ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1975*

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

CONTENTS

---

*Organic Reactions of Selected π-Complexes, Annual Survey Covering the Year 1974 see J. Organometal. Chem., 103 (1975) 197.

1. REVIEWS

Settineri and McKeever presented a review entitled Electrolytic Synthesis and Reactions of Organometallic Compounds. The review contained a section on electrochemical reactions and preparation of organo-transition metal compounds[1]. The chemistry of cyclobutadiene complexes of transition metals has been surveyed by Rybin [2]. The Moessbauer spectroscopy of metal sandwich compounds has been surveyed in a short review by Good, Buttone and Foyt [3]. The chemistry of mono-η-cyclopentadienyl complexes of transition metals has been discussed at length by Nikitina [4].

Perevalova and Nikitina have surveyed extensively the chemistry of bis(η-cyclopentadienyl) transition metal compounds [5]. Bochvar and Gambaryan have discussed bonding in (η-cyclopentadienyl)-transition metal and related compounds [6]. Watts has surveyed the literature for 1973 covering η-cyclopentadienyl, η-arene and related complexes [7]. Silverthorn has reviewed arene transition metal chemistry. The article covered all complexes in which a transition metal was π-bonded to a six-membered aromatic hydrocarbon ring. The literature coverage was through December, 1973 [8]. Klabunde has presented a review entitled the Reactions of Metal Atoms with Fluorocarbons. The review included a section on the formation of bis(η-arene) complexes [9].

The chemistry of (η-acetylene) transition metal complexes has been reviewed exhaustively by Yur'eva [10]. The chemistry of transition metal carbonyls and related organometallic compounds has been surveyed by Cross [11]. Baker, Halstead and Raymond have reviewed briefly the structure and bonding of 4f and 5f π-sandwich organometallic compounds [12]. The polymerization of olefins in the presence of bis(η-benzene)chromium was reviewed by Hagihara [13]. At the symposium on metal carbonyl chemistry, dedicated to Professor Walter Hieber, Werner discussed the substitution of metal carbonyl complexes of chromium, molybdenum and tungsten. (η-Benzene)tricarbonylchromium complexes were included [14]. Anisimov and Valueva have reviewed extensively the chemistry of cymantrene [15].

The toxicology of methylcymantrene emitted from internal combustion engines has been surveyed. Related antiknock compounds are also discussed [16]. The X-ray diffraction studies carried out on manganese, technetium and rhenium complexes and organometallic compounds were reviewed [17]. Deganello and co-workers have reviewed the chemistry of the cyclic polyolefin-carbonyl derivatives of iron, ruthenium and osmium. The review concentrated on derivatives of cyclic polyolefins containing more than six carbon atoms in the ring with at least three carbon-carbon double bonds [18]. In the one hundredth volume of this journal Pettit discussed the role of tricarbonyl(η-cyclobutadiene)iron in the cyclobutadiene problem. The discovery and the chemistry of this molecule was described [19]. The use of iron-cyclobutadiene complexes in synthesis has been discussed in a review by Pettit [20]. Cotton and Frenz have discussed the structures and conformations of compounds containing cyclobutane rings including iron carbonyl complexes [21].

Also in the one hundredth volume of this journal Wilkinson recalled the early days of ferrocene chemistry in an article entitled 'The Iron Sandwich. A Recollection of the First Four Months.' In this article he also describes the first preparations of ruthenocene, ruthenicinium salts and cobalticinium ion [22]. The X-ray diffraction studies carried out on iron, ruthenium and osmium complexes and organometallic compounds were reviewed [23]. The X-ray diffraction studies carried out on cobalt, rhodium and iridium complexes and organometallic compounds were reviewed [24]. As part of Gmelin's Handbook of Inorganic Chemistry a supplementary work was produced entitled Organonickel Compounds [25].

2. GENERAL RESULTS

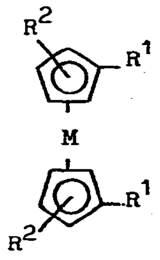
The metal-ligand bonding interactions in several η-diene and η-dienyl manganese complexes including cymantrene have been studied by MO calculations checked by reference to photoelectron spectra. Deviations from Koopmans theorem were reasonably constant in these complexes and the photoelectron spectra were adequately assigned by the results of the calculations. It was concluded that the principal bonding interaction between the organic ligand and the metal arose from the interaction of the pentadienyl a'(e_1") level with the metal d_{xz} orbital and this was more important than the a"(e_1")-d_{yz} interaction [26].

Johnson has calculated core electron binding energies for a number of "solid" ligand molecules together with ESCA chemical shifts for the formation of transition metal complexes from these ligands. Benchrotrene, cymantrene and metallocenes were included among the complexes discussed. The results were used to compare the electronegativities of the ligands and the bonding in the complexes [27]. Elian and Hoffmann have discussed in detail the bonding capabilities of transition metal carbonyl fragments. The valence molecular orbitals for several geometrical configurations of the $M(CO)_3$, $M(CO)_4$ and $M(CO)_5$ fragments have been considered in terms of the ordering of energy levels, symmetry and spatial distribution and extent. Among the characteristics analysed were: stabilization of fragments towards umbrella distortion, the difference between $M(CO)_n$ fragments and ML_n fragments where L is a π-donor ligand and why $Cr(CO)_4$ interacts preferentially with unconjugated dienes whilst $Fe(CO)_3$ prefers to be coordinated with conjugated dienes [28].

The CNDO/2 method with Gaussian type AO's was used to calculate the electronic structures of six π-organometallic complexes of chromium. The results indicated that the chromium-ligand bond had high π-character and negligible δ-character. Charge transfer was almost exclusively from ligand to metal in sandwich compounds while in half-sandwich compounds ligand to metal charge transfer was greater than metal to ligand transfer [29].

Self-consistent charge and configuration molecular orbital calculations have been performed on the isoelectronic series of complexes: $(\eta\text{-}C_6H_6)Cr(CO)_3$, $(\eta\text{-}C_5H_5)Mn(CO)_3$, $(\eta\text{-}C_4H_4)Fe(CO)_3$, $(\eta\text{-}C_3H_5)Co(CO)_3$ and the hypothetical complex $(\eta\text{-}C_2H_4)Ni(CO)_3$. The calculated decrease in the M-C(O) overlap population and in the π^* population followed the increase in the atomic number of the metal atom and indicated progressive weakening of the metal-carbonyl bond across the series which in turn suggested an increasing tendency for an S_N2 mechanism to be favoured at the expense of S_N1 for carbonyl substitution in these complexes [30].

Koehler has measured the Fourier transform ^{13}C NMR and the continuous wave ^1H NMR spectra of bis(η-t-butylcyclopentadienyl)-vanadium. The dipolar and contact contributions to the observed line width were separated and the electron-spin relaxation time was calculated. The author concluded that the ^{13}C NMR spectra of paramagnetic metallocenes should be observed easily with the exception of the cyclopentadienyl ring carbon atoms of nickelocene [31]. Kohler has reported and interpreted the ^{13}C Fourier transform NMR spectra of several substituted metallocenes (2.1; M = V, Cr, Co, Ni; R^1 = Ph, Et; R^2 = H, Ph, Et). Attention was



(2.1)

given to the resolution of multiplets by selective proton decoupling and by selective off-resonance experiments [32]. The infrared spectra (400-3100 cm^{-1}; at 293 and 77°K) of crystalline nickelocene and cobaltocene, together with the Raman spectrum of nickelocene were recorded. The bands in the spectra were assigned [33]. He(I) photoelectron spectra of the compounds $(\eta\text{-}C_5H_5)\text{-}M(\eta\text{-}C_7H_7)$ (M = Zr, Nb, Mo) were recorded and the results were compared with those for the corresponding 3d transition metal compounds. It was concluded: (i) that there was a stronger interaction between the metal orbitals and the $\underline{e}_1$ orbitals of the $\eta\text{-}C_5H_5$ ring in the 4d than in the 3d compounds; (ii) that in the compounds $(\eta\text{-}C_5H_5)M(\eta\text{-}C_7H_7)$ (M = Zr, Nb, Mo) both metal and ligand contribute substantially to the molecular orbitals of δ-symmetry and (iii) that for the a'_1 orbital there is a smaller pairing energy of the electrons in the 4d transition metals than in the 3d series [34].

Analysis of the ESR spectra at liquid helium temperatures and the anisotropic Zeeman effects of the orbitally degenerate low spin complexes $(\eta\text{-}C_5H_5)_2Mn$, $(\eta\text{-}C_5H_5)_2Fe^+$ and $(\eta\text{-}C_5H_5)_2Co$ $(\eta\text{-}C_5H_5)_2Ni^+$ indicated that the Jahn-Teller distortions were dynamic. Covalent delocalisation of singly occupied degenerate 3d metal orbital over the cyclopentadienyl rings was correlated with the Jahn-Teller distortions and increased in the order: $(\eta\text{-}C_5H_5)_2Fe^+ < (\eta\text{-}C_5H_5)_2Mn < (\eta\text{-}C_5H_5)_2Co < (\eta\text{-}C_5H_5)_2Ni^+$ [35]. The mass spectra of tricarbonyl(η-cyclopentadienyl)manganese and (η-benzene)tricarbonylchromium were compared. The decompositions of these two molecules in the mass spectrometer were analogous. The potentials for the appearance of the main ions were given and these were used to calculate dissociation energies [36]. In the mass spectra of the π-complexes $(\eta\text{-}C_5H_5)Cr(\eta\text{-}C_6H_6)$, $(\eta\text{-}C_5H_5)Mn(\eta\text{-}C_6H_6)$, $(\eta\text{-}C_5H_5)V(\eta\text{-}C_7H_7)$ and $(\eta\text{-}C_5H_5)Cr(\eta\text{-}C_7H_7)$ binuclear secondary ions appeared, for example:

$$C_5H_5M^+ + C_5H_5MC_7H_7 \longrightarrow (C_5H_5)_2M_2C_7H_7^+$$

$$C_5H_5M^+ + C_5H_5MC_7H_7 \longrightarrow C_{17}H_{15}M_2^+ + H_2$$

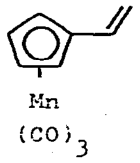
Also a large number of ion-molecule reactions occurred between the molecular or fragment ions of the π-complexes and neutral σ- or π-donors in the ion source of the mass spectrometer [37], for example:

$$C_5H_5CrC_6H_6^+ + O{=}C(CH_3)_2 \longrightarrow C_5H_5CrOC(CH_3)_2^+ + C_6H_6$$

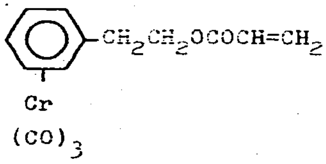
$$C_5H_5CrC_6H_6^+ \xrightarrow{-C_6H_6} C_5H_5Cr^+ \xrightarrow{O=C(CH_3)_2} C_5H_5CrOC(CH_3)_2^+$$

Enthalpies of combustion for chromocene, manganocene, ferrocene, cobaltocene and nickelocene were measured by a calorimetric method and the standard enthalpies of formation together with the dissociation energies were calculated for these five metallocenes [38]. Borrell and Henderson have determined the quantum yields for photodecomposition of bis(η-benzene)chromium, ferrocene, ruthenocene, cobaltocene, nickelocene and their corresponding cations. In general, the compounds with noble gas configurations showed good photo-stability while the remainder, with unpaired electrons, were photo-labile. The results were interpreted on the basis of the electronic structures of the compounds and cations [39].

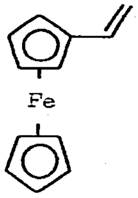
The polymerization of butadiene and isoprene in the presence of a π-organometallic compound and an organic halide has been studied by Kubota and Atsu. Nickelocene, ferrocene and bis(η-benzene)chromium were used in addition to η-cyclopentadienyl halides of titanium and zirconium. Conversions of up to 96% with a trans-1,4 content of 88% were obtained with nickelocene and an organic iodide [40]. The unsaturated organometallic compounds (2.2, 2.3 and 2.4) and related compounds were incorporated into organic copolymers and linseed oil films. Films containing the benchrotrene moiety (2.3) gave chromium oxide on exposure to light [41].



(2.2)

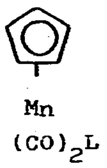


(2.3)

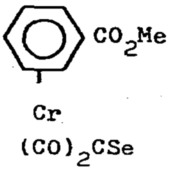


(2.4)

The copyrolysis of diisopropylnickelocene with bis(η-diethylbenzene)chromium was examined and found to obey first order kinetics in the temperature range 320-380° [42]. Cymantrene was converted by photolysis to the THF complex (2.5; L = THF) and this was treated with carbon diselenide in the presence of triphenylphosphine to give the selenocarbonyl manganese complex (2.5; L = CSe). The selenocarbonyl analogue of benchrotrene (2.6) was prepared in the same way. The IR frequencies of the coordinated groups were in order of decreasing energy CO $\gg$ CS $>$ CSe. Mass spectrometric results indicated a strong Mn-CSe bond in the manganese complex [43]. Cobaltocene and chromocene readily formed intercalation complexes with the layered transition

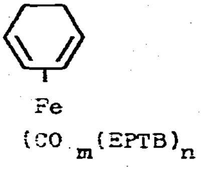


(2.5)

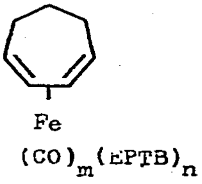


(2.6)

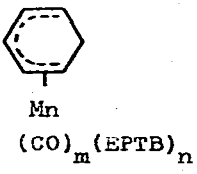
metal derivatives TiS_2, ZrS_2, HfS_2, $NbSe_2$, TaS_2 and also with SnS_2. X-ray studies showed complete intercalation, with the five-membered rings of the metallocene situated perpendicular to the sheets of the host [44]. Whitesides and Budnik have prepared the η-cyclohexadiene (2.7; m = 2, n = 1; m = 1, n = 2) and the η-cycloheptadiene (2.8; m = 2, n = 1; m = 1, n = 2) iron complexes together with the corresponding ruthenium complexes.



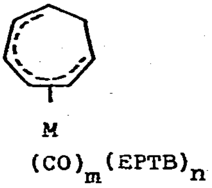
(2.7)



(2.8)

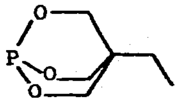


(2.9)



(2.10)

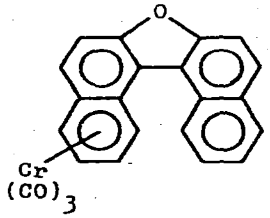
EPTB =



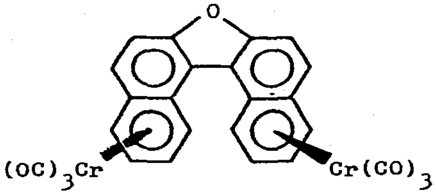
The analogous η-cyclohexadienyl and η-cycloheptadienyl complexes of manganese (2.9; m = 2, n = 1; m = 1, n = 2 and 2.10; m = 2, n = 1; m = 1, n = 2) were also characterized along with the rhenium, iron$^+$ and ruthenium$^+$ complexes. ^{31}P NMR studies at several temperatures indicated that most of the compounds existed as mixtures of ligand isomers which underwent rapid interconversion at room temperature. Kinetic parameters for the interconversions were determined and rates were dependant principally on the metal and decreased in the order: $Mn \sim Re \gg Fe^+ \gg Ru^+$ for dienyl compounds and $Fe \gg Ru$ for diene compounds [45].

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

Six isomeric dinaphthofurans were treated, in turn, with chromium hexacarbonyl in dibutyl ether at the reflux temperature. The usual product was the chromium tricarbonyl complex although in two cases the bis(chromium tricarbonyl) compound was obtained. Thus dinaphtho 2,7-b:7',2'-d furan gave the complexes (3.1 and 3.2) [46]. King and von Stetten have prepared chromium tricarbonyl complexes of some nitrogen mustard anti-leukaemia agents in order to evaluate the effects of the metal carbonyl residue

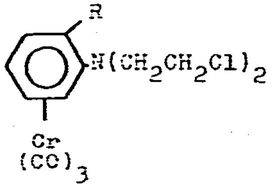


(3.1)

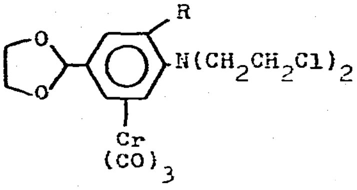


(3.2)

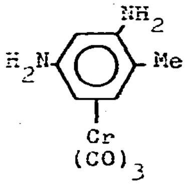
on their pharmacological activity. The N,N-bis(2-chloroethyl)-aniline complexes (3.3; R = H, Me) were formed from chromium hexacarbonyl and the ligand while the benzaldehyde ethylene acetal complexes (3.4; R = H, Me) were obtained from <u>fac</u>-$(MeCN)_3Cr(CO)_3$ and the ligand in boiling THF. The complexes did not exhibit significant antileukaemia activity.[47].



(3.3)

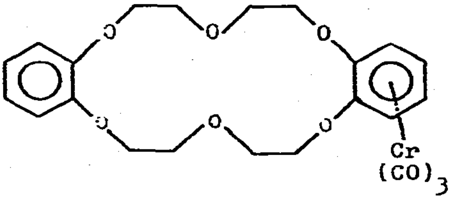


(3.4)

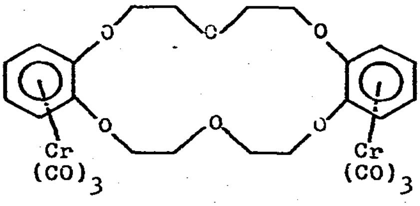


(3.5)

Seven η-bisaminobenzene complexes of chromium tricarbonyl have been prepared by treatment of the appropriate phenylenediamine with chromium hexacarbonyl in decalin and diglyme. A typical product was the 2,4-bisaminotoluene complex (3.5) [48]. The irradiation of hexacarbonylchromium with dibenzo-18-crown-6 gave the mono- and bis-(tricarbonylchromium) compounds (3.6 and 3.7). The ether complexes (3.6 and 3.7) exhibited a decreased ability to extract alkali metal salts into organic solvents which



(3.6)



(3.7)

was attributed to electron withdrawal from the oxygen crown by the $Cr(CO)_3$ substituents [49].

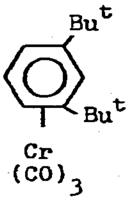
Pittman, Patterson and McManus have prepared polytetramethyl-p-silphenylenesiloxane and polymethylphenylsiloxane and converted these to the chromium tricarbonyl complexes by heating with chromium hexacarbonyl in glyme. Chain scission and decomposition of the organometallic groups were in competition with the complexation process to give lower molecular weights for the complexed polymers [50]. Chromium hexacarbonyl was heated with swollen 1% divinylbenzene cross-linked polystyrene to give a polymer with chromium tricarbonyl groups bonded to the phenyl rings. This heterogenized catalyst was active in the selective conversion of methyl sorbate to (Z)-methyl 3-hexenoate (97%) at 160° and 500 psi of hydrogen [51, 52].

(ii) Spectroscopic and Physico-chemical Studies

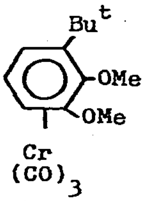
The crystal and molecular structure of dicarbonyl (η-methylbenzoate)(triphenylphosphine)chromium was determined by X-ray diffraction. The $Cr(CO)_2PPh_3$ fragment was in an eclipsed orientation relative to the η-methylbenzoate ligand and the bond lengths and angles were those usually found in this type of molecule [53]. NMR broad line measurements were made on crystalline benzenetricarbonylchromium at various temperatures and two narrowings of the proton absorption line width were observed at -165 and -45°C. The corresponding activation energies were $E_1 = 3.4$ and $E_2 = 7.2$ kcal mol^{-1}. The lower temperature narrowing for which a more accurate activation energy (4.2 kcal mol^{-1}) was obtained from the spin-lattice relaxation time, was attributed to rotation of the arene group. It was thought that most of the rotational hindrance was due to the crystal environment rather than to intramolecular forces [54].

The ^{1}H NMR spectra of the 1-(*p*-tolyl)ethyl- and di-(*p*-tolyl methyl-tricarbonylchromium cations were recorded in HSO$_3$F at -50°. These spectra were compared with those of the free ligand ions and the parent alcohols. In the cations charge migration towards the metal occurred as shown by a downfield shift of all the signals on passing from the parent alcohols to the 1-(*p*-tolyl)ethyl- and di(*p*-tolyl)methyl-tricarbonylchromium cations. It was concluded that the chromium atom participated directly in the stabilization of the cations [55].

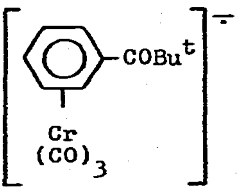
^{13}C NMR spectra were recorded for a series of (η-arene)-tricarbonylchromium derivatives. The spectra were interpreted in terms of electronic effects of the substituent together with effects arising from conformational preferences of the tricarbonylchromium group. The t-butyl derivatives (3.8) and (3.9) were prepared but there was no evidence from the ^{13}C NMR spectra of restricted rotation of the η-arene groups[56]. The ^{19}F NMR chemical shifts obtained for free fluoroarenes were correlated



(3.8)



(3.9)

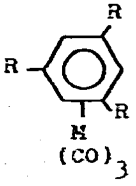


(3.10)

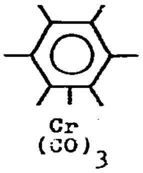
with the Swain-Lupton field and resonance parameters. Comparison of these data with those from the corresponding tricarbonylchromium complexes showed little change in the transmission of mesomeric effects by para-substituents. Meta-substituents which interacted primarily by a field effect had little or no influence on the fluorine chemical shift in the chromium complexes suggesting that the σ-framework of the ring interacted with the chromium [57].

The ESR spectrum of the benchrotrene radical anion (3.10) was compared with that of the ligand radical anion. The spectrum of the ligand showed an increased extension span and two additional ring-proton hyperfine splittings relative to the spectrum of the complex [58]. The IR and Raman spectra of the (η-arene) complexes (3.11; R = H, Me; M = Cr, Mo, W) have been measured in the solid phase and in solution. The ligand and skeletal vibrations were assigned and some force constants calculated. The arene-metal bond force constants for the complexes (3.11; R = H; M = Cr, Mo, W) decreased in the order W $>$ Cr $>$ Mo whilst the carbonyl-metal bond force constants were in the order W $>$ Mo $>$ Cr. The linear correlation between the carbonyl frequencies and the parameter σ_p^o was used as evidence for the inductive transmission of substituent effects through the metal atom. The complexes (3.11; R = H; M = Mo, W) underwent reversible protonation at the metal atom in trifluoroacetic acid solution while benchrotrene was not protonated in this way [59].

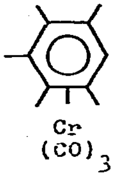
The infrared spectra of the complexes $[(\eta\text{-}\underline{p}\text{-}RC_6H_4)Cr(CO)_3]_2Hg$ (R = H, F, Me, MeO, CO_2Et, Me_2N) were recorded and correlated with the Hammett substituent constants. The chromium-carbon



(3.11)



(3.12)



(3.13)

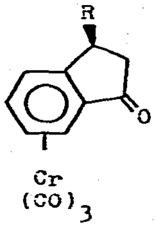
vibrations were less affected by the changes in the ligand than the C-O vibrations. The deformational δ-Cr-CO vibration was independent of the substituent attached to the η-arene group [60]. Single-crystal Raman studies of the vibration of the chromium tricarbonyl group in the isomorphous compounds (η-hexamethylbenzene)- and (η-pentamethylbenzene)-chromium tricarbonyl (3.12, 3.13) suggested that while the absorption at 2000 cm^{-1} was best discussed by a vibrational factor-group approach, several features revealed by the study remained unexplained by it [61].

The infrared and Raman spectra of (η-benzene)tricarbonylchromium as a crystalline solid, as a solid solution in EtOH - Et_2O - Me_2CHEt at $85^{\circ}K$ and as a vapour at $500^{\circ}K$ were recorded and the C-O force constants were calculated [62]. Adams and co-workers presented an approximate vibrational analysis of the complete (η-benzene)tricarbonylchromium molecule and its deuterated analogue. It was found that in most cases kinematic coupling effects were insufficient to explain the frequency shifts which were observed on coordination of the benzene moiety to the tricarbonylchromium group. The effects of ligation on the force constants of the benzene ring were evaluated [63].

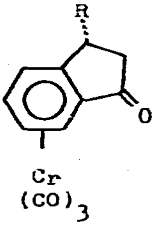
The following standard enthalpies of formation of some (η-arene)tricarbonylchromium complexes were determined by thermochemical techniques $\Delta H_f^\circ[(\eta\text{-}C_6H_5Me)Cr(CO)_3,c] = -114 \pm 1.5$ kcal mol^{-1}, $\Delta H_f^\circ[(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cr(CO)_3,c] = -136.5 \pm 2$ kcal mol^{-1} $\Delta H_f^\circ[(\eta\text{-}C_6H_5Cl)Cr(CO)_3,c] = -111.5 \pm 5$ kcal mol^{-1}. A microcalorimetric vacuum sublimation technique was used to obtain the enthalpies of sublimation for $(\eta\text{-}C_6H_6)Cr(CO)_3$, $(\eta\text{-}C_6H_5Me)Cr(CO)_3$, $(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cr(CO)_3$, $(\eta\text{-}C_6Me_6)Cr(CO)_3$, $(\eta\text{-}C_6H_5Cl)Cr(CO)_3$ and $(\eta\text{-cyclo-}C_7H_8)Cr(CO)_3$. Values were obtained for arene-Cr bond enthalpy contributions in (η-arene)$Cr(CO)_3$ molecules in the gas phase: these decreased along the series $[(\eta\text{-}C_6Me_6)\text{-}Cr] \gg [(\eta\text{-}C_6H_3Me_3)\text{-}Cr] > [(\eta\text{-}C_6H_5Me)\text{-}Cr] \approx [(\eta\text{-}C_6H_6)\text{-}Cr] > [(\eta\text{-}C_6H_5Cl)\text{-}Cr] > [(\eta\text{-cyclo-}C_7H_8)\text{-}Cr]$ [64].

The electrochemical reduction of a series of (η-arene)-tricarbonylchromium complexes was examined using a dropping mercury electrode in dimethylformamide solution, benchrotrene had a reversible two electron reduction.and the reduction took place stepwise with the intermediate formation of an anion-radical [65]. A variety of (η-arene)tricarbonylchromium complexes were studied electrochemically in nonaqueous media. The polarographic constants for pulse polarography were measured and it was found that the complexes underwent reduction by a transfer of two electrons to give stable (η-arene)tricarbonylchromium(-II) dianions [66].

Correlations were established between the substituent parameters σ_I, σ_P, σ_R^P, σ_P^0 and σ_R^0 and the carbonyl stretching force constant, <u>k</u>(CO), for a series of mono- and poly-substituted tricarbonylchromium-complexed arene compounds. A poor correlation was obtained with σ_I but a much better correlation was apparent for σ_p. It was concluded that the overall electronic substituent effect transmitted to the carbonyl groups involved both mesomeric and inductive mechanisms. The results also supported appreciable participation of the ring carbon σ-framework in metal-ring bond formation [67]. Caro and Jaouen have investigated the effect of increasing size of substituent on the borohydride reduction of the exo- (3.14) and endo-isomer (3.15) of β-alkylindenone complexes. The enthalpy and entropy of the reduction of the isomer (3.14; R = Me, Et, Pr^i) decreased with increasing size of the alkyl group while the same parameters were virtually unaltered in the same reaction of the endo-isomer (3.15; R = Me, Et, Pr^i). The mechanism of the reaction was discussed in terms of transition state changes with substitution [68].

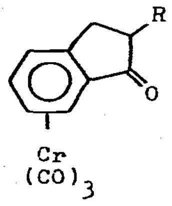


(3.14)

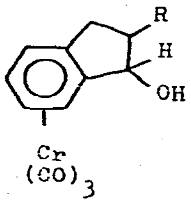


(3.15)

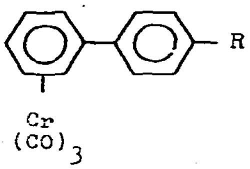
The rate of reduction of the indanone (3.16) to the endo-alcohol (3.17) with sodium borohydride was dependent on the nature of the substituent R. The rate decreased in the order of increasing size of substituent: R = exo-Me > endo-Me > endo-Et > endo-CHMe$_2$. Thermodynamic parameters were determined in each case and the mechanistic implications of the results were discussed [69]. The ionization constants of the benchrotrene



(3.16)



(3.17)



(3.18)

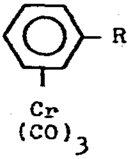
compounds (3.18; R = OH, NH_2) and of 4-hydroxy- and 4-aminodiphenyl have been determined. The hydroxy compound (3.18; R = OH) was a stronger acid than 4-hydroxydiphenyl and phenol while the amino compound (3.18; R = NH_2) was a weaker base than 4-aminodiphenyl and aniline. The σ_p^- and σ_R^- constants were determined for the $(\eta\text{-}C_6H_5)Cr(CO)_3$ group and demonstrated weak conjugation between the group and electron releasing substituents [70]. The vapour phase molecular structure of (η-benzene)-tricarbonylchromium was studied by electron diffraction. On the basis of these results and of auxiliary vibrational calculations it was concluded that in the vapour phase the molecule was nearly an unhindered internal rotor. In the vapour phase it consisted of a mixture of several conformations which differed from each other by the rotational arrangement of the benzene ring with respect to the carbonyl groups. In the solid state the molecule was in the staggered form. The C-C bond distance of the benzene ring was slightly larger than that in free benzene. It was thought that the bond elongation was probably due to the donation of electrons from the metal d-orbitals into the benzene π^*-antibonding orbitals [71].

Mechanisms have been considered for the stabilization of chromium-arene fragment ions formed during the mass spectrometric breakdown of bis(η-arene)chromium and (η-arene)tricarbonylchromium complexes. The first mechanism requires distribution of excess energy between the covalent bonds of the fragment ion, the second involves stabilization by structural distortion of the fragment [72].

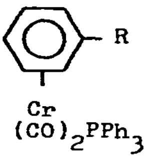
The X-ray photoelectron spectra for fifty molybdenum compounds including tricarbonyl(η-mesitylene)molybdenum, tricarbonyl-(η-cycloheptatriene)molybdenum and the corresponding tropylium ion were reported. Strong σ-donor ligands were effective in increasing the electron density around the metal atom [73].

(iii) General Chemistry

Mercuration of benchrotrene and the benchrotrene analogue (3.20; R = H) with mercury(II) acetate and then calcium chloride gave the mercurichlorides (3.19; R = HgCl and 3.20; R = HgCl) respectively. Tricarbonyl(η-toluene)chromium (3.19; R = Me) was not mercurated under the same conditions [74].

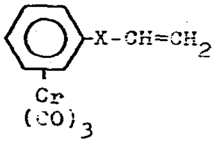


(3.19)

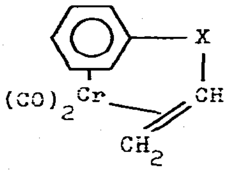


(3.20)

(η-Areneolefin)tricarbonylchromium complexes [3.21; X = CH_2, OCH_2, $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_4$] were prepared from the parent olefin and chromium hexacarbonyl. Irradiation of these complexes in petroleum ether gave the corresponding dicarbonylchromium complexes [3.22; X = CH_2, OCH_2, $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_4$] [75].



(3.21)

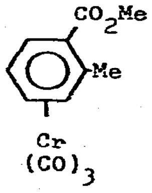


(3.22)

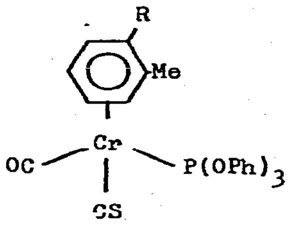
The reactions between (η-benzene)chromium tricarbonyl and its derivatives with butyllithium in THF have been examined. At temperatures below -20° efficient ring metallation was observed with the parent compound and in the presence of methyl and fluoro substituents. Tricarbonyl(η-mesitylene)chromium underwent α-metallation. At temperatures above 0° the principal product was n-butylbenzene [76]. A quantitative study was made of the photosubstitution of carbon monoxide in tricarbonyl(η-mesitylene)chromium by N-dodecylmaleimide in benzene. In benzene the reaction was clear and a quantum yield of 0.90 ± 0.09 at 313 nm was obtained. An attempt was made to study the same reaction in cyclohexane but some decomposition of the reagents occurred [77]. The catalytic activity of tricarbonylchromium complexes of phenanthrene, naphthalene and anthracene in the hydrogenation of dienes was studied. The solvent effect on the hydrogenation kinetics of methyl sorbate in the presence of (η-phenanthrene)- and (η-naphthalene)tricarbonylchromium indicated that the longest Cr-C (arene) was displaced by the incoming diene ligand; the longer the Cr-C (arene) bond the easier the displacement. The hydrogenation of 2,4-hexadiene, 1,4-cyclohexadiene, dimethylmuconate and 1,4-diphenyl-1,3-butadiene was studied also [78].

Enantiomeric chromium complexes with chirality based on an asymmetric metal centre have been formed from disubstituted benchrotrene compounds. The optically pure benchrotrene methylester (3.23) was converted to the pair of internal diastereoisomers (3.24 and 3.25; R = CO_2H) by the stepwise replacement of two carbonyl ligands with thiocarbonyl and triphenyl phosphite. The diastereoisomers were separated by TLC on silica gel and the ester group on each was removed by reduction with lithium aluminium hydride and aluminium chloride to leave the pair of enantiomeric complexes (3.24 and 3.25; R = H) [79].

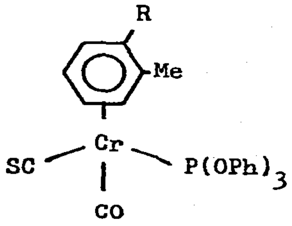
(η-Benzyl acrylate)tricarbonylchromium (3.26) was prepared from (η-benzyl alcohol)tricarbonylchromium and acryloyl chloride. Homopolymerization of the acrylate (3.26) gave polymers of



(3.23)

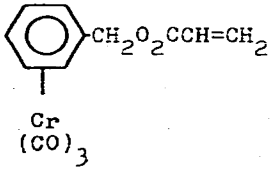


(3.24)



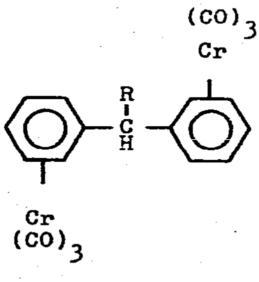
(3.25)

molecular weight 7,700-60,000. The acrylate (3.26) was copolymerized with methylacrylate and styrene [80]. The treatment of diphenylmercurybis(η-chromium tricarbonyl) with $Co_2(CO)_8$ gave benzophenonebis(η-chromium tricarbonyl) and the reduction of this ketone produced the alcohol (3.27; R = OH). The carbonium ion salt (3.28), a royal-blue solid was obtained by the reaction of

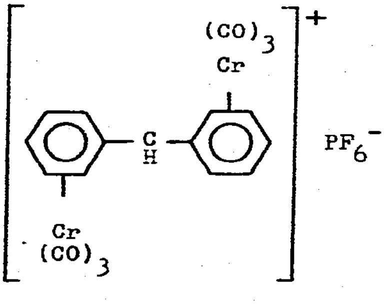


(3.26)

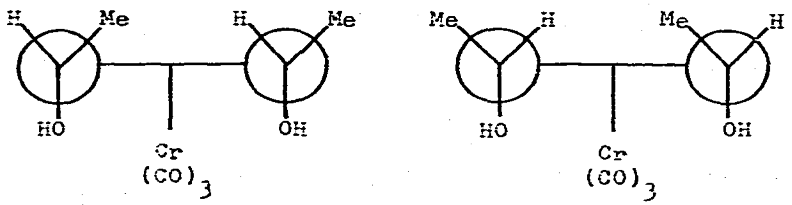
the alcohol (3.27; R = OH) with hexafluorophosphoric acid. The salt (3.28) was found to alkylate ethanol, diethylamine, and pyrrole to give the derivatives (3.27; R = OEt, NEt_2 and C_4H_3NH) respectively [81]. The reduction of 1,2-diacetylbenchrotrene and the treatment of 1,2-diformylbenchrotrene with methylmagnesium iodide gave three stereoisomeric glycols; the racemic mixture (3.29) and two meso (pseudoasymmetric) forms (3.30 and 3.31).



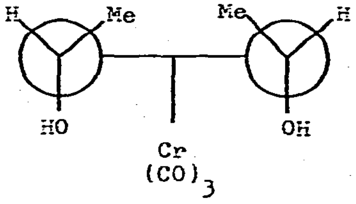
(3.27)



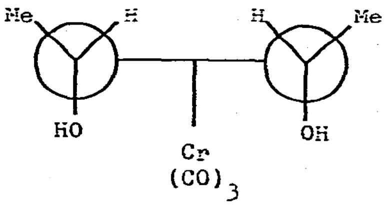
(3.28)



(3.29)



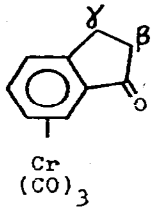
(3.30)



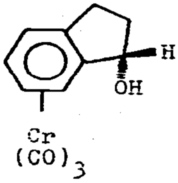
(3.31)

The irradiation of these glycols gave the corresponding benzene glycols [82]. The structure of the glycol (3.31) was determined by X-ray diffraction [83].

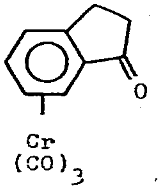
Jaouen and Dabard have reduced tricarbonyl(η-indanone)-chromium compounds (3.32) substituted in either the β- or γ-positions of the cyclopentenone ring with an endo- or exo-methyl group or substituted in the benzene residue with a methoxy group. Reduction with potassium borohydride or lithium aluminium hydride gave only the endo-alcohol (3.33) [84]. Optically pure 1-indanone- and tetralone-tricarbonylchromium (3.34 and 3.35) were obtained via oxidation of 1-endo-indanoltricarbonylchromium and 1-endo-tetraloltricarbonylchromium respectively. These complexes were used as precursors to chiral arene compounds difficult to prepare by other routes. The tricarbonylchromium moiety was removed from



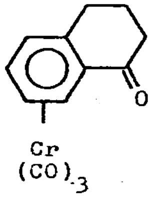
(3.32)



(3.33)



(3.34)

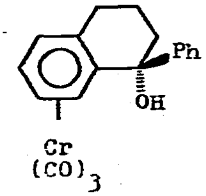


(3.35)

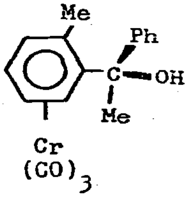
the arene ligands by exposure of ether solutions of the chromium complexes to sunlight [85].

Tertiary alcohols derived from η-benzene-tricarbonylchromium (for example complexes 3.36 and 3.37) were used as a source of the tricarbonylchromium group in the direct preparation of η-arene-tricarbonylchromium derivatives bearing cyano, nitro or hydroformyl groups. Little reaction occurred with arenes having only electron-withdrawing groups (methylbenzoate) but in the presence of electron donating groups (2-methoxy aniline, 3-aminotoluene, 4-amino-benzonitrile) satisfactory yields of the η-arene derivatives were obtained [86].

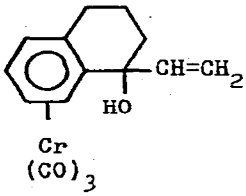
The tricarbonylchromium group was exchanged from η-arene ligands which were part of a tertiary alcohol group to new arene



(3.36)



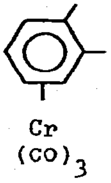
(3.37)



(3.38)

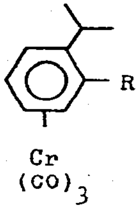
ligands in the presence of 2-methyl-1,3-cyclopentadione which behaved as a proton donor. For example, the alcohol (3.38) underwent reaction with 1,2-dimethylbenzene to give the chromium complex (3.39) [87]. Stanger has investigated the ligand displacement reactions of several chromium and molybdenum tricarbonyl complexes including η-arene complexes. The ligands were classified on the basis of π-acceptor ability while the metal carbonyl derivatives, fac-$L_3M(CO)_3$, were classified by lability. It was found that chromium exhibited a preference for arene and olefin ligands while molybdenum preferred "n"-type donor ligands. The solution IR spectra of metal tricarbonyl compounds were only slightly dependent on the solvent [88].

The reaction of tetracyanoquinodimethan (TCNQ) (3.40) with tricarbonyl(η-toluene)chromium in acetonitrile gave toluene, carbon monoxide and $Cr(MeCN)_2(TCNQ)_2$. Magnetic susceptibility measurements indicated the presence of chromium(III) in this complex showing that the TCNQ had behaved as an oxidizing agent [89]. η-Arenetricarbonylchromium compounds formed charge-transfer complexes with 1,3,5-trinitrobenzene (TNB) but these complexes were not formed by η-arenetricarbonyl -molybdenum and -tungsten



(3.39)

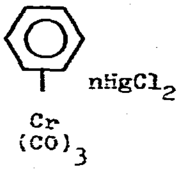
(3.40)



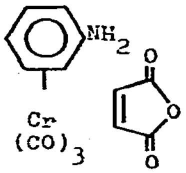
(3.41)

derivatives. However η-arenetricarbonyl-chromium, -molybdenum and -tungsten all formed charge-transfer complexes with tetracyanoethylene (TCNE). With TNB, complex formation with the molybdenum and tungsten compounds occurred via the coordinated arene and this was inhibited by the reduced electron density on the coordinated arene due to intramolecular charge transfer. In the case of TCNE the complex was formed by an inner-sphere charge-transfer interaction with the metal atom. Therefore the stability of the TCNE charge-transfer complexes was dependant on the charge density on the metal atom and not the coordinated arene [90].

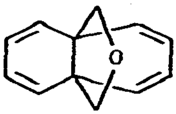
The benchrotrene derivatives (3.41; R = NH_2, NMe_2, OMe) were obtained in the exchange reactions between benchrotrene and the appropriate o-substituted iso-propylbenzene [91]. Benchrotrene derivatives such as $(\eta\text{-}C_6H_5NMe_2)Cr(CO)_3$ gave 1:1 and 1:2 complexes of mercury(II) chloride by treatment of the organometallic compound with mercury(II) acetate and then calcium chloride [92]. Electron acceptors, such as mercury(II) chloride and maleic anhydride, formed complexes with benchrotrene and its derivatives Thus benchrotrene combined with two or three moles of mercury(II) chloride to form the complexes (3.42; n = 2, 3) while the



(3.42)



(3.43)



(3.44)

complex (3.43) was obtained with maleic anhydride and (η-aniline)-tricarbonylchromium [93]. Uranyl complexes were prepared with (η-benzoic acid)tricarbonylchromium and (η-benzoylacetone)-tricarbonylchromium as the ligands. The infrared spectra indicated that all the complexes had a pentagonal bipyramidal configuration around the uranium atom. All the complexes were less stable in solution than the corresponding ligands [94].

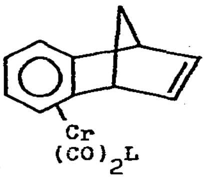
Aromatic compounds such as benzene, naphthalene and 2-methyl-naphthalene were hydroxylated by molecular oxygen in acetonitrile and in the presence of molybdenum hexacarbonyl. The reactions involved (η-arene)Mo(CO)$_3$ intermediates [95]. Selective reduction of the propellane derivative (3.44) has been achieved by using hydrogen and a (η-arene)tricarbonylchromium catalyst. Reduction occurred by 1,4-addition of hydrogen to the ether-bridge side of each cyclohexadiene ring [96].

Stille and Nelb have incorporated the chromium tricarbonyl group into removable arene complexes in order to improve the solubility during polymerization of monomers to poly(p-phenylene) [97]. η-Arenetricarbonyl-chromium, -molybdenum and -tungsten were shown to be active homogeneous catalysts in the linear polymerization of acetylenes to relatively high molecular weight polymers. With the molybdenum catalysts the reactions were very fast and often quantitative but with the less active chromium and tungsten catalysts the intermediates of the polymerizations were isolated. These intermediates were shown to be ladder compounds composed of fused cyclobutane rings [98].

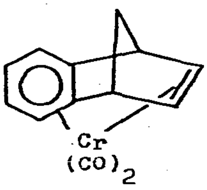
(iv) Analogues

Kinetics of hydrogen-deuterium exchange of $(\eta\text{-Ph-Ph})Cr(CO)_3$ and $(\eta\text{-Ph-Ph})Cr(CO)_2PPh_3$ were determined in acid media. The reactivity of the coordinated and uncoordinated phenyl rings was approximately the same [99]. The $Cr(CO)_2L$ unit L = CO, CS, PPh_3, $P(OPh)_3$ was used to increase reactivity, enhance selectivity and protect the substituents of complexed arene rings with respect to alkylation. For example $(\eta\text{-PhCOMe})Cr(CO)_3$ was rapidly converted into $(\eta\text{-PhCOPr}^i)Cr(CO)_3$ in dimethylformamide with methyl iodide and sodium hydride. Free $PhCH_2CO_2Me$ was inert to methyl iodide and sodium iodide but the complex $(\eta\text{-PhCH}_2CO_2Me)Cr(CO)_3$ rapidly gave $(\eta\text{-PhCMe}_2CO_2Me)Cr(CO)_3$ when treated with these reagents. The activating power of the carbonylchromium group was modified by photochemical replacement of one of the carbonyl groups. Polarographic and p*K*a data indicated the following order of activating power of the $Cr(CO)_2$ units: $Cr(CO)_2CS > Cr(CO)_3 > Cr(CO)_2P(OPh)_3 > Cr(CO)_2PPh_3$ [100].

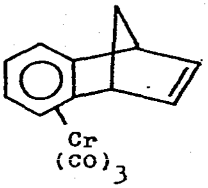
The benchrotrene compound (3.45; L = CO) was converted to the η-benzonorbornadiene compound (3.46) by photolysis in ether at room temperature. This compound was attacked by effective π-acceptor ligands at the metal-norbornadiene bond to give the benchrotrene analogues [3.45; L = RNC, Ph_3P, $(MeO)_3P$, PF_3, $(MeO)_3As$] but it was inert towards ligands such as pyridine, THF and acetonitrile which are good σ-donors but weak π-acceptors. The IR spectra of the benzonorbornadiene compounds (3.46) suggested that chromium-carbonyl π-bonding was stronger than in the benchrotrene compounds (3.45) [101].



(3.45)



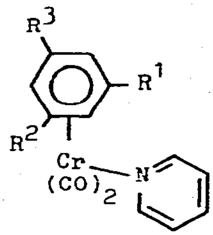
(3.46)



(3.47)

A series of (η^8-alkenylbenzene)dicarbonylchromium complexes was prepared via irradiation of the corresponding tricarbonylchromium derivative. For example, the irradiation of the benzonorbornadiene complex (3.47) gave (η^8-benzonorbornadiene)-dicarbonylchromium (3.46) in 49% yield. The ^1H NMR spectra of the dicarbonylchromium complexes suggested that the carbon-carbon double bond was parallel to the benzene ring [102].

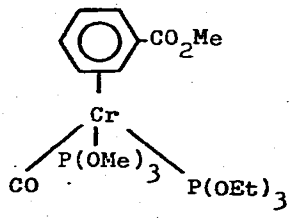
The photochemical formation of the η-arene complexes (3.48; $R^1 = R^2 = R^3 = H, Me$) from the corresponding chromium tricarbonyl complexes was investigated. The quantum efficiency of this reaction was independent of the pyridine concentration in the range 0.008-0.17M. The (η-arene)$Cr(CO)_3$ complexes quenched triplet excited benzil at a diffusion controlled rate and the quenching was accompanied by reaction of the chromium complex. The triplet



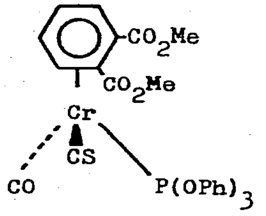
(3.48)

sensitized reaction only occurred with a quantum efficiency of 0.15 as compared to the high substitution efficiency of 0.72 upon direct irradiation of (η-arene)Cr(CO)$_3$ [103].

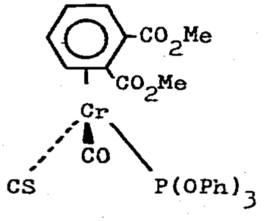
(η-$C_6H_5CO_2Me$)Cr(CO)$_3$ was irradiated in the presence of P(OEt)$_3$ and then irradiated with P(OMe)$_3$ to give the chromium complex (3.49). The complex [η-$C_6H_4(CO_2Me)_2$]Cr(CO)(CS)[P(OPh)$_3$] was prepared similarly and it was separated into the diastereoisomers (3.50 and 3.51) by thin layer chromatography [104]. The ^{31}P NMR spectra of the complexes (η-C_6H_5X)Cr(CO)$_2$PPh$_3$, (X = H, Me, OMe, NMe$_2$, COOMe); (η-p-$C_6H_4X_2$)Cr(CO)$_2$PPh$_3$, (X = COOMe) and (η-$C_6H_3X_3$)Cr(CO)$_2$PPh$_3$, (X = Me) were recorded in neutral and acidic media. All the compounds showed a narrow singlet in the ^{31}P- ^{1}H spectra in carbon disulphide suggesting that fast internal



(3.49)



(3.50)



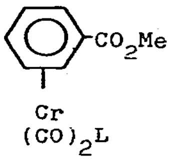
(3.51)

rotation about the Ar-Cr π-bond was taking place. In the presence of trifluoroacetic acid some of the complexes were protonated at the metal which resulted in the upfield shielding of the ^{31}P- ^{1}H signal. Temperature-dependence of the ^{31}P- ^{1}H NMR spectra was investigated and the degree of protonation was found to increase with decreasing temperature [105].

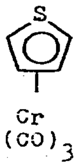
The complexes $(\eta\text{-}C_6Me_6)Cr(CO)_2L$ where L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OPh)_3$ and $P(OMe)_3$, when treated with nitrosyl hexafluorophosphate gave the salts $[(\eta\text{-}C_6Me_6)Cr(CO)L(NO)]PF_6$ and $[(\eta\text{-}C_6Me_6)\text{-}Cr(CO)_2(NO)]PF_6$. Treatment of the same complexes with benzenediazonium hexafluorophosphate gave the paramagnetic derivatives $[(\eta\text{-}C_6Me_6)Cr(CO)_2L]PF_6$ where L = PPh_3, $PMePh_2$ and PMe_2Ph or $[(\eta\text{-}C_6Me_6)Cr(CO)L(N_2Ph)]PF_6$ and $[(\eta\text{-}C_6Me_6)Cr(CO)_2(N_2Ph)]PF_6$ where L = $P(OMe)_3$ and $P(OPh)_3$. Cyclic voltammetric studies showed that the oxidation of the complex $(\eta\text{-}C_6Me_6)Cr(CO)_2L$ to $[(\eta\text{-}C_6Me_6)\text{-}Cr(CO)_2L]^+$ was a reversible one electron process [106].

The crystal and molecular structure of dicarbonyl(η-methylbenzoate)thiocarbonylchromium was determined by a single-crystal X-ray study. The $Cr(CO)_2CS$ group had C_s symmetry with a Cr-C(S) bond length of 1.792 Å and a Cr-C(O) mean bond length of 1.849 Å [107]. Caillet and Jaouen have reported detailed assignments of the infrared and Raman spectra of the benchrotrene analogue (3.52; L = CS). Comparisons with the spectra of methyl benzoate and the benchrotrene complex (3.52; L = CO) were made [108].

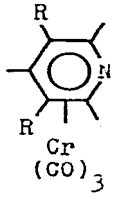
The IR and Raman spectra of tricarbonyl(η-thiophen)chromium (3.53) were recorded for solid and solution samples. The vibrational modes were assigned and compared with the corresponding absorptions for benchrotrene [109].



(3.52)



(3.53)



(3.54)

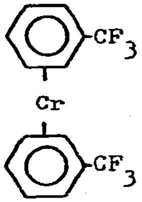
Tri- and penta-methylpyridine gave the π-complexes (3.54; R = H, Me) rather than the alternative σ-nitrogen complexes [110]. A series of previously unknown (η-arene)tricarbonylmolybdenum complexes was prepared by the reaction of tripyridinemolybdenum tricarbonyl with boron trifluoride etherate in the presence of the arene ligand.

$$(Py)_3Mo(CO)_3 + \text{arene} + 3BF_3 \xrightarrow[20^\circ]{Et_2O} (\eta\text{-arene})Mo(CO)_3 + 3PyBF_3$$

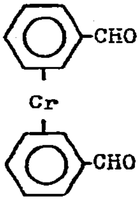
This method of preparation was shown to be superior to the direct synthesis in that it gave higher yields, a shorter reaction time was required and the reaction could be carried out at room temperature. An attempt was made to extend the method to the synthesis of (η-arene)tungsten tricarbonyl complexes but only low yields of product were obtained [111]. The crystal structure of trimethylenemethanechromiumtricarbonyltriphenylphosphine was determined by conventional Patterson and Fourier methods. Carbon-carbon bond distances in the trimethylenemethane ligand, as well as metal-ligand π-bonding distances, were equivalent with mean values of 1.42 Å and 2.23 Å respectively. The trimethylenemethane ligand was not quite planar with the central atom displaced 0.28 Å from the plane of the other three carbon atoms [112].

4. $(\eta\text{-}C_6H_6)_2Cr$

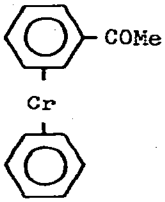
Halogenated arenes were cocondensed with chromium vapour to yield bis(η-arene)chromium compounds such as bis(η-benzotrifluoride)chromium (4.1). When two trifluoromethyl groups were present in the arene ligand then products with good air and temperature stability were obtained. However IR spectroscopy indicated that the metal-arene bonding was weaker in such complexes than in bis(η-benzene)chromium [113].



(4.1)



(4.2)

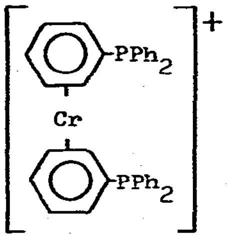


(4.3)

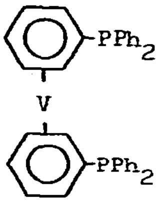
Chromium underwent reaction with excess ethylbenzoate at -196°, in vacuo, to give bis(ethylbenzoate)chromium. This complex was oxidized in air in the presence of water to give $Cr(PhCO_2Et)_2OH$ and decomposed thermally at 260° to form chromium(III) compounds [114]. Bis(η-benzene)chromium was metallated with n-butyllithium in tetramethylethylenediamine and the lithio intermediate was treated with dimethylformamide to give the symmetrical dialdehyde (4.2) in 65% yield. The acetyl derivative (4.3) was prepared in the same way [115]. Symmetry coordinates of the molecular vibrations of trigonal XY_6 prism (D_{3h}) and antiprism (D_{3d}) models of organometallic compounds, for example di(η-benzene)chromium, were calculated [116]. A complete harmonic force field was constructed for di(η-benzene)chromium with symmetry coordinates that preserved the ligand identity and the molecular vibrations were analyzed by treating the whole, eclipsed D_6 , molecule. The calculated mean amplitudes agreed with those obtained from electron diffraction studies [117].

The thermal decomposition of bis(η-benzene)chromium, bis(η-ethylbenzene)chromium and bis(η-ethylbenzene)vanadium were studied. The activation energies of the decompositions were approximately 22.5 kcal mol^{-1}. The change of metal from vanadium to chromium increased the rate of decomposition approximately ten times [118]. Second order rate constants and activation parameters were obtained for the reaction of oxygen with bis(η-benzene)-, bis(η-ethylbenzene)-, bis(η-cumene)- and bis(η-p-xylene)-chromium and other η-benzene complexes of chromium and molybdenum [119].

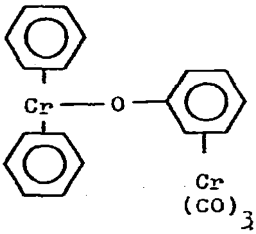
The thermal decomposition of several ethyl derivatives of bis(η-benzene)chromium was investigated by statistical and by flow techniques. The reactions were heterogeneous and adsorption of the compound on the reaction surface was followed by decomposition. The two techniques used gave similar results [120]. Highly active catalysts for low pressure ethylene polymerization were formed when bis(η-benzene)-, bis(η-cumene)-chromium or bis(η-cyclopentadienyl)chromium were deposited on high surface area silica or silica-alumina supports. The (η-arene)chromium complexes required an acidic support (silica-alumina) or thermal aging with silica to form a highly active catalyst [121]. The cationic bis(η-benzene)chromium compound (4.4) was labile to solvolytic cleavage of the C-(η-Ar)-P bond while the same bond in the iso-electronic vanadium compound (4.5) was inert [122]. The helium(I) and helium(II) photoelectron spectra of benchrotrene and



(4.4)



(4.5)



(4.6)

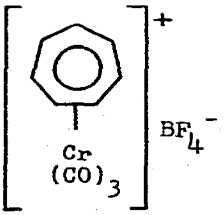
bis(η-benzene)chromium have been measured and rationalized in terms of all electron ab initio SCF MO calculations. The ionization potentials were interpreted with the aid of Koopmans theorem which permitted effects arising from the ligand molecular orbitals to be included [123].

The reaction of $(\eta\text{-}C_6H_6)_2CrOH$ with $(\eta\text{-}C_6H_5OH)Cr(CO)_3$ at room temperature gave good yield of the binuclear complex (4.6). Thermolysis of this complex in a sealed tube gave chromium carbonyl, di(η-benzene)chromium, chromium(II) phenoxide and benzene [124]. Cosolubility of $(\eta\text{-PhH})_2CrI$, $(\eta\text{-PhMe})_2CrI$, bis(η-mesitylene)CrI and $(\eta\text{-}C_6H_4Me_2)_2CrI$ in water was investigated between 10-40°, under these conditions the ratios of the solubilities were virtually constant [125]. A mixture of bis(η-arene)chromium iodides was resolved by thin layer chromatography on silica gel containing gypsum (13%). The developing solvent was a mixture of acetone, benzene and water [126]. Mass-spectrometric analysis of trace amounts of bis(η-arene)chromium(I) iodide was carried out by field ionization. By using tungsten emitters in weak fields in the range 25-200° spectral lines corresponding to $[(\eta\text{-arene})_2Cr]^+$ were obtained. In a strong electric field, simultaneous ionization and dissociation of the bis(η-arene)chromium(I) iodide took place *on the emitter surface* [127].

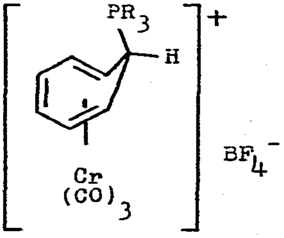
The redox behaviour of bis(η-biphenyl)chromium(I) iodide in water was studied by polarography, cyclic voltammetry, large scale electrolysis and pulse voltammetric methods. The voltammetric behaviour was complicated by adsorption phenomena of both the oxidized and reduced forms. The redox potential obtained was regarded as the surface redox potential of the two adsorbed forms [128].

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

A kinetic study was made of the addition of acetylacetone and methoxide ion to the cations $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, W) under pseudo first order conditions using a large excess of nucleophile. The rate of addition of both nucleophiles was almost independent of the nature of the central metal decreasing slightly in the order W>Mo$\geqslant$Cr. This data supported a mechanism involving direct nucleophilic attack at the tropylium ring [129]. The η-cycloheptatrienyl complex (5.1) was attacked by trialkyl- and triaryl-phosphines to form the derivatives (5.2). ^{1}H NMR spectroscopy indicated that the phosphonium group occupied an



(5.1)



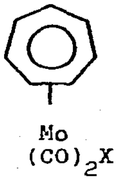
(5.2)

<u>exo</u>- position relative to the chromium atom [130]. The decomposition of tricarbonyl(η-cycloheptatriene)chromium has been studied by the chemical vapour deposition technique. The complex decomposed above 300° to give deposits containing principally chromium and carbon. Labelling experiments with ^{13}C confirmed the cycloheptatriene group as the major source of the carbon [131].

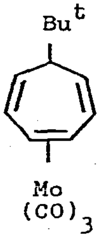
The ^{13}C NMR spectra of some tricarbonyl(η^6-cyclopolyene) complexes of Cr, Mo and W (cyclopolyene = 1,3,5-cycloheptatriene, 1,3,5-cyclooctatriene and 1,3,5,7-cyclooctatetraene) were recorded. Hindered rotation of the cyclopolyene ligands around the prolonged 3-fold axis of the tricarbonylmetal groups was detected and the 1,3,5-cyclooctatriene ligand in $C_8H_{10}Cr(CO)_3$ was frozen at -120°C into a chiral conformation [132].

Irradiation of a boiling solution of [2.2]paracyclophane and chromium-, molybdenum-, or tungsten-hexacarbonyl gave the corresponding complexes tricarbonyl(η-[2.2]paracyclophane)metal. The molybdenum complex decomposed to the starting materials and free molybdenum by a first order reaction [133]. Ligand displacement reactions of (η-cycloheptatrienyl)molybdenum complexes have been used as a convenient route to other (η-cycloheptatrienyl)-molybdenum compounds [134] as previously described [135].

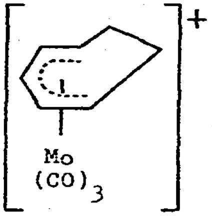
An X-ray crystal structure and molecular structure determination on the η-cycloheptatrienyl compound (5.3; X = $SnCl_3$) confirmed discrete molecules with a molybdenum-tin covalent bond and a planar cycloheptatrienyl ring [136]. The structures of the analogous compounds (5.3; X = Cl, Br) were determined in the same way. The molybdenum-bromine bond was shorter than the molybdenum-chlorine bond because of stronger $d_\pi - d_\pi$ interaction between molybdenum and the heavier halogen [137]. The crystal and molecular structure of the (η-t-butylcycloheptatriene)-molybdenum complex (5.4) was confirmed by single crystal X-ray methods [138].



(5.3)



(5.4)



(5.5)

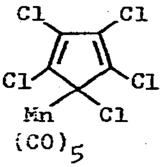
Compounds of the type (η-C_7H_7)Mo$(CO)_2MR_3$ (M = Ge, Sn, R = Ph) were prepared by treatment of the anion [η-C_7H_7Mo$(CO)_2]^-$ with $ClMR_3$ [139]. Trichlorotin and trichlorogermanium derivatives were prepared by the insertion of $SnCl_2$ or $GeCl_2$, as in the following reaction:

$$(\eta\text{-}C_7H_7)Mo(CO)_2Cl + HGeCl_3 \longrightarrow (\eta\text{-}C_7H_7)Mo(CO)_2GeCl_3 + HCl$$

Salzer and Werner have studied the addition of electrophilic reagents to the hydrocarbon ligand in tricarbonyl(η-cycloheptatriene)molybdenum. The acids HBF_4 and HCl were effective in protonating the ring to form the η-cycloheptadienyl complex cation (5.5). Treatment of this cation with triphenylphosphine gave nucleophilic addition to the seven-membered ring and breakdown of the complex [140].

6. $(\eta\text{-}C_5H_5)Mn(CO)_3$ (i) Formation

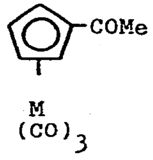
The reaction of diazotetrachlorocyclopentadiene with pentacarbonylchloromanganese gave $(\eta\text{-}C_5Cl_5)Mn(CO)_3$ and the σ-bonded complex (6.1) [141]. Wiles has examined the effects of nuclear recoil in organometallic compounds by using the $^{56}Fe(\underline{n}, \underline{p})^{56}Mn$ reaction with bis(η-cyclopentadienyl)diiron tetracarbonyl as the target. A very low yield of cymantrene-^{56}Mn and the manganese pentacarbonyl-^{56}Mn radical was obtained indicating that recoil was not important in the formation of organometallic species in nuclear reactions [142].



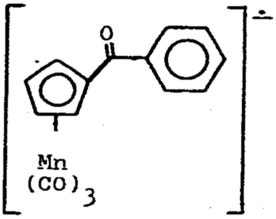
(6.1)

(ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structure of acetylcymantrene (6.2; M = Mn) and its rhenium analogue (6.2; M = Re) have been determined by X-ray crystallography. Acetylcymantrene shows the same orientation of carbonyl groups to the cyclopentadienyl ring as cymantrene itself. However the rhenium compound (6.2; M = Re) is less symmetrical than tricarbonyl(η-cyclopentadienyl)rhenium [143]. ^{55}Mn, ^{185}Re, ^{187}Re and ^{127}I NQR spectra of tricarbonyl-(η-cyclopentadienyl)-manganese and -rhenium derivatives were recorded. The spectra were more affected by the conjugation



(6.2)



(6.3)

characteristics of the substituents than the inductive effects. From the spectra it was concluded that the $(CO)_3ReC_5H_4$ group was a stronger electron acceptor than the $(CO)_3MnC_5H_4$ group [144]. Good agreement was obtained between the hyperfine constants determined by ESR spectroscopy and calculated by the extended Huckel molecular orbital method for the radical anion of the cymantrene derivative (6.3). Extensive electron delocalization over the molecule was indicated with most of the spin density on the manganese atom, the ketone group and the phenyl ring [145].

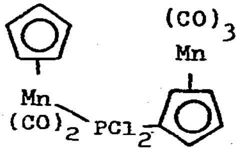
The rate of isotopic exchange of hydrogen atoms of cymantrenylferrocene and ferrocene in $CF_3COOD-(CH_2Cl)_2$ was determined by mass spectrometry, NMR and EPR analysis [146]. The mass spectra of the manganese complexes $(\eta-RC_5H_4)Mn(CO)_2CX$ (X = S, O; R = H, Me) were recorded and the appearance potentials of most of the metallic fragment ions determined. The manganese to carbonyl and thiocarbonyl ionic bond dissociation energies were estimated and it was concluded that the Mn-CS bond was stronger than the Mn-CO bond. It was suggested that the thiocarbonyl group was primarily a σ-donor ligand [147]. Cymantrene was included with ferrocene into a clathrate compound with thiourea and the incorporation of cymantrene was confirmed by photochemical degradation. When ferrocene was absent then cymantrene was not taken up into the clathrate [148].

The first order kinetics for the thermal decomposition of tricarbonyl(η-cyclopentadienyl)manganese were determined at 410-460°. The products of thermal decomposition were manganese, carbon monoxide and cyclopentadiene [149].

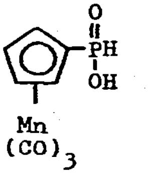
(iii) <u>General Chemistry</u>

Tricarbonyl(η-cyclopentadienyl)manganese, nickelocene and ferrocene formed adducts with thiourea. This reaction was used to separate tricarbonyl(η-cyclopentadienyl)manganese from (η-acetylcyclopentadienyl)tricarbonylmanganese [150]. Treatment of cymantrene with phosphorus trichloride and aluminium(III) chloride in isopentane gave the phosphorus bridged binuclear complex (6.4). The same reaction in the absence of solvent and at a high temperature gave the phosphine oxide derivatives (6.5 and 6.6) in low yields [151].

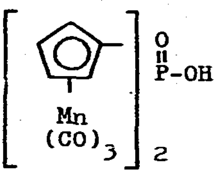
Irradiation of tricarbonyl(η-cyclopentadienyl)manganese in the presence of cycloheptatrienes gave the neutral diamagnetic complexes (6.7; R = H, 7-Me, 1-Me, 7-Ph, 7-<u>t</u>-Bu). Treatment of



(6.4)

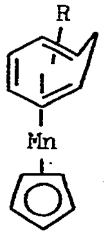


(6.5)

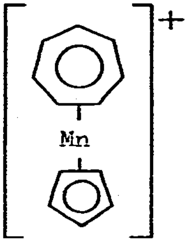


(6.6)

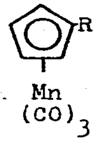
the complex (6.7; R = H) with triphenylmethyl salts gave the cation (6.8) which was reduced by lithium aluminium hydride to give the neutral complex (6.7; R = H). (η-Cyclooctatriene)- and (1-6-η-cyclooctatetraene)-(η-cyclopentadienyl)manganese were prepared similarly but they were much less stable than their cycloheptatriene analogues [152].



(6.7)



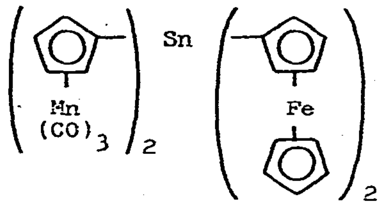
(6.8)



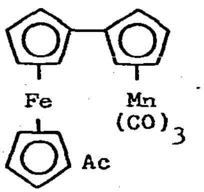
(6.9)

The ultraviolet irradiation of an equimolar mixture of cymantrene and $Ph_2PCH_2CH_2PPh_2$ gave the bidentate complex (η-C_5H_5)Mn(CO)($Ph_2PCH_2CH_2PPh_2$). The reaction was thought to proceed stepwise and this was supported by the isolation of the monodentate complex (η-C_5H_5)$Mn(CO)_2$ $Ph_2PCH_2CH_2P(O)Ph_2$ [153]. The reaction of lithiated cymantrene (6.9; R = Li) with chlorosilanes gave the corresponding methylsilanes (6.9; R = $SiHMe_2$, SiHMePh) [154]. Lithiocymantrene was dimerized in the presence of copper(I) bromide at -10° to 100° [155].

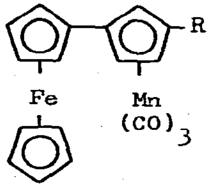
Tricarbonyllithiocyclopentadienylmanganese was condensed with biferrocenyltin(IV) chloride to give the organo-tin derivative (6.10). Reaction of this latter compound with mercury(II) chloride gave cymantrenyl- and ferrocenyl-mercury(II) chlorides [156]. Cymantrenylferrocene was acetylated by acetic anhydride and



(6.10)



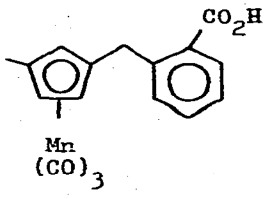
(6.11)



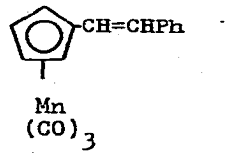
(6.12)

phosphoric acid in the unsubstituted cyclopentadienyl ring to form the acetylferrocene (6.11). Metallation of cymantrenylferrocene with butyllithium afforded the intermediate (6.12; R = Li) which was converted to the boronic acid [6.12; R = $B(OH)_2$] with tri-n-butylborate. The boronic acid was converted into the bromocymantrene (6.12; R = Br) and the mercurichloride (6.12; R = HgCl) with copper(II) bromide and mercury(II) chloride respectively [157].

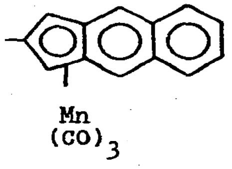
Methylcymantrene was treated with enamines, such as PhCH=NPh to give the corresponding vinylcymantrene compounds, such as the trans-olefin (6.13) [158]. The benzylcymantrene (6.14) was prepared from the corresponding benzoylcymantrene by esterification, lactonization and reduction. This intermediate was then



(6.14)

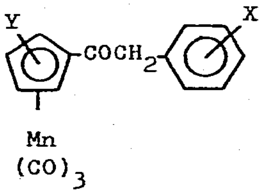


(6.13)

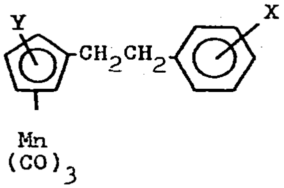


(6.15)

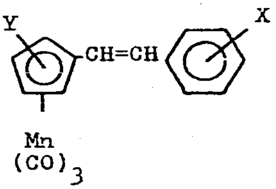
cyclized, the ketone group was reduced to the hydroxyl group and the alcohol was dehydrated to give the cymantro naphthalene (6.15). An isomer, with the methyl group in the alternative position of the cyclopentadienyl ring, was prepared in the same way [159]. A series of cymantrene derivatives (6.16; X = H, Me, OMe, Cl; Y = H, Me) was prepared by Friedel-Crafts benzoylation of tricarbonyl(η-cyclopentadienyl)manganese. These compounds were used to prepare the cymantrene derivatives (6.17) and (6.18). These compounds were studied by UV, IR and ^{1}H NMR spectroscopy [160].



(6.16)



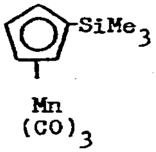
(6.17)



(6.18)

The addition of 0.01-1% trimethylsilylcymantrene (6.19) to organosilicon elastomers was effective in increasing their thermo-oxidative stability [161]. Petroleum reforming which led to high octane gasolines also gave enhanced concentrations of polynuclear aromatic hydrocarbons including benzo[a]pyrene. The concentration of this last compound in the exhaust emissions from such gasolines was reduced by 30% when cymantrene was added [162].

Rats were dosed orally and intravenously with ^{54}Mn labelled methylcymantrene and the whole-body retention, tissue distribution and excretion of manganese was followed. Initial rapid excretion

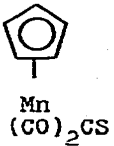


(6.19)

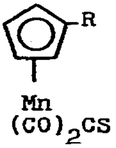
of most of the manganese was observed. The methylcymantrene was metabolized in the liver, lung and kidney and excreted in inorganic form. High levels of ^{54}Mn were found in the urine and this atypical behaviour was explained by bioconversion of methylcymantrene in the kidney [163].

(iv) Analogues

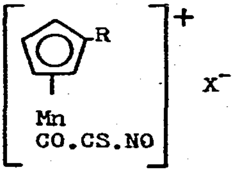
The absolute integrated IR intensities of the carbonyl and thiocarbonyl groups in the cymantrene analogue (6.20) have been compared and confirm that the thiocarbonyl group is a better π-acceptor than the carbonyl group [164]. The (η-cyclopentadienyl)-manganese salts (6.22; R = H, Me; X = SbF_6^-, PF_6^-) were formed by treatment of the neutral complexes (6.21; R = H, Me) with $NO^+SbF_6^-$ and $NO_2^+PF_6^-$. The remaining carbonyl group in each of the salts



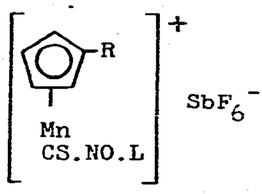
(6.20)



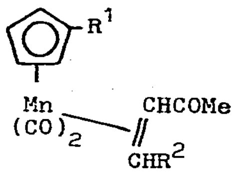
(6.21)



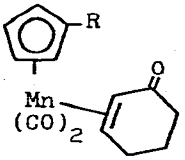
(6.22)



(6.23)



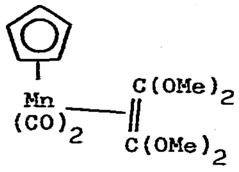
(6.24)



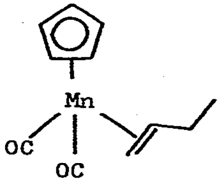
(6.25)

(6.22) was displaced with Lewis bases to give the products (6.23; R = H, Me; L = PPh_3, $AsPh_3$, $SbPh_3$) [165]. The structure of dicarbonyl(η-cyclopentadienyl)(benzoylphenylcarbene)manganese was determined by X-ray methods. The Mn-C distance of 1.88 Å was the shortest Mn-carbene distance recorded. The data obtained indicated that there was no π-interaction between either the phenyl or benzoyl groups and the carbene carbon atom [166].

The cymantrene analogues (6.24; R^1 = H, Me; R^2 = H, Ph), (6.25; R = H, Me) have been synthesized by photolysis of cymantrene or methylcymantrene with the appropriate α,β-unsaturated ketone [167]. Dicarbonyl(η-cyclopentadienyl)tetramethoxyethylenemanganese (6.26) was prepared by the irradiation of cymantrene in the presence of tetramethoxyethylene. The ^1H NMR spectrum of the tetramethoxyethylene derivative (6.26) showed a definite temperature dependence. The NMR data was explained on the basis of two mutually independent ligand movements. One being a hindered rotation of the olefin ligand around the metal-ligand bond ($\Delta G^{+}_{194} \sim 9.8$ kcal/mol) and the other a hindered movement of the four methoxy groups ($\Delta G^{+}_{263} \sim 13.8$ kcal/mol) [168]. The crystal and molecular structure of the cymantrene analogue (6.27) has been determined by X-ray



(6.26)

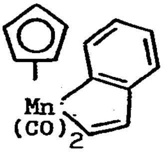


(6.27)

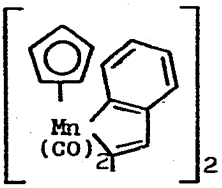
methods. The methylvinyl ketone ligand was bound to manganese through the olefinic double bond. The bonding between the manganese atom and the (η-cyclopentadienyl) and carbonyl groups was similar to that in the parent cymantrene [169]. The reversible equilibrium of $(\eta\text{-}C_5H_5)Mn(CO)_2N_2$ and tetrahydrofuran (THF) with $(\eta\text{-}C_5H_5)Mn(CO)_2THF$ and nitrogen was investigated [170].

Cymantrene was converted to the reactive etherate (6.28; R = THF) by irradiation in THF and this intermediate was treated with the organometallic acetylenes $Ph_3MC{\equiv}CPh$, where M = Si, Ge, Sn, to give the cymantrene analogues (6.28; R = $Ph_3MC{\equiv}CPh$). The tin-containing product decomposed under the reaction conditions used to give the organic cymantrene derivatives (6.29 and 6.30)[171] The tetrahydrofuran complexes (6.31; R = H, Me) behaved as carbene

(6.28)



(6.29)

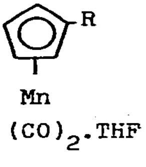


(6.30)

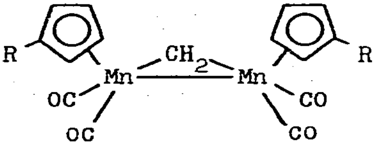
trapping reagents when treated with diazomethane. When the reactions were carried out at low temperatures the dimeric complexes (6.32 and 6.33; R = H, Me) were isolated together with the olefin complex $(\eta\text{-}RC_5H_4)Mn(CO)_2(\eta\text{-}C_2H_4)$, [172].

The complexes $LMn(CO)_2THF$ ($L = \eta\text{-}C_5H_5$, $\eta\text{-}MeC_5H_4$) were treated with aliphatic diazo compounds. Substitution of the THF ligand occurred to give the corresponding olefin, ketimine or carbene complex. In the reaction with 3-diazo-2-butanone or 3-diazocamphor the THF was replaced by 2-butenone or 3-iminocamphor respectively whilst diaryldiazomethanes gave the corresponding carbenes [173].

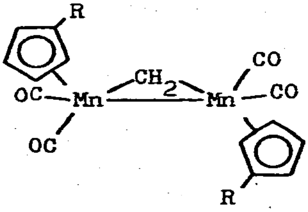
The organosulphide complexes $(\eta\text{-}C_5H_5)Mn(CO)_2(SR_2)$ (R = Me, Et, n-Pr, n-Bu, Ph, CH_2Ph) and $(\eta\text{-}C_5H_5)Mn(CO)_2C_4H_8S$ were prepared photochemically from cymantrene and the appropriate ligand. The



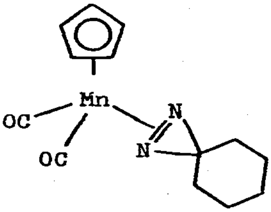
(6.31)



(6.32)



(6.33)

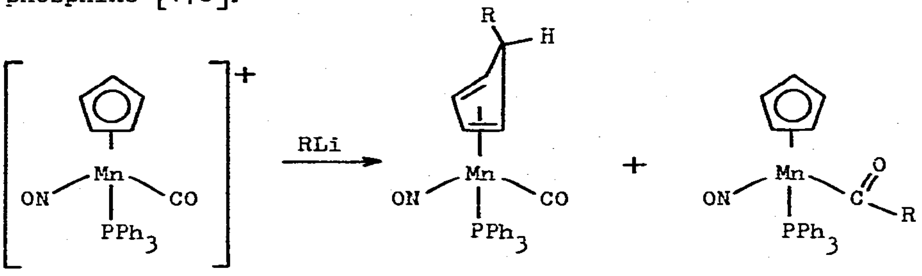


(6.34)

kinetics for the reaction of the sulphide complexes with tertiary phosphines and phosphites were studied. The reaction rates were first order in substrate and independent of both the nature and concentration of the phosphorus ligand, and increased with changes in the organosulphide ligand in the order $SMe_2 < C_4H_8S < SEt_2$ $S(n\text{-}Bu)_2 < S(n\text{-}Pr)_2 < S(CH_2Ph)_2 \ll SPh_2$. An SN1 dissociative mechanism was proposed with cleavage of the manganese-sulphur bond as the rate determining step [174].

^1H NMR spectroscopy was used to follow the deuteration of tricarbonyl(η-pyrrolyl)manganese with $MeCO_2D$-CF_3CO_2D in ethylene dichloride. Deuteration occurred initially on the manganese atom [175]. Several diazirine complexes have been prepared including the cymantrene complex (6.34) [176]. The reaction of $(\eta\text{-}C_5H_5)$-$M(CO)_2NO$ (M = Mo, W) with nitrosyl hexafluorophosphate afforded the ionic compounds $[(\eta\text{-}C_5H_5)M(NO)_2CO]PF_6$ (M = Mo, W) in good yields. These compounds underwent facile carbonyl substitution with neutral ligands [L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$] and anions (X = Cl^-, Br^-, I^-) to give $[(\eta\text{-}C_5H_5)M(NO)_2L]PF_6$ and and $(\eta\text{-}C_5H_5)M(NO)_2X$ respectively. The carbonyl group in the complexes $[(\eta\text{-}C_5H_5)M(NO)_2CO]^+$ was replaced rapidly by coordinating solvents such as methyl cyanide and acetone [177].

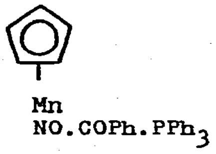
The optically active cymantrene analogue (6.35) was attacked by methyllithium, phenyllithium and p-substituted phenyllithiums to give mixtures of the η-cyclopentadiene complexes (6.36; R = Me, Ph, p-XC_6H_4) and the acyl complexes (6.37; R = Me, Ph, p-XC_6H_4). The η-cyclopentadiene complexes (6.36) were optically stable but the acyl complexes racemized in solution. Electron releasing substituents X in the acyl group COC_6H_4X of the complex increased the rate of the first-order racemization while electron withdrawing groups decreased it. The reaction was interpreted in terms of initial loss of triphenylphosphine followed by inversion of configuration at manganese and recombination with triphenylphosphine [178].



(6.35) (6.36) (6.37)

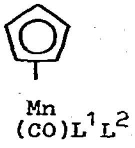
The racemization of the optically active (η-cyclopentadienyl)-manganese complex (6.38) was followed in toluene at 20°. The reaction was first order and was retarded by the addition of triphenylphosphine. A dissociative mechanism was proposed involving loss of the triphenylphosphine ligand [179].

At the symposium on Metal Carbonyl Chemistry, dedicated to Professor Walter Hieber, Brunner presented a paper on manganese esters of the type $(\eta\text{-}C_5H_5)Mn(COOR)(NO)(PPh_3)$ and $(\eta\text{-}C_5H_5)Mn\text{-}(CO\text{-}\underline{p}\text{-}C_6H_4X)(NO)(PPh_3)$. The possible mechanism for the racemisation

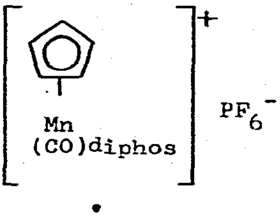


(6.38)

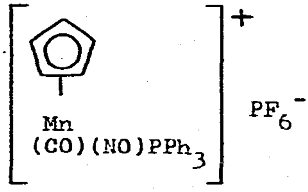
of these optically active complexes was discussed [180]. The half-wave potentials of the cymantrene analogues (6.39; $L^1 = L^2 = PPh_3$; L^1, L^2 = diphos.; $L^1 = PPh_3$, L^2 = CO) were determined by cyclic voltammetry and indicated that these compounds should undergo easy oxidation. This was found to be the case with the complex (6.39; L^1, L^2 = diphos.) which was oxidized with silver hexafluorophosphate to the paramagnetic salt (6.40). The complex (6.39; $L^1 = L^2 = PPh_3$) was oxidized in the same way with nitrosyl hexafluorophosphate to the salt (6.41) [181].



(6.39)

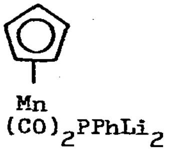


(6.40)

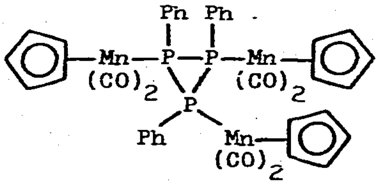


(6.41)

Pure *cis*- and *trans*-(η-C_5H_5)M(CO)$_2$(PPh$_3$)X (M = Mo, X = I or Br; M = W, X = I) were separated by chromatography on alumina. The *cis*/*trans* isomer ratio was a function of the halogen and the method of preparation [182].

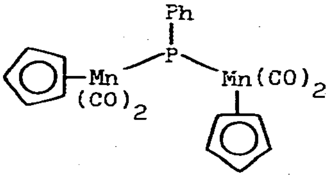


(6.42)

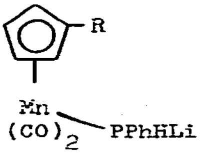


(6.43)

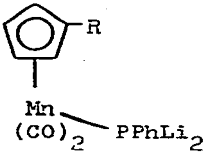
The delithiation of the dilithiophenylphosphane (6.42) gave tris[dicarbonyl(η-cyclopentadienyl)manganese]triphenylcyclotriphosphane (6.43) which on thermolysis gave the phosphindene complex (6.44). The phosphindene complex (6.44) was claimed to be the first compound in which phosphorus(I) had a trigonal planar coordination which was stabilized by metal-dπ-phosphorus-pπ bonds [183, 184].



(6.44)

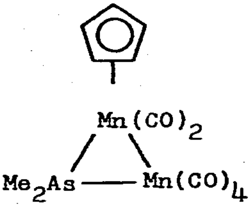


(6.45)

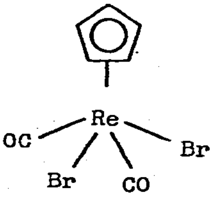


(6.46)

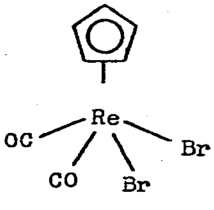
The phosphine complexes, $(\eta\text{-}C_5H_5)(CO)_2MnPPhH_2$ and $(\eta\text{-}MeC_5H_4)$-$(CO)_2MnPPhH_2$ were treated with n-BuLi to give the corresponding lithio-phosphines (6.45 and 6.46; R = H, Me) [185]. The crystal and molecular structure of the stereochemically crowded cymantrene analogue (6.47) has been determined by X-ray crystallography. A terminal Mn-C-O group was distorted to a bond angle of 160° by steric interactions [186].



(6.47)

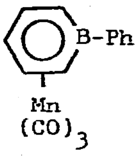


(6.48)

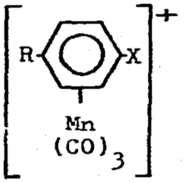


(6.49)

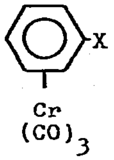
The diagonal (6.48) and lateral (6.49) isomers of dibromo-(η-cyclopentadienyl)dicarbonylrhenium were separated by chromatography on a Florisil column in dichloromethane. The isomers (6.48 and 6.49) were stable in the solid state at room temperature but the lateral isomer (6.49) readily isomerized to the diagonal isomer (6.48) when heated in chloroform [187]. Huttner and Gartzke have determined the crystal and molecular structure of the cymantrene analogue (6.50). The carbon-carbon distances in the ligand indicated cyclic conjugation although the phenyl group was twisted 14° out of the ligand plane [188].



(6.50)

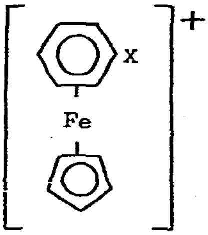


(6.51)

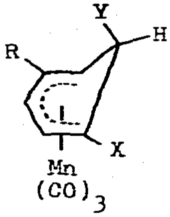


(6.52)

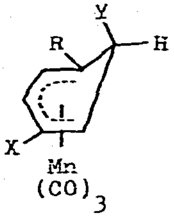
Tricarbonyl(η-methoxy-) and tricarbonyl(η-halogeno-benzene)-manganese salts were prepared by the reaction of the appropriate arene with bromopentacarbonylmanganese in the presence of aluminium chloride. Nucleophilic substitution of the chlorine atom in the cation (6.51; R = H, X = Cl) proceeded readily with a variety of nucleophiles (methoxide, phenoxide, benzenethiolate and azide) to give the expected substitution products (6.51; R = H, X = MeO, PhO, PhS and N_3). It was established for arene complexes with the same halogen (X) that there was a sharp increase in reactivity in the order (6.52) < (6.53) < (6.51). The high reactivity of the manganese complexes was utilized in the preparation of other functionally substituted arene complexes by reaction with amines [189]. The reaction of the manganese salts (6.51; R = Me, X = Cl, NMe_2) and (6.51; R = H, X = OMe) with lithium aluminium hydride, methyllithium and phenyllithium gave the corresponding cyclohexadienyl complexes (6.54; Y = H, Me, Ph) and (6.55; Y = H, Me, Ph) [190].



(6.53)



(6.54)



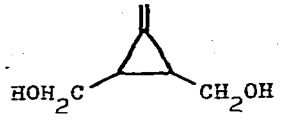
(6.55)

The mass spectra of the seven coordinate rhenium complexes, (η-RC_5H_4)$Re(CO)_2XY$ (R = H, Me, CO_2Me; X, Y = H, Me, COMe, Br, I, HgCl), have been recorded and interpreted. The main fragmentation paths were a successive expulsion of the carbonyl groups together with the parallel elimination of the substituents X and Y from the molecular ion of the complex [191].

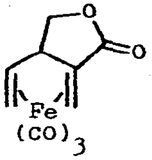
7. (Acyclic-η-diene)$Fe(CO)_3$ and (η-trimethylenemethane)$Fe(CO)_3$ complexes

Amine oxides, preferably trimethylamine oxide, induced a fast reaction between iron pentacarbonyl and various dienes to give tricarbonyl(η-diene)iron complexes in good yields according to the equation:

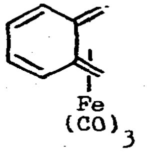
$$L + Fe(CO)_5 + Me_3NO \longrightarrow LFe(CO)_3 + Me_3N + CO_2 + CO$$



(7.1)

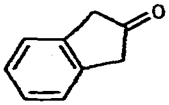


(7.2)

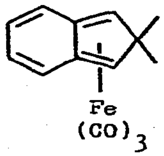


(7.3)

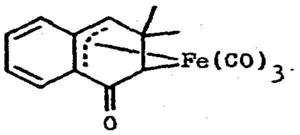
Practically instantaneous complexation was achieved with some ligands at low temperatures [192]. *Cis*- and *trans*-2,3-bis-(hydroxymethyl)methylenecyclopropanes (7.1) underwent ring opening with diiron nonacarbonyl to yield the 3-methylene-4-vinyldihydrofuran complex (7.2) which was characterized by X-ray crystallography. A mechanistic pathway for the reaction was proposed [193]. The synthesis of cyclopentenones from tricarbonyl-(η-1,3-diene)iron complexes has been studied. The quinodimethane compound (7.3) was treated with aluminium chloride in benzene at room temperature to give 2-indanone (7.4). A reaction between the isoindene complex (7.5) and aluminium chloride did not give the expected bicyclic ketone but gave the iron tricarbonyl complex (7.6). A mixture of 2- and 3-cyclopentenone was obtained in low



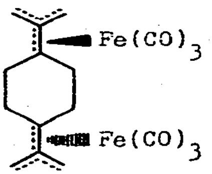
(7.4)



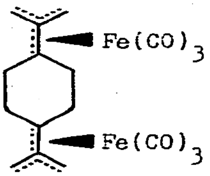
(7.5)



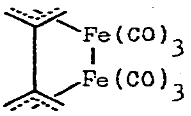
(7.6)



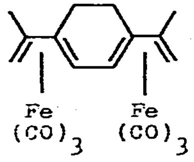
(7.7)



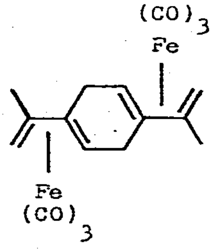
(7.8)



(7.9)



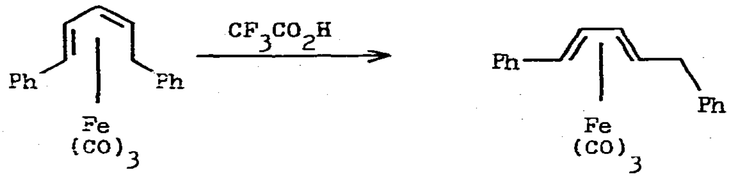
(7.10)



(7.11)

yield from tricarbonyl(η-butadiene)iron under the same conditions [194]. The reaction of 2,3-bis(bromomethyl)-1,3-butadiene with diiron nonacarbonyl gave two isomeric trimethylene methane complexes (7.7 and 7.8) together with the allyl complex (7.9). Treatment of (7.7) with sulphuric acid gave a 1/1 mixture of the bis-diene complexes (7.10 and 7.11) [195].

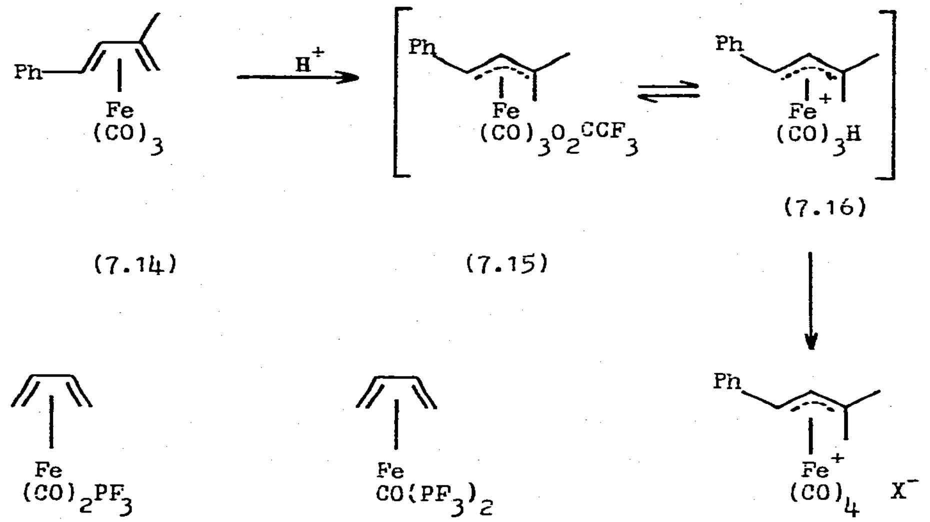
Whitesides and Neilan have studied the acid-catalyzed cis-trans isomerization of substituted (η-butadiene)iron tricarbonyl complexes. Trifluoroacetic acid catalyzed the reaction which proceeded by rate determining protonation of the iron atom in the cis-complex (7.12) followed by hydrogen transfer to carbon-4 and formation of an η-allyl intermediate. This intermediate rearranged to the trans form which then transferred hydrogen from the ligand



(7.12) (7.13)

to the metal to reform the protonated η-butadiene complex and thence the trans-isomer (7.13). The isotope effect in the initial protonation was unusually large [196]. The protonation of tricarbonyl(η-diene)iron complexes by strong acids has been re-examined by Whitesides and Arhart. The phenylbutadiene complex (7.14) was treated with fluoroboric acid in trifluoroacetic acid to form an equilibrium mixture of the allyl cations (7.15 and 7.16) which decomposed slowly to the iron tetracarbonyl complex (7.17) [197].

Busch and Clark have prepared ten methyl substituted tricarbonyl(η-butadiene)iron complexes by photochemical reaction of the appropriate diene with iron pentacarbonyl or by thermal reaction with diiron nonacarbonyl. Carbonyl stretching force constants were determined from the IR spectra of the complexes and were found to vary in an additive manner with the number and position of the methyl groups on the η-butadiene ligand. On irradiation with phosphorus trifluoride several of the complexes were converted to the mono- or di-phosphorus trifluoride derivatives (7.18 and 7.19). The IR spectra of these derivatives were compared with the spectra of the parent tricarbonyl(η-butadiene)iron compounds [198].



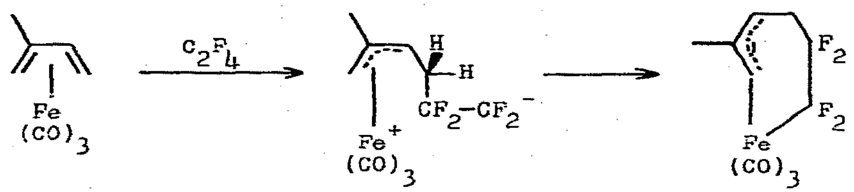
(7.14) (7.15) (7.16)

(7.18) (7.19) (7.17)

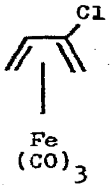
It was shown that the phosphorus trifluoride ligand preferred the apical position over either of the two basal sites and this was confirmed by ^{19}F NMR spectroscopy. A second phosphorus trifluoride group preferred the basal position trans to the methyl group in asymmetric diene complexes. The examination of NMR spectra recorded at several temperatures gave information on the general nature of the nonrigid process [199].

The iron tricarbonyl complexes of butadiene and methylbutadienes including penta-1,3-diene, isoprene and 2,3-dimethylbuta-1,3-diene combined with tetrafluoroethylene on UV irradiation to yield (η-allyl)iron(II) complexes with a C_2F_4 bridge between the ligand and iron. It was suggested that the reaction involved endo-attack by tetrafluoroethylene on a coordinated double bond in a cisoid

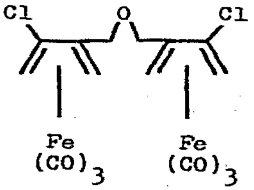
1,2-η-bonded species (7.21) formed by irradiation. The iron tricarbonyl group then migrated to stabilize the charge formed. Thus the (η-isoprene) complex (7.20) was converted to the bridged (η-allyl) complex (7.22) through the intermediate (7.21). Attack by tetrafluoroethylene took place preferentially at the least-substituted end of the complexed diene. Related reactions with cyclic diene, cinnamaldehyde, and styryldiphenylphosphine complexes were also examined [200]. The reaction of 2,3-dichlorobutadiene with diiron nonacarbonyl gave the diene complexes (7.23) and (7.24) together with some (η-butatriene)hexacarbonyldiiron(0). No complex of the reactant diene was isolated. However reaction of the same diene with $Fe_3(CO)_{12}$ gave the dichlorobutadiene complex (7.25). These results were discussed in terms of accepted bonding models for coordinated alkenes and 1,3-dienes [201].



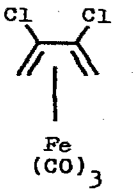
(7.20) (7.21) (7.22)



(7.23)

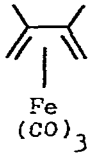


(7.24)

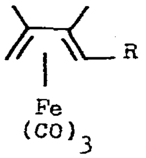


(7.25)

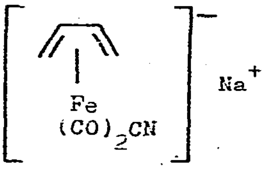
Friedel-Crafts acetylation of the tricarbonyl(η-butadiene)iron complex (7.26) in the presence of aluminium chloride gave exclusively the anti-form of the complex (7.27; R = MeCO). On reduction of this complex with lithium aluminium hydride-aluminium chloride an equimolar mixture of the syn- and anti-forms of the complex (7.27; R = Et) was obtained. Other acylation reactions of the (η-butadiene)iron complex (7.28) and related complexes were described [202].



(7.26)



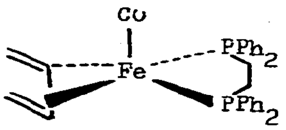
(7.27)



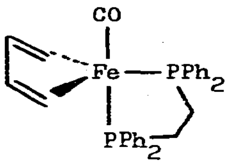
(7.28)

Iron(III) chloride complexed with the dienes L (L = butadiene, isoprene, 1,3-pentadiene) and carbon monoxide to give the compounds $L_2Fe(CO)$. The compound bis(η-butadiene)carbonyliron was a good catalyst for the polymerization of butadiene [203]. Acyclic and cyclic (η-diene)iron complexes were treated with sodium bis-(trimethylsilyl)amide to form anionic cyanide complexes. Thus (η-butadiene)tricarbonyliron gave the complex (7.28) [204].

The reaction of bis(η-cyclooctatetraene)iron 1,3-butadiene and carbon monoxide gave (η-CH_2=CHCH=CH_2)(η-C_8H_8)Fe(CO). The latter complex was a good catalyst for the polymerization of butadiene to give 4-vinylcyclohexene and 1,5-cyclooctadiene [205]. The reaction of bis(η-butadiene)carbonyliron with $(Ph_2PCH_2)_2$ gave a 4/1 mixture of two isomers of the phosphine complex (7.29 and

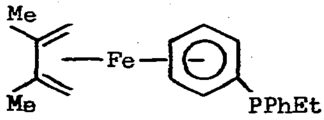


(7.29)

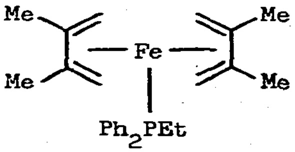


(7.30)

7.30) as shown by ^{31}P NMR spectroscopy [206]. Irradiation of the iron complex (7.31) in the presence of 2,3-dimethylbutadiene gave the diene complex (7.32) [207]. El-Awady has calculated the relative stabilities of the isomeric iron tricarbonyl complexes which may be formed with 9-methyl-2,4,6,8-nonatetraenal. A



(7.31)

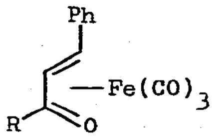


(7.32)

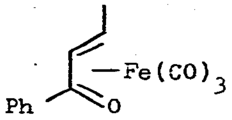
semiempirical extended Hueckel AVE charge SCF MO method was used and the isomers were placed in the order of stability:

2,3,4,5->4,5,6,7->6,7,8,9-tetrahapto.

where the iron tricarbonyl group was bound to a butadiene residue in each case. The susceptibility of the complexes to substitution was related to the electron densities calculated for the atoms of the complexes [208]. The electric dipole moments of the complexes η-LFe(CO)$_3$ (L = trans-PhCH=CHCHO, trans-PhCH=CHCOMe, *trans*-PhCH=CHCOPh, *trans*, *trans*-PhCH=CH-CH=CHPh and CH$_2$=CHCHO were measured. A vectorial analysis of the results led to the conclusion that the ligands were bound to the iron via the olefinic and carbonylic bonds as shown for (η-PhCH=CHCOR)Fe(CO)$_3$ (7.33) and that the lone pairs on the oxygen of the carbonyl group were not involved. It was also concluded that the metal to ligand back-bonding was stronger in the aldehyde and ketone complexes than in the butadiene complexes [209].

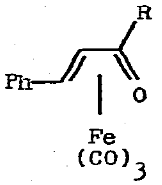


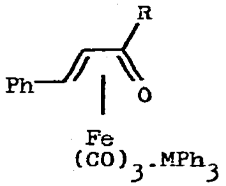
(7.33)

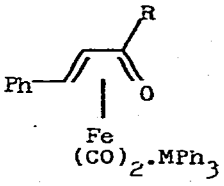


(7.34)

Treatment of the (η-allyl)tricarbonyliron anion with benzoyl chloride gave the (η-diene)iron complex (7.34) as a minor product [210]. Cardaci and Concetti have investigated the reaction between the olefin-iron tricarbonyl complexes (7.35; R = H, Me, Ph) and the Group V ligands MPh$_3$, where M = P, As, Sb. The first formed products were the complexes (7.36; R = H, Me, Ph; M = P, As, Sb) obtained through an associative mechanism. The second stage of the reaction gave the iron tricarbonyl complexes Fe(CO)$_3$(MPh$_3$)$_2$ where M = Ph, As, Sb and the olefin compounds (7.37; R = H, Me, Ph; M = P, As, Sb). The kinetic results indicated that three different pathways were involved in this step [211]. The reaction of 4-vinylcyclohexene with diiron nonacarbonyl or triiron dodecacarbonyl in benzene gave 3:1 mixtures of tricarbonyl

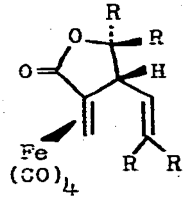

(7.35)

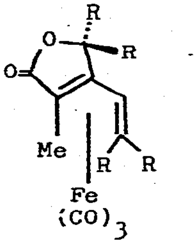

(7.36)

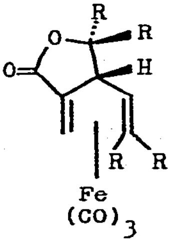

(7.37)

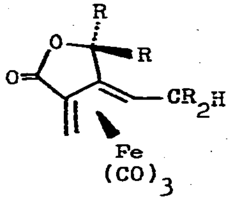
1- and 2-ethylcyclohexadieneiron. The 1-ethyl isomer was converted to the 2-ethyl isomer by treatment with concentrated sulphuric acid [212].

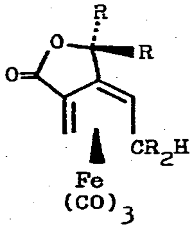
The iron complex (7.38; R = H) rearranged slowly in refluxing ether to give the diene complex (7.39; R = H). The corresponding deuterated complex (7.38; R = D) rearranged to the complex (7.39;


(7.38)


(7.39)


(7.40)


(7.41)

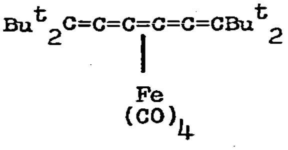

(7.42)

R = D) with no deuterium scrambling. The optically active complex (7.38; R = H) therefore rearranged regiospecifically, but with extensive racemisation. In contrast the complex (7.40; R = H) rearranged rapidly to give a mixture of the diene complexes (7.41; R = H) and (7.42; R = H). The corresponding deuterated complex (7.40; R = D) rearranged with no deuterium scrambling. This rearrangement occurred regiospecifically without extensive racemisation. Possible mechanisms for these rearrangements were proposed [213].

King and Harmon have described the formation of iron carbonyl complexes of tetra-t-butylhexapentaene (7.43) by direct reaction of the ligand with diiron nonacarbonyl or triiron dodecacarbonyl. The yellow monoolefin complex (7.44) was obtained together with the red butatriene complex (7.45). In each case, ^{13}C NMR spectroscopy was used to demonstrate that the centre double bonds of the pentaene were bonded to the iron carbonyl residues in the complexes, suggesting that the bulky t-butyl groups prevented access of the metal to the outer olefinic double bonds. A tetramethylhexapentaene diironhexacarbonyl complex was obtained from 2,7-dichloro-2,7-dimethyl-3,5-octadiyne and triiron dodecacarbonyl in the presence of zinc dust, this product was not a simple analogue of

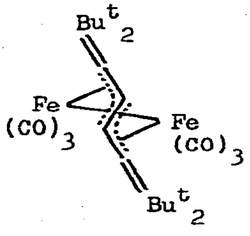
$Bu^t{}_2C{=}C{=}C{=}C{=}C{=}CBu^t{}_2$

(7.43)



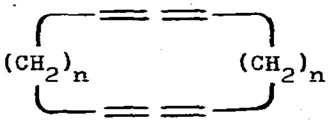
$Bu^t{}_2C{=}C{=}\underset{\substack{|\\ Fe(CO)_4}}{C{=}C}{=}C{=}CBu^t{}_2$

(7.44)

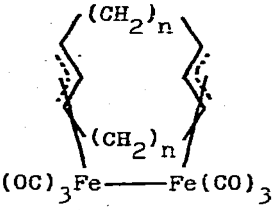


(7.45)

the tetra-t-butyl complex (7.45) [214]. King and Harmon have described the intramolecular transannular cyclization of the macrocyclic diallenes (7.46; n = 2, 5) with triiron dodecacarbonyl to form the bicyclic tetramethyleneethane diiron hexacarbonyl complexes (7.47; n = 2, 5). Degradation of the complex (7.47; n = 2) with cerium(IV) gave 1,2,3,4-tetrahydronapthalene [215].



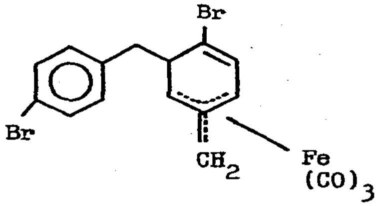
(7.46)



(7.47)

An approximate valence force field was calculated for tricarbonyl(trimethylenemethane)iron and it satisfactorily reproduced the observed wavenumbers. Many of the observed wavenumbers were shown to be due to complex normal modes which involved several different types of internal coordinate [216].

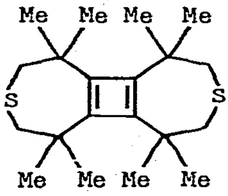
The trimethylenemethane complex (7.48) was formed in low yield from diiron nonacarbonyl and p-bromobenzylbromide at 45° in hexane [217].



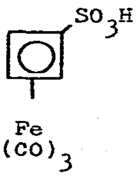
(7.48)

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

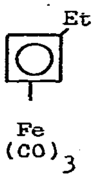
The palladium chloride complex of the fused cyclobutadiene (8.1) when treated with iron pentacarbonyl gave the iron tricarbonyl complex of (8.1). In the latter complex the iron atom was displaced from a central position above the cyclobutadiene ring due to interactions between carbonyl carbon atoms and the cyclobutadiene ring atoms and between carbonyl and methyl groups. The four-membered ring had a trapezoidal shape with C-C double bond lengths of 1.455 and 1.485 Å and C-C single bond lengths of 1.479 Å [218]



(8.1)



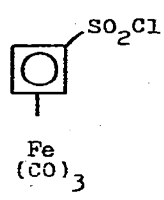
(8.2)



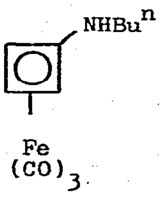
(8.3)

Tricarbonyl(η-cyclobutadiene)iron was treated with a sulphuric acid-acetic anhydride mixture to give the sulphonic acid (8.2) which was isolated as the p-toluidine salt. Tricarbonyl(η-ethylcyclobutadiene)iron (8.3) was treated similarly to give a mixture with the sulphonic acid group in the 2- and 3- positions of the ethylcyclobutadiene ring [219]. The (η-cyclobutadienesulphonic acid) iron complex (8.2) was converted to the chlorosulphonate (8.4) with phosphorus pentachloride and this intermediate was treated with butylamine to give the aminoalkyl derivative (8.5) [220].

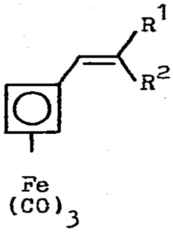
Biehl and Reeves have used the Wittig reagent of tricarbonyl-(η-formylcyclobutadiene)iron to form the tricarbonyl(η-vinyl



(8.4)

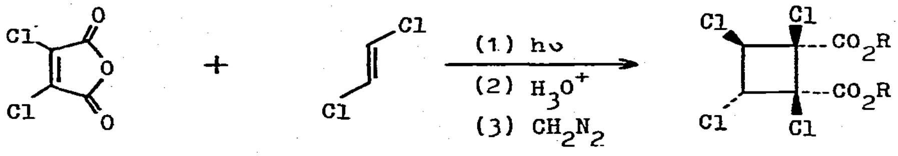


(8.5)



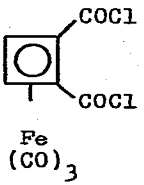
(8.6)

cyclobutadiene)iron derivatives (8.6; R^1, R^2 = H, Me, Ph, CO_2Et) [221]. The 1,2- disubstituted cyclobutadiene complex (8.7) was prepared from the tetrahalocyclobutane (8.8) by treatment with sodium tetracarbonylferrate(-II) (Scheme 8.1). The structure of the complex (8.7) was established by chemical correlation with the known tricarbonyl(η-1,2-dimethylcyclobutadiene)iron. The bis(acid chloride) (8.9) was prepared and this was used as the

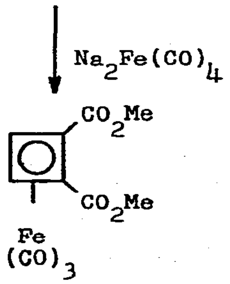


(8.8)

Scheme 8.1



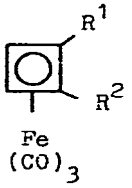
(8.9)



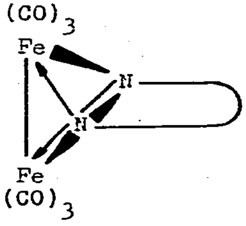
(8.7)

starting material for the preparation of a series of 1,2-disubstituted tricarbonyl(η-cyclobutadiene)iron complexes [222].

Berens has prepared several tricarbonyl(η-cyclobutadiene) iron complexes with vicinal substituents (8.10). The complex (8.10; $R^1 = NMe_2$, $R^2 = CN$) with adjacent electron releasing and withdrawing groups was oxidized in attempts to form the free butadiene complex which was not obtained. The di-t-butyl complex (8.10; $R^1 = R^2 = Bu^t$) was prepared and converted to the tri-t-butyl derivative but the tetra-t-butyl compound could not be formed [223].

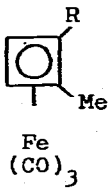


(8.10)

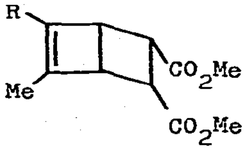


(8.11)

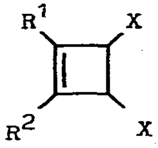
The synthesis of tricarbonyl(η-phenylcyclobutadiene)iron has been reported by Devon. The reactions of trieneiron tricarbonyl compounds with olefins, acetylenes and 1,2- and 1,3-dipolar species were studied [224]. The reaction of μ-(*cis*-azo)hexacarbonyldiiron complexes of the type (8.11) with diphenylacetylene gave tricarbonyl tetraphenylcyclobutadieneiron. The mechanism of this reaction was discussed [225]. The (η-cyclobutadiene)iron complexes (8.12; R = Me, Et) were oxidized with cerium(IV) ammonium nitrate in the presence of dimethyl maleate to give the corresponding bicyclo-[2.2.0]hexanes (8.13; R = Me, Et). Similar adducts were formed in



(8.12)



(8.13)

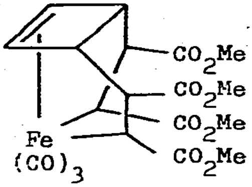


(8.14)

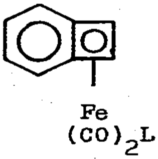
the presence of dimethylfumarate and maleic anhydride. The oxidation of the resolved complex (8.12; R = Et) gave racemic adducts which indicated the intermediacy of free cyclobutadienes [226]. In a separate paper Schmidt described the oxidation of the (η-cyclobutadiene)iron complexes, (8.10; $R^1 = R^2 = H$; R^1 = Me, R^2 = Me and R^1 = Me, R^2 = Et) with cerium(IV) ammonium nitrate, bromine or iodine, when the oxidation products of the corresponding cyclobutadienes (8.14; X = ONO_2, Br, I) were obtained. The formation of optically active cyclobutenes from chiral (8.10; R^1 = Me, R^2 = Et) showed that this process involved reaction of cyclobutadiene still attached to iron in contrast to the Diels-Alder reaction which involved liberated cyclobutadiene [227].

The He(I), He(II) and X-ray photoelectron spectra of tricarbonyl(η-cyclobutadiene)iron were recorded. It was necessary to take into account deviations from Koopman's theorem in order to interpret the low energy spectra. All electron ab initio SCF MO calculations were made using Gaussian-type functions and a large negative charge on the cyclobutadiene ring was indicated [228]. The He(I) and He(II) photoelectron spectra of tricarbonyl-(η-cyclobutadiene)iron were recorded and interpreted with the aid of *ab initio* SCF MO calculations. The calculated charge distribution in the complex was similar to that found for (η-butadiene)-tricarbonyliron with a net negative charge on the η-C_4H_4 ligand which was the result of metal to ligand pi-electron donation into the $1e_g$ molecular orbitals. The application of Koopman's theorem to the interpretation of the bands arising from the metal molecular orbitals was found to lead to inaccuracies [229].

The crystal and molecular structure of a 1:2 tricarbonyl-(η-cyclobutadiene)iron tricarbonyl-dimethyl maleate photoadduct, $C_{16}H_{20}O_8Fe(CO)_3$ (8.15), was determined by single-crystal X-ray diffraction techniques [230].



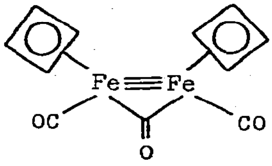
(8.15)



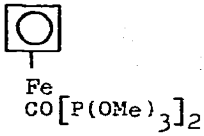
(8.16)

The ^1H NMR spectrum of tricarbonyl(η-cyclobutadiene)iron in nematic solution has been measured in order to determine the effect of vibrational averaging on the geometry of the molecule. A normal coordinate analysis was made and the ratio of dipolar coupling constants for a square structure corrected for harmonic vibrations was obtained. The cyclobutadiene ring had lower than D_{4h} symmetry [231]. Efraty, Huang and Weston have investigated the mass spectral fragmentation of the benzocyclobutadiene complexes (8.16; L = CO, PPh_3, $AsPh_3$, $SbPh_3$) at 80eV. The complexes undergo sequential unimolecular loss of carbon monoxide and elimination of MPh_3 (M = P, As, Sb), the benzocyclobutadiene and benzyne cations were also formed. Detailed fragmentation pathways were proposed [232].

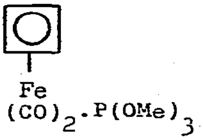
The interesting binuclear(η-cyclobutadiene)iron compound (8.17) was obtained by irradiation of tricarbonyl(η-cyclobutadiene)-iron in THF at -40° and under nitrogen. The product was converted back to tricarbonyl(η-cyclobutadiene)iron by treatment with carbon monoxide, while with trimethyl phosphite it gave the derivatives (8.18) and 8.19) [233].



(8.17)



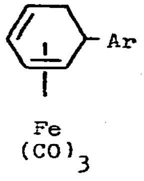
(8.18)



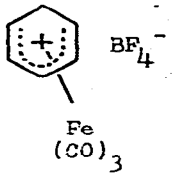
(8.19)

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

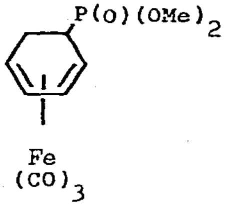
The tricarbonyl(η-cyclohexadienyl)iron cation has been used as an electrophile to attack the organometallic aryls $ArMMe_3$ (Ar = Ph, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, 2-furyl, 2-thienyl; M = Si, Sn) and form the tricarbonyl(η-cyclohexadiene)iron derivatives (9.1; Ar = Ph, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, 2-furyl, 2-thienyl) by cleavage of the Ar-M bond. The order of reactivity of the arene substrates was Ar = Ph < 4-$MeOC_6H_4$ < 4$Me_2NC_6H_4$ and the aryltin compounds were more reactive than the arylsilanes [234]. Reaction of tricarbonyl-(η-cyclohexadienyl)iron tetrafluoroborate (9.2) with trimethylphosphite gave the phosphonate diester (9.3). The tricarbonyliron



(9.1)

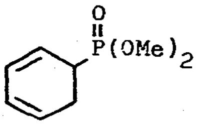


(9.2)

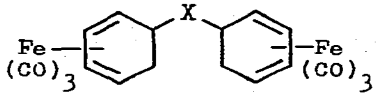


(9.3)

group was removed readily from the diester (9.3) by aqueous methanolic iron(III) chloride to give the phosphonate (9.4). Treatment of the complex (9.2) with sodium hydrogen carbonate and sodium sulphide gave the dimers (9.5; X = O and S) respectively [235].

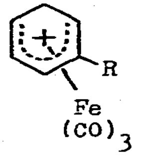


(9.4)

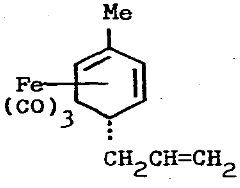


(9.5)

The cationic complexes (9.6; R = H, Me, OMe) were alkylated by organo-zinc and -cadmium reagents. For example the complex (9.6; R = Me) when treated with $Zn(CH_2CH{=}CH_2)_2$ gave the diene complex (9.7). Alkylation occurred on the opposite side of the ring to the $Fe(CO)_3$ group [236]. The η-cyclohexadienone complexes (9.8; R = H, Me) have been used as arylating agents for amines such as aniline. Thus the complex (9.8) was converted to the

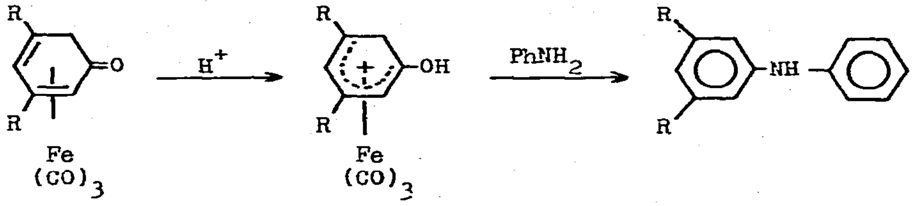


(9.6)



(9.7)

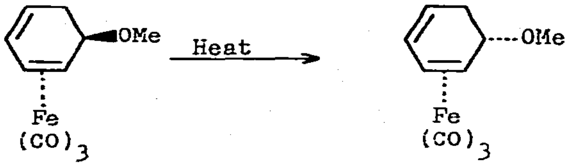
intermediate η-cyclohexadienyl cation (9.9) which attacked aniline to form the secondary amine (9.10) [237]. A solution of the cyclohexadienyliron cation (9.2) in methanol was heated to give,



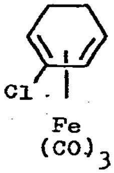
(9.8) (9.9) (9.10)

as the initial product, the exomethoxycyclohexadiene complex (9.11) which isomerized slowly to the endomethoxy complex (9.12). The reaction was extended to give the corresponding endo-ethoxy and endo-malononitrile compounds [238].

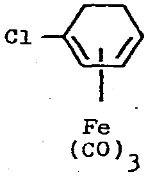
2-Chloro-1,3-cyclohexadiene was partially isomerized to the 1-chloro compound on heating with triiron dodecacarbonyl in boiling benzene and the complexes (9.13 and 9.14) were formed at the same time [239]. The substituted tricarbonyl(η-cyclohexadiene)-iron compounds (9.15; M = Si, Ge, Sn) were formed by treatment of the tricarbonyl(η-cyclohexadienyl)iron cation with the



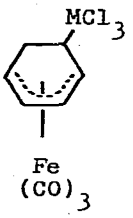
(9.11) (9.12)



(9.13)

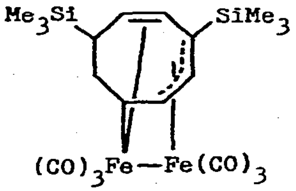


(9.14)

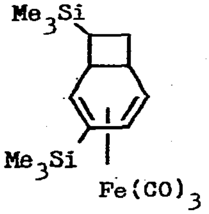


(9.15)

triethylammonium salts, $Et_3NH^+MCl_3^-$ (M = Si, Ge, Sn) [240]. The treatment of bis-5,8-trimethylsilyl-1,3,6-cyclooctatriene with diiron nonacarbonyl and triiron dodecacarbonyl gave the tricarbonyliron complexes (9.16) and (9.17). Fluxional behaviour was not observed with either of these complexes [241]. The reaction of phenyl- and carbomethoxy-cyclooctatetraenes with equimolar

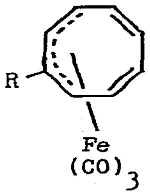


(9.16)

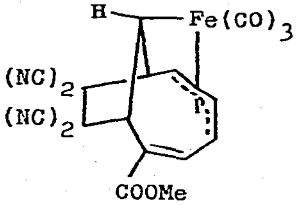


(9.17)

amounts of diiron nonacarbonyl gave the complexes (9.18; R = Ph) and (9.18; R = $COOCH_3$) respectively. The reaction of these complexes and similar compounds with tetracyanoethylene was investigated. The cycloaddition of tetracyanoethylene occurred via an unusual 1,3 bonding process with the formation of products in which the iron atom was both σ- and π-bonded, for example the addition product (9.19) was obtained [242].

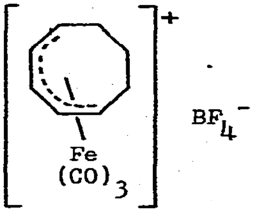


(9.18)

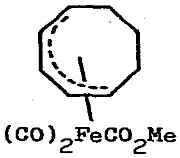


(9.19)

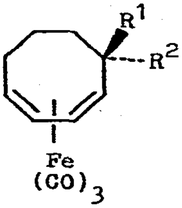
The reaction of the complex cation (9.20) with methoxide ion gave the cyclooctadienyl complex (9.21) and the irontricarbonyl complexes (9.22; $R^1 = H$, $R^2 = MeO$ and $R^1 = MeO$, $R^2 = H$) [243]. The (η-cyclooctatetraene)iron complexes (9.23; M = Si, Ge, Sn) were formed from the appropriately substituted cyclooctatetraene and diiron nonacarbonyl, in two cases the diiron complexes (9.24;



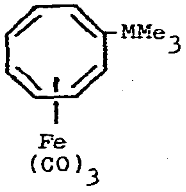
(9.20)



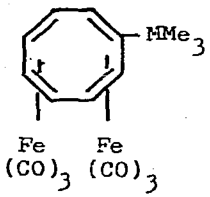
(9.21)



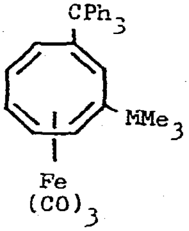
(9.22)



(9.23)

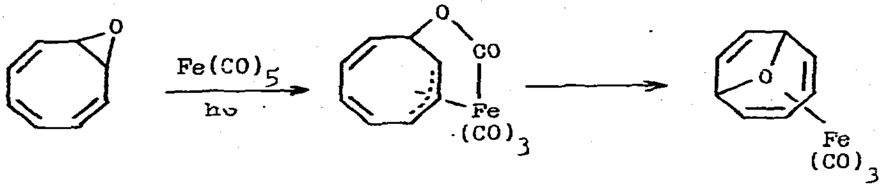


(9.24)



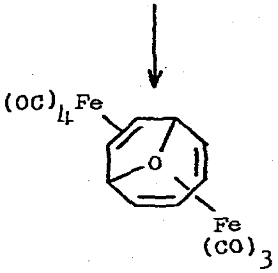
(9.25)

M = Si, Sn) were also obtained. Treatment of the silicon and germanium derivatives (9.23; M = Si, Ge) with triphenylmethyltetrafluoroborate gave tetrafluoroborate salts which were hydrolysed to neutral complexes containing the disubstituted cyclooctatetraene ligands (9.25; M = Si, Ge) [244]. The reaction of bis(η-cyclooctatetraene)iron with Lewis bases L, where L = F_3P, $(MeO)_3P$,



(9.26) (9.27) (9.28)

(9.30)

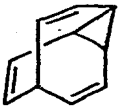


(9.29)

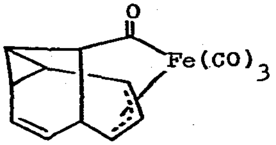
$(EtO)_3P$, $(C_3H_7O)_3P$ under mild conditions produced complexes of the type $Fe(C_8H_8)L_3$ [245].

Irradiation of the bicyclononatriene (9.26) with iron pentacarbonyl gave initially the ferralactone (9.27) which was rapidly transformed into the bicyclononatriene irontricarbonyl complex (9.28) and then the diironheptacarbonyl complex (9.29). Degradation of this product (9.29) with trimethylamine oxide in ether formed the novel bicyclononatriene (9.30) [246].

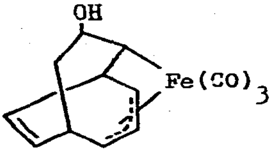
Photolysis of bullvalene (9.31) and iron pentacarbonyl in moist benzene gave the iron tricarbonyl derivatives (9.32) and (9.33). The treatment of the complex (9.32) with $Fe_2(CO)_9$ gave the complex (9.34) which underwent valence isomerism to give the compound (9.35) [247]. The irontricarbonyl derivatives (9.37 and 9.38) of the propellane methylimide (9.36) were prepared and their reactions with cerium(IV) and a dienophile were investigated [248].



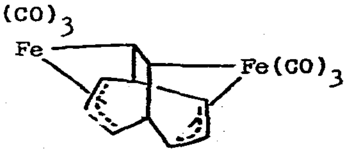
(9.31)



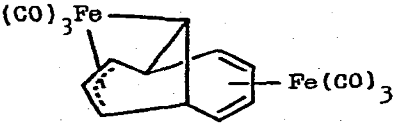
(9.32)



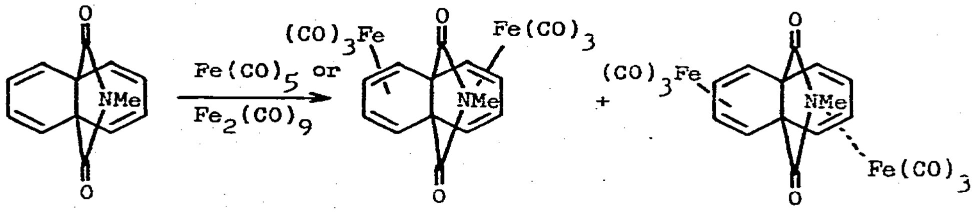
(9.33)



(9.34)

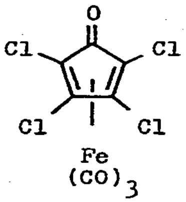


(9.35)

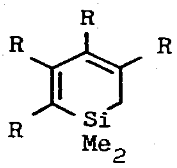


(9.36) (9.37) (9.38)

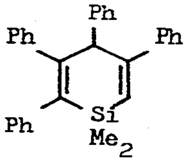
The reaction between dichloroacetylene and diiron nonacarbonyl gave the cyclopentadienone complex (9.39) [249]. The silacyclohexadiene (9.40; R = Ph) was isomerized in the presence of iron



(9.39)

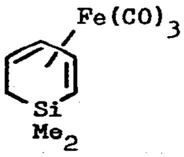


(9.40)

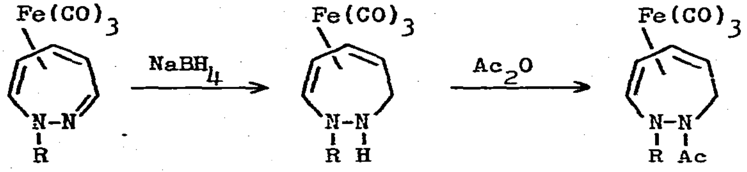


(9.41)

pentacarbonyl to give the diene (9.41) whereas the diene (9.40; R = H) formed the complex (9.42) [250]. The tricarbonyl diazepine iron complexes (9.43; R = COMe, CO$_2$Et) were prepared and their



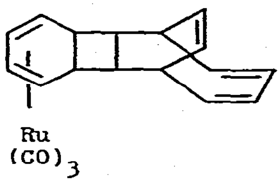
(9.42)



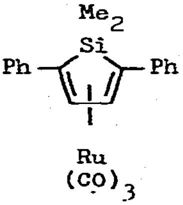
(9.43)

Scheme 9.1

reactions with sodium borohydride and acetic anhydride were investigated (Scheme 9.1) [251]. The reaction of cyclooctatetraene with the hydrido-carbonylruthenium cluster $[H_4Ru_4(CO)_{12}]$ gave the ruthenium complex (9.44). The ruthenium tricarbonyl group was removed from the complex (9.44) with cerium(IV) to give the dimer of cyclooctatetraene [252].

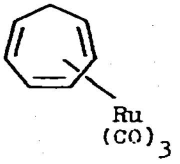


(9.44)

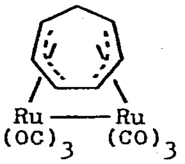


(9.45)

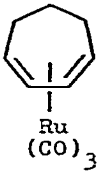
The tricarbonylruthenium complex (9.45) was prepared by the reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene with dodecacarbonyltriruthenium in toluene. The crystal structure of the complex (9.45) was determined by X-ray analysis. In the uncomplexed ligand the bond lengths within the cyclopentadiene ring were consistent with complete localization of the double bonds. The butadiene unit was planar with the silicon atom displaced from this plane by 0.08 Å. In the presence of the metal considerable perturbation of the bond lengths in the silole ring occurred and the silicon atom was displaced from the plane of the butadiene unit by 0.72 Å. [253]. Cycloheptatriene was heated with triruthenium dodecacarbonyl in hexane to give a cluster compound $Ru_3(CO)_6(\eta-C_7H_7)(\eta-C_7H_9)$ as the principal product together with low yields of the η-cycloheptatriene (9.46 and 9.47) and η-cycloheptadiene (9.48) complexes. These three complexes (9.46 - 9.48) were analogous to well known iron complexes. Several alkyl and halogeno derivatives were characterized [254].



(9.46)



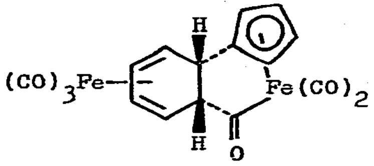
(9.47)



(9.48)

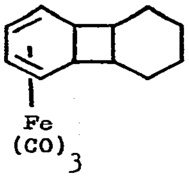
(ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structure of the complex $(C_5H_4C_6H_6CO)Fe_2(CO)_5$, (9.49) prepared by the reaction of diiron nonacarbonyl with spiro(2,4-cyclopentadiene-1,7'-norcara-2',4'-diene) (9.50) [255], was determined by X-ray crystallography. The structural analysis showed that the original spironorcaradiene (9.50) had undergone 1,6' bond scission with the incorporation of a -C(=O)- moiety at the 6'- position [256]. Chiang has carried out X-ray crystallographic studies on the iron tricarbonyl complexes of bullvalene and barbaralone, in each case π-allyl-C-O



(9.49)

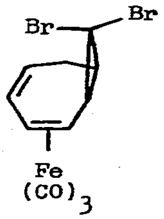
(9.50)



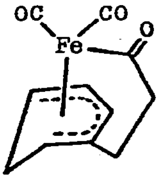
(9.51)

type bonding was observed [257]. The molecular structure and conformation of the tricarbonyl(η-cyclohexadiene)iron complex (9.51) has been determined by single crystal X-ray diffractometry. The preferred conformations of the two cycloalkane rings are mutually incompatible which has resulted in a compromise with the cyclobutane folded by 15° along its diagonal and the cyclohexane having a conformation intermediate between planarity and a chair [258].

The crystal and molecular structure of the η-bicyclooctadiene complex (9.52) has been determined by single crystal X-ray analysis. The molecule is strained due to intramolecular repulsion between the endo-bromine atom and the cycloheptadiene ring. The complex (9.52) was debrominated by methyllithium in ether and rearranged



(9.52)

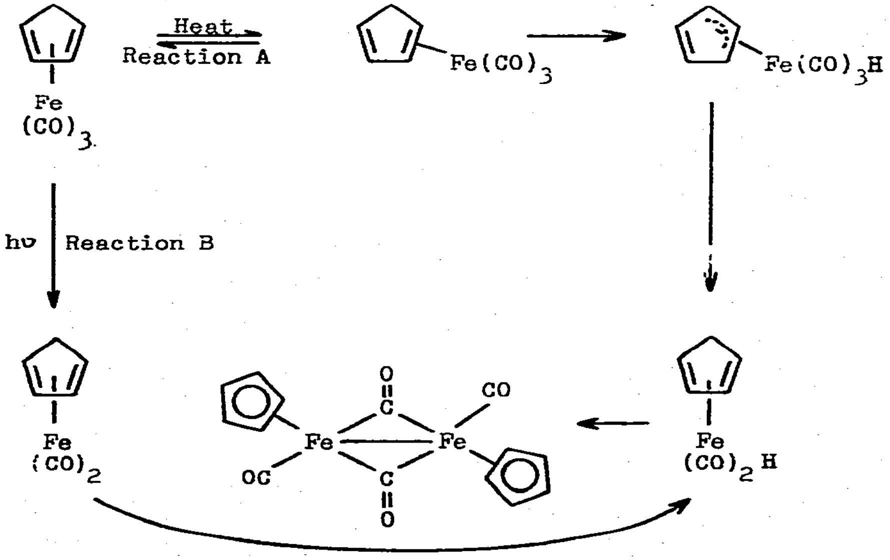


(9.53)

to the η-cyclohexadienyl compound (9.53) through a spirocyclopropene intermediate [259].

The ^1H and ^{13}C NMR spectra of tricarbonyl(1-methoxy-1,3-cyclohexadiene)iron have been reinvestigated. The magnitude of the $^1J(CH)$ coupling constants at C-2, C-3 and C-4 indicated trigonal hybridization at these centres. The energy barrier for basal-apical exchange of the carbonyl ligand was $\Delta G_c = 7.3$ kcal mol^{-1}. Electronic charge densities were discussed and compared with values obtained previously by INDO calculations [260].

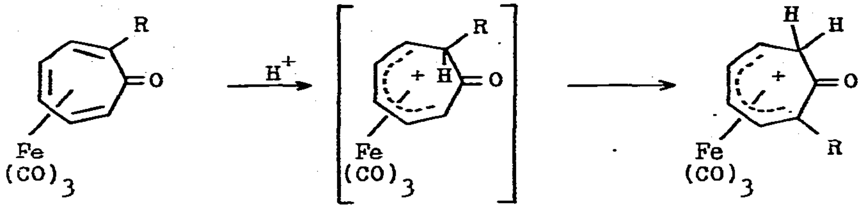
Thermal and photochemical conversion of tricarbonyl(η-cyclopentadiene)iron to dicarbonyl(η-cyclopentadienyl)iron dimer has been investigated by a ^1H NMR analysis of the deuterated reactant. Stereospecific free radical chain abstraction of the deuterium by an Fe(I) species was proposed for the thermal



Scheme 9.2

process (Reaction A, Scheme 9.2). The photochemical reaction, by contrast, appeared to proceed by intramolecular hydrogen transfer following loss of carbon monoxide (Reaction B) [261].

The 2-substituted troponeiron tricarbonyls (9.54; R = Me, Cl, Ph) were extracted into concentrated sulphuric acid and the ^{1}H NMR spectra were recorded. Spectra of the completely isomerized ions (9.55; R = Me, Cl, Ph) were observed. The isomerization was shown to take place through a cation of the type (9.56) [262].

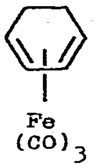


(9.54) (9.56) (9.55)

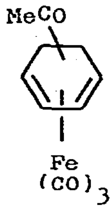
The infrared and Raman spectra of norbornadiene complexes of Fe, Rh, Pd and Pt were recorded. The normal modes were assigned and the ligand vibrations in the complexes were compared with those for uncomplexed norbornadiene [263].

(iii) General Chemistry

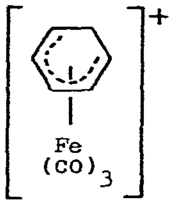
Acylation of the tricarbonyliron complex (9.57) with acetyl chloride in the presence of aluminium chloride gave the acetyl derivative (9.58) and the cation (9.59), formed by hydride abstraction. Similarly acylation of the complex (9.60) gave the tricarbonyliron derivatives (9.61 and 9.62) [264]. The thermochemistry of tricarbonyl (trans, cis-1,5-diphenyl-1,3-



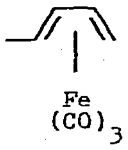
(9.57)



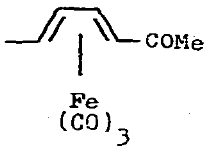
(9.58)



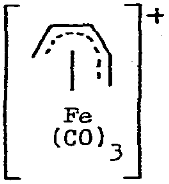
(9.59)



(9.60)



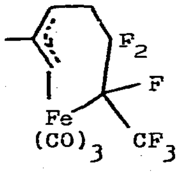
(9.61)



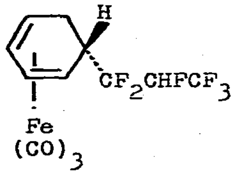
(9.62)

pentadiene)iron was studied. When this complex was heated in solution an irreversible first-order conversion occurred to give tricarbonyl(trans, trans-1,5-diphenyl-1,3-pentadiene)iron. The thermolyses of a variety of tricarbonyl cyclohexadieneiron complexes were studied and they were shown to undergo isomerizations resulting from overall [1,5] hydrogen migrations [265].

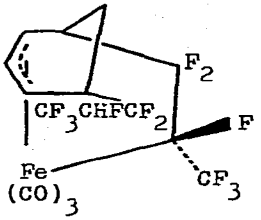
Hexafluoropropene attacked the iron tricarbonyl complexes of butadiene, isoprene, 2,3-dimethylbutadiene, and cyclohexa-1,3-diene on UV irradiation to give 1:1 complexes. The X-ray crystal and molecular structure of the isoprene adduct (9.63) was determined in order to establish the direction of addition of the fluoroolefin which was found to link the iron atom to the



(9.63)



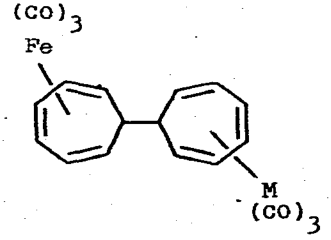
(9.64)



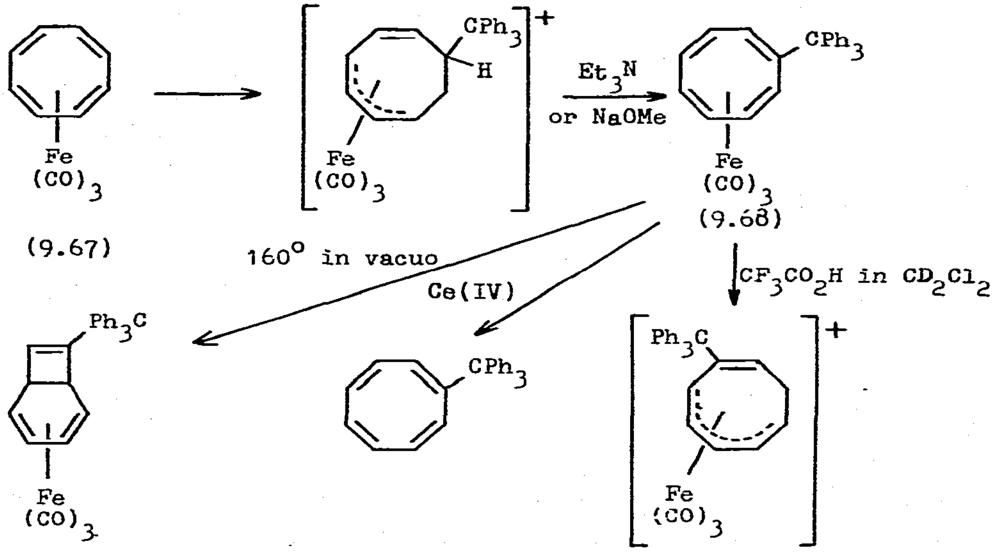
(9.65)

hydrocarbon ligand. However, the cyclohexadiene adduct (9.64) contained only a singly bound fluorocarbon residue. Addition of a further molecule of hexafluoropropene gave the bridged 1:2 adduct (9.65). Several similar reactions were reported and discussed [266].

The reaction between tricarbonyl(η-cycloheptatriene)iron and diphenylacetylene gave tricarbonyl(η-tetraphenylferrole)iron the structure of which has been confirmed by X-ray crystallography [267]. Reaction of the anion $[(\eta\text{-}C_7H_7)Fe(CO)_3]^-$ with allyl halides gave the ditropylium complex (9.66; M = Fe) whilst reaction with $[(\eta\text{-}C_7H_7)M(CO)_3]^-$ (M = Cr, Mo, W) gave the mixed metal carbonyl derivatives (9.66; M = Cr, Mo, W)[268]. The reaction of triphenylmethylium tetrafluoroborate with the cyclooctatetraene



(9.66)

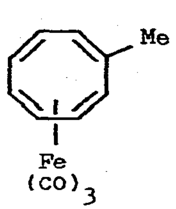


Scheme 9.3

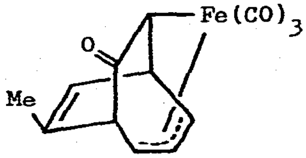
derivative (9.67) followed by a base gave the complex (9.68). The reactions of the complex were investigated (Scheme 9.3). The ^{13}C and ^{1}H NMR spectra of the new compounds were reported [269].

The reaction of the tricarbonyl(η-cyclooctatetraene)iron (9.69) with aluminium chloride in benzene at 10° gave the bicyclononadienyl complex (9.70) which had been obtained previously by treatment of barbaralone with diiron nonacarbonyl. The complex (9.70) liberated barbaralone (9.71) (95%) with carbon monoxide at 100 atmospheres pressure and 120°. The reaction was extended to the formation of other cyclic ketones [270].

The reaction of tricarbonyl(η^4-1,2,3,4-cyclooctatetraene)-iron with diiodomethane in the presence of a zinc/copper couple



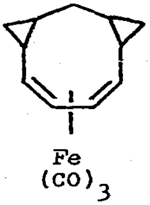
(9.69)



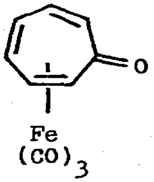
(9.70)

(9.71)

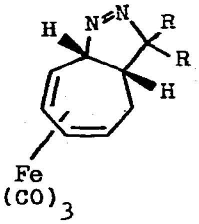
and a trace of iodine gave the irontricarbonyl complex (9.72) [271]. The cycloheptatrienone complex (9.73) with R_2CN_2 (R = H, Me) in diethyl ether gave the 1-pyrazolines (9.74; R = H, Me) in good yields. The iron tricarbonyl moiety behaved as a protecting group for the tropone diene unit while the other double bond



(9.72)



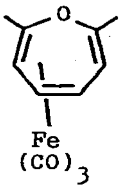
(9.73)



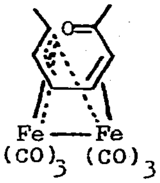
(9.74)

underwent regiospecific cycloaddition [272]. The (η-oxepine)iron complex (9.75) underwent a multistage valence isomerism to give the ketocarbene complex (9.76) which was characterized by X-ray crystallography [273].

The reaction of N-carbomethoxy-1,2- and -1,4-dihydropyridines (9.77 and 9.78; R = Me, Et) with diiron nonacarbonyl gave the N-carbomethoxy-1,2-dihydropyridine complexes (9.79; R = Me, Et). The iron tricarbonyl fragment was easily removed from these

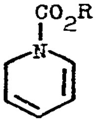


(9.75)

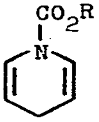


(9.76)

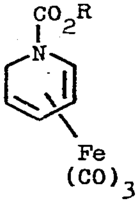
complexes in the presence of trimethylamine oxide to give the 1,2-dihydropyridines (9.77; R = Me, Et) [274]. The reaction of tricarbonyl(η-cycloocta-1,5-diene)ruthenium with olefin (olefin = cyclohexa-1,3-diene, cyclo-octatetraene, cyclo-octa-1,3,6-triene, cyclohepta-2,4,6-triene-1-one, cyclohepta-1,3-diene or cycloheptatriene) in benzene gave the appropriate [(olefin)Ru(CO)$_3$]



(9.77)



(9.78)

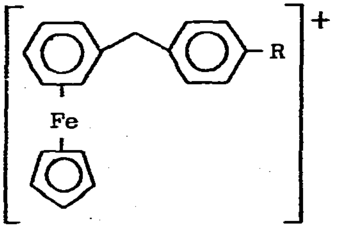


(9.79)

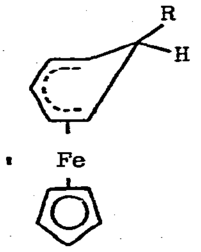
complex in good yield. Many of these complexes were inaccessible or obtained in low yields by the usual route of direct reaction of diene with triruthenium dodecacarbonyl [275].

10. (η-C_5H_5)Fe(η-C_6H_6)

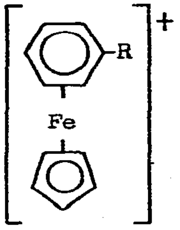
The (η-benzene)iron cation (10.1; R = H) was acetylated and benzoylated with the appropriate acyl chloride and aluminium



(10.1)



(10.2)

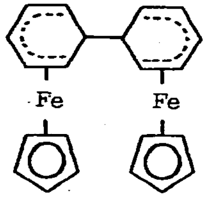


(10.3)

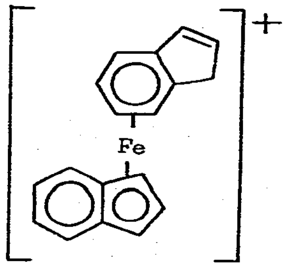
chloride in nitromethane to form the cations (10.1; R = COMe, COPh) [276]. Reaction of (η-benzene)(η-cyclopentadienyl)iron tetrafluoroborate with ethyllithium at 0° and -25° in ether and 20° in tetrahydrofuran gave $(\eta\text{-}C_6H_6)Fe(\eta\text{-}C_5H_5)$, the exo-substituted derivative (10.2; R = Et) and ferrocene respectively. Reaction with benzylmagnesium chloride and cyclopentadienylsodium gave the exo-benzyl and exo-cyclopentadienyl derivatives (10.2; R = CH_2Ph and C_5H_5) respectively [277].

The oxidation of exo- substituted (η-cyclohexadienyl)(η-cyclopentadienyl)iron compounds (10.2) by triphenylmethyl tetrafluoroborate has been studied. In the presence of a methyl group (10.2; R = Me) only the (η-cyclopentadienyl)(η-toluene)iron cation (10.3; R = Me) was obtained but in the presence of larger groups (10.2; R = Et, Bz, C_5H_5) elimination of a carbanion competed with hydride ion elimination to give a mixture of benzene substituted cations (10.3; R = Et, Bz, C_5H_5) respectively and the parent cation (10.3; R = H) [278].

Paramagnetic (η-benzene-η-cyclopentadienyl)iron gave the binuclear η-cyclohexadienyl complex (10.4) after 15 h in pentane at room temperature. Oxidation of this complex with N-bromo-



(10.4)



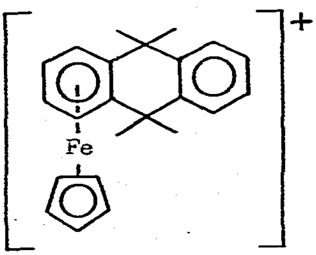
(10.5)

succinimide or oxygen gave the (η-benzene)(η-cyclopentadienyl)-iron cation, which was isolated as the tetraphenylborate, while oxidation with iodine gave the corresponding iodide, $[(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)Fe]I$ [279].

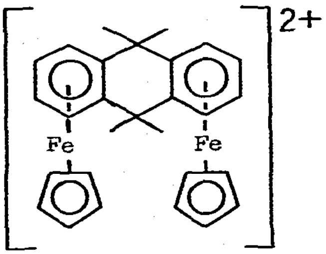
Treichel and Johnson have protonated bis(η-indenyl)iron in the five-membered ring with hydrogen chloride or trifluoroacetic acid in benzene to give the cation (10.5). Evidence was offered in support of endo-protonation. n-Butyllithium was effective in deprotonating the cation to the initial neutral complex [280].

The reaction of ferrocene with anthracene in the presence of $AlCl_3$-Al gave the mono- and di-cations (10.6 and 10.7) respectively which were identical with those derived from 9,10-dihydroanthracene. A similar reaction with naphthalene in tetralin gave both the tetralin complex (10.8) and the naphthalene complex (10.9). The ^1H and ^{13}C NMR spectra of the complexes were discussed. [281].

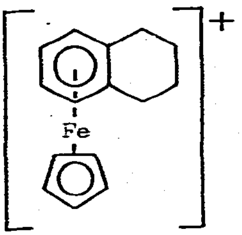
Seven (η-arene)bis(η-cyclopentadienyl)diiron dications including the η-biphenyl (10.10) and the η-phenanthrene (10.11) cations have been prepared and compared with the corresponding (η-arene)(η-cyclopentadienyl)iron cations. The UV spectra of



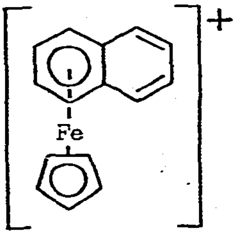
(10.6)



(10.7)



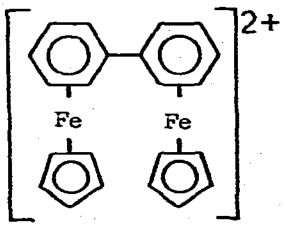
(10.8)



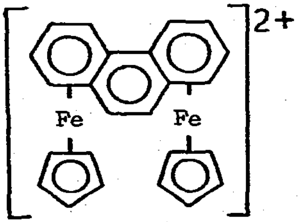
(10.9)

the dications showed d-d transitions analogous to ferrocene while the ^{57}Fe Moessbauer results were similar to those for (η-arene)(η-cyclopentadienyl)iron cations [282]. Polarographic results indicated important differences between the two in that the dications exhibited two iron reduction waves which were represented by the processes:

$$Fe^{II}Fe^{II} \xrightarrow{e^-} Fe^{II}Fe^{I} \xrightarrow{e^-} Fe^{I}Fe^{I}$$

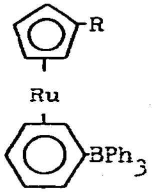


(10.10)



(10.11)

Haines and Du Preez obtained the arylboron substituted ruthenium complex (10.12; R = H) by treatment of Ru(η-C_5H_5)-$(PPh_3)_2Cl$ with sodium tetraphenylborate in methanol. The methyl derivative (10.12; R = Me) was formed in the same way [283].



(10.12)

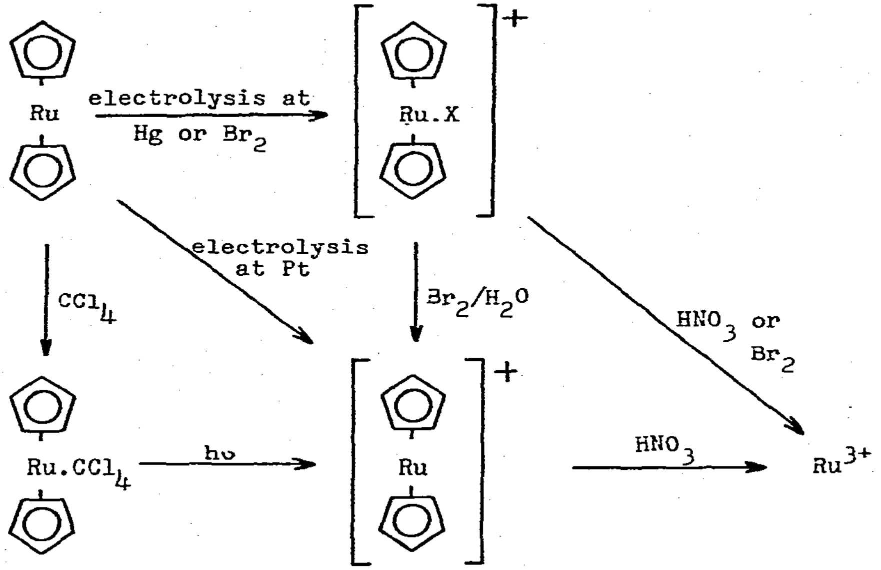
11. (η-C_5H_5)$_2$Ru

Mono- and di-substituted ruthenocenes labelled with radioactive ^{103}Ru were prepared by treatment of the corresponding ferrocene with $^{103}RuCl_3$. Yields were in the range 5-70%. Labelled osmocenes were obtained in 1% yield by using $^{191}OsCl_4$. Thin-layer chromatography was used to separate the labelled metallocenes [284]. Complexes containing ruthenium-mercury bonds were synthesised by treating ruthenocene with mercury(II) salts. These compounds were studied with electronic, infrared, Raman and Mössbauer spectroscopy and it was concluded that the metal-metal bonds were relatively weak [285].

The protonation of ruthenocene and ferrocene was investigated in media of varying acid strengths using ^{1}H NMR spectroscopy. Protonation of the metal atom in ruthenocene only occurred in the most strongly protonating media, H_2SO_4-CF_3CO_2H and $BF_3.H_2O$-CF_3CO_2H, and the cation was characterised by an absorption strongly upfield from TMS. Hydrogen-deuterium exchange was studied for ruthenocene under conditions where metal protonation was incomplete. As the acid concentration was increased the rate of exchange decreased. From these results it was argued that the reaction mechanism of this process was similar to that of electrophilic substitution in benzenoid systems [286]. The solution Raman spectra of ferrocene, ruthenocene and osmocene have been re-investigated. The band at 1186 cm^{-1} in the ferrocene spectrum has been reassigned and the skeletal modes for osmocene have been assigned. Metal-η-cyclopentadienyl ring bond force constants have been calculated and increase in the order $(\eta\text{-}C_5H_5)_2Fe < (\eta\text{-}C_5H_5)_2Ru < (\eta\text{-}C_5H_5)_2Os$ [287].

The UV spectrum of ruthenocene in halocarbon solvents showed a band at 285 nm characteristic of electron transfer-to-solvent and indicating formation of charge-transfer complexes with the solvents. Irradiation of the charge-transfer complex gave the ruthenicinium cation [288]. Ruthenocene forms charge-transfer complexes with halocarbon solvents and the equilibrium constant was determined for the solution in carbon tetrachloride. UV irradiation of the carbon tetrachloride at the charge-transfer absorption frequency gave the ruthenicinium cation which decomposed to ruthenium trichloride and ruthenocene and then formed the complex $(\eta\text{-}C_5H_5)_2Ru.RuCl_4$ [289].

Borrell and Henderson have investigated the photolysis and the naphthalene-photosensitized reaction of the ruthenocene-carbon tetrachloride charge-transfer complex. The ruthenicinium cation was formed in the primary photochemical process. The naphthalene-photosensitized oxidation proceeded through a triplet state and it was inhibited at high concentrations by competitive quenching of the naphthalene singlet state by ruthenocene. The authors



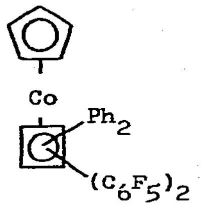
Scheme 11.1

used photo-oxidation, electrochemical and chemical oxidation results to construct an oxidation scheme for ruthenocene (Scheme 11.1) [290].

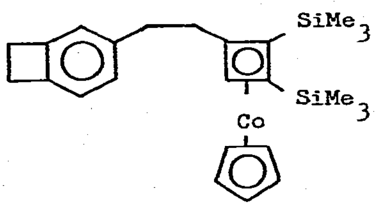
The photochemical preparation of $(\eta-C_5H_5)_2RuL$ (L = fumaronitrile, tetracyanoethylene and tetracyanocyclopropane) and the ultraviolet and infrared spectra of these complexes were examined. The donor excited states in the ruthenocene complexes were associated with either (or both) the 240 and 278 nm intramolecular bands [291].

12. $(\eta-C_4H_4)Co(\eta-C_5H_5)$

When (η-cyclopentadienyl)cobalt dicarbonyl was heated with pentafluorophenylphenylacetylene the η-cyclobutadiene complex



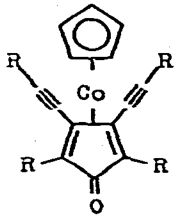
(12.1)



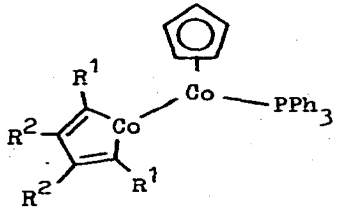
(12.2)

(12.1) was obtained in addition to η-cyclopentadienone complexes and polynuclear complexes [292].

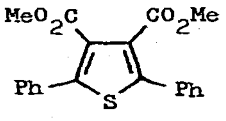
In the reaction between 1,5-hexadiyne and bis(trimethylsilyl)-acetylene, in the presence of catalytic amounts of dicarbonyl-(η-cyclopentadienyl)cobalt, the cyclobutadiene complex (12.2) was isolated [293]. The (η-cyclopentadienone)cobalt complexes (12.3; R = Me, Ph) were obtained by treatment of (η-cyclopentadienyl)cobalt dicarbonyl with 2,4-hexadiyne and 1,4-diphenylbutadiyne respectively [294].



(12.3)



(12.4)



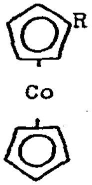
(12.5)

The (η-cyclopentadienyl)cobalt complexes (12.4) were converted to 5- or 6-membered heterocycles by heating with sulphur or nitrogen compounds. Thus the complex (12.4; R^1 = Ph, R^2 = CO_2Me) was heated with sulphur and benzene in a sealed tube at 150°

to give the substituted thiophen (12.5) [295]. The effect of the lanthanide shift reagents Eu(fod)$_3$ and Pr(fod)$_3$ on the ^1H NMR spectra of some (η-cyclopentadienone)(η-cyclopentadienyl)-cobalt complexes was investigated. The shift reagents complexed with the lone pairs of the carbonyl group. Pseudo contact shifts were observed for the hydrogen atoms of each ring and also for the hydrogen atoms in the substituents on the cyclopentadienone ring [296].

13. $(\eta-C_5H_5)_2Co$ and $[(\eta-C_5H_5)_2Co]^+$

The cobaltocene derivatives [13.1; R = CCl_3, CH_2CN, CH(CN)Me, C(CN)=CH_2, C≡CPh] were obtained by treating cobaltocene with the alkyl compounds RH in the presence of oxygen [297].



(13.1)

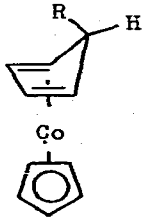
X-ray crystallography has been used to obtain details of the crystal and molecular structure of cobaltocene. The η-cyclopentadienyl rings were parallel and staggered with respect to one another [298]. The molecular structure of gaseous cobaltocene was investigated by electron diffraction. The gaseous molecule had a sandwich structure and the data showed that any distortion from D_{5h} or D_{5d} molecular symmetry was small. It was concluded that the barrier to internal rotation was small enough to allow large amplitude torsional motion and that the minimum energy conformation of the rings could not be distinguished. The metal-carbon bond length in cobaltocene was 0.05 Å longer than that in ferrocene and 0.08 Å shorter than that in nickelocene. The weakening of the metal-cyclopentadienyl bond in cobaltocene relative to that in ferrocene was due to the antibonding effects of e_{1g} orbitals which were singly occupied in cobaltocene but empty in ferrocene [299].

The enthalpies and entropies of phase transitions at temperatures below 200° were determined for several sandwich compounds including cobaltocene and nickelocene. Heat capacities (C_p), free energy functions and other thermodynamic functions were given for these compounds in the temperature range 5-298.15°K [300]. Wide-line ^1H NMR spectra of the intercalation complex $TaS_2(\text{cobaltocene})_{\frac{1}{4}}$ were recorded and interpreted. It was concluded that the C_5 symmetry axis of the cobaltocene molecule was parallel to the TaS_2 layers. The spectra also revealed changes in the dynamics of the guest species as the temperature was lowered and they suggested a possible rearrangement of the molecules within the layers [301].

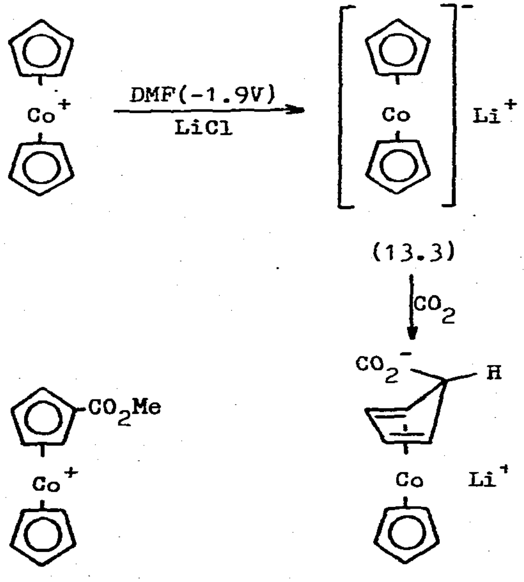
The basicities of three aminocobalticinium cations have been determined, all were much less basic than the corresponding ferrocenyl- and phenyl-amines. Thus the aminocobalticinium cation had $p\underline{K}_b = 15.6$. By contrast, alkylcobalticinium ions were strongly acidic and the methyl hydrogen atoms in 1,1'-dimethylcobalticinium ion exchanged with 1.02 M NaOD at 80°C to give a half-life of 18 min and $E_a = 25.4$ kcal mol^{-1} [302]. The rate of decomposition of the cobalticinium ion in water has been determined as a function o pH and temperature. It was dependent on the concentration of undissociated $[(\eta\text{-}C_5H_5)_2Co]OH$ while the order of reaction varied with the pH and the temperature [303].

Electrolysis of the cobalticinium ion in the presence of an alkyl halide gave the corresponding alkylated derivative (13.2; R = CH_2Ph, CHClPh, CCl_3, CH_2Br) in good yield. The cobaltocene anion (13.3) generated electrochemically, in the presence of lithium chloride, when treated with carbon dioxide gave the salt (13.4). The salt was converted to the corresponding methyl ester (13.5) which gave the cobalticinium derivative (13.6) on reaction with triphenylmethane tetrafluoroborate [304].

The reaction of 1,1'-bis(carboxy)cobalticinium hexafluorophosphate with R_2SnCl_2 (R = Ph, Bu, Et, octyl, benzyl and Me) gave the tin poly(cobalticinium esters) (13.7). The yields of



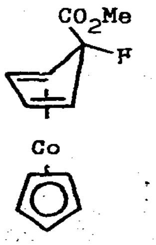
(13.2)



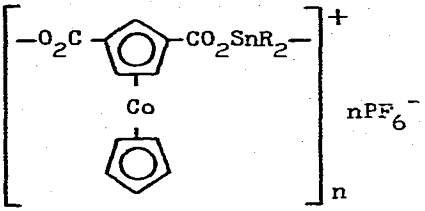
(13.3)

(13.6)

(13.4)



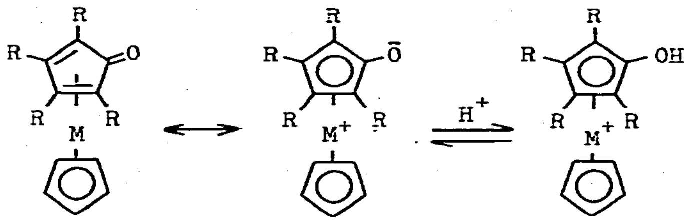
(13.5)



(13.7)

the polyesters (13.7) varied with R in the series Ph>Bu>Et>octyl=benzyl>Me [305]. Bis(η-cyclopentadienyl)titanium bis(hexafluorophosphate) was copolymerized with cobalt bis-(η-cyclopentadienylcarboxylate) hexafluorophosphate to give poly(cobalticinium) esters containing titanium. The polymers were characterized by spectroscopy, molecular weight measurements and thermogravimetric analysis [306].

In the polymerization of alkyl or acyl derivatives of cobalticinium salts they were treated with benzene derivatives, such as p-dichlorobenzene or acetophenone in the presence of a catalyst, to increase the yield of the polymer [307]. The infrared spectra of the tetraaryl- or tetraalkyl-cyclopentadienone complexes (13.8: M = Co, R = Me or Ph) and (13.8; M = Co or Rh, R = C_6F_5) showed an absorption characteristic of a C=O group between 1570-1620 cm^{-1}. On treatment with concentrated hydrochloric or fluoroboric acid this absorption disappeared and a new peak appeared in the region 1430-1485 cm^{-1} together with an OH stretch in the region 3500-2500 cm^{-1}. In acid conditions the hydroxy cobalticinium and rhodicinium ions (13.9; M = Co, Rh) were formed. The acidity constants of these hydroxymetallocinium

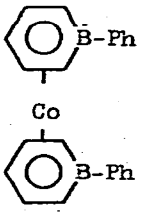


(13.8) (13.9)

salts (13.9; M = Co, Rh) were determined spectrophotometrically [308]. Parallel changes in the electronic spectra of ferrocene and cobalticinium chloroplatinate were observed on the introduction of an ethyl substituent into each metallocene [309].

Treatment of the η-borabenzene complex (13.10) with iron(III) chloride gave the corresponding cation. This cation gave the mixed η-cyclopentadienyl-η-borabenzene complex in the presence of methanol [310].

$$\begin{aligned}3[Co(C_5H_5BPh)_2]PF_6 + 2MeOH \rightarrow 2Co(C_5H_5BPh)_2 + [Co(C_5H_5)(C_5H_5BPh)]PF_6 \\ 2HPF_6 + PhB(OMe)_2\end{aligned}$$



(13.10)

The treatment of the borabenzene complex (13.10) with potassium cyanide gave the salt $K[C_5H_5BPh]$ [311]. The electron spin resonance spectrum of bis(1-phenylborabenzene)cobalt(II) (13.10) was recorded and interpreted. From the results it was concluded that the bonding in this molecule (13.10) was very similar to that in ferrocene and the cobalticinium cation. Ligand electrons were donated into metal d_{z^2}, d_{xz} and d_{yz} orbitals with the populations in d_{z^2} and d_{xz} only slightly greater than those in ferrocene. Considerable back bonding occurred from filled metal $d_{x^2-y^2}$ and d_{xy} orbitals to the ligands, approximately 0.6 electrons back bonded to each borabenzene ring. This value was only slightly less than that for ferrocene [312].

The crystal and molecular structure of 2-methyl-1,7-bis-(η-cyclopentadienyl)-1,7,2,4-dicobaltdicarbaheptaborane(7) has been determined by X-ray diffraction. This compound was shown to be a triple-decker sandwich containing a central planar ring formally designated in the parent molecule as $C_2B_3H_5^{4-}$, isoelectronic with η-$C_5H_5^-$. All three rings were planar and nearly parallel, the cyclopentadienyl rings were tilted by approximately 3.2° with respect to the central ring [313].

Friedel-Crafts acetylation of (η-cyclopentadienyl)[η-(3)-1,2-dicarbaundecaborane(11)]cobalt $[(\eta\text{-}C_5H_5)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}]$ with aluminium chloride in carbon disulphide gave $[(\eta\text{-}C_5H_5)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}Cl\}]$, $[(\eta\text{-}C_5H_5)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(8\text{-}OCOMe)\}]$, $[(\eta\text{-}C_5H_5)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(8\text{-}OH)\}]$ and $[(\eta\text{-}C_5H_5)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(8\text{-}COMe)\}]$. The complexes were characterized by infrared, ^1H NMR mass spectrometry and X-ray analysis. From these results it was concluded that the π-electrons of the η-C_5H_5 group in $[(\eta\text{-}C_5H_5)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}]$ were transferred to some extent to the cobalt rendering the η-C_5H_5 group less susceptible to electrophilic substitution [314].

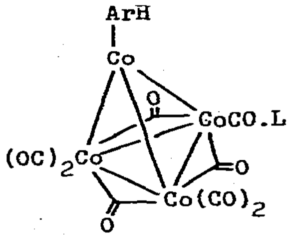
14. Cobalt-carbon Cluster Compounds

Reaction between fluoroalkyltetracarbonylcobalt derivatives $[(RCF_2)Co(CO)_4]$ and either sodium tetracarbonylcobaltate(-1) or octacarbonyldicobalt gave the cluster compounds $[RCCo_3(CO)_9]$ ($R = F, CHF_2, CF_3, C_2F_5$). An effort was made to extend the scope of the reaction between fluoroalkylcobalt carbonyls and $Na[Co(CO)_4]$ the reaction between this salt or $Na[Co(CO)_3(PPh_3)]$ and $[(CF_3)Co(CO)_3(PPh_3)]$ was investigated but no evidence for cluster formation was obtained [315].

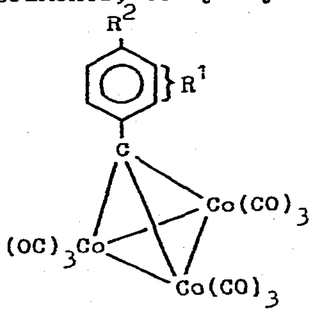
Direct reaction between the tricobalt carbon cluster and the dienes bicyclo[2.2.1]hepta-2,5-diene (bhd) and cyclohexa-1,3-diene afforded the dark green complexes $[YCCo_3(CO)_7(diene)]$ (Y = alkyl, aryl, F). No comparable derivatives were formed in reactions with cyclo-octadienes, cycloheptadiene and butadiene and the coordinated bhd was not replaced by any of these dienes. An X-ray analysis of $[Et_3CCo_3(CO)_7(bhd)]$ showed that the chelating bhd coordinated to one cobalt atom in the basal triangle with the ring in a <u>cis</u>-<u>cis</u> (<u>cis</u> with respect to the apical substituent) orientation [316].

(η-Arene)nonacarbonyltetracobalt complexes (14.1; ArH = mono-, di-, and tri-alkylbenzene, anisole, biphenyl, fluorene, phenanthrene; L = CO) were treated with phosphites to give the corresponding derivatives [14.1; L = $P(OR)_3$]. Displacement of the arene ligand took place with carbon monoxide, phosphines and acetylenes to form known derivatives of dicobalt octacarbonyl and tetracobalt dodecacarbonyl [317].

The benzylidynetricobalt nonacarbonyl cluster compounds (14.2; R^1 = <u>o</u>-, <u>m</u>-Me; <u>o</u>-, <u>m</u>-Cl; R^2 = H) were acetylated with acetyl chloride in the presence of aluminium chloride to give the *para*-derivatives (14.2; R^1 = *o*-, *m*-Me; *o*-, *m*-Cl; R^2 = COMe). The benzyl group was introduced in the same way although the chlorine-substituted cluster compounds were inert to benzoyl chloride. Formylation of the benzylidyne cluster compound (14.2; $R^1 = R^2 = H$) was achieved with $MeOCHCl_2$ and aluminium chloride. In competitive acetylation experiments, benzylidynetricobalt nonacarbonyl was of comparable reactivity to ferrocene and dimethylaniline and much more reactive than anisole. The reactions were rationalized in terms of the stable $[(OC)_9Co_3C]^+$ cluster [318].

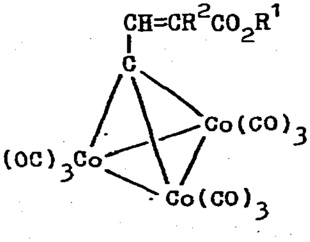


(14.1)

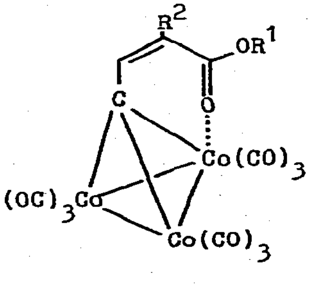


(14.2)

Palyi and Varadi have prepared eight acrylate derivatives of methylidinetricobalt nonacarbonyl (14.3; R^1 = H, R^2 = H, Me, Pr^n, Ph; R^1 = Me, R^2 = H, Me, Pr^n, Ph). All of the compounds showed splitting of some terminal carbonyl stretching frequencies



(14.3)

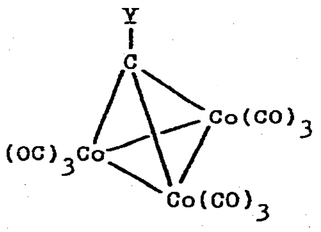


(14.4)

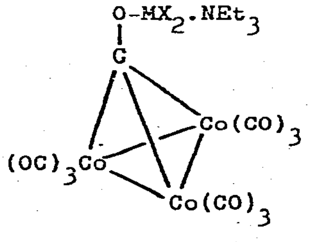
in the IR and these were interpreted in terms of direct interaction between the ester carbonyl group and cobalt (14.4) [319]. Substitution of tertiary phosphine for carbonyl in the methylidynetricobalt nonacarbonyl cluster compounds (14.5; Y = H, Me, Ph, F) has been studied in detail by Cartner, Cunninghame and Robinson. Rates of reaction and activation parameters were determined, the activation energies increased in the order of substituents: $F < Ph < H < Me$. A simple dissociative mechanism was indicated with loss of a molecule of carbon monoxide before attack by the phosphine [320].

Boron and aluminium substituted methylidinetricobalt nonacarbonyl compounds (14.6) have been described. The boron difluoride derivative (14.6; M = B, X = F) was obtained by fluorination of the corresponding bromine compound (14.6; M = B, X = Br) with silver tetrafluoroborate. The boron diiodide derivative (14.6; M = B, X = I) and the aluminium dichloride derivative (14.6; M = Al, X = Cl) were formed by treatment of dicobalt octacarbonyl with $BI_3.NEt_3$ and $AlCl_3.NEt_3$ respectively [321].

Apical cluster ^{13}C NMR resonances in some neutral complexes $RCCo_3(CO)_9$ [R = C_5H_{11}, $C_{10}H_{21}$, n-$C_9H_{19}CH(OH)$, $Me_3Si(H)C{=}CH$,



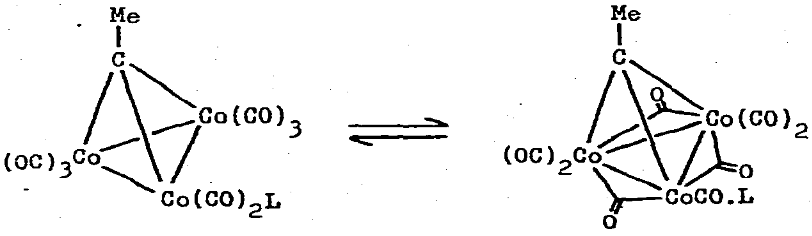
(14.5)



(14.6)

$n\text{-}C_6H_{13}C(O)$, $C_9H_{19}C(O)$, $C_2H_5OC(O)$, $n\text{-}C_{10}H_{21}OC(O)$] were observed in the region δ(C) 255-310 ppm by using either neat samples or very concentrated solutions in $CDCl_3$. The ^{13}C chemical shifts were far downfield from those of most carbon atoms in the organic and organometallic compounds except for those of alkyl substituted carbenium ions and some transition metal-carbene complexes. The ^{13}C NMR spectra of some cobalt cluster substituted carbenium ions were recorded in concentrated sulphuric acid. It was concluded that the positive charge in these carbenium ions resided mainly on the cobalt atom [322].

Matheson and Robinson have investigated the equilibria between bridged and non-bridged forms of methinyltricobaltnonacarbonyl compounds by measuring IR and ^1H, ^{13}C and ^{31}P NMR spectra at several temperatures. The complexes [14.7; L = $P(C_6H_{11})_3$, PBu_3] each exist as a mixture of bridged and non-bridged forms at room temperature in the solid state and in solution. The proportion of the non-bridged complex [14.7; L = $P(C_6H_{11})_3$] at 295°K was 66% and the equilibrium shifted towards the bridged isomer [14.8; L = $P(C_6H_{11})_3$] as the temperature was lowered. At 195°K the proportion of the non-bridged isomer was 12%. The activation parameters determined for the reaction were



(14.7) (14.8)

$\Delta H = -8.6$ kJ mol^{-1}, $\Delta S = 23$ J mol^{-1} k^{-1}. Alternative mechanisms for the interconversion were discussed [323].

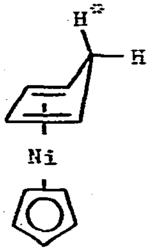
A solution calorimetric method was used to determine the standard enthalpies of formation of the crystalline complexes $[Co_3(CBr)(CO)_9]$, $[Co_3(CCl)(CO)_9]$ and $[Co_2(CO)_8]$, the values were -284.3, -283.5 and -298.9 kcal mol^{-1} respectively. The enthalpies of sublimation of the same compounds were determined by effusion manometry as 23.8, 28.1 and 15.6 kcal mol^{-1} respectively. Bond energies were derived from the gas phase enthalpies and for the bromo- cluster it was concluded that the metal-carbon bond energy was probably greater than the metal-carbon monoxide bond energy [324].

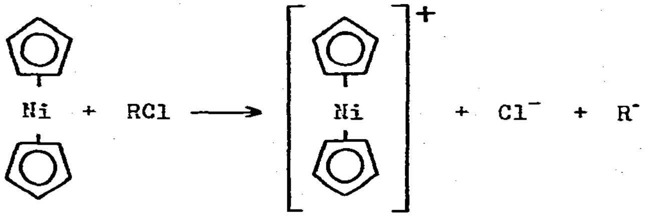
15. $(\eta\text{-}C_5H_5)_2Ni$

The second volume of the book, The Organic Chemistry of Nickel, entitled Organic Synthesis has been published [325]. Nickelocene was prepared directly from finely divided nickel metal, produced by an electric arc, and cyclopentadiene [326]. The separation of organo-nickel derivatives obtained in the preparation of bis(η-isopropylcyclopentadienyl)nickel was studied by adsorption-partition chromatography [327].

Treatment of a solution of the nido-borane anion, $B_9H_{12}^-$, and nickelocene in acetonitrile with sodium amalgam gave the two isomeric closo- metalloboranes $[(\eta\text{-}C_5H_5)\text{-}2\text{-}Ni(\eta\text{-}B_9H_9)]^-$ and $[(\eta\text{-}C_5H_5)\text{-}1\text{-}Ni(\eta\text{-}B_9H_9)]^-$. The former compound, in which the nickel atom was coordinated to five boron atoms, was converted quantitatively on heating to the latter compound, in which the nickel atom was coordinated to four boron atoms [328].

Protonation of nickelocene occurred in trifluoroacetic acid to give $[(\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_6)]^+$ (15.1). Deuteration experiments showed that the entering proton (H^*) occupied the exo-methylene position and that attack of the electrophile occurred at one of the ring ligands and not at the metal [329].

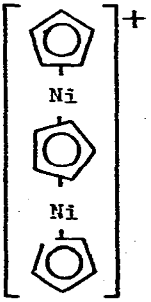




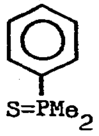
(15.1) (15.2) (15.3)

Traverso and Rossi have reassigned the absorption at 307 nm in the UV spectrum of nickelocene. This band was attributed previously to intramolecular-charge transfer but is now regarded as a nickelocinium band. Nickelocene (15.2) in haloalkane solvents underwent dissociative charge transfer to the cation (15.3) which in turn formed the triple-decker sandwich complex (15.4) by a secondary thermal process [330].

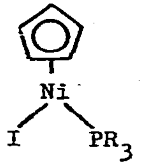
The hydrogenation of hydrochloric acid lignin of wood and its model compounds was carried out in the presence of nickelocene.



(15.4)



(15.5)



(15.6)

A semimicro method was used to investigate the effect of time, temperature and pressure on the output of phenols in this system [331, 332]. Triphenylphosphine was converted to triphenylphosphine oxide by stirring with nickelocene in benzene in the presence of oxygen. Trialkylphosphines and tri-alkyl and -arylphosphates were oxidized in the same way [333].

Mathey has reported the attack by alkyl and aryl phosphine sulphides such as the compound (15.5) on nickelocene in the presence of methyl or allyl iodide to form the (η-cyclopentadienyl)nickel complexes (15.6) in yields of up to 70% [334]. The structure of gaseous (η-cyclopentadienyl)nitrosylnickel was determined by electron diffraction. The hydrogen atoms were in the plane of the η-cyclopentadienyl ring, the Ni-N-O moiety was linear, and the Ni-C and Ni-N bond distances were 2.128 and 1.58 Å respectively [335].

16. Uranocene

Streitwieser has reviewed the chemistry of uranocene [336]. Bis(1,3,5,7-tetraphenylcyclooctatetraene)uranium was prepared by the reaction of potassium 1,3,5,7-tetraphenylcyclooctatetraene with uranium(IV) chloride. The uranocene derivative was air stable and it was sublimed unchanged. The unusual stability of this compound was attributed to steric blocking of the central uranium by the phenyl substituents [337].

The magnetic susceptibility of uranocene was measured between 1.25 and 298^{o}K and these results were correlated with a systematic study of the crystal field splitting [338].

REFERENCES

1 W. J. Settineri and L. D. McKeever, Tech. Chem. (N.Y.) 5 (1975) Pt. 2. (Tech. Electroorg. Synth.) 397

2 L. V. Rybin, Metody Elementoorg. Khim., Tipy Metalloorg, Soedin, Perekhodnykh Met., 2 (1975) 542.

3 M. L. Good, J. Buttone and D. Foyt, Ann. N.Y. Acad. Sci., 239 (1974) 193.

4 T. V. Nikitina, Metody Elementoorg. Khim., Tipy Metalloorg. Soedin, Perekhodnykh Met., 2 (1975) 585.

5 E. G. Perevalova, T. V. Nikitina, Metody Elementoorg. Khim., Tipy Metalloorg. Soedin. Perekhodnykh Met., 2 (1975) 687.

6 D. A. Bochvar and N. P. Gambaryan, Metody Elementoorg. Khim., Tipy Metalloorg. Soedin, Perekhodnykh Met., 1 (1975) 9.

7 W. E. Watts, Organometal. Chem., 3 (1975) 342.

8 W. E. Silverthorn, Adv. Organometal. Chem., 13 (1975) 47.

9 K. J. Klabunde, Angew. Chem., 87 (1975) 309.

10 L. P. Yur'eva, Metody Elementoorg. Khim., Tipy Metalloorg. Soedin, Perekhodnykh Met., 1 (1975) 384.

11 R. J. Cross, Annu. Rep. Prog. Chem., Sect. A: Phys. Inorg. Chem., 70 (1974) 419.

12 E. C. Baker, G. W. Halstead and K. N. Raymond, Proc. Rare Earth Res. Cong., 11th, 1 (1974) 284.

13 N. Hagihara, Mem. Inst. Sci. Ind. Res., Osaka Univ., 32 (1975) 45; Chem. Abstr., 83 (1975) 152937.

14 H. Werner, J. Organometal. Chem., 94 (1975) 285.

15 K. Anisimov and Z. P. Valueva, Metody Elem.-Org. Khim., 2 (1974) 781; Chem. Abstr., 82 (1975) 125425.

16 J. Starr, W. Moore, D. Hysell, S. Lee, J. Lewkowski, L. Hall, K. Campbell and M. Wiester, Proc. Annu. Conf. Environ. Toxicol., 4th, (1973) 251; Chem. Abstr., 82 (1975) 119647.

17 Lj. Manojlovic-Muir, Mol. Struct. Diffr. Methods, 2 (1974) 248.

18 G. Deganello, P. Uguagliati, L. Calligaro, L. Sandrini and F. Zingales, Inorg. Chim. Acta, 13 (1975) 247.

19 R. Pettit, J. Organometal. Chem., 100 (1975) 205.

20 R. Pettit, Proc. Robert A. Welch Found. Conf. Chem. Res., 17 (1973) 227.

21 F. A. Cotton and B. A. Frenz, Tetrahedron, 30 (1974) 1587.

22 G. Wilkinson, J. Organometal. Chem., 100 (1975) 273.

23 W. S. McDonald, Mol. Struct. Diffr. Methods, 2 (1974) 261.

24 Lj. Manojlovic-Muir and K. W. Muir, Mol. Struct. Diffr. Methods,2 (1974) 297.

25 Gmelin's Handbook of Inorganic Chemistry, Supplementary Work, Vol 17; Organonickel Compounds, Pt. 2. 8th Edit., Springer, Berlin, 1974.

26 T. H. Whitesides, D. L. Lichtenberger and R. A. Budnik, Inorg. Chem., 14 (1975) 68.

27 O. Johnson, Chem. Scr., 8 (1975) 166.

28 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.

29 J. Y. Saillard, D. Grandjean, F. Choplin and G. Kaufmann, J. Mol. Struct., 23 (1974) 363.

30 D. A. Brown, N. J. Fitzpatrick and N. J. Mathews, J. Organometal. Chem., 88 (1975) C27.

31 F. H. Koehler, Z. Naturforsch., Teil B, 29 (1974) 708.

32 F. H. Kohler, J. Organometal.Chem., 91 (1975) 57.

33 V. Bohm, B. F. Gaechter, M. Shushani, J. A. Koningstein, E. M. Smirnova, Ya. M. Kimel'feld, E. V. Bykova and V. T. Aleksanyan, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 572.

34 C. J. Groenenboom, H. J. De Liefde Meijer, F. Jallinek and A. Oskam, J. Organometal. Chem., 97 (1975) 73.

35 J. H. Ammeter, N. Oswald and R. Bucher, Helv. Chim. Acta, 58 (1975) 671.

36 P. E. Gaworonskii, Tr. Khim. Khim. Tekhnol., (1974) 136.

37 J. Muller, W. Holzinger and W. Kalbfus, J. Organometal. Chem., 97 (1975) 213.

38 V. I. Tel'noi, K. V. Kir'yanov, V. I. Ermolaev and I. B. Rabinovich, Doklady Akad. Nauk SSSR, 220 (1975) 1088.

39 P. Borrell and E. Henderson, Inorg. Chim. Acta, 12 (1975) 215.

40 S. Kubota and T. Otsu, Kobunshi Ronbunshu, 31 (1974) 759; Chem. Abstr., 82 (1975) 112312.

41 C. U. Pittman, P. Grube and R. M. Hanes, J. Paint Technol., 46 (1974) 35.

42 L. M. Pudeev, L. M. Diagileva and Yu. A. Aleksandrov, Zh. Obshch. Khim., 45 (1975) 245.

43 I. S. Butler, D. Cozak and S. R. Stobart, J. Chem. Soc., Chem. Commun., (1975) 103.

44 M. D. Dines, Science, 188 (1975) 1210.

45 T. H. Whitesides and R. A. Budnik, Inorg. Chem., 14 (1975) 664.

46 E. Frauendorfer, R. E. Lopez, X. Figarella, S. Fontana and

J. L. Calderon, J. Organometal. Chem., 90 (1975) 53.

47 R. B. King and O. Von Stetten, Synth. React. Inorg. Met.-Org. Chem., 4 (1974) 447.

48 W. Cho and J. E. Fernandez, Syn. React. Inorg. Metal-Org. Chem., 4 (1974) 403.

49 K. H. Pannell, D. H. Hambrick and G. S. Lewandos, J. Organometal. Chem., 99 (1975) C21.

50 C. U. Pittman, W. J. Patterson and S. P. McManus, J. Polym. Sci., Polym. Chem. Ed., 13 (1975) 39.

51 C. U. Pittman, B. T. Kim and W. M. Douglas, J. Org. Chem., 40 (1975) 590.

52 C. U. Pittman, B. T. Kim and W. M. Douglas, USNTIS, AD/A Rep. 1975, No. 004945/2GA; From Gov. Rep. Announce. Index (US), 75 (1975) 69; Chem. Abstr., 83 (1975) 65421.

53 V. G. Andrianov, Yu. T. Struchkov, N. K. Baranetzkaya, V. N. Setkina and D. N. Kursanov, J. Organometal. Chem., 101 (1975) 209.

54 P. Delise, G. Allegra, E. R. Mognaschi and A. Chierico, J. Chem. Soc., Faraday Trans. 2, 71 (1975) 207.

55 M. Acampora, A. Ceccon, M. Dal Farra and G. Giacometti, J. Chem. Soc., Chem. Commun., (1975) 871.

56 W. R. Jackson, C. F. Pincombe, I. D. Rae and S. Thapebinkarn, Aust. J. Chem., 28 (1975) 1535.

57 J. L. Fletcher and M. J. McGlinchey, Can. J. Chem., 53 (1975) 1525.

58 A. Ceccon, C. Corvaja, G. Giacometti and A. Venzo, J. Chim. Phys., Phys.-Chim. Biol., 72 (1975) 23.

59 B. V. Lokshin. E. B. Rusach, V. S. Kaganovich, V. V. Krivykh,

A. N. Artemov and N. I. Sirotkin, Zh. Strukt. Khim., 16 (1975) 592.

60 N. R. Rudnevskii, N. N. Vyshinskii, I. I. Grinval'd, A. N. Artemov and N. I. Sirotkin, Tr. Khim. Khim. Tekhnol. (1974) 127; Idem ibid (1974) 130.

61 H. J. Buttery, S. F. A. Kettle and I. Paul, J. Chem. Soc., Dalton Trans., (1975) 969.

62 M. Bigorgne, O. Kahn, M. F. Koenig and A. Loutellier, Spectrochim. Acta, Part A, 31A (1975) 741.

63 D. M. Adams, R. E. Christopher and D. C. Stevens, Inorg. Chem., 14 (1975) 1562.

64 F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. L. Leung, I. M. Andrade and H. A. Skinner, J. Organometal. Chem., 97 (1975) 221.

65 I. A. Suskina, L. I. Denisovich and S. P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 471.

66 R. D. Rieke, J. S. Arney, W. E. Rich, B. R. Willeford and S. Poliner, J. Amer. Chem. Soc., 97 (1975) 5951.

67 E. W. Neuse, J. Organometal. Chem., 99 (1975) 287.

68 B. Caro and G. Jaouen, Tetrahedron Lett., (1974) 2061.

69 B. Caro and G. Jaouen, Tetrahedron Lett., (1974) 3539.

70 A. Z. Kreindlin, V. S. Khandkarova and S. P. Gubin, J. Organometal Chem., 92 (1975) 197.

71 N. S. Chiu, L. Schafer and R. Seip, J. Organometal. Chem., 101 (1975) 331.

72 A. N. Artemov, N. N. Byshinskii, I. I. Grimval'd and N. I. Sirotkin, Fiz. Mat. Metody Koord Khim., Tezisy Dokl., Vses. Soveshch., 5th (1974) 161; Chem. Abstr., 82 (1975) 160469.

73 S. O. Grim and L. J. Matienzo, Inorg. Chem., 14 (1975) 1014.

74 G. I. Magomedov, V. G. Syrkin, A. S. Frenkel, Yu. S. Nekrasov and T. A. Zavina, Zh. Obshch. Khim., 45 (1975) 2533.

75 A. N. Nesmeyanov, M. I. Rybinskaya, V. V. Krivykh and V. S. Kaganovich, J. Organometal. Chem., 93 (1975) C8.

76 R. J. Card, Diss. Abstr. Int. B 36 (1975) 2219.

77 J. Nasielski and O. Denisoff, J. Organometal. Chem., 102 (1975) 65.

78 M. Cais, D. Fraenkel and K. Weidenbaum, Coord. Chem. Rev., 16 (1975) 27.

79 G. Simonneaux, A. Meyer and G. Jaouen, J. Chem. Soc., Chem. Commun., (1975) 69.

80 C. U. Pittman and R. L. Voges, Macromol. Synth., 3 (1972) 175; Chem. Abstr., 83 (1975) 28633.

81 D. Seyferth and C. S. Eschbach, J. Organometal. Chem., 94 (1975) C5.

82 J. Besancon, S. Top, J. Tirouflet and B. Gautheron, J. Organometal. Chem., 94 (1975) 35.

83 Y. Dusausoy, J. Protas, J. Besancon and S. Top, J. Organometal. Chem., 94 (1975) 47.

84 G. Jaouen and R. Dabard, Bull. Soc. Chim. France, (1974) 2009.

85 G. Jaouen and A. Meyer, J. Amer. Chem. Soc., 97 (1975) 4667.

86 A. Meyer and G. Jaouen, J. Organometal. Chem., 97 (1975) C21.

87 F. Goasmat, R. Dabard and H. Patin, Tetrahedron Lett., (1975) 2359.

88 C. W. Stanger, Diss. Abstr. Int. B, 35 (1974) 2092.

89 A. R. Siedle, J. Amer. Chem. Soc., 97 (1975) 5931.

90 H. Kobayashi, M. Kobayashi and Y. Kaizu, Bull. Chem. Soc. Jap., 48 (1975) 1222.

91 G. Barbieri and R. Benassi, Synth. React. Inorg. Met.-Org. Chem., 4 (1974) 545.

92 G. K. Magomedov, V. G. Syrkin, A. S. Frenkel and A. V. Medvedeva, Zh. Obshch. Khim., 44 (1974) 2277.

93 G. I. Magomedov, V. G. Syrkin, A. S. Frenkel and O. A. Zakharchenko, Zh. Obshch. Khim., 45 (1975) 2530.

94 U. Casellato, P. A. Vigato and M. Vidali, J. Inorg. Nucl. Chem., 37 (1975) 1181.

95 A. A. Akhrem, M. L. Abeliovich, S. N. Kovalenko and D. I. Metelitsa, Neftekhimiya, 14 (1974) 746.

96 C. Amith, M. Cais, D. Fraenkel and D. Ginsburg, Heterocycles, 3 (1975) 25.

97 J. K. Stille and R. G. Nelb, USNTIS, AD Rep. 1974 No. 781546/7GA; Chem. Abstr., 82 (1975) 58165.

98 P. S. Woon, Diss. Abstr. Int. B, 35 (1975) 5321.

99 N. K. Baranetskaya, A. A. Tsoi, V. N. Setkina, E. I Fedin and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser Khim., (1975) 1494.

00 G. Jaouen, A. Meyer and G. Simmonneaux, J. Chem. Soc., Chem. Commun., (1975) 813.

01 B. A. Howell and W. S. Trahanovsky, J. Amer. Chem. Soc., 97 (1975) 2136.

02 W. S. Trahanovsky and R. A. Hall, J. Organometal. Chem., 96 (1975) 71.

103 M. S. Wrighton and J. L. Haverty, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 30B (1975) 254.

104 G. Jaouen, A. Meyer and G. Simonneaux, Tetrahedron, 31 (1975) 1889.

105 L. A. Fedorov, P. V. Petrovskii, E. I. Fedin, N. K. Baranetskaya, V. I. Zdanovich, V. N. Setkina and D. N. Kursanov, J. Organometal. Chem., 99 (1975) 297.

106 N. G. Connelly, Z. Demidowicz and R. L. Kelly, J. Chem. Soc., Dalton Trans., (1975) 2335.

107 J. Y. Saillard, G. Le Borgne and D. Grandjean, J. Organometal. Chem., 94 (1975) 409.

108 P. Caillet and G. Jaouen, J. Organometal. Chem., 91 (1975) C53.

109 B. V. Lokshin, E. B. Rusach and Yu. D. Konovalov, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 84.

110 H. G. Biedermann, K. Oefele, N. Schuhbauer and J. Tajtelbaum, Angew. Chem., 87 (1975) 634.

111 A. N. Nesmeyanov, V. V. Krivykh, V. S. Kaganovich and M. I. Rybinskaya, J. Organometal. Chem., 102 (1975) 185.

112 W. W. Henslee, Diss. Abstr. Int. B, 35 (1975) 3772.

113 K. J. Klabunde and H. F. Efner, Inorg. Chem., 14 (1975) 789.

114 G. A. Razuvaev, G. A. Domrachev and V. D. Zinov'ev, Doklady Akad. Nauk SSSR, 223 (1975) 617.

115 A. N. Nesmeyanov, L P. Yur'eva, S. N. Levchenko and N. N. Zeitseva, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 2865.

116 J. Brunvoll, B. N. Cyvin, S. J. Cyvin, G. Hagen and L. Schaefer, Mol. Struct. Vib., (1972) 261, Chem. Abstr., 83 (1975) 77919.

117 L. Schaefer, J. Brunvoll and S. J. Cyvin, Mol. Struct. Vib., (1972) 272; Chem. Abstr., 83 (1975) 77920.

118 L. M. Dyagileva and L. M. Pudeev, Zh. Prikl. Khim., 48 (1975) 1367.

119 Yu. A. Aleksandrov, V. M. Fomin and A. V. Lunin, Kinet. Katal., 16 (1975) 618.

120 S. M. Vlasov, G. G. Devyatykh, G. V. Almazov, S. M. Mazavin and A. A. Morozov, Zh. Fiz. Khim., 49 (1975)87.

121 F. J. Karol and R. N. Johnson, J. Polym. Sci., Polym. Chem. Ed., 13 (1975) 1607.

122 C. Elschenbroich and F. Stohler, Chimia, 28 (1974) 730.

123 M. F. Guest, I. H. Hillier, B. R. Higginson and D. R. Lloyd, Mol. Phys., 29 (1975) 113.

124 G. G. Petukhov, A. N. Artemov, B. I. Rabosin, N. I. Sirotkin, A. S. Senyushkin and A. A. Alad'in, Tr. Khim. Khim. Tekhnol., (1974) 26.

125 B. G. Gribov, L. L. Ivanov, B. I. Kozyrkin, A. S. Pashinkin and V. A. Nikol'skii, Zh. Neorg. Khim., 20 (1975) 2574.

126 D. A. Vyakhirev, A. V. Buntova and A. I. Subbotina, Tr. Khim. Tekhnol., (1974) 110.

127 I. L. Agafonov and V. I. Faerman, Zh. Anal. Khim., 30 (1975) 396.

128 G. Gritzner, Monatsh. Chem., 106 (1975) 947.

129 K. M. Al-Kathumi and L. A. P. Kane-Maguire, J. Organometal. Chem., 102 (1975) C4.

130 P. Hackett and G. Jaouen, Inorg. Chim. Acta, 12 (1975) L19.

131 T. J. Truex, R. B. Saillant and F. M. Monroe, J. Electrochem. Soc., 122 (1975) 1396.

132 C. G. Kreiter, M. Lang and H. Strack, Chem. Ber., 108 (1975) 1502.

133 F. Cristiani, D. Filippo, P. Deplano, F. Devillanova, A. Diaz, E. F. Trogu and G. Verani, Inorg. Chim. Acta., 12 (1975) 119.

134 E. F. Ashworth, M. L. H. Green and J. Knight, Chem. Uses Molybdenum, Proc. Conf., 1st (1973) 114; Chem. Abstr., 82 (1975) 57866.

135 E. F. Ashworth, M. L. H. Green and J. Knight, J. Less-Common Metals, 36 (1974) 213.

136 M. L. Ziegler, H. E. Sasse and B. Nuber, Z. Naturforsch., Teil B, 30B (1975) 22.

137 M. L. Ziegler, H. E. Sasse and B. Nuber, Z. Naturforsch., Teil B, 30B (1975) 26.

138 K. Weidenhammer, H. Weinand and M. L. Zeigler, Z. Naturforsch., B, Anorg. Chem., Org. Chem., 30B (1975) 699.

139 E. E. Isaacs and W. A. G. Graham, Can. J. Chem., 53 (1975) 975.

140 A. Salzer and H. Werner, J. Organometal. Chem., 87 (1975) 101.

141 K. J. Reimer and A. Shaver, Inorg. Chem., 14 (1975) 2707.

142 D. R. Wiles, J. Inorg. Nucl. Chem., 36 (1974) 2405.

143 T. L. Khotsyanova, S. I. Kuznetsov, E. V. Bryukhova and Yu. V. Makarov, J. Organometal. Chem., 88 (1975) 351.

144 E. V. Bryukhova, G. K. Sernin, I. M. Alymov, S. I. Kuznetsov, K. N. Anisimov, N. E. Kolobova and Yu. V. Makarov, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 797.

145 N. J. Gogan, C. K. Chu and P. A. Narayana, J. Organometal. Chem., 92 (1975) 207.

146 A. N. Nesmeyanov, D. N. Kursanov, V. N. Setkina, V. A. Sazonova, E. I. Fedin, P. V. Petrovskii, N. N. Sedova and Yu. V. Volgin, Doklady Akad. Nauk SSSR, 221 (1975) 854.

147 A. Efraty, M. H. A. Huang and C. A. Weston, Inorg. Chem., 14 (1975) 2796.

148 R. E. Bozak and A. D. Barone, Chem. Lett., (1975) 75.

149 I. L. Gaidyt and A. K. Baev, Zh. Fiz. Khim., 49 (1975) 794.

150 A. N. Nesmeyanov, G. B. Shul'pin and M. I. Rybinskaya, Doklady Akad. Nauk SSSR, 221 (1975) 624.

151 A. N. Nesmeyanov, K. N. Anisimov and Z. P. Valueva, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 2790.

152 P. L. Pauson and J. A. Segal, J. Chem. Soc., Dalton Trans., (1975) 2387.

153 I. B. Nemirovskaya, A. G. Ginzburg, V. N. Setkina and D. N. Kursanov, Zh. Obshch. Khim., 45 (1975) 893.

154 I. M. Gverdtsiteli, L. P. Asatiani and S. Kh. Kiladze, Zh. Obshch. Khim., 45 (1975) 1648.

155 G. K. Vasilevskaya, R. A. Kasperovich and G. I. Sukhinina, USSR Pat., 484222, Sep. 15, 1975; From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 52 (1975) 58; Chem. Abstr., 83 (1975) 193514.

156 A. N. Nesmeyanov, T. P. Tolstaya, V. V. Korol'kov and A. N. Yarkevich, Doklady Akad. Nauk SSSR, 221 (1975) 1337.

157 A. N. Nesmeyanov, N. N. Sedova, V. A. Sazonova, I. F. Leshcheva and I. S. Rogozhin, Doklady Akad. Nauk SSSR, 218 (1974) 356.

158 R. Eberhardt and K. Schlögl, Synth. React. Inorg. Met.-Org. Chem., 4 (1974) 317.

159 A. Tartar and E. Cuingnet, C. R. Hebd, Seances Acad. Sci., Ser. C, 279 (1974) 1057.

160 N. J. Gogan and C-K. Chu, J. Organometal. Chem., 93 (1975) 363.

161 F. A. Galil-Ogly, A. S. Shapatin, A. S. Dmitriev, I. N. Kas'yanova, L. V. Kireeva, E. A. Chernyshev, D. Ya. Zhinkin, E. P. Nikitenko and L. L. Polstyanko, USSR Pat. 465132, 1975 Sep. 25; Chem. Abstr., 84 (1976) 6285.

162 M. O. Lerner, V. V. Goncharov, A. Ya. Khesina and A. M. Bokaleinik, Eksph-Tekh. Svoistva Priman. Avtomob. Topl., Smaz. Mater. Spetszhidk., 8 (1974) 51; Chem. Abstr., 84 (1976) 49360.

163 W. Moore, L. Hall, W. Crocker, J. Adams and J. F. Stara, Environ. Res., 8 (1974) 171.

164 I. S. Butler and D. A. Johanson, Inorg. Chem., 14 (1975) 701.

165 A. Efraty, R. Arneri and J. Sikora, J. Organometal. Chem., 91 (1975) 65.

166 A. D. Redhouse, J. Organometal. Chem., 99 (1975) C29.

167 M. Giffard and P. Dixneuf, J. Organometal. Chem., 85 (1975) C26.

168 M. Herberhold, C. G. Kreiter, S. Stuber and G. O. Wiedersatz, J. Organometal. Chem., 96 (1975) 89.

169 G. Le Borgne, E. Gentric and D. Grandjean, Acta Crystallogr., Sect. B, B31 (1975) 2824.

170 B. Bayerl, K. Schmidt and M. Wahren, Z. Chem., 15 (1975) 277.

171 A. N. Nesmeyanov, N. E. Kolobova, A. B. Antonova and K. N. Anisimov, Doklady Akad. Nauk SSSR, 220 (1975) 105.

172 W. A. Herrmann, B. Reiter and H. Biersack, J. Organometal. Chem., 97 (1975) 245.

173 W. A. Herrmann, Chem. Ber. 108 (1975) 486.

174 I. S. Butler and T. Sawai, Inorg. Chem., 14 (1975) 2703.

175 V. N. Setkina, N. I. Pyshnograeva, P. V. Petrovskii, N. E. Kolobova and D. N. Kursanov, Doklady Akad. Nauk SSSR, 220 (1975) 123.

176 W. Beck and W. Danzer, Z. Naturforsch., B, Anorg. Chem., Org. Chem., 30B (1975) 716.

177 R. P Stewart and G. T. Moore, Inorg. Chem., 14 (1975) 2699.

178 H. Brunner and M. Langer, J. Organometal. Chem., 87 (1975) 223.

179 H. Brunner, J. Aclasis, M. Langer and W. Steger, Angew. Chem., 86 (1974) 864.

180 H. Brunner, J. Organometal. Chem., 94 (1975) 169.

181 P. M. Treichel, K. P. Wagner and H. J. Much, J. Organometal. Chem., 86 (1975) C13.

182 D. L. Beach and K. W. Barnett, J. Organometal. Chem., 97 (1975) C27.

183 G. Huttner, H. D. Mueller, A. Frank and H. Lorenz, Angew. Chem., 87 (1975) 597.

184 G. Huttner, H. D. Mueller, A. Frank and H. Lorenz, Angew. Chem., 87 (1975) 714.

185 G. Huttner and H. D. Mueller, Z. Naturforsch., B Anorg. Chem., Org. Chem., 30B (1975) 235.

186 H. Vahrenkamp, Chem. Ber., 107 (1974) 3867.

187 R. B. King, R. H. Reimann and D. J. Darensbourg, J. Organometal. Chem., 93 (1975) C23.

188 G. Huttner and W. Gartzke, Chem. Ber., 107 (1974) 3783.

189 P. L. Pauson and J. A. Segal, J. Chem. Soc., Dalton Trans., (1975) 1677.

190 P. L. Pauson and J. A. Segal, J. Chem. Soc., Dalton Trans., (1975) 1683.

191 V. F. Sizoi, Yu. S. Nekrasov, Yu. V. Makarov and N. E. Kolobova, J. Organometal. Chem., 94 (1975) 425.

192 Y. Shvo and E. Hazum, J. Chem. Soc., Chem. Commun., (1975) 829.

193 M. Green, R. P. Hughes and A. J. Welch, J. Chem. Soc., Chem. Commun., (1975) 487.

194 B. F. G. Johnson, J. Lewis and D. J. Thompson, Tetrahedron Lett., (1974) 3789.

195 S. Sadeh and Y. Gaoni, J. Organometal. Chem., 93 (1975) C31.

196 T. H. Whitesides and J. P. Neilan, J. Amer. Chem. Soc., 97 (1975) 907.

197 T. H. Whitesides and R. W. Arhart, Inorg. Chem., 14 (1975) 209.

198 M. A. Busch and R. J. Clark, Inorg. Chem., 14 (1975) 219.

199 M. A. Busch and R. J. Clark, Inorg. Chem., 14 (1975) 226.

200 A. Bond, B. Lewis and M. Green, J. Chem. Soc., Dalton Trans., (1975) 1109.

201 S. M. Nelson, C. M. Regan and M. Sloan, J. Organometal. Chem., 96 (1975) 383.

202 N. S. Nametkin, A. I. Nekhaev, V. D. Tyurin and S. P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 2067.

203 Montedison S.p.A., Ital. Pat., 907326, 1972, Feb. 15; Chem. Abstr., 83 (1975) 59055.

204 H. Behrens and M. Moll, Z. Anorg. Allg. Chem., 416 (1975) 193.

205 Montedison S.p.A., Ital. Pat., 907325, 1972, Feb. 15; Chem. Abstr., 83 (1975) 59056.

206 C. B. Ungermann and K. G. Caulton, J. Organometal. Chem., 94 (1975) C9.

207 I. Fischler and E. A. Koerner von Gustorf, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 30 (1975) 291.

208 A. A. El-Awady, J. Inorg. Nucl. Chem., 36 (1974) 2185.

209 S. Sorriso and G. Cardaci, J. Organometal. Chem., 101 (1975) 107.

210 A. N. Nesmeyanov, N. P. Avakyan, G. M. Babakhina and I. I. Kritskaya, Izv. Akad. Nauk SSSR, Ser, Khim., (1975) 2133.

211 G. Cardaci and G. Concetti, J. Organometal. Chem., 90 (1975) 49.

212 N. S. Nametkin, A. I. Pekhaev, V. D. Tyurin, S. P. Gubin and L. P. Kolesnikova, Neftekhimiya, 15 (1975) 380.

213 M. Green and R. P. Hughes, J. Chem. Soc., Chem. Commun., (1975) 619.

214 R. B. King and C. A. Harmon, J. Organometal.Chem., 86 (1975) 93.

215 R. B. King and C. A. Harmon, J. Organometal. Chem., 86 (1975) 239.

216 D. C. Andrews, G. Davidson and D. A. Duce, J. Organometal. Chem., 97 (1975) 95.

217 A. N. Nesmeyanov, G. P. Zol'nikova, I. F. Lesheheva and I. I. Kritskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 2388.

218 H. Irngartinger, H. Kimling, A. Krebs and R. Maeusbacher, Tetrahedron Lett., (1975) 2571.

219 P. Marcinal and E. Cuingnet, Tetrahedron Lett., (1975) 1223.

220 P. Marcinal and E. Cuingnet, Tetrahedron Lett., (1975) 3827.

221 E. R. Biehl and P. C. Reeves, Synthesis, (1974) 883.

222 G. Berens, F. Kaplan, R. Rimerman, B. W. Roberts and A. Wissner, J. Amer. Chem. Soc., 97 (1975) 7076.

223 G. Berens, Diss. Abstr. Int. B 36 (1975) 231.

224 T. J. Devon, Diss. Abstr. Int. B 35 (1975) 3625.

225 A. Albini and H. Kisch, J. Organometal. Chem., 101 (1975) 231.

226 E. K. G. Schmidt, Chem. Ber., 108 (1975) 1401.

227 E. K. G. Schmidt, Chem. Ber., 108 (1975) 1598.

228 J. A. Connor, L. M. Derrick, M. B. Hall, I. H. Hillier, M. F. Guest, B. R. Higginson and D. R. Lloyd, Mol. Phys., 28 (1974) 1193.

229 M. B. Hall, I. H. Hillier, J. A. Connor, M. F. Guest and D. R. Lloyd, Mol. Phys., 30 (1975) 839.

230 P. E. Riley and R. E. Davis, Inorg. Chem., 14 (1975) 2507.

231 J. W. Emsley and J. C. Lindon, Mol. Phys., 28 (1974) 1373.

232 A. Efraty, M. H. A. Huang and C. A. Weston, J. Organometal. Chem., 91 (1975) 327.

233 K. Hildenbrand and E. K. Von Gustorf, Angew. Chem. 87 (1975) 35.

234 G. R. John, L. A. P. Kane-Maguire and C. Eaborn, J. Chem. Soc., Chem. Commun., (1975) 481.

235 A. J. Birch, I. D. Jenkins and A. J. Liepa, Tetrahedron Lett., (1975) 1723.

236 A. J. Birch and A. J. Pearson, Tetrahedron Lett., (1975) 2379.

237 A. J. Birch and I. D. Jenkins, Tetrahedron Lett., (1975) 119.

238 K. E. Hine, B. F. G. Johnson and J. Lewis, J. Chem. Soc., Chem. Commun., (1975) 81.

239 N. S. Nametkin, V. D. Tyurin, M. Slupczynski and A. I. Nekhaev, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 2131.

240 N. S. Nametkin, V. D. Tyurin and V. I. Ivanov, Izv. Akad. Nauk SSSR Ser. Khim., (1975) 1911.

241 J. B. Davison and J. M. Bellama, Inorg. Chim. Acta, 14 (1975) 263.

242 L. A. Paquette, S. V. Ley, S. Maiorana, D. F. Schneider, M. J. Broadhurst and R. A. Boggs, J. Amer. Chem. Soc., 97 (1975) 4658.

243 G. Schiavon, C. Paradisi and C. Boanini, Inorg. Chim. Acta, 14 (1975) L5.

244 M. Cooke, C. R. Russ and F. G. A. Stone, J. Chem. Soc., Dalton Trans., (1975) 256.

245 M. T. Mocella, Diss. Abstr. Int. B, 35 (1975) 5312.

246 R. Aumann and H. Averbeck, J. Organometal. Chem., 85 (1975) C4.

247 R. Aumann, Chem. Ber., 108 (1975) 1974.

248 C. Amith and D. Ginsburg, Tetrahedron, 30 (1974) 3415.

249 C. G. Krespan, J. Org. Chem., 40 (1975) 261.

250 W. Frink, Helv. Chim. Acta, 58 (1975) 1205.

251 T. Tsuchiya and V. Snieckus, Can. J. Chem., 53 (1975) 519.

252 R. Goddard, A. P. Humphries, S. A. R. Knox and P. Woodward,

J. Chem. Soc., Dalton Trans., (1975) 507.

253 K. W. Muir, R. Walker, E. W. Abel, T. Blackmore and R. J. Whitley, J. Chem. Soc., Chem. Commun., (1975) 698.

254 J. C. Burt, S. A. R. Knox and F. G. A. Stone, J. Chem. Soc., Dalton Trans., (1975) 731.

255 R. M. Moriarty, K.-N. Chen, M. R. Churchill and S. W.-Y. Chang, J. Amer. Chem. Soc., 96 (1974) 3661.

256 M. R. Churchill and W. Y. Shirley, Inorg. Chem., 14 (1975) 1680.

257 C. C. T. Chiang, Diss. Abstr. Int. B, 36 (1975) 2238.

258 F. A. Colton, V. W. Day and K. I. Hardcastle, J. Organometal. Chem., 92 (1975) 369.

259 P. Skarstad, P. Janse-van Vuuren, J. Meinwald and R. E. Hughes, J. Chem. Soc., Perkin Trans, 2, (1975) 88.

260 J.-Y. Lallelemand, P. Laszlo, C. Muzette and A. Stockis, J. Organometal. Chem., 91 (1975) 71.

261 T. H. Whitesides and J. Shelly, J. Organometal. Chem., 92 (1975) 215.

262 A. Eisenstadt, J. Organometal. Chem., 97 (1975) 443.

263 I. A. Zakharova, Ya. V. Salyn, I. A. Garbouzova, V. T. Aleksanyan and M. A. Prianichnicova, J. Organometal. Chem., 102 (1975) 227.

264 N. S. Nametkin, A. I. Nekhaev, V. D. Tyurin and S. P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 676.

265 J. P. Neilan, Diss. Abstr. Int. B, 36 (1975) 1225.

266 M. Green, B. Lewis, J. J. Daly and F. Sanz, J. Chem. Soc., Dalton Trans., (1975) 1118.

267 P. E. Riley and R. E. Davis, Acta Crystallogr., Sect. B, B31 (1975) 2928.

268 G. Deganello, T. Boschi and L. Toniolo, J. Organometal. Chem., 97 (1975) C46.

269 B. F. G. Johnson, J. Lewis and J. W. Quail, J. Chem. Soc., Dalton Trans., (1975) 1252.

270 B. F. G. Johnson, J. Lewis, D. J. Thompson and B. Heil, J. Chem. Soc., Dalton Trans., (1975) 567.

271 D. L. Reger and A. Gabrielli, J. Amer. Chem. Soc., 97 (1975) 4422.

272 M. Franck-Neumann and D. Martina, Tetrahedron Lett., (1975) 1759.

273 R. Aumann, H. Averbeck and C. Krueger, Chem. Ber., 108 (1975) 3336.

274 H. Alper, J. Organometal. Chem., 96 (1975) 95.

275 A. J. P. Domingos, B. F. G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1975) 2288.

276 A. N. Nesmeyanov, N. A. Vol'kenau, I. N. Bolesova, L. S. Polkovnikova and L. S. Kotova, Koord. Khim., 1 (1975) 1465.

277 A. N. Nesmeyanov, N. A. Vol'kenau, L. S. Shilovtseva and V. A. Petrakova, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 1151.

278 A. N. Nesmeyanov, N. A. Vol'kenau, L. S. Shilovtseva and V. A. Petrakova, J. Organometal. Chem., 85 (1975) 365.

279 A. N. Nesmeyanov, N. A. Vol'kenau and V. A. Petrakova, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 2159.

280 P. M. Treichel and J. W. Johnson, J. Organometal. Chem., 88 (1975) 207.

281 R. G. Sutherland, S. C. Chen, J. Pannekoek and C. C. Lee,

J. Organometal. Chem., 101 (1975) 221.

282 W. H. Morrison, E. Y. Ho and D. N. Hendrickson, Inorg. Chem., 14 (1975) 500.

283 R. J. Haines and A. L. Du Preez, J. Organometal. Chem., 84 (1975) 357.

284 D. Langheim, H. Wenzel and E. Nipper, Chem. Ber., 108 (1975) 146.

285 W. H. Morrison, Diss. Abstr. Int. B, 35 (1975) 5314.

286 G. Cerichelli, A. M. Giuliani, G. Illuminati and G. Ortaggi, Ann. Chim. (Rome) 64 (1974) 125.

287 B. V. Lokshin, V. T. Alexanian and E. B. Rusach, J. Organometal. Chem., 86 (1975) 253.

288 O. Tràverso, S. Sostero and G. A. Mazzocchin, Inorg. Chim. Acta, 11 (1974) 237.

289 O. Traverso and S. Sostero, Ann. Univ. Ferrara, Sez. 5, 3 (1974) 91.

290 P. Borrell and E. Henderson, J. Chem. Soc., Dalton Trans., (1975) 432.

291 O. Traverso, E. Horvath and S. Sostero, Ann. Univ. Ferrara Sez. 5, 3 (1974) 175; Chem. Abstr., 83 (1975) 27221.

292 S. A. Gardner, E. F. Tokas and M. D. Rausch, J. Organometal. Chem., 92 (1975) 69.

293 W. G. L. Aalbersberg, A. J. Barkovich, R. L. Funk, R. L. Hillard and K. P. C. Vollhardt, J. Amer. Chem. Soc., 97 (1975) 5600.

294 R. S. Dickson and L. J. Michel, Aust. J. Chem., 28 (1975) 285.

295 Y. Wakatsuki and H. Yamazaki (Inst. of Phys. and Chem. Res.),

Japan Pat. 74100073, 1973, Sep. 20; Chem. Abstr., 82 (1975) 86419.

296 R. S. Dickson, S. H. Johnson and I. D. Rae, Aust. J. Chem., 28 (1975) 1681.

297 N. Hagiwara, H. Yamazaki, S. Takahashi and H. Kojima, (Osaka University), Japan. Pat., 7416854, 1974, Apr. 25; Chem. Abstr., 82 (1974) 86418.

298 W. Bunder and E. Weiss, J. Organometal. Chem., 92 (1975) 65.

299 A. K. Hedberg, L. Hedberg and K. Hedberg, J. Chem. Phys., 63 (1975) 1262.

300 V. P. Nistratov, M. S. Sheiman, V. A. Maslova, G. V. Burchalova, A. N. Lineva and I. B. Rabinovich, Tr. Khim. Khim. Tekhnol., (1974) 64; Chem. Abstr., 82 (1975) 65230.

301 B. G. Silbernagel, Chem. Phys. Lett., 34 (1975) 298.

302 J. E. Sheats, W. Miller and T. Kirsch, J. Organometal. Chem., 91 (1975) 97.

303 N. V. Bychkov, N. N. Rukhlyada, A. I. Kasperovich, E. V. Leonova and N. S. Kochetkova, Zh. Fiz. Khim., 49 (1975) 2291.

304 N. El Murr and E. Laviron, Tetrahedron Lett., (1975) 875

305 C. E. Carraher, G. F. Peterson and J. E. Sheats, Amer. Chem. Soc., Div. Org. Coat. Plast. Chem., Pap. 33 (1973) 427; Chem. Abstr., 83 (1975) 28608.

306 C. E. Carraher and J. E. Sheats, Amer. Chem. Soc., Div. Org. Coat. Plast. Chem., Pap., 33 (1973) 634.

307 A. N. Nesmeyanov, N. N. Rukhlyada, E. V. Leonova, N. S. Kochetkova and N. V. Bychkov, USSR Pat., 480733, Aug. 15; 1975; From Otkrytiya, Izobret., Prom. Obraztsy,

Tovarnye Znaki, 52 (1975) 78; Chem. Abstr., 83 (1975) 194056.

308 J. E. Sheats, W. Miller, M. D. Rausch, S. A. Gardner, P. S. Andrews and F. A. Higbie, J. Organometal. Chem., 96 (1975) 115.

309 A. N. Nesmeyanov, B. M. Yavorski, N. S. Kochetkova, G. B. Zaslavskaya, N. P. Gambaryan and E. I. Afrina, Doklady Akad. Nauk SSSR, 291 (1974) 361.

310 G. E. Herberich and W. Pahlmann, J. Organometal. Chem., 97 (1975) C51.

311 G. E. Herberich and H. J. Becker, Angew. Chem., 87 (1975) 196.

312 G. E. Herberich and T. Lund and J. B. Raynor, J. Chem. Soc., Dalton Trans., (1975) 985.

313 W. T. Robinson and R. N. Grimes, Inorg. Chem., 14 (1975) 3056.

314 T. Totani, H. Nakai, M. Shiro and T. Nakagawra, J. Chem. Soc., Dalton Trans., (1975) 1938.

315 B. L. Booth, R. N. Haszeldine and T. Inglis, J. Chem. Soc., Dalton Trans., (1975) 1449.

316 P. A. Elder, B. H. Robinson and J. Simpson, J. Chem. Soc., Dalton Trans., (1975) 1771.

317 A. Sisak, C. Sisak, F. Ungvary, G. Palyi and L. Marko, J. Organometal. Chem., 90 (1975) 77.

318 D. Seyferth, G. H. Williams, A. T. Wehman and M. O. Nestle, J. Amer. Chem. Soc., 97 (1975) 2107.

319 G. Palyi and G. Varadi, J. Organometal. Chem., 86 (1975) 119.

320 A. Cartner, R. G. Cunninghame and B. H. Robinson, J. Organometal. Chem., 92 (1975) 49.

321 G. Schmidt, V. Batzel, G. Etzrodt and R. Pfeil, J. J. Organometal. Chem., 86 (1975) 257.

322 D. Seyferth, C. S. Eschbach and M. O. Nestle, J. Organometal. Chem., 97 (1975) C11.

323 T. W. Matheson and B. H. Robinson, J. Organometal. Chem., 88 (1975) 367.

324 P. J. Gardner, A. Cartner, R. G. Cunninghame and B. H. Robinson, J. Chem. Soc., Dalton Trans., (1975) 2582.

325 P. W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol. 2, Organic Synthesis, Academic Press, New York, 1975.

326 J. L. Lang, U.S. Pat., 3880743, 1975, Apr. 29; Chem. Abstr., 83 (1975) 97557.

327 A. I. Bruk, Z. P. Vetrova, D. A. Vyakhirev, N, T. Karabanov, and Ya. I. Yashin, Tr. Khim. Khim. Tekhnol., (1974) 139.

328 R. N. Leyden and M. F. Hawthorne, J. Chem. Soc., Chem. Commun., (1975) 310.

329 G. K. Turner, W. Klaui, M. Scotti and H. Werner, J. Organometal. Chem., 102 (1975) C9.

330 O. Traverso and R. Rossi, Ann. Univ. Ferrara, Sez. 5, 3 (1974) 167.

331 P. Hoffmann and W. Schweers, Holzforschung, 29 (1975) 18; Chem. Abstr., 83 (1975) 12512.

332 P. Hoffmann and W. Schweers, Holzforschung, 29 (1975) 73.

333 N. Hagiwara, N. Takahashi and H. Kojima (Osaka University), Japan, Pat., 7424900, 1974, Jun. 26; Chem. Abstr., 82 (1975) 86404.

334 F. Mathey, J. Organometal. Chem., 87 (1975) 371.

335 I. A. Ronova, N. V. Alekseeva, N. N. Veniaminov and M. A. Kravers, Zh. Strukt. Khim., 16 (1975) 476.

336 A. Streitwieser, Proc. Rare Earth Res. Conf., 11th 1 (1974) 278.

337 A. Streitwieser and R. Walker, J. Organometal. Chem., 97 (1975) C41.

338 H. D. Amberger, R. D. Fischer and B. Kanellakopulos, Theor. Chim. Acta, 37 (1975) 105.