ORGANIC REACTIONS OF SELECTED π-COMPLEXES

ANNUAL SURVEY COVERING THE YEAR 1976*

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

CONTENTS

---

* Organic Reactions of Selected π-Complexes, Annual Survey Covering the Year 1975 see J. Organometal. Chem., 126 (1977) 227.

1. Reviews

Seyferth has reviewed progress in the chemistry of carbon-functional alkylidynetricobalt nonacarbonyl cluster compounds [1]. The papers presented at the symposium "Metal Atoms in Chemical Synthesis" which took place at Darmstadt, Germany, in May 1974 have recently been collected together in book form [2]. Several of the papers dealt with the synthesis of π-bonded organometallic derivatives [3, 4, 5].

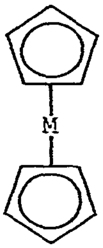
Koerner von Gustorf has presented a review of "Synthetic Applications of Photochemical Ligand Substitution in Organoiron Compounds" at the Dublin Conference on Coordination Chemistry [6]. The use of tricarbonyl(η-cyclopentadienyl)manganese as an antiknock agent in petrol was reviewed. Economic data was given and two major case studies were summarised [7]. Bennett has provided a review entitled "Aromatic Compounds of the Transition Elements" as part of Rodd's Chemistry of Carbon Compounds. The review covered compounds in which a benzene ring was either π- or σ-bonded to a transition metal [8].

Knox and Watts have reviewed the chemistry of η-cyclopentadienyl complexes from 1969 until early 1973, some earlier references were included where these were relevant to later work. The review was not comprehensive but concentrated attention upon reactions in which the η-cyclopentadienyl ligand was involved specifically [9]. Stevenson has discussed the literature of metal compounds containing six-electron and seven-electron organic ligands from 1971 until early 1973 [10]. Watts has reviewed the literature for 1974 covering the chemistry of η-cyclopentadienyl, η-arene and related complexes [11].

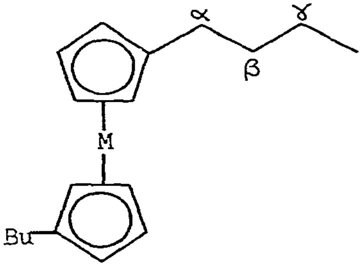
2. General Results

Armstrong, Fortune and Perkins have used the CNDO-MO formalism to study the ground- and excited-state properties of the metallocenes formed by the first transition series elements (2.1; M = V, V^+, V^{2+}, Cr, Cr^+, Mn, Fe, Fe^+, Co, Co^+, Ni). The multielectron configuration interaction method has been used to calculate both photoelectron and absorption spectra, satisfactory agreement with experimental determinations was obtained. The electronic properties of the metallocenes were described and variations in bonding within the series were explained [12].

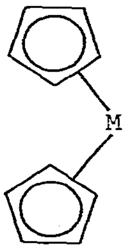
The 1,1'-di(η-n-butylcyclopentadienyl)metal complexes (2.2; M = vanadium, chromium, cobalt, nickel) were prepared. The ^{13}C NMR spectra of these paramagnetic metallocenes were recorded in order to study C-C hyperconjugation. The selective transfer of unpaired electron spin density to C-β (2.2) by C-C hyperconjugation was detected [13].



2.1



2.2



2.3

Lauher and Hoffmann have constructed the molecular orbitals for the bent bis(η-cyclopentadienyl)metal group (2.3) and have used this approach to analyze several problems concerned with the electronic structure of the molecules η-Cp_2ML_n where n = 1-3. Among the areas discussed were: the relationship between the geometry of these molecules and the d-electron configuration; bonding with π-acceptor and donor ligands; geometrical distortions of the bis(η-cyclopentadienyl)metal group; insertion reactions of olefins coordinated to the group; insertion reactions of carbonyls; oxidative coupling and allyl and tetrahydroborate complexes. The metallocenes containing titanium, hafnium, zirconium, vanadium, niobium and molybdenum received most emphasis [14].

Ring-metal bond dissociation energies together with heats and entropies of solid state transitions have been obtained for five metallocenes [15]. The combustion enthalpies of the metallocenes (η-$C_5H_5)_2M$ (M = Cr, Mn, Fe, Co, Ni) were determined so that the metal-(η-cyclopentadienyl) bond dissociation energies could be calculated. The bond dissociation energies showed maxima for vanadium and iron and a deep minimum for manganese [16].

Nickelocene, (η-benzene)tricarbonylchromium, (η-cyclopentadienyl)tricarbonylmanganese and ferrocene all form thiourea complexes. The complexes which are relatively insoluble in organic solvents, were used to separate these organometallic compounds from mixtures. Treatment of the thiourea complexes with boiling water gave the pure parent organometallic compound [17, 18]. The electronic configurations of several η-organometallic complexes including ferrocene, benchrotrene, cymantrene and bis(η-benzene)chromium tetrafluoroborate have been investigated by X-ray photoelectron spectroscopy [19].

The ^1H NMR chemical shifts for protons on the α-, β- and 1'-positions have been used to investigate the transmission of electronic effects in substituted ferrocenes, (η-benzene)(η-cyclopentadienyl)iron cations, cobalticinium ions and cymantrenes. Correlation of the shifts with Hammett parameters indicated that while the inductive effect was transmitted more strongly to the α- than to the β-position, the resonance effect was transmitted equally to these two positions. Interaction across the iron atom resembled that across a p-phenylene group [20].

The mass spectra of zero-valent transition metal complexes were obtained in order to investigate the relationship between the average dissociation energies of the complexes and the relative intensities of the metal ions. A quantitative relationship was found in carbonyl, η-benzene and η-cyclopentadienyl complexes where there was a relatively simple fragmentation scheme [21].

3. $(\eta\text{-}C_5H_5)V(CO)_4$

UV irradiation of tetracarbonyl(η-cyclopentadienyl)vanadium in the presence of the phosphines $Ph_2P(CH_2)_nPPh_2$ gave the phosphine complex cis-$[(\eta\text{-}C_5H_5)V(CO)_2Ph_2P(CH_2)_nPPh_2]$ when n = 1, 2, 4 and when n = 3 the polymeric compound cis-$[(\eta\text{-}C_5H_5)V(CO)_2Ph_2P(CH_2)_3PPh_2]_m$ was formed. ^{51}V NMR spectroscopy indicated that there was a relationship between ^{51}V chemical shifts and the ring size of the chelated structure [22]. ^{51}V NMR spectra were recorded for a series of vanadium complexes $(\eta\text{-}C_5H_5)V(CO)_3L$. (L = substituted phosphine, $SbPh_3$, $AsPh_3$, CN^-). From the ^{51}V chemical shift parameters the ligands L were arranged in sequence of their π-acceptor ability, which was $P(OR)_3 > CN^- > PR_3 \sim SbPh_3 \sim PPhF_2 > P(i\text{-}Bu)_3 \sim P(NR_2)_3 > PPh_3 > AsPh_3$ [23].

Cyclic voltammetric studies on the complexes $(\eta\text{-}C_5H_5)V(CO)_3$ L, where L = PPh_3, $PMePh_2$, PEt_3, $P(NMe_2)_3$, $P[(OCH_2)_3CMe]$, $P(OPh)_3$ and on the diphosphine $(\eta\text{-}C_5H_5)V(CO)_2(Ph_2PCH_2CH_2PPh_2)$ showed that they underwent one electron oxidation processes at a platinum electrode [24].

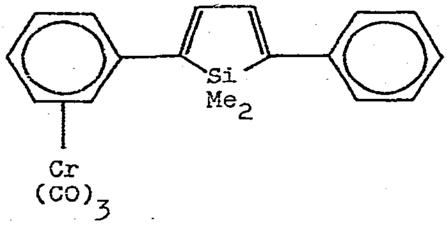
Tricarbonyl(η-hexaphenylbenzene)vanadium the first uncharged six-member arene carbonyl complex of vanadium, was prepared in low yield by the reaction of vanadium carbonyl with diphenylacetylene in the absence of light and air [25].

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

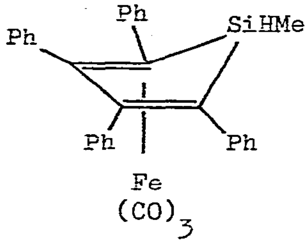
The complexes $(\eta\text{-}PhSiCl_3)Cr(CO)_3$, $(\eta\text{-}PhSiMeCl_2)Cr(CO)_3$, $(\eta\text{-}Ph.SiMe_2Cl)Cr(CO)_3$ and $(\eta\text{-}PhSiMe_3)Cr(CO)_3$ were prepared from hexacarbonylchromium and the corresponding arylsilane. The reaction of the complexes with hydrogen chloride under high pressure was studied. Pressures up to 4000 atmospheres increased the rate of cleavage of the phenyl-silicon bond in the complexes and in the uncoordinated arylsilane ligands. Coordination with the $Cr(CO)_3$ moiety facilitated the bond cleavage and the order of reactivity in the free and coordinated ligands was $PhSiMe_3 >$

PhSiMe$_2$Cl > PhSiMeCl$_2$ > PhSiCl$_3$ [26, 27].

Reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene with chromium hexacarbonyl gave the tricarbonylchromium complex (4.1). Similarly, 1-hydrido-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene underwent reaction with triiron dodecacarbonyl to form the complex (4.2) [28]. Addition of 2-pentyne to the aromatic ligand in the complex PhC(OMe):Cr(CO)$_5$ gave the chromium complex (4.3) [29].

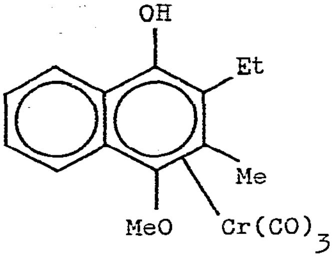


4.1

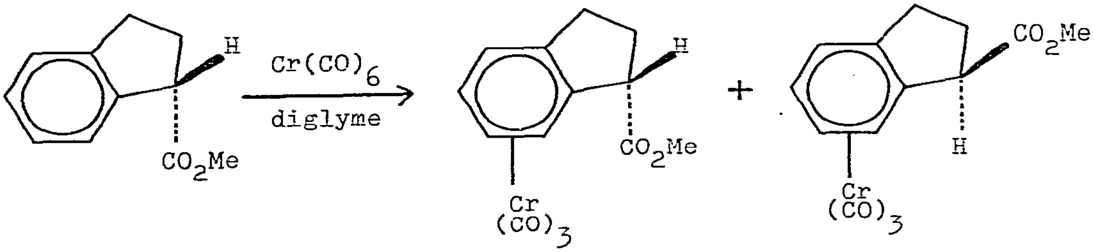


4.2

Methyl indan-1-carboxylate (4.4) which was enriched in the (-)-enantiomer was treated with hexacarbonylchromium to give the complexes (4.5 and 4.6). The complexes (4.5) and (4.6) underwent epimerization in the reaction to give the chromium complexes (4.6) and (4.5) respectively [30]. The benchrotrene complex (4.7) was obtained by heating *trans*-azobenzene with chromium hexacarbonyl in diglyme. Under photolytic conditions the same two reactants gave a binuclear σ-complex of azobenzene [31]. The preparation and acetolysis of some (tricarbonyl-η-phenylchromium)-benzyl-*p*-toluenesulphonates (4.8) and the noncomplexed analogues were reported. The ability of the α-(tricarbonyl-η-phenylchromium) group to stabilize electrophilic centres was compared with that of α-ferrocenyl. It was concluded that the tricarbonyl-η-phenylchromium group was a poorer electron donor than the ferrocenyl group but it was comparable to it as a conjugative substituent [32].



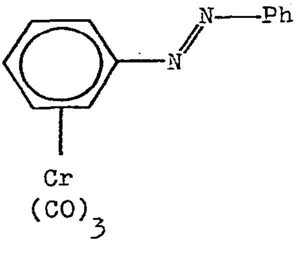
4.3



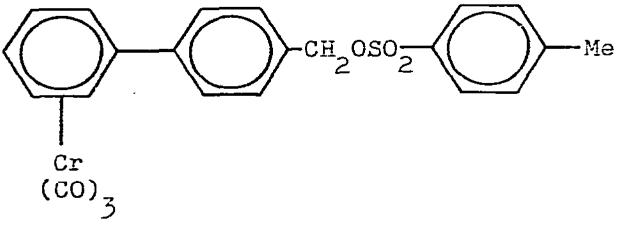
4.4

4.5

4.6



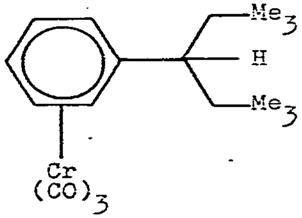
4.7



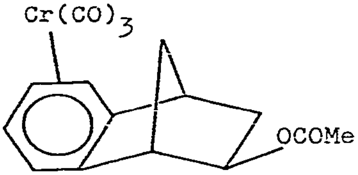
4.8

(ii) Spectroscopic and Physico-chemical Studies

The molecular structure of (1'-t-butyl-2',2'-dimethylpropyl)-(tricarbonylchromium)benzene (4.9) was determined from three dimensional X-ray data. Any strain in the molecule was relieved by a deviation of the CH-t-Bu$_2$ group and the tricarbonylchromium group from their usual position. The α-carbon atom was forced out of the η-arene ring plane by 0.41Å. The dihedral angle between the plane of the benzene ring and the plane through the oxygen atoms was 8°. The tricarbonylchromium group was twisted away from the electronically favoured conformation (i.e. eclipsed with respect to the alkyl group) by 44.4° [33]. The crystal and molecular structure of tricarbonyl(η-methylbenzoate)chromium was determined by X-ray analysis and compared with the structure of dicarbonyl(η-methylbenzoate)thiocarbonylchromium [34]. The crystal and molecular structure of (η-exo-2-acetoxybenzonorbornenyl)-exo-tricarbonylchromium (4.10) has been determined by X-ray crystallography [35]. ESCA was used to study the effect of substitution on the aromatic ring in arenetricarbonylchromium complexes, (η-ArX)Cr(CO)$_3$ (X = Me, Et, Pr, F, Cl, MeO). The chemical shifts of the core ionization energies (C 1s, O 1s, Cr 3s) were measured and discussed in relation to the bonding in these complexes [36].

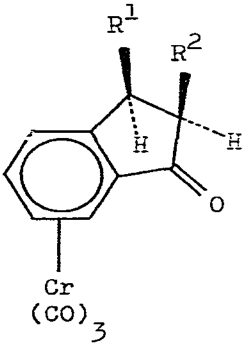


4.9

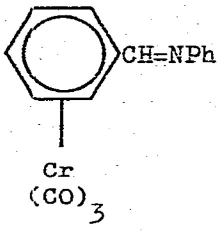


4.10

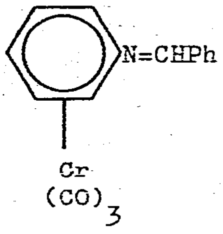
Tetracyanoethylene charge transfer complexes of (η-benzene)-tricarbonylchromium compounds were studied by an electron spectroscopic method. A linear relationship was obtained between the charge-transfer frequencies and σ_π^+ substituent constants which indicated that the tetracyanoethylene interacted with the η-benzene ligand [37]. Rate constants were determined spectrophotometrically for the reduction of the η-indanonechromium complexes (4.11; $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = Et$, $R^2 = H$; $R^1 = Pr^i$, $R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = H$, $R^2 = Et$; $R^1 = H$, $R^2 = Pr^i$) by sodium borohydride and sodium borohydride-d_4. The k_H/k_D values varied significantly as the degree of steric hindrance around the ketone group changed. It was concluded that a displacement of the transition state occurred in this type of reaction [38]. The wavenumbers and half-band widths of the infrared carbonyl stretching vibrations for the alkyl-substituted (η-benzene)tricarbonylchromium complexes were recorded. Only small perturbations of C_{3v} symmetry were observed. A satisfactory correlation was obtained between the CO force constants and electronic substituent parameters for the monosubstituted complexes. For the di- and tri-alkylsubstituted benzene complexes the substituent effects were approximately additive [39]. The ^1H NMR and infrared spectra of the tricarbonylchromium complexes (4.12, 4.13 and 4.14) were discussed. The C-O stretching frequencies at 1958-86 cm^{-1} indicated that the transmission of electronic substituent effects to the carbonyl group involved a mesomeric mechanism comprising both the substituent and the arene ligand [40]. The ^1H NMR spectrum of the tricarbonylchromium complex (4.9) was studied over the temperature range 0-115°C. The spectra indicated that there were two rotamers present (4.15 and 4.16) which exchanged slowly at 0°. At higher temperatures the exchange rate increased and the $\Delta G^{\ddagger}$ value for the interconversion was 16.9 kcal mol^{-1} which was smaller than the



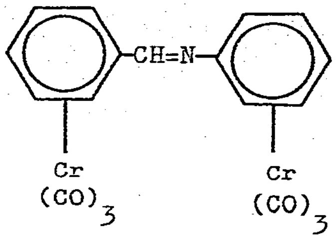
4.11



4.12

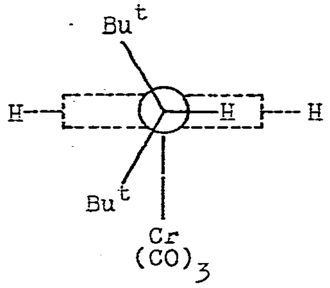


4.13

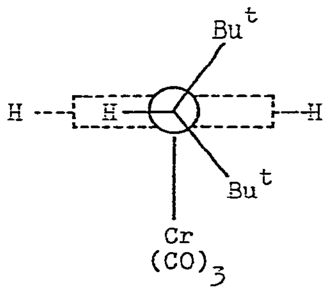


4.14

corresponding value for the free ligand. This decrease was ascribed to additional steric strain between the alkyl and the tricarbonylchromium groups in the conformers of the complex [41].

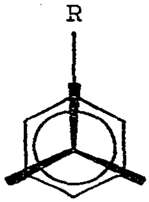


4.15

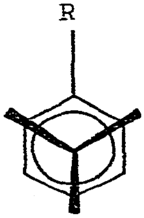


4.16

A series of alkyl-substituted (η-benzene)tricarbonylchromium complexes was prepared and the ^{1}H NMR spectra were recorded. It was concluded that the alkyl group tended to orientate the $Cr(CO)_3$ into conformation (4.17). The adverse steric interaction of a bulky aryl with a superimposed carbonyl ligand favoured conformation (4.18). The bulkiness of the alkyl group helped to determine the conformational equilibrium constant [42]. ^{1}H NMR spectroscopy has been used to investigate hindered rotation in dimesitylmethane chromium complexes such as the ketone (4.19; X = O) and the hydrocarbon complex (4.19; X = H_2).

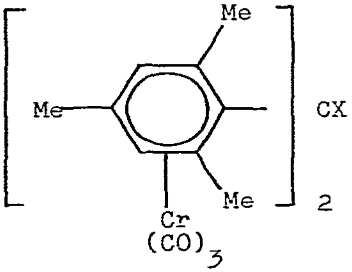


4.17

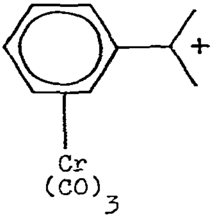


4.18

The complexes adopted helical conformations and the energy barrier for rotation of the ketone was 5 kcal mol $^{-1}$ greater than that for the hydrocarbon complex. Tricarbonylchromium complexes of biphenyls were also studied [43]. The tricarbonyl-(η-cumyl)chromium cation (4.20) was obtained by treatment of the corresponding cumyl alcohol complex with fluorosulphuric acid in liquid sulphur dioxide at -80°C. ^{1}H and ^{13}C NMR spectroscopy indicated that the cation was stabilized by back donation of electron density from the chromium atom to the arene ligand. On the basis of the spectroscopic measurements the σ^{+} substituent constant for the tricarbonylchromium group was estimated as -1.8 [44].

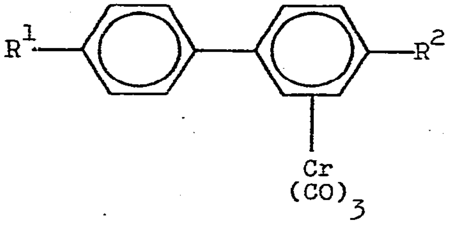


4.19

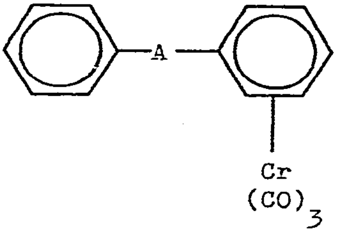


4.20

The ^{13}C NMR chemical shifts of the benzene ring carbon atoms in a series of (η-diphenyl)chromium tricarbonyl and related complexes have been determined. Large upfield shifts in the carbon resonances of the complexed ring were observed while the resonances in the uncomplexed ring showed only very small shifts. The results indicated the importance of σ-effects in the transmission of substituent effects. Typical complexes investigated were the biphenyls (4.21; R^1 = H, F, Cl, Me; R^2 = H, F, Me) and the diphenylalkanes (4.22; A = CH_2, CH_2CH_2, CH=CH, CO) [45].



4.21

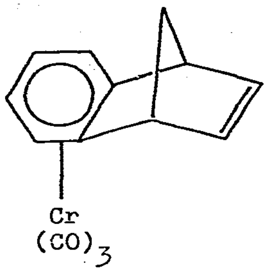


4.22

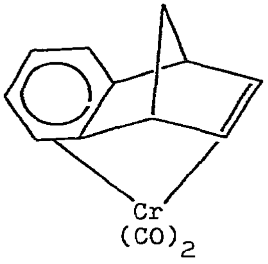
The ^{13}C NMR spectra of benzonorbornadiene and the two chromium complexes (4.23 and 4.24) were recorded. The spectra suggested that there was little molecular distortion on the formation of the complex (4.23) from benzonorbornadiene but on conversion of complex (4.23) to the complex (4.24) appreciable strain was introduced into the alkyl portion of the ligand. It was concluded that in complex (4.24) the chromium atom was not symmetrically placed with respect to the benzene ring and that it was strongly bound to the carbon-carbon double bond [46]. Olah and Yu have used ^{13}C NMR spectroscopy to show that (η-anisole)-tricarbonylchromium was protonated exclusively on the chromium atom in sulphur dioxide containing fluorosulphonic acid at -80° [47].

(iii) General Chemistry

The phenylboronic acid [4.25, R = $B(OH)_2$] prepared from phenylboronic acid and triamminetricarbonylchromium was converted

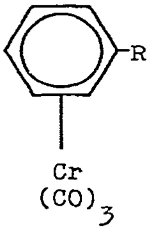


4.23

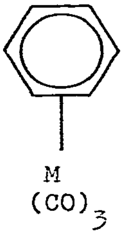


4.24

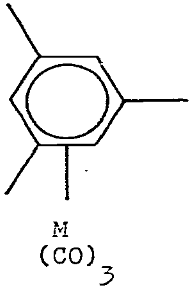
to the anhydride (4.25, R = BO) on heating *in vacuo*. It formed the ester [4.25, R = $B(OPr^n)_2$] with propanol in boiling benzene and the mercurichloride (4.25, R = HgCl) with mercury (II) chloride [48]. The interaction of the (η-arene)carbonylchromium complexes



4.25



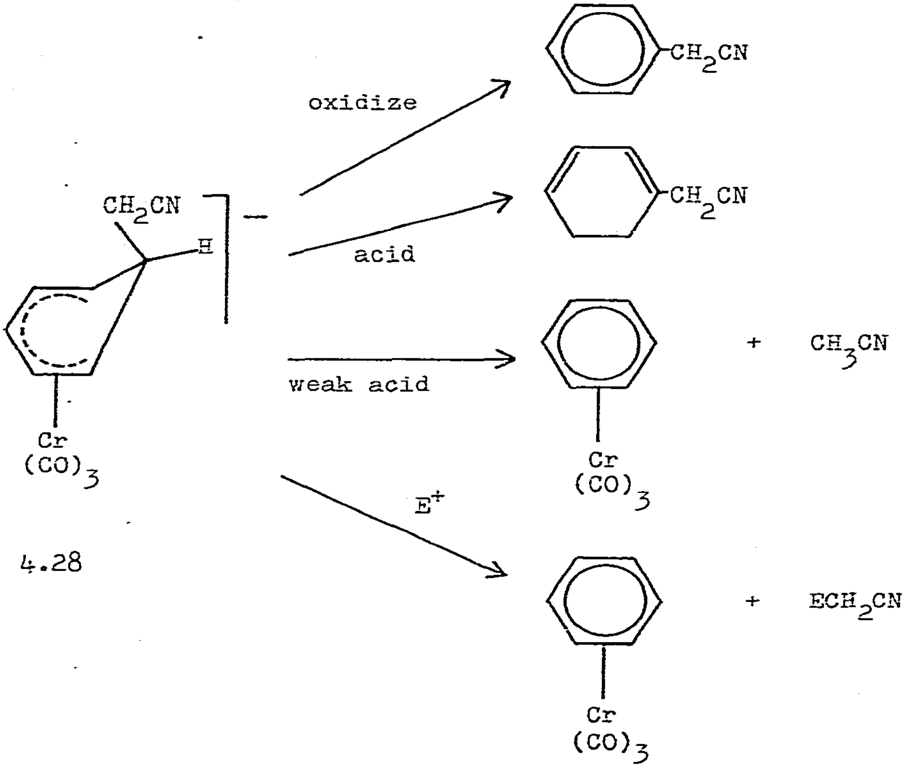
4.26



4.27

$XArCr(CO)_2L$ where L = CO, PPh_3; X = H, 3(Me), OMe, CO_2Me and COMe with visible light was investigated by measurement of the electronic absorption spectra. Photo-decomposition occurred and this followed first order kinetics. (η-Benzene)tricarbonylchromium decomposed to give benzene and hexacarbonylchromium and the introduction of a substituent into the benzene ring had no effect upon the rate of decomposition. Substitution of a carbonyl group by a triphenylphosphine ligand increased the rate of decomposition [49]. The formation of adducts between benchrotrenes and Lewis acids in solution has been investigated by infrared spectroscopy. The arene complexes (4.26, 4.27; M = Cr, Mo, W) gave adducts with titanium tetrachloride and tin (IV) chloride containing a transition metal-Lewis acid bond. When one carbonyl group in the arenes (4.26, 4.27) was replaced by a triphenylphosphine group then stronger adducts were formed [50].

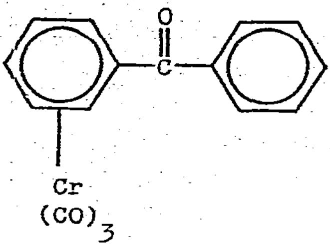
The reaction of carbanions with (η-arene)tricarbonylchromium compounds was studied by ^1H NMR spectroscopy. (η-Benzene)tricarbonylchromium was treated with lithiocyanomethane and it was concluded that exo attack of the carbanion occurred to give the intermediate (4.28). The reactivity of the intermediate (Scheme 4.1) was generally consistent with the η-cyclohexadienyl structure [51]. The mechanism of electrolytic reduction of benzyl chlorides,



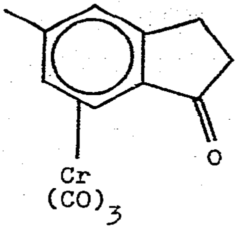
Scheme 4.1

free and complexed with tricarbonylchromium was investigated. The fission of the carbon to chlorine bonds in the complexed chlorides occurred at less negative potentials than those of the uncomplexed compounds [52]. The polarographic reduction of (η-benzophenone)tricarbonylchromium (4.29) and related compounds in dimethylformamide has been investigated. The polarograms showed two well defined waves, the first corresponding to formation of the radical anion and the second to the dianion [53]. Thermolysis of the sodium salt of tricarbonyl(η-acetophenone)chromium p-tosylhydrazone was studied in pyridine in the presence and absence of 1,1-diphenylethylene and cyclohexene. The products isolated were rationalized in terms of a diazo intermediate and tricarbonyl-(η-methylphenylcarbene)chromium [54]. The (-)-tricarbonyl-(η-indanone)chromium compound (4.30) of known configuration and optical purity was condensed with 2-formyl-4-methylbenzoic acid, esterified and reduced with hydrogen over a catalyst to form the ester (4.31). This intermediate (4.31) was saponified and cyclized to give a mixture of the (-)-trans- (4.32), and (-)-cis--spirobiindanone from which the free chiral spiroindanone ligands were liberated and reduced to yield the (-)(S)- (4.33) and (+)(R)--spirobiindanes respectively [55].

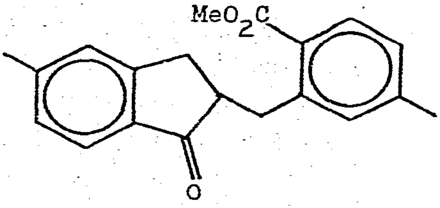
The (η-indane)chromium complex (4.34; R = H) was formed from the free optically active ligand and chromium hexacarbonyl. Treatment with base and the appropriate halide led to stereospecific introduction of substituents to form the alkylated ester complexes (4.34; R = Me, CH_2Ph, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$, CH_2CO_2Me). The tricarbonylchromium group was removed by photo-induced oxidation to leave the corresponding optically active indan-1-carboxylic ester [56]. The effect of pH on deuterium exchange reactions of the chromium complexes (4.25, 4.35 and 4.36; R = H, Me, OMe, CO_2Me, COMe) was investigated. The rate of exchange between the complex (4.25; R = H) and CF_3CO_2D was almost the same as that of benzene whereas the rate with the complex (4.36; R = H) increased three-fold. Substituent effects with the complex (4.25; R = H) were negligible. The rate of deuterium exchange for the complexes (4.36) was higher than for the corresponding complexes (4.25 and 4.35) [57]. The π-complexes of phosphorins (4.37; M = Cr, Mo, W; R^1 = Ph, R^2 = Ph, Me, CH_2Ph, CMe_3; X = F, OMe) were obtained as air-stable solids by heating the phosphorin with the appropriate metal carbonyl or with



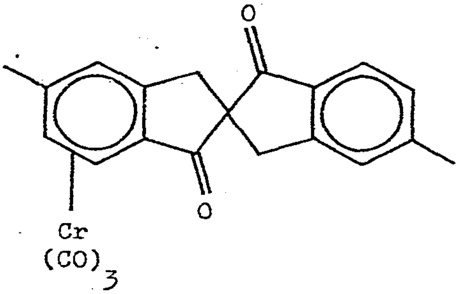
4.29



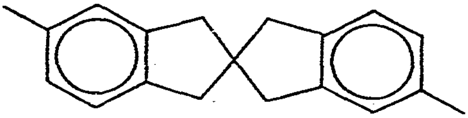
4.30



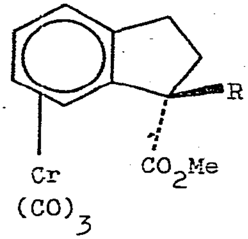
4.31



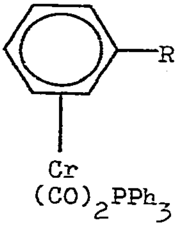
4.32



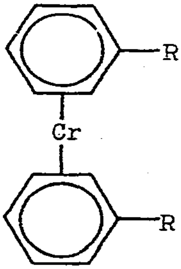
4.33



4.34

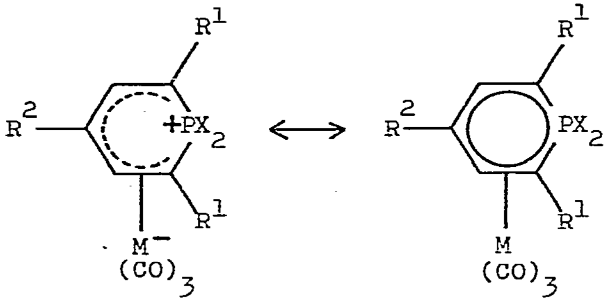


4.35

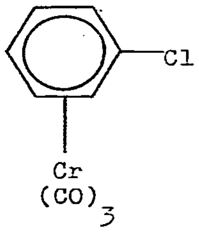


4.36

$M(CO)_3(MeCN)_3$. X-ray structure analysis showed that the phosphorin-ring remained planar on complex formation but it was not possible to decide to what extent the ylide form (4.37) or the arene form (4.38) participated in the ground state bonding of the complex [58].



4.37 4.38



4.39

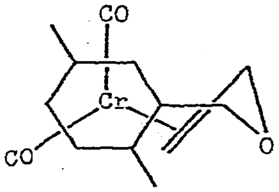
Unsaturated vegetable oils, such as soyabean oil, were hydrogenated at 180-250° and under pressure (30 atmos) in the presence of a benchrotrene catalyst (4.39) [59]. Tricarbonyl-tris(1,2-diphenylacrylonitrile)molybdenum was prepared by the addition of tricarbonyl(η-mesitylene)molybdenum to 1,2-diphenylacrylonitrile. It was suggested that the ligand was bound to the metal by the alkene double bond [60]. Polystyrene beads were treated with hexacarbonylmolybdenum to give (η-polystyrene)tricarbonylmolybdenum. The polymer anchored tricarbonylmolybdenum behaved as a Friedel-Crafts catalyst for acylation and alkylation and it also catalysed the bulk polymerization of benzyl chloride. The anchored catalyst showed decreased activity when compared with the corresponding homogeneous system. Exchange and leaching experiments on the catalyst indicated that the tricarbonylmolybdenum group remained attached to the polystyrene when it was used as a catalyst. When the polymer anchored catalyst was reused six times, in the alkylation of anisole with t-butyl chloride it showed no loss in activity [61].

The early stages in the polymerization of phenylacetylene by tricarbonyl(η-toluene}molybdenum have been studied using diphenylacetylene as a model monomer. Among the products isolated were hexaphenyl-Dewar-benzene, carbonyl(η-diphenylacetylene)-

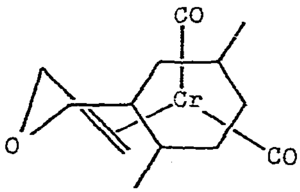
(η-tetraphenylcyclobutadiene)molybdenum and a trinuclear complex containing two molecules of diphenylacetylene. It was concluded that the (η-toluene)-molybdenum bond remained intact during the polymerization of phenylacetylene [62]. Molybdenum hexacarbonyl has been used to generate in situ (η-arene)tricarbonylmolybdenum catalysts which were used for acylation, alkylation, dehydrohalogenation, polymerization and sulphonation of benzenoid aromatics such as toluene and anisole [63,64]. (η-Arene)tricarbonylmolybdenum compounds, when used as Friedel Crafts catalysts in the alkylation, acylation and sulphonation of aromatic substrates, showed improved selectivity in product formation leading to p-isomers as the principal products [65].

(iv) Analogues

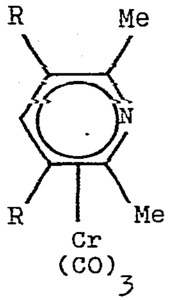
Dicarbonyl[η-(2,5-dimethylbenzyl)allyl ether]chromium was prepared as a mixture of two diastereoisomeric pairs of enantiomers. The structure of the principal enantiomeric pair (4.40 and 4.41) was established by X-ray analysis [66]. η-Complexes of methylpyridines have been obtained by direct combination of hexacarbonylchromium with the ligand. Thus the tricarbonylchromium complexes (4.42; R = H, Me) were formed from 2,6-dimethylpyridine and 2,3,5,6-tetramethylpyridine. The spectroscopic properties of these and other tricarbonyl(η-pyridine)chromium complexes were discussed [67]. The thiophene complexes (4.43; R^1, R^2 = H, Me, OMe, CO_2Me, Br) were formed by treatment of tricarbonyltripyridine-



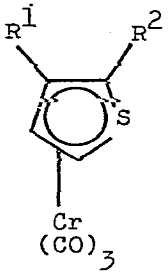
4.40



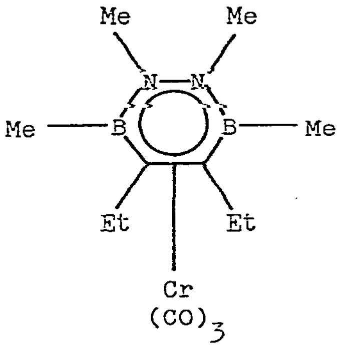
4.41



4.42

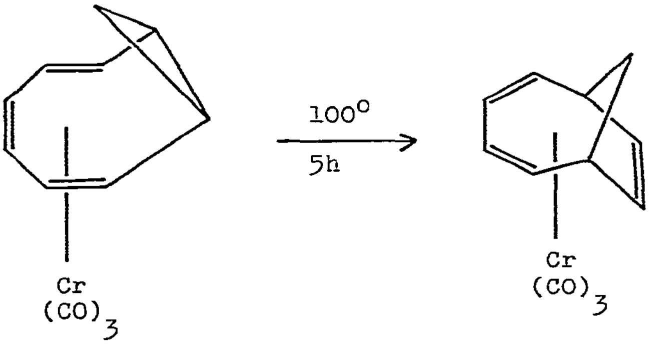


4.43



4.44

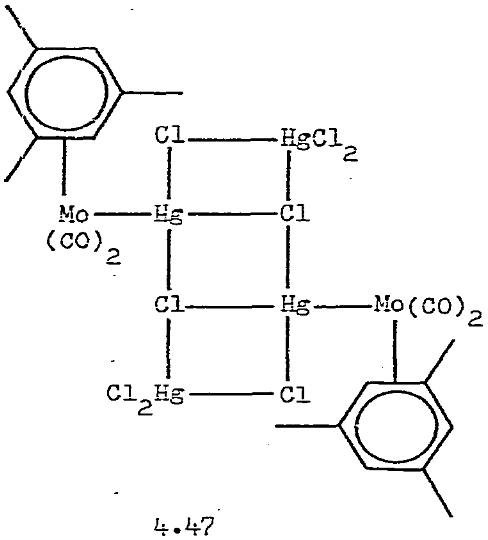
chromium with the free substituted thiophene [68]. Treatment of triacetonitriletricarbonylchromium with an alkyl substituted 1,2-diaza-3,6-dibora-4-cyclohexene gave the benchrotrene analogue (4.44) [69]. A series of (η-triene)Cr(CO)$_3$ complexes of bicyclic derivatives of cycloocta-1,3,5-triene were prepared. The complex (4.45) rearranged at 100° to give {η-bicyclo[4.2.1]nona-2,4,7-triene}Cr(CO)$_3$ (4.46) in almost quantitative yield. The reaction of (MeCN)$_3$Cr(CO)$_3$ or (diglyme)$_2$Mo(CO)$_3$ with cycloocta-1,3,6-triene gave the corresponding tricarbonylmetal compounds [70].



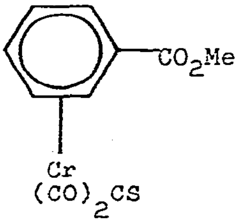
4.45

4.46

(η-Mesitylene)molybdenum tricarbonyl formed a 1 : 2 adduct with mercuric chloride in acetone and the structure of this complex was determined by X-ray crystallography as the dimer (4.47). The two molybdenum atoms are bridged by an Hg_2Cl_2 four-membered ring. Mercury-chlorine distances varied between 2.317 and 3.038 Å [71].



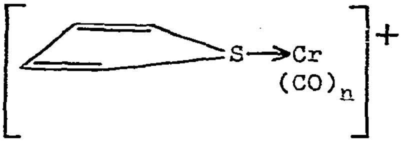
4.47



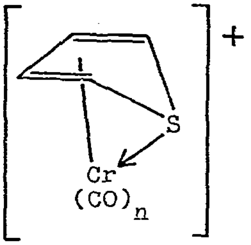
4.48

The valence force field of the thiocarbonyl benchrotrene compound (4.48) has been calculated and has confirmed results obtained from the vibrational spectra of this compound and benchrotrene. It was demonstrated that the thiocarbonyl group was a better σ-electron donor and π-acceptor than the carbonyl group [72]. The mass spectrum of tricarbonyl(η-thiophene)chromium was similar to that of (η-benzene)tricarbonylchromium in that there was successive elimination of three carbonyl groups and of the ligand molecule. The cation CrS^+ was formed in the fragmentation and this suggested that part of the ion $[(\eta\text{-}C_4H_4S)Cr(CO)_n]^+$ where $n = 0, 1$ was subject to σ-type coordination (4.49) or both π- and σ-coordination (4.50) [73].

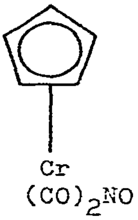
Reaction of (η-arene)tricarbonylchromium complexes with nitrosyl chloride at room temperature led to complete decarbonylation but at -30^{o} $[CrCl(CO)_2NO]$ was formed as the main product. Reaction of this nitrosyl complex with cyclopentadienylsodium gave the chromium complex (4.51). Analogous reactions with



4.49

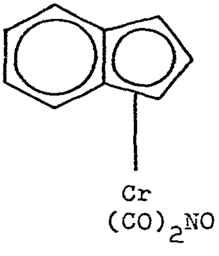


4.50

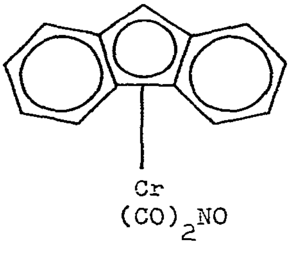


4.51

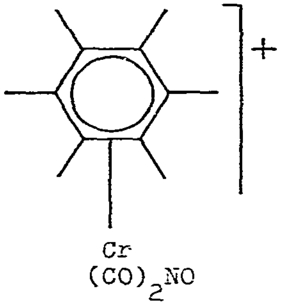
indenyl- and fluorenyl-lithium led to the complexes (4.52) and (4.53) [74]. The (η-arene)chromium cation (4.54) was attacked by chloride, bromide and iodide ions with displacement of the arene ligand and formation of a chromium-halogen bond [75].



4.52



4.53

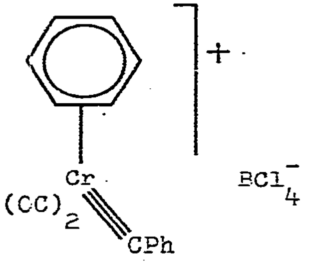


4.54

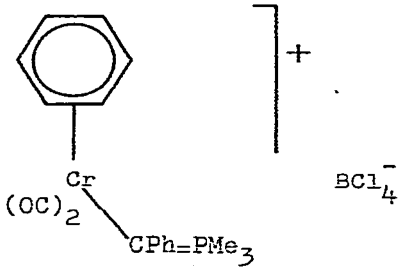
The tricarbonylchromium complexes (4.55; Ar = PhH, PhMe, 1,4-$Me_2C_6H_4$, 1,3,5-$Me_3C_6H_3$) were converted into the corresponding carbene complexes (4.56) by treatment with phenyllithium followed by alkylation. Treatment of the carbene complexes (4.56) with boron trichloride gave the cationic carbyne complexes (4.57). Aminolysis with ammonia or dimethylamine led to the aminocarbene complexes (4.58; R = H, Me) [76].

$$\begin{tikzcd}
\underset{4.55}{\eta\text{-ArCr(CO)}_3} \arrow[r] & \eta\text{-ArCr(CO)}_2[\text{C(Ph)OMe}] \arrow[d, "4.56"] \\
\underset{4.58}{\eta\text{-ArCr(CO)}_2[\text{C(Ph)NR}_2]} & \underset{4.57}{[\eta\text{-ArCr(CO)}_2(\text{CPh})]^+\text{BCl}_4^-} \arrow[l]
\end{tikzcd}$$

The chromium substituted ylid (4.60) has been obtained by treatment of the carbyne chromium complex (4.59) with trimethylphosphine [77].



4.59



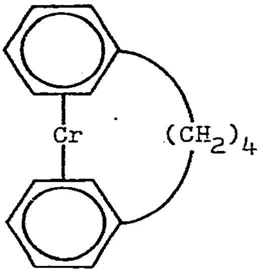
4.60

The kinetics of hydrogen-deuterium exchange of trifluoroacetic acid-d_1 with tricarbonyl-(η-thiophene)-(η-2-bromothiophene)- and -(η-2-chlorothiophene)-chromium have been determined at 25° [78]. A tricarbonyl (η-mesitylene)molybdenum-phenol mixture was an active, selective, homogeneous catalyst for the metathesis of acetylenes in boiling toluene [79].

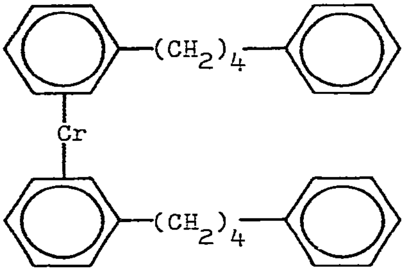
5. $(\eta\text{-C}_6\text{H}_6)_2\text{Cr}$

Addition of 1,4-diphenylbutane to chromium vapour gave the bridged di(η-benzene)chromium derivatives (5.1, 5.2 and 5.3).

These derivatives were converted to their iodides and then separated by preparative thin layer chromatography [80].

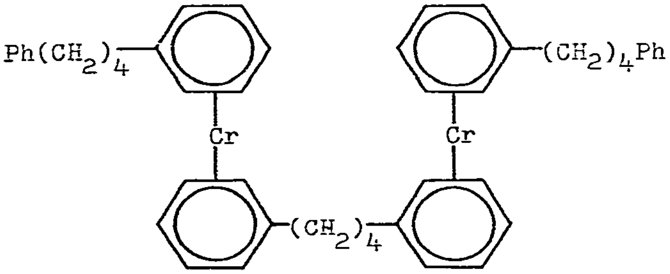


5.1

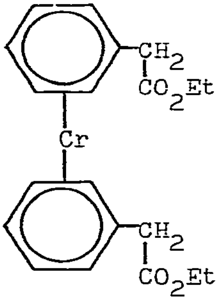


5.2

Low temperature condensation of chromium vapour with ethyl phenylacetate and phenylpropionate gave the chromium complexes (5.4 and 5.5) respectively. These complexes were oxidized in water to give the hydroxo derivatives which were treated with potassium iodide to give the corresponding iodides L_2CrI where $L = \eta\text{-}PhCH_2CO_2Et$, $\eta\text{-}PhCH_2CH_2CO_2Et$ [81]. The chromium complexes



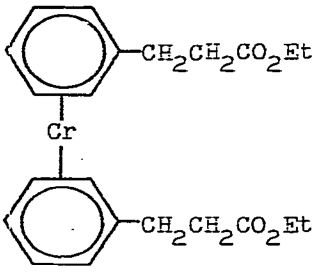
5:3



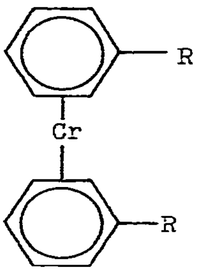
5.4

(5.6; R = Me, Et) were prepared by the cocondensation of chromium with the appropriate ligand. These complexes were oxidized to the iodides (η-MeC$_6$H$_5$)$_2$Cr$^+$I$^-$ and (η-EtC$_6$H$_5$)$_2$Cr$^+$I$^-$ respectively [82].

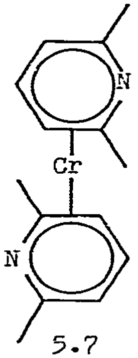
A thermodynamic study was carried out on the equilibrium in the direct-synthesis reaction of bis(η-benzene)chromium. The reaction of gaseous chromium with the solid ligand was shown to be the most probable mechanism for this process. The thermodynamic and kinetic stabilities of bis(η-benzene)chromium were also discussed [83]. Chromium atoms were condensed with 2,6-dimethylpyridine at 77° K to give the bis (η-pyridine)chromium compound (5.7). The structure of the complex was determined by X-ray methods, the two pyridine rings were parallel and the complex was analogous to bis(η-benzene)chromium [84].



5.5

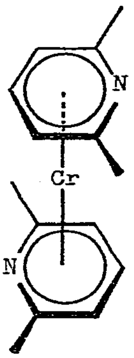


5.6

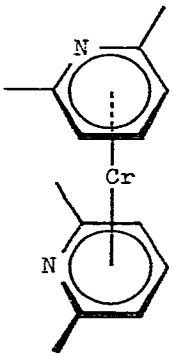


5.7

The molecular structure of bis(η-2,6-dimethylpyridine)chromium was determined by X-ray analysis. Two crystal modifications were examined and these were found to be the rotameric conformers (5.8 and 5.9). In both forms the molecule was a true sandwich complex with the chromium atom symmetrically π-bonded to two 2,6-dimethylpyridine ligands [85]. The ^{1}H NMR spectra of a series of bis(η-arene)chromium complexes were recorded at 100 MHz and interpreted. Simple first order spectra were obtained for most of the compounds. A reduction in *J*(HH)-values, relative to the free ligand, was found for the complexed arenes and H-H coupling was limited to adjacent hydrogen atoms [86].



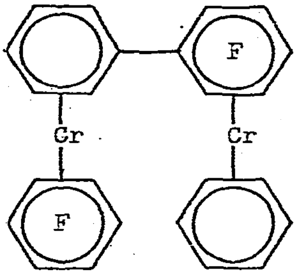
5.8



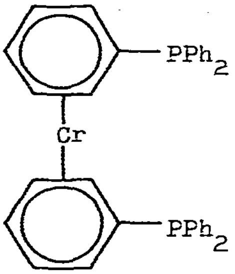
5.9

Graves and Lagowski have recorded the ^{13}C NMR spectra of thirty eight bis(η-arene)chromium compounds with the alkyl, F, Cl, CF_3, $N(alkyl)_2$ and ester groups as substituents. Where a single substituent group was present, analysis of the C-4 chemical shift indicated that there was no transmission of the substituent effect across the arene ring. It was suggested that donation of π-electron density from the arene ring to the chromium atom appreciably reduced the ring aromaticity [87]. Details were given of an apparatus for the thermal decomposition of bis(η-ethylbenzene)chromium in a strong electric field. Chromium was deposited in both globular and whisker form during the decomposition [88]. The rate of pyrolysis of bis(η-ethylbenzene)vanadium was increased by the addition of bis(η-ethylbenzene)chromium [89]. The heat capacity and magnetic susceptibility of bis(η-benzene)chromium iodide were measured so that the long-range antiferromagnetic ordering of the compound could be studied [90]. The thermodynamic properties of bis(η-benzene)chromium iodide have been determined. The heats of combustion and formation were 7049.6 and 42.0 kJmol^{-1} respectively [91].

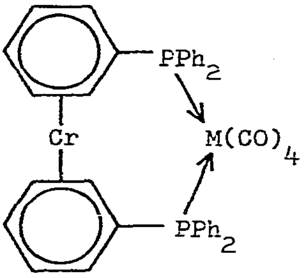
McGlinchey and Tan have observed that fluoride ions were displaced from bis(η-benzene)chromium complexes by nucleophiles. Thus bis(η-fluorobenzene)chromium was attacked by sodium methoxide to form bis(η-methoxybenzene)chromium while (η-benzene)(η-hexafluorobenzene)chromium underwent replacement of one, two or four fluoride ions by alkyl or aryl groups when treated with organolithium reagents at -78°. In addition, t-butyllithium was effective in metallating (η-benzene)(η-hexafluorobenzene)-chromium and the lithio intermediate combined with a second molecule of the fluoro complex to form the biphenyl complex (5.10) [92]. The bisbenzenechromium complex (5.11) was attacked by chromium, molybdenum and tungsten hexacarbonyls to give the binuclear complexes (5.12; M = Cr, Mo, W) [93].



5.10



5.11



5.12

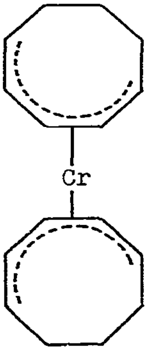
Treatment of bis(η-benzaldehyde)chromium with acetophenone or ethyl acetate in the presence of base gave the β-substituted styrene complexes $(\eta\text{-PhCH=CHCOPh})_2Cr$ and $(\eta\text{-PhCH=CHCO}_2Et)_2Cr$ respectively [94].

Bis(η-ethylcinnamate)chromium was hydrogenated, in the presence of tris(triphenylphosphine)rhodium (I) chloride and palladium (II) chloride as catalysts, to give the η-arene complex (5.5). Hydrogenation over platinum (IV) oxide, Pd/Al_2O_3 or nickel led to breakdown of the chromium complex [95].

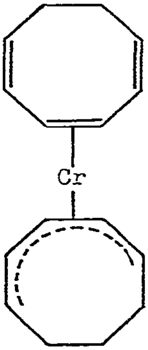
The intercalation compounds $[(\eta\text{-}C_6H_6)_2M]_{1/6}ZrS_2$ where M = Cr, Mo, $[(\eta\text{-arene})_2Mo]_xZrS_2$ where arene = toluene, mesitylene and $x = < 1/6$, $[(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)Cr]_{1/4}ZrS_2$, $[(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)Cr]_{1/4}ZrS_2$, $[(\eta\text{-}C_5H_5)_2Cr]_{1/4}ZrS_2$ and $[(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)Ti]_{1/4}ZrS_2$ were prepared by heating ZrS_2 with a solution of the appropriate sandwich compound in a sealed ampoule [96]. Dry, microspheroidal silica was treated with tetraisopropyl titanate and calcined. The treated silica was then impregnated with a hexane solution of di(η-benzene)chromium and exposed to dry air to give a catalyst with good activity for the preparation of polythene [97]. The possibility of separating bis(η-arene)-chromium complexes by crystallization from a melt was investigated and shown to be practicable [98]. The melting points, densities and viscosities of some di(η-ethylbenzene)-chromium and-molybdenum complexes were measured. The magnitudes of the physical parameters decreased as the number of ethyl groups increased [99]. Solid supports which had been treated with di(η-ethylbenzene)-chromium at 250-350° were used in the gas chromatographic separation of thermally unstable organometallic compounds [100].

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

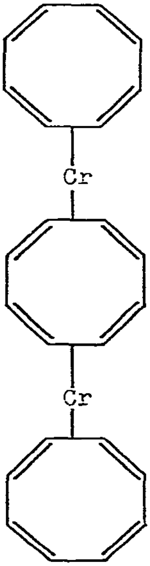
The cocondensation of chromium atoms and styrene at -196°C and subsequent warm-up to room temperature in an atmosphere of carbon monoxide gave tricarbonyl(η-styrene)chromium and tricarbonyl-(η-polystyrene)chromium. A similar reaction using trifluorophosphine instead of carbon monoxide gave (η-styrene)tris(trifluorophosphine)chromium and (η-polystyrene)tris(trifluorophosphine)-chromium [101]. Treatment of chromium (III) chloride with iso-propylmagnesium bromide in a mixture of 1,3-cyclooctadiene and 1,3,5-cyclooctatriene gave the chromium complexes (6.1 and 6.2). Similarly, treatment of chromium (III) chloride and the Grignard reagent with cyclooctatetraene gave the chromium



6.1

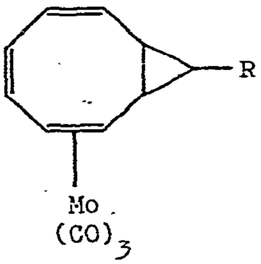


6.2

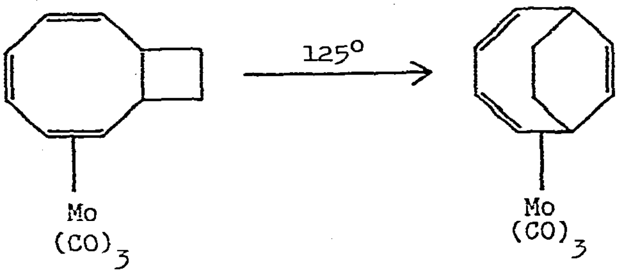


6.3

complex (6.3) [102]. Salzer has described the formation of some molybdenum tricarbonyl complexes of bicyclic derivatives of cyclooctadiene. The complexes (6.4; R = H, Me, Cl, CO_2Et) were stable towards valence isomerism while the complex (6.5) rearranged at 125° to the (η-bicyclo[4.2.2]decatriene) complex (6.6) [103].



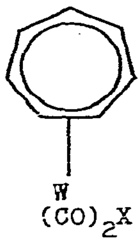
6.4



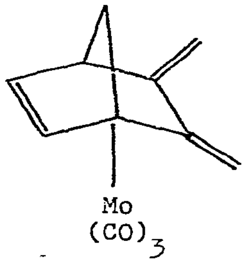
6.5

6.6

The halide and pseudohalide (η-cycloheptatrienyl)tungsten complexes (6.7; X = Cl, Br, OCN, N_3) were formed by treatment of the tricarbonyl(η-cycloheptatrienyl)tungsten fluoroborate with the appropriate halide ion [104]. The crystal structure of the molybdenum complex (6.8) has been determined by X-ray analysis [105]. INDO calculations on the cation $[(\eta\text{-}C_7H_7)Cr(CO)_3]^+$



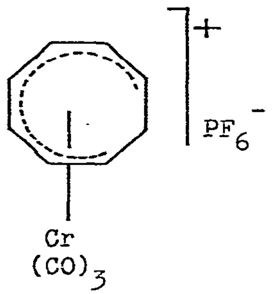
6.7



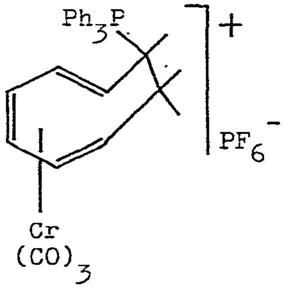
6.8

showed that, despite an increase in ring carbon positive charge, the decrease in reactivity of the ligand $C_7H_7^+$ towards nucleophiles upon coordination could be explained in terms of increased bond index values. The site of nucleophilic attack in the cations $[(C_7H_6X)Cr(CO)_3]^+$ where X = OMe, CO_2Me did not correlate with any specific electronic parameter and it was thought that several factors were involved [106]. The complexes $(\eta\text{-}C_5H_5)M(\eta\text{-}C_7H_7)$ where M = Ti, Zr, Cr, Mo were investigated by ^{13}C NMR spectroscopy. In the complex M = Cr the carbon atoms of the η-cyclopentadienyl ring were more shielded than those of the seven-membered ring while for M = Ti the reverse was true. From the chemical shifts it was clear that for M = Cr the carbon atoms of the five-membered ring were more negatively charged than those of the η-cycloheptatrienyl ring. The replacement of chromium by molybdenum in the complexes caused a down-field shift of the signals for the five-membered ring and an upfield shift of the signals for the seven membered ring [107].

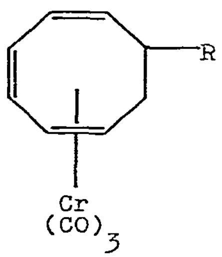
The addition of triphenylphosphine to the chromium complex (6.9) gave the phosphonium salt (6.10). The chromium complex (6.9) also behaved as an electrophilic reagent with aromatic compounds and β-diketones to give the η-cyclooctatriene complexes (6.11; R = indole, acetylacetone, dimedone) [108]. Reaction of tricarbonyl(η-cycloheptatrienyl)molybdenum (I) hexafluorophosphate with bis(diphenylphosphino)methane (dpm) and



6.9

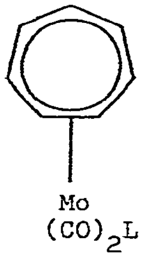


6.10



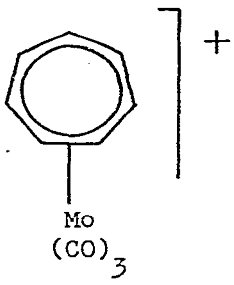
6.11

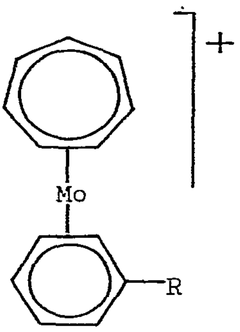
bis(diphenylphosphino)ethane (dpe) gave products of three types; the monosubstituted complex $[(\eta\text{-}C_7H_7)Mo(CO)_2(dpm)]PF_6$, the chelated complexes $[(\eta\text{-}C_7H_7)Mo(CO)(dpm)]PF_6$ and $[(\eta\text{-}C_7H_7)Mo(CO)(dpe)]PF_6$, and the dinuclear complex $[\{(\eta\text{-}C_7H_7)Mo(CO)_2\}_2\text{-}\mu\text{-}Ph_2PCH_2CH_2PPh_2](PF_6)_2$. The spectroscopic properties, including the ^{31}P NMR spectra of these complexes, were reported [109]. The neutral tropylium complexes (6.12; L = SO_2Ph, $SO_2C_6H_4Me$) were obtained by treatment of dicarbonyl(η-cycloheptatrienyl)molybdenum iodide with $AgSO_2R$. The sulphinate group was bound to molybdenum through sulphur. The thioaryl complexes (6.12; L = SPh, SC_6H_4Me, SC_6F_5, $SC_6H_4NO_2$) were prepared in the same way from dicarbonyl (η-cycloheptatrienyl)-molybdenum iodide and arylmercaptans [110].

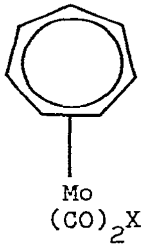


6.12

Treatment of the (η-cycloheptatrienyl)molybdenum cation (6.13) with benzene or alkylbenzenes gave the mixed sandwich compounds (6.14; R = H, Me) whilst treatment with trimethylhalogenosilane gave the halides (6.15; X = Cl, Br, I). Several transformations of these compounds were reported together with the X-ray crystal and molecular structures of two examples [111]. The protonation of organometallic compounds by HBF_4-propionic anhydride has been investigated. Protonation of tricarbonyl(η-cycloheptatriene)-molybdenum occurred to give $[(\eta\text{-}C_7H_9)Mo(CO)_3]BF_4$. Protonation of η-cyclopentadienyl-cobalt-phosphonate cluster compounds proceeded via protonation of the P=O moiety [112]. The reaction of tricarbonyl-(η-cycloheptatriene)-molybdenum with maleic acid or fumaric acid esters (L) at 60-80^0 gave binuclear carbonyl-bridged complexes







6.13

6.14

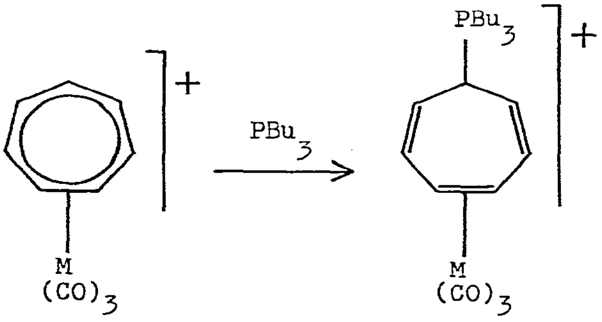
6.15

in which the ester molecules were π-coordinated across the olefinic double bond.

$$2(\eta\text{-}C_7H_8)Mo(CO)_3 + 4L \longrightarrow [Mo(CO)_3L_2]_2 + 2C_7H_8$$

Reaction with dimethyl fumarate (L') at 100° gave a polymeric complex, $[Mo(CO)_3(L')_2]_x$, which also contained carbonyl bridges [113].

It has been confirmed that the first products formed by treatment of the (η-tropylium)metal cations (6.16; M = Cr, Mo, W) with tributylphosphine were the adducts (6.17; M = Cr, Mo, W). These products decomposed with cleavage of the cycloheptatriene--metal bond [114]. The cycloheptatriene group in tricarbonyl-(η-cycloheptatriene)molybdenum was displaced by phenylurea and other arylureas in benzene at -5° to give the corresponding arylureapentacarbonylmolybdenum complexes [115].

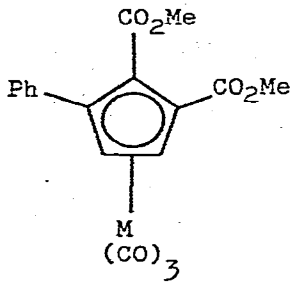


6.16

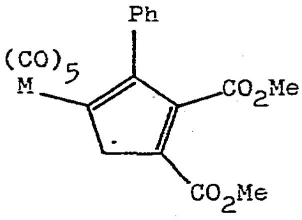
6.17

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

The η-cyclopentadienyl derivatives (7.1; M = Mn, Re) were prepared by the cycloaddition of $PhC{\equiv}CCH_2M(CO)_5$ to $MeO_2CC{\equiv}CCO_2Me$. The reaction proceeded via the σ-bonded intermediate (7.2) [116].

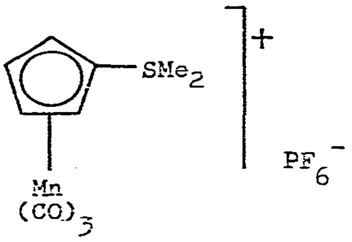


7.1

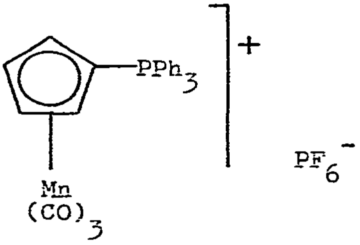


7.2

Insertion reactions of diazocyclopentadienes with manganesepentacarbonyl halides afforded chloro-, bromo-, iodo-, pentachloro-, and bromotetrachloro-cymantrene [117]. The salt $[(MeCN)_3Mn(CO)_3]^+$ PF_6^- was treated with dimethylsulphonium- and triphenylphosphonium-cyclopentadienylide in diglyme at room temperature to form the corresponding cymantrene salts (7.3 and 7.4) as crystalline solids [118].



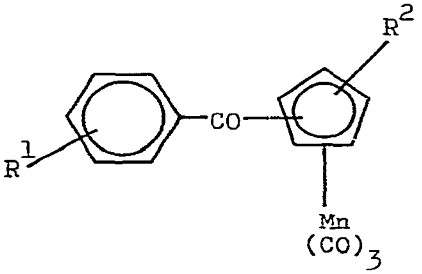
7.3



7.4

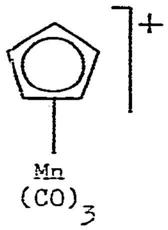
(ii) Spectroscopic and Physico-chemical Properties

The He(I) photoelectron spectra of $(\eta\text{-}C_5H_5)Mn(CO)_2CS$, $Cr(CO)_5CS$ and $W(CO)_5CS$ were recorded. The ionizations that were associated with the highest occupied σ and π levels of the thiocarbonyl ligand were separated from the other ionizations and they displayed different band envelopes. The remaining ionization bands were comparable to the bands found in the ionization spectra of the corresponding carbonyl complexes. It was concluded that the thiocarbonyl ligand was a better π-electron acceptor than the carbonyl ligand. Also, that the occupied thiocarbonyl σ and π levels interacted more strongly with the metal and the electron density increased at the carbon atom of the thiocarbonyl group [119]. Lichtenberger and Fenske have obtained the He(I) photoelectron spectra of cymantrene and related complexes and interpreted these in terms of electronic structures based on ab initio calculations for the cyclopentadienide ion and the complexes. The low energy ionization bands (binding energies 7 - 13eV) were sensitive to both ligand and metal substitution. Degenerate ionizations, associated with the metal d orbitals in $M(CO)_6$ compounds, are substantially similar in these lower symmetry $(\eta\text{-}C_5H_5)M(CO)_3$ complexes. A consistent description of the electronic structure and bonding in d^6 (η-cyclopentadienyl) metal complexes was derived and this suggested that important errors could arise when ionization potentials were interpreted exclusively on the basis of Koopmans' theorem [120]. The ESR spectra of the anions of the complexes (7.5; R^1 = H, o-, m-, p-Me; R^2 = H, α-Me, β-Me) and the corresponding tricarbonylchromium complexes were recorded. All the spectra showed splitting from the manganese nucleus and most exhibited proton splittings. Computer simulation was used to determine the hyperfine splitting constants [121].

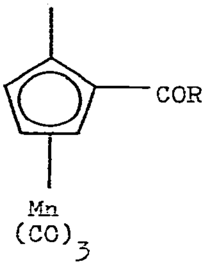


7.5

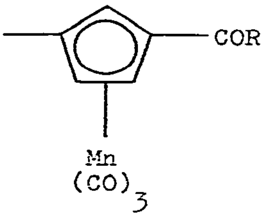
The ^{13}C NMR spectra of some α-cymantrenylcarbenium ions and the parent alcohols were recorded and compared with the spectra of ferrocenylmethyl cations. The values of the spin-spin coupling constants in the α-cymantrenyl- and α-ferrocenyl--carbenium ions did not exclude the possibility of direct Metal$\rightarrow C^+$ interaction. The possible mechanism by which metallocenyl radicals stabilized an adjacent carbenium centre was discussed [122]. Parker has recorded the IR and Raman spectra of methylcymantrene and has made new assignments for several modes on the basis of C_s symmetry [123]. The blue-red cymantrene cation (7.6) was generated by electrochemical oxidation of cymantrene at a platinum electrode in trifluoroacetic acid-tetrabutylammonium tetrafluoroborate and it was of appreciable stability in this medium [124]. Reduction of the chiral cymantrenyl ketones (7.7; R = Me, Ph, CH_2Ph, Et) with potassium borohydride was markedly stereoselective while reduction of the corresponding isomeric ketones (7.8) showed little stereoselectivity. When the same ketones were treated with the Grignard reagent then the reactions were highly stereoselective although selectivity varied with the ketone and with the reagent. The asymmetric synthesis of optically active cymantrenylcarbinols was described [125].



7.6

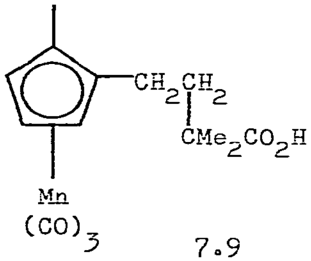


7.7

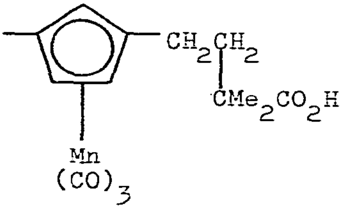


7.8

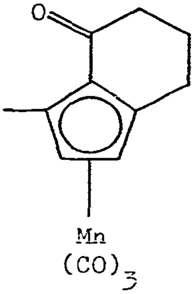
Le Plouzennec and Dabard have determined the absolute configurations of several 1,2- and 1,3-disubstituted cymantrene compounds by chemical correlation with (-)2-methylcymantrenoic acid of known absolute configuration. Thus the configurations of the 2- and 3-methylcymantrenyl propionic acids (7.9 and 7.10) together with some related cyclohexenone (7.11) and cyclohexenol (7.12) compounds were obtained. The wide range of results obtained enabled the authors to discuss the relative usefulness of the available physico-chemical methods, including circular dichroism and Horeau's method, for the investigation of the stereochemistry of cymantrene compounds [126].



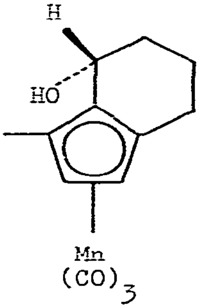
7.9



7.10



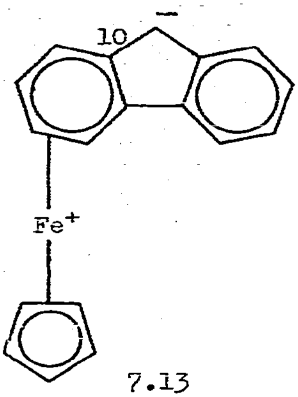
7.11



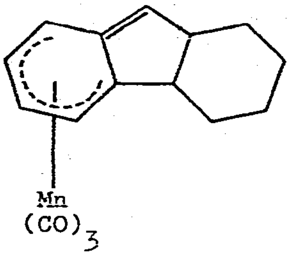
7.12

(iii) General Chemistry

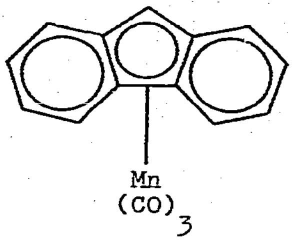
The complexes [Mn(η-fluorene)(CO)$_3$]PF$_6$ and [Fe(η-C$_5$H$_5$)-(η-fluorene)]PF$_6$ were deprotonated with t-butoxide to give the neutral compounds (7.14 and 7.13) respectively where metal coordination to one of the six membered rings was maintained. X-ray analysis of the complex (7.13) showed that the iron atom was slightly displaced from C(10). The manganese compound (7.14) rearranged thermally to the isomeric species (7.15) [127]. The cymantrenyl alcohols [7.16; R = H, Me, Et, Ph; ML$_n$ = Mn(CO)$_3$, Mn(CO)$_2$PPh$_3$ and Fe(η-C$_5$H$_5$)] and the corresponding carbenium ions (7.17) were investigated by ^{13}C NMR and infrared spectroscopy. The spectra indicated that the positive charge of the carbenium ion (7.17) was delocalised into both metallocene moieties [128].



7.13

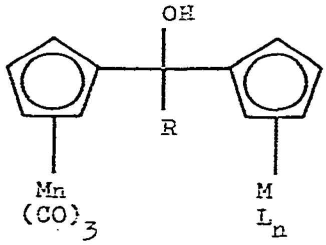


7.14

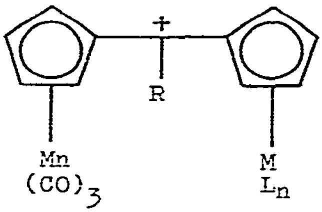


7.15

The ^1H NMR and ultraviolet spectra of the cymantrenyl alcohols (7.18; R^1 = H, Me, Ph; R^2 = Et, Ph) in sulphuric or trifluoroacetic acid confirmed the presence of the α-cymantrenylcarbenium



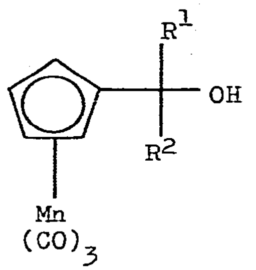
7.16



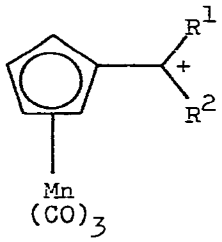
7.17

ions (7.19; R^1 = H, Me, Ph; R^2 = Et, Ph). Evidence was presented to demonstrate that these carbenium ions were stabilized in the same way as ferrocenylcarbenium ions [129].

Cymantrene, methylcymantrene and ferrocene were treated with boron triiodide, boron tribromide, phenylboron diiodide and methylboron diiodide in carbon disulphide or cyclohexane to give the corresponding metallocenylhaloboranes. Treatment of the cymantrenylborondiiodide with arsenic (III) fluoride or chloride resulted in halogen exchange and treatment with tetramethyltin,

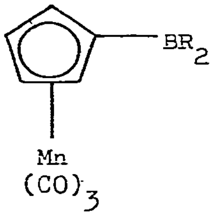


7.18

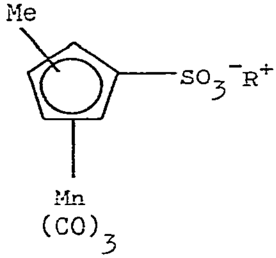


7.19

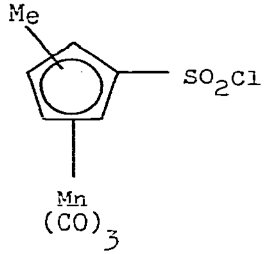
diethylether, $(MeS)_2$ and a dialkylamine (R^1_2NH) gave the metallocene derivatives (7.20; R = Me, OEt, SMe, NR^1_2) respectively [130].



7.20



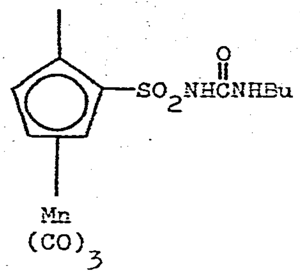
7.21



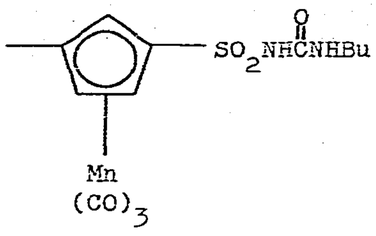
7.22

Methylcymantrene was sulphonated by reaction with sulphuric acid--acetic anhydride and with Me_3SiSO_3Cl. Treatment of the sulphonic acid salts (7.21; R = p-toluidine, p-chloroaniline) with phosphorus (V) chloride gave the acid chlorides (7.22) which were converted to the cymantrene analogues of tolbutamide (7.23 and 7.24). Both the isomers (7.23 and 7.24) were pharmacologically active [131].

The photochemical substitution of the carbonyl ligands of cymantrene, by various phosphines and phosphites, was investigated. The reactions are summarised in Schemes 7.1 and 7.2 where R^1

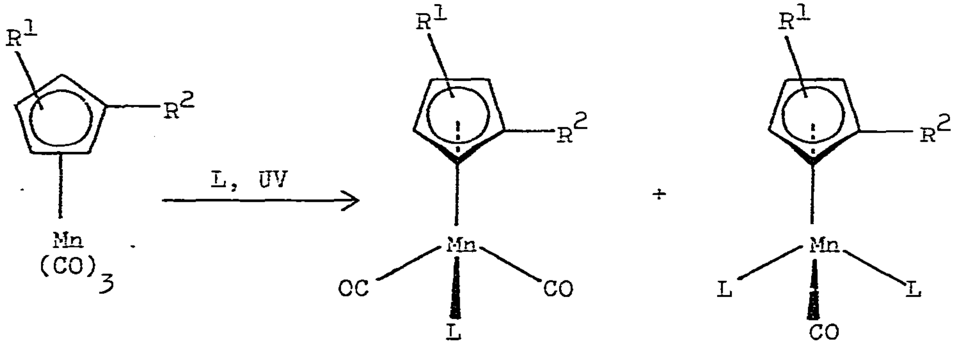


7.23

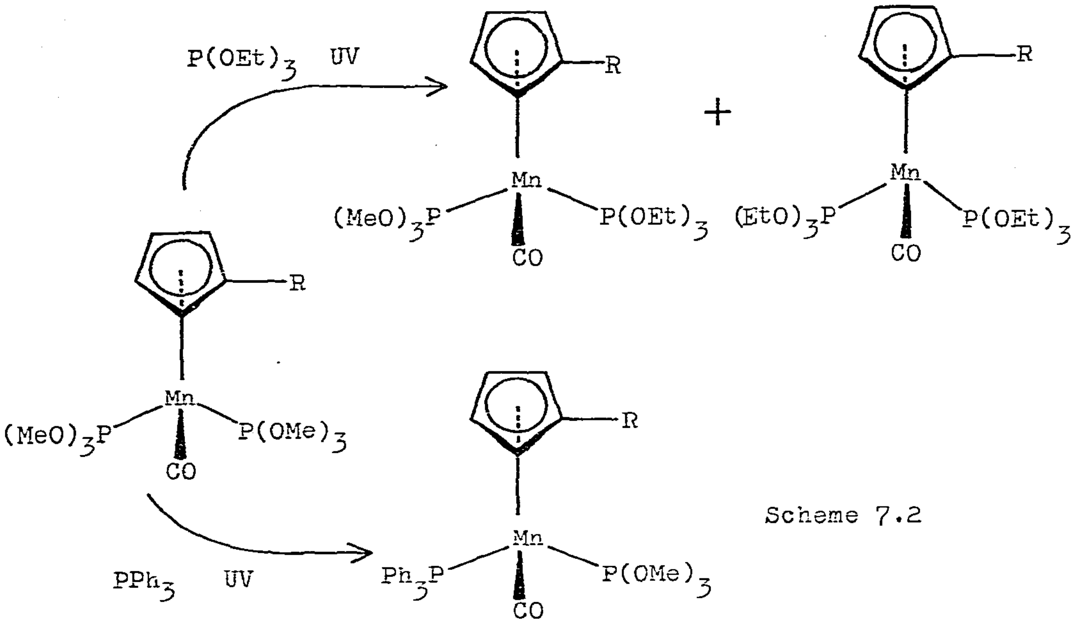


7.24

and R^2 were combinations of the following groups H, Me, COMe, CO_2Me, $CO(CH_2)_2CO_2Me$; R = CO_2Me or $CO(CH_2)_2CO_2Me$ and L = PPh_3, $P(OMe)_3$ or $P(OEt)_3$. The optical activity of these compounds was investigated [132]. The treatment of acetylcymantrene with $BrMgC{\equiv}CCR^1R^2(OMgBr)$ followed by hydrolysis gave the diols [7.25; $R^1 = R^2$ = Me, Pr; R^1 = Me, R^2 = Et; $R^1R^2 = (CH_2)_4$, $(CH_2)_5$] [133].

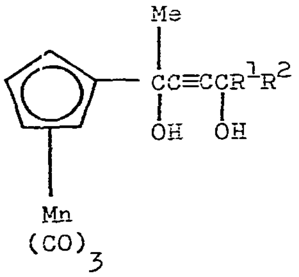


Scheme 7.1

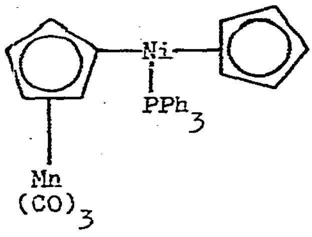


Scheme 7.2

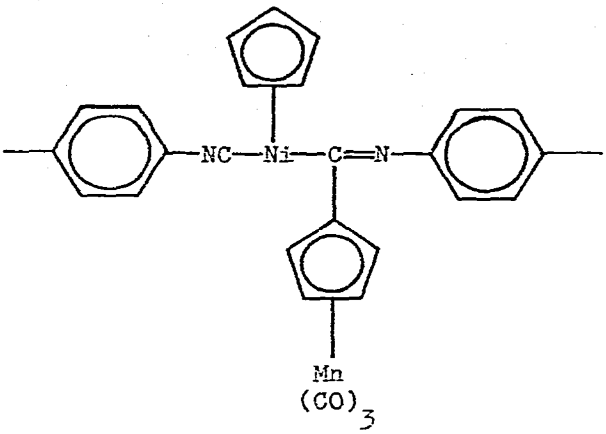
Reaction of the cymantrene derivative (7.26) with *p*-tolylisonitrile gave the nickel complex (7.27) [134]. Reactivity ratios have been determined for the copolymerization of vinylcymantrene and other vinyl monomers with vinylferrocene [135]. The reduction of tetracarbonyl(η-cyclopentadienyl)vanadium and cymantrene with sodium in hexamethylphosphoramide gave mainly $[(\eta\text{-}C_5H_5)V(CO)_3]^{2-}$ and $[Mn(CO)_4]^{3-}$ respectively [136].



7.25



7.26



7.27

(iv) Applications

The potential usefulness of methylcymantrene as a gasoline additive continues to be an active area of investigation. However, sharply conflicting results have been reported on the toxicological properties of the additive and its combustion products and the resolution of the conflict must await more definitive studies.

Moran reviewed the use of tricarbonyl(η-methylcyclopentadienyl)-manganese as an antiknock agent. The possible effects on public health of the large scale use of this compound were discussed [137]. The recommended use of methylcymantrene as a gasoline antiknock additive has been challenged by Calabrese and Sorensen on the grounds of the health hazard posed by manganese and its catalytic properties [138]. A toxicologic evaluation was carried out on tricarbonyl(η-methylcyclopentadienyl)manganese which is used as a fuel additive. Oral administration to rats produced clinical symptoms including tremors, huddling together and roughened hair coats. Histopathological examination of the rats showed pulmonary alveolar haemorrhage and edema, hepatic necrosis and renal lesions. Exposure of hamsters and rats to exhaust fumes from an engine where the manganese complex had been used as a fuel additive did not cause growth retardation or any gross abnormalities [139].

Exhaust gases from the combustion of gasoline containing methylcymantrene as an antiknock were found to contain 98.7% of the manganese in inorganic form, principally as Mn_3O_4.

This intermediate oxide was decomposed in air and sunlight. It was concluded that the low toxicity of manganese together with the low concentration of the additive required would ensure that no hazard to human health arose from its use in gasoline [140]. Methylcymantrene has been tested as an antiknock additive for gasoline. Good octane response was obtained at a level of 0.125g manganese per gallon of gasoline. There were no adverse effects on the engine and exhaust catalyst performance was satisfactory. The manganese was exhausted as Mn_3O_4 which had no harmful potential. General use of this antiknock would result in airborne concentrations of manganese of the order $0.05 \mu g/m^3$ in urban areas [141]. When tricarbonyl(η-methylcyclopentadienyl)manganese was used as the antiknock agent in petrol the useful life of the exhaust-gas catalyst in the exhaust system of the engine was improved by also adding glyceryl triacetate to the fuel [142]. A mixture of methylcymantrene and triethyl citrate has been proposed as an alternative to lead compounds for addition to gasoline as an antiknock agent and to improve the octane number [143]. Cymantrene mixed with tetrabutyltin may also be used to improve the octane number of gasoline [144].

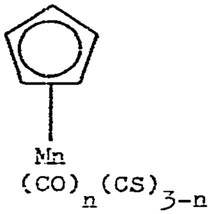
The useful life of catalytic converters in the exhaust systems of motor vehicles was extended by the addition of nitrilotriacetic acid esters to gasoline containing methylcymantrene as the antiknock [145]. Plugging of motor vehicle exhaust gas catalysts was reduced by the addition of triethylmethanetricarboxylate and mercurymethylcymantrene to the fuel [146]. The concentration of sulphur trioxide in flue gases from the combustion of coal was reduced by 66% when methylcymantrene (20g) was added to each ton of coal. Smoke formation was also reduced [147]. The potential role of methylcymantrene in gasoline as a catalyst for the oxidation of atmospheric sulphur dioxide to sulphate has been investigated. No measurable effect on the oxidation of sulphur dioxide was observed [148].

(v) Analogues

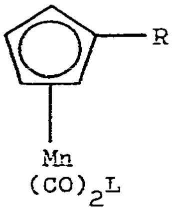
The vapour phase, solution and solid-state IR and laser Raman spectra for the thiocarbonyl complex (7.28; n = 2) have been measured and assigned in terms of the C_{5v} and C_S local symmetries of the (η-cyclopentadienyl)manganese and the dicarbonylthiocarbonylmanganese groups respectively. Solid-state spectra for the dithiocarbonylcomplex (7.28; n = 1) were recorded and interpreted in the same way [149]. The electron withdrawing power of some π-bonding ligands has been compared by ^{13}C NMR spectroscopy and found to be:

$$CSe > CS > CO$$

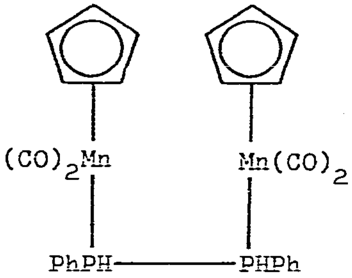
Measurements were made on the (η-cyclopentadienyl)manganese compounds (7.29; L = CO, CS, CSe; R = H, Me) and on the corresponding rhenium compounds [150]. The crystal structure of $PhP[\eta\text{-}C_5H_5(CO)_2MnFe_2(CO)_6]$ was determined by X-ray analysis. The compound contained a three-membered metallocycle formed from two iron atoms and one manganese atom. Each iron atom had three terminal carbonyl groups and the two carbonyl groups of the $\eta\text{-}C_5H_5Mn(CO)_2$ fragment formed unsymmetrical bridges with the two iron atoms. The three membered metallocycle was capped by a Ph-P group with a triply bridging phosphorus atom [151]. The crystal structure of bis[dicarbonyl(η-cyclopentadienyl)-manganese]-1,2-diphenylphosphine (7.30) was determined by X-ray analysis. The compound was shown to contain a meso-1,2-diphenylphosphine ligand [152].



7.28



7.29



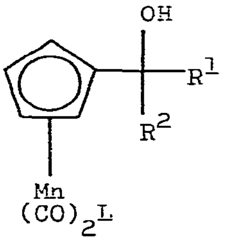
7.30

A series of cymantrenyl-alcohols [7.31; L = PPh_3, $P(i\text{-}C_3H_7)_3$; R^1 and R^2 = H, Me, Et, Ph] was prepared and on dissolution of the alcohols in $CF_3COOH\text{-}CH_2Cl_2$ the corresponding carbenium ions were formed. Spectroscopic evidence indicated that substitution of a carbonyl group by a tertiary phosphine increased the stability of the cymantrenyl-carbenium ions also, that the positive charge was delocalised extensively throughout the molecule [153].

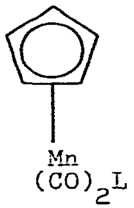
Alkylation of the metal sulphide complexes $(\eta\text{-}C_5H_5)Mn(CO)_2SR^1R^2$ where $R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Ph$; $(\eta\text{-}MeC_5H_4)Mn(CO)_2SMe_2$ and $(\eta\text{-}C_6H_6)Cr(CO)_2SMe_2$ occurred at the sulphur atom with the formation of coordinated sulphonium cations. Spectroscopic evidence indicated that even though the sulphonium ligand behaved as an electron donor it was also strongly electron withdrawing. In comparison, the sulphonium ligand was similar to PCl_3 and $PhPCl_2$ but it was not as electron withdrawing as PF_3. The sulphonium ligand was replaced easily by neutral ligands to give the corresponding monosubstituted neutral complex (equation) [154].

$$[MeC_5H_4Mn(CO)_2SMe_3]^+ + L \longrightarrow MeC_5H_4Mn(CO)_2L + SMe_3^+$$

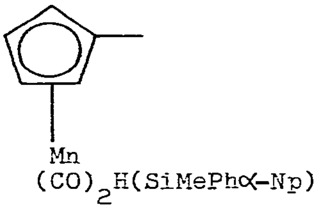
The reduction of the manganese complexes (7.32, L = PPh_2Cl, $PPhEtCl$, $PPhCl_2$) with sodium in liquid ammonia gave the corresponding sodio-phosphine complexes (7.32, L = PPh_2Na, $PPhEtNa$, $PPhNa_2$). Some reactions of these complexes and the amine complex (7.32; L = NMe_2H) were described [155].



7.31



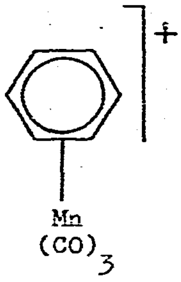
7.32



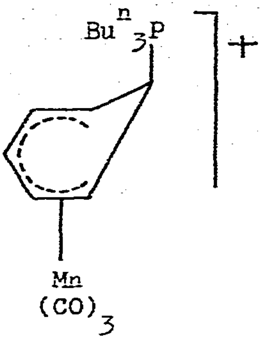
7.33

Electrophilic and nucleophilic cleavage of the manganese-silicon bond in the optically active methylcymantrene analogue (7.33) has been investigated [156].

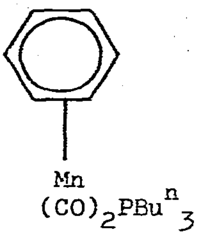
The (η-benzene)manganese tricarbonyl cation (7.34) underwent nucleophilic ring addition with tri-n-butylphosphine to give the phosphonium cation (7.35) which was rapidly converted by light in the absence of air to the (η-benzene)manganese dicarbonyl complex (7.36) [157]. Reaction of the tetrahydrofuran complexes (7.37; R = H, Me) with 1,1,1-trifluorodiazoethane gave the



7.34

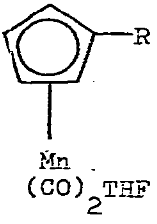


7.35

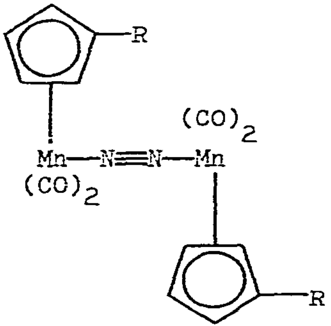


7.36

diamagnetic dinitrogen complexes (7.38; R = H, Me). The reaction was thought to proceed by nitrogen transfer from the diazoalkane to the metal with terminal attack of the diazo function on the organometallic fragment ($(\eta\text{-RC}_5H_4)Mn(CO)_2$) as the primary step [158]. The first transition metal-carbene complexes (7.39; R = Me, Ph) in which a dialkyl or an alkylarylcarbene was stabilized as a ligand to a metal atom were prepared by reaction of the cationic carbyne complexes (7.40, R = Me, Ph) with methyllithium [159].

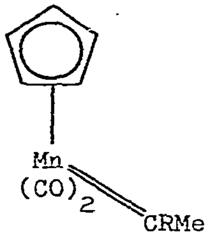


7.37

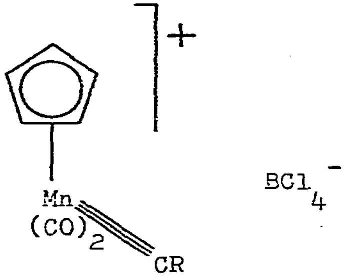


7.38

The reaction of the manganese complex (7.41) with nonacarbonyldiiron gave the stable binuclear complex (7.42). The structure of this molecule (7.42) was confirmed by X-ray analysis. The trimethylenemethane type structure was supported by the distance

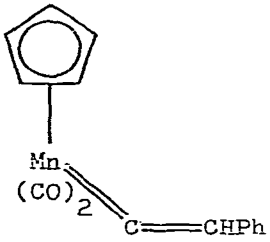


7.39

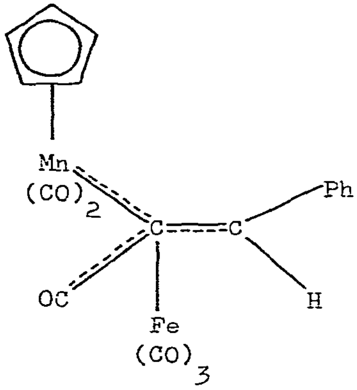


7.40

of the iron atom from the central carbon atom Fe-C 2.00 Å which was shorter than the distances to the peripheral carbon atoms. Electron delocalisation over the whole five-centred central part of the molecule was supported by the shortened metal-metal distance as compared to that found in other complexes

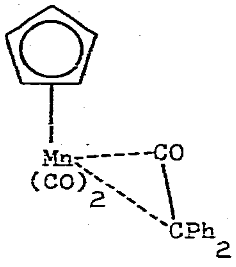


7.41

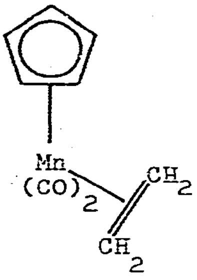


7.42

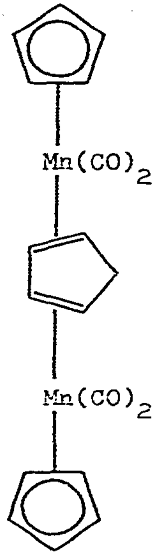
with Fe-Mn bonds [160]. The structure of the diphenylketene complex (7.43) was determined by X-ray analysis. It was found that the heterocumulene framework of the ligand was not linear and that the oxygen atom did not participate in the bonding to the manganese [161]. The effect of one, two and four methoxy groups bound to ethylene on the coordinating power of this ligand in the cymantrene analogue (7.44) has been studied by variable-temperature ^1H NMR spectroscopy. Restricted



7.43



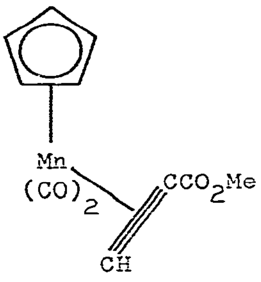
7.44



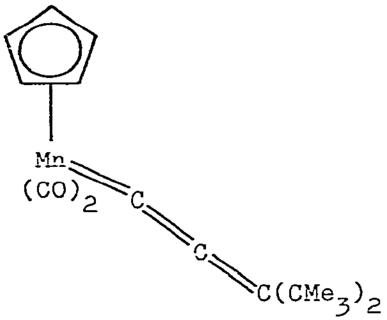
7.45

rotation of the η-ethylene group about the metal-olefin bond was observed in solution at room temperature. Charge density at the manganese atom was increased when the ligand was methylvinyl ether or 1,1-dimethoxyethylene, while a decrease in charge density was observed in the presence of tetramethoxyethylene [162]. The structure of the manganese complex (7.45) was determined by X-ray analysis. The metal atoms were arranged trans relative to the bridging ring and the carbon to carbon double bonds in the bridging ring were lengthened to 1.41 Å by the metal interaction. All three rings were planar and the Mn-$C_{C_5H_6}$ distance was 2.21 Å while the Mn-$C_{C_5H_5}$ distance was 2.14 Å [163].

Reaction of tricarbonyl(η-cyclopentadienyl)manganese with cis-cyclooctene (L) gave (η-C_5H_5)Mn(CO)$_2$L which on further reaction with triphenylphosphine and carbon disulphide gave dicarbonyl(η-cyclopentadienyl)thiocarbonylmanganese (I) [164]. Irradiation of the cymantrene complex (7.37; R = H) and phenylacetylene gave three manganese complexes. The molecular structure of the product (7.41) was established by X-ray crystallography and it contained the unusual phenylvinylidene ligand. The remaining two products were binuclear and one at least included the same phenylvinylidene group [165]. Irradiation of cymantrene followed by treatment with methyl propiolate gave the manganese complex (7.46). Treatment of the complex (7.46) with <u>tert</u>-butyllithium followed by acid gave the dialkylallenylidene complex (7.47) [166].

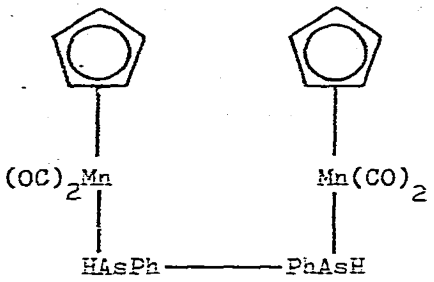


7.46

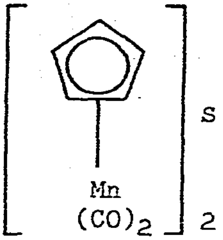


7.47

The tetrahydrofuran ligand in the dicarbonyl(η-cyclopentadienyl)manganese complex (7.37; R = H) was displaced by phenylarsine to form the binuclear arsenic compound (7.48) the structure of which was confirmed by X-ray crystallography. The epimerisation of the compound was investigated [167]. Treatment of the tetrahydrofuran complex (7.32; R = THF) with $(Et_2N)_2SO$ gave the manganese compound [7.32; L = $SO(NEt_2)_2$] which was converted to the sulphur dioxide complex (7.32; L = SO_2) with ethanolic hydrochloric acid. Reaction of the complex (7.32; L = THF) with thionyl fluoride gave the corresponding thionyl fluoride complex (7.32; L = SOF_2) whereas treatment with $(Et_2N)_2S_2$ gave the sulphide (7.49) [168]. The (η-cyclopentadienyl)manganesedicarbonylnitrosyl cation (7.50) combined with <u>p</u>-substituted triarylphosphines to give the asymmetric monosubstitution products (7.51; R = F, Cl, CF_3, Me, OMe, Ph, NMe_2) which were then converted to the neutral diastereoisomeric esters (7.52) with sodium menthoxide. These esters (7.52) were separated by fractional crystallization and resolved into the enantiomeric cations (7.51) by cleavage with HCl. The cations (7.51), which

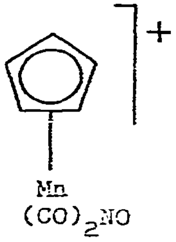


7.48

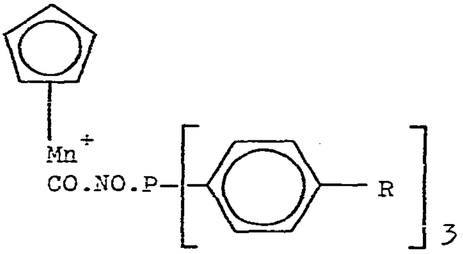


7.49

were configurationally stable, were subjected to ring- and carbonyl-addition reactions [169].

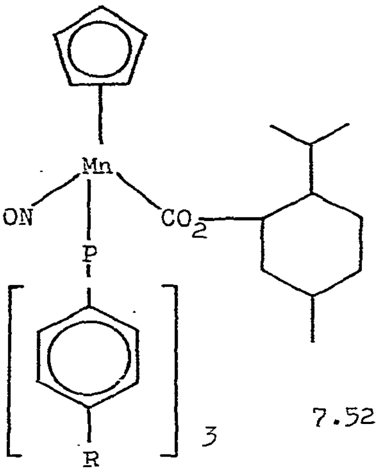


7.50

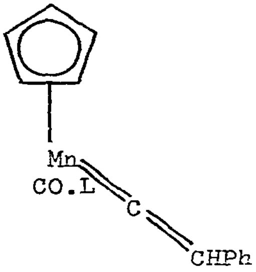


7.51

The He(I) photoelectron spectra of (η-C_5H_5)Mn(CO)$_2N_2$ and (η-C_5H_5)Mn(CO)$_2NH_3$ were measured and the Fenske method of molecular orbital calculation was used to interpret the results. The spectra resembled those of cymantrene and the major differences appeared in the ionizations associated with the metal d levels. It was concluded that N_2 was a poorer π-acceptor and poorer σ-donor than CO [170]. Reaction of dicarbonyl-η-cyclopentadienyl-(phenylvinylidene)manganese with a phosphorus ligand L = PPh_3, $P(OPh)_3$ gave the complexes [7.53; L = PPh_3, $P(OPh)_3$] [171]. Reaction of the (η-cyclopentadienyl)manganese complex (7.54;

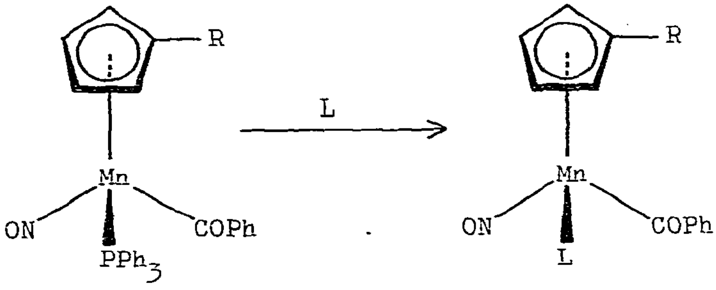


7.52



7.53

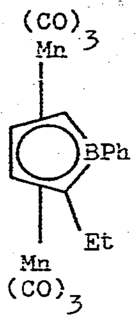
R = H, Me) with a ligand L = $P(4\text{-}C_6H_4OMe)_3$, $P(n\text{-}Bu)_3$, $P(OEt)_3$, CNC_6H_{11}, CO gave the corresponding manganese complexes (7.55). The exchange of PPh_3 by a ligand L was shown to occur with retention of configuration at the manganese atom [172].



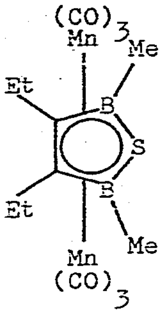
7.54

7.55

Herberich and co-workers reported that the triple-decker complex (7.56) was formed as the main product in the reaction of 1-phenyl-4,5-dihydroborepin with $Mn_2(CO)_{10}$ in boiling mesitylene. The structure of the complex (7.56) was confirmed by X-ray analysis [173]. Siebert and Kinberger reported a similar triple decker complex (7.57) which was prepared by the reaction of 1,2,5-thiadiborolene with manganese carbonyl [174]. The (η-cyclohexadienyl)manganese tricarbonyl complex (7.58) underwent hydrogen migration on heating, the 6-endo hydrogen

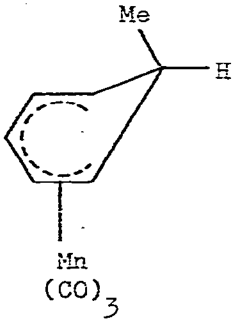


7.56

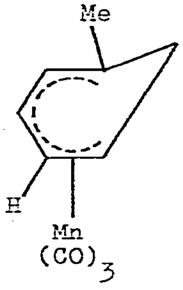


7.57

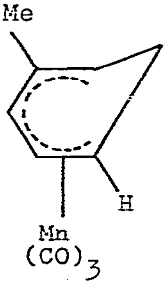
migrated to give equal proportions of the isomers (7.59 and 7.60). In arene solvents, the η-cyclohexadienyl ligand was replaced partly by the solvent. A metal hydride complex was proposed as the intermediate in these rearrangements [175].



7.58

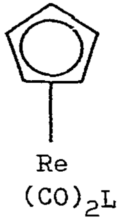


7.59

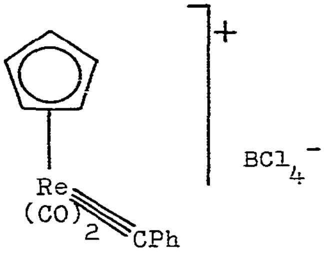


7.60

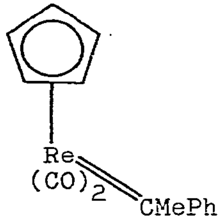
Irradiation of η-cyclopentadienyltricarbonylrhenium with tetrahydrofuran gave the complex (7.61; L = THF). The η-cyclopentadienylrhenium complexes [7.61; L = PPh_3, $P(OEt)_3$, $P(OPh)_3$, PhC≡CPh, $AsPh_3$, pyridine, urotropine] were prepared by treatment of the tetrahydrofuran complex (7.61; L = THF) with the appropriate ligand. An infrared study of the complexes in CF_3CO_2H showed that the basicity of the Re atom increased with increasing electron donor properties of the ligands [176]. Low temperature reaction of the cationic carbyne complex (7.62) with



7.61

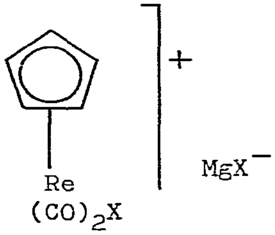


7.62

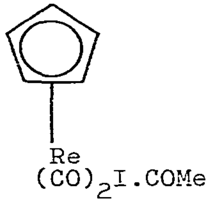


7.63

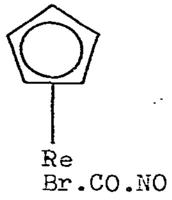
methyllithium gave the aryl, alkyl carbene complex (7.63) [177]. Treatment of the rhenium carbonyl (7.64; X = I) with acetyl chloride gave the complex (7.65). Reaction of the corresponding bromo derivative (7.64; X = Br) with nitrosyl chloride gave the rhenium derivative (7.66) [178].



7.64



7.65

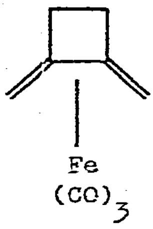


7.66

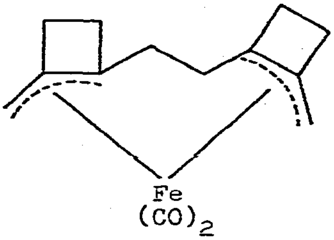
8. (Acyclic-η-dienyl)Fe(CO)$_3$ and (η-trimethylenemethane)Fe(CO)$_3$ Complexes

(i) Formation

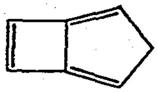
King and Harmon have examined the reactions of dimethylene-cyclobutanes and -cyclobutenes with iron carbonyls. 1,2-Dimethylenecyclobutane combined with triiron dodecacarbonyl in boiling benzene to give both the simple (η-1,3-diene)iron compound (8.1)



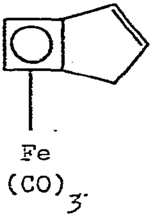
8.1



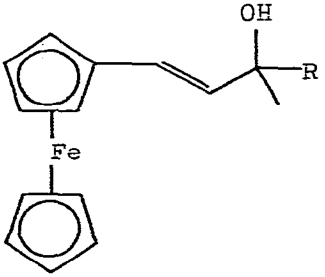
8.2



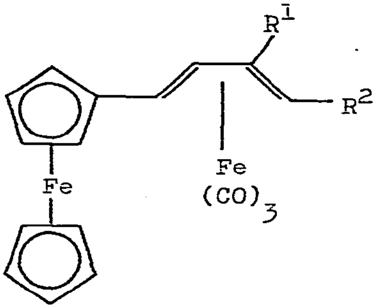
8.3



8.4

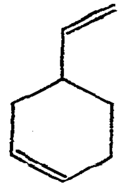


8.5

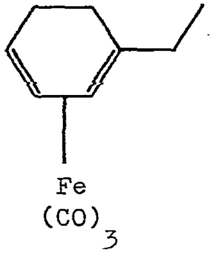


8.6

and the iron complex (8.2) containing a symmetrical bis(η-allyl) ligand. 1,3-Dimethylenecyclobutane was inert under the same conditions. The bicycloheptatriene (8.3) was treated with the same carbonyl to give the iron tricarbonyl complex (8.4) containing a novel bicyclic cyclobutadiene ligand which had been formed by hydrogen migration [179]. Ferrocenyl-α- or β-unsaturated alcohols have been treated with polynuclear iron carbonyls in the presence of copper (II) sulphate to give (η-diene)iron tricarbonyl complexes. Thus the alcohols (8.5; R = H, CH_2CN) were converted to the complexes (8.6; R^1 = H, Me; R^2 = H, CN). Cyclic and acyclic non-conjugated dienes were converted to iron carbonyl complexes of conjugated dienes by direct treatment with iron carbonyls. The cyclohexadiene complex (8.8) was obtained from vinyl-4-cyclohexene (8.7) and diiron nonacarbonyl in this way [180]. An equimolar mixture of 1,3-butadiene and 1,3-butadiene-1,1,4,4-d_4 and pentacarbonyliron was irradiated. The results indicated that deuterium substitution did not exert any significant influence on the rate of formation of (η-butadiene)-



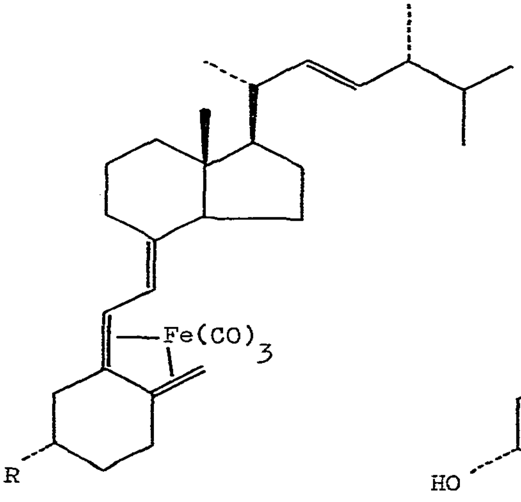
8.7



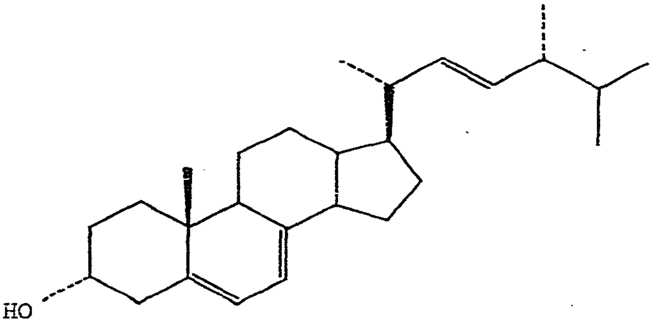
8.8

tricarbonyliron [181].

Reaction of nonacarbonyldiiron with caliciferol in toluene gave a 2 : 1 mixture of the α- and β-tricarbonyliron complexes (8.9; R = H). Oxidation of the mixture affected only the α-complex to give the ketone (8.9; R = O). The tricarbonyl-

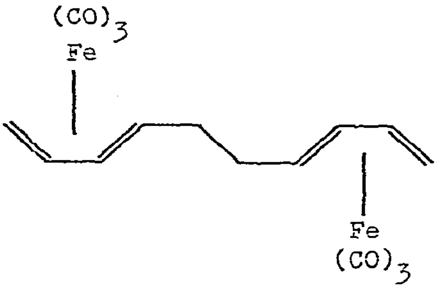


8.9

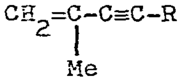


8.10

iron complex of ergosterol was formed and oxidised to give the 3-ketone which was then reduced by lithium hydridotri-t-butoxyaluminate to afford the new epiergosterol (8.10) in good yield [182]. Penta-1,4-dien-3-ol combined with iron pentacarbonyl to give a mixture of two diastereoisomers of di(pentadienyliron tricarbonyl) (8.11) [183]. The hex-1-ene-3-yne ligands (8.12; R = Et, Bu^t) combined with diiron nonacarbonyl to give the binuclear complexes (8.13; R = Et, Bu^t) in which a carbonyl group was bound to the ligand. The CH_2CMeC- fragment behaved as an η-allyl donor towards one iron atom whilst the -CR=C-CO group was intermediate in character between a η-allyl and an η-olefin -σ-donor [184]. Iron atoms produced by laser evaporation of iron were cocondensed with butadiene and styrene at -196°C and then treated with carbon monoxide to give the corresponding tricarbonyliron complexes [185].

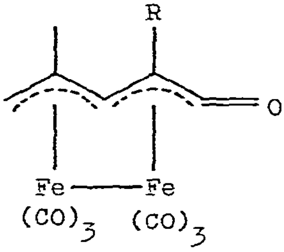


8.11



$CH_2{=}\underset{\displaystyle Me}{C}{-}C{\equiv}C{-}R$

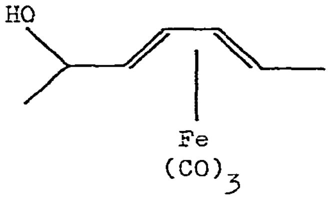
8.12



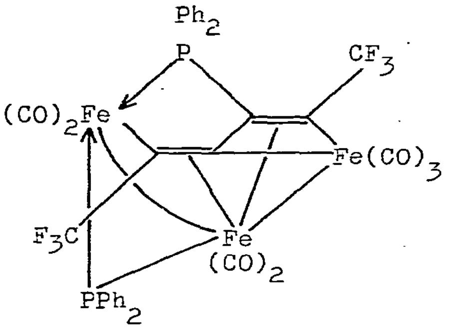
8.13

(ii) Spectroscopic and Physico-chemical Properties

The crystal and molecular structure of the (η-diene)iron complex (8.14) has been determined by X-ray crystallography with confirmation of the trans, trans geometry of the ligand [186]. Several trinuclear complexes have been obtained from triiron dodecacarbonyl and 1-diphenylphosphino-2-trifluoromethylacetylene including the ferracyclobutene (8.15) which was characterized by X-ray crystallography [187]. INDO molecular orbital calculations were carried out on (η-butadiene)tricarbonyliron, nickel tetracarbonyl and chromium hexacarbonyl. The Koopmans-theorem values of ionization potentials were found to be in good agreement with



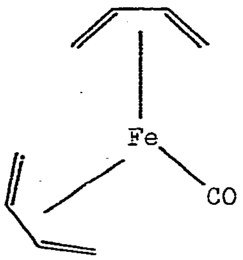
8.14



8.15

the observed photoelectron spectroscopic data except when the orbital relaxation upon ionization was substantial [188]. Debye-Waller factors of monolayer films of (η-butadiene)tricarbonyliron on exfoliated graphite sheets were measured by Moessbauer spectroscopy. The results indicated a melting transition, that was a change of fluidity in the plane of the film [189].

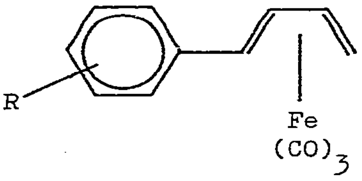
The polarographic reduction of tricarbonyl(η-diene)iron complexes proceeded through two one-electron steps with the formation of an anion-radical in the first step [190]. The electric dipole moments of several (η-diene)iron complexes have been measured and interpreted. (η-Cyclobutadiene)iron tricarbonyl, (η-cyclooctatetraene)iron tricarbonyl and (η-methyl 1,3--pentadienoate)iron tricarbonyl were included together with bis(η-diene)iron carbonyl compounds and methyltricobalt nonacarbonyl derivatives. The iron-carbonyl group moment in bis(η-1,3--butadiene)iron carbonyl (8.16) was determined as ~2D (from iron to carbonyl) [191]. The enthalpies of thermal decomposition for (η-butadiene)tricarbonyliron and some related complexes were determined with a Calvet high temperature calorimeter [192]. Microcalorimetry has been used to investigate the thermal decomposition of (η-diene)iron complexes. (η-Butadiene)tricarbonyliron decomposed at temperatures above 500 K to give a diffuse metallic mirror of iron, butadiene as the dimer, and polymers.



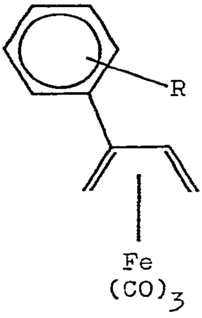
8.16

The diene-iron bond enthalpy was ΔH^{298} = 48.0 kcal mol^{-1}. Bis(η-butadiene)carbonyliron decomposed above the melting point ca. 400 K to give a black powder of metallic iron and the dimer and trimer of butadiene, $\Delta H^{298} \sim 44$ kcal mol^{-1}. Tetracarbonyl (η-ethylene)iron decomposed cleanly to give a bright metallic mirror of iron with ΔH^{298} = 23.1 kcal mol^{-1} for the olefin-iron bond enthalpy [193].

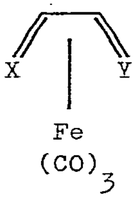
Contact shift reagents have been used to reexamine the NMR spectra of diastereoisomeric tricarbonyl(η-trans-3,5-hexadienyl--2-ol)iron complexes and related hexadienol complexes. The previous assignments of relative configurations were confirmed [194]. The effect of (η-butadiene)tricarbonyliron substituents on the polarographic oxidation potentials of the ferrocene nucleus and the ^{19}F NMR chemical shifts in meta and para substituted fluorobenzene has been investigated. The ferrocenyl oxidation potential changed by 0.09V when it was transferred from position 1 to position 2 of the butadienyl system which indicated that there was an essential charge separation in the dienic system. It was concluded that coordination of the butadiene with the $Fe(CO)_3$ group caused charge transfer from the ligand to the metal similar to that found in other metal carbonyl π-complexes. Also, it was concluded that all the carbon atoms in coordinated butadiene were sp^2 hybridized [195]. ^{19}F NMR data for the fluorine complexes (8.17 and 8.18; R = m-F, p-F) indicated that the π-electron density was not evenly distributed throughout the butadienyl ligand whereas the σ-electron density was evenly distributed [196]. The intramolecular exchange of carbonyl



8.17



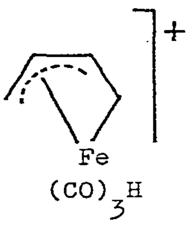
8.18



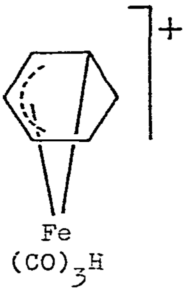
8.19

groups in (η-diene)iron tricarbonyl compounds (8.19) with hetero-atoms in either the 1- or 4-positions or in both positions has been investigated by variable temperature ^{13}C NMR spectroscopy. High activation energies (10-14 kcal mol^{-1}) were observed for the diene compounds with polar bonds (8.19; X = O, N-R, Y = CH-R) and simple diene compounds (8.19; X = Y = CH-R). By contrast, the diazadienecompounds (8.19; X = Y = N-R) showed low activation energies (<9 kcal mol^{-1}). These observations were in agreement with the local C_{3v} symmetry of the iron tricarbonyl group in these compounds [197].

The species generated by protonation of (η-butadiene)tricarbonyl-iron and tricarbonyl(η-cyclohexadiene)iron instrongly acidic media

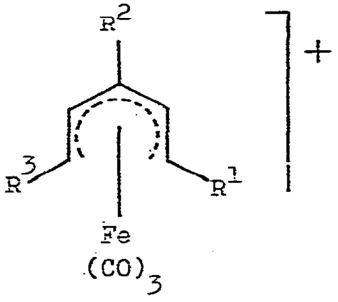


8.20

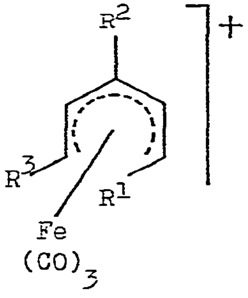


8.21

were studied by ^{13}C NMR and infrared spectroscopy. The data supported structures (8.20 and 8.21) in which iron was σ-bonded to a terminal carbon atom and π-bonded to the remaining allyl moiety [198]. Variable temperature ^{13}C NMR spectroscopy was used to study the fluxional behaviour of a series of tricarbonyl-(η-diene)-iron and -ruthenium complexes. A large increase in fluxionality was noted when a conjugated 1,3-diene was replaced by either a nonconjugated 1,4- or 1,5-diene. This increased activation barrier for carbonyl scrambling in tricarbonyl(η-1,3-diene)iron complexes was attributed to the mixing of six coordinate character into the formally five coordinate molecules. Possible mechanisms for the intramolecular rearrangements were discussed [199]. ^{13}C NMR spectra were recorded for a series of tricarbonyl(η-dienyl)iron cations (8.22; R^1 = Me, $R^2 = R^3$ = H; $R^1 = R^3$ = Me, R^2 = H; $R^1 = R^2 = R^3$ = Me and 8.23; $R^1 = R^3$ = Me, R^2 = H; $R^1 = R^2 = R^3$ = Me). The $^1J_{C-H}$ values for the dienyl carbons fell within the range 165±6 Hz which was consistent with sp^2 hybridization. It was concluded that atomic charge was an important factor in determining the ^{13}C chemical shifts in tricarbonyl(η-dienyl)iron cations [200].



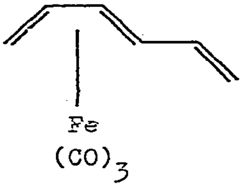
8.22



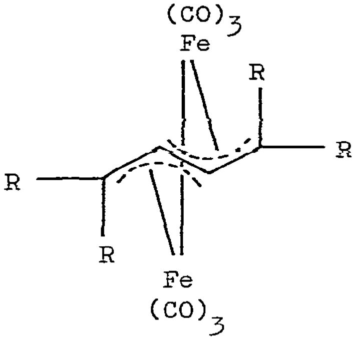
8.23

(iii) General Chemistry

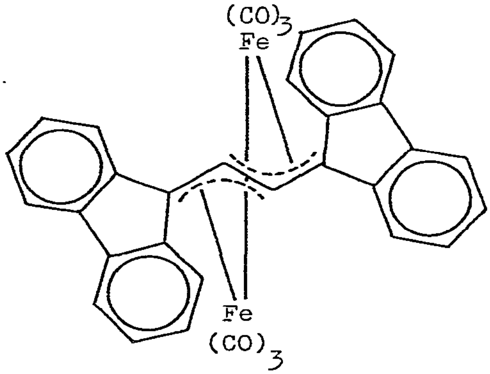
Slow heating under reduced pressure of the trimethyl- and triethyl-amine adducts of tricarbonyl(hexa-1,3-dienium)iron hexafluorophosphate gave the η-triene complex (8.24) [201]. Reaction of the η-butatriene complexes (8.25; R = H, Ph) and (8.26) with triphenyl-phosphine and -phosphite resulted in displacement of the carbonyl ligand <u>trans</u> to the iron-iron bond and the kinetics of these reactions were investigated. The crystal and molecular structure of one of the products (8.27) was determined by X-ray analysis. Each iron atom was in an



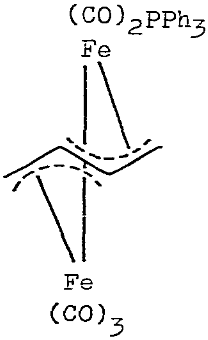
8.24



8.25

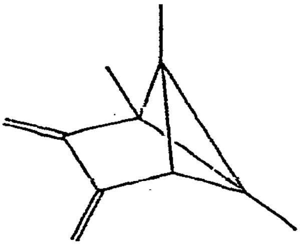


8.26

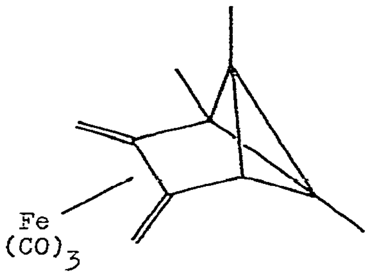


8.27

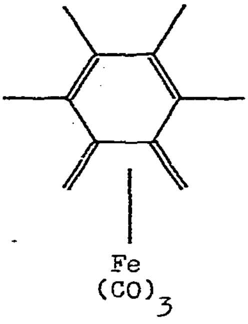
octahedral environment with an iron-iron bond of 0.263 nm. The bridging butatriene had a planar carbon skeleton but it was twisted end for end by 90^0 which suggested an η-allyl bond to each iron atom [202]. Irradiation of the diene (8.28) in the presence of pentacarbonyliron gave the tricarbonyliron complex (8.29). Treatment of this complex with a catalytic amount of silver (I) perchlorate gave a mixture containing the tricarbonyliron complexes (8.30 and 8.31) together with some hexamethylbenzene. The energy of activation for rotation of the tricarbonyliron group in the complex (8.29) was determined by ^{13}C NMR spectroscopy and was found to be 12.8 kcal mol^{-1}. This energy of activation was about 3 kcal mol^{-1} higher than that for (η-butadiene)tricarbonyliron and this was attributed to increased steric hindrance to rotation [203].



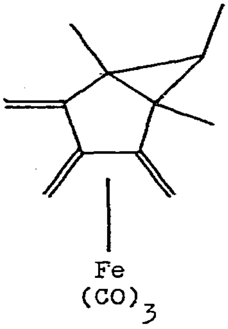
8.28



8.29

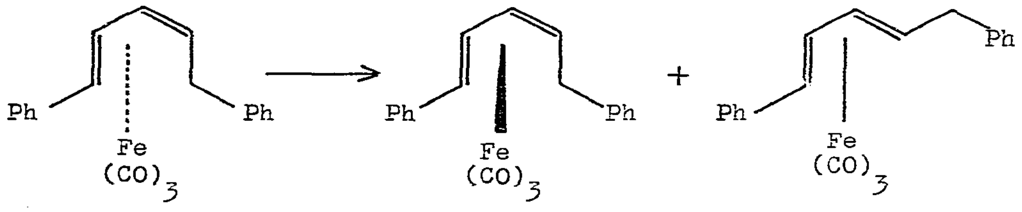


8.30



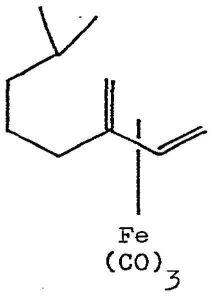
8.31

Whitesides and Neilan have investigated the thermolysis of several acyclic and cyclic (η-diene)iron tricarbonyl complexes.

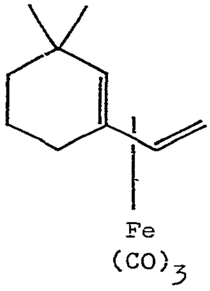


8.32 8.33 8.34

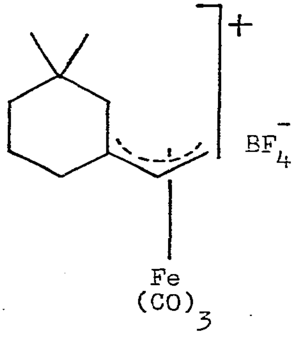
Thus the (η-1,5-diphenylpentadiene)iron complex (8.32) on heating in benzene underwent metal epimerization to form the complex (8.33) and isomerization to the trans-isomer (8.34). Kinetic and deuterium labelling evidence was used to indicate a mechanism involving a coordinately unsaturated dihapto iron tricarbonyl intermediate [204]. A general method for the preparation of cyclic hydrocarbons via intramolecular coupling of bis(η-pentadienyl)iron tricarbonyl cations has been described (Scheme 8.1). Five-, six- and ten-membered cycloalkane derivatives were prepared [205]. Tricarbonyl(η-myrcene)iron (8.35) was pro-



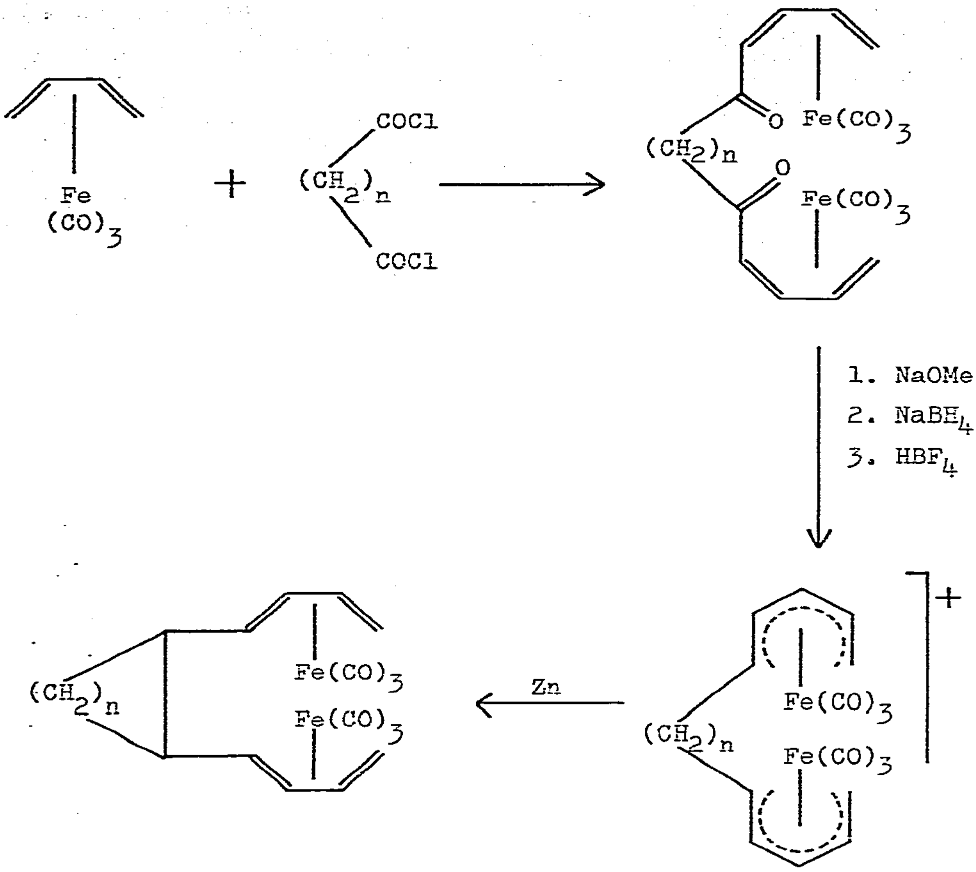
8.35



8.36



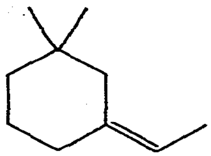
8.37

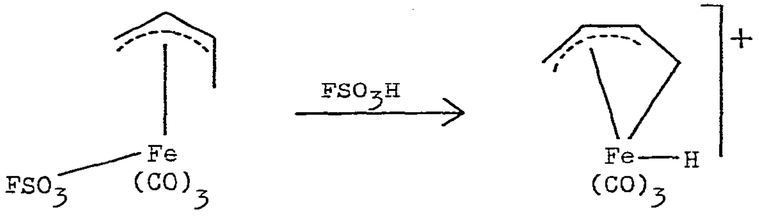


Scheme 8.1

tonated with tetrafluoroboric acid in dichloromethane and the intermediate carbenium ion cyclized to give the (η-vinylcyclohexene)iron complex (8.36). With an excess of tetrafluoroboric acid this product formed the (η-allyl) complex (8.37) which was, in turn, reduced with sodium borohydride to the ethylidenecyclohexane (8.38) [206]. Olah and co-workers used ^{13}C NMR spectroscopy to study the protonation of (η-butadiene)tricarbonyliron by fluorosulphonic acid in sulphur dioxide. In the presence of one equivalent of acid the η-allyl complex (8.39) was formed which ionized in the presence of excess FSO_3H to give the monoprotonated complex (8.40) [207].

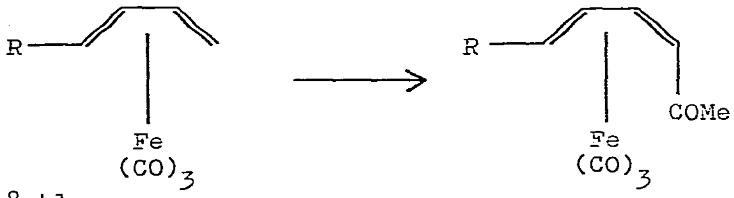
Acylation of the (η-diene)iron tricarbonyl complexes (8.41; R = H, Me, p-BrC_6H_4, p-$MeCOC_6H_4$ and 8.42; R^1 = Me, R^2 = H;





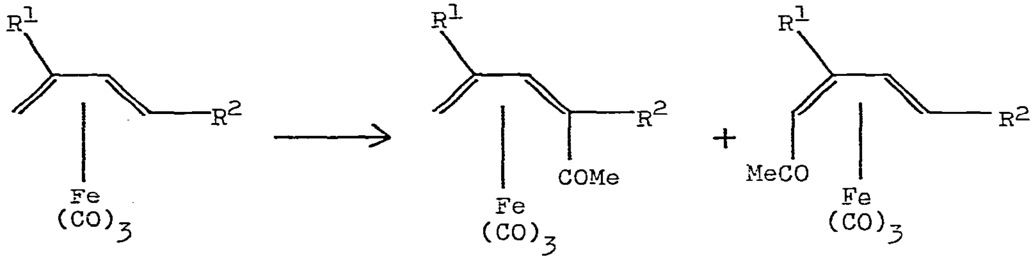
8.38 8.39 8.40

R^1 = MeO, R^2 = H; R^1 = Me, R^2 = Me) with acetyl chloride and aluminium chloride gave dienone complexes in good yields (Schemes 8.2 and 8.3). Substitution only occurred at the unsubstituted



8.41

Scheme 8.2



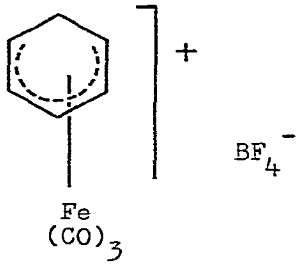
8.42

Scheme 8.3

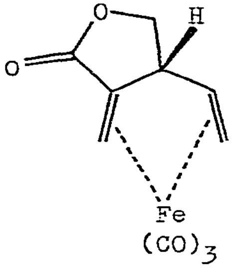
terminal carbon atoms of the η-diene ligand and if the reaction mixtures were quenched in cold aqueous ammonia only the <u>cis</u>-dienone complexes were isolated. The <u>cis</u>-complexes were isomerized to the <u>trans</u>-dienone complexes in methanolic sodium methoxide. Formylation of (η-diene)iron tricarbonyl complexes was effected with dichloromethylmethylether-aluminium chloride to give <u>trans</u>-η-dienal complexes [208]. Arhart has examined the behaviour of tricarbonyl(η-diene)iron complexes in trifluoroacetic acid. Complete conversion to a tricarbonyl(η-allyl)iron complex occurred and this intermediate decayed to a tetracarbonyl(η-allyl)iron complex with $t_{\frac{1}{2}} \sim 20$ min at 35°. When tetrafluoroboric acid and carbon monoxide were also present high yields of the tetracarbonyl (η-allyl)iron tetrafluoroborate salts were isolated. These salts were formed with retention of the stereochemistry of the diene ligand. Protonation of tricarbonyl(η-cyclohexadiene)iron in trifluoroacetic acid was reversible and stereospecific (<u>endo</u>) [209].

The kinetics of reaction of the η-cyclohexadienylium complex (8.43) with pyrrole, indole, methylindoles, furan, di- and trimethoxybenzene and thiophene was investigated. It was concluded that rate determining addition of the complex (8.43) to the heterocycles occurred, followed by rapid proton loss [210]. Reaction of <u>trans</u>- or <u>cis</u>-bis(hydroxymethyl)methylenecyclopropane with diiron nonacarbonyl gave the complexes (8.44 and 8.45). The structures of these complexes were established by X-ray analysis and a possible mechanism for their formation was presented [211]. The tetracarbonyliron complex (8.45) rearranged regiospecifically at 35° via a 1,3-hydrogen shift to give the tricarbonyliron complex (8.46). The complex (8.44) also rearranged regiospecifically under similar conditions to give a mixture of the isomeric complexes (8.47 and 8.48) [212]. Tricarbonyl(η-myrcene)iron (8.49) was treated with an acetyl chloride-aluminium chloride Perrier complex at 0° to give three tricarbonyliron compounds (8.50, 8.51 and 8.52). Similarly, treatment of the complex (8.49) with oxalyl chloride-aluminium chloride gave the cyclohexene complexes (8.53 and 8.54) after treatment of the reaction mixture with ethanolic silver nitrate [213].

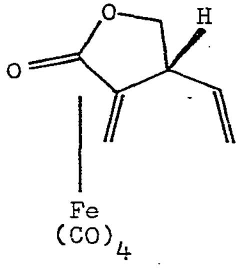
The mechanism of partial substitution of the (η-heterodiene)iron complex (8.55; R = H, Me, Ph) with triphenylantimony to form the (η-olefin)iron complex (8.56; R = H, Me, Ph) has been



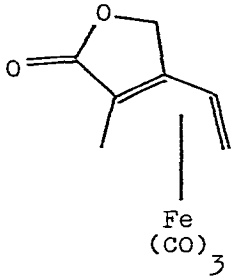
8.43



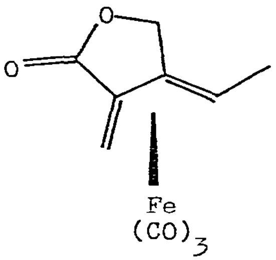
8.44



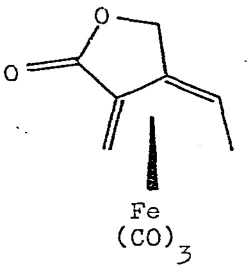
8.45



8.46



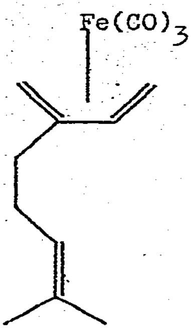
8.47



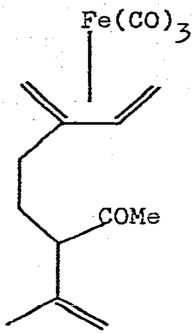
8.48

investigated. The reaction was first order in the complex (8.55) and in triphenylantimony. Equilibrium constants for the reaction were determined and it was confirmed that the products (8.56) were more stable than initial diene complexes (8.55) [214]. The solvolysis of exo- (8.57; $R^1 = H$, $R^2 = Me$) and endo-dienol ester iron complexes (8.57; $R^1 = Me$, $R^2 = H$) normally proceeds stereospecifically to give dienol iron complexes with the same configuration (8.58; $R^1 = H$, $R^2 = Me$; $R^1 = Me$, $R^2 = H$) through intermediate trans-diene cations. However the endo-dienol ester (8.59) was solvolyzed slowly to give both the exo- and endo-dienols (8.60; $R^1 = H$, $R^2 = Me$; $R^1 = Me$, $R^2 = H$) respectively. Evidence was presented for non-stereospecific ionization of the ester (8.59) as the most probable mechanism for stereochemical leakage [215].

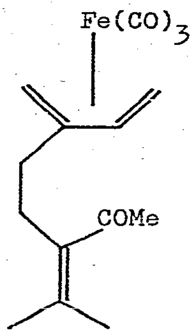
Treatment of the diene-irontricarbonyl complex (8.61) with a ligand L, L = PMe_2Ph, $P(OMe)_3$ gave the irondicarbonyl



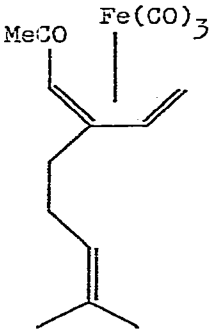
8.49



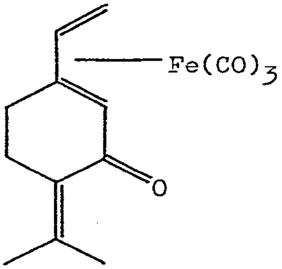
8.50



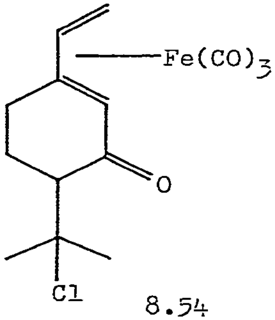
8.51



8.52

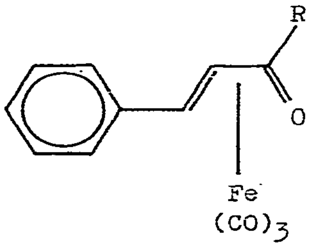


8.53

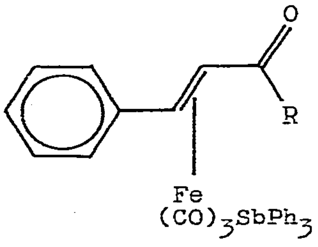


8.54

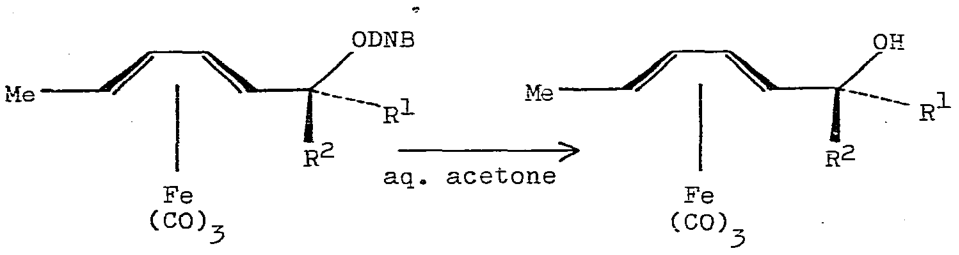
complexes (8.62) [216]. Rubbery (η-polybutadiene)irontricarbonyl complexes were prepared from polybutadiene and triiron dodeca-



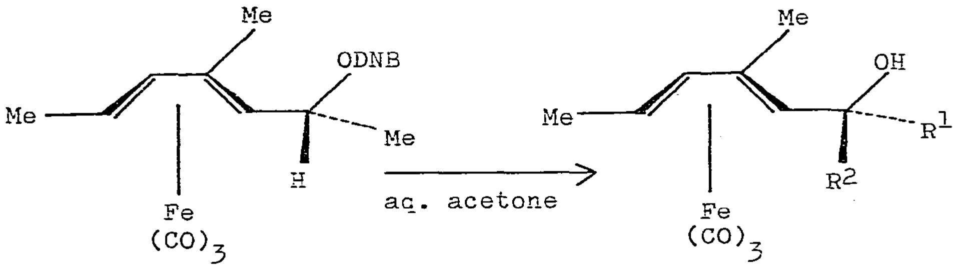
8.55



8.56



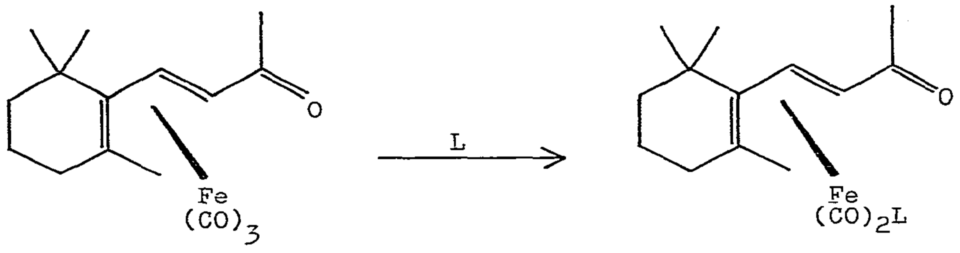
8.57 8.58



8.59 8.60

DBN = 3,5-dinitrobenzoyl

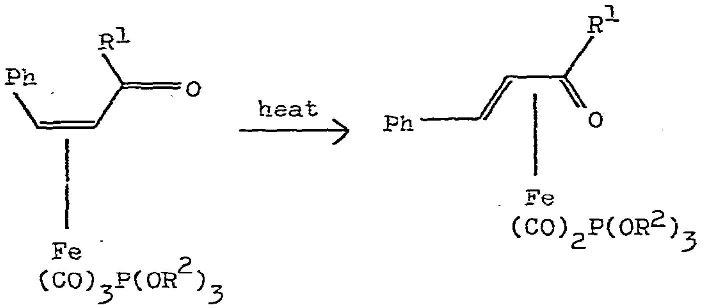
carbonyl. The irontricarbonyl complexes were used as high burning rate additives or plasticizers for carboxylated polybutadiene propellant binders [217].



8.61 8.62

Diene iron complexes such as tricarbonyl(η-hexadiene)iron, tricarbonyl(η-2,3-dimethylbutadiene)iron and tricarbonyl(3-methylpentadiene)iron were analyzed by decomposition over heated iron (III) chloride and gas chromatography of the volatile products [218]. This procedure was also the subject of a patent [219].

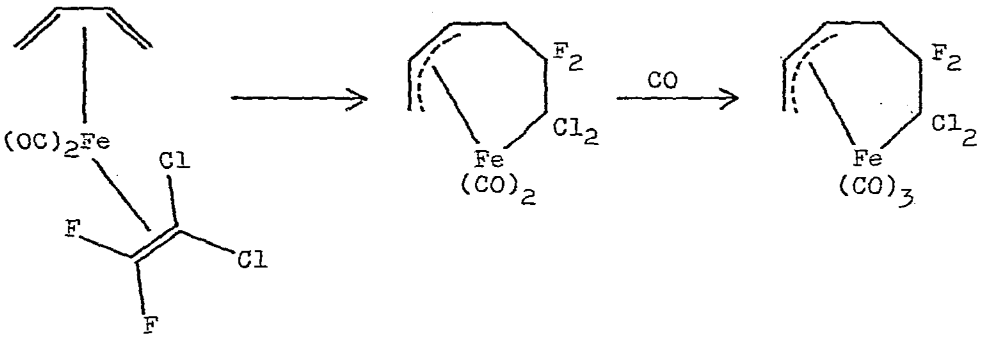
The (η-diene)iron complexes (8.64; R^1 = H, Me, Ph; R^2 = Me, Ph) were prepared by thermolysis of the corresponding (η-α-enone)iron tricarbonyl phosphites (8.63). The (η-diene) complexes (8.64) underwent enone exchange in boiling benzene [220]. Kerber and Von Gustorf have reexamined the mechanism of photoinsertion of fluoroalkenes into tricarbonyl(η-diene)iron complexes. The reaction was shown to be regiospecific with respect to both diene and fluoroalkene. After preliminary photodissociation of a carbonyl group from iron, the haloalkene formed a η-complex (8.65) which underwent η-σ rearrangement to form the η-allyl complex (8.66). Carbon monoxide reattachment gave the product (8.67) [221].



8.63

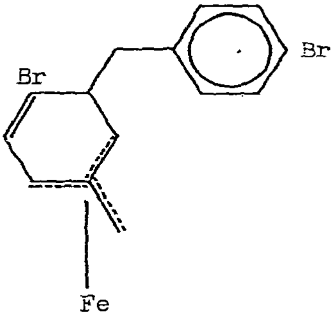
8.64

CNDO calculations on the nature of the metal-ligand bonding in tricarbonyl(η-trimethylenemethane)iron suggested that the principal bonding interactions were between the iron atom and the three methylene groups. The central carbon atom was bonded quite weakly to iron although the interatomic distance was short [222]. The crystal and molecular structure of the trimethylenemethane compound (8.68) has been determined by X-ray crystallography. The iron atom was bound to the trimethylenemethane group of the ligand [223]. The complete vibrational spectra of tricarbonyl(η-trimethylenemethane)iron

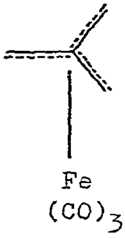


8.65 8.66 8.67

and its perdeutero derivative were presented and vibrational assignments were made for most of the active modes. A force field was deduced which reproduced the observed frequencies



8.68



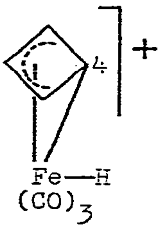
8.69

and provided descriptions of the normal modes. From the results it was concluded that (a) all the C-H stretches were above 3000 cm^{-1} which indicated that the methylene carbons were unsaturated; (b) the C-C average stretching frequency, force constant and bond distance all indicated that these bonds were unsaturated; and (c) the iron-ligand stretching and tilting force constants were relatively large and indicated a strong metal-ligand bond. It was thought that a model of the molecule with bonds between iron and the three C-C orbitals was better than one with a bond along the iron-central carbon line [224].

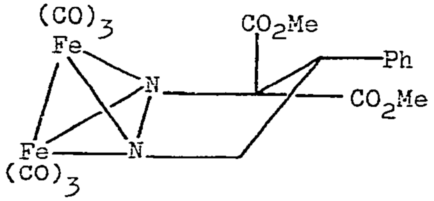
The helium (I), helium (II) and X-ray photoelectron spectra of tricarbonyl(η-trimethylenemethane)iron (8.69) have been obtained. These results have been used in conjunction with all-electron ab initio SCF MO calculations to discuss the electronic structure of the complex. Negative charge was localized on the terminal methylene groups of the ligand and arose by donation of π-electron density from iron to the half filled ligand 5e molecular orbitals. Koopmans theorem was unsuccessful in predicting the positions of the low-energy bands arising from the metal obitals [225]. ^{13}C NMR spectra were measured for several tricarbonyl (η-trimethylenemethane)-iron complexes and three separate metal carbonyl resonances were observed at room temperature. As the temperature was raised the three resonances coalesced to give a single peak. The results indicated a relatively high barrier to rotation [226].

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

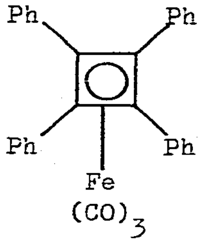
Natural abundance ^{13}C-^{57}Fe and ^{13}C-^{13}C satellite spectra obtained from ^{13}C Fourier transform NMR spectroscopy were reported for tricarbonyl(η-cyclobutadiene)iron, ferrocene and 1,1'-dimethylferrocene. Analysis of the spectra gave the ^{13}C-^{57}Fe and ^{13}C-^{13}C coupling constants and the one- and two--bond ^{13}C-$^{13}C(^{12}C)$ isotope shifts [227]. An ^{1}H and ^{13}C NMR spectroscopic study of tricarbonyl(η-cyclobutadiene)iron in fluorosulphuric acid was carried out at low temperatures. On protonation the complex underwent π-σ isomerisation to give the complex (9.1). The observation of geminal $^{1}H_4$-Fe-$^{1}H_x$ (29 Hz) and ^{13}C-Fe-H_x (81.2 Hz) coupling substantiated the



9.1



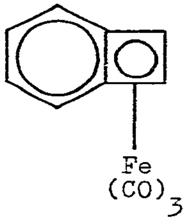
9.2



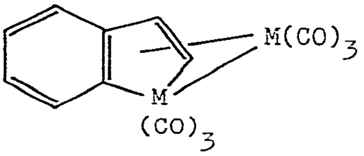
9.3

structure of the complex [228]. Reaction of the tricarbonyliron complex (9.2) with diphenylacetylene at 150° gave the cyclobutadiene complex (9.3) [229].

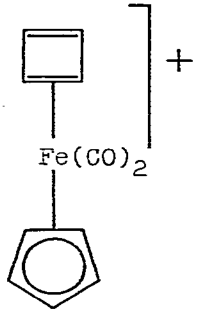
1,4-Dibromocyclooctatetraene was debrominated by stirring with diiron enneacarbonyl in hexane to give the benzocyclobutadiene complex (9.4) as the product. When the same two reactants were heated in heptane then the metallaindenyl complex (9.5; M = Fe) was obtained. Presumably the former complex (9.4) was converted to the latter complex (9.5; M = Fe) on heating in the second reaction. In the same way, 1,4-dibromocyclooctatetraene was heated with triruthenium dodecacarbonyl to give



9.4



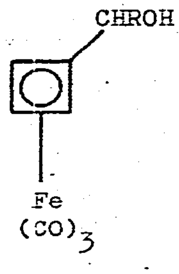
9.5



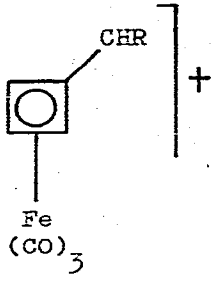
9.6

the metallaindenyl complex (9.5; M = Ru). Several related complexes of osmium were also described [230]. Sanders and Giering have obtained the η^2-cyclobutadiene complex (9.6) as a highly reactive intermediate which was trapped by dienes as the Diels-Alder adducts. Several other (η^2-cyclobutadiene)iron compounds were described [231].

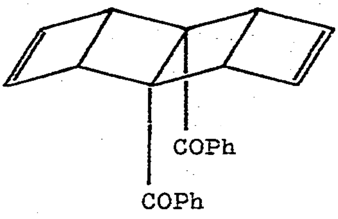
The ^{13}C NMR spectra of the (η-α-hydroxymethylcyclobutadiene)-iron complexes (9.7; R = H, Me, Ph) and the corresponding carbenium ions (9.8; R = H, Me, Ph) have been recorded. Analysis of the spectra indicated considerable donation of electron density from the iron atom to the α-carbenium centre through the η-cyclobutadiene group to give an effectively stabilized carbenium ion [232]. Meinwald and Mioduski have oxidized (η-cyclobutadiene)iron tricarbonyl with cerium (IV) and in the presence of half an equivalent of dibenzoylacetylene. The intermediate bicyclohexadiene formed by addition of the



9.7



9.8



9.9

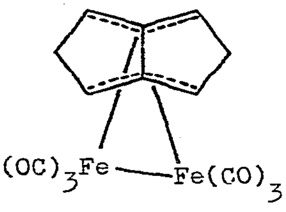
acetylene to cyclobutadiene was attacked by a second molecule of cyclobutadiene to form the tetracyclodeca-3,8-diene compound (9.9) [233].

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

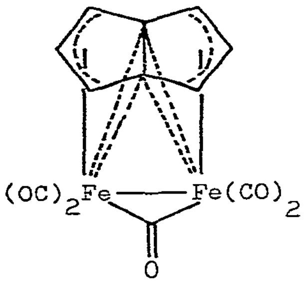
(i) Formation

A suspension of 1,4-dihydropentalene in ether was warmed with diiron nonacarbonyl to form a mixture of (η-pentalene)- and (η-dihydropentalene)-iron complexes. A bis-η-allyl structure (10.1) was proposed for the (η-dihydropentalene) complex and for one of the (η-pentalene) complexes (10.2) with the η-tetraene structure (10.3) as a possible alternative to (10.2). The second (η-pentalene) complex was assigned the (η-cyclopentadienyl) structure (10.4) [234]. King and Harmon have obtained the tricarbonyl(η-cyclopentadienone)iron compound (10.5; R = Et_2N) by heating or irradiating bis(diethylamino)-acetylene with iron pentacarbonyl [235]. Ultraviolet irradiation of pentacarbonyliron and dimethyldiacetylene (DMDA) gave (DMDA) $Fe_2(CO)_6$ (10.6) as the only product. The thermal reaction of DMDA with pentacarbonyliron gave three isomeric forms of the tricarbonylferroleiron tricarbonyl (10.7; $R^1 = R^3 = Me$, $R^2 = R^4 = C{\equiv}CMe$; $R^1 = R^4 = Me$, $R^2 = R^3 = C{\equiv}CMe$ and $R^1 = R^4 = C{\equiv}CMe$, $R^2 = R^3 = Me$) [236].

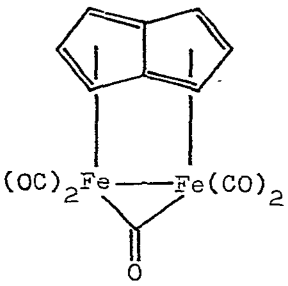
Hexafluorobut-2-yne added to cyclopentadiene to give the ligand (10.8) which underwent reaction with diiron nonacarbonyl to give the metal complex (10.9) [237]. Reaction of methoxy-



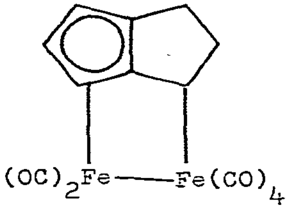
10.1



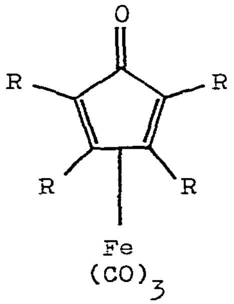
10.2



10.3

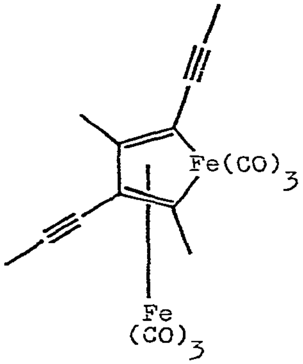


10.4

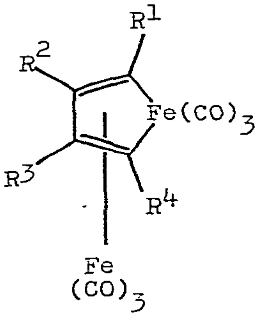


10.5

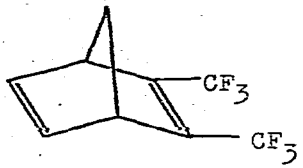
cyclo-octatetraene with triiron dodecacarbonyl gave the tricarbonyliron complexes (10.10 and 10.11). Acid-catalysed



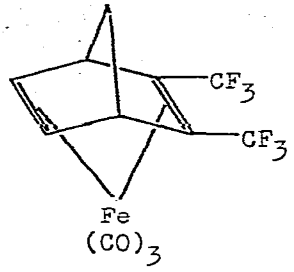
10.6



10.7

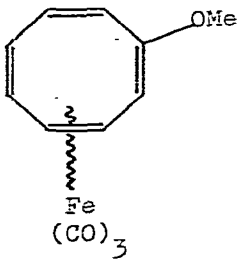


10.8

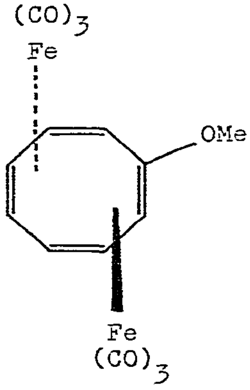


10.9

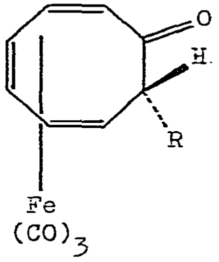
hydrolysis of the complex (10.10) gave tricarbonyl(η-cyclo-octa-2,4,6-trienone)iron (10.12; R = H) use of deuteriated acid gave the complex (10.12; R = D) stereospecifically monodeuteriated in the *anti* -8-position. When cyclooctatrienone was heated with (benzylideneacetone)-tricarbonyliron the bicyclic



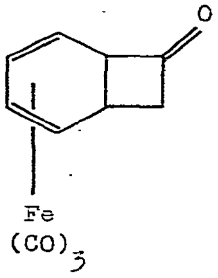
10.10



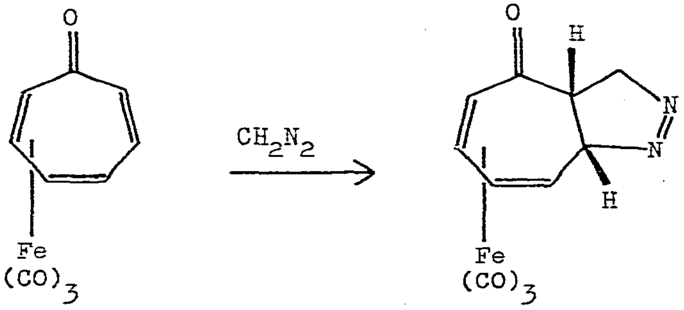
10.11



10.12



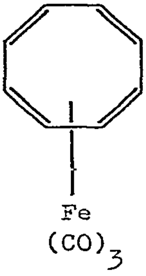
10.13



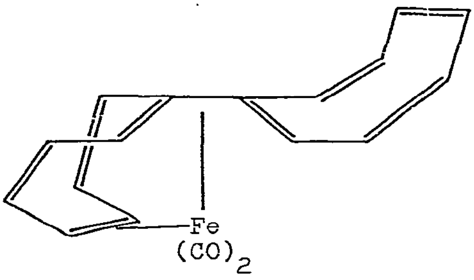
10.14

10.15

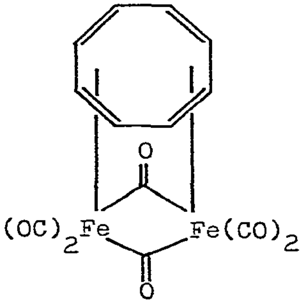
complex (10.13) was obtained whilst treatment with hexacarbonylchromium gave (η-benzene)tricarbonylchromium and tricarbonyl(η-cycloheptatriene)chromium. Treatment of the tropone complex (10.14) with diazomethane did not lead to ring expansion but regiospecific 1,3-dipolar cycloaddition occurred to give the complex (10.15) [238].



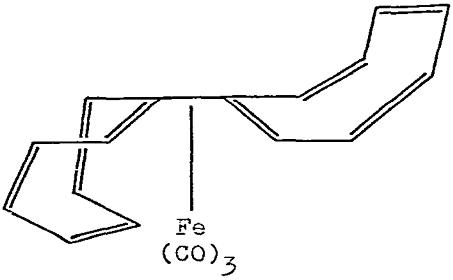
10.16



10.18



10.17

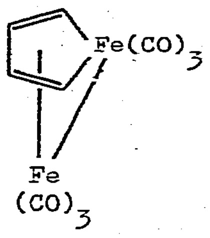


10.19

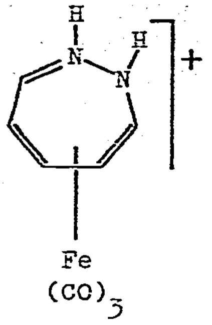
Treatment of bicyclooctatetraenyl with iron carbonyls gave known complexes of cyclooctatetraene as the principal products (10.16 and 10.17) while complexes of the intact ligand were formed only as minor products (10.18 and 10.19). Several related ruthenium complexes were characterized [239].

(ii) <u>Spectroscopic and Physico-Chemical Properties</u>

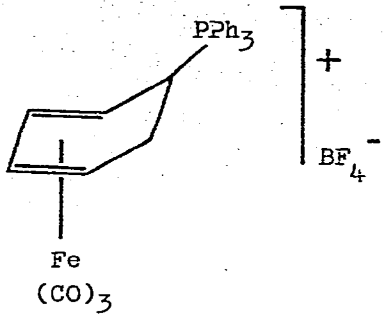
The ferracyclopentadiene complex (10.20) was formed by heating thiophene with triiron dodecacarbonyl and its crystal and molecular structure were determined by X-ray methods [240].



10.20



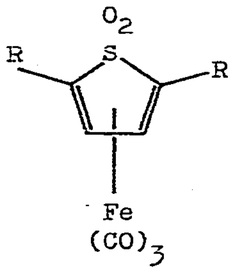
10.21



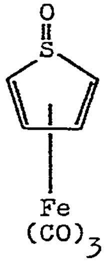
10.22

The crystal and molecular structure of the diazepiniumiron trifluoroacetate (10.21) has been determined by X-ray crystallography. The results confirmed that protonation of tricarbonyl $[\eta^4$-1(1H), 2-diazepine]iron occurred on the imine nitrogen [241]. The crystal and molecular structure of (5-*exo*-triphenylphosphinocyclohexa-1,3-diene)tricarbonyliron tetrafluoroborate (10.22) was determined by X-ray analysis. The diene was symmetrically bound to the tricarbonyliron group with the phosphorus attached to one of the two adjacent saturated carbon atoms [242].

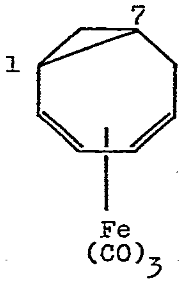
The ESCA spectra of the (η-diene)iron tricarbonyl compounds (10.23; R = H, Me and 10.24) have been recorded, assigned and interpreted. The ionization potentials of the atoms in each complex were determined [243]. Aumann has elucidated the



10.23



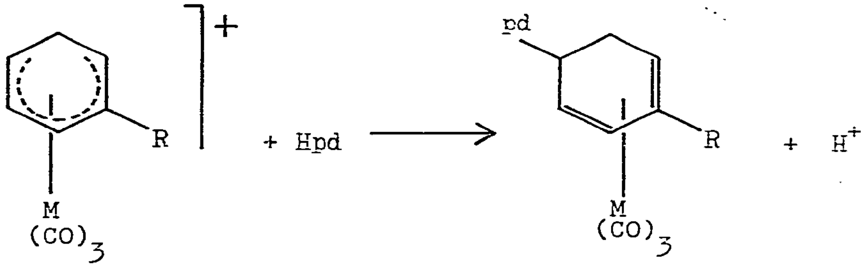
10.24



10.25

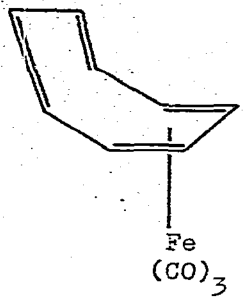
stereo-chemical course of the valence isomerization of the bicyclooctadiene complex (10.25). Two processes were observed, migration of the cyclopropane ring with retention of configuration at C (1) and C (7) and 1,5-hydride shifts on the <u>endo</u>-face of the ligand [244]. The out of plane bending of the saturated carbon atom in (η-cyclobutenyl), (η-cyclohexadienyl) and (η-cyclooctatrienyl) transition metal complexes has been discussed on a molecular orbital basis. It was predicted that (η-cyclobutenyl) and (η-cyclooctatrienyl) groups should be less bent than (η-cyclohexadienyl) while (η-cyclopentadienyl) carbenium ion ligands should be bent towards the metal atom [245].

The kinetics of addition of pentane-2,4-dione (Hpd) to the tricarbonyliron complexes (10.26; M = Fe; R = H, OMe) to form the (η-cyclohexadiene)iron complexes (10.27; M = Fe; R = H, OMe) were studied and the effects of variation in solvent, added acid, added base and deuteration were investigated. The reactions were not sensitive to solvent changes and the effects of acid, base and of deuteration were explained by a mechanism that involved rapid pre-equilibrium dissociation of Hpd to give pd^- which then added directly to the dienyl ring [246]. The kinetics of addition of indoles to the dienyl cations (10.26; M = Fe, Ru; R = H) were studied. The results indicated that direct electrophilic attack of the dienyl cation at C^3 of indole occurred and this was followed by rapid proton loss [247].

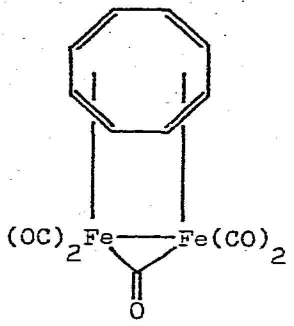


10.26 10.27

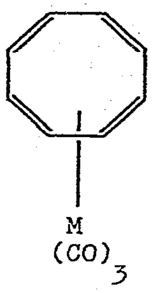
A pulsed NMR study of the (η-cyclooctatetraene)iron compounds (10.28 and 10.29) over a wide temperature range has confirmed that they show fluxional behaviour in the solid state. Measurements of the spin-lattice relaxation time were made and activation energies were calculated as 9.4 and 2 kcal mol^{-1}



10.28

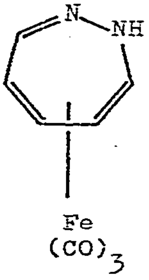


10.29

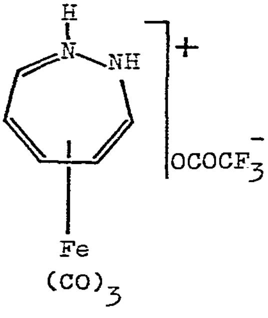


10.30

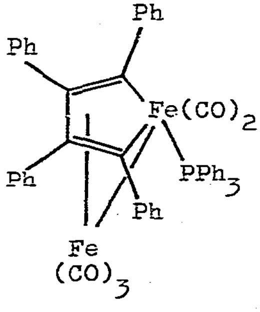
for the compounds (10.28 and 10.29) respectively. The implications of these results were discussed in terms of structure and bonding [248]. Cotton and Hunter have used ^{13}C NMR spectroscopy to reinvestigate the fluxional behaviour of tricarbonyl(η-cyclooctatetraene)-iron and -ruthenium (10.30; M = Fe, Ru). Rearrangements in the iron compound has been shown to take place by a 1,2-shift mechanism [249]. The solvent and concentration dependence of the ^{1}H NMR spectra of the tricarbonyl (η-diazepine)iron complex (10.31) indicated that its fluxional behaviour involved intermolecular proton transfer. The fluxional process was catalysed strongly by acids and proceeded through a fluxional imminium ion which has been characterized as the trifluoroacetate (10.32) [250].



10.31

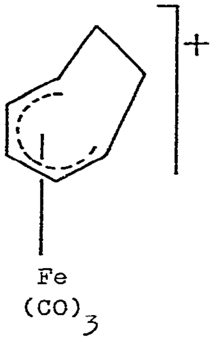


10.32

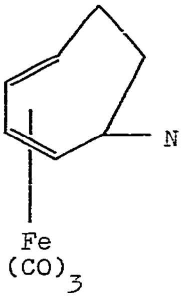


10.33

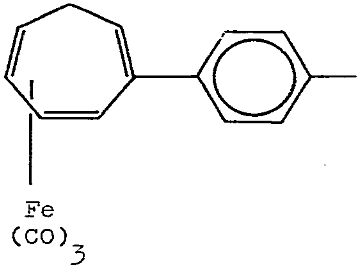
The dicarbonylferrole iron tricarbonyl complex (10.33) and related compounds were examined by ^{13}C NMR spectroscopy in the temperature range -125 to $+95^{0}$ C for fluxional behaviour. The dicarbonylferrole group was found to be static while the irontricarbonyl group was fluxional. The ferrole ring carbon and carbonyl carbon resonances were assigned and the structure of the complex (10.33) confirmed by single crystal X-ray measurements [251]. The reaction of the complex cation (10.34) with a series of nucleophiles, N = N_3^-, OEt^-, PEt_3, PBu_3 to give ring addition products (10.35), was followed by infrared and ^{1}H NMR spectroscopy. From the results it was suggested that attack by the nucleophile occurred at the metal atom and this preceded ring addition [252]. ^{1}H NMR studies on unequal mixtures of the complexes (10.36 and 10.37) in trifluoroacetic



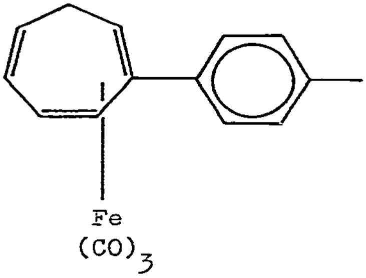
10.34



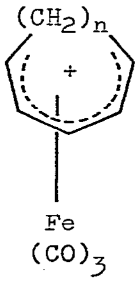
10.35



10.36



10.37

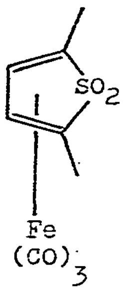


10.38

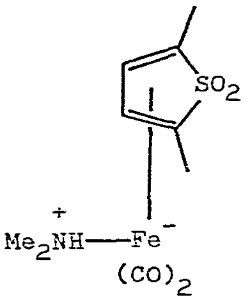
acid showed that protonation occurred at the uncoordinated double bonds. This indicated deactivation of the coordinated double bond by the tricarbonyliron group. The complexes (10.38; $n = 2$, 3 and 4) were hydrolysed by water to the corresponding alcohols whereas the complex (10.38; $n = 1$) was stable to hydrolysis which suggested that homoaromaticity contributed to the stability of the molecule [253].

(iii) General Chemistry

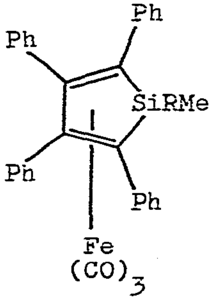
The addition of NOX where $X = BF_4$ or PF_6 to the iron complex $Fe(CO)_2L(C_nH_m)$ where C_nH_m = cyclic polyolefin gave either the nitrosyl cation $Fe(CO)L(NO)(C_nH_m)^+$ where L = CO; C_nH_m = norbornadiene; $L = PPh_3$, C_nH_m = tetraphenylcyclobutadiene) or the cation $Fe(CO)_2L(C_nH_{m+1})^+$ in which protonation of the polyene ligand had occurred. It was shown that in the presence of oxidizing agents such as silver (I) or the nitrosyl cation that the paramagnetic cations $Fe(CO)_2L(C_nH_m)^+$ were generated and these abstracted a proton from the solvent to give the protonated product $Fe(CO)_2L(C_nH_{m+1})^+$ [254]. In the decomplexation of the tricarbonyliron complex (10.39) by trimethylamine oxide the intermediate (10.40) was isolated. Treatment of this complex (10.40) with an excess of trimethylamine oxide gave the ligand 2,5-dimethylthiophen-SS-dioxide and inorganic products [255]. Twelve derivatives of tricarbonyl(η-tetraphenylcyclopentadiene)iron (10.41) have been prepared



10.39



10.40

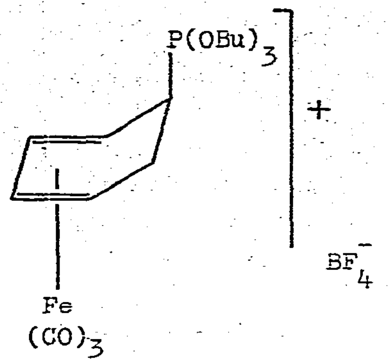


10.41

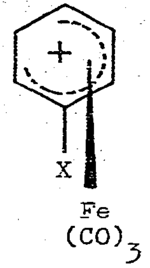
and substitution at silicon has been examined. The exo-substituents (10.41; R = Me, OH, OMe) were displaced readily by groups such as F, Cl, OH,OMe and Me_2CHO [256].

Tetracarbonyl(η-methyl acrylate)iron combined with isoprene on photolysis to give a tricarbonyl(η-diene)iron complex in which the ligand incorporated an adduct between isoprene and the acrylate. Similar reactions were carried out with related iron complexes and olefins. The mechanism for the thermal and photolytic conversion of tricarbonyl(η-cyclopentadiene)-iron to dicarbonyl(η-cyclopentadienyl) iron dimer has been investigated. The thermal route involved stereospecific free radical abstraction of hydrogen by an iron (I) species while the photolytic pathway involved intramolecular hydrogen transfer [257]. Addition of tri-n-butylphosphite to $[(\eta\text{-}C_6H_7)Fe(CO)_3]BF_4$ gave the stable adduct (10.42). Similar adducts were isolated from the reaction of the same phosphite with $[(\eta\text{-}C_6H_6OMe)Fe(CO)_3]BF_4$ and $[(\eta\text{-}C_7H_7)Cr(CO)_3]BF_4$ [258]. The kinetics of phosphonium adduct formation by attack of tri-n-butylphosphine on the cations $[(\eta\text{-}C_7H_7)M(CO)_3]^+$ where M = Cr, Mo, W, obeyed the rate law, Rate = $\underline{k}$ [complex][PBu_3]. The rates of the reaction were almost independent of the nature of the metal which indicated that the tropylium rings in the different complexes had similar electrophilicities and also that the phosphine added directly to the ring. It was established in this reaction that the ratio of the reactivities was $[(\eta\text{-}C_6H_7)Fe(CO)_3]^+$: $[(\eta\text{-}C_7H_7)Cr(CO)_3]^+$: $[(\eta\text{-}C_6H_6)Mn(CO)_3]^+$, 160 : 60 : 1 [259].

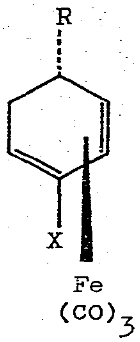
Reaction of (η-2-pyrone)tricarbonyliron complexes with hydroxide ion and acylation of the intermediate η-allyl anion gave a reactive anhydride intermediate which was used to prepare butadienes substituted with amide, azide, ester, acid, amine and alkyl groups [260]. The reaction of tricarbonyl(η-cyclohexadienyl)iron salts (10.43) with a series of cadmium reagents (R_2Cd, R = Ph, $PhCH_2$, Me_2CH, $CH_2{=}CHCH_2$, $MeCH{=}CHCH_2$, $MeCH{=}CH$) gave the products (10.44) of alkylation at the terminal carbon atom of the dienyl system. The reaction proceeded stereospecifically on the face opposite to the tricarbonyliron group. Similar reactions were carried out with the acyclic tricarbonylpentadienyliron salts (10.45) but the yields of the butadiene complexes (10.46 and 10.47) were variable and regioselectivity



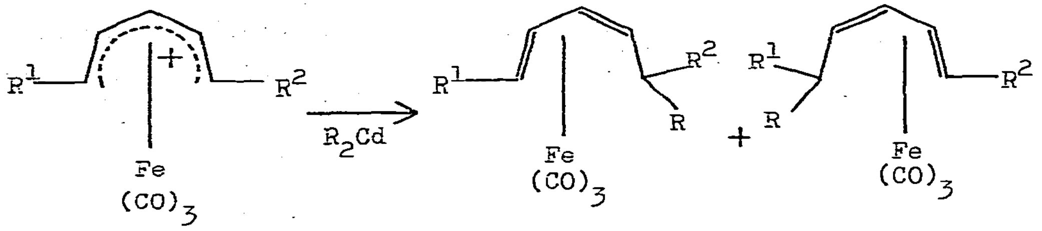
10.42



10.43

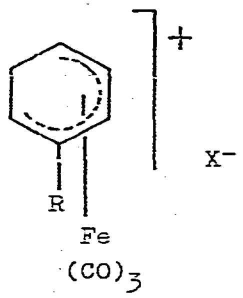


10.44

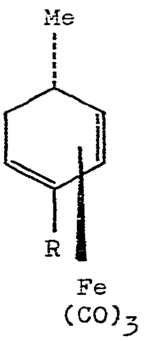


10.45 10.46 10.47

was poor [261]. Methylation of the tricarbonyliron complex (10.48; R = Me, OMe; X = BF_4^-, PF_6^-) with lithium dimethylcuprate proceeded stereospecifically to give the corresponding



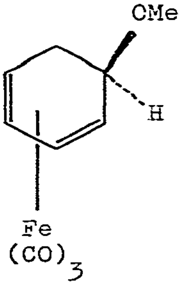
10.48



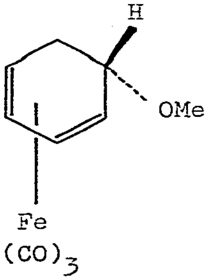
10.49

cyclohexadiene complexes (10.49). Experiments using deuterium labelled compounds established that alkylation occurred at the face of the η-cyclohexadienyl ring opposite to that occupied by the tricarbonyliron group [262].

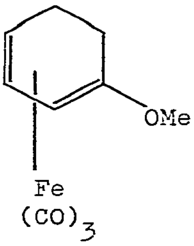
The relative thermal reactivities of the 5-<u>exo</u>- and 5-<u>endo</u>-methoxycyclohexa-1,3-diene complexes of iron tricarbonyl (10.50 and 10.51) were investigated. Thermal isomerization of the complex (10.50) gave a mixture of the 1- and 2- methoxy-isomers (10.52 and 10.53) together with some tricarbonyl(η-cyclohexa-1, 3-diene)iron. Attempted thermal isomerization of the complex (10.51) under the same reaction conditions gave mainly uncharged starting material together with a small amount of tricarbonyl-(η-cyclohexa-1,3-diene)iron. These results were interpreted in terms of a reaction mechanism where only migration of the C^5 <u>endo</u>-hydrogen occurred [263]. (η-Benzylideneacetone)tricarbonyliron underwent ligand exchange with 2,4,6-cyclooctatrienone



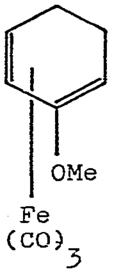
10.50



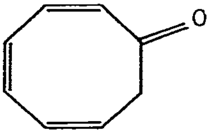
10.51



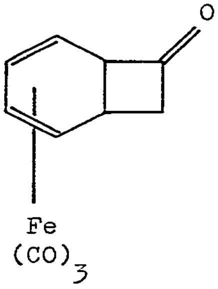
10.52



10.53



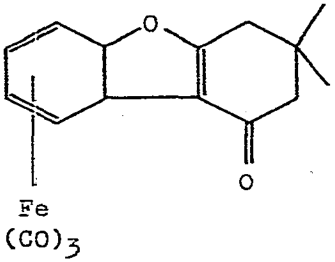
10.54



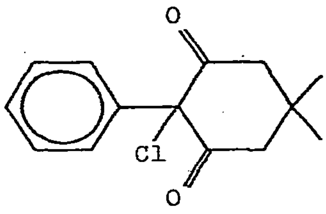
10.55

(10.54) in benzene at 55° to give the iron tricarbonyl complex (10.55) of the less stable bicyclic tautomer bicyclo[4.2.0]octa-2,4-dien-7-one and the complex was degraded with cerium (IV) at -30° to give the free bicyclic ligand [264].

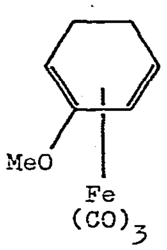
The tricarbonyliron group was efficiently removed from tricarbonyl(η-cyclohexadiene)iron complexes with copper (II) chloride in ethanol at room temperature. In two cases the ligand underwent modification, thus the chlorinated ligand (10.57) was obtained from the complex (10.56), and the ether linkage in the complex (10.58) was broken to give cyclohexenone



10.56



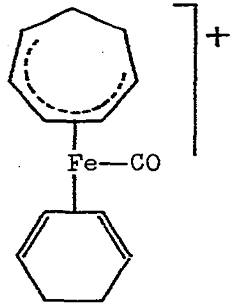
10.57



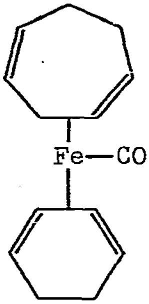
10.58

[265]. The cycloheptadienyl cation (10.59) was reduced with sodium borohydride in water to give the cycloheptadiene complex (10.60) together with a small proportion of the isomeric cycloheptadiene complex (10.61). The first order isomerization of the complex (10.60) to (10.61) was investigated kinetically and a cycloheptadienyl intermediate was proposed. Evidence was obtained for the *exo*-addition of hydride followed by migration of an *endo*-hydrogen in the reduction of the cation (10.59). Further reactions of the cycloheptadiene (10.60) were described [266].

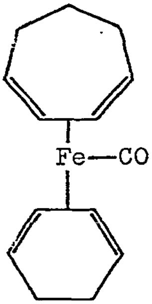
Abstraction of a hydride ion from the silacyclohexadiene complex (10.62) gave the 1,1-dimethyl-1-silacyclohexadienyl-tricarbonyliron cation [267]. Excess tricarbonyl (η-cycloheptatriene)iron was added to the tricarbonyliron complex (10.63; R = H) to give a polymeric product (10.64; n > 30). A similar product was obtained from the reaction of tricarbonyl-η-cyclo-



10.59

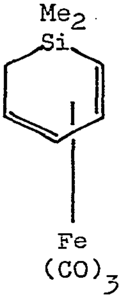


10.60

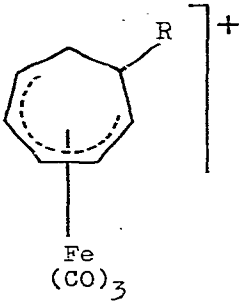


10.61

heptatrieneiron with the cationic tricarbonyliron complex (10.63; R = C_7H_7) [268]. (η-Tropone)tricarbonyliron (10.65)

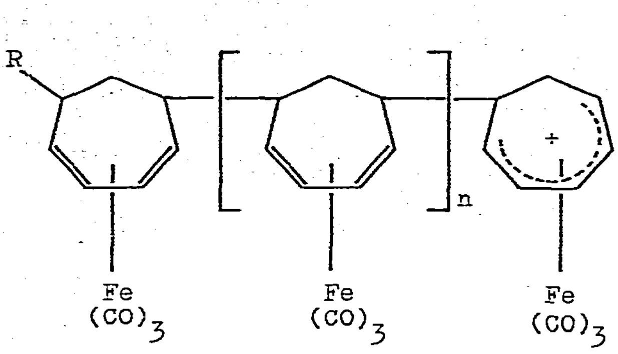


10.62

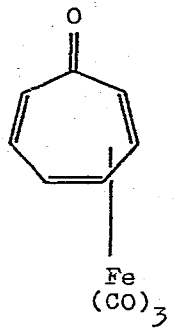


10.63

underwent a 1,5-cycloaddition with tetracyanoethylene to give the tricarbonyliron complex (10.66). ^1H NMR studies showed that the cycloaddition involved initial electrophilic addition to a non-coordinated double bond [269]. The reaction of tricarbonyl(η-cycloheptatrienyl)ferrate (-1) $[C_7H_7Fe(CO)_3]^-$ with Me_3MCl, where M = Si, Ge, gave the 7-substituted η-cycloheptatriene derivatives (10.67; M = Si, Ge). The ^1H and ^{13}C NMR spectra of these molecules (10.67; M = Si, Ge) showed that they exhibited fluxional behaviour when heated above room temperature. The origin of this temperature dependence of the NMR spectra was discussed and it was thought to be due

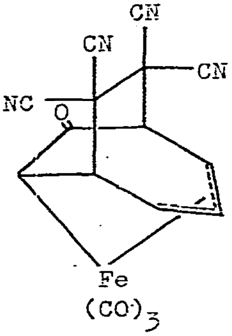


10.64

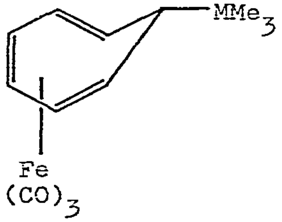


10.65

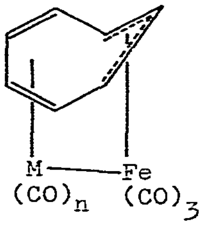
to oscillatory motion of the tricarbonyliron moiety having the effect of a 1,3-shift [270].



10.66

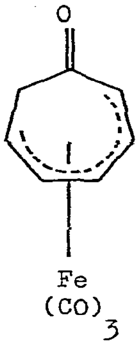


10.67

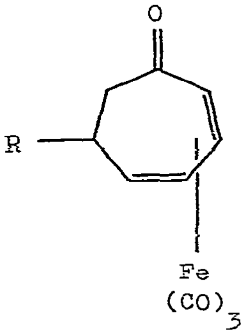


10.68

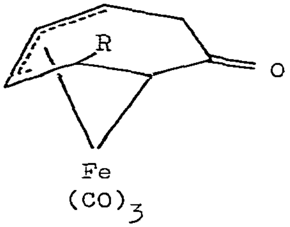
The reaction of tricarbonyl(η-cycloheptatrienyl)iron anion with metal carbonyl halides gave a series of heterodimetallic η-cycloheptatrienyl complexes (10.68; M = Mn, Re, n = 3; M = Rh, n = 2). The mass spectra and ^{1}H and ^{13}C NMR spectra of these compounds were discussed and it was concluded that all of the complexes adopted a cis arrangement of the carbonyl moieties with respect to the seven-membered ring [271]. Nucleophilic addition to protonated tricarbonyl(η-tropone)iron (10.69) by methanol, primary amines and azide ion gave the expected η-cycloheptadienone products (10.70; R = OMe, NHPh, NHBu^t, N$_3$). However treatment with cyanide and borohydride gave the η-cycloheptenyl complexes (10.71; R = CN, H) as the major products together with small amounts of the η-cycloheptadienone complexes (10.70; R = H, CN) [272]. Addition of a proton, using



10.69

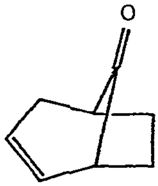


10.70

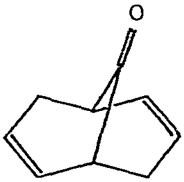


10.71

fluoroboric acid, and then a hydride ion, using sodium borohydride, to tricarbonyl(η-cycloheptatriene)iron followed by carbonylation gave the bicyclooctenone (10.72) in 57% yield. Treatment of tricarbonyl(η-cyclooctatetraene)iron in the same way gave the bicyclononadienone (10.73) in 62% yield [273].

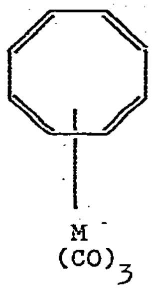


10.72

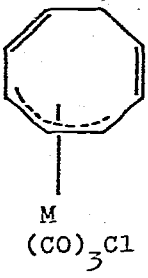


10.73

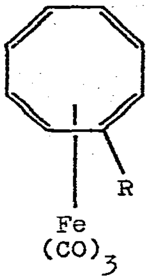
Treatment of the η-cyclooctatetraene complex (10.74; M = Fe) with dry hydrogen chloride gave the η-allyl complex (10.75). The corresponding ruthenium complex (10.74; M = Ru) underwent a similar reaction [274]. Bis(η-1,5-cyclooctadiene)iron, Fe(1,5-COD)$_2$ was treated with trimethylphosphite to give (1,3-COD)Fe[P(OMe)$_3$]$_3$. It was concluded that the isomerization of the 1,5- to the 1,3-species occurred on warming the complex in the presence of phosphite [275]. The (η-cyclooctatetraene)-



10.74

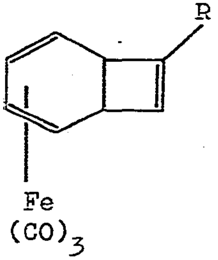


10.75

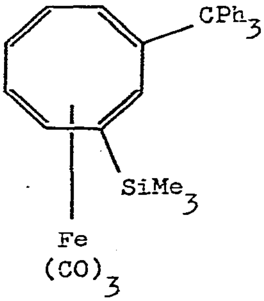


10.76

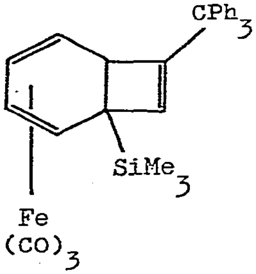
iron complexes (10.76; R = $SiMe_3$, $GeMe_3$, Ph_3C) isomerized on heating in octane to give the corresponding complexes (10.77; R = $SiMe_3$, $GeMe_3$, CPh_3) of the bicyclo[4.2.0]octa-2,4,7-triene ligand. The disubstituted cyclooctatetraene complex (10.78) also gave a bicyclooctatriene complex (10.79) whose structure was determined by X-ray crystallography. The ligand had a long bridgehead bond (1.58 Å) and the triphenylmethyl group was <u>trans</u> to the trimethylsilyl group and the folded hexadiene ring presented a convex face to the iron atom. Several related ruthenium complexes were described [276]. Treatment of triruthenium dodecacarbonyl with 1,5-cyclooctadiene (L) gave the complex $LRu(CO)_3$ in good yield [277].



10.77

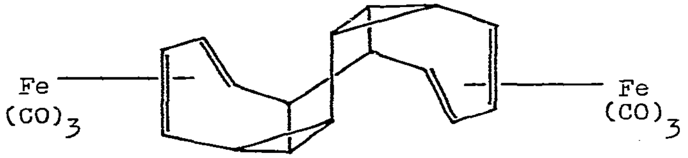


10.78



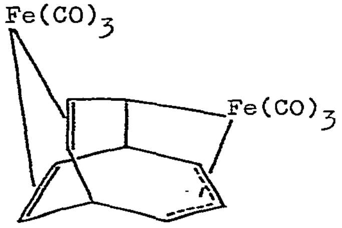
10.79

Tricarbonyl(η-cyclooctatetraene)iron has been treated with a tungsten hexachloride, ethanol, ethylaluminium dichloride mixture under olefin metathesis conditions to form the binuclear complex (10.80) with five fused rings in the ligand. The molecular structure was confirmed by X-ray crystal analysis [278].

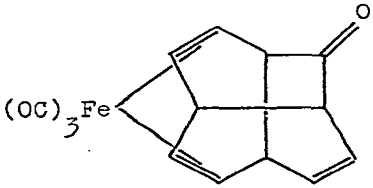


10.80

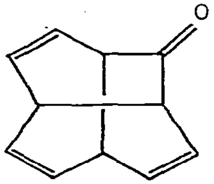
Treatment of the iron complex (10.81) with carbon monoxide gave the mononuclear carbonyliron complex (10.82) which underwent oxidative decomposition with iron (III) chloride to give the triene (10.83) [279].



10.81



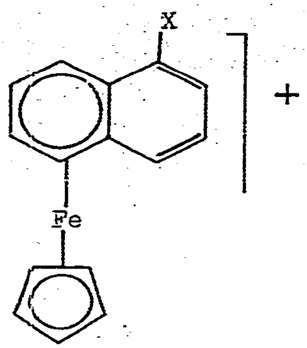
10.82



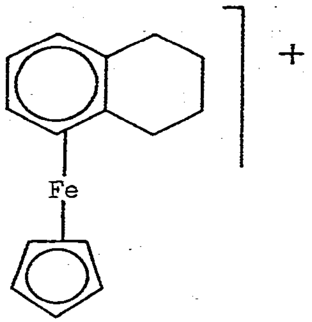
10.83

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

Reaction of 1-fluoro-, 1-chloro- and 1-bromo-naphthalene with ferrocene and an aluminium chloride-aluminium mixture gave the η-cyclopentadienyl-η-1-halonaphthaleneiron cations (11.1; X = F, Cl, Br) in which the η-cyclopentadienyliron group



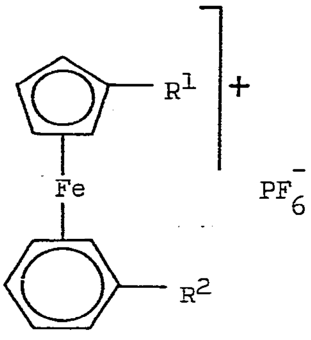
11.1



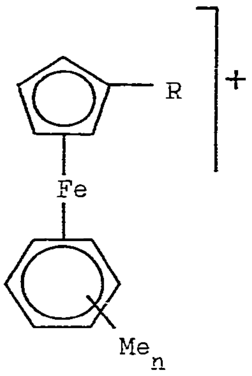
11.2

was complexed only to the unsubstituted aromatic ring. When the same reaction was carried out with 2-methylnaphthalene two complexes were isolated in which either the substituted or the unsubstituted ring was complexed to the η-cyclopentadienyliron group. With 1-bromonaphthalene the ion (11.1; X = Br) was isolated together with the dehalogenated (η-cyclopentadienyl)(η-naphthalene)iron cation and the hydrogenated derivative (11.2). To account for these results a hydrogenation mechanism involving radical ions as key intermediates was postulated [280]. Cyclic voltammetry showed that (η-arene)(η-cyclopentadienyl)iron salts were reduced reversibly to the parent complex. In water or aqueous ethanol a second irreversible reduction occurred to give metallic iron and the free ligands [281].

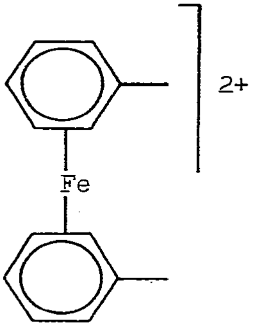
The exchange of ligands between alkylferrocenes and arenes was investigated. The ease of substitution of η-cyclopentadienyl moieties from a series of ferrocenes by benzene and alkylbenzenes decreased in the order $FcCOCH_3 \gg C_{10}H_8FeR_2 > FcH \gg C_{10}H_8Fe(COMe)_2$ (R = alkyl). The reaction of ferrocene and substituted ferrocenes with a series of alkylbenzenes, as solvents, in the presence of aluminium chloride gave the salts (11.3; R^1 = H, Me, Et, Pr, Me_2CH, CH_2Ph, COMe; R^2 = Me, Et, Pr, Me_2CH) [282]. Astruc and Dabard have investigated the exchange of cyclopentadienyl for arene in substituted ferrocenes. The products obtained were dependent on the nature of the arene, the reaction temperature and the nature of the ferrocene substituents. Thus acetylferrocene was heated to 80° with benzene and aluminium chloride to give the η-benzene complexes (11.4; R = COMe, H, CPh_2Me;



11.3



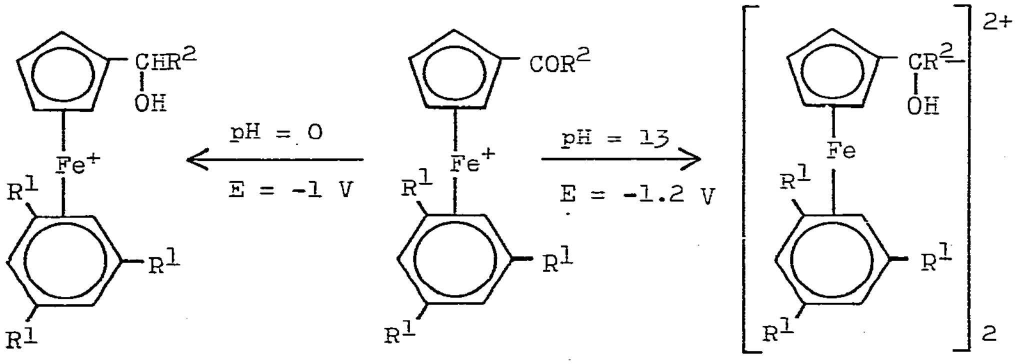
11.4



11.5

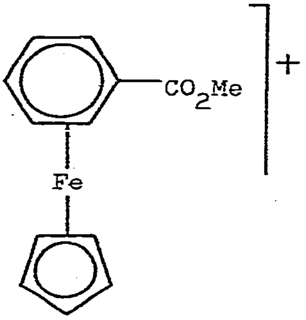
n = 0). With toluene as the reagent the η-benzene complexes [11.4; R = COMe, H, C(p-tolyl)$_2$Me; n = 1] were obtained together with the bis(η-benzene) complex (11.5). Increasing substitution with alkyl groups in the arene reagent lead to an increased proportion of bis(η-benzene) products (11.5) at the expense of the mixed complexes (11.4). Similar studies were carried out with formylferrocene, benzoylferrocene, 1,1'-diacetylferrocene, 1,1'-dibenzoylferrocene, diferrocenylketone and 1,1'-bis(α-hydroxyethyl)ferrocene [283].

Specific reduction of the carbonyl group in cationic (η-acylcyclopentadienyl)(η-arene)iron complexes was achieved electrochemically whilst the organometallic part of the molecule remained unchanged. When the ketones (11.6; R^1 = H, R^2 = Me;

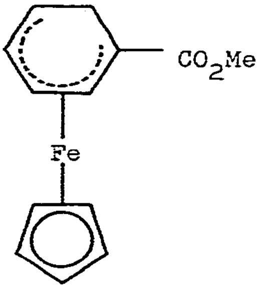


11.7 11.6 11.8

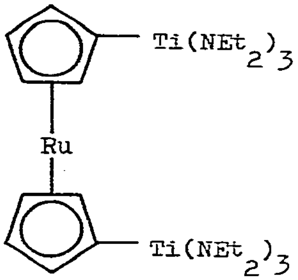
$R^1 = H$, $R^2 = Ph$; $R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Ph$) were reduced the monocationic alcohols (11.7) or the dicationic dinuclear pinacols (11.8) were obtained depending on the pH and the potential used [284]. The addition of hydride ion to the (η-methylbenzoate)iron cation (11.9) took place exclusively in the benzene ring to give a mixture of the <u>ortho-</u>, <u>meta-</u>, and <u>para-</u> products with the <u>ortho</u>-ester (11.10) strongly favoured over the other two isomers [285]. The reaction of bis(η-mesitylene)-iron (II) hexafluorophosphate with a series of nucleophiles was studied. Relatively weak carbanion nucleophiles formed 1 : 1 adducts which when oxidized with ceric ion gave a mixture of mesitylene and the 2-substituted mesitylene [286].



11.9



11.10

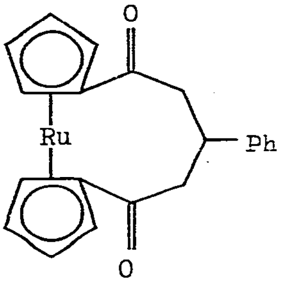


12.1

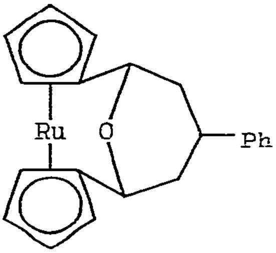
12. <u>$(\eta\text{-}C_5H_5)_2Ru$</u>

The structure of the ruthenocene-titanium complex (12.1) was investigated by ^1H- and ^{13}C-NMR and infrared spectroscopy [287]. The electronic and magnetic circular dichroism (mcd) spectra of ruthenocene and ferrocene were measured in solution, Perspex films at 4.2 K and rare-gas matrices at 20 K. Extensive calculations of the mcd parameters for the d – d transitions were carried out and it was concluded that the experimental results could be explained by inclusion of significant ligand character into the d orbitals [288]. The Raman spectra of ruthenocene and osmocene have been obtained for solid and liquid samples and compared with the corresponding spectra of other metallocenes. The assignments of some cyclopentadienyl vibrations have been revised [289]. The irradiation of solutions of ruthenocene in halocarbon solvents lead to the formation of the ruthenocinium and chloride ions [290].

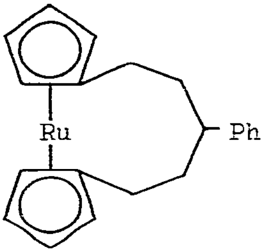
Ruthenocene in chlorocarbon solvents (RCl) absorbed radiation strongly in the 285-300 nm region. This absorption was absent in alcohol and hydrocarbon solvents and it was attributed to the formation of a charge transfer complex ($C_{10}H_{10}Ru.RCl$) [291]. 1,1'-Diacetylruthenocene was treated with benzaldehyde in ethanolic potassium hydroxide to form the [5]ruthenocenophane diketone (12.2). Reduction of the diketone (12.2) with sodium borohydride and treatment with hydrochloric acid gave the cyclic ether (12.3) which was in turn reduced with borohydride and aluminium chloride to the [5]ruthenocenophane (12.4) [292]. The elution behaviour of ruthenocene, ferrocene and a series of substituted ferrocenes on a gel permeation chromatographic support, cross-linked poly(acryloyl morpholine) (Enzacryl® Gel) was investigated. For most of the solutes an approximately linear relationship was obtained between log molecular weight and the Wheaton Baumann absolute distribution coefficient (Kd), which indicated that the separations were effected via a molecular sieving mechanism [293].



12.2



12.3



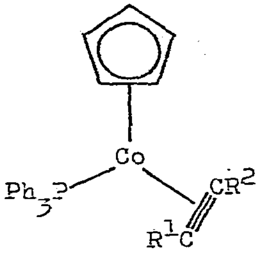
12.4

Acetylruthenocene-^{103}Ru was administered to rats and mice and scintigraphic studies showed that it accumulated mainly in the adrenal glands, liver and to a less extent in the kidneys. There was relatively little accumulation in the muscles and blood. Ferrocene-^{59}Fe was tested similarly but its persistence in the body was low. It was concluded that acetylruthenocene-^{103}Ru might be a useful diagnostic tool for adrenal disorders [294]. The reaction of areneruthenium (II) complexes

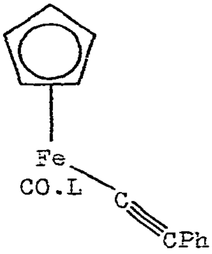
$[RuCl_2(arene)]_2$ and $RuCl_2$(arene)(pyridine) with alkali metal salts of cyclooctatetraene (cot) gave the air-sensitive compounds Ru(arene)(cot), (arene = PhH, 1,3,5-$C_6H_3Me_3$, C_6Me_6). An X-ray diffraction study of the hexamethylbenzene derivative showed that the arene ring was planar and that the cyclooctatetraene was 1-4-η-bonded. The barrier to intramolecular exchange of the bound and unbound halves of the eight-membered ring was very low (< 6 kcal mol^{-1}) [295].

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

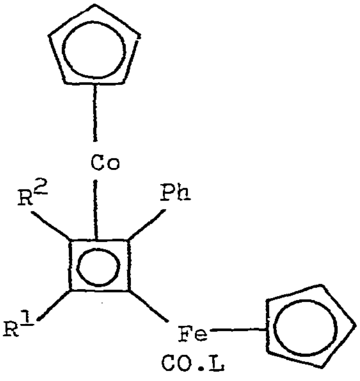
The reaction of the cobalt complexes (13.1; R^1 and R^2 = Ph, CO_2Me) with the ethynyl complexes (13.2; L = CO, PPh_3) gave the corresponding η-cyclobutadiene complexes (13.3). The nickel complexes (13.4; $R^1 = R^2$ = Ph, $R^3 = CO_2Me$; R^1, R^3 = Ph, $R^2 = CO_2Me$; R^1, $R^3 = CO_2Me$, R^2 = Ph; R^1, $R^2 = CO_2Me$, R^3 = Ph) were prepared by a similar route [296]. The sandwich



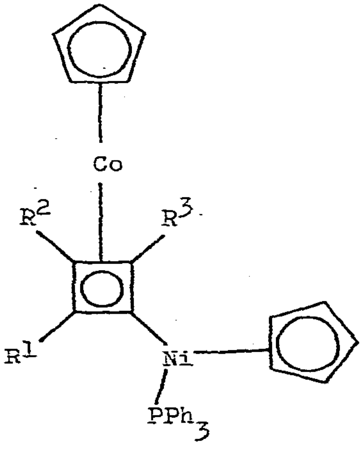
13.1



13.2



13.3

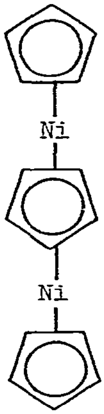


13.4

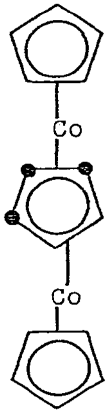
structure of (η-cyclobutadiene)(η-cyclopentadienyl)cobalt has been confirmed by a single crystal X-ray diffraction study at -35°C. The cobalt atom is bound symmetrically to each ring with typical carbon-cobalt internuclear distances [297].

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

Extended Hueckel molecular orbital calculations and frontier orbitals for the metal(η-cyclopentadienyl) and metal tricarbonyl groups have been used to analyze and discuss the electronic structures of the triple-decker sandwich complexes (14.1, 14.2 and 14.3). Two series of stable structures were predicted, containing thirty and thirtyfour valence electrons respectively. The similarities between these triple-decker complexes and the well known triply-bridged binuclear metal carbonyls such as diiron nonacarbonyl were considered. The structures of several triple-decker complexes which should be stable on theoretical grounds, but which have not yet been synthesised, were described [298]. The molecular structure of cobaltocene has been studied by gas phase electron diffraction, the sandwich structure with eclipsed η-cyclopentadienyl rings was indicated although the alternative staggered structure was not ruled out. The high value obtained for the C - C vibrational amplitude confirmed the presence of a dynamic Jahn-Teller effect [299]. The magnetic susceptibilities of cobaltocene and chromocene were measured by the Gouy method. For cobaltocene an effective magnetic moment of 1.70-1.90 BM was obtained between 83 and

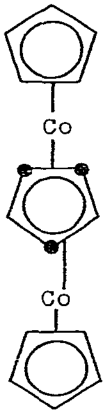


14.1



14.2

● = Boron

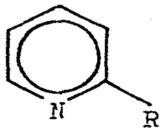


14.3

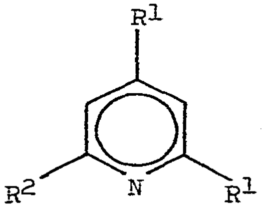
293 K. It was concluded that there was an appreciable orthorhombic splitting of $^2\Pi(\sigma^2\pi\delta^4)$ ground state [300].

Combustion and formation enthalpies together with mean bond dissociation energies were determined for cobaltocene, nickelocene and several other bis(η-cyclopentadienyl) transition metal complexes [301]. Several thermodynamic functions such as Cp and the energies for solid state transitions have been determined for cobaltocene, nickelocene and other metallocenes [302]. The ^{1}H and ^{13}C NMR spectra of twenty paramagnetic mono- and di-alkylated bis(η-cyclopentadienyl)complexes of vanadium, chromium, cobalt and nickel have been recorded. The chemical shifts were assigned completely and arranged systematically allowing the convenient identification of these paramagnetic complexes in solution [303]. Di(η-iso-propylcyclopentadienyl)cobalt was prepared and its ^{13}C and ^{1}H NMR spectra were recorded and interpreted [304]. Metallocenes, $(\eta\text{-}C_5H_5)_2M$ where M = Co, Cr, were treated with metal disulphides and diselenides, M^1X_2 where M^1 = Ta, Zr, Hf, Nb, Ti, Sn; X = S, Se to give the complexes $MX_2[M^1(\eta\text{-}C_5H_5)_2]_n$ where n = 0.2-0.38 [305].

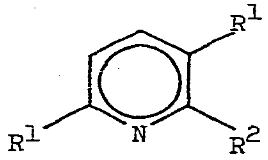
Acetylene and cyanides, RCN where R = C_{1-3} alkyl, $CH_2{=}CH$, Ph, $PhCH_2$, combined in benzene or toluene in the presence of cobaltocene to give substituted pyridines (14.4). In a similar reaction cocyclotrimerization of acetylenes, $R^1C{\equiv}CH$ where R^1 = C_{1-4} alkyl, with cyanides, R^2CN where R^2 = Me, Pr) gave mixtures of the pyridine isomers (14.5 and 14.6) [306].



14.4

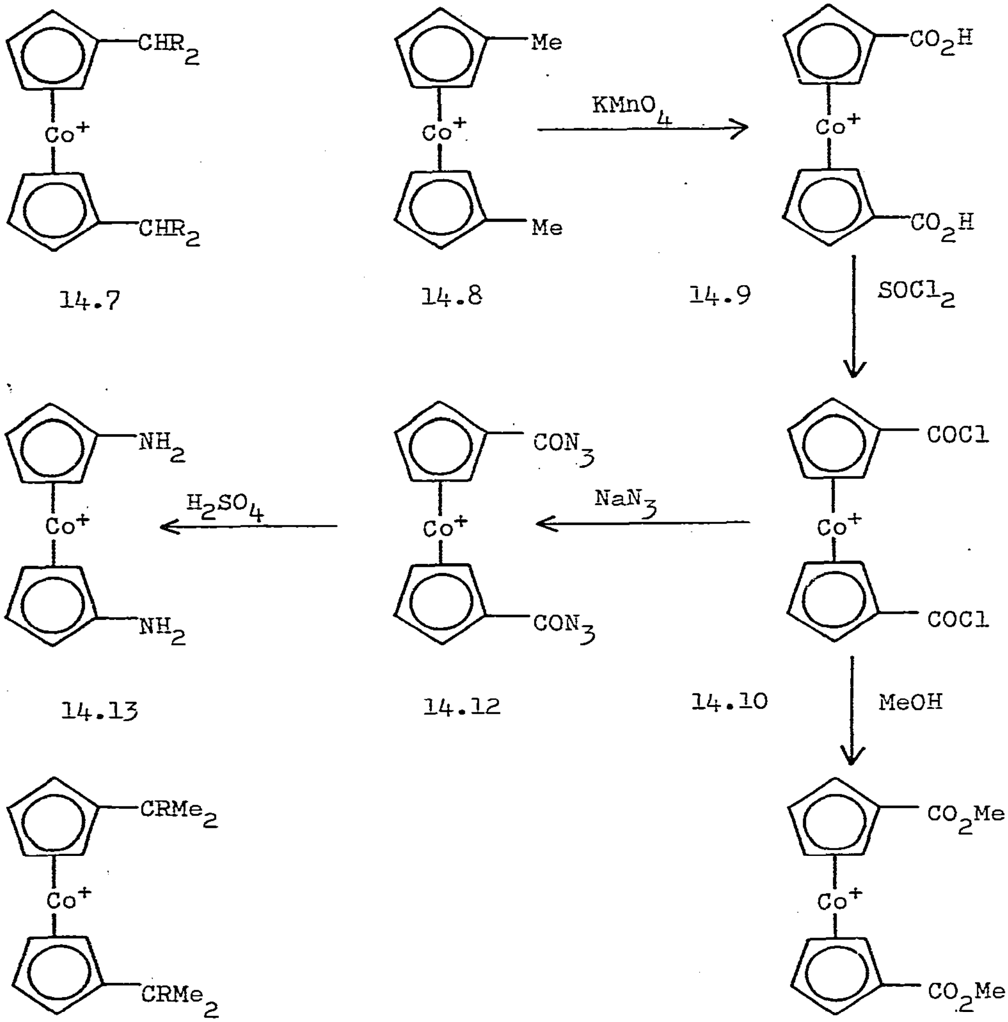


14.5



14.6

1,1'-Disubstituted cobalticinium cations (14.7; R = H, Me, Et, Ph) have been prepared by treatment of the appropriate cyclopentadienide anions with cobalt (II) under oxidizing conditions. Mono-, 1,2-, and 1,3-disubstituted compounds were obtained by oxidation of the mono- or di-substituted cyclopentadienide anions with cobalt (II) and cyclopentadiene in the presence of



14.7

14.8

14.9

14.13

14.12

14.10

14.14

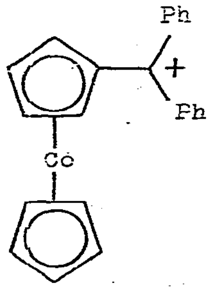
14.11

pyrrolidine. The 1,1'-dimethylcobalticinium ion (14.8) was oxidized to the carboxylic acid (14.9) with potassium permanganate, converted to the acid chloride (14.10) with thionyl chloride and then to either the methyl ester (14.11) with methanol or to the amine (14.13) through the azide (14.12). The isopropyl groups in the cation (14.14; R = H) were oxidized to the tertiary alcohol (14.14; R = OH) with permanganate and esterified with acetyl chloride to give the acetate (14.14; R = OCOMe); some related reactions were described [307].

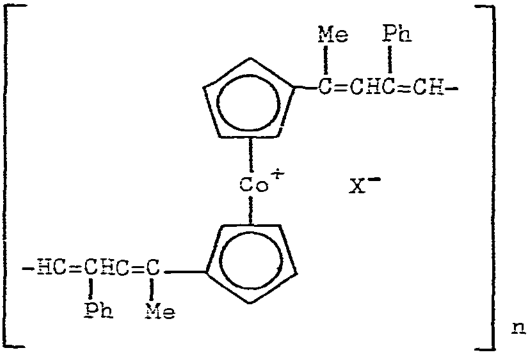
The polarographic reduction of six monosubstituted and eight disubstituted cobalticinium cations has been investigated. Two successive cathodic waves were observed at the dropping mercury electrode, the first corresponded to formation of cobaltocene and the second to the cobaltocene anion:

$$(\eta\text{-}C_5H_5)_2Co^+ \overset{e-}{\rightleftharpoons} (\eta\text{-}C_5H_5)_2Co \overset{e-}{\rightleftharpoons} (\eta\text{-}C_5H_5)_2Co^-$$

The UV, IR and ^{1}H NMR spectra of the cations were recorded and discussed [308]. The stability of the α-cobalticinium-carbenium ion (14.15) was determined spectrophotometrically in 80-96% sulphuric acid and compared with the stability of the ferrocenyl and phenyl analogues. The relative stability constants for RPh_2C^+ were; R = cobalticinium, 1; R = H, 10^2; R = phenyl 5×10^8; R = ferrocenyl, 10^{16}. ^{1}H and ^{13}C NMR spectroscopy indicated that in the carbenium ion (14.15)



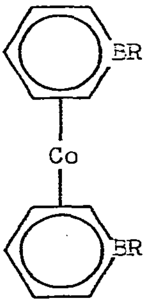
14.15



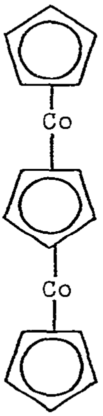
14.16

positive charge was more delocalized on to the phenyl groups than on to the cobalticinium group [309]. The acylcobalticinium--alkyl aryl ketone copolymer (14.16; X = Cl, OH) molecular weight 2500-5000 was prepared for use as a heat-resistant material [310]. Zirconocene poly(cobalticinium dicarboxylate) was prepared by the reaction of 1,1'-dicarboxycobalticinium hexafluorophosphate with zirconocene dichloride. The polymer was not very soluble in organic solvents and there was no tendency to form filaments [311].

The bonding and electronic structure of the triple-decker sandwich metallocarboranes (14.2 and 14.3) has been investigated by ^{11}B and ^{1}H Fourier transform NMR spectroscopy and comparisons made with the triple-decker cobalticinium sandwich (14.17). Alkyl, halogeno and trimethylsilyl groups were introduced into the central $(C_2B_3H_5)^{4-}$ ring or end $(C_5H_5)^-$ rings in order to determine substituent effects on the spectra. Medium and large changes in chemical shift were observed at all boron positions and at all hydrogens in each ring for both the 1,7,2,3- (14.2) and 1,7,2,4- (14.3) isomers when groups were present on a carboranyl ring carbon atom. Substitution on the end ring carbon atoms gave large chemical shift changes in the carboranyl ring. It was concluded that the 1,7,2,4-isomer (14.3) contained a metallocene-like carboranyl ring with strong electron delocalization while the 1,7,2,3-isomer (14.2) showed more localized cobalt-olefin and cobalt-boron bonding in the central ring [312].



14.18

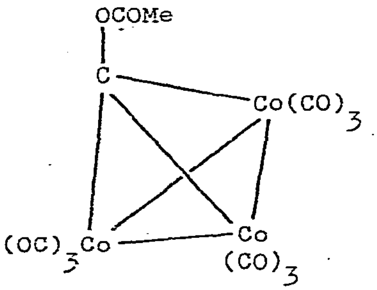


14.17

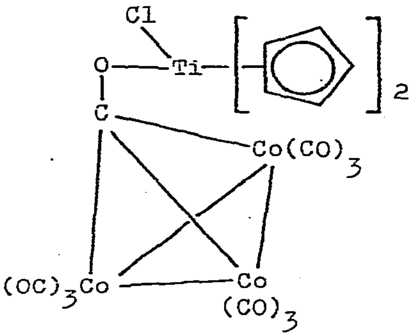
Degradation of the cobalt complexes (14.18; R = Ph, Me) with an alkali metal cyanide gave the corresponding metal borinate which was used to prepare $(\eta\text{-}C_5H_5BPh)_2Os$, $(\eta\text{-}C_5H_5BPh)PtMe_3$, $(\eta\text{-}C_5H_5BR)_2Ru$ and $1,5\text{-}C_8H_{12}RhC_5H_5BR$ (R = Ph, Me) [313].

15. Cobalt-carbon Cluster Compounds

The methylidyne nonacarbonyltricobalt acetate (15.1) has been prepared in high yield by treatment of $Li[Co_3(CO)_{10}]$ with acetylbromide [314]. Treatment of dicobaltoctacarbonyl with bis(η-cyclopentadienyl)titanium dichloride gave the titanocenyl cobalt cluster complex (15.2). The structure was determined by X-ray crystallography, the interatomic distances and bond angles about titanium were close to those observed in the starting material [315]. Treatment of trihalomethyl compounds RCX_3 where R = Cl, Br, Ph, $COOCMe_3$, CH_2OH with cobalt carbonyl in benzene-aqueous sodium hydroxide mixtures using benzyltriethylammonium chloride as a phase transfer catalyst afforded the cobalt cluster compounds (15.3) [316]. The crystal and molecular structure of the cobalt cluster complex (15.4) has been determined by X-ray crystallography [317].

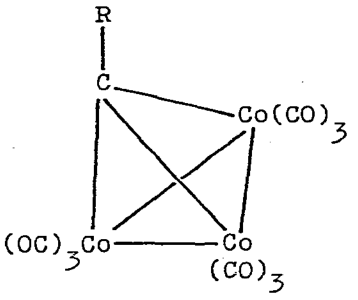


15.1

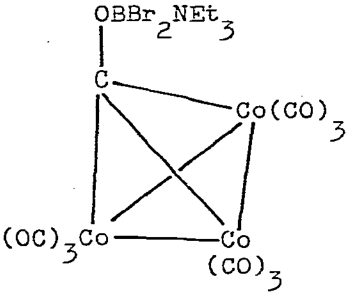


15.2

A series of cobalt cluster complexes of the type $XCCo_3(CO)_9$ where X = H, halogen, alkyl, aryl, C(OH)HR, OMe, $C(O)SCMe_3$ were examined by cyclic voltammetry at a hanging mercury drop or platinum bead electrode. The characteristic reduction pattern was a reversible, one electron reduction in the range of -0.7 to



15.3



15.4

-0.9 V measured against a saturated calomel electrode followed by an irreversible, multi-electron reduction at about -1.5 to -1.8 V. Clusters with more electronegative substituents were reversibly reduced around -0.7 V whilst those with electron--donating substituents were reduced at approximately -0.9 V. ESR spectra of the reduced clusters consisted of at least 16 lines, and the hyperfine structure and coupling constant changed little with the substituent [318]. The ^{13}C NMR apical carbon resonances for the cobalt complexes $Co_3(CO)_9CY$ where Y = H, Me, Ph, CF_3, CO_2Me, F, Cl, Br, I were observed in the lowfield region (310-230 ppm). The signals were quite difficult to detect due to spin-spin coupling with the three cobalt atoms which underwent quadrupole induced relaxation. Variable temperature spectra showed thermal decoupling of carbon from cobalt and scrambling of the carbonyls [319].

Seyferth and co-workers found that molecular hydrogen would reduce aroylmethylidynetricobalt nonacarbonyls (15.3; R = COPh, p-MeC_6H_4CO, p-BrC_6H_4CO) in the absence of a catalyst to produce the corresponding α-hydroxybenzylidynetricobalt nonacarbonyls in good yields. Hydrogenation of the ferrocene derivative (15.3; R = $COC_5H_5FeC_5H_4$) gave the alcohol [15.3; R = $CH(OH)C_5H_5FeC_5H_4$] and the cluster compound (15.3; R = $C_5H_4FeC_5H_5$) which was shown to be produced by thermal decarbonylation of the ketone [320]. Bromomethylidynetricobalt nonacarbonyl underwent a rapid reaction with ammonia and primary and secondary aliphatic amines to give the corresponding amides

(R^1, R^2 = H or alkyl).

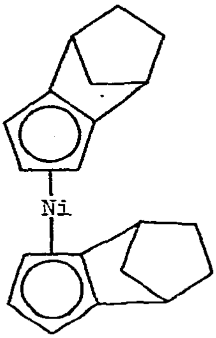
$$(OC)_9Co_3CBr + R^1R^2NH \longrightarrow (OC)_9Co_3CC(O)NR^1R^2$$

The slow room temperature reaction of methanol with $(OC)_9Co_3CBr$ was accelerated when it was carried out in the presence of triethylamine under an atmosphere of carbon monoxide. Triethylamine also accelerated the reactions between $(OC)_9Co_3CBr$ and other alcohols, phenol, anilines and indole [321].

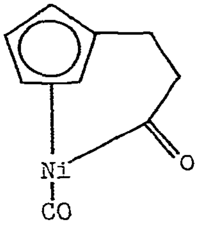
16. $(\eta\text{-}C_5H_5)_2Ni$

An X-ray powder diffraction study was carried out on nickelocene in the temperature range 5 to 295° K. The temperature dependence of the cell parameters and the principal thermal expansion coefficients were explained in terms of an order - disorder transition in the range 240-170° K. It was thought that nickelocene was eclipsed (D_{5h}) in the ordered phase [322]. The heat capacity curve for nickelocene has been determined in the temperature range 130-300° K and previous proposals on the nature of solid state transitions in this compound were substantiated [323]. Contact shifts for the cyclopentadienyl and substituent hydrogen atoms have been determined for seven alkyl and alkylene substituted nickelocenes. The cyclopentadienyl hydrogen atoms showed constant contact shifts (250 ± 19 ppm) while the β-hydrogen atoms on carbons attached directly to the metallocene nucleus showed shifts which were dependent on the dihedral angle between the cyclopentadienyl p_z orbital and the C-H_β bond. The structure of one of the compounds (16.1) was determined by X-ray crystallography [324].

Corderman and Beauchamp have used ion cyclotron resonance spectroscopy to examine the gas-phase ion chemistry of nickelocene. Total rate constants for the further reactions of primary fragment ions such as $(C_5H_5)Ni^+$ and $(C_3H_3)Ni^+$ have been obtained by trapped-ion techniques. The nickelocene anion $(\eta\text{-}C_5H_5)_2Ni^-$ was formed by electron attachment, it was long-lived and unreactive towards hydrogen chloride, nitric oxide, and ammonia. Nickelocene was found to be a strong base in the gas phase with a proton affinity of 218.9 kcal mol^{-1} which was determined from equilibrium proton transfer reactions with trimethylamine [325]. The d-d spectra of nickelocene and the carborane analogue $[Ni(B_9C_2H_{11})_2]^{2-}$ were analysed. The spin-

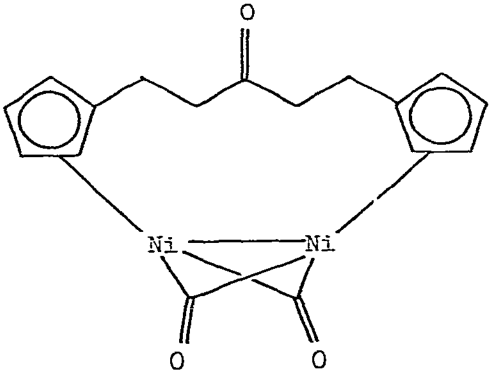


16.1

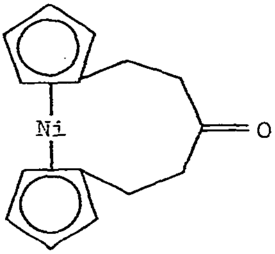


16.2

-orbit coupling constants and nephelauxetic parameters were estimated for the two complexes [326]. A rate expression was derived for the thermal decomposition of diisopropylnickelocene which was thought to decompose via a radical mechanism [327].

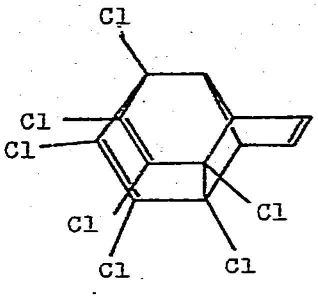


16.3

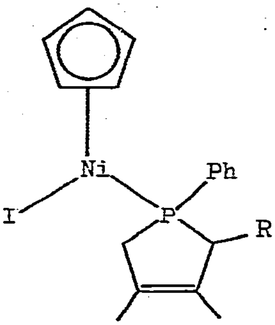


16.4

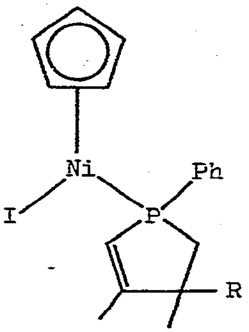
Reaction of tetracarbonylnickel with spiro[2.4]hepta-4,6-diene gave the nickel complexes (16.2 and 16.3). Treatment of the complex (16.2) with triphenylphosphine gave the nickelocenophane (16.4) [328]. Treatment of nickelocene with octachlorocycloheptatriene in dry ether at room temperature formed a cyclopentadienylcycloheptatriene which underwent an intramolecular Diels Alder reaction to give a heptachlorotetracyclododecatriene (16.5) [329]. Nickelocene was degraded by phosphine sulphides in the presence of allyl iodide to give (η-cyclopentadienyl)nickel trialkylphosphine complexes [16.6;



16.5



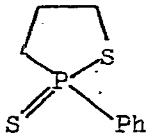
16.6



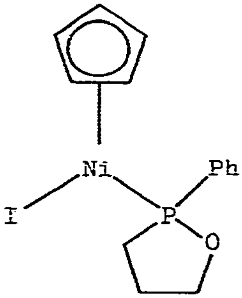
16.7

R = H, C(alkyl)$_2$OH, COPh, CO$_2$Et and 16.7; R = C(alkyl)$_2$OH]. The ester, ketone and alcohol functions did not interfere with the reaction. The complexes (16.6 and 16.7) were decomposed by sodium cyanide to give the free phosphines [330].

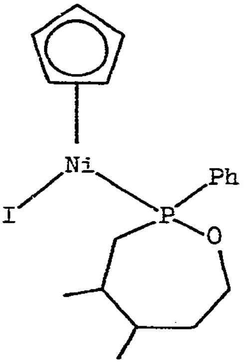
The cyclic phosphinate (16.8) was treated with nickelocene and allyl iodide to give the η-cyclopentadienyl complex (16.9). A 1-oxa-2-phosphacycloheptadiene underwent the same reaction to give the η-cyclopentadienyl complex (16.10) [331]. Nickelocene was attacked by bis(trifluoromethyl)acetylene at 80° to give the mono- (16.11) and di-acetylene (16.12) adducts as the principal products. The mechanisms of these and related reactions were discussed [332].



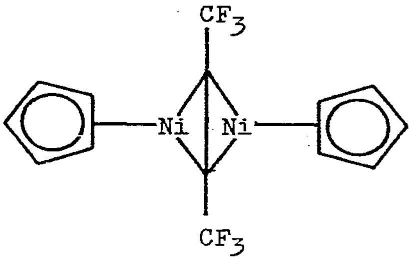
16.8



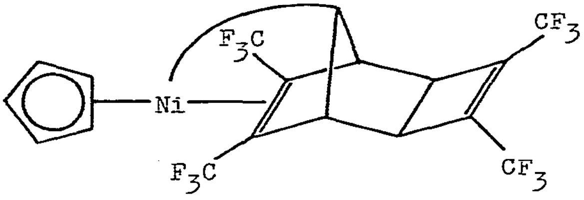
16.9



16.10



16.11



16.12

17. Uranocene

The crystal and molecular structure of bis[η-(1,3,5,7-tetraphenylcyclooctatetraene)]uranium was determined by X-ray analysis. The molecule crystallized with completely disordered molecular packing. The molecule itself was a sandwich compound with the C_8 rings in a nearly eclipsed configuration and with the phenyl rings tilted at an average of 42° from the plane of the C_8 ring in a staggered configuration [333]. The low temperature magnetic susceptibilities of methyl and phenyl substituted uranocenes have been determined and were in accord with the calculations of Hayes and Edelstein [334] and their MO description of metal-ligand bonding [335]. The helium I photoelectron spectra of uranocene, $(\eta\text{-}C_8H_8)_2U$, and thorocene, $(\eta\text{-}C_8H_8)_2Th$ have been measured and the ionization energies determined. Striking resemblences were observed between these spectra and those of other transition metal sandwich compounds. The lowest bands were assigned to electrons ionized from molecular orbitals localized on the metal and demonstrated the electron rich character of the metal and the very low ionization energies associated with such orbitals [336].

References

1 D. Seyferth, Adv. Organomet. Chem., 14 (1976) 97.
2 New Synth. Methods, Vol. 3, Verlag Chemie, Weinheim, 1975.
3 P.S. Skell and M.J. McGlinchey, New Synth. Methods, 3 (1975) 7.
4 E. Koerner von Gustorf, O. Jaenicke, O. Wolfbeis and C. R. Eady, New Synth. Methods, 3 (1975) 107.

5 K. J. Klabunde, New Synth. Methods, 3 (1975) 135.

6 E.A. Koerner von Gustorf, I. Fischler and R. Wagner, Proc. Int. Conf. Coord. Chem., 16th (1974) 4. 20.

7 J.D. Bailie, Oil Gas J., 74 (1976) 69.

8 M.A. Bennett, Rodd's Chem. Carbon Compd., 2nd Ed., Pt. B, 3 (1974) 357; Edited by S. Coffey, Elsevier, Amsterdam.

9 G.R. Knox and W.E. Watts, MTP Int. Rev. Sci., Inorg. Chem., Ser. Two; 6 (1975) 219.

10 T.A. Stevenson, MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two; 6 (1975) 287.

11 W.E. Watts, Organometal. Chem., 4 (1975) 353.

12 D.R. Armstrong, R. Fortune and P.G. Perkins, J. Organometal. Chem., 111 (1976) 197.

13 K. Eberl, F.H. Koehler and L. Mayring, Angew. Chem., 88 (1976) 575.

14 J.W. Lauher and R. Hoffmann, J. Amer. Chem. Soc., 98 (1976) 1729.

15 I.B. Rabinovich, V.P. Nistratov, M.S. Shaiman and G.V. Burchalova, Conf. Int. Thermodyn. Chim., (C.R.), 4th, 2 (1975) 136; Chem. Abstr., 84 (1976) 150069.

16 V.I. Telnoi, K.V. Kir'yanov, E.I. Ermolaev and I.B. Rabinovich, Tr. Khim. Khim. Tekhnol., (1975) 3.

17 Japan Pat. 7632544, 1976, Mar 19; Chem. Abstr., 85 (1976) 143306.

18 A.N. Nesmeyanov, M.I. Rybinskaya and G.B. Shul'pin, Ger. Pat. 2438427, 1976, Feb. 19; Chem. Abstr., 85 (1976) 5887.

19 A.T. Shuvaev, I.A. Zarubin, V.N. Uvarov, B. Yu. Khelmer, S.P. Gubin, N.E. Kolobova and V.M. Danyushin, Izv. Akad. Nauk SSSR, Ser. Fiz., 40 (1976) 333.

20 S. Toma, E. Salcaniova and A. Maholanyiova, Chem. Zvesti, 29 (1975) 526.

21 P.E. Gaivoronskii and N.V. Larin, Tr. Khim. Khim. Tekhnol., (1975) 92.

22 D. Rehder, L. Dahlenburg and I. Muller, J. Organometal. Chem., 122 (1976) 53.

23 D. Rehder, W.L. Dorn and J. Schmidt, Transition Met. Chem., 1 (1976) 74.

24 N.G. Connelly and M.D. Kitchen, J. Chem. Soc., Dalton Trans., (1976) 2165.

25 M. Schneider and E. Weiss, J. Organometal. Chem., 114 (1976) C43.

26 A.P. Hagen and H.W. Beck, Inorg. Chem., 15 (1976) 1512.

27 H.W. Beck, Diss. Abstr. Int. B, 36 (1976) 5021.

28 E.W. Abel, T. Blackmore and R.J. Whitley, J. Chem. Soc., Dalton Trans., (1976) 2484.

29 K.H. Doetz, R. Dietz, A. Von Imhof, H. Lorenz and G. Huttner, Chem. Ber., 109 (1976) 2033.

30 H. des Abbeyes and M.A. Boudeville, Tetrahedron Lett., (1976) 1189.

31 M. Herberhold and K. Leonhard, Angew. Chem., 88 (1976) 227.

32 R.S. Bly, K-K. Tse and R.K. Bly, J. Organometal. Chem., 117 (1976) 35.

33 F. Van Meurs and H. Van Koningsveld, J. Organometal. Chem., 118 (1976) 295.

34 J.Y. Saillard and D. Grandjean, Acta Crystallogr. Sect B, B32 (1976) 2285.

35 I.F. Taylor, E.A.H. Griffith and E.L. Amma, Acta Crystallogr., Sect. B, B32 (1976) 653.

36 C. Azokpota, C. Pommier, Y. Limouzin and J.C. Maire, J. Organometal. Chem., 117 (1976) 349.

37 A.N. Egorochkin, V.A. Kuznetsov, A.N. Artemov, N.I. Sirotkin, V.G. Kirilicheva and G.A. Razuvaev, Dokl. Akad. Nauk SSSR, 227 (1976) 878.

38 B. Caro and G. Jaouen, J. Chem. Soc., Chem. Commun., (1976) 655.

39 F. van Meurs, J.M.A. Baas and H. van Bekkum, J. Organometal. Chem., 113 (1976) 353.

40 E.W. Neuse, J.S. Afr. Chem. Inst., 28 (1975) 365.

41 F. Van Meurs, J.M.A. Baas, J.M. Van Der Toorn and H. Van Bekkum, J. Organometal. Chem., 118 (1976) 305.

42 F. Van Meurs, J.M. van der Toorn and H. van Bekkum, J. Organometal. Chem., 113 (1976) 341.

43 D.J. Kowalski, Diss. Abstr. Int. B, 36 (1976) 3389.

44 G.A. Olah and S.H. Yu, J. Org. Chem., 41 (1976) 1694.

45 D.A. Brown, N.J. Fitzpatrick, I.J. King and N.J. Mathews, J. Organometal. Chem., 104 (1976) C9.

46 B.A. Howell and W.S. Trahanovsky, J. Magn. Reson., 20 (1975) 141.

47 G.A. Olah and Simon H. Yu, J. Org. Chem., 41 (1976) 717.

48 G.A. Razuvaev, A.N. Artemov, A.A. Aladjin and N.I. Sirotkin, J. Organometal. Chem., 111 (1976) 131.

49 V.N. Trembovler, N.K. Baranetskaya, N.V. Fok, G.B. Zaslavskaya, B.M. Yavorskii and V.N. Setkina, J. Organometal. Chem., 117 (1976) 339.

50 B.V. Lokshin, E.B. Rusach, N.E. Kolobova, Yu. V. Makarov, N.A. Ustynyuk, V.I. Zdanovich, A. Zh. Zhakaeva and V.N. Setkina, J. Organometal. Chem., 108 (1976) 353.
51 M.F. Semmelhack, H.T. Hall and M. Yoshifuji, J. Amer. Chem. Soc., 98 (1976) 6387.
52 A. Ceccon, A.M. Romanin and M. Gentiloni, Gazz. Chim. Ital., 106 (1976) 291.
53 A. Ceccon, A. Romanin and A. Venzo, Transition Met. Chem., 1 (1976) 25.
54 M. Ashraf, Can. J. Chem., 54 (1976) 448.
55 A. Meyer, H. Neudeck and K. Schloegl, Tetrahedron Lett., (1976) 2233.
56 H. Des Abbeyes and M.A. Boudeville, Tetrahedron Lett., (1976) 2137.
57 V.N. Setkina, N.K. Baranetskaya, V.I. Zdanovich and D.N. Kursanov, Proc. Int. Conf. Coord. Chem., 16th (1974) R57.
58 T. Debaerdemaeker, Angew. Chem., 88 (1976) 544.
59 E. Ucciani and G. Devinat (Institut Français du Petrole), Fr. Pat., 2262690, 1975 Sep. 26; Chem. Abstr., 84 (1976) 61663.
60 A.H. Westlake, Chem. Ind. (London), (1976) 372.
61 C.P. Tsonis and M.F. Farona, J. Organometal. Chem., 114 (1976) 293.
62 G.M. Holtzapple, P.S. Woon and M.F. Farona, Inorg. Nucl. Chem. Lett., 12 (1976) 623.
63 M.F. Farona and J.F. White (Akron Univ.), U.S. Pat., 3946072, 1976, Mar. 23; Chem. Abstr., 84 (1976) 179845.
64 M.F. Farona and J.F. White (University of Akron) US Pat. 3912788, 1975 Oct 14; Chem. Abstr., 84 (1976) 30618.
65 M.F. Farona and J.F. White (University of Akron), US Pat. 3933752, 1975, Jan. 20; Chem. Abstr., 84 (1976) 105170.
66 Yu. T. Struchkov, V.G. Andrianov, A.N. Nesmeyanov, V.V. Krivykh, V.S. Kaganovich and M.I. Rybinskaya, J. Organometal. Chem., 117 (1976) C81.
67 H.G. Biedermann, K. Oefele and J. Tajtelbaum, Z. Naturforsch. B. Anorg. Chem., Org. Chem., 31B (1976) 321.
68 M. Novi, G. Guanti and C. Dell'Erba, J. Heterocycl. Chem., 12 (1975) 1055.
69 W. Siebert and R. Full, Angew. Chem., 88 (1976) 55.
70 A. Salzer, J. Organometal. Chem., 117 (1976) 245.

71 A.M. Ciplys, R.L. Geue and M.R. Snow, J. Chem. Soc., Dalton Trans., (1976) 35.

72 P. Caillet, C.R. Hebd. Seances Acad. Sci., Ser., C 281 (1975) 1057.

73 Yu. S. Nekrasov and N.I. Vasyukova, J. Organometal. Chem., 122 (1976) 228.

74 M. Herberhold and W. Bernhagen, Angew. Chem., 88 (1976) 651.

75 N.G. Connelly, B.A. Kelly, R.L. Kelly and P. Woodward, J. Chem. Soc., Dalton Trans., (1976) 699.

76 E.O. Fischer, P. Stueckler, H.J. Beck and F.R. Kreissl, Chem. Ber., 109 (1976) 3089.

77 F.R. Kreissl and P. Stuckler, J. Organometal. Chem., 110 (1976) C9.

78 D.N. Kursanov, V.N. Setkina, Yu. D. Konovalov, M.N. Nefedova, N.K. Baranetskaya and G.A. Panosyan, Doklady Akad. Nauk SSSR, 227 (1976) 1365.

79 A. Mortreux, N. Dy and M. Blanchard, J. Mol. Catal., 1 (1976) 101.

80 A.N. Nesmeyanov, N.N. Zaitseva, G.A. Domrachev, V.D. Zinov'ev, L.P. Yur'eva and I.I. Tverdokhlebova, J. Organometal. Chem., 121 (1976) C52.

81 G.A. Domrachev, V.D. Zinov'ev, L.P. Yur'eva and N.N. Zaitseva, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 1638.

82 G.A. Domrachev and V.D. Zinov'ev, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 951.

83 G.A. Domrachev and V.D. Zinov'ev, J. Organometal. Chem., 117 (1976) 241.

84 L.H. Simons, P.E. Riley, R.E. David and J.J. Lagowski, J. Amer. Chem. Soc., 98 (1976) 1044.

85 P. E. Riley and R.E. Davis, Inorg. Chem., 15 (1976) 2735.

86 V. Graves and J.J. Lagowski, J. Organometal. Chem., 120 (1976) 397.

87 V. Graves and J.J. Lagowski, Inorg. Chem., 15 (1976) 577.

88 L.M. Bessmertnaya, I.L. Agafonov, V.I. Faerman and B.S. Kaverin, Tr. Khim. Khim. Tekhnol., (1975) 93; Chem. Abstr., 85 (1976) 167659.

89 L.V. Burmistrova, Tr. Khim. Khim. Tekhnol., (1975) 90; Chem. Abstr., 85 (1976) 123087.

90 S.A. Friedberg, L.G. Polgar and T. Smith, Tr. Mezhdunar. Konf. Magn. 1 (1974) 320; Chem. Abstr. 85 (1976) 27946.

91 I.B. Rabinovich, G.V. Burchalova, K.V. Kir'yanov, V.P. Nistratov, V.I. Tel'noi and M.S. Sheiman, Tr. Khim. Khim. Tekhnol., (1975) 57.

92 M.J. McGlinchey and T.-S. Tan, J. Amer. Chem. Soc., 98 (1976) 2271.

93 C. Elschenbroich and F. Stohler, Angew. Chem., 87 (1975) 198.

94 A.N. Nesmeyanov, L.P. Yur'eva and N.N. Zaitseva, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 922.

95 A.N. Nesmeyanov, L.P. Yureva, N.N. Zaitseva, V.K. Latov, S.D. Soinov, L.M. Samoilenko, K.K. Babievskii and A.G. Makarovskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 924.

96 W.B. Davies, M.L.H. Green and A.J. Jacobson, J. Chem. Soc., Chem. Commun., (1976) 781.

97 J.A. Delap (Phillips Petroleum Co.) US Pat. 3976632, 1976, Aug. 24; Chem. Abstr., 85 (1976) 143835.

98 V.A. Umilin and Yu. B. Zverev, Tr. Khim. Khim. Tekhnol., (1975) 113.

99 V.A. Umilin and I.N. Tyutyaev, Tr. Khim. Khim. Tekhnol., (1975) 96; Chem. Abstr., 85 (1976) 149358; V.A. Umilin and Yu. B. Zverev, Tr. Khim. Khim. Tekhnol., (1975) 98; Chem. Abstr., 85 (1976) 149359.

100 A.D. Zorin, V.A. Umilin and U.K. Vanchagova, USSR Pat. 519628, 1976, Jun. 30; Chem. Abstr., 85 (1976) 153565.

101 J.R. Blackborow, R. Grubbs, A. Miyashita and A. Scrivanti, J. Organometal. Chem., 120 (1976) C49.

102 J. Mueller, W. Holzinger and F.H. Koehler, Chem. Ber., 109 (1976) 1222.

103 A. Salzer, J. Organometal. Chem., 107 (1976) 79.

104 G. Hoch, R. Panter and M.L. Zeigler, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 294.

105 B.F. Anderson, G.B. Robertson and D.N. Butler, Can. J. Chem., 54 (1976) 1958.

106 D.W. Clack, M. Monshi and L.A.P. Kane-Maguire, J. Organometal. Chem., 120 (1976) C25.

107 C.J. Groenenboom, H.J. De Liefde Meyer and F. Jellinek, Proc. Int. Conf. Coord. Chem., 16th (1974) R2.

108 A. Salzer, Inorg. Chim.Acta, 18 (1976) L31.

109 E.E. Isaacs and W.A.G. Graham, J. Organometal. Chem., 120 (1976) 407.

110 D. Mohr, H. Wienand and M.L. Ziegler, Z. Naturforsch., B; Anorg. Chem., Org. Chem., 31B (1976) 66.

111 M. Bochmann, M. Cooke, M. Green, H.P. Kirsch, F.G.A. Stone and A.J. Welch, J. Chem. Soc., Chem. Commun., (1976) 381.

112 A. Salzer and H. Werner, Proc. Int. Conf. Coord. Chem., 16th 1974 4.24; Chem. Abstr., 85 (1976) 76909.

113 H. Schaper and H. Behrens, J. Organometal. Chem., 113 (1976) 361.

114 D.A. Sweigart, M. Gower and L.A.P. Kane-Maguire, J. Organometal. Chem., 108 (1976) C15.

115 S.C. Tripathi, S.C. Srivastava, R.D. Pandey and R.P. Mani, J. Organometal. Chem., 110 (1976) 67.

116 J.P. Williams and A. Wojcicki, Inorg. Chim. Acta. 15 (1975) L19.

117 K.J. Reimer, Diss. Abstr. Int. B 36 (1976) 3948.

118 A.N. Nesmeyanov, N.E. Kolobova, V.I. Zdanovich and A. Zh. Zhakaeva, J. Organometal. Chem., 107 (1976) 319.

119 D.L. Lichtenberger and R.F. Fenske, Inorg. Chem., 15 (1976) 2015.

120 D.L. Lichtenberger and R.F. Fenske, J. Amer. Chem. Soc., 98 (1976) 50.

121 N.J. Gogan, C.K. Chu and P.A. Narayana, Proc. Int. Conf. Coord. Chem., 16th, (1974) 2.5b.

122 N.M. Loim, P.V. Petrovskii, V.I. Robas, Z.N. Parnes and D.N. Kursanov, J. Organometal. Chem., 117 (1976) 265.

123 D.J. Parker, Spectrochim. Acta, Part A, 31A (1975) 1789.

124 C.J. Pickett and D. Pletcher, J. Chem. Soc., Dalton Trans., (1976) 636.

125 M. Le Plouzennec, F. Le Moigne and R. Dabard, J. Organometal. Chem., 111 (1976) C38.

126 M. Le Plouzennec and R. Dabard, J. Organometal. Chem., 112, (1976) 333.

127 J.W. Johnson and P.M. Treichel, J. Chem. Soc., Chem. Commun., (1976) 688.

128 A.G. Ginzburg, V.N. Setkina, Sh. G. Kasumov, G.A. Panosyan, P.V. Petrovskii and D.N. Kursanov, Dokl. Akad. Nauk SSSR, 228 (1976) 1368.

129 N.M. Loim, L.A. Malutschenko, Z.N. Parnes and D.N. Kursanov, J. Organometal. Chem., 108 (1976) 363.

130 T. Renk, W. Ruf and W. Siebert, J. Organometal. Chem., 120 (1976) 1.

131 C. Sergheraert, P. Marcincal and E. Cuingnet, J. Organometal. Chem., 120 (1976) 329.

132 F. Le Moigne, R. Dabard and M. Le Plouzennec, J. Organometal. Chem., 122 (1976) 365.

133 I.M. Gverdsiteli, L.P. Asatiani and A.A. Tskhvaradze, Soobshch. Akad. Nauk Gruz. SSR, 87 (1976) 353.

134 A.N. Nesmeyanov, L.I. Leont'eva and L.I. Khomik, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 1656.

135 C.U. Pittman and T.D. Rounsefell, Macromolecules, 9 (1976) 936.

136 J.E. Ellis, R.A. Faltynek and S.G. Hentges, J. Organometal. Chem., 120 (1976) 389.

137 J.B. Moran, SAE [Tech. pap.] (1975) 750926; Chem. Abstr., 85 (1976) 162960.

138 E.J. Calabrese and A. Sorensen, J. Air Pollut. Control Assoc., 25 (1975) 1254.

139 W. Moore, J.F. Stara, D. Hysell, M. Malanchuk, J. Burkart and R. Hinners, SAE [Tech. Pap.] (1975) 750927; Chem. Abstr., 85 (1976) 41693.

140 G.L. Ter Haar, M.E. Griffing, M. Brandt, D.G. Oberding and M. Kapron, J. Air Pollut. Control Assoc., 25 (1975) 858.

141 J.E. Faggen, J.D. Bailie, E.A. Desmond and D.L. Lenane, SAE (Tech. Pap.), (1975) 750925 43pp; Chem. Abstr. 86 (1977) 19227.

142 L.M. Niebylski (Ethyl Corp.) US Pat. 3948618, 1975, Jun. 5; Chem. Abstr., 85 (1976) 80772.

143 J.W. Sprague, D.W. Feldman and F. Veatch (Standard Oil Co.), Ger. Pat., 2521892, 1975, Dec. 4; Chem. Abstr., 84 (1976) 153031.

144 J.W. Sprague, D.W. Feldman and F. Veatch (Standard Oil Co.), Ger. Pat., 2521988, 1975, Dec. 4; Chem. Abstr., 84 (1976) 153032.

145 L. Plonsker (Ethyl Corp.), U.S. Pat., 3926581, 1975, Dec. 16; Chem. Abstr., 84 (1976) 167188.

146 L.M. Niebylski (Ethyl Corp), US Pat. 3950145, 1976, Aug. 24; Chem. Abstr., 86 (1977) 19347.

147 R.V. Kerley (Ethyl Corp.) US Pat. 3927992, 1975 Dec. 23; Chem. Abstr., 84 (1976) 124353.

148 G.L. Ter Haar, M.E. Griffing, M. Brandt, D.G. Oberding and M. Kapron, J. Air Pollut. Control Assoc., 25 (1975) 1255.

149 G.G. Barna, I.S. Butler and K.R. Plowman, Can. J. Chem., 54 (1976) 110.

150 D. Cozak and J.S. Butler, Spectrosc. Lett., 9 (1976) 673.

151 G. Huttner, A. Frank and G. Mohr, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 1161.

152 G. Huttner, H.D. Mueller, V. Bejenke and O. Orama, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 1166.

153 A.G. Ginzburg, V.N. Setkina, P.V. Petrovskii, Sh. G. Kasumov, G.A. Panosyan and D.N. Kursanov, J. Organometal. Chem., 121 (1976) 381.

154 R.D. Adams and D.F. Chodosh, J. Organometal. Chem., 120 (1976) C42.

155 M. Hoefler, H. Hausmann and W. Saal, Z. Naturforsch B: Anorg. Chem., Org. Chem., 31 (1976) 790.

156 E. Colomer, R. Corriu and A. Vioux, J. Chem. Soc., Chem. Commun., (1976) 175.

157 D.A. Sweigart and L.A.P. Kane-Maguire, J. Chem. Soc., Chem. Commun., (1976) 13.

158 M.L. Ziegler, K. Weidenhammer, H. Zeiner, P.S. Skell and W.A. Herrmann, Angew. Chem., 88 (1976) 761.

159 E.O. Fischer, R.L. Clough, G. Besl and F.R. Kreissel, Angew. Chem., 88 (1976) 584.

160 V.G. Andrianov, Yu. T. Struchkov, A.B. Antonova and N.S. Obezyuk, J. Organometal. Chem., 122 (1976) C33.

161 A.D. Redhouse and W.A. Herrmann, Angew. Chem., 88 (1976) 652.

162 M. Herberhold, G.O. Wiedersatz and C.G. Kreiter, J. Organometal. Chem., 104 (1976) 209.

163 G. Huttner, V. Bejenke and H.D. Mueller, Cryst. Struct. Commun., 5 (1976) 437.

164 I.S. Butler, N.J. Coville and A.E. Fenster, Inorg. Synth., 16 (1976) 53.

165 A.N. Nesmeyanov, G.G. Aleksandrov, A.B. Antonova, K.N. Anisimov, N.E. Kolobova and Yu. T. Struchkov, J. Organometal. Chem., 110 (1976) C36.

166 H. Berke, Angew. Chem., 88(1976) 684.

167 G. Huttner, H.G. Schmid and H. Lorenz, Chem. Ber., 109 (1976) 3741.

168 M. Hoefler and A. Baitz, Chem. Ber., 109 (1976) 3147.

169 H. Brunner and J.A. Aclasis, J. Organometal. Chem., 104 (1976) 347.

170 D.L. Lichtenberger, D. Sellmann and R.F. Fenske, J. Organometal. Chem., 117 (1976) 253.

171 A.N. Nesmeyanov, N.E. Kolobova, A.B. Antonova, N.S. Obezyuk and K.N. Anisimov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 948.

172 H. Brunner and W. Steger, J. Organometal. Chem., 120 (1976) 239.

173 G.E. Herberich, J. Hengesbach, U. Koelle, G. Huttner and A. Frank, Angew. Chem., 88 (1976) 450.

174 W. Siebert and K. Kinberger, Angew. Chem., 88 (1976) 451.

175 G.A.M. Munro and P.L. Pauson, J. Chem. Soc., Chem. Commun., (1976) 134.

176 A.N. Nesmeyanov, N.E. Kolobova, Yu. V. Makarov, B.V. Lokshin and E.B. Rusach, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 629.

177 E.O. Fischer, R.L. Clough and P. Stuckler, J. Organometal. Chem., 120 (1976) C6.

178 A.N. Nesmeyanov, N.E. Kolobova, Yu. V. Makarov and E.I. Kazimirchuk and K.N. Anisimov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 159.

179 R.B. King and C.A. Harmon, J. Amer. Chem. Soc., 98 (1976) 2409.

180 N.S. Nametkine, V.D. Tyurine, A.I. Nekhaev, V.I. Ivanov and F.S. Bayaouova, J. Organometal. Chem., 107 (1976) 377.

181 R. Noyori and K. Yokoyama, Bull. Chem. Soc. Jpn., 49 (1976) 1723.

182 D.H.R. Barton and H. Patin, J. Chem. Soc., Perkin Trans. 1, (1976) 829.

183 R.W. Jotham, S.F.A. Kettle, D.B. Moll and P.J. Stamper, J. Organometal. Chem., 118 (1976) 59.

184 F.A. Cotton, J.D. Jamerson and B.R. Stults, Inorg. Chim. Acta., 17 (1976) 235.

185 J.R. Blackborow, C.R. Eady, E.A.K. Von Gustorf, A. Scrivanti and O. Wolfbeis, J. Organometal. Chem., 111 (1976) C3.

186 P.E. Riley and R.E. Davis, Acta Crystallogr., Sect, B, B32 (1976) 381.

187 R.J. Restivo and G. Ferguson, J. Chem. Soc., Dalton Trans., (1976) 893.

188 K. Tatsumi and T. Fueno, Bull. Chem. Soc., Jpn., 49 (1976) 929.

189 H. Shechter, J. Suzanne and J.G. Dash, Phys. Rev. Lett., 37 (1976) 706.

190 L.I. Denisovich, I.A. Suskina and S.P. Gubin, Nov. Polyarogr., Tezisy Dokl. Vses. Soveshch. Polyarogr., 6th (1975) 133; Chem. Abstr., 86 (1977) 23505.

191 H. Lumbroso and D.M. Bertin, J. Organometal. Chem., 108 (1976) 111.

192 F.A. Adedeji, L.D.S.Brown, J.A. Connor, M. Leung, I.M. Paz-Andrade and H.S. Skinner, Conf. Int. Thermodyn. Chim., (C.R.), 4th, 1 (1975) 85.

193 D.L.S. Brown, J.A. Connor, M.L. Leung, M.I. Paz-Andrade and H.A. Skinner, J. Organometal. Chem., 110 (1976) 79.

194 M.R. Willcott, W.H. Bearden, R.E. Davies and R. Pettit, Org. Magn. Reson., 7 (1975) 557.

195 N.S. Nametkin, S.P. Gubin, A.I. Nekhaev and V.D. Tyurin, J. Organometal. Chem., 114 (1976) 299.

196 N.S. Nametkin, A.I. Nekhaev, S.P. Gubin and V.D. Tyurin, Izv. Akad. Nauk SSSR., Ser. Khim., (1976) 1636.

197 D. Leibfritz and H. tom Dieck, J. Organometal. Chem., 105 (1976) 255.

198 M. Brookhart, T.H. Whitesides and J.M. Crockett, Inorg. Chem., 15 (1976) 1550.

199 L. Kruczynski and J. Takats, Inorg. Chem., 15 (1976) 3140.

200 P.A. Dobosh, D.G. Gresham, C.P. Lillya and E.S. Magyar, J. Amer. Chem. Soc., 15 (1976) 2311.

201 P. McArdle and H. Sherlock, J. Chem. Soc., Chem. Commun., (1976) 537.

202 J.N. Gerlach, R.M. Wing and P.C. Ellgen, Inorg. Chem., 15 (1976) 2959.

203 J. Elzinga and H. Hogeveen, Tetrahedron Lett., (1976) 2383.

204 T.H. Whitesides and J.P. Neilan, J. Amer. Chem. Soc., 98 (1976) 63.

205 R.S. Sapienza, P.E. Riley, R.E. Davis and R. Pettit, J. Organometal. Chem., 121 (1976) C35.

206 A.J. Pearson, Aust. J. Chem., 29 (1976) 1841.

207 G.A. Olah, G. Liang and S.H. Yu, J. Org. Chem., 41 (1976) 2227.

208 R.E. Graf and C.P. Lillya, J. Organometal. Chem., 122 (1976) 377.

209 R.W. Arhart, Diss. Abstr. Int. B,36 (1976) 4475.

210 C.A. Mansfield, K.M. Al-Kathumi and L.A.P. Kane-Maguire, Proc. Int. Conf. Coord. Chem., 16th, (1974) 4.21.

211 B.M. Chisnall, M. Green, R.P. Hughes and A.J. Welch, J. Chem. Soc., Dalton Trans., (1976) 1899.

212 M. Green and R.P. Hughes, J. Chem. Soc., Dalton Trans., (1976) 1907.

213 A.J. Birch and A.J. Pearson, J. Chem. Soc., Chem. Commun., (1976) 601.

214 G. Cardaci and S. Sorriso, Inorg. Chem., 15 (1976) 1242.

215 J.W. Burrill, B.R. Bonazza, D.W. Garrett and C.P. Lillya, J. Organometal. Chem., 104 (1976) C37.

216 A. Vessieres, D. Touchard and P. Dixneuf, J. Organometal. Chem., 118 (1976) 93.

217 D.C. Sayles (US Dept. of the Army) US Pat., 3954527, 1976, May 4; Chem. Abstr., 85 (1976) 162920.

218 N.S. Nametkin, L.P. Kolesnikova, V.D. Tyurin, A.I. Nekhaev and L.G. Potapova, Neftekhimiya, 15 (1975) 763.

219 N.S. Nametkin, L.P. Kolesnikova, V.D. Tyurin, A.I. Nekhaev,

A.V. Topchiev and I.M. Gubkin (Institute of Petrochemical Synthesis) USSR Pat. 449639, 1975 Sept. 5; Chem. Abstr., 84 (1976) 98945.

220 A. Vessieres and P. Dixneuf, J. Organometal. Chem., 108 (1976) C5.

221 R.C. Kerber and E.A.K. Von Gustorf, J. Organometal. Chem., 110 (1976) 345.

222 J.M. Savariault and J.F. Labarre, Inorg. Chim. Acta, 19 (1976) L53.

223 G.G. Alexandrov, G.P. Zol'nikova, I.I. Kritskaya and Yu. T. Struchkov, Koord, Khim., 2 (1976) 272.

224 D.H. Finseth, C. Scurisseau and F.A. Miller, J. Phys. Chem., 80 (1976) 1248.

225 J.A. Connor, L.M.R. Derrick, I.H. Hillier, M.F. Guest and D.R. Lloyd, Mol. Phys., 31 (1976) 23.

226 E.S. Magyar and C.P. Lillya, J. Organometal. Chem., 116 (1976) 99.

227 P.S. Nielson, R.S. Hansen and H.J. Jakobsen, J. Organometal. Chem., 114 (1976) 145.

228 G.A. Olah and G. Liang, J. Org. Chem., 41 (1976) 2659.

229 H. Kisch, Proc. Int. Conf. Coord. Chem., 16th (1974) 3.21.

230 P.J. Harris, J.A.K. Howard, S.A.R. Knox, R.P. Phillips, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1976) 377.

231 A. Sanders and W.P. Giering, J. Organometal. Chem., 104 (1976) 49.

232 C.S. Eschbach, D. Seyferth and P.C. Reeves, J. Organometal. Chem., 104 (1976) 363.

233 J. Meinwald and J. Mioduski, Tetrahedron Lett., (1974) 3839.

234 D.F. Hunt and J.W. Russell, J. Organometal. Chem., 104 (1976) 373.

235 R.B. King and C.A. Harmon, Inorg. Chem., 15 (1976) 879.

236 F.R. Young, D.H. O'Brien, R.C. Pettersen, R.A. Levenson and D.L. von Minden, J. Organometal. Chem., 114 (1976) 157.

237 A.R.L. Bursics, E. Bursics-Szekeres, M. Murray and F.G.A. Stone, J. Fluorine Chem., 7 (1976) 619.

238 B.F.G. Johnson, J. Lewis and D. Wege, J. Chem. Soc., Dalton Trans., (1976) 1874.

239 J.D. Edwards, J.A.K. Howard, S.A.R. Knox, V. Riera, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1976) 75.

240 G. Dettlaf and E. Weiss, J. Organometal. Chem., 108 (1976) 213.

241 A.J. Carty, N.J. Taylor and C.R. Jablonski, Inorg. Chem., 15 (1976) 1169.

242 J.J. Guy, B.E. Reichert and G.M. Sheldrick, Acta Crystallogr., Sect. B, B32 (1976) 2504.

243 J.H. Eekhof, H. Hogeveen, R.M. Kellogg and G.A. Sawatzky, J. Organometal. Chem., 111 (1976) 349.

244 R. Aumann, Chem. Ber., 109 (1976) 168.

245 R. Hoffmann and P. Hofmann, J. Amer. Chem. Soc., 98 (1976) 598.

246 C.A. Mansfield and L.A.P. Kane-Maguire, J. Chem. Soc., Dalton Trans., (1976) 2187.

247 L.A.P. Kane-Maguire and C.A. Mansfield, J. Chem. Soc., Dalton Trans., (1976) 2192.

248 A.J. Campbell, C.E. Cottrell, C.A. Fyfe and K.R. Jeffrey, Inorg. Chem., 15 (1976) 1321.

249 F.A. Cotton and D.L. Hunter, J. Amer. Chem. Soc., 98 (1976) 1413.

250 A.J. Carty, C.R. Jablonski and V. Snieckus, Inorg. Chem., 15 (1976) 601.

251 L.J. Todd, J.P. Hickey, J.R. Wilkinson, J.C. Huffman and K. Folting, J. Organometal. Chem., 112 (1976) 167.

252 D.A. Brown, S.K. Chawla and W.K. Glass, Inorg. Chim. Acta., 19 (1976) L31.

253 P. McArdle and H. Sherlock, Proc. Int. Conf. Coord. Chem., 16th, (1974) R89.

254 N.G. Connelly and R.L. Kelly, J. Organometal. Chem., 120 (1976) C16.

255 J.H. Eekhof, H. Hogeveen and R.M. Kellogg, J. Chem. Soc., Chem. Commun., (1976) 657.

256 H. Sakurai, J. Hayashi and T. Kobayashi, J. Organometal. Chem., 110 (1976) 303.

257 J. Shelly, Diss. Abstr. Int. B, 36 (1976) 4496.

258 G.R. John and L.A.P. Kane-Maguire, J. Organometal. Chem., 120 (1976) C45.

259 G.R. John, L.A.P. Kane-Maguire and D.A. Sweigart, J. Organometal. Chem., 120 (1976) C47.

260 A.R. Banks, Diss. Abstr. Int. B, 36 (1976) 5584.

261 A.J. Birch and A.J. Pearson, J. Chem. Soc., Perkin Trans. 1 (1976) 954.

262 A.J. Pearson, Aust. J. Chem., 29 (1976) 1101.

263 K.E. Hine, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1976) 1702.

264 M. Brookhart, G.O. Nelson, G. Scholes and R.A. Watson, J. Chem. Soc., Chem. Commun., (1976) 195.

265 D.J. Thompson, J. Organometal. Chem., 108 (1976) 381.

266 B.F.G. Johnson, J. Lewis, J.E. Ryder and M.V. Twigg, J. Chem. Soc., Dalton Trans., (1976) 421.

267 W. Firk, Helv. Chim. Acta, 59 (1976) 276.

268 P. McArdle and H. Sherlock, J. Organometal. Chem., 116 (1976) C23.

269 Z. Goldschmidt and Y. Bakal, Tetrahedron Lett., (1976) 1229.

270 L.K.K. Li Shing Man and J. Takats, J. Organometal. Chem., 117 (1976) C104.

271 M.J. Bennett, J.L. Pratt, K.A. Simpson, L.K.K. Li Shing Man and J. Takats, J. Amer. Chem. Soc., 98 (1976) 4810.

272 A. Eisenstadt, J. Organometal. Chem., 113 (1976) 147.

273 R. Aumann and J. Knecht, Chem. Ber., 109 (1976) 174.

274 A.D. Charles, P. Diversi, B.F.G. Johnson and J. Lewis J. Organometal. Chem., 116 (1976) C25.

275 A.D. English, J.P. Jesson and C.A. Tolman, Inorg. Chem., 15 (1976) 1730.

276 M. Cooke, J.A.K. Howard, C.R. Russ, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1976) 70.

277 A.J.P. Domingos, J.A.S. Howell, B.F.G. Johnson and J. Lewis, Inorg. Synth., 16 (1976) 103.

278 H.A. Bockmeulen, R. Grant Holloway, A.W. Parkins and B.R. Penfold, J. Chem. Soc., Chem. Commun., (1976) 298.

279 R. Aumann, Angew. Chem., 88 (1976) 375.

280 R.G. Sutherland, S.C. Chen, W.J. Pannekoek and C.C. Lee, J. Organometal. Chem., 117 (1976) 61.

281 D. Astruc and R. Dabard, Bull. Soc. Chim. Fr., 1-2 (1976) 228.

282 D. Astruc and R. Dabard, Bull. Soc. Chim. Fr., (1975) 2571.

283 D. Astruc and R. Dabard, Tetrahedron, 32 (1976) 245.

284 E. Roman, D. Astruc and A. Darchen, J. Chem. Soc., Chem. Commun., (1976) 512.

285 J.F. McGreer and W.E. Watts, J. Organometal. Chem., 110 (1976) 103.

286 G.G. Cash, Diss. Abstr. Int. B, 36 (1976) 63156.

287 H. Buerger and C. Kluess, Z. Anorg. Allg. Chem., 423 (1976) 112.

288 T.J. Barton, I.N. Douglas, R. Ginter and A.J. Thomson, J. Chem. Soc., Dalton Trans., (1976) 1948.

289 V.T. Aleksanyan, B.N. Lokshin, G.K. Borisov, G.G. Devyatykh, A.S. Smirnov, R.V. Nazarova, J.A. Koningstein and B.F. Gachter, J. Organometal. Chem., 124 (1977) 293.

290 O. Traverso, S. Sostero and R. Rossi, Proc. Int. Conf. Coord. Chem. 16th (1974) 3.39.

291 S. Sostero, O. Traverso and G.A. Mazzochin, Atti Accad. Peloritana Pericolanti, Cl. Sci. Fis., Mat. Nat., 54 (1974) 367; Chem. Abstr., 85 (1976) 10853.

292 A.N. Nesmeyanov, G.B. Shul'pin, D.V. Zagorevskii and M.I. Rybinskaya, Dokl. Akad. Nauk SSSR, 229 (1976) 881.

293 R. Epton, S.R. Holding, G. Marr, J.V. McLaren and G.J. Morgan, J. Organometal. Chem., 112 (1976) 89.

294 M. Wenzel, N. Subramanian and E. Nipper, Naturwissenschaften, 63 (1976) 341.

295 M.A. Bennett, T.W. Matheson, G.B. Robertson, A.K. Smith and P.A. Tucker, J. Organometal. Chem., 121 (1976) C18.

296 K. Yasufuku and H. Yamazaki, J. Organometal. Chem., 121 (1976) 405.

297 P.E. Riley and R.E. Davis, J. Organometal. Chem., 113 (1976) 157.

298 J.W. Lauher, M. Elian, R.H. Summerville and R. Hoffmann, J. Amer. Chem, Soc., 98 (1976) 3219.

299 A. Almenningen, E. Gard, A. Haaland and J. Brunvoll, J. Organometal. Chem., 107 (1976) 273.

300 K.R. Gordon and K.D. Warren, J. Organometal. Chem., 117 (1976) C27.

301 V.I. Telnois, I.B. Rabinovich and K.V. Kiryanov, Conf. Int. Thermodyn. Chim., (C.R.), 4th, 9 (1975) 12; Chem. Abstr., 84 (1976) 96268.

302 I.B. Rabinovich, V.P. Nistratov, M.S. Sheiman and G.V. Burchalova, Conf. Int. Thermodyn. Chim., (C.R.), 4th, 9 (1975) 69; Chem. Abstr., 84 (1976) 96307.

303 F. H. Kohler, J. Organometal. Chem., 110 (1976) 235.

304 F.H. Kohler, J. Organometal. Chem., 121 (1976) C61.

305 M.B. Dines, Ger. Pat., 2551409, 1976, Aug. 12; Chem. Abstr., 85 (1976) 192898.

306 Y. Wakatsuki and H. Yamazaki, Synthesis (1976) 26.

307 N. El Murr, J. Organometal. Chem., 112 (1976) 177.

308 N. El Murr, J. Organometal. Chem., 112 (1976) 189.

309 J.E. Sheats, E.J. Sabol, D.Z. Denney and N. El Murr, J. Organometal. Chem., 121 (1976) 73.

310 A.N. Nesmeyanov, N.N. Rukhlyada, E.V. Leonova, N.S. Kochetkova and N.V. Bychkov, USSR Pat. 494397, 1975, Dec. 5; From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki, 52 (1975)

67; Chem. Abstr., 85 (1976) 6350.
311 J.E. Sheats, C.H. Carraher, D. Bruyer and M. Cole, Am. Chem. Soc., Div. Org. Coat. Plast. Chem., Pap., 34 (1974) 474; Chem. Abstr., 85 (1976) 33435.
312 R. Weiss and R.N. Grimes, J. Organometal. Chem., 113 (1976) 29.
313 B. Walther, R. Mahrwald, C. Jahn and W. Klar, Chem. Ber., 109 (1976) 2382.
314 V. Baetzel and G. Schmid, Chem. Ber., 109 (1976) 3339.
315 G. Schmid, V. Baetzel and B. Stutte, J. Organometal. Chem., 113 (1976) 67.
316 H. Alper, H. Des Abbayes and D. Des Roches, J. Organometal. Chem., 121 (1976) C31.
317 V. Baetzel, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 31B (1976) 342.
318 J.C. Kotz, J.V. Petersen and R.C. Reed, J. Organometal. Chem., 120 (1976) 433.
319 S. Aime, L. Milone and M. Valle, Inorg. Chim. Acta, 18 (1976) 9.
320 D. Seyferth, M.O. Nestle and C.S. Eschbach, J. Amer. Chem. Soc., 98 (1976) 6724.
321 D. Seyferth and C.L. Nivert, J. Organometal. Chem., 113 (1976) C65.
322 G. Calvarin and D. Weigel, J. Appl. Crystallogr. 9 (1976) 212.
323 C. Azokpota, G. Calvarin and C. Pommier, J. Chem. Thermodyn., 8 (1976) 283.
324 W.T. Scroggins, M.F. Rettig and R.M. Wing, Inorg. Chem., 15 (1976) 1381.
325 R.R. Corderman and J.L. Beauchamp, Inorg. Chem., 15 (1976) 665.
326 I. Pavlik and E. Kustkova-Maxova, Sb. Ved. Pr., Vys. Sk. Chemickotechnol., Pardubice, 32 (1974) 11; Chem. Abstr., 85 (1976) 93221.
327 L.M. Dyagileva and L.M. Pudeev, Tr. Khim. Khim. Tekhnol., (1975) 86; Chem. Abstr., 85 (1976) 123085.
328 P. Eilbracht, Chem. Ber., 109 (1976) 3136.
329 C. Moberg and M. Nilsson, Tetrahedron Lett., (1974) 4521.
330 F. Mathey and G. Sennyey, J. Organometal. Chem., 105 (1976) 73.
331 F. Mathey and D. Thavard, J. Organometal. Chem., 117 (1976) 377.
332 J.L. Davidson and D.W.A. Sharp, J. Chem. Soc., Dalton Trans., (1976) 1123.
333 L.K. Templeton, D.H. Templeton and R. Walker, Inorg. Chem., 15 (1976) 3000.
334 R.G. Hayes and N. Edelstein, J. Am. Chem. Soc., 94 (1972) 8688.
335 N. Edelstein, A. Streitwieser, D.G. Morrell and R. Walker, Inorg. Chem., 15 (1976) 1397.
336 J.P. Clark and J.C. Green, J. Organometal. Chem., 112 (1976) C14.