ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1973

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CONTENTS

1. Reviews 348
2. General Results 349
3. (i) $(\pi\text{-}C_6H_6)Cr(CO)_3$ 350
(ii) $[\pi\text{-}C_7H_7Cr(CO)_3]^+$, $(\pi\text{-}C_7H_8)Cr(CO)_3$ 365
(iii) $(\pi\text{-}C_6H_6)_2Cr$ 367
4. $(\pi\text{-}C_5H_5)Mn(CO)_3$ 373
5. (i) $(\pi\text{-}C_4H_4)Fe(CO)_3$ 385
(ii) (Acyclic π-diene)$Fe(CO)_3$ and (π-trimethylenemethane)$Fe(CO)_3$ complexes 389
(iii) (Cyclic π-diene)$Fe(CO)_3$ complexes 394
(iv) $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_6)$ 410
(v) $(\pi\text{-}C_5H_5)_2Ru$ 411
6. (i) $(\pi\text{-}C_4H_4)Co(\pi\text{-}C_5H_5)$ 411
(ii) $(\pi\text{-}C_5H_5)_2Co$ and $[(\pi\text{-}C_5H_5)_2Co]^+$ 413
(iii) Cobalt-carbon cluster compounds 418
7. (i) $(\pi\text{-}C_5H_5)_2Ni$ 422
(ii) Nickel-carbon cluster compounds 425
8. Uranocene 427
References 427

1. REVIEWS

Nesmeyanov, Rybinskaya and co-workers have discussed the synthesis and reactions of transition metal complexes containing a dimetallic group with each metal bound to a common organic ligand. Both σ, π-and π,π- complexes are included[1]. Mawby has outlined the synthesis and chemistry of π-cyclopentadienyl, π-arene and π-carborane transition metal complexes[2]. Vosniuc has discussed the chemistry of π-cyclopentadienyl complexes of the transition metals[3].

The applications of Mössbauer spectroscopy to the chemistry of organometallic compounds of iron has been reviewed by Herber[4]. The organometallic chemistry of the transition elements reported during 1971 has been surveyed by Candlin, Taylor and Parkins[5]. The chemistry of π-olefin and π-alkynyl transition metal complexes has been reviewed by Bennett[6].

The structural features characteristic of organometallic compounds have been summarized by Bryan in a general discussion on the use of X-ray and electron diffraction methods[7]. Bruce has surveyed the electrophilic substitution of hydrocarbon ligands in π-hydrocarbon-transition metal complexes[6]. π-Ligand transfer reactions were reviewed by Efraty. The review included a section on π-cyclobutadiene transfer which is one of the more important routes for the preparation of π-cyclobutadiene metal complexes[9].

A valuable survey of polynuclear organocobalt compounds is presented in Gmelin's Handbook of Inorganic Chemistry[10]. Penfold and Robinson have discussed the structure and chemistry of tricobaltcarbon cluster compounds. The coordination chemistry of the basal triangle of cobalt atoms receives particular emphasis as does the reactivity of the apical carbon atom to substitution by electrophiles and nucleophiles. The electron withdrawing character of the cobalt tricarbonyl groups is used to rationalize the reactivity at the apical site[11].

2. GENERAL

The protonation of $(\pi\text{-}C_5H_5)M(CO)_4$ (M = V, Nb) and $(\pi\text{-}C_5H_5)Re(CO)_3$ and their phosphine derivatives in acidic media ($CF_3COOH\text{-}CH_2Cl_2$) was studied by infrared spectroscopy. The results obtained in this study and other investigations indicated that for cyclopentadienyl carbonyl complexes of Groups V and VII elements with the same ligand L, the basicity of the metal atom increases in the series $C_5H_5Mn(CO)_2L < C_5H_5V(CO)_3L < C_6H_6Cr(CO)_2L < C_5H_5Re(CO)_2L < C_5H_5Nb(CO)_3L$[12].

Complete ligand field perturbation calculations, including spin-orbit coupling, using the strong field formalism have been carried out for $\underline{d}^1(\underline{d}^9)$, $\underline{d}^2(\underline{d}^8)$ and $\underline{d}^3(\underline{d}^7)$ configurations in axial C_{∞} symmetry. These results were applied to the interpretation of the d-d electronic spectra of metal sandwich complexes with particular reference to bis(cyclopentadienyl)-vanadium, -cobalt and -nickel[13].

The X-ray photoelectron spectra of the metallocenes: vanadocene, chromocene, manganocene, ferrocene, cobaltocene and nickelocene have been measured. The experimental core binding energies have been interpreted with the aid of approximate m.o. calculations to provide a description of the charge distribution within the series. Net electron transfer from metal to ligand was observed in each case. The values of the metal 3s multiplet splittings were discussed in terms of delocalization of the unpaired electrons, approximate m.o. calculations and effective values of the metal 3s-3d exchange integral derived from experimental data on the appropriate fluorides. Good agreement was obtained between the experimental and calculated splittings, except in the case of nickelocene[14].

Begun and Compton have carried out a detailed study of the electron impact ionization of metallocenes. Collisions between monoenergetic electrons and ferrocene, cobaltocene and nickelocene gave the ions $[(C_5H_5)_2M]^+$, $[(C_5H_5)M]^+$ and M^+, the appearance potentials for these ions, relative to the ionization potential for krypton, have been determined. Good agreement was obtained with values obtained recently by photoelectron spectroscopy. The negative ions $[(C_5H_5)_2M]^-$, $(C_5H_5)^-$, and in the case of cobaltocene $[(C_5H_5)Co]^-$, were also obtained by electron impact. The cyclopentadienyl ions were formed at low electron energies and the long-lived parent negative ion of nickelocene was observed at thermal electron energies. It was suggested that the captured electron in the negative ions occupied one of the $\underline{e}_{1g}$ or $\underline{e}_{2u}$ orbitals of the parent molecule[15].

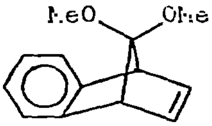
3. (i) $(\pi\text{-}C_6H_6)Cr(CO)_3$.

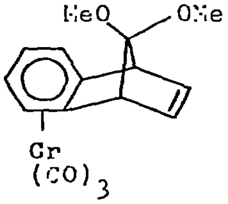
Benchrotrene derivatives and the corresponding molybdenum and tungsten compounds were formed by heating anisole or $PhCH_2CH_2OMe$ with the appropriate metal hexacarbonyl at 140°[16]. The acetal (3.1) was heated with chromium hexacarbonyl to give the arene complex (3.2) (1%) and the complex (3.3) (36%). Hydrolysis of the complexed acetal (3.2) gave tricarbonylnaphthalenechromium. When 7-anti-benzonorbornadienyl acetate was heated with chromium hexacarbonyl the arene complexes (3.4 and 3.5) were obtained. Treatment of the complexes (3.4 and 3.5) with methylmagnesium iodide gave the corresponding alcohols[17].

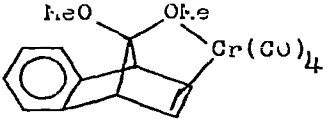
The reaction of excess 1,3,5-triphenylbenzene (TPB) with chromium hexacarbonyl in boiling dibutyl ether gave $TPB.Cr(CO)_3$

(3.6). In the presence of excess chromium hexacarbonyl TPB.2Cr(CO)$_3$ (3.7) and TPB.3Cr(CO)$_3$ (3.8) were formed[18].

Chromium hexacarbonyl was condensed with optically pure (S)-PhCH$_2$CHMeCO$_2$Me and the product was saponified to give the optically pure acid (3.9). This acid was cyclized by polyphosphoric acid to form the ketones (3.10 and 3.11)[19].







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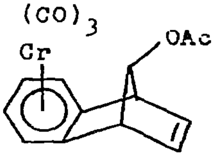

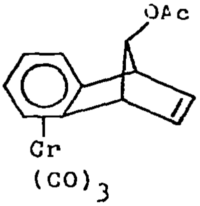

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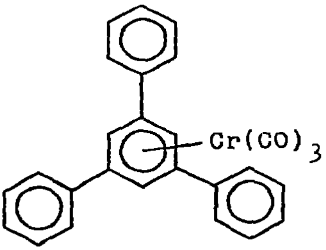

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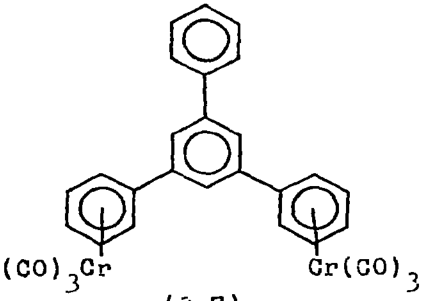

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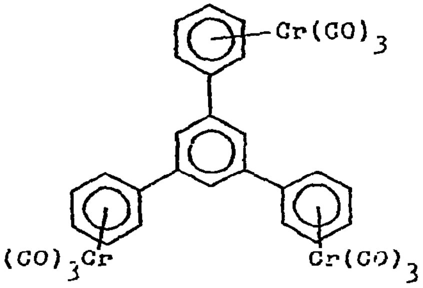

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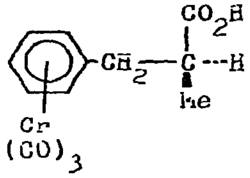

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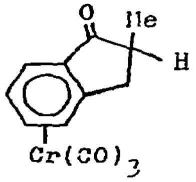

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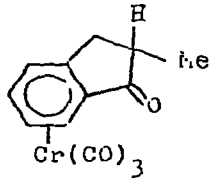

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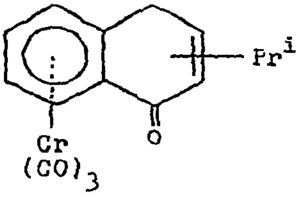
Organosilicon compounds with chromium tricarbonyl groups attached were prepared by the reaction of Ph_nSiR_{4-n} (R = OH, halogen, alkyl; n = 1-3) with chromium hexacarbonyl in diglyme or in an autoclave at 160-70° [20]. Triphenylstannylbenzenechromium tricarbonyl was prepared by the reaction of tetraphenyltin with chromium hexacarbonyl in diglyme. Treatment of the tin derivative with mercury(II) chloride gave phenylmercurichloride and triphenyltin chloride. Similarly, treatment with acetic acid gave triphenyltin acetate; these two reactions showed that the phenyl groups coordinated to chromium are more susceptible to cleavage than those that are uncoordinated[21].

Chromium hexacarbonyl was treated with dihydroisopropylnaphthalenones to give the corresponding chromium tricarbonyl derivatives (3.12). The *exo-* and *endo-* forms of (3.12; i-Pr at 2,3,4 positions) were prepared, when the iso-propyl group was in the 2 or 4 positions the endo form was obtained preferentially. When the iso-propyl group was in the 3 position the exo form was obtained[22].

Deberitz and Noth have investigated the reactions between phenylpyridines and chromium hexacarbonyl. Two complexes were formed from 2,6-diphenylpyridine (DPP) with the stoichiometry DPP.$Cr(CO)_3$ and DPP.$2Cr(CO)_3$ while with 2,4,6-triphenylpyridine (TPP) three complexes were obtained, TPP.$Cr(CO)_3$, TPP.$2Cr(CO)_3$ and TPP.$3Cr(CO)_3$. In each case the chromium tricarbonyl groups



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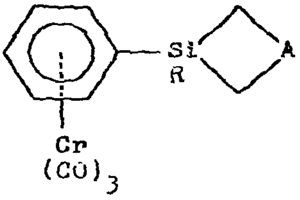


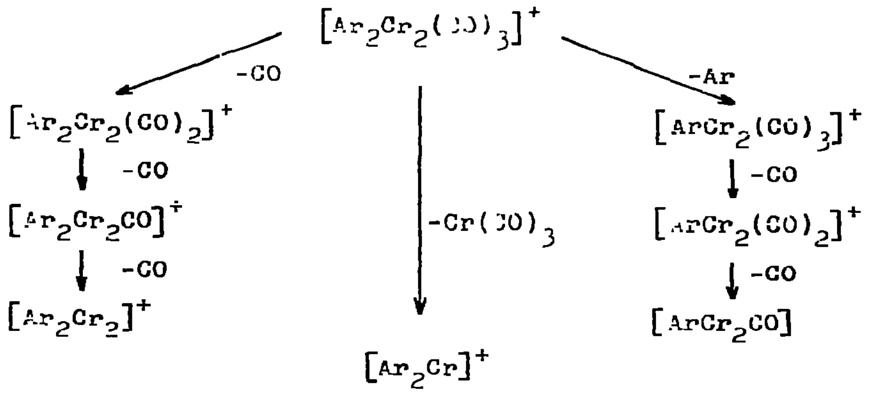
(3.13)

were π-bonded to the phenyl groups and not to the central pyridine ring. Chromium hexacarbonyl combined with 4-phenylpyridine (PP) to give only the σ-complex PP.$Cr(CO)_5$[23].

The direct reaction of chromium hexacarbonyl with 1,1-diphenyl-1-silacyclobutane in the presence of dioctylamine at 105° for 40 hours gave the π-arene complex (3.13; R = Ph; A = CH_2). The same procedure was used to prepare the disilacyclobutane complex (3.13; R = Me; A = $SiMe_2$). PMR spectroscopy confirmed that the geminal methylene protons in the first complex were equivalent[24]. The reactions of substituted arenechromium tricarbonyl derivatives in a mass spectrometer source have been studied. Secondary ions of the types $[Ar_2Cr_2(CO)_3]^+$ and $[Ar_2Cr_3(CO)_6]^+$ were shown to arise from ion-molecule reactions at pressures of 5×10^{-6} to 2×10^{-5} mm Hg. Appearance potentials were measured and used to confirm the reactant ions and also to provide information on the fragmentation paths of the secondary ions. The fragmentation of $[Ar_2Cr_2(CO)_3]^+$ was formulated as shown (Scheme 3.1)[25].

Mass spectrometry has been used to measure the ionization potentials and the appearance potentials for the ions that arose from the sequential loss of carbonyl groups from several benchrotrene derivatives. Good correlations were obtained between the values obtained for the loss of one and two carbonyl groups and both the carbonyl stretching force constant and the Hammett constant for the benchrotrene substituent. $[Arene]^+$ ions were obtained at energies intermediate between those found for the loss of two and three carbonyl groups[26].

Information on the bonding in the complexes $(C_6H_6)_2Cr$, $C_6H_6Cr(CO)_3$, $MeOOCC_6H_5Cr(CO)_3$ and $Cr(CO)_6$ was obtained by

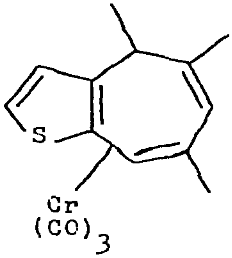


Scheme 3.1

measuring the chemical shifts of the core ionization energies for these compounds. In the spectra of these complexes the main peaks were often accompanied by smaller ones, whose intensities and energies were dependant on the structure. An attempt was made to assign these smaller peaks[27].

The crystal and molecular structures of the two isomeric thiophenotropilidenechromium tricarbonyl complexes (3.14 and 3.15) have been determined by X-ray methods. In each case the chromium tricarbonyl group was bound to the cycloheptatriene group of the ligand. The conformations of the complexed and free ligands were different and isomerization on complex formation was also observed. Potential mechanisms for these processes were discussed[28].

X-ray and neutron diffraction methods have been used by Rees and Coppens to investigate the detailed structure of benchrotrene at 78°K. The symmetry of the benzene ring was C_{3v} with slight bond alternation (average difference in C-C bond length 0.017Å), the shortest bonds were <u>trans</u> to the carbonyl groups.



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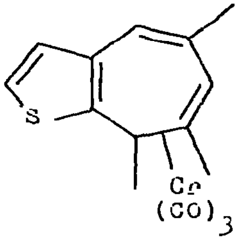

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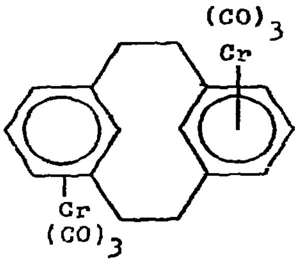
Semi-empirical m.o. calculations were in good agreement with the observed bond lengths. The hydrogen atoms were displaced slightly out of the plane of the benzene ring and towards the chromium atom by an average of 0.03Å [29].

The electric dipole moments of benchrotrene and sixteen benchrotrene derivatives have been measured in benzene solution at 25°. The (π-arene)$Cr(CO)_3$ group moment was found to depend on the nature of the substituent in a precise manner. The measurements allowed conformations to be assigned to (π-aniline)$Cr(CO)_3$

and (π-p-phenylenediamine)$Cr(CO)_3$ and confirmed that the metal was bound to the benzene rather than the thiophene residue in (π-benzo[b]thiophene)$Cr(CO)_3$. The dipole moment of benchrotrene was lower than that of (π-thiophene)$Cr(CO)_3$ by 0.95D despite the lower π-basicity of thiophene and this was explained in terms of the high S-Cr bond moment[30].

Transannular π-π interactions in [2.2]metacyclophane, [2.2]paracyclophane and 2,2'-spirobiindane have been studied by measuring the ratio of the dissociation constants (K_1/K_2) for the equilibria between the bis-chromium tricarbonyl and mono-chromium tricarbonyl complexes, and between the mono-chromium tricarbonyl complex and the free ligand. The equilibria for the metacyclophanes are 1; (3.16) $\rightleftharpoons$ (3.17) + $Cr(CO)_3$ and 2; (3.17) $\rightleftharpoons$ (3.16) + $Cr(CO)_3$. In this case the ratio $K_1/K_2 = 9.0 \pm 1.9$ which suggested that there was no interaction between the benzene rings. These results were supported by the IR carbonyl stretching frequencies for the chromium tricarbonyl complexes[31].

Benchrotrene and its derivatives form charge transfer complexes with electron acceptor species such as tetracyanoethylene (TCNE) and 1,3,5-trinitrobenzene (TNB) but do not combine with electron donors. The charge-transfer transition energies in the complexes were determined and used to obtain the ionization potentials of



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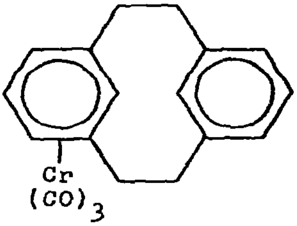

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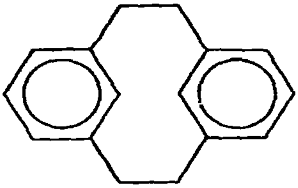
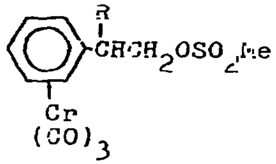


(3.18)

the parent benchrotrene compounds. It is suggested that in the case of TC[illegible] interaction between the chromium atom and the electron donor is of major importance while with TNB the donor interacts most strongly with the π-benzene ring of the organometallic compound[32].

In an attempt to determine the relative importance of steric and electronic effects of chromium tricarbonyl participation in the solvolysis of β-[(π-aryl)chromium tricarbonyl]alkyl derivatives, the acetolysis and formolysis rates and products for these reactions have been studied. The chromium complex (3.19: R = H) was ten times more reactive than the free ligand and the complex (3.19; R = Me) was six times more reactive than the free ligand towards acetolysis at 90°. These reactions proceeded without rearrangement while the formolysis of the complex (3.19; R = Me) gave 17% of the (π-phenyl)chromium tricarbonyl-migrated product. Estimates of anchimeric assistance to product formation were made and the results were rationalized in terms of electron donation by the π-complexed group[33].

Treatment of the ketones (3.20; R^1 = Me, OMe; R^2 = Me, Ph, Et) with the Grignard reagent gave a mixture of two diastereomeric alcohols (3.21 and 3.22; R^2 = Me, OMe; R^2 = Me, Ph, Et). The reduction was stereoselective and the proportions of the two products were determined by the nature of the substituents R^1



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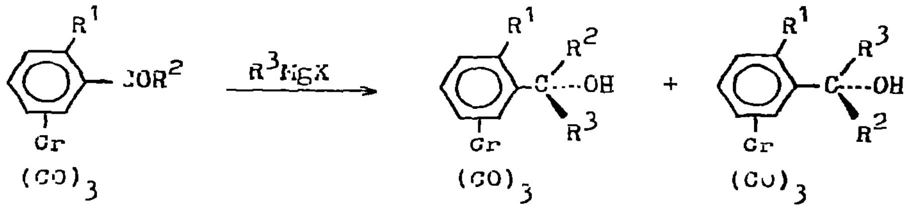
and R^2 and the Grignard reagent. Thus the methyl ketone (3.20; R^1 = OMe, R^2 = Me) with phenylmagnesium bromide gave the alcohols (3.21 and 3.22; R^1 = OMe, R^2 = Me, R^3 = Ph) in the ratio 93:7 while the ketone (3.20; R^1 = R^2 = Me) with ethylmagnesium bromide gave the products (3.21 and 3.22; R^1 = R^2 = Me, R^3 = Et) in the proportion 8:92[34].

The mechanistic interpretation offered by the authors was supported by an X-ray crystallographic determination of the structures of the diastereoisomeric alcohols (3.21 and 3.22; R^1 = Me, R^2 = Et, R^3 = Ph)[35]. The selectivities observed in the Grignard reactions and the hydride reduction of the ketones (3.23 and 3.24) were explained in terms of the preferred molecular conformations of these compounds which were determined from the X-ray crystal and molecular structures[36].

Dusausoy and co-workers have now determined the crystal structure and stereochemistry of one of the diastereoisomeric



(3.20) (3.21) (3.22)

forms of the alcohol (3.25) by X-ray diffraction. The structure obtained supported the mechanistic schemes presented in earlier papers mentioned above[37].

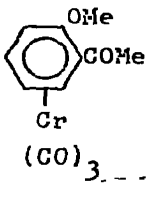
X-ray crystal structure methods were used to determine the absolute configuration of the (+)-2-methoxy-(1-hydroxyethyl)-benchrotrene enantiomer of melting point 70°; the absolute configuration was (1R)-2-methoxy-[(S)1-hydroxyethyl]benchrotrene[38]. Rate constants were obtained for the solvolysis of $RC_6H_4CMe_2Cl$ [R = H, p-$PhCr(CO)_3$, p-Ph] and $Cr(CO)_3PhCMe_2Cl$ in aqueous acetone at -15 to +25°. The rate of solvolysis of the cumyl chloride containing the $Cr(CO)_3$ group was 28 times faster than that of cumyl chloride, and that of $Cr(CO)_3PhCMe_2Cl$ was 2.4 times faster than $PhCMe_2Cl$[39].

The pH dependence of the kinetics of the hydrolysis of $PhCH{=}NC_6H_4Cr(CO)_3$ and other Schiff bases was studied polarographically. In acid, the protonated base was attacked by water. In weakly basic media, hydroxyl ion attacked the protonated base, while in strongly basic media the hydroxyl ion attacked the free base[40].

Rate constants have been determined for the decomposition of benchrotrene and $(\pi\text{-}C_6H_6)Cr(CO)_2PPh_3$ to benzene in cyclohexane at 25°. The values are 4×10^{-3} and 1×10^{-3} min^{-1} respectively. Progressive changes in the UV spectra of the compounds during the reactions allowed the band at 315-325 nm to be assigned to the $(\pi\text{-}C_6H_6)Cr$ group[41]. The voltammetric oxidation of arene, cycloheptatriene, and cycloheptatrienyl tricarbonyl complexes of chromium was investigated. The π-arene chromium tricarbonyl complexes underwent two one-electron oxidation processes. The $E_{\frac{1}{2}}$ values for the oxidation waves were dependent on the nature of the substituent in the benzene ring but they were independent of ring substituent positional isomerism. There was a linear relationship between $E_{\frac{1}{2}}$(complex) and $E_{\frac{1}{2}}$(free arene) and between $E_{\frac{1}{2}}$(complex) and the ionization energies of the complexes $[(\pi\text{-}C_6H_nMe_{6-n})Cr(CO)_3]$ and of the free arenes. The cycloheptatriene and cycloheptatrienyl chromium tricarbonyl complexes studied underwent one electron reduction processes[42].

The chromium tricarbonyl complexes, $PhNHRCr(CO)_3$ (R = H, Me) were treated with $M(CO)_6$ (M = Cr, Mo, W) in ethanol and irradiated with ultra-violet light. Complexes of the type $(CO)_3Cr(PhNHR)M(CO)$ were formed in which the benzene ring was π-bonded to the chromium and the NHR group was σ-bonded to the metal M[43]. The <u>ortho</u>-metallation of the chromium tricarbonyl complex of benzo[<u>h</u>]quinolin with methylmanganese pentacarbonyl has been carried out in toluene to form the mixed metal complex (3.26) in 35% yield[44].

Ethylbenchrotrene was treated with <u>tert</u>-butyllithium in pentane-THF followed by ceric ammonium nitrate to give a mixture of <u>m</u>- and <u>p</u>-ethyl-<u>tert</u>-butylbenzene in the ratio 7:2. The free ligand was alkylated with the same reagent only under forcing conditions and the electron withdrawing chromium tricarbonyl group in the complex facilitates nucleophilic attack on the benzene ring[4



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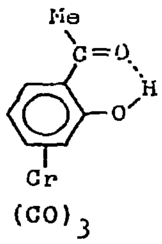

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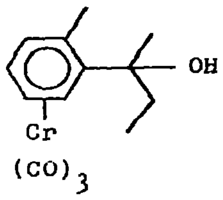
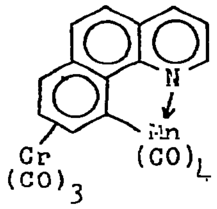


(3.25)

Mercuration of benchrotrene was achieved by heating it with mercury(II) acetate in ethanol under an argon atmosphere. The product was treated with ethanolic calcium chloride to give (π-$C_6H_5HgCl)Cr(CO)_3$ in 43% yield. The compound failed to symmetrize with sodium thiosulphate; instead cleavage of the carbon-mercury bond was observed[46]. The reaction of chromium carbonyl with diarylmercury derivatives $(p\text{-}XC_6H_4)_2Hg$ (X = Me_2N, MeO, Me, H, F) gave the chromium carbonyl derivatives (3.27). The infrared spectra of these compounds showed a decreasing electron donor ability of X in the order given. Pyrolysis of (3.27; X = H) gave Hg, Cr, PhH, Ph_2 and non-volatile products[47].

White and Farona have shown that (π-toluene)molybdenum tricarbonyl acts as a homogeneous catalyst in the Friedel-Crafts alkylation, acylation, sulphonation and polymerization of benzenoid aromatics. The catalyst may be added directly to the reaction mixture or generated *in situ* from toluene and molybdenum hexacarbonyl. Evidence was presented to support ionic intermediates and several mechanistic possibilities were discussed. (π-Arene)-molybdenum tricarbonyl catalysts were comparable in efficiency with aluminium trichloride but were more convenient to handle, store and recover[48,49].

Chromium hexacarbonyl was heated with a series of indans (3.28; R = H, Me, X = CH_2; R = H, X = $GeMe_2$, $SiMe_2$) to give the complexes $(indan)Cr(CO)_3$. The NMR spectra and thermogravimetric curves were recorded for these compounds[50]. The chromium tricarbonyl complexes of 9,10-dihydro-1,4-disubstituted-9,10-*o*-benzoanthracenes have been prepared by direct reaction between the ligand and chromium hexacarbonyl. The 1,4-dimethoxy complex was isolated as a mixture of two isomers separable by liquid chromatography which had the chromium tricarbonyl group directed toward or away from the methoxylated ring, the 1,4-dimethyl complex existed in three isomeric forms[51].



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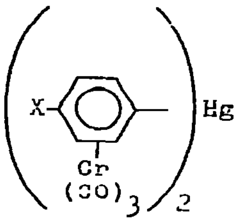

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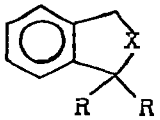


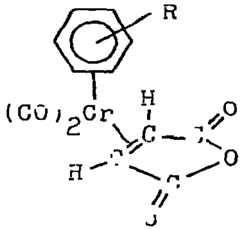
(3.28)

A series of stable maleic anhydride ($C_4H_2O_3$) complexes of the general type $ArCr(CO)_2C_4H_2O_3$ (3.29) were prepared photochemically from $ArCr(CO)_3$ and maleic anhydride. A comparison of the infrared and NMR data for the compounds $ArCr(CO)_3$ and $ArCr(CO)_2C_4H_2O_3$ indicated that the π-bonded maleic anhydride was a more powerful electron withdrawing ligand in these compounds than carbon monoxide[52]. The reaction of polymethylated arenechromiumtricarbonyls $Cr(CO)_3(C_6Me_{6-n}H_n)$, n = 0 - 3, with $NOPF_6$ gave air-stable, yellow salts $[Cr(CO)_2NOC_6Me_{6-n}H_n)]PF_6$ (3.30). Attempts to prepare cationic arenechromium acetylene nitrosyls from $Cr(CO)_2(PhC{\equiv}CPh)(C_6Me_{6-n}H_n)$, n = 0 and 1, and $NOPF_6$ afforded the hydrido complexes $Cr(H)(CO)_2(PhC{\equiv}CPh)(C_6Me_{6-n}H_n)$ PF_6. The treatment of the cations (3.30) with nucleophiles (X^-) gave neutral substituted cyclohexadienyl complexes of the type $Cr(CO)_2(NO)(C_6Me_{6-n}H_nX)$[53].

Bowden and Colton have prepared the interesting binuclear π-complexes (3.31; Ar = Ph, R^1 = R^2 = H; Ar = *m*-tolyl, R^1 = Me, R^2 = H; Ar = *p*-tolyl, R^1 = H, R^2 = Me) by treatment of chromium hexacarbonyl with the appropriate triarylphosphine in decalin at the reflux temperature. The normal mononuclear compounds (π-triarylphosphine)$Cr(CO)_3$, were formed as intermediates in the reactions. The bridged complexes (3.31) were broken down by carbon monoxide in chloroform at room temperature and pressure to form the simple complexes (triarylphosphine)Cr(CO)$_5$[54].

The crystal and molecular structure of the dimer $\{[(\pi\text{-}C_5H_5)P(C_6H_5)_2]Cr(CO)_2\}_2$ (3.31) has been investigated by X-ray crystallography. The molecule contains two Cr(CO)$_2$ groups bridged by two triphenylphosphine groups where each triphenylphosphine group is bonded to one chromium atom by phosphorus and is involved in π-benzene bonding to the second chromium atom[55].

Jaouen and Dabard have discussed the effect of substituting PPh$_3$, P(OMe)$_3$ or P(OEt)$_3$ for one of the carbonyl groups in benchrotrene and benchrotrene derivatives. The decrease in the terminal carbonyl IR stretching frequency for the esters [3.32; R^1 = H, R^2 = Me, X = PPh$_3$, P(Oalkyl)$_3$] from that for the benchrotrene ester was explained in terms of an increase in charge density on chromium and increased M→C back donation. The pK$_a$ values



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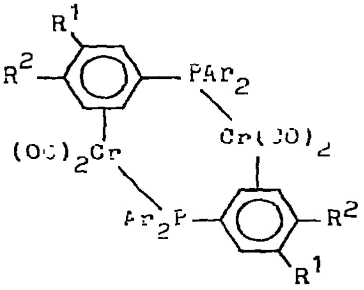

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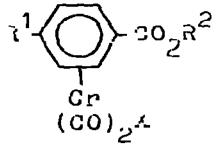


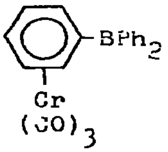
(3.32)

for the acids (3.32; R^1 = R^2 = H) increased in the order of the substituents, X = CO$<$P(OMe)$_3$$<$P(OEt)$_3$$<PPh_3$[56].

The chemical properties of benchrotrene are also modified by substitution of PR$_3$ for CO, thus the ester (3.32; R^1 = Me$_3$C, R^2 = Me, X = PPh$_3$) was reduced rapidly and quantitatively to the corresponding methyl complex. By contrast, the analogous benchrotrene ester was reduced slowly and incompletely under the same conditions. Substituent constants (σ^+) were determined for $Cr(CO)_3$, (+0.06) and $Cr(CO)_2P(OEt)_3$, (-0.53) from IR carbonyl frequencies for the substituted ketones (π-PhCOMe)$Cr(CO)_2X$[57].

The rate of hydrogen exchange in the π-benzene ring of $(C_6H_6)Cr(CO)_2PPh_3$, using CF_3CO_2D, was approximately three times as fast as with benzene-chromium tricarbonyl. This was attributed to the increased nucleophilicity of the aromatic ligand. When the reaction was carried out with EtONa in EtOD the insertion of a triphenylphosphine ligand retarded the rate of hydrogen exchange about twenty times. In this case the reaction was considered to be protophilic hydrogen exchange[58].

The triphenylborane complex (3.33) was prepared from bromodiphenylborane and $Hg[(\pi-C_6H_5)Cr(CO)_3]_2$ in cyclohexane. Boron-phenyl π-bonding was weaker in the complex (3.33) than in triphenylborane[59]. The tricarbonylchromium derivatives of hexamethyl-, B-monophenylpentamethyl-, B-monoethylpentamethyl- and N-triethyl-B-trimethyl-borazine were prepared. The infrared, NMR and visible-ultraviolet spectra of these complexes were interpreted in terms of a puckered borazine ring σ-bonded through the ring nitrogen atoms. The results suggested that when the borazine ring was complexed to chromium it was a poorer π-acceptor

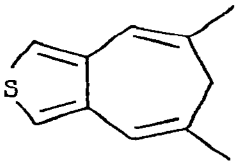


(3.33)

than the corresponding arene[60].

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

The molecular orbital diagrams for several dimethyl- and trimethyl-cyclohepta[c or b]thiophenes (such as 3.34 and 3.35) have been calculated by an ω-Huckel method in order to explain the nature and characteristics of the products obtained by treatment of the cycloheptathiophenes with chromium hexacarbonyl. The structures and conformations of the π-complexes were found to show good correlations with the calculated parameters of the ligands. In the same way, the characteristics of the thiophenotropylium ion formed in each series were correlated with the structure of the only π-complex formed in each case[61].



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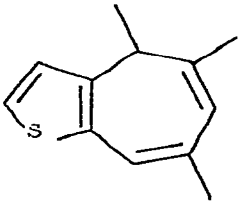
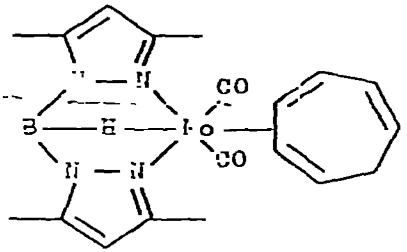


(3.35)

The crystal and molecular structure of $\underline{h}^3$-cycloheptatrienyl molybdenum complex (3.36) has been determined by single crystal X-ray diffraction methods. The cycloheptatrienyl ligand is a trihapto species. The molybdenum-nitrogen-boron ring in the bidentate pyrazolylborate group adopted a boat conformation which permitted a B-H-Mo three-centre two-electron bond and allowed the metal atom to gain the eighteen-electron configuration[62].

Clark and Palenik have determined the crystal and molecular structure of π-cycloheptatrienyliumtricarbonylmolybdenum tetrafluoroborate by X-ray diffraction. The cation (3.37) had the expected 'piano stool' arrangement with the planar seven-membered ring as the 'seat' and the three carbonyl groups as 'legs'. The C-C distances in the cycloheptatrienylium ring fell within the range 1.366-1.425Å (average 1.400Å) which were similar to those found in other cycloheptatrienylium complexes. The metal atom was almost equidistant from each of the ring carbon atoms, average 2.314Å, while the molybdenum-ring plane distance was 1.650Å. The molybdenum-C(carbonyl) was found to be 2.032Å, the longest yet observed in a molybdenum tricarbonyl complex. This observation coupled with the rather short molybdenum-C(ring) distance indicated a stronger than normal interaction between the metal atom and the ring[63].



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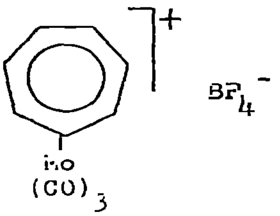
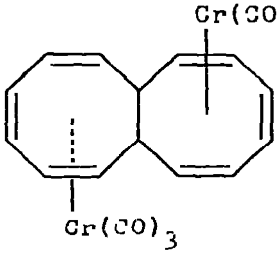


(3.37)

The reaction of [14] annulene with triamminetricarbonylchromium gave hexacarbonyl-trans-6a,12a-dihydro-octalenedichromium(0 (3.38). The reaction of monodehydro[14]annulene with triacetonitriletricarbonylchromium gave tricarbonyl-1,4-dihydrophenanthrenechromium(0) and tricarbonylphenanthrenechromium(0). The crystal structures of these complexes were determined by X-ray diffraction[64]

Protonation of bicyclo[6,1,0]nonatrienemolybdenum tricarbonyl (3.39) in degassed $HSO_3F-SO_2F_2$ at -120° gave the rearranged product (3.40) where the additional proton was bound to molybdenum. The metal atom was σ-bonded to carbon(2) and π-bonded to the pentadienyl group, carbon(3)-carbon(7)[65].



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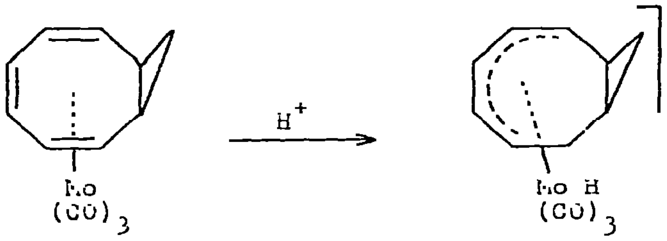


(3.39) (3.40)

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

The standard entropies $[S^o_{298(g)}]$ of the gaseous bis(π-benzene complexes of vanadium, molybdenum and tungsten were calculated in the rigid rotor-harmonic oscillator approximation. The values of the standard entropies of the solid compounds $[S^o_{298(s)}]$ were obtained using previously published data. The results obtained for $S^o_{298(g)}$ were considerably higher than those for $S^o_{298(s)}$ and this was attributed to the high symmetry and high stability of the complexes[66].

Solid state transitions of bis(arene)chromium halides were studied by Nikolaev et al. The specific heat against temperature plots for bis(π-benzene)chromium chloride, bromide and iodide and bis(π-mesitylene)chromium iodide exhibited breaks or maxima at 160, 230, 240 and 255-262°K respectively. These discontinuities were caused by transitions in the solid state[67].

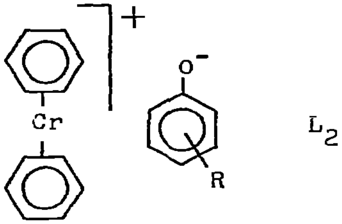
A calorimetric method has been used to determine standard enthalpies of combustion and formation together with mean bond dissociation energies for the following π-arene complexes: bis(π-ethylbenzene)chromium, bis(π-o-diethylbenzene)chromium, (π-iso-propylbenzene)(π-o-diisopropylbenzene)chromium and bis(π-o-diisopropylbenzene)chromium[68].

The thermal decomposition of bis(π-benzene)chromium in air or in an inert atmosphere was facilitated by chromium(II) iodide. The reaction mechanism involved the initial loss of benzene and formation of π-PhHCrI which was oxidized to chromium(III) oxide in air. In the absence of air the intermediate gave bis(π-benzene)chromium and chromium(II) iodide, the former finally gave metallic chromium and benzene. Increasing alkylation of the starting material by methyl and ethyl groups caused an increase in the temperature required for thermolysis[69].

Pyrolysis of the bis(arene)chromium phenolates [3.41; R = H, L = PhOH; R = OH, L = $C_6H_4(OH)_2$; R = NO_2, L = m-NO_2.C_6H_4OH] gave a mixture of benzene, phenol or the monosubstituted phenol and $Cr(OC_6H_4R)_2$ together with minor amounts of bis(benzene)chromium and hydrogen. A disproportionation mechanism was proposed for the simplest phenolate (3.41; R = H, L = PhOH). Oxidation of bis(benzene)chromium by phenol was observed at 200° with the evolution of hydrogen and loss of the sandwich structure to form the phenolate $Cr(OC_6H_4R)_2$. The phenols of highest acidity were most active in the oxidation and in the case of m-nitrophenol nearly quantitative formation of phenolate $Cr(OC_6H_4R)_2$ and benzene was achieved[70].

The pyrolysis of bis(ethylbenzene)chromium at 160, 170 and 180° gave ethylbenzene and Cr_7C_3[71]. The thermal decomposition of bis(benzene)chromium was studied at 340-400° and 100-300 mm pressure. The pyrolysis was autocatalytic and the rate was unaffected if the products of pyrolysis for example chromium and benzene, were coated on the vessel walls. This indicated that the effect of the chromium atoms was only important at the instant they were released. Each mole of substrate gave more than two moles of gas. The gases released included hydrogen, ethylene, methane, ethane, propylene, propane and toluene together with traces of butane and benzene[72].

Pyrolysis of bis(π-benzene)chromium and its symmetrical di-, tetra- and hexa-ethyl derivatives at 340-400° and 100-300 mm pressure gave the free ligands C_6H_6, C_6H_5Et, $C_6H_4Et_2$ and $C_6H_3Et_3$ together with chromium. Up to 50% conversion was achieved and the reaction obeyed first order kinetics with an activation energy of 22.5 kcal mole^{-1} [73]. Thermal decomposition studies and measurements of the heats of reaction with iodine vapour were carried out for bis(benzene)chromium, bis(benzene)chromium iodide and some (arene)chromium tricarbonyls using high temperature microcalorimetry. The standard enthalpies of formation $\Delta H^o_{f(cryst)}$/kcal mole^{-1} obtained were as following, $Cr(C_6H_6)_2$, +34; $Cr(C_6H_6)_2I$, +12; $Cr(C_6H_6)(CO)_3$, -106; $Cr(C_6H_5CH_3)(CO)_3$, -112; $Cr[C_6(CH_3)_6](CO)_3$, -171; $Cr(cyclo\text{-}C_7H_8)(CO)_3$, -74. The total enthalpies of disruption of the Cr-ligand bonds in these molecules were calculated. For the (arene)chromium tricarbonyls, the ligand binding energy was increased substantially by replacing benzene with hexamethylbenzene[74].



(3.41)

The formation of bis(tetrahydronaphthalene)chromium iodide and benzene(tetrahydronaphthalene)chromium iodide from chromium(III) chloride and 1,4-diphenylbutane has been reported. Chromium(III) chloride, aluminium chloride, aluminium dust and 1,4-diphenylbutane were heated to reflux in octane, the reaction mixture was treated with aqueous-methanolic potassium hydroxide and formamidinesulphinic acid and then with potassium iodide. The products were separated by chromatography on alumina[75].

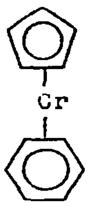
The autoxidation of bis(ethylbenzene)chromium was investigated, at 19° over a period of 40 hours acetophenone (7%), ethylbenzene (30%) and an unstable solid $[(PhEt)_2Cr]_2CrO_4$ were formed. The unstable solid gave ethylbenzene on further oxidation. It was concluded that the autoxidation was a bimolecular heterolysis reaction passing through an intermediate complex which decomposed to give ethylbenzene and acetophenone by oxidation[76]. The autoxidation of (π-diethylbenzene)(π-ethylbenzene)molybdenum proceeded smoothly, even at -70°C to give ethylbenzene, diethylbenzene and an oxide of molybdenum in quantitative yields. The reaction was first order in oxygen and in the arene complex. Free radical inhibitors did not affect the rate and the solid products of the reaction did not catalyze it[77].

The autoxidation of bis(π-benzene)chromium and its di- and tri-ethyl derivatives proceeds readily in dry hydrocarbon solvents at room temperature by a second order heterolytic reaction to give free ligand and a solid product $[(PhH)_2Cr]_2CrO_4$. A free radical mechanism was excluded and the reaction was catalysed by water[76].

The kinetics of the autoxidation of bis(benzene)chromium was studied at 40° in p-xylene at concentrations of 1.44-4.6×10^{-2} moles/l and an oxygen pressure of 300 mm. The activation energy for the reaction was found to be 22 kcal/mole

The mass spectra of bisarene chromium compounds $CrAr_2$ ($Ar = C_6H_6$, $C_6H_5CH_3$, xylene and mesitylene) were recorded and the appearance potentials of Cr^+ were determined. The relative abundance of the ions decreased in the order $CrL^+ > CrL_2^+ > Cr^+$. The relative intensity of Cr^+ decreased whilst its appearance potential increased as the number of alkyl groups increased in the benzene ring of the ligand. This indicated that the strength of the Cr-ligand bond increased in the same direction[80].

The ESR spectra of the mixed sandwich compounds (3.42 and 3.43) have been obtained at -150° in solid solution and at -55° in liquid solution. Good agreement with the theoretically predicted spectra was obtained. The wide line ^1H NMR spectra of the polycrystalline solid compounds were also measured. These results together with previously published data for the bis(π-benzene)chromium cation were used to compare the magnetic parameters of the complexes with the ring size of the aromatic ligands and the total charge on the molecule[81].



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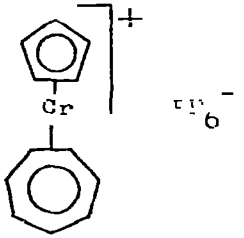

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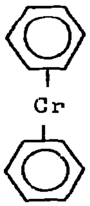

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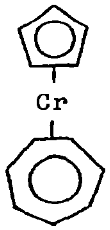


(3.45)

The X-ray photoelectron spectra of the chromium complexes (3.42, 3.44 and 3.45) and the hexafluorophosphate and tetrafluoroborate salts of (3.44 and 3.45) showed that the chemical shifts of the electron bond energies is <0.5 eV. Therefore the charge distribution between the ligands in the complexes (3.42 and 3.45) was nearly balanced. The chromium atom was shown to carry a partial positive charge even in the neutral complexes[82].

Cocondensation of chromium atoms with arenes gave good yields of bis(arene)chromium complexes. Conventional methods of making bis(arene)chromium complexes failed when the arene possessed a strongly electron-withdrawing substituent but with the cocondensation method chlorobenzene, fluorobenzene and even p-difluorobenzene gave bis(arene)chromium compounds[63]. Bis-π-arene complexes of molybdenum were separated from aromatic hydrocarbons and purified by distillation under reduced pressure[64].

Pavlik and Klikorka have investigated π-complexes as catalysts in homogeneous polymerization and hydrogenation. Bis(π-benzene)chromium was used in the polymerization of ethylene in heptane at 250° and 200 atmospheres of nitrogen. A trans-polymer was obtained with a molecular weight of 37,000. The selective hydrogenation of $MeCH{=}CHCH{=}ChO_2Me$ to $MeCH_2CH{=}CHCH_2CO_2Me$ was achieved with benchrotrene as the catalyst. Bis(π-benzene)-chromium was also used for selective hydrogenation, in the presence of hydrogen and carbon monoxide, the effective catalyst was $(\pi\text{-}C_5H_5)Cr(CO)_3H$[65].

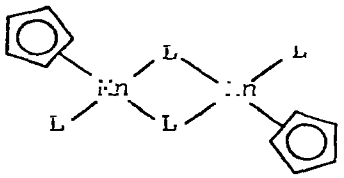
The concentrations of trace elements in metals may be significantly reduced when the metal is converted to an organometallic compound. Non-transition metal impurities in particular were reduced when a transition metal was incorporated into a π-complex. Among the systems investigated was the formation of bis(π-ethylbenzene)chromium from chromium(III) chloride, aluminium and ethylbenzene[66].

Bis(π-arene)chromium compounds were found to be active as catalysts in the coupling of alkyl and aralkyl halides to form dimeric products after the elimination of halogen. Thus a benzene solution of Ph_2CHCl containing $(\pi\text{-}PhEt)_2Cr$ gave $Ph_2CHCHPh_2$ (66%) and similar reactions were carried out with $PhCH_2Cl$, Ph_3CCl, $CH_2{=}CHCH_2Br$ and MeI. Using the same conditions $PhCCl_3$ gave $PhCCl_2CCl_2Ph$ while Ph_2CCl_2 gave $Ph_2C{=}CPh_2$ and ethyl iodide gave a mixture of ethane and ethylene[67].

4. $(\pi\text{-}C_5H_5)Mn(CO)_3$

Kirchner, Marks, Kristoff and Ibers have used the X-ray technique to confirm the *trans* configuration (4.1) for the dimeric cymantrene analogue $[(\pi\text{-}C_5H_5)_2Mn(CO)(NO)]_2$. One of the bridging ligands was a carbonyl and the other a nitrosyl group. In solution the compound existed as a mixture of *cis* (4.2; L = CO, NO) and *trans* (4.1; L = CO, NO) ligand bridged dimers in dynamic equilibrium. *Cis*-*trans* interconversion and bridge-terminal ligand interchange occurred through symmetrical bridge cleavage followed by rotation about the metal-metal bond. Bridge-terminal ligand interchange was faster for the *trans* than for the *cis* isomer and these two reactions were faster than *cis*-*trans* interconversion. The equilibrium constant K = [*trans*]/[*cis*] varied from 2.1 in DMSO to 71.6 in cyclohexane, the thermodynamic parameters for the equilibrium were ΔH = -0.16 kcal mole^{-1}, ΔS = 0.93 eu, ΔG = -0.44 kcal mole^{-1} at 298°K. Comparisons with the isoelectronic chromium and iron complexes were made[88].

In a parallel investigation Adams and Cotton propose similar mechanistic schemes to account for the PMR spectra of the compounds (4.1 and 4.2; L = CO, NO) and related iron compounds[89].



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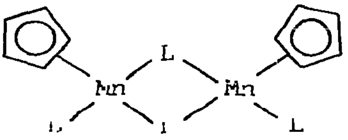


(4.2)

The crystal and molecular structure of (cyclopentadienyl)-dicarbonyl(triphenylphosphine)manganese has been determined by X-ray crystallography. The molecule had parameters that were almost identical with those of $C_5H_5Mn(CO)_3$ except for the Mn-C bond lengths which changed from 1.80 to 1.73Å. The P-Mn distance of 2.234Å and the unchanged parameters for the Mn-C_5H_5 group confirmed the strong electron donating power of the cyclopentadienyl group[90]

The X-ray method has been used to determine the crystal and molecular structure of π-cyclopentadienyl-σ-methylrhenium dicarbonyl bromide in which rhenium was bound to five ligands. The average distance between the metal atom and the cyclopentadienyl ring was 2.31Å, the rhenium-methyl bond length was 2.32Å. The molecule had the half-sandwich structure that is characteristic of the analogous complex cymantrene[91].

X-ray fluorescene has been found to provide a rapid and convenient method for the determination of heavy elements in organometallic polymers. In a typical experiment, iron and manganese were determined accurately and precisely by soaking filter paper discs in an aqueous solution containing a known concentration of vinylcymantrene-vinylferrocene copolymer and then subjecting the discs to X-ray fluorescene[92].

Adams and Squire have reexamined the vibrational spectra of cymantrene and its methyl derivative in the solid, liquid and solution phases. They conclude that the π-C_5H_5 part of the spectrum cannot be assigned on the basis of "local" C_{5v} symmetry and offer a reinterpretation of previous results together with new evidence[93].

The interaction of phosphine derivatives of cyclopentadienylmanganese tricarbonyl with tin(IV) chloride and other Lewis acids [antimony(III) chloride mercury(II) chloride and germanium(IV) chloride] in the dichloromethane solution was studied by infrared spectroscopy. Complex formation was favoured by electron donor substituents in the cyclopentadienyl ring and also by an increase in the electron donor properties of the phosphine ligand attached to the manganese. The ability of Lewis acids to undergo complex formation followed the series $SnCl_4 > SbCl_3 > HgCl_2 > GeCl_4$[94].

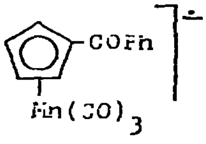
The IR and Raman spectra were obtained for π-cyclopentadienylrhenium tricarbonyl in solution and in the solid state. The normal modes of vibration were assigned in terms of local symmetry and comparisons were made with cymantrene. The increase in M-CO bond strength in going from manganese to rhenium was demonstrated by the frequencies and force constants for this group and by the relative ease of photochemical substitution of carbon monoxide by other ligands[95].

The ^{13}C NMR chemical shifts of a series of monosubstituted cymantrene derivatives were reported. The average shielding of the carbon atoms at the 2- and 3- positions was increased by alkyl substituents that had a greater electron-donor ability than the methyl group and was decreased by electron acceptor substituents[96].

The NMR spectrum of cymantrene enriched with ^{13}C so that 20% of the molecules were $(\pi\text{-}C_5H_5)Mn(CO)_2(^{13}CO)$ was recorded at 12° and 23°C in a nematic solvent [N-(p-methoxybenzylidene)-p-n-butylamine]. Some geometrical parameters of the molecule were calculated from the results and the OC-Mn-CO bond angle compared well with values obtained by X-ray crystallography[97]. The polarographic reduction of $C_5H_4HgClM(CO)_3$ (M = Mn, Re) and ferrocenylmercurichloride was investigated and the pK_a values for these molecules as C-H acids were determined. The mercury derivatives of cyclopentadienylmanganese and rhenium tricarbonyls were much more readily reduced than phenylmercury chloride which indicated that the respective radicals were stronger electron acceptors than the phenyl radical. The values of pK_a estimated from the $E_{\frac{1}{2}}$ values showed that cyclopentadienylmanganese and rhenium tricarbonyls were less acidic than benzene whilst ferrocene was more acidic[98,99].

The kinetics of hydrogen-deuterium exchange in tricarbonyl-π-pyrrolylmanganese with CF_3CO_2D in benzene were studied. All four positions on the pyrrolyl ring were very reactive and they were equally deuterated[100]. The reaction of bromopentacarbonylmanganese(I) with either potassium 1,2,4-tricyanocyclopentadienide or tetraethylammonium pentacyanocyclopentadienide gave the bright yellow complexes $[Mn(L)(CO)_3]_n$. Spectroscopic evidence indicated that these polymeric complexes contained nitrogen-bonded bridging cyanocyclopentadienyl groups. There was no evidence for the formation of π-bonded complexes with these ligands[101].

Benzoyl-, 1-benzoyl-2-methyl- and 1-benzoyl-3-methylcymantrene were reduced by sodium or potassium in 1,2-dimethoxyethane or THF to the corresponding radical anions (4.3); electrolytic reduction was effective also in forming the radical ions. Solutions of the radical anion were purple and slowly changed to red on standing in contact with the reducing agent with the formation of the diamagnetic dinegative ion. The ESR spectrum of the radical anion had a *g*-value of 2.00006 and



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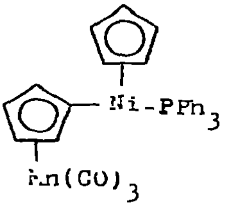
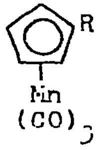


(4.4)

was split into six components by the ^{55}Mn nucleus. Each component showed fine structure from the o- and p-protons on the phenyl group. The unpaired spin density was largely on the manganese atom, the phenyl ring and perhaps on the ketonic carbonyl group[102].

Lithiated cymantrene was treated with (π-C_5H_5)Ni(PPh_3)Cl to give the nickel complex (4.4). The reaction of the complex (4.4) with excess mercury(II) chloride gave chloromercuricymantrene in good yield[103]. Kovar and Rausch have described the preparation of chloromercuricymantrene(4.5; R = HgCl) by direct mercuration of cymantrene in the presence of perchloric acid. The intermediate (4.5; R = HgCl) was converted to the iodide (4.5; R = I) and dicymantrenylmercury (4.6) by standard methods. Pyrolysis of this compound (4.6) with diferrocenylmercury in the presence of silver powder gave the unsymmetrical coupling product cymantrenylferrocene (4.7, 39%) together with biferrocene and bicymantrene. The useful Grignard (4.5; R = MgI) and lithio (4.5; R = Li) intermediates have been prepared. The first was obtained from iodocymantrene, ethylene bromide and magnesium powder and the second from either of the mercurials (4.5; R = HgCl) or (4.6) and n-butyllithium. Bicymantrene was acetylated with acetyl chloride in the presence of aluminium chloride[104].



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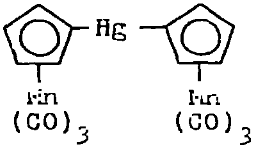

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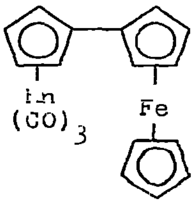


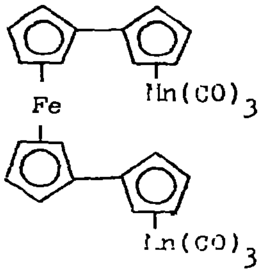
(4.7)

The reaction of bis(bromomercuri)cymantrene with copper(II) bromide gave cymantrene (1.2%), bromo- (12.4%), 1,3-dibromo- (4.3%), 1,2-dibromo- (26%), 1,2,4-tribromo- (4.3%), 1,2,3-tribromo- (21.6%), tetrabromo- (16.2%) and pentabromo-cymantrene (14%)[105] Di(cymantrenyl)mercury was treated with tin(II) chloride in tetrahydrofuran and gave dicymantrenyldichlorostannane. This cymantrene-tin derivative was slowly hydrolysed in air and when treated with cold alcoholic ammonium hydroxide or sodium carbonate gave dicymantrenyltin oxide[106].

The treatment of cymantrenyl-copper or -silver with 1,1'-dibromoferrocene in the presence of copper(I) bromide gave the dicymantrene (4.8), 15% and the intermediate complex (4.9; R = Br), 36%. With metallic copper the bromide (4.9; R = Br) gave the product (4.9; R = H). The acetate (4.9; R = OAc) was formed in 76% yield by heating the same bromide with copper(II) acetate in ethanol. The corresponding reaction with copper(II) phthalimide at 130-150° gave the phthalimide (4.9; R = phthalimido) and this was converted to the amine (4.9; R = NH_2), 68% with ethanolic hydrazine[107].

Cyclization of the two α-disubstituted cymantrenes (4.10; R^1 = H, R^2 = Me and 4.10; R^1 = Me, R^2 = H) under Friedel Crafts conditions followed by reduction with zinc amalgam gave a simple cyclohexene product in each case while cyclization of the two β-disubstituted cymantrenes (4.11; R^1 = H, R^2 = Me and 4.11; R^1 = Me, R^2 = H) and reduction gave two cyclohexene products from each reactant. Thus the acid (4.11; R^1 = H, R^2 = Me) gave the products (4.12 and 4.13). The cymantrene (4.12) was also formed from the acid (4.10; R^1 = Me, R^2 = H). The product distributions and a detailed analysis of the IR and NMR spectra were used to confirm the structures[106].

The condensation of trialkyl- and triaryl-halosilanes with alkali metal-substituted cyclopentadienyltricarbonylmanganese gave a series of organosilylcyclopentadienyltricarbonylmanganese compounds[109].



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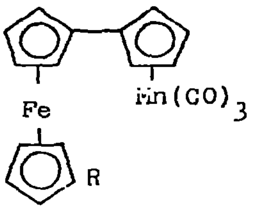

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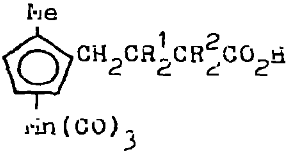

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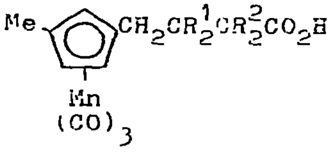

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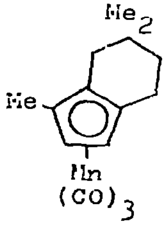

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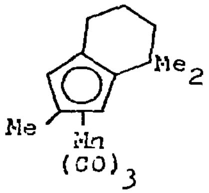


(4.13)

Anderson has described the application of light-sensitive resin compositions to the preparation of printing plates. A mixture of an epoxy resin (81.5%), a polymercaptan or reactive anhydride curing agent (16%) and methylcymantrene (2.5%) was used to coat tinplate. The plate was exposed through a stencil to a mercury arc lamp and cured at 125°. The uncured resin was removed by washing. In the absence of light the uncured resin was stable for several weeks[110].

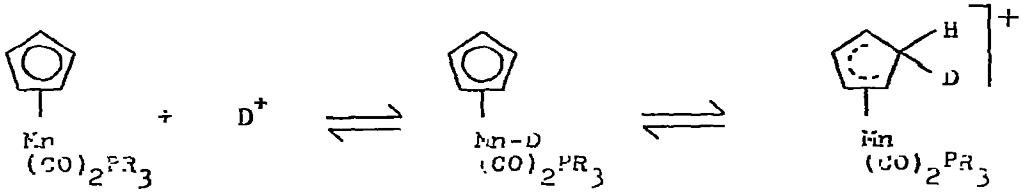
Cymantrene was confirmed as an effective antiknock additive for aromatic petroleums with research octane numbers $\leqslant 90$, it was particularly effective at high speeds and it decreased the fuel sensitivity to service conditions. Pollution problems suggested that its use would be restricted to special circumstances[111].

The concentration of atmospheric manganese, as manganese dioxide, was proportional to the traffic density when measurements were made near to highways carrying traffic that used cymantrene as the petroleum antiknock. Cymantrene was considered to be less toxic than tetraethyl lead[112]. (Vinylcyclopentadienyl)tricarbonylmanganese was dissolved in alkali refined linseed oil and this was drawn into films. The drying rate of the film did not appear to be retarded by the presence of the organometallic derivative. After drying, chips of the film were extracted with either boiling acetone or benzene, no organometallic compounds were extracted. This suggested that the (vinylcyclopentadienyl)-tricarbonylmanganese had been chemically cross-linked into the film matrix[113].

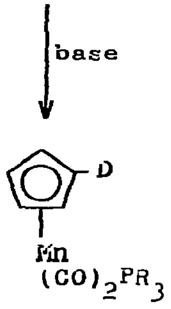
Mixtures of cymantrene with ethyl bromide, tricresylphosphate and toluene have been evaluated as antiknock additives for petroleum Light stability and toxicity of the mixtures were also examined[114]. A mixture of cymantrene, as an oxidation catalyst, and tris-(β-chloroisopropyl)thionophosphate, as a detergent, have been found to cause the almost complete elimination of carbon monoxide and hydrocarbons when added to gasoline[115].

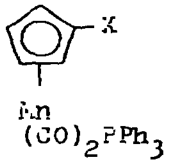
Copolymers have been formed with vinylcymantrene and styrene methylacrylate, acrylonitrile, vinylacetate and vinylferrocene using azobisisobutyronitrile as the initiator. Reactivity ratios were obtained and the copolymers were film-forming and insulating. The films showed high anti-fungal activity[116]. Setkina and co-workers have examined the effect of substituting donor ligands for CO in cymantrene and benchrotrene. Replacement of one carbonyl group in cymantrene by tertiary phosphine, arsine or stibine increased the rate of hydrogen isotope exchange (HIE) between two and four orders of magnitude using trifluoroacetic acid in methylene dichloride. The increase in rate of HIE at the cyclopentadienyl ring was accompanied by a decrease in the IR carbonyl stretching frequency which confirmed the donor character of the Group V ligands. The effect of a change in the donor atom from phosphorus to arsenic or antimony was much smaller than the effect of changes in the substituent on phosphorus. The rate of HIE increased in the order $OPh < Ph < CH_2Ph < Pr^i <$ cyclohexyl. Introduction of a second tertiary phosphine caused a marked decrease in the rate of HIE under the same conditions although the IR carbonyl stretching frequency showed a decrease confirming the increased basicity of the manganese atom. When the acidity of the medium was increased by the incremental addition of D_2SO_4 the rate of HIE decreased and in media of high acidity the exchange was almost completely suppressed. By contrast, the rate of HIE for cymantrene and the monophosphine analogue $(\pi\text{-}C_5H_5)\text{-}Mn(CO)_2PPh_3$ increased with an increase in acidity. These observations were accommodated by a mechanism involving rapid initial protonation to give the cation (4.14) followed by slow hydrogen transfer from metal to ring to form (4.15) and subsequent loss of a proton to give the product (4.16). IR evidence was used to support the formation of the protonated intermediate (4.14); high frequency shifts for the carbonyl stretching modes were observed on the addition of CF_3CO_2H to those complexes that underwent HIE. Replacement of CO by PR_3 increased the basicity of manganese, facilitated initial protonation and increased the rate of HIE, introduction of two PR_3 groups caused a large increase in metal basicity, formation of a stable protonated complex and inhibition of the metal-ligand proton shift. Experiments with cymantrene and its mono- and di-phosphine analogues labelled with deuterium and tritium in the cyclopentadienyl ring confirmed the existence of a kinetic isotope effect in HIE and demonstrated that the final step (proton abstraction) was rate-determining.

The rate of HIE in the complexes (4.17) has been determined



(4.14) (4.15)

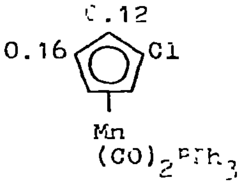




(4.17) (4.16)

for five substituents. Although the overall rates of exchange varied by three orders of magnitude, the difference between the rates at the α and β positions remained small. Some partial rate constants (relative to cymantrene) are given in complexes (4.18, 4.19 and 4.20). The trends observed here are similar to those obtained in the ferrocene series.

The rate of HIE at the benzene ring of benchrotrene was sensitive to replacement of carbonyl groups by tertiary phosphines. Replacement of one carbonyl caused a rate enhancement of three orders of magnitude. At the same time the carbonyl stretching frequencies decreased. Protonation of the chromium atom was demonstrated by NMR spectroscopy and mechanistic arguments were used similar to those invoked for the corresponding cymantrene complexes. Substitution in the π-benzene ring of benchrotrene had almost no effect on the rate of HIE. This finding contrasts sharply with the large change in rate observed on substitution into the free benzene ligand where the introduction of three methyl groups enhanced the rate by 10^7. Ring substitution of $(\pi\text{-PhH})Cr(CO)_2PPh_3$ was similar in its effect on the rate of HIE and no adequate explanation for these results could be offered[117].



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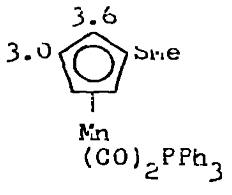

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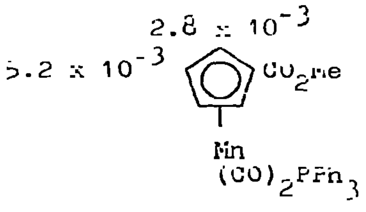
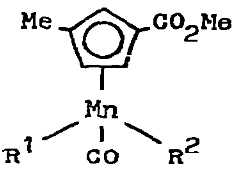


(4.20)

Moigne and Dabard have introduced two asymmetric centres into the cymantrene molecule and isolated the product as a pair of diastereoisomers [4.21 and 4.22; $R^1 = P(OMe)_3$, $R^2 = PPh_3$]. The racemic ester (4.21; $R^1 = R^2 = CO$) was irradiated with trimethylphosphite to give the diphosphite [4.21; $R^1 = R^2 = P(OMe)_3$] which was, in turn, irradiated with triphenylphosphine to form the diastereoisomeric complexes[118].

Rhenium tricarbonyl and bis(rhenium tricarbonyl) complexes of mesoporphyrin IX dimethyl ester have been prepared. Several alternative structures for the complexes were discussed and rhenium was assigned the formal oxidation state +1[119].



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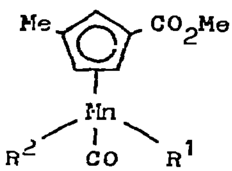

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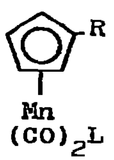


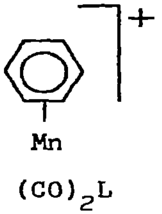
(4.23)

Irradiation of the monosubstituted cymantrenes (4.23; R = H, Et, CH_2Ph, CO_2Me, SMe, Cl, Br, I; L = CO) in cyclohexane-benzene solution with triphenylphosphine, led to displacement of one carbonyl ligand by triphenylphosphine and formation of the cymantrene analogues (4.23; L = PPh_3).[120]

Poly(1-pyrazolyl)boratotricarbonylmanganese derivatives were prepared photochemically and the chemical, physical and electronic properties of these compounds were compared with those of the analogous π-cyclopentadienyltricarbonylmanganese compounds[121] Benzonorbornadienone has been isolated for the first time as a π-complex in which the olefinic bond is linked to the manganese atom of a (π-methylcyclopentadienyl)manganese dicarbonyl group[122].

Smith has prepared a number of (π-arene)manganese complexes such as the cation (4.24; L = CNMe, PPh_3). Nucleophilic attack on these compounds by methyllithium, n-butyllithium and pentafluorophenyllithium gave the cyclohexadienyl complexes (4.25; L = CNMe, PPh_3)[123]. Biehl and Reeves reported a convenient, high yield synthesis of cyclopentadienylmanganese tricarbonyl carboxylic acid. Treatment of $C_5H_5Mn(CO)_3$ with o-ClC_6H_4COCl and aluminium trichloride gave the ketone (4.26) in 87% yield. The ketone (4.26) was hydrolysed by Me_3COK - $MeOCH_2CH_2OMe$ to give the corresponding acid in good yield[124].

The cymantrene analogue (4.27) was obtained in 84% yield by



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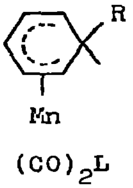

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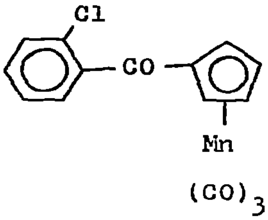

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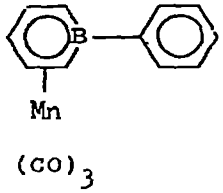
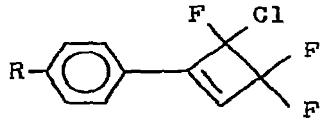


(4.27)

heating bis(1-phenylborinato)cobalt with manganese carbonyl in toluene. The borinate group is a planar and a hexahapto ligand[125]

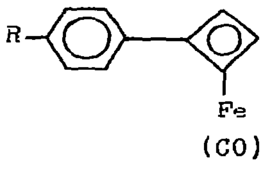
5. (i) $(\pi\text{-}C_4H_4)Fe(CO)_3$

Para-substituted phenyl acetylenes were treated with CF_2CFCl to give the cyclobutenes (5.1). These were hydrolysed with sulphuric acid to form the diketones, the ketones were reduced and the cis-diols produced were treated with phosphorus(III) bromide to give the corresponding trans dibromo derivatives. Treatment of the dibromo compounds with $Fe_2(CO)_9$ gave the para-substituted phenylcyclobutadieneiron tricarbonyls (5.2). Infrared, ^{13}C and PMR spectra indicated that there was no conjugative interaction between the π-electron system of cyclobutadiene and the phenyl ring[126].



R = Me, F, Cl, Br,
MeO, Me_2N

(5.1)



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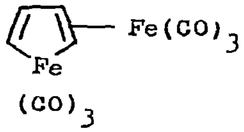
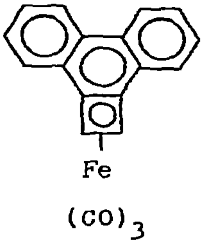


(5.3)

When iron pentacarbonyl was heated under pressure with a saturated solution of acetylene in tetrahydrofuran low yields of cyclobutadieneiron tricarbonyl were obtained together with tricarbonyl(ferracyclopentadiene)iron tricarbonyl (5.3), γ-butyrolactone, quinhydrone and polymeric material[127].

The cyclobutadieneiron tricarbonyl derivative (5.4) was obtained by stirring 1,2-dichloro-1,2-dihydrocyclobuta[l]phenanthrene with diiron enneacarbonyl in hexane at 50°. Oxidative decomposition of the complex with cerium(IV) liberated the free cyclobutadiene ligand which was trapped as the corresponding cyclopentadiene adduct[128].



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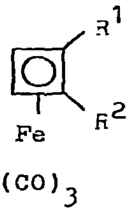
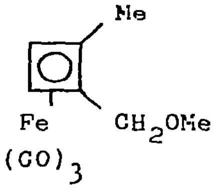


(5.5)

Schmidt has prepared the optically active (-)cyclobutadiene (5.5; R^1 = Me, R^2 = Et) by reduction of the corresponding (-) acid (5.5; R^1 = CO_2H, R^2 = COMe) and oxidized it with cerium(IV) in the presence of $MeO_2CCH{=}CHCO_2Me$ to form the butadiene adduct which was 40% racemic. In the same way, oxidation in the presence of tetracyanoethylene gave wholly racemic adducts. These results were used as evidence for the formation of free butadiene during the oxidation[129].

An optically active cyclobutadieneiron tricarbonyl (5.6) was decomposed with ceric ammonium sulphate in acetone solution in the presence of the symmetrical dieneophiles tetracyanoethylene, benzoquinone and N-phenylmaleimide. The Diels-Alder adducts of the liberated cyclobutadiene were examined and there was no evidence for the retention of optical activity. This suggested that the cyclobutadiene was free from the metal's influence when the adducts were formed[130].

Grubbs and Grey have resolved the disubstituted cyclobutadiene complex (5.7; R = OMe) into optically stable enantiomers by conversion of the methoxyl group to the dimethylamino group (5.7; R = NMe$_2$) through a bromo intermediate (5.7; R = Br) and formation



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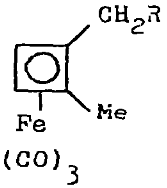
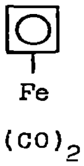


(5.7)

of the (+)-camphor-10-sulphonate of the dimethylamine. The resolved amine was reconverted to the starting material (5.7; R = OMe) by treatment of the methiodide (5.7; R = NMe$_3$I) with methoxide. The resolved complex showed less than 5% racemization when it was heated to 120° for 46 hours. By contrast, a butadiene complex, (+)-(methyl 5-formylpenta-2,4-dienoate)iron tricarbonyl racemized with $t_{\frac{1}{2}}$ = 46.5 hours at 119.4°. The optical stability of the cyclobutadiene complex was ascribed to the requirement for the ligand to become completely detached from the metal atom for racemization to occur[131].

The reaction of cyclobutadieneiron tricarbonyl with nitrosonium hexafluorophosphate gave the air stable, yellow orange complexes of cyclobutadieneiron dicarbonyl nitrosyl hexafluorophosphate $[R_4C_4Fe(CO)_2NO]^+PF_6^-$ (R = H, Me, Ph). These complexes readily underwent monocarbonyl substitution with various Lewis bases (L) to afford products of the type $[R_4C_4Fe(CO)_2(NO)L]^+PF_6^-$ (R = H, L = Ph_3P, Ph_3As, Ph_3Sb; R = Ph, L = Ph_3P, Ph_3As). A dicarbonyl substitution product $[R_4C_4Fe(NO)L_2]^+PF_6^-$ [R = Ph, L = $(PhO)_3P$] was also obtained[132].

UV irradiation of matrix isolated π-cyclobutadiene iron-



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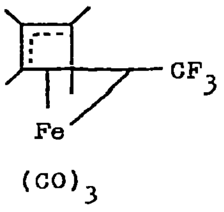

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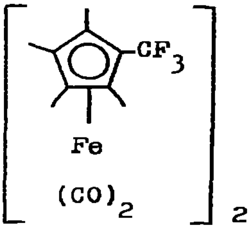


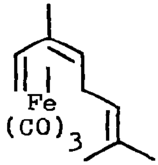
(5.10)

carbonyl in krypton at 8°K gave the dicarbonyl (5.8) as the primary photochemical product. The authors suggest that this intermediate forms adducts with dienophiles directly without generation of free cyclobutadiene[133].

The UV irradiation of (π-tetramethylcyclobutadiene)iron tricarbonyl with trifluoroethylene in hexane led to the formation of the bridged complex (5.9) by insertion of 1,1,1-trifluoroethylidene. Thermolysis of this product led to ring expansion and gave the dinuclear complex (5.10)[134].

5. (ii) (Acyclic π-diene)$Fe(CO)_3$ and (π-trimethylenemethane)$Fe(CO)_3$ complexes

Dieneiron tricarbonyl adducts were formed by treatment of five monoterpenes with iron carbonyls. The cis-ocimene (5.11) and cis-allo-ocimene complexes (5.12) underwent both skeletal and double bond rearrangement on heating, treatment with alumina and treatment with triphenylmethyl fluoroborate followed by borohydride. The mechanism of the thermal isomerization was determined by tracer studies. Hydroboronation of the adducts (5.11 and 5.12) gave products which were decomposed under mild conditions to form novel dihydromonoterpenes[135].



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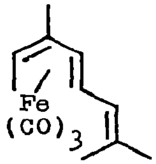

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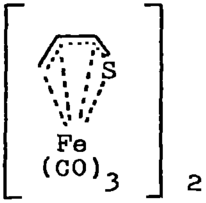

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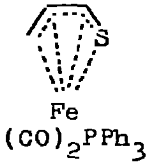
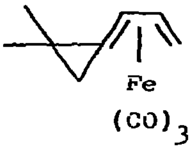


(5.14)

Treatment of thiacyclobutene with either diiron nonacarbonyl (thermally) or with iron pentacarbonyl (photochemically) gave the iron complex (5.13) which was converted to the monomeric complex

(5.14) on treatment with triphenylphosphine[136]. A series of dienes, for example butadiene, cyclopentadiene, 1,3-hexadiene, and $Fe_2(CO)_9$ were heated together in an autoclave or alternatively in benzene to give diene π-complexes of iron[137].

Heating a mixture of the *syn* and *anti* isomers of 2,2-dimethylallylidenecyclopropane with diiron nonacarbonyl gave the diene complex (5.15) together with the trimethylenemethane complexes (5.16 and 5.17) by ligand rearrangement. The products (5.15 and 5.16) were formed from the *syn* isomer while the product (5.16) together with traces of (5.17) were obtained from the *anti* isomer[138].



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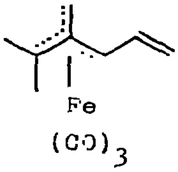

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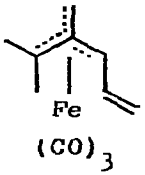


(5.17)

The crystal and molecular structure of the mixed complex (π-1,4-diphenyl-1,3-butadiene)iron tricarbonyl.$\frac{1}{2}$(1,4-diphenyl-1,3-butadiene) has been determined. The complexed butadiene ligand was cis and planar, it was bonded to the iron atom in the usual way with Fe-C distances of 2.076, 2.079. 2.165 and 2.165Å. The uncomplexed butadiene molecule was trans and planar and the two species were held together in the crystal by Van der Waals forces[139].

The crystal and molecular structure of cinnamaldehydeiron tricarbonyl was determined by X-ray methods. The π-diene character of the ligand was confirmed and the oxygen atom was not bonded to iron. The similarity between this structure and that of π-N-cinnamylideneanilineiron tricarbonyl was noted[140].

The crystal and molecular structure of 1,4-diphenylbutadieneiron tricarbonyl has been determined by X-ray crystallograpny. The butadiene group was bound to iron in the form of a tetragonal pyramid with two different iron-carbon bond lengths, 2.12 and 2.14Å. The phenyl rings were twisted appreciably out of the plane of the butadiene group[141].

The PMR spectra of trismethylenemethaneiron tricarbonyl $[(CH_2)_3CFe(CO)_3]$ (5.18) and $(CH_2)_3CFe(CO)_2(^{13}CO)$ (5.19) in N-(p-methoxybenzylidene)-p-n-butylaniline were recorded at 220 MHz. The observed spectrum of (5.19) resembled a broadened spectrum of (5.18) and this could have arisen from an intermediate rate of rotation or from insufficient resolution[142].

The complexes formed between butadiene, methylbutadienes or trimethylenemethane ligands and iron tricarbonyl groups or their trifluorophosphine and mixed carbonyl-trifluorophosphine analogues were investigated by IR and NMR spectroscopy. Trimethylenemethaneiron tricarbonyl was the only tricarbonyl with all of the carbonyls equivalent and C_{3v} symmetry. The remaining compounds were based on a square pyramid with one carbonyl group occupying an apical position and the other two on basal sites. Carbon-oxygen stretching force constants were calculated for apical and basal carbonyls and used to predict the most stable isomers of the trifluorophosphine derivatives. A Huckel MO description of the diene ligands was used to explain the changes observed in the force constants for the complexes. ^{19}F NMR spectroscopy showed that intramolecular exchange of PF_3 and CO was taking place in mixed complexes by concerted rotation of the ligands about the iron atom so that their relative positions remained fixed[143].

The separation of dieneiron tricarbonyl complexes by gas chromatography has been described. In the absence of air, quantitative separations were achieved on methylsilicone gum in teflon columns at temperatures up to 150° [144].

Mixtures containing diene- and dienone-iron tricarbonyl complexes were separated rapidly and quantitatively by reversed phase liquid chromatography. The technique was convenient for use with compounds that were of low stability at temperatures required for gas chromatography[145].

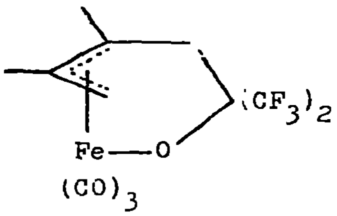
The kinetics of the substitution of olefinic ligands by triphenylantimony in (π-monoolefin)tetracarbonyliron

$$Fe(CO)_4(CH_2{=}CHX) + SbPh_3 \rightarrow Fe(CO)_4SbPh_3 + CH_2{=}CHX$$

$$(X = OEt,\ Ph,\ Bu,\ Cl,\ Br,\ CN,\ CO_2Me)$$

was studied in toluene solution. The reaction proceeded by a dissociative mechanism and there was an appreciable mass law retardation effect which indicated that $Fe(CO)_4$ was produced as an intermediate. The results also led to the conclusion that π-backbonding between the metal and the olefinic ligand was the major contributor to the strength of the metal-olefin bond[146].

Hexafluoroacetone has been shown to insert into a carbon-hydrogen bond in the diene ligands of methyl and dimethylbutadiene complexes. The UV irradiation of (π-2,3-dimethylbutadiene)iron tricarbonyl with hexafluoroacetone gave the bridged π-allyl complex (5.20)[147]. The acylation of the irontricarbonyl complexes (5.21) followed by reduction gave the alcohols (5.22) and then dehydroxylation with fluoroboric acid produced the salts (5.23). Treatment of the salt (5.23a) with a tertiary amine gave the complex (5.24) whilst under similar conditions (5.23b) and (5.23c) gave the quaternary ammonium salts (5.25)[148].



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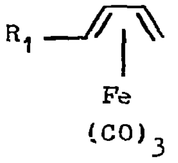

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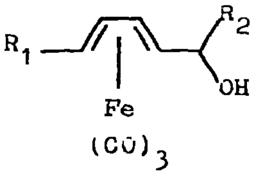

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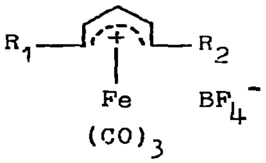
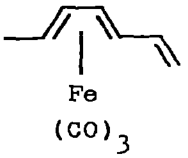


(5.23)

(a) $R_1 = R_2 = Me$
(b) $R_1 = H$, $R_2 = Me$
(c) $R_1 = H$, $R_2 = Et$



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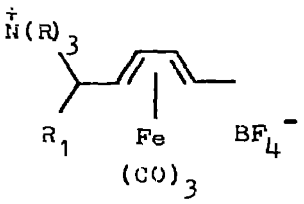

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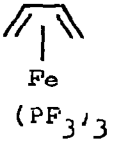
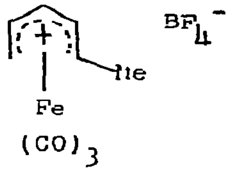


(5.26)

The Friedel Crafts acetylations of the (syn-)1- and 2-acetoxybutadieneiron tricarbonyl complexes were investigated[149]. The molecular structure of tetrafluoroethyleneiron tetracarbonyl was investigated by gas-phase electron diffraction. The data obtained was consistent with a distorted octahedral complex of iron with C_{2v} symmetry. The results suggested that the C_2F_4 unit resembled a fragment of perfluorocyclopropane rather than perfluoroethylene, and that the complexing with the iron was sigma, rather than pi, in character[150].

The UV irradiation of butadiene and $Fe(PF_3)_5$ in ether gave the π-butadiene complex (5.26). Similar reactions were carried out with twelve other conjugated dienes and in each case the product was an air-stable compound that was sublimed unchanged[151]

syn-(1-Methylpentadienyl)iron tricarbonyl fluoroborate (5.27) was prepared by dissolving the alcohol (5.28) in anhydrous fluoroboric acid. When a suspension of (5.27) in methylene chloride was treated with basic alumina for one hour the volatile



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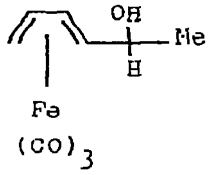

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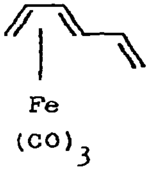

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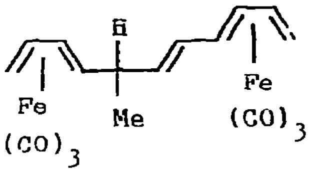


(5.30)

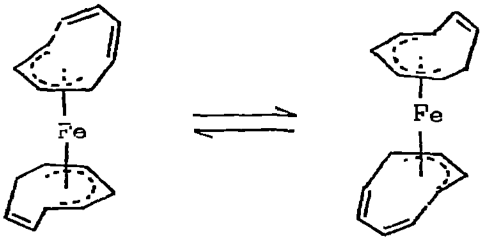
syn complex (5.29) was isolated. If the reaction was allowed to continue for 60 hours two closely related isomers of syn,syn-1,3,8,10-(5-methyl-1,3,6,10-undecapentaene)diiron hexacarbonyl (5.30) were isolated[152].

5. (iii) (Cyclic π-diene)$Fe(CO)_3$ complexes

The crystal structure of bis(cyclooctatetraene)iron was determined by X-ray analysis. In the monoclinic cell of $(C_8H_8)_2Fe$

(space group C/2c a = 25.13, b = 10.68, c = 13.98 Å; β = 99.6°, z = 12) there were two non-equivalent molecules one of which showed evidence of disorder. Broad line PMR spectra of a polycrystalline sample indicated that the molecules were undergoing a dynamic rearrangement as shown (5.31)[153].

The reaction of 1,7-cyclododecadiyne with $Fe(CO)_5$ gave $C_{12}H_{16}Fe_2(CO)_6$ (major product) and $C_{12}H_{16}Fe(CO)_3$. The structure of the major product (5.32) was determined by X-ray diffraction techniques and this was found to be different from the structure (5.33) originally proposed by King and Haiduc[154,155].



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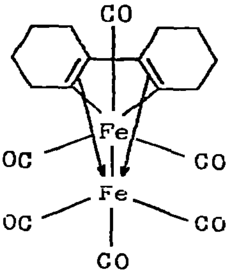

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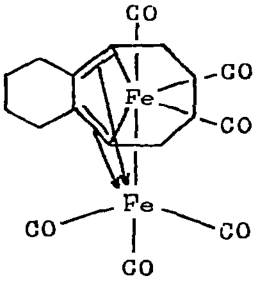
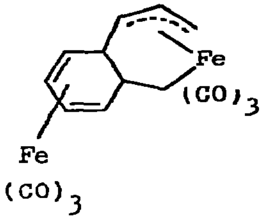


(5.33)

Churchill and DeBoer have determined the crystal and molecular structure of heptafulveneiron tricarbonyl by X-ray methods and have shown that iron is bound to a trimethylenemethane group in the hydrocarbon ligand. The bond lengths in the 1,6,7,8-tetrahaptoheptafulveneiron tricarbonyl were Fe-C-(central) 1.946 Å and Fe-C(peripheral) 2.120-2.192 Å [150].

At least four products were formed when diiron nonacarbonyl was treated with bicyclo[6.2.0]deca-2,4,6-triene; one of those which involved ligand rearrangement has been investigated structurally by X-ray diffraction. It contained a 1,3-cyclohexadiene group bonded to iron together with a second iron tricarbonyl



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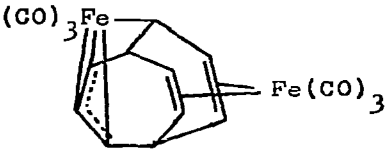


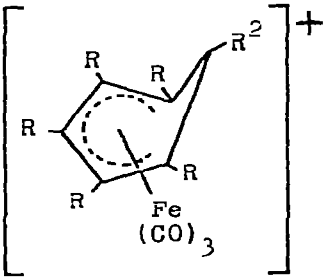
(5.35)

residue linked through a σ-bond to methylene and a π-bond to an allyl group (5.34)[157].

An X-ray single crystal study of the bullvalene complex (5.35) showed that the three membered ring in bullvalene was opened to give the bicyclo[3,3,2]deca-3,6,9-triene-2,8-diyl ligand. This ligand was π-bonded to one iron tricarbonyl group through two olefinic bonds and to a second iron tricarbonyl group by an iron-carbon σ-bond and a π-allyl group[158].

The ^{13}C NMR spectra were reported for the irontricarbonyl complexes (5.36; R = H, Me) and they were compared with the spectra of the cation (5.37). It was concluded that the irontricarbonyl group participated in the delocalization of the positive charge in the complexes (5.36)[159].

Cycloheptatrienyliron tricarbonyl anion was prepared by the reaction of alkyllithium reagents with cycloheptatrieneiron tricarbonyl. The room temperature PMR spectrum of the anion displayed a singlet at $\tau = 5.35$ which was indicative of a fluxional structure. The stable anion underwent oxidation as well as nucleophilic substitution to produce the 7-substituted derivatives[160]



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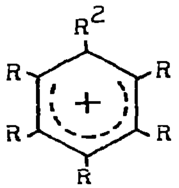


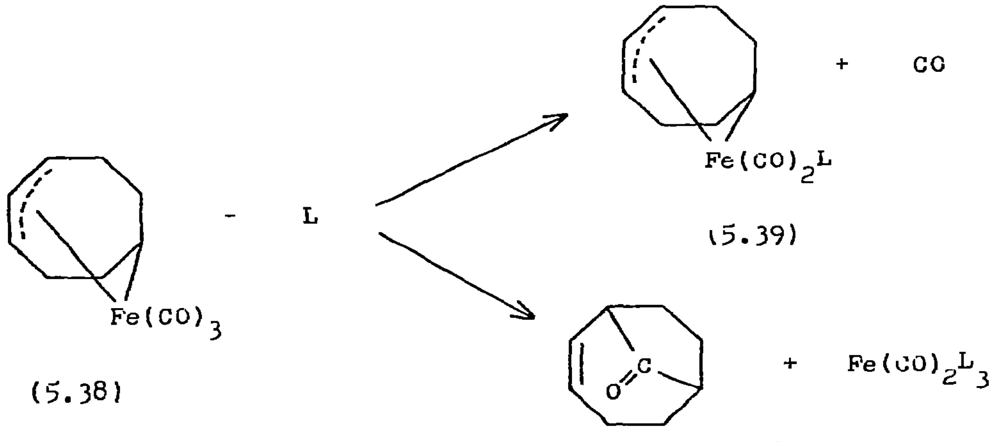
(5.37)

The NMR spectrum of polycrystalline tricarbonyl(π-cyclooctatetrene iron at 200° was examined in detail. Previously derived equations for the NMR line shapes were reviewed[161,162]. Fourier transform ^{13}C NMR spectroscopy has been used to investigate the fluxional behaviour of (π-cyclooctatetraene)iron tricarbonyl. The spectrum recorded at temperatures of -120° and below was in agreement with the rigid structure of the molecule and the multiplicity of the carbonyl resonances demonstrated the absence of exchange at these temperatures. At higher temperatures, both ring-atom and carbonyl exchange processes were operating independently[163].

Deganello has used room temperature ^{13}C NMR spectroscopy to distinguish between fluxional and non-fluxional π-cycloheptatriene and π-cyclooctatriene diiron hexacarbonyl complexes. Observation of the spectra over a range of temperatures indicated that at least two rearrangement processes were involved[164].

Chierico and Mognaschi have investigated the origin of the structural disorder observed in bis(cyclooctatetraene)iron and the motion that may take place in the crystal, by wide line NMR spectroscopy. The second moment has been calculated for the rigid lattice and compared with the experimental second moment. Below -165° the line width was constant and the rate of the motions in the crystal was not great enough to affect the second moment. At higher temperatures the molecules began to move at a greater rate. It was concluded that the disorder observed at room temperature was dynamic, rather than static, in character. The only type of motion at this temperature was completely activated and consisted of small oscillations of the cyclooctatetraene rings and not rotations of the rings[165].

The kinetics of the reaction of the iron-carbonyl complex (5.38) with a number of substituted phosphines and phosphites was examined under pseudo first order conditions using infrared spectroscopy. With PPh_3 or $P(OPh)_3$ substitution of the carbon monoxide molecule *trans* to the iron-carbon bond took place via a CO dissociative mechanism. The reaction of (5.38) with more nucleophilic ligands (alkylphosphines and phosphites) followed two distinct reaction paths. One involved the dissociative path to give (5.39; L = phosphine) and one in which the transannular ketone (5.40) was formed[166].

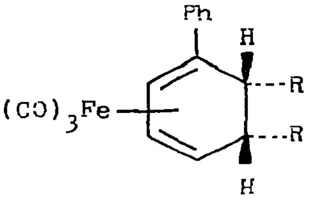


(5.38)

(5.39)

(5.40)

The 1,5 migration of hydrogen in cyclic-diene iron tricarbonyl complexes was investigated. For example the complex (5.41) isomerized to give a mixture of (5.41 and 5.42) when heated in xylene. On the basis of stereochemical studies and isotope effects a mechanism was proposed for this unusual reaction[107].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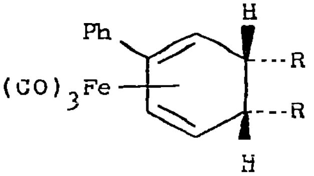
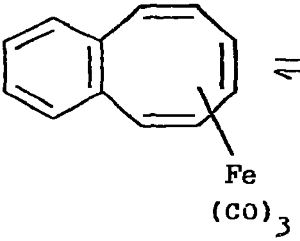

(5.42)

R = H or D

Whitlock and Stucki have reinvestigated shift isomerism in the benzocyclooctatetraene complex (5.43) and its 2,3-naphtho analogue and demonstrated that both are fluxional molecules. The low temperature limiting NMR spectra were reached at -15° and 70° respectively. Line shape analysis of the tetradeuterio derivative of the complex (5.43) enabled the activation energy for the process ($5.43 \rightleftharpoons 5.44 \rightleftharpoons 5.45$) to be determined as 16.6 kcal mole^{-1}. The rate of shift isomerism for the 2,3-naphtho analogue of (5.43) was estimated and gave an activation energy of 31 kcal mole^{-1}. Comparison of these activation energies with the value for the same process in cyclooctatetraeneiron tricarbonyl (7.2 kcal mole^{-1}) indicates that the large difference may be ascribed to the energy of the ortho quinoidal intermediate (5.44) and its analogue in the 2,3-naphtho compound. These results may also be contrasted with the facile shift isomerism in the benzocyclooctatetraene diiron complex (5.46) which has an activation energy of 8.1 kcal mole^{-1} and where isomerisation may involve a "twitch"



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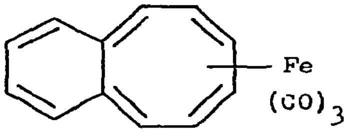

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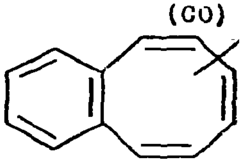

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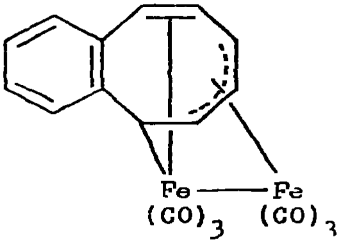
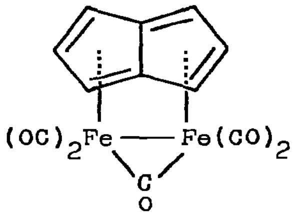


(5.46)

mechanism[168].

Hunt and Russell have described the formation of a stable π-complex of 1-phenylpentalene. Iron pentacarbonyl was stirred with 3-phenyl-1,2-dihydropentalene in methylcyclohexane at 110° to give the octahapto diiron complex (5.47) in 12% yield[169]. The reactions of bis-trimethylsilylacetylene and bis-trimethylsilylbutadiyne with $Fe_3(CO)_{12}$, $Co_2(CO)_8$ and $C_5H_5Mn(CO)_3$ was studied. Both the acetylenes with $Fe_3(CO)_{12}$ gave the stable complexes $Fe(CO)_4(Me_3SiC_2SiMe_3)$ and 2,5-bis-trimethylsilylcyclopentadienone iron tricarbonyl dimer (5.48) respectively. Both the acetylenes with $Co_2(CO)_8$ gave the familiar bridging acetylene complexes and the reaction of bis-trimethylsilylacetylene with cyclopentadienylmanganese tricarbonyl gave $C_5H_5Mn(CO)_2$-$(Me_3SiC_2SiMe_3)$[170].

King and Ackermann have reported the direct formation of tricarbonylferrole-iron tricarbonyl derivatives (5.49) from



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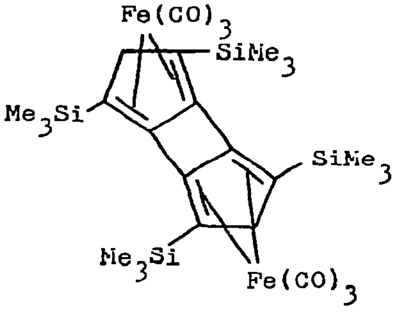
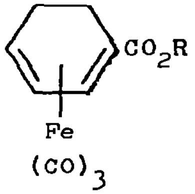


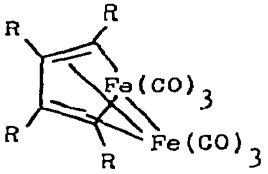
(5.48)

alkynes or macrocyclic alkadiynes and the benzalacetone complex (π-PhCH=CHCOMe)Fe$(CO)_3$ in boiling benzene. The benzalacetone complex provides a convenient source of Fe$(CO)_3$ groups free from Fe$(CO)_4$ groups and side reactions were insignificant.

Kruck and Knoll have reported the formation of the yellow crystalline complex π-C_5H_6Fe$(PF_3)_3$ on UV irradiation of cyclopentadiene and Fe$(PF_3)_5$ in ether. The cyclopentadiene complex



(5.50)

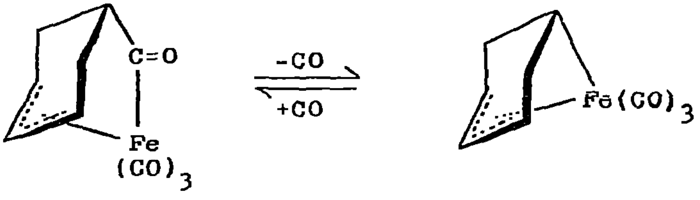


(5.49)

was converted to a cyclopentadienyl derivative, π-C_5H_5Fe$(PF_3)_2$H, on treatment with triethylamine[172].

Diene iron tricarbonyl complexes were formed by treatment of the isomeric methyl cyclohexadienecarboxylates with iron pentacarbonyl. The 'conjugated' complex (5.50; R = Me) was the most stable and was obtained from the others by heating with methanolic acid or methoxide. Isomerization was accompanied by hydrogen-deuterium exchange to give a monodeuterated product at the *endo*-6-H position. On this basis a π-allyl intermediate was suggested for the exchange process. The carboxyl group in the acid (5.50; R = H) was reduced to a primary alcohol by diborane while the ester (5.50; R = Me) was inert towards lithium aluminium hydride. Abstraction of a hydride ion from either one of two non-equivalent positions allylic to the diene group in the ester (5.50; R = Me) gave the corresponding π-cyclohexadienyliron tricarbonyl cations. Diene iron tricarbonyl complexes were also formed from three isomeric dihydro-*o*-toluic esters and iron pentacarbonyl[173].

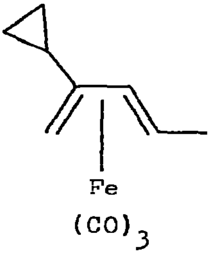
Aumann has isolated several π-complexes from the reaction between the vinylcyclopropane , bicyclo[3.1.0]hex-2-ene, and diiron nonacarbonyl in ether. One product contained the ligand bound to the $Fe(CO)_4$ group through the double bond. A second product with the same stoichiometry (5.51) contained the rearranged hydrocarbon moiety and this complex lost carbon monoxide to give a third π-complex (5.52). π-(1,3-Cyclohexadiene)iron tricarbonyl was formed from the π-allyl complex (5.52) by a further rearrangement. Similar transformations were achieved with the iron carbonyl complex of bicyclo[4.1.0]hept-2-ene and the same products were obtained by the borohydride reduction of the (π-cycloheptadienyl)-iron tricarbonyl cation[174].



(5.51) (5.52)

Sarel, Ben-Shoshan and Kirson have observed independently the formation of dieneiron tricarbonyl complexes from vinylcyclopropanes and iron pentacarbonyl. 1-Phenyl-1-cyclopropylethylene and its p-chloro derivatives were each heated with iron pentacarbonyl in di-n-butyl ether to give the 2-arylpenta-1,3-dienes in 55-61% yield. 1,1-Dicyclopropylethylene gave the expected product (5.53) on treatment with iron pentacarbonyl for 6 hours, but after heating for a further 10 hours the dienone complex (5.54) was formed by ring opening of the second cyclopropane ring with carbonyl insertion. The cyclohexenone derivative (5.54) was not formed on heating the diene complex (5.53) with iron pentacarbonyl[175].

The treatment of semibullvalene with iron enneacarbonyl gave four iron carbonyl complexes (5.55, 5.56. 5.57) and an unstable yellow oil which was not characterized[176]. In the reaction between cyclohexa-1,3-diene and $Ru_3(CO)_{12}$, Whitesides and Budnik have observed the catalytic cleavage of the cyclohexadiene ring and



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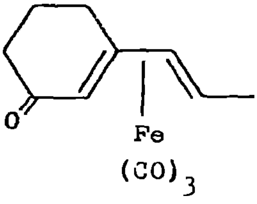

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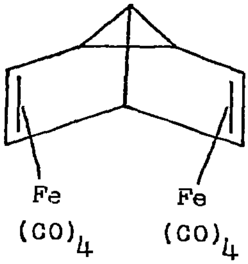
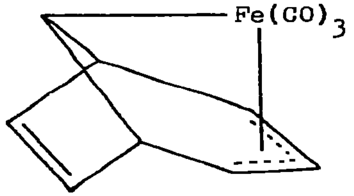


(5.55)

the formation of (cyclohexa-1,3-diene)ruthenium tricarbonyl. The latter product was favoured by a large excess of cyclohexadiene or by the use of benzene as a solvent. The cyclohexadiene complex was found to be an active catalyst for inter- and intra-molecular



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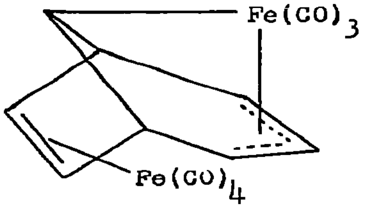
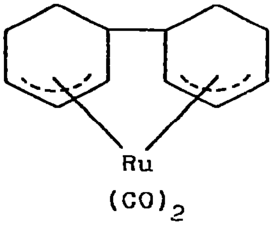


(5.57)

hydrogen transfer reactions. Treatment of the complex with cyclohexa-1,3-diene at the reflux temperature lead to the formation of benzene, cyclohexa-1,4-diene and cyclohexene together with a new ruthenium complex (5.58)[177].

Treatment of 1,3,5-trimethyl-1,4-cyclohexadiene with triiron dodecacarbonyl gave a mixture of the endo- (5.59; $R^1 = H$, $R^2 = Me$) and exo- (5.59; $R^1 = Me$, $R^2 = H$) diene iron compounds in the



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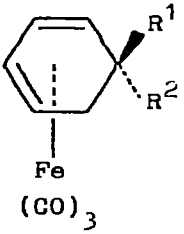

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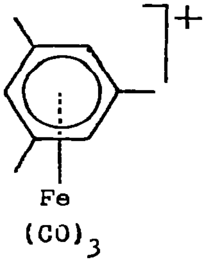
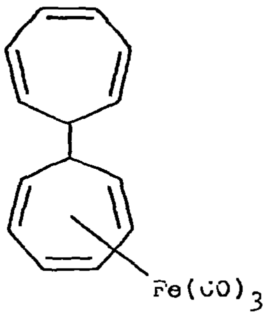


(5.60)

proportion 1:4. Hydride ion abstraction from the exo- isomer was achieved smoothly to yield the benzenonium complex (5.60) when the mixture was stirred with triphenylmethyl fluoroborate while the endo- isomer was recovered unchanged. The dimethylcyclohexadiene complex (5.59; $R^1 = R^2 = Me$) was also resistant to hydride ion abstraction[178].

The ditropyl iron complex (5.61) when treated with a molar quantity of tetracyanoethylene gave the complex (5.62). Treatment of complex (5.62) with an excess of tetracyanoethylene gave the di-adduct (5.63). The initial isolation of the complex (5.62)



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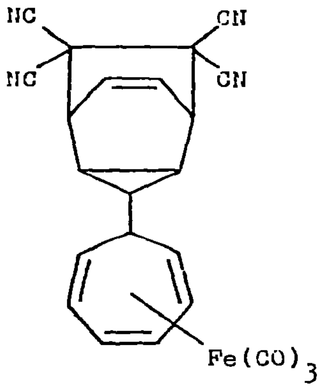

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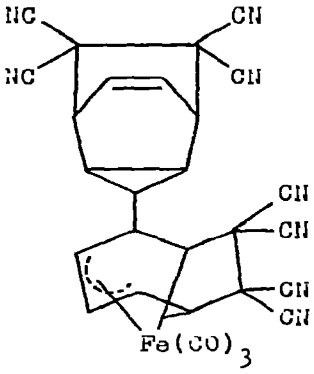
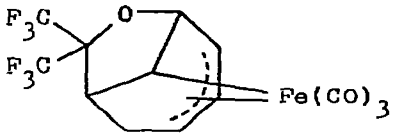


(5.63)

indicated that the tricarbonyliron group had deactivated the cycloheptatriene ring, to which it was coordinated, towards electrophilic attack[179].

The reaction of tricarbonylcycloheptatrieneiron with hexafluoroacetone, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, trans-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene and tetracyanoethylene gave the crystalline compounds (5.64-5.67) respectively. Similar adducts were formed when tricarbonyl-



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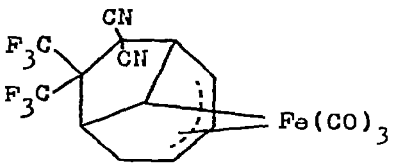
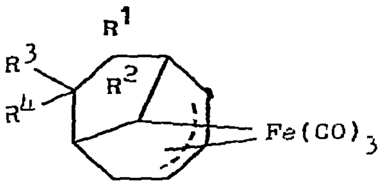


(5.65)

(methyl-, bromo-, and phenyl-cyclooctatetraene)iron were treated with tetracyanoethylene[180].

The complex 1,5-cyclooctadieneruthenium tricarbonyl has been



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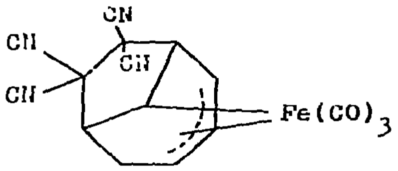


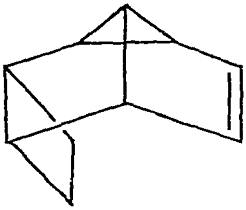
(5.67)

a; $R^1 = R^4 = CN$, $R^2 = R^3 = CF_3$
b; $R^1 = R^4 = CF_3$, $R^2 = R^3 = CN$
c; $R^1 = R^3 = CF_3$, $R^2 = R^4 = CN$

used as the source of several dieneruthenium tricarbonyl complexes. The new complexes were formed by heating the starting material with the appropriate ligand in benzene. Side reactions and polymerization were insignificant and high yields of products were obtained after short reaction times (~30 min). In this way, ruthenium tricarbonyl complexes were prepared of 1,3-cyclohexadiene 1,3-cycloheptadiene, cycloheptatriene, tropone, cyclooctatetraene and some dicyclic dienes[181].

In order to investigate the possible intermediate formation of σ- and π-allyl bonded iron in the reaction of vinylcyclopropane systems with iron carbonyls, rigid tricyclic hydrocarbons have been used as starting materials. Thus the tetracyclodecene (5.68) gave the complex (5.69) with diiron nonacarbonyl. Rearrangement of this product to the corresponding π-diene complex was inhibited by its structure and the intermediate role of σ and π-allyl bonding to iron in the formation of π-diene iron carbonyls was supported

Treatment of the bicyclononatriene (5.70) with diiron nonacarbonyl at room temperature led to extensive rearrangement of the hydrocarbon with the formation of four isomeric $(\pi\text{-}C_9H_{10})Fe(CO)_3$ complexes together with $Fe(CO)_4$ and $Fe_2(CO)_6$ complexes of C_9H_{10}[183].



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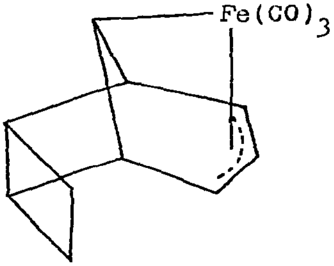
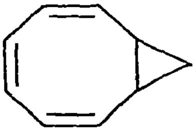


(5.69)

cis^4-Cyclononatetraeneiron tricarbonyl (5.71) was prepared from the reaction of *cis*-bicyclo[6.1.0]nonatriene either photochemically with iron pentacarbonyl or thermally with diiron nonacarbonyl. Additional complexes isolated from these reactions included the iron tricarbonyl complexes (5.72-5.74). The *cis*^{4}-cyclononatetraene complex (5.73) was a stable solid at room temperature but at 101° it underwent electrocyclic ring closure to give *cis*-dihydroindeneiron tricarbonyl (5.72). The complex (5.73) underwent protonation at -120° in FSO_3H-SO_2ClF to give the monocyclic cation (5.75)[124].



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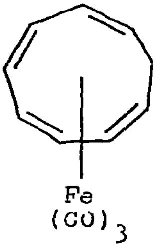

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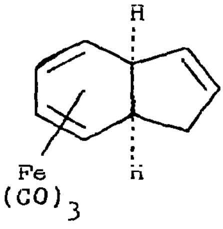
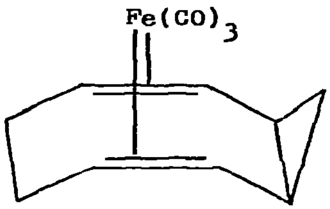


(5.72)

King, Haiduc and Eavenson have continued their investigations of intramolecular transannular cyclization in the reactions between macrocyclic alkadiynes and transition metal compounds.



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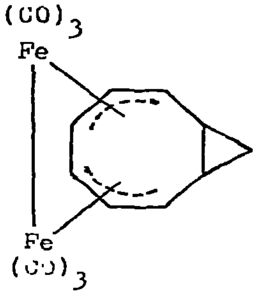

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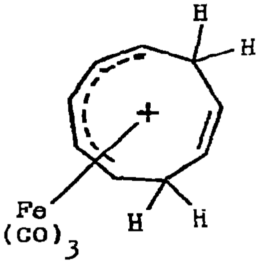
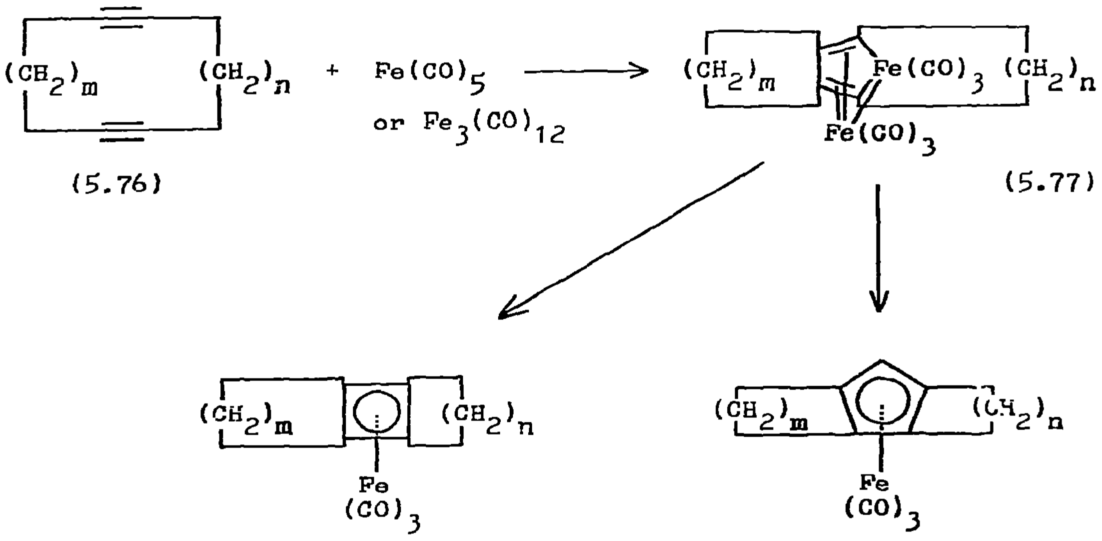


(5.75)

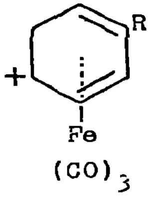
The alkadiynes (5.76; $m = 4$, $n = 4$, 5 and 6; $m = 5$, $n = 5$ and 6) were heated with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ to form initially the metallacyclopentadienes (5.77). These intermediates then lost a metal atom to form either the tricyclic cyclobutadiene derivatives (5.78) or the tricyclic cyclopentadienyl compounds (5.79). It was necessary for one bridge of at least five methylene groups to be present in the complex (5.77) for collapse of the ferracyclopentadiene to occur. When one bridge length was five (m or $n = 5$) then collapse to the cyclopentadienyl derivatives



(5.76) (5.77) (5.78) (5.79)

(5.79) was preferred[185].

Birch, Chamberlain and Thompson have investigated the oxidative cyclization of π-cyclohexadiene iron tricarbonyl complexes (5.81). Thus the cation (5.80; R = H,OMe) was treated with acetylacetone to give the diketone (5.81; R = H,OMe) and this compound was heated with manganese dioxide in benzene to form the dihydrofuran complex (5.82; R = H,OMe). Deuteration confirmed that cyclization proceeded stereospecifically with loss of the 6-endo-proton[186].



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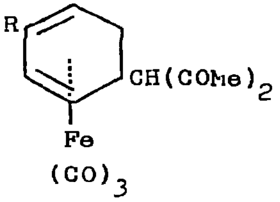
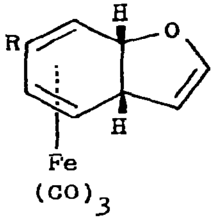


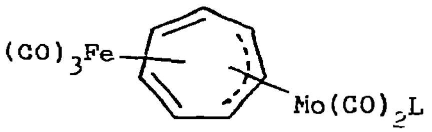
(5.81)



(5.82)

Compounds of the type LMo(CO)$_2$C$_7$H$_7$ [L = B(C$_3$N$_2$H$_3$)$_4$, HB(C$_3$N$_2$H$_3$)$_3$, HB(3,5-Me$_2$C$_3$N$_2$H$_2$)$_3$ and H$_2$B(3,5-C$_3$N$_2$H$_2$)$_2$] were treated with Fe(CO)$_5$ to give the corresponding Fe(CO)$_3$ adducts. The starting compounds and the adducts were fluxional molecules with the C$_7$H$_7$ ring resonances appearing as singlets in the PMR spectra. It was thought that the Fe(CO)$_3$ group was attached to the butadiene portions of the C$_7$H$_7$ rings (5.83)[187].

Graf and Lillya reported the electrophilic substitution of tricarbonyl(norbornadiene)iron. Treatment of this complex with equivalent amounts of dichloromethyl methyl ether and titanium tetrachloride gave the aldehyde (5.84). Reduction of the aldehyde (5.84) with lithium aluminium hydride - aluminium chloride gave the corresponding methyl derivative[188, 189].



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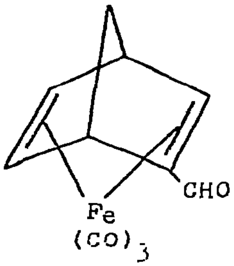
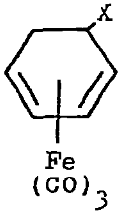


(5.84)



(5.85)

The cation $[C_6H_7Fe(CO)_3]^+$ was shown to behave as an electrophile with a wide variety of aromatic compounds to give the iron carbonyl complexes (5.85; X = indolyl, methylindolyl, pyrrolyl, furyl, thienyl, imidazolyl and ferrocenyl). The reactions were carried out in water of polar organic solvents but no reaction was observed with benzene, alkylbenzene, anisole or phenol[190].

The chromatographic separation of 1- and 2-methoxy derivatives of cyclohexa-1,3-diene iron tricarbonyl complexes has been described and the site of hydride ion abstraction from them by triphenylmethyl fluoroborate determined. The resulting cyclohexadienyl complexes have, in turn, been treated with borohydride, hydroxide and morpholine in order to define the sites of nucleophilic addition. The reactions of enamines and ketones with cyclohexadienyl iron complexes have also been examined[191].

5. (iv) $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_6)$

When benzenecyclopentadienyliron was heated to 40° in tetrahydrofuran it gave ferrocene (51%).

$$2C_6H_6FeC_5H_5^+ \longrightarrow (C_5H_5)_2Fe + 2C_6H_6 + Fe^{2+}$$

In a similar manner naphthalenecyclopentadienyliron was converted to ferrocene[192].

5. (v) $(\pi\text{-}C_5H_5)_2Ru$

Electron delocalization in ruthenocene and ferrocene was studied by the attachment of a variety of spin label systems to the cyclopentadienyl ring. The spin label systems used included semidione radical anions, semiquinone radical anions, ketyl radical anions and naphthyl radical anions. Ruthenocene and ferrocene were found to be relatively inefficient in the delocalization of electron spin density regardless of the spin label employed[193].

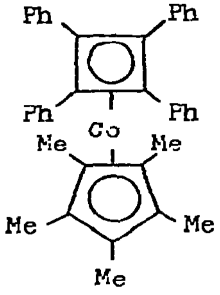
Decachlororuthenocene has been prepared from ruthenocene by seven successive lithiation and chlorination steps. Each step involved the heteroannular dilithiation of the metallocene with n-butyllithium-TMEDA in hexane or THF and addition of the lithiation mixture to hexachloroethane. In the early reactions, polylithiation and metal-halogen exchange combined to give complex mixtures of products. Decachlororuthenocene was obtained in 14% yield overall. In the corresponding synthesis of decachloroferrocene, the product was obtained in 42% yield from 1,1'-dichloroferrocene. The decachlorometallocenes were heteroannularly dimetallated with n-butyllithium and the lithio intermediates were treated with iodine to give the 1,1'-diiodooctachlorometallocenes. The physical properties of the decachloro- and the intermediate polychloro-compounds were reported[194].

Radioactive methylruthenocenecarboxylate ^{103}Ru was prepared by heating methylferrocenecarboxylate with $^{103}RuCl_3$[195].

6. (i) $(\pi\text{-}C_4H_4)Co(\pi\text{-}C_5H_5)$

The crystal and molecular structure of (π-cyclopentadienyl)-[π-trans-diphenyl-bis(trimethylsilyl)cyclobutadiene]cobalt has been confirmed by a single crystal X-ray investigation. These results[196] concur with the independent structural studies on both the *cis*- and *trans*-isomers reported by Kabuto and co-workers[197].

King and co-workers reported the reaction of $(Me)_5C_5Co(CO)_2$ with diphenylacetylene to give the tetraphenylcyclobutadiene derivative (6.1), and with 1,7-cyclododecadiyne to give the tricyclicbutadiene derivative (6.2). The manganese compounds $(Me)_5C_5Mn(CO)_2PPh_3$, $[(Me)_5C_5Mn(CO)_2NO]PF_6$ and $[(Me)_5C_5Mn(CO)(NO)PPh_3]PF_6$ were prepared from $(Me)_5C_5Mn(CO)_3$ by routes that were analogous to those used for the preparation of the corresponding unsubstituted cyclopentadienyl derivatives using $C_5H_5Mn(CO)_3$[196].



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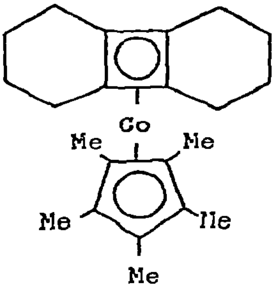
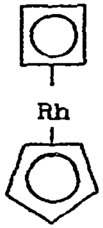


(6.2)

The photolysis of photo-α-pyrone and π-cyclopentadienyldicarbonylrhodium in benzene solution gave π-cyclopentadienyl-π-cyclobutadienerhodium (6.3) and a dinuclear complex (6.4). The treatment of the complex (6.3) with acetic anhydride and tin(IV) chloride gave π-cyclopentadienyl-π-acetylcyclobutadienerhodium which illustrated the great reactivity of the π-cyclobutadiene ring towards electrophilic substitution[199].



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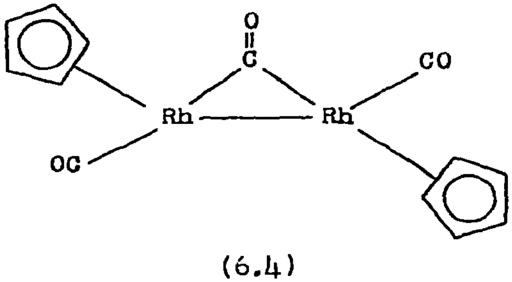


(6.4)

6. (ii) $(\pi-C_5H_5)_2Co$ and $[(\pi-C_5H_5)_2Co]^+$

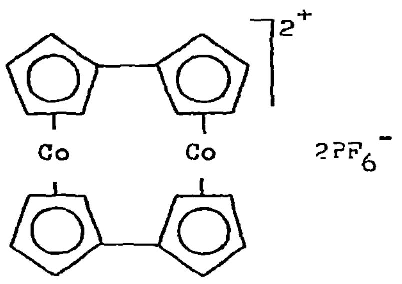
The half-wave potential of the cobalticinium-cobaltocene couple at a dropping mercury electrode was used as a reference potential against which the potential of a glass electrode was measured. This was utilized for the determination of hydrogen ion activity in basic media such as aqueous hydrazine and aqueous ethylenediamine[200].

The g values and the hyperfine structure parameters for the orbitally degenerate doublet ground state of cobaltocene were determined by electron paramagnetic resonance and compared with the theoretically predicted values[201].

An EPR study of cobaltocene complexed with tetracyanoethylene (TCNE), tetracyanoquinodimethane, 2,3-dichloro-5,6-dicyanoquinone and chloranil has been carried out. The last three complexes gave only single line spectra but the spectrum of the TCNE complex was complex and was assigned to contributions from three sources[202].

Davison and Smart have developed a convenient procedure for the synthesis of the bisfulvalene complexes (6.5 and 6.6). Dihydrofulvalene was formed in THF at -78° by the reaction of iodine with two equivalents of sodium cyclopentadienide and was deprotonated to the corresponding dianion with n-butyllithium. Anhydrous cobalt chloride was stirred into the reaction mixture and after twelve hours it was acidified and oxidized with gaseous oxygen. The addition of ammonium hexafluorophosphate gave the product (6.5). Different proportions of the same reactants led to the complex (6.6) rather than (6.5)[203].

Sheets and Kirsch have described a convenient procedure for the synthesis of cobalticinium salts in 30-50% yield, neither an inert atmosphere nor anhydrous conditions are required. Mono- and



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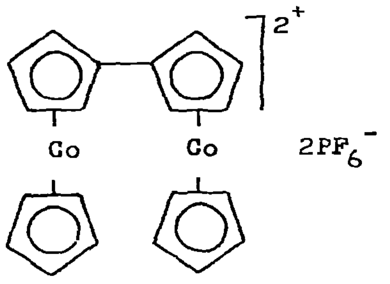

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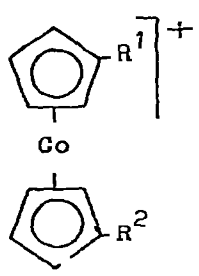


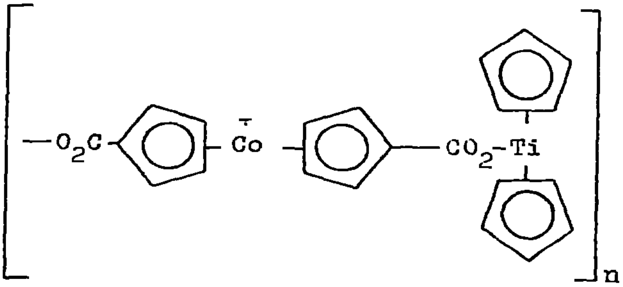
(6.7)

di-substituted compounds (6.7; R^1 = Me, R^2 = H; R^1 = CO_2H, R^2 = H; $R^1 = R^2$ = H, Me, CO_2H) were prepared from cyclopentadienylthallium which was generated in situ. Thus methylcyclopentadiene, cyclopentadiene and anhydrous TlOH in ethanol were stirred together to give the intermediate thallium complex. A solution of cobalt chloride in aqueous dimethylsulphoxide was added to give a mixture of the three products (6.7; R^1 = Me, R^2 = H; $R^1 = R^2$ = H, Me) in 50% yield[204].

The electronic absorption spectra of cobalticinium salts, recorded in ethanol at room temperature, showed similarities to the spectra of the corresponding ferrocenes in both the number and form of the bands. The effect of electron donating substituents in increasing the electron density on the cyclopentadienyl ring was more important for the cobalticinium ion than for ferrocene. The absorption band at 400 nm, which was assigned to the $A_{2g}(1_{2g} \rightarrow 1_{2g}^{+})$ transition in ferrocene, corresponded to a similar transition in the cobalticinium ion[205].

The interfacial condensation of 1,1'-dicarboxycobalticinium hexafluorophosphate disodium salt with dicyclopentadienyltitanium hexafluorophosphate in nitrobenzene to water mixtures gave poly-{bis(oxycarbonylcyclopentadienyl)cobalt(III)[dicyclopentadienyltitanium(IV)]hexafluorophosphate} (6.8). The thermal stability of the polymer (6.8) was higher in nitrogen than in air and it underwent anion exchange in aqueous salt solutions to give soluble products[206].

(Trichloromethyl)cyclopentadiene was displaced from the cobaltocene (6.9) by treatment with iodine, silver nitrate, tetracyanoethylene or sulphur dioxide[207].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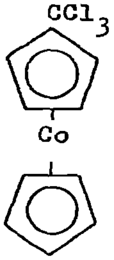
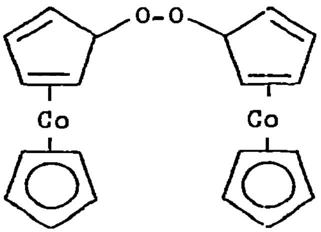

(6.9)

The reactivity of ferrocene and cobaltocene towards picric and trichloroacetic acids has been compared. A radical anion species was not formed from cobaltocene since the cobalticinium product from the reaction with trichloroacetic acid was diamagnetic. It was found that hydroxide ion did not reduce cobalticinium salts to cobaltocene although the ferricinium ion was reduced by this reagent[208].

Brown has investigated the reaction between cobaltocene and trimethylsilyl halides. Cobaltocene is rapidly oxidized to the cobalticinium ion by trimethylsilyl bromide and iodide at room temperature or below with the formation of $Me_3SiSiMe_3$. Trimethylsilyl chloride is inert in the absence of oxygen. A cobalticinium superoxide was proposed as the intermediate in this reaction in the presence of oxygen, it was detected by the NMR paramagnetic contact shift and was trapped as an adduct[209].

Leonova and Kochetkova have reviewed the reaction chemistry of cobaltocene and nickelocene. This is a good review and it has sections on, (i) substitution reactions of the carbon atoms, (ii) reactions in the side chains of substituted cobalticinium salts, (iii) reactions involving addition to the cyclopentadienyl ligand, (iv) ligand exchange reactions and (v) electron donating properties of cobaltocene and nickelocene[210].

Oxygen was taken up by a dry ethereal solution of cobaltocene to form the peroxide adduct (6.10) as an orange solid. This species had been proposed previously as an intermediate in the reaction of cobaltocene with compounds containing an active hydrogen atom in the presence of oxygen. The adduct (6.10) decomposed rapidly in air and slowly under nitrogen[211].



(6.10)

The oxygen adduct of cobaltocene, $[(C_5H_5)_2Co]_2O_2$, was found to be a good reagent for the oxidative cleavage of a carbon-carbon bond in α-diketones and o-quinones to give cobalticinium carboxylates. The oxidation also occurred when a mixture of cobaltocene and α-diketone (or o-quinone) was treated with molecular oxygen at a low temperature. For example benzil gave cobalticinium benzoate, $[(C_5H_5)_2Co]^+PhCOO^-$, which when treated with hydrogen chloride in ether produced benzoic acid and cobalticinium chloride in quantitative yields[212].

A series of cobalticinium hexafluorophosphates was prepared and used in the preparation of polyesters. For example 1,1'-

dichloroformylcobalticinium hexafluorophosphate was added to 1,4-butanediol to give the 1,4-butanediol-1,1'-dichloroformylcobalticinium hexafluorophosphate copolymer[213].

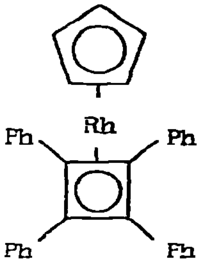
Cobaltocene mixed with activated halogen compounds was used as a photosensitive catalyst for the polymerization of vinyl monomers by ultraviolet irradiation. For example cobaltocene mixed with benzenesulphonyl chloride was used as a catalyst for the polymerization of hydroxyethyl acrylate by ultraviolet radiation[214].

Imai and Koizumi have used a catalyst prepared from cobaltocene and triisobutylaluminium in toluene under a nitrogen atmosphere for the isomerization of 5-alkenyl-2-norbornenes. Thus 5-vinyl-2-norbornene was converted to ethylidene-2-norbornene in 82.4% yield over 2 hours at 150° [215].

The reactivities towards triphenylphosphine shown by π-allylcobalt tricarbonyl (fast reaction with first-order kinetics) and π-cyclopentadienylcobalt dicarbonyl (slow reaction with second-order kinetics) were explained by IR and theoretical SCCCMO investigation of the compounds. The π-cyclopentadienyl ligand acted as an electron donor and facilitated a build up of electronic charge in the carbonyl π_t^* orbitals via the metal d_{xy} and d_{yz} orbitals. This led to a high M-C bond order and low C-O bond order as confirmed by the IR measurements. The high orbital population of the π_t^* orbitals caused the incoming nucleophile to be diverted towards the positive metal centre to give a slow bimolecular reaction[216].

Treatment of (π-cyclopentadienyl)(π-1,5-cyclooctadiene)rhodium(I) with diphenylacetylene at 180° under pressure gave (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)rhodium(I) in 3% yield. The crystal and molecular structure of this complex

(6.11) was determined by X-ray diffraction. The rhodium-cyclopentadienyl distance was 1.868 Å and the metal-cyclobutadiene distance was 1.826 Å. The planes of the two ligands were almost parallel and the planes of the phenyl groups were twisted with respect to the cyclobutadiene ring and bent away from the metal atom[217].

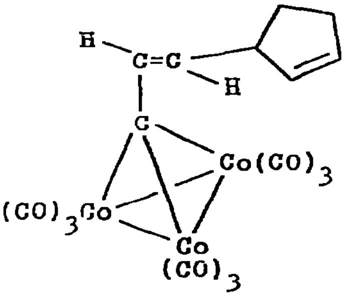


(6.11)

6. (iii) Cobalt-carbon cluster compounds

The reaction of norbornadiene with $XCCo_3(CO)_9$ (X = Me, Ph, MeO_2C, EtO_2C, F) gave the complexes $XCCo_3(CO)_7$(Norbornadiene). In contrast, the reaction of norbornadiene with $HCCo_3(CO)_9$ gave the complexes (6.12 and 6.13) and with $BrCCo_3(CO)_9$ and $ClCCo_3(CO)_9$ the norbornadiene dimerized to give Binor S (6.13a)[216].

Seyferth, Hallgren and co-workers have continued their



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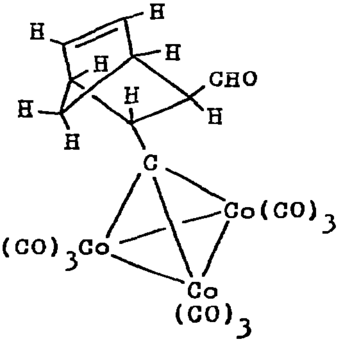

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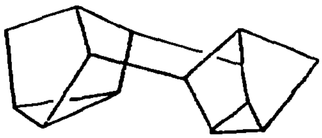

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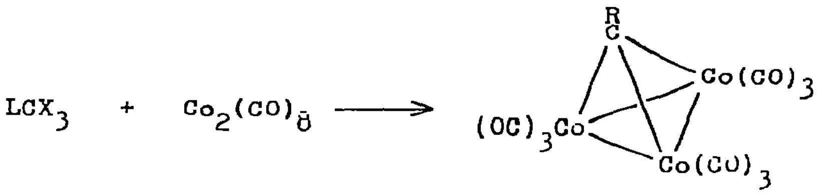
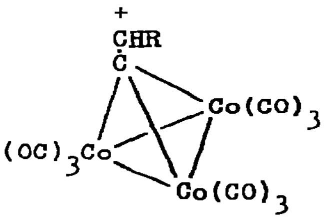


(6.14)

investigations of alkylidynetricobalt nonacarbonyl complexes and report the preparation of a number of functionally substituted complexes (6.14) from dicobalt octacarbonyl and alkyltrihalomethanes or alkyldihalomethanes in THF. The ratio of reactants preferred was 9 moles of dicobalt octacarbonyl to 5 moles of alkyl halide and the reactions proceeded at room temperature or on gentle heating (50°) to give yields of up to 50%. Compounds prepared by this method were as follows: [6.14; R = D, R_3Si, $(RO)_2P(O)$, $Me_3COC(O)$, $Me_3SiOC(O)$, $Et_2NC(O)$, RC(O), $Me_2COC(O)$, $HOCH_2$, HC(O), MeO, and Me_2N][219].

In a later paper from the same laboratory evidence was offered to support this mechanism and in particular the carbonium ion intermediate (6.15). Thus treatment of the ketones (6.14; R = CHO, COMe, COPh) with triethylsilane in benzene without the addition of trifluoroacetic acid gave the alcohols (6.14; R = CH_2OH, CHOHMe, CHOHPh) as was anticipated from the mechanism proposed. The alcohols were convenient starting materials for the preparation of the carbonium ions (6.15) by treatment with propionic anhydride and then aqueous HPF_6 under nitrogen. The PF_6^- salt of the carbonium ion (6.15; R = Me) was obtained as a black solid which was quite stable in the absence of air and moisture. The stability of the carbonium ions was attributed to σ-π overlap which was favoured by its structure. The salts, in either the solid state or in benzene solution were attacked by nucleophiles such as methanol, thiophenol and aniline to form the ether [6.14; R = CH(Me)OMe], the sulphide [6.14; R = CH(Me)SPh] and the secondary amine [6.14; R = CH(Me)NHPh] respectively. N,N-Dimethylaniline suffered electrophilic substitution by the carbonium ions (6.15; R = H, Ph) to form the p-substituted anilines [6.14; R = $CH_2C_6H_4NMe_2$-p, $CH(Ph)C_6H_4NMe_2$-p]^{220}.



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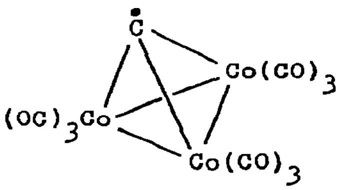
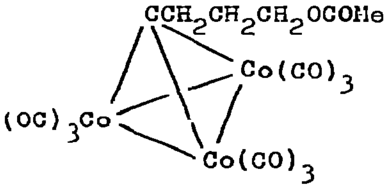


(6.16)

In addition to α-alkylidynetricobalt nonacarbonyl carbonium ions, the accessibility of the corresponding radical (6.16) has also been demonstrated this year by Seyferth and Hallgren. Methylidynetricobalt nonacarbonyl was stirred with allyl acetate and a catalytic quantity of azobisisobutyronitrile (AIBN) under reflux for nine days to form the olefin addition product (6.17) in 21% yield. A similar reaction with allyl ethyl ether gave the corresponding addition product $(OC)_9Co_3C(CH_2)_3OEt$. In the absence of the free radical initiator, AIBN, no reaction took place^{221}.

Seyferth, Hung and Hallgren have reported a new route to alkylidynetricobalt nonacarbonyl complexes. The readily available ketones (6.18; R = COalkyl, COaryl)were reduced to the products (6.18; R = alkyl, CH_2aryl) with triethylsilane and trifluoroacetic acid in THF at reflux temperature. Yields were good and fell within the range 67-92% for the ten compounds prepared. It was proposed that the reduction proceeded by addition of triethylsilane across the ketone double bond with subsequent loss of the triethylsiloxy anion and reduction of the resulting carbonium ion



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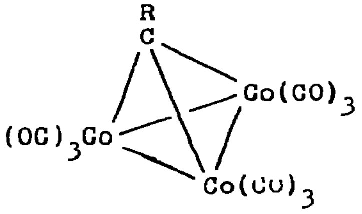

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(6.18; $R = \overset{+}{C}HR^1$) with a second molecule of triethylsilane[222].

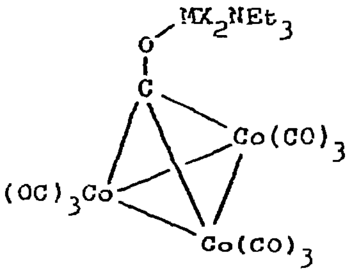
Methylidynetricobalt nonacarbonyl cluster compounds (6.19; M = B, X = Cl, Br; M = Al, X = Br) have been formed by heating dicobalt octacarbonyl with Cl_3BNEt_3, Br_3BNEt_3 or Br_3AlNEt_3 in benzene at 60°. The reaction mechanism was investigated by heating the same cobalt carbonyl with aluminium(III) bromide in benzene and isolation of the intermediate complexes $Co_2(CO)_8AlBr_3$ and $Co_3(CO)_9AlBr_2$ as well as the product $Co_3(CO)_9AlBr_2AlBr_3$[223].

Alkyl and alkenyl substituted methinyltricobalt enneacarbonyls were prepared by the reaction of $XCCo_3(CO)_9$ (X = H, D) with mono- and di-olefins in an autoclave at approximately 130°. It was

$$C_2H_4 + XCCo_3(CO)_9 \longrightarrow XCH_2CH_2CCo_3(CO)_9$$

thought that this reaction proceeded <u>via</u> a radical mechanism[224].

Radical anions $YCCo_3(CO)_9^-$, where Y = Et, F, $SiMe_3$, were obtained by reduction of the parent cluster compounds with sodium in ether. The deep red solutions of the radical anions were stable for several hours in the absence of air and each gave a complex ESR spectrum which confirmed interaction between the unpaired electron and the three equivalent cobalt nuclei and suggested that the $CCo_3(CO)_9$ cluster was an electron-withdrawing group[225].



(6.19)

Tricobaltcarbon cluster compounds, $RCCo_3(CO)_9$, R = H, Me, Et, F, Cl, Br, have found application as dimerization catalysts for cyclic dienes. For example bicyclo[2.2.1]hepta-2,5-diene was heated to reflux with the catalyst in methylene dichloride for 3 hours to give the corresponding dimer in 94% yield[226].

Halogenomethinyltricobalt enneacarbonyls were treated with aryl Grignard reagents to give the corresponding aryl-clusters in good yield. Substitution with alkyl Grignard reagents was

$$RMgBr + BrCCo_3(CO)_9 \longrightarrow RCCo_3(CO)_9 + MgBr_2$$

not possible. Treatment of the halogen-cluster compounds with organolithium reagents under a carbon monoxide atmosphere gave the corresponding acid, in good yield, which resulted from carbon

$$BrCCo_3(CO)_9 \xrightarrow[(ii)\ H_2O]{(i)\ RLi} HO_2CCCo_3(CO)_9$$

monoxide insertion. Grignard reactions carried out under a carbon monoxide atmosphere gave the acid in small yield[227].

7. (i) $(\pi\text{-}C_5H_5)_2Ni$

The rates of exchange of deuterium and tritium were determined for systems of nickelocene with Me_3COOH-Me_2SO-Me_3COK and

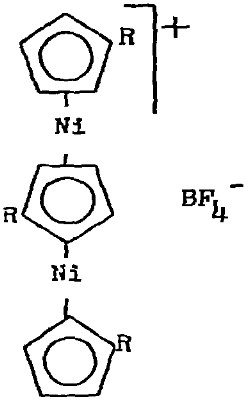
$O(CH_2CH_2OH)_2$-Me_3COH-Me_3COK. These rates were compared with the rates of exchange in ferrocene, triphenylmethane and diphenylmethane. The kinetic acidity of these compounds increased in the order: ferrocene $<$ $C_5H_5Mn(CO)_3$ $<$ Ph_2CH_2 $<$ Ph_3CH $<$ nickelocene. The kinetic isotope effect of nickelocene was determined and the reaction was found to proceed as a protophilic replacement of H[228].

Kobinata has used configurational interaction techniques to probe the electronic structure of nickelocene. Charge-transfer configurations involving ligand to metal electron transfer as well as locally-excited configurations of the metal ion were considered. In order to achieve the best correlation between the calculated and experimentally obtained *d*-*d* transition energies, the Racah parameters, the resonance integrals and the energies of the charge-transfer configurations were determined[229].

A PMR investigation of polycrystalline nickelocene and chromocene has confirmed that the resonance line shape and position and paramagnetism for each metallocene was independent of the temperature between 1.6 and 20°K. The observed and calculated line shapes for nickelocene at 4.2°K were compared, the best fit was obtained for the case where the electronic spin densities on nickel and each carbon atom were 1.5 and 0.05 respectively[230].

Symmetrically trisubstituted triple decker sandwich compounds (7.1; R = Me, Bu^t) have been prepared by Salzer and Werner by treatment of the appropriately 1,1'-disubstituted nickelocene with tetrafluoroboric acid, nearly quantitative yields were obtained The reaction involved a primary one-electron transfer and subsequent radical addition, or direct attack by the proton to give the diene (dienyl) cation $[Ni(C_5H_5)(C_5H_6)]^+$ which then underwent an ion-molecule reaction with a second molecule of nickelocene to give the product (7.1)[231].

The reaction of nickelocene with phosphites $(RO)_3P$ (R = Me, Ph) and carbon tetrachloride gave the non-ionic complexes π-$C_5H_5Ni[P(OR')_3]Cl$[232]. The reaction of nickelocene with the square-planar complex $(diphos)_2NiX_2$ [diphos = 1,2-bis(diphenylphosphino)ethane, X = I, Cl] gave the bridged bimetallic complexes $(C_5H_5NiX)_2$-μ-diphos. The corresponding chloro and bromo complexes gave the novel ionic compounds $[(C_5H_5)Ni(diphos)]_2NiX_4$ (X = Cl, Br) (7.2) which contained nickel(II) cations and anions of different coordination geometries[233].



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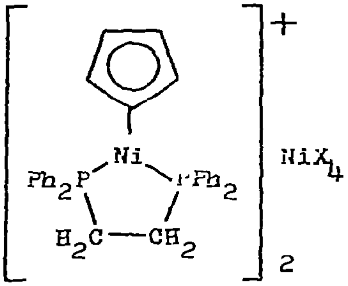


(7.2)

The reaction of nickelocene with carbon tetrachloride, carbon tetrabromide or trichloromethylbenzene in the presence of triphenylphosphine gave (trihalogenomethyl)cyclopentadiene and the corresponding (π-cyclopentadienyl)triphenylphosphinenickel halide. The analogous reaction of nickelocene with allyl bromide gave allylcyclopentadiene; triphenylphosphine was not necessary for the cleavage in this case. Alternative mechanistic schemes involving attack at either the nickel atom or a cyclopentadienyl ring carbon atom were compared[234].

The reaction of nickelocene with thiols RSH (R = i-C_3H_7,

$t\text{-}C_3H_9$, $C_{12}H_{25}$ and p-MeC_6H_4) gave the corresponding thiolate derivatives $(C_5H_5NiSR)_2$ (equation 1). The treatment of nickelocene

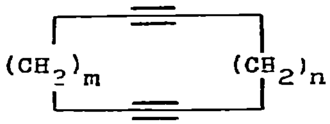
$$2(C_5H_5)_2Ni + 2RSH \longrightarrow (C_5H_5NiSR)_2 + 2C_5H_6 \qquad (1)$$

with methanol in the presence of oxygen gave a deep red liquid the analysis of which indicated monomethoxy nickelocene[235]. Nickelocene has been investigated as a catalyst for the homogeneous dimerization of ethylene. At 200° and 43 atmospheres under nitrogen a heptane solution of ethylene was converted to 1-butene[85].

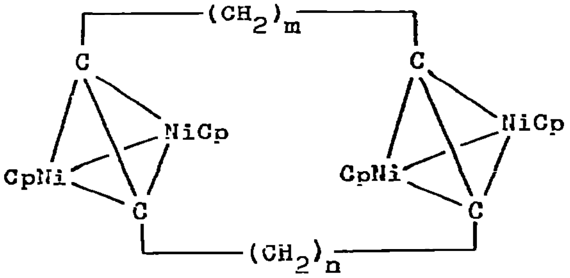
Nickelocene complexes have been used as stereospecific catalysts for the polymerization of butadiene. Treatment of nickelocene with an equimolar amount of either titanium tetrachloride or aluminium bromide gave the corresponding 1:1 complexes. With an excess of titanium tetrachloride a 2:1 complex was formed while excess aluminium bromide gave a complex with a ratio of 1.5:1, the 1:1 complexes were also formed in each case. The catalysts $(\pi\text{-}C_5H_5)_2NiTiCl_4$ and $(\pi\text{-}C_5H_5)_2NiAlBr_3$ were used as suspensions in benzene or toluene and an induction period was observed before the initiation of the reaction. At 8-10% conversion of monomer to polymer the catalyst passed into solution and the reaction continued in homogeneous medium. It was proposed that the reactive sites in the organometallic species were π-allylic in character since $(\pi\text{-}C_5H_5)NiClAlBr_3PPh_3$ was an active catalyst while $(\pi\text{-}C_5H_5)NiPPh_3$ was inert[236].

7. (ii) Nickel-carbon cluster compounds

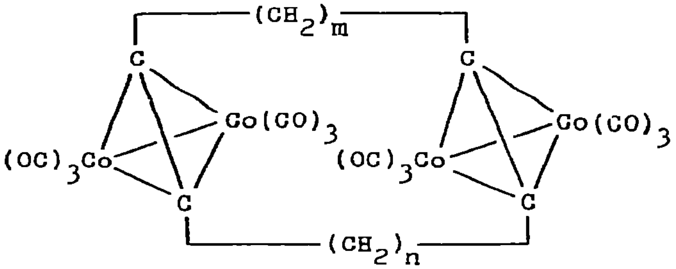
King and co-workers have continued their investigations of the reactions between macrocyclic alkadiynes and transition metal organometallic compounds or metal carbonyls. The diynes (7.3: m = 4, n = 4, 5 and 6) were treated with the cyclopentadienyl



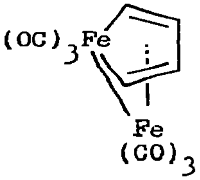
(7.3)



(7.4)



(7.5)



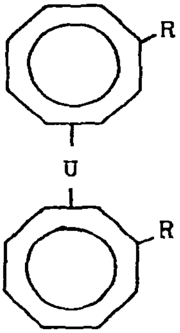
(7.6)

complex, $(\pi\text{-}C_5H_5NiCO)_2$ and dicobalt octacarbonyl in hydrocarbon solvents to give the tetrametallic complexes (7.4 and 7.5) respectively in which the macrocyclic alkadiyne structure was retained. In the case of the alkadiyne (7.3; m = n = 4) dimetallic complexes were isolated where only one of the two carbon-carbon triple bonds in the ligand was bonded to transition metals[237].

The formation of dimetallic complexes from alkynes and nickelocene or dicobalt octacarbonyl has been reported by Wiles and Massey. With 1-(phenylethynyl)-4-chlorotetrafluorobenzene the reagents gave $C_6H_5C_2C_6F_4Cl(NiC_5H_5)_2$ and $C_6H_5C_2C_6F_4ClCo_2(CO)_6$ respectively, the acetylene group bridged the two metal atoms in each case. Treatment of the same diphenylacetylene with triiron dodecacarbonyl gave a complex mixture of products including isomeric derivatives of the binuclear complex (7.6)[238].

8. Uranocene

Streitwieser and Harmon have prepared a number of uranocenes with hydrocarbon substituents (8.1; R = Et, CH_2=CH, Bu^n, Ph, cyclo-C_3H_5) by direct reaction between the dianion of the appropriate cyclooctatetraene and uranium(IV) chloride in THF. 1,1'-Diethyl- and 1,1'-dibutyl-uranocene did not exchange ligands on heating for several hours in diglyme. Divinyluranocene was reduced to the diethyl derivative by hydrogen over a palladium catalyst and with the Simmons-Smith reagent it gave dicyclopropyluranocene. The metallocene group in the alkyluranocenes was as labile to oxidation and acid cleavage as the parent metallocene. The visible spectra of these compounds showed bathochromic shifts which were interpreted as charge transfer transitions[239].



(8.1)

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