ORGANIC REACTIONS OF SELECTED π-COMPLEXES

ANNUAL SURVEY COVERING THE YEAR 1972

BERNARD W. ROCKETT and GEORGE MARR
Department of Physical Sciences, The Polytechnic
Wolverhampton, WV1 1LY (Great Britain).

CONTENTS

I. REVIEWS

The structures of mononuclear and polynuclear complexes containing π-hydrocarbon and carbonyl ligands have been discussed[1]. The chemistry of transition metal complexes containing arene, cycloheptatriene, cyclooctatriene, cyclooctatetraene and larger ring trienes has been reviewed by Stephenson[2]. The chemistry of organometallic compounds containing four-electron ligands has been the subject of a general survey[3]. In a review on the electronic effects in metallocenes and related systems, Slocum and Ernst dealt briefly with cobalticinium salts and cymantrene[4]. The ring-ligand displacement reactions of many of the more common arene-metal complexes were discussed by Werner[5]. The preparations and properties of organic π-complexes of the iron triad carbonyls were reviewed by Smik and Juluvka[6]. Rausch has presented a valuable survey of much of the recent work involving metal-π-cyclopentadienyl and metal-arene compounds[7].

Perevalova and Nikitina have reviewed the structure and properties of the metallocenes but the methods of preparation and the physical properties of these compounds were not discussed. The article discussed the properties of the metallocenes according to the types of reaction that they underwent, the chapter headings were: hydrogen-substitution reactions of five membered metallocene rings; substituent-exchange reactions of the cyclopentadienyl ring; reactions involving the metal-ring bond and oxidation-reduction reactions of the metallocenes. The authors covered the literature on the subjects under discussion up to 1967 and there was also a summary of results published in 1968 and 1969 and partly in 1970[8]. Green surveyed briefly molybdenum chemistry and then discussed bonding in bent bis(π-cyclopentadienyl)metal compounds, new reactions of bis(π-cyclopentadienyl)molybdenum and (tungsten) complexes and arenemolybdenum chemistry were discussed in more detail[9]. Ligand exchange and replacement reactions in transition metal π-complexes were discussed by Rubezhov and Gubin with the emphasis on π-arene and π-cyclopentadienyl complexes[10]. Barnett and Slocum have published an authoritative survey of the chemistry of π-cyclopentadienyl complexes of chromium, molybdenum and tungsten.

II. (i) $(\pi\text{-}C_6H_6)Cr(CO)_3$

Benchrotrene derivatives have been formed from α,β,γ,δ-tetraphenylporphin and its Cr(II), Mn(III), Ni(II), Cu(II) and Zn(II) chelates. The NMR and IR spectra were used to confirm the structures proposed and the invariance of the carbonyl stretching frequencies showed that the benzene ring in the π-complex was not in conjugation with the chelated transition metal through the porphin system[12].

The distortion of the benzene ring in benzenechromium tricarbonyl was determined by X-ray and neutron-diffraction methods at 78°K. It was found that of the six C-C bonds three were lengthened by approximately 0.02Å and that of the six hydrogen atoms, three were displaced towards the chromium atom. These distortions only became evident at low temperatures and it was suggested that the details of the bonding in many organometallic complexes might be elucidated if structural analyses were performed routinely at low temperatures[13]. The crystal structures of the two racemic diastereoisomers of the benchrotrene derivative (1.1) have been determined by X-ray crystallography. The relative configurations obtained confirmed the assignments made previously on the basis of spectroscopic results[14].

The Raman spectra of benchrotrene were obtained for solid and solution samples, the bands were assigned and compared with the infrared spectra[15]. In a similar investigation the Raman spectra and the low temperature infrared spectra of $(C_6D_6)Cr(CO)_3$ and $(C_6H_6)Cr(CO)_3$ were recorded and interpreted[16]. These results were compared with those from the earlier work by Fritz and

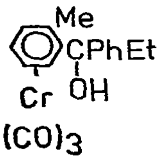
Manchot[17] and some changes in the interpretation of the spectra were made. A complete set of symmetry coordinates of molecular vibrations have been constructed for a C_{3V} model of benzene-chromium tricarbonyl on the basis of conventional valence coordinates A second set has been determined, where the identity of the benzene ligand was preserved as far as possible, for use in a normal coordinate analysis and the same group described this analysis in the succeeding paper. The calculations showed similar kinematic coupling to that described previously for transition metal sandwich complexes. The mean amplitudes of vibration and selected shrinkage effects were determined and compared with the corresponding quantities in the related molecules, benzene, bis(π-benzene)-chromium and chromium hexacarbonyl[19].

In the mass spectrometer, bimolecular ion-molecule reactions occur and substituent effects on such reactions using the arene-chromium tricarbonyl system (equation 1) have been studied. The rate of this bimolecular reaction was correlated with substituent

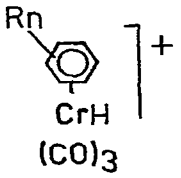
$$[ArCr(CO)_3]^+ + ArCr(CO)_3 \longrightarrow [Ar_2Cr_2(CO)_3]^+ + 3CO \qquad (1)$$

effects in the arene. The Hammett ρ constant was large and negative and this was taken as evidence that the reaction was facilitated by electron donation at the site of attack by the cation and that it was sensitive to the electrical effects of the substituent[20].

Tris(dipivalomethanato)europium, a paramagnetic shift reagent, has been used to investigate 1,2-(α-oxotetramethylene) substituted ferrocene, benchrotrene and cymantrene through their NMR spectra. The reagent was effective in facilitating structural analysis and the analysis of mixtures[21]. Trimethyl-, hexamethyl-, and trimethoxy-benchrotrene undergo protonation with FSO_3H in liquid sulphur dioxide. In each case, NMR spectroscopy suggested that the cation (1.2) was dominant over (1.3) and in the presence of the methoxy group, the only species present was (1.2). The mechanism for proton exchange was discussed[22]. IR[23] and NMR[24] spectroscopy have been used to investigate the protonation of the



1.1



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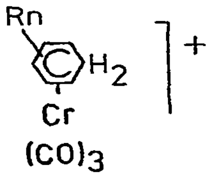
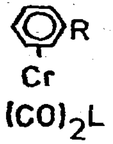


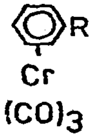
1.3

benchrotrene derivatives (1.4; R = H, Me, OMe, CO_2Me, NMe_2) in BF_3-CF_3CO_2H mixtures and the arenechromium dicarbonyl triphenylphosphines (1.5; R = H, Me, OMe, CO_2Me, NMe_2) in CF_3CO_2H. Benchrotrenes were not protonated in the latter solvent. In each case, protonation at the metal atom was observed and the reaction was facilitated by electron-releasing groups on the benzene ring or by substitution of carbonyl with triphenylphosphine. Ashraf has examined base catalysed hydrogen-deuterium exchange in the benchrotrene derivatives (1.6; R = OMe, CO_2Et) using sodium ethoxide in ethanol-O-$\underline{d}_1$ at 100°. Exchange of aromatic protons in the o-, m- and p-positions relative to the substituent was observed. In the presence of the electron releasing methoxy group (1.6; R = OMe) o-exchange was dominant whereas random substitution was observed for the complex (1.6; R = CO_2Et) with the electron withdrawing ester group. In each case extensive decomposition of the complexes was observed (85%) under the conditions used although the ester was recovered partially as the carboxylic acid[25]. Trahanovsky



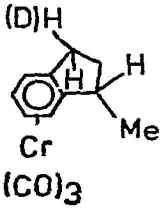
1.4 L = CO

1.5 L = PPh_3



1.6

and Card have observed the stereospecific hydrogen-deuterium exchange of benzylic protons in benchrotrene complexes under basic conditions (potassium t-butoxide in DMSO-$\underline{d}_6$). Experiments with the methylindan complexes (1.7 and 1.8) demonstrated that only protons anti to the tricarbonylchromium group underwent exchange. The reaction was complete within 15 min at room temperature when 0.5M potassium t-butoxide was used. It was suggested that overlap of the anionic charge with chromium in the intermediate anion was favoured when an anti proton was removed, although steric control of the reaction was not excluded[26].



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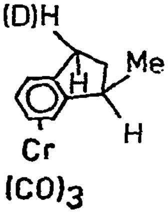
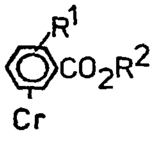


1.8

The pK_a values of a series of m- and p-alkylbenzoic acids in aqueous ethanol were compared with the values for the corresponding benchrotrene complexes (1.9). The complexes (1.9) were stronger acids than the parent acids although the substituent effects showed a different trend. Thus the p-Bu^t substituent caused an increase in acid strength from pK_a 6.22 in the free acid to 5.32 in the complex (1.9; $R^1 = Bu^t$) while the p-Me group showed an increase from pK_a 5.92 to 5.57. These differences were rationalized in terms of the polarizability differences between the methyl and t-butyl groups. Conformational preferences of the $Cr(CO)_3$ group were shown to be unimportant in influencing the stability of the carboxylate anions. By contrast, the NMR spectra of the complexes (1.9) were best interpreted in terms of the conformational influence of the alkyl groups on the $Cr(CO)_3$ moiety[27]. A related study by Reeves and co-workers compared the

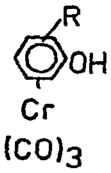


1.9

R^1 = p-Me, p-Et, p-Pr^i, p-Bu^t, m-Me, m-Pr^i

R^2 = H

1.10 R^1 = o-, m-, p-F, R^2 = Me

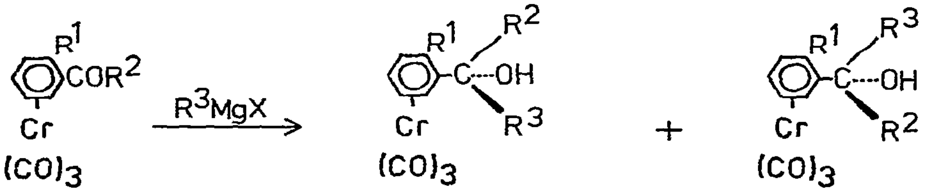


1.11

pK_a values of substituted phenols in aqueous ethanol with those for the chromium complexed ligands (1.11; R = p-Me, H, p-, m-CO_2Me, p-, m-COMe). The results demonstrated that complexing markedly increased the acidity of the phenols. The good correlation observed between pK_a values for the complexes or the free phenols and the Hammett σ^- values show the transmission of the substituent effect to the reaction centre. It was also found that the two sets of pK_a values were linearly related for the six substituents investigated[28].

The nucleophilic displacement of fluoride by methoxide in the disubstituted benchrotrenes (1.11) has been investigated kinetically by a potentiometric technique. The second order rate constants and the thermodynamic parameters for the reactions were calculated. Racemization of these compounds was studied under similar conditions and possible mechanisms were discussed[29]. The rates of elimination with sodium ethoxide in ethanol for (2-phenylethylbromide)- and (2-phenylethyl-*p*-toluenesulphonate)-chromium tricarbonyl, to give the corresponding styrene (1.6; $R = CH{=}CH_2$) were determined over a range of temperatures. These results were compared with the rates of elimination of the uncomplexed 2-phenylethy and 2-(*p*-nitrophenyl)ethylbromides and tosylates. The introduction of π-chromiumtricarbonyl increased the rate of elimination but the effect was much less marked than that of a *p*-nitro group. The increase in rate on going from $Cr(CO)_3$ to *p*-nitro was thought to be due to the lower capacity of the chromium tricarbonyl to stabilize the developing negative charge at the α-carbon in this base induced E_2 reaction[30].

Reduction of the chiral benchrotrenes (1.12) with the Grignard reagent gave a mixture of the diastereoisomeric alcohols (1.13 and 1.14). The proportions of the products were dependent on the nature of the substituents R^1 and R^2 (1.12) and on the reagent. These differences were explained in terms of the steric requirements of the transition state[31]. The effect of two different substituents

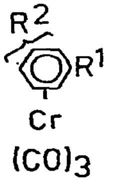


1.12 1.13 1.14

R^1 = Me, OMe

R^2, R^3 = Me, Et, Ph

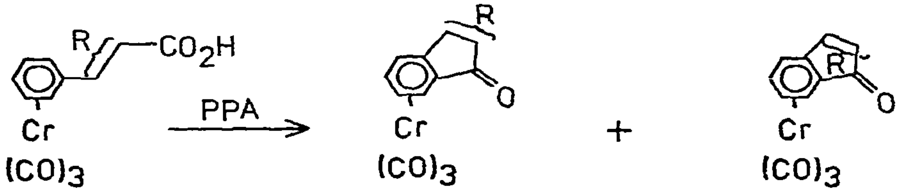
in the benzene ring of benchrotrene on the nucleophilic substitution of the complex has been investigated. The derivatives (1.15) were inert to substitution while the esters (1.10) were attacked by Me_2NH, NaSMe, NaOEt and $NaOPr^i$ with displacement of the fluoride ion and the reaction of optically active esters was accompanied by racemization[32].



1.15

$R^1 = NH_2$, R^2 = o-, m-, p-F
R^1 = Me, R^2 = o-, m-, p-F

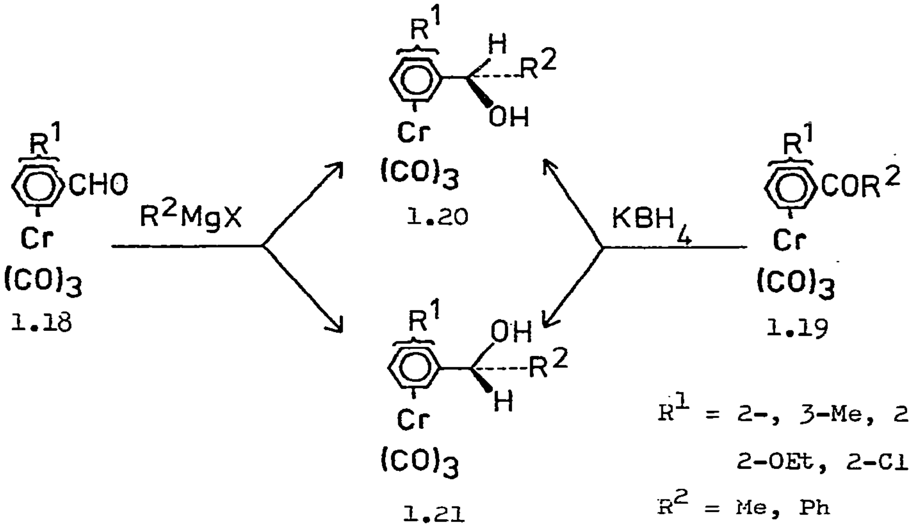
Cyclization of the α- or β-alkyl propionic acids (1.16) gave a mixture of isomeric ketones (1.17) in each case with the alkyl group either endo or exo to the metal atom. The exo product was preferred and the percentage was greater for α- than for β-substitution. α-Et, 80% exo; β-Et, 60%. An increase in the size of the substituent also gave an enhanced yield of this product, β-Pr^i, 75% exo; β-Bu^t, 95%. Reduction of the ketones (1.17) with potassium borohydride in aqueous methanol was stereospecific; the reagent attacked the face of the ligand remote from the chromium tricarbonyl group to give the cis alcohol[33]. Meyer and Dabard



1.16 1.17 (exo) 1.17 (endo)

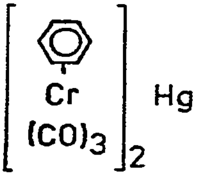
R = Et, Pr^i, Bu^t

have investigated the formation of a series of diastereoisomeric benchrotrene derivatives (1.20 and 1.21) by either the Grignard reaction of the aldehydes (1.18) or the borohydride reduction of the ketones (1.19). The proportions of the two isomeric products (1.20 and 1.21) were dependent on the reagent and on the nature and position of the substituents. The steric and electronic effects of ortho-substituents determined the conformation of the carbonyl group and the product proportions. In the case of meta-substituents the conformations of the chromium tricarbonyl residue were invoked in order to explain the stereoselectivity[34].



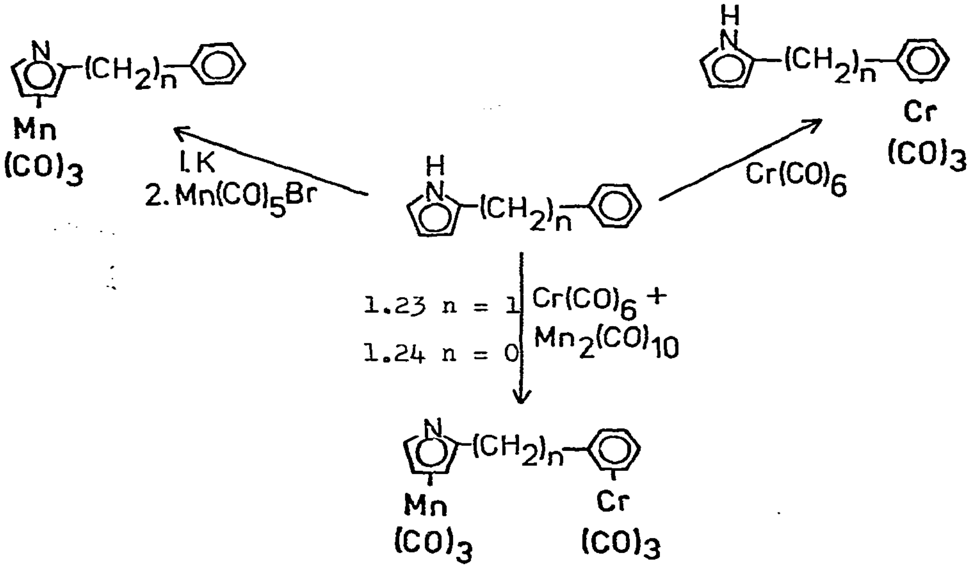
R^1 = 2-, 3-Me, 2-, 3-OMe, 2-OEt, 2-Cl

R^2 = Me, Ph



1.22

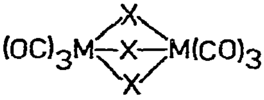
The binuclear complex (1.22) was obtained by heating diphenylmercury with chromium hexacarbonyl in diglyme-octane, it was used to prepare the benchrotrene complexes (1.6; R = H, I, HgCl) by treatment with lithium aluminium hydride, iodine and mercury (II) chloride respectively[35]. When mesitylene- or hexamethylbenzene-chromium tricarbonyl in THF was irradiated in a nitrogen atmosphere $[ArCr(CO)_2]_2N_2$ was formed. The nitrogen molecule bridged the two chromium atoms[36]. The $Cr(CO)_3$ and $Mn(CO)_3$ complexes



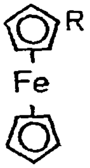
Scheme 1.I

of 2-benzylpyrrole (1.23) and 2-phenylpyrrole (1.24) and the complexes in which both a $Cr(CO)_3$ and a $Mn(CO)_3$ group are attached to a ligand were prepared (see Scheme 1.I). In each complex the $Cr(CO)_3$ group is π-bonded to the phenyl ring and the $Mn(CO)_3$ group is π-bonded to the pyrrolyl ring. The NMR spectra of these molecules were interpreted in terms of electronic effects transmitted through the 6-electron system and in ring current effects[37]. A series of compounds of general formula $(R_4N)_3[(CO)_3MX_3M(CO)_3]$ (1.25) where M = Cr, Mo, W; X = F, Cl, Br, I, OH, SCN, N_3, OC_2H_5 were prepared by allowing $AreneM(CO)_3$ to react with a tetraalkylammonium halide. Some compounds with two membered bridges with the formula $(R_4N)_2[(CO)_3MX_2M(CO)_3]$ were prepared by a similar route. The ease with which this reaction took place was taken as evidence for the strong Lewis acid properties of $AreneM(CO)_3$ compounds[38].

π-(Benzylacrylate)chromium tricarbonyl was prepared by treating $Cr(CO)_6$ with benzyl alcohol to give π-(benzylalcohol) chromium tricarbonyl which was esterified with $H_2C{=}CHCOCl$ to yield the acrylate The acrylate was homopolymerized in the presence of azobis(isobutyronitrile) and it was copolymerized with styrene, methylacrylate or 2-ferrocenylethyl-acrylate[39]. The organometallic monomers (1.26, 1.6; R = $CH_2O_2CCH{=}CH_2$, 1.27) were synthesized and homopolymerized, (1.6; R = $CH{=}CH_2$, 1.27) were copolymerized and the monomers (1.26; R = $CH_2O_2CCH{=}CH_2$, R = $CH{=}CH_2$, 1.27) were each copolymerized with styrene and methylacrylate[40]. The polymers were evaluated as catalysts and as components of surface coatings[41]. The benchrotrene derivative (1.6; R = $CH{=}CH_2$) was converted to the acetylenes (1.6; R = $C{\equiv}CH$, $C{\equiv}CSiMe_3$) and attempts were made to polymerize the olefin



1.25



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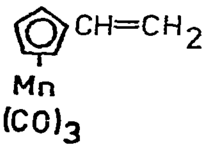
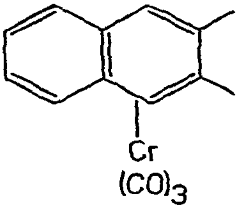


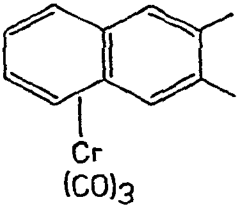
1.27

(1.6; R = $CH{=}CH_2$) with free radical and anionic initiators, only low yields of polynuclear products were obtained. Reduction and hydration of the acetylene (1.6; R = $C{\equiv}CSiMe_3$) gave π-ethylbenzene- and π-acetophenone-chromium tricarbonyl respectively[42].

1,3,7-Octatriene was hydrogenated, in the presence of methylbenzoatechromium tricarbonyl as a catalyst, to give 1,5-octadiene and 1,6-octadiene which were useful as comonomers in the preparation of vinyl polymers and ethylene elastomers[43]. Benchrotrene supported on dried aluminosilicate was found to be an effective catalyst for the polymerization of ethylene[44]. A mixture of the two isomers of (2,3-dimethylnaphthalene)-chromium tricarbonyl (1.28) and (1.29) was separated by high speed column liquid chromatography. The mixture which was prepared from chromium hexacarbonyl was found to contain 73% of isomer (1.28)[45].



1.28



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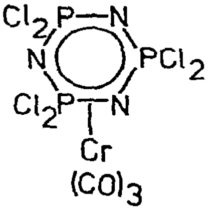


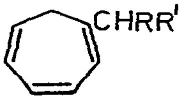
1.30

The cyclotriphosphazene analogue (1.30) of benchrotrene has been formed by heating cyclo-$(PNCl_2)_3$ with $(MeCN)_3Cr(CO)_3$ in THF or diethyl ether. Although these compounds were predicted theoretically in 1966 this is the first example to be synthesized[46].

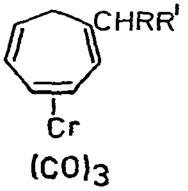
II (ii) $[(\pi\text{-}C_7H_7)Cr(CO)_3]^+$, $(\pi\text{-}C_7H_8)Cr(CO)_3$

Treatment of the heptafulvene (2.1) with tris(acetonitrile) chromium tricarbonyl gave the complex (2.2) which on reaction with Ph_3CBF_4 gave the tropylium salt (2.3). Proton abstraction with

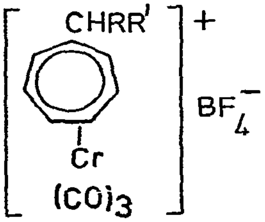
1,8-bis(dimethylamino)naphthalene yielded the heptafulvene (2.4). Treatment of the complex (2.4) with HPF_6 regenerated the tropylium derivative (2.3). These chromium complexes also functioned as sources of the heptafulvene by displacement of the ligand in an appropriate arene solvent in the presence of a dienophile[47]. Pauson and his group have studied the specific hydrogen migration of the equatorial



2.1



2.2



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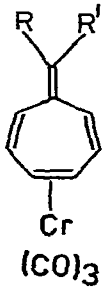
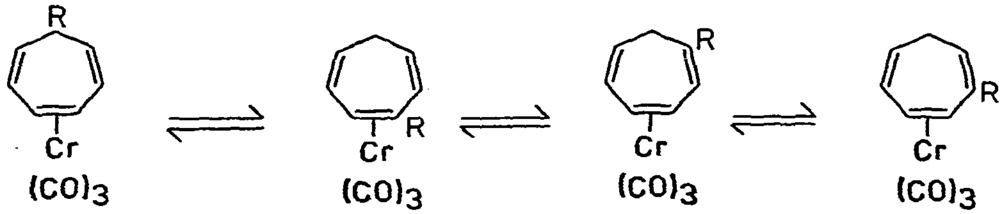


2.4

7-endo-hydrogen in chromium tricarbonyl complexed cycloheptatrienes. They showed that the process involved a series of sequential [1,5] hydrogen migrations (Scheme 2.1) which gave first the 3-, then 1- and finally 2-substituted products[48]. The photochemical reaction of cycloheptatriene chromium tricarbonyl with triphenylphosphine and triphenyl phosphite gave $C_7H_8Cr(CO)_2P(C_6H_5)_3$ and $C_7H_8Cr(CO)_2P(OC_6H_5)_3$ respectively. The cycloheptatriene complexes were inert towards



Scheme 2.1

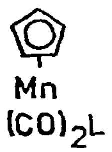
acetonitrile, benzonitrile and pentamethyldiethylenetriamine and this suggested that the strengths of the chromiumcycloheptatriene bonds were increased by the replacement of a carbonyl group with $P(C_6H_5)_3$ or $P(OC_6H_5)_3$[49].

II (iii) $(\pi\text{-}C_6H_6)_2Cr$

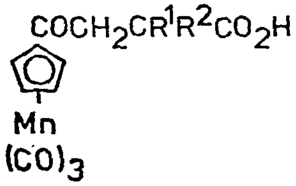
Evans, Green and Jackson have measured the He(I) photoelectron spectra of bis(π-benzene)chromium, bis (π-toluene)chromium and some related bis-π-arene complexes. The ionization energies obtained were compared with the values obtained by mass spectrometry and interpreted in terms of the electronic structures of the complexes[50]. The EPR spectra of a series of bis(arene)chromium (I) complexes have been measured; the hyperfine structure could not be explained by configuration interaction over the π-system or by direct metal--hydrogen interaction[51]. The mass spectra of a series of chromium bisarene complexes ArCrAr' (where Ar = Ar' or Ar ≠ Ar' and Ar and Ar' = C_6H_6, C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$, C_6Me_6, C_6H_5Et, $C_6H_4Et_2$) were recorded. From the spectra it was concluded that the strength of the chromium--ligand bond increased as the number of alkyl substituents increased[52]. Thermal decomposition of the tetraphenylborate salts of some alkyl--substituted bis(π-benzene) chromium cations gave the free organic ligands at 195-210° and $CrBPh_4$[53]. The reaction of dibenzene chromium tetraphenylborate with mercury (II) chloride in methanol contained in a sealed tube at 100° for 65h gave CH_3Cl, PhH, PhHgCl, Hg and HgCl. After a reaction time of 3h $(Ph)_2CrCl$ was formed in isolable amounts which indicated that the reaction proceeded *via* $(Ph)_2CrCl$ and Ph_4BHgCl[54]. The thermal decomposition of bis(benzene) chromium phenolate at 80-135° proceeded by disproportionation to yield PhH, $(Ph)_2Cr$, PhOH and $Cr(OPh)_2$. At 200-260° the phenol oxidized the bis(benzene)-chromium to give PhH, H_2 and $Cr(OPh)_2$[55]. The bisarenechromium salts $(Arene_2Cr)^+X^-$ (Arene = PhH, Ph_2, MePh) were pyrolysed directly in the cavity of an EPR spectrometer. The resul indicated that when X = halogen the salt decomposed to give CrX_3, $Arene_2Cr$ and two molecules of the uncomplexed aromatic species. Whe $X = Ph_4B^-$ a different mode of pyrolysis was observed. Apparently the salt decomposed to give $CrBPh_4$ and two molecules of the uncomplexed aromatic species[56]. Treatment of cumene with chromium chloride in the presence of aluminium chloride and aluminium under Friedel-Crafts conditions gave mixtures of mono and polysubstituted bis(π-benzene) chromium compounds. The products were analysed by gas chromatography[57]. Bis(isopropylbenzene) chromium was separated successfully from other isopropylbenzene-chromium compounds by fractional distillation on a column with thirty five theoretical plates[58]. The quantitative analysis of complex isomeric mixtures of π-arenechromium complexes by mass spectrometry has been described[59]

II (iv) $(\pi\text{-}C_5H_5)Mn(CO)_3$

The preparation, physical and chemical properties and application of cymantrene have been reviewed with particular emphasis on its use as an antiknock additive in petroleum[60]. The carbonyl IR stretching frequencies and the ^{55}Mn NQR spectra were measured for a series of cymantrene derivatives (4.1). The IR intensities were insensitive to changes in the ligand L suggesting that the cyclopentadienyl ring bufferred the vibronic contribution made by the ligand. The NQR results confirmed the expected trends in σ-donor and π-acceptor character of the ligand[61]. Tris(acetylacetonato) chromium (III) was found to be a shiftless relaxation reagent for ^{13}C magnetic resonance of some organometallic carbonyl compounds. For example with $(\pi\text{-}MeC_5H_4)Mn(CO)_3$ a ^{13}C NMR spectrum was obtained by Fourier transform methods but in the absence of the complex neither the cyclopentadienyl C-1 nor the CO resonances were observed. In the absence of the relaxation reagent these resonances saturate. An added effect of the reagent was to ensure that on signal integration accurate intensity ratios were obtained since the Overhauser effect had been undermined[62]. The ^{19}F NMR spectra of m- and p- $-FC_6H_4C_5H_4Mn(CO)_3$ and the Re analogues were reported. It was found that the inductive effect substituent constant for the $(CO)_3MnC_5H_4$ group agreed with values obtained from redox potential data. In the Re analogue the electrophilic nature of the carbon atoms in the cyclopentadienyl ring increased but the electron density remained unchanged. There was a large change in the inductive effect constant when the anion was coordinated with $Mn(CO)_3$ or $Re(CO)_3$. This confirmed the participation in the metal bonding of both the π-electrons and the 6-ring skeleton[63]. The PMR chemical shifts of the cyclopentadienyl ring protons in the complexes $C_5H_5Mn(CO)_2L$ (L = CO, Bu_3P, Ph_3P, Pr^i_3P, Ph_3As and tricyclohexylphosphine) were reported. These spectra were compared with those for $RC_5H_4Mn(CO)_2L$ (R = Me, $PhCH_2$ and Et)[64]. Budesinsky and Svec have determined the effective and overall stability constants for the π-cyclopentadienyl complexes of Mn, Fe, CO, Ni and Pd in water and DMF[65]. The acylation of cymantrene with 2,2-disubstituted succinic anhydrides under Friedel-Crafts conditions gave the isomeric ketones (4.2 and 4.3; $R^1 = R^2$ = Me, Ph) with methylcymantrene as the substrate, both 2- and 3-substitution was observed[66].



4.1 L = R_3P, R_3As,
RCN, $[(CH_2)_n$ n = 3,4,6



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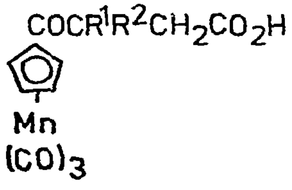
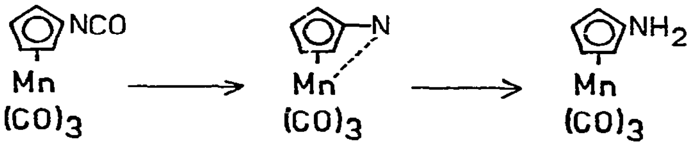


4.3

The presence of a chiral centre in the substituent of monosubstituted derivatives of cymantrene [4.4; R = $CHOHCF_3$, CHOHMe, CHOHPh, $CMe(OH)PO(Oalkyl)_2$] induced both the α and β ring protons to be diastereotopic and show chemical shift differences in the PMR spectra for either the α protons or both the α and β protons[67]. Thermolysis of cymantrenyl isocyanate (4.5) gave a mixture of the corresponding amine (4.7) and the symmetrical urea; the proportions of products were dependent on the solvent. It was suggested that a metal-nitrene complex (4.6) was the intermediate and this formed the amine product by hydrogen abstraction from the solvent and the urea by attack on the starting material[68]. The photolysis of cymantrene in petroleum gave the binuclear complex $[\pi\text{-}C_5H_5Mn(CO)_2]_2$ which decomposed on further irradiation to form a brown precipitate[69].

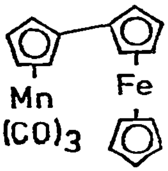
Cymantrenecopper was formed in low yield from cymantreneboronic acid and alkaline copper acetate at room temperature. The compound gave cymantrene with hydrochloric acid, chloromercuricymantrene with mercury (II) chloride in benzene, iodocymantrene

4.4



4.5 4.6 4.7

and dicymantrene with iodine and it ignited on heating[70]. The same group reported the reaction of cymantrenecopper with chloro- or bromo-ferrocene to give the stable ferrocenylcyclopentadienylmanganese tricarbonyl (4.8)[71]. Treatment of the ketone (4.9) in chloroform with CF_3CO_2H and triethylsilane gave the reduction product (4.10; R = Me, Ph, H). When the ketone (4.9; R = CF_3) was reduced with the same reagents the corresponding carbinol was obtained[72]. The reaction of acetylcyclopentadienylmanganese tricarbonyl with 1,3,5-trinitrobenzene gave an ionic adduct and this was treated with tropylium tetrafluoroborate to give (2,4,6--trinitrophenylacetyl)cyclopentadienylmanganese tricarbonyl (4.11) in 80% yield[73].



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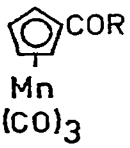

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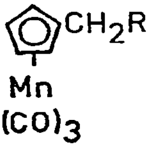


4.10

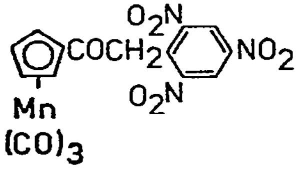
The manganese complexes $[(\pi\text{-arene})Mn(CO)_3]^+$ combine with primary alkylamines as shown in the equation:

$$[(\text{arene})Mn(CO)_3]^+ + 2RNH_2 \longrightarrow (\text{arene})Mn(CO)_2CONHR + RNH_3^+$$

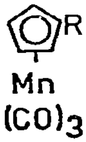
The carboxamide complex was not usually isolable because the reversibility of the reaction gave only starting material $[(\text{arene})Mn(CO)_3]^+$ when the solutions were evaporated to dryness. Qualitative equilibrium studies indicated that the reaction proceeded further to the right when the electron density at the carbonyl carbon atom was reduced by decreasing the number of CH_3 groups on the arene. When the $[(\text{arene})Mn(CO)_3]^+$ complexes were treated with hydrazine they gave $(\text{arene})Mn(CO)_2(NCO)$ derivatives[74].

The photolysis of cymantrene or methylcymantrene in a methylcyclohexane/nujol glass gave matrix trapped CO and $(\pi\text{-}C_5H_5)Mn(CO)_2$ and $(\pi\text{-}C_5H_4CH_3)Mn(CO)_2$ respectively[75]. The irradiation of a mixture containing cymantrene and PF_3 induced CO-PF_3 exchange to give $(\pi\text{-}C_5H_5)Mn(PF_3)_3$. The intermediate compounds $(\pi\text{-}C_5H_5)Mn(CO)_2PF_3$

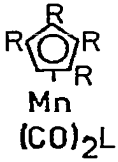
and $(\pi\text{-}C_5H_5)Mn(CO)(PF_3)_2$ were also obtained by changing the reaction conditions[76]. In a series of papers[77-88] several Russian groups report a number of investigations into the mechanism, the effects of substituents and additives and long term tests on the application of cymantrenes (4.12; R = H, alkyl, alkenyl, Ac, COPh, CH_2Oalkyl, CH_2OAc, CH_2CH_2Cl) as antiknock additives for petroleum.



4.11



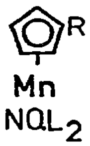
4.12



4.13; L = CO

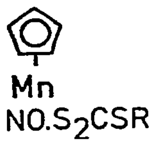
4.14; L = PAr_3

The protonation of cymantrenes (4.13; R = H, Et) and cymantrene analogues (4.14; R = H, Et) in CF_3CO_2H was favoured by electron-releasing groups on the cyclopentadienyl ring and by substitution of triarylphosphine for carbonyl. IR spectroscopy suggested that protonation occurred at the metal atom[88]. The attack of nucleophiles (C_6H_5Li and $NaBH_4$) on the cymantrene analogues (4.15; R = H, Me) has been investigated by Benedict. Reaction at both the cyclopentadienyl and the carbonyl or isocyanide ligands was observed, the site of reaction was determined by the steric and electronic properties of the group L[89].



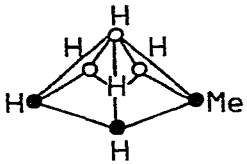
4.15

L = CO, CNMe, PR_3



4.16

The thioxanthate cymantrene analogues (4.16) were shown, by voltammetry, to undergo reversible one-electron oxidation in which the $(\pi\text{-}C_5H_5)Mn(NO)$ group played a significant role[90]. Some interesting carboranyl π-complexes, isoelectronic with cymantrene, have been described. Thus 2-methyl-2,3,4-tricarba-*nido*-hexaborane (4.17) was treated with manganese carbonyl in the gas phase to give the half sandwich complex (4.18). In diglyme, the carborane (4.17) gave the anion (4.19) with sodium hydride and this was converted to the yellow product (4.18) on heating with bromomanganese pentacarbonyl. ^{11}B NMR and mass spectrometry confirmed the cage structure of the complex (4.18)[91].



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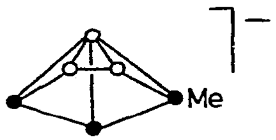

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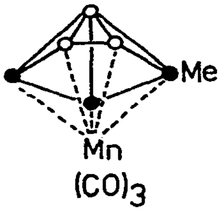
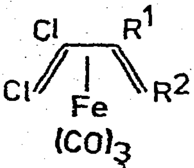


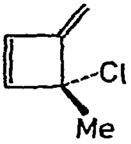
4.18

II(v) $(\pi\text{-}C_4H_4)Fe(CO)_3$

Maitlis and Eberius have reviewed extensively the chemistry of π-cyclobutadiene metal complexes[92]. The sites of the chloro-substituents were important in determining the reactivity of trichlorobutadienes towards triirondodecacarbonyl. Thus the 1,2,3- and the 1,2,4-trichlorobutadienes each gave the corresponding irontricarbonyl complexes (51 and 5.2) respectively while the 1,1,4-trichloro compound was inert under the same conditions[93]. A further report from the same laboratory confirmed that a cyclobutadiene complex (5.4), rather than a butadiene complex was obtained from the reaction between the cyclobutene (5.3) and diironenneacarbonyl[94].

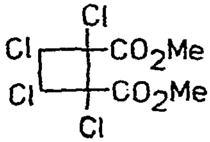

5.1 $R^1 = Cl$ $R^2 = H$

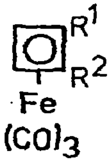
5.2 $R^1 = H$ $R^2 = Cl$


5.3

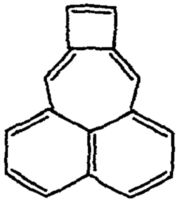

5.4

The dicarboxylic ester (5.6), synthesized from the tetrachlorocyclobutane (5.5) and diiron nonacarbonyl in the presence of zinc and acetic acid, has been used as the precursor of a variety of 1,2-disubstituted π-cyclobutadiene complexes (5.7)[95]. The generation of dimethylenecyclobutenes from cyclobutadieneiron tricarbonyl complexes was reported and this route was used to prepare cyclobutadienopleiadiene (5.8) and α,α'-diphenyldimethylenecyclobutene (5.9)[96].


5.5


5.6 $R^1 = R^2 = CO_2Me$

5.7 $R^1 = R^2 = CO_2H$, COCl, CH_2OH, CH_2Cl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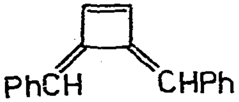
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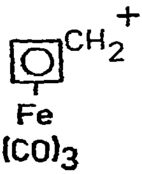
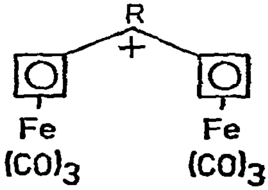
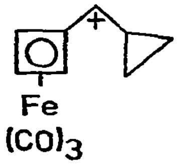

5.10


5.11

The IR and Raman vibrational spectra of cyclobutadieneiron tricarbonyl have been recorded and the vibrations of the (π-C_4H_4)Fe group have been assigned in detail. The assignments confirm strong bonding interactions between the iron atom and the ring. The vibrational frequencies of the iron tricarbonyl group are similar to those observed previously for other (π-hydrocarbon) $Fe(CO)_3$ molecules[97]. The rate of solvolysis of chloromethyl-cyclobutadiene-iron tricarbonyl was found to be 10^8 times faster than that of benzyl chloride. From this result it was concluded that the primary carbonium ion (5.10) was unusually stable. The nature of the electronic interaction that could lead to the delocalization of the positive charge was investigated by an X-ray study of several salts of these carbonium ions (5.11; R = H, Me, Ph) and (5.12). From the results it was concluded that the major effect leading to stabilization of the cation involved interaction of a filled metal orbital with the four carbon atoms of the cyclobutadiene ring and that electrons were transmitted to the electron deficient exocyclic carbon atom by a π-π carbon—carbon interaction[98]. Oxidation with ceric ion of cyclobutadieneiron tricarbonyl in the presence of 2,5-diphenyl-3,4-diazanorcarane (5.13) afforded the azo derivative (5.14). Further reactions of this derivative were studied and discussed in detail[99].



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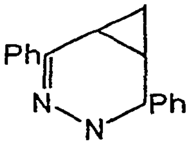

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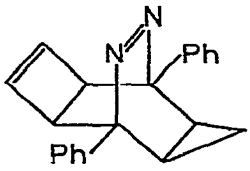
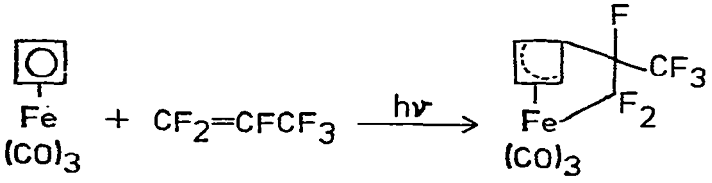
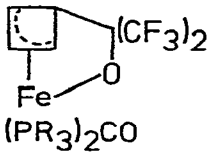


5.14

Bond and Green have shown that fluoro-olefins add to cyclobutadieneiron tricarbonyl on irradiation to form π-cyclobutenyl complexes in which the fluorocarbon group bridges the metal and the carbocyclic ligand. In a typical reaction hexafluoropropene and the complex (5.15) in hexane gave the yellow crystalline adduct (5.16) in 27% yield. Hexafluoroacetone formed an adduct on irradiation with the tetramethylbutadiene complex in which the four-membered ring remained intact. Subsequent treatment of this intermediate with a phosphine gave a bridged π-cyclobutenyl complex (5.17). In every case a two membered bridge was formed[100].



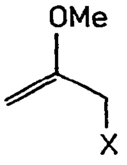
5.15 5.16

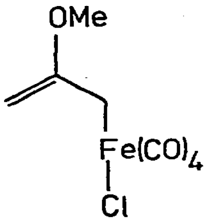


5.17

II (vi) Acyclic(π-diene)Fe(CO)$_3$ and (π-trimethylenemethane) Fe(CO)$_3$ complexes

Hill and Hoffmann have prepared a stable vinylketen complex (6.3) by heating the allyl chloride (6.1; X = Cl) with diiron nonacarbonyl in benzene. The reaction involved a novel carbonylation with the σ-complex (6.2) as a probable intermediate. The allyl bromide and iodide (6.1; X = Br, I) gave the π-allyl complexes (6.4; X = Br, I) under similar conditions[101]. Compounds of the type LFe(CO)$_3$ (where L was benzylideneacetone, chalcone, 2'-hydroxychalcone and 2,6-dibenzylidenecyclohexanone) were prepared by direct reaction of the ligand with diironenneacarbonyl in toluene under mild conditions. Under milder preparative conditions chalcone


6.1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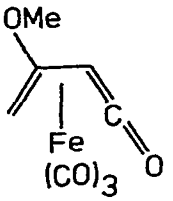
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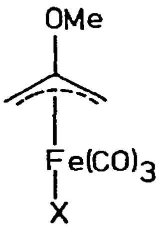
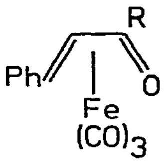

6.4

gave the complex (6.6). The IR and NMR spectra of these compounds were discussed[102]. It was suggested by Nelson and Sloan that the products of reaction of methyl substituted conjugated dienes with $Fe(CO)_5$ were determined by kinetic rather than thermodynamic factors.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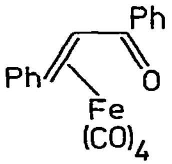
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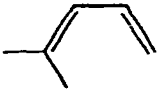
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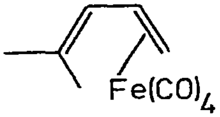
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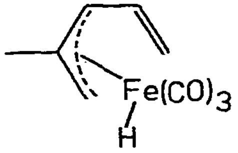
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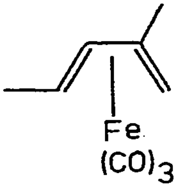
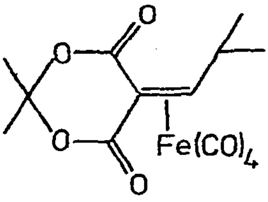

6.10

In the reaction of 4-methylpenta-1,3-diene (6.7) with $Fe(CO)_5$ isomerization was thought to occur through the monodentate intermediate (6.8), followed by loss of CO, transfer of hydrogen and formation of a π-allylic bond (6.9). A reversed metal-carbon hydrogen transfer in the allyl complex (6.9), to the other terminal carbon atom then gave the product (6.10)[103]. Direct reaction of the ligand with diironenneacarbonyl gave the π-complex (6.11) which on irradiation lost a further molecule of carbon monoxide to give (6.12)[104].

Iron atoms obtained by evaporation of the metal in a high vacuum were allowed to react with butadiene and then carbon monoxide to give bis(butadiene)monocarbonyliron. When PF_3 was introduced instead of CO bis(butadiene)trifluorophosphaneiron was obtained[105]. A series of iron tricarbonyl derivatives of α-β-unsaturated ketones were prepared by the treatment of $Fe_2(CO)_9$ with benzylideneacetone (BDA), chalcone, dypnone or 2,6-dibenzylidenecyclohexanone. (BDA)$Fe(CO)_3$ was useful as a source of the iron tricarbonyl moiety in the preparation of dieneiron tricarbonyl complexes. For example, the reaction of (BDA)$Fe(CO)_3$ with 8,8-diphenylheptafulvene gave a good yield (70%) of tricarbonyl (8,8-diphenylheptafulvene)iron. This reagent possessed several advantages over other iron carbonyl reagents in that the reactions with a diene could be carried out under mild conditions, there was no formation of colloidal iron and other iron carbonyls were not formed as by-products[106]. The iron complexes (diene)$_2$FeCO (diene = $CH_2{=}CHCH{=}CH_2$, isoprene, $CH_2{=}CMeCMe{=}CH_2$, 1,3-cyclohexadiene and methyl sorbate) were formed by UV irradiation of a solution of $Fe(CO)_5$ and the diene in benzene or pentane. The diene complexes were useful as catalysts for the oligomerization of unsaturated hydrocarbons[107]. The reaction of 2,4-hexadiyne with dodecacarbonyltriiron gave an unusual trimetallic product $(C_6H_6)_3Fe_3(CO)_{10}$. The spectral data were in accord with structure (6.13) although it was recognised that there were fifteen alternatives to this structure which differed only in the position of the two non-equivalent



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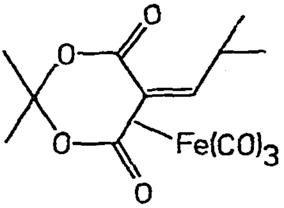

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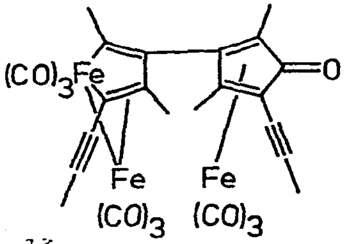
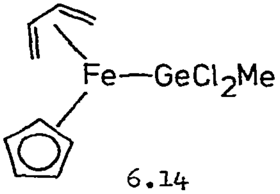


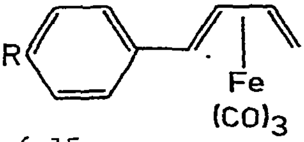
6.13

substituents in each of the two non-equivalent halves of the two non-equivalent five-membered rings[108]. An unsuccessful attempt was made to prepare (hexachlorobuta-1,3-diene)iron tricarbonyl from hexachlorobuta-1,3-diene and $Fe_3(CO)_{12}$. The steric effects of the chloro substituents in this synthesis were discussed[109].

The X-ray crystal structure of the complex (6.14) which exists in two polymorphic forms showed dihedral angles between the ligand planes of 16° in one form and 18° in the other. The Fe-Ge bond length was shortened to 2.28Å and 2.29Å in each of the two forms respectively[110]. The crystal structure of bis(butadiene)iron monocarbonyl has been determined by Whiting, the two hydrocarbon ligands are planar but not parallel, they are arranged so that the molecule has two-fold symmetry[111].

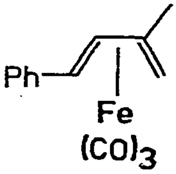


6.14

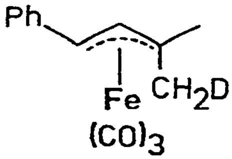


6.15

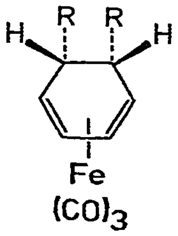
Landsberg and Katz have obtained a linear relationship between the carbonyl IR stretching frequencies and the Hammett substituent constant σp, for a series of p-substituted phenylbutadieneiron tricarbonyl complexes (6.15; R = NH_2, OMe, H, NHCOMe, Br, COMe, CN). Lower frequencies were observed in the presence of electron releasing groups which correspond to a high CO bond order through dπ-pπ interaction between the metal and the carbonyl group^{112} The frequencies of carbonyl stretching vibrations and the relative yields in the syntheses of trans(1,2-dichlorobuta-1,3-diene)iron tricarbonyl and trans(1-chlorobuta-1,3-diene)iron tricarbonyl were discussed with respect to the steric effects of the chloro substituents on the formation of trans,trans(1,2,3,4-tetrachlorobuta-1,3-diene)iron tricarbonyl^{113}. Davidson and Duce have proposed an assignement for the vibrational spectrum of bis(butadiene) iron monocarbonyl. The internal butadiene modes showed that there was little interaction between the two butadiene ligands and that each is very similar to the same ligand in butadieneiron tricarbonyl^{11} Whitesides and Arhart^{115} have produced evidence to show that deuteration of the diene-iron complex (6.16) using dry hydrogen chloride, gave the allyl complex (6.17) with the deuterium located exclusively on the anti-methyl group. These results were inconsistent with the mechanism proposed previously by Pettit and coworkers^{116}. Protonation of the diene complex (6.18; R = H) in CF_3CO_2D led to the rapid uptake of two deuterium atoms into the methylene groups and endo to



6.16



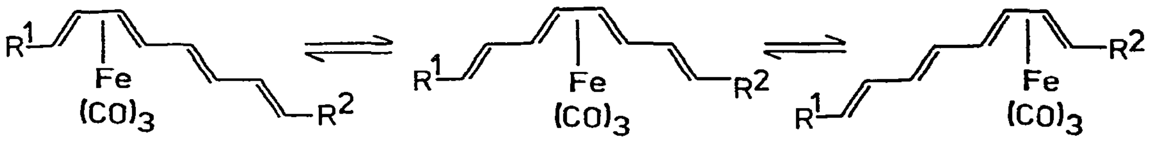
6.17



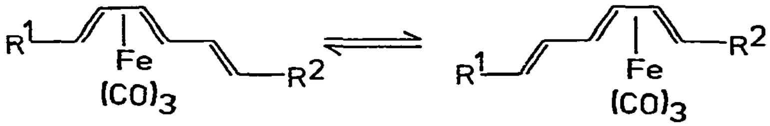
6.18

the metal atom (6.18; R = D) as demonstrated by NMR spectroscopy.

Whitlock and Markezich have studied the relationship between racemization and isomer shift interconversion in the octatetraene (6.19; $R^1 = CO_2CH_3$, $R^2 = CO_2CD_3$) and hexatriene (6.20; $R^1 = CO_2CH_3$, $R^2 = CO_2CD_3$) complexes of iron. The interconversion and racemization processes each followed first order kinetics and interconversion of (6.19a) and (6.19b) was faster than could be explained by a linear (6.19a) ⇌ (6.19c) ⇌ (6.19b) mechanism. In the triene case interconversion of (6.20a) and (6.20b) was 2.6 times faster than racemization and was consistent with movement of the $Fe(CO)_3$ group along the face of the triene.. The two series of reactions were discussed in terms of dissociation of a diene-*tetrahapto*iron tricarbonyl to an *s*-*cis*-diene-*dihapto*iron tricarbonyl complex; rotation about σ bonds that were not components of the ene-iron group; or direct interconversion of two *s*-*trans*-diene-1,2-*dihapto* complexes[117].

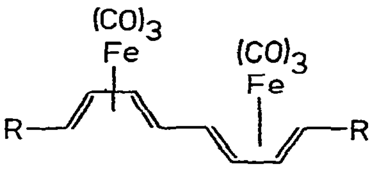


6.19a 6.19c 6.19b

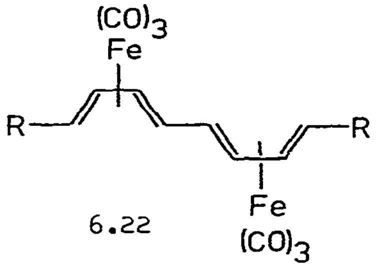


6.20a 6.20b

The same authors have investigated the thermal racemization of the optically active (-)-tetraene complex (6.21; $R = CO_2Me$) and its isomerization to the meso complex (6.22; $R = CO_2Me$). The first order rate constants for each process were very similar and suggest that formation of the meso complex was the dominant and probably the only pathway for racemization. Thus racemization proceeded by a mechanism localized in the 1,3-butadiene group of the complex and not by the iron tricarbonyl groups passing one another on opposite side of the conjugated tetraene chain[118].

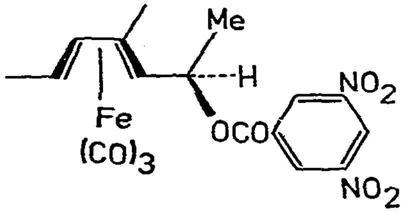


6.21



6.22

The ψ-*endo*,(6.23) ψ-*exo* (6.24) iron tricarbonyl complexes were synthesised stereospecifically and solvolysed in 80% aqueous acetone. The measured first order rate constants showed that the ψ-*exo* ester was solvolysed much more rapidly than the ψ-*endo* isomer, rate ratio 2500. Stereospecific reduction of *trans*, *trans*-dienone complexes (6.25) with sodium borohydride to give ψ-*endo* alcohols of the ester (6.23) was also observed. These results were used with NMR vicinal coupling constants to confirm the configurations and preferred conformations of the isomers (6.23 and 6.24), and to demonstrate that the leaving group departs *exo* in the solvolyses[119]. Protonation of (*trans*, *trans*-2,4-hexadienyl)iron tricarbonyl (6.26) gave two *trans*-pentadienyliron cations, an *s*-*cis* form (6.27) and an *s*-*trans* form (6.28) in an approximately equal ratio. This ratio represented a kinetically controlled product distribution and



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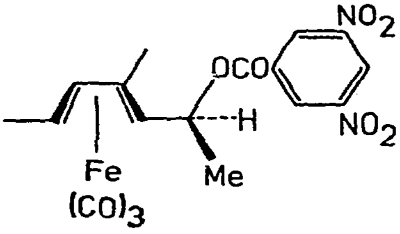

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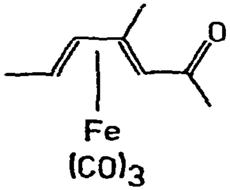
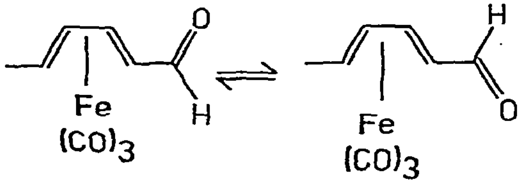


6.25

indicated that the originally unprotonated aldehyde complex was present in equally populated s-cis and s-trans forms. Both the trans ions (6.27) and (6.28) isomerized to the cis ion. From an analysis of the kinetics and NMR line widths the barrier to rotation about the C_1-C_2 bond in the cations was at least 15 kcal/mole. At temperatures below -100° the OH protons of (6.27) and (6.28) could be observed due to slow exchange at this temperature. The chemical shifts of these protons indicated extensive charge delocalization[120].



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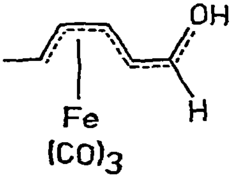
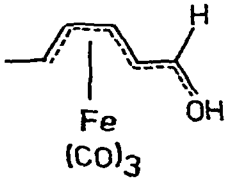


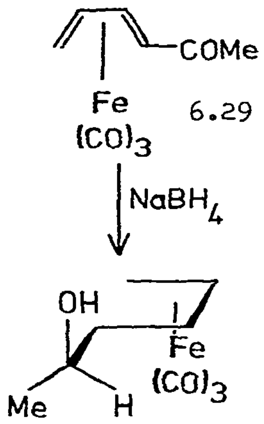
6.27



6.28

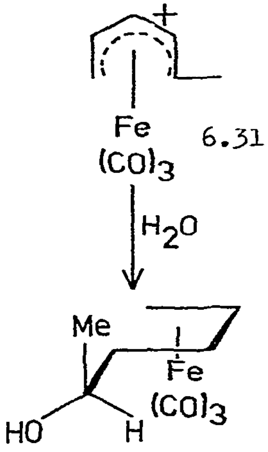
The alcohols (6.30) and (6.32) formed by the hydrolysis of the iron tricarbonyl cation (6.31) and reduction of the ketone (6.29) were examined by NMR spectroscopy. The spectra obtained in the presence of the shift reagent tris(1,1,1,2,2,3,3-heptafluoro-

-7,7-dimethyl-4,6-octanedionato)europium (III) indicated that the alcohol (6.30) had the ψ-exo configuration and (6.32) the ψ-endo form[121]. These assignments differ from those previously suggested[122,123]. The bisbutadiene complexes (6.33; $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = H$, $R^2 = Me$) were effective in the oligomerization of butadiene and in its polymerization in the presence of protic acids. On the other hand the cyclooctatetraene complexes (6.34; $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = H$, $R^2 = Me$) were transformed into stable π-allylic derivatives. Possible mechanisms for the reactions were discussed[124].



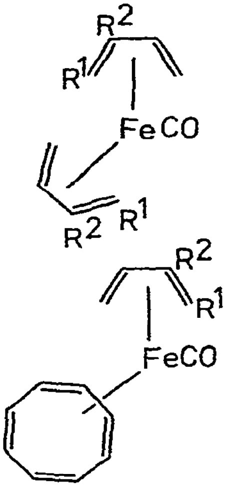
6.29

6.30



6.31

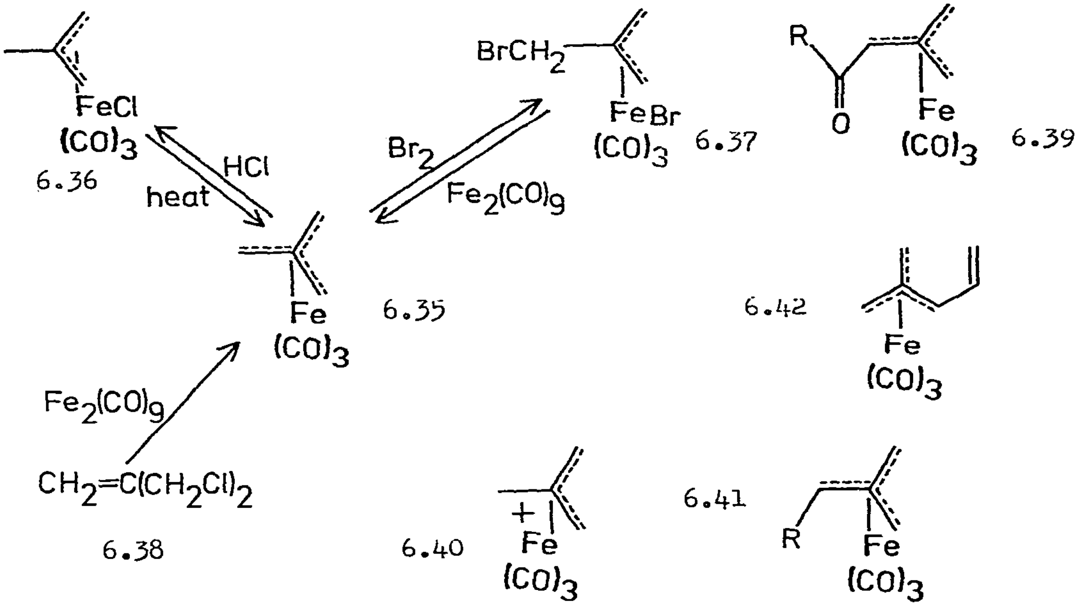
6.32



6.33

6.34

Further details of the synthesis and reactions of the interesting trimethylenemethane complexes of iron have been presented by Ehrlich and Emerson. The parent compound (6.35) was obtained by disproportic ation of 2-methylallyliron tricarbonyl complexes (6.36 and 6.37) or by dehalogenation of 3-halo-2-halomethylpropenes (6.38) with diiron nonacarbonyl. Friedel-Crafts acylation of the π-complex (6.35) with acetyl and benzoyl chlorides gave the acyl derivatives (6.39; R = Me, Ph) in 5-10% yields. Other attempted electrophilic

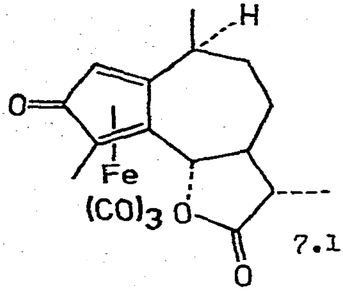


6.36 6.37 6.39 6.35 6.42 6.38 6.40 6.41

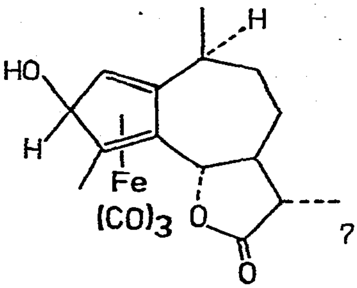
substitutions were unsuccessful and protonation of the complex in concentrated sulphuric acid gave the allyl compound (6.40). Dilution of the acid solution with water failed to regenerate the starting material. Substituted trimethylenemethane complexes (6.41; R = Me, Ph, Cl, MeCHOH, CO_2Me, CO_2H) were prepared by methods similar to those used for the parent compound (6.35). Mechanisms for the formation of the complexes (6.35 and 6.41) from allylic dihalides and allyl halides were discussed. The NMR and IR spectra of twelve compounds were analysed[125]. The reaction of methylene(vinyl)-cyclopropane with $Fe_2(CO)_9$ gave the stable complex dimethylene-(2-propylidene)methanetricarbonyliron (6.42)[126].

II (vii) (Cyclic π-diene)Fe(CO)$_3$

Treatment of santonin with $Fe_2(CO)_9$ in benzene gave $Fe(CO)_3$ complexes of the rearrangement (7.1) and the rearrangement-reduction (7.2) products. Previously the organic ligand in the complex (7.1) had been obtained only on solid state photolysis of santonin[127].

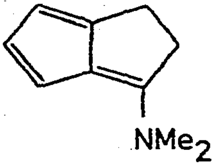


7.1

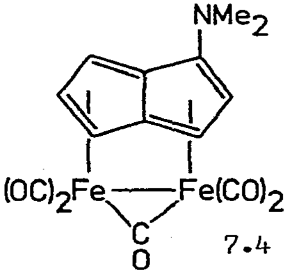


7.2

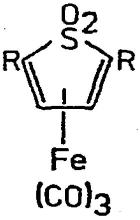
Hunt and Russell have reported the oxidation of the dihydropentalene (7.3) to the pentalene complex (7.4) (11%) on heating with iron pentacarbonyl in methylcyclohexane[128].



7.3



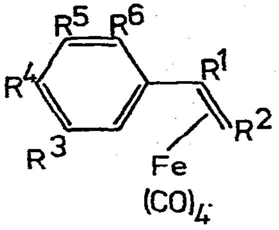
7.4



7.5

The thiophen dioxide complexes (7.5; R = H, Me, Ph) were formed in 50-90% yield on irradiation of the thiophen dioxide and iron pentacarbonyl in dilute benzene solution[129]. The irradiation of styrene and other vinylbenzenes with iron pentacarbonyl gave complexes using two (7.6), four (7.7) and eight (7.8) electrons of the eight

π-electron system. The classical diene structure given for (7.7) and (7.8) was supported by chemical and spectral evidence which indicated that the aromatic character of the original substrate was not present[130]. The treatment of diiron nonacarbonyl with *cis*-bicyclo [6.2.0] deca-2,4,6-triene gave the iron carbonyl derivatives



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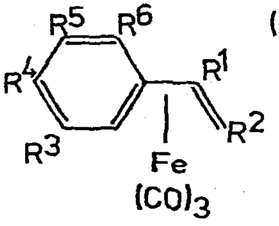

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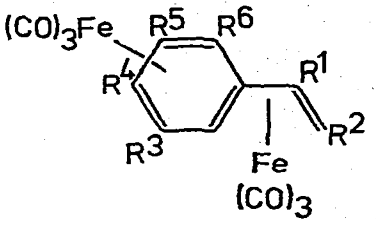
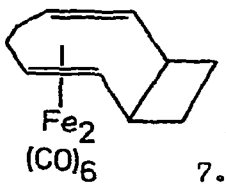
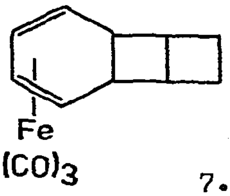


7.8

(7.9) and (7.10) as well as some unidentified products[131].



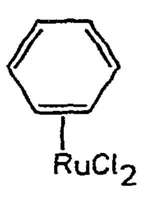
7.9



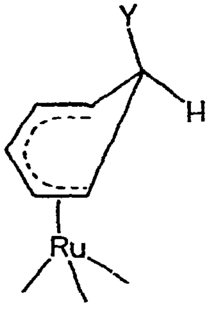
7.10

The ruthenium (II) π-complex (7.11), obtained from cyclo-1,3-hexadiene and ruthenium (III) chloride in aqueous ethanol, was monomeric in water and polar organic solvents. Adducts were formed with group V donors such as PEt_3 and while electrophilic attack on the benzene ring (mercuration, acylation, deuteration in acid) was unsuccessful, nucleophiles added smoothly to the ring. Cyanide and hydroxide gave the cyclohexadienyl complexes (7.12; Y = CN, OH) but borohydride gave the π-cyclohexadieneruthenium (0) complex (7.13).

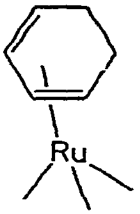
Comparisons were made with the corresponding iron complexes[132].



7.11

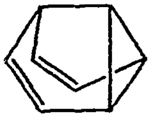


7.12

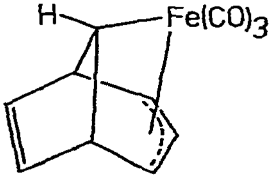


7.13

Moriarty and co-workers have described the formation of the green liquid complex (7.15) in 70% yield from semibullvalene (7.14) and diiron nonacarbonyl at reflux temperature in benzene. The metal-ligand bond contains π-allyl and σ components[133]. Tropone-Fe(CO)$_3$

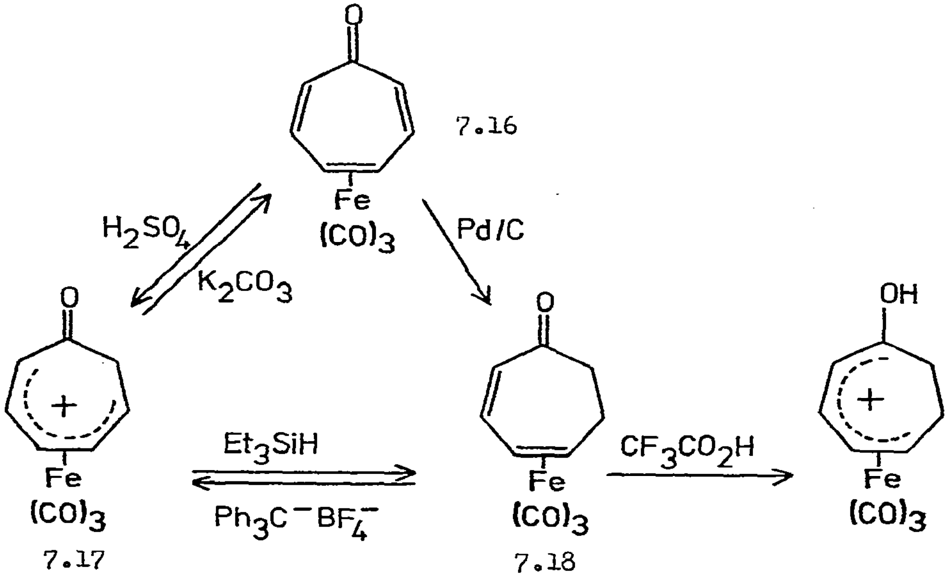


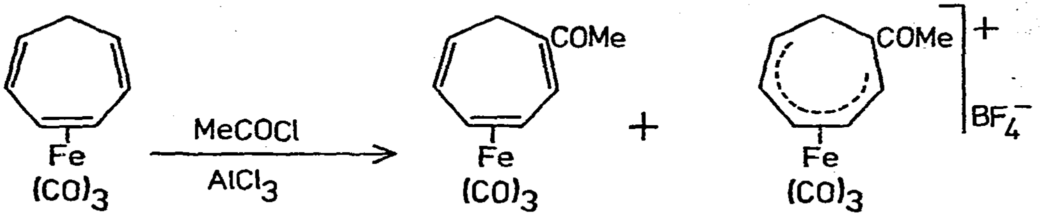
7.14



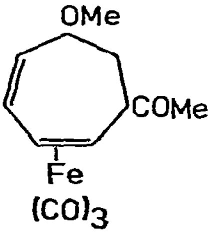
7.15

(7.16) was prepared in high yield (62%) from diiron enneacarbonyl and tropone and the NMR spectrum was investigated in highly acidic media. On treatment with either sulphuric or trifluoroacetic acid protonation occurred to give the cation (7.17) and treatment of this species with triethylsilane gave (7.18). In trifluoroacetic acid protonation occurred from the <u>exo</u> side of the ring at a coordinated double bond and in sulphuric acid the protonation was non-stereoselective. The hydride ion was transferred from triethylsilane onto the exo side of the ring. Protonation of the dienone complex (7.18) was at the oxygen atom of the ketone group[134]. Friedel-Crafts acylation of the cycloheptatriene complex (7.19) gave the products of addition (7.20) and substitution (7.21), while treatment with acyl tetrafluoroborates gave only the addition products (7.20). These salts formed ethers (7.22) with the methoxide ion. Spin decoupling experiments confirmed that addition of a proton to complex (7.19) gave the cation (7.23) and demonstrated that the added proton was exo[135], in contrast to the previously proposed[136] endo addition. The tricarbonyl complexes of cyclohexa-2,4-dienone and cyclohepta-2,4-dienone were found to undergo the Reformatskii reaction with methyl α-bromoacetate and zinc to give the expected hydroxy-esters. Treatment of the esters





7.19 7.21 7.20



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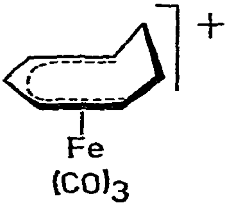

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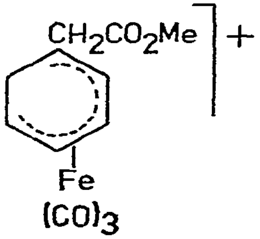
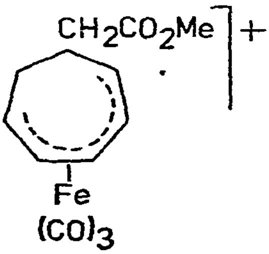


7.24

with trityl tetrafluoroborate resulted in the loss of the hydroxy groups to give dienyl salts (7.24, 7.25). These salts were readily deprotonated to give neutral complexes with a substituted exocyclic double bond. (Cyclohepta-2,4-dienone)iron tricarbonyl underwent the Mannich reaction with dimethylammonium chloride and paraformaldehyde to give the α-dimethylaminomethyl derivative (7.26) but the six membered ketone did not undergo aminomethylation[137]. The preparatio



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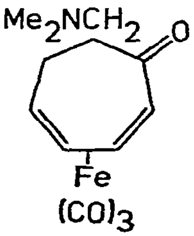

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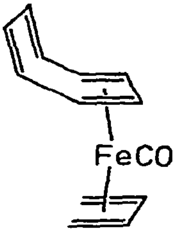


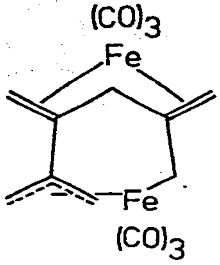
7.27

and characterization of three heptafulvene complexes of iron has been reported, the ligands contained tropylium, trimethylenemethane and diene together with trimethylenemethane groups bound to iron[138].

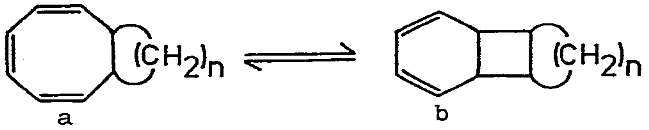
Cyclooctatetraene complexes of iron and nickel have been obtained by an electrochemical method employing a solution of the ligand in an aprotic organic solvent and the appropriate transition metal as anode. Complexes of Ti, Zr, Co and Ni were synthesized in a divided cell or by the use of an oxidizable anode[139]. The reaction between allene and $Fe_3(CO)_{12}$ gave a complex (7.28) containing two irontricarbonyl groups π-bonded to the trimer of allene. The complex (7.28) was isomerized on heating to give two different forms, each of these contained irontricarbonyl bound to a conjugated diene group and one contained the π-allyl ligand while the other used π-trimethylenemethane in bonding to iron. The structure of each complex was confirmed by X-ray crystallography[140].

Jones and Mawby have invoked interaction between the six-membered ring and the iron atom in π-indenylirondicarbonyl iodide to explain the high rate of carbonyl substitution by a first order reaction. The rates of substitution in the corresponding π-cyclopentadienyl and π-tetrahydroindenyl complexes were lower by a factor of 600 at 95°[141]. Aromatization of the hydrocarbon ligand in the mass spectrometric fragmentation of π-cyclohexadieneiron tricarbonyl takes place by stereoselective abstraction of the hydrogen atoms endo to the metal atom. As the coordinative unsaturation of the iron atom increased by sequential loss of carbonyl groups, the selectivity decreased[142].

Bassi and Scordamaglia have determined the crystal and molecular structures of the butadieneiron complex (7.27). The iron atom is bonded to four coplanar carbon atoms in both the butadiene and the cyclooctatetraene ligands[143]. The wide line



7.28

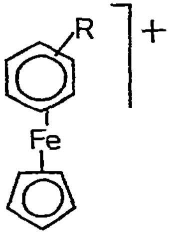


7.29 n = 2
7.30 n = 3
7.31 n = 4

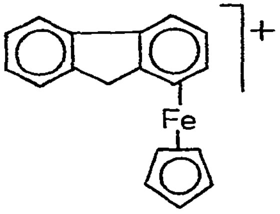
NMR spectra for the fluxional molecules π-$C_8H_8Fe(CO)_3$ and π-$C_8H_8Fe_2(CO)_5$ in the solid state show that while the iron carbonyl groups are fixed in the crystal lattice, the cyclooctatetraene ligand moves by a simultaneous rotation and distortion. In this way each carbon atom occupies a position previously occupied by another carbon atom[144]. The thermodynamic equilibrium between the members of the three pairs of bicyclic and tricyclic tautomers (7.29, 7.30 and 7.31) has been kinetically investigated by Cotton and Deganello. The equilibrium between the isomers (7.29a and 7.29b) lies exclusively with (7.29b), through ring strain. The tricyclic tautomer (7.30b) is more stable than the bicyclic form (7.30a), ratio 7.30b/7.30a $\sim$32 and $\Delta G^o \sim -2.0$ kcal.mol.$^{-1}$ The equilibrium ratio 7.31b/7.31a $\sim$1 was reached by equilibration of the two isomers at 114°, interconversion was slow at lower temperatures. The cyclohexadiene ring in the tautomers (b) imposed planarity on the four membered ring and the cyclopentane ring in (7.30) favoured the planarity of the C-4 ring and stabilized the (7.30b) tautomer. The cyclohexane group was less efficient in stabilizing the tautomer (7.31b) because fusion to a C-4 ring forces the cyclohexane to adopt a half-chair conformation. Each of the compounds (7.29, 7.30 and 7.31) was isolated and characterized as the $Mo(CO)_3$, $Fe_2(CO)_6$ or $Fe(CO)_3$ complexes[145].

II (viii) $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_6)]^+$

The reaction of the arenecyclopentadienyliron cations (8.1; R = Ph, CH_2Ph) and (8.2) with ferrocene in the presence of aluminium chloride and aluminium gave the corresponding bis(π-arene-π-cyclopentadienyliron) dications (8.3) and (8.4) which were isolated as the bishexafluorophosphates[146]. The Mössbauer spectra of three series of compounds (8.1, 8.5 and 8.6), where the R group varied



8.1



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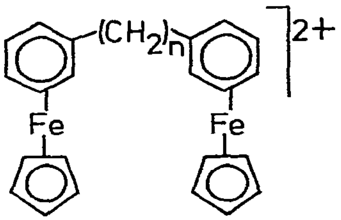
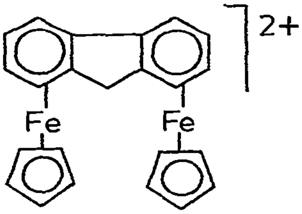


8.3



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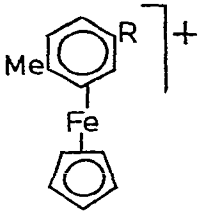

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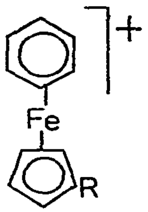


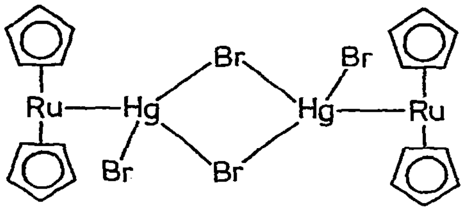
8.6

from strongly electron withdrawing to strongly electron releasing in character, were determined at several temperatures as frozen solutions in acetone. The isomer shifts decreased slightly with increasing temperature and were almost independent of the substituent, values of 0.77-0.83 mm. $sec.^{-1}$ were obtained at 80°K. An increase in electron-withdrawing power of the substituent caused the quadrupole splitting to decrease when the substituent was in the benzene ring and to increase when it was in the cyclopentadienyl ring. The quadupole splittings showed a linear correlation with the Hammett--Taft substituent constants[147].

II (ix) Ruthenocene

Adams and Fernando have interpreted the Raman and infrared spectra of ruthenocene at ambient and liquid nitrogen temperatures. A Raman single-crystal study was used to aid the complete assignment of the spectra. The infrared-active ring tilt mode in ruthenocene was observed at a lower frequency than the metal-ring bond stretch which was the reverse of the accepted order[148]. The helium (I) photoelectron spectra of several metallocenes, ferrocene, ruthenocene, 1,1'-dimethylruthenocene and 1,1'-dimethylosmocene were measured and compared. The spectra were interpreted in terms of a simple molecular orbital model and discussed on the basis of ligand field theory predictions[149]. Wulfsberg and West reported the first measurements of ^{35}Cl nuclear quadrupole resonance frequencies in halogen-substituted metallocenes. The spectrum for decachloro-ruthenocene showed the expected three line pattern of intensity 2:2:1 at 38.61, 38.66 and 38.74 MHz. These frequencies were similar to those of C_6Cl_6 and more than 3 MHz higher than those of C_5Cl_5. This increase in the frequency for decachlororuthenocene was thought to be caused by a Stark effect repulsion of the p_z lone pairs on chlorine by filled girdle d orbitals around the metal atom[156].

The acylmetallocenes $RCOC_5H_4MC_5H_5$ (M = Ru, Os; R = Me, Ph) were treated with MeCN-NaNH$_2$ to give the carbinol adducts which were dehydrated with phosphorus oxychloride to form cis- and trans--$C_5H_5MC_5H_4CR{=}CHCN$[151]. Ruthenocene in dioxane was treated with sulphur trioxide in 1,2-dichloroethane to give ruthenocenesulphonic acid which was converted to the sulphonyl chloride. Ruthenocene was lithiated with n-butyl-lithium and treatment of the lithiation mixture with carbon dioxide or $B(OBu)_3$ gave the ruthenocene-carboxylic acid and -boronic acid respectively. Treatment of the boronic acid with CuX_2 (X = Cl, Br) formed the corresponding halogenated ruthenocene. Bromoruthenocene was converted conventionally into phenylruthenocene and ruthenocenylacetate. Treatment of the boronic acid with mercuric chloride gave ruthenocenylmercuric chloride which was converted into diruthenocenylmercury on stirring with sodium thiosulphate. In a competitive reaction ruthenocene was found to be more reactive than ferrocene towards metallation[152]. Ruthenocene was treated with a stoichiometric quantity of mercuric halide to give the diamagnetic compound $Ru(C_5H_5)_2.HgX_2$, excess halide led to the incorporation of additional molecules of mercuric halide[153]. The 1:1 materials were essentially simple adducts of mercuric halide and ruthenocene and X-ray analysis showed them to be dimeric with a halogen bridge (9.1)[154]. The infrared and Raman spectra of these compounds were recorded and interpreted in terms of structure (9.1). An intense Raman band at 137 cm^{-1} was assigned to the Ru-Hg stretch.

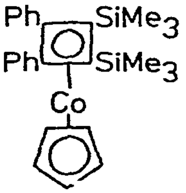


9.1

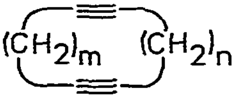
II (x) $(\pi-C_4H_4)Co(\pi-C_5H_5)$

The chemistry of rhodium and iridium π-complexes has been discussed, particular emphasis was placed on their reactions with cyclic and acyclic olefins and acetylenes[155]. The molecular and crystal structures of cis- (10.1) and trans- (π-cyclopentadienyl)-[π-bis(trimethylsilyl)diphenylcyclobutadiene]cobalt have been determined by X-ray crystallography. The sandwich structure was confirmed with each ligand planar and parallel to the other. The centres of the two rings were equidistant (1.68Å) from the cobalt atom. Small distortions in the ring bond lengths and angles were ascribed to the effect of the bulky trimethylsilyl groups[156].

Treatment of π-cyclopentadienylcobaltdicarbonyl with macrocyclic alkadiynes (10.2; m = n = 4, 5; m = 4, n = 5, 6; m = 5, n = 6) gave the products (10.3; m = n = 4, 5; m = 4, n = 5, 6; m = 5, n = 6) in which the alkadiyne ligand had undergone a novel intramolecular transannular cyclization to form the tricyclic cyclobutadiene group. IR and NMR spectroscopy and mass spectrometry were used to confirm the structures of the products. In the case of 1,8-cyclotetradecadiyne a cluster compound (10.4) was obtained in which the macrocyclic ligand had not rearranged[157]. Cyclobutadiene(cyclopentadienyl)cobalt (10.7) was formed by the photolysis of the dicarbonyl (10.6) with photo-α-pyrone (10.5) Two other



10.1



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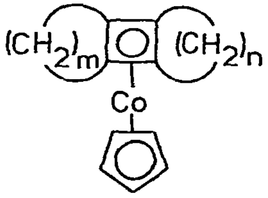
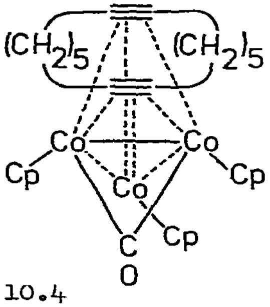


10.3

π-complexes (10.8 and 10.9) were also isolated from the reaction. The dinuclear complex (10.9) exhibited fluxional behaviour at elevated temperatures by intramolecular exchange of the structurally non-equivalent cyclopentadienyl rings. Rates and thermodynamic parameters for the exchange reaction were determined from the temperature dependence of the NMR spectra. The complex (10.7) was a yellow, crystalline, air stable solid. With acetyl chloride under Friedel-Crafts conditions only the monosubstituted complex (10.10; R^1 = H, R^2 = COMe) was isolated (5%), although metallation with n-butyl lithium followed by carbonation gave the mono and dicarboxylic acids (10.10; R^1 = H, R^2 = CO_2H; R^1 = R^2 = CO_2H) respectively confirming preferential reaction at the cyclobutadiene ring. Oxidation of the complex (10.7) led to decomposition rather than the cation and the instability of the ion was demonstrated by the two irreversible electron transfer processes observed by cyclic voltammetry[158].



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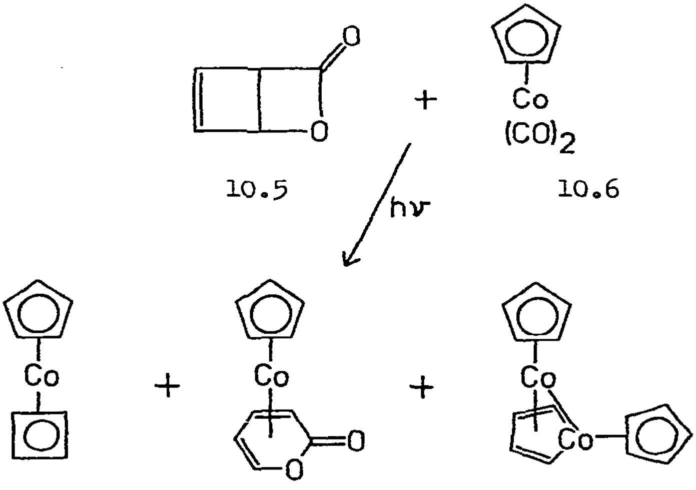
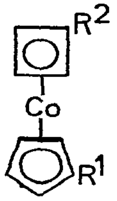


10.5 10.6

10.7 10.8 10.9

The reaction of $(\pi\text{-}C_5H_5)Co(CO)_2$ (10.6) with $PhC{\equiv}CSiMe_2R$ (R = Me, $SiMe_3$) gave two isomeric cyclobutadiene complexes (10.11) and (10.1) in almost quantitative yields. When (10.6) was treated with bis(trimethylsilyl)acetylene the dinuclear complex (10.12) was obtained. It was thought that complexes such as (10.12) might be intermediates in the formation of the cyclobutadiene complexes, and when (10.12) was treated with diphenylacetylene the cyclobutadiene complexes (10.1) and (10.13) were obtained[159].



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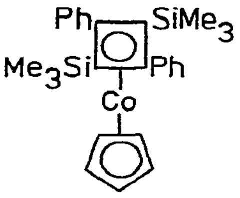

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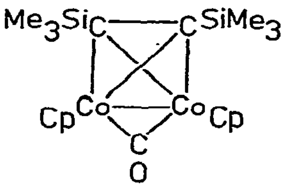
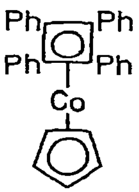


10.12

The π-cyclo-octatriene complexes (10.14; M = Co, Rh, Ir) have been described, they undergo protonation to form the cations (10.15; M = Co, Rh, Ir). The C_8H_{11} ligand was able to adopt several bonding modes and the interconversions between these modes were examined. Nucleophilic addition to the cations (10.15) gave the corresponding complexes (10.16; M = Co, Rh, Ir) or isomers, the temperature and the nature of the nucleophile were important in determining the site of substitution[160].



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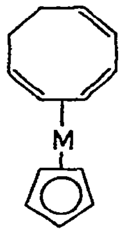

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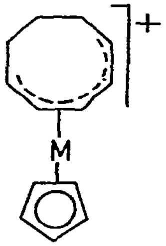
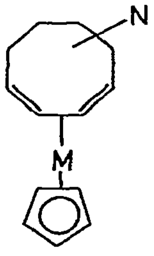


10.15



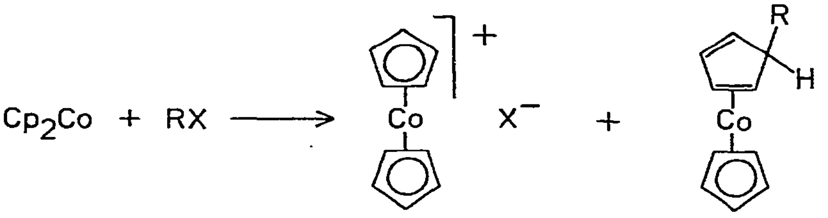
10.16

N = CN, OMe

II (xi) Cobaltocene and the cobalticinium ion

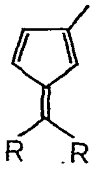
The reactions between halosilanes and cobaltocene have been reviewed briefly[161]. An attempt was made to obtain quantitative information about the nature of chemical bonding in metallocenes by a study of the cobaltocene molecule using EPR and magnetic susceptibility measurements at 4.2°K and by optical spectroscopy at 77°K. From the EPR data it was concluded that covalency effects and vibronic interactions were of comparable importance and resulted in a drastic modification of the magnetic parameters compared with a free cobalt (II) ion in a static crystal field. In agreement with earlier work considerable covalency of the singly occupied $e_{1g}{}^*$ orbital was found[162]. The enthalpy of formation of the cyclopentadienyl radical (47 ± 4 kcal mol^{-1}) was obtained from threshold appearance potential data for cobaltocene and the ionization potential of the metal in an electron impact study. The observed first two ionization potentials were 5.95 and 7.60 eV and they were assigned to ionization of the $e_{1g}{}^*$ and a_{1g} orbitals respectively[163]. A comparative study of the NMR spectra of isoelectronic ferrocene and cobalticinium salt homologues was carried out. The introduction of a positive charge on the cobalticinium salts lead to a decrease in the ring proton shielding and the introduction of alkyl groups had a similar effect for both the cobalticinium cation and ferrocene. It was found that the introduction of primary and secondary alkyl groups caused proton signal shifts in both the substituted and unsubstituted cyclopentadienyl rings. It was concluded that the heteroannular effect of alkyl substituents was governed mainly by conjugation[164]. The crystal and molecular structure of the cobalticinium salt $(\pi\text{-}C_5H_5)_2Co^+(Ph_3PCoI_3)^-$ was confirmed by X-ray analysis[165].

Dicyclopentadienylcobalt was prepared from cobalt chloride which was made *in situ*. Hydrogen chloride was bubbled into methanol in the presence of powdered cobalt metal to give methanolic cobalt chloride. Sodium methoxide and cyclopentadiene were then added to give cobaltocene (74%)[166]. The addition of trifluoro- or trichloro-acetic acid to cobaltocene in dry benzene gave cobalticinium salts with either diamagnetic or paramagnetic anions. The two salts were formulated as $Cp_2Co^+B^-(BH)_2$ and $Cp_2Co^+(BH^-)(BH)_2$ respectively on the basis of their magnetic, spectral and chemical properties, $B = Cl_3C.CO_2$ or $F_3C.CO_2$. It was suggested that the paramagnetic salt was formed by donation of an electron from cobaltocene to an undissociated molecule of the acid[167]. The rate of reaction between cobaltocene and di-, tri-, and tetra-halogenomethanes or *p*-substitute benzylbromides to give cobalticinium salts (11.1) and the *exo*-substituted complexes (11.2) was found to depend on the concentratio of each reactant. The enthalpy and entropy of the process were determined for the reaction with $CHCl_2Br$ (13.6 kcal mol^{-1}, -16.7 cal mol^{-1} deg^{-1}) and CCl_4 (12.8 kcal mol^{-1}, -18.7 cal mol^{-1} deg^{-1}). A mechanism was discussed involving radical intermediates[168].



11.1 11.2

The fulvene (11.3; R = Me, Ph) was reduced with lithium aluminium hydride and then condensed with cobalt chloride in the presence of the cyclopentadienide ion. The reaction mixture was treated with a solution of $NaPF_6$ to give the 1,3-disubstituted cobalticinium salt (11.4 and 11.7; R = Me). The cation (11.4) was oxidised with alkaline permanganate to the carbinols (11.5; R = Me, CO_2H) and these were converted to the corresponding esters (11.6; R = Me, CO_2H) with acetyl chloride. Oxidation of the cation (11.7; R = Me) under the same conditions gave the carboxylic acid (11.7; R = CO_2H).and this was esterified to the methyl ester (11.7; R = CO_2Me) with diazomethane[169].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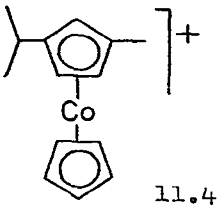
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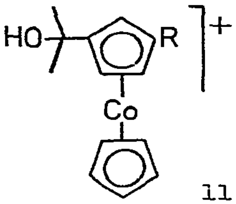
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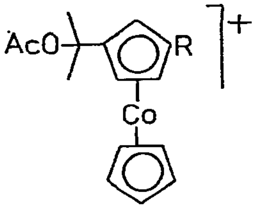
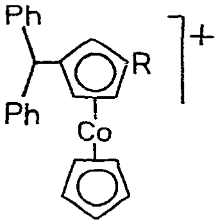

11.6


11.7

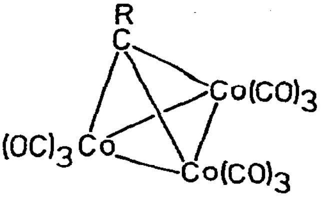
II (xii) Cobalt-carbon cluster compounds

The crystal and molecular structure of $PhCCo_3(CO)_6$-π-$C_6H_3Me_3$, a product from the reaction of $PhCCo_3(CO)_9$ with mesitylene, was determined. The crystals were orthorhombic with four molecules in a unit cell of dimensions a = 19.259, b = 13.088, c = 8.731Å. The mesitylene molecule had replaced the three carbonyl groups which were bonded to one cobalt atom in the parent compound $PhCCo_3(CO)_9$[170]. The formation of a number of complexes from trienes, norbornadiene, cyclopentadiene, cyclooctadiene and alkenes with methinyltricobalt enneacarbonyl has been reported by Elder and Robinson. The stoichiometry of the complexes was $YCCo_3(CO)_nL$ where Y = Me, Ph and halogen, n = 4, 6 and 7, and L was the hydrocarbon ligand. The nature and conformation of the products was determined by intramolecular steric effects, the susceptibility of the ligand (L) to carbonylation and the nature of the apical substituent (Y)[171]. Investigation of the fluxional behaviour of the cobalt complex $PhCCo_3(CO)_6C_8H_8$, where the cycloooctatetraene is bound to the three basal cobalt atoms, showed that rearrangement took place by a series of 1,2-shifts. Reversible dissociation also occurred at temperatures above 0°[172].

The Friedel-Crafts reaction of mono- and di-substituted arenes with halogenomethinyltricobalt enneacarbonyls $XCCo_3(CO)_9$ (X = Cl, Br) afforded a wide range of aryl clusters $ArCCo_3(CO)_9$. It was found that these derivatives could be purified easily using gas-liquid chromatography, and that they underwent complete degradation in the presence of Ce^{4+} (equation 2) as in the following equation[173].

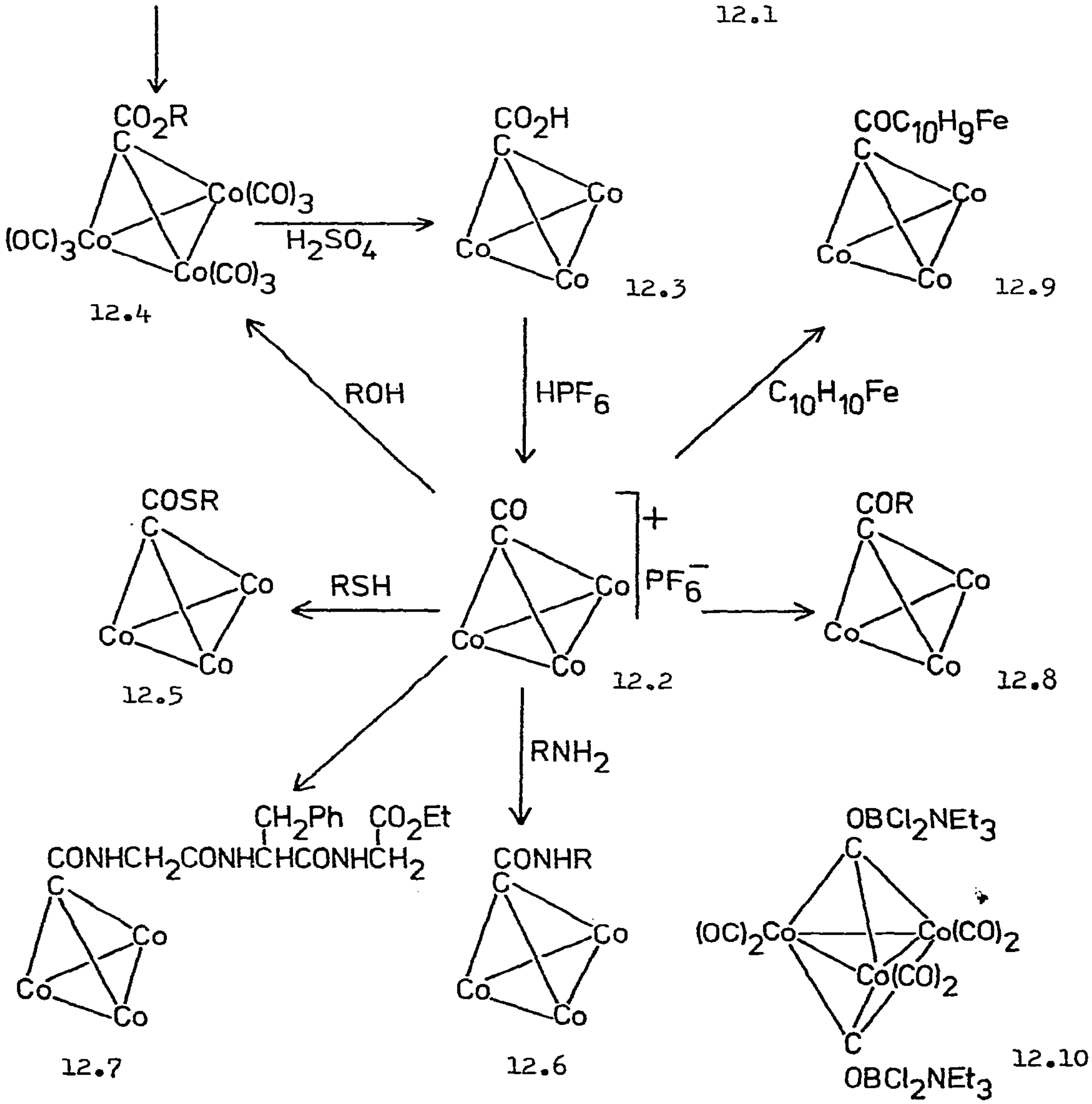
$$ClC_6H_4CCo_3(CO)_9 \xrightarrow{Ce^{4+}} ClC_6H_4CO_2H + 3Co^{2+} + 9CO \qquad (2)$$

Electrophilic substitutions at the apical carbon atom in the cobalt cluster compounds (12.1) have been described. The halides (12.1; R = Cl, Br) with a Friedel-Crafts catalyst, carbon monoxide and water or an alcohol, gave insertion of carbon monoxide and lead to carboxyli esters or acids (12.4; R = H, Et, Ph) in yields of 50-70%. In the absence of a hydroxy compound the same reaction gave the acylium ion (12.2). With nucleophilic reagents such as the Grignard reagent, alkyl-lithiums, water, hydroxide or alkoxide ions, the bromide (12.1; R = Br) again suffered carbonyl insertion to give the corresponding products (12.4). However with a large excess of the Grignard reagent



12.1

$Co_2(CO)_8 + Cl_3CCO_2R$



(AlkylMgX) the bromide (12.1; R = Br) gave the alkyl derivative (12.1; R = Alkyl)[174]. The cobalt cluster acylium ion (12.2) has been used as an acylating agent to give a number of cobalt cluster derivatives, with water the acid (12.3) was obtained while alcohols and thiols gave the esters (12.4 and 12.5) respectively. Amides (12.6) including the tripeptide derivative (12.7) were formed by treatment of the salt with amines, the ketone (12.8; R = Et) was obtained with the ethyl Grignard reagent and a methyl group was cleaved from tetramethyltin to form the methylketone (12.8; R = Me). The electrophilic substitution of ferrocene with the reagent gave the acylferrocene (12.9). The acylium salt was obtained by treating esters of trichloroacetic acid with dicobalt octacarbonyl in THF to form the complexes (12.4), hydrolysis with concentrated sulphuric acid to the carboxylic acid (12.3) and treatment with hexafluorophosphate in propionic anhydride[175]. The same group has reported a new route to C-carbonyl derivatives of the methylidynetricobalt nonacarbonyl cluster. The cobalt carbonyl (12.1; R = Cl) was treated with $AlCl_3$ and tetramethyltin to give $CH_3COCCo_3(CO)_9$ rather than the expected methyl derivative $CH_3CCo_3(CO)_9$. The reagent formed from (12.1) and $AlCl_3$ was $[(OC)_9Co_3CCO^{+}\text{---}Cl\text{-}AlCl_3^{-}]$[176].

The paramagnetic cobalt-carbon cluster compound (12.10) (μ = 1.9BM) was obtained by heating $Co_2(CO)_8$ and Cl_3BNEt_3 in benzene[17

II (xiii) Nickelocene

The NMR spectra (30MHz) of polycrystalline nickelocene and cobaltocene were measured at 4.2-100°K. When the temperature was decreased the NMR lines broadened and their centres of gravity shifted to high-field. The values of the bond isotropic constants agreed with those obtained by high-resolution NMR spectroscopy. For nickelocene a significant difference between the measured and calculated values of isotropic shifts was observed at very low temperatures because of the susceptibility anisotropy of the molecule which caused a pseudocontact shift[178].

The mean amplitudes of vibration for nickelocene were calculated and these values were compared with those obtained by electron diffraction. The agreement between the observed and calculated values was only fair[179]. The d-d transitions found in the longwave region of the electronic spectra of some d^6- and d^8-metallocenes, e.g. nickelocene, were discussed[180].

The mass spectra and fragmentation mechanisms of ferrocene, nickelocene and ruthenocene were reinvestigated with emphasis on the interpretation of the ionization efficiency (IE) data. It was found from the IE data that the ionic bond dissociation energy for the loss of the first cyclopentadienyl ring, $D(CpM^+-Cp)$ was 6-7eV, while that for the loss of the second cyclopentadienyl ring, $D(M^+-Cp)$ was in the 4-5eV range[181]. This second value differed from those reported earlier[182, 183] which were <leV. Methane chemical ionization (CI) mass spectra were recorded for a series of diene $Fe(CO)_3$ complexes, the iron group metallocenes, nickelocene, cobaltocene and several other organometallic molecules. Methane CI spectra usually exhibit abundant ions at high mass and a smaller number of fragment ions. For example with cobaltocene and the iron group metallocenes only three ions occurred at m/e values corresponding to M^+, M+1 and M+29, Table 1. Nickelocene afforded the same three ions but in addition also gave the fragments Ni^+ and $C_5H_5Ni^+$, and the dimeric species $(C_5H_5)_2Ni_2^+$ and $(C_5H_5)_3Ni_2^+$.

TABLE 1

Methane Chemical Ionization Mass Spectra of some Metallocenes (m/e ratios, relative abundance %)

Metallocene		Additive ionization	
	M^+	M+1	M+29
Ferrocene	37	62	1.0
Ruthenocene	43	52	4.2
Osmocene	48	47	5.0
Cobaltocene	94	5.8	0.2
Nickelocene	62	32	0.3

Proton transfer to the metallocenes from CH_5^+ and $C_2H_5^+$ yields the abundant M+1 ions (equation 3) and electrophilic addition of $C_2H_5^+$ affords the M+29 ions (equation 4). The generation of abundant M^+ ions probably occurred *via* an electron transfer reaction between the metallocene and the ethyl cation (equation 5)[184].

$$(C_5H_5)_2M + CH_5^+(C_2H_5^+) \longrightarrow (C_5H_5)_2MH^+ + CH_4(C_2H_4) \qquad (3)$$

$$(C_5H_5)_2M + C_2H_5^+ \longrightarrow (C_5H_5)_2MC_2H_5^+ \qquad (4)$$

$$(C_5H_5)_2M + C_2H_5^+ \longrightarrow (C_5H_5)_2M^+ + C_2H_5 \qquad (5)$$

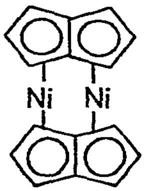
The ring-exchange reactions between LiC_5D_5 and $M(C_5H_5)_2$ (M = V, Cr, Mn, Ni) were followed by observing the rate of disappearance of the first overtone of the metallocene C-H stretching vibration at about 5300cm^{-1}. The exchange of $Ni(\pi\text{-}C_5D_5)_2$ with $M(\pi\text{-}C_5H_5)_2$ (M = Cr, Mn) were studied in a similar manner except that $Ni(C_5H_5)_x(\pi\text{-}C_5D_5)_{2-x}$ was isolated before infrared analysis[185]. The kinetic acidity (isotope exchange) of nickelocene was determined at 75° in $MeOD\text{-}(CD_3)_2SO\text{-}MeOK$. The acidity of the metallocene, pKa = 22.6, was found to be less than that of fluorene in this system. In Et_2NH-Et_2NLi the relative acidities of nickelocene and fluorene were reversed[186]. When ferrocene or nickelocene was treated with atomic oxygen the principal low boiling product was $CH_2{=}CHC{\equiv}CH$[187].

The reaction between nickelocene and Me_2AlSPh in benzene solution gave $[Ni(\pi\text{-}C_5H_5)SPh]_2$ together with dimethylaluminium cyclopentadienide[188]. The magnetic susceptibility of cotton fibres was increased by imbibition of nickelocene or ferrocene in benzene or toluene solutions[189]. Ling proposed that metallocenes could function as positive charge scavengers and to test this hypothesis ferrocene and nickelocene solutions in glassy hydrocarbon matrices were subjected to gamma-radiolysis from a cobalt-60 source. Doses up to 5×10^{19} eVg^{-1} gave no detectable concentration of metallocinium ion $(C_5H_5)_2M^+$. Further experiments were initiated such that irradiation and subsequent spectroscopic monitoring were accomplished in the absence of bleaching light and the results indicated that the metallocenes were scavenging electrons[190].

Bis(pentalenylnickel) (13.2) was prepared by treating nickelocene or $NiCl_2(CH_3OCH_2)_2$ with dilithium pentalenide (13.1). This is the first purely pentalene-metal complex and it is stable in air for a few hours[191]. The reaction of nickelocene with carbonium ions such as $(Ph_3C)^+$ and $(C_7H_7)^+$ gave the double sandwich complex $[Ni_2(C_5H_5)_3]^+$ and which formed stable salts with tetrafluoroborate and hexafluorophosphate anions[192]. Treatment of the double sandwich complex (13.3)

$$2Ni(C_5H_5)_2 + [Ph_3C]PF_6 \longrightarrow [Ni_2(C_5H_5)_3]PF_6 + C_5H_5CPh_3$$

13.1



13.2

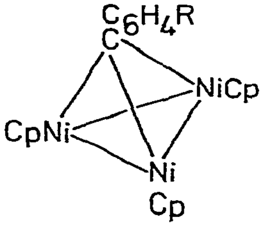
with Lewis-bases such as PBu^n_3, $P(OMe)_3$, $P(OEt)_3$ $P(OPh)_3$, $AsPh_3$, pyridine gave compounds of the type $(C_5H_5NiL_2)BF_4$ (where L = monodentate ligand). Similarly bidentate ligands displaced two cyclopentadienyl groups to give compounds of the type $(C_5H_5NiL\text{-}L)BF_4$ (where L-L = bidentate ligand) and in all of these reactions nickelocene was also obtained.

$$[Ni_2(C_5H_5)_3]BF_4 + 2L \longrightarrow [C_5H_5NiL_2]BF_4 + Ni(C_5H_5)_2$$

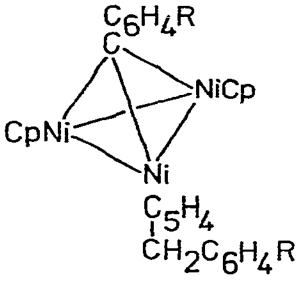
II (xiv) Nickel-carbon cluster compounds

Treatment of nickelocene with benzylmagnesium chloride at room temperature gave a mixture of the trinuclear cluster compounds

13.3



14.1



14.2

(14.1; R = H, Me) a mixture of (14.2; R = H, Me) was obtained with p-methylbenzylmagnesium chloride. The black, crystalline, diamagnetic complexes (14.1 and 14.2; R = H, Me) were characterized by absorption spectroscopy and mass spectrometry. Substitution in the cyclopentadienyl ring to give (14.2; R = H) was achieved by heating the complex (14.1; R = H) with benzylmagnesium chloride[194].

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