ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1978*

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

CONTENTS

---

* Selected π-Complexes, Annual Survey covering the year 1977 see J. Organometal. Chem., 163(1978)325-452.

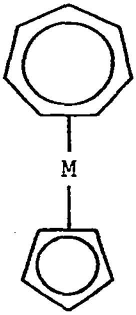
1. REVIEWS

Klabunde has surveyed the types of reactions that may occur between metal atoms and organic ligands. The reaction types have been classified as cluster formation, oxidative addition, abstraction, electron transfer and simple orbital mixing (π or σ complexation). Bis(η-arene) complexes of titanium, vanadium and chromium were discussed under the last heading [1]. The hydrogenation of aromatic ligands during the arene-cyclopentadienyl ligand exchange reactions of ferrocene and arenes in the presence of aluminium chloride has been surveyed [2]. Sarel has surveyed metal induced rearrangements and insertions into cyclopropylolefins. The similarity between cyclopropyl rings and olefins was emphasized [3]. Kochetkova and Krynkina have reviewed the uses of η-cyclopentadienyl-transition metal complexes [4].

The use of (η-arene)metal complexes in the synthesis of organic compounds has been discussed by Semmelhack [5]. The 1976 literature of η-cyclopentadienyl, η-arene and related complexes has been reviewed briefly [6]. The organometallic chemistry of the transition metals for the year 1976 has been reviewed by Pearce, Thompson and Twigg [7]. Allen and Palmer have reviewed the chemistry of the borabenzene anion and some of its transition metal complexes [8]. The applications of cobalt carbonyl acetylene complexes to organic synthesis have been discussed by Pauson and Khand [9]. Noyori has discussed the use of iron carbonyls in organic synthesis [10]. Davidson has reviewed substitution reactions of organometallic compounds including cymantrene, tricarbonyl(η-cyclobutadiene)iron, ferrocene and tricarbonyl(η-diene)-iron complexes [11]. The same author has discussed the reactions of ligands, including η-polyenes, coordinated to transition metals [12]. The chemistry of (η-cyclopentadienyl)metal complexes with simple ligands has been surveyed [13].

2. GENERAL RESULTS

Clack and Warren have carried out INDO SCF MO calculations for several d^6 sandwich complexes including $(\eta\text{-}C_5H_5)_2Fe$, $(\eta\text{-}C_6H_6)_2Cr$, $(\eta\text{-}C_6H_6)(\eta\text{-}C_7H_7)Cr$, $(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)Mn$ and $(\eta\text{-}C_5H_5)_2Co^+$ and for complexes derived from these species by addition of an electron. In each case, with the exception of $(\eta\text{-}C_5H_5)_2Co$, the additional electron was expected to lie in a ligand orbital and the complex formed to be less stable than the parent d^6 system [14]. INDO SCF MO calculations on the neutral compounds (2.1; M = Ti,V,Cr) and on the cations of the vanadium and chromium compounds have predicted correctly $^1A_1$ ground states for the species (2.1; M = Ti,Cr) and for the cation of the vanadium compound. The $^2A_1$ ground states for the neutral compound (2.1; M = V) and the cation of the chromium compound were confirmed. The sequence of energy levels for the formal metal d-orbitals was $e_2 < a_1 < e_1$ and the important bonding interactions were between metal e_2 and η-cycloheptatrienyl ligand π-orbitals and between metal e_1 and η-cyclopentadienyl π-orbitals. The calculations indicated also that



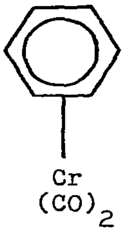
2.1

metal e_2-ligand interactions became more important and metal e_1-ligand interactions less important as the size of the ligand ring increased [15].

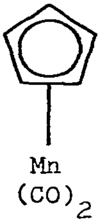
Thorn and Hoffmann have carried out a systematic MO study of the electronic structure of complexes containing the $M_2(CO)_6$ binuclear transition-metal fragment bonded to a variety of ligands. Orientational preferences of ligands such as acetylene, dienes, tetramethyleneethane, cyclobutadiene, pentalene, cycloheptatrienyl, azulene and cyclooctatetraene were discussed and the reactivity and stability of known and uncharacterized complexes were considered [16]. INDO SCF molecular orbital calculations have been carried out for a number of diamagnetic sandwich, mixed sandwich and related tricarbonyl complexes of the first row transition elements and for the free ligands. The π-bond orders of the C-C linkages of the ligands all showed a reduction on complex formation, and the ^{1}H NMR shift for a given proton, relative to that of the free ligand showed a linear correlation with the corresponding change in the charge density at the proton. It was concluded that there was an appreciable diminution in the aromatic character of the ligands on complex formation [17].

Self consistent charge and configuration molecular orbital theory (SCCCMO method) has been used to obtain values of half the partial valence-inactive populations ($\underline{P}_A{}^{LUMO}$) for two series of polyene-$M(CO)_3$ complexes, $AM(CO)_3$ where $AM = (\eta\text{-}C_6H_6)Cr$, $(\eta\text{-}C_5H_5)Mn$, $(\eta\text{-}C_4H_4)Fe$, $(\eta\text{-}C_3H_5)Co$, $(\eta\text{-}C_2H_4)Ni$ and $[BFe(CO)_3]^+$ where $B = \eta\text{-}C_5H_5$, $\eta\text{-}C_6H_7$, $\eta\text{-}C_7H_9$. The $\underline{P}_A{}^{LUMO}$ values were used as a measure of frontier electron density for nucleophilic reactions to give an indication of the relative $\underline{S}_N2$ reactivity in these molecules. It was concluded for both series $AM(CO)_3$ and $[BFe(CO)_3]^+$ that nucleophilic substitution by an $\underline{S}_N2$ process would probably occur by initial attack at the metal atom [18]. Pauling has used the theory of hybrid bond orbitals to obtain a relationship between the metal-carbonyl bond number and the OC-M-CO bond angle in compounds containing a transition metal tricarbonyl group with the metal in an enneacovalent or octacovalent form. The values obtained for the iron tricarbonyl and cobalt tricarbonyl groups were 94.5° and 101.9° respectively and were within 1° of the experimental values. The experimental values for chromium tricarbonyl and manganese tricarbonyl indicated the average covalence to be about 7.7 and 8.4 respectively [19].

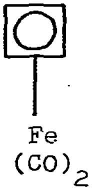
The UV photolysis of benchrotrene, cymantrene, tricarbonyl(η-cyclobutadiene)iron and tricarbonyl(η-trimethylenemethane)iron in argon and methane matrices at 12° K gave the corresponding coordinatively unsaturated dicarbonyl species (2.2, 2.3, 2.4, 2.5) respectively. The reactions were reversed by visible light for the chromium and iron complexes but not for the manganese complex. The results were discussed in terms of coordinatively unsaturated species as intermediates in solution-phase ligand displacement reactions [20]. Green



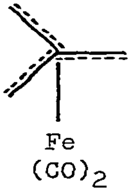
2.2



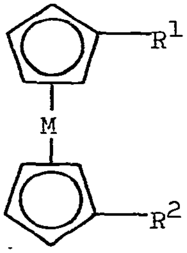
2.3



2.4



2.5

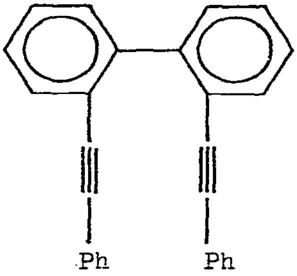


2.6

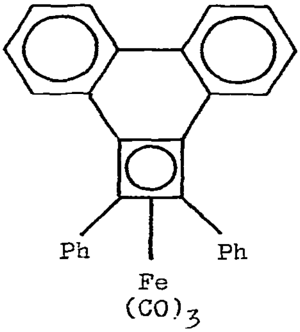
has claimed a process for the manufacture of bis(η-arene)transition metal complexes in which metal atoms and the hydrocarbon ligand were evaporated successively under vacuum on to the liquid nitrogen cooled wall of a rotating flask [21]. Heat capacity measurements on chromocene, ruthenocene, cobaltocene and nickelocene were made in the temperature range $120-200^{\circ}$ K using a microcalorimeter. Cp curves were obtained for all four metallocenes and first-order phase transitions were observed for chromocene and nickelocene with entropies of transition of 1.5 and 5.2 J K^{-1}mol^{-1} respectively [22].

Disubstituted metallocenes (2.6; R^1, R^2 = H, OH, CHO, CO$_2$H, halogen, CO halogen, α-hydroxyalkyl, alkoxycarbonyl; M = Cr, Mn, Fe, Ru, Co, Ni) have been used in radiation resist compositions for the fabrication of semiconductor devices and integrated circuits [23]. The electronic spectra of the metallocenes and 1,1'-dimethylmetallocenes (2.6; $R^1 = R^2$ = H, Me; M = V, Cr, Mn, Fe, Co, Ni) have been measured in isooctane and assignments have been made for the d-d and charge-transfer transitions observed. The charge-transfer bands for the vanadium, chromium, manganese and iron metallocenes corresponded to ligand → metal excitations ($e_{2u} \rightarrow e_{2g}$, a_{1g}, e_{1g}) while for cobaltocene and possibly nickelocene evidence was obtained also for metal → ligand excitations ($e_{1g} \rightarrow e_{2u}$). Paramagnetic susceptibilities were measured by the NMR or Gouy methods for the vanadium, chromium, cobalt and nickel metallocenes. The Curie-Weiss law was obeyed by the vanadium, chromium and nickel compounds while cobaltocene showed substantial deviation from it [24].

The bonding in several open-shell metallocenes, their molecular ions and ferrocenes have been investigated by CNDO and INDO molecular orbital calculations. Unrestricted eigen functions were obtained and it was concluded that the INDO calculations gave a more satisfactory description of the ground and open-shell states [25]. The mass spectra of cobaltocene, nickelocene and several other metallocenes have been recorded and studied [26]. The diphenyldiacetylene (2.7) combined with iron pentacarbonyl to form the (η-cyclobuta[l]phenanthrene) complex (2.8) by intramolecular cyclodimerization. The corresponding (η-cyclobuta[l]phenanthrene)(η-cyclopentadienyl)cobalt complex was formed when the reagent was dicarbonyl(η-cyclopentadienyl)cobalt.



2.7

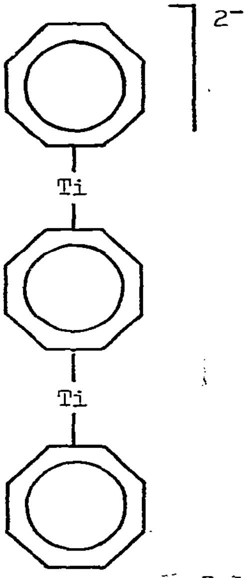


2.8

The crystal and molecular structure of the analogous rhodium complex was determined by X-ray crystallography [27].

3. $(\eta\text{-}C_8H_8)_3Ti$

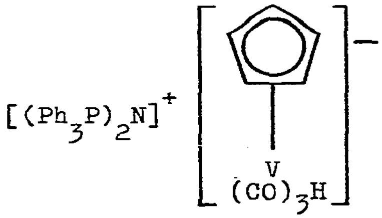
Tris(cyclooctatetraene)titanium was reduced by potassium to give a green diamagnetic anion the properties of which were consistent with the formulation of the species as the triple-decker dianion (3.1) [28].



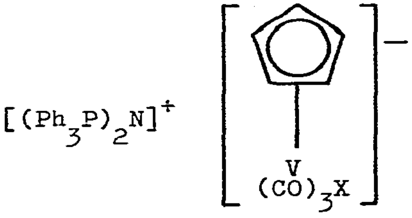
3.1

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

Reduction of tetracarbonyl(η-cyclopentadienyl)vanadium gave the corresponding dianion as the sodium salt. Protonation of the sodium salt with water followed by cation exchange with $[(Ph_3P)_2N]^+Cl^-$ gave the hydrido-vanadate (4.1). The hydride (4.1) was treated with a wide range of organic halides to give the corresponding halide complex (4.2; X = halogen) together with the parent hydrocarbon. The mechanism of this halide exchange reaction was discussed and compared with halide reductions carried out with tri-_n_-butyltin hydride [29, 30]. When tetracarbonyl(η-cyclopentadienyl)vanadium was irradiated in the presence of the bidentate ligands L-L [L-L = $Ph_2AsCH_2CH_2AsPh_2$ (dpase), $Ph_2AsCH_2CH_2PPh_2$ (arphos) and _o_-phenylenebis(dimethylarsine) (diars)] the corresponding dicarbonylvanadium derivatives (4.3) were formed. ^{51}V NMR shifts were used to place the ligands arphos, dpase and diars

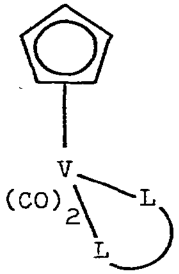


4.1

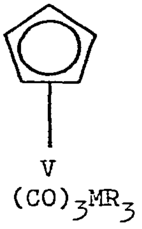


4.2

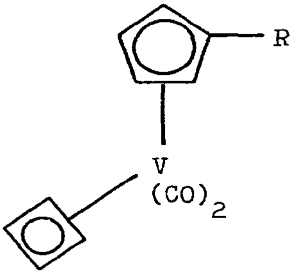
in a series of increasing ligand strength which was $Ph_3As \approx dpase \approx$ arphos (As) $<$ diars $<$ arphos (As,P) $<$ arphos (P) $\approx PEtPh_2$ [31].



4.3



4.4



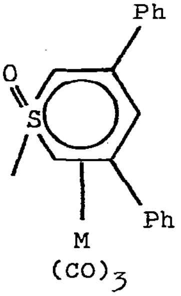
4.5

Tetracarbonyl(η-cyclopentadienyl)vanadium was irradiated in the presence of the ligands MR_3 [MR_3 = $AsPh_3$, $AsMe_2Ph$, $AsEt_3$, $As(OEt)_3$, $SbPh_3$, $SbEt_3$, $Sb(OEt)_3$, $BiEt_3$] to give the corresponding tricarbonyl complexes (4.4). Infrared evidence was used to arrange the ligands in the order of their increasing π-acceptor strength: $MEt_3 < MEt_2Ph \leqslant MPh_3 < M(OEt)_3$ where M = As, Sb or Bi. This order was independent of the donor atom M. On the basis of ^{51}V NMR chemical shifts the ligands were arranged in the following sequences of increasing overall ligand strength: $MPh_3 < MMe_2Ph = MEt_3 < M(OEt)_3$ (M = P, As), and $BiEt_3 < AsR_3 < PR_3 < SbR_3$ [32]. The (η-cyclobutadiene)(η-cyclopentadienyl)vanadium complexes (4.5; R = H, COMe) were formed by photolysis of α-pyrone with tetracarbonyl(η-cyclopentadienyl)vanadium or the acetyl derivative [33].

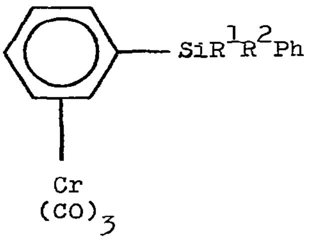
5. $(\eta\text{-}C_6H_6)Cr(CO)_3$

(i) Formation

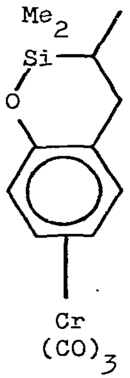
1-Methyl-3,5-diphenylthiabenzene-1-oxide was treated with the tris(acetonitrile)tricarbonyl-metal complexes of chromium, molybdenum and tungsten to give the corresponding tricarbonyl-metal complexes (5.1; M = Cr, Mo, W). An X-ray analysis was carried out on the two isomers of the complex (5.1; M = Cr) and it was found that the heterocyclic ligand was non-planar and that there was no bonding between the metal and the sulphur atom [34]. (η-Arsabenzene)tricarbonylmolybdenum was prepared by the reaction of the arene with hexacarbonylmolybdenum. Tricarbonyl(η-stibabenzene)molybdenum was prepared by the boron trifluoride ether catalysed reaction of stibabenzene with



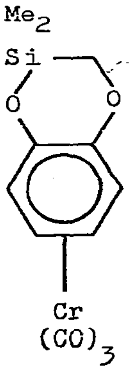
5.1



5.2



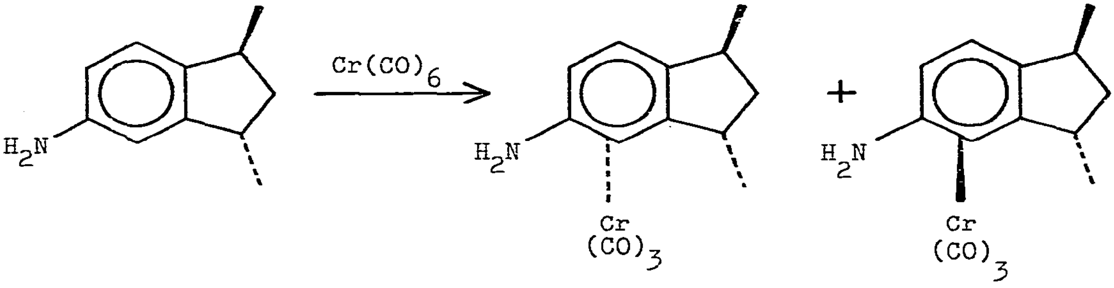
5.3



5.4

tricarbonyltris(pyridine)molybdenum. ^{13}C NMR and infrared data indicated that stibabenzene was a more powerful π-base than arsabenzene [35]. Hexacarbonylchromium was treated with phenylsilanes to give the tricarbonylchromium derivatives (5.2; $R^1 = R^2 = OH$; $R^1 = H$, $R^2 = Me$; 5.3 and 5.4) [36], Reaction of [2.2]orthocyclophane with hexacarbonylchromium gave [2]orthocyclo[2](1,2)benchrotrenophane which was used for configurational and conformational studies [37].

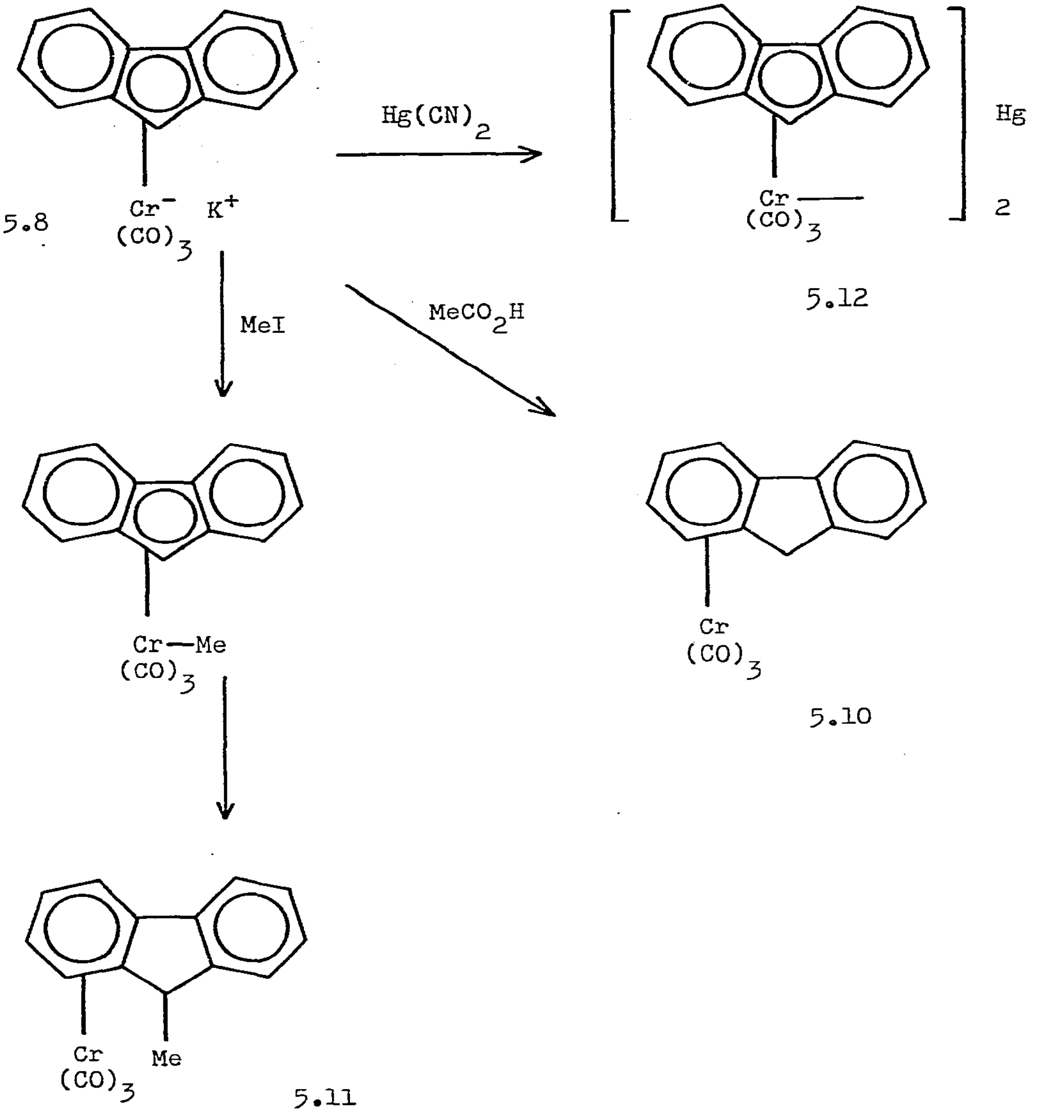
Reaction of trans-1,3-dimethylindan-5-amine (5.5) with hexacarbonylchromium gave a mixture of the diastereoisomers (5.6 and 5.7) [38].



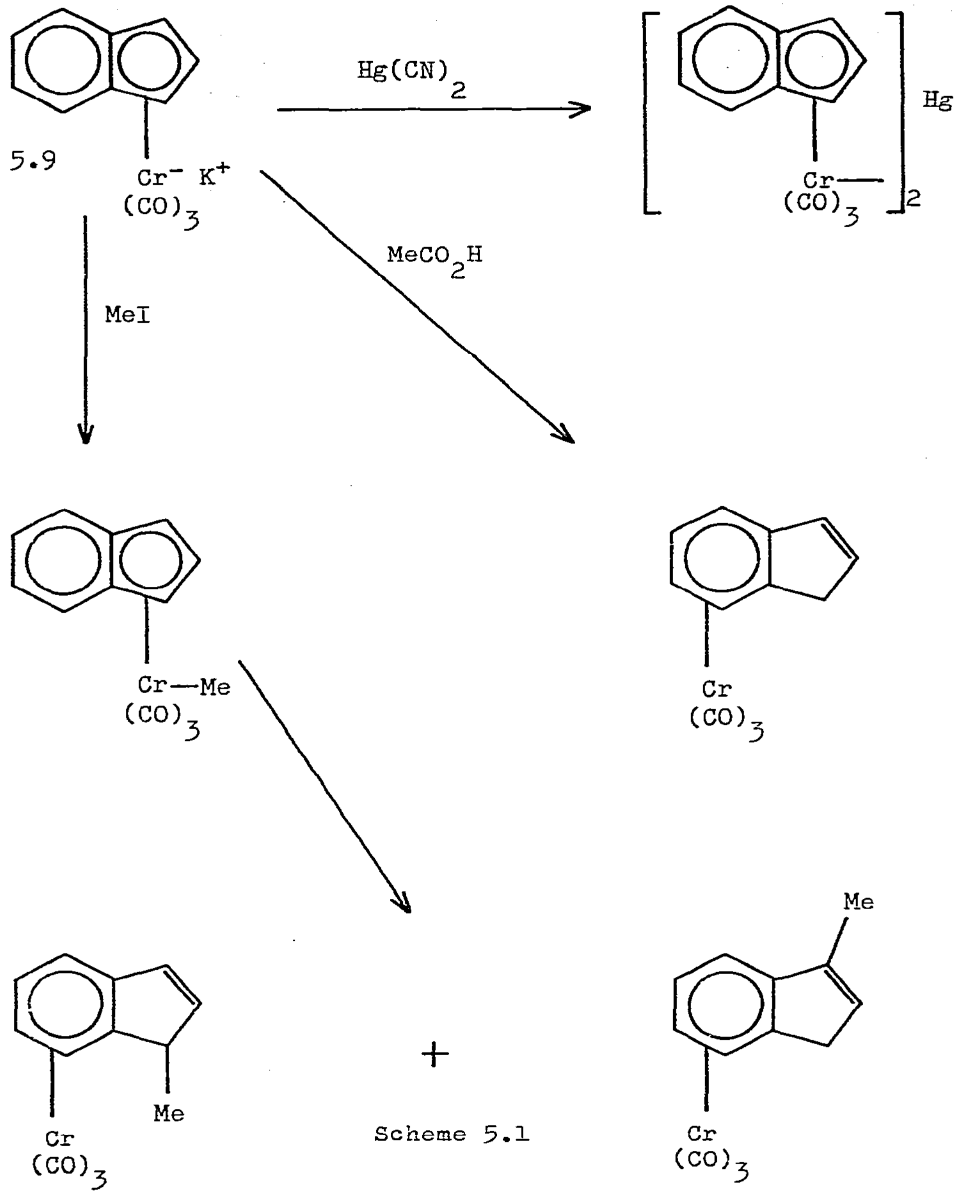
5.5 5.6 5.7

The η-fluorenyl and η-indenyl anions (5.8 and 5.9; M = Cr, Mo, W) were prepared. The reactions of these anions (5.8 and 5.9) with acetic acid, methyl iodide and mercury (II) cyanide were investigated. The first two reagents caused reduction of the cyclopentadienyl ring of the ligand to give the benchrotrenes (5.10 and 5.11) while mercury (II) cyanide gave the binuclear complex (5.12). Similar reactions were observed for the (η-indenyl)chromium complex (5.9) as outlined in Scheme 5.1 [39]. The reaction between bis(diethylamino)acetylene and pentacarbonyl[methoxy(phenyl)carbene]chromium at 14^{o} gave the pentacarbonylchromium carbene, $(OC)_5Cr{=}C(NEt_2)C(NEt_2){=}C(OMe)Ph$ which on heating to 75^{o} was converted to the metallocyclobutene (5.13). Further heating at 125^{o} gave the tricarbonyl(η-indene)chromium complex (5.14) in 75% yield [40].

Tricarbonylchromium complexes of benzodiazaboroles and phenylboranes were obtained by treatment of the appropriate ligand with hexacarbonylchromium or tris(acetonitrile)tricarbonylchromium. Where the tricarbonylchromium group was able to select between arene and heterocyclic rings then the former were invariably chosen. ^{11}B NMR chemical shifts were discussed in terms of chromium 3d orbital

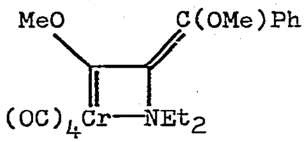


interaction with the arene $\pi^*\perp$ orbital. The benzodiazaborole (5.15) and the phenylborane (5.16) were typical of the complexes examined [41]. Treatment of the carbenes $(CO)_5Cr{=}C(OMe)R$, (R = p-MeC_6H_4, p-$CF_3C_6H_4$, 1-, 2-naphthyl, 2-, 3-furyl, 2-thienyl, cyclopentyl) and $(CO)_5Cr{=}CR^1R^2$ (R^1 = Ph, p-MeC_6H_4, R^2 = 2-furyl, 2-naphthyl) with the acetylenes $R^3C\equiv CR^4$ gave the tricarbonylchromium complexes (5.17; $R^3 = R^4$ = Ph, R^5 = Me, CF_3), (5.18; $R^3 = R^4$ = Ph, $R^6 = R^7$ = OH, OMe), (5.19; X = O, S; R^3 = Ph, Pr; R^4 = H, Ph; R^6, R^7 = OH, OMe) and (5.20; R^2 =

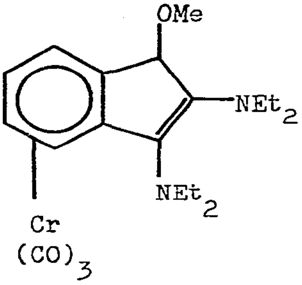


Scheme 5.1

2-furyl, 2-naphthyl, p-MeC_6H_4; $R^3 = R^4 = Ph$, $R^5 = H$, Me). In these reactions the phenyl group in the carbenes $(OC)_5Cr:CR^1R^2$ was anellated rather than the furyl and naphthyl rings [42]. Reaction of benzo-1,2,3,6-diazaborines with the hexacarbonyls of chromium, molybdenum and tungsten gave the corresponding tricarbonylmetal complexes (5.21; M = Cr, Mo, W; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = Me$, $R^2 = H$).

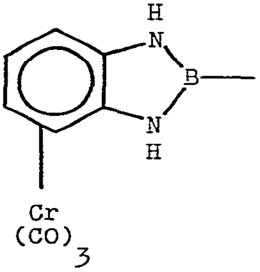


5.13

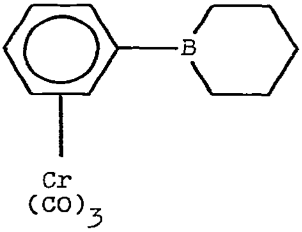


5.14

It was concluded that benzo-1,2,3,6-diazadiborine ligands exhibited better π-donor properties than benzene [43].

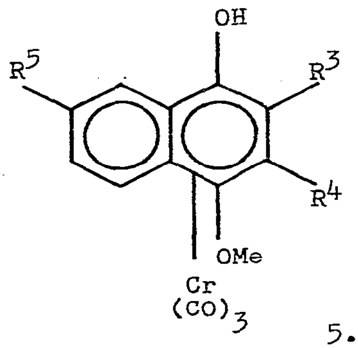


5.15

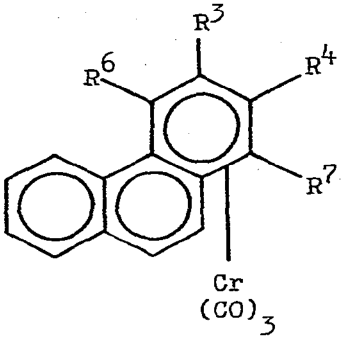


5.16

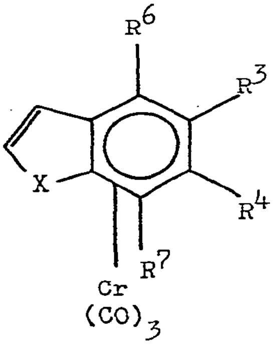
Several arenotropones have been heated with chromium hexacarbonyl to form the corresponding tricarbonyl (η-triene) chromium complexes. Benzotropones formed complexes such as the dimethyl derivative (5.22) in which the benzene ring was bound to chromium while thiopheno- and furano-tropones formed complexes such as (5.23; X = O, S) respectively in which the tropone ring was bound to the metal [44]. Treatment of trichlorotris(tetrahydrofuran)-molybdenum with tertiary phosphines gave the molybdenum complexes $MoCl_3(PR_3)(C_4H_8O)_2$ where $PR_3 = PMe_3$, PMe_2Ph. Alkylation of these latter complexes with dimethylmagnesium in the presence of an arene gave the corresponding η-arene-methyl complexes (5.24; $R^1 = R^2 = R^3 = H$; $R^1 = R^2 = Me$, $R^3 = H$; $R^1 = R^3 = Me$, $R^2 = H$). Reaction of the η-benzene complex (5.24; $R^1 = R^2 = R^3 =$



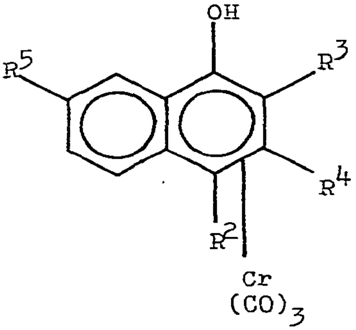
5.17



5.18

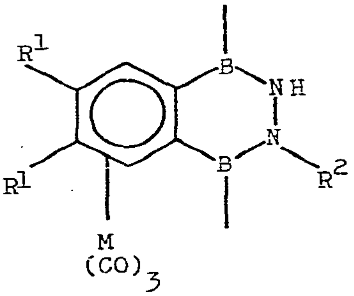


5.19

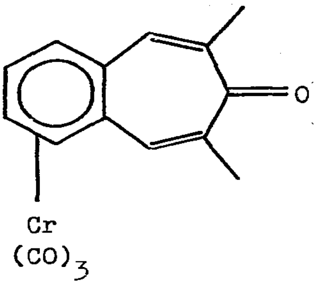


5.20

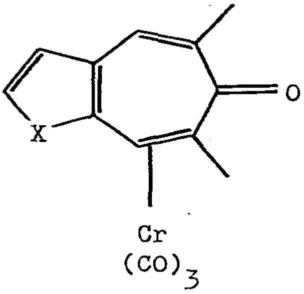
H; PR_3 = PMe_2Ph) with carbon monoxide gave the corresponding carbonyl complex (5.25) which was converted in acetone to the tris(tertiary



5.21

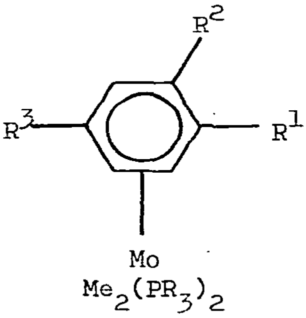


5.22

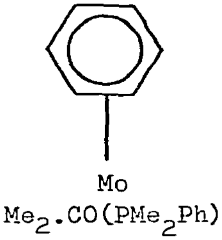


5.23

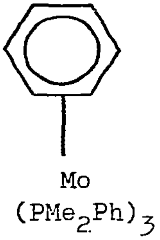
phosphine) complex (5.26) [45]. Reaction of tricarbonyltris(methyl cyanide)chromium with azulene and 4,6,8-trimethylazulene gave the



5.24



5.25

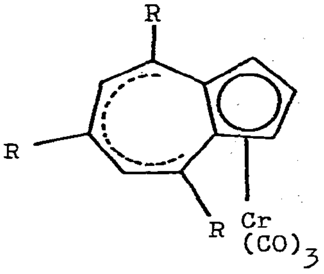


5.26

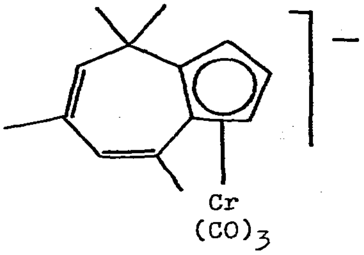
corresponding tricarbonylchromium complexes (5.27; R = H, Me). The complex (5.27; R = Me) underwent nucleophilic addition on treatment with methyllithium to give the anion (5.28) which was isolated as the tetramethylammonium salt [46].

(ii) Spectroscopic and Physico-chemical Studies

Clack and Kane-Maguire have carried out INDO molecular orbital calculations on the benzyl carbenium ion and the (η-benzyl)tricarbonylchromium cation (5.29). The results indicated that the high stability of the cation was derived to a large extent from back donation of electron density from the metal $d_{x^2-y^2}$ orbital to the non-bonding π-orbital of the benzyl ligand in which C(7) is strongly implicated [47]. The crystal and molecular structures of the two isomeric tricarbonylchromium

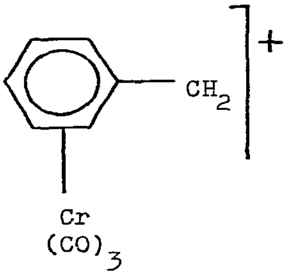


5.27

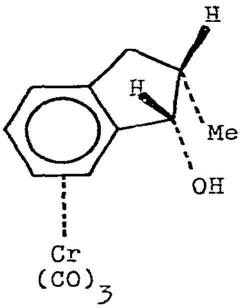


5.28

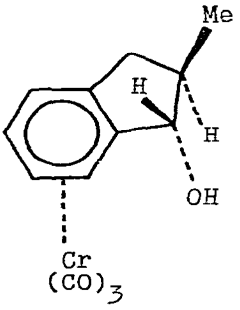
complexes (5.30 and 5.31) were determined by X-ray analysis [48].



5.29



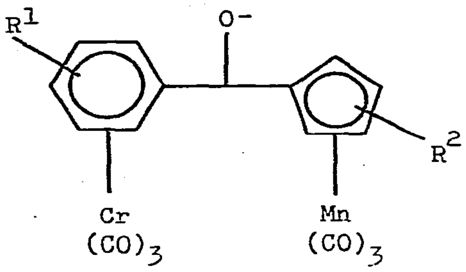
5.30



5.31

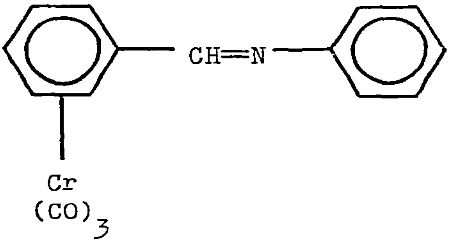
The ESR spectra for several tricarbonylchromium(benzoylcyclopentadienyl)manganese tricarbonyl complexes (5.32; R^1 = H, *o*-, *m*-, *p*-Me, *p*-MeO; R^2 = H, α-, β-Me) have been measured and interpreted. The tricarbonylchromium group withdrew spin density from both the phenyl protons and the manganese atom to the extent that the hyperfine coupling constant A(H) was reduced by one half and A(Mn) by one third. Comparison of the experimental results with values calculated by the extended Hückel method indicated that there was extensive delocalization of spin density over the organic moiety and considerable π-overlap between the chromium atom and the benzene ring [49].

An electron impact study was carried out on the two isomeric tricarbonylchromium complexes of N-benzylideneaniline (5.33 and 5.34). Under electron impact the complexes (5.33 and 5.34) decarbonylated completely before the chromium-ring bond broke and the azomethine ligand

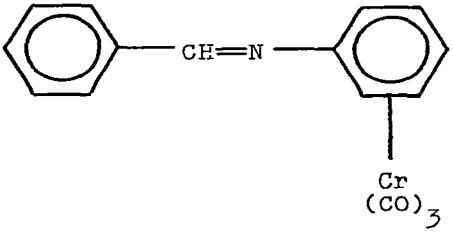


5.32

underwent further fragmentation. The stable benzylideneaniline-chromium cations decomposed mainly by fission of the metal-ring bond

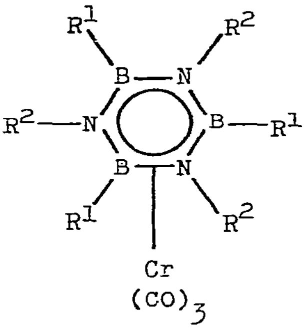


5.33

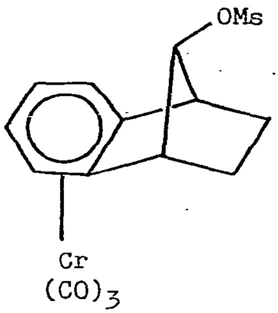


5.34

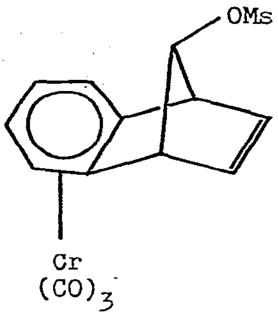
although other fragmentation pathways were observed [50]. A kinetic study of the displacement of the borazole ligand from the (η-borazole)-chromium complexes (5.35; R^1 and R^2 = Me, Et, Pr^n, Pr^i) by tertiary phosphines indicated that steric factors were dominant in determining the rate of reaction. The ligand-metal bond enthalpy was determined as 25±3 kcal mol^{-1} which was appreciably less than the value for the corresponding (η-hexaalkylbenzene)chromium bond [51]. The rates of formolysis of the <u>endo</u>-tricarbonyl(η-benzonorbornenyl)-chromium complexes (5.36 and 5.37; MS = methanesulphonate) have been compared with the rates for the corresponding <u>exo</u>-complexes and for the free benzonorbornene ligands. Direct d-orbital participation in the reaction was not observed and the rate differences for formation of the unrearranged ester products were explained on the basis of ion-



5.35



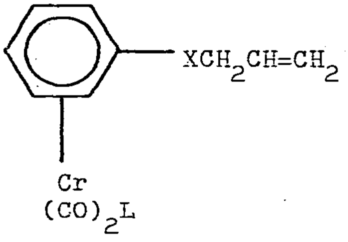
5.36



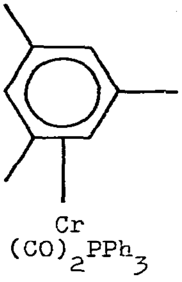
5.37

-dipole interactions in the transition state [52].

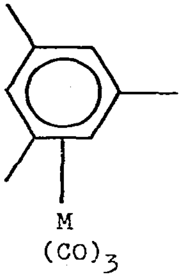
Ultraviolet irradiation of the dicarbonylchromium complexes



5.38



5.39



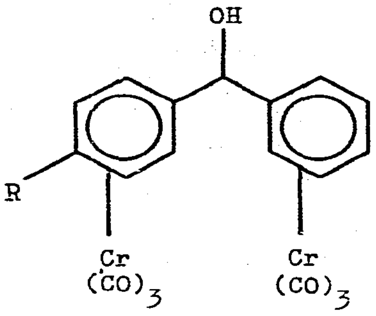
5.40

[5.38; X = O, CH_2; L = PPh_3, $P(OPh)_3$, P $(OEt)_3$, PMe_2Ph] resulted in rapid displacement of the ligand L and coordination of the pendant olefin. Displacement of the phosphine also occurred on irradiation of the complex (5.39) in the presence of <u>cis</u>-cyclooctene. The two complexes (5.38; X = O, CH_2; L = CS) decomposed when irradiated [53]. Tricarbonyl(η-mesitylene)chromium (5.40; M = Cr) and the corresponding molybdenum and tungsten complexes (5.40; M = Mo, W) formed a continuous range of mixed crystals. The last two complexes were isomorphous but the chromium complex (5.40; M = Cr) showed a different crystal form. The solid state IR and Raman spectra of the mixed crystals showed one-mode behaviour for the ν(CO) modes while all other modes showed two-mode behaviour [54].

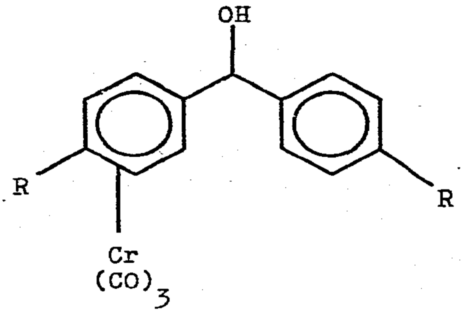
The ^{13}C NMR spectra of (η-indane)-, (η-biphenyl)-, (η-naphthalene)- and (η-phenanthrene)-chromiumtricarbonyl have been measured and assigned. It was found that the ^{13}C shift induced by the chromium tricarbonyl group in the coordinated ring was little affected by the structure of the other parts of the ligand. The upfield shift of the coordinated ring carbon resonances was ~35ppm relative to the free ligand while the shift for the uncomplexed parts of the ligand was much smaller. It was concluded that there was no metal exchange between the rings of the ligand [55]. The rate constants $\underline{k}_{ex}$ for electron exchange between the bis(η-arene)chromium complexes (arene = toluene, p-xylene, mesitylene, durene) and the corresponding radical cations were calculated from ^{1}H NMR line broadening data. The values obtained, $\underline{k}_{ex} = 3.8 \times 10^{8}$ l mol^{-1} sec^{-1} and $\underline{E}_{a} = 8.6$ kJ mol^{-1} approached values for diffusion controlled reactions. The degree of methylation of the η-arene group had little effect on the rate of electron exchange [56].

The large upfield change in ^{13}C chemical shifts in aromatic ring systems when they are incorporated into transition metal π-complexes was investigated by solid state NMR studies of (η-ArH)Cr(CO)$_3$ (ArH = benzene, hexamethylbenzene, hexaethylbenzene). The shift was attributed to a large (>50ppm) increase in screening when the external magnetic field was in the plane of the aromatic ring along the bonds to the substituents [57]. Polarographic reduction of alkylbenchrotrenes gave a single two-electron wave while acetylbenchrotrene showed two consecutive one-electron waves. Both alkyl and acetyl complexes showed reversible cyclic voltammograms. Tricarbonyl(η-cycloheptatriene)-chromium displayed a single irreversible wave on cyclic voltametry. Electrochemical reduction of tricarbonyl(η-naphthalene)chromium gave a stable dianion which was electrochemically oxidized to the original complex. Alkali metal reduction of the 2,3-dimethyl derivative of this complex gave first a Cr(-I) species and than a Cr(-II) dianion [58]. A series of arylmethanol derivatives complexed with the tricarbonylchromium group (5.41; R = H, Me, OMe), (5.42; R = H, Me, OMe) and (5.43; R = H, Me) and attached to ferrocene (5.44; R = H, Me) were prepared. The $\underline{pK}_{R^+}$ values of ionization of these metallocenylmethyl alcohols were measured to give data on the relative stabilities of the corresponding carbenium ions. It was concluded that the cation stabilizing ability of the tricarbonylchromium group was much lower than that of the ferrocenyl group [59].

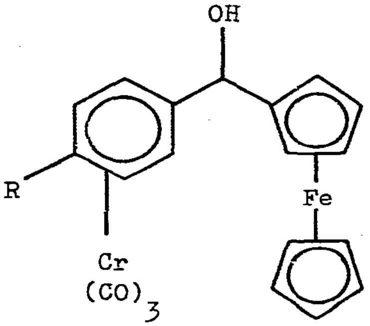
The coordination site of the tricarbonylchromium group and the nature of the metal-ligand bond have been explored by examining



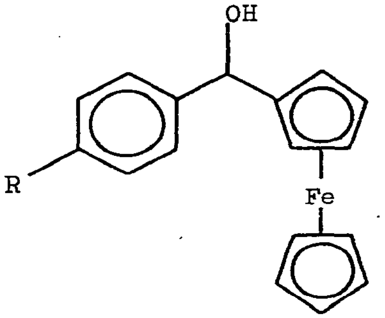
5.41



5.42

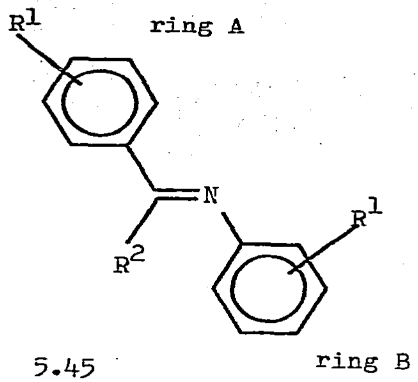


5.43

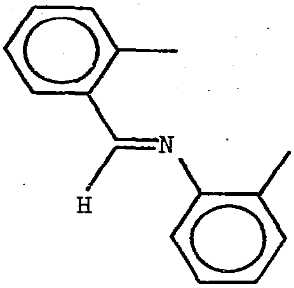


5.44

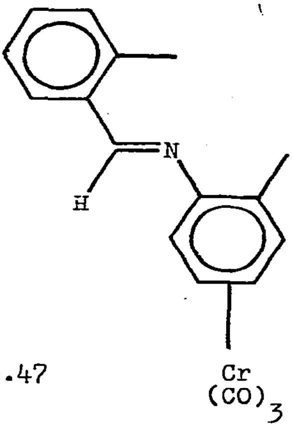
competition between two or three benzene rings in the same ligand for the tricarbonylchromium group. The complexes were formed by treatment of the ligand with chromium hexacarbonyl and complexation was observed on ring A, ring B or on both rings in the aldimines and ketimines (5.45; R^1 = H, Me; R^2 = H, Ph). Thus the aldimine (5.46) gave the complexes (5.47, 5.48 and 5.49) in yields of 77, 16 and 7% respectively. It was concluded that the three π-orbitals of the preferred benzene ring were selected on the basis of energy, representivity and symmetry and not simply on the basis of electron density [60]. Complexation with the chromium tricarbonyl group of one benzene ring in a rigid diaryl ketone followed by addition to the ketone group of a chiral and optically pure reagent gave ~40% asymmetric induction. Thus the chromium tricarbonyl complexes (5.50 and 5.51) were treated with the optically pure ester $BrMgCH_2CO_2$menthyl to form the β-hydroxy esters



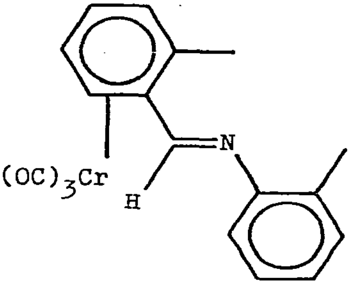
5.45



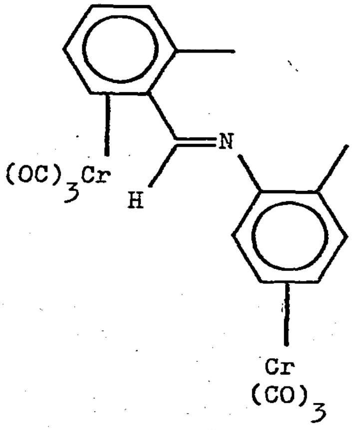
5.46



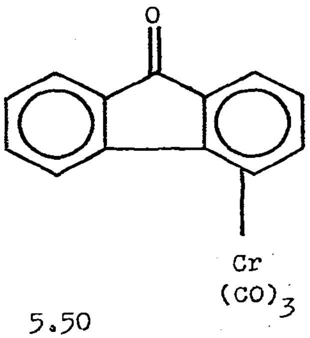
5.47



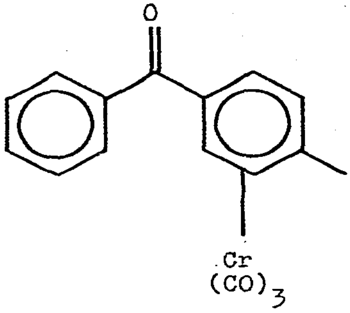
5.48



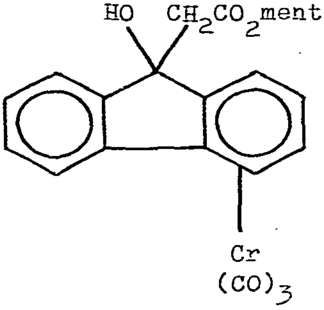
5.49



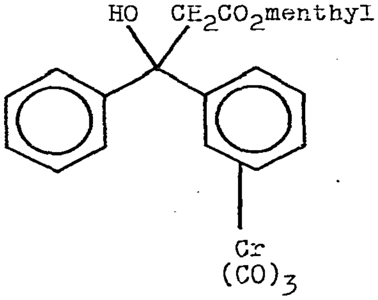
5.50



5.51



5.52

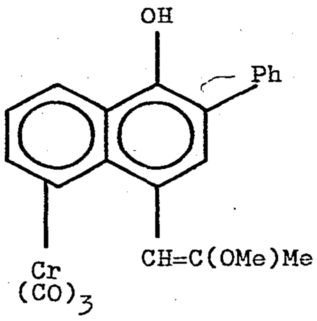


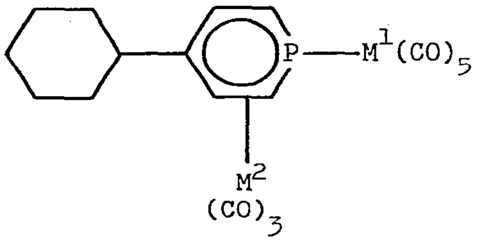
5.53

(5.52 and 5.53) as mixtures of diastereoisomers. The proportions of the isomers were determined by ^{13}C NMR spectroscopy. A symmetric induction in the non-rigid complex (5.53) was significantly smaller than for the rigid complex (5.52) [61]. Benchrotrene derivatives have been separated by gas chromatography using hydrocarbon stationary phases. The retention volumes were obtained and Kovats indexes were calculated. Chromatograms were recorded at several temperatures and used to calculate sorption heats for the compounds [62].

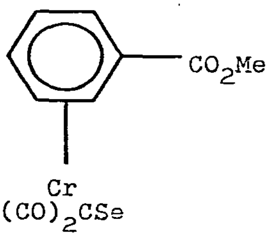
(iii) General Chemistry

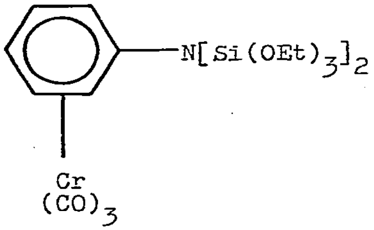
Jaouen has surveyed the applications of tricarbonyl(η-arene)-chromium compounds to the synthesis of organic compounds [63]. The reaction of pentacarbonyl(methoxymethylcarbene)chromium with phenylacetylene gave the tricarbonylchromium complex (5.54) [64]. The mixed σ,π-complexes of the 4-cyclohexylphosphorin ligand (5.55; $M^1 = M^2 =$ Cr, Mo) were formed by heating the ligand with the metal hexacarbonyl.


5.54

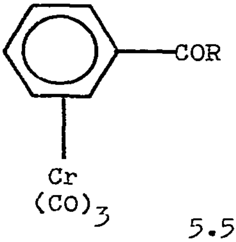

5.55

The mixed metal complex (5.55 M^1 = W, M^2 = Cr) was obtained by using σ-cyclo-$C_6H_{11}.C_5H_4P.W(CO)_5$ as the ligand and chromium hexacarbonyl as the reagent [65]. The crystal and molecular structure of selenocarbonyl benchrotrenyl analogue (5.56) has been determined by X-ray crystallography. It was concluded that the selenocarbonyl group was a stronger ligand than carbonyl [66].

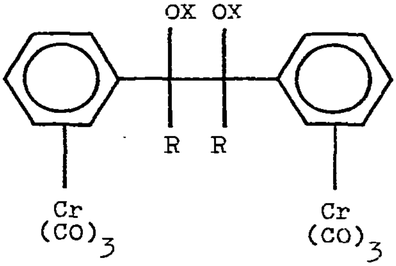

5.56


5.57

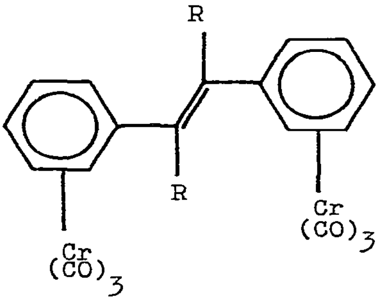
Nucleophilic aromatic substitution was achieved by sequential treatment of an (η-arene)tricarbonylchromium complex with a carbanion and iodine. Ester-, nitrile- and sulphur-stabilized carbanions, organo-lithium and -magnesium reagents all effected nucleophilic substitution. When the η-arene group had an electron donating substituent the ortho or para product was favoured but in the presence of an electron withdrawing substituent, the trimethylsilyl group, the para isomer was favoured [67]. Dicobalt octacarbonyl was active as a catalyst for the silylation of (η-aniline) tricarbonylchromium with triethoxysilane to give the N,N-disubstituted (η-aniline)chromium complex (5.57). Aniline and aliphatic amines were less reactive in the silylation than the (η-aniline)chromium complex [68]. Reductive dimerization of the benchrotrenyl ketones (5.58; R = Me, Et, Pr, Bu) with the titanium complex Mg-Hg-$TiCl_4$ gave the meso and racemic forms of the benchrotrenyl diol (5.59; R = Me, Et, Pr, Bu; X = H) together with the cis- and trans-benchrotrenyl ethylene (5.60; R = Me, Et, Pr, Bu). The isolation of both the meso and racemic forms of the diol (5.59; X = H) suggested that the titanium complex (5.59; R = Me, Et, Pr, Bu; X = $TiCl_2$) was an intermediate



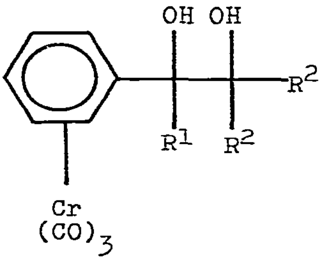
5.58



5.59

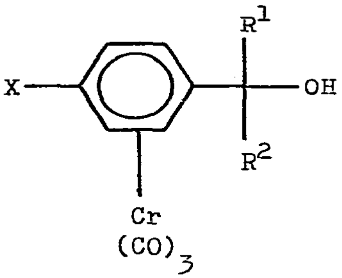


5.60

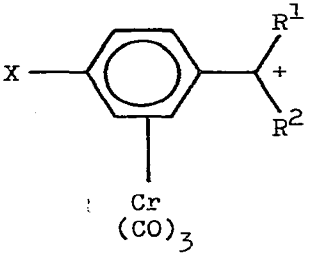


5.61

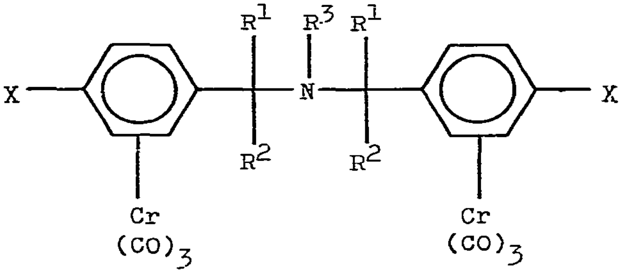
in the reaction. Reduction of the benchrotrenyl ketones (5.58) mixed with the aliphatic ketones R_2CO, where R = Me, Et, Pr, Bu gave the cross coupled diols (5.61; R^1 = Me, Et, Pr, Bu; R^2 = Me, Et, Pr, Bu) [69].



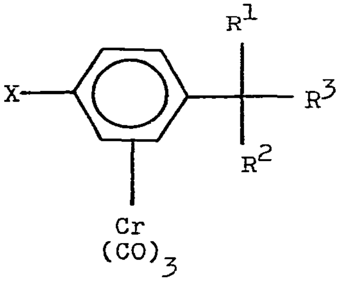
5.62



5.63

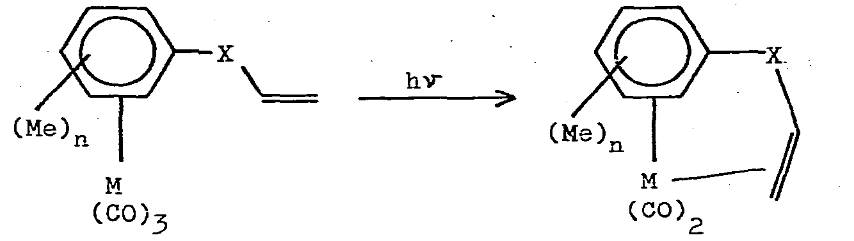


5.64

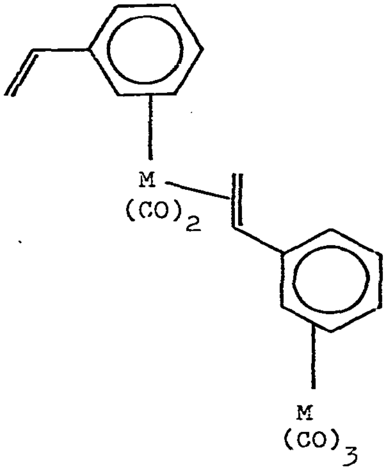


5.65

Reaction of the primary, secondary and tertiary alcohols (5.62; X = OMe, $R^1 = R^2 = H$; X = OMe, $R^1 = H$, $R^2 = Me$; X = OMe, $R^1 = R^2 =$ Me; X = H, $R^1 = H$, $R^2 = Ph$) with HPF_6 gave the corresponding carbenium ions (5.63). Treatment of these carbenium ions with ammonia, methylamine, dimethylamine, methanol and ethanol gave the tricarbonylchromium derivatives (5.64; R^3 = H, Me) and (5.65; $R^3 = NMe_2$, OMe, OEt) respectively [70]. A series of (η-alkenylarene)tricarbonylchromium, -molybdenum and -tungsten complexes [5.66; M = Cr, Mo, W; n = 0, 2, 3, 5; X = OCH_2, CH_2CH_2, CH_2OCH_2, $(CH_2)_3$, $(CH_2)_4$] were irradiated. Intramolecular cyclization occurred to give the corresponding dicarbonylmetal derivatives (5.67). Chelate compounds (5.67) were formed only if the bridging group X contained two or three atoms. Irradiation of tricarbonyl(η-styrene)-chromium and -molybdenum gave the corresponding dinuclear species (5.68; M = Cr, Mo) [71]. Photolysis of the (η-arene)-tricarbonylchromium complexes (arene = hexamethylbenzene, mesitylene, benzene) in the presence of cyclooctene followed by reaction with



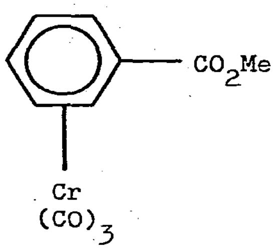
5.66 5.67



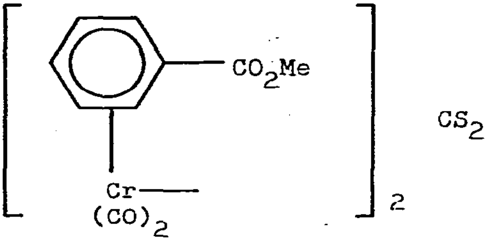
5.68

carbon disulphide gave the corresponding (η-arene)(carbon disulphide)-dicarbonylchromium complexes. Treatment of the latter compounds with trimethylphosphine gave the (η-arene)dicarbonylthiocarbonylchromium derivatives. In the analogous reaction of carbon disulphide with the chromium complex (5.69) the binuclear derivative (5.70) was formed which had a carbon disulphide bridge [72].

Ultraviolet irradiation of the tricarbonylchromium complexes (5.71; R = OPh, Ph n = 4, 5) gave the corresponding cyclic-chromium derivatives (5.72). Irradiation of the complex (5.73) gave the cyclic derivative (5.74) in only low yield (1%) [73]. Ultraviolet irradiation of the tricarbonylchromium complex (5.75) resulted in displacement of

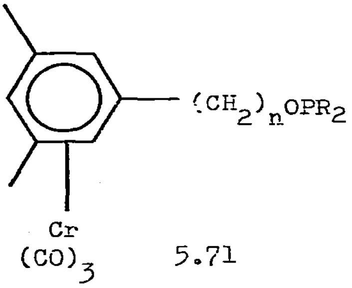


5.69

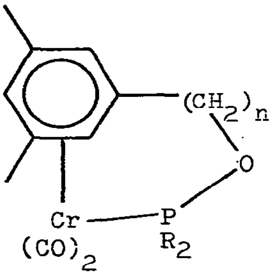


5.70

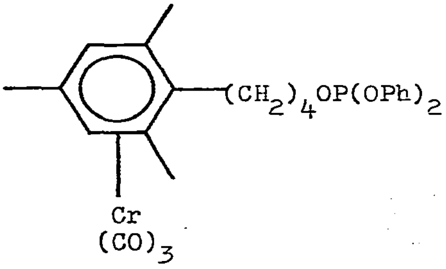
the three carbonyl groups to give the difluorophosphite derivative (5.76) [74]. Ultraviolet irradiation of the chromium complexes $(CO)_3$



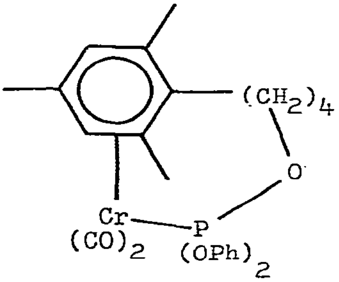
5.71



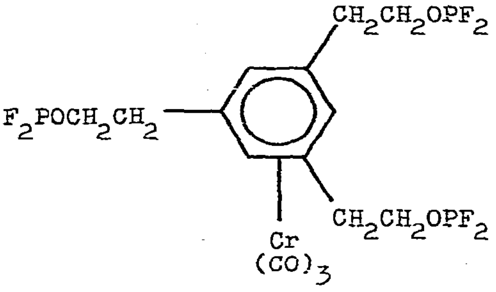
5.72



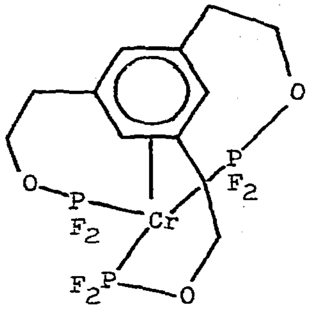
5.73



5.74

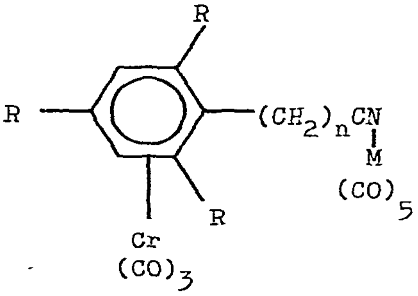


5.75

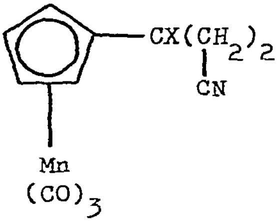


5.76

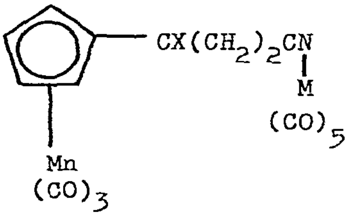
$Cr[C_6H_5(CH_2)_nCN]$ (n = 1, 3) in the presence of the metal carbonyls $M(CO)_6$ (M = Cr, W) gave the corresponding dimetal complexes (5.77).



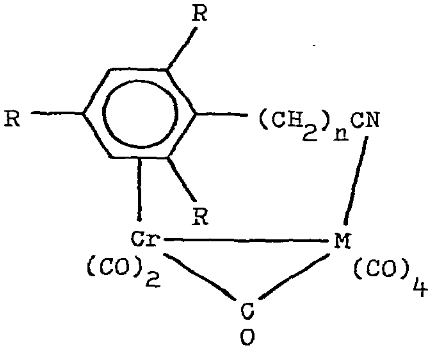
5.77



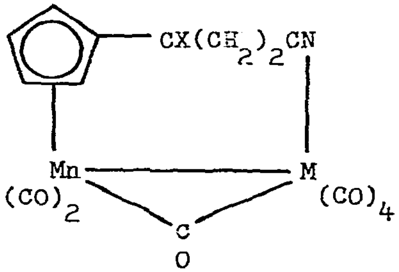
5.78



5.79



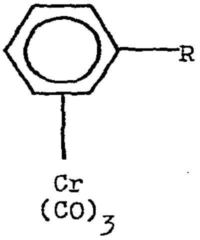
5.80



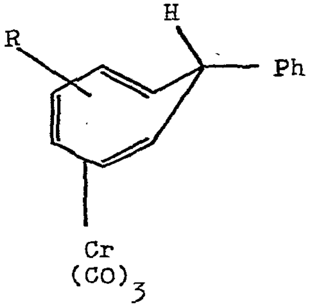
5.81

Similarly, irradiation of the cymantrene derivatives (5.78; X = H_2, O) in the presence of the same metal carbonyls gave the manganese complexes (5.79; M = Cr, W). Irradiation of the complexes (5.77 and 5.79) gave the cyclic species (5.80 and 5.81) respectively [75].

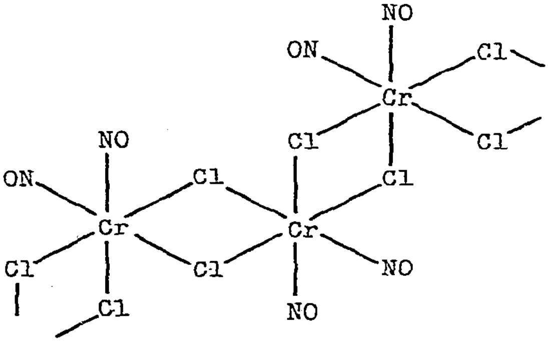
Stereospecific ring expansion of the tricarbonylchromium complexes (5.82; R = H, Et, Ph, $PhCH_2$, CH_2OH, NMe_2) by treatment with $PhCH_2Cl$--$LiN(CHMe_2)_2$ gave the corresponding endo-η-cycloheptatriene derivatives (5.83) with R in the 2 or 3 position [76]. Polymeric dichlorodinitrosyl chromium (5.84) was prepared by treating (η-benzene)tricarbonylchromium with nitrosyl chloride. This oxidative nitrosylation was studied in both tetrahydrofuran and dichloromethane. Solvent stabilized intermediates of the type [$CrCl(CO)_2NO$] were formed at low temperatures and converted into dinitrosylchromium complexes [$CrCl_2(NO)_2$] by further



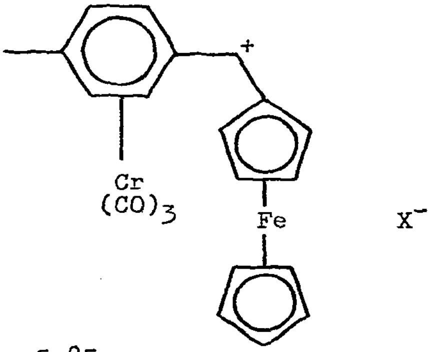
5.82



5.83



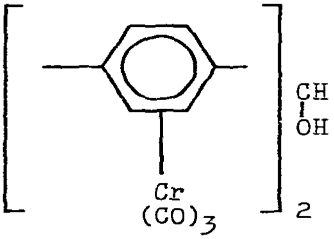
5.84



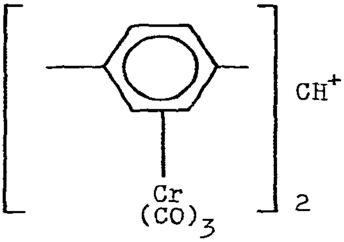
5.85

reaction with nitrosyl chloride [77]. Tricarbonyl (η-toluene)molybdenum and tricarbonyl(η-benzene)molybdenum have been used as catalysts for the epoxidation of cyclohexene with ethylbenzene hydroperoxide [78].

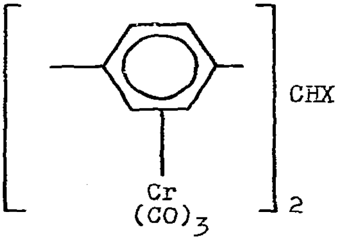
The reaction product of benchrotrene and the dimer $[Fe(NO)_2Cl]_2$ was a selective catalyst for the cyclodimerization of butadiene to 4-vinylcyclohexene at 80°. The same reaction of isoprene was also investigated. The catalyst was not efficient at room temperature [79]. Hydrogen tetrafluoroborate in propanoic acid anhydride was added to ferrocenyl-*p*-tolyltricarbonylchromium carbonyl and the carbenium ion (5.85; $X = BF_4^-$) was formed. When the same reaction was carried out in trifluoroacetic acid the carbenium ion (5.85; $X = CF_3CO_2^-$) was formed [80]. Di-*p*-tolylcarbinol combined with an excess of chromium hexacarbonyl in a diglyme-octane mixture to give bis(tricarbonyl-*p*-tolylchromium)carbinol (5.86) which was treated with hexafluorophosphoric



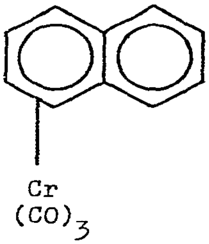
5.86



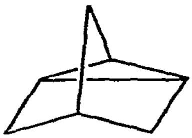
5.87



5.88



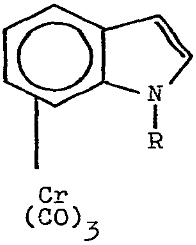
5.89



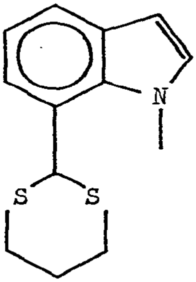
5.90

acid in propionic anhydride to form the carbenium ion (5.87) as the blue hexafluorophosphate. The carbenium ion (5.87) was attacked by alcohols, primary amines and secondary amines to form the derivatives (5.88; X = OR, NHR, NR_2) and was effective in alkylating highly nucleophilic aromatic and heterocyclic compounds such as N,N-dimethylaniline, pyrrole and N-methylpyrrole. Evidence for extensive delocalization of positive charge from carbon to chromium in the carbenium ion was obtained from ^{13}C NMR and infrared spectroscopy [81].

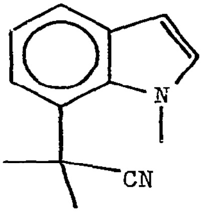
The tricarbonylchromium complexes of phenanthrene and naphthalene (5.89) have been used as catalysts for the stereospecific and regioselective hydrogenation of olefins. 1,4-Disubstituted butadienes underwent 1,4-addition of hydrogen with 95% regioselectivity while norbornadiene gave both the 1,4-adduct (5.90) in 80% yield and norbornene in 20% yield [82]. The tricarbonylchromium complexes (5.91; R = COMe, CO_2Et, Me) were prepared. Reaction of the complex (5.91, R = Me) with 2-lithio-1,3-dithian resulted in formation of the 7-substituted indole (5.92). A similar reaction of the complex (5.91; R = Me) with the anion prepared from isobutyronitrile gave the indole (5.93) [83]. Benchrotrene underwent ligand exchange with diphenylmercury to form bis(η-phenyltricarbonylchromium)mercury (5.94) which was then treated with n-butyllithium at -20° to give tricarbonyl(η-phenyllithium)chromium (5.95; R = Li). This intermediate was treated with carbon dioxide, trimethylchlorosilane, acetyl chloride, pyridine and diphenylchlorophosphine to form the benzoic acid (5.95; R = CO_2H), the trialkylsilane (5.95; R = $SiMe_3$), the acetophenone (5.95; R = COMe), the 2-pyridyl derivative (5.95; R = 2-C_5H_4N) and the triphenylphosphine (5.95; R = PPh_2) respectively [84].



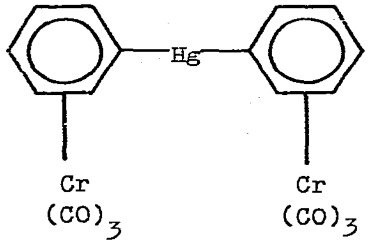
5.91



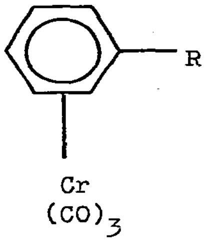
5.92



5.93

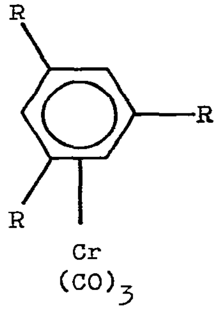


5.94

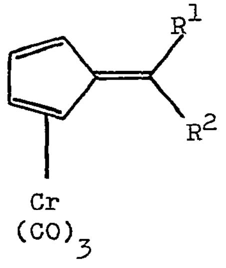


5.95

Displacement of the arene ligand from benchrotrenes (5.96; R = H, Me) by substituted fulvenes gave the (η-fulvene)chromium complexes (5.97; R^1 = Me, R^2 = Ph; $R^1 = R^2$ = p-ClC_6H_4) in quantitative yield [85]. The organic ligand was removed from a series of

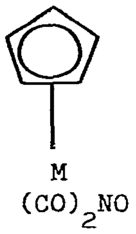


5.96

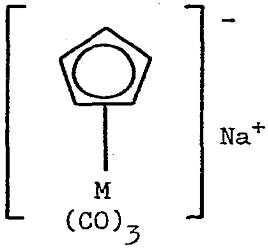


5.97

(η-arene)$Cr(CO)_3$ complexes (Arene = $PhNEt_2$, thiophen, PhCl, PhF, PhOMe, C_6H_6, naphthalene) by reaction with pyridine. The tricarbonylchromium part of the molecule was recovered in high yield as tricarbonyltris-(pyridine)chromium which was recycled to make new (η-Arene)$Cr(CO)_3$ complexes [86]. Dicarbonylnitrosyl(η-vinylcyclopentadienyl)chromium was homopolymerized and copolymerized with styrene, N-vinyl-2-pyrrolidone and vinylcymantrene in the presence of azo initiators. The molecular weight of the homopolymer increased with an increasing monomer-initiator ratio which suggested that the rate was not first order in initiator [87]. The preparation of the nitrosyl complexes (5.98; M = Cr, Mo, W) from the corresponding sodium salts (5.99) was



5.98

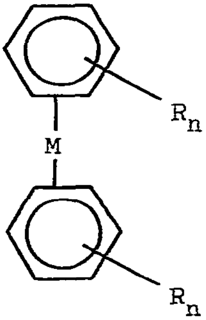


5.99

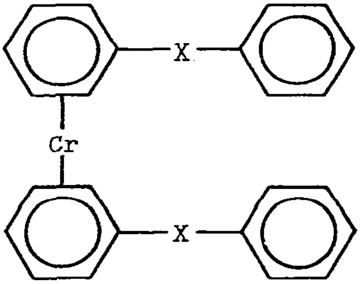
described in detail [88].

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

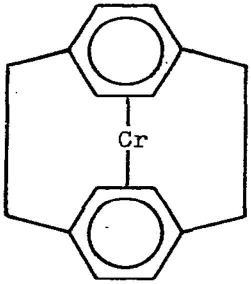
A study has been made of the composition of the organic impurities present in bis(η-ethylbenzene)chromium when it was prepared by the Friedel-Crafts reaction. The composition of the organic impurities was found to be independent of the metal present when molybdenum or tungsten replaced chromium in the reaction [89]. Bis(η-arene)metal complexes, including bis(η-1-methylnaphthalene)chromium and bis(η-toluene)-chromium and -molybdenum have been prepared by condensing potassium atoms into solutions containing arenes and metal halides at -100° [90]. Iron atoms and chromium atoms were cocondensed at low temperatures with toluene vapour and the vapours of the benzenoid



6.1



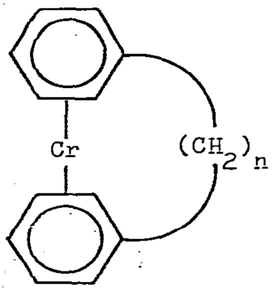
6.2



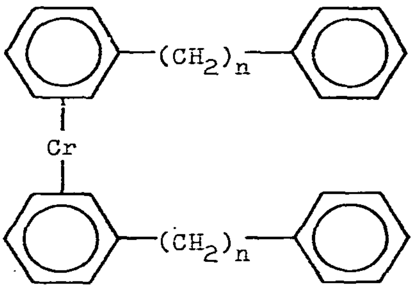
6.3

ligands 1,3,5-$Me_3C_6H_3$ and 1,2,4,5-$Me_4C_4H_2$ to form the corresponding bis(η-arene)metal complexes such as the (η-toluene) complexes (6.1; M = Cr, Fe; R = Me; n = 1). The identities of the complexes were confirmed by IR spectroscopy [91].

The cocondensation of chromium atoms with diphenylmethane, 1,4-diphenylbutane and benzyl ether afforded the corresponding chromium complexes [6.2; X = CH_2, $(CH_2)_4$, $(CH_2)_2O$]. Reaction of chromium atoms with benzyl sulphide resulted in desulphurization of the potential ligand [92]. Chromium atoms and [2,2]paracyclophane were cocondensed at low temperatures to give the chromium complex (6.3) together with a bis(η-paracyclophane)chromium complex [93]. Low temperature cocondensation of chromium atoms with acetophenone gave low yields (3%) of the chromium complex (6.1; M = Cr; R = COMe; n = 1) together with considerable amounds of (HO)MePhCCPhMe(OH) [94]. Cocondensation of 1,4-diphenylbutane and 1,5-diphenylpentane with chromium atoms at liquid nitrogen temperatures gave the [4]- and [5]-dibenzenechromocenophanes (6.4; n = 4, 5) respectively in addition to the disubstituted bis(η-benzene)chromium complexes (6.5; n = 4, 5), binuclear complexes were also isolated. The compounds were separated as the iodides $[(\eta\text{-Arene})_2\ Cr^+\ I^-]$ and converted back to the neutral complexes by reduction [95].

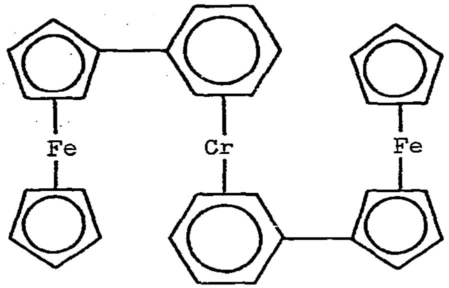


6.4

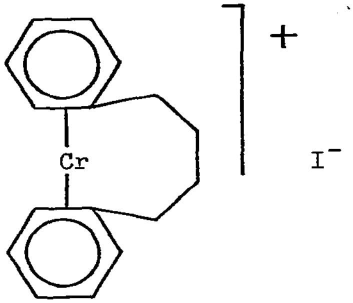


6.5

Reaction of phenylferrocene with chromium (III) chloride in the presence of aluminium chloride and aluminium gave the mixed ferrocene-chromium complex (6.6) [96]. Tungsten has been evaporated at rates of 5g h^{-1} with an electron gun and the tungsten atoms formed were cocondensed with benzene, toluene and mesitylene to give the bis(η-arene)



6.6



6.7

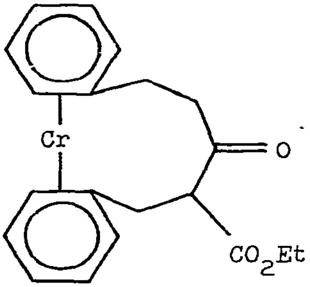
-metal complexes (6.1; M = W; R = H, Me; n = 1, 3) [97]. The ground state electronic structure of bis(η-benzene)chromium and the corresponding cation have been investigated by molecular orbital calculations based on the all-electron self-consistent-field multiple scattering $X\alpha$ method. In the ground state of both complexes, the level ordering for the highest occupied orbitals and the lowest unoccupied one was found to be:

$$e_{1u}(\eta\text{-}C_6H_6) < e_{1g}(\eta\text{-}C_6H_6) < e_{2g}(3d) < a_{1g}(3d) < e^*_{1g}(3d)$$

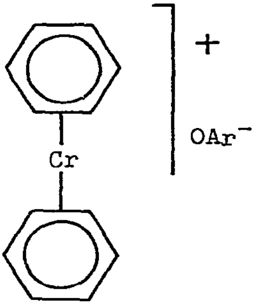
which was in agreement with experimental determinations. Ionization energies for bis(η-benzene)chromium were calculated and found to agree satisfactorily with photoelectron results. Calculated electronic excitation energies for both complexes enabled the optical and UV absorption spectra to be satisfactorily interpreted [98].

An attempt has been made to correlate the oxidative stability of the bis(η-arene)chromium compounds with the sum of the inductive parameters, the Hammett σ_m values, of the substituents. It was shown that the sum of the Hammett parameters, $\Sigma\sigma_m$, gave a good indication of the oxidative stability of a given bis(η-arene)chromium compound. It was also shown that ^1H and ^{13}C NMR chemical shifts for a series of unsymmetrical bis(η-arene)chromium derivatives correlated with $\Sigma\sigma_m$ and with the oxidative stability of the complex [99]. The crystal and molecular structure of the bis(η-benzene)chromium salt (6.7) has been determined by X-ray methods. The phenyl rings were found to be parallel indicating a strainless tetramethylene bridge [100]. X-ray crystallography has been used to determine the crystal and molecular structure of bis(η-ethylbenzene)chromium iodide monohydrate. The bis(η-ethylbenzene)chromium cations formed alternate layers with the iodide anions [101].

The heat capacity of bis(η-benzene)chromium has been determined over the temperature range 110-300°K. The heat capacity vs. temperature curve indicated that no phase transitions occurred in the range examined and was consistent with an ordered structure for the solid at room temperature. Enthalpy and entropy values were determined [102]. Bis(η-benzaldehyde)chromium has been condensed with carbomethoxymethylenetriphenylphosphorane to form bis(η-methylcinnamate)-chromium (6.1; M = Cr; R = $CH{=}CHCO_2Me$, n = 1) in 60% yield. Bis(η-ethyl-β-phenylpropionate)chromium was treated with potassium hydride to give the [5]dibenzenechromocenophane (6.8) [103]. Bis(η-ethylbenzene)chromium has been treated with organic hydroperoxides (Me_3COOH and $PhMe_2COOH$) to give 1:3 complexes [104]. Bis(η-benzene)-chromium was oxidized with 2,4,6-tri-tert-butylphenoxyl (ArO•, a stable phenoxyl radical) to give the chromium complex (6.9) [105].



6.8

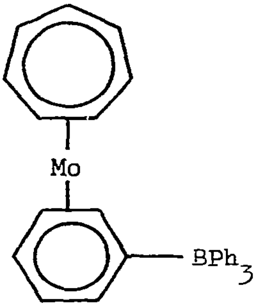


6.9

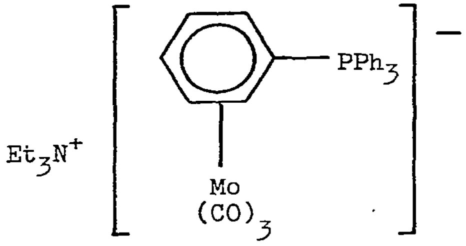
7. $[(\eta\text{-}C_7H_7)Cr(CO)_3]^+$ and $(\eta\text{-}C_7H_8)Cr(CO)_3$

Ab Initio calculations have been carried out on the mixed sandwich complexes $(\eta\text{-}C_5H_5)M(\eta\text{-}C_7H_7)$ (M = Ti, V, Cr). It was shown that the negative charge on the C_7H_7 ring decreased in the order Ti > V > Cr while the charge on the C_5H_5 ring increased in the order Ti < V < Cr. The trends in the calculated ionization energies only agreed partly with the values obtained from photoelectron spectra [106]. Extended Hückel calculations have been carried out for η-cycloheptatriene and η-fulvene tricarbonylchromium complexes and the conformational preferences of these molecules were considered [107].

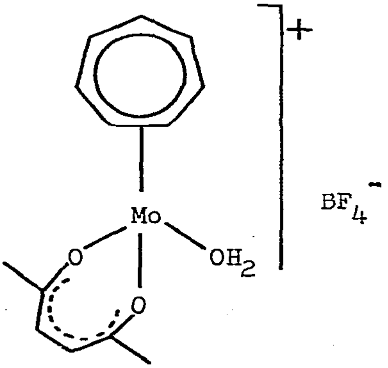
The crystal and molecular structures of the two (η-arene) molybdenum complexes (7.1 and 7.2) were determined by X-ray analysis. In the (η-cycloheptatrienyl)molybdenum complex (7.1) all the C-H bonds in the two rings were significantly bent towards the metal atom. In the (η-arene)molybdenum complex (7.2), the phenyl ring and the three carbonyl ligands formed a near-staggered geometry around the molybdenum [108]. Treatment of the η-cycloheptatrienyl complex (7.3) with anionic



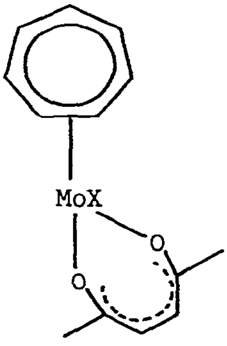
7.1



7.2



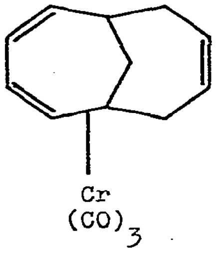
7.3



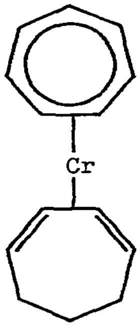
7.4

nucleophiles gave the neutral seventeen-electron paramagnetic compounds (7.4; X = Cl, Br, I, NCS). The crystal structure of the thiocyanate complex (7.4; X = NCS) was determined. The thiocyanate group was nonlinear and bound to the molybdenum by the nitrogen atom [109]. Conjugated dienes, for example 1,3-butadiene or trans, trans-2,4-hexadiene underwent [4s + 6s] cycloaddition with tricarbonyl (η-cycloheptatriene)chromium on irradiation with ultraviolet light to give chromium complexes. Thus the product formed from butadiene was the tricarbonylchromium complex (7.5) [110].

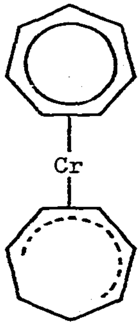
Tetraisopropylchromium combined with cycloheptatriene in THF to give the (η-cycloheptatrienyl)chromium complexes (7.6 and 7.7). These two complexes were interconverted through the cation derived from (η-cycloheptadienyl)(η-cycloheptatrienyl)chromium (7.7) [111].



7.5



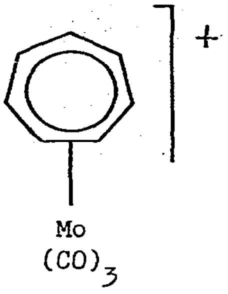
7.6



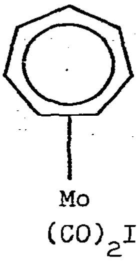
7.7

The nature of the intermediates formed in the reaction of the (η-cycloheptatrienyl)molybdenum cation (7.8) with iodide to form the iodo complex (7.9) have been investigated by flow ^{1}H NMR, spectroscopy and stopped-flow spectrophotometry. Two intermediates were indicated, an iodo-molybdenum species was formed initially by attack at the metal and this then rearranged to the iodo-cycloheptatriene species (7.10) before forming the product (7.9). Similar intermediates were suggested for the same reaction of the corresponding tungsten complex [112].

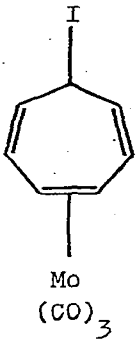
Substitution of (η^6-bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum with ^{13}CO gave stereospecific incorporation of the labelled ligand into an axial position with the formation of an (η^4-bicyclononatriene)molybdenum complex (7.11). Displacement of the hydrocarbon ligand from this product by ligands, L = norbornadiene, diamines,



7.8

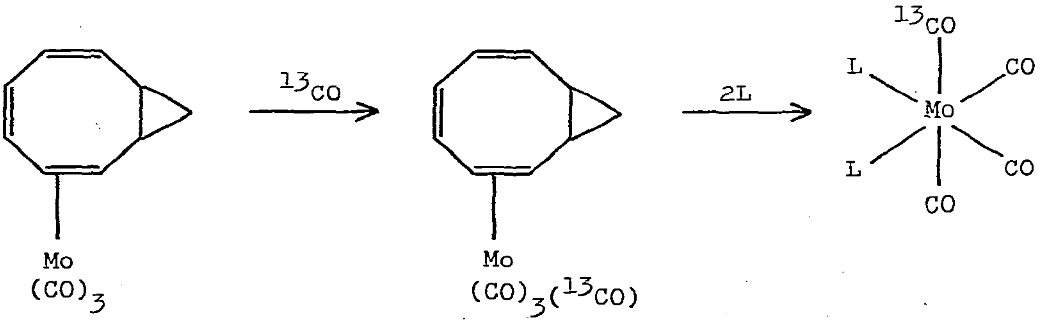


7.9



7.10

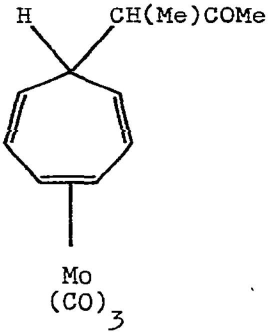
phosphines and triphenylantimony gave the stereospecific ^{13}CO labelled cis-disubstituted complexes $MoL_2(CO)_3(^{13}CO)$ in high yield. The



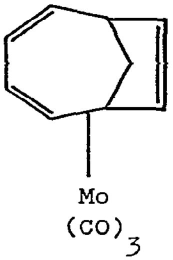
7.11

mechanism of the displacement was discussed and rationalized in terms of the rigidity of substituted 5-coordinate molybdenum carbonyl intermediates in the presence of ligands which have weak σ-donor and weak π-acceptor character [113]. Electrolysis of the (η-cycloheptatrienyl)-molybdenum cation (7.8) in the presence of a ketone and hydrogen bromide gave the (η-cycloheptatriene) molybdenum complexes $(\eta\text{-}RC_7H_7)Mo(CO)_3$, where $R = CH_2COMe$, $CHMeCOMe$, $CH(CHMe_2)COMe$. X-ray analysis of the complex (7.12) confirmed that the MeCOCHMe group was bound to the η-cycloheptatriene ligand by the α-carbon atom of the ethyl group [114].

Lewis has studied the thermal rearrangement of (η^6-bicyclo[6.1.0] nonatriene)tricarbonylmolybdenum to (η-bicyclo[4.2.1]nonatriene)tri-



7.12



7.13

carbonylmolybdenum (7.13). The mechanism of the apparent sigmatropic shift at C_9 was examined by selective deuteration and ^1H NMR analysis of the rearranged complex. The fluxional cation, tricarbonyl(σ-methyltropylium)iron existed in three of the four possible isomeric forms at -102° which on warming underwent three time-averaging processes at sequentially higher temperatures [115]. Tricarbonyl(η-cycloheptatriene)tungsten has been reduced electrochemically and with sodium in liquid ammonia to give the anion $[(\eta\text{-}C_7H_9)W(CO)_3]^-$ which on treatment with methyl iodide gave the neutral complex $(\eta\text{-}C_7H_9)W(CO)_3Me$. A possible mechanism for the electrochemical reduction was proposed [116].

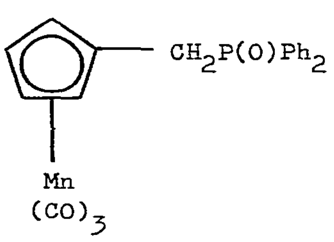
8. $(\eta\text{-}C_5H_5)Mn(CO)_3$

(i) Formation

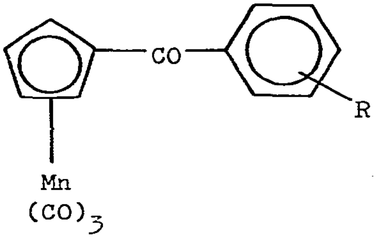
Treatment of diphenyl(cyclopentadienylmethyl)phosphine with manganese carbonyl gave the cymantrene derivative (8.1) [117].

(ii) Spectroscopic and Physico-chemical Studies

The crystal and molecular structure of bis(cymantrenyl)tin (IV) chloride has been determined by X-ray crystallography. Tin was found to be in a similar coordination environment to that reported previously for bis(ferrocenyl)tin (IV) chloride [118]. The mechanism of mass spectrometric fragmentation of benzoylcymantrenes (8.2; R = H, Me, OH, o-, m-, p-F) has been investigated. Two carbonyl groups were lost in a single step and then the third carbonyl was lost. Subsequent fragmentation involved rearrangement and cyclization. The nature of the substituent R determined whether the positive charge was localized on the manganese atom or on the ligand [119]. The mass spectra of a series of manganese and rhenium vinylidene complexes, $(\eta\text{-}C_5H_5)_nM_n(CO)L^1L^2$ [M = Mn, Re; n = 1, 2; L^1 = CO, PPh_3, $P(OPh)_3$; L^2 = a vinylidene



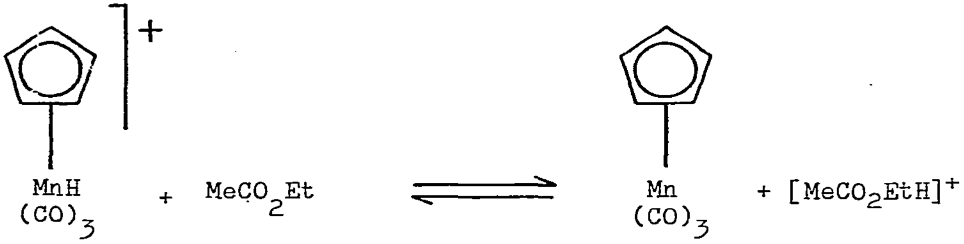
8.1



8.2

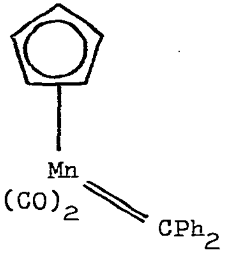
ligand] were recorded. The spectra of the rhenium complexes were characterised by strong dehydrogenation and in the bimetallic compounds it was concluded that the Re-Re bond was stronger than the Mn-Mn bond [120].

The gas phase Bronsted basicity of methylcymantrene has been determined at 296°K by ion cyclotron resonance measurements on the equilibrium between the protonated (8.3) and non-protonated (8.4) forms of the complex. The proton affinity was determined as 825 kJ mol^{-1} [121]. The electronic absorption spectrum of the diphenylcarbene



8.3 8.4

complex (8.5) exhibited an intense maximum at 380nm which was assigned to a metal to ligand charge transfer transition in which the empty orbital on the carbene carbon was populated. When the complex was irradiated it decomposed rapidly. In the charge transfer excited state the electron distribution was described as $(\eta\text{-}C_5H_5)(CO)_2Mn\text{-}\dot{C}(Ph)_2$ containing $\underline{d}^5$ Mn(II) and a carbene radical anion ligand. The

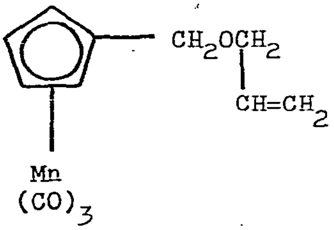


8.5

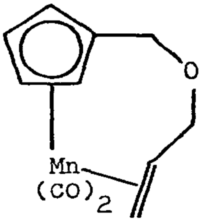
excited complex decomposed to give Mn(II) and a free carbene radical anion which underwent secondary reactions [122]. Organometallic haptotropic shifts in η-cyclopentadienyl complexes ($(C_5H_5)X$) have been analyzed by examining the interactions which take place when the group X^+ moves across the face of the $C_5H_5^-$ ring. When the group in transit was $Mn(CO)_3^+$ the interactions of the ligand were dominated by a set of acceptor orbitals of a + e symmetry, the e component of which stabilized the most symmetrical η^5 coordination [123]. The concentration of (η-methylcyclopentadienyl)tricarbonylmanganese in petrol was determined by gas chromatography with interfaced specific manganese detection by means of direct current argon plasma emission spectroscopy. This method was rapid, free from interferences, specific and it required very little sample preparation. The limit of detection was approximately 12ng of (η-methylcyclopentadienyl)tricarbonylmanganese [124].

(iii) General Chemistry

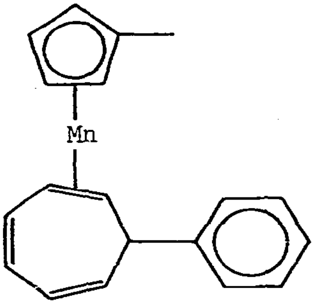
UV irradiation of the vinylcymantrene (8.6) caused the elimination of carbon monoxide and the formation of the olefin-manganese complex (8.7) [125]. Methylcymantrene was irradiated with 7-phenylcyclohepta-1,-3,5-triene to form the (η-cycloheptatriene)(η-cyclopentadienyl)-manganese complex (8.8). The structure of the complex was confirmed by X-ray diffraction methods [126]. Reaction of the manganese complexes (8.9; R = H, COMe, Et, COBu, C_5H_{11}) and (η-benzene)tricarbonylchromium with the phosphine ligands L (L = PFc_nPh_{3-n}, Fc = ferrocenyl, n = 0-3) gave the dicarbonyl-metal derivatives (8.10 and 8.11) respectively [127]. The tricarbonylmanganese cations (8.12; R = H, Me, X = N_3) were reduced to the corresponding η-aniline and η-toluidine complexes by lithium aluminium hydride or azide ion in polar solvents. Treatment of the complexes (8.12; R = H, Me, X = N_3) with sodium methoxide resulted in



8.6

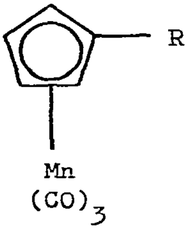


8.7

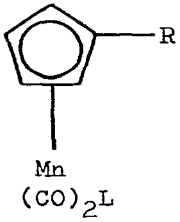


8.8

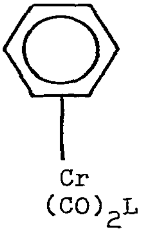
direct replacement of the azide group by methoxy. Pyrolysis of the azido compounds (8.12; R = H, Me, X = N_3) at 132° gave the



8.9



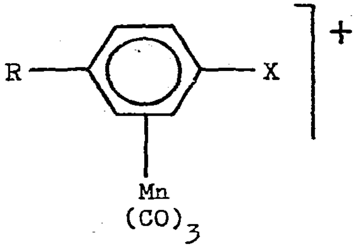
8.10



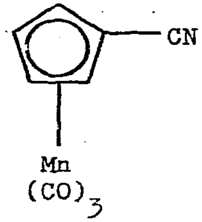
8.11

η-cyanocyclopentadienyl complexes (8.13 and 8.14) respectively [128].

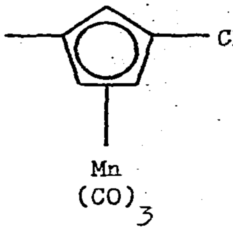
The electrochemical oxidation of cymantrene and substituted cymantrenes to the corresponding cations has been studied at a rotating platinum electrode in acetonitrile by voltammetry, coulometry, oscillopolarography and controlled potential electrolysis. A diffusion-controlled wave corresponding to a reversible one-electron oxidation was observed in each case except for cymantrenes with diphosphine ligands. These complexes showed two waves, each corresponding to a one-electron oxidation. The most negative wave was reversible and was interpreted in terms of a stable product, while the least negative wave was irreversible and explained as an unstable



8.12



8.13



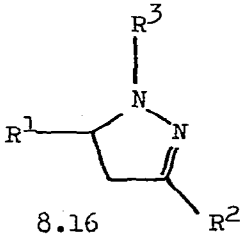
8.14

product. The values of the half-wave potentials of the reversible process were correlated with the distribution of electron density in the initial complex and in the cation product. Increased electron--donating power of substituents caused the half wave potentials to be shifted to more negative values [129]. The addition of acetylenic Grignard reagents to acylcymantrenes has been examined in a range of solvents, reduction of the adducts was also examined [130].

The kinetics of homopolymerization of tricarbonyl(η-vinylcyclopentadienyl)manganese in the presence of azobisisobutyronitrile in benzene, benzonitrile or acetone were studied. In each solvent the rate was 0.5 order in initiator and 1.5 order in monomer [131]. Cyclization of the olefins (8.15; R^1 = cymantrenyl, ferrocenyl, Ph; R^2 = cymantrenyl, ferrocenyl) with hydrazine gave the corresponding pyrazolines (8.16; R^3 = H). Acetylation of the pyrazoline (8.16; R^3 = H) gave the acetyl derivative (8.16; R^3 = $COCH_3$). Thermolysis

$R^1CH{=}CHCOR^2$

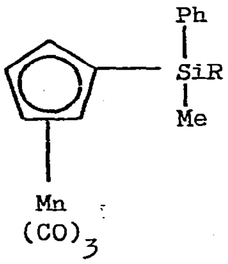
8.15



8.16

8.17

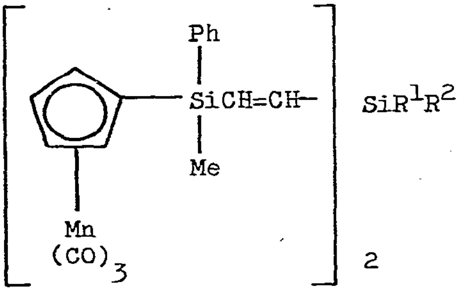
of the pyrazolines (8.16; R^3 = H) in the presence of Pt-C-KOH gave the corresponding <u>trans</u>-cyclopropanes (8.17) [132]. Hydrosilylation of the substituted acetylenes $HC{\equiv}CR$ ($R = SiPh_3$, Ph, ferrocenyl) with (cymantrenyl)phenylmethylsilane in the presence of Speier's catalyst proceeded regioselectively to give the corresponding olefins [8.18;



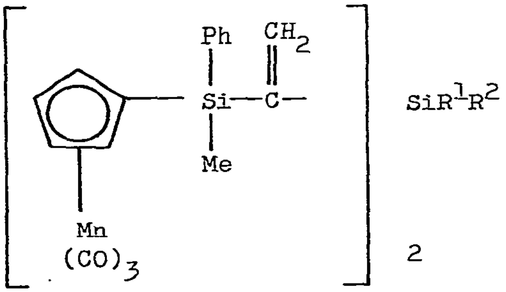
8.18

R = CH=CHSiPh$_3$, CH=CHPh, CH=CH(η-C$_5$H$_4$)Fe(η-C$_5$H$_5$)][133].

The cymantrenyl-silane (8.18; R = H) added to the silicon-acetylides $R^1R^2Si(C\equiv CH)_2$ (R^1 = R^2 = Et, Ph; R^1 = Me, R^2 = Ph) in the presence of Speier's catalyst to give the diene (8.19) as the major product together with a small proportion of the diene (8.20) [134].



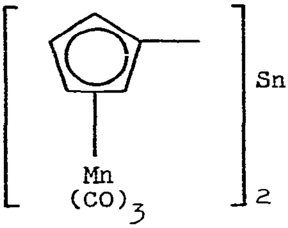
8.19



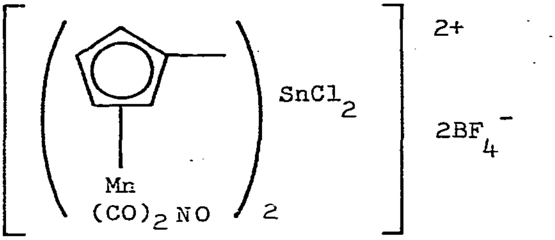
8.20

The cymantrenyl-stannane (8.21) formed unstable 1:1 and 1:2 complexes with dimethylformamide and 1:2 complexes with dimethylsulphoxide. Reaction of the stannane (8.21) with O_2NBF_4 gave the tetrafluoroborate salt (8.22) [135]. Reaction of bis(cymantrenyl)mercury with CH_3AuPPh_3 in the presence of hydrogen tetrafluoroborate gave the cationic organo-gold complex (8.23). The general applicability of this reaction to other organo-mercury derivatives was investigated [136].

Reaction of the manganese and rhenium complexes (8.24; X = HgCl; M = Mn, Re; L = CO, PPh$_3$) with tris(triphenylphosphine)platinum at -20° gave the corresponding complexes [8.24; X = HgPt(PPh$_3$)$_2$Cl; M = Mn, Re; L = CO, PPh$_3$] which when heated to 20° eliminated mercury

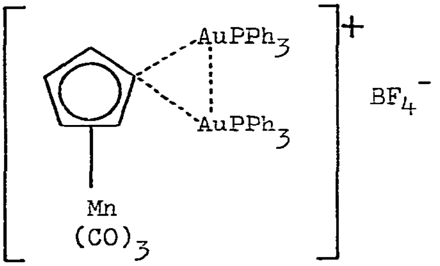


8.21

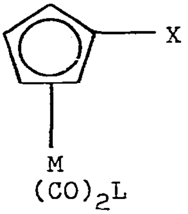


8.22

to give the complexes [8.24; X = Pt(PPh_3)$_2$Cl; M = Mn, Re; L = CO, PPh_3]. The carbon-platinum bonds in these latter complexes were cleaved with trifluoroacetic acid to give cymantrene or tricarbonyl-(η-cyclopentadienyl)rhenium. Treatment of the complexes [8.24;



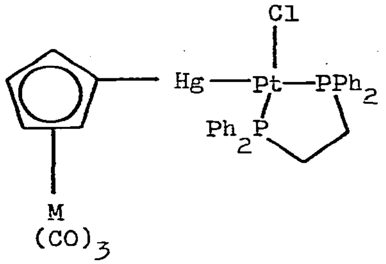
8.23



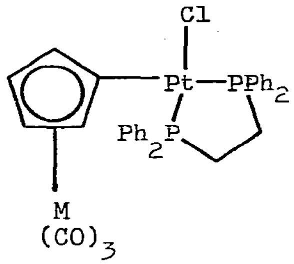
8.24

X = HgPt(PPh_3)$_2$Cl, M = Mn, Re; L = CO] with 1,2-bis(diphenylphosphino)-ethane gave the corresponding chelate complexes (8.25) which eliminated mercury on warming to give the complexes (8.26) [137]. Reaction of the lithio-derivatives (8.27; M = Mn, Re) with acetylcymantrene or formylcymantrene gave the corresponding alcohols (8.28; R = Me, H; M = Mn, Re) respectively [138].

Reaction of the mercury-bridged manganese and rhenium complexes (8.29; M = Mn, Re; X = Hg) with tris(triphenylphosphine)platinum at -20° gave the corresponding platinum compounds (8.29; M = Mn, Re, X = HgPt(PPh_3)$_2$]. When these latter complexes were heated to 20°

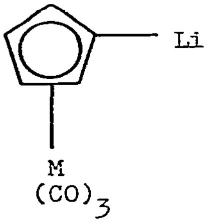


8.25

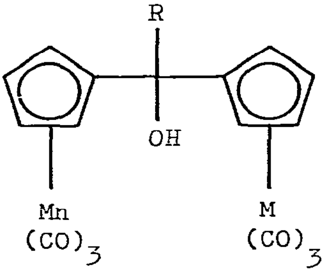


8.26

mercury was eliminated to give the platinum-bridged derivatives [8.29; M = Mn, Re; X = $Pt(PPh_3)_2$] [139]. The binuclear cymantrene



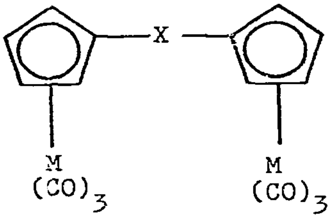
8.27



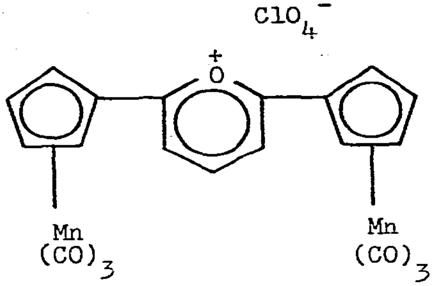
8.28

derivative (8.30) was treated with palladium (II) chloride in the presence of sodium carbonate to give the η-allyl complex [8.31; R = $(\eta\text{-}C_5H_4)Mn(CO)_3$] in good yield. Treatment of the complex (8.30) with thallium cyclopentadienyl at room temperature gave the η-allyl complex [8.32; R = $(\eta\text{-}C_5H_4)Mn(CO)_3$] [140]. Dicymantrenyl (8.33) was formed by treatment of metallated cymantrenes with halides or halogens. Thus cymantrenyllithium was treated with copper (II) chloride to give the dimer (8.33) in 69% yield; cymantrenylsilver combined with cymantrenylbromide to give the same product in 23% yield and cymantrenylcopper was attacked by bromine to give a 50% yield of the dimer [141].

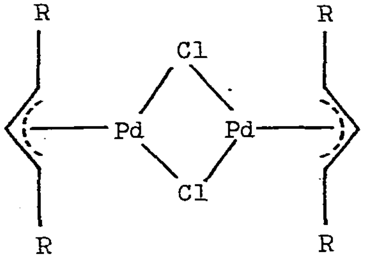
The trinuclear cymantrenyl complexes (8.34; M = Sb, Bi) were formed from the trivalent metal chlorides and lithiocymantrene in



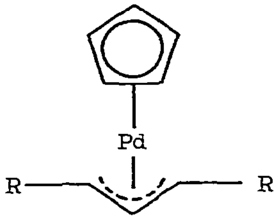
8.29



8.30

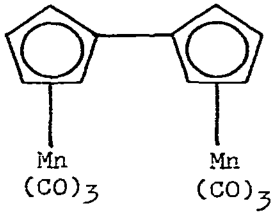


8.31

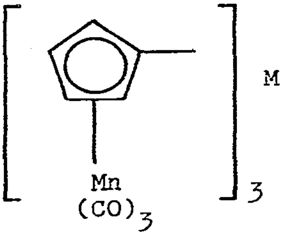


8.32

yields of 75 and 81% respectively. Thermal degradation of the bismuth compound (8.34; M = Bi) at 300° gave dicymantrenyl (8.33) while the

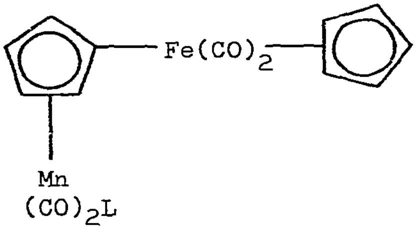


8.33

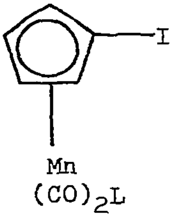


8.34

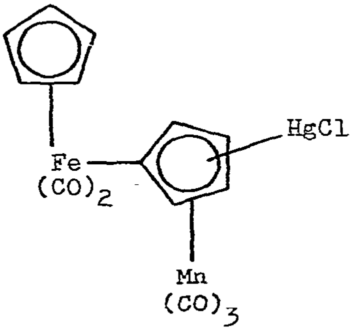
antimony compound (8.34; M = Sb) gave manganese, antimony, carbon monoxide and organic products [142]. The mixed (η-cyclopentadienyl)-iron-manganese complexes (8.35; L = CO, PPh_3) were treated with iodine in chloroform to give iodocymantrène (8.36; L = CO) and the triphenylphosphine analogue (8.36; L = PPh_3) respectively. The other major product in each case was (η-cyclopentadienyl)irondicarbonyl iodide. The complex (8.35: L = CO) was attacked by acetyltetrafluoroborate in acetonitrile to form dicymantrene (8.33) [143]. Mercuration of dicarbonyl(η-cyclopentadienyl)(η-cymantrenyl)iron with mercury (II) acetate followed by treatment with a metal chloride gave the mercuri--chloride derivative (8.37). Reaction of this mercurated cymantrene (8.37) with sodium thiosulphate produced the symmetrical derivative (8.38) [144].



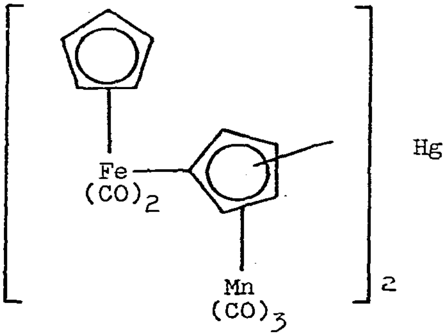
8.35



8.36

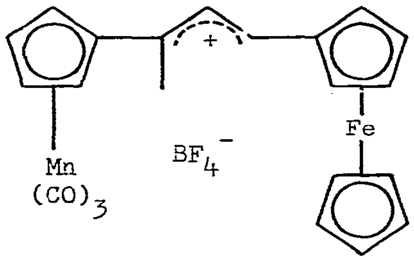


8.37

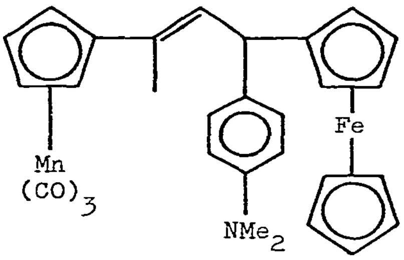


8.38

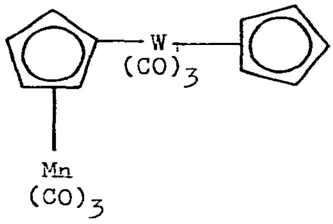
Treatment of 1-methyl-1-cymantrenyl-3-ferrocenylallyl alcohol with fluoroboric acid in acetic anhydride gave the cymantrenylallyl cation (8.39) which attacked dimethylaniline to form the p-substituted aniline (8.40) in high yield [145]. The cymantrenyltungsten complex



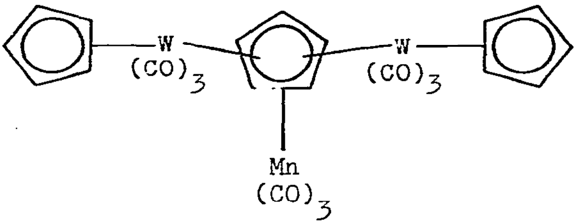
8.39



8.40



8.41

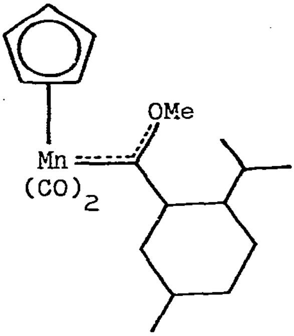


8.42

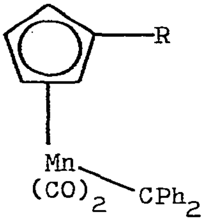
(8.41) on heating at 200° gave a mixture of cymantrene and the cymantrenylbistungsten complex (8.42) together with two tungsten complexes [146].

(iv) Analogues

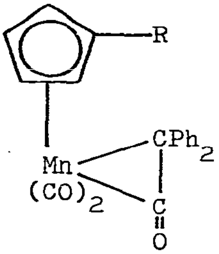
Cymantrene has been treated with (+)-menthyllithium and then methylated with $(Me_3O)BF_4$ to form (-)(η-cyclopentadienyl)dicarbonylmenthylmethoxycarbenemanganese (8.43), the absolute configuration of this complex was determined by X-ray crystallography [147]. High-pressure carbonylation of the diphenylcarbenemanganese complexes (8.44; R = H, Me) gave the corresponding diphenylketene complexes (8.45). The ketene complexes (8.45; R = H, Me) were hydrogenoly-



8.43

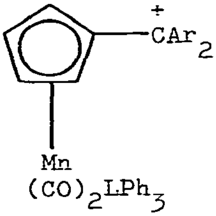


8.44

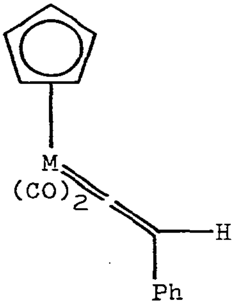


8.45

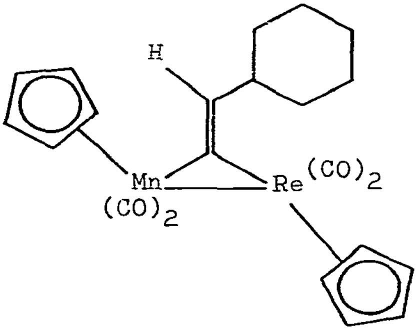
tically degraded under high pressure to give diphenylacetaldehyde and 2,2-diphenylethanol respectively [148]. The infrared spectra of several carbenium ions (8.46; L = P, Sb) derived from diarylcymantrenylcarbinols have been recorded and interpreted [149]. The



8.46



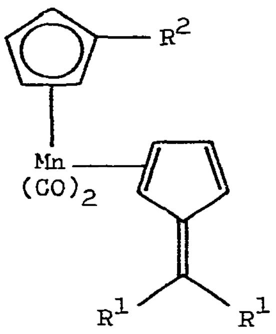
8.47



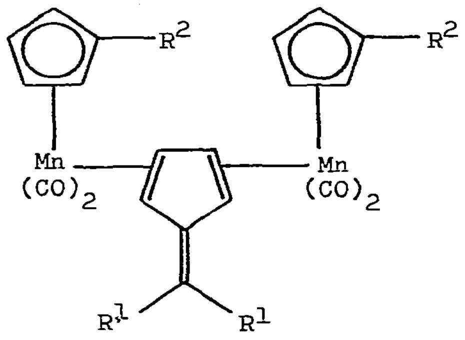
8.48

manganese phenylvinylidene complex (8.47; M = Mn) combined with the tetrahydrofuran adduct of dicarbonyl(η-cyclopentadienyl)rhenium to form the binuclear complex (8.48) which contained a bridging phenylvinylidene ligand. On standing at room temperature the complex (8.48) was slowly converted to the rhenium phenylvinylidene complex (8.47; M = Re) [150].

Irradiation of cymantrene or methylcymantrene with fulvenes gave mixtures of the mono- and di-nuclear complexes [8.49 and 8.50; R^1 = Me, cyclopropyl, Ph; $R^1_2 = (CH_2)_5$; R^2 = H, Me]. The fulvene ligand L was exchanged from the complex (8.49; R^1 = Ph, R^2 = Me) to diironenneacarbonyl to give the complex $LFe_2(CO)_5$ in good yield [151].

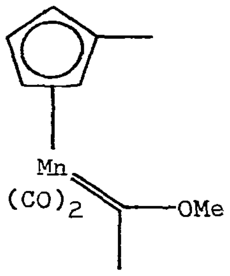


8.49

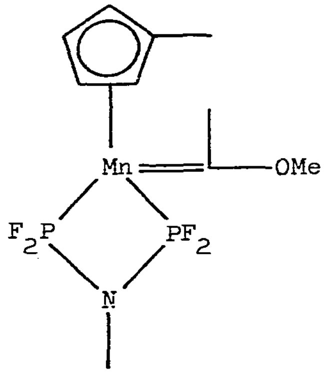


8.50

Irradiation of dicarbonyl(η-methylcyclopentadienyl)methylmethoxycarbenemanganese (8.51) with methylaminobis(difluorophosphine) gave the fluorophosphine manganese complex (8.52) [152]. Methylcymantrene has been converted to the THF analogue (8.53) which induced the fragmentation of diazocyclopentadiene and gave the binuclear carbocyclic

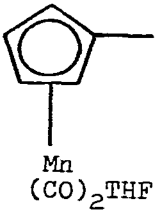


8.51

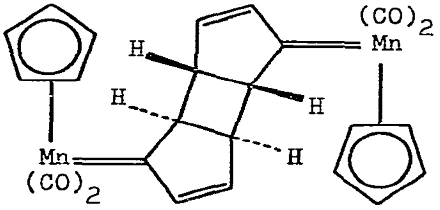


8.52

carbene complex (8.54). The crystal and molecular structure of the complex has been determined by X-ray crystallography. The same reaction was carried out with cymantrene [153].

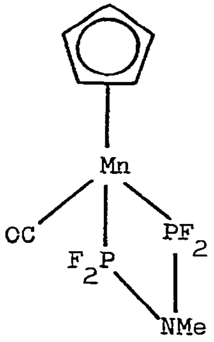


8.53

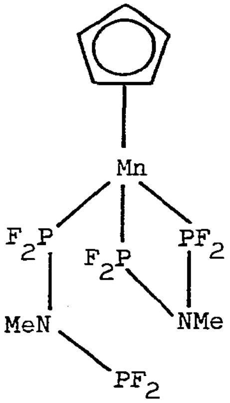


8.54

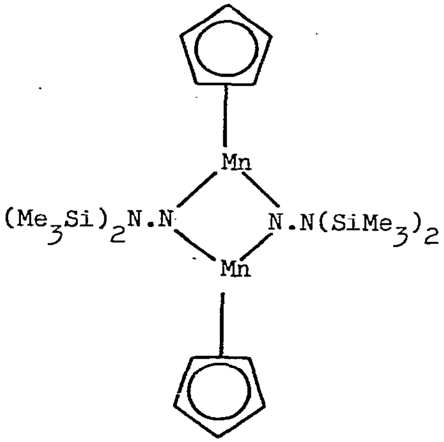
Ultraviolet irradiation of cymantrene with methylaminobis(difluorophosphine) gave successively the monocarbonyl derivative (8.55) and the carbonyl-free complex (8.56). The ^1H, ^{13}C and ^{31}P NMR spectra of these and related complexes were recorded [154]. Reaction of



8.55



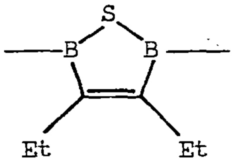
8.56



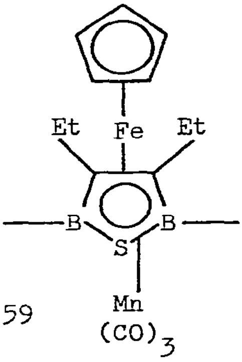
8.57

bis(η-cyclopentadienyl)manganese with $Me_3SiN{=}NSiMe_3$ gave the (η-cyclopentadienyl)manganese complex (8.57) [155]. Simultaneous reaction of the thiadiborolene derivative (8.58) with dicarbonyl(η-cyclopentadienyl)-iron dimer and manganese carbonyl gave the triple-decker complex (8.59). Treatment of the latter complex (8.59) with aluminium chloride in benzene gave the triple-decker salt (8.60) which underwent thermal decomposition in vacuo to give the tetradecker complex (8.61). The structure of the complex (8.61) was confirmed by X—ray structural analysis [156].

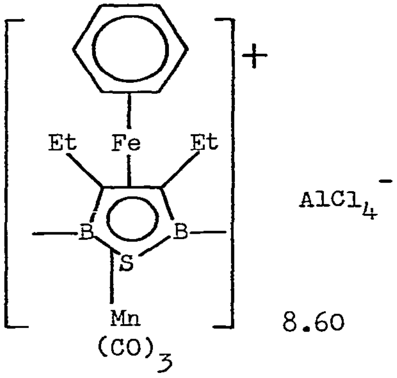
The reaction of manganese carbonyl with 1-phenyl-3,4-dimethylphosphole at 150° in xylene gave the phosphacymantrene (8.62; R^1 =



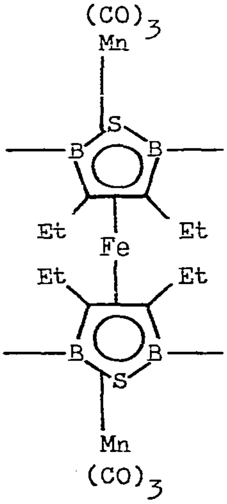
8.58



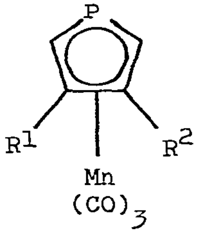
8.59



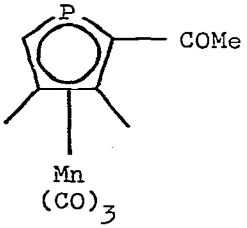
8.60



8.61

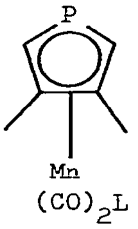


8.62

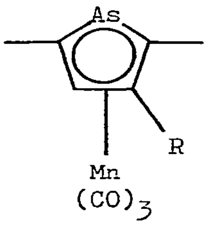


8.63

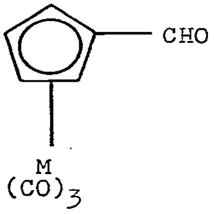
R^2 = Me) as the major product. In similar reactions 1-phenylphosphole and 1-phenyl-3-methylphosphole gave the phosphacymantrenes (8.62; $R^1 = R^2 = H$, $R^1 = Me$, $R^2 = H$) respectively. Friedel-Crafts acylation of 3,4-dimethylphosphacymantrene gave the acetyl derivative.(8.63). Treatment of 3,4-dimethylphosphacymantrene with n-butyllithium resulted in cleavage of the phospholyl-manganese bond and 1-butyl-3,4-dimethylphosphole was formed [157]. Irradiation of the phosphacymantrene (8.64; L = CO) in cyclohexane solution and in the presence of phosphine ligands gave the monosubstituted derivatives [8.64; L = PPh_3, PMe_2Ph, PPh(cycloalkene)]. When trimethylphosphite was the ligand then both monosubstituted [8.64; L = $P(OMe)_3$] and disubstituted products were obtained [158]. Reaction of 1-phenyl-2,5-dimethylarsole with manganese carbonyl gave the arsacymantrene (8.65; R = H).



8.64



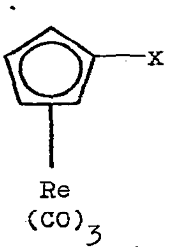
8.65



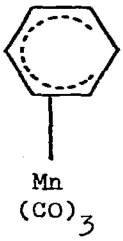
8.66

Acetylation of the arsacymantrene (8.65; R = H) with acetyl chloride-aluminium chloride gave the monoacetylated derivative (8.65; R = COMe) [159].

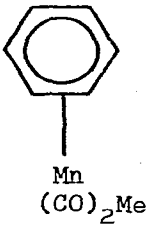
(η-Lithiocyclopentadienyl)tricarbonylrhenium was treated with dimethylformamide at -10° to give the formyl derivative (8.66; M = Re) in good yield. The corresponding manganese complex (8.66; M = Mn) was prepared in the same way [160]. Reaction of diazocyclopentadiene with $XRe(CO)_5$ (X = Cl, Br, I) gave the corresponding (η-halocyclopentadienyl)rhenium complex (8.67) [161]. The reduction of (η-arene)tricarbonylmanganese cations afforded the corresponding (η-cyclohexadienyl)manganese complexes together with (η-arene)dicarbonylmethylmanganese compounds formed by reduction of a metal carbonyl. Thus the (η-benzene)tricarbonylmanganese cation was reduced with lithium aluminium hydride to form the η-cyclohexadienyl complex (8.68) and the methylmanganese complex (8.69) [162].



8.67



8.68



8.69

(v) Applications

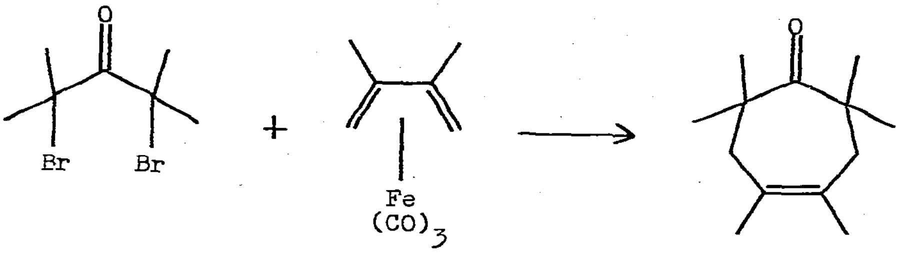
The use of tricarbonyl(η-methylcyclopentadienyl)manganese as a gasoline and fuel additive continues to receive attention. Effort has been focussed on the efficiency of the additive as an antiknock compound and problems centred around the plugging of exhaust purification catalysts have been investigated. Several reports show that mixing esters with the cymantrene additive gave some control of plugging. Thus when the tertiary amines $N(CH_2CO_2R)_3$, where R = H or a hydrocarbon group, were combined with cyclopentadienylcymantrene then plugging was minimised and pollution by exhaust gases was reduced [163]. A related patent described similar applications for the compound $RO_2CCH_2CH(CO_2R)OCH_2CO_2R$, where R = H or a hydrocarbon group was used in combination with cymantrene [164]. Mono- and di-esters of succinic acid were effective in the same way [168].

Methylcymantrene was effective in reducing smoke and sulphur trioxide emission when added to fuel oil. It promoted more efficient combustion of the fuel [165]. Manganese emission from vehicles using gasoline with the same additive has been monitored [166] and the effect of the additive on octane number and the nature of the exhaust gases determined. Concentrations of 0.0625g. methylcymantrene per gallon of gasoline did not affect the emissions from vehicles fitted with catalytic converters. The additive was found to be three-five times more effective when used in unleaded rather than leaded gasoline [167]. However hydrocarbon emissions from engine and tailpipe were doubled when methylcymantrene was added to gasoline. The same study indicated that emission levels of carbon monoxide and nitrogen oxides were not affected and that catalyst efficiency was maintained in the presence of the additive

[169]. Reports describing the effect of methylcymantrene on the plugging of exhaust catalysts do not present a clear picture. While vehicle performance was regarded as satisfactory [170] one study [171] found no increase in catalyst plugging but other workers [172, 173, 174] have reported a significant effect. Two reports [173, 174] agreed that plugging was a result of physical deposition of material on the catalyst rather than chemical attack but they differed in their conclusions on the nature of the deposit. Metallic manganese was found in one case [173] while Mn_3O_4 was implicated by the second study [174]. An investigation into the causes of catalyst plugging has shown that the catalyst inlet temperature and the concentration of the antiknock agent were important. It was observed that the deposits tended to collect on the inlet edge of the converter [174]. The effect of methylcymantrene additives on spark plug life has been examined. One study found that spark plug life was not affected [171] while excessive spark plug deposits were found with cars tested for 80,000km using a driving schedule which included steady driving at 133km h^{-1} [172]. The oxidation of methylcymantrene, present in gasoline as an octane number improver, was inhibited by the addition of 0.5-2.0% 2-ethylhexanoic acid [175]. Waste water from plants producing cymantrene as an antiknock was treated to remove organic matter by extraction with gasoline fractions. Organic contamination was reduced to 0.3-1.5 mg l^{-1} [176].

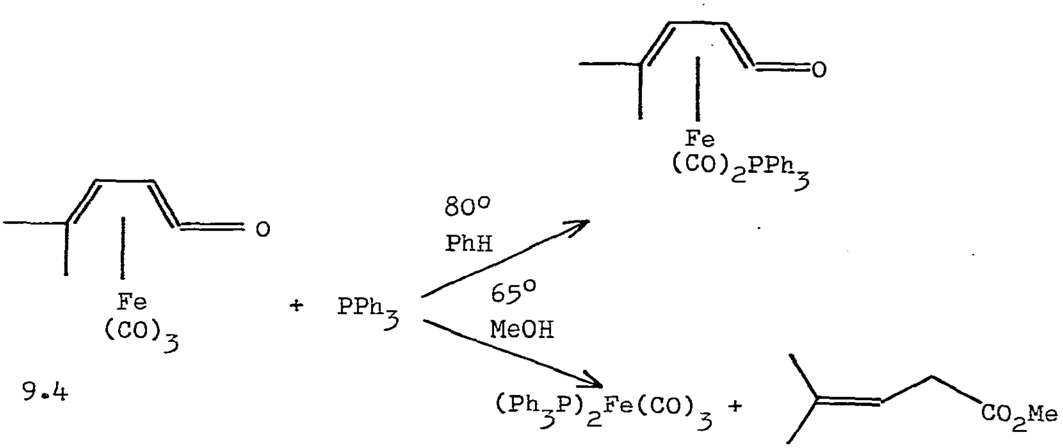
9. Acyclic-η-diene)Fe(CO)$_3$

The addition of α,α'-dibromoketones to 1,3-dienes to give cycloheptenones was facilitated by converting the diene to the tricarbonyliron complex and using this complex as the reagent. In a typical reaction, the dibromide (9.1) combined with 2,3-dimethylbutadiene in the presence of diiron nonacarbonyl to form the cycloheptenone (9.3) in 71% yield while the same dibromide (9.1) combined with the (η-butadiene) iron complex (9.2) to form the cycloheptenone (9.3) in quantitative yield. Ten alkylsubstituted cycloheptenones were prepared in this way [177]. Treatment of nonacarbonyldiiron with excess 3,3-dimethylcyclopropene gave tricarbonyl(4,4-dimethylbuta-1,3-dienone)iron (9.4) in variable yield depending on the solvent used. The reaction of the diene



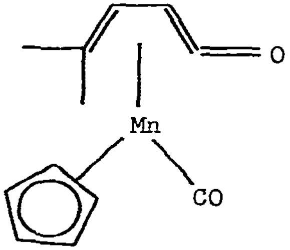
9.1 9.2 9.3

complex (9.4) with triphenylphosphine was also solvent dependent (Scheme 9.1). Dicarbonyl(η-cyclopentadienyl)(tetrahydrofuran)manganese



9.4

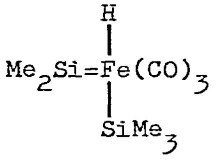
Scheme 9.1



9.5

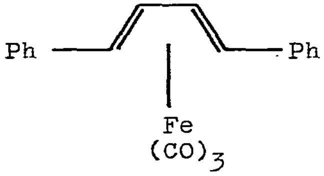
underwent a similar reaction with 3,3-dimethylcyclopropene to give the manganese complex (9.5) [178].

The reaction of (η-benzylideneacetone)tricarbonyliron with trans, trans- 2,4-hexadiene, trans-1,3-pentadiene,2,3-dimethylbutadiene and trans,trans-2,4-hexadienal gave the corresponding tricarbonyl(η-diene)-iron complexes. Similarly treatment of (η-benzylideneacetone)-tricarbonyliron with norbornadiene, cyclooctatetraene and cycloheptatriene gave the corresponding tricarbonyl(η-diene)iron complexes. Irradiation of pentacarbonyliron with 2,4,6-cyclooctatrienone gave tricarbonyl(η-2,3,4,5-cyclooctatrienone)iron. Thermal reaction of the same ketone with (η-benzylideneacetone)tricarbonyliron or tricarbonyl-(η-3-penten-2-one)iron produced (η-bicyclo[4.2.0]octa-2,4-dien-7-one)-tricarbonyliron [179]. Reaction of pentamethyldisilane with $Fe_2(CO)_9$ gave the dimethylsilanediyliron complex (9.6) which when treated with 1,4-diphenylbuta-1,3-diene gave the corresponding (η-butadiene)tricarbonyliron complex (9.7) [180].

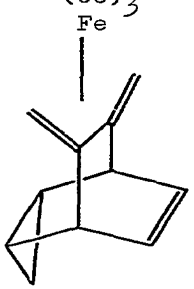


$$\overset{H}{\underset{SiMe_3}{Me_2Si{=}Fe(CO)_3}}$$

9.6

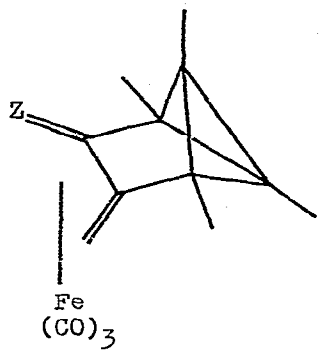


9.7



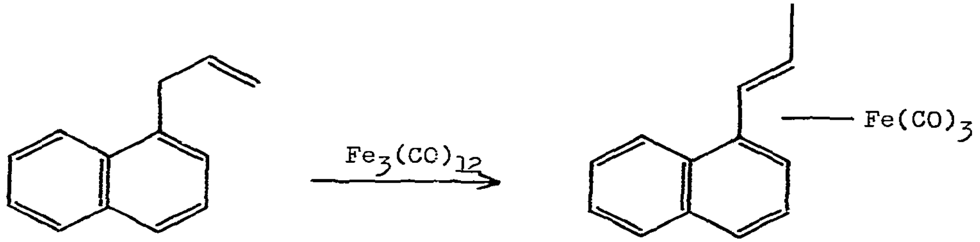
9.8

The (η-homobarrelene)iron complex (9.8) has been formed by treatment of the free ligand with iron pentacarbonyl [181]. Irradiation of the appropriate diene ligand with pentacarbonyliron gave the iron-tricarbonyl complex (9.9; Z = CH_2). However the corresponding enone ligand when treated under similar conditions did not form the complex (9.9; Z = O) but gave a lactone by carbonyl insertion [182]. Reaction of α-allylnaphthalene (9.10) with $Fe_3(CO)_{12}$ gave the tricarbonyliron derivative (9.11). Extension of this procedure to allylbenzene gave no isolable product. However, irradiation of allylbenzene with pentacarbonyl iron gave the bis(tricarbonyliron)derivative (9.12) in low



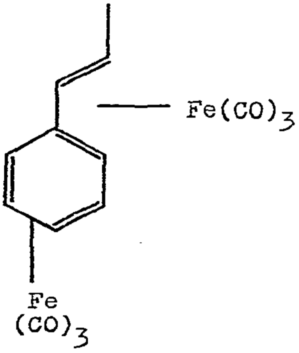
9.9

yield. The reaction of m-diallylbenzene with $Fe_3(CO)_{12}$ gave the corresponding bis(tricarbonyliron) complex (9.13) [183].

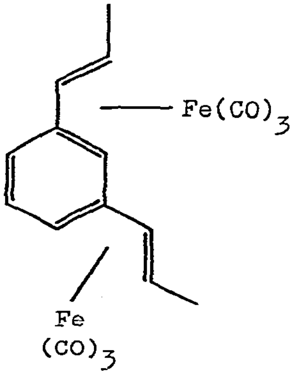


9.10

9.11

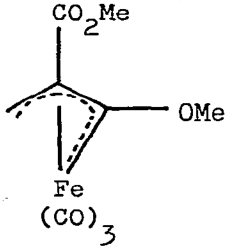


9.12

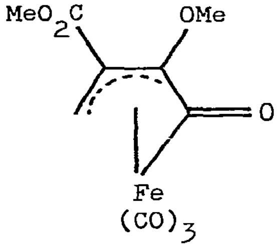


9.13

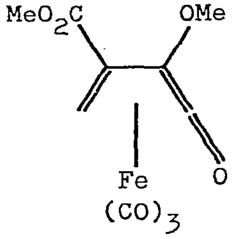
Carbonylation of the (η^3-vinylcarbene)iron complex (9.14) gave a product in which the η^3-allyl-η^1-acyl structure (9.15) was preferred over the alternative η^4-vinylketen structure (9.16). The structure (9.15) was confirmed by an X-ray crystallographic analysis [184].



9.14

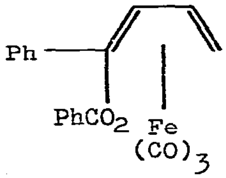


9.15

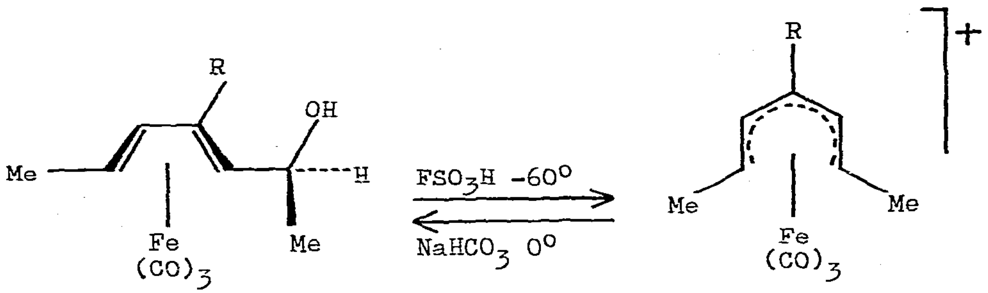


9.16

The crystal and molecular structure of the (η-butadiene)iron complex (9.17) has been determined by X-ray crystallography. The dihedral angle between the butadiene group and the phenyl substituent was ~73° [185]. The ^{13}C NMR spectra of a series of acyclic η-dienetricarbonyliron complexes were recorded. The effects of alkyl substituents (particularly methyl groups) on the chemical shift positions of the ligand carbon atoms were discussed. It was suggested that steric factors played a significant role in determining chemical shift positions of the diene carbon centres in the complexes [186].

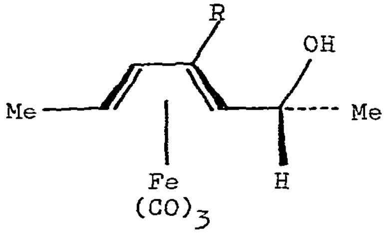


9.17

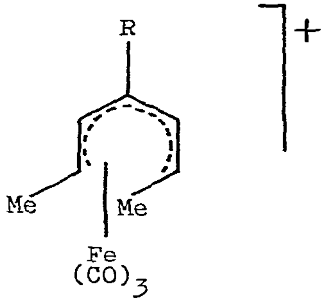


9.18

9.19



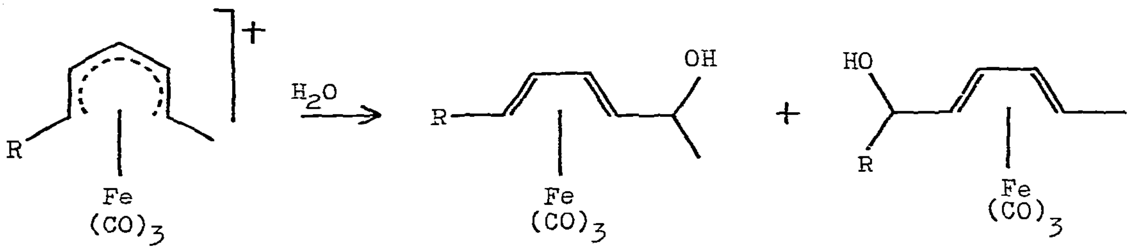
9.20



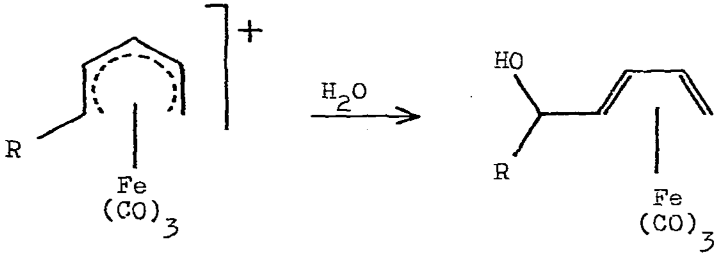
9.21

The ψ-*exo*-*trans*-dienoliron tricarbonyl complexes (9.18; R = H, Me) gave the *syn,syn*-dienyliron tricarbonyl cations (9.19; R = H, Me) with high stereospecificity in fluorosulphonic acid at -60° while the ψ-*endo*-*trans*-dienoliron complexes (9.20; R = H, Me) gave the *syn,anti*-dienyliron cations (9.21; R = H, Me). The cation (9.21; R = Me) was configurationally stable for several hours at room temperature. On long standing it was slowly converted to the *syn,syn*-dienyliron cation (9.19; R = Me). Water or methanol quenching of the cations (9.19 and 9.21) at 0° or below proceeded with high stereospecificity to the original dienoliron complexes and their methyl ethers respectively. The mechanism of ionization involved preferential departure of *exo* leaving groups followed by *trans*-*cis* isomerization about the(C3)-C(4) bond in the case of *cis* cations [187].

Bayoud, Biehl and Reeves have investigated the hydrolysis of unsymmetrically substituted tricarbonyl(η-pentadienyl)iron cations in order to elucidate the role of electronic and steric effects in the reaction. The cations used were formed from the corresponding alcohols by treatment with a mixture of acetic anhydride and fluoroboric acid. The (η-pentadienyl)iron cations (9.22; R = Me, Et, $\mathrm{Pr^i}$, Ph) underwent hydrolysis to give a mixture of the alcohols (9.23 and 9.24; R = Me, Et, $\mathrm{Pr^i}$, Ph) in which the proportion of the isomer (9.23) increased with increasing size of the substituent R. Hydrolysis of a second series of (η-pentadienyl)iron cations (9.25; R = Me, Et, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$, Ph) gave only the alcohols (9.26; R = Me, Et, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$, Ph). The results were rationalized in terms of an (η-allyl)iron intermediate which suffered attack at the least substituted terminal carbon atom when two terminal substituents were present as in the cations (9.22). When only one end of the cation carried a substituent, cation (9.25), then attack occurred at the substituted position because of the ability of the substituent to stabilize the reactive intermediate [188].

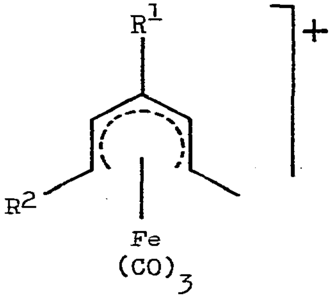


9.22 9.23 9.24

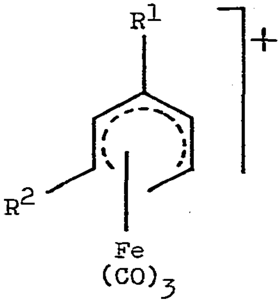


9.25 9.26

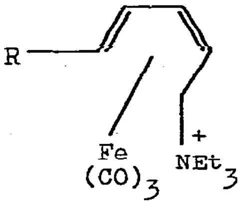
The tricarbonyl(η-dienyl)iron cations (9.27; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; $R^1 = R^2 = Me$; $R^1 = H$, $R^2 = Ph$) and (9.28; $R^1 = H$, $R^2 = Me$; $R^1 = R^2 = Me$; $R^1 = H$, $R^2 = Ph$) were generated from the corresponding alcohols in FSO_3H-SO_2-$CDCl_3$ mixtures and the ^{13}C NMR spectra of these species were recorded. The ^{13}C chemical shifts and molecular orbital calculations indicated an alternation of charge along the dienyl ligand with carbon atoms 1, 3 and 5 being less electron deficient than carbon atoms 2 and 4. It was also concluded that site exchange of the carbonyl ligands occurred via tricarbonyliron rotation or via a process which approximated to a Berry pseudorotation process [189]. Dehydration of the alcohols (9.23; R = H, Me) or thermal degradation of the amine salts (9.29; R = H, Me) *in vacuo* gave the corresponding triene complexes (9.30). The amine salts (9.29) were formed by treatment of the cation (9.22) with triethylamine. The reaction of the cation (9.22) with other amines, triphenylphosphine and triphenylarsine was investigated [190].



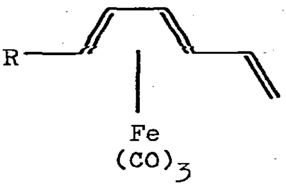
9.27



9.28

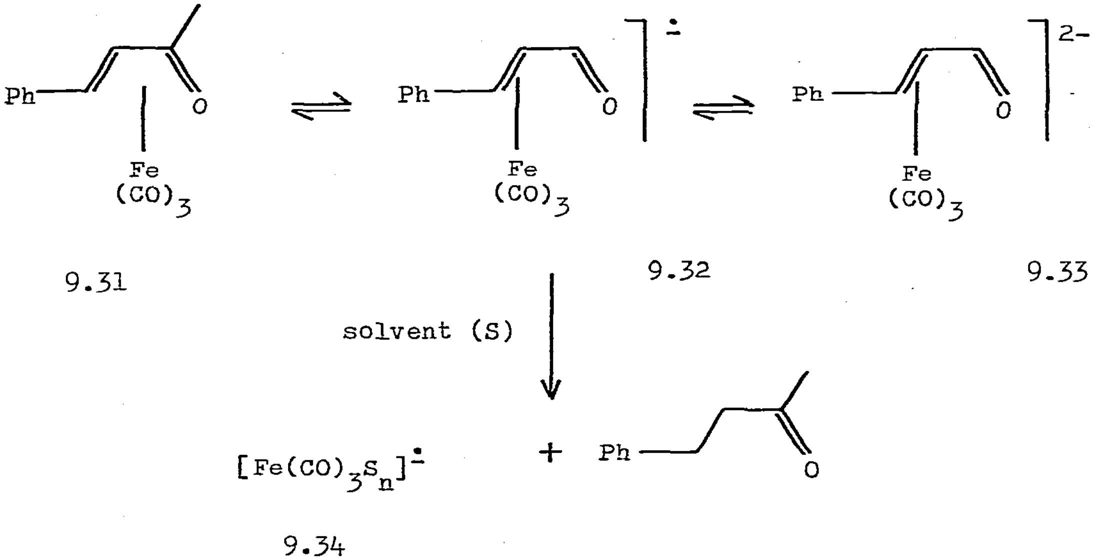


9.29

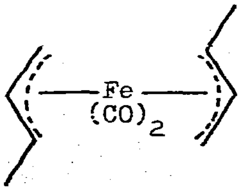


9.30

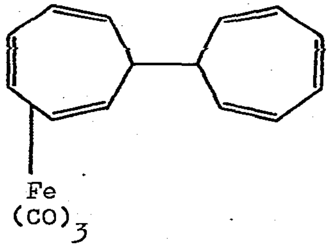
Electrochemical reduction of the tricarbonyliron complex (9.31) gave the anionic species (9.32, 9.33 and 9.34) (Scheme 9.2). Reaction of the anionic species (9.32 and 9.33) with crotyl halides gave the complex (9.35) and reaction of the radical anion (9.34) with the tropylium cation gave the tricarbonyliron complex (9.36) [191]. The mechanism of ligand exchange between tricarbonyl(η-enone)iron complexes (9.37; R = H, Me, Ph) and cycloheptatriene has been investigated. The reactions were carried out in toluene at 90° and the results suggested a mechanism with alternative dissociative and



Scheme 9.2

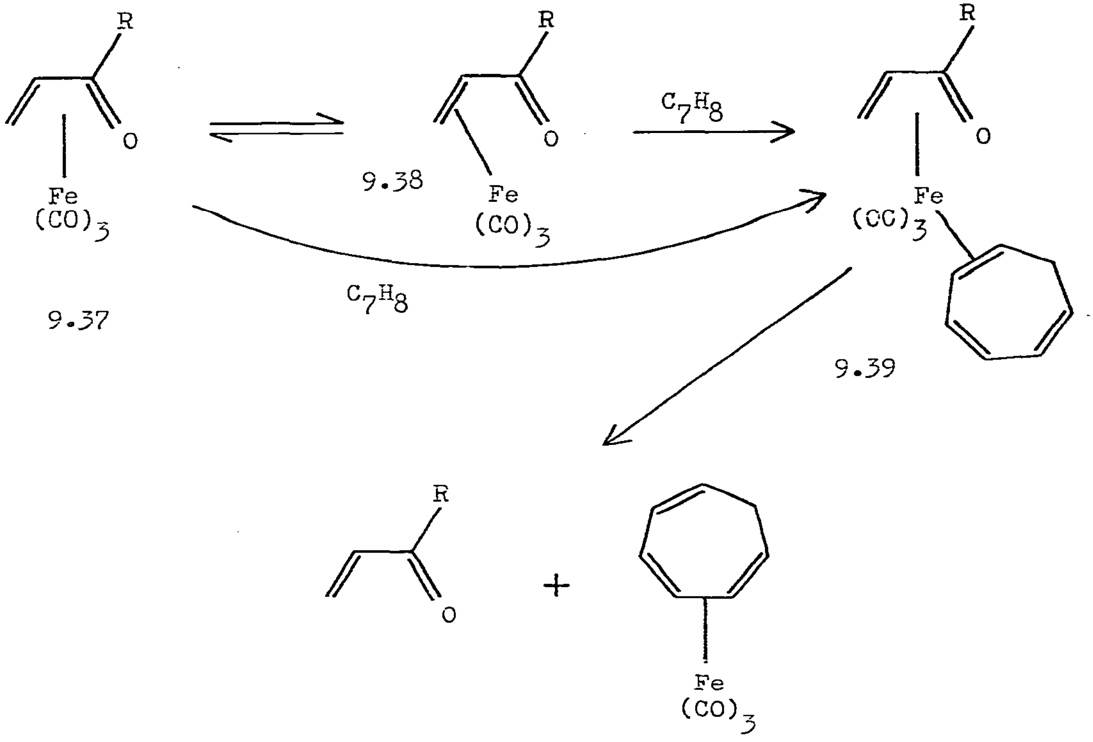


9.35



9.36

associative pathways involving the intermediates (9.38 and 9.39) respectively. The product was tricarbonyl(η-cycloheptatriene)iron (9.40) and the reaction was facilitated by increasing electron donation by the substituent R [192].



9.37

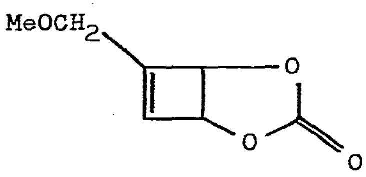
9.38

9.39

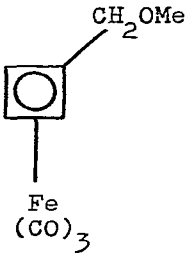
9.40

10. (η-C_4H_4)Fe(CO)$_3$

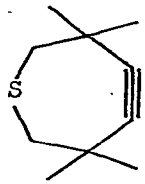
Treatment of the cyclobutene (10.1) with sodium tetracarbonylferrate (II) gave the η-cyclobutadiene complex (10.2) [193]. Reaction of the cycloheptyne (10.3) with palladium (II) chloride gave the tetrasubstituted η-cyclobutadiene complex (10.4; M = $PdCl_2$) which when treated with pentacarbonyliron gave the tricarbonyliron derivative [10.4; M = Fe(CO)$_3$]. When the palladium complex (10.4; M = $PdCl_2$) was treated with 1,2-bis(diphenylphosphino)ethane the free cyclobutadiene derivative (10.5) was released which was isolable at room temperature [194]. The He (I) and Ne (I) photoelectron



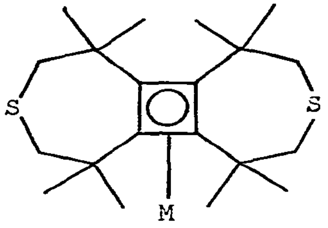
10.1



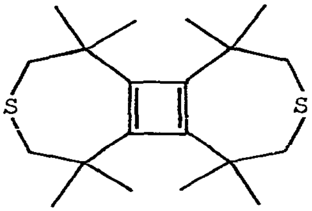
10.2



10.3



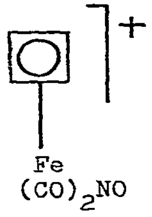
10.4



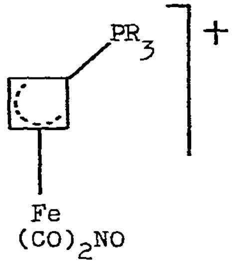
10.5

spectra of the ferraborane $B_4H_8Fe(CO)_3$ and (η-cyclobutadiene)tricarbonyliron have been recorded and assigned. The results indicated that the metal atom interacted more strongly with the B_4H_8 borane ring than with the cyclobutadiene ring. This gave a lower energy for the ring-metal orbital in the ferraborane and the iron appeared to be more cagelike in the ferraborane than in the cyclobutadiene complex [195].

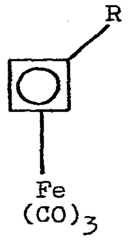
The far-IR, Raman and inelastic neutron scattering spectra of (η-cyclobutadiene)tricarbonyliron in the solid phase have been recorded. Two low frequency vibrations were reassigned and the torsion of the cyclobutadiene about the C_4 axis has been assigned. Force constants have been calculated [196]. A kinetic study of the addition of tertiary phosphines to the dicarbonylnitrosyl(η-cyclobutadiene)iron cation (10.6) indicated direct bimolecular attack on the cyclobutadiene ring to form the (η-cyclobutenyl)iron cations (10.7; R = Ph, p-Cl.C_6H_4). These results and those from a parallel study on the tricarbonyl(η-cycloheptatriene)manganese cation enabled the following reactivity



10.6

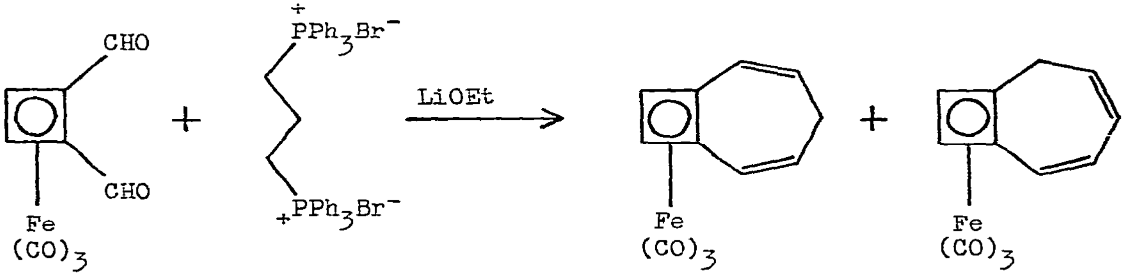


10.7

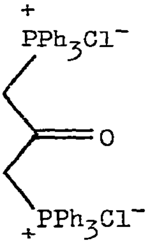


10.8

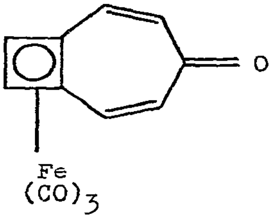
sequence towards nucleophilic attack by phosphines to be constructed:



10.9 10.10 10.11 10.12



10.13

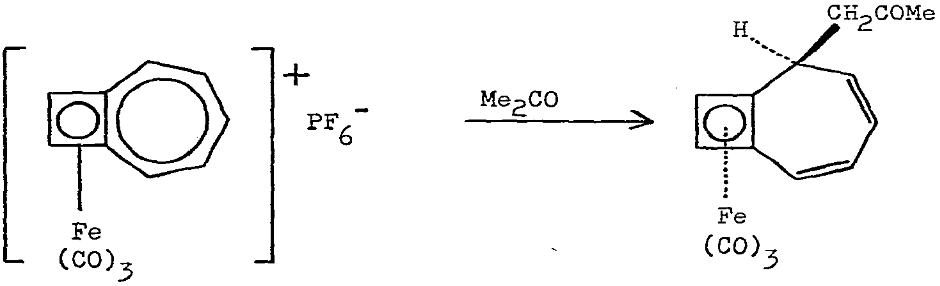


10.14

$[(\eta\text{-}C_7H_8)Mn(CO)_3]^+ > [(\eta\text{-}C_4H_4)Fe(CO)_2NO]^+ > [(\eta\text{-}C_6H_7)Fe(CO)_3]^+ >$ $[(\eta\text{-}C_6H_6OMe)Fe(CO)_3]^+ \gtrsim [(\eta\text{-}C_7H_7)M(CO)_3]^+$ where M = Cr, Mo, W $>$ $[(\eta\text{-}C_6H_6)Mn(CO)_3]^+$ [197].

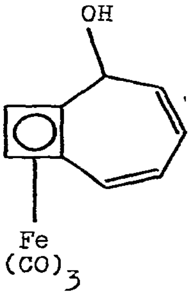
Direct sulphonation of tricarbonyl(η-cyclobutadiene)iron gave the sulphonic acid (10.8; $R = SO_3H$) which was converted, through the sulphonyl chloride (10.8; $R = SO_2Cl$), to amines such as the benzylamines (10.8; $R = NHCH_2Ph$) and the dimethylamine (10.8; $R = NMe_2$) and to the sulphide and mercaptan. Similar reactions were described for tricarbonyl(η-ethylcyclobutadiene)iron [198].

A Wittig reaction between the dialdehyde (10.9) and the ylid generated *in situ* from the phosphonium salt (10.10) gave a mixture of the isomers (10.11 and 10.12). A similar reaction of the dialdehyde (10.9) with the phosphonium salt (10.13) gave the tropone (10.14). Treatment of the isomers (10.11 and 10.12) with triphenylmethyl hexafluorophosphate gave the salt (10.15). This salt (10.15)

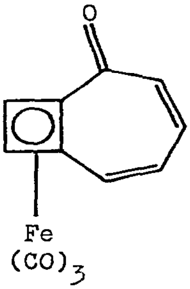


10.15

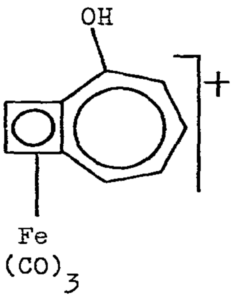
10.16



10.17

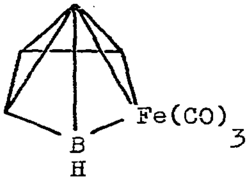


10.18



10.19

underwent rapid reaction with acetone to give the acetonyl derivative (10.16). Treatment of the salt (10.15) with sodium hydrogencarbonate gave the unstable alcohol (10.17) which was readily oxidized to the tropone (10.18). The tropone (10.18) was protonated readily by trifluoroacetic acid to give the cation (10.19) [199]. The crystal structure of the tricarbonyliron derivative (10.14) has been determined by X-ray analysis. The iron atom was symmetrically bound to the four carbon atoms of the cyclobutadiene ring with an iron--carbon distance of 0.205 nm [200]. Irradiation of (η-cyclobutadiene)tricarbonyliron with pentaborane (9) in diethyl ether gave a

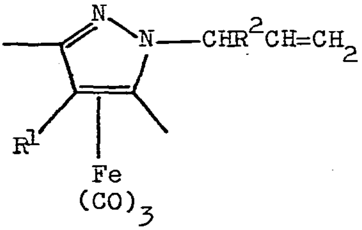


10.20

metallocarborane $BC_4H_5Fe(CO)_3$ with the probable structure (10.20) [201].

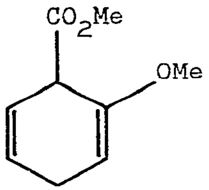
11. (Cyclic-η-diene)Fe(CO)$_3$

The photochemical reaction of ironpentacarbonyl with substituted 1-allylpyrazoles gave the (η-1-allylpyrazole)iron complexes (11.1; R^1 = H, Me, Br; R^2 = H, Me; R^1 = NO_2; R^2 = H). The ^1H and ^{13}C NMR spectra of the complexes have been analyzed and the olefinic nuclei

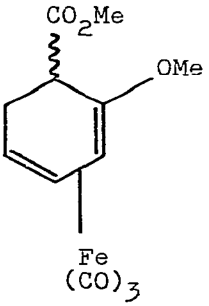


11.1

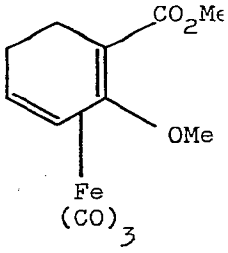
show upfield shifts by comparison with the free ligands. These shifts were not influenced by the substituents on the pyrazole ring [202]. Thiobenzophenones combined with the dicarbonyl(η-cyclopentadienyl)iron anion to form fulvenes as the major products. (η-Cyclopentadiene)iron complexes were invoked as possible intermediates in the reactions [203]. Reaction of the methyl ester (11.2) with pentacarbonyliron gave the (η-cyclohexadiene)iron complex (11.3) as a mixture of exo- and endo-isomers. Treatment of this isomer mixture with methanolic sulphuric acid gave the isomer (11.4). Reaction of the ester (11.4) with nonacarbonyliron gave the tricarbonyliron complex (11.5) which isomerised in sulphuric acid to the complex (11.6). The complexes (11.4, 11.5 and 11.6) underwent hydride abstraction in the presence of trityl fluoroborate to give the corresponding cations [204].



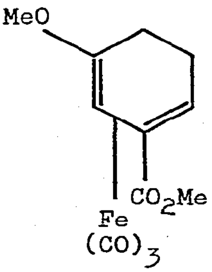
11.2



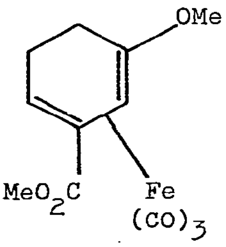
11.3



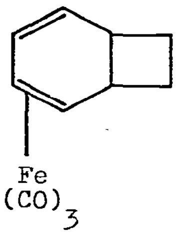
11.4



11.5

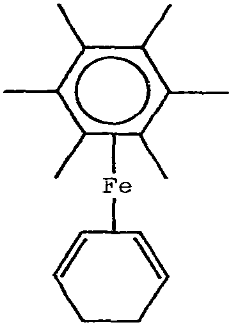


11.6

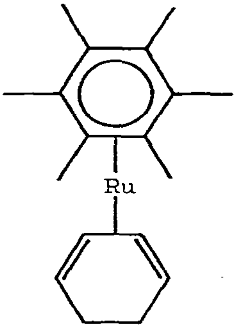


11.7

Graham has investigated the reactions of (η-benzylidene acetone)-tricarbonyliron [BDA.Fe.$(CO)_3$] with cyclic polymers. Thus cyclooctatriene was selectively trapped by BDA.Fe.$(CO)_3$ as the iron complex of the diene valence tautomer (11.7). This tautomer was present in equilibrium with the triene in only small proportion [205]. Norbornadiene combined with acetylenes on irradiation in the presence of iron pentacarbonyl to give a variety of polycyclic hydrocarbons and ketones. η-Polyeneiron complexes were presumably involved as intermediates in these reactions [206]. Synthetic approaches to mixed (η-arene)(η-diene)-iron and -ruthenium complexes have been reported by Bennett and Matheson. Reduction of the bis(η-hexamethylbenzene)iron cation with sodium amalgam and treatment of the neutral complex formed with 1,3- and 1,4-cyclohexadiene, gave the mixed complex (11.8). Cycloheptatriene and cyclooctatetraene complexes were also prepared. The dimeric ruthenium complex $[(\eta\text{-}C_6Me_6)RuCl_2]_2$ combined with 1,3-cyclohexadiene in the presence of ethanol and zinc dust to give the (η-cyclohexadiene)ruthenium complex (11.9). Several related ruthenium complexes were also characterized [207].

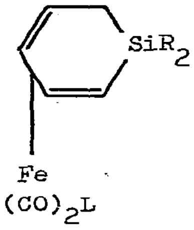


11.8

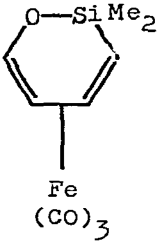


11.9

The (η-silacyclohexadiene)iron complexes (11.10; R = Me, Ph, Cl; L = CO) were obtained by reaction of the appropriate silacyclohexadiene with $Fe_3(CO)_{12}$. The crystal and molecular structure of one of the complexes (11.10; R = Ph; L = CO) has been determined by X-ray crystallography. Irradiation of the complexes (11.10) with triphenylphosphine gave the derivatives (11.10; R = Me, Ph; L = PPh_3) [208]. Treatment of 1,1-dimethyl-1-sila-2-oxa-cyclohexa-

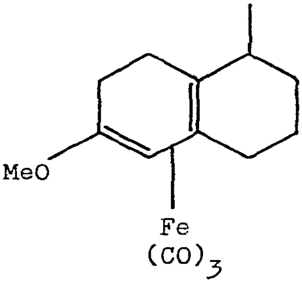


11.10

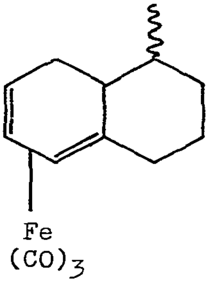


11.11

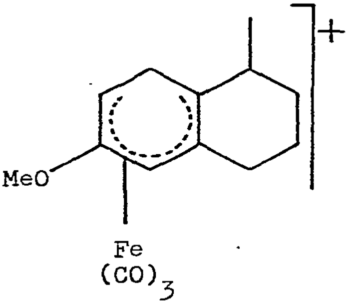
-3,5-diene with triiron dodecacarbonyl gave the tricarbonyliron complex (11.11) [209]. Reaction of 3-methoxy-7-methylbicyclo [4.4.0]deca-



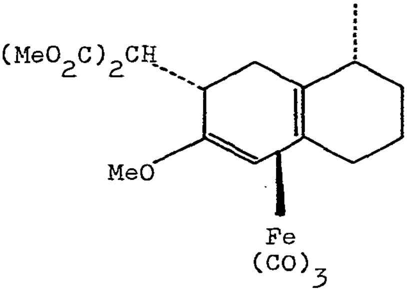
11.12



11.13



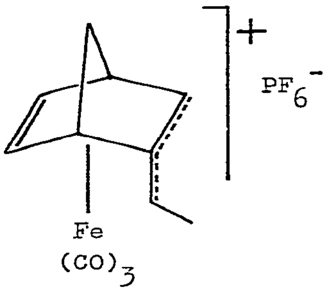
11.14



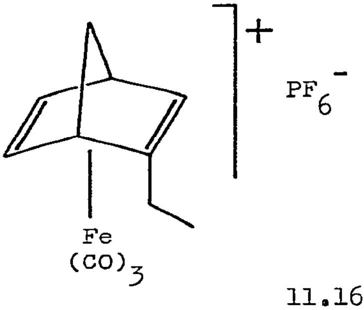
11.15

-1(6),3-diene with pentacarbonyliron gave a mixture of the endo- and exo-methyl isomers of the tricarbonyliron complex (11.12) together with a small quantity of the complex (11.13). Reaction of complex (11.12) with triphenylmethylium tetrafluoroborate gave the endo- and exo-methyl isomers of the dienylium complex (11.14) which was easily converted to the corresponding hexafluorophosphate. Treatment of the exo-isomer of the complex (11.14) with dimethyl sodiomalonate gave the diene complex (11.15). Similarly, reaction of the complex (11.12) with dimethyl sodiomalonate led to the (η-cyclohexadiene)iron complex (11.15) together with two isomers of this complex [210].

The chiral cationic (η-bicycloheptadienyl)iron complex (11.16) was obtained by treating the appropriate 1-ethanol complex with concentrated sulphuric acid and hexafluorophosphate. The ^{1}H NMR spectrum indicated that the allyl canonical form (11.16a) was preferred over the carbenium canonical form (11.16b) [211]. The bicyclooctadiene ligand (11.17) combined with iron pentacarbonyl to give a σ-η-allyl complex (11.18) by rearrangement rather than an η-diene complex [212]. Several (η-arenotropilidene)tricarbonyliron complexes have been formed from the appropriate arenotropilidene ligand and iron pentacarbonyl. Typical of the complexes characterized were the benzo-, furano-, and thiopheno-tropilidene compounds (11.19, 11.20; X = O and S) respectively. The structure of the thiophenotropilidene compound (11.20; X = S) was confirmed by an X-ray crystallographic analysis [213].

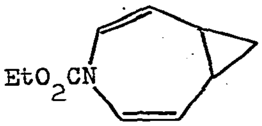


11.16a

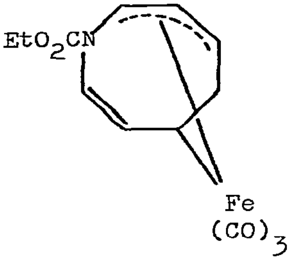


11.16b

Reaction of cyclonona-1,3,6-triene with diiron nonacarbonyl at 70° gave the tricarbonyliron complex (11.21) which rearranged to the bicycloderivative (11.22) at 100°. Treatment of bicyclo [6.1.0]-nona-2,4,6-triene (11.23) with diiron nonacarbonyl gave three products (Scheme 11.1) [214]. Diphenylketene added to tricarbonyl(η-cyclo-

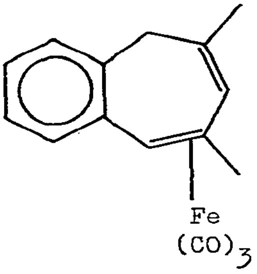


11.17

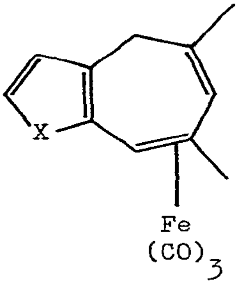


11.18

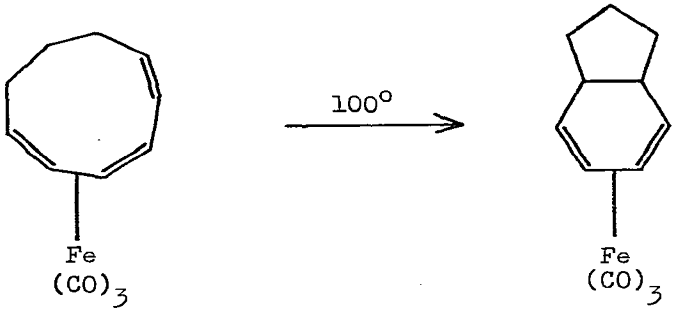
heptatriene)iron to give the dienone-iron complex (11.24) which rearranged in hot benzene to give the σ,η-allyliron complex (11.25).



11.19

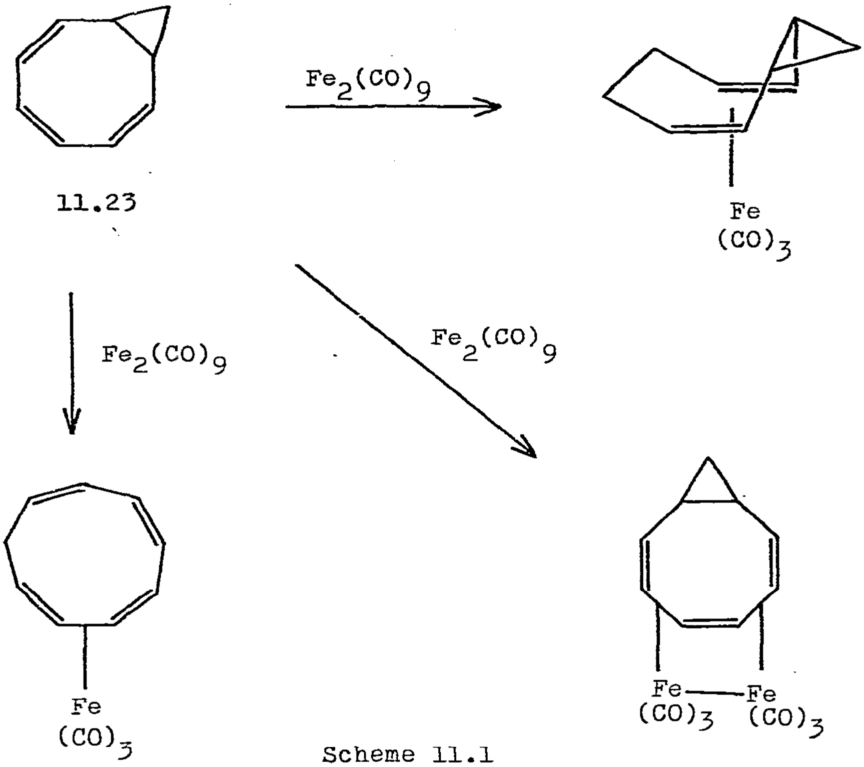


11.20



11.21

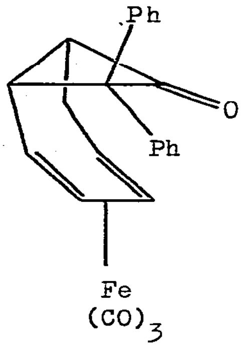
11.22



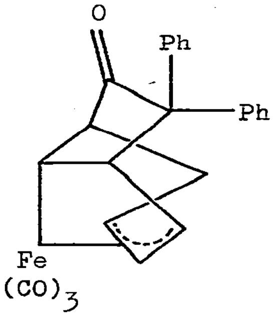
Scheme 11.1

Treatment of the complex (11.25) with cerium (IV) gave the dione (11.26) [215]. The tricyclic vinylcyclopropane (11.27) isomerized on irradiation with iron pentacarbonyl to give, among other products, the (η-diene)iron complex (11.28). The same complex (11.28) was obtained by irradiating the free ligand with iron pentacarbonyl [216]. The hexacyclictetraene iron complex (11.29) was formed from the corresponding ligand and diiron nonacarbonyl [217].

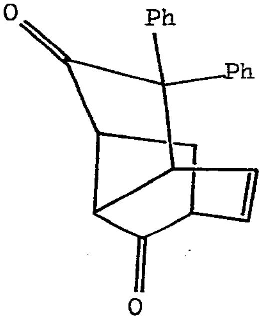
When cyclooctatetraene was heated with the hydridometal cluster $[Ru_4H_4(CO)_{12}]$ the Diels-Alder dimer of cyclooctatetraene (11.30) was formed together with the ruthenium carbonyl complexes (11.31) and (11.32). The reaction of cyclooctatetraene with $[Fe(CO)_3(\eta^4-C_8H_8)]$ gave the tricarbonyliron complex (11.33) [218].



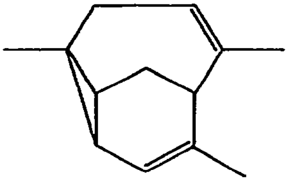
11.24



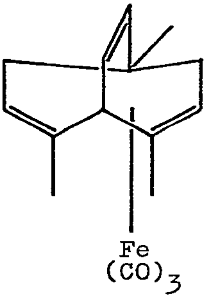
11.25



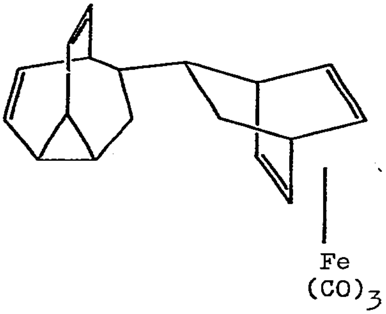
11.26



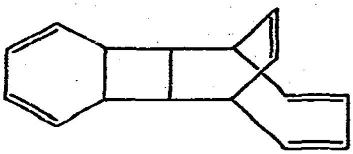
11.27



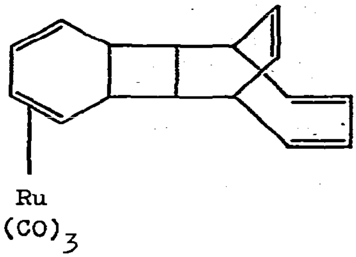
11.28



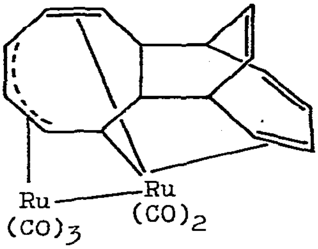
11.29



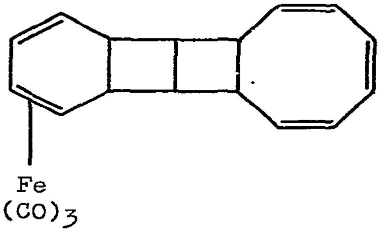
11.30



11.31



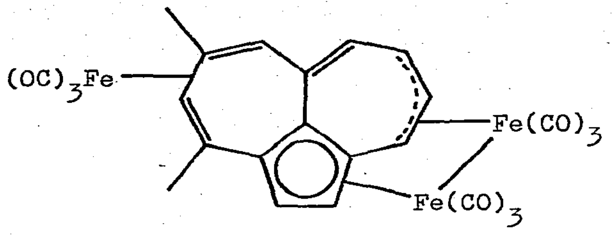
11.32



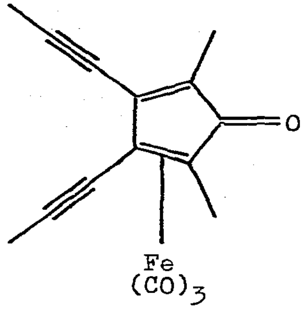
11.33

(ii) Spectroscopic and Physico-chemical Properties

Molecular orbital calculations were carried out for the (η-cycloheptatrienide)tricarbonyliron anion [(η-C_7H_7)Fe(CO)$_3$]$^-$. It was predicted that the η^3-allyl anion complex with an uncoordinated diene part of the η-C_7H_7 ligand was more stable than the alternative η^4-butadiene form. There was only a small energy difference between the two coordination modes and this was used to account for the high fluxionality of the complex anion [219]. Extended Hückel calculations indicated that there were substantial barriers to internal rotation in tricarbonyl(η-thiadiborolene)iron and tricarbonyl(η-diazaborolene)-chromium complexes and that the equilibrium geometry of these molecules differed. The results were explained and the rotational barriers in η-heterocyclopentadienyl and substituted η-cyclopentadienyl-ML$_3$ and -ML$_2$ complexes were considered [220].

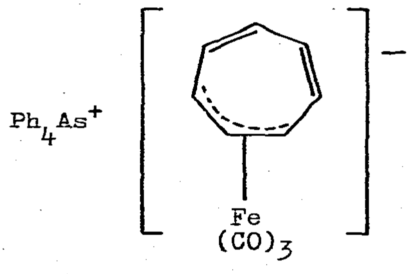


11.34

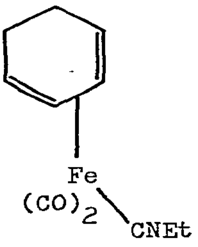


11.35

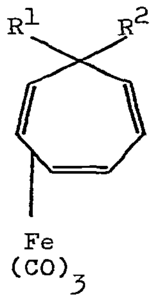
The (η-3,5-dimethylaceheptylene)nonacarbonyltriiron complex (11.34) has been identified and characterized by a single crystal X-ray structural analysis. The three iron atoms were each bonded in different ways, one to an η-cyclopentadienyl group, the second to an η-allyl group and the third to an η-*cis*-diene residue [221]. The (η-cyclopentadienone)iron complex (11.35), prepared from iron pentacarbonyl and 2,4-hexadiyne, has been characterized by X-ray crystallography. The butadiene fragment of the ligand was planar with the ketonic carbonyl group bent away from the iron atom by 14.1° [222].



11.36



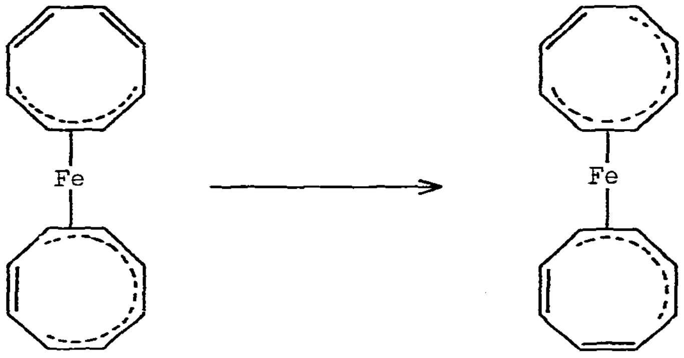
11.37



11.38

The crystal and molecular structure of the tricarbonyl(η-cycloheptatrienyl)iron complex (11.36) has been determined by X-ray crystallography. The tricarbonyliron group was bound to an allyl anion group while the remaining diene group in the ligand was uncoordinated [223]. The crystal structure of the η-1,3-cyclohexadiene complex (11.37) has been determined by X-ray analysis. The iron atom was pentacoordinate with the isonitrile ligand, a carbonyl group and two carbon atoms of the diene part of the η-C_6H_8 ring occupying the basal positions of a square pyramid. Vibrational and ^{13}C NMR spectra indicated that the molecule was fluxional in solution [224].

Cotton and Hanson have called attention to the wide range of rates observed for the localized scrambling of carbonyl groups in (η-cyclodiene)- and (η-cyclotriene)-iron tricarbonyl complexes. Possible pathways for the stereodynamic processes were discussed and the most favourable pathway identified. The activation energy for carbonyl scrambling was found to increase with an increase in the π-acceptor ability of the ligand [225]. Karel and Brookhart have used a ^1H NMR spin saturation transfer technique to measure the 1,3-iron shift in the fluxional (η-cycloheptatriene)iron complexes (11.38). The free energy of activation for the complex containing an unsubstituted ligand (11.38; $R^1 = R^2 = H$), $\Delta G^{\ddagger} = 22.3$ kcal mol^{-1}, was lower than for the substituted complex (11.38; $R^1 = Ph$, $R^2 = CO_2Me$), $\Delta G^{\ddagger} = 23.9$ kcal mol^{-1}. A symmetrical tricarbonyl(η^2-cycloheptatriene)iron species and a tricarbonyl(η^4-bicyclo[4.2.0]octa-2,4--diene)iron species were considered as possible intermediates in the



11.39a

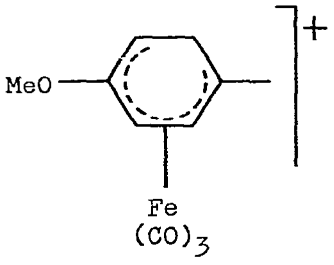
11.39b

rearrangement [226].

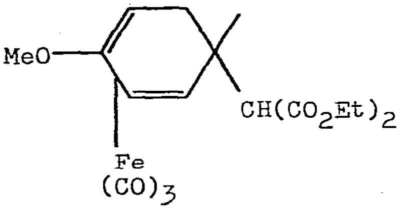
A ^{13}C NMR investigation was carried out on the ring exchange in the iron complex (11.39a). It was concluded that the site exchange (11.39a→11.39a) between the η^4- and η^6-rings in the complex occurred *via* a mechanism where the transition state retained the differentiation between the four different types of CH groups in the η^6-C_8H_8 ring with $\Delta G^{\ddagger} = 10.9$ kcal mol^{-1}. There was no evidence for any shifts within the η^6-C_8H_8 ring, while the shifts within the η^4-C_8H_8 ring had $\Delta G^{\ddagger} < 5.4$ kcal mol^{-1} [227].

(iii) General Chemistry

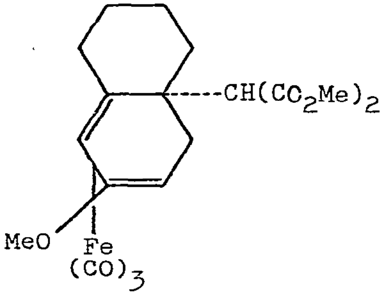
The (η-methylcyclohexadienyl)iron cation (11.40) underwent addition of carbanions derived from 1,3-dicarbonyl compounds, such as diethyl malonate, exclusively at the methylated ring position to form neutral complexes such as the (η-methylcyclohexadiene)iron complex (11.41). The tricarbonyliron group was removed from the product (11.41) on heating with trimethylamine N-oxide in benzene to give diethyl 4-methoxy-1-methylcyclohexa-2,4-dienylmalonate. The same reaction has been employed to introduce angular substituents into bicyclic complexes to give products such as the (η-4-methoxybicyclo-[4.4.0]deca-3,5-diene)iron complex (11.42) [228]. Iron pentacarbonyl



11.40

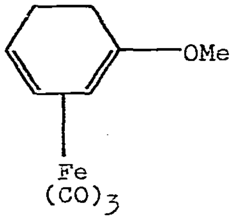


11.41

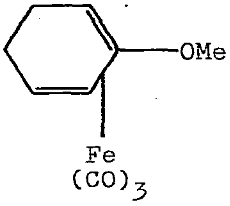


11.42

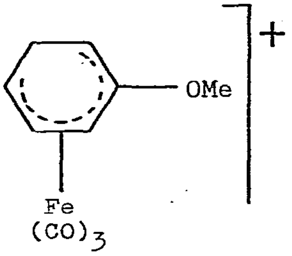
combined with 1-methoxy-1,4-cyclohexadiene to form a mixture of the isomeric (η-cyclohexadiene)iron complexes (11.43 and 11.44) which on treatment with $Ph_3C^+BF_4^-$ underwent hydride abstraction to give the (η-cyclohexadienyl)iron cations (11.45 and 11.46). Hydrolysis of the cation (11.45) gave the (η-cyclohexadienone)iron complex (11.47) [229].



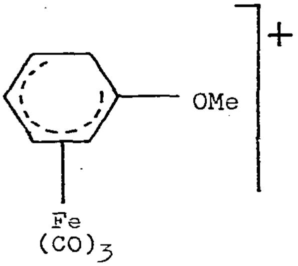
11.43



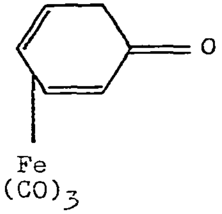
11.44



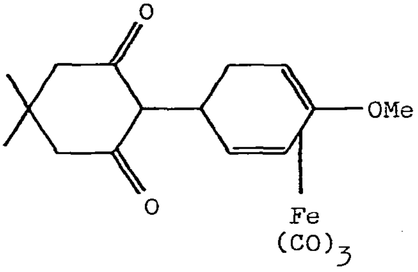
11.45



11.46

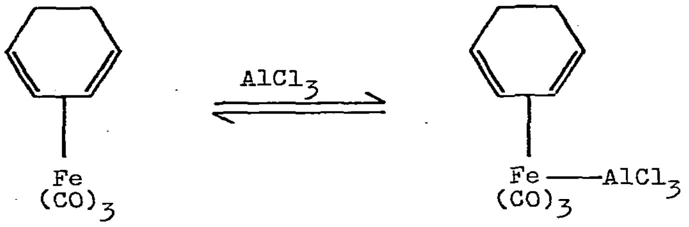


11.47



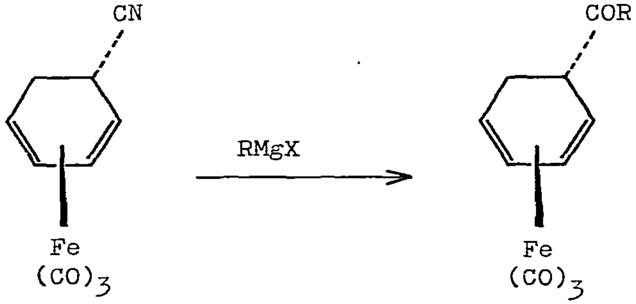
11.48

The (η-cyclohexadienyl)iron cation (11.46) has been used as an alkylating agent for dimedone when the (η-cyclohexadiene)iron derivative (11.48) was obtained [230]. The tricarbonyl(η-cyclohexadienyl)iron cation has been used also as an alkylating agent for adenine, guanine, cytosine, adenosine and guanosine. Both mono- and di-alkylation were observed in the first two cases [231]. An aluminium trihalide was added gradually to the η-cyclohexadiene complex (11.49) and the reaction was monitored by IR spectroscopy. It was suggested that an aluminium halide adduct (11.50) was formed. Tricarbonyl(η-cycloheptatriene)iron and tricarbonyl(η-cyclooctatetraene)iron formed similar adducts with aluminium halides [232]. The crystal and molecular structure of tricarbonyl(η-5-exo-cyanocyclohexa-1,3-diene)iron (11.51) has been determined by X-ray crystallography and this compound has been used for the stereospecific synthesis of (η-5-exo-acylcyclohexa-1,3-diene)iron complexes (11.52; R = Me, Et, Pr^n, Bu^n, Ph) by treatment with the appropriate Grignard reagent [233].



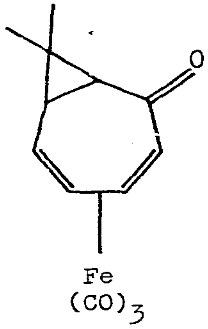
11.49 11.50

The photolysis of (η-1,3-diene)tricarbonyliron complexes bearing electron-withdrawing groups on the 1-position was carried out in acetic acid to give regioselective hydrogenation and cleavage of the metal-ligand bond. Thus (η-benzoylcyclobutadiene)tricarbonyliron gave 3-benzoylcyclobutene in 85% yield, the (η-cycloheptadienone)iron

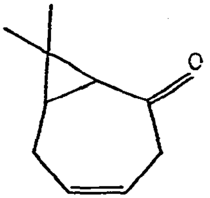


11.51 11.52

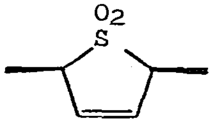
complex (11.53) gave the cycloheptenone (11.54) in 90% yield, (η-2,5-dimethylthiophene-1,1-dioxide)tricarbonyliron gave the dihydrothiophene-1,1-dioxide (11.55), 75% yield and the (η-butadiene)tricarbonyliron complex (11.56) gave the butene (11.57), 80% yield. Under the same conditions an (η-bicycloheptadiene)tricarbonyliron complex underwent carbonylation as well as reduction [234]. The tropone-tricarbonyliron complex (11.58) has been irradiated with left or right circularly polarized light at λ = 380-500 nm. Photolytic destruction of one enantiomer of the tropone complex (11.58) occurred to give stable optical activity in the complex. The observation



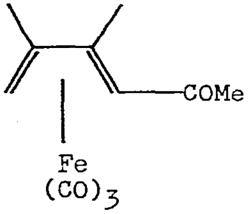
11.53



11.54



11.55



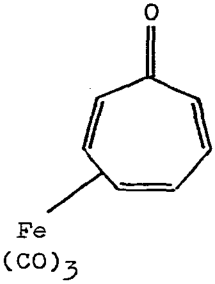
11.56

$CMe_2=CMeCH_2COMe$

11.57

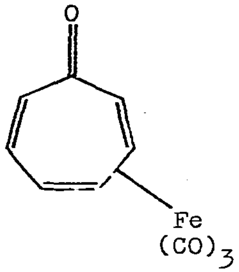
of this stable optical activity confirmed the existence of chirality in the molecule induced by metal coordination [235].

High performance liquid chromatography was used to study the thermal rearrangements of four isomers of (η-phenylcycloheptatriene)-tricarbonyliron (11.59, 11.60, 11.61 and 11.62). Rearrangement of the four pure isomers (11.59, 11.60, 11.61 and 11.62) in isooctane at 90° gave an equilibrium mixture of three of the isomers (11.60, 11.61 and 11.62) [236]. Reaction of the η-tropone complex (11.63) with diphenylketene and diphenyleneketene gave the tricarbonyliron complexes (11.64 and 11.65) respectively [237]. Some preliminary results of a systematic study of 1,3-dipolar and Diels-Alder cyclo-additions with tricarbonyl(η-tropone)iron (11.66) were reported. Benzonitrile oxide and 2,4,6-trimethylbenzonitrile oxide added regiospecifically and stereospecifically to give the adducts (11.67, R = Ph) and (11.67; R = 2,4,6-$Me_3C_6H_2$) respectively. Reaction of the dimer of (11.68) with the complex (11.66) gave the tricarbonyl-iron derivative (11.69) together with the tropone derivative (11.70). The products obtained by treatment of the adducts with cerium (IV) were examined [238].

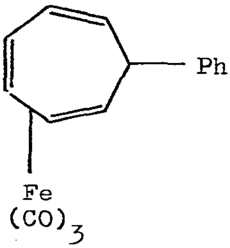


11.58a

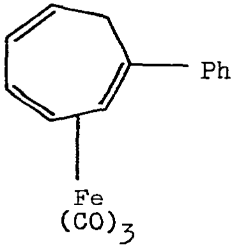
mirror
plane



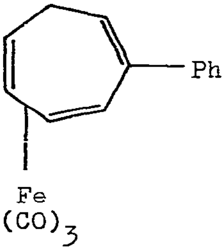
11.58b



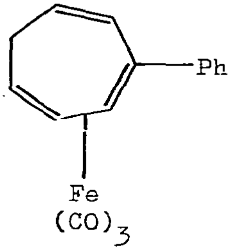
11.59



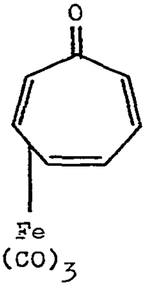
11.60



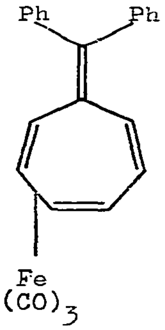
11.61



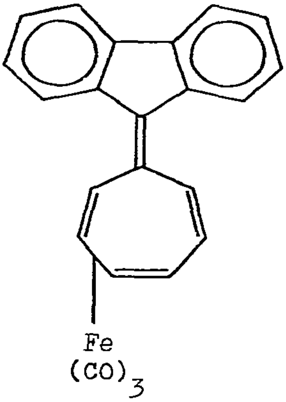
11.62



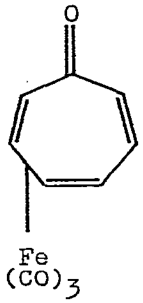
11.63



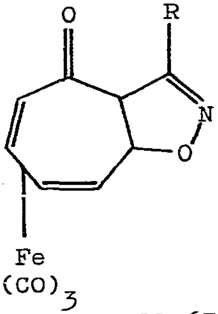
11.64



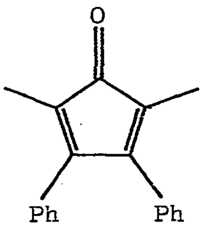
11.65



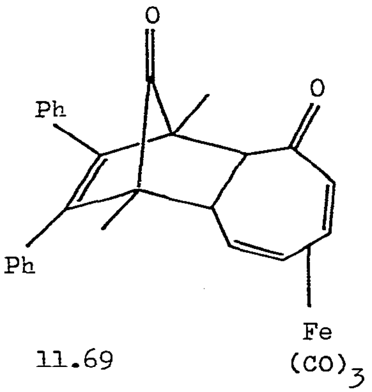
11.66



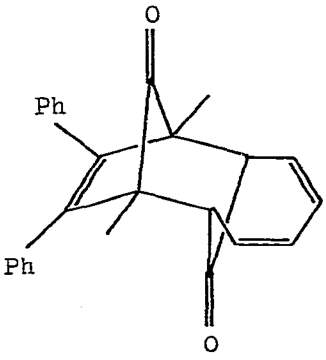
11.67



11.68

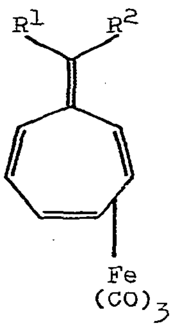


11.69

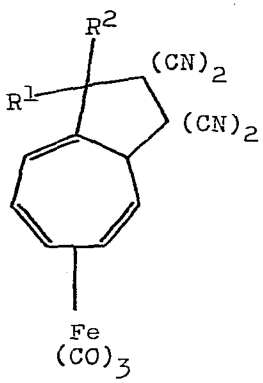


11.70

McArdle has investigated the mode of addition of tetracyanoethylene to 7-methylenecycloheptatriene iron complexes (11.71; R^1 = Me, Ph, R^2 = H; R^1 = Ph, R^2 = Me) and has obtained the products (11.72; R^1 = Me, Ph, R^2 = H; R^1 = Ph, R^2 = Me) [239]. Aluminium chloride was an effective catalyst for the carbonylation of tricarbonyl(η-cyclohexadiene)iron to the (η-cycloheptenediyl)iron complex (11.73) which on heating at 110°C in the presence of carbon monoxide at 100 atmospheres pressure gave the bicyclooctenedione (11.74). The intermediate (11.73) isomerized in hot benzene to form the (η-cycloheptadienone)iron complex (11.75) [240]. Treatment of tricarbonyl(η-cyclooctatetraene)iron with acetyl chloride under Friedel-Crafts conditions gave the cation (11.76) as the major product. X-ray analysis of the hexafluorophosphate salt of the cation (11.76) showed that the acetyl group was endo to the localized double bond and the PF_6^- anion was disordered [241].

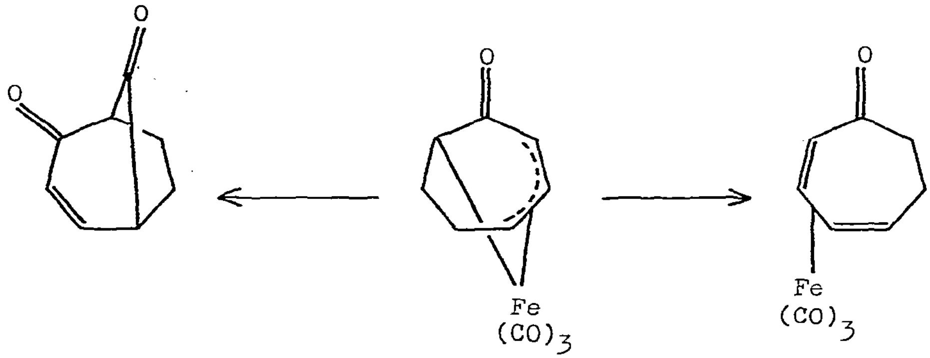


11.71

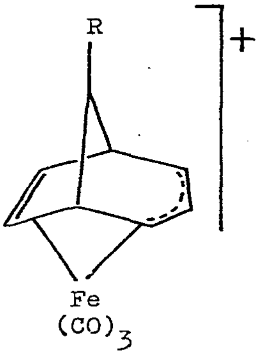


11.72

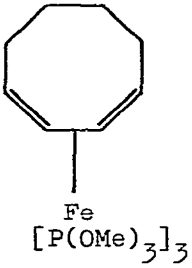
Protonation of the (η-1,3-cyclooctadiene)iron complex (11.77) with acids such as acetic acid and fluoroboric acid gave the (η-cyclooctenyl)iron cation (11.78), the first example of a 16-electron (η-enyl)iron complex [242]. Treatment of the heterobicyclic compound (11.79) with diiron nonacarbonyl gave three products (11.80, 11.81 and 11.82). A similar reaction between the diene (11.83) and diiron nonacarbonyl gave a complicated mixture of products. The structures of these products were discussed and a mechanism was proposed for their formation. It was proposed that an initial oxidative insertion of iron into the >N—O bond occurred, followed by several competing reactions [243]. Asymmetric hydrogenation catalysts analogous to (η-arene)(η-cycloocta-1,5-diene)ruthenium were prepared using polystyrene [244].



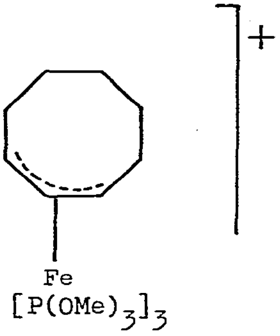
11.74 11.73 11.75



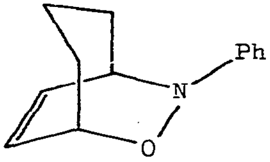
11.76



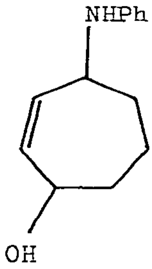
11.77



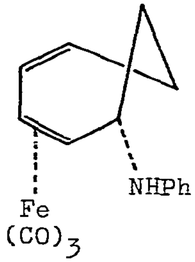
11.78



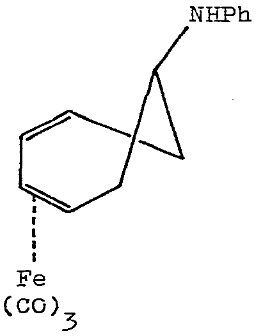
11.79



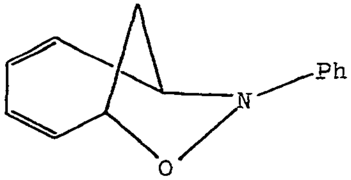
11.80



11.81



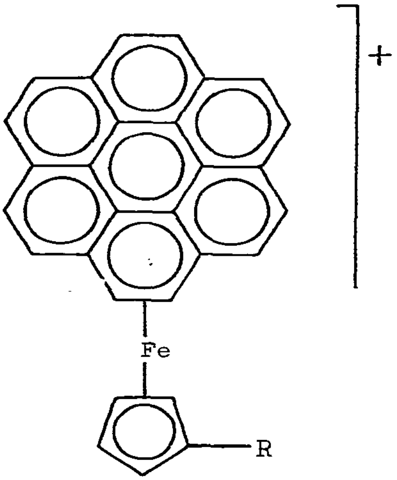
11.82



11.83

12. $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_6H_6)]^+$

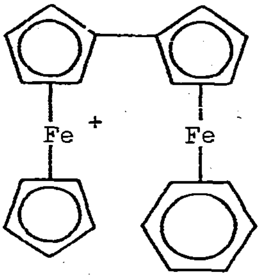
Ferrocene and 1,1'-dimethylferrocene underwent ligand exchange with coronene in the presence of aluminium chloride to form the cations (12.1; R = H, Me) which were isolated as the hexafluorophosphate salts. ^1H and ^{13}C NMR spectroscopy indicated that the (η-cyclopentadienyl)iron group was bonded to an outer ring of the coronene ligand and this finding was supported by calculations based on the iterative extended Hueckel model which determined the energy contents, bond orders, and charge distributions for four different coordination positions of the (η-cyclopentadienyl)iron group [245].



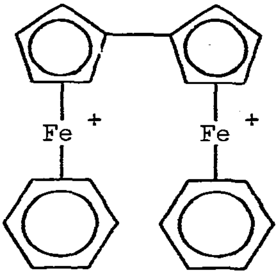
12.1

The ligand exchange reaction between biferrocenyl and arenes such as benzene, mesitylene, naphthalene and tetralin was catalysed by aluminium chloride. It was possible to exchange either one or two moles of arene for cyclopentadienyl to give two products. Thus benzene underwent exchange to give the (η-benzene)iron cation (12.2) and the di(η-benzene)iron dication (12.3)[246].

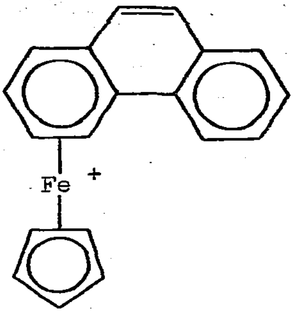
The reaction of ferrocene with phenanthrene in the presence of aluminium chloride-aluminium in decalin (molar ratio 1:1:2:1) gave a mixture of cations (12.4 and 12.5). The effect of solvent and temperature on this reaction was investigated. When the molar ratio of ferrocene-phenanthrene-aluminium chloride-aluminium was 5:1:10:1 the dications (12.6 and 12.7) were isolated. Similar reactions with 9,10-dimethylphenanthrene were investigated [247]. Reduction of



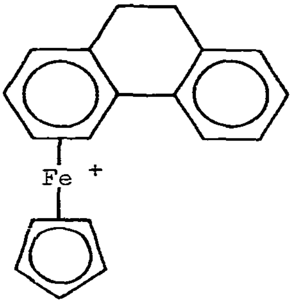
12.2



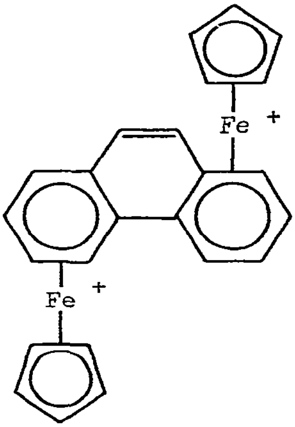
12.3



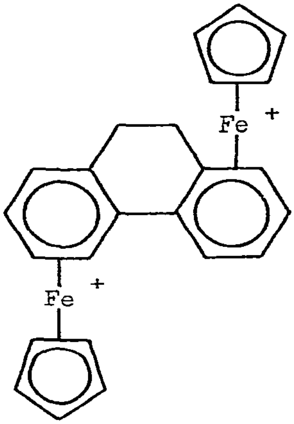
12.4



12.5



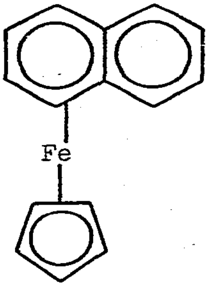
12.6



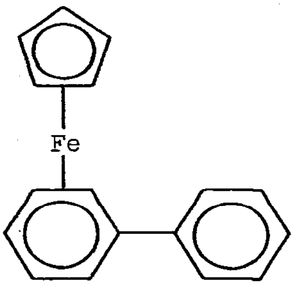
12.7

(η-cyclopentadienyl)(η-naphthalene)iron tetrafluoroborate with sodium amalgam in dimethoxyethane gave neutral (η-cyclopentadienyl)(η-naphthalene)iron (12.8) in 70% yield. The complex (12.8) was paramagnetic and the EPR spectrum indicated that the unpaired electron was on the $a_{1g}(3d_{z^2})$ metal orbital. The complex (12.8) was oxidized in air to form the initial cationic complex and hydrolyzed in water with loss of both ligands together with the formation of some ferrocene. The corresponding (η-cyclopentadienyl)(η-tetralin)iron complex showed similar properties to (η-benzene)(η-cyclopentadienyl)iron [248].

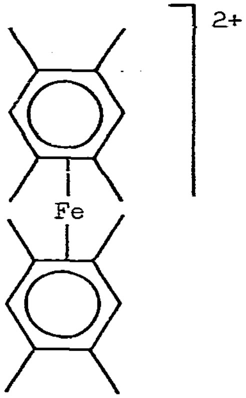
The (η-biphenyl)(η-cyclopentadienyl)iron complex (12.9) was obtained in good yield by reduction of the corresponding cation with sodium amalgam in THF. The biphenyl ligand was displaced by benzene to form (η-benzene)(η-cyclopentadienyl)iron [249]. The bis(η-durene)-iron dication (12.10) was reduced with sodium amalgam or sodium dithionite to the corresponding monocation while reduction with sodium



12.8

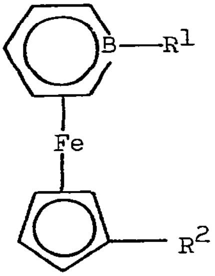


12.9

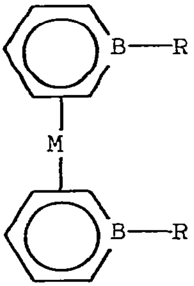


12.10

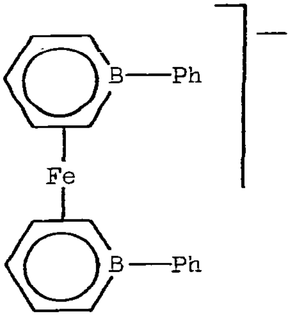
borohydride caused one of the arene ligands to be reduced to a cyclohexadienyl ligand. A similar effect was observed in the borohydride reduction of the bis(η-benzene)iron dication [250]. Cyclic volt-



12.11



12.12



12.13

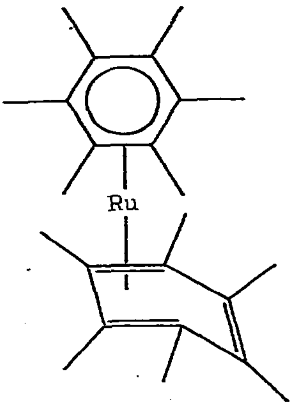
ammetry of (η-borinato)(η-cyclopentadienyl) and of bis(η-borinato) complexes (12.11; R^1 = Me, R^2 = H; R^1 = Ph, R^2 = H; $R^1 = R^2$ = Ph) and (12.12; M = Fe, R = Ph, Me; M = Cr, R = Ph, Me; M = V, R = Me) respectively was carried out at a platinum electrode. Oxidation of the iron complexes occurred with varying degrees of reversibility depending on the solvent. The iron complex (12.12; R = Ph, M = Fe) was reduced reversibly in tetrahydrofuran to give the corresponding anion (12.13). The chromium complexes gave anions and cations reversibly, and the vanadium compound formed an anion [251].

13. $(\eta\text{-}C_5H_5)_2Ru$ and $(\eta\text{-}C_5H_5)_2Os$

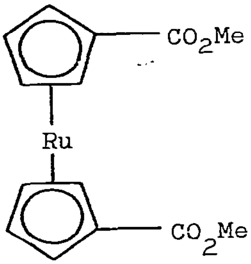
Iodoruthenocene was prepared from lithioruthenocene and the reaction conditions were optimised to give the monoiodo product exclusively. Iodoruthenocene was separated from 1,1'-diiodoruthenocene by high pressure liquid chromatography. Synthetic methods were described for the preparation of biruthenocene, biruthenocenylene and ferrocenyl-ruthenocene [252]. The formation of [3]- and [4]-ruthenocenophanes required more vigorous conditions than the formation of the corresponding ferrocenophanes. Ring-tilting was observed in both the tri- and tetra-bridged species and it was more significant in the former than in the latter [253]. Ferrocene derivatives, ruthenocene derivatives and osmocene have been used as quenching agents for the uranyl ion. Quenching constants (k_Q) were determined both from luminescence intensity and lifetime measurements. An electron-transfer mechanism was supported by the correlation between $\log_{10}k_Q$ and the oxidation potentials of the metallocenes and by photoreaction studies where either the $[UO_2]^+$ ion or uranium (IV) species were observed [254].

The variable-temperature ^1H NMR spectra of the fluxional ruthenium complex (13.1) were recorded. The effect of added trimethylaluminium on these spectra was discussed and a mechanism that accounted for the fluxional behaviour of the molecule (13.1) was proposed [255]. Benzoylruthenocene labelled with ^{103}Ru was prepared by a ligand exchange reaction between benzoylferrocene and $^{103}RuCl_3$ at 180° [256]. Estrone 3-ruthenocenecarboxylate and 17β-estradiol 3-ruthenocenecarboxylate labelled with ^{103}Ru have been obtained by exchange from the corresponding ferrocene compounds and $^{103}RuCl_3$. The organ distribution and excretion of these labelled compounds in mice has been compared with ruthenocenecarboxylic acid and methyl ruthenocenecarboxylate [257]. The fate of ^{103}Ru-labelled ruthenocene administered to mice has been investigated. Most of the ^{103}Ru was eliminated from the body within twenty four hours. The remainder which was located in the liver, gastrointestinal tract and fat was excreted slowly. The ^{103}Ru was excreted in the bile and urine as ruthenocene O-glucuronide [258].

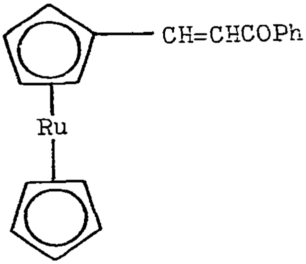
The tissue distributions of ^{103}Ru radioactivity from 1,1'-ruthenocene-^{103}Ru-dicarboxylic acid dimethylester (13.2) and benzoyl-vinyl-ruthenocene-^{103}Ru (13.3) were compared with those of ^{67}Ga citrate which is frequently used in scintigraphy. In mice with solid



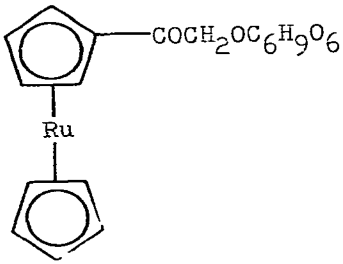
13.1



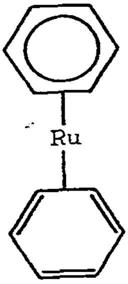
13.2



13.3



13.4

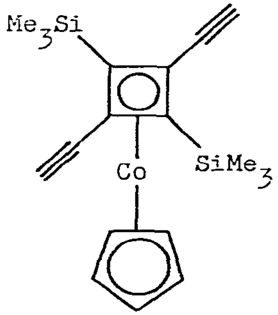


13.5

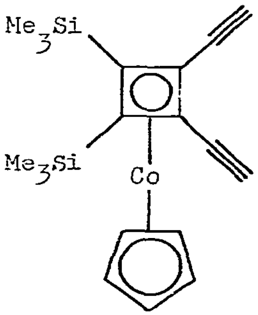
Ehrlich carcinomas, the tumor to muscle ratio was approximately 4:1 for the three compounds. The ruthenocene derivatives (13.2 and 13.3) concentrated preferentially in the small tumors and the ^{67}Ga citrate accumulated uniformly in both the large and small tumors [259]. ^{103}Ru-labelled acetylruthenocene was administered orally to rats. The major metabolite detected in both the bile and urine was the glucuronide (13.4) [260]. Ruthenium vapour has been generated by resistive heating of tungsten filaments coated with a mixture of ruthenium powder and epoxy resin ('Araldite'). The cocondensation of the ruthenium vapour with benzene gave the ruthenium complex (13.5). The 1—4-η:1—6-η structure of the complex (13.5) was supported by ^{1}H NMR evidence [261].

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

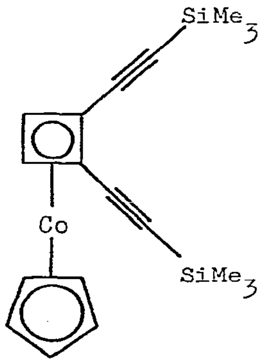
Heating bis(trimethylsilyl)butadiyne with dicarbonyl(η-cyclopentadienyl)cobalt in decane gave a mixture of the isomeric (η-cyclobutadiene)(η-cyclopentadienyl)cobalt complexes (14.1 and 14.2). The unsymmetrical isomer (14.2) underwent an interesting rearrangement on heating to 525° *in vacuo* to form the complex (14.3). A bicyclobutadienylene complex was proposed as a possible intermediate in the reaction [262]. Dicarbonyl(η-cyclopentadienyl)cobalt was heated with diferrocenylacetylene in xylene to form the (η-tetraferrocenylcyclobutadiene)iron complex (14.4; R^1 = R^2 = R^3 = ferrocenyl). When ferrocenylphenylacetylene was used as the reagent then a mixture of the structural isomers (14.4; R^1 = ferrocenyl, R^2 = R^3 = Ph; R^1 = R^3 = Ph, R^2 = ferrocenyl) was obtained. The structure of one of these



14.1

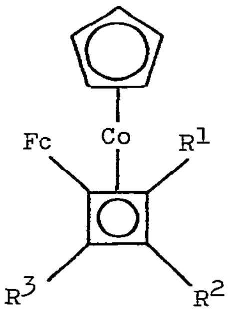


14.2



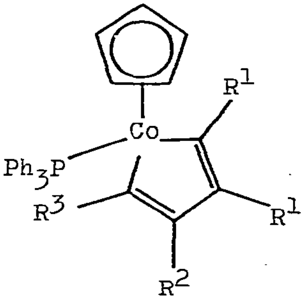
14.3

isomers (14.4; $R^1 = R^3 = Ph$, R^2 = ferrocenyl) has been determined by X-ray crystallography [263].

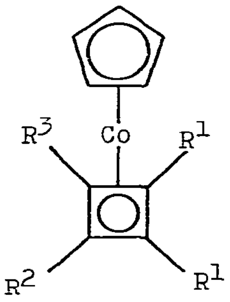


14.4

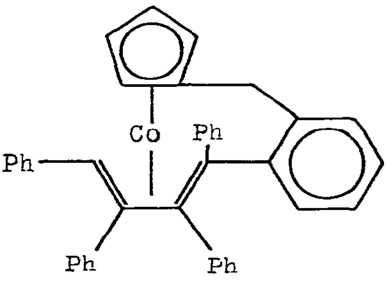
Thermolysis of (η-cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene complexes (14.5; R^1, R^3 = Ph, $R^2 = CO_2Me$; R^1 = Ph, R^2 = Me, $R^3 = CO_2Me$; R^1 = Ph, R^2, $R^3 = CO_2Me$) by heating the solids to just above the melting point or the benzene solutions to 150° for several hours in a sealed tube gave the corresponding (η-cyclobutadiene)(η-cyclopentadienyl)cobalt complexes (14.6; R^1, R^3 = Ph, $R^2 = CO_2Me$; R^1 = Ph, R^2 = Me, $R^3 = CO_2Me$; R^1 = Ph, R^2, $R^3 = CO_2Me$). Similar treatment of benzyl-substituted cyclopentadienyl derivatives gave diene complexes such as the tetraphenyl complex (14.7) which were formed by addition of the ortho-hydrogen of the benzyl group to the cobaltacyclopentadiene ring [264]. The formation of several related



14.5



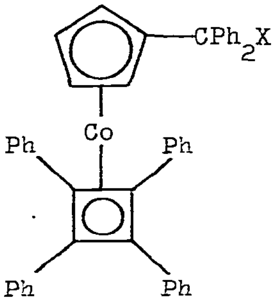
14.6



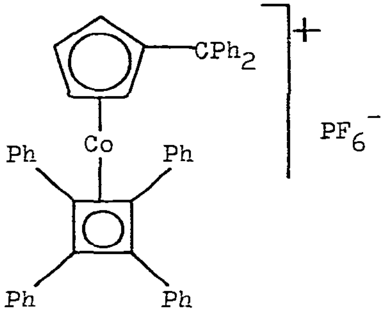
14.7

(η-butadiene)(η-cyclopentadienyl)cobalt complexes containing heteroatoms (sulphur, nitrogen, silicon) has been described [265].

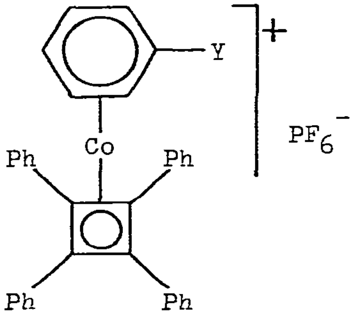
Treatment of (η-diphenylhydroxymethylcyclopentadienyl)(η-tetraphenylcyclobutadiene)cobalt (14.8, X = OH) with diethyloxonium hexafluorophosphate gave the corresponding carbenium ion salt (14.9). This salt (14.10) behaved as a carbon electrophile with methanol, methylamine and N-methylpyrrole to give the complexes (14.8; X = OMe, NHMe and C_4H_3NMe) respectively and as a cobalt electrophile with N,N-dimethylaniline and anisole to give the complexes (14.10; Y = NMe_2 and OMe) respectively. Similar reactions with benzene, toluene and mesitylene only occurred in the presence of aluminium chloride [266].



14.8



14.9

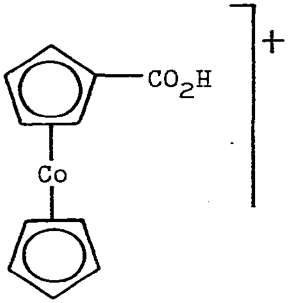


14.10

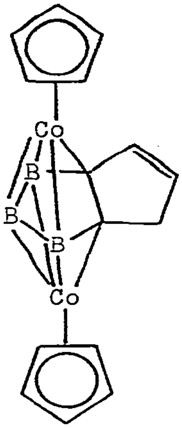
Clack and Warren have continued their theoretical studies of transition metal complexes with INDO SCF MO calculations on the formally d^6 complex, (η-cyclobutadiene)(η-cyclopentadienyl)cobalt, which have indicated a diamagnetic ground state. The calculated charge distributions on the cyclobutadiene ligand were interpreted in terms of its behaviour as a π-donor [267].

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

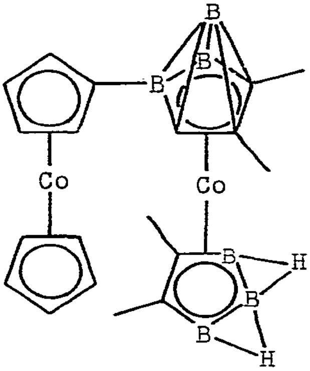
Extended X-ray absorption fine structure spectroscopy has been used to determine the metal-ligand distance in cobaltocene and in a number of cobalt complexes [268]. The crystal and molecular structure of carboxycobalticinium hexafluorophosphate has been determined by single crystal X-ray diffraction. The structure consisted of hydrogen-bonded dimers of the cation (15.1) and discrete PF_6^- anions. The η-cyclopentadienyl rings adopted a staggered configuration and the mean



15.1



15.2



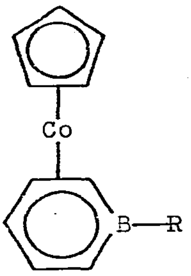
15.3

cobalt-ring carbon distance was appreciably shorter than in cobaltocene [269]. The crystal and molecular structure of the triple-decker sandwich metallocarborane (15.2) has been determined by X-ray methods. The complex contained a seven-vertex pentagonal bipyramid with the two cage carbon atoms bridged by an exo-polyhedral propenylene group [270]. The crystal and molecular structure of the cobalticinium cobaltacarborane zwitterion (15.3) has been determined by X-ray crystallography [271].

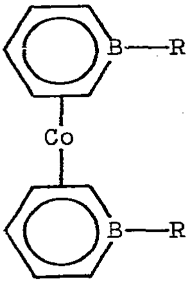
Cyclic voltammetry of the (η-borabenzene)cobalt complexes (15.4 and 15.5; R = Me, Ph) at a platinum electrode in acetonitrile has revealed reversible one-electron oxidation in each case to the corresponding cations and reversible one-electron reduction to the anions [272].

The temperature dependent paramagnetic ^{13}C and ^{1}H NMR spectra of the cobaltocenes (15.6; R = H, Me, Et, i-Pr, n-Bu, t-Bu) have been recorded. From the results it was concluded that cobaltocenes could be classified as nonrigid molecules [273]. ^{13}C NMR spectra have been recorded for a series of metallocenes and perdeuterated cobaltocene as part of an investigation into isotope effects in the NMR of paramagnetic compounds. An isotope shift was observed and it increased with the number of unpaired electrons and with the efficiency of electron delocalization [274].

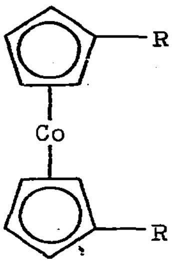
The ligand exchange reactions of cobaltocene and nickelocene have been investigated. Ligand exchange between the metallocenes and a



15.4



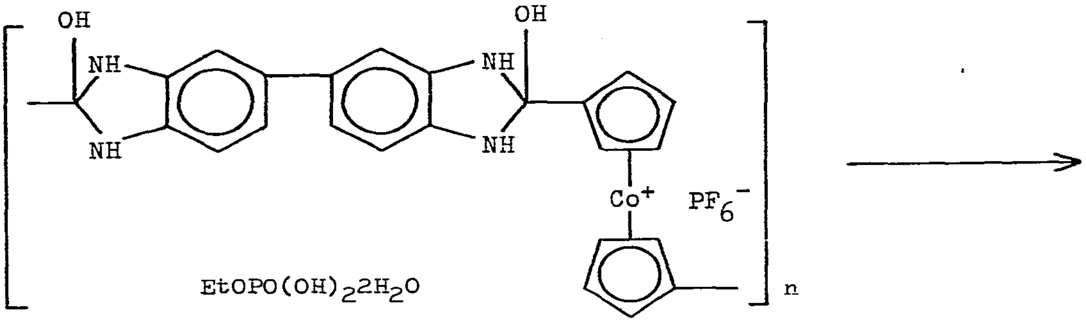
15.5



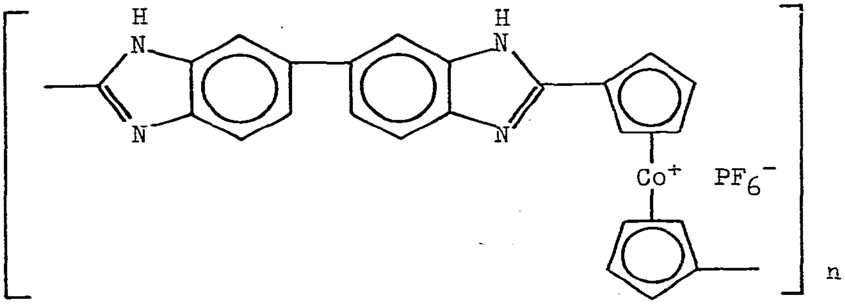
15.6

diene, with concurrent reduction of the metal atom, gave the corresponding (η-cyclopentadienyl)(η-diene)cobalt (I) complexes (diene = duroquinone, 2,5-ditertiarybutyl-p-benzoquinone, 3-p-biphenyltetracyclone, 3,4-bis-p-chlorotetracyclone, tetracyclone and 2-methyl-3,4,5-triphenylcyclopenta-2,4-diene-1-one) and $(\eta\text{-diene})_2Ni(0)$ complexes (diene = duroquinone, tetracyclone) [275]. The decomposition of organic hydroperoxides on a series of transition metal π-complexes was investigated. The catalytic activities, for the decomposition of $PhCMe_2OOH$, were in the orders; ferrocene > acetylferrocene > 1,1'-diacetylferrocene and ferrocene > cobaltocene > nickelocene [276].

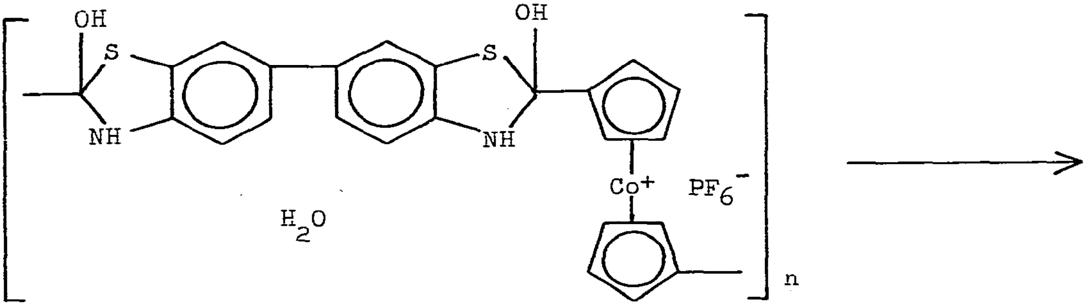
Cobalt was coated on a copper surface activated with palladium by decomposition of cobaltocene with hydrogen at 150-350°C. The coated surface was solderable [277]. 1,1'-Dicarboxycobalticinium hexafluorophosphate was polycondensed with 3,3'-diaminobenzidine in ethylated polyphosphoric acid at 100-240° to give linear, soluble polymers (15.7). The polymer (15.7) was heated at 250-300° in the solid state, aromatization occurred to give the polybibenzimidazole (15.8). In a similar reaction 1,1'-dicarboxycobalticinium hexafluorophosphate was condensed with 3,3'-dimercaptobenzidine to give the polymer (15.9) which when heated was converted to the corresponding polymeric benzothiazole (15.10) [278]. 1,1'-Dicarboxycobalticinium chloride was copolymerized with 1,4-phenylenediamine, 4,4'-biphenylenediamine or 4,4'-methylenedianiline in antimony (III) chloride to give a polyamide containing the cobalticinium tetrachloroantimonate salt system in the recurring unit. The copolymers were soluble and film-forming [279].



15.7

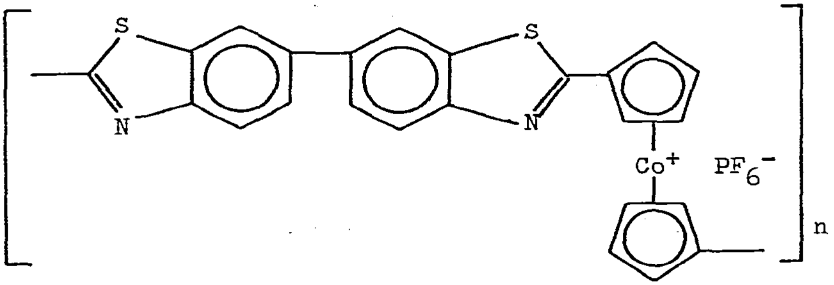


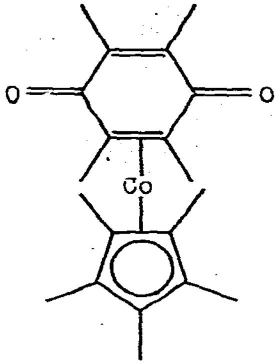
15.8



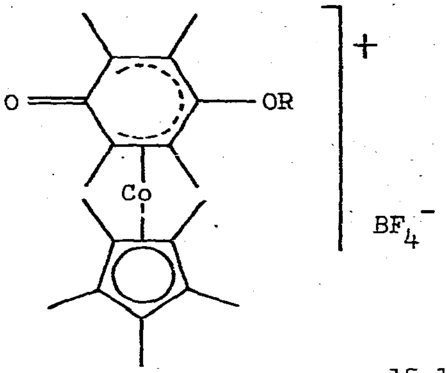
15.9

15.10

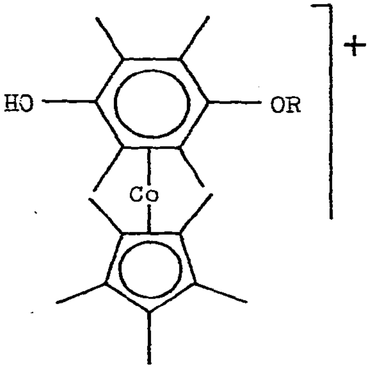




15.11

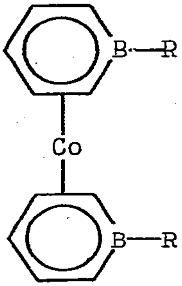


15.12



15.13

It has been shown that the addition of cobaltocene, nickelocene or ferrocene inhibits the formation of powdery surface layers during the weathering of polyurethane rubbers [280]. When duroquinone was heated with $[Co(\eta\text{-}C_5Me_5)(CO)_2]$ the cobalt complex (15.11) was formed. This complex (15.11) underwent reversible protonation to give the salt (15.12; R = H) and diprotonation to give the η-tetramethylbenzene derivative (15.13; R = H). Methylation of the complex (15.11) with methyliodide-silver hexafluorophosphate gave the salt (15.12; R = Me) which underwent protonation in trifluoroacetic acid to give the cation (15.13; R = Me) [281]. The bis(borinato)cobalt complexes (15.14; R = Me, Ph) were reduced by sodium amalgam to give the corresponding anions (15.15) which are twenty electron species. Metathesis of the anion (15.15; R = Ph) with tetraphenylphosphonium bromide gave a stable tetraphenylphosphonium salt of the anion. Treatment of the anions (15.15; R = Me, Ph) with electrophiles E^+



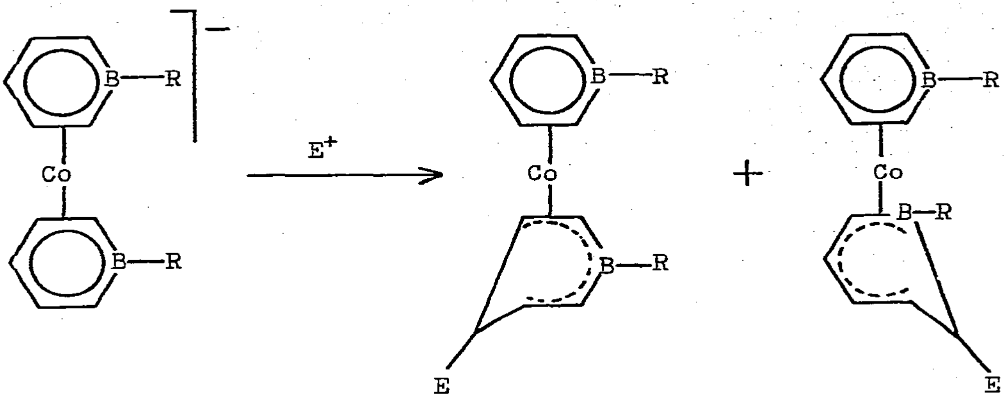
15.14

(Scheme 15.1) gave the corresponding substitution products (15.16 and 15.17; R = Ph, E = H; R = Me, E = Ph) [282]. The electrochemical oxidation of the triple-decker complex (15.18) gave the corresponding dication which was a thirty four electron species. The mechanism of the two electron transfer process was discussed [283].

16. Cobalt-carbon Cluster Compounds

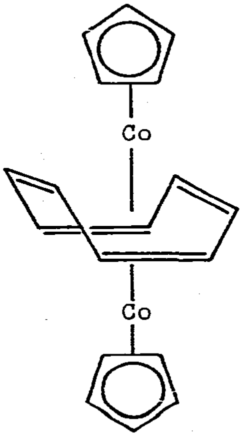
η-Cyclopentadienyltitanium trichloride was treated with sodium tetracarbonylcobaltate(-1) to give the cobalt complex $[(CO)_9Co_3CO]_2$-$(\eta$-$C_5H_5)Ti$-$Co(CO)_4$. In this complex the titanium atom was surrounded tetrahedrally by two oxymethylidynenonacarbonyltricobalt groups, one π-bonded cyclopentadienyl group and one $Co(CO)_4$ group. A titanium-cobalt covalent bond was shown to be present [284]. Neutral and cationic transition metal carbyne complexes such as trans-$Br(CO)_4$-$Cr{\equiv}CMe$ and $[(\eta$-$C_5H_5)(CO)_2Mn{\equiv}CPh]^+$ underwent carbyne ligand transfer with octacarbonyldicobalt under mild conditions to form the methylidynenonacarbonyltricobalt cluster complexes (16.1; R = Me, Ph) [285]. Reaction of alkyldichloromethyl ethers, Cl_2CHOR (R = Me, Et, Pr^i), with dicobalt octacarbonyl gave the corresponding alkoxymethylidynetricobalt nonacarbonyls (16.2) [286].

Molecular orbital calculations on the carbenium ion (16.3) indicated that the C-CH_2 unit does not stand upright but that it is bent away from the central perpendicular to the Co_3 plane (16.4) [287]. The crystal structure of bis(η-cyclopentadienyl)(methylmethinyl)-



15.15 15.16 15.17

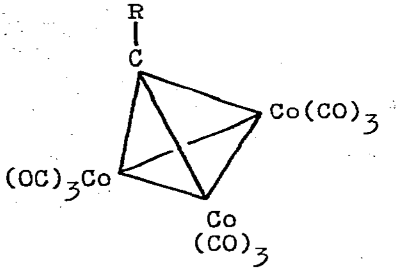
Scheme 15.1



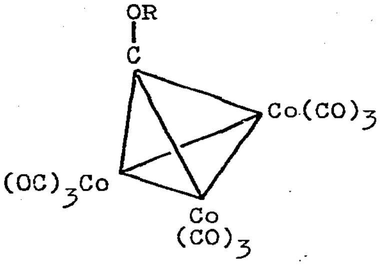
15.18

tetracarbonyltricobalt was determined by X-ray analysis. The η-cyclopentadienyl groups were bonded to two cobalt atoms of the CCo_3 unit and the same two cobalt atoms were bridged by one carbonyl group. The third cobalt atom had three terminal carbonyl groups [288]. The crystal structure of the η-norbornadiene complex (16.5) has been determined by X-ray analysis. On two of the cobalt atoms there were three terminal carbonyl groups (2 equatorial and 1 axial) and on the third cobalt atom the η-norbornadiene molecule replaced the two equatorial carbonyl groups [289].

The ground-state electronic structure of alkylidynetricobalt nonacarbonyl cluster compounds (16.1; R = H, Me, CF_3, Cl, MeO, Et_3Si, $MeCO_2$, $EtCO_2$, Ph, PhCO) has been investigated by ^{59}Co NQR spectroscopy. The nuclear quadrupole coupling constants were found to

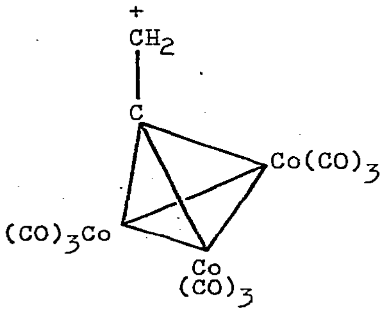


16.1

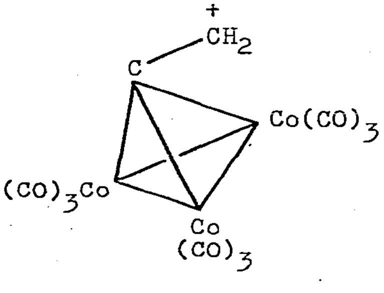


16.2

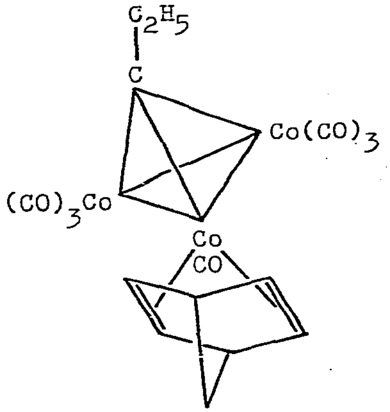
correlate with the Hammett σ constants and the σ_R^- constants for the substituent groups. It was therefore concluded that the apical carbon atom transmitted the electronic effect of the substituent R to the cobalt atoms by a π-resonance mechanism rather than by a through-bond inductive mechanism [290]. Bromomethylidynetricobaltnonacarbonyl combined with alkenethiols and lithium alkane- and arene-thiolates in the presence of carbon monoxide and triethylamine to form the thioesters (16.6; R = Me_3C, Bu^n, Et). However arenethiols gave, under the same conditions, the thioethers (16.7; R = H, Me) together with the products of partial cluster degradation.



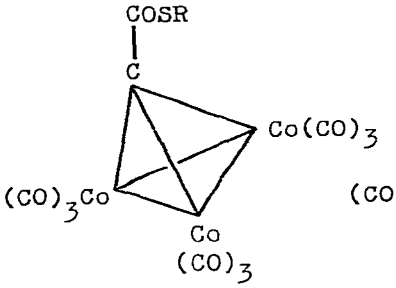
16.3



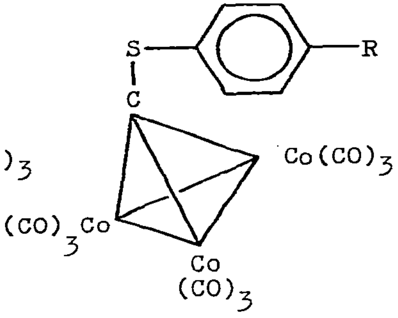
16.4



16.5



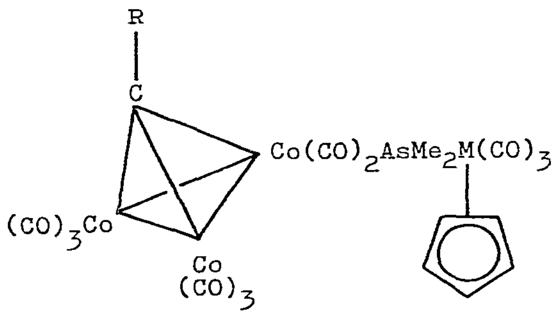
16.6



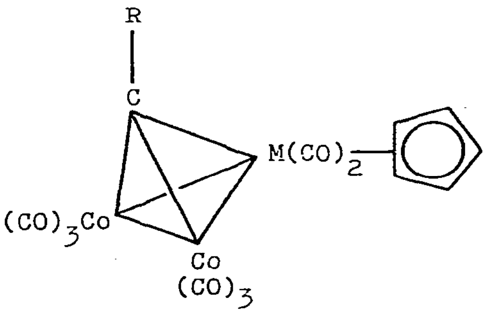
16.7

The thioesters underwent decarbonylation on heating to form the corresponding thioethers [291].

The methylidyneoctacarbonyltricobalt complexes (16.8; R = H, Me, Ph, *p*-Me, C_6H_4; M = Mo, W) underwent exchange of cobalt for molybdenum or tungsten on heating in cyclohexane at 40° for 8 days to form the heteronuclear cobalt cluster complexes (16.9; R = H, Me, Ph, *p*-Me.C_6H_4; M = Mo, W). The crystal and molecular structure of one of the products (16.9; R = Ph; M = Mo) has been determined

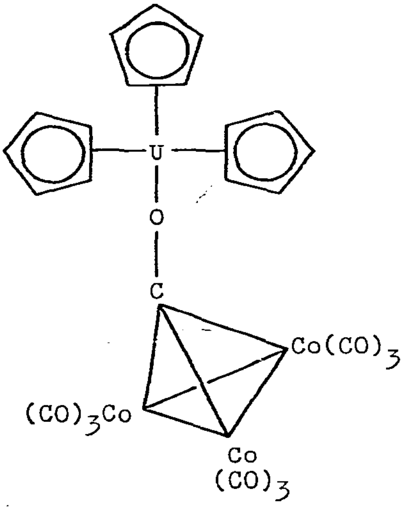


16.8



16.9

by X-ray methods [292]. Reaction of $[(CO)_9Co_3CO]Li$ with chlorotris(η-cyclopentadienyl)uranium gave the cobalt cluster-uranium derivative (16.10). This uranium compound (16.10) was paramagnetic, $\mu_{eff.}$ = 3.0 BM and infrared data showed that the complex was a typical oxymethylidyne cluster compound [293]. The thermolysis of the methylidyne cobalt cluster compound (16.1; R = H) gave a mixture of the

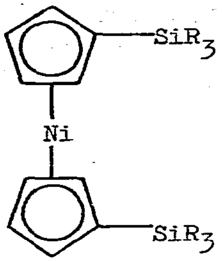


16.10

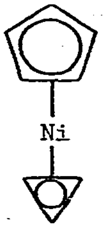
corresponding methyl and ethyl derivatives (16.1; R = Me, Et). A reaction mechanism was proposed that involved the generation of a carbyne, $H\dot{C}:$, and its addition to the $Co(CO)_3$ core of the parent molecule, followed by extrusion of $Co(CO)_3$ to give acetylenehexacarbonyldicobalt which decomposed to give $MeCCo_3(CO)_9$ [294].

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

Nickel (II) chloride has been treated with trialkylsilylcyclopentadienides to form the 1,1'-disubstituted nickelocenes (17.1; R = alkyl, aryl, alkoxy, aryloxy, amino) [295]. Clack and Warren have carried out INDO SCF molecular orbital calculations for (η-cyclopentadienyl)-(η-cyclopropenyl)nickel (17.2) and found a formally $\underline{d}^{10}$ configuration to be indicated for the nickel. Ionization energy calculations showed that electron loss should take place first from the set of predominantly d-orbitals and then from a cyclopentadienyl e orbital. This latter level mixed only slightly with the metal d-orbitals to give a small ligand→metal electron donation. However substantial



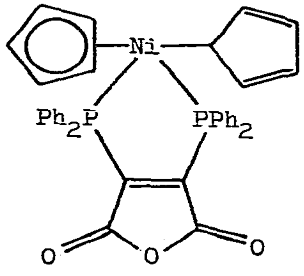
17.1



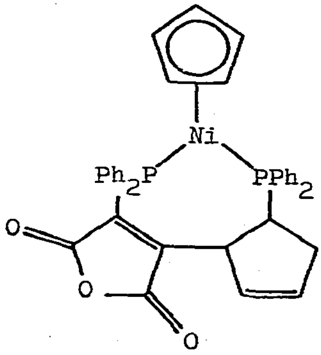
17.2

metal→ligand donation resulted from interaction between the cyclopropenyl $\underline{e}$ level and the nickel $3d_{xz}$ and $3d_{yz}$ orbitals [296].

A vacuum adiabatic calorimeter has been used to measure the heat capacities of the bis(η-cyclopentadienyl)metal compounds, $(\eta\text{-}C_5H_5)_2M$ where M = V, Cr, Mn, Co, Ni, at 4.5-300°K [297]. The reaction of nickelocene with hexachlorocyclopentadiene gave 1,2,3,4,5-pentachloro-5-(2,4-cyclopentadienyl)-1,3-cyclopentadiene [298]. Nickelocene and cobaltocene have been used as the metal vertex source in the



17.3

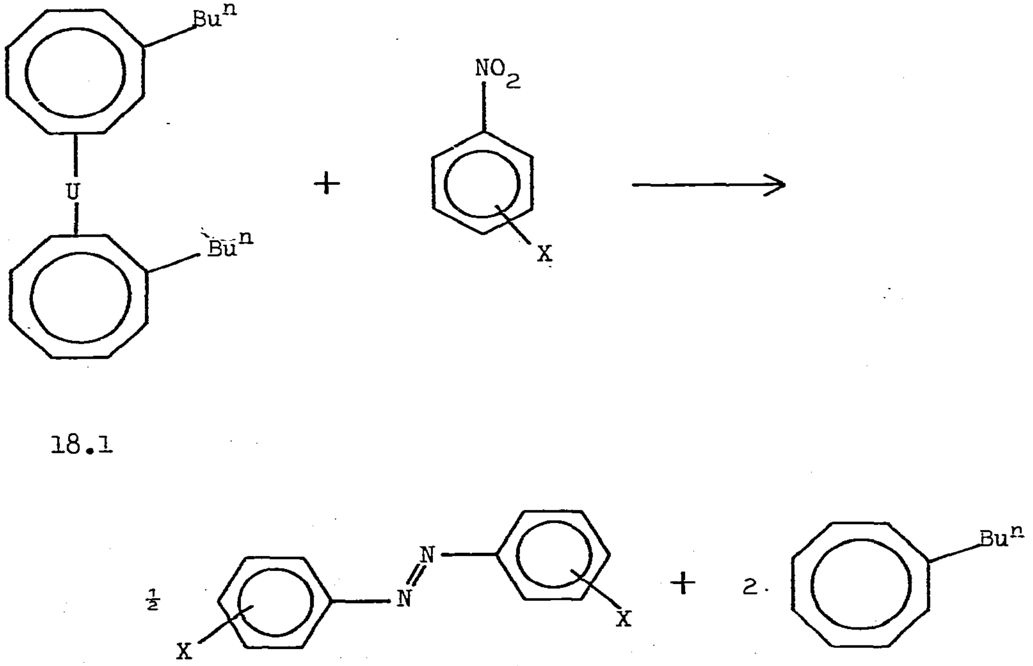


17.4

formation of a number of ten- and twelve-vertex *closo*- and *nido*-metalloboranes. In a typical reaction nickelocene combined with *nido*-$(B_{11}H_{13})^{2-}$ in the presence of a catalytic amount of sodium amalgam in glyme to give *closo*-$[(\eta^5-C_5H_5Ni)B_{11}H_{11}]^-$ [299]. Reaction of bis(diphenylphosphino)maleic anhydride with nickelocene gave the nickel derivative (17.3) which rearranged to give the complex (17.4) [300].

18. $(\eta-C_8H_8)_2$

Uranocenes were attacked rapidly by aromatic and aliphatic nitro compounds to yield azo compounds and the free cyclooctatetraene ligand. Thus di-n-butyluranocene (18.1) combined with nitrobenzenes to form the azobenzenes (18.2; X = *p*-MeO, *p*-I, *o*-I, *o*-Ph, H). Evidence was produced to implicate nitroso compounds as the reaction intermediates [301]. The anodic oxidation of uranocene gave the



18.1

18.2

unstable uranocene cation which decomposed rapidly to a stable but uncharacterized cluster cation containing two or more uranium atoms and cyclooctatetraene [302].

References

1. K. J. Klabunde, Ann. N.Y. Acad. Sci., 295 (1977) 83.
2. R. G. Sutherland, W. J. Pannekoek and C. C. Lee, Ann. N.Y. Acad. Sci., 295 (1977) 192.
3. S. Sarel, Acc. Chem. Res., 11 (1978) 204.
4. N. S. Kochetkova and Yu. K. Krynkina, Usp. Khim., 47 (1978) 934.
5. M. F. Semmelhack, Ann. N.Y. Acad. Sci., 295 (1977) 36.
6. W. E. Watts, Organomet. Chem., 6 (1978) 319.
7. R. Pearce, D. J. Thompson and M. V. Twigg, Annu. Rep. Prog. Chem., Sect. B, 73 (1976) 99.
8. C. W. Allen and D. E. Palmer, J. Chem. Educ., 55 (1978) 497.
9. P. L. Pauson and I. U. Khand, Ann. N. Y. Acad. Sci., 295 (1977) 2.
10. R. Noyori, Ann. N.Y. Acad. Sci., 295 (1977) 225.
11. J. L. Davidson, Inorg. React. Mech., 5 (1977) 305.
12. J. L. Davidson, Inorg. React. Mech., 5 (1977) 383.
13. P. C. Bharara, V. D. Gupta and R. C. Mehrotra, J. Organomet. Chem. Libr., 5 (1977) 259.
14. D. W. Clack and K. D. Warren, J. Organometal. Chem., 152 (1978) C60.
15. D. W. Clack and K. D. Warren, Theor. Chim. Acta, 46 (1977) 313.
16. D. L. Thorn and R. Hoffmann, Inorg. Chem., 17 (1978) 126.
17. D. W. Clack and K. D. Warren, J. Organometal. Chem., 162 (1978) 83.
18. D. A. Brown, J. P. Chester and N. J. Fitzpatrick, J. Organometal. Chem., 155 (1978) C21.
19. L. Pauling, Proc. Natl. Acad. Sci. USA, 75 (1978) 12.
20. A. J. Rest, J. R. Sodeau and D. J. Taylor, J. Chem. Soc., Dalton Trans., (1978) 651.
21. M. L. H. Green (National Research Development Corp.), Brit. Pat., 1483459, 1977, Aug. 17; Chem. Abstr., 88 (1978) 74462.
22. C. Pommier and C. Azokpota, Journ. Calorim. Anal. Therm., [Prepr.], 7 (1976) 3/6/1.
23. M. Miyamura, A. Miura and O. Tada (Tokyo Shibaura Electric Co.) Japan Pat., 77117616, 1977, Oct. 3; Chem. Abstr., 88 (1978) 144343.
24. K. R. Gordon and K. D. Warren, Inorg. Chem., 17 (1978) 987.
25. D. R. Armstrong, R. Fortune and P. G. Perkins, Rev. Roum. Chim.,

23 (1978) 1179.
26. Yu. A. Andrianov and O. N. Druzhkov, Khimiya Elementoorgan. Soedin., (1977) 78; Chem. Abstr., 90 (1979) 5470.
27. M. D. Rausch, S. A. Gardner, E. F. Tokas, I. Bernal. G.M. Reisner and A. Clearfield, J. Chem. Soc., Chem. Commun., (1978) 187.
28. S. P. Kolesnikov, J. E. Dobson and P. S. Skell, J. Am. Chem. Soc., 100 (1978) 999.
29. R. J. Kinney, W. D. Jones and R. G. Bergman, J. Am. Chem. Soc., 100 (1978) 7902.
30. R. J. Kinney, W. D. Jones and R. G. Bergman, J. Am. Chem. Soc., 100 (1978) 635.
31. W. R. W. Roose, D. Rehder, H. Luders and K. H. Theopold, J. Organometal. Chem., 157 (1978) 311.
32. R. Talay and D. Rehder, Chem. Ber., 111 (1978) 1978.
33. M. D. Rausch and A. V. Grossi, J. Chem. Soc., Chem. Commun., (1978) 401.
34. L. Weber, C. Krueger and Y-H. Tsay, Chem. Ber., 111 (1978) 1709.
35. J. C. Colburn, Diss. Abstr. Int. B, 39 (1978) 745.
36. G. I. Magomedov, Ya. M. Paushkin, N. I. Kirklina, V. D. Shuludyakov, E. G. Gorlov and A. S. Frenkel, Dokl. Akad. Nauk SSSR, 241 (1978) 853.
37. M. Benedikt and K. Schloegl, Monatsh. Chem., 109 (1978) 805.
38. C. M. Ashraf and W. Roy, Aust. J. Chem., 31 (1978) 1845.
39. A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, S. Andre, Yu. A. Ustynyuk, L. N. Novikova and Yu. N. Luzikov, J. Organometal. Chem., 154 (1978) 45.
40. K. H. Doetz and D. Neugebauer, Angew. Chem., 90 (1978) 898.
41. R. Goetze and H. Nöth, J. Organometal. Chem., 145 (1978) 151.
42. K. H. Doetz and R. Doetz, Chem. Ber., 111 (1978) 2517.
43. H. Schmidt and W. Siebert, J. Organometal. Chem., 155 (1978) 157.
44. M. El. Borai, R. Guilard and P. Fournari, J. Organometal. Chem., 148 (1978) 277.
45. E. Carmona-Guzman and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1978) 1139.
46. F. Edelmann and U. Behrens, Chem. Ber., 111 (1978) 3001.
47. D. W. Clack and L. A. P. Kane-Maguire, J. Organometal. Chem., 145 (1978) 201.
48. E. Gentric, G. Le Borgne and D. Grandjean, J. Organometal. Chem., 155 (1978) 207.
49. M. J. Gogan, C. K. Chu and P. A. Narayana, J. Organometal. Chem., 144 (1978) 125.

50. E. W. Neuse, Can. J. Chem., 55 (1977) 3384.

51. M. Scotti, H. Werner, D. L. S. Brown, S. Cavell, J. A. Connor and H. A. Skinner, Inorg. Chim. Acta, 25 (1977) 261.

52. R. S. Bly and T. L. Maier, J. Org. Chem., 43 (1978) 614.

53. G. P. Donnini and A. Shaver, Can. J. Chem., 56 (1978) 1477.

54. D. N. Kariuki and S. F. A. Kettle, J. Chem. Soc., Dalton Trans., (1978) 262.

55. F. Coletta, A. Gambaro, G. Rigatti and A. Venzo, Spectrosc. Lett., 10 (1977) 971.

56. Ch. Elschenbroich and U. Zenneck, J. Organometal. Chem., 160 (1978) 125.

57. M. M. Maricq, J. S. Waugh, J. L. Fletcher and M. J. McGlinchey, J. Am. Chem. Soc., 100 (1978) 6902.

58. J. S. Arney, Diss. Abstr. Int. B, 37 (1976) 1254.

59. A. Ceccon, A. Gobbo and A. Venzo, J. Organometal. Chem., 162 (1978) 311.

60. A. Solladié-Cavallo, G. Solladié and E. Tsamo, J. Organometal. Chem., 144 (1978) 181.

61. C. Mioskowski, A. Solladié-Cavallo and G. Solladié, J. Organometal. Chem., 149 (1978) C63.

62. L. P. Prokhorova, N. I. Sirotkin, Ya. I. Yashin and A. N. Artemov, Khim. Elementoorg. Soedin., 4 (1976) 105.

63. G. Jaouen, Ann. N.Y. Acad. Sci., 295 (1977) 59.

64. R. Dietz, K. H. Doetz and D. Neugebauer, Nouv. J. Chim., 2 (1978) 59.

65. K. C. Nainan and C. T. Sears, J. Organometal. Chem., 148 (1978) C31.

66. J. Y. Saillard and D. Grandjean, Acta Crystallogr., Sect. B, B34 (1978) 3772.

67. G. R. Clark, Diss. Abstr. Int. B, 39 (1978) 234.

68. G. I. Magomedov and O. V. Shkol'nik, Koord. Khim., 4 (1978) 1039.

69. J. Besancon and J. Tirouflet, C. R. Hebd. Seances Acad. Sci. Ser. C, 287 (1978) 113.

70. S. Top, B. Caro and G. Jaouen, Tetrahedron Lett., (1978) 787.

71. A. N. Nesmeyanov, V. V. Krivykh, P. V. Petrovskii, V. S. Kaganovich and M. I. Rybinskaya, J. Organometal. Chem., 162 (1978) 323.

72. M. Herberhold and M. Suess-Fink, Chem. Ber., 111 (1978) 2273.

73. A. N. Nesmeyanov, V. V. Krivykh and M. I. Rybinskaya, Dokl. Akad. Nauk SSSR, 239 (1978) 1363.

74. A. N. Nesmeyanov, V. V. Krivykh and M. I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 975.
75. A. N. Nesmeyanov, M. I. Rybinskaya, V. S. Kaganovich and L. M. Korneva, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 722.
76. G. Simonneaux, G. Jaouen, R. Dabard and M. Louer, Nouv. J. Chem., 2 (1978) 203.
77. M. Herberhold and L. Haumaier, J. Organometal. Chem., 160 (1978) 101.
78. V. N. Sapunov, I. Yu. Litvintsev, G. I. Magomedov and I. Margitfal'vi, Deposited Doc., (1976) VINITI 1451; Chem. Abstr., 88 (1978) 61797.
79. D. Huchette, B. Thery and F. Petit, J. Mol. Catal., 4 (1978) 433.
80. A. Ceccon, M. Gentiloni, L. Sella and A. Venzo, Gazz. Chim. Ital., 107 (1977) 439.
81. D. Seyferth, J. S. Merola and C. S. Eschbach, J. Am. Chem. Soc., 100 (1978) 4124.
82. Y. Eden, D. Fraenkel, M. Cais and E. A. Halevi, Isr. J. Chem., 15 (1977) 223.
83. A. P. Kozikowski and K. Isobe, J. Chem. Soc., Chem. Commun., (1978) 1076.
84. M. D. Rausch and R. E. Gloth, J. Organometal. Chem., 153 (1978) 59.
85. F. Edelmann, D. Wormsbaecher and U. Behrens, Chem. Ber., 111 (1978) 817.
86. G. Carganico, P. Del Buttero, S. Maiorana and G. Riccardi, J. Chem. Soc., Chem. Commun., (1978) 989.
87. C. U. Pittman, T. D. Rounsefell, E. A. Lewis, J. E. Sheats, B. H. Edwards, M. D. Rausch and E. A. Mintz, Macromolecules, 11 (1978) 560.
88. J. K. Hoyano, P. Legzdins and J. T. Malito, Inorg. Synth., 18 (1978) 126.
89. A. D. Zorin, V. A. Umilin, V. K. Vanchagova, P. E. Gaivoronskii, Zh. Obshch. Khim., 48 (1978) 1092.
90. P. N. Hawker, E. P. Kundig and P. L. Timms, J. Chem. Soc., Chem. Commun., (1978) 730.
91. H. Noeth and S. N. Sze, Z. Naturforsch., B. Anorg. Chem., Org. Chem., 33B (1978) 1313.
92. J. A. Gladysz, J. G. Fulcher and A. B. Bocarsly, Tetrahedron Lett., (1978) 1725.
93. C. Elschenbroich, R. Moeckel and U. Zenneck, Angew. Chem., 90 (1978) 560.

94. G. A. Domrachev, Yu. A. Shevelev and V. D. Zinov'ev, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 227.

95. A. N. Nesmeyanov, L. P. Yur'eva, N. N. Zaitseva, G. A. Domrachev and V. D. Zinov'ev, J. Organometal. Chem., 153 (1978) 181.

96. A. N. Nesmeyanov, N. N. Zaitseva, L. P. Yur'eva and R. A. Stukan, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1428.

97. F. G. N. Cloke, M. L. H. Green and G. E. Morris, J. Chem. Soc., Chem. Commun., (1978) 72.

98. J. Weber, M. Geoffroy, A. Goursot and E. Penigault, J. Am. Chem. Soc., 100 (1978) 3995.

99. N. Hao and M. J. McGlinchey, J. Organometal. Chem., 161 (1978) 381.

100. T. N. Sal'nikova, V. G. Andrianov, Yu. T. Struchkov, L. P. Yur'eva and N. N. Zaitseva, Koord. Khim., 4 (1978) 288.

101. V. A. Lebedev, V. P. Golovachev and E. A. Kuz'min, Zh. Strukt. Khim., 18 (1977) 1073.

102. C. Azokpota and C. Pommier, J. Chem. Thermodyn., 9 (1977) 1121.

103. A. N. Nesmeyanov, L. P. Yur'eva, N. N. Zaitseva and N. I. Vasyukova, J. Organometal. Chem., 153 (1978) 341.

104. Yu. A. Aleksandro, A. V. Lunin, V. M. Fomin, I. O. Grinval'd and V. G. Tsvetkov, Zh. Obshch. Khim., 48 (1978) 936.

105. A. Yu. Sorokin, A. Yu. Shevelev and G. A. Domrachev, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 713.

106. J. D. Zeinstra and W. C. Nieuwpoort, Inorg. Chim. Acta, 30 (1978) 103.

107. T. A. Albright, R. Hoffmann and P. Hofmann, Chem. Ber., 111 (1978) 1591.

108. M. B. Hossain and D. Van der Helm, Inorg. Chem., 17 (1978) 2893.

109. M. Green, H. P. Kirsch, F. G. A. Stone and A. J. Welch, Inorg. Chim. Acta, 29 (1978) 101.

110. S. Özkar, H. Kurz, D. Neugebauer and C. G. Kreiter, J. Organometal. Chem., 160 (1978) 115.

111. J. Mueller and W. Holzinger, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 33B (1978) 1309.

112. P. Powell, L. J. Russell, E. Styles, A. J. Brown, O. W. Howarth and P. Moore, J. Organometal. Chem., 149 (1978) C1.

113. D. J. Darensbourg and A. Salzer, J. Am. Chem. Soc., 100 (1978) 4119.

114. M. Sommer, K. Weidenhammer, H. Wienand and M. L. Ziegler, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 33B (1978) 361.

115. C. P. Lewis, Diss. Abstr. Int. B, 38 (1977) 692.

116. N. El Murr, M. Riveccie and A. Salzer, Inorg. Chim. Acta, 29 (1978) L213.
117. C. Charrier and F. Mathey, Tetrahedron Lett., (1978) 2407.
118. N. G. Bokii and Yu. T. Struchkov, Koord. Khim., 4 (1978) 134.
119. N. J. Gogan and C.-K. Chu, Org. Mass Spectrom., 12 (1979) 343.
120. V. F. Sizoi, Yu. S. Nekrasov, Yu. N. Sukharev, N. E. Kolobova, O. M. Khitrova, N. S. Obezyuk and A. B. Antonova, J. Organometal. Chem., 162 (1978) 171.
121. J. Fernando, G. Faigle, A. M. da C. Ferreira, S. E. Galembeck and J. M. Riveros, J. Chem. Soc., Chem. Commun., (1978) 126.
122. R. E. Wright and A. Vogler, J. Organometal. Chem., 160 (1978) 197.
123. N. T. Anh, M. Elian and R. Hoffmann, J. Am. Chem. Soc., 100 (1978) 110.
124. P. C. Uden, R. M. Barnes and F. P. DiSanzo, Anal. Chem., 50 (1978) 852.
125. A. N. Nesmeyanov, M. I. Rybinskaya and L. M. Korneva, Dokl. Akad. Nauk SSSR, 237 (1977) 1373.
126. J. A. D. Jeffreys and J. MacFie, J. Chem. Soc., Dalton Trans., (1978) 144.
127. A. N. Nesmeyanov, D. N. Kursanov, V. D. Vil'chevskaya, N. K. Barentskaya, A. I. Krylova, V. I. Losilkina and V. N. Setkina, Dokl. Akad. Nauk SSSR, 241 (1978) 111.
128. G. A. M. Munro and P. L. Pauson, J. Organometal. Chem., 160 (1978) 177.
129. S. P. Gubin, L. I. Denisovich, N. V. Zakurin and A. G. Ginzburg, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1322.
130. I. M. Gverdtsiteli and L. P. Asatiani, Tezisy Dokl.-Vses. Konf. Khim. Atsetilena 5th, (1975) 237; Chem. Abstr., 88 (1978) 152760.
131. C. U. Pittman, C.-C. Lin and T. D. Rounesfall, Macromolecules, 11 (1978) 1022.
132. A. N. Nesmeyanov, V. A. Sazonova, V. N. Postnov, A. M. Baran, Ya. A. Angelyuk and B. A. Surkov, Dokl. Akad. Nauk SSSR, 241, (1978) 1099.
133. L. P. Asatiani, A. A. El-Agami and I. M. Gverdtsiteli, Soobshch. Akad. Nauk Gruz. SSR, 90 (1978) 61.
134. L. P. Asatiani, A. A. El-Agamy and I. M. Gverdtsiteli, Soobshch. Akad. Nauk Gruz. SSR, 90 (1978) 589.
135. A. N. Nesmeyanov, T. P. Tolstaya and V. V. Korol'kov, Dokl. Akad. Nauk SSSR, 241 (1978) 1103.
136. A. N. Nesmeyanov, E. G. Perevalova, O. B. Afanasova, M. V.

Tolstaya and K. I. Grandberg, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1118.
137. O. A. Reutov, G. Z. Suleimanov, I. A. Amiraslanov, V. V. Bashilov and V. I. Sokolov, Zh. Org. Khim., 14 (1978) 1802.
138. N. E. Kolobova, Z. P. Valueva, K. N. Anisimov and G. Z. Suleimanov, Izv. Akad. Nauk. SSSR, Ser. Khim., (1978) 910.
139. G. Z. Suleimanov, V. V. Bashilov, V. I. Sokolov and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1670.
140. L. Yu. Ukhin, V. V. Krasnikov and G. N. Dorofeenko, Koord. Khim., 4 (1978) 455.
141. A. N. Nesmeyanov, N. N. Sedova, Yu. V. Volgin and V. A. Sazonova, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2353.
142. G. A. Razuvaev, G. A. Domrachev, V. V. Sharutin and O. N. Suvarova, Dokl. Akad. Nauk SSSR, 237 (1977) 852.
143. E. V. Shumilina, Vestn. Mosk. Univ. Ser. 2: Khim., 18 (1977) 476.
144. E. G. Perevalova, E. V. Shumilina and L. I. Leont'eva, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1438.
145. A. N. Nesmeyanov, V. N. Postnov, V. A. Sazonova, T. N. Galakhova and A. A. Kuznetsov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 2172.
146. A. N. Nesmeyanov, E. G. Perevalova, L. I. Leont'eva and E. V. Shumilina, Dokl. Akad. Nauk SSSR, 238 (1978) 588.
147. S. Fontana, U. Schubert and E. O. Fischer, J. Organometal. Chem., 146 (1978) 39.
148. W. A. Herrmann and J. Plank, Angew. Chem., 90 (1978) 555.
149. D. N. Kursanov, A. G. Ginzburg, V. N. Setkina and Sh.G. Kasumov, Dokl. Akad. Nauk SSSR, 240 (1978) 1368.
150. N. E. Kolobova, A. B. Antonova and O. M. Khitrova, J. Organometal. Chem., 146 (1978) C17.
151. F. Edelmann, K. J. Jens and U. Behrens, Chem. Ber., 111 (1978) 2895.
152. E. O. Fischer and G. Besl, J. Organometal. Chem., 157 (1978) C33.
153. W. A. Herrmann, J. Plank, M. L. Ziegler and K. Weidenhammer, Angew. Chem., 90 (1978) 817.
154. R. B. King and J. Gimeno, Inorg. Chem., 17 (1978) 2396.
155. N. Wiberg, H. Haering, G. Huttner and P. Friedrich, Chem. Ber., 111 (1978) 2708.
156. W. Siebert, C. Boehle, C. Krueger and Y. -H. Tsay, Angew. Chem., 90 (1978) 558.
157. F. Mathey, A. Mitschler and R. Weiss, J. Am. Chem. Soc., 100 (1978) 5748.

158. A. Breque and F. Mathey, J. Organometal. Chem., 144 (1978) C9.
159. G. Thiollet, R. Poilblanc, D. Voigt and F. Mathey, Inorg. Chim. Acta, 30 (1978) L294.
160. N. E. Kolobova, M. Ya. Solodova and Z. P. Valueva, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 735.
161. W. A. Herrmann, Chem. Ber., 111 (1978) 2458.
162. G. A. M. Munro and P. L. Pauson, Isr. J. Chem., 15 (1978) 258.
163. Anon. (Ethyl Corporation), Japan. Pat., 77 40504, 1977, Mar. 29; Chem. Abstr., 88 (1978) 92030.
164. Anon. (Ethyl Corporation), Japan. Pat., 77 40503, 1977, Mar. 29; Chem. Abstr., 88 (1978) 92031.
165. J. D. Bailie and A. H. Zeitz, Energy Technol. Handbook, D. M. Considine (Ed.), McGraw-Hill, New York, pp. 9, 349.
166. W. R. Pierson, D. E. McKee, W. W. Brachaczek and J. W. Butler, J. Air. Pollut. Control Assoc., 28 (1978) 692.
167. J. D. Bailie, G. W. Michalski and G. H. Unzelman, Natl. Pet. Refiners Assoc., [Tech. Pap.], (1978) AM-78-36; Chem. Abstr., 89 (1978) 132000.
168. Ethyl Corp., Japan Pat., 77126404,1977, Oct. 24; Chem. Abstr., 89 (1978) 77503.
169. L. J. Faix (Gen. Mot. Corp.) SAE [Tech. Pap.], (1978) 780002; Chem. Abstr., 89 (1978) 116966.
170. D. L, Lenane, SAE [Tech. Pap.], (1978) 780003; Chem. Abstr., 89 (1978) 134823.
171. D. L. Lenane, SAE [Tech. Pap.], (1977) 770656; Chem. Abstr., 89 (1978) 27152.
172. J. D. Benson, SAE [Tech. Pap.], (1977) 770655; Chem. Abstr., 89 (1978) 27153.
173. I. E. Lichtenstein and J. P. Mundy, SAE [Tech. Pap.], (1978) 780005; Chem. Abstr., 89 (1978) 134822.
174. R. L. Furey and J. C. Summers, SAE [Tech. Pap.] (1978) 780004; Chem. Abstr., 89 (1978) 165776.
175. R. J. Lukasiewicz (Union Oil Co.), US Pat., 4067699, 1978, Jan. 10; Chem. Abstr., 88 (1978) 194305.
176. G. K. Goncharenko, V. Ya. Shuteev, S. T. Shebanova and V. P. Mikhailichenko, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 20 (1977) 1731; Chem. Abstr., 88 (1978) 125948.
177. H. Takaya, S. Makino, Y. Hayakawa and R. Noyori, J. Am. Chem. Soc., 100 (1978) 1765.

178. P. Binger, B. Cetinkaya and C. Kruger, J. Organometal. Chem., 159 (1978) 63.
179. G. O. Nelson, Diss. Abstr. Int. B, 39 (1978) 237.
180. H. Sakurai, Y. Kamiyama and Y. Nakadaira, Angew. Chem., 90 (1978) 718.
181. J. Daub, J. Kappler, K. P. Krenkler, S. Schreiner and V. Trautz, Justus Liebigs Ann. Chem., (1977) 1730.
182. J. Elzinga and H. Hogeveen, J. Org. Chem., 43 (1978) 745.
183. P. Boudjouk and S. Lin, J. Organometal. Chem., 155 (1978) C13.
184. T. -A. Mitsudo, T. Sasaki, Y. Watanabe, Y. Takegami, S. Nishigaki and K. Nakatsu, J. Chem. Soc., Chem. Commun., (1978) 252.
185. L. G. Kuz'mina, Yu. T. Struchkov and I. I. Kritskaya, Koord. Khim., 4 (1978) 293.
186. D. H. Gibson and T. -S. Ong, J. Organometal. Chem., 155 (1978) 221.
187. D. G. Gresham, D. J. Kowalski and C. P. Lillya, J. Organometal. Chem., 144 (1978) 71.
188. R. S. Bayoud, E. R. Biehl and P. C. Reeves, J. Organometal. Chem., 150 (1978) 75.
189. P. A. Dobosh, D. G. Gresham, D. J. Kowalski, C. P. Lillya and E. S. Magyar, Inorg. Chem., 17 (1978) 1775.
190. P. McArdle and H. Sherlock, J. Chem. Soc., Dalton Trans., (1978) 1678.
191. N. El Murr, M. Riveccie and P. Dixneuf, J. Chem. Soc., Chem. Commun., (1978) 552.
192. J. A. S. Howell and P. M. Burkinshaw, J. Organometal. Chem., 152 (1978) C5.
193. R. H. Grubbs and T. S. Pancoast, Synth. React. Inorg. Met. -Org. Chem., 8 (1978) 1.
194. A. Krebs, H. Kimling and R. Kemper, Justus Liebigs Ann. Chem., (1978) 431.
195. J. A. Ulman, E. L. Andersen and T. P. Fehlner, J. Am. Chem. Soc., 100 (1978) 456.
196. J. Howard and T. C. Waddington, Spectrochim. Acta, Part A, 34A (1978) 445.
197. D. M. Birney, A. M. Crane and D. A. Sweigart, J. Organometal. Chim., 152 (1978) 187.
198. P. Marcinal and E. Cuingnet, Bull. Soc. Chim. Fr., (1977) 489.
199. M. B. Stringer and D. Wege, Aust. J. Chem., 31 (1978) 1607.
200. S. R. Hall, B. W. Skelton and A. H. White, Aust. J. Chem., 31 (1978) 1619.

201. T. P. Fehlner, J. Am. Chem. Soc., 100 (1978) 3250.
202. K. Fukoshima, T. Miyamoto and Y. Sasaki, Bull. Chem. Soc., Jpn. 51 (1978) 499.
203. H. Alper and H. -N. Paik, J. Am. Chem. Soc., 100 (1978) 508.
204. A. J. Birch and A. J. Pearson, J. Chem. Soc., Perkin Trans. 1, (1978) 638.
205. C. R. Graham, Diss. Abstr. Int. B, 38 (1977) 688.
206. K. Hayakawa and H. Schmid, Helv. Chim. Acta, 60 (1977) 2160.
207. M. A. Bennett and T. W. Matheson, J. Organometal. Chem., 153 (1978) C25.
208. E. A. Chernyshev, O. B. Afanasova, N. G. Komalenkova, A. I. Gusev and V. A. Sharapov, Zh. Obshch. Khim., 48 (1978) 2261.
209. A. A. Bykovets, M. O. Labartkava, T. L. Krasnova and E. A. Chernyshev, Zh. Obshch. Khim., 48 (1978) 930.
210. A. J. Pearson, J. Chem. Soc., Perkin Trans. 1, (1978) 495.
211. I. T. Chizhevsky and A. A. Koridze, J. Organometal. Chem., 153 (1978) C28.
212. R. Aumann and J. Knecht, Chem. Ber., 111 (1978) 3429.
213. M. El Borai, R. Guilard, P. Fournari, Y. Dusausoy and J. Protas, J. Organometal. Chem. 148 (1978) 285.
214. A. Salzer and W. Von Philipsborn, J. Organometal. Chem., 161 (1978) 39.
215. Z. Goldschmidt and S. Antebi, Tetrahedron Lett., (1978) 271.
216. K. Hayakawa and H. Schmid, Helv. Chim. Acta, 60 (1977) 1942.
217. J. Daub, U. Erhardt, M. Michna, J. Schmetzer and V. Trautz, Chem. Ber., 111 (1978) 2877.
218. A. P. Humphries and S. A. R. Knox, J. Chem. Soc., Dalton Trans., (1978) 1514.
219. P. Hofmann, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 33B (1978) 251.
220. T. A. Albright and R. Hoffmann, Chem. Ber., 111 (1978) 1578.
221. M. R. Churchill and S. A. Julis, Inorg. Chem., 17 (1978) 1453.
222. G. C. Cash and R. C. Pettersen, Inorg. Chem., 17 (1978) 650.
223. E. Sepp, A. Puerzer, G. Thiele and H. Behrens, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 33B (1978) 261.
224. H. Behrens, G. Thiele, A. Purzer, P. Wurstl and M. Moll, J. Organometal. Chem., 160 (1978) 255.
225. F. A. Cotton and B. E. Hanson, Isr. J. Chem., 15 (1977) 165.
226. K. J. Karel and M. Brookhart, J. Am. Chem. Soc., 100 (1978) 1619.
227. B. E. Mann, J. Chem. Soc., Dalton Trans., (1978) 1761.

228. A. J. Pearson, J. Chem. Soc., Perkin Trans. 1, (1977) 2069.
229. A. J. Birch and K. B. Chamberlain, Org. Synth., 57 (1977) 107.
230. A. J. Birch and K. B. Chamberlain, Org. Synth., 57 (1977) 16.
231. F. Franke and I. D. Jenkins, Aust. J. Chem., 31 (1978) 595.
232. K. D. Karlin, B. F. G. Johnson and J. Lewis, J. Organometal. Chem., 160 (1978) C21.
233. B. F. G. Johnson, J. Lewis, D. G. Parker, P. R. Raithby and G. M. Sheldrick, J. Organometal. Chem., 150 (1978) 115.
234. M. Franck-Neumann, D. Martina and F. Brion, Angew. Chem., 90 (1978) 736.
235. S. Litman, A. Gedanken, Z. Goldschmidt and Y. Bakal. J. Chem. Soc., Chem. Commun., (1978) 983.
236. A. Pryde, J. Chromatogr., 152 (1978) 123.
237. Z. Goldschmidt and S. Antebi, Tetrahedron Lett., (1978) 1225.
238. M. Bonadeo, R. Gandolfi and C. De Micheli, Gazz. Chim. Ital., 107 (1977) 577.
239. P. McArdle, J. Organometal. Chem., 144 (1978) C31.
240. B. F. G. Johnson, K. D. Karlin and J. Lewis, J. Organometal. Chem., 145 (1978) C23.
241. A. V. Rivera and G. M. Sheldrick, Acta Crystallogr., Sect. B, B34 (1978) 1716.
242. S. D. Ittel, F. A. Van-Catledge, C. A. Tolman and J. P. Jesson, J. Am. Chem. Soc., 100 (1978) 1317.
243. Y. Becker, A. Eisenstadt and Y. Shvo, J. Organometal. Chem., 155 (1978) 63.
244. E. Benedetti, C. Carlini, F. Ciardelli, P. Pertici and G. Vitulli, Chem. Ind. (Milan), 60 (1978) 408.
245. G. Schmitt, W. Keim, J. Fleischhauer and U. Walbergs, J. Organometal. Chem., 152 (1978) 315.
246. C. C. Lee, K. J. Demchuk and R. G. Sutherland, Synth. React. Inorg. Met.-Org. Chem., 8 (1978) 361.
247. C. C. Lee, K. J. Demchuk, W. J. Pannekoek and R. G. Sutherland, J. Organometal. Chem., 162 (1978) 253.
248. A. N. Nesmeyanov, S. P. Solodovnikov, N. A. Volkenau, L. S. Kotova and N. A. Sinitsyna, J. Organometal. Chem., 148 (1978) C5.
249. A. N. Nesmeyanov, N. A. Vol'kenau and L. S. Kotova, Koord. Khim., 4 (1978) 1699.
250. A. N. Nesmeyanov, N. A. Vol'kenau, I. N. Bolesova and L. S. Polkovnikova, Dokl. Akad. Nauk SSSR, 236 (1977) 1130.
251. U. Koelle, J. Organometal. Chem., 157 (1978) 327.

252. J. Park, Diss. Abstr. Int. B, 38 (1978) 5385.

253. S. Kamiyama, T. M. Suzuki, T. Kimura and A. Kasahara, Bull. Chem. Soc., Jpn., 51 (1978) 909.

254. O. Traverso, R. Rossi, L. Magon, A. Cinquantini and T. J. Kemp, J. Chem. Soc., Dalton Trans., (1978) 569.

255. M. Y. Darensbourg and E. L. Muetterties, J. Am. Chem. Soc., 100 (1978) 7425.

256. E. A. Stadlbauer, E. Nipper and M. Wenzel, J. Labelled Compd. Radiopharm., 13 (1977) 491.

257. B. Riesselmann and M. Wenzel, Hoppe-Seyler's Z. Physiol. Chem., 358 (1977) 1353.

258. A. J. Taylor and M. Wenzel, Xenobiotica, 8 (1978) 107.

259. M. Wenzel, Strahlentherapie, 154 (1978) 506.

260. A. J. Taylor and M. Wenzel, Biochem. J., 172 (1978) 77.

261. P. L. Timms and R. B. King, J. Chem. Soc., Chem. Commun., (1978) 898.

262. J. R. Fritch and K. P. C. Vollhardt, J. Am. Chem. Soc., 100 (1978) 3643.

263. M. D. Rausch, F. A. Higbie, G. F. Westover, A. Clearfield, R. Gopal, J. M. Troup and I. Bernal, J. Organometal. Chem., 149 (1978) 245.

264. H. Yamazaki and Y. Wakatsuki, J. Organometal. Chem., 149 (1978) 377.

265. Y. Wakatsuki and H. Yamazaki, J. Organometal. Chem., 149 (1978) 385.

266. D. Seyferth and J. S. Merola, J. Organometal. Chem., 160 (1978) 275.

267. D. W. Clack and K. D. Warren, Inorg. Chim. Acta, 27 (1978) 105.

268. B. -K. Teo, P. Eisenberger and B. M. Kincaid, J. Am. Chem. Soc., 100 (1978) 1735.

269. P. E. Riley and R. E. Davis, J. Organometal. Chem., 152 (1978) 209.

270. J. R. Pipal and R. N. Grimes, Inorg. Chem., 17 (1978) 10.

271. J. R. Pipal, W. M. Maxwell and K. N. Grimes, Inorg. Chem., 17 (1978) 1447.

272. U. Koelle, J. Organometal. Chem., 152 (1978) 225.

273. F. H. Kohler, J. Organometal. Chem., 160 (1978) 299.

274. F. H. Kohler and W. Prossdorf, J. Am. Chem. Soc., 100 (1978) 5970.

275, M. B. Moronski, Diss. Abstr. Int. B, 39 (1978) 754.

276. Yu. A. Aleksandrov and A. O. Kolmakov, Zh. Obshch. Khim., 48 (1978) 1653.

277. Yu. A. Kaplin, L. S. Chernyshova, G. V. Belyskeva and I. F. Solov'ev, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 20 (1977) 944; Chem. Abstr., 88 (1979) 93400.
278. E. W. Neuse and G. Horlbeck, Polym. Eng. Sci., 17 (1977) 821.
279. E. W. Neuse, Organomet. Polym. [Symp.], 1977 (Pub. 1978) 95; Edited by C. E. Carraher, J. E. Sheats and C. U. Pittman, Academic Press, New York.
280. Union Carbide Corp., Belg. Pat., 857038, 1978, Jan. 23; Chem. Abstr., 89 (1978) 25820.
281. G. Fairhurst and C. White, J. Organometal. Chem., 160 (1978) C17.
282. G. E. Herberich, W. Koch and H. Lueken, J. Organometal. Chem., 160 (1978) 17.
283. J. Moraczewski and W. E. Geiger, J. Am. Chem. Soc., 100 (1978) 7429.
284. G. Schmid, B. Stutte and R. Boese, Chem. Ber., 111 (1978) 1239.
285. E. O. Fischer and A. Daeweritz, Chem. Ber., 111 (1978) 3525.
286. A. Bou, M. A. Pericas and F. Serratosa, Afinidad, 35 (1978) 134.
287. B. E. R. Schilling and R. Hoffmann, J. Am. Chem. Soc., 100 (1978) 6274.
288. R. S. McCallum and B. R. Penfold, Acta Crystallogr., Sect. B, B34 (1978) 1688.
289. Y. S. Ng and B. R. Penfold, Acta Crystallogr., Sect. B, B34 (1978) 1978.
290. D. C. Miller and T. B. Brill, Inorg. Chem., 17 (1978) 240.
291. D. Seyferth, C. N. Rudie and J. S. Merola, J. Organometal. Chem., 144 (1978) C26.
292. H. Beurich and H. Vahrenkamp, Angew. Chem., 90 (1978) 915.
293. B. Stutte and G. Schmid, J. Organometal. Chem., 155 (1978) 203.
294. D. Seyferth, C. N. Rudie and J. S. Merola, J. Organometal. Chem., 162 (1978) 89.
295. N. A. Varfolomeeva, V. N. Lizina, B. K. Kabanov and E. A. Chernyshev, USSR Pat. 572463, 1977 Sep. 15; Chem. Abstr., 88 (1978) 37971.
296. D. W. Clack and K. D. Warren, J. Organometal. Chem., 149 (1978) 401.
297. I. B. Rabinovich, V. P. Nistratov, M. S. Sheiman and G. V. Burchalova, J. Chem. Thermodyn., 10 (1978) 523.
298. C. Moberg, Acta. Chem. Scand., Ser. B, B32 (1978) 149.
299. R. N. Leyden, B. P. Sullivan, R. T. Baker and M. F. Hawthorne, J. Am. Chem. Soc., 100 (1978) 3758.

300. W. Bensmann and D. Fenske, Angew. Chem., 90 (1978) 488.
301. C. B. Grant and A. Streitwieser, J. Am. Chem. Soc., 100 (1978) 2433.
302. J. A. Butcher, J. Q. Chambers and R. M. Pagni, J. Am. Chem. Soc., 100 (1978) 1012.