η-arene) and (η-arene)tricarbonyl complexes of Cr, Mn and Fe were measured in the solid state. The binding energies were interpreted with the aid of ab initio SCF MO calculations for (η-C_6H_6)Cr(CO)$_3$ and (η-C_6H_6)$_2$Cr and semi-empirical MO calculations on most of the other compounds. In neutral bis(η-arene)metal complexes the arene ring carried a small negative charge and the electron density on the ring was higher than in the comparable (η-arene)tricarbonyl complex[86]. Simple mass spectra were obtained, for a series of bis(η-arene)-chromium and -molybdenum complexes, at 60° for the chromium compounds and at 100° for the molybdenum compounds, by the use of a field-ionization source. The ions (5.1; M = Cr, Mo) were formed preferentially and the method was suitable for qualitative and quantitative analysis. Mass spectrometry with field ionization was also used for studying the thermal decomposition of these compounds[87]. The dependence of the hyperfine structure of EPR signals of bis(η-arene)chromium compounds [e.g. (η-PhH)$_2$Cr$^+$, (η-PhMe)$_2$Cr$^+$, (η-PhPh)$_2$Cr$^+$] on temperature ($-160°$–$+70°$), viscosity, solvent and magnetic field was studied. The line width temperature dependence was explained by the relaxation mechanisms: when $\omega\tau > 1$, an anisotropic Zeeman interaction; when $\omega\tau < 1$, a modulation of spin reversalinteraction[88]. A synthetic mixture of bis(η-arene)chromium iodides was resolved by partition liquid chromatography and the chromium content in each fraction was determined by atomic absorption spectrometry[89].



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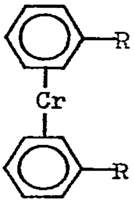

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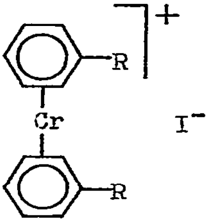
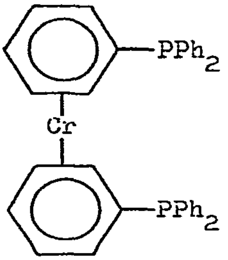


5.3

The kinetics of hydrogen-deuterium exchange for the complexes (5.2; R = H, Me, Et) in EtOD-EtONa and for the salt (5.3; R = H, Me) in D_2O-KOD were studied. In both reactions deuterium entered both the aromatic nucleus and the side chain[90]. The kinetics for the thermal decomposition of the diarene complex (η-PhEt)$_2$Cr was correlated with its field mass spectrum[91]. The saturated vapour pressures for a series of bis(η-arene)molybdenum complexes were determined and the heats of evaporation were calculated[92]. The saturated vapour pressures of the benzene complexes (η-PhH)$_2$Cr, (η-PhH)(η-PhEt)Cr, (η-PhEt)(η-$C_6H_4Et_2$)Cr and (η-$C_6H_3Me_3$)$_2$ Cr were determined at 20-110° and the heats of evaporation were measured[93]. Expressions have been derived to correlate the physicochemical properties, such as density and vapour pressure, of bis(η-arene)metal complexes. The arene ligands were benzene and substituted benzenes and the metals were chromium, molybdenum and tungsten[94].

Bis(η-benzene)chromium was heteroannularly dilithiated with a mixture of butyllithium and TMEDA in cyclohexane at 70°. The lithio intermediate was stirred with diphenylchlorophosphine to give the diphosphine (5.4) which was converted to the dimethiodide[95]. Mixed sandwich complexes of chromium have been formed by direct reaction between chromium salts and acetylenes. Treatment of 2-butyne with chromium (III) chloride and trialkylaluminium gave the η-benzene cation (5.5; R^1 = Me, R^2 = Me, Et, Pr). The cation was reduced with lithium aluminium hydride to the neutral sandwich compound (5.6; R = Me). Replacement of 2-butyne with 2-hexyne in the same reaction gave the η-benzene cation (5.5; R^1 = Et, R^2 = Me, Et, Pr) which on reduction formed the η-benzene complex (5.6; R = Et). It was suggested that the polyalkylbenzene ligands were formed by cyclotrimerization of the acetylenes while the cyclopentadienyl groups arose by cleavage of the acetylenes at the triple bond[96]. Bis(η-diphenyl)chromium was oxidized with a stream of oxygen in the presence of 1,3-diphenyltriazine to give the salt (5.7) which was isolated as the sesquihydrate[97]. Bis(η-ethylbenzene)chromium was



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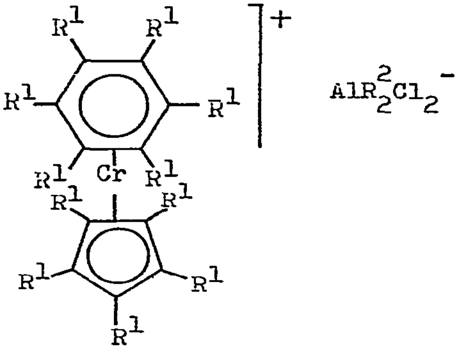

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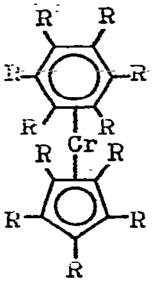

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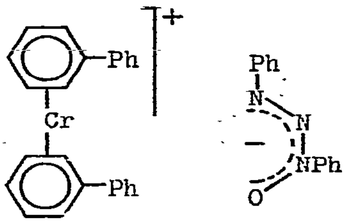


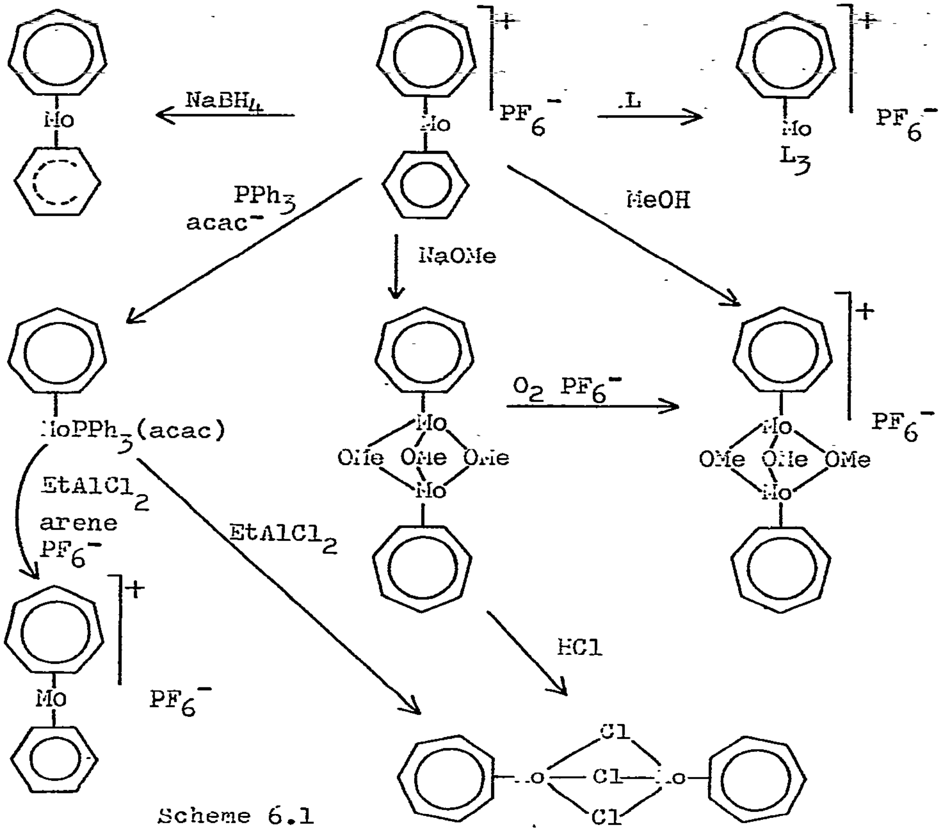
5.7

pyrolysed at 350-450° for 10h to give methane, C_2-C_4 hydrocarbons and chromium as the main products together with minor amounts of hydrogen, toluene and ethylmethylbenzene[98].

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

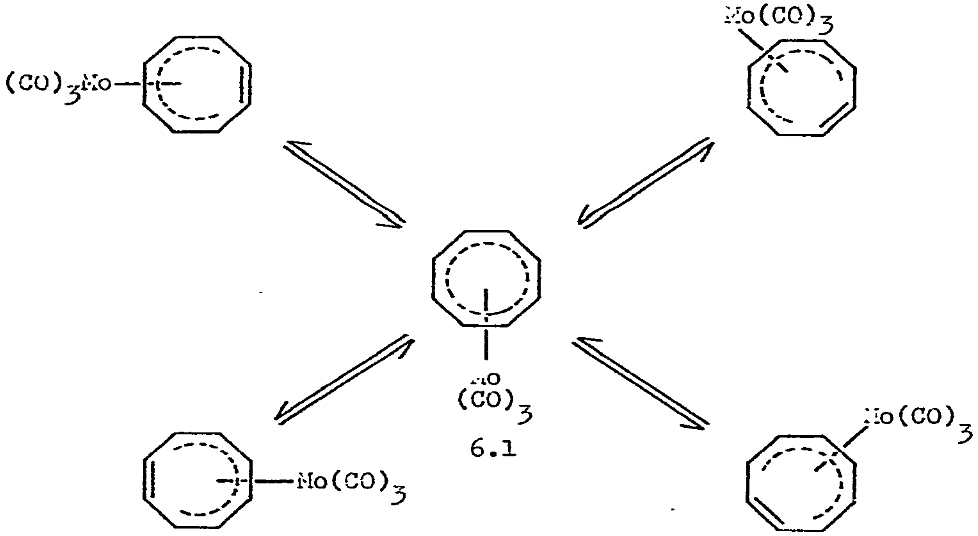
An improved synthesis for the compounds $(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)M$ (M = Cr, Mo) was reported from $MCl_3.3THF$, C_7H_8, C_5H_6 and $i\text{-}C_3H_5MgBr$. The reactants were mixed together in THF-diethylether at -20°. The product was purified by sublimation and subsequent recrystallization. The synthesis and properties of $(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)M$, (M = Zr, Nb) were reported[99]. Green and co-workers have reported a general route for preparing non-carbonyl cycloheptatrienyl molybdenum compounds <u>via</u> the facile displacement of the arene ligand from the complexes $[(\eta\text{-}C_7H_7)(\eta\text{-arene})\,Mo]^+PF_6^-$ as shown in Scheme 6.1[100].

The crystal structure of 1,3,3,5-tetramethyl-6-(1',2'-naphtho)bicyclo[3,2,1]octenechromium (0) tricarbonyl was determined by X-ray analysis. The crystal data was as follows: space group <u>C</u>2/<u>c</u>, a = 19.66, b = 14.35, c = 16.44Å, = 120.1°, Z = 8. The cyclohexane ring was distorted from the normal chair form due to the steric interaction of an



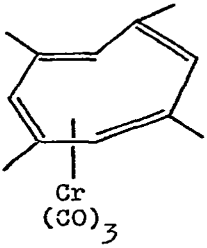
Scheme 6.1

axial methyl group with the naphthalene moiety and the strain of fusion through a five-membered ring to the naphthalene moiety. The chromium atom was complexed to the ring of the naphthalene that was fused to the aliphatic part of the molecule[101]. X-ray photoelectron spectra (ESCA) on (η-C_5H_5)(η-C_7H_7)M, (M = Ti, V, Cr) and some related compounds showed that the oxidation state of the metal increased in the sequence $Cr < V < Ti$. This resulted in an increased electron density on the ligands in the same sequence. In the Cr compound the cyclopentadienyl ring was more negative than the cycloheptatrienyl ring; for the V compound about equal negative charges were found on the two rings; while for the Ti compound the highest negative charge was found on the seven membered ring[102]. ^{13}C and ^{1}H NMR spectra of the compounds $(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)M$, (M = Ti, Zr, Mo, Cr) were recorded. For the chromium compound the ^{13}C resonance of the $\eta\text{-}C_7H_7$ ring was at lower field than that for the $\eta\text{-}C_5H_5$ ring, whilst for the molybdenum compound the two signals were close together. It was concluded that the $\eta\text{-}C_5H_5$ ring was more negatively charged than the $\eta\text{-}C_7H_7$ ring in the chromium compound. ^{1}H NMR spectra indicated hindered rotation of the rings in the chromium and molybdenum compounds[103]. The mechanism of fluxional rearrangement in (η-cyclooctatetraene)tricarbonylmolybdenum was investigated using ^{13}C NMR spectroscopy. The results ruled out a 1,2 shift and it was proposed that the rearrangement process involved a symmetrical "piano stool" intermediate (6.1), Scheme 6.2, with the metal atom lying over the centre of a flat octagonally symmetric C_8H_8 ring[104].



Scheme 6.2

The fluxional behaviour of the chromium tricarbonyl derivative (6.2) was reexamined with ^{13}C NMR and it was proved that a 1,2-shift process occurred. For the chromium tricarbonyl derivative (6.3), ^{13}C NMR showed that 1,2-shifts were not the pathway and that only 1,3-shifts or a process resulting in random shifts were admissible[105].



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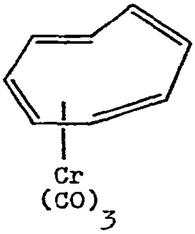
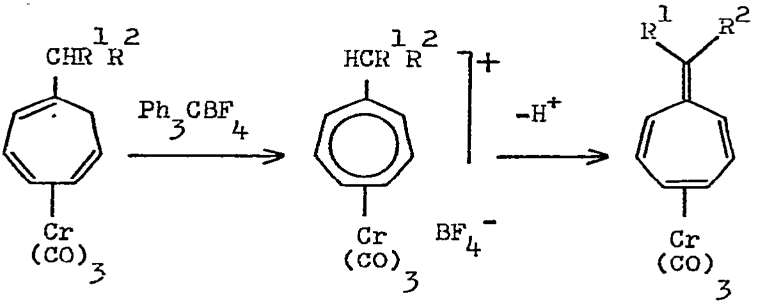


6.3

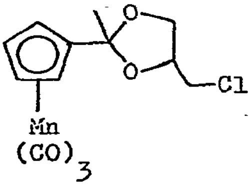
The reaction of (η-cycloheptatriene)metal tricarbonyl (where metal = chromium, molybdenum or tungsten) with acetonitrile obeyed third-order kinetics. The reaction was interpreted in terms of pre-equilibrium association between the π-complex and acetonitrile which was followed by rate-determining addition of a further molecule of acetonitrile. The ease of displacement of the ligand decreased in the order Mo > W > Cr. Displacement of the aromatic ligand from the complex $(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Mo(CO)}_3$ by acetonitrile followed second-order kinetics and led to the following order of displacement of ligands (L) from the complexes LMo(CO)_3^{n+} where n = 0,1; $\eta\text{-C}_7\text{H}_8 > \eta\text{-C}_6\text{H}_3\text{Me}_3 > \eta\text{-C}_7\text{H}_7$[106]. The reaction of $[(\eta\text{-C}_7\text{H}_7)\text{Mo(CO)}_3]\text{BF}_4$ with triphenylphosphine gave $[(\eta\text{-C}_7\text{H}_7)\text{Mo(CO)}_2\text{PPh}_3]\text{BF}_4$ which was reduced with sodium borohydride to give $(\eta\text{-C}_7\text{H}_8)\text{Mo(CO)}_2\text{PPh}_3$[107]. Hepta-fulvene complexes of chromium (6.6; R^1 = Ph, Me, H; R^2 = Ph, Me, H) have been obtained from the 1-substituted cycloheptatriene compounds (6.4) by hydride ion abstraction with triphenylmethyl fluoroborate to form the tropylium salts (6.5) which were treated with 1,8-bis(dimethylamino)naphthalene, a strong non-nucleophilic base, to abstract a proton and give the products (6.6). These compounds resembled free heptafulvenes in their reactivity towards electrophiles with exclusive attack at the exocyclic double bond[108].



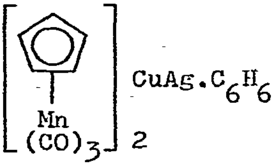
6.4 6.5 6.6

7. $(\eta-C_5H_5)Mn(CO)_3$. (i) Formation

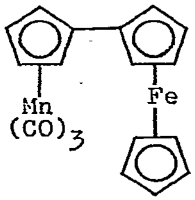
[η-(Triorganosilyl)cyclopentadienyl]tricarbonylmanganese compounds were prepared by treating a (triorganosilyl)-cyclopentadiene with an alkali metal, heating the resultant metal derivative with manganese (II) salts and treating the intermediate bis(η-cyclopentadienyl)manganese with carbon monoxide at 100-200° and 50-200 atmospheres[109]. The dioxolanylcymantrene (7.1) was prepared by condensation of acetylcymantrene with epichlorhydrin in the presence of tin (IV) chloride using carbon tetrachloride as solvent[110]. Bis(cymantrenyl) copper silver (7.2) was formed by treatment of cymantrenylsilver with copper (I) iodide in benzene. The complex (7.2) was converted to benzoylcymantrene with benzoylchloride, to phenylcymantrene with iodobenzene and to ferrocenylcymantrene (7.3) with ferrocenylbromide. Yields were in the range 70-83%[111]. King and Ackermann have investigated



7.1

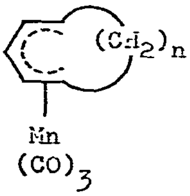


7.2



7.3

the reactions of olefins and acetylene with $[HMn(CO)_4]_3$ under mild conditions. Dienylmanganese tricarbonyl compounds (7.4) were formed in several cases, thus 1,3-cyclohexadiene give the cyclohexadienyl compound (7.4; n = 1). The cycloheptadienyl compound (7.4; n = 2) was formed from both cycloheptatriene and 1,3-cycloheptadiene. The same reaction with 1,3,5-cyclooctatriene gave the cyclooctadienyl compound (7.4; n = 3) together with other manganese complexes. The dienyl complex (7.5) was formed in addition to a fluxional dimanganese complex when cyclooctatetraene was the reactant. When dimethylaminofulvene was used then the cymantrene derivative (7.6) was obtained[112].



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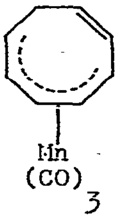

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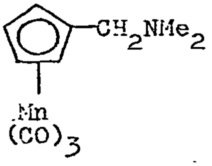
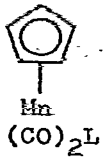


7.6

(ii) Spectroscopic and Physico-chemical Studies

Cymantrene was irradiated with X-rays or electrons and the free radicals formed were examined by EPR spectroscopy. The anisotropic spectrum of the final, stable paramagnetic species was compared with the theoretical model based on the crystal field approximation modified for covalency effects[113]. The frequencies of the metal-cyclopentadienyl and metal-carbonyl stretching modes in (η-cyclopentadienyl)tricarbonyl-manganese and -rhenium were compared. The frequencies of the manganese-ring stretching vibrations increased whilst those of manganese-carbonyl decreased with an increase in π-acceptor properties of the substituent R in the ring. The frequency of the rhenium-ring stretching vibrations was independent of the substituent R. These differences showed that the dative $d\pi$(metal)-$p\pi$(CO) was more important in the formation of the metal-ring bond in (η-RC_5H_4)$Mn(CO)_3$ than in the corresponding rhenium compound[114]. Parker has obtained the IR and laser Raman spectra of cymantrene and (η-C_5D_5)$Mn(CO)_3$. The solution spectra may be assigned approximately on the basis of C_{5v} 'local' symmetry but this approach cannot be used for the assignment of the solid state spectra[115]. The protonation of the manganese-η-cyclopentadienyl complexes (7.7 and 7.8) was studied with ^{13}C and ^{31}P NMR techniques. The complexes were subject to rapid reversible protonation at the metal atom in the presence of trifluoroacetic acid. The protonation was governed by the basicity of the manganese atom which depended on the number and nature of the phosphine ligands. The basicity of the diphosphine complexes (7.8) was higher than that of the monophosphine complexes (7.7) and the alkylphosphines were better electron donors than triphenylphosphine[116].



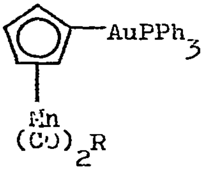
7.7 L = $P(C_6H_{11})_3$, $P(i\text{-}C_3H_7)_3$, $P(CH_2Ph)_3$, PPh_3

7.8 L = PPh_3
L_2 = $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH_2CH_2CH_2PPh_2$

The ^1H NMR spectra of cymantrene and fifteen monosubstituted cymantrenes have been compared with the spectra of the corresponding rhenium compounds. In each case the electron density on the η-cyclopentadienyl group was higher in the cymantrene compounds than in their rhenium analogues[117].

(iii) General Chemistry

Treatment of the (η-cyclopentadienyl)manganese complexes (7.9) with hydrogen borofluoride in tetrahydrofuran gave the gold complexes (7.10; R = CO, PPh_3)[118]. Tricarbonyl(η-cyclopentadienyl)manganese was treated with Et_2NPCl_2 to give $[(CO)_3Mn(\eta\text{-}C_5H_4)]_3P$. Treatment of this phosphine with H_2O_2, Cl_3PS and methyl iodide gave $[(CO)_3Mn(\eta\text{-}C_5H_4)]_3PO$, $[(CO)_3\text{-}Mn(\eta\text{-}C_5H_4)]_3PS$ and $[(CO)_3Mn(\eta\text{-}C_5H_4)]_3\overset{+}{P}MeI^-$ respectively[119].
The photochemical reactions of $(\eta\text{-}C_5H_5)Mn(CO)_3$ and $(\eta\text{-}C_5H_5)Mn(CO)_2(CS)$ with $(Ph_2PCH_2CH_2)_2\dot{P}Ph$ (triphos) gave $(\eta\text{-}C_5H_5)Mn(CO)(\text{triphos})$, as two isomers (7.11 and 7.12) and



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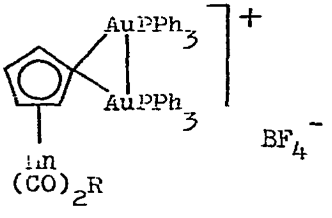
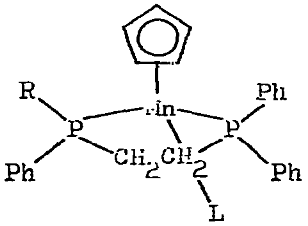
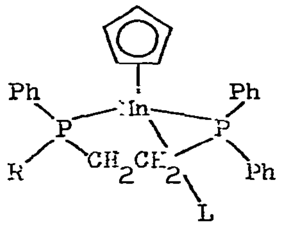


7.10

$(\eta\text{-}C_5H_5)Mn(CS)(triphos)$ as two isomers, (7.11 and 7.12) respectively. The presence of one uncoordinated phosphorus atom in the complexes was confirmed by their reactions with $Cr(CO)_5(THF)$ and $(\eta\text{-}C_5H_5)Mn(CO)_3$ to give the bimetallic species, $(\eta\text{-}C_5H_5)(CO)Mn(triphos)Cr(CO)_5$, $(\eta\text{-}C_5H_5)(CS)Mn(triphos)Cr(CO)_5$, $(\eta\text{-}C_5H_5)(CO)Mn(triphos)Mn(CO)_2(\eta\text{-}C_5H_5)$ and $(\eta\text{-}C_5H_5)(CS)Mn(triphos)Mn(CO)_2(\eta\text{-}C_5H_5)$. The reaction of $(\eta\text{-}C_5H_5)Mn(CO)_2CS$ with $Ph_2PCH_2CH_2PPh_2$ gave $(\eta\text{-}C_5H_5)Mn(CS)Ph_2PCH_2CH_2PPh_2$. The absence of any CS substitution by the phosphorus ligands demonstrated the stronger metal-carbon bonding in metal thiocarbonyls as compared to metal carbonyls[120].



7.11.

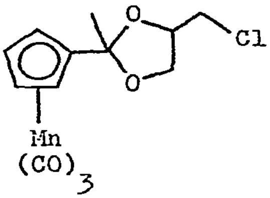


7.12

L = CO, CS

R = $CH_2CH_2PPh_2$

$(\eta$-Methylcyclopentadienyl)tricarbonylmanganese was fed orally to rats and it caused histopathological changes in the lungs, liver and kidney. The degree of severity was related to the dose. Manganese concentrations in the tissues of the animals given 15-150 mg/kg was high, those that survived the treatment had normal manganese levels fourteen days after the complex had been administered. The results indicated that manganese metabolism was homeostatically controlled and that the manganese was transported in the tissues as a metabolite of the original complex[121]. The thermal stability of siloxanes containing tricarbonyl(η-cyclopentadienyl)manganese was reviewed[122]. Acetylcymantrene was converted to the ketal (7.13) by treatment with epichlorohydrin and tin (IV) chloride in carbon tetrachloride[123]. Silvercymantrene was treated with trinitrobenzene and tropylium tetrafluoroborate to give the anion (7.14) which was oxidized to 1(2,4,6-trinitrophenyl)-cymantrene[124]. The cymantrene gold complex (7.15; X = CO) was irradiated with triphenylphosphine in benzene to give the cymantrene analogue (7.15; X = PPh_3). When an excess of triphenylphosphine was used in the reaction then gold-carbon cleavage was observed rather than replacement of a second carbonyl group by triphenylphosphine[125].



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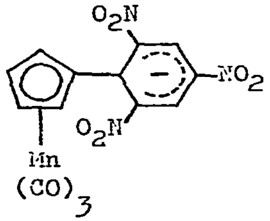

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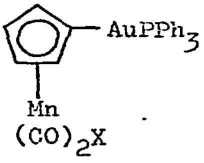
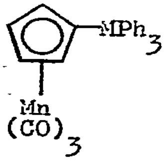


7.15

The effect of manganese based additives, e.g. (η-methylcyclopentadienyl)manganese tricarbonyl on the mass, size distribution and the chemical composition of particulate emissions from gas turbine combustors was investigated. The presence of large amounts of (η-methylcyclopentadienyl)-manganese tricarbonyl increased the mass of the emissions with the manganese being discharged as MnO[126]. Lithiocymantrene was treated with triphenylsilicon-, triphenylgermanium-, triphenyltin- and triphenylead-chloride to give the cymantrenes (7.16; M = Si, Ge, Sn, Pb). The tin-cyclopentadienyl bond in the tin compound (7.16; M = Sn) was cleaved with dry HCl to form cymantrene[127]. Metal carbonyls and organometallic compounds, including methylcymantrene, have been incorporated into polymeric analogues of benzyldiphenylphosphine. The polymer-bound complexes have been evaluated as hydroformylation and olefin isomerization catalysts[128].



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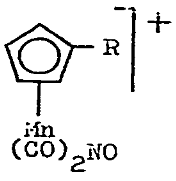
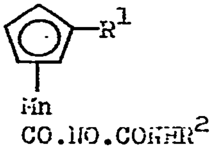


7.17

$[(\eta\text{-MeC}_5H_4)Mn(CO)_2NO]^+ PF_6^-$ was treated with (S)-(+)--MePhCHNMe(PPh$_2$) (ligand L) in acetone in the absence of air to give the pair of diastereoisomers of the tetrahedrally coordinated complex $[(\eta\text{-MeC}_5H_4)Mn(CO)(NO)L]^+PF_6^-$. The isomers were separated by fractional crystallization[129]. Details have been given for the preparation of $[(\eta\text{-C}_5H_5)Mn(CO)_2NO]PF_6$ from $(\eta\text{-C}_5H_5)Mn(CO)_3$ and $NOPF_6$[130]. The cymantrene analogues (7.17; R = H, Me) gave the carboxamides (7.18; R^1 = H, Me, R^2 = alkyl, aryl) on treatment with primary amines in ether[131]. Reaction of $(\eta\text{-MeC}_5H_4)Mn(CO)_2THF$ with an excess of α-diazodeoxybenzoin gave the phenylcarbene complex 7.19[132].



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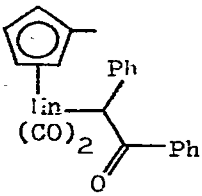

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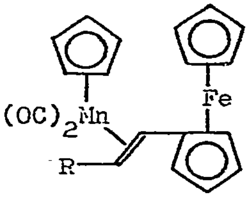
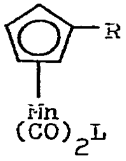


7.20

Treatment of cymantrene with substituted vinylferrocenes gave the mixed complexes (7.20; R = H, acyl) in yields of 21-25%[133].

The ^{1}H NMR spectra of the isoelectronic complexes $(\eta\text{-}C_5H_5)Mn(CO)_2CH_2{=}CH_2$ and $(\eta\text{-}C_5H_5)Cr(CO)(NO)CH_2{=}CH_2$ were analysed. The temperature dependence of these spectra indicated that the ethylene ligand underwent hindered rotation around the metal-olefin bond axis. The activation barrier for the ligand motion in the manganese complex was $\Delta G^{\ddagger}_{168} = 8.4$ kcal/mole and in the chromium complex $\Delta G^{\ddagger}_{238} = 11.4$ kcal/mole[134]. The formation of the cymantrene analogues (7.21; R = H, Me; L = CS, CS_2; 7.22 and 7.23) has been reported[135]. The reaction of $LMn(CO)_2THF$ (L = η-cyclopentadienyl and η-methylcyclopentadienyl) with $PhMeCN_2$ gave the acetophenone imine complexes (7.24; R = H and Me). The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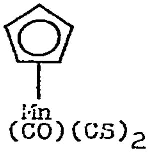
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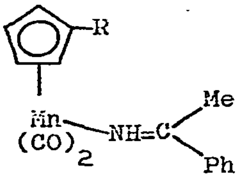
7.23

expected carbene complexes were not isolated[136]. ^{13}C NMR spectra were obtained for a series of complexes of the type $(\eta\text{-}C_5H_5)Mn(CO)_2L$, [L = CS, CO, $P(OPh)_3$, $P(OMe)_3$, PPh_3, PBu_3, $C_5H_{10}NH$, C_8H_{14}]. The results suggested that the order of increasing electron density at the transition metal was $CS < CO < P(OPh)_3 < P(OMe)_3 < PBu_3 < PPh_3 < C_8H_{14} < C_5H_{10}NH$ and that the CS ligand was a better π-acceptor than CO[137].

The reaction of the (η-cyclopentadienyl)manganese complex

(7.25; L = CO) with triphenylphosphine in the presence of ultraviolet light gave the complex (7.25; L = PPh_3). A similar replacement reaction was carried out with diphenylacetylene. Treatment of the complex (7.25; L = PPh_3) with hydrochloric acid gave $(\eta\text{-}C_5H_5)Ni(PPh_3)Cl$ and $(\eta\text{-}C_5H_5)Mn(CO)_2\text{-}PPh_3$ in good yields[138]. The crystal and molecular structure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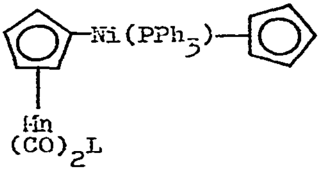
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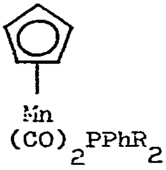
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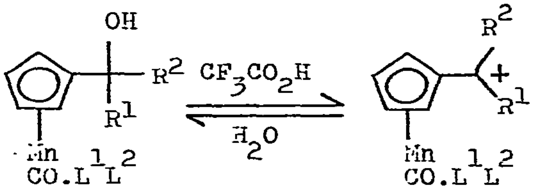
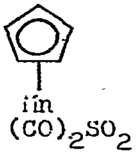
of carbonyl(η-cyclopentadienyl)bis(triphenylphosphine)-manganese benzate $(\eta\text{-}C_5H_5)MnCO(PPh_3)_2.C_6H_6$, has been obtained from three dimensional X-ray data. The compound has space group $P\bar{1}$ with unit cell dimensions a = 9.83, b = 14.79, c = 11.36 Å; $\alpha = 69.44^\circ$, $\beta = 66.48$, $\gamma = 67.57^\circ$; Z = 2. The P-Mn-P bond angle was 104° and this large bond angle was considered to be a consequence of electrostatic repulsion between the two phosphorus atoms[139]. The rate of proton exchange in $(\eta\text{-}C_5H_5)Mn(CO)(Ph_2PCH_2CH_2PPh_2)$ decreased in acetic acid-trifluoroacetic acid mixtures as the acidity increased. When sulphuric acid was added the reaction almost stopped[140]. The rate of hydrogen-deuterium exchange in the same molecule passed through a maximum as the acidity was increased. The maximum occurred when the concentrations of the protonated and nonprotonated forms were about equal[141]. The cymantrene analogues (7.26; R = CN, NCO, NCS, N_3) underwent addition reactions at the R group with alcohols, amines and carbon monoxide[142].

Tertiary and secondary carbinols of cyclopentadienylmanganese carbonyls (7.27) when treated with trifluoroacetic acid give stable carbenium ions (7.28). The carbenium ions were identified by infrared spectroscopy and when one of the carbonyl groups was substituted by a phosphine ligand the stability of the carbenium ion increased[143]. The addition





7.27 7.28 7.29

L^1, L^2 = CO, PR_3

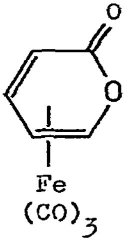
of excess trifluoroacetic acid to solutions of (η-cyclopentadienyl)phosphinemanganese complexes $(\eta\text{-}C_5H_5)MnCOL_2$ and $(\eta\text{-}C_5Et_5)Mn(CO)_2L$, where L = substituted phosphine and diphosphine ligands, gave rise to a Mn-H proton NMR signal at δ = -4 to -6 ppm. The stereochemistry of the protonated forms was determined from the ^1H-^{31}P coupling patterns[144]. The structure and bond lengths in the η-cyclopentadienyl compound (7.29) have been determined by X-ray methods. The manganese-cyclopentadienyl carbon distance was 2.09 Å and appreciably shorter than in cymantrene compounds while the manganese-sulphur distance was shorter than the normal covalent bond length by 0.3 Å [145].

The infrared and Raman spectra of $(\eta\text{-}C_4H_4N)Mn(CO)_3$ and the infrared spectrum of $(\eta\text{-}C_4D_4N)Mn(CO)_3$ were recorded.

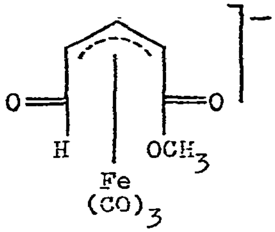
and the vibrational frequencies were assigned. The frequencies of the C_4H_4N ligand closely resembled those of the cyclopentadienyl ring in $(\eta-C_5H_5)Mn(CO)_3$. The replacement of a CH group by nitrogen had little effect on the mechanical properties of the ring and the lowering of the local symmetry of the ligand from $\underline{C}_{5v}$ to $\underline{C}_s$ did not split the degenerate modes. However, the modes, active only in the Raman spectrum of the cyclopentadienyl ring, for the pyrrolyl ligand also appeared in the infrared spectrum[146]. Nucleophiles were shown to combine with the cationic complex $[(\eta-C_6H_6)Mn(CO)_3]^+$ in four different ways; (a) by addition to the arene; when the complex was treated with $(EtO_2C)CH^-$ it gave $[\eta-C_6H_6CH(CO_2Et)_2]Mn(CO)_3$; (b) by attack at the metal with displacement of a carbonyl ligand; treatment of the complex with triphenylphosphine gave $[\eta-C_6H_6Mn(CO)_2PPh_3]^+$; (c) by attack at the metal with liberation of arene; treatment of the complex with methyl cyanide gave $[Mn(CO)_3(MeCN)_3]^+$; (d) by addition to the carbon atom of a carbonyl group; treatment of the complex with methanol gave $(\eta-C_6H_6)Mn(CO)_2-CO_2Me$[147].

8. <u>(Acyclic-η-diene)Fe(CO)$_3$ and (η-trimethylenemethane)Fe(CO)$_3$ complexes</u>

When α-pyrone was heated with diironennea carbonyl the tricarbonyliron complex (8.1) was obtained. The ester group in this complex was highly reactive and underwent cleavage with methoxide to give the allyl anion (8.2). Treatment of this anion with acetic anhydride gave the ester (8.3) and treatment with lithium aluminium hydride gave the aldehyde (8.4)[148]. The reaction of $MeCH=CHCH=CHCH(Me)NR_2$ (R = H, Me)



8.1



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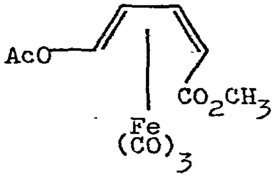
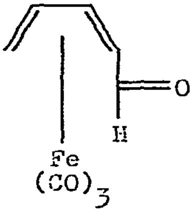


8.3

with pentacarbonyliron gave the tricarbonyliron complex (8.5). Alternative routes to this complex were also presented[149]. The reaction of $Fe_2(CO)_9$ with the olefin FcCH=CHCH(OH)Me (Fc = ferrocenyl) in the presence of copper (II) sulphate gave (η-FcCH=CHCH=CH_2)Fe$(CO)_3$. In a similar manner FcCMe(OH)CH=CH_2 gave (η-H_2C=CFcCH=CH_2)Fe$(CO)_3$. The dehydration



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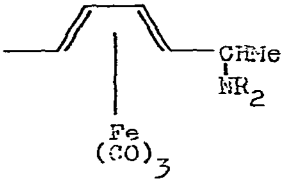
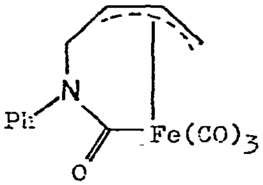


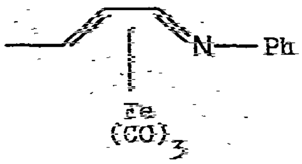
8.5



8.6

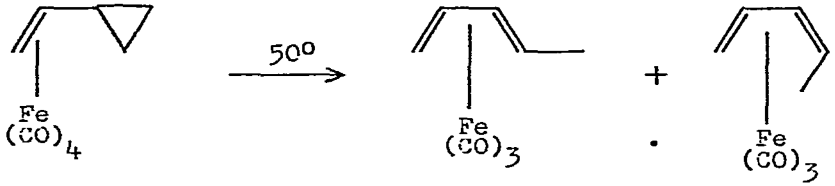
of p-FC_6H_4CH=CHCH(OH)Me with copper (II) sulphate gave p-FC_6H_4CH=CHCH=CH_2 which when treated with $Fe_3(CO)_{12}$ formed the complex (η-p-FC_6H_4CH=CHCH=CH_2)Fe$(CO)_3$[150]. The π-allyl lactam (8.6) when heated in methanol gave the iron tricarbonyl complex (8.7)[151].

Aumann has obtained the vinylcyclopropane complex of iron (8.8) from the parent hydrocarbon on irradiation with iron



8.7

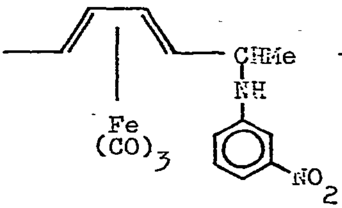
pentacarbonyl. When the cyclopropane (8.8) was heated in benzene it gave a mixture of the (η-diene)iron compounds (8.9 and 8.10)[152]. Mantzaris and Weissberger have investigated



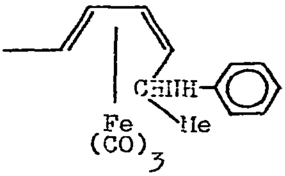
8.8 8.9 8.10

the mechanism by which cyclopentanones are formed through coupling of olefins to carbon monoxide on irradiation with iron pentacarbonyl. Photolytically generated iron tetracarbonyl first formed a (η-olefin)iron tetracarbonyl complex which was converted to a bis(η-olefin)iron tricarbonyl complex through the intermediate (η-olefin)iron tricarbonyl. Cyclization to a metallocycle followed by migratory insertion of carbon monoxide led to the product[153].

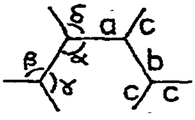
The structures of two diene-iron tricarbonyls (8.11 and 8.12) having substituents in the _syn_ and _anti_ positions were determined by X-ray diffraction. These compounds were used as models for the parent compound (η-butadiene)iron tricarbonyl and on the basis of their structures, the structure (8.13) for the butadiene molecule bonded to $Fe(CO)_3$ (C_s symmetry) was proposed[154]. (η-Pentadienyl)iron tricarbonyl cations may



8.11



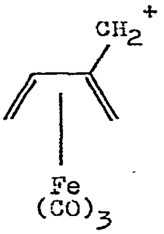
8.12



8.13

a = 1.404 Å
b = 1.415
c = 1.08
α = 119.8°
β = 117°
γ = 119°
δ = 118°

have the structures (8.14, 8.15 or 8.16), the diene (8.14) and trimethylenemethane (8.15) structures are consistent with the EAN rule with an 18-electron configuration at iron. However, the allyl structure (8.16) with a 16-electron configuration at iron is consistent with the Dewar-Chatt-Duncanson theory of bonding in transition metal π-complexes. Structure (8.16) permits free rotation about the C_2-C_3 bond while this is not permitted by structures (8.14 and 8.15). Evidence for free rotation has been obtained by Bonazza and Lillya on treatment of the (η-butadiene)iron complex (8.17) with FSO_3H in sulphur dioxide. The low-temperature ^1H NMR spectrum of the cation formed from the complex (8.17) was not wholly consistent with a (η-allyl)iron cation[155].



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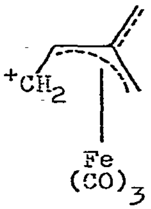

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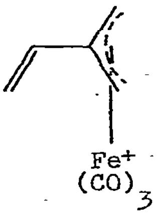

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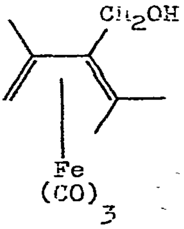
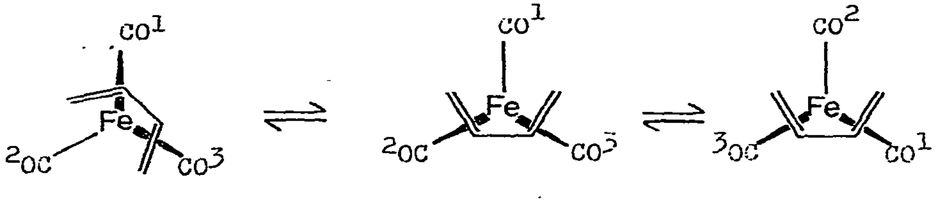
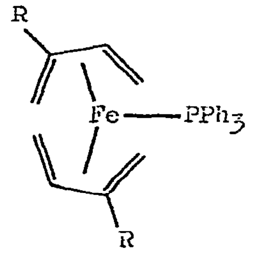


8.17

The ^{13}C NMR spectra of (η-butadiene)iron tricarbonyl and some of its derivatives have been reported and interpreted[156]. Kruczynski and Takats have investigated the fluxional behaviour of several (η-diene)iron tricarbonyl compounds by variable temperature ^{13}C NMR spectroscopy. A low-temperature limiting spectrum was obtained in each case with a 2 : 1 ratio of basal ; apical carbonyl groups. A mechanism (8.18⇌8.19⇌8.20) was suggested for the basal-apical exchange[157]. The iron complexes (8.21; R = H and Me) were characterized by protolytic reactions, mass spectrometry and ^1H and ^{31}P NMR spectroscopic studies[158].

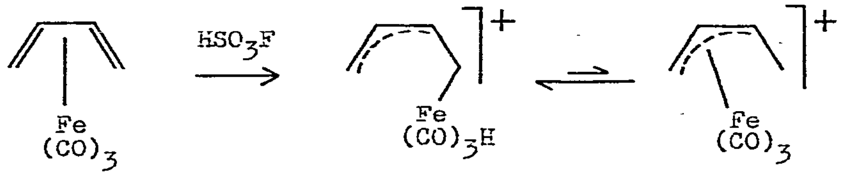


8.18 8.19 8.20



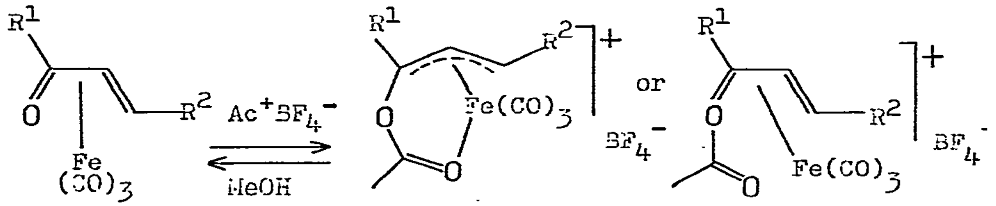
8.21

Brookhart and Harris have reinterpreted earlier results on the protonation of polyolefinic metal complexes in terms of a general π to σ change in metal ligand bonding. This has been exemplified for (η-butadiene)iron tricarbonyl (8.22) which gives the η-allyl σ-iron cation (8.23) that undergoes intramolecular proton scrambling by equilibration with a small proportion of the η-allyl cation (8.24)[159]. Iron



8.22 8.23 8.24

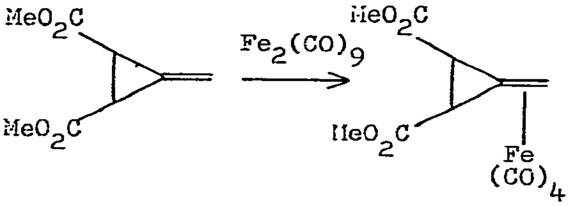
tetracarbonyl and iron tricarbonyl complexes (8.25) of α,β-unsaturated carbonyl compounds have been treated with acetylium tetrafluoroborate to give yellow, crystalline air-labile salts which may be formulated as either allyl (8.26) or enone (8.27) complexes. These salts are decomposed easily by nucleophiles such as methanol and water to give the original enone complexes (8.25)[160]. Whitesides and Slaven



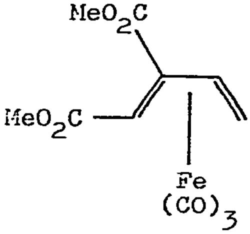
8.25 8.26 8.27

have investigated complex formation between the <u>cis</u>- and <u>trans</u>-isomers of Feist's ester (8.28) and diironnonacarbonyl. The first formed products are <u>cis</u>- and <u>trans</u>-(η-olefin)iron tetracarbonyl compounds (8.29) which then undergo ring opening and a series of stereospecific reactions to give eventually anti- and syn-(η-diene)iron tricarbonyl complexes (8.30 and 8.31) respectively. The photochemical reactions of the cis isomer (8.29) parallel the thermal reactions while the trans isomer (8.29) gave a η-allyl complex[161].

The attack of several open-chain pentadienyltricarbonyliron cations (8.32) on 1,3-dimethoxybenzene has been studied kinetically. The trans-pentadienyltricarbonyliron cation



8.28 8.29



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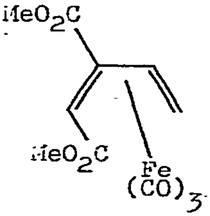
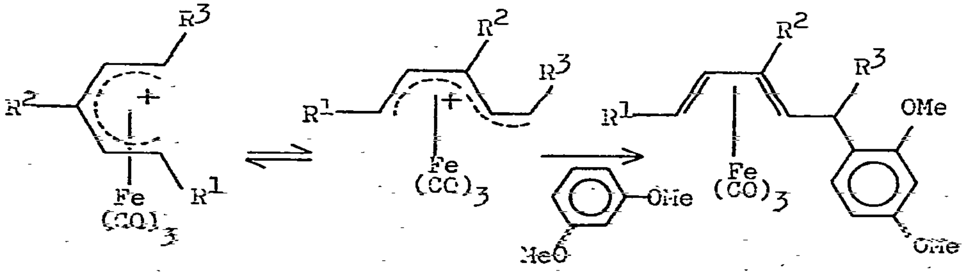


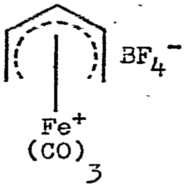
8.30

(8.33) was postulated as the reaction intermediate and only one product (8.34) was isolated[162]. Pentadienyltricarbonyliron tetrafluoroborate (8.35) was treated with a series of



8.32 8.33 8.34

amines to give four different dieneaminetricarbonyliron species (8.36, 8.37, 8.38 and 8.39)^{163}. The photoreaction of pentacarbonyliron with 4-methylenedispiro [2,1,2,3] decane (8.40) gave mainly the tricarbonyliron complex (8.41) together with a small amount of the complex (8.43). Hydrogen scrambling has been observed in the thermal degenerate rearrangement of the dimethylenecyclobutane complex (8.42). The rearrangement afforded the products (8.44 and 8.45) and this suggested that



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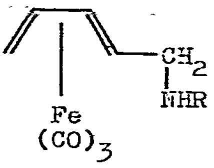

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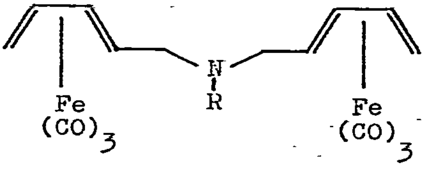

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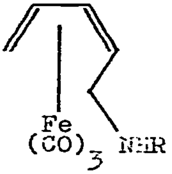

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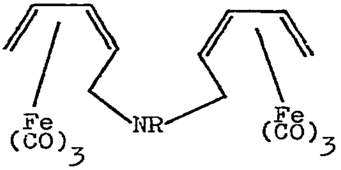

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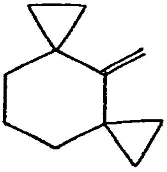

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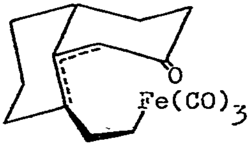

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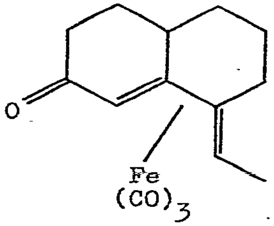
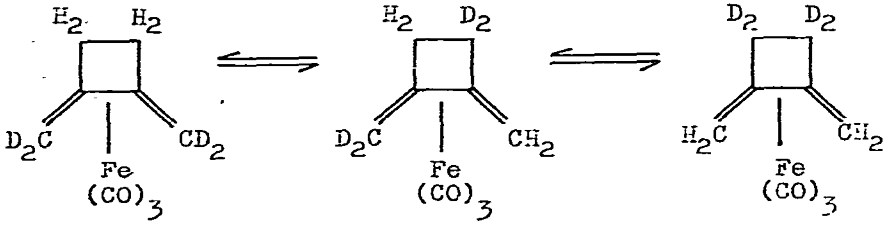


8.42

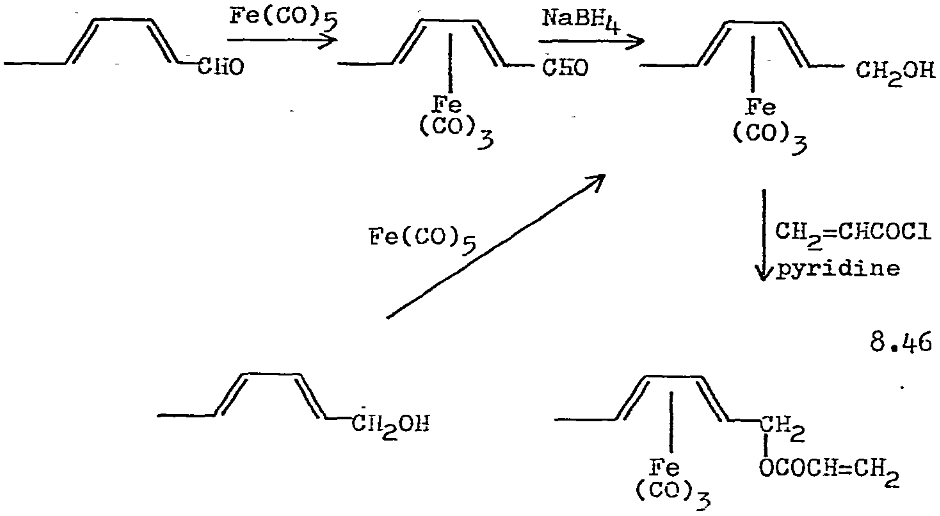
either one exomethylene group exchanged with one ring methylene or that the hydrogen atoms were reversibly exchanged between the ring carbon atoms and the exocyclic carbons[165]. The



8.43 8.44 8.45

monomer (η-2,4-hexadiene-1-yl acrylate)tricarbonyliron (8.46) was prepared from pentacarbonyliron by the routes shown (Scheme 8.1). The monomer (8.46) was homopolymerized and copolymerized with acrylonitrile, vinylacetate, styrene and methyl acrylate in the presence of azobisisobutyronitrile as the initiator. The polymers were characterized by infrared, gel permeation chromatography, viscosity and differential scanning calorimetry studies. When the polymers were decomposed thermally in air iron (III) oxide was formed[166].

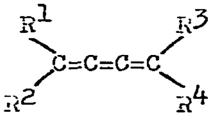
The crystal and molecular structure of a η-trimethylenemethane complex of iron has been determined by X-ray methods. The complex was formed from diironnonacarbonyl and 1-bromo--2(bromomethyl)naphthalene[167]. The gas-phase infrared and Raman spectra of trimethylenemethaneiron tricarbonyl were recorded and interpreted[168]. The butatriene derivatives



8.46

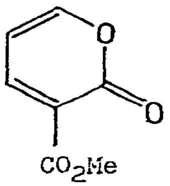
Scheme 8.1

(8.46a; R^1 = Ph; R^2 = t-Bu, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, Ph, α-naphthyl; R^3 = Ph, t-Bu, *p*-MeC_6H_4, *p*-$MeOC_6H_4$; R^4 = t-Bu, Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, α-naphthyl) gave a series of complexes with $Fe_3(CO)_{12}$[169].

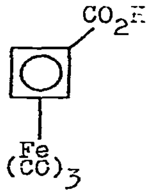


8.46a

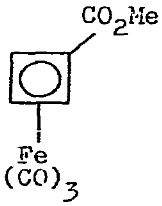
9. $(\eta\text{-}C_4H_4)Fe(CO)_3$



9.1

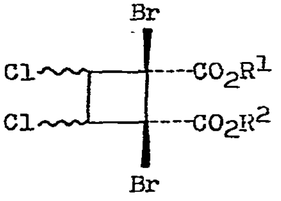


9.2



9.3

The carboxylic acid (9.2) has been synthesized conveniently by irradiation of the pyrone (9.1), addition of an excess of iron pentacarbonyl to the photoproduct and further irradiation. The product (9.2) was obtained in 21% yield after saponification and the intermediate ester (9.3) was also isolated as a light sensitive oil[170]. The isomeric tetrahalocyclobutanes (9.4; $R^1 = R^2$ = H or Me) were treated with $Fe_2(CO)_9$ to give the cyclobutadiene complex (9.5; $R^1 = R^2 = CO_2Me$). This complex was converted to the optically pure complexes (9.5; R^1 = Et, R^2 = Me; $R^1 = CO_2Me$, R^2 = COMe and $R^1 = CO_2H$, R^2 = COMe)[171]. Methoxymethyl-3, 4-carbonyldioxycyclobutene was treated with disodium tetracarbonylferrate to give (η-methoxymethylcyclobutadiene)iron tricarbonyl which was converted to the bromomethyl derivative (9.6) by hydrobromic acid. The treatment of this derivative (9.6) with potassium



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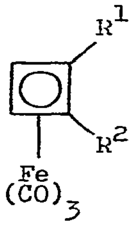

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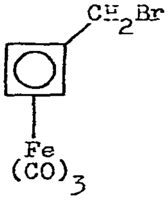

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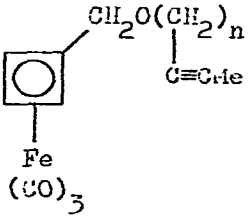

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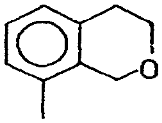

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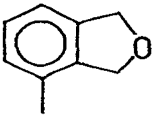

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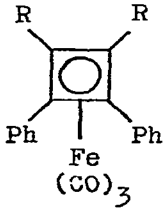

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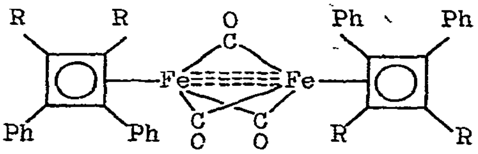
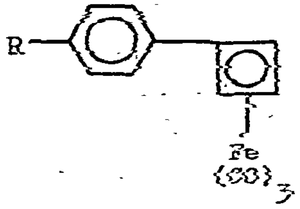


9.11

alkoxides gave the complexes (9.7; n = 1, 2). Successive photolysis and Ce (IV) oxidation of the complexes (9.7; n = 1, 2 gave 5-methylisochroman (9.8) and 4-methylphthalan (9.9) respectively[172].

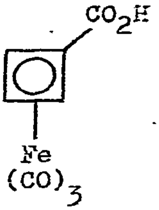
By the use of reasonable approximations a valence force field has been calculated for tricarbonyl(η-cyclobutadiene)-iron using $\underline{C}_{4v}$ symmetry for the C_4H_4 group and $\underline{C}_{3v}$ for the $RFe(CO)_3$ moiety. The results obtained reproduced the observed vibrational frequencies very closely and were consistent with those known for related systems[173]. Irradiation of the complexes (9.10; R = Bu^t or Ph) in hexane afforded the binuclear derivatives (9.11; R = Bu^t or Ph), these complexes were converted back to the starting materials by treatment with carbon monoxide. The crystal structure of the compound (9.11; R = Bu^t) was determined by X-ray diffraction. The two iron atoms were bridged by three carbonyl groups and the cyclobutadiene ring was essentially square planar. The Fe-Fe bond was extremely short, 2.177 Å, and it was thought that a triple bond existed between the two iron atoms. This gave the iron atoms eighteen electron configurations and it also accounted for the diamagnetic behaviour of the complex[174].

The structure of (η-cyclobutadiene)iron tricarbonyl has been studied by microwave spectroscopy and it has been



9.12

confirmed as symmetric top molecule[175]. The IR and Raman spectra of (η-cyclobutadiene)iron tricarbonyl have been obtained for the liquid and solid phases and the vibrational frequencies assigned[176]. Brune and Horlbeck have used ^1H and ^{13}C NMR spectroscopy to investigate electronic interactions between the phenyl substituent and the (η-cyclobutadiene)iron tricarbonyl group in the complexes (9.12; R = H, F, Cl, Br). The (η-C_4H_3)$Fe(CO)_3$ group donates electrons by conjugation and accepts electrons through the sigma skeleton of the molecule[177]. The 100 MHz ^1H NMR spectra of chloro-, bromo- and methyl-cyclobutadieneiron tricarbonyl were recorded and analyzed[178].



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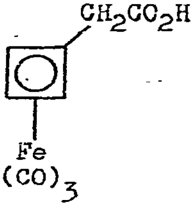
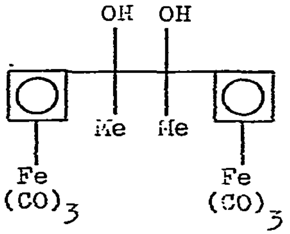


9.14

The carboxylic acid (9.13) has been prepared by Hoesch addition of trichloroacetonitrile to (η-cyclobutadiene)iron tricarbonyl and alkaline hydrolysis of the resulting trichloroacetyl intermediate. The acetic acid derivative (9.14) was obtained by displacement of chloride from (η-chloromethylcyclobutadiene)iron tricarbonyl with cyanide and hydrolysis of the acetonitrile derivative. The pK_a values for the two acids (9.13 and 9.14) were measured in 50% aqueous ethanol as 5.01 and 5.56 respectively. On the basis of these measurements it was concluded that (η-cyclobutadiene)iron tricarbonyl is an electron releasing group by resonance and a weak electron withdrawing group by induction[179]. Pinacol reduction of (η-acetylcyclobutadiene)iron tricarbonyl gave the α-diol (9.15) which was dehydrated to the diene (9.16) and underwent pinacol rearrangement to the ketone (9.17). Reduction of the same acetyl derivative with diborane gave (η-ethylcyclobutadiene)-iron tricarbonyl and acetylation of this product gave a 9 : 11 mixture of the 2- and 3-acetyl derivatives. Treatment of (η-acetylcyclobutadiene)iron tricarbonyl with base led to the isomeric dypnones (9.18)[180]. Grey has described the



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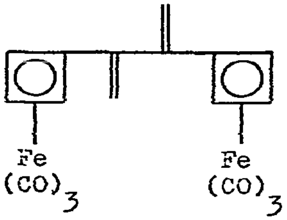

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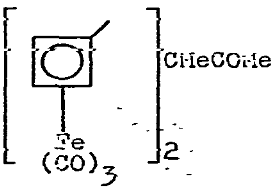

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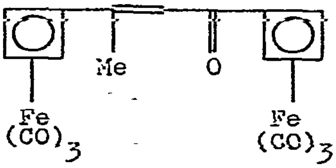
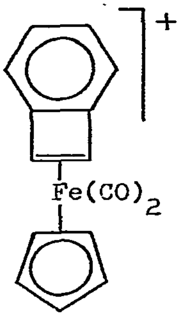


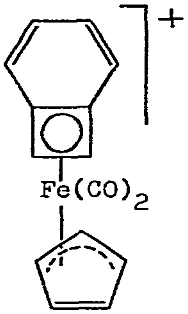
9.18

decomposition of an optically active (η-cyclobutadiene)iron tricarbonyl derivative with ceric ammonium nitrate in the presence of dienophiles to give totally racemic products. These results supported a mechanism of decomposition where free cyclobutadiene was an intermediate[181].

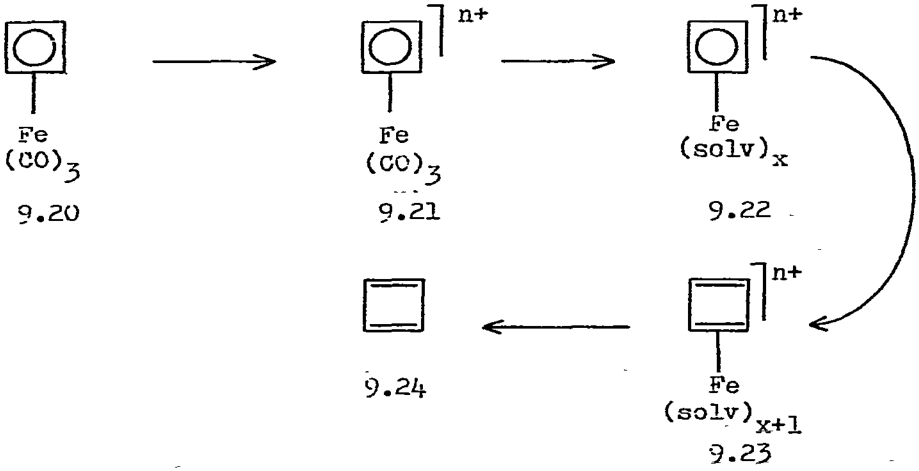
The iron carbonyl cation (9.19) has been formed by hydride abstraction from a benzocyclobutenyl precursor. The structure (9.19a) is preferred to the alternative (9.19b) on chemical grounds and it may be an intermediate in the oxidative degradation of (η-cyclobutadiene)iron tricarbonyl complexes through the sequence (9.20→9.24)[182]. Irradiation of the



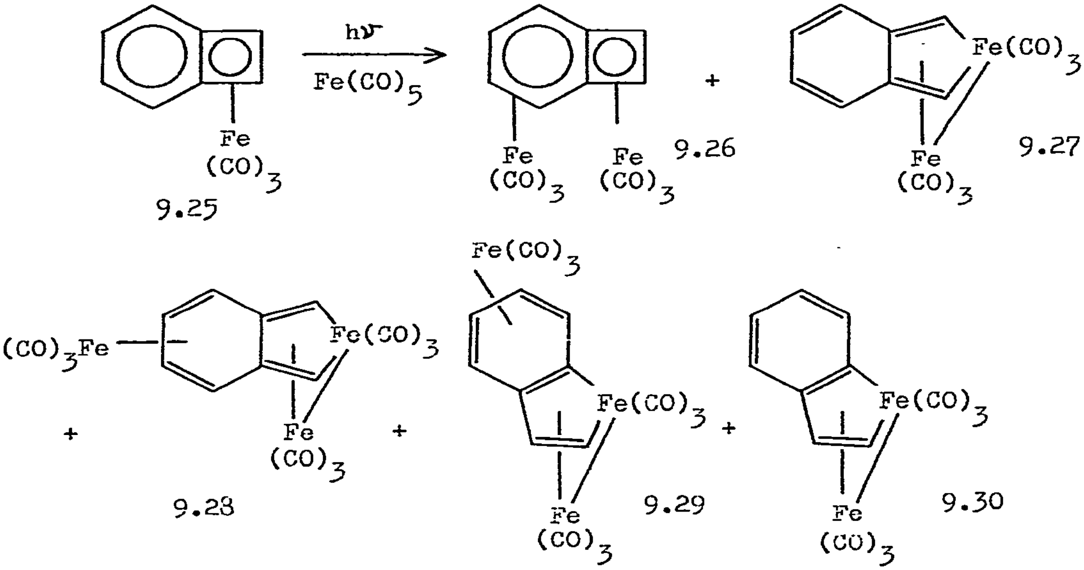
9.19a



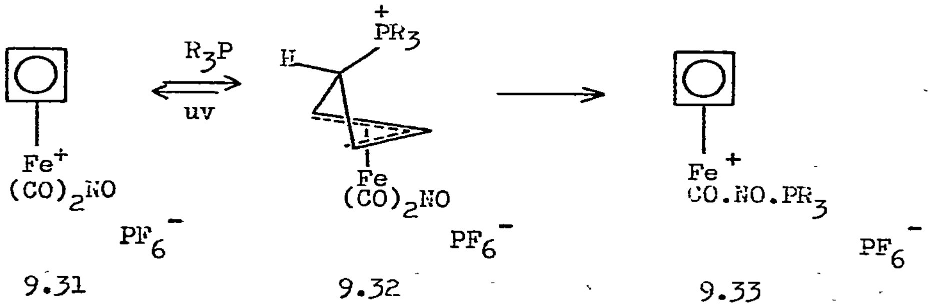
9.19b



benzocyclobutadiene complex (9.25) with iron pentacarbonyl gave the diiron complex (9.26) as the major product together with minor amounts of two isomeric diiron complexes (9.27 and 9.28) and two triiron complexes (9.29 and 9.30). The complexes (9.27 and 9.28) were formed by an unusual ring-opening of the cyclobutadiene group and gave the triiron complexes (9.29 and 9.30) respectively by coordination of a third iron tricarbonyl residue[183].



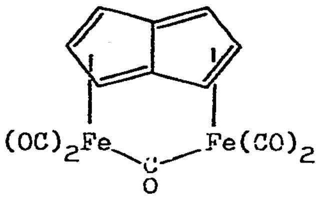
(η-Cyclobutadiene)iron tricarbonyl was stirred with nitrosonium hexafluorophosphate in acetonitrile to give the



air-stable crystalline complex (9.31)[184]. Nucleophilic addition of trialkyl or triaryl phosphines to the η-cyclobutadiene cation (9.31) gave the η-cyclobutenyl complex (9.32). When the hydrocarbon groups (R) were phenyl then the complex (9.32) was converted by heating in acetone to the η-cyclobutadiene complex (9.33)[185].

10. (Cyclic-η-diene)Fe(CO)$_3$ Complexes. (i) Formation

Pentalene dimer was cleaved with diiron nonacarbonyl in methylcyclohexane under an atmosphere of carbon monoxide to give the pentalene complex (10.1)[186]. An iron carbonyl derivative (10.2) was obtained from the reaction of bicyclo [4.1.0]heptane with diiron nonacarbonyl. The light-induced reaction of homosemibullvalene (10.3) with pentacarbonyliron under kinetic control gave the iron carbonyl compounds (10.4, 10.5 and 10.6)[187]. The reaction of iron pentacarbonyl or diiron nonacarbonyl with benzo[b] thiophen-1,1-dioxide gave



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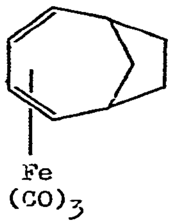

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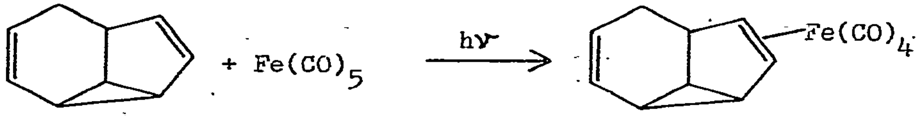

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10.4

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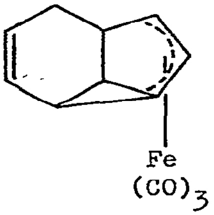

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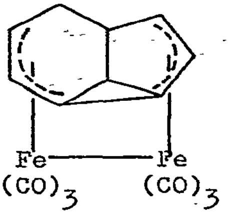
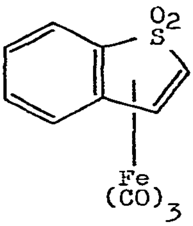


10.5

the two complexes (10.7 and 10.8). The structure of complex (10.8) was confirmed by X-ray crystallography[188]. The diene



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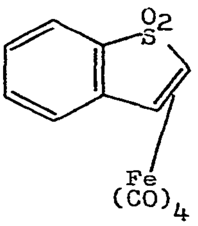

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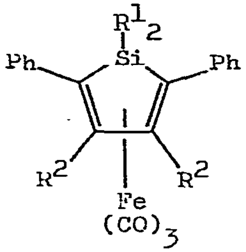
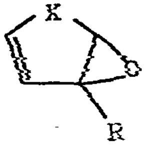


10.9

iron carbonyl complex (10.9; R^1 = alkyl, R^2 = H) was formed by treatment of the appropriate silacyclopentadiene with diiron nonacarbonyl[189]. The same complex (10.9; R^1 = alkyl, R^2 = H) was prepared independently by a second group using the same reactants. The corresponding tetraphenyl complex (10.9; R^1 = alkyl, R^2 = Ph) was also prepared from the tetraphenylsilacyclopentadiene and iron pentacarbonyl. The complex (10.9; R^1 = Me, R^2 = Ph) was obtained from 1,1-dimethyl-2, 5-diphenylsilacyclopentadiene by treatment with bromine to form a mixture of the 2,3- and 2,5-dibromo adducts which were then heated with diiron nonacarbonyl[190].

Photolysis of pentacarbonyliron and the 2-vinyloxiranes (10.10; R = H, Me; X = CH_2, CH_2CH_2) gave the lactones (10.11).

When the lactone (10.11; R = H, X = CH_2CH_2) was heated in benzene the complex (10.12) was formed[191]. Treatment of the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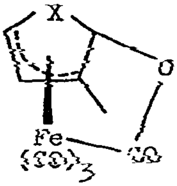
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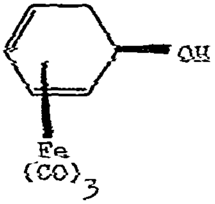
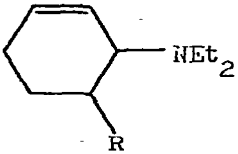

10.12

cyclohexene (10.13), prepared from 1(diethylamino)butadiene and CH_2=CHR, with $Fe_3(CO)_{12}$ gave the irontricarbonyl complex (10.14; R = CHO, COMe)[192]. The cyclohexa-2, 4-diene complex (10.15)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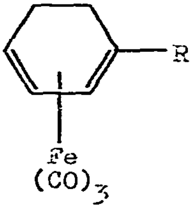
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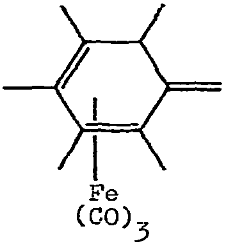
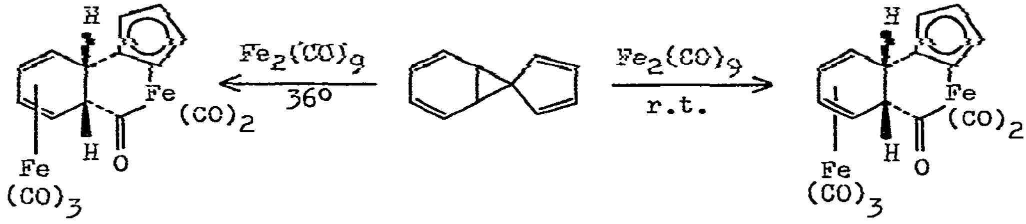
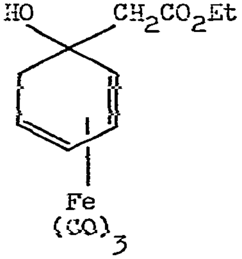

10.15

was prepared by heating the corresponding cyclohexa-2,5-diene with iron pentacarbonyl. The rearrangement may occur by a 1,5-hydride shift from a methyl group to the exomethylene group in which the iron carbonyl group participates[193]. The stereochemistry of the interaction between diiron nonacarbonyl and cisoid or transoid divinylcyclopropyl ligands has been examined by using the spironorcaradiene (10.16) as the ligand since this ligand contains both cisoid and transoid systems in the same molecule. Mild conditions (room temperature, 48 h) favoured the product (10.17) while gentle heating (36°, 30 h) led to the isomer (10.18). The crystal structure and molecular geometry of the complex (10.18) was determined by X-ray crystallography[194].



10.18 10.16 10.17

Details were given for the preparation of tricarbonyl-(η-2,4-cyclohexadienone)iron and tricarbonyl(η-2-methoxy-1,3-cyclohexadienylium)iron hexafluorophosphate from anisole[195,196]. Their conversion to tricarbonyl(1-ethoxycarbonylmethyl-1-hydroxy-2,4-cyclohexadiene)iron (10.19) and tricarbonyl [5-(2-hydroxy-4,4-dimethyl-6-oxo-1-cyclohexen-1-yl)-2-methoxy-1,-3-cyclohexadiene]iron (10.20) respectively was described[197,198].



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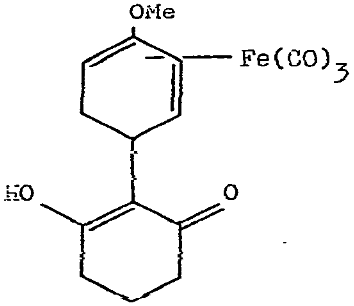

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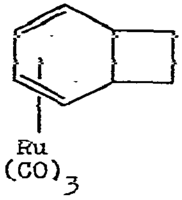
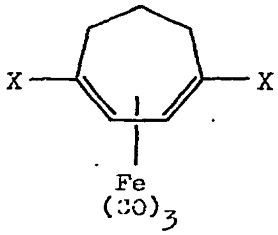


10.21

Cyclooctatrienes combine with $Ru(SiMe_3)_2(CO)_4$ to give hydrocarbon ruthenium carbonyl complexes, with isomerization of the ligand, including the bicyclooctadiene complex (10.21)[199].

Dodman and Tatlow have described the preparation of some (η-polyfluoro-1,3-cycloheptadiene)iron tricarbonyl complexes (10.22; X = H, F) from triirondodecacarbonyl and the ligand in sealed tubes at 130°. Pyrolysis of the complexes at 440° C under nitrogen gave polyfluorobenzenes, presumably by loss of iron tricarbonyl and fluorine to form polyfluorocycloheptatrienes and then ring contraction[200]. Wang and Paul have prepared an iron tricarbonyl complex of barbaralone in which the hydrocarbon



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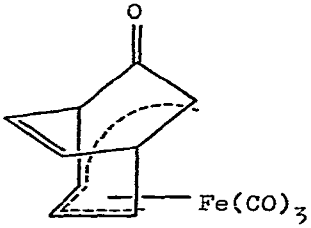
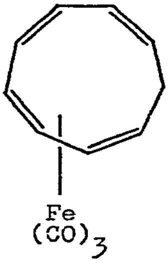


10.23

may be bound as a "homobutadiene" ligand (10.23). This proposal is supported by X-ray structure analysis and molecular spectra[201]. Details have been given for the synthesis of bis(η-1,3,5,7-cyclooctatetraene)iron (0) from tris(2,4-pentanedionato)iron, 1,3,5,7-cyclooctatetraene and triethylaluminium[202].

The *cis*^{4}-cyclononatetraene complex (10.24) has been prepared from *cis*-bicyclo[6.1.0]nonatriene either thermally with diiron nonacarbonyl or photochemically with iron pentacarbonyl. Three other (η-C_9H_{10})iron carbonyl complexes were isolated and characterized from the same reactions. While the parent hydrocarbon ligand underwent rapid electrocyclic ring closure to dihydroindene at 23° ($t_{\frac{1}{2}}$ = 50 min,

$\Delta F^{\ddagger}$ = 23 kcal mol^{-1}), the complex is stable at room temperature for several days but underwent first-order isomerization to the dihydroindene complex (10.25) at 101° ($k = 2.4 \times 10^{-4}$ sec^{-1}, $\Delta F^{\ddagger}$= 28.4 kcal mol^{-1}). Protonation of the tetraene compound (10.24) occurred at C_6 in FSO_3H at -120° to give the dienyl cation (10.26)[203]. The reaction of 1,7-cyclododecadiyne (10.27) with $Fe(CO)_5$ unexpectedly gave the ferrole (10.28) rather than the ferrole (10.29)[204]. It was suggested that the formation of (10.28) proceeded through the (η-cyclobutadiene)iron tricarbonyl complex (10.30) from (10.27) and $Fe(CO)_5$, and further reaction of the complex (10.30) with $Fe(CO)_5$ to give the ferrole (10.28). This suggestion was supported by the combination of the iron tricarbonyl derivative (10.31) with excess $Fe_3(CO)_{12}$ to afford a mixture of the sym- and unsym-benzoferroles (10.32) and (10.33) respectively[205].



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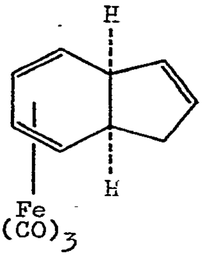

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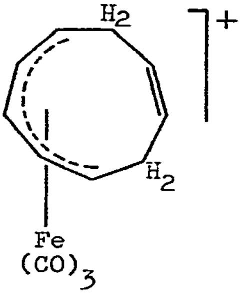

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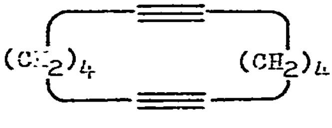

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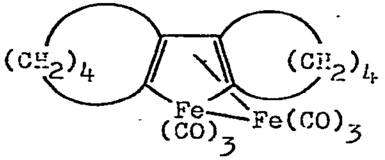

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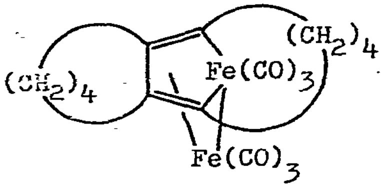

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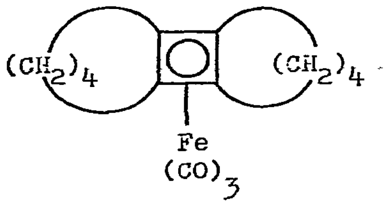

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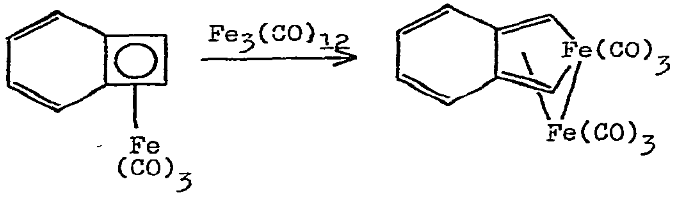
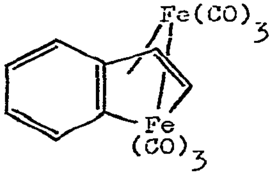
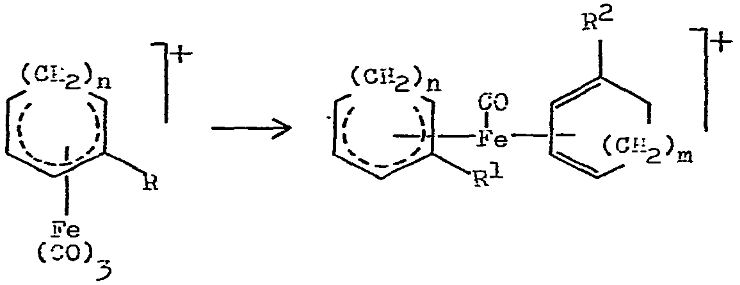


10.31 10.32



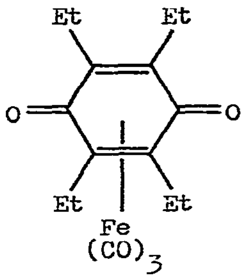
10.33

Irradiation of (η-dienyl)tricarbonyl iron cations (10.34; n = 1-3, R = H, OMe) in the presence of the appropriate 1,3-diene gave the cations (10.35; n = 1-3; m = 0, 2, 3; R^1 = H, OMe; R^2 = H, Me) in good yields. The reactivity of these cations towards nucleophilic and electrophilic reagents was examined[206]. In an investigation of the photo-



10.34 10.35

-reactions of cyclopropylacetylenes with iron carbonyl, 3-hexyne was irradiated with iron pentacarbonyl in methylene chloride to form the benzoquinone adduct (10.36) in addition to the free benzoquinone[207]. The irradiation of $Fe(CO)_5$



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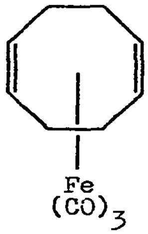

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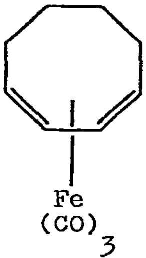
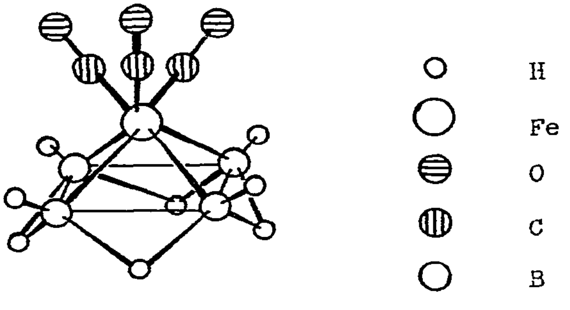


10.38

with cycloocta-1,5-diene and cycloocta-1,3-diene gave the corresponding (η-diene)irontricarbonyl complexes (10.37 and 10.38). On reaction of complex (10.38) with Ph_3CBF_4 hydride-ion abstraction occurred to give the cyclooctadienylium complex $[(\eta\text{-}C_8H_{11})Fe(CO)_3]^+$ [208].

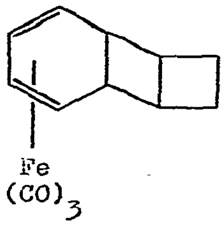
The direct reaction of pentaborane (9) with $Fe(CO)_5$ or the reaction of tetraborane (10) with $Fe_2(CO)_9$ gave the stable ferraborane $B_4H_8Fe(CO)_3$ (10.39). Spectroscopic evidence showed that the $Fe(CO)_3$ group had replaced the apical BH group in B_5H_9 and that the compound had structural and bonding affinities with $(\eta\text{-}C_4H_4)Fe(CO)_3$ and $Fe_5(CO)_{15}C$ [209].



10.39

(ii) Spectroscopic and Physico-chemical Studies

The structure of the tricarbonyliron complex (10.40) was determined from X-ray data. The $Fe(CO)_3$ moiety was bound to the diene portion of the cyclohexadiene ring and this six-membered ring was cis-fused to a four-membered ring, which in turn was cis-fused to a second four membered ring. Both four membered rings were essentially planar[210]. The molecular structure of the (η-diene)iron compound (10.41) has been determined by single-crystal X-ray analysis. The ligand adopts the boat conformation[211]. The crystal and molecular structure of 3,3'-bis(η-bicyclo[4.2.0]octa-2,4-diene-tricarbonyl-iron), $[(\eta\text{-}C_8H_9)Fe(CO)_3]_2$ was determined by X-ray analysis. The structure consisted of two bicyclo[4.2.0]octa-2,4-diene-tricarbonyliron moieties related by an inversion centre[212]. Struchkov has reported bond lengths based on X-ray measurements for the iron complex (10.42)[213]. Struchkov has determined the bond lengths and interatomic distances in the cyclopentadiene complex (10.43) by X-ray methods[213]. The structure of the iron complex (10.44), containing two different valence-tautomeric forms of the η-C_8H_{10} ligand, has been determined by X-ray crystallography. Bond length alternation in the parts of the ligands bonded to the iron atom was not observed and these parts of the ligands were planar[214]. The crystal and molecular structure of a tri-



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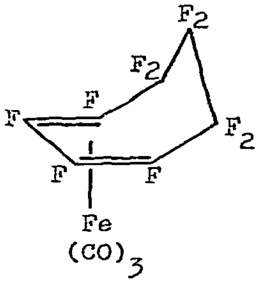

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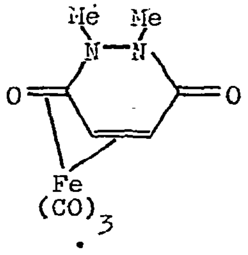
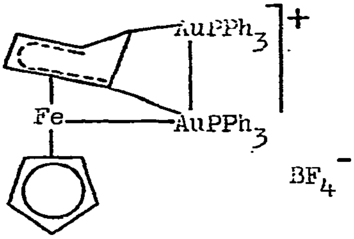


10.42

carbonyliron derivative of barbarlone (10.45) has been determined by X-ray crystallography. The compound crystallized



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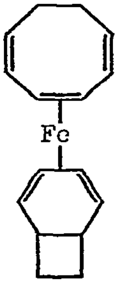

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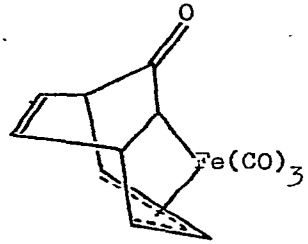
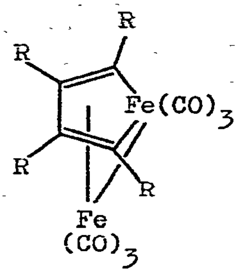


10.45

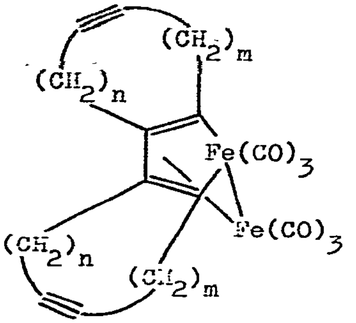
from pentane at -5° in the triclinic system with unit cell dimensions a = 7.48, b = 11.91, c = 6.61 Å, α= 94.55°, β= 110.17°, γ= 92.38°, Z = 2 space group $\underline{P}_1$. The three carbonyl groups were mutually *cis*. The allyl group was *trans* to two of them and the Fe-C sigma bond was *trans* to the third carbonyl group[215].

The ^{57}Fe Moessbauer spectra obtained on glassy n-butylbenzene matrices of the tricarbonylferroleiron tricarbonyl derivatives (10.46, 10.47 and 10.48) were analysed. The two nonequivalent iron atoms were resolved and the doublet with a quadrupole splitting in the range 1.22-1.26 mm/sec was assigned to the iron atom of the iron tricarbonyl group bonded to all four carbon atoms of the ferrole ring. The doublet at a less positive isomer shift with a quadrupole splitting in the range 0.94/1.02 mm/sec was assigned to the iron atom in the ferrole ring[216].

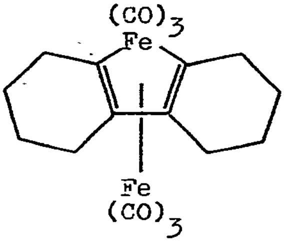
The electron-impact induced fragmentation of thirty derivatives of the styrene complex (10.49) has been studied



10.46 R = Me, Et, Ph



10.47 n = 4, 5, 6 m = 4, 5, 6



10.48

by mass spectrometry. In each case the complex underwent stepwise loss of carbon monoxide groups followed by loss of iron atoms as in the following scheme (Scheme 11.1)

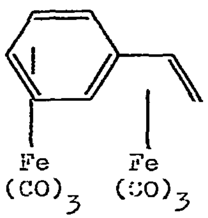
$$\begin{tikzcd}
{[(\eta\text{-vinylstyrene})Fe_2(CO)_6]^{\dot{+}}} \arrow[r] & {[(\eta\text{-vinylstyrene})Fe_2]^{\dot{+}}} \arrow[d, bend left] \\
{[\eta\text{-vinylstyrene}]^{+}} & {[(\eta\text{-vinylstyrene})]Fe^{\dot{+}}} \arrow[l]
\end{tikzcd}$$

Fragmentation of the organic ligand was sensitive to the nature and position of the substituent, at least four modes of breakdown were observed[217].

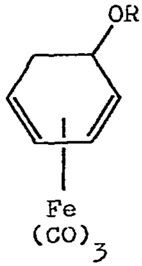
Infrared and Raman spectra of (η-N-methylmaleimide)-iron tetracarbonyl (solid, solution) and of N-methylmaleimide (solid, solution, gas) were recorded. An assignment of the normal modes of both molecules was made and compared with the data for (η-maleic anhydride)iron tetracarbonyl. The C=C stretching vibration in the complex occurred at 1370 cm^{-1} as compared with 1585 cm^{-1} in the free ligand[218]. Andrews and Davidson have also investigated the vibrational spectrum of (η-maleic anhydride)iron tetracarbonyl. On the basis of solid-phase infrared and Raman spectra, together with some solution data for the infrared, a complete vibrational assignment was made for the modes of maleic anhydride in the complex. Shifts in ν(C=C) and δ(CH) were consistent with a strong interaction with the metal, but relatively little coupling between the modes[219]. These results agreed in all essential details with those presented by Lokshin and co-workers[218].

10. (iii) General Chemistry

Treatment of the (η-cyclohexadienyl)iron tricarbonyl cation with sodium alkoxide (NaOR) gave the iron containing cyclohexadiene ethers (10.50; R = Ph, p-$MeOC_6H_4$, 3,5-$Me_2C_6H_3$) in good yield. Treatment of the same cation with (η-5-hydroxy-1,3-cyclohexadienyl)iron tricarbonyl gave the ether (10.51)[220].



10.49



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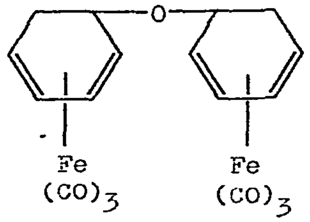
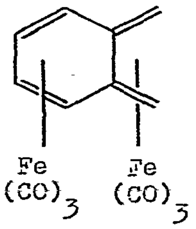


10.51

Irradiation of (η-o-quinodimethane)tricarbonyliron in the presence of pentacarbonyliron gave the three isomeric complexes



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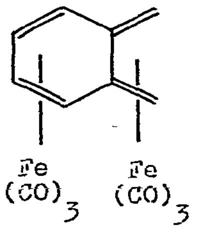

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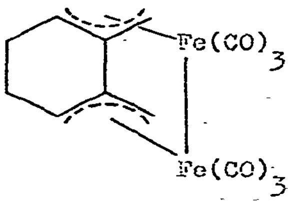
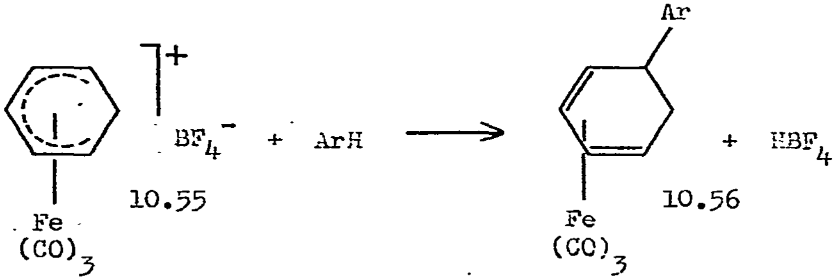


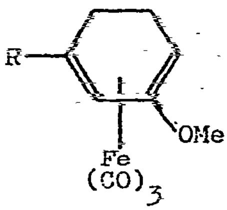
10.54

(10.52, 10.53 and 10.54)[221]. The dienyl cation (10.55) has been shown to act as an electrophile towards benzenoid aromatics. Thus 1,3-dimethoxybenzene and 1,3,5-trimethoxybenzene gave the diene substituted products (10.56) in the following reaction (Scheme 10.2). Rate constants for the reactions were measured and compared with the rate constants for the reaction of the cation (10.55) with some heterocycles to give the order of reactivity: pyrrole > indole > furan > 1,3,5-trimethoxybenzene > 1,3-dimethoxybenzene > thiophen. Preliminary experiments indicated that $[(\eta\text{-}C_7H_7)Cr(CO)_3]^+$ was also an active electrophile towards heterocycles such as indole[222].



Scheme 10.2

The pentadienyl cation (10.59; R = H) was formed from the diene complexes (10.57; R = H and 10.58) by treatment with triphenylmethyl fluoroborate. The methylpentadienyl cation (10.59; R = Me) was formed under the same conditions from the diene complex (10.57; R = Me). The reactions of these cations (10.59) with enamines, alkoxides and alkyllithiums have been studied. The cation (10.59; R = H) gave the diene complex (10.60) on treatment with alkoxide ion and



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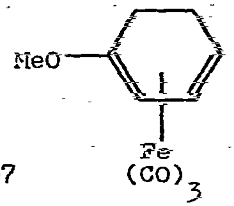

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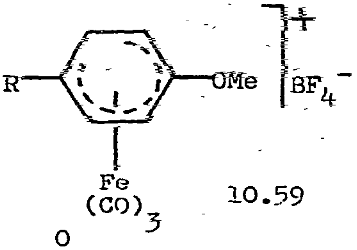

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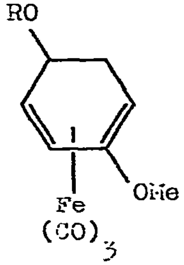
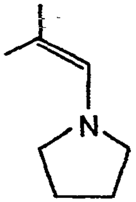
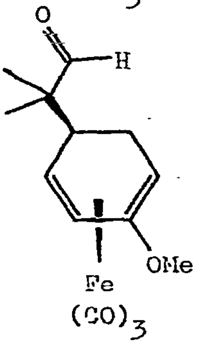


10.60

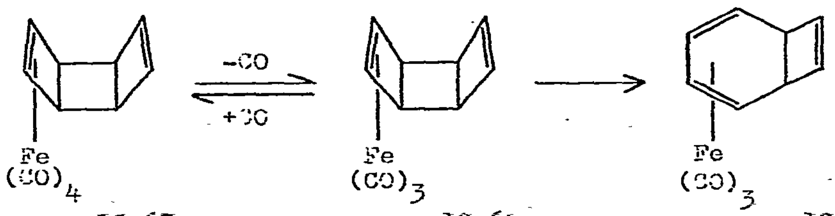


10.61



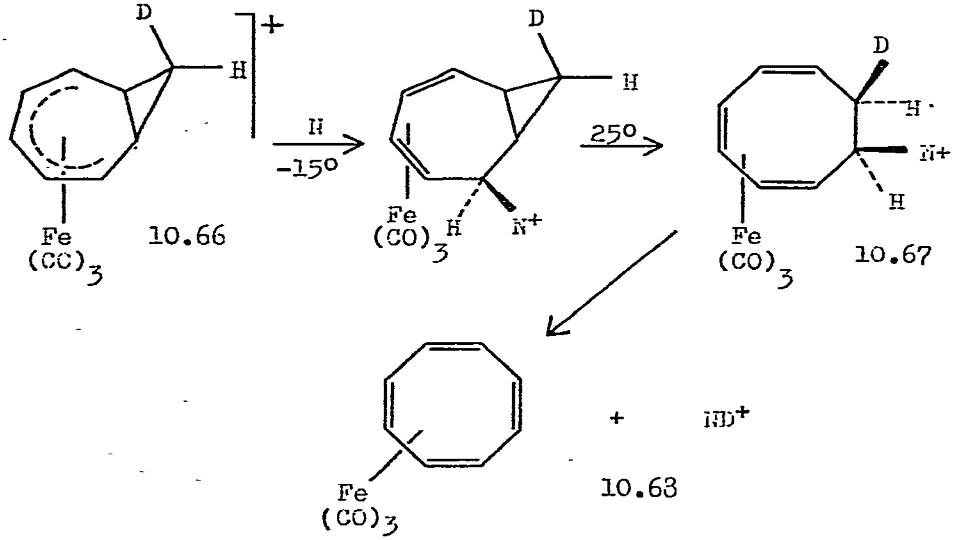
10.62

with the enamine (10.61) it gave the complex (10.62) after hydrolysis[223]. Experimental evidence has been offered to support the hypothesis that (η-cyclobutene)metal complexes can undergo a facile, disrotatory, concerted ring opening of the four-membered ring to give (η-butadiene)metal complexes. The iron-olefin complex (10.63) has been heated in hexane to form the iron-diene complex (10.65) presumably through the intermediate (10.64). The rate of conversion is insensitive to solvent polarity and the reaction is inhibited by carbon monoxide and added olefins[224].

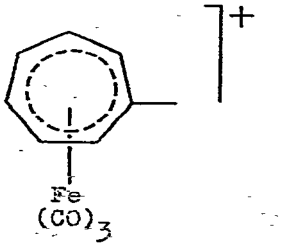


10.63 10.64 10.65

The reaction of (η-bicyclo[5.1.0]octadienyl)Fe(CO)$_3^+$ (10.66) with pyridine gave the cyclooctatriene complex (10.67) which was transformed into the corresponding cyclooctatetraene complex (10.68). The addition of iodide ion to the complex (10.66) caused the cyclopropane ring to open to give (3,4,5-η-octatrienyl)Fe(CO)$_3$I[225]. The fluxional cation



(10.69) was prepared by acid treatment (HBF$_4$-Ac$_2$O) of the alcohol (10.70) or its isomer (10.71). Treatment of the cation (10.69) with triethylamine gave the dimer (10.73) <u>via</u> the unstable (η-heptafulvene)iron tricarbonyl complex (10.72). The structure of the dimer (10.73) was confirmed by an X-ray investigation[226].



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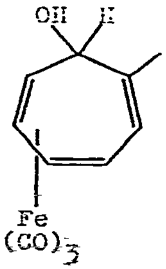
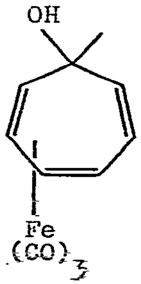
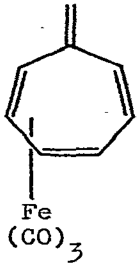


10.70



10.71



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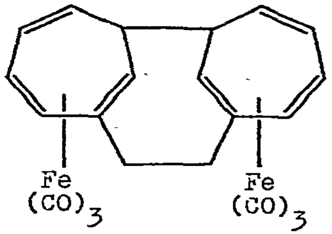
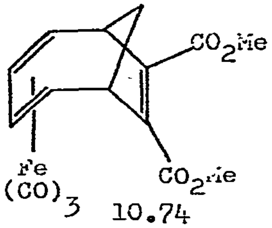
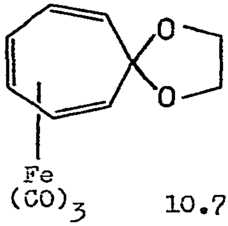


10.73

Irradiation of solutions of (η-cycloheptatriene)iron tricarbonyl and acetylene dicarboxylic ester in tetrahydrofuran gave the complex (10.74). The isolation of this compound demonstrated that $[2\pi + 6\pi]$ addition had taken place and X-ray data indicated that the acetylene moiety had added to the triene on the same face to which the iron atom was bonded. This suggested that at some point in the reaction the acetylene was bonded to the iron atom. Irradiation of the complex (10.75) with acetylene carboxylic ester gave the complex (10.76)^{227}. The reduction of tricarbonyl(1-5-η-cycloheptadienylium)iron with sodium tetrahydroborate resulted in nucleophilic attack at both the 1- and 2-positions to generate a mixture of tricarbonyl(η-cyclohepta-1,3-diene)iron (10.77) and tricarbonyl(3-5-η,1-σ-cyclo-heptenyl)iron (10.78). Tricarbonyl(1-5-η-cyclohexadienylium)iron and its dicarbonyl-(triphenylphosphine) analogue both gave the corresponding



10.74



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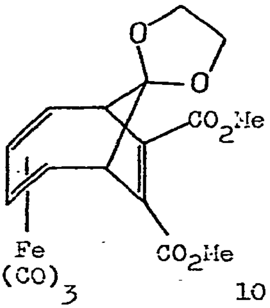

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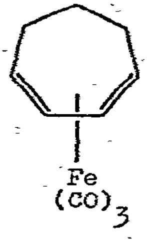

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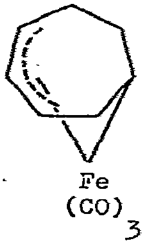
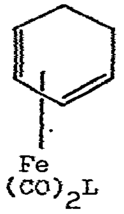


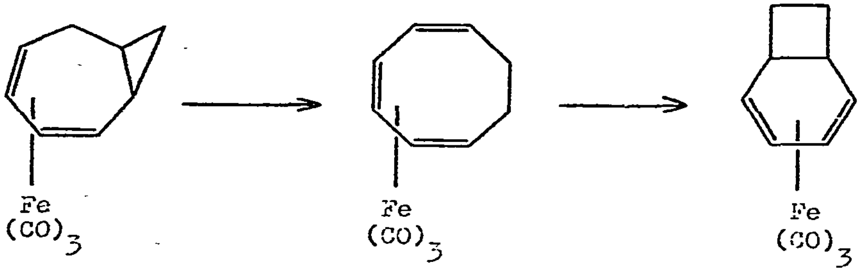
10.78



10.79

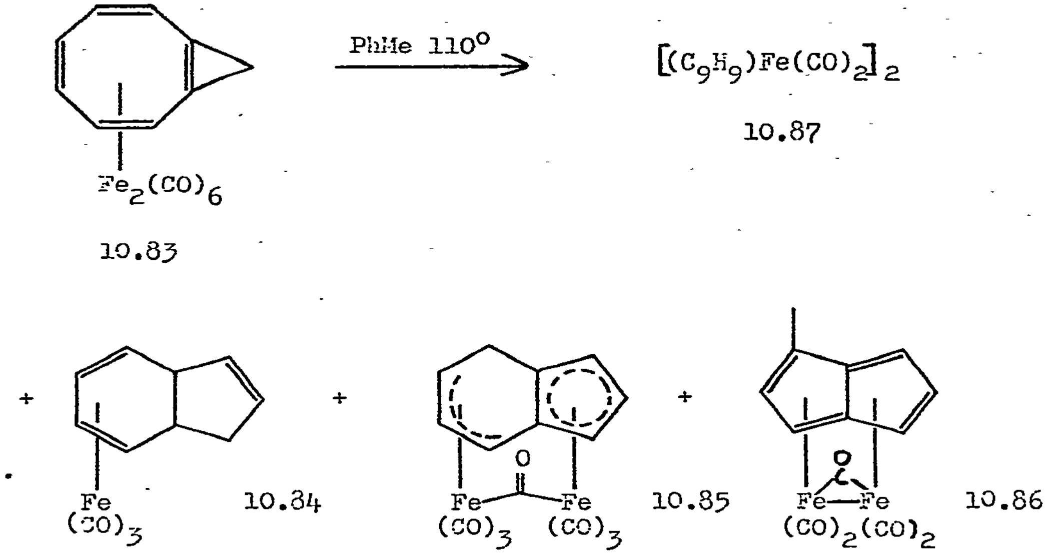
cyclohexa-1,3-diene product (10.79; L = CO and PPh_3) when treated with sodium tetrahydroborate[228].

The mechanism of the thermal isomerization of the octadiene complex (10.80) to the more stable complex (10.82) has been investigated. The reaction followed first-order kinetics with a free energy of activation of 31.8 kcal mol^{-1}. Both kinetic and analytical evidence indicated that the cyclooctatriene complex (10.81) was the intermediate in the rearrangement[229]. Thermolysis of (η-*cis*-bicyclo[6.1.0]



10.80 10.81 10.82

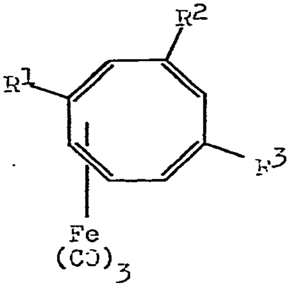
nonatriene)diiron hexacarbonyl (10.83) involved rearrangement of the organic ligand to give four iron carbonyl complexes (10.84, 10.85, 10.86 and 10.87)[230]. When the cyclooctatetraene complexes (10.88; R^1 = H, $SiMe_3$, R^2 = H, CPh_3, R^3 = H, CPh_3) were heated in a sealed tube in octane they rearranged to give the isomeric bicyclo [4.2.0] 2,4,7-octatriene compounds (10.89; R^1 = $SiMe_3$, CPh_3, R^2 = H,$SiMe_3$). The crystal and



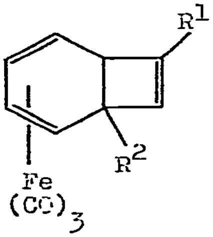
$[(C_9H_9)Fe(CO)_2]_2$

10.83 10.87 10.84 10.85 10.86

molecular structure of the complex (10.89) was determined by X-ray analysis[231].



10.88



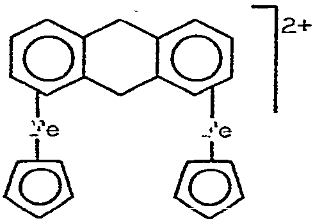
10.89

The synthesis of bicyclo [6.2.0]decapentaene derivatives *via* the tricarbonyliron complexes has been reported[232]. Kinetic studies were carried out on the reactions of tricarbonyl(η-cycloocta-1,3-diene)-, tricarbonyl(η-cyclohexa-1,3-diene)-, and tricarbonyl(η-cyclohepta-1,3,5-triene)-iron complexes with triphenylphosphine. In the presence of excess triphenylphosphine tricarbonyl(η-cycloocta-1,3-diene)iron underwent a second-order process to form *trans*-$[Fe(CO)_3(PPh_3)_2]$.

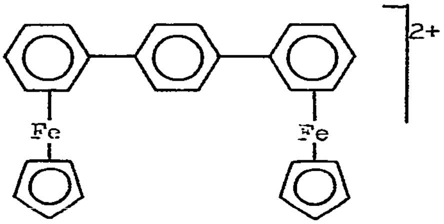
In contrast, tricarbonyl(η-cyclohepta-1,3-diene)iron and tricarbonyl(η-cyclohexa-1,3-diene)iron did not combine with PPh_3 under these conditions. The latter complex underwent a CO-dissociative reaction at high temperatures with retention of the olefin. Tricarbonyl(η-cyclohepta-1,3,5-triene)iron was similarly unreactive but it underwent reaction with PPh_3 at 154°C *via* first and second order processes[233].

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

Ferrocene, in the presence of aluminium chloride and aluminium, attacked a number of polyaromatic molecules to give derivatives of the (η-benzene)(η-cyclopentadienyl)iron cation. Biphenyl, diphenylmethane, fluorene, 9,10-dihydroanthracene, *p*-terphenyl, anthracene, phenanthrene, pyrene, chrysene and other aromatics each bonded two (η-cyclopentadienyl)iron groups to give dications which were isolated as the yellow hexa-fluorophosphate salts. The structures of the salts were determined by ^{13}C NMR spectroscopy and those for the complexes of 9,10-dihydroanthracene (11.1), terphenyl (11.2) and phenanthrene (11.3) are typical[234]. Electron-rich aromatic compounds behave as donors towards bis(η-hexamethylbenzene)-iron (II) hexafluorophosphate and give 1 : 1 molecular complexes,

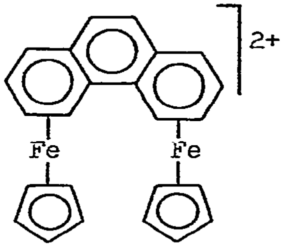


11.1

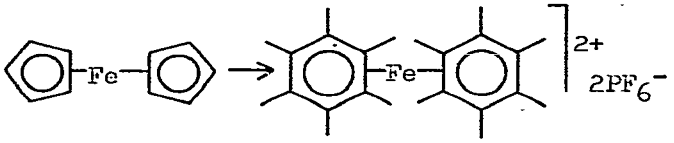


11.2

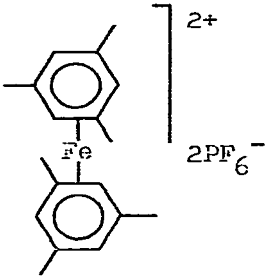
Benzene, anthracene, anilines, hydroquinone, pyridine, furan and ferrocene have been used as donors. In the last case the complex (11.4) appears to have four stacked rings^{235}.



11.3



11.4



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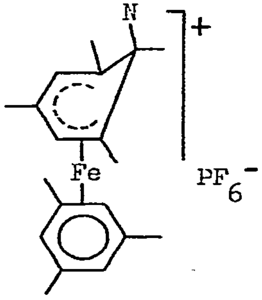
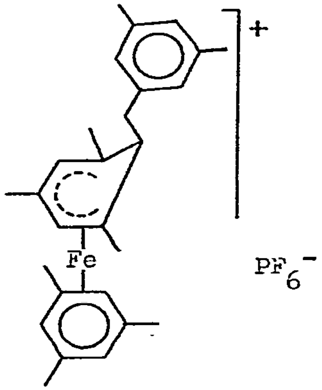


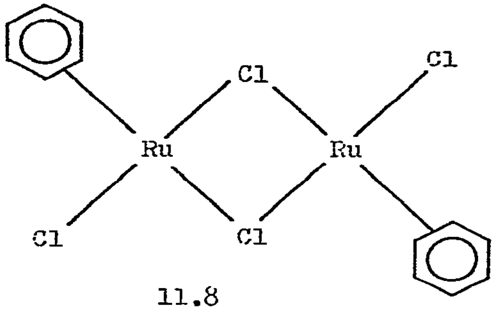
11.6



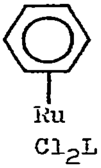
11.7

The treatment of bis(η-mesitylene)iron (II) hexafluorophosphate (11.5) with a series of nucleophiles (N) gave the mono adducts (11.6; N = CN, CH$_2$NO$_2$, CHMeNO$_2$, CH$_2$CO$_2$Bu^t). The reaction of (11.5) with several oxygen and nitrogen nucleophiles (e.g. MeOLi and H$_2$NLi) gave the same product (11.7) which was thought to be formed by the initial attack of a base on an α-proton of (11.5) followed by carbanion addition to another ion (11.5) and finally fragmentation^{236}. (η-Benzene)(η-cyclopentadienyl)iron exhibited a reversible anodic polarographic wave at $E_{\frac{1}{2}} = 1.23$ V and an irreversible cathodic wave at $E_{\frac{1}{2}} = -2.19$ V, both of these waves involved a single electron[237].

Bennett and Smith have prepared (η-arene)di-μ-chloro--ruthenium complexes (11.8) by dehydrogenation of the appropriate cyclohexadiene with ruthenium (III) chloride in ethanol. These complexes are cleaved with group V ligands to form mononuclear complexes (11.9; L = PR_3, AsR_3, pyridine) that are formally analogous to benchrotrene. The arene groups in the complexes (11.9) may be exchanged on heating or irradiation in an aromatic solvent[238].



11.8

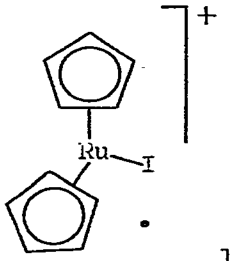


11.9

12. $(\eta-C_5H_5)_2Ru$

Methylferrocene carboxylate was treated with $^{103}RuCl_3$ to give methylruthenocene carboxylate $-^{103}Ru$[239]. The IR spectra of ferrocene, ruthenocene and osmocene were obtained from monocrystal films and the Laser-Raman spectra were also obtained from solid samples. The IR spectrum of nickelocene was recorded for a solid film. Fundamental symmetry forbidden modes were observed for these solid state spectra and the fundamental vibrational modes were assigned[240]. The temperature dependence of the photoluminescence of ruthenocene has been investigated by analysis of the luminescence decay times in the temperature range 4.2-77° K. The energy levels of the lowest excited states together with their decay characteristics were obtained and were used to describe the splitting of a $^3E_1(dd)$ term into $A_2 + A_1 + E_1 + E_2$ components by spin-orbital coupling. A Franck-Condon analysis of the luminescence spectrum at 4.2° K was made[241].

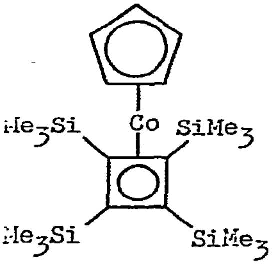
The gel chromatography of ferrocene, ruthenocene and osmocene on polystyrene beads crosslinked with 2% divinylbenzene and swollen in cyclohexane has been examined. The three metallocenes have different distribution coefficients indicating that separation occurs by solute-gel interaction rather than by molecular sieving[242]. The crystal and molecular structure of the cation (12.1), formed by the oxidation of ruthenocene with iodine, has been determined by X-ray crystallography. The cyclopentadienyl rings are eclipsed and tilted back from the iodine ligand by 16°. The metal-carbon bond distances are reduced by 0.01 Å. This shortening is less than would have been expected in view of the increase in the formal oxidation state of ruthenium from Ru (II) to Ru(IV)[243].



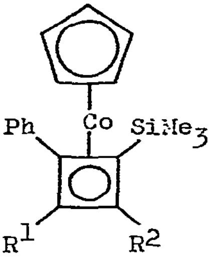
12.1

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

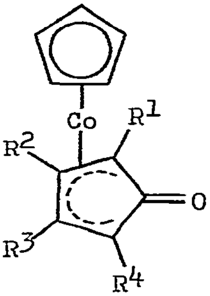
Further routes to the η-cyclobutadiene complex (13.1) have been reported. η-Cyclopentadienylcobalt dicarbonyl was treated with bis(trimethylsilyl)acetylene to give a binuclear intermediate which formed the product (13.1) after reaction with a second molecule of the acetylene. Heating cobaltocene with the same acetylene also gave the complex (13.1). Low yields were obtained in each case[244]. The reaction between



13.1



13.2

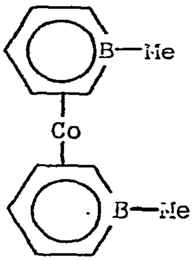


13.3

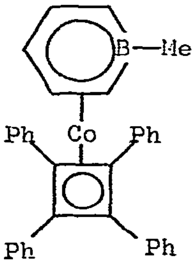
(η-cyclopentadienyl)dicarbonylcobalt and phenylethynyltrimethylsilane produced a number of organometallic products (13.2, R^1 = Ph, $SiMe_3$, R^2 = Ph, $SiMe_3$; 13.3, R^1, R^3 = Ph, R^2, R^4 = $SiMe_3$; R^2, R^4 = Ph, R^1, R^3 = $SiMe_3$; R^2, R^3 = Ph, R^1, R^4 = $SiMe_3$) but no cyclotrimerization products were isolated. The structure of one of these products (13.2, R^1 = $SiMe_3$, R^2 = Ph was determined by X-ray analysis. The cyclopentadienyl ring was planar and had normal Co-C and C-C distances. The cyclobutadiene ring was planar and the four C-C bond distances were equal. The internal angles of the ring were not 90° but the two angles at the carbon atoms bonded to phenyl rings were 88.1° and 88.4° while those bonded to silicon had values of 91.6° and 91.8°[245].

1,4-Dilithiotetraphenylbutadiene combined with (η-C_5H_5)Co(PPh_3)I_2 to give (η-cyclopentadienyl)(η-tetraphenylcyclobutadiene)cobalt[246]. X-ray diffraction data has been used to determine the crystal and molecular structures of

(η-cyanocyclopentadienyl)(η-tetraphenylcyclobutadiene)cobalt, (η-iodocyclopentadienyl)(η-tetraphenylcyclobutadiene)cobalt and (η-1,2-diiodocyclopentadienyl)(η-tetraphenylcyclobutadiene)-cobalt. In these compounds the cobalt atom was sandwiched between parallel η-cyclopentadienyl and η-tetraphenylcyclobutadiene rings which were planar. The perpendicular distances from cobalt to the plane defined by the five- and four-membered rings were 1.68 and 1.70 Å respectively. The phenyl groups were slightly bent away from cobalt with respect to the plane of the cyclobutadiene and they were twisted about their respective axes by an average of 35° in a propeller configuration[247]. The borabenzene sandwich complex (13.4) when treated with diphenylacetylene in a sealed tube for seven days at 150° gave (η-1-methylborinato)(η-tetraphenylcyclobutadiene)cobalt (13.5)[248]. King and co-workers have extended their investigations of macrocyclic alkadiyne-transition metal complexes to include the complexes (η-C_5H_5)Rh(alkadiyne) which were formed by heating (η-C_5H_5)Rh$(CO)_2$ with alkadiynes in cyclooctane. Five alkadiynes were used and in each case intramolecular transannular cyclization was observed to give the tricyclic η-cyclobutadiene compounds (13.6; $m = 4$, $n = 4$, 5 and 6, $m = 5$, $n = 5$ and 6)[249].



13.4



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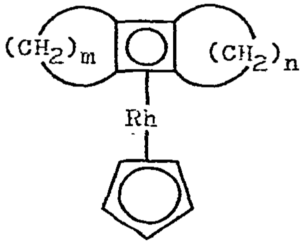
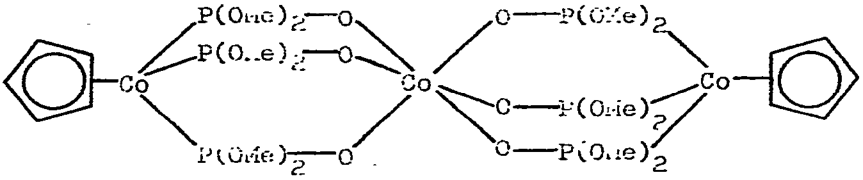


13.6

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

Harder, Dubler and Werner have reported the preparation and characterization of the trinuclear cobaltocene analogue (14.1)[250]. The crystal and molecular structure of $(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4.B_9C_2H_{11})$ was determined by X-ray diffraction.

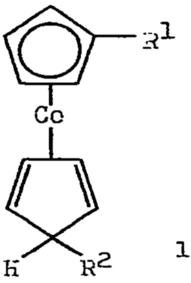


14.1

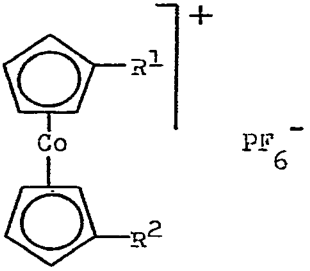
The species crystallized in the centrosymmetric monoclinic space group $P2_1/c$ with a = 10.02, b = 10.99, c = 14.55 Å, β = 98.57°, V = 1585.2 Å and Z = 4. The molecule was zwitterionic and was formed from a cobalticinium cation and a $[B_9C_2H_{12}]^-$ anion which were linked via a carbon-carbon bond with concomitant loss of a terminal hydrogen atom from each species to give the molecule $(\eta\text{-}C_5H_5)Co(\eta\text{-}C_5H_4.B_9C_2H_{11})$[251].

Cobaltocene isolated in neon, argon and krypton matrices was studied by ESR at 4.2° K. Earlier results were also considered and it was concluded that the orthorhombic splitting parameter δ (measuring the deviation from exact five-fold symmetry) increased in the host series ruthenocene ~ nickelocene < neon < argon < krypton from 100 cm^{-1} to approximately 350 cm^{-1}. However the host system had little effect on the bonding parameters and the vibronic coupling strength[252]. The ^{13}C NMR spectra of $(\eta$-indenyl)chromium tricarbonyl, bis(η-indenyl)iron, bis(η-indenyl)cobalt hexafluorophosphate and bis(η-indenyl)nickel were recorded and analysed with reference to the metal ligand bonding. In the case of the nickel complex, the η-indenyl group was shown to be a trihapto ligand[253]. The rate of hydrogen--deuterium exchange in cobaltocene in basic media was slower than that of cobalticinium tetrafluoroborate. It was concluded that in this reaction the oxidation state of the cobalt atom was important[254].

The heterogeneous electron transfer at a mercury-acetonitrile interface for cobaltocene, nickelocene and their dicarbollide analogues has been investigated kinetically using a.c. polarography. The rate constants obtained were correlated with the molecular structures of the complexes[255]. Murr, Laveron and Dabard have investigated the chemical (O_2, or H^+) and electrochemical oxidation of the cobalt complexes (14.2; $R^1 = R^2 = H, Me, CO_2Me$). In each case the cobalticinium ion was obtained. The oxidation with aqueous acid was first order in the complex (14.2)[256]. 1,1'-Diethylcobalticinium cation was oxidized with potassium permanganate in acid to a mixture of the diketone (14.3; $R^1 = R^2 = COMe$) and the diacid (14.3; $R^1 = R^2 = CO_2H$). When the oxidizing agent was a nitric acid-potassium permanganate mixture then



14.2



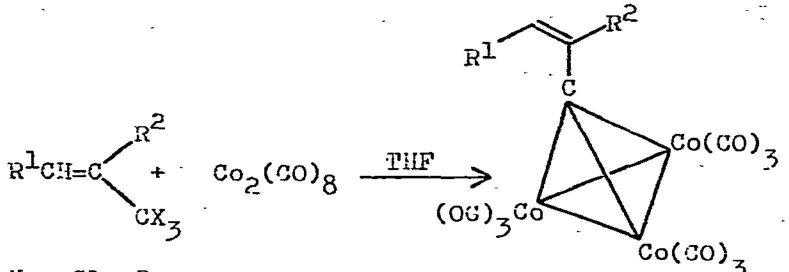
14.3

the mixed acetyl carboxy salt (14.3; R^1 = COMe, R^2 = CO_2H) was formed in addition to the previous two products[257].

Geiger has generated the first metallocene anion, η-Cp_2Co^- by electrochemical reduction of the cobalticinium ion in dimethoxyethane. The anion was stable in dimethoxyethane but decomposed in acetonitrile[258]. The reaction of molten 1,1'-bis(carbethoxy)cobalticinium hexafluorophosphate with equimolar amounts of 1,10-decanediol and 1,4-bis(hydroxymethyl)benzene gave the polyesters poly(cobalticinium-1,1'-diylcarbonyloxydecamethyleneoxycarbonyl hexafluorophosphate) and poly(cobalticinium-1,1'-diylcarbonyloxymethylene-1,4-phenylenemethyleneoxycarbonyl hexafluorophosphate) respectively. Attempts were made to prepare polyamides from 1,1'-dicarboxycobalticiniumdiamine salts by melt techniques but extensive decomposition occurred and pure polyamides could not be isolated[258a].

15. Cobalt-carbon Cluster Compounds

Methylidynetricobalt nonocarbonyl derivatives were the important products from the reactions of cobalt carbonyl or $NaCo(CO)_4$ and chlorosilanes. The course of the reaction was dependent on solvent basicity, the nature of the chlorosilane and the cobalt carbonyl species. Thus silicon tetrachloride and cobalt carbonyl or $NaCo(CO)_4$ in THF or diethyl ether gave the trichloride $Cl_3SiOCCo_3(CO)_9$[259]. α,β-Unsaturated methylidynetricobalt nonacarbonyl complexes (15.1) were prepared by the reaction between dicobalt octacarbonyl and the appropriate vinylic trihalomethyl derivative (Scheme 15.1). Protonation of the methyl derivative (15.1; R^1 = H, R^2 = Me) with HPF_6-propionic anhydride gave the hexafluorophosphate salt of the

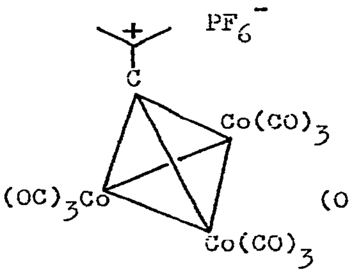


15.1

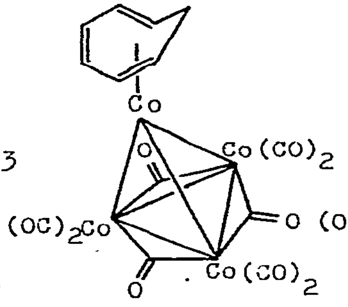
X = Cl, Br

Scheme 15.1

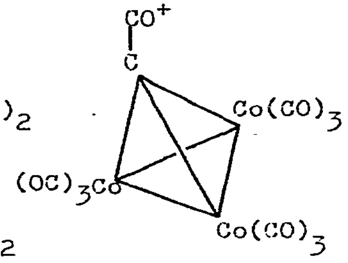
carbenium ion (15.2). Treatment of this salt with methanol gave $MeOCC(Me)_2CCo_3(CO)_9$ and treatment with aniline gave $PhNHC(Me)_2CCo_3(CO)_9$[260]. The η-cycloheptatriene complex (15.3) was formed by heating dodecacarbonyltetracobalt and cycloheptatriene in hexane. The physical properties of the complex showed some resemblences to (η-cycloheptatriene)-chromium tricarbonyl[261]. The preparation of the cobalt cluster acylium ion (15.4) from carboxymethylidynetricobalt nonocarbonyl and its esters with sulphuric acid has been



15.2



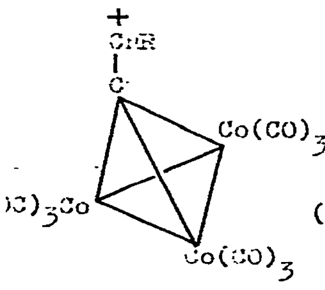
15.3



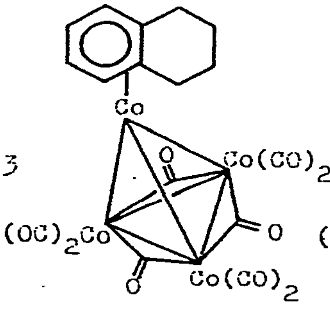
15.4

reported with full experimental details by Seyferth, Hallgren and Eschbach. The reactions of the acylium ion (15.4) with alcohols, phenols, thiols, amines, Grignard reagents and organometallic compounds which were outlined in the preliminary communication[263] have been extended and described in detail[262].

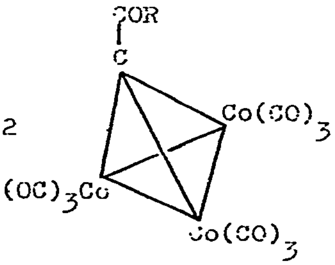
The crystal and molecular structure of the mixed crystal (η-*o*- and *m*-xylene)enneacarbonyltetracobalt was determined by X-ray analysis. The unit cell data were, space group $P2_1/c$ with a = 10.03, b = 9.86, c = 20.24 Å, β= 96.4°, Z = 4. The unit cell data for (η-benzene)enneacarbonyltetracobalt were, space group *R*3 with a = 9.79 Å, = 82.95°, Z = 2. Both the structures consisted of a tetrahedral cobalt cluster with one cobalt atom π-bonded to the arene moiety, while the other three are each bonded to two terminal and two bridging carbonyl groups. The aromatic rings showed no significant distortion from local six-fold symmetry[264]. Charge delocalization in the cluster carbenium ions (15.5; R = H, Me, Ph) has been investigated by ^1H and ^{13}C NMR spectroscopy. The results suggested extensive charge delocalization from carbon to cobalt and comparisons with ferrocenylcarbenium ions indicated that the cluster cations were stabilized at least as efficiently as their ferrocene analogues[265]. Differences between the mass spectra of the complexed and free tetrahydronaphthalene ligand have been observed. The ligand in the cobalt complex (15.6) loses small neutral molecules (H_2) with aromatization while atomic hydrogen is lost from the free ligand The results are explained in terms of the activation energies of possible fragmentation routes of the molecular ion[266].



15.5



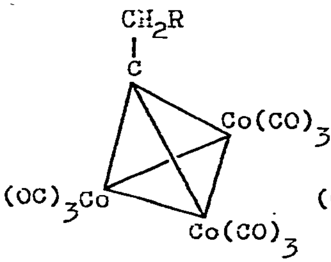
15.6



15.7

The reaction of cobalt complexes of the type $[YCCo_3(CO)_9]$ (Y = Cl, Me, Ph), $[(\eta\text{-}C_5H_5)NiCo_3(CO)_9]$ $[SCo_3(CO)_9]$, $[SCo_2Fe(CO)_9]$ and $[Co_4(CO)_{12}]$ with isocyanides, RNC (R = Me, Bu^t), was studied by Newman and Manning. The reactions took place under mild conditions and up to five carbonyl ligands were displaced by isocyanide with retention of the XCo_3 or SCo_2Fe cluster (X = C, Ni, S or Co). The structures of the products were discussed on the bases of their infrared spectra[267]. The reduction of the acyl cluster compounds (15.7; R = alkyl or aryl) to the respective alkyl or aralkyl compounds (15.8; R = alkyl or aryl) was achieved under acid conditions, triethylsilane and trifluoroacetic acid in THF, yields were good (67-92%). The secondary alcohols (15.9; R = alkyl or aryl) were obtained when the cluster ketones (15.7) were reduced with triethylsilane in boiling benzene followed by sulphuric acid and hydrolysis, yields varied between 46 and 90%[268].

Seyferth and his co-workers have continued their investigations of methylidynetricobalt nonacarbonyl cluster compounds. Arylation of methylidynetricobalt nonacarbonyl with diarylmercurials and arylmercuric halides in benzene or THF proceeded in good yield at the reflux temperature. The yields were maximised when the reactions were carried out under an atmosphere of carbon monoxide which suppressed the reversible loss of carbon monoxide from the starting material and its subsequent irreversible degradation. Fourteen aryl complexes (15.10) were formed in this way in yields of up to 96%. The aryl groups (Ar) introduced were methoxy-, methyl-, halogeno- and amino-phenyl and perfluorophenyl. The ferrocenyl group was also introduced, althought in rather low yield. By contrast, alkylation reactions with dialkylmercurials and alkylmercuric halides were slow and gave poor yields of products. Arylation of the halogeno cluster compounds (15.11; Hal = Cl, Br, I) with diphenylmercury was also achieved. The structurally related acetylenedicobalt hexacarbonyl cluster



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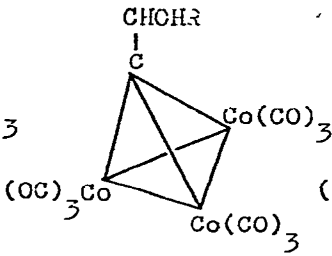
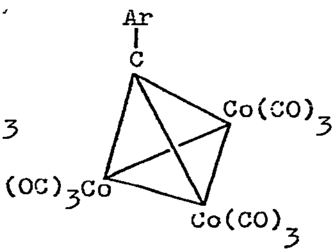


15.9



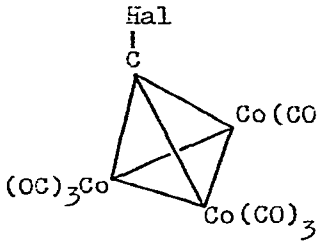
15.10

compound was phenylated with diphenylmercury to give both the mono- (15.12) and di-aryl (15.13) derivatives in yields of 21% and 10% respectively. Alternative radical and ionic mechanisms for these arylations were discussed[269]. Oxidative (ceric salts) and thermal degradation of the methylidynenonacarbonyltricobalt compounds $RCCo_3(CO)_9$ (R = Ph, CH_2Ph) gave the acetylenes $RC{\equiv}CR$. It was thought that these acetylenes were formed by the coupling of the two methinyl fragments[270].

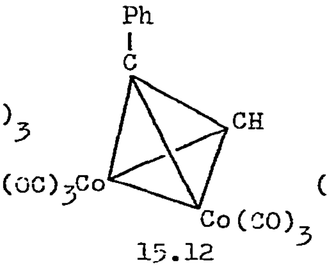
16. $(\eta\text{-}C_5H_5)_2Ni$

Barnett has reviewed the chemistry of nickelocene. The survey was divided into the following sections: structure and bonding, ring-addition, ring cleavage and finally ligand transfer reactions. The literature survey was complete up to the end of 1973[271]. Undergraduate experiments for the preparation of nickelocene and the reaction of nickelocene with dimethylacetylene dicarboxylate have been described by Barnett[272].

The reduction of $(\eta\text{-}C_5H_5)NiNO$ with lithium aluminium hydride-aluminium chloride gave paramagnetic $[(\eta\text{-}C_5H_5)Ni]_4H_3$ and some nickelocene. The structure of $[(\eta\text{-}C_5H_5)Ni]_4H_3$ was shown to consist of a slightly distorted Ni tetrahedron with $\eta\text{-}C_5H_5$ groups at the apices. The hydrogen atoms lay over three tetrahedron faces[273]. The X-ray structure analysis of the triple-decker sandwich complex (16.1) has confirmed the previous proposals based on other evidence. The three ligands and two nickel atoms are colinear with staggered cyclopentadienyl rings. The average nickel-carbon distances for the two terminal rings are 2.09 and 2.08 Å and for the bridging ring are 2.13 and 2.16 Å. These bond distances are consistent with the substitution patterns of the complex (16.1) with Lewis bases[274]. Court and Werner have presented ^{1}H NMR evidence to support an ionic mechanism for the formation of the triple decker sandwich (16.4) from nickelocene. A solution of nickelocene in anhydrous hydrogen fluoride contained the ring-protonated cation (16.2). Addition of boron trifluoride to the solution gave the cation (16.3), isolated as the brown tetrafluoroborate. The ion (16.3) attacked a further molecule of nickelocene to form the triple-decker complex (16.4). Although this route to the product was favoured by the authors, the alternative route through attack of the diene complex (16.2) on nickelocene was not excluded[275].



15.11



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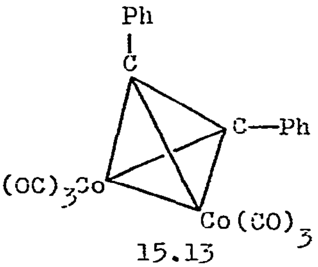

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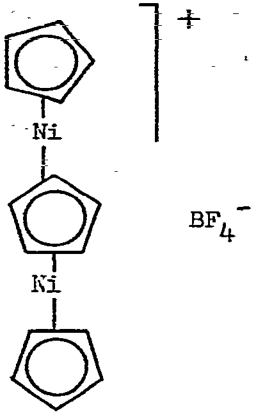
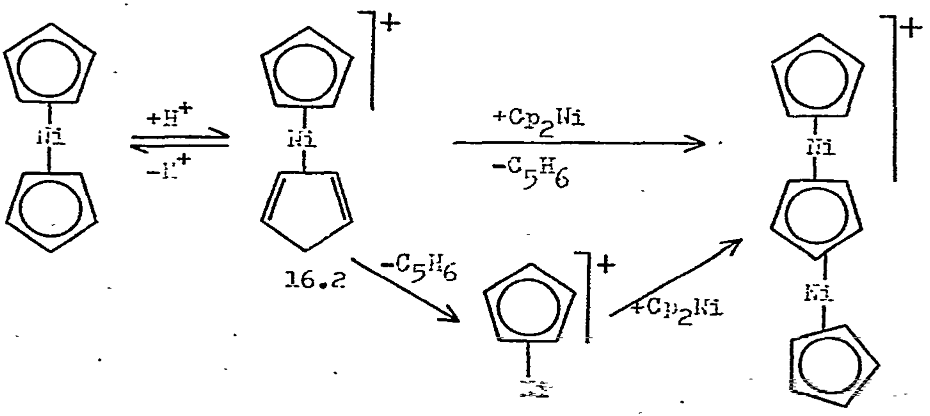


16.1

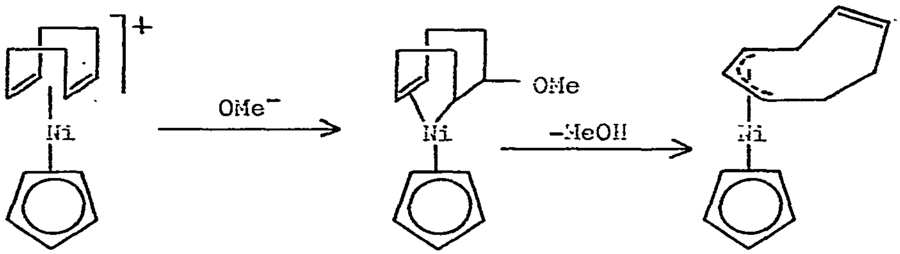
The cationic complex (16.5) was converted to the neutral olefin complex (16.6) on treatment with methoxide ion in methanol. Abstraction of methanol from this product gave the η-allyl compound (16.7). The ^1H NMR spectra of these complexes were discussed with particular reference to their stereochemistry[276]. The reaction between nickelocene and dimethylketene has been reinvestigated by Young. The orange solid obtained by mixing the reactants in benzene was first assigned a π-complexed lactone structure by Sato, Ichibori and Sato[278]. It has now been reassigned as the structure (16.8)



16.2 16.3 16.4

formed by cycloaddition of one ketene molecule to a cyclopentadienyl ring of nickelocene followed by insertion of a second ketene molecule into a nickel-carbon bond[277].

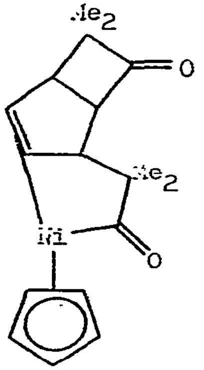
The reaction of nickelocene with PBu_3 or Ph_2PBu in hexane gave the complexes $Ni(PBu_3)_4$ and $Ni(PPh_2Bu)_4$ respectively. A similar reaction with $RPBu_2$ (R = Ph, p-tolyl) gave the complexes $(\eta\text{-}C_5H_5)Ni(RPBu_2)_2$[279]. Nickelocene combined with $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$ to give the η-cyclopentadienylnickel complex (16.9). The tertiary phosphorus atom in this molecule was shown to be uncoordinated, by quaternization with methyl iodide and ethyl bromide[280]. Nickelocene was attacked



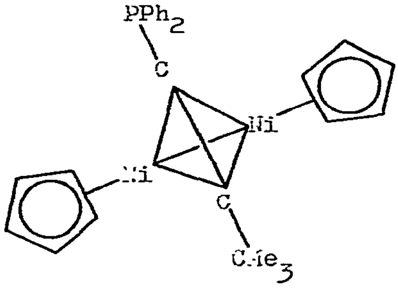
16.5 16.6 16.7

by bis(trifluoromethyl)diazomethane to give a 1:2 adduct with a nickel-cyclopentadiene bridge (16.10)[281].

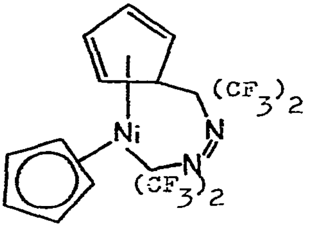
The kinetics of ligand exchange between nickelocene and (a) lithium cyclopentadienide (LiC_5D_5), (b) the tetramethylethylenediamine adduct of LiC_5D_5 and (c) bis(η-cyclopentadienyl)manganese, have been studied. For reaction (a) the rate law suggested that exchange proceeded by two paths. The first path involved rate determining association of nickelocene and LiC_5D_5 and the second involved similar association of nickelocene with $(LiC_5D_5)_2$, a dimer. The dimer was at least forty times as reactive as the monomer[282]. Ferrocene readily formed a clathrate complex with thiourea but nickelocene did not form such a complex. However nickelocene was included when it accompanied ferrocene. All attempts form clathrates with ruthenocene were unsuccessful[283]. Polypropylene films were stabilized against degradation by ultraviolet radiation with a thin coating of nickelocene which behaved as an energy transfer agent[284].



16.3



16.9



16.10

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