ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1982*

Bernard W. Rockett and George Marr
Department of Physical Sciences, The Polytechnic,
Wolverhampton, WV1 1LY (Great Britain).

CONTENTS

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* Organic reactions of selected π-complexes; Annual Survey covering the year 1981, G. Marr and B.W. Rockett, J. Organometal. Chem., 242 (1983) 1.

1. Reviews

The Nobel Lecture by Professor Hoffmann entitled "Building Bridges Between Inorganic and Organic Chemistry" is of interest to all organometallic chemists. The application of the frontier orbital approach to inorganic and organic moieties was discussed [1].

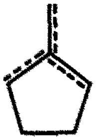
Watts has reviewed the chemistry of η-cyclopentadienyl, η-arene and related complexes published in 1980 [2]. Reissova and Capka have surveyed the applications of metallocenes containing titanium, zirconium, hafnium, chromium, iron, cobalt and nickel as homogeneous catalysts and reagents [3].

The use of magnetic resonance techniques in the investigation of paramagnetic metallocenes and di(η-arene)-transition metal complexes has been the subject of a review of Solodovnikov [4]. Volume 2 of "The Organic Chemistry of Iron" has been published, it contains several useful reviews including one on the chemistry of iron complexes formed by trienes, tetraenes and polyenes by Kerber [5]. Complexes formed between metallocenes and inorganic acceptors have been discussed in a survey by Dyagileva and Alexsandrov [6]. Hoppe has reviewed syntheses involving the use of tricarbonyl-(η-1,3-diene)iron complexes [7]. The properties of unsaturated ketones of cymantrene and ferrocene have been reviewed briefly [8].

2. General Results

The International Union of Pure and Applied Chemistry has published recommendations for measuring and reporting electrode potentials in non-aqueous solvents against the reference systems; ferrocene/ferrocenium ion and bis(η-biphenyl)-chromium(0)/bis(η-biphenyl)chromium (I) [9]. A range of organometallic compounds, for example, metal carbonyls, bis(η-cyclopentadienyl)complexes, arene complexes, arene-carbonyl complexes and ferrocene, has been incorporated into polymer films or sheets. Laser irradiation of the polymer sheets, for example, polythene, produced opaque metal or metal oxide particles within the polymer sheet [10]. Calculations of triplet to singlet and other excitation energies have been carried out on the two trimethylenemethane derivatives (2.1 and 2.2). The triplet-singlet energy for derivative (2.2) was calculated as 11.7 kcal mol^{-1} which was only 3.2 kcal mol^{-1} lower than that of trimethylenemethane [11].

A semiempirical INDO Hamiltonian has been used to examine the Hartree-Fock instabilities in a series of bimetallocenes and bimetallocenylenes of chromium, iron, cobalt and nickel. The Hartree-Fock approach was found to be valid only for the iron metallocenes and strong correlation effects were observed for the chromium, cobalt and nickel compounds [12]. Synthetic procedures for the decamethylmetallocenes $(\eta\text{-}Me_5C_5)_2M$, where M = V, Cr, Co, Ni, and the decamethylmetallocene salts $[(\eta\text{-}Me_5C_5)_2M]PF_6$, where M = Cr, Co, Ni and $[(\eta\text{-}Me_5C_5)_2Ni](PF_6)_2$ have been detailed. The compounds were found to be D_{5d} or D_{5h} with low spin electronic configurations. Cyclic voltammetry was used to confirm the reversibility of the one-



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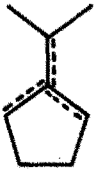

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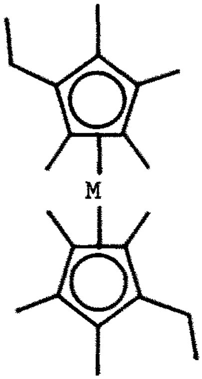

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-electron redox reactions:

$$(\eta\text{-}Me_5C_5)_2M \rightleftharpoons [(\eta\text{-}Me_5C_5)_2M]^+$$

where M = Cr, Fe, Co, Ni

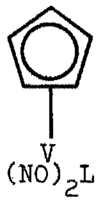
$$[(\eta\text{-}Me_5C_5)_2Ni]^+ \rightleftharpoons [(\eta\text{-}Me_5C_5)_2Ni]^{2+}$$

The neutral decamethylmetallocenes were more easily oxidized than their unsubstituted homologues due to electron donation from the methyl groups. The UV-visible absorption spectra for the 15-, 18- and 20- electron species were reported and assigned [13].

The metallocenes (2.3; M = V, Cr, Co, Ni) have been prepared and the effects of peralkylation studied by ^1H and ^{13}C NMR spectroscopy. The redox properties of the compounds were changed with an enhancement of the reducing power for the cobaltocene and nickelocene derivatives (2.3; M = Co, Ni). Hindered rotation of the cyclopentadienyl rings was observed with $C\beta$ of the ethyl group turned away from the metal. $C\beta$ allowed the sign of the electron spin density in the ligand π-system to be determined selectively [14].

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

A series of vanadium complexes [3.1; L = $P(OMe)_3$, SEt_2, pyridines, Me_2SO] has been prepared in solution by treatment of carbonyl(η-cyclopentadienyl)dinitrosylvanadium with the Lewis base. These compounds were characterised by ^{51}V, ^{13}C and ^1H NMR and infrared spectroscopy. The shielding of the ^{51}V and ^{13}C nuclei decreased as the electronegativity of the ligand atom bound to the metal increased [15]. The photolysis of tetracarbonyl(η-cyclopentadienyl)vanadium in the presence of bis(pentafluorophenyl)acetylene produced the acetylene complex (3.2; L = CO). Irradiation of this complex with triphenylphosphine yielded the monocarbonyl compound (3.2; L = PPh_3). In vacuo, melt-phase thermolysis of the complex (3.2; L = CO) with bis(pentafluorophenyl)acetylene produced the diacetylenic complex (3.2; L = $C_6F_5C{\equiv}CC_6F_5$) [16].



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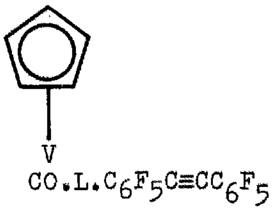

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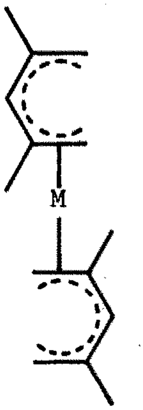
Ernst and coworkers have extended their syntheses of "open metallocenes" to include the vanadium and chromium complexes (3.3; M = V, Cr) respectively. The complexes were obtained by treatment of the potassium salt of the 2,4-dimethylpentadienyl anion with the metal dichloride in THF. The corresponding reaction with manganese(II)chloride and the potassium salt of the 3-methylpentadienyl anion gave the tri-nuclear complex (3.4) which has been characterized by X-ray crystallography [17]. In the same way the reaction between



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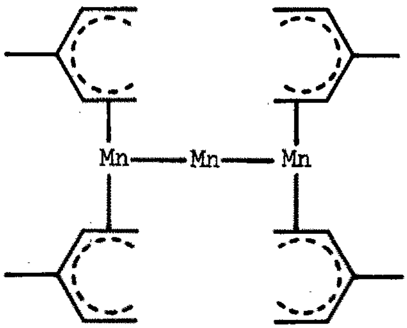

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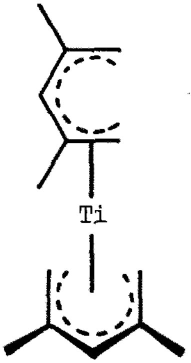
titanium(II) chloride and the potassium salt of the 2,4-dimethylpentadienyl anion gave the green, pyrophoric, 14-electron "open metallocene" complex (3.5) with appreciable thermal stability. The complex adopted a staggered conformation in the solid state (3.5) and gave a monocarbonyl adduct, $(\eta\text{-}2,4\text{-}C_7H_{11})_2Ti(CO)$ with carbon monoxide [18].



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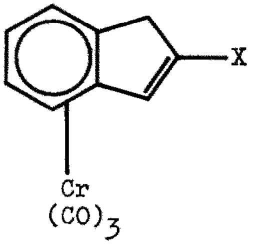
4. $(\eta\text{-}C_6H_6)Cr(CO)_3$

(i) Formation

Benchrotrene has been prepared by treatment of hexacarbonylchromium with benzene at 150-170°C in the presence of 1-2% $(pyridine)_nCr(CO)_{6-n}$, where n = 1-3 [19]. The tricarbonylchromium complexes $Me_2MPh_2[Cr(CO)_3]_x$ where M = C, Si, Ge, Sn, Pb, $Me_2Sn(CH_2Ph)_2[Cr(CO)_3]_x$ and $Me_2Sn(\underline{p}\text{-}MeC_6H_4)_2[Cr(CO)_3]_x$ where x = 1, 2, have been prepared by reaction of the ligand with $Cr(CO)_6$ in tetrahydrofuran-diglyme or with $Cr(CO)_3(NH_3)_3$ in dioxan. The NMR, Moessbauer, infrared and Raman spectra of the complexes were recorded and interpreted [20]. The tricarbonylchromium complexes of acenaphthene and acenaphthylene have been prepared. When an attempt was made to form the tricarbonylchromium complex of 5-nitroacenaphthene, reduction of the nitro group occurred and the 5-aminoacenaphthene complex was formed with the metal bonded to the unsubstituted arene ring. The tricarbonylchromium complexes of fluorene, 9-phenylfluorene and 9-p-tolylfluorene were prepared. In the arylfluorenes the tricarbonylchromium moiety was bonded to one of the fluorene aromatic rings. The molecular structure of tricarbonyl-(η^6-fluorenyl)manganese was determined by X-ray analysis. The fluorenyl ligand had considerable cyclohexadienyl character with one carbon atom (C-10) in the complexed ring was bent away from the manganese atom [21].

An improved procedure for the preparation of triamminetricarbonylchromium in high yield has been reported. The reaction of this complex with some indenes and dehydronaphthalenes in dioxane in the dark produced the corresponding tricarbonylchromium complexes (4.1; X = H, CO_2Me and 4.2; X = R = H; X = CO_2Me, R = H; X = CO_2Me, R = Me) in good yields [22]. The treatment of 1,1-dimethylindane with hexacarbonylchromium produced the tricarbonylchromium complex (4.3). Reaction of this complex with the nucleophile $LiC(Me)_2CN$ followed by oxidation of the initially formed anion with iodine gave the 5-substituted product (4.4) in good yield. Formation of this product was caused by nucleophilic attack at a carbon which was eclipsed by a chromium-carbonyl bond. Electrophilic substitution of the complex (4.3) with acetyl chloride-aluminium chloride occurred predominantly at the C-4 and the C-6 positions which were not eclipsed by chromium-carbonyl bonds. This showed that conformational effects were important in directing the regio selectivity of attack by both electrophilic and nucleophilic reagents on (η-arene)tricarbonylchromium complexes



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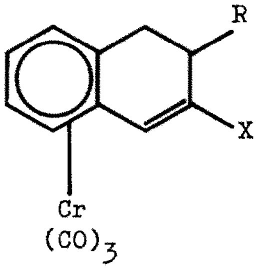

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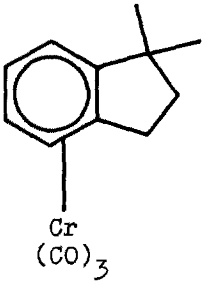

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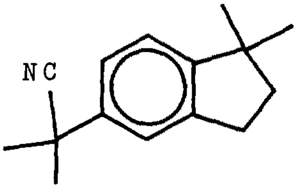
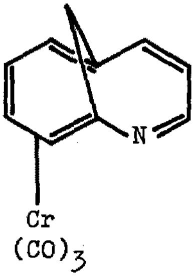


4.4

[23]. Reaction of 2,7-methanoaza[10]annulene with triamminetricarbonylchromium produced the tricarbonylchromium complex (4.5). This complex was stable in air and it was claimed to be the first transition-metal π-complex of an aza[4n + 2) annulene with $n > 1$. The structure of the complex (4.5) was determined by X-ray analysis [24].

Several indenyl and fluorenyl complexes of chromium have been obtained by treatment of 1-azafluorene, 3-methyl-1-azafluorene, 4-azafluorene, 7-methyl-4-azafluorene and [2,3]benzo-4-azafluorene with hexacarbonylchromium, or $(NH_3)_3Cr(CO)_3$. Thus, 3-methyl-2-azafluorene gave the tri-



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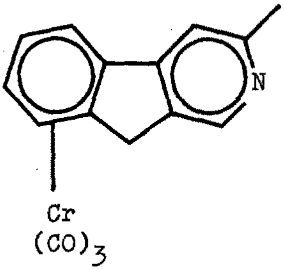

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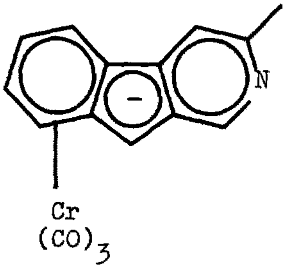

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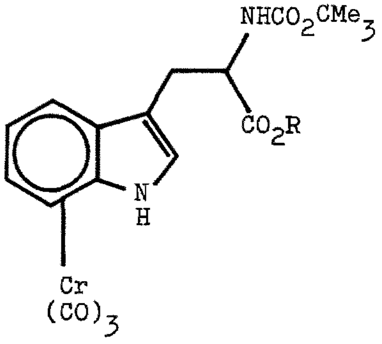
carbonylchromium complex (4.6) which was deprotonated with THF and t-BuOK to form the η^6-anion and this reversibly isomerized to the η^5-anion (4.7). Several related reactions were reported [25]. Reaction of hexacarbonylchromium with N-t-butoxycarbonyl-L-tryptophanmethyl ester produced the tricarbonylchromium complex (4.8; R = Me) and this was converted to the para-nitrophenol ester (4.8; R = $\underline{p}$-$NO_2C_6H_4$). The activated ester was used in the solid phase synthesis of a peptidic hormone (LHRH) analogue with the object of



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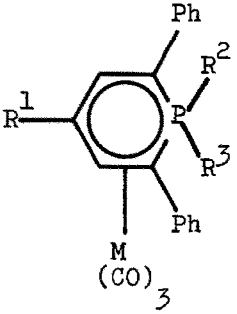
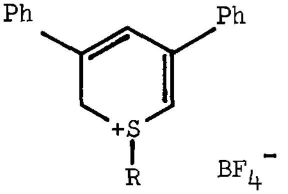


4.9

decreasing tryptophan alkylation. The overall yield of LHRH was not improved and additional byproducts were obtained [26].

Twenty-four λ^5-phosphorin complexes (4.9; R^1 = Me, Me_3C, Ph; R^2, R^3 = Me, Et, Me_3C, OMe, F, Et_2N; M = Cr, Mo, W) have been obtained in yields of up to 65% by treatment of the appropriate phosphorins with group VI metal carbonyls, $M(CO)_6$ [27]. The thiabenzene salts (4.10; R = Me, Et) have been treated with $L_3M(CO)_3$, where L = MeCN, cycloheptatriene; M = Cr, Mo, W, to give the corresponding tricarbonylmetal complexes (4.11). The 1-methyl thiabenzene derivatives (4.11; R = Me, M = Cr, Mo, W) were lithiated with t-butyllithium to give the lithio-intermediates (4.12) which were condensed with electrophiles [28]. The reaction of hexaethylidenecyclohexane (4.13) with triacetonitriletricarbonylchromium produced the tricarbonylchromium complex (4.14) via a double 1,5-sigmatropic hydrogen migration. When the latter



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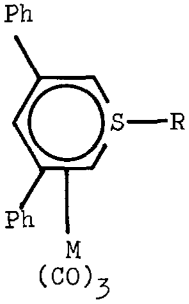

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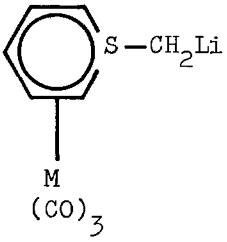
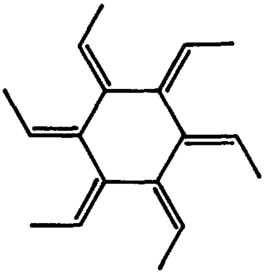


4.12

complex was heated further, rearrangement occurred to give the 1,3,5-triethyl-2,4,6-trivinylbenzene complex (4.15) [29].



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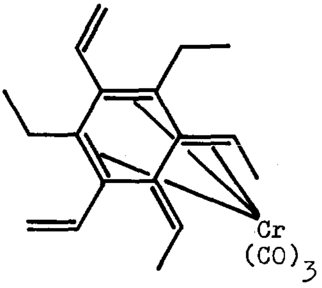

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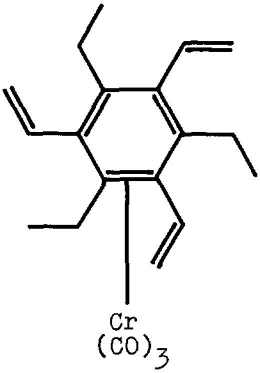
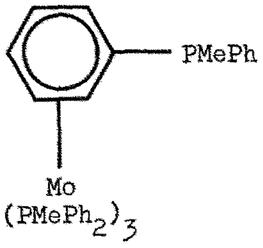


4.15

The (η-arene)molybdenum complex, $(\eta\text{-4-MeOC}_6\text{H}_4)\text{P(4-MeOC}_6\text{H}_4)_2$ Mo(triphos), where triphos = $\text{PhP(CH}_2\text{CH}_2\text{PPh}_2)_2$, has been prepared by sodium amalgam reduction of MoCl_3(triphos) in the presence of $(\text{4-MeOC}_6\text{H}_4)_3\text{P}$ [30]. The reduction of $\text{Mo}_2\text{Cl}_{10}$ with magnesium in the presence of PMePh_2 under nitrogen or argon produced the dinitrogen complex trans-$\text{Mo(N}_2)_2(\text{PMePh}_2)_4$ or the η^6-arene complex (4.16) respectively. The dinitrogen complex readily rearranged and coordinated η^6-arene ligands. For example, when the complex was heated in benzene

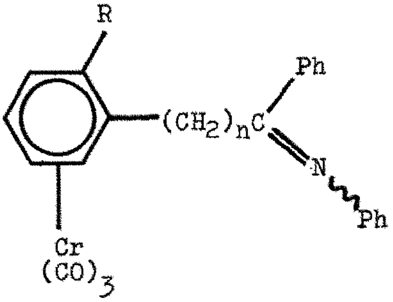


4.16

$(\eta^6\text{-}C_6H_6)Mo(PMePh_2)_3$ was produced [31].

(ii) Spectroscopic and Physico-chemical Studies

Irradiation of the tricarbonylchromium complexes (4.17; R = H, n = 2, 3; R = Me, n = 2) produced the corresponding chelate compounds (4.18). The structure of the complex (4.18; R = H, n = 2) was determined by X-ray analysis [32]. The crystal and molecular structure of dicarbonyl(η-hexaethylbenzene)triethylphosphine chromium has been determined by X-ray crystallography. Two different conformations were



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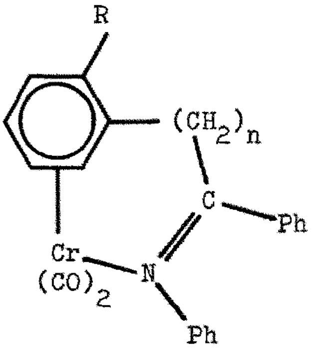
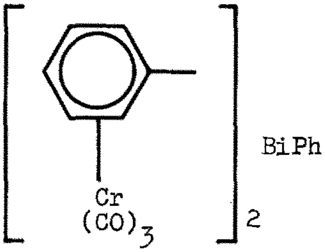


4.18

present in equal populations [33]. X-ray crystallography has been used to determine the crystal and molecular structure of the bis(benchrotrene)bismuth complex (4.19) [34].



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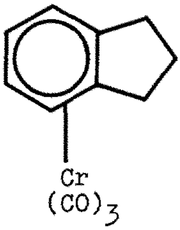

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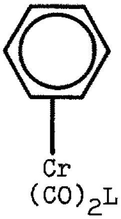
The electronic structure and nucleophilic reactivity of tricarbonyl(η-indanyl)chromium (4.20) has been investigated by He(I) and He(II) photoelectron spectroscopy and by EHT calculations. Nucleophilic reactivity was correlated with molecular conformations and the regioselectivity of electrophilic attack was explained by the eclipsed position of the tricarbonylchromium group and the localization of arene molecular orbitals under the influence of the alkyl substituents on the benzene ring [35].

A study of low frequency motions in (η-C_6H_6)M(CO)$_3$, where M = Cr, Mo, W, has been made by Raman and quasielastic neutron scattering [36]. The IR and laser Raman spectra for benchrotrene and its chalcocarbonyl analogues (4.21; L = CO, CS, CSe) have been measured in solution and in the solid state. Assignments have been proposed for most of the fundamental modes based on general quadratic compliance and force field calculations. The net π-acceptor/σ-donor capacity of the ligands increased in the order:

$$CO < CS < CSe$$

Comparisons of the general quadratic and energy-factored force fields for the CX modes showed the former to be favoured [37]. Electronic and IR spectroscopy have been used to provide evidence for 1:1 adduct formation between (η-arene)tricarbonylchromium complexes, where arene = acetophenone, benzaldehyde, and the europium β-diketonate complex Eu(fod)$_3$. The η-arene complex behaved as a Lewis base in adduct formation. Photolytic degradation of the Eu(fod)$_3$ adduct of the acetophenone complex was much less efficient than the photolysis of the free complex. This was explained in terms of excited state reordering in the complex on adduct formation and the implications of this effect were discussed [38].



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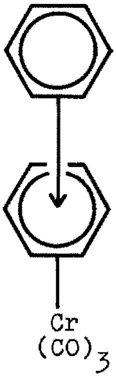
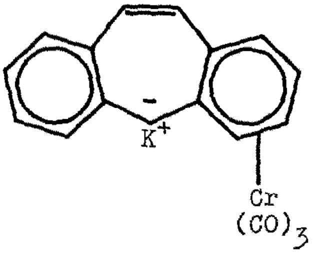


4.22

The formation of a 1:1 complex (4.22) between benzene-d$_6$ and (η^6-arene)Cr(CO)$_3$ complexes where arene = C_6H_5R(R = H, Me, OMe, Cl), $C_{10}H_8$, has been observed by ^{1}H NMR spectroscopy. From the results it was concluded that the Cr(CO)$_3$ unit exerts an electron withdrawing effect upon aromatic rings which is approximately equal to that of a nitro group [39]. Venzo and co-workers have reported on the kinetic acidity and the ^{1}H NMR spectrum of the tricarbonylchromium complex (4.23). The presence of the tricarbonylchromium group strongly stablized the 5H-dibenzo[a, d]cyclo-



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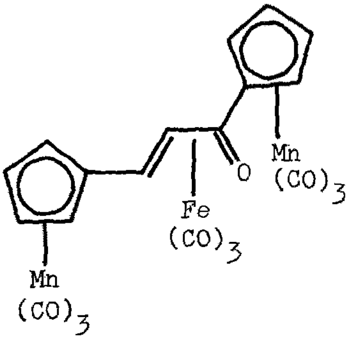
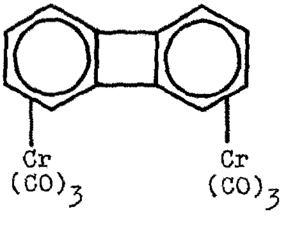


4.24

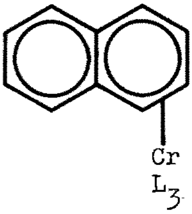
heptenyl anion. The NMR results for the free and the complexed ligand were explained in terms of a substantial reduction of the paratropic character of the ligand anion upon complexation [40]. An NMR study on the complex (4.24) showed that protonation, followed by treatment with aqueous sodium hydrogen carbonate removed the tricarbonyliron moiety [41].



4.25

The ^{1}H and ^{13}C NMR spectra of the tricarbonylchromium complexes of biphenylene have been recorded and interpreted. The data suggested that there was a substantial reduction in the paratropic character of the molecule on complex formation. In the bis-complexed biphenylene (4.25) the two electronic sextets behaved as separate non-interacting systems [42].

The ^{13}C NMR spectra of several (η^6-naphthalene)chromium complexes [4.26; L = CO, $P(OMe)_3$, PF_2OMe, PF_3] and (4.27) have been measured and assigned with the use of deuterium labelled naphthalene ligands. The coordinated ring resonances were found to shift to higher field with an increase in electron donation from the ligand (L). The naphthalene group in complexes containing strong acceptor ligands was activated to attack by nucleophiles [43]. ^{13}C NMR studies on tricarbonyl-(η-hexaethylborazine)chromium in CD_2Cl_2 indicated the presence of two conformers. In one conformer two terminal methyl groups on N-Et moieties were proximal to the chromium atom whereas in the other conformer only one such group was proximal [44].



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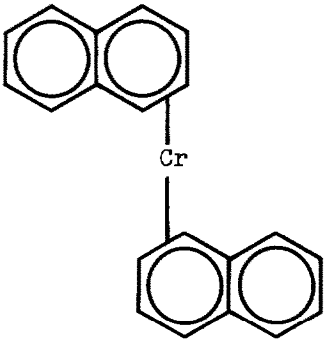
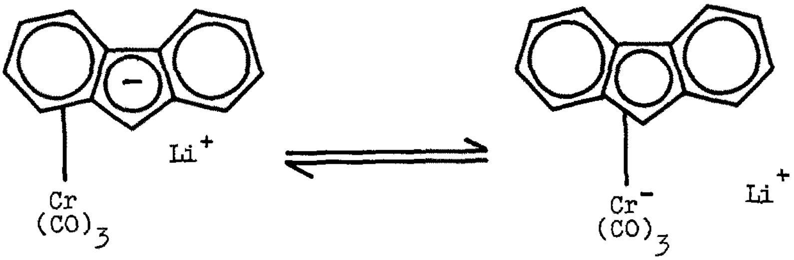


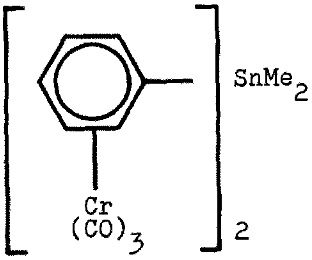
4.27

The reversible isomerization of the η^6- and (η^5-fluorenyl)-chromiumtricarbonyl anions (4.28 and 4.29) respectively has been examined by ^{13}C NMR spectroscopy. The π-electron density distribution in the fluorenyl anion has been calculated using the INDO method [45]. The complex (4.30) and related compounds have been studied by cyclic voltammetry. The compounds underwent a reversible one electron oxidation per $Cr(CO)_3$ moiety. The $Cr(CO)_3$ groups were essentially noninteracting and adhered to the Bard-Anson-Saveant model. Similar results were obtained for the bis- and tris-$Cr(CO)_3$ complexes of $MeSnPh_3$ where a dication and a trication were



4.28 4.29

formed respectively [46]. The (η-arene)tricarbonylchromium complexes (4.31; X = H, COMe, NMe_2) in N,N-dimethylformamide exhibited a three electron irreversible oxidation at a glassy carbon electrode. The first electron loss was followed by decomposition of the chromium(I) complex with the formation of chromium(III). The presence of an electron-donating group on the η-arene ring did not improve the stability of the intermediate chromium(I) species [47].



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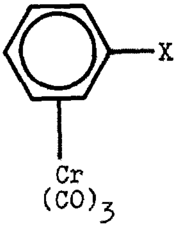
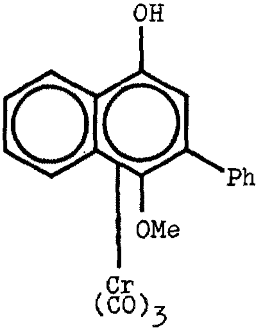
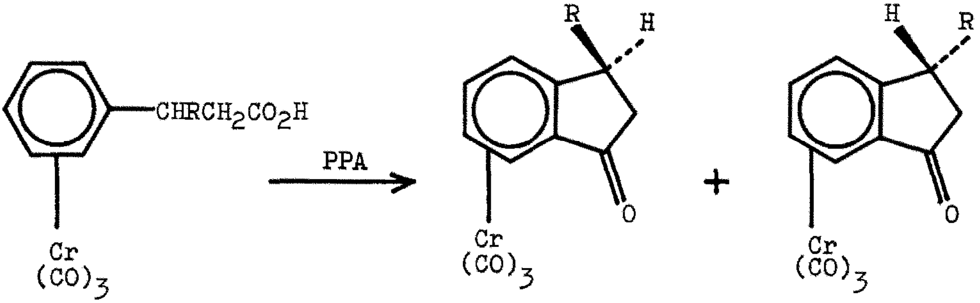


4.31



4.32

The electron-donating properties of cymantrene and the corresponding rhenium complex to aluminium bromide and gallium (III) chloride have been determined. For example, the heat of formation for coordination of the carbonyl groups in cymantrene with aluminium bromide was 18.9 kcal mol^{-1} [48]. The kinetics and mechanism have been investigated for the reaction of pentacarbonyl[(methoxy)(phenyl)carbene]chromium with alkynes to give tricarbonyl(η-naphthol)chromium complexes of the type (4.32). The reaction rate increased with an increase in the electron density within the triple bond of the alkyne [49]. The cyclization of the tricarbonylchromium



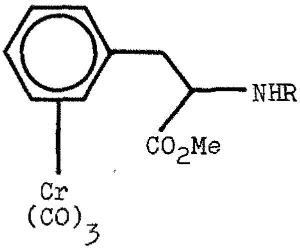
4.33 4.34 4.35

complexes of β-alkyl-β-phenylpropionic acids (4.33; R = Me, Et, Pr^i) with polyphosphoric acid (PPA) gave the exo- and endo-diastereoisomers of the indanone complexes (4.34 and 4.35; R = Me, Et, Pr^i). The mechanism of the reaction appeared to be under steric control and the configurations of the indanone complexes (4.34 and 4.35) were determined by the use of optically active substrates. The cyclization of tricarbonylchromium complexes of α-alkyl-β-phenylpropionic acids were the subject of a parallel study [50].

The basicity of the metal in (η^6-arene)Cr(CO)$_3$ and Fe(CO)$_{5-n}$L$_n$, where L = phosphine or phosphite and n = 2, 3 complexes has been investigated. The variations in basicity of the metal centre were small and this was attributed to the ability of the carbonyls to moderate the effect of the ligands, so that the electron density around the metal remained relatively constant [51].

(iii) General Chemistry

Reaction of phenylalanine derivatives and phenylalanine-containing cyclic dipeptides with hexacarbonylchromium in water-tetrahydrofuran mixtures gave the corresponding stable tricarbonylchromium complexes (4.36; R = CHO, COMe, 5-butyloxycarbonyl and 4.37). Photolytic elimination of the tricarbonylchromium moiety from these complexes regenerated the free ligand with full optical activity indicating that no racemization had occurred [52]. Irradiation of the tricarbonylchromium complex (4.38) produced the η-acetylene complex (4.39) which underwent a reversible rearrangement to give a mixture of the two η-allene complexes (4.40 and 4.41) [53]. Reaction of the carbon disulphide complexes (4.42; $R^1 = R^2 = R^3 = H$; $R^1 = R^2 = Me$, $R^3 = H$; $R^1 = R^2 = H$, $R^3 = OMe$) with the activated acetylenes $R^4C{\equiv}CR^5$, where R^4, R^5 = CO_2Me, CO_2Me; CH_2OH, Ph; CO_2Et, H, afforded the 1,3-dithiol-2-ylidene derivatives (4.43). Irradiation of these complexes in the presence of phosphites



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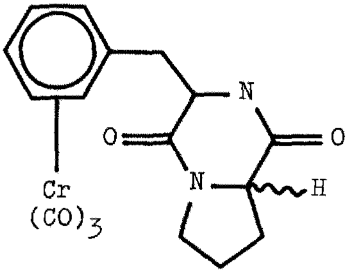

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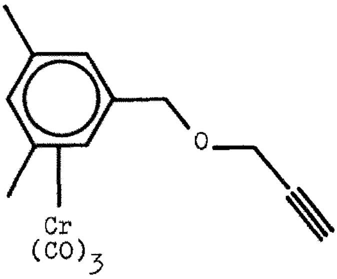

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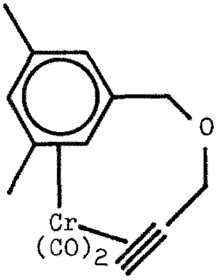

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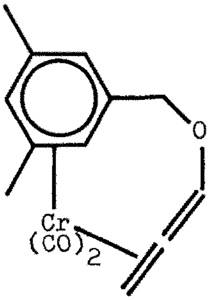

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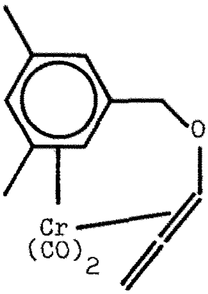
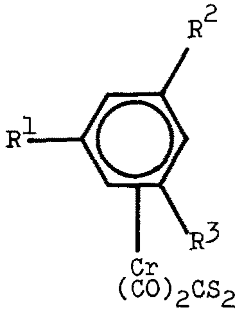


4.41

resulted in replacement of the carbonyl groups by phosphite ligands but the chromium-carbene bond was unaffacted [54].

The (η-octamethylnaphthalene)metal complexes (4.44; M = Cr, Mo, W) have been characterized. Triphenylphosphine displaced one carbonyl ligand from the chromium complex (4.44; M = Cr) under photochemical conditions while trimethylphosphite displaced the naphthalene ligand on heating to form the derivative $Cr(CO)_3[P(OMe)_3]_3$. Maleic anhydride underwent Diels-Alder addition to the naphthalene ligand in the chromium complex(4.44; M = Cr)to form two isomeric products [55]. Reaction of the tricarbonylchromium complex (4.45) with chiral amines gave the optically active imides, for example, reaction with (S)(-)- and (R)(+)-phenylalaninol



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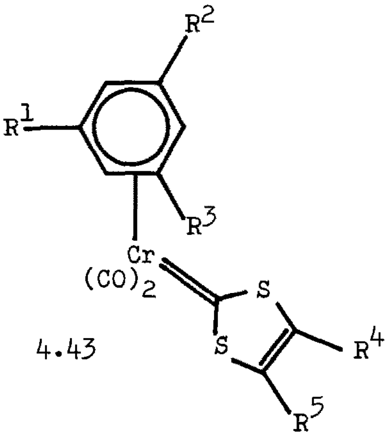
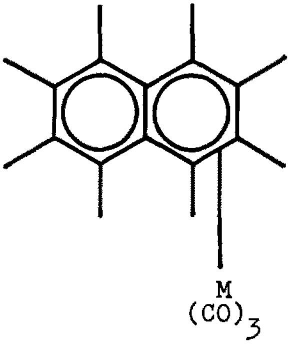


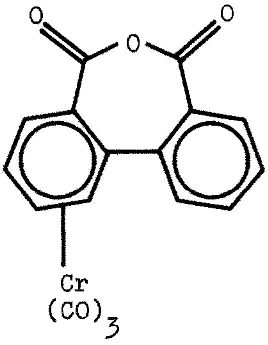
4.43

produced the imides (4.46 and 4.47) respectively. The absolute configurations of the complex and axial-chiral parts of the diphenyl system were ascertained from the circular dichroism spectra. The ligands were removed from the tricarbonylchromium moieties photochemically. The optically active biphenyl (4.48) was prepared by a similar route [56].



4.44

The tricarbonylchromium complex of indole (4.49; X = NH) was converted easily into a series of N-protected compounds (4.49; X = NMe, NCH_2Ph, $NSiPh_2$-t-Bu) by deprotonation with sodium hydride followed by addition of the appropriate electrophile. Addition of reactive carbon nucleophiles to



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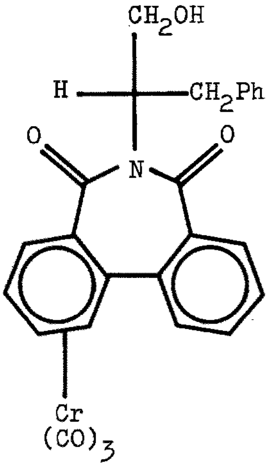

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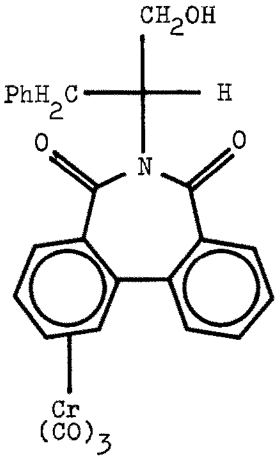
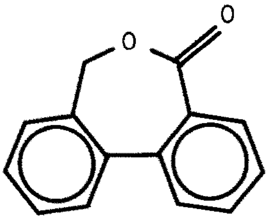


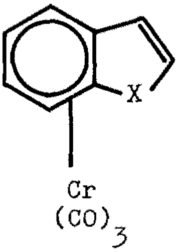
4.47



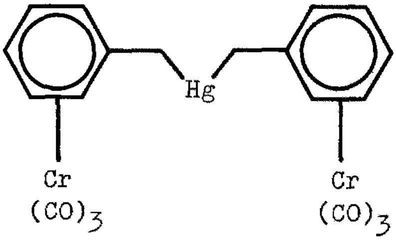
4.48

the N-protected compounds led to substitution in the coordinated ring at C-4 and sometimes at C-7. Oxidation of the intermediate cyclohexadienyl anionic complexes produced substituted indoles in good yield [57].

Treatment of the tricarbonylchromium complex (4.50) with iodine, lithium aluminium hydride or mercury(II) or copper(II) chloride produced the iodide (4.51; R = I), the hydride (4.51; R = H) and the mercurichloro derivative (4.51; R = HgCl) respectively [58]. Garcia has explored the reaction of nucleophiles with a series of (η-arene)tricarbonylchromium complexes. Nucleophilic aromatic substitution was considered to involve charge control and frontier



4.49



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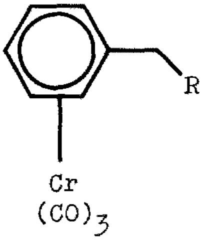
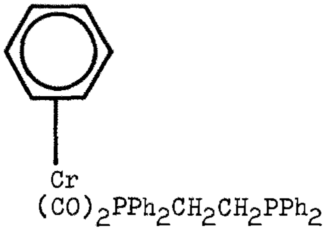


4.51

orbital control. These ideas together with steric considerations were used to explain the regiochemistry of the nucleophilic substitutions [59]. The phosphine complex (4.52), obtained by irradiation of benchrotrene with 1,2-bis(diphenylphosphino)ethane, has been attacked by the carbon nucleophiles, $LiCMe_2CN$ and $LiCHMeCO_2Bu^t$ to form the derivatives (4.53; R = CMe_2CN, $CHMeCO_2Bu^t$) after oxidative cleavage of the first formed complex [60].



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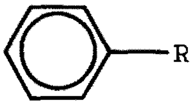
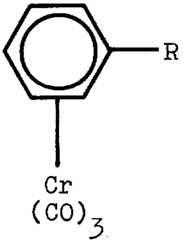
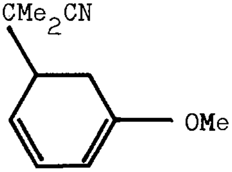


4.53

The addition of carbon nucleophiles to (η-arene)tricarbonylchromium complexes has been investigated. The addition of $LiCMe_2CO_2CMe_3$ to the complex (4.54; R = Me) followed by iodine oxidation gave 96% of 3:97 mixture of



4.54



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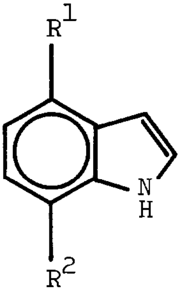
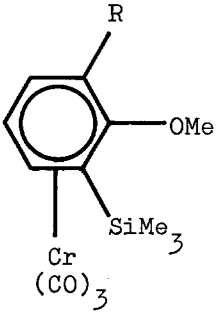


4.56

2- and 3-$MeC_6H_4CMe_2CO_2CMe_3$. The addition of $LiCMe_2CN$ to the complex (4.54; R = OMe) followed by protonation and oxidation gave a good yield of the cyclohexadiene (4.55). The addition of $LiCMe_2CO_2CMe_3$ to tricarbonyl(η-indole)chromium produced 92% of a 99:1 mixture of the indoles (4.56; $R^1 = CMe_2CO_2CMe_3$ R^2 = H; R^1 = H, $R^2 = CMe_2CO_2CMe_3$) respectively [61]. Treatment of the tricarbonylchromium complex (4.57; R = H) sequentially with n-butyl lithium, copper(I) iodide and (E)-$BrCH_2CH=CHPr$ gave the complex [4.57; R = $CH_2CH=CHPr$-(E)]. The latter compound was used as an intermediate



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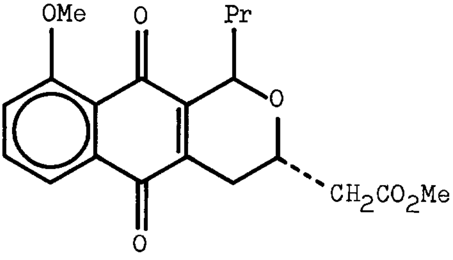
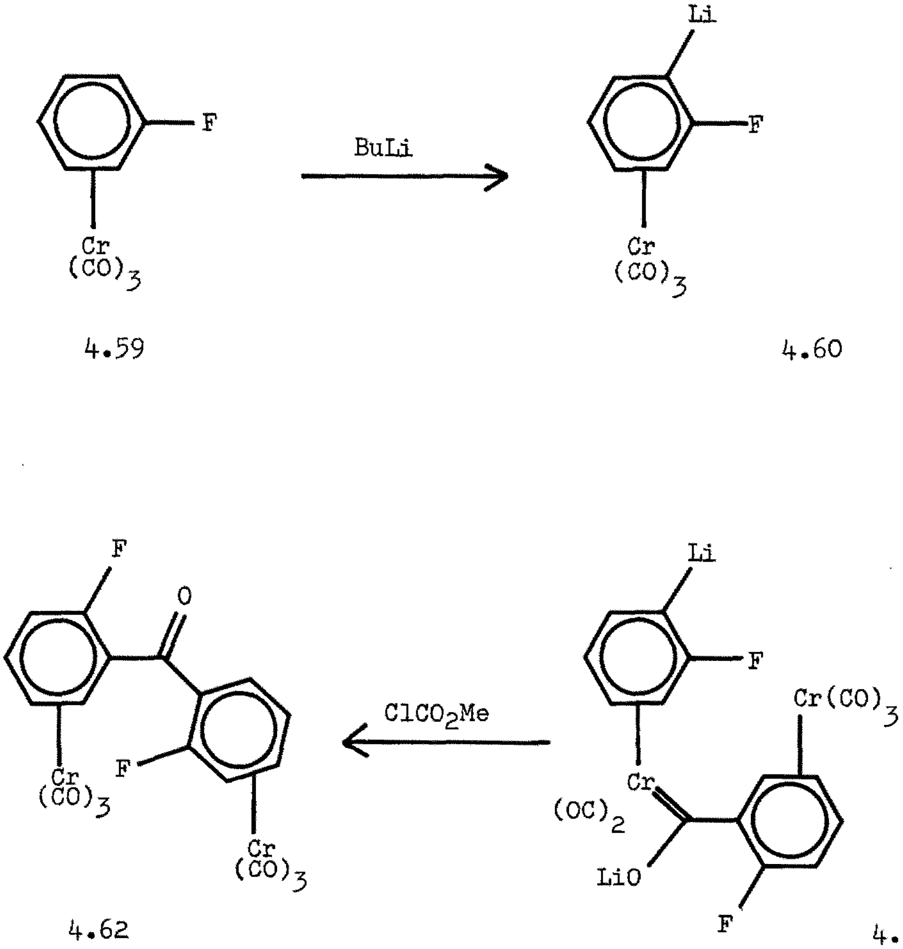


4.58

in the preparation of the naphthaquinone (4.58) which is a known precursor to frenolicin [62].

Tricarbonyl(η-fluorobenzene)chromium (4.59) has been treated with butyllithium in diethylether at -78°C to form the lithioarene complex (4.60) which gave, with methyl chloroformate, the binuclear product (4.62) apparently by way of the carbene-bridged dimer (4.61). The crystal and molecular structure of the dimethyl derivative of the product (4.62) was determined by X-ray methods [63]. The decomposition of (η^6-2-lithiochlorobenzene)tricarbonylchromium has been studied between -50°C and +33°C in ether. The decomposition



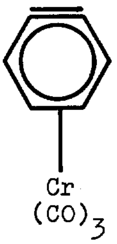
4.59

4.60

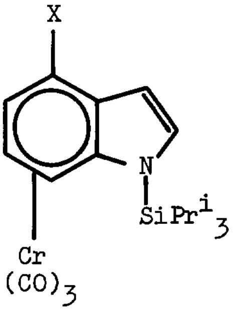
4.62

4.61

was found to follow first order kinetics $\underline{k}_{dec}$ = 5.1×10^{-3} min^{-1} at 0°C. The results suggested the presence of the intermediate η^6-benzyne complex (4.63), however attempts to capture this intermediate were inconclusive [64]. The (η-indole)chromium complex (4.64; X = H) underwent selective lithiation in the 4-position to give the



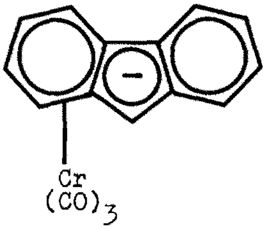
4.63



4.64

intermediate (4.64; X = Li) which was treated with electrophilic halides to form the products (4.64; X = CO_2Me, CO_2Et, $SiMe_3$, SPh, $CH_2CH{=}CMe_2$). These products were **subsequently deprotected and decomplexed under mild conditions** [65].

The complex anion (4.65) was prepared from tricarbonyl(η-fluorene)chromium by metallation with potassium or sodium t-butoxide in tetrahydrofuran. The tautomer (4.66) was obtained by treatment of bis[tricarbonyl(η-fluorenyl)-chromium]mercury with sodium, potassium, or lithium amalgam [66]. The thermal decomposition of bis[tricarbonyl(η-phenyl)chromium]-mercury (4.67) at 200°C gave benchrotrene (25%) and bisbenchrotrenyl (4.68)(51%). The mechanism involved homolytic cleavage of the mercury-phenyl bond with formation of the intermediate benchotrenyl radical [67]. The optically active tricarbonyl(η-arene)chromium alcohols (4.69; n = 1, 2) have been oxidized to the corresponding optically active ketones (4.70) in good yields by a mixture of acetic anhydride



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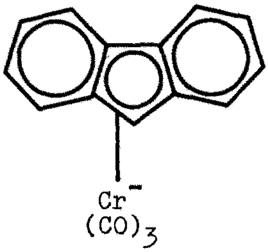
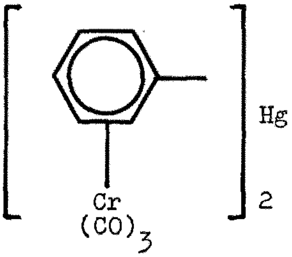


4.66

and dimethylsulphoxide. Other alcohols were oxidized without the loss of the $Cr(CO)_3$ group and the yields were dependent on the nature of the starting alcohol [68].



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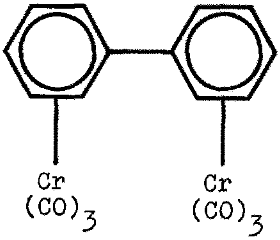
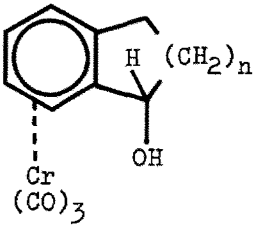


4.68

The tricarbonyl(η^5-indenyl)chromium anion (4.71) as the potassium salt underwent alkylation with methyliodide to form initially the σ-alkyl complex (4.72) which formed the tricarbonyl(η^6-indenyl)chromium complexes (4.73 and 4.74) by an innersphere "ricochet" rearrangement. Alkylation of the anion (4.71) with benzylbromide was carried out in the same way and the <u>endo</u>-benzyl configuration of the product was confirmed by X-ray crystallography. The anion obtained from tricarbonyl(η^5-fluorene)chromium consisted of tricarbonyl(η^5- and η^6-fluorenyl)chromium in tautomeric equilibrium



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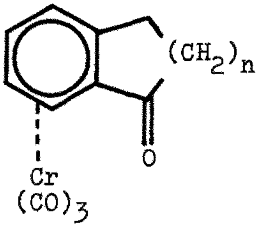
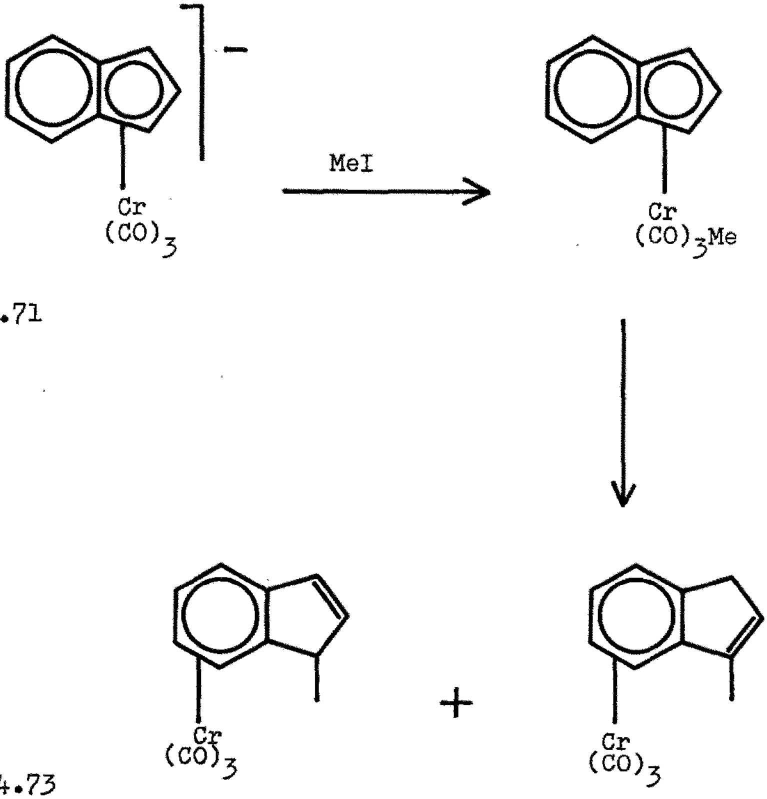


4.70

and it underwent alkylation in the same way [69]. Synthetic routes to (η-cyclopentadienyl)dicarbonylnitrosylchromium,

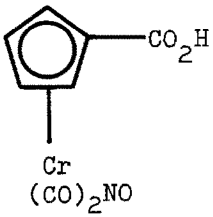


4.71

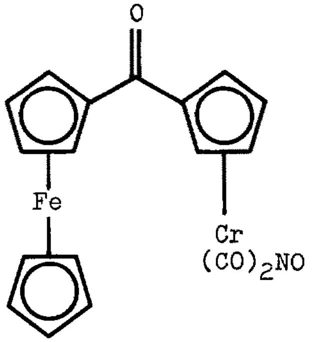
4.72

4.73

4.74



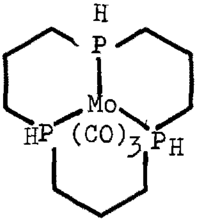
4.75



4.76

cynichrodene, derivatives have been explored. Cynichrodenic acid (4.75) was found to behave as a typical aromatic carboxylic acid and was useful as an intermediate. The acid chloride, amide, anhydride and ester were prepared. The acid chloride was used as an electrophile to attack ferrocene and form the cyninchrodenylferrocenyl ketone (4.76) [70].

The reaction of (η-benzene)tricarbonylchromium with NOCl or $NOPF_6$ led to solvated mono- and di-nitrosylchromium intermediates which were used in the synthesis of a variety of Me_3CNC (L) complexes, for example, $CrCl_2(NO)_2L_2$ and $CrCl(CO)_n(NO)L_{4-n}$ ($n = 0$-2) [71]. Tricarbonyl(η-phenanthrene)-chromium has been used as a hydrogenation catalyst for α-terpinene and 2,3-dihydroanisole in cyclohexane. The catalytic reaction was accelerated by the addition of a small proportion of acetone or 3-methylcyclohexanone [72]. Reaction of tricarbonyl(η-mesitylene)molybdenum with allylphosphine produced fac-$(CO)_3Mo(H_2PCH_2CH{=}CH_2)_3$ and when this was heated with [2,2'-azobis(isobutyronitrile)] gave the macrocyclic triphosphine-molybdenum complex (4.77) [73]. The benzylcobalt tetracarbonyl compound (4.78) has been obtained by treatment of (η-benzylchloride)tricarbonylchromium with $Na[Co(CO)_4]$ in ether [74].



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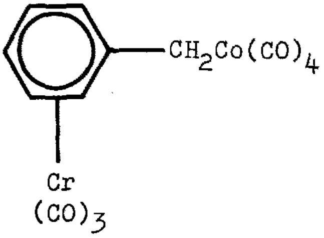
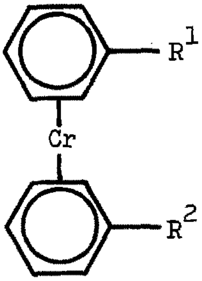


4.78

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

Several bis(η-arene)chromium complexes (5.1; R^1, R^2 = H, NMe_2, CO_2Me, CO_2Et, CH_2CO_2Me, CH_2CO_2Et, $CH_2CH_2CO_2Me$, $CH_2CH_2CO_2Et$) have been obtained by cocondensation of chromium atoms with the ligand vapour at low temperatures and pressures. These complexes were oxidized to the corresponding bis(η-arene)chromium(I) iodides with iodine. IR carbonyl frequencies demonstrated that the (η-arene)Cr(0) group was a powerful electron donor while the (η-arene)Cr(I)



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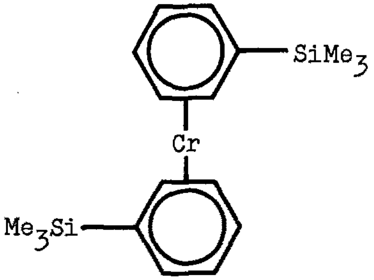
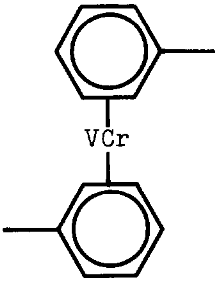


5.2

group was strongly electron withdrawing. The redox potential Cr(O)/Cr(I) was determined by cyclic voltammetry and showed marked dependence on the type and number of the substituents [75]. Chromium atoms have been cocondensed with the appropriate ligand vapour at low temperatures to form bis(η-trimethylsilylbenzene)chromium (5.2), bis[η-1,4-bis-(trimethylsilyl)benzene] chromium and bis[η-1,3,5-tris(trimethylsilyl)benzene]chromium. The complexes have been characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and ESR spectroscopy. Theyunderwent desilylation with reagents as mild as methanol, they were oxidized by pyridine-4-aldehyde to radical cations and reduced at a potassium mirror to radical anions [76].

Cocondensation of chromium atoms with disubstituted pyridines at low temperatures and pressures gave bis(η--pyridine)chromium complexes. Cocondensation of iron atoms with alkynes gave substituted ferrocenes and cyclooctatetraene oligomers [77]. Cocondensation of tungsten vapour with an excess of the arenes, C_6H_6, m-(iPr)$_2C_6H_4$, C_6H_5Me, 1,3,5-$Me_3C_6H_3$, C_6H_5OMe, C_6H_5F, produced the corresponding bis(η-arene)tungsten complexes. These compounds protonated readily in dilute aqueous acids to form the bent bis(η-arene)hydrido-cations $[W(\eta\text{-arene})_2H]^+$ [78]. Some cyclopropyl-containing bis(η-arene)-chromium and titanium complexes have been prepared by low temperature cocondensation of the metal with the ligand [79].

Bis(η^6-toluene)chromium dissolved in methylcyclohexane at 140-160 K has been treated with vanadium or chromium atoms to give the heterodimetallic species (5.3 and 5.4). It was proposed that the arene-stabilized dimetal complexes were produced <u>via</u> a one step addition of a metal atom to the metal centre of $(\eta^6\text{-toluene})_2Cr$ [80]. The competition reactions between two substituted arenes for molybdenum atoms were investigated by the condensation of a mixture of the two arenes, with a metal to ligand ratio of 20-50:1 at temperatures near -196°C. The mixtures of sandwich complexes were analyzed by NMR spectroscopy. The relative rates of reaction were spaced over the small overall range of 3.7 for the following arenes: toluene, $\alpha,\alpha,$-trifluorotoluene, t-butyl-



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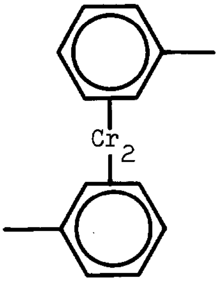
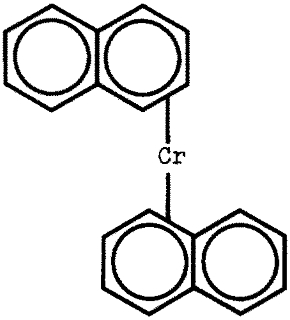


5.4

benzene, o-xylene, fluorobenzene, N,N-dimethylaniline, fluorobenzene, methylbenzoate and anisole [81]. The decompositions of (η-PhH)$_2$Cr,(η-PhEt)$_2$Cr, (η-PhH)Cr(CO)$_3$, Cr(CO)$_6$ and (η-C_5H_5)$_2$Cr have been studied in a pulsed electrical discharge [82].

The bonding in some bis(η-arene)chromium compounds has been investigated by ultra-violet photoelectron spectroscopy. It was concluded that (i) the ionizations from the a_{1g} and e_{2g} molecular orbitals localized on the chromium were governed mainly by ligand electronegativity with some evidence for the operation of conjugative effects, and (ii) the ionization energies of the free and coordinated arenes were similar [83].

Substituent effects in a series of monosubstituted bis(η-arene)chromium cations were investigated via their electronic and ESR spectra. The ultraviolet ligand-metal charge transfer band and ESR parameters did not depend on the nature of the ring substituents. As the number of electron--donating groups increased so did the significance of the inductive effects. The structure of bis(η-1,3,5-triisopropylbenzene)chromium was determined by X-ray analysis. The molecule had a staggered conformation which was stabilized by steric factors [84].



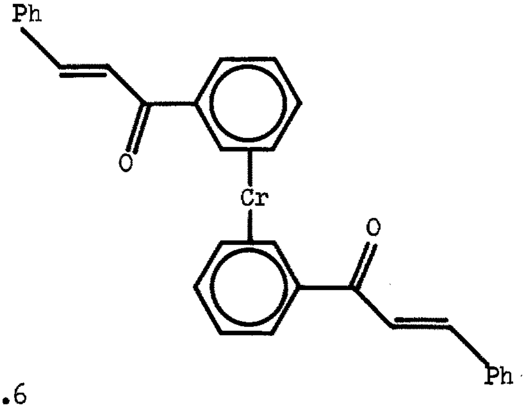
5.5

The kinetics of electron exchange between (η-arene)$_2$Cr^I and (η-arene)$_2$Cr^0, where arene=benzene, toluene, methoxybenzene, ethyl benzoate, chlorobenzene and biphenyl, have been determined by an ESR line broadening technique and comparisons made with electron-transfer theory. The solvent dependence of the rate constants for the exchange using (η-biphenyl)$_2$Cr$^{I/0}$ were found to be in reasonable agreement with the predictions of the dielectric continuum model [85].

The inelastic neutron scattering spectra of benchrotrene, bis(η-benzene)chromium and bis(η-benzene)chromium iodide have been measured in the range 0-875cm^{-1}. The low frequency modes which involved appreciable benzene-ligand displacement were assigned. The energy barriers for benzene-group rotation have been determined as 27.5, 12.6 and 15.5 kJ mol^{-1} respectively and compared with values obtained by NMR spectroscopy [86, 87]. The incoherent inelastic neutron scattering (INS) spectra of low frequency motions in $Mn_{0.84}PS_3[Co(\eta\text{-}C_5H_5)_2]_{0.32}$ and $Mn_{0.86}PS_3[Cr(\eta\text{-}C_6H_6)_2]_{0.28}$ have been investigated. By comparing the far infrared, low frequency Raman and INS results, an assignment was proposed for the internal torsion and for the librational motions in the intercalated organometallic cations [88].

The crystal and molecular structure of bis(η-toluene)tungsten has been determined by X-ray crystallography. The structures of the hydrides $[WH(\eta^6-C_6H_5Me)_2]PF_6$, $[WH(\eta^6-C_6H_5F)_2]PF_6$ and several related complexes were also determined. No evidence was obtained to indicate that the arene ligands behaved as dienes [89]. The structures of bis(η-1,3,5-triisopropylbenzene)chromium and bis(η-1,3,5-triisopropylbenzene)chromium(I) iodide have been determined by X-ray crystallography and dynamic NMR spectroscopy. The staggered conformation was stabilized by steric factors both in the solid and in solution [90]. The crystal and molecular structure of bis(η-naphthalene)chromium (5.5) has been determined by X-ray crystallography. Naphthalene ligands in individual molecules were found to be syn-oriented [91].

The electrochemical reduction of benzalacetophenone and bis(η-benzalacetophenone)chromium (5.6) has been studied by the rotating disc and rotating ring-disc electrode techniques.



5.6

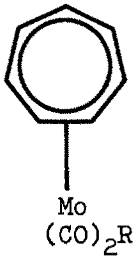
The free ligand showed two, and the complex three, cathodic waves on the polarization curves. In both cases reversible one electron transfer was followed by dimerization of the primary products of the electrode reaction. The presence of the chromium atom exerted little influence on the mechanism of the process but it reduced the reactivity of the complex [92]. In a related study of a series of bis(η-arene)chromium complexes and the corresponding ligands the role of the chromium atom in the transfer of electronic effects from one ligand to another was discussed. The results obtained provided experimental support for the conclusion that electron density in bis(η-benzene)chromium was shifted to the ligands so that the chromium atom was carrying a positive charge [93].

The electrochemical reduction of nine bis(η-arene)-chromium complexes, where the arene was a hydrocarbon with condensed benzene rings such as fluorene, naphthalene, chrysene, has been studied by cyclic voltammetry. Each complex exhibited a reversible one-electron reduction step. The half-wave potentials were independent of the ligands and contrasted with the behaviour of bis(η-arene)chromium complexes with alkyl- and aryl-substituted benzenes which depended largely on the ligands. The ESR spectra of the nine complexes were measured and showed only ^1H hyperfine lines due to a pair of benzene ligands bonded to Cr, in addition to the expected ^{53}Cr hyperfine lines. It was concluded that the HOMO of $Cr(\eta\text{-arene})_2$ was composed mainly of metal $3d_z2$ and ligand σ-orbitals [94].

In a study of the reaction of bis(η-ethylbenzene)chromium and other bis(η-arene)chromium complexes with organosilicon peroxides, a bis(η-arene)chromium cation was identified as an intermediate [95, 96]. A mechanistic model has been proposed to explain the amount of carbon formed during the degradation of bis(η-ethylbenzyl)chromium [97, 98]. Thermolysis of bis(η^6-acylbenzene)chromium complexes afforded ethene derivatives as the main products. It was suggested that the reaction proceeded via arylcarbenes formed by deoxygenation of the η-acylbenzene ligand by chromium(0) [99].

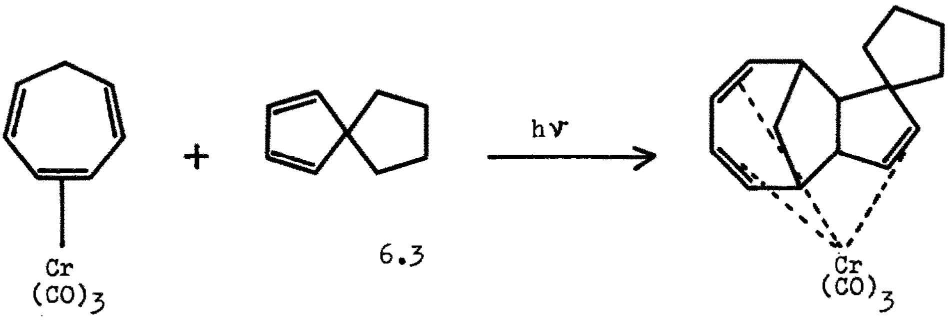
6. $[(\eta\text{-}C_7H_7)Cr(CO)_3]^+$ and $(\eta\text{-}C_7H_8)Cr(CO)_3$

The (η-cycloheptatrienyl)molybdenum complexes (6.1; R = Me, Ph) have been prepared and subjected to insertion of SO_2 into the Mo-R bond which took place in ether solution. Insertion of SeO_2 and TeO_2 required forcing conditions [100].

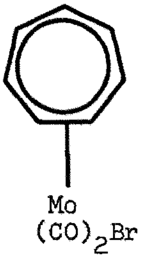


6.1

UV irradiation of tricarbonyl(η-cycloheptatriene)chromium (6.2) with cyclic dienes gave complexes with tetracyclic ligands. Thus, spiro[4.4]nona-1,3-diene (6.3) gave the tricarbonylchromium complex (6.4). The mechanism of cycloaddition was investigated by deuterium labelling and by ^1H NMR spectroscopy [101]. Treatment of the (η-cycloheptatrienyl)molybdenum complex (6.5) with sodium amides $NaNR_2$ gave the mixed-valence binuclear complexes (6.6; R = H, p-$NO_2.C_6H_4$; NR_2 = pyrrole) [102].



6.2 6.3 6.4



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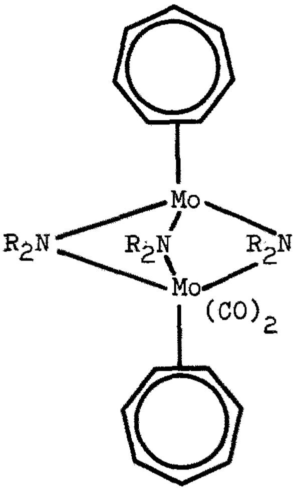
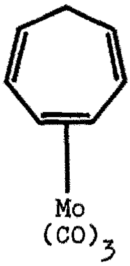


6.6

The (η-1,3,5-cycloheptatriene-3,7-$^{13}C_2$)molybdenum complex (6.7) has been subjected to thermolysis in benzene-$\underline{d}_6$ and the redistribution of the isotopic labels followed by ^{13}C NMR spectroscopy. Comparisons with predicted rearrange-



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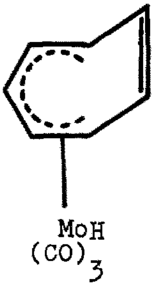
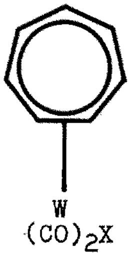


6.8

ment pathways indicated that 1,5-hydride shifts were involved. Thermal redistribution in an (η-cycloheptatriene)-rhodium complex occurred with randomisation of the label [103]. Infrared spectra of matrices obtained by cocondensing sublimed (η^6-C_7H_8)Mo(CO)$_3$ with matrix gas at 12K indicated the presence of a new species produced by thermal rearrangement in the gas phase. It was proposed that the new species was the hydride complex (6.8) [104].

Ultraviolet irradiation of the η^6-cycloheptatriene complex (6.7) in methane and argon matrices at 12K resulted in the reversible formation of (Mo(η^6-C_7H_8)(CO)$_2$ via photodissociation of carbon monoxide. Stepwise photoelimination of cycloheptatriene occurred in a carbon monoxide matrix to give hexacarbonylmolybdenum [105]. Dicarbonyl(η-cycloheptatrienyl)iodotungsten (6.9; X = I) has been attacked by the anions OR$^-$, SR$^-$, SeR$^-$ and TeR$^-$, where R is alkyl or aryl, to form the derivatives (6.9; X = OR, SR, SeR and TeR) together with some related polynuclear complexes [106].

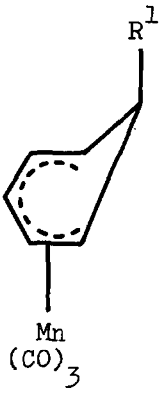


6.9

7. (η-C_5H_5)Mn(CO)$_3$

(i) Formation

Reaction of [(η^6-C_6H_6)Mn(CO)$_3$]$^+$ with Grignard reagents produced the corresponding η-cyclohexadienyl complexes (7.1; R^1 = Me, Ph). Treatment of these latter complexes with



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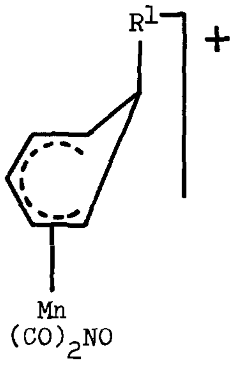

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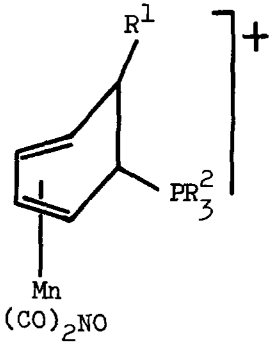
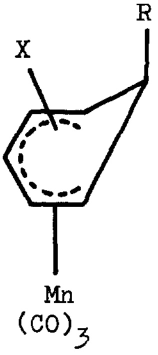


7.3

NOPF$_6$ gave almost quantitative yields of the nitrosyl containing cations (7.2). The cyclohexadienyl ring in these cations (7.2) was readily attacked by nucleophiles to give coordinated dienes. For example, treatment of the cations (7.2) with tertiary phosphines, PR^2_3 where R^2 = Ph, Bu, gave the corresponding phosphonium salts (7.3) [107].



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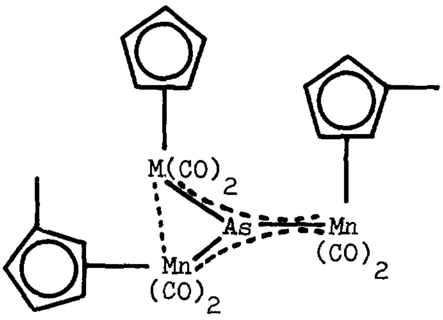
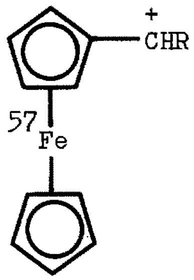


7.5

Grignard reagents and ketone enolates have been shown to add to the η-arene ring in the complexes $[LMn(CO)_3]^+$, where L = PhH, PhCl, p- MeC_6H_4Cl, PhMe, PhOMe, to give the cyclohexadienyl complexes (7.4; X = H; 1,4-Cl, Me; 2-MeO; R = Me, Ph) in good yields. A method to release the arene to recycle the $[Mn(CO)_3]^+$ moiety was described [108]. The trinuclear metal complexes (7.5; M = Mo, W) were prepared by reaction of $ClAs[Mn(CO)_2(\eta-C_5H_4Me)]$ with $(\eta-C_5H_5)M(CO)_3$ [109].

(ii) Spectroscopic and Physico-chemical Studies

The ^{13}C-[^{57}Fe] chemical shifts in the NMR spectra of the binuclear α-ferrocenylcarbenium ions (7.6; R = cymantrenyl, ferrocenyl, ruthenocenyl) have been studied [110]. An infrared and ^1H NMR spectroscopy study has shown that on addition of trifluoroacetic acid to the manganese complex (7.7), protonation of position 9 of the fluorenyl ligand occurred with simultaneous migration of the metal to form the cation (7.8) [111]. A neutron diffraction study has been carried out on the manganese complex (7.9). The silicon to hydrogen distance was found to be shorter than the sum of the van der Waals radii. The nature of the silicon to hydrogen interaction was discussed and one possibility considered was the presence of an incipient three centre/two-electron bond



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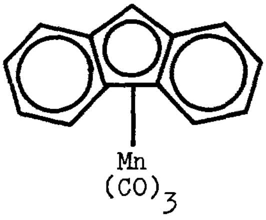

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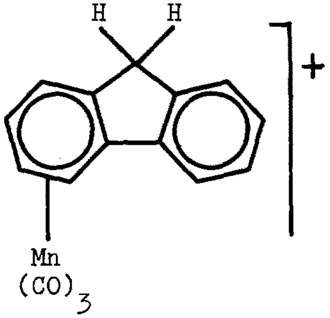
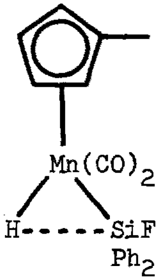


7.8

in the Mn-H-Si triangle [112].

The structure of the manganese complex (7.10) has been determined by X-ray analysis. The orientation of the methyl group was trans with respect to the phosphine ligand [113].



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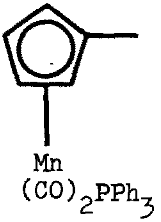
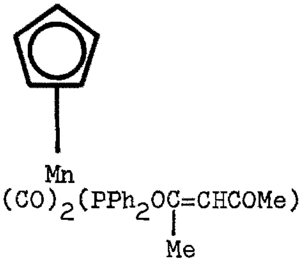


7.10

The crystal and molecular structure of μ-[(1-oxoethyl)-cyclopentadienyl](tricarbonylmanganese)tricarbonylcyclopentadienyltungsten has been determined by X-ray analysis [114]. The structure of tricarbonyl(η^6-fluorenyl)manganese has been determined by X-ray analysis. The structure was intermediate between an η^6-zwitterionic complex and an η^5-cyclohexadienyl complex. Five carbon atoms of the six-membered ring were coplanar and the sixth carbon atom [C(10)] was bent out of the plane by 15° [115].

Dicarbonyl(chlorodiphenylphosphine)(η-cyclopentadienyl)-manganese combined with acetylacetone to give the cymantrene derivative (7.11). Determination of the structure by X-ray methods confirmed the coplanarity of the acetylacetonate residue and the cis-configuration of the double bonds [116].



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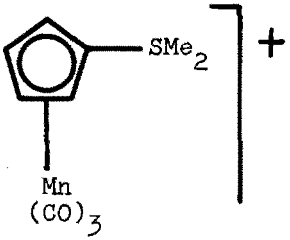
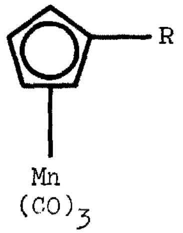


7.12

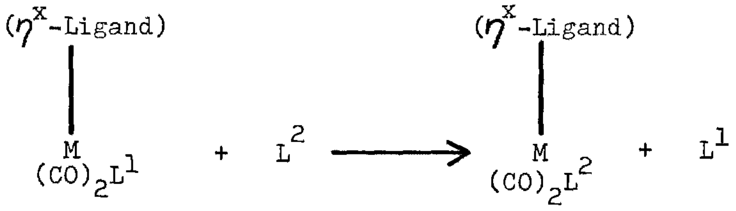
Treatment of $Me_2\overset{+}{S}.C_5\overset{-}{H_4}$ with $[(MeCN)_3Mn(CO)_3]^+PF_6^-$ gave the cationic complex (7.12), the crystal and molecular structure of which has been confirmed by X-ray methods. Comparisons were made with the corresponding chromium, molybdenum and tungsten complexes [117]. The mass spectra of the cymantrene derivatives [7.13; R = H, CO_2Me, Br, Cl, COMe, COCl, CHPh(OH), SO_2Cl] have been recorded [118], and the spectra of a further twenty six derivatives have been recorded and interpreted [119].

Ligand substitution in cymantrene has been discussed as part of a kinetic and mechanistic investigation of transition metal carbonyl complexes. The radical chain process for the conversion of the complexes (7.14; M = Cr, Mo, W; x = 6; M = Mn; x = 5; L^1 = MeCN, pyridine, THF) into the derivatives [7.15; M = Cr, Mo, W; x = 6; M = Mn; x = 5; L^2 = PPh_3, $P(OMe)_3$, $P(OPh)_3$, PEt_3, Me_3CNC] was induced chemically or electrochemically. The first-formed intermediate was a 17-electron complex cation. This participated in the chain propagation steps which were:



7.13

(a) facile ligand exchange of the intermediate with L^2 to form the cation of complex (7.15);
(b) reduction of this cation by either an homogeneous or a heterogeneous electron transfer step [120].

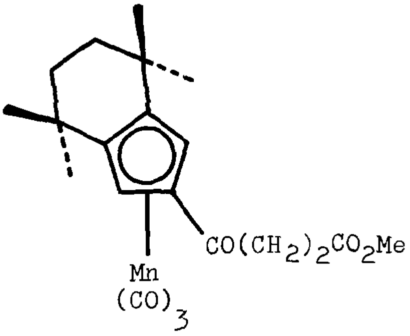


$$(\eta^x\text{-Ligand})\text{M}(\text{CO})_2L^1 + L^2 \longrightarrow (\eta^x\text{-Ligand})\text{M}(\text{CO})_2L^2 + L^1$$

7.14 7.15

(iii) General Chemistry

The reaction of cymantrene with t-butyl chloride and aluminium chloride produced a series of cymantrene complexes with one or two t-butyl substituents and/or one or two COBu groups on the η-cyclopentadienyl ring together with three complexes in which the η-cyclopentadienyl ring was fused with



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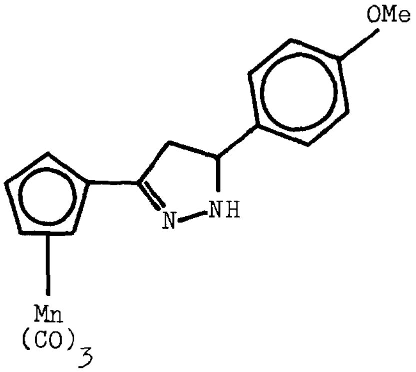

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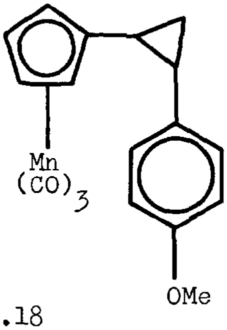

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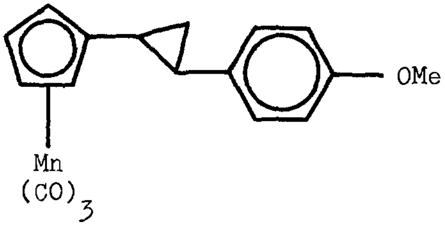
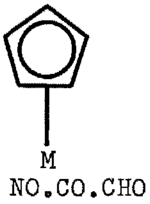


7.19

an acyclic ring and substituted by COBu groups. It was concluded that formation of cyclized products only occurred when the η-cyclopentadienyl contained an acyl group. The structure of the complex (7.16) was determined by X-ray analysis [121]. Thermolysis of the cymantrene derivative (7.17) in the presence of NaOH/Ag or Pt/C produced a mixture of cis- and trans-1-cymantrenyl-2-p-anisylcyclopropane (7.18 and 7.19) [122]. The pyrolysis of cymantrene at 400-420°C and 10^{-3}-10^{-2}mm pressure gave biscyclopentadienyl which was condensed at liquid nitrogen temperatures [123].

The kinetically unstable neutral formyl complexes (7.20; M = Mn, Re) have been obtained by treatment of the appropriate metal carbonyl cations with $LiBHEt_3$ and by transformylation from a stable neutral complex. The rhenium complex (7.20;

M = Re) decomposed on warming in dilute solution by decarbonylation to a metal hydride but the manganese complex (7.20; M = Mn) did not follow a simple decomposition pathway [124].



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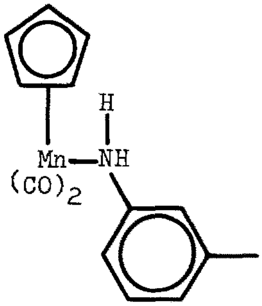

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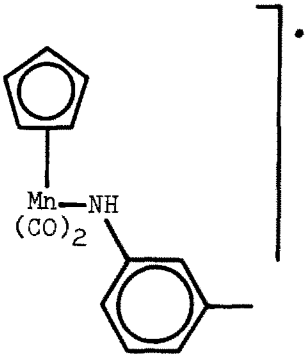
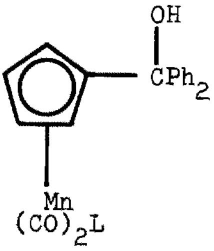


7.22

Oxidation of the m-toluidine complex (7.21) with air or H_2O_2 produced the m-toluidinyl compound (7.22). This was claimed to be the first isolable aminyl complex [125]. The solid cymantrenylcarbenium ion salts (7.24; L = CO, PPh_3, PEt_3) have been prepared by treating the corresponding alcohols (7.23) in propionic anhydride with aqueous tetrafluoroboric



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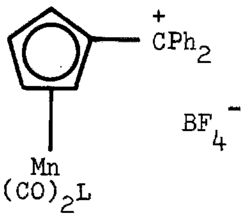

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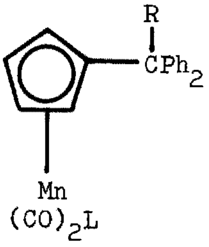
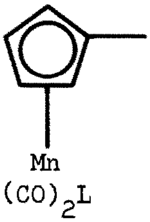


7.25

acid. Treatment of the salt (7.24; L = CO) with nucleophiles RH, where R = MeO, PrO, PhNH, $C_6H_4NMe_2$, produced the corresponding neutral complexes (7.25) [126]. The methylcymantrene derivative (7.26; L = MeCN) underwent electrocatalytic nucleophilic substitution with PPh_3 and Bu^tNC to form the products (7.26; L = PPh_3, Bu^tNC). The reaction was complete in 10 min at 22°C. Cyclic voltammetry was used to demonstrate that the reaction involved a cationic chain mechanism based on the cation derived from the reactant

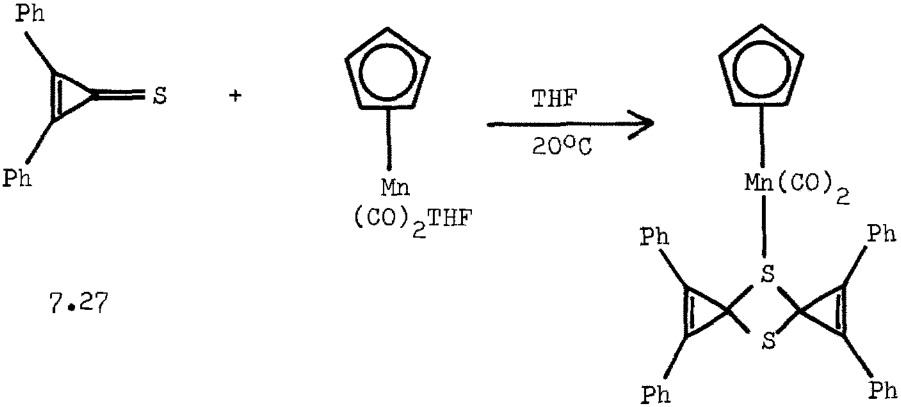


7.26

(7.26; L = MeCN) [127].

Diphenylcyclopropenethione (7.27) combined with $(\eta\text{-}C_5H_5)Mn(THF)(CO)_2$ under mild conditions to form the cymantrene analogue (7.28) [128]. The Grignard reaction has been used to prepare trimethylsilyl derivatives of cymantrene including the tertiary alcohol (7.29) [129].

The UV irradiation of methylcymantrene in ethanol gave the intermediate (7.30) which combined with 4-vinylpyridine to form the η^2-olefin complex (7.31). Products with Mn-N bonds were also obtained [130]. Ultraviolet irradiation of cymantrene or the corresponding rhenium complex in tetrahydrofuran followed by treatment with nitrosobenzene produced the corresponding dicarbonylmetal complexes (7.32; M = Mn, Re) [131]. UV irradiation of the allyloxymethylcymantrene complex (7.33) gave the chelate complex (7.34), the



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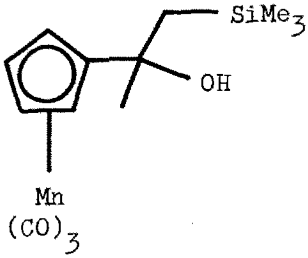
7.28

propargyl complex (7.35) and the σ-cyanoalkyl complexes (7.36; n = 2, 3, 4, 6) were obtained in the same way [132].



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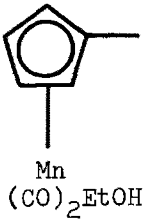

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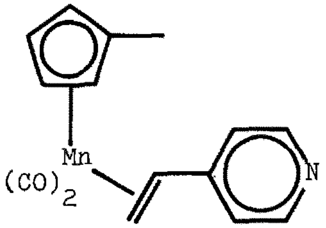
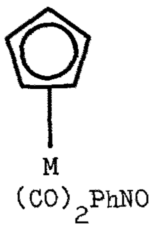


7.31

The solution and low temperature matrix photochemistry of cymantrene and the isoelectronic complexes (7.37 and 7.38) has been investigated. The primary photoreaction was the elimination of a carbonyl ligand. Photolysis of cymantrene in the presence of triethylphosphine led to the stepwise replacement of one or two carbonyl groups by the phosphine ligand [133]. Reaction of dicarbonyl(η-cyclopentadienyl)phenylethenylidenemanganese with tetrakis(triethyl-



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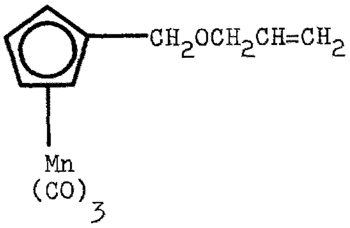
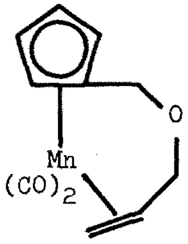


7.33

phosphite)platinium(0) produced the manganesecarbonyl complexes (7.39 and 7.40) [134]. Treatment of the manganese complex (7.41) with two equivalents of Me$_3$P=CH$_2$ produced the neutral complex (7.42) via ylide addition at the carbonyl carbon atom and transylidation [135].



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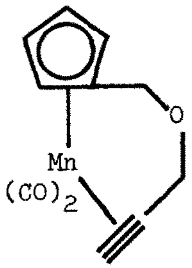

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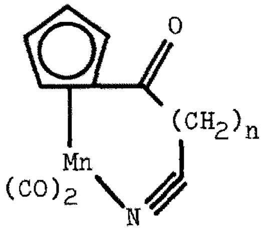
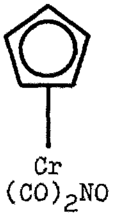


7.36

An undergraduate laboratory experiment has been described in which sunlight was used to promote the photochemical substitution of triphenylphosphine for carbon monoxide in methylcymantrene [136]. Reaction of the manganese



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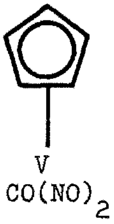
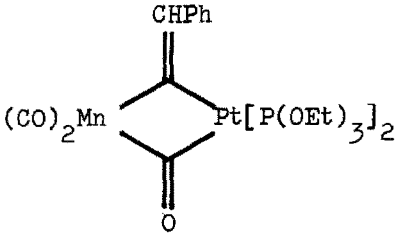


7.38

complex (7.43) with PPh_3 or $(Ph_2PCH_2)_2$ gave rise to rearrangement of the methylpropiolate ligand to produce the corresponding phosphonium ylide complexes (7.44; R = Ph, $CH_2CH_2PPh_2$). The structure of the complex (7.44; R = Ph) was determined by X-ray analysis [137]. Cymantrene and methylcymantrene have been treated with the phosphorane, $Ph_3P{=}CH_2.LiBr$ to give the derivatives (7.45 and 7.46; R = H, Me), the latter involving an unexpected acylation [138].



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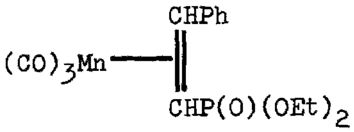

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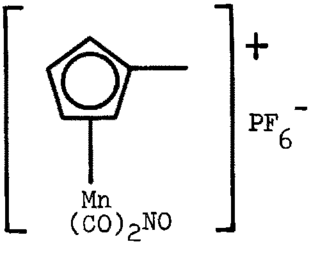
Hydride reduction of the (η-benzene)tricarbonylmanganese cation produced the highly reactive tricarbonyl(η-1,3-cyclo-



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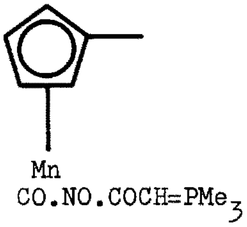
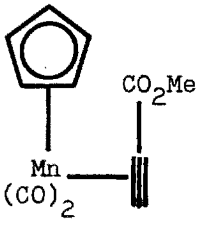


7.42

hexadiene)manganese anion. The mechanism of hydrogen migration in tricarbonyl(η-cyclohexadienyl)manganese was investigated [139]. Treatment of $[(\eta\text{-}C_6H_6)Mn(CO)_3]^+$ with lithium dimethylcuprate produced the methylarene complex (7.47) which was formed via intramolecular methyl migration in the presence of triphenylphosphine [140].



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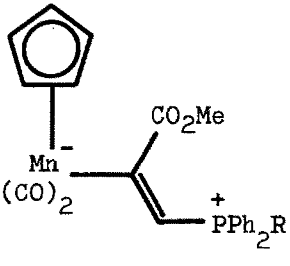

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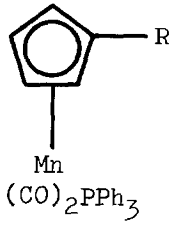
Cymantrene has been used in an analytical procedure for the determination of nitrogen-containing organic compounds [141]. The administration of tricarbonyl(η-methylcyclo-



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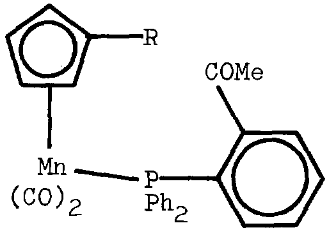
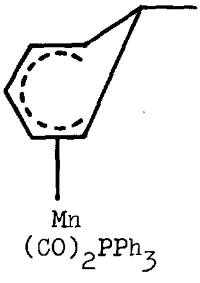


7.46

pentadienyl)manganese to young female mice, albino rats or Syrian hamsters resulted in lung cell damage followed by cellular proliferation. It was found that the mouse, rat and hamster had different susceptibilies to the effect of the methylcymantrene [142].

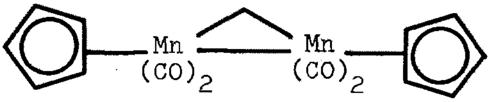


7.47

8. Polynuclear (η-C_5H_5)$Mn(CO)_3$ Complexes

An X-ray photoelectron spectroscopic study has been carried out on the μ-methylene manganese complex (8.1)

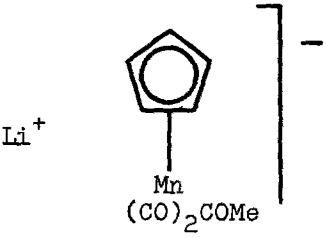
and several related methylene bridged complexes. The gas-phase core-electron binding energies indicated that the methylene group was highly negatively charged [143].
The structure and the experimental electron-distribution of **the manganese complex (8.1) have been determined from single-crystal** X-ray diffraction data. Theoretical calculations have predicted a large negative charge on the methylene carbon but the experimental charge found in this study was not significantly different from zero [114]. The Mn-Mn interatomic distance 2.779 Å was within the range expected for a single metal-metal bond [145].



8.1

The lithium salt (8.2) was attacked by $(CF_3SO_2)_2O$ and 1,8-bis(dimethylamino)naphthalene to form the binuclear vinylidene bridged complex (8.3) [146]. Diketene underwent decarboxylation with the cymantrene complex (8.4) to form the cymantrene derivative (8.5) which was in turn attacked by a second molecule of the complex (8.4) to give the binuclear manganese complex (8.6). Decarbonylation then gave the carbonyl-bridged binuclear complex (8.7) the structure of which was confirmed by X-ray crystallography [147].

Room temperature Moessbauer spectra of the phosphine bridged complexes [8.8, 8.9 and 8.10; L = CO, $P(OMe)_3$, PPh_3, $AsPh_3$, $SbPh_3$] have been recorded and interpreted [148].



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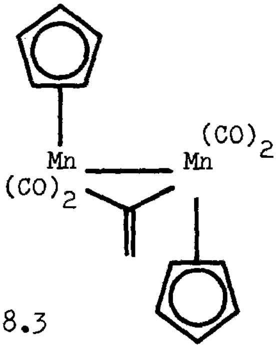
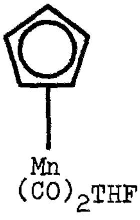


8.3

The reaction of the cymantrene derivative (8.11) with enneacarbonyldiiron gave the binuclear μ-vinylidene complex



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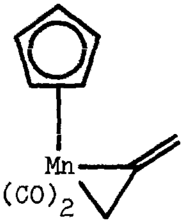

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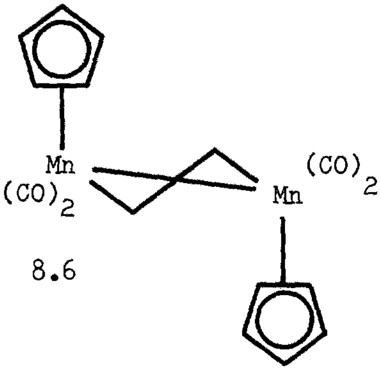

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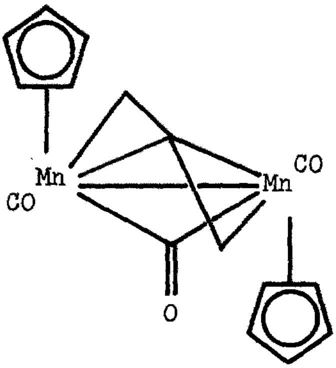

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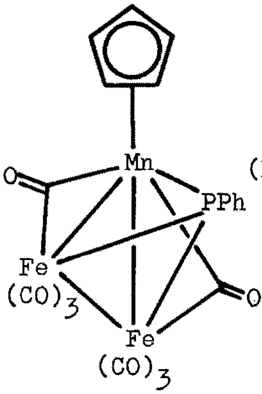

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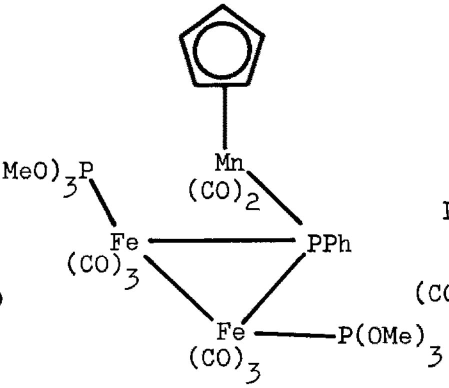

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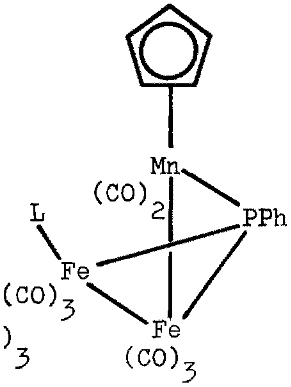
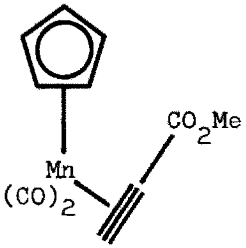


8.10

(8.13) which had been previously reported and the trinuclear cluster complex (8.12) containing a three-membered Fe$_2$Mn ring and a bridging $\pi,2\sigma$-olefin ligand. The crystal and molecular structure of the complex (8.12) has been determined by X-ray crystallography [149].



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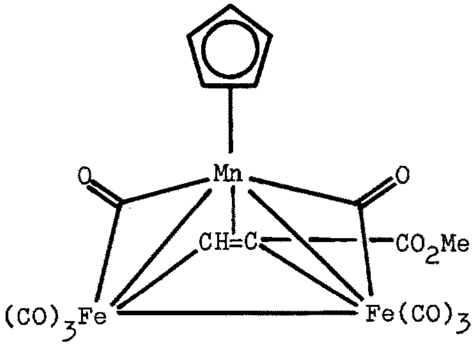

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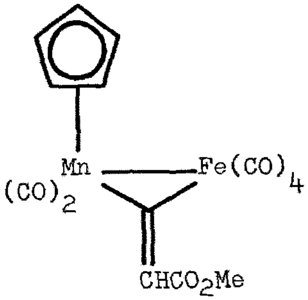

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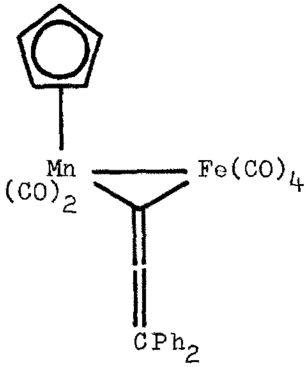
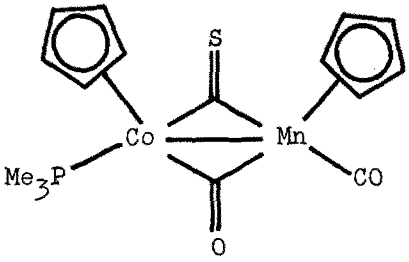


8.14

The vinylidene complex, $(\eta\text{-}C_5H_5)(CO)_2Mn{=}C{=}CHCO_2Me$ and the acetylene complex, $(\eta\text{-}C_5H_5)(CO)_2Mn(HC{\equiv}CCO_2Me)$ combined with enneacarbonyldiiron in hexane to give the



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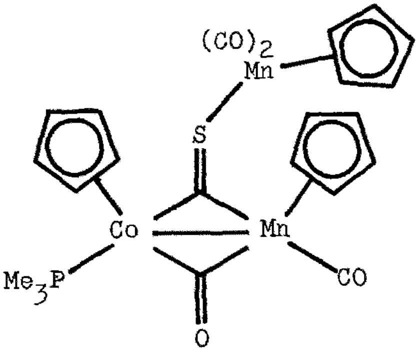

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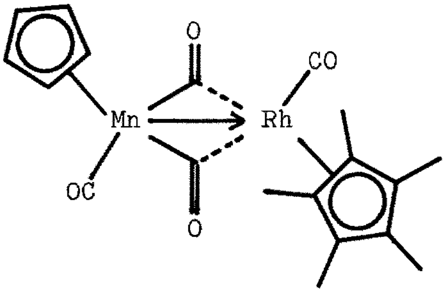
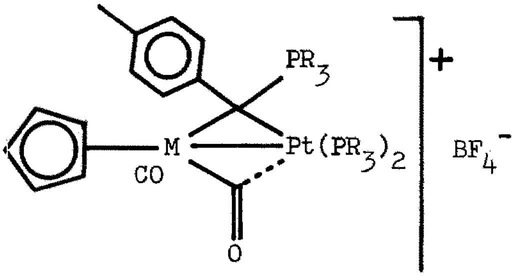


8.17

binuclear vinylidene complex (8.13) as a mixture of two isomers. The structure of one isomer was confirmed by X-ray crystallography. The allenylidene complex, (η-C_5H_5)(CO)$_2$Mn=C=C=CPh$_2$ combined with the same carbonyl to form the corresponding product (8.14) [150]. The complex (η-C_5H_5)Co(PMe$_3$)CS combined with the cymantrene derivative (η-C_5H_5)Mn(CO)$_2$THF in the proportions 1:1 and 1:2 to give di- and tri-nuclear complexes (8.15 and 8.16) respectively [151].



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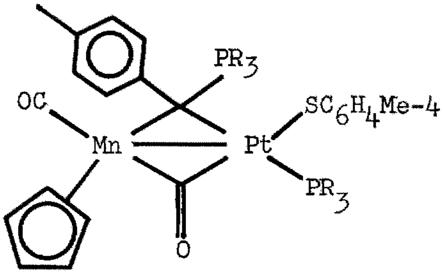
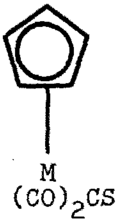


8.19

Treatment of dicarbonyl(η-pentamethylcyclopentadienyl)-rhodium with dicarbonyl(η-cyclopentadienyl)tetrahydrofuran-manganese afforded the carbonyl bridged complex (8.17). The structure of this compound was determined by X-ray analysis [152]. The complexes (8.18; M = Mn, Re; R_3 = Me_3, Me_2Ph and 8.19; R_3 = Me_3, Me_2Ph) have been prepared. The structures of the complexes (8.18; M = Mn, R = Me and 8.19; R = Me) were determined by X-ray analysis [153]. Addition



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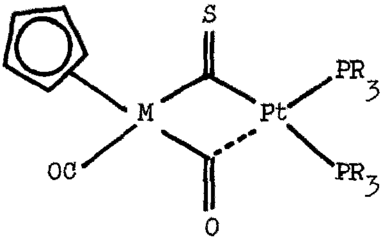

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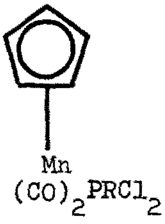

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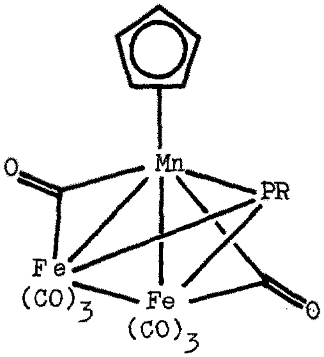

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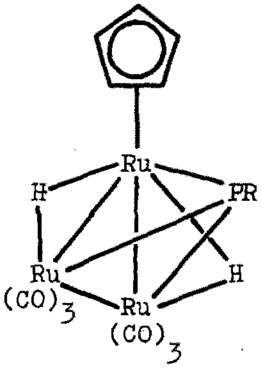
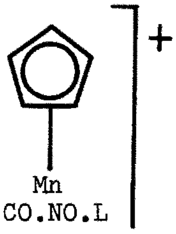


8.24

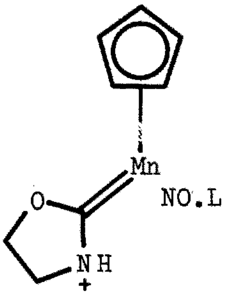
of the manganese and rhenium complexes (8.20; M = Mn, Re) to the **platinum** derivatives $[Pt(\eta-C_2H_4)(PR_3)_2]$ afforded the corresponding binuclear species (8.21; M = Mn, PR_3 = PMe_2Ph, $PMePh_2$; M = Re, PR_3 = PMe_2Ph). The structure of the complex (8.21; M = Mn, PR_3 = $PMePh_2$) was established by X-ray diffraction [154]. Reaction of the cymantrenyl phosphine (8.22; R = Et, Bu, Me_3C, cyclohexyl, p-anisyl, Me_2CH, Ph) with $Fe_2(CO)_9$ or reaction of $(\eta-C_5H_5)(CO)_2MnP(R)H_2$ with $Fe_3(CO)_{12}$ produced the corresponding heterometallic clusters (8.23). When the latter reaction was carried out with $Ru_3(CO)_{12}$ the manganese-ruthenium clusters (8.23; M = Ru) were obtained together with small amounts of the homo-metallic clusters (8.24) [155].

9. Carbene and Carbyne $(\eta-C_5H_5)Mn(CO)_3$ Complexes

Carbonyl ligands in (η-hydrocarbon)metal carbonyls have been converted to cyclic aminooxocarbene ligands by treatment with $\overset{+}{N}H_3CH_2CH_2Br$ and a base such as sodium hydride or triethylamine. Thus the (η-cyclopentadienyl)manganese complexes [9.1; L = CO, $P(OPh)_3$] were converted to the carbene (9.2). A number of related reactions were reported and it was concluded that an electropositive carbonyl group in the

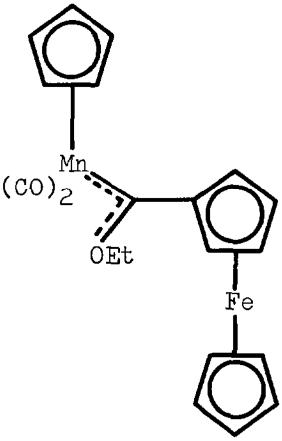


9.1



9.2

reactant was essential [156]. Cymantrene has been converted to neutral carbene and cationic carbyne complexes. In a typical reaction cymantrene was treated with lithioferrocene



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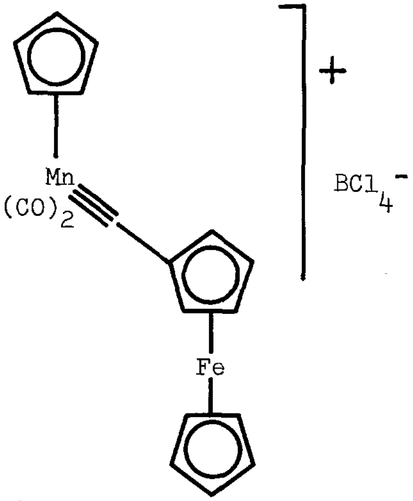
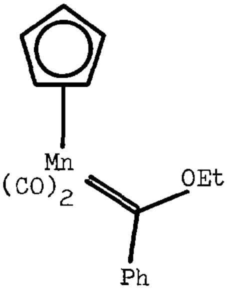


9.4

and then Et_3O^+ BF_4^- to form the carbene (9.3) and this was then converted to the carbyne (9.4) with borontrichloride [157].



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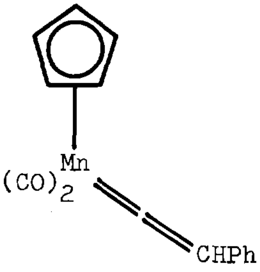

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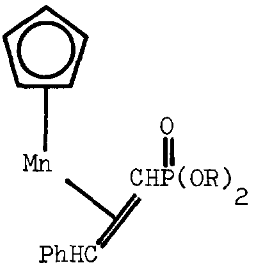
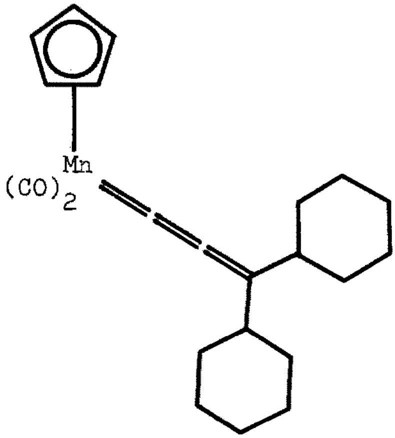


9.7

The structure of the cymantrene carbene complex (9.5) has been determined by X-ray analysis [158].

The manganese vinylidene complex (9.6) has been converted into the η-olefin complex (9.7) by treatment with phosphites $P(OR)_3$, where R = Et, Ph [159]. The crystal and molecular structure of the allenylidene complex (9.8) has been determined by X-ray crystallography. The complex was attacked by anionic nucleophiles such as OMe^- and NMe_2^- to form, after protonation, vinylcarbene or vinylidene complexes. By contrast, phosphine nucleophiles such as PPh_3 and PEt_3 attacked the terminal position of the cumulene chain [160].

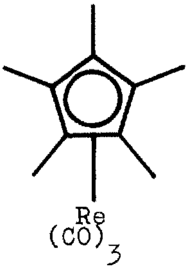


9.8

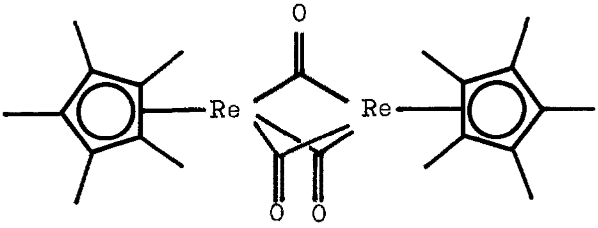
10. $(\eta\text{-}C_5H_5)Re(CO)_3$

UV irradiation of the (η-pentamethylcyclopentadienyl)-rhenium complex (10.1) in cyclohexane gave the binuclear complex (10.2) the structure of which was confirmed by X-ray crystallography. A second binuclear complex, $(\eta\text{-}C_5Me_5)_2Re_2(\mu\text{-}CO)(CO)_4$, was also obtained [161].

Reduction of the (η-cyclopentadienyl)rhenium complex (10.3; L = CO) with sodium borohydride took place in discrete steps to form successively the complexes (10.4; L = CHO, CH_2OH and CH_3). Complexation with rhenium was

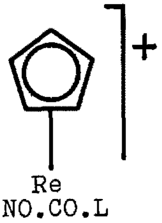


10.1



10.2

effective in activating the formyl and hydroxymethyl groups to reduction [162]. The (η-cyclopentadienyl)rhenium cation (10.5) was attacked by the borohydride, $HB(OR)_3^-$, to form the neutral formyl complex (10.4; L = CHO) which underwent disproportionation to give the metallo ester (10.6).



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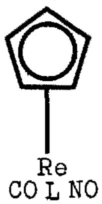
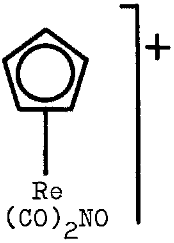
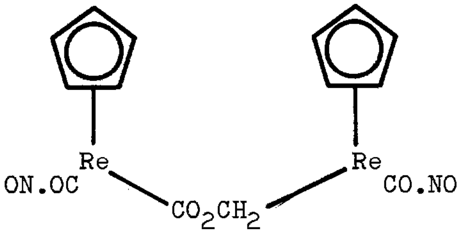


10.4

Hydrolysis of this metallo ester afforded the hydroxymethyl derivative (10.4; L = CH_2OH). Several related reactions were reported [163]. Treatment of the cation (10.5) with aqueous triethylamine in acetone afforded the hydride (10.4; L = H). The metallocarboxylic acid (10.4; L = CO_2H) was



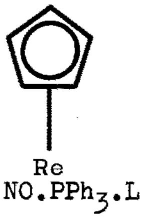
10.5



10.6

produced in the absence of acetone. The hydride (10.4; L = H) was thermally stable and when treated with tetrabromomethane, bromine or N-bromosuccinimide the bromide (10.4; L = Br) was produced in excellent yield [164].

The neutral rhenium formyl complex (10.7; L = CHO) has been obtained by treatment of the nitrosyl cation (10.3; L = CO) with $PhI^{+}O^{-}$/MeCN and PPh_3 to form the phosphine (10.3; L = PPh_3) which was then reduced with borohydride in aqueous THF. The formyl complex underwent disproportionation with trifluoroacetic acid to give the methyl derivative (10.7; L = Me) and the carbonyl (10.3; L = CO). The mechanism



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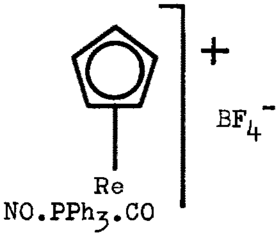
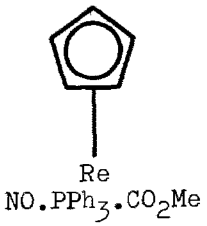


10.8

of this reaction was investigated and several reactions of the formyl complex (10.7; L = CHO) were reported [165].



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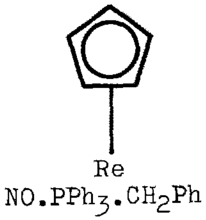
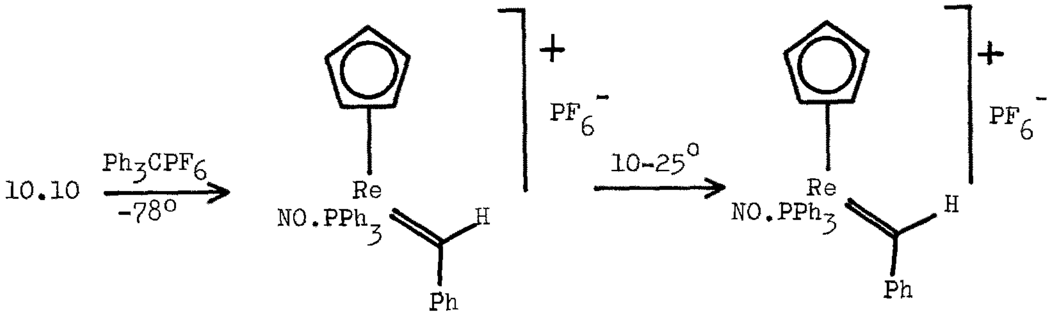


10.10

Reaction of the rhenium complex (10.8) with sodium methoxide in methanol produced the ester (10.9). Treatment of the ester with (-)-(S)- or (+)-(R)-α-(1-naphthyl)ethylamine gave the corresponding amides, the diastereoisomers of which were separated. The least soluble diastereoisomers were treated with CF_3CO_2H and $NaBF_4$ to give (-)-(R)- and (+)-(S)-(10.8).

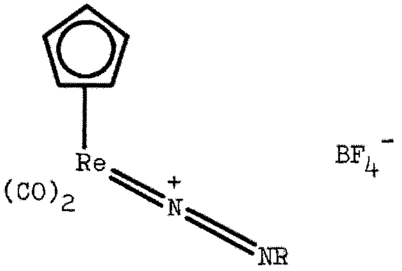


10.11

10.12

The resolved complex (10.8) was used to prepare several optically active derivatives, for example the benzyl complex (10.10). The structure of (-)-*R*)-(10.10) was determined by X-ray analysis [166].

Hydride abstraction from the rhenium complex (10.10) with Ph_3CPF_6 produced the benzylidene complex (10.11) which isomerized on warming to give the Re=C isomer (10.12). Treatment of the isomer (10.12) with nucleophiles (Nu), $Li(Et)_3BD$, MeLi, EtMgBr, $PhCH_2MgCl$, PMe_3 and MeONa gave diastereomerically pure adducts $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHNuC_6H_5)$ in which a new chiral centre was generated stereospecifically [167]. Treatment of dicarbonyl(η-cyclopentadienyl)-tetrahydrofuranrhenium with arenediazonium tetrafluoroborate salts produced the corresponding aryldiazenido complexes (10.13; R = C_6H_4X with X = *p*-Me, *p*-OMe, *o*-OMe, *p*-NEt_2, *o*-CF_3; R = $C_6H_3X_2$ with X_2 = 2,6-Me_2, 3,5-Me_2). These complexes were treated with sodium borohydride or methyllithium to give the aryldiazene (10.14) and the arylhydrazido (10.15) complexes respectively [168].



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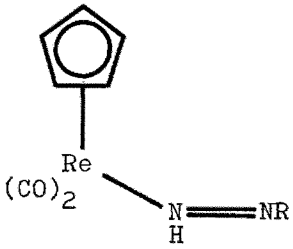

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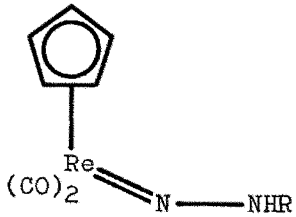
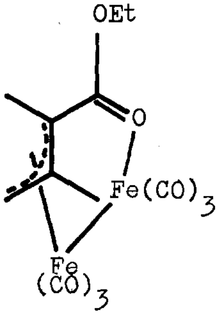


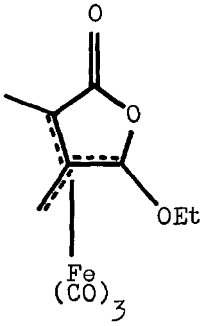
10.15

11. (η-Trimethylenemethane)Fe$(CO)_3$

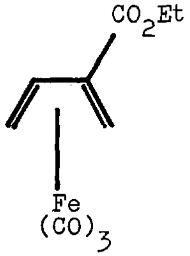
Slow addition of 1-carbethoxy-1,2-butadiene to enneacarbonyldiiron followed by heating to 80°C for 15 min. afforded the dinuclear complex (11.1). When the same reaction was carried out but the reactants were heated quickly at 70°C for 5 min. a mixture of the complexes (11.2 and 11.3) was produced. The structures of the complexes (11.1 and 11.2)



11.1

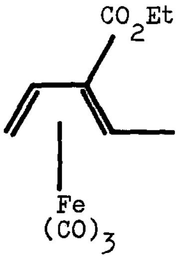


11.2

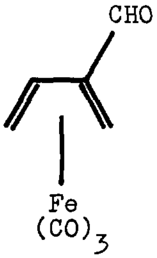


11.3

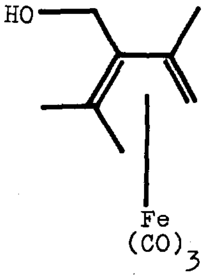
were determined by X-ray analysis [169]. The trimethylenemethane complex (11.2) was converted to the butadiene derivative



11.4



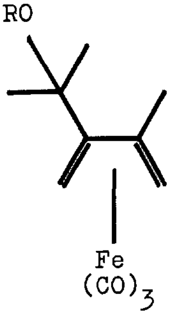
11.5



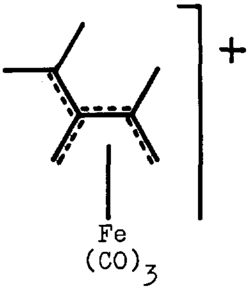
11.6

(11.3) by reaction with an excess of boron trifluoride etherate. In a similar reaction, $Fe_2(CO)_9$ was treated with 3-carbethoxy-1,2-pentadiene followed by boron trifluoride to afford the 1,3-butadiene complex (11.4) [170].

The ester (11.3) was hydrolysed with aqueous potassium hydroxide and reduced with lithium aluminium hydride to the corresponding acid and alcohol. The alcohol was oxidized to the aldehyde (11.5) and some reactions of this aldehyde were investigated [171]. Treatment of the (η-butadiene)iron complex (11.6) with fluorosulphonic acid in SO_2 at -65°C gave an equilibrium mixture of the (η-trimethylenemethane)iron analogues (11.8 and 11.9). The same equilibrium mixture was obtained from the alcohol complex (11.7; R = H) and the ether complex (11.7; R = Me) under the same conditions. This evidence, together with the observed formation of the ether complex (11.7; R = Me) from the cation derived from the alcohol complex (11.6), indicated facile isomerization about the C_2-C_3 bond at low temperatures [172].



11.7



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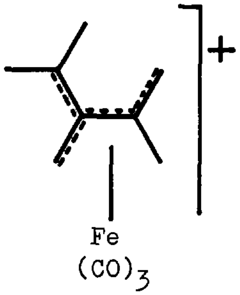
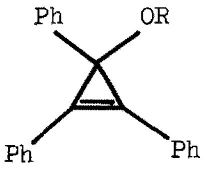


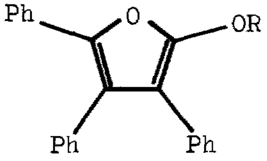
11.9

12. (Acyclic-η-diene)Fe(CO)$_3$

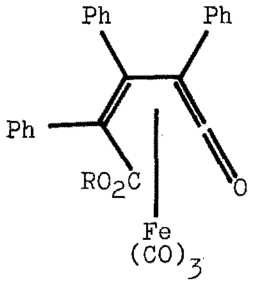
Treatment of the cyclopropenes (12.1; R = Me, Et, Me_3C, Ph) with $Fe_2(CO)_9$ produced the corresponding furan derivatives (12.2). The diene complex (12.3) was isolated as one of the intermediates in this reaction [173]. Reaction



12.1



12.2

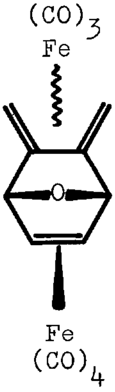


12.3

of 5,6-bis(methylene)-7-oxabicyclo-[2.2.1]hept-2-ene with $Fe_2(CO)_9$ in pentane gave the tricarbonyliron complexes (12.4 and 12.5). The same reaction in methanol afforded the complex (12.6) together with the uncomplexed organic ligand. Some reactions of these compounds were investigated [174]. Nonacarbonyldiiron induced ring opening of the spirocyclopropene (12.7) to give the tricarbonyliron complexes (12.8 and 12.9). The crystal structure of the latter compound was determined by X-ray analysis [175].

Treatment of the (η^3-allyl)iron complex (12.10) with ethylene under mild conditions caused isomerization of the ethylene to an ethylidene moiety which was incorporated into the (η^4-1,3-diene)iron product (12.11). The crystal and molecular structure of the complex (12.11) has been determined by X-ray spectroscopy [176].

The crystal and molecular structure together with the absolute configuration (1S, 2R) for the (+)-enantiomer of the (η-dimethylidenenorbornyl)iron complex (12.12) has been determined by X-ray crystallography. The absolute configurations of several norbornyl ligands were established by relating them to the complex (12.12) [177]. The structures of some carbonyl(1,4-diaza-1,3-diene)(1,3-diene)iron complexes have been determined by X-ray analysis. There were two types of structure, one where the 1,4-diaza-1,3-diene ligand exhibited N,N' apical/basal coordination and the other with



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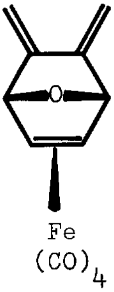

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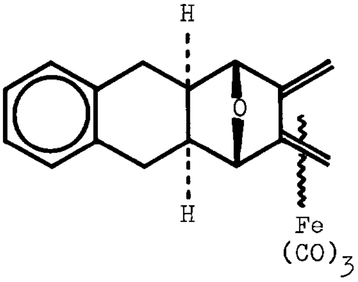

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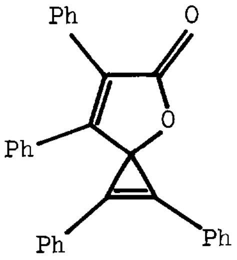

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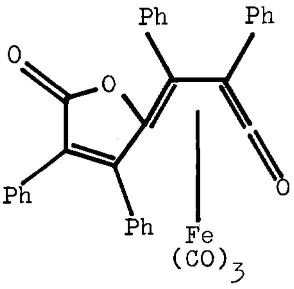

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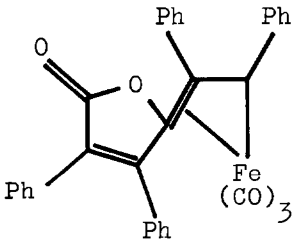

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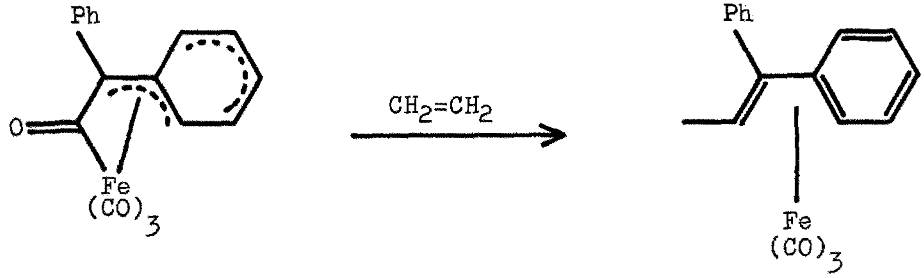
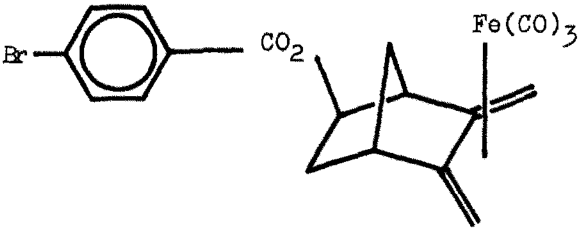


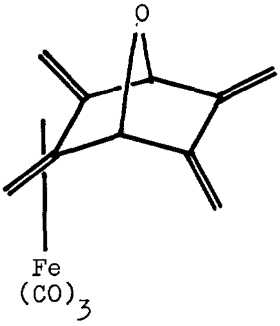
12.10 12.11

N,N' basal/basal coordination. The nature of the 1,3-diene ligand determined the structure adopted by the complex [178].

Dependence of the iron-butadiene interactions on the stereochemistry of irontricarbonyl complexes of 2,3,5,6-tetrakis(methylene)-7-oxabicyclo[2.2.1]heptane has been investigated by He(I) photoelectron spectroscopy. The results suggested a stronger iron-butadiene interaction in the *endo*-isomer (12.13) than in the *exo*-isomer. The perturb-



12.12



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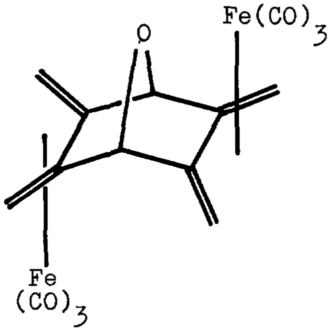
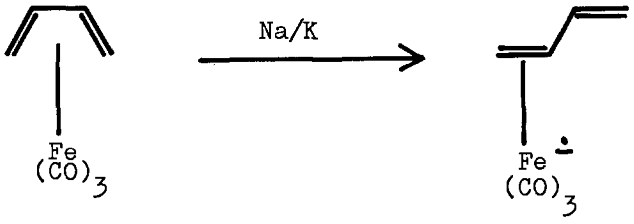


12.14

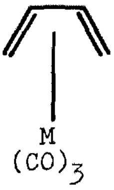
ations which arose when two irontricarbonyl groups were present were additive in the low symmetry endo-exo complex (12.14) while in the high symmetry exo-exo complex an extra perturbation was observed [179]. Radical anions were obtained by the Na/K alloy reduction of tricarbonyl(η-diene)iron complexes at -80°C. Thus (η-butadiene)tricarbonyliron (12.15) gave the 17-electron species (12.16) which was characterized by ESR spectroscopy. Similar results were obtained with methyl- and



12.15

12.16

dimethyl-butadiene complexes [180]. One bond $^{13}C-^{13}C$ spin coupling constants have been obtained for the (η^4-butadiene)metal complexes (12.17; Fe, Ru, Os) and for η^3-enyl and η^2-ene complexes. The results were used to discuss substituent effects [181].



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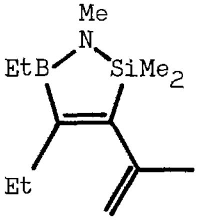

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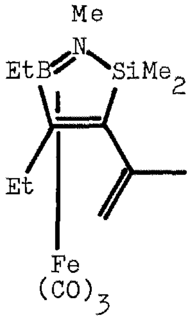

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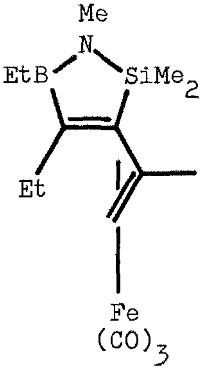

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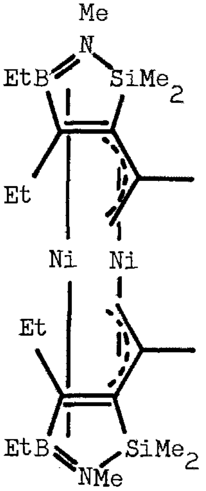
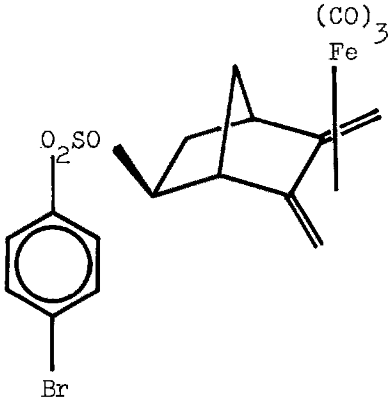


12.21

The boron-silicon heterocycle (12.18) combined with enneacarbonyldiiron to give a mixture of the two (η-butadiene)-iron complexes (12.19 and 12.20). The same ligand (12.18) combined with (1,5,9-cyclododecatriene)nickel to form the binuclear complex (12.21) [182]. The acetolysis of several exocyclic (η-diene)iron complexes including the exo- and endo-norbornyl complexes (12.22 and 12.23) respectively has



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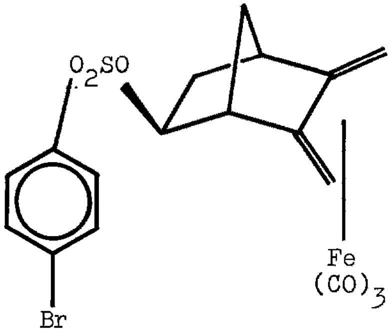
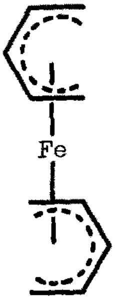


12.23

been the subject of a kinetic investigation. An electrostatic field effect model has been used to discuss the results and it supported competitive inductive destabilization and charge-induced dipole stabilization of the carbenium intermediate [183]. The oxidation of functionalized (η^3:η^1-allyl-carbonyl)iron tricarbonyl complexes with trimethylamine oxide or iron(III) chloride gave (η-butadiene)irontricarbonyl products in some cases [184].

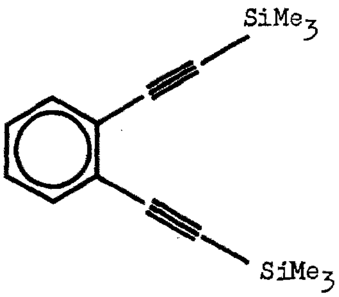
Activation parameters have been determined for the intramolecular site exchange of carbonyl groups in a series of symmetrically substituted tricarbonyl(η-1,3-diene)iron complexes. The parameters were discussed in terms of a turnstile-type mechanism for the exchange process and of the differences in the ground state and transition state stabilities of the complexes [185]. The electronic structure of bis-(η^5-pentadienyl)iron (12.24) and its dimethyl and tetramethyl derivatives has been the subject of a detailed investigation by He(I) photoelectron spectroscopy and by semiempirical LCAO calculations of the INDO and charge-iterative extended Hueckel type. The calculations indicated a significant barrier to rotation of the ligands and a very large degree of metal-ligand coupling by comparison with ferrocene. A bonding interaction of partial δ character was observed as a result of the large flexibility of the 3d basis functions, this contrasted with the behaviour of ferrocene [186].



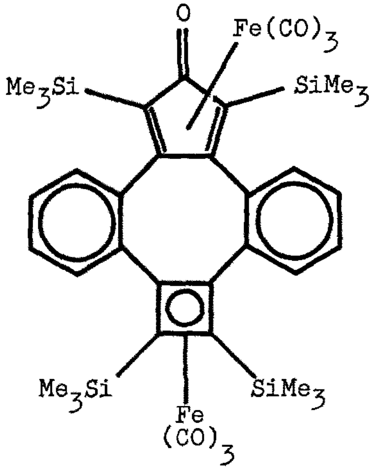
12.24

13. (η-C_4H_4)$Fe(CO)_3$

The reaction of o-bis(trimethylsilylethynyl)benzene (13.1) with nonacarbonyldiiron gave several (η-diene)iron

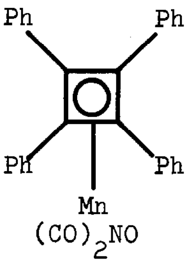


13.1



13.2

complexes including the (η-cyclobutadiene)iron complex (13.2) [187]. The reaction of Mn(CO)$_4$NO with diphenylacetylene produced the η^4-tetraphenylcyclobutadiene-manganese complex (13.3). X-ray analysis showed that the cyclobutadiene ring was planar [188]. A molecular orbital study has been carried out on tricarbonyl(η-cyclobutadiene)iron. It was concluded that the η-cyclobutadiene-iron bond was highly covalent [189]. Valence bond structure-resonance theory has been used to calculate bond orders in tricarbonyl(η-cyclobutadiene)iron complexes. C-Fe bond lengths showed a linear correlation with the bond orders. C-Fe bond lengths in two η-benzocyclobutadiene complexes were also rationalized [190].



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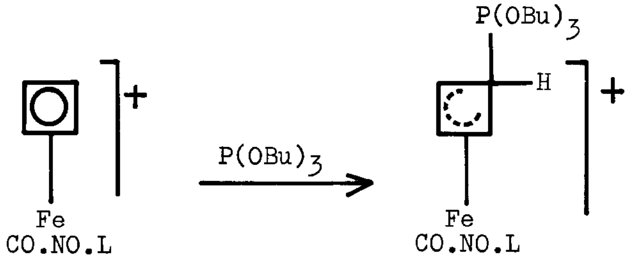


13.4

13.5

(Benzo- and benzoyl-cyclobutadiene)tricarbonyliron undergo facile insertion of a cyclopentadienylcobalt moiety to produce *sym*- and *unsym*-[tricarbonyl(benzoferracyclopentadiene)]-η^5-cyclopentadienylcobalt, [tricarbonyl(2-benzoylferracyclopentadiene)]-η^5-cyclopentadienylcobalt and [tricarbonyl-(3-benzoylferracyclopentadiene)]-η^5-cyclopentadienyl cobalt [191]. The (η-cyclobutadiene)iron cations (13.4; L = CO, PR$_3$, AsPh$_3$, SbPh$_3$) underwent rapid reversible addition of phosphines to form *exo*-phosphonium salts (13.5). A kinetic study of the reaction in nitromethane with several nucleophiles gave the following order of cyclobutadiene ring electrophilicity:

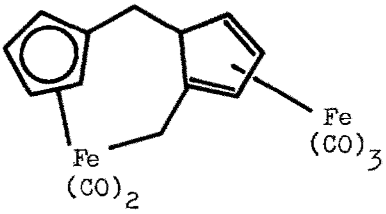
$CO > P(CH_2CH_2CN)_3 \sim P(4\text{-}Cl.C_6H_4)_3 > P(4\text{-}F.C_6H_4)_3 > AsPh_3 \sim PPh_3 > SbPh_3 \sim P(4\text{-}Me.C_6H_4)_3 > P(4\text{-}MeO.C_6H_4)_3$.

Broenstead, Hammett and rate-equilibrium constant correlations have indicated that rehybridization of the carbon reaction centre from sp^2 to sp^3 and bond formation were 33% complete in the transition state for the reaction [192].

14. (Cyclic-η-diene)$Fe(CO)_3$

i) Formation

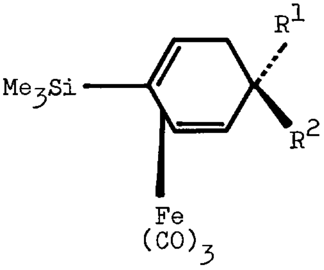
The disproportionation of *cis*-bicyclo[4.3.0]nona-3,7-diene catalyzed by pentacarbonyliron and tetracarbonylbis(η-cyclopentadienyl)diiron has been studied. The first step in the disproportionation was hydrogen migration to give a conjugated diene followed by reaction with pentacarbonyliron to produce diene-$Fe(CO)_3$ complexes which were not isolated [193].



14.1

The reaction of fulvene with $Fe_2(CO)_9$ produced the dimeric fulvene complex (14.1) [194]. The preparation of dicarbonyl-(η-cyclopentadienyl)iron complexes of diphenylcyclopropenone, phenalenone and tropone has been reported. The crystal and molecular structure of the tropone complex has been determined by X-ray crystallography and the presence of Fe-O σ-bonding was demonstrated [195].

Reductive silylation of benzene produced cis, trans-3,6-bis(trimethylsilyl)-1,4-cyclohexadienes which underwent reaction with pentacarbonyliron to give the tricarbonyliron complexes (14.2; $R^1 = SiMe_3$, $R^2 = H$; $R^1 = H$, $R^2 = SiMe_3$ and 14.3). Treatment of the complex (14.2; $R^1 = SiMe_3$, $R^2 = H$) with triphenylmethyl tetrafluoroborate produced the isomeric cations (14.4 and 14.5) [196]. The reaction between cyclohexadiene esters and pentacarbonyliron was stereoselective and gave mixtures of isomeric tricarbonyl(η-cyclohexadiene)iron complexes with the proportions determined by the steric and polar nature of substituents on the cyclohexadiene ester and on the conditions used. Thus the ester (14.6) gave three products with the (η-cyclohexadiene)iron complex (14.7) as the dominant product [197].



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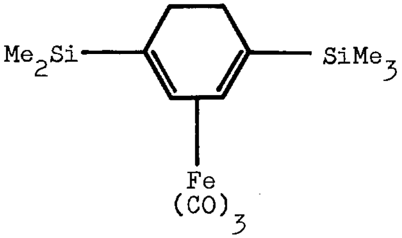

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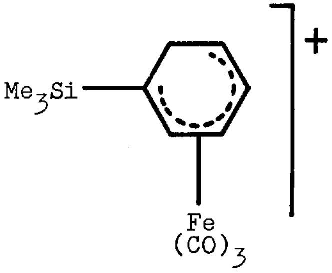

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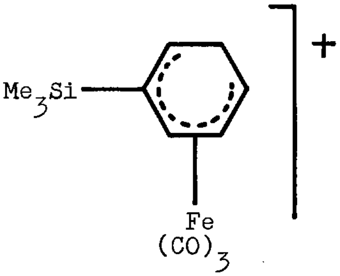

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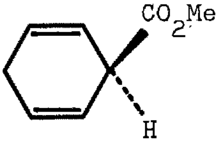

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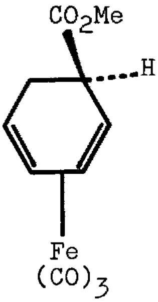

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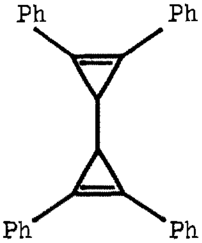
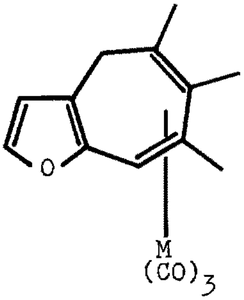


14.8

Reaction of the bicyclopropene (14.8) with $Fe_2(CO)_9$ produced tricarbonyl (4-7-η^4-2,3,5,7-tetraphenyl-2,4,6-cycloheptatriene-1-one)iron. The structure of this complex was determined by X-ray analysis [198].

The reaction of 5,6,7-trimethylfuro[b]tropylidene with $Cr(CO)_6$ or $Fe_2(CO)_9$ produced the corresponding tricarbonylmetal derivatives (14.9; M = Cr, Fe) [199]. Treatment of methyl-



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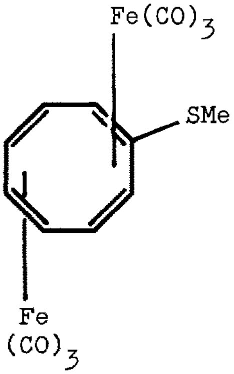

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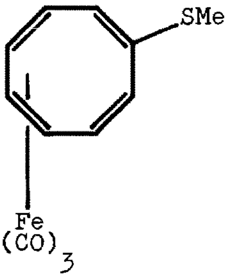


14.11

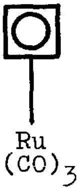
thiocyclooctatetraene with $Fe_2(CO)_9$ gave the bis(tricarbonyliron) complex (14.10) as the major product together with a small proportion of complex (14.11) [200].

(ii) Spectroscopic and Physico Chemical Studies

The structures of tricarbonyl[2-5-η-(dimethyl 2,4-cyclohexadiene-1α, 2-dicarboxylate)]iron and tricarbonyl[2-5-η--(dimethyl 2,4-cyclohexadiene-1β, 2-dicarboxylate)] iron have been determined by X-ray analysis. In the latter compound an unusually short O....C=O contact generated an appreciable pyramidal distortion of the 4-atom C-(1β-carboxylate) set [201]. The structure of tricarbonyl[2-5-η-(methyl-3, 5-dimethoxy-1α-methyl-2, 4-cyclohexadiene-1β-carboxylate]iron has been determined by X-ray analysis. The metal-ligand bonding was as expected for 1,3-dienetricarbonyliron complexes [202]. The structure of [(3,4,5,6-η)-1-oxacyclohexa-3, 5-dien-2-one[tricarbonyliron (α-pyronetricarbonyliron) has been determined by X-ray analysis. The C(3), C(4), C(5) and C(6) carbon atoms of the diene moiety were coplanar but the C(6), O(1), C(2), C(3) moiety was slightly distorted from planarity [203].

The He(I) photoelectron spectra for η-butadiene-, η-cyclooctatetraene-, and η-cyclobutadiene-rutheniumtricarbonyl (14.12) have been measured and assigned. Ionization energies were determined and the results indicated that the perturbation--extrapolation method for the prediction of electronic structures was less valid for the η-butadiene- and η-cyclobutadiene--ruthenium complexes than for the corresponding iron complexes [204]. Mass spectrometric fragmentation of the tricarbonyl-(η-1-sila-2,4-cyclohexadiene)iron complexes (14.13; R = H, Me, Ph, OH, OEt, Cl) has been investigated. The principal pathway involved three sequential decarbonylations, followed by loss of RH [205].

The mechanism of 1,3-iron shifts in the fluxional (η-cycloheptatriene)iron complexes (14.14; $R^1 = R^2 = H$; R^1 = Ph, Me, $R^2 = CO_2Me$) has been studied by ^1H NMR spin saturation transfer. The free energy for the process was determined for each complex; $\Delta G^{\ddagger} = 22.3$ (14.4; $R^1 = R^2 = H$),



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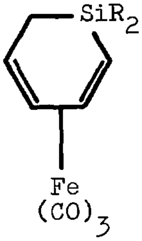

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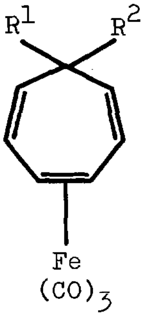
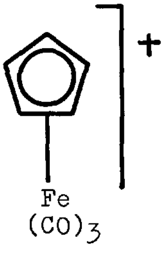


14.14

23.9 (14.14; R^1 = Ph, R^2 = CO_2Me), 23.3. and 23.6 kcal mol^{-1} (14.14; R^1 = Me, R^2 = CO_2Me, two isomers). These results and the values for (η-oxepine)-, (η-azepine)-, and (η-tropone)-iron tricarbonyl were consistent with an intermediate having an



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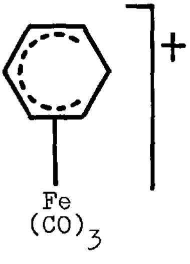

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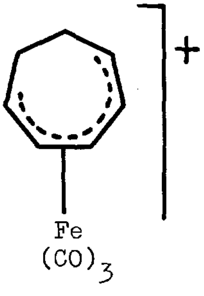
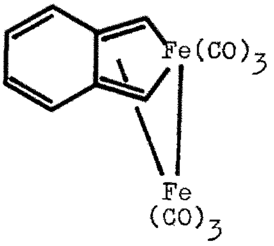


14.17

η^2-geometry and the tricarbonyliron group shifted towards the centre of the cycloheptatriene ring rather than an (η-norcaradiene)iron tricarbonyl intermediate [206].

The steric configuration of a substituent attached to an sp^3 carbon atom in tricarbonyl(η-cyclohexadiene)iron complexes has been examined by ^{1}H NMR spectroscopy. It was concluded that the most useful parameter for distinguishing the α-(exo) and β- (endo) stereochemistry of a substituent adjacent to CH_2 was the coupling constants of these H atoms. Those on the same side as the metal had a vicinal coupling constant of approximately 10-12 Hz while for the α-H it was approximately 8 Hz [207]. The self-consistent charge and configuration molecular orbital method has been used to calculate ^{13}C NMR paramagnetic shielding in the η-cyclopentadienyl, η-cyclohexadienyl and η-cycloheptadienyl cations (14.15, 14.16 and 14.17) respectively. Downfield shifts in the ^{13}C carbonyl spectra of the complexes were calculated although the observed shifts showed little variation in the series of three complexes. However, the cation (13.20) showed both the predicted and calculated least downfield shift [208].



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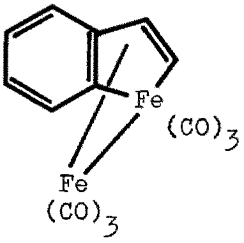
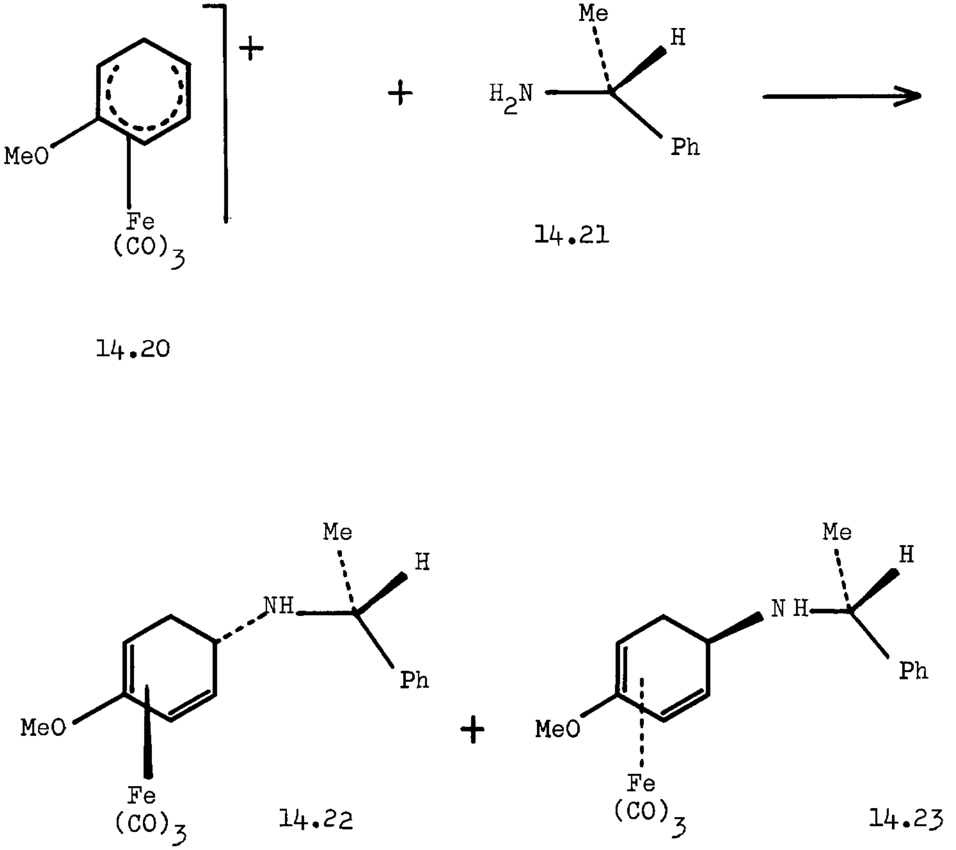


14.19

The electrochemical reduction of sym-benzoferrole (14.18) and unsym-benzoferrole (14.19) have been the subject of a voltammetric investigation. While both complexes underwent reduction in two reversible one-electron steps, the sym--complex (14.18) underwent the two steps at the same potential to give a stable dianion and the unsym-complex (14.19) showed seperate reduction potentials yielding a relatively stable radical anion and a dianion that rapidly decomposed. These observations were correlated with spectroscopic properties and MO calculations [209]. The reactivities of ester groups in



14.20

14.21

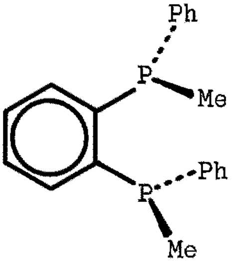
14.22

14.23

tricarbonyl(η-cyclohexadiene)iron complexes have been determined by comparing the alkaline hydrolyses of the esters. Steric and electronic effects were evaluated and the role of the tricarbonyliron group evaluated. The half-hydrolysis of dicarboxylic ester complexes was achieved in cases where it was not possible with the free ligands [210].

It has been shown that kinetic diastereotopic discrimination occurred in the reaction of the cation (14.20) with ($\underline{R}$)-$(+)_{589}$-1-phenylethylamine (14.21) in methyl cyanide.

Initial attack of the amine (14.21) occurred at C(5) in the dienyl ring to give the diastereomeric cations $[Fe(CO)_3\{PhCH(Me)NH_2.C_6H_6OMe\}]^+$. In the presence of excess amine deprotonation of these cations occurred to give the corresponding neutral diastereoisomers (14.22 and 14.23) [211]. The racemic cation (14.20) has also been treated with (*S*,*S*)(-)$_{589}$-*o*-phenylenebis(methylphenylphosphine) (P$\sim$P) (14.24). A 50/50 mixture of the two diastereoisomers (14.25 and 14.26) was obtained, this mixture equilibrated over three days in acetonitrile to give a 60/40 mixture. When the reaction of



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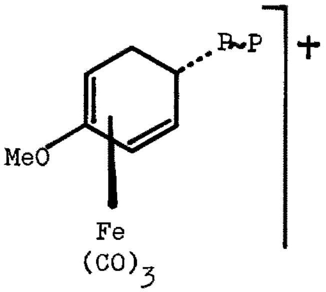

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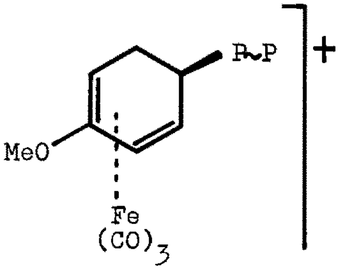
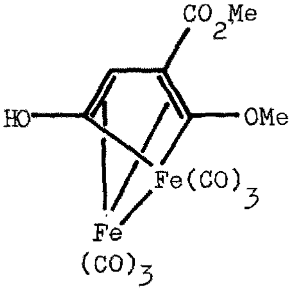


14.26

the cation (14.20) with the phosphine (14.24) was carried out in dichloromethane about half of the original salt was solubilized and optically active (14.20) remained [212]. Selective crystallization has been used to resolve the enantiomers of tricarbonyl[1-5-η-(2-methoxy-5-methylcyclohexadienyl)]iron hexafluorophosphate and the absolute configuration of the (-)-enantiomer was determined as 2R,5S. The optically active salt was reduced to corresponding (η-cyclohexadiene)iron complex [213].

(iii) General Chemistry

The binuclear ferrole (14.27) has been formed from an (η^3-vinylcarbene)iron complex by treatment with enneacarbonyldiiron. The hydroxyl group of the complex underwent methylation with diazomethane [214]. Hydride ion abstraction with



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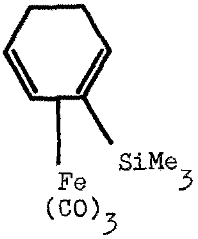

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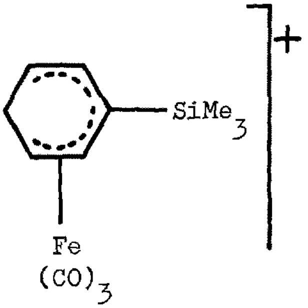
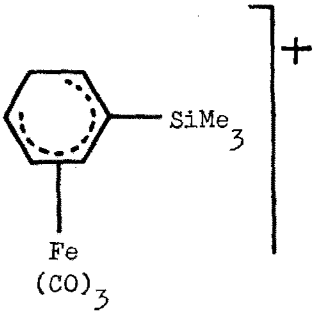


14.29

the triphenylmethylium ion from (η-trimethylsilylcyclohexadiene)iron complexes, such as the 1,3-cyclohexadiene complex (14.28), was regiospecific to form exclusively silyl-symmetrical (η^5-cyclohexadienyl)iron cations, such as the complex (14.29). Nucleophilic addition to the cations, such as the complex (14.29), was also regiospecific with the formation of isomerically pure products [215]. Hydride abstraction from tricarbonyl[2-(trimethylsilyl)-1,3-cyclohexadiene]iron (14.28) produced the isomeric cationic complexes (14.29 and 14.30) in



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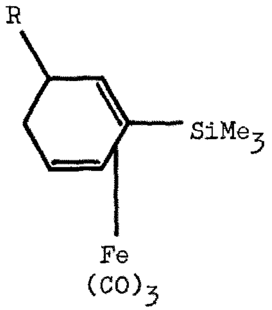

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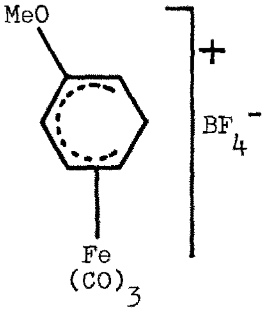
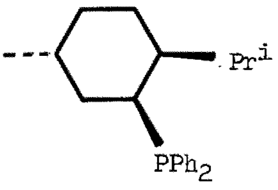


14.32

the ratio 97:3. Treatment of the cation (14.29) with nucleophiles gave good yields of the corresponding complexes [14.31; R = Bu, $CH(CO_2Me)_2$, CN, p-$Me_2NC_6H_4$, morpholino, $P(O)(OMe)_2$, $CH(COMe)_2$, 2-oxocyclohexyl, 2,6-dioxo-4,4-dimethylcyclohexyl]. Oxidative removal of the $Fe(CO)_3$ group from the latter complexes followed by aromatization of the dienes produced the corresponding 3-substituted trimethylphenylsilanes [216].

Treatment of six- and seven-membered ring dienyl complexes of tricarbonyliron with tertiary phosphines produced the corresponding phosphoniodiene salts. These salts were protonated on treatment with n-butyllithium or sodium hydride and underwent a subsequent reaction with aldehydes to give the appropriate olefinic complexes [217]. Reaction of the racemic complex (R,S)-$[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_5)][BF_4]$ (14.32) with the optically active tertiary phosphines (14.33 and 14.34) produced the corresponding monomeric phosphonium salts (14.35). Some chiral discrimination was observed in these reactions [218].



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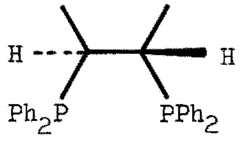

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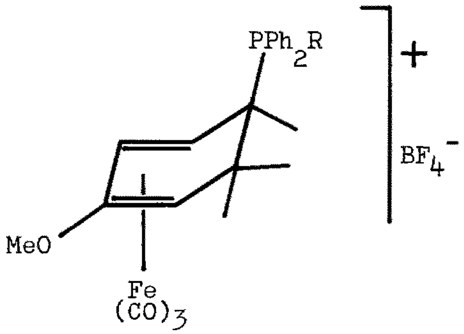
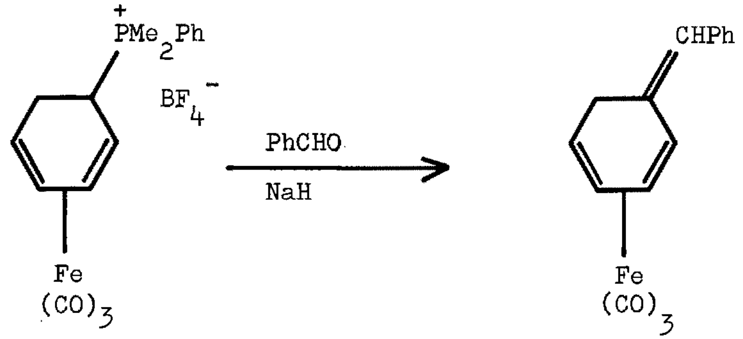


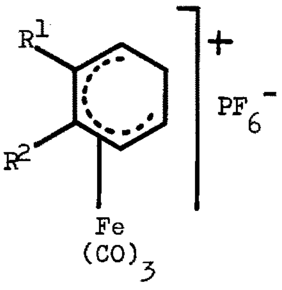
14.35

Tricarbonyl(η-2,4-cyclohexadien-1-yl)iron combined with dimethylphenylphosphine to form the phosphonium tetrafluoroborate (14.36) which was attacked by benzaldehyde in the presence of base to form (η-1-benzylidene-2,4-cyclohexadiene)tricarbonyliron (14.37) in 90% yield [219].



14.36 14.37

Kelly has demonstrated the use of the $Fe(CO)_3$ group as an agent for lateral control and activation in the reactivity of cyclohexa-1,3-dienes. The η-cyclohexadienyliron salts (14.38; R^1 = H, OMe; R^2 = H, OMe) were treated with a solution of the anion of methylphenylsulphonyl acetate when a mixture of the diastereoisomers (14.39) was obtained. Desulphonylation with sodium amalgam produced the corresponding arylacetic acid precursors (14.40; R^1 = H, R^2 = R^3 = OMe; R^1 = OMe, R^2 = R^3 = H) [220]. The η-cyclohexadienylium salts (14.41; n = 2,3) have



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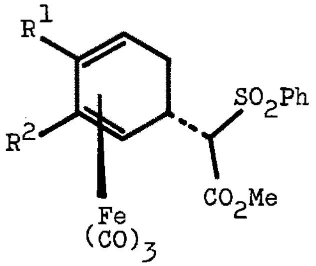

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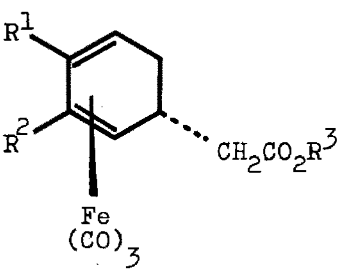
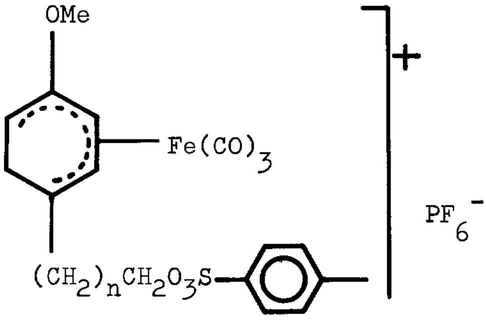


14.40

been prepared from the tricarbonyliron complexes (14.42; n = 2,3) by sequential reduction, esterification, treatment with Ph_3CBF_4 and anion exchange. Cyclization with $NaCH(CN)_2$ or $NaCH(CN)CO_2Me$ produced the spiro compounds (14.43; n = 1,2; R = CN, CO_2Me). Removal of the tricarbonyliron group with Me_3NO gave the corresponding enones (14.44) [221]. The diester



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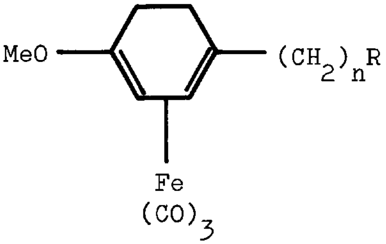
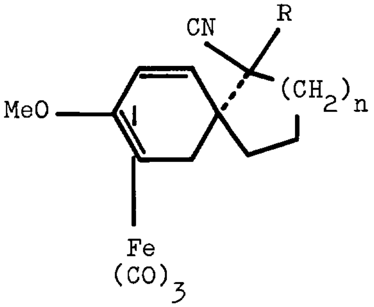


14.42



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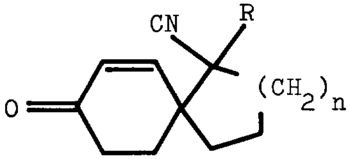
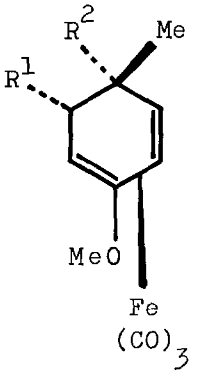
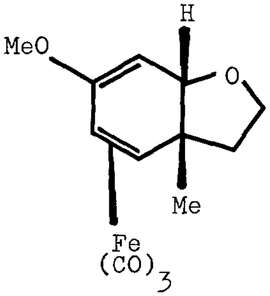


14.44

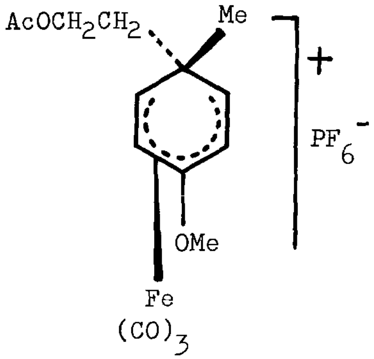
complex [14.45; $R^1 = H$, $R^2 = CH(CO_2Me)_2$] has been decarbomethoxylated by using tetramethylammonium acetate in hexamethylphosphoramide to give the monoester (14.45; $R^1 = H$, $R^2 = CH_2CO_2Me$). The monoester was reduced to the corresponding primary alcohol and this was treated with manganese dioxide to afford the tetrahydrobenzofuran complex (14.46). The latter was transformed into the dienylium complex (14.47) by treatment



14.45



14.46

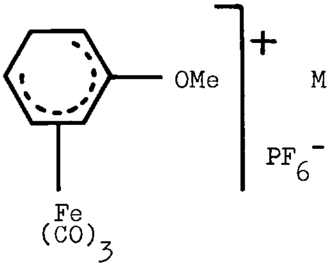


14.47

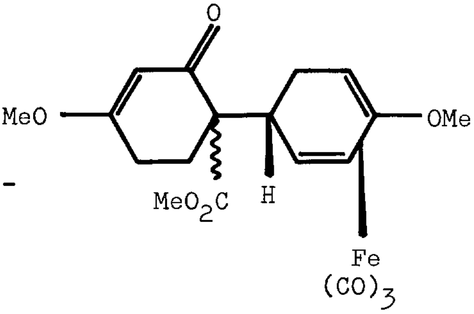
with hexafluorophosphoric acid in acetic anhydride. Reaction of the cationic derivative (14.47) with dimethylsodiomalonate produced the cyclohexadiene complex [14.45; $R^1 = CH(CO_2Me)_2$, $R^2 = CH_2CH_2OAc$] [222].

Addition of ammonium thiocyanate to the tricarbonyl(η-cyclohexadienyl)iron and tricarbonyl(η-cycloheptadienyl)iron cations gave initially the 5-*exo*-isothiocyanate (NCS) compounds $(\eta\text{-}C_6H_7NCS)Fe(CO)_3$ and $(\eta\text{-}C_7H_9NCS)Fe(CO)_3$. The isothiocyanate groups isomerised to give the corresponding 5-*exo* thiocyanate derivatives $(\eta\text{-}C_6H_7SCN)Fe(CO)_3$ and $(\eta\text{-}C_7H_9SCN)Fe(CO)_3$ on exposure to air [223]. The dienyl complex (14.48) which is the synthetic equivalent of the *p*-methoxyphenyl cation, was treated with the potassium enolate of methyl 4-methoxy-2-oxocyclohex-3-enecarboxylate to give the diastereoisomeric complexes (14.49). These complexes were used in a synthetic approach to the sceletium alkaloid (±)-*O*-methyljoubertiamine [224]. The (η-cyclohexadiene)iron complex (14.50) has been used as an intermediate in the multistage synthesis of the aspidospermine precursor (14.51). The utility of (η-cyclohexadiene)iron complexes in natural-product synthesis was discussed [225]. A total synthesis of the aspidosperma alkaloid, (±)-limaspermine has been achieved using the (η-cyclohexadienvl)iron cation (14.52) as an intermediate [226].

Regiochemical control has been achieved in the addition of stable enolate nucleophiles to tricarbonyl(η-cyclohexadienyl)-

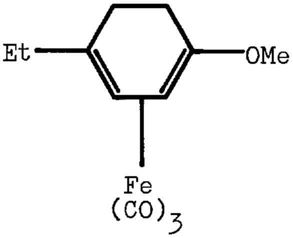


14.48

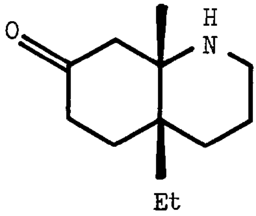


14.49

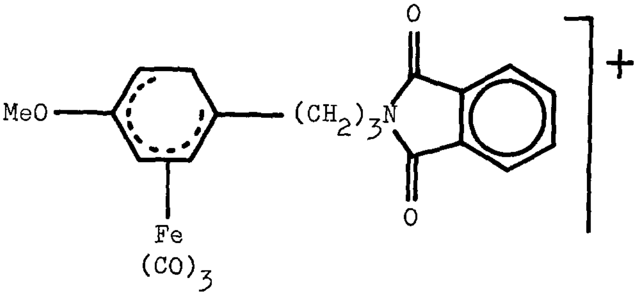
iron cations [14.53; R^1 = Et, $(CH_2)_2CO_2Me$] to form the (η-cyclohexadiene)iron products [14.54 and 14.55; R^2 = $CH(CO_2Me)_2$, $CH(CN)_2$, $CH(COMe)CO_2Me$] by changing the enolate countercation. Steric, coulombic and frontier orbital effects were implicated in the bond forming reaction [227]. Room temperature addition of the (η-cyclohexadienyl)iron salt (14.56) to aniline, p-toluidine and p-anisidine gave only the



14.50

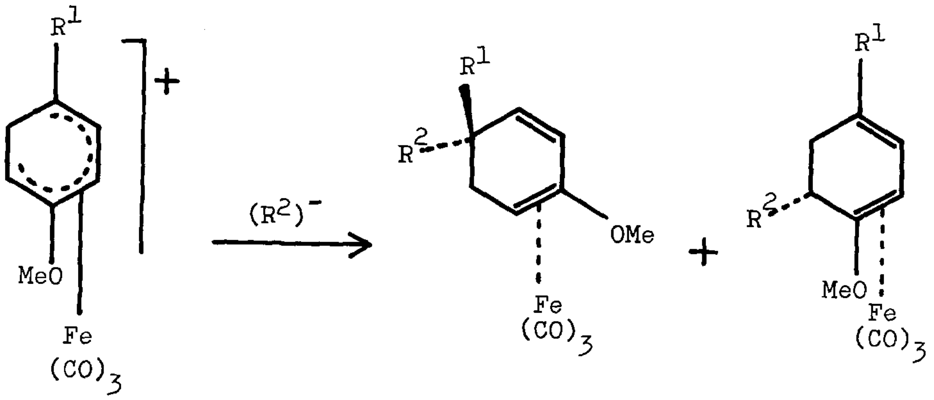


14.51

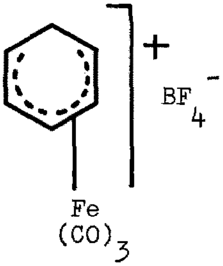


14.52

products of N-alkylation (14.57; R = H, Me and OMe) respectively. When the reaction mixture was heated, electrophilic attack on the aromatic ring occurred and C-alkylation products were obtained. Aniline was attacked at either the ortho- or the para-position and a mixture of products was obtained. When the para-position was blocked, mainly the ortho-substituted products (14.58; R = Me, OMe) were obtained [228].



14.53 14.54 14.55



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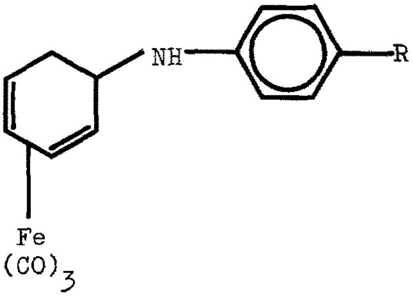

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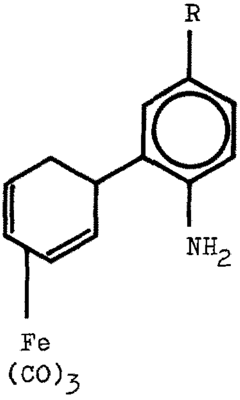

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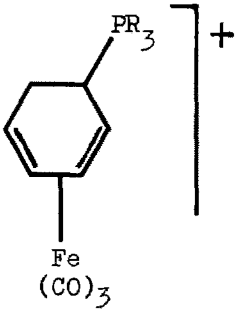
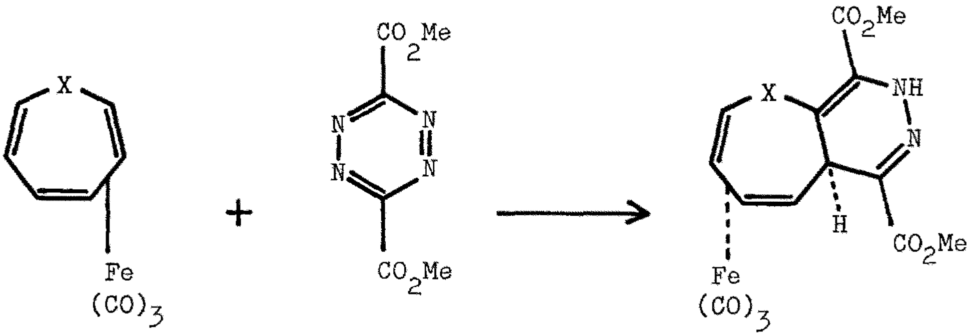


14.59

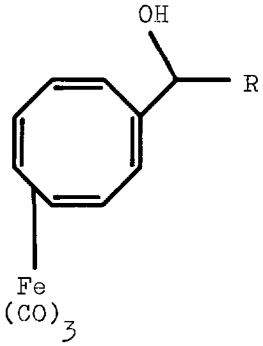
Kinetic studies have been carried out on the addition of a wide range of tertiary phosphines and phosphites to the dienyl ring of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ to give the corresponding diene complexes (14.59; R = 2- and $4\text{-}MeOC_6H_4$, $4\text{-}FC_6H_4$, $2\text{-}MeC_6H_4$, Bu, C_6H_{11}, CH_2CH_2CN, OEt, OMe). All the reactions obeyed the rate expression $k_{obs} = k_1[PR_3]$ except for the reversible additions of $P(CH_2CH_2CN)_3$ and $P(2\text{-}MeC_6H_4)_3$ which followed the equation $k_{obs} = k_1[PR_3] + k_{-1}$ where k_1 and k_{-1} were the forward and reverse rate constants. The reactivity of the phosphorus nucleophiles decreased in the order: $P(2\text{-}MeOC_6H_4)_3 > PBu_3 > PEt_2Ph > P(4\text{-}MeOC_6H_4)_3 > P(4\text{-}MeC_6H_4)_3 >$ $PPh_3 > P(4\text{-}FC_6H_4)_3 > P(C_6H_{11})_3 > P(CH_2CH_2CN)_3 > P(OBu)_3 > P(OEt)_3 >$

$P(OMe)_3 > P(2\text{-}MeC_6H_4)_3$ [229]. The cycloaddition of tricarbonyl(η-cycloheptatriene)iron (14.60; X = CH_2) to 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine (14.61) has been the subject of a kinetic and structural study. The crystal and molecular structure of the product (14.62; X = CH_2) was confirmed by X-ray crystallography. The kinetic results indicated a concerted reaction mechanism with a very rigid transition state and periselective addition at the C(2)-C(3) position in high yield was demonstrated. Several related tricarbonyliron complexes (14.60; X = NCO_2Et, C=O, $C{=}N{-}C_6H_4Me$) underwent the same reaction to give the corresponding adducts (14.62) [230].

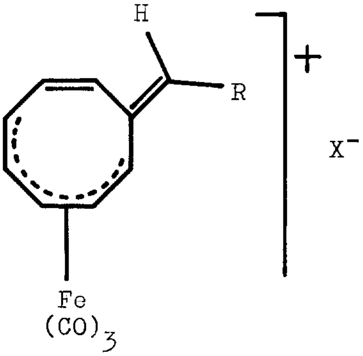


14.60 14.61 14.62

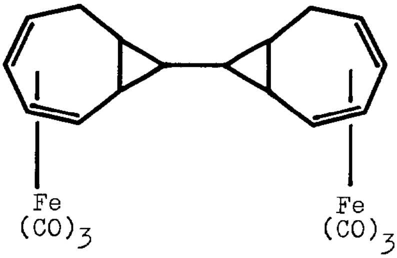
Treatment of the (η-alkylcyclooctatetraenylmethanol)-tricarbonyliron complexes (14.63; R = Et, n-Bu) with Ph_3CBF_4 or HPF_6 produced the corresponding salts (14.64; X = BF_4 or PF_6). The structure of these salts was investigated by ^1H NMR spectroscopy and it was thought to involve a pentadienyl fragment and an uncoordinated double bond within the eight membered ring system together with an exocyclic double bond [231]. The binuclear tricarbonyliron complexes (14.65 and 14.66) have been shown to undergo stereospecific oxidative cyclopropane ring-opening to give the cationic complexes (14.67 and 14.68) with an exocyclic <u>trans</u>- and a <u>cis</u>- double bond respectively [232]. The nucleophilic substitution and addition reactions of the (tricarbonyl)(η-1,5-cycloheptadienylium)-



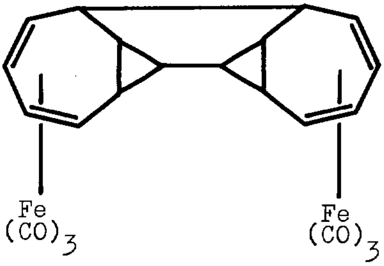
14.63



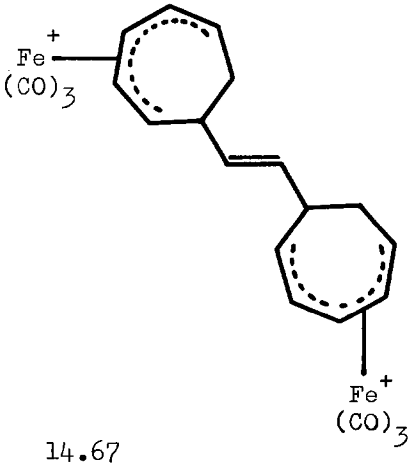
14.64



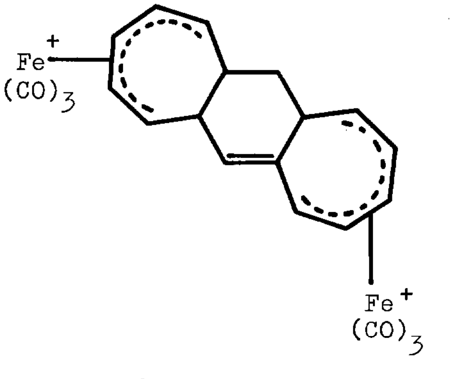
14.65



14.66



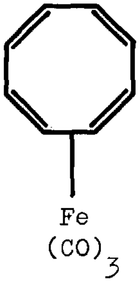
14.67



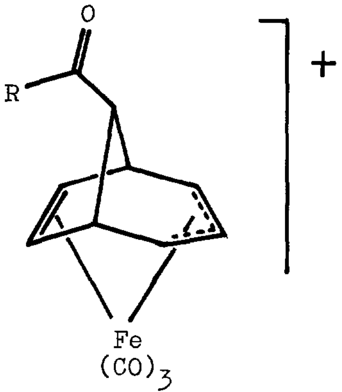
14.68

iron cation have been investigated. Amines attacked the ring directly to give 5-exo ring products and alkoxides attacked the carbonyl groups at low temperatures to give carbalkoxy derivatives which rearranged spontaneously with an increase in temperature to give 5-exo ring alkoxy derivatives. By careful choice of both the phosphine and solvent, both 5-exo and 5-endo phosphine ring adducts were obtained [233].

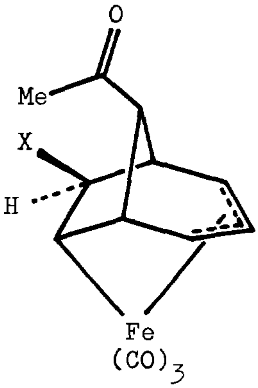
(1-2:5-6-η-Cyclooctadiene)(1-2:3-4:5-6-η-cyclooctatriene)-ruthenium has been used as the starting material for the synthesis of a number of ruthenium (0) and ruthenium hydride phosphine complexes [234]. Friedel-Crafts acylations of the (η-cyclooctatetraene)iron complex (14.69) produced the cations (14.70; R = Me, Ph) in which the C(8) acyl group was stereospecifically



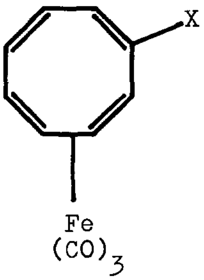
14.69



14.70



14.71

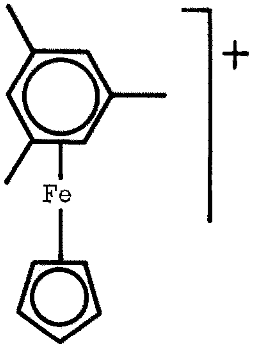


14.72

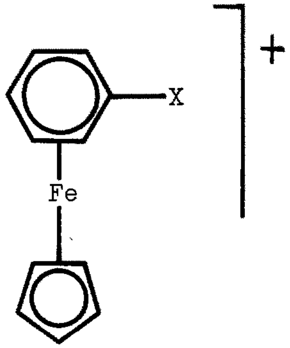
endo to the C(6), C(7) double bond. Reaction of the cation (14.70; R = Me) with BH_4^- or CN^- gave as major products the corresponding complexes (14.71; X = H, CN) while iodide ion replaced one of the carbonyl ligands [235]. Formylation of the substituted (η-cyclooctatetraene)iron complexes (14.72; X = Me, Ph, CPh_3, Br) under Vilsmeir conditions gave products that corresponded in each case to attack by the electrophile at the least sterically hindered sites on the cyclooctatetraene ligand. The bulk of both the tricarbonyliron group and the substituent were important in this respect [236].

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

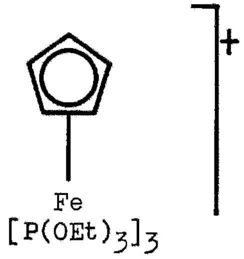
Azaferrocene has been attacked by benzene and substituted benzenes in the presence of aluminium chloride to form the corresponding (η-arene)(η-cyclopentadienyl)iron cations. Thus mesitylene gave the cation (15.1) in 80% yield [237]. Ferrocene underwent ligand exchange with monosubstituted benzenes in the presence of aluminium powder and aluminium chloride to give the (η-benzene)iron cations (15.2; X = F, Cl, NH_2, $NHNH_2$, NHAc) which were isolated as the light sensitive and explosive picrates [238]. Aromatic compounds in crude oil and petroleum products underwent ligand exchange with ferrocene to form (η-arene)(η-cyclopentadienyl)iron hexafluorophosphates which were then analyzed by thin-layer chromatography [239]. The nitroarene and aminoarene complexes (15.2; X = NO_2, NH_2)



15.1

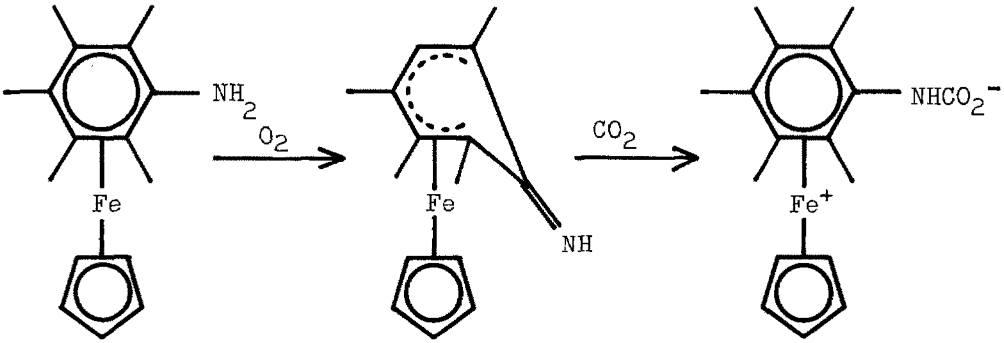


15.2



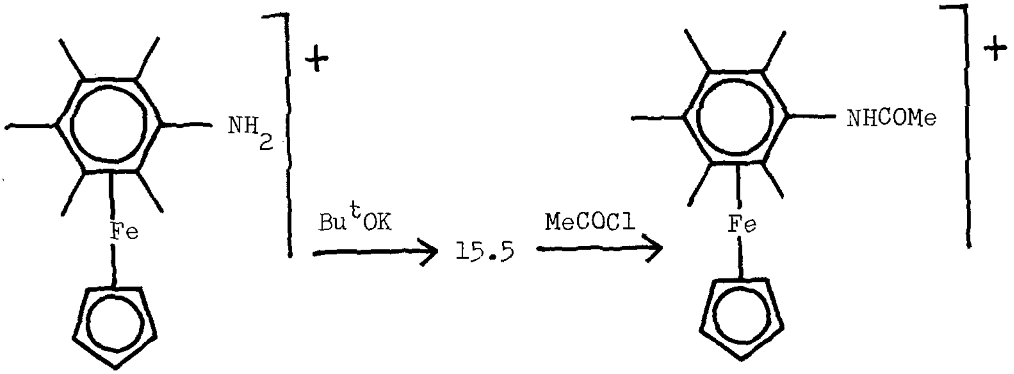
15.3

respectively underwent ring replacement when heated with $P(OEt)_3$ to form the product (15.3). Several related complexes underwent the same reaction while the chlorine atom in the chloroarene complex (15.2; X = Cl) and related species was readily displaced by amines such as methylamine, cyclohexylamine, benzylamine and pyrrolidine to give the derivatives [15.2; NHMe, NHC_6H_{11}, $NHCH_2Ph$, $N(CH_2)_4$] [240].



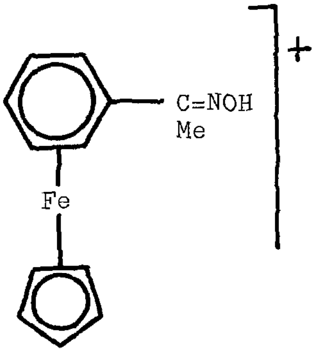
15.4 15.5 15.6

The 19-electron iron complex (15.4) was converted by oxygen to the intermediate imine complex (15.5), the NH_2 group being activated by oxygen. Attack by carbon dioxide on the intermediate (15.5) afforded the zwitterion (15.6). An electron transfer mechanism was invoked for the process [241]. Ligand exchange between ferrocene and pentamethylaniline has been used to form the (η-pentamethylaniline)iron cation (15.7) which has been deprotonated with Bu^tOK in THF to the imine (15.5) and then treated with acetyl chloride to give the amide (15.8). Other acid chlorides took part in the reaction to give similar products [242]. Deprotonation of the (η-ethylbenzene)(η-cyclopentadienyl)iron cation with t-BuOK followed by treatment with ethylnitrite, C_2H_5ONO, gave the oxime (15.9) which was reduced electrochemically to the corresponding primary amine (15.10). The oximes of benzophenone and fluorenone complexes has been obtained in the same way [243].



15.7 15.8

Treatment of (η^6-benzene)(η^5-cyclopentadienyl)iron with oxygen under aprotic conditions gave the crystalline peroxidic dimer (15.11) which was attacked at C-6 by chloroform and acetone to form the products (15.12 and 15.13) respectively. Reaction of the dimer (15.11) with water, ethanol, thiophenol and halides gave the salts (15.14), peroxides (15.15) were also formed [244]. It has been shown that the reduction of a variety of monocationic organoiron complexes by lithium aluminium hydride and/or sodium borohydride could proceed via



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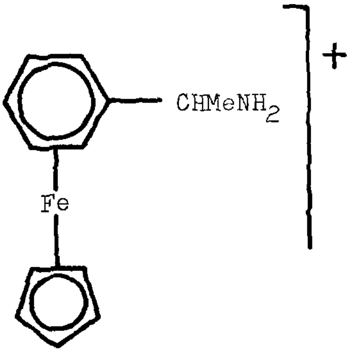

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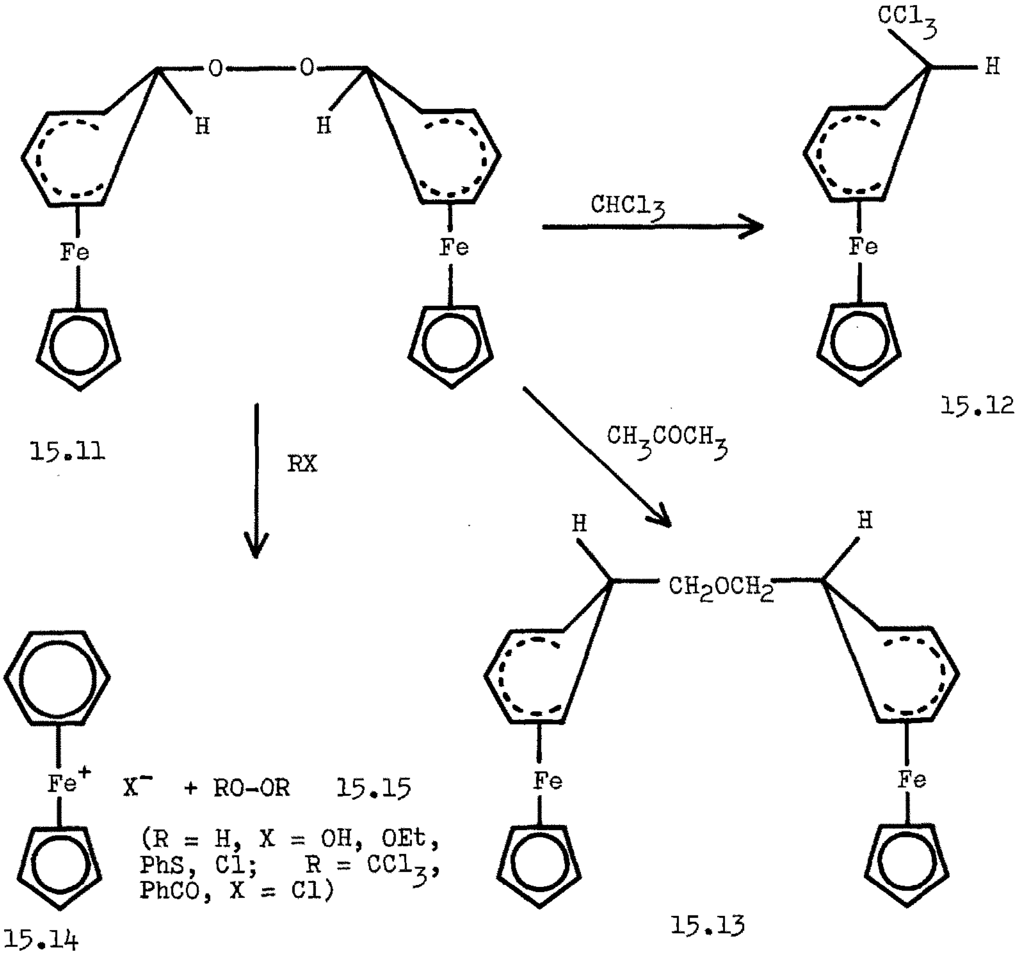
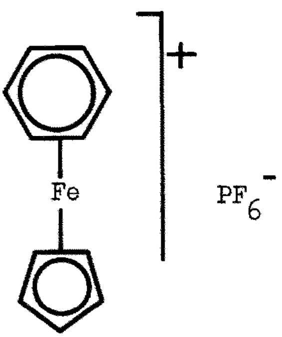


a single electron transfer. For example, in the reduction of the salt (15.16) by lithium aluminium hydride at -60°C the unstable d^7 complex $(\eta^5-C_5H_5)Fe^I(\eta^6-C_6H_6)$ was formed by electron transfer. When the solution warmed to -30°C hydrogen atom transfer occurred to give the (η-cyclohexadienyl)iron complex (15.17) [245]. Hydrogenation of the (η-pentamethylcyclohexadienyl)iron complex (15.18) over palladium gave initially the (η-hexamethylbenzene)iron complex (15.19) and then the (η-hexamethylcyclohexadienyl)iron product (15.20) [246].

The peralkylation of the poly(methyl)arene ligand in $[(\eta-C_5H_5)Fe(\eta-arene)]^+$ complexes has been carried out by reaction with excess t-BuOK and an alkyl halide. For example, treatment of the η-hexamethylbenzene complexes (15.21; R = H, Me) with t-BuOK and methyl iodide produced the corresponding



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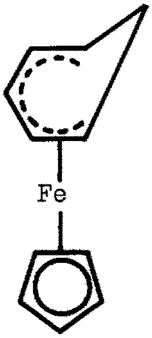
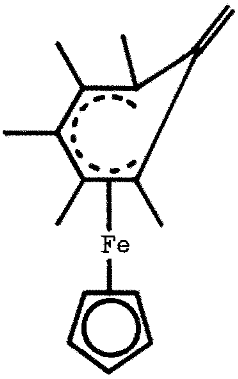


15.17

hexaethyl complexes (15.22). The structure of the complex (15.22; R = H) was determined by X-ray analysis. Three of the arene carbon atoms were eclipsed or nearly eclipsed by η-cyclopentadienyl ligand carbon atoms. The ethyl groups on these carbon atoms were directed away from the iron atom and only two ethyl groups pointed towards the metal atom with unusually large C-CH_2-CH_3 angles (118.6°) [247]. The reduction



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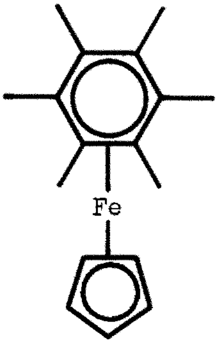

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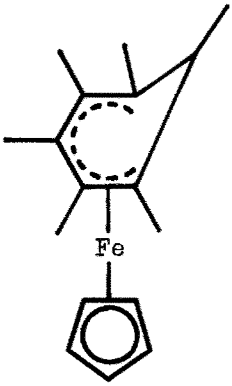

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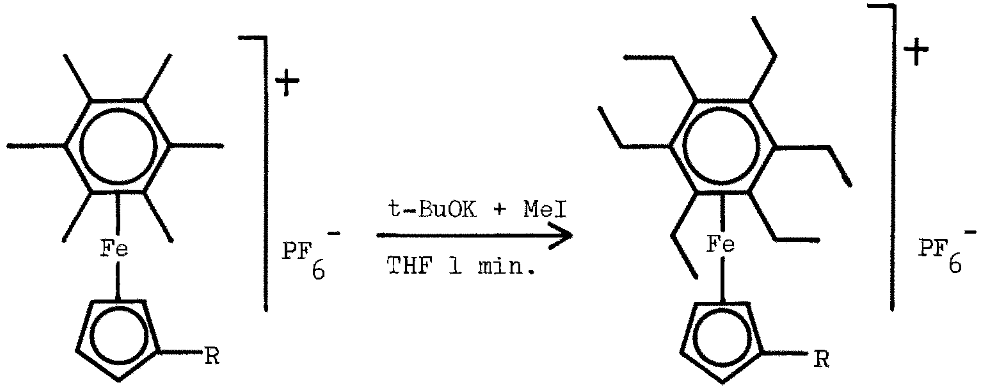
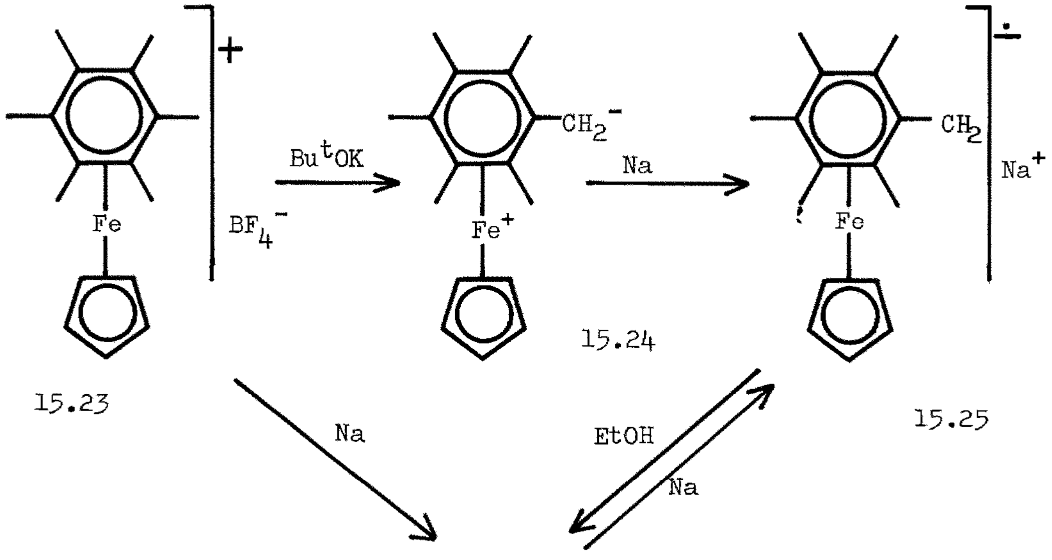


15.21 15.22

of deprotonated (η-arene)(η-cyclopentadienyl)iron borofluorides, where arene = diphenylmethane, fluorene, hexamethylbenzene, with sodium gave paramagnetic d^7 complexes. These complexes were attacked by ethanol to form neutral d^7 species which were also formed by direct reduction of the initial cations with

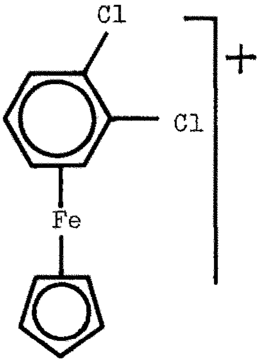


15.23 15.24 15.25

15.19

sodium. Thus the (η-hexamethylbenzene)iron cation (15.23) was deprotonated to the zwitterion (15.24) which was reduced with sodium to the d^7 radical anion (15.25) and converted to the neutral d^7 species (15.19) with ethanol. The direct attack of sodium on the cation (15.23) gave the product (15.19). The paramagnetic species were characterized by ESR spectroscopy [248].

The (η-benzene)iron cation (15.26) has been cyclized with the *o*-disubstituted benzene compounds (15.27) in the presence of potassium carbonate to form the (η-arene)iron cations (15.28; X = Y = O; X = NH, Y = O, S; X = S, Y = O) in yields of up to 82% [249]. Photolysis studies have been carried out on dilute solutions of (η^6-*o*-, *m*- or *p*-azidotoluene)-(η^5-cyclopentadienyl)iron hexafluorophosphate in cyclohexane or dichloromethane as solvent. 1-Cyano-2-methylferrocene and 1-cyano-3-methylferrocene were obtained from the *ortho*- and *para*-derivatives respectively whilst a mixture of the same two ferrocene derivatives was obtained on irradiation of the *m*-azidotoluene complex [250]. Irradiation of the (η-cyclopentadienyl)(η-*p*-toluene)iron cation with cyclophanes in dichloromethane gave the corresponding (η-cyclophane)iron complexes (15.29; X = H, R = H, Me; X = OMe, R = Me). When ferrocene replaced the *p*-toluene complex then the triple-layered complexes (15.30; R = H, Me) were obtained under thermal conditions.



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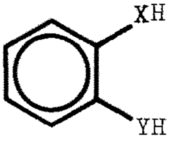

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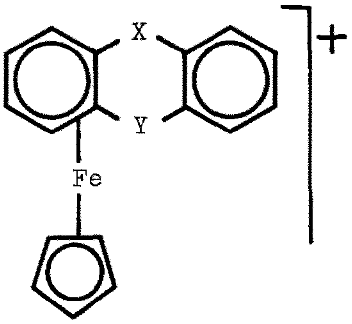

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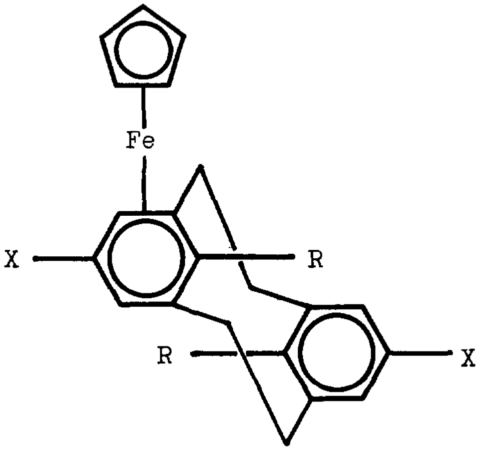

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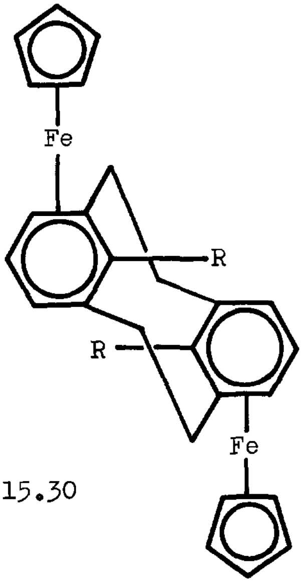
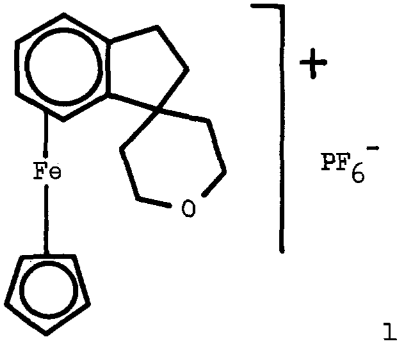


15.30

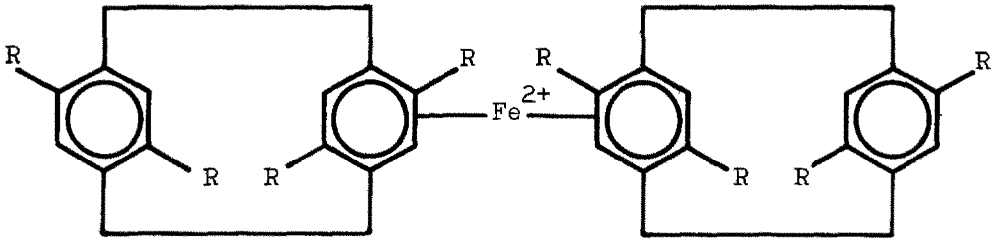
^{1}H NMR spectroscopy was used to analyze the nature of the metal-cyclophane bonding in these complexes [251].

The structure of (η^6-[2.2]paracyclophane)(η^5-cyclopentadienyl)iron(II) tetrafluoroborate has been determined by X-ray analysis [252]. The crystal and molecular structure of the



15.31

(η-spiroindene)iron salt (15.31) has been determined by X-ray crystallography. The reaction of the salt (15.31) with the anion $(CHMeCN)^-$ was rationalized in terms of its structure [253]. Reaction of [2.2]paracyclophane with iron(II) chloride in the presence of aluminium chloride and $Me_3Al_2Cl_3$ produced

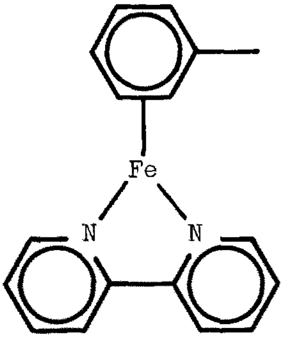


15.32

the unstable complex (15.32; R = H). When the same reaction was carried out with 4,7,12,15-tetramethyl-[2.2]paracyclophane the stable complex (15.32; R = Me) was obtained [254].

Thermally unstable complexes were generated by the codeposition of iron, cobalt or nickel with toluene at -196°C. The iron complex decomposed at -30°C [255]. Cocondensation of iron atoms and toluene at -196°C gave a brown complex Fe(η--toluene)$_x$ which was treated with 2,2-bipyridyl to form the product (15.33). The crystal and molecular structure of the complex has been determined by X-ray crystallography. The Fe-N bond was unusually short and transfer of electron density from iron to the π^* orbitals of bipyridyl was indicated [256]. The 19- and 20- electron complexes (15.34; n = 1, 0) have been prepared in high yield by Na/Hg reduction of $[Fe(\eta\text{-}C_6Me_6)_2]^{2+}$ $[PF_6^-]_2$. The Moessbauer spectra of these complexes indicated high metal character for the antibonding e_1^* orbital and rhombic distortion of the Jahn-Teller active complex (15.34; n = 1) [257].

A variable temperature, 4-300°K, ESR study has been made of the 19-electron iron sandwich complexes (15.34; n = 1 and



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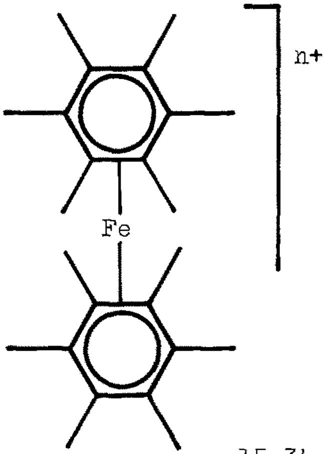
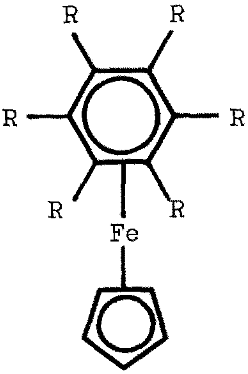
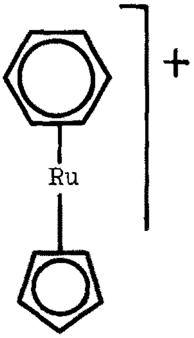


15.34

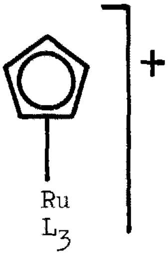
15.35; R = H, Me, Et) and some related derivatives. The results suggested a d^7 configuration for iron with the unpaired electron in a metal-centred (d_{xz}, d_{yz}) molecular orbital. Differences in g values between the complexes and their host lattice dependence were rationalized in terms of dynamic Jahn--Teller coupling and rhombic splitting caused by the unsymmetrical ligands [258]. A series of new (η^6-arene)FeL_2 (L = phosphine ligand) complexes, for example (η^6-C_6H_6)$Fe[P(OMe)_3]_2$, has been



15.35

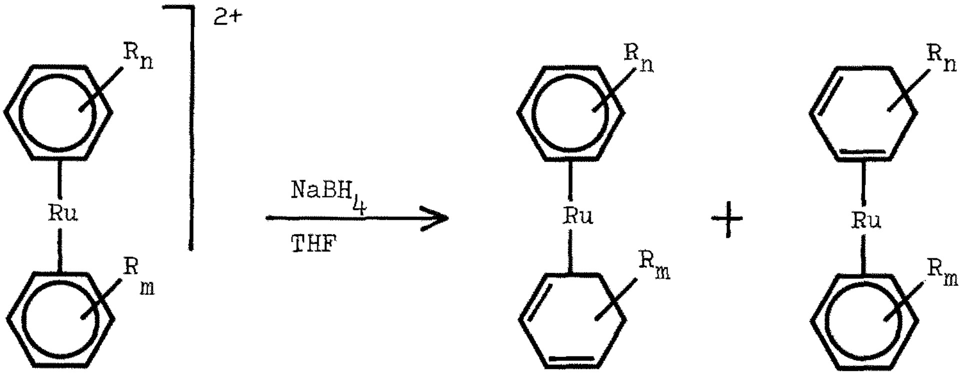


15.36



15.37

prepared by cocondensing iron atoms simultaneously with arene and the ligand L or condensation of iron atoms with the arene followed by low-temperature reaction of the condensate with the phosphine ligand. A series of (η^6-arene)Fe(η^4-diene) complexes was prepared similarly [259]. The (η-benzene)-ruthenium cation (15.36) underwent photolysis in acetonitrile to form the acetonitrile-ruthenium cation (15.37; L = MeCN) in quantitative yield. Procedures have been developed for the selective displacement of one, two or three acetonitrile ligands to give products such as the phosphite [15.37; L = $P(OMe)_3$], the arene (15.37; L_3 = η-Me_6C_6) and the cyclooctatetraene complex (15.37; L_3 = η^6-cyclooctatetraene) [260].

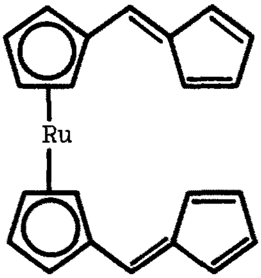


13.38 13.39 13.40

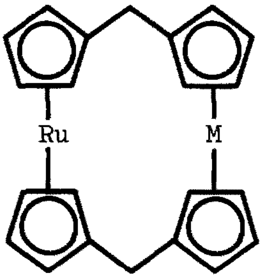
The reduction of the symmetrical and unsymmetrical bis-(η-arene)ruthenium cations (15.38; $R_n = R_m$ = 1,3,5-Me_3; R_n = 1,3,5-Me_3, R_n = 1,4-Me_2, R_n = Me, R_m = H) with sodium borohydride to give the (η-cyclohexadiene)ruthenium complexes (15.39 and 15.40) has been studied. Hydride hydrogen added preferentially to the less alkylated ring. It was shown that the reaction proceeded via intermediate (η-arene)(cyclohexadienyl)-ruthenium cationic complexes [261]. A series of (η^6-cyclophane)(η^6-arene)ruthenium complexes [arene = C_6H_6, *p*-cymene, mesitylene, C_6Me_6; cyclophane = [2.2]paracyclophane, *anti*-[2.2]metacyclophane, and $[2_3]$(1,3,5)-, $[2_3]$(1,2,4)(1,2,5)-, $[2_4]$(1,2,3,4)-, $[2_4]$(1,2,3,5)-, $[2_4]$(1,2,4,5)-, $[2_5]$(1,2,3,4,5) and $[2_6]$(1,2,3,4,5,6)cyclophane] has been prepared. The cyclic voltammetry and spectral properties of these molecules were described [262].

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

1,1'-Bis(6-fulvenyl)ruthenocene (16.1) has been prepared by either adding 1,1'-dilithioruthenocene to 6-dimethylfulvene or by treating the ligand anion fulvenyl cyclopentadienide with dichlorotetrakis(dimethylsulphoxide)ruthenium. The bis-fulvene (16.1) was converted to the metallocenophanes (16.2; M = Ru, Fe) [263]. The electrochemistry of these two metallocenephanes was investigated by cyclic voltammetry. For the iron-ruthenium complex (16.2; M = Fe) there was found to be a ferrocene-centred reversible one-electron oxidation and a ruthenocene-centred irreversible two-electron oxidation which showed the independence of the two metallocenes in this molecule. By contrast in [1.1]ruthenocenophane (16.2, M = Ru) the two ruthenocenes appeared to interact strongly as indicated by a quasi-reversible two-electron oxidation at a relatively low potential [264]. Trichlorosilylruthenocene,1,1'-dicarboxyruthenocene and a series of ferrocene compounds were prepared and used for derivatization of n-type silicon electrodes. The derivatized electrodes exhibited a wide range of responses but none of the systems investigated showed a photoresponse which lasted beyond several hundred cycles [265].

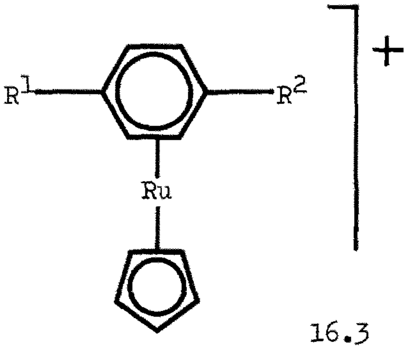


16.1



16.2

Acetylruthenocene was heated with $^{97}RuCl_3$ to give acetylruthenocene-^{97}Ru and this compound underwent H-exchange in KOH-T_2O to give the corresponding t_3 tritiated compound. In a similar reaction acetylruthenocene underwent H-exchange

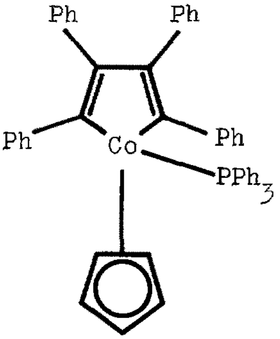


16.3

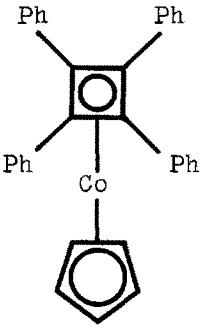
in KOH-D_2O to give d_3-acetylruthenocene [266]. Several (η-arene)ruthenium cationic complexes (16.3; R^1 = H, OMe, R^2 = H; R^1 = Me, R^2 = Pr^i) have been prepared by treatment of $[Ru(\eta\text{-arene})Cl_2]_2$ with $Tl(C_5H_5)$. The hexamethylbenzene complex and two analogous osmium complexes were prepared in the same way. The complexes did not undergo electroreduction [267]. Ruthenocene underwent enzymic hydroxylation with mouse liver microsomes more slowly than osmocene although both had the same value of $K_m = 1.4 \times 10^{-4}$M. Ruthenocene and osmocene in buffer of pH 7.4 alone at 37°C and without microsomes were much more stable than ferrocene under the same conditions [268]. Intraveneous injection of ^{103}Ru-labelled acetylruthenocene produced high concentrations of ^{103}Ru in the adrenal cortex of female mice. High ^{103}Ru accumulations did not occur in the adrenals of male mice or rats but very high concentrations were found in the kidney. The ^{103}Ru concentration in the kidney of the female rats was only 5% that of the male. After the application of testosterone to female mice or estradiol to male rats the ^{103}Ru radioactivity in the adrenals and the kidneys was greatly reduced [269].

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

The cobaltacyclopentadiene complex (17.1) has been converted to the (η-cyclobutadiene)cobalt complex (17.2) on UV irradiation in benzene or dichloromethane. When oxygen was present in the irradiated system an (η-enone)cobalt complex was formed in addition to the previous product (17.2) [270].



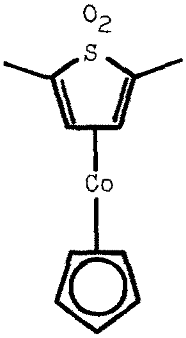
17.1



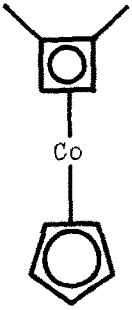
17.2

The reaction of 2-cyclopropene-1-carbonyl chlorides with cobalt anions produced η^3-cyclobutenonylcobalt complexes. Treatment of these complexes with trialkyloxonium salts afforded a variety of cationic (η^4-cyclobutadiene)cobalt compounds [271]. Irradiation of dicarbonyl(η-cyclopentadienyl)-cobalt in the presence of 2,5-dimethylthiophene-1,1-dioxide produced the (η-cyclopentadienyl)cobalt complex (17.3). Flash vacuum pyrolysis of this latter complex gave the 1,2-dimethyl-cyclobutadiene complex (17.4) via sulphur dioxide extrusion [272].

It has been shown that isomerization of the diastereoisomers (17.5 and 17.6; R^1 = OH, OMe, Ph; $R^2 = R^3$ = $SiMe_3$, $SiEt_3$) in the gas phase by flash photolysis or in solution proceeds via a bisalkyne cobalt complex [273]. The rearrangement of the η-cyclobutadiene ligand in (η-1,2-diethynylcyclobutadiene)cobalt complexes has been reinvestigated. Flash vacuum thermolysis of the complexes promoted a clean rearrangement whereby the four sp hybridized carbon atoms in the ethynyl groups cyclized to form a new cyclobutadiene ring while the

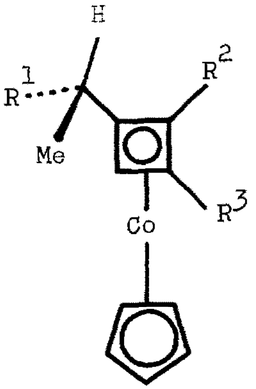


17.3

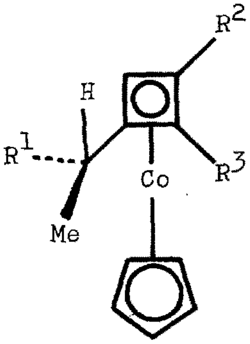


17.4

old cyclobutadiene ring opened to form two new ethynyl groups. Thus the complex (17.7; $R^1 = SiMe_3$, $R^2 = H$) rearranged to give the product (17.7; $R^1 = H$, $R^2 = SiMe_3$) and in the same way the deutero complex (17.7; $R^1 = H$, $R^2 = D$) underwent equilibration with the product (17.7; $R^1 = D$, $R^2 = H$) [274,275] Carbon-carbon and carbon-hydrogen coupling constants in [η-1,3-bis(silyl)cyclobutadiene]cobalt complexes have been



17.5



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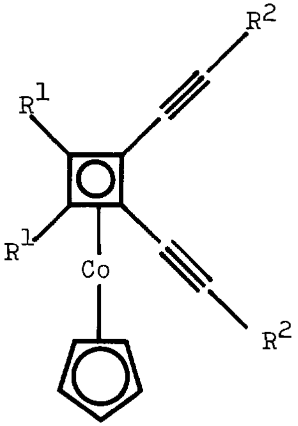
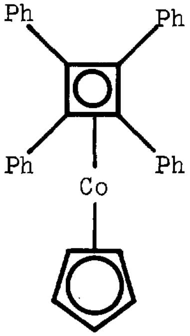


17.7



17.8

17.9

measured by ^{13}C NMR spectroscopy. The values obtained were significantly lower than those reported previously [276]. Metal-ligand bonding in cobalt complexes has been investigated by ^{59}Co nuclear quadrupole resonance spectroscopy. Electron redistribution was compared in the cobaltocenium ion and the (η-cyclobutadiene)cobalt complex (17.8). The electron density was significantly asymmetric in complexes containing localized cyclic olefins. The cobalt-diene bond strength in the (η-cyclopentadienyl)cobalt complexes (17.9) was found to fall in the order:

L = cyclooctadiene > duroquinone > cyclopentadienone.

The order was interpreted in terms of the ability of the ligand to distort and thereby maximize overlap between the π-orbitals of the ligand and the d_{xz} orbital of cobalt [277].

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

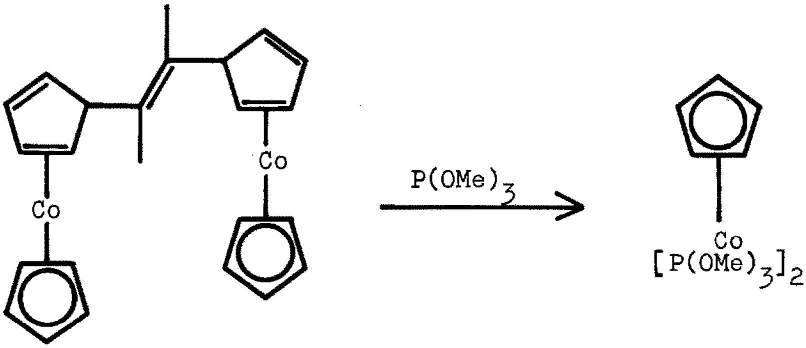
Ferrocene and cobaltocene have been synthesized electrochemically from cyclopentadiene monomer and the appropriate metal anode. Several related syntheses were described [278]. Azulene has been obtained in 21% yield by heating cobaltocene in acetonitrile [279]. The electronic structure of cobaltocene has been investigated by comparison of the results of multiple-scattering X_α calculations with various other techniques. The order for the penultimate orbitals of the $^2E_{1g}$ ground state

(D_{5d} notation) was calculated as:

$$4a_{1g}(L\pi) < \ldots < 4a_{2u}(L\pi) \ll 3e_{1g}(L\pi) < 4e_{1u}(L\pi) < 3e_{2g}(Md\delta) < 5a_{1g}(Md\sigma) \ll 4e_{1g}(Md\pi).$$

The last antibonding orbital with an unpaired electron was appreciably delocalized over the cyclopentadienyl rings. Qualitative structural predictions were made on the basis of a diagram that represented the electronic energy levels of cobaltocene as a function of metal-to-ring distance [280]. The all-electron self-consistent-field multiple scattering $X\alpha$ model has been used to calculate and predict the magnetic properties, such as the hyperfine interaction tensor on metal, of several organometallic compounds. Metal hyperfine tensor components were calculated for cobaltocene and were found to agree well with values obtained by EPR spectroscopy [281].

A theoretical study of the electronic structure of cobaltocene has been made using the LCAO Hartree-Fock-Slater approach. The metal-ring bonding was discussed in detail and the experimental photoelectron and optical absorption spectra were assigned satisfactorily. It was confirmed that the π-component of the metal-ring bond was dominant over the σ- and δ-components [282].

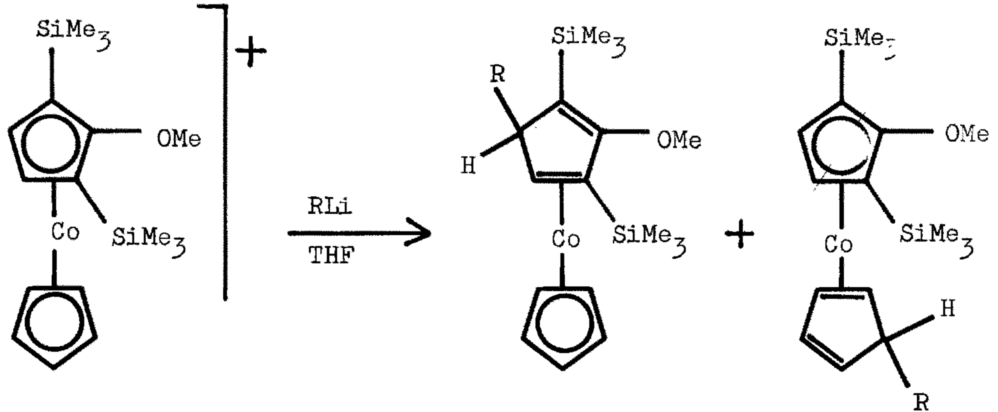


18.1

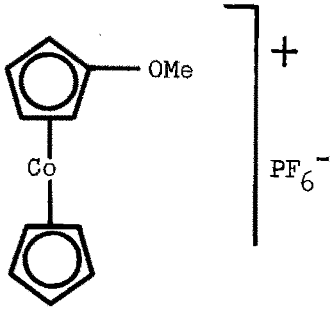
18.2

Cyclic voltammetry and polarography have been used in an electrochemical investigation of metallocarboranes. The results were compared with those obtained for the corresponding metallocenes, cobaltocene and ferrocene [283].

The reaction of cobalt(II) bromide with sodium cyclopentadienyl followed by addition of a diene or acetylene gave the complexes $(\eta\text{-}C_5H_5)(\eta\text{-diene})Co$. Cobaltocene and the cobaltocenium ion were also isolated in some of these reactions [284]. Cobaltocene has been attacked by 2-butyne to form the binuclear-(η-cyclopentadiene)cobalt complex (18.1) which was subsequently cleaved by trimethylphosphite to form the product (18.2) [285]. Treatment of neutral [η^4-2,5-bis(trimethylsilyl)cyclopenta-



18.3 18.4 18.5



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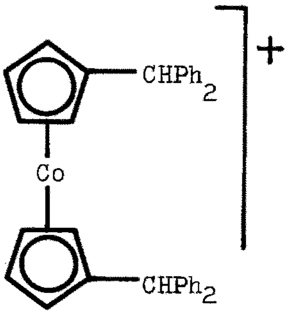
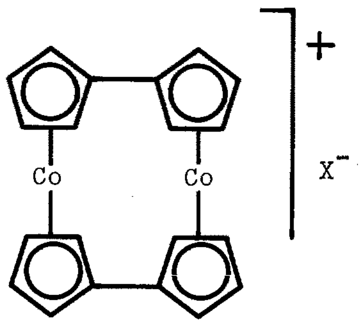


18.7

dienone](η^5- cyclopentadienyl)cobalt with dimethyl sulphate produced the cobaltocenium cation (18.3) which was converted by organolithium reagents, RLi, for example, R = t-Bu, Me, $Me_3SiC{\equiv}C$, into mixtures of the η^4-cyclopentadiene complexes (18.4 and 18.5). The reaction of the cobaltocenium salt (18.6) with organolithium reagents was also investigated [286].

A series of cobaltocenium salts, $(Me_nC_5H_{5-n})_2CoX$ where n = 0-5; X = Br, PF_6, has been prepared and steric effects in these molecules have been examined by ^1H and ^{13}C NMR spectroscopy [287]. The reaction of 6,6-diphenylfulvene with cobalt (II) chloride and $Me_2CHMgBr$ followed by oxidation produced the cobaltocenium cation (18.7). The crystal structure of this cation as the PF_6^- salt was determined by X-ray analysis [288]. The mixed valence cobaltocenylene complexes (18.8; X = 3TCNQ, 3TBDQ) where TCNQ = tetracyano-p-quinodimethane and TBDQ = tetrabromodiphenoquinone have been obtained by treatment of the salt (18.8; X = PF_6) with TCNQ and TBDQ. The TCNQ units in the complex (18.8; X = 3TCNQ) stacked to form an alternating chain with interplanar spacings [289]. Polymers obtained from chlorocarbonylcobaltocenium hexafluorophosphate and poly(ethylenimine) have been used to modify the properties of glassy carbon and static mercury drop electrodes [290].



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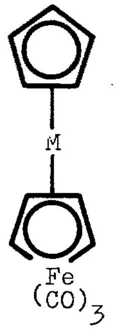
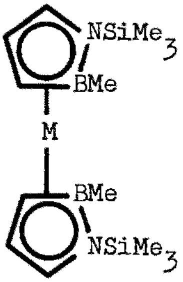


18.9

Ferracobaltocene (18.9; M = Co) and ferrarhodocene (18.9; M = Rh) have been prepared by two routes: (i) reaction of tricarbonyl(η-cyclobutadiene)iron with (η-C_5H_5)M(CO)$_2$ and (ii) reaction of tricarbonyl(tricarbonylferracyclopentadiene)iron with (η-C_5H_5)M(CO)$_2$. X-ray data showed that these molecules had sandwich-like structures and that there was substantial electron delocalization. The compounds (18.9; M = Co, Rh) underwent Friedel-Crafts acylation which suggested aromatic character [291]. The azaborolinyl sandwich complexes (18.10; M = Fe, Co) have been obtained by cocondensation of the free ligand in methylcyclohexane with metal atoms at -130°C and 10^{-4} Torr. The structures of the complexes have been confirmed by X-ray crystallography [292]. Seventeen Co, Rh, Ni and Pt complexes of 1,4-diboracyclohexadiene and 1,4-diborabenzene have been prepared. Attempts to acetylate the complex (18.11) under Friedel-Crafts conditions brought about substitution of a ring member to form a cationic borabenzene complex [293]. The reaction of the Δ^4-1,3-diborolenes (18.12, R^1 = Et, R^2 = Me; R^1 = Me, R^2 = H) with (η^5-cyclopentadienyl)bis(ethene)cobalt has been shown to proceed via the cobalt complexes (18.13) to give the corresponding triple-decker complexes (18.14; M = Co). The structure of the complex (18.13; R^1 = Et, R^2 = Me) was determined by X-ray analysis. The two cyclic ligands were coplanar and the distances of the ring planes from the



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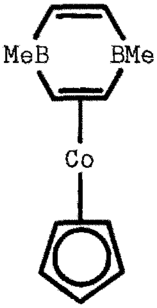

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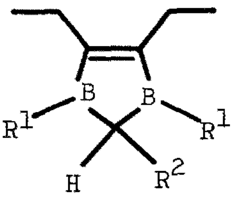

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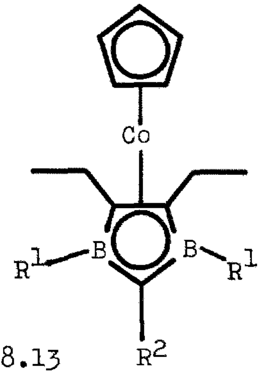
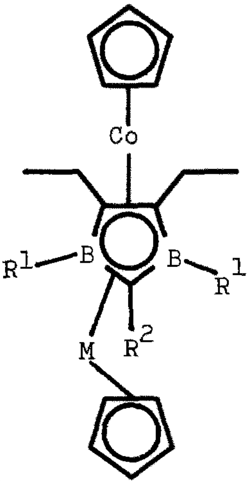
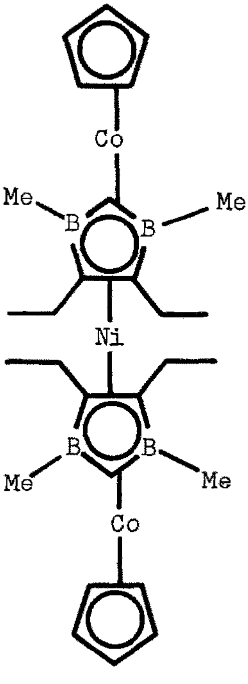


18.13



18.14

cobalt atom were 1.66Å [Co—(η-C_5H_5)] and 1.56Å [Co—(η-C_2B_2C)] [294]. Reaction of the triple decker sandwich complex (18.14; R^1 = Me, R^2 = H; M = Ni) with potassium unexpectedly produced



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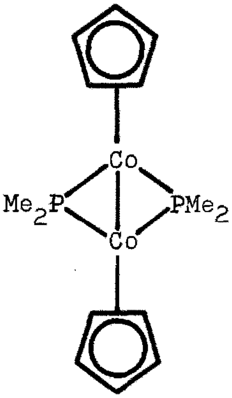

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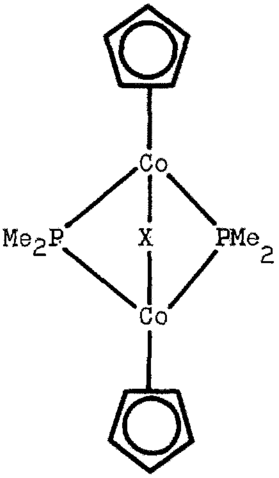
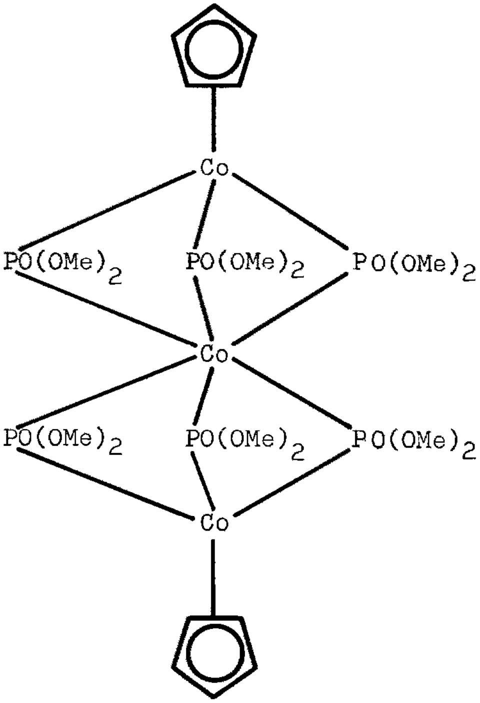


18.17

the tetradecker complex (18.15). The structure of the complex (18.15) was confirmed by X-ray analysis [295]. When the compound (18.13; R^1 = Et, R^2 = Me) was heated with tetracarbonylnickel it produced a dicarbonyldinickel complex which underwent reaction with the diboralene (18.12; R^1 = Me, R^2 = H) to give a penta-decker sandwich complex [296].

The metal-metal bond in the cobalt complex (18.16) underwent electrophilic addition with sulphur, selenium and tellurium to form the derivatives (18.17; X = S, Se, Te) [297]. Carbonyl(η-cyclopentadienyl)diiodocobalt has been treated with an excess of trimethylphosphite and the intermediate obtained has been pyrolyzed or combined with anhydrous cobalt chloride

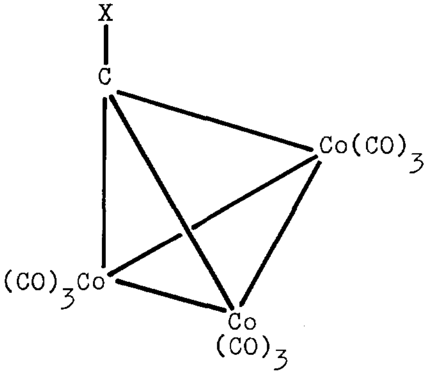


18.18

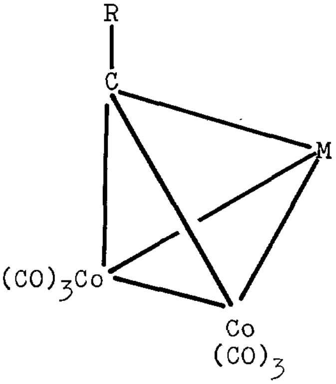
to form the cobalt "supersandwich" complex (18.18) [298].

19. Cobalt-carbon Cluster Compounds

The reaction of cobalt carbonyl with XCY_3 (X = Ph, Cl, H, CO_2Et; Y = halide) in the presence of a phase transfer catalyst produced the corresponding cobalt cluster compounds (19.1). The latter compounds were catalysts for the hydroformylation of terminal, internal and cyclic alkenes; the activities decreased in the order 1-hexane > 2-octene >> cyclohexene [299].



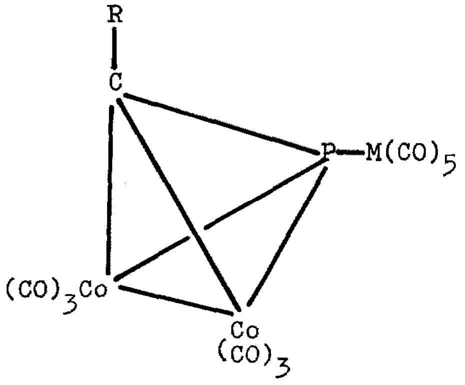
19.1



19.2

The reaction of cobalt carbonyl with $RCCl_2MCl_2$ (M = P, As) at low temperatures produced the corresponding hexacarbonyl complexes (19.2; M = P, As). The arsenic derivative was devoid of electron donor properties but the phosphorus compound formed adducts with chromium, molybdenum and tungsten carbonyls (19.3; M = Cr, Mo, W) [300]. The cobalt-iron complexes (19.4; R^1 = H, $OCOCH_3$, Me, R^2 = H, $OCOCH_3$) have been prepared from $HCCo_3(CO)_9$ and the appropriate ferrocenylmercurichloride. Cyclic voltammograms of the complex (19.14; $R^1 = R^2$ = H) exhibited two reversible waves in the potential range 1.0 to -1.0V due to the formation of a radical anion, the CCo_3-$CCo_3{}^{\bullet -}$ couple and a cation, the ferricinium-ferrocene couple. The cyclic voltammograms of the complex (19.4; R^1 = H, R^2 = $OCOCH_3$) were characterised by three redox processes. From the results it was concluded that metal carbonyl clusters were suitable redox centres for incorporation in multiple-redox and mixed-valence compounds [301].

Hydroformylation of the alkylidynenonacarbonyltricobalt cluster complex (19.1; X = OH) in the presence of dicobalt octacarbonyl gave methanol and ethanol while the same reaction with the methoxycomplex (19.1; X = OMe) gave acetone, $MeOCH_2CH_2OH$ and $MeOCH_2CH_2OCHO$ [302]. The molybdenum and tungsten tetrahedral cluster cations (19.5; M = Mo, W; R = H, Me) have been formed from the corresponding alcohols with HBF_4. The cationic charge was stabilized by the neighbouring cluster [303]. Treatment of the cobalt cluster complex (19.6) with the radical anion, sodium diphenylketyl, followed by reaction with $P(OC_6H_4Me\text{-}\underline{p})_3$ and $P(OMe)_2Ph$ produced the complex (19.7) [304]. The tetrahedral cobalt cluster compound (19.8) underwent metal exchange with the dinuclear (η-cyclopentadienyl)metal carbonyls $[(\eta\text{-}C_5H_5)M(CO)_{n+1}]_2$ (M = Mo, W, Fe, Ni) when one $Co(CO)_3$ unit was replaced by an isoelectronic $(\eta\text{-}C_5H_5)M(CO)_n$ unit [305].



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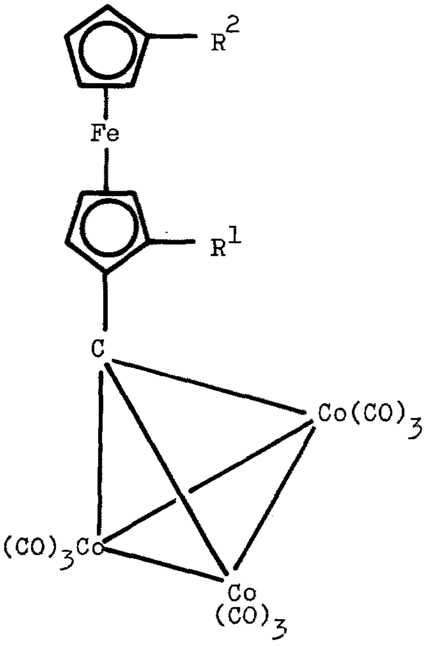

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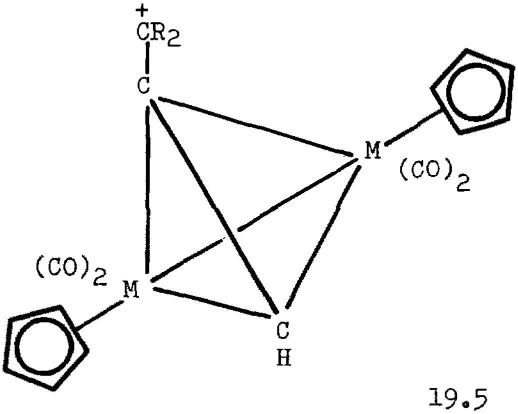
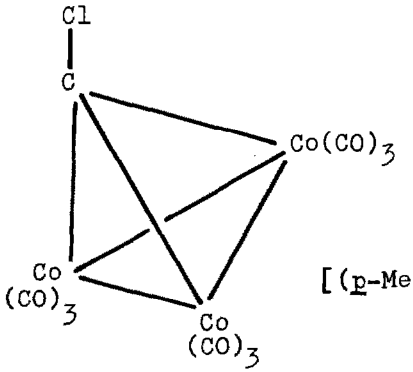


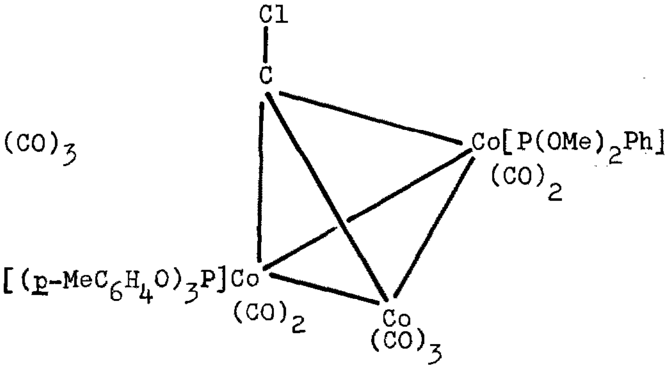
19.5

Treatment of octacarbonyldicobalt with $(\eta\text{-}C_5H_5)Fe(CO)_2SiH_3$ produced the μ^3-metallosilylidene tricobalt cluster (19.9) [306].

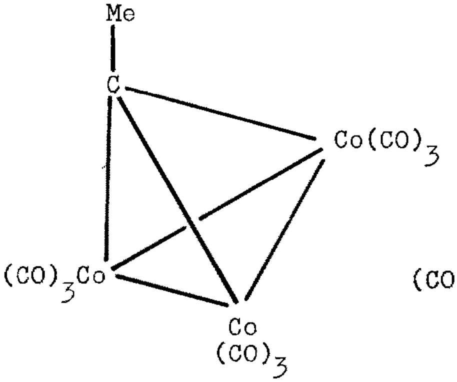
UV and photoelectron spectroscopy have been used to investigate the bonding in alkylidynetricobalt nonacarbonyl complexes (19.1; X = Cl, Br, OMe, NMe_2). The core-electron binding energy of the methylidyne carbon atom was found to be a function of the electronegativity of the group X. The core



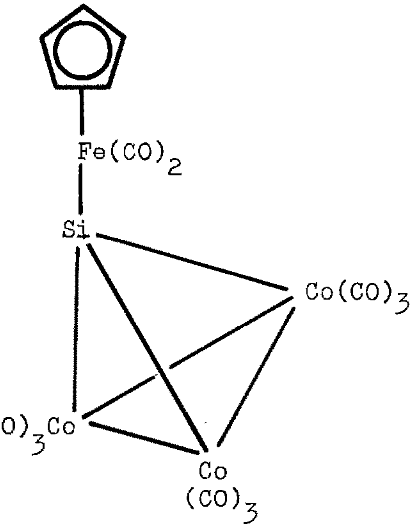
19.6



19.7



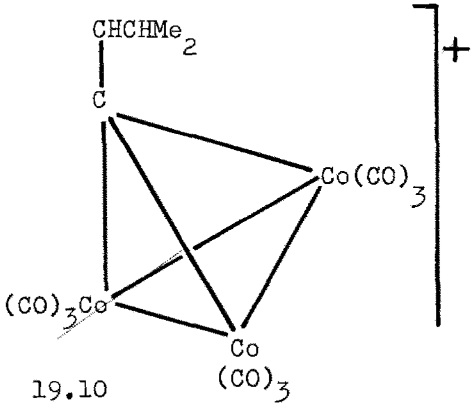
19.8



19.9

binding energies of the $[Co(CO)_3]_3$ cluster were subject to a similar, but less marked, variation. Evidence was obtained to suggest that the chloro, bromo, methoxy and dimethylamino groups behaved as π-donors towards the $[Co(CO)_3]_3$ cluster [307].
The gas-phase He(I) photoelectron spectra of the methinyltricobaltenneacarbonyl cluster complexes (19.1; X = H, Me, CF_3, CO_2Me, F, Cl, Br, I) have been measured and interpreted. The results have been used to construct a qualitative MO energy level diagram for the complexes. It was proposed that a MO of e symmetry accounted for a large part of the interaction between the triangle Co_3 and the apical carbon atom and for the electron transmission from the substituent X and the cobalt atoms by a resonance mechanism. Evidence was found for appreciable substituent X$\longrightarrow$ apical carbon atom π-bonding donation when X = Cl, Br, I [308].

He(I) photoelectron spectroscopy has been used to measure changes in the ionization behaviour of a carbyne carbon substituent as a function of the number of transition metal atom nearest neighbours in some cobalt cluster complexes including tricobaltalkylidenenonacarbonyl. The results obtained indicated that it became progressively easier to remove an electron from a localized π-orbital on a phenyl group attached to a carbyne carbon atom as the number of near neighbour cobalt atoms per



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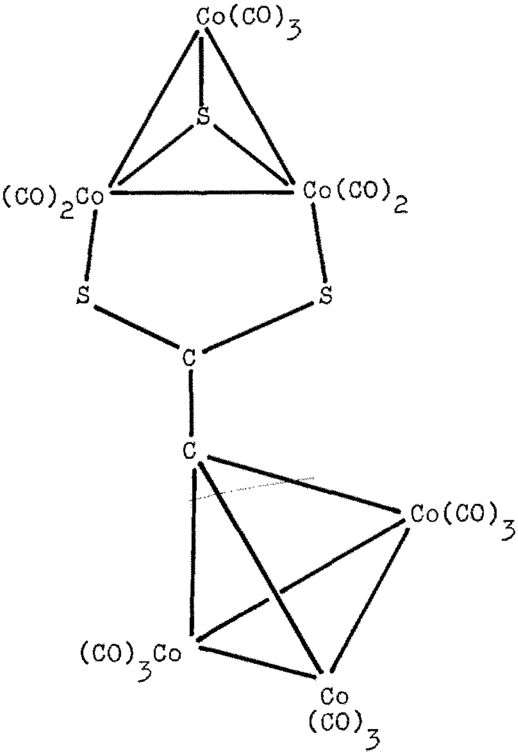
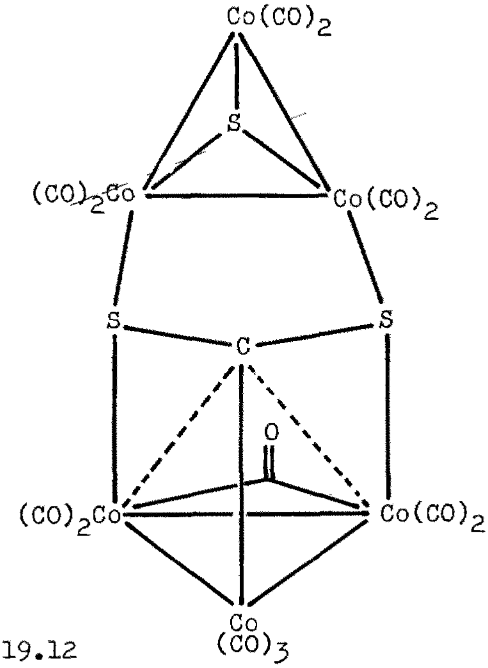


19.11



19.12

carbyne carbon increased. This suggested an increase in negative charge on the carbyne carbon as the ionization potential decreased [309]. The He(I), and in some cases He(II), photoelectron spectra of the enneacarbonylmethylidynetricobalt complexes (19.1; X = H, Me, CF_3 F, Cl, Br, I) have been measured and assigned. Ionizations corresponding to the CX moiety have been observed and the level of the bridge C $2p_{\pi}$

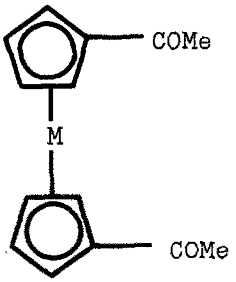
character has been observed in all of the complexes. The values of the ionization energies of this and other levels have been used to demonstrate the considerable delocalization of the p_π levels of the substituent groups X over the molecules. SCC calculations have been carried out and show good correlations with the observed results [310].

The fluxional behaviour of the carbenium ion (19.10) has been studied by variable temperature NMR spectroscopy. The methyl groups were anisochronous at -65°C which was consistent with a tilted rather than an upright side chain. The methyl resonances coalesced at higher temperatures indicating enantiomerization of the cation. The energy barrier to site exchange was determined as $\Delta G^{\ddagger} = 10.5$ kcal mol^{-1} at -52°C [311]. The structures of two compounds (19.11 and 19.12) obtained from the reaction of cobalt carbonyl with carbon disulphide have been determined by X-ray analysis. In the cobalt-cluster compound (19.12) a $(CO)_8Co_3CS_2$ entity was found in which the CS_2 fragment was bonded through the carbon atom and both the sulphur atoms to an isosceles Co_3 triangle containing an extremely short Co-Co bond [312].

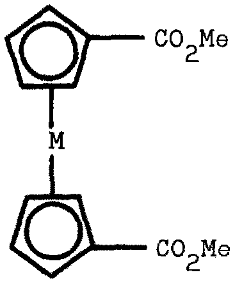
20. $(\eta\text{-}C_5H_5)_2Ni$

Nickelocene has been prepared in good yield by the reaction of nickel(II) chloride and cyclopentadiene with diethylamine in dimethylsulphoxide [313]. Sodium cyclopentadienide combined with ethyl acetate and dimethyl carbonate to form the sodium salts of the acetyl- and carbomethoxy-cyclopentadienide ions. Subsequent treatment with cobalt(II) chloride and the nickel(II) bromide-dimethoxyethane complex gave the metallocenes (20.1 and 20.2; M = Co, Ni) respectively. Several related syntheses were reported [314]. Nickelocene has been formed as one of the products from the disproportionation of the neutral (η-cyclooctadiene)(η-pentadienyl)nickel radical which was in turn generated by electrochemical reduction of the corresponding cation [315].

Nickelocene has been treated with the phosphines $Ph_2P(CH_2)_nPPh_2$, where n = 1, 2, and tetrachloromethane or tetrabromomethane in acetonitrile to form the complexes $(\eta\text{-}C_5H_5)Ni[Ph_2P(CH_2)_nPPh_2]X$, where X = Cl, Br [316]. The treatment of

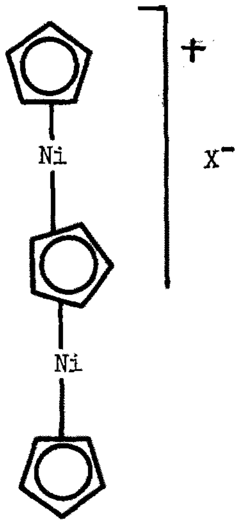


20.1

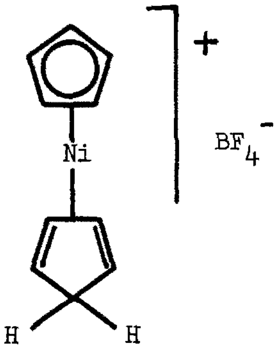


20.2

nickelocene with aluminium bromide produced the triple decker sandwich complex (20.3; X = $AlBr_4$) [317]. The reaction of nickelocene with 4-tolyl azide produced [1,4-bis(4-tolyl)tetraazabutadiene](η^5-cyclopentadienyl)nickel. The structure of this latter complex was determined by an X-ray diffraction study [318].



20.3



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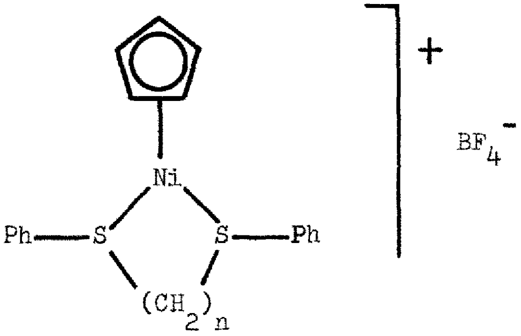
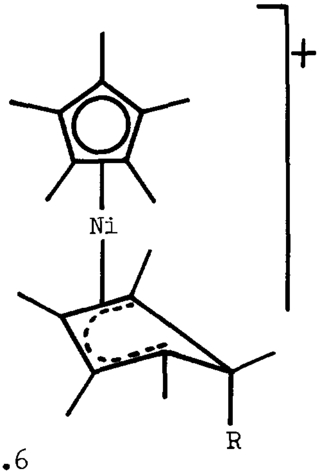


20.5

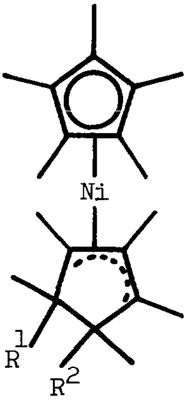
Treatment of nickelocene with tetrafluoroboric acid gave the salt (20.4) which underwent reaction with the bis(phenylthio)alkylidenes $PhS(CH_2)_nSPh$ (n = 1, 2) to give the corresponding nickel complexes (20.5). Reaction of the salt (20.5; n = 1) with nickelocene produced the triple decker complex (20.3; $X = BF_4$) [319].

Decamethylnickelocene has been shown to exist as the stable neutral sandwich complex with 20 valence electrons, as the 19-electron monocation and as the 18-electron dication. Reaction of decamethylnickelocene with electrophiles, RX (R = H, CCl_3, Bz, $PhCH_2$) gave the cations (20.6). Reaction of the cations (20.6) with strong nucleophiles, for example H^- or CN^-, produced the neutral complexes (20.7; $R^1 = H$, R^2 = H, Me, CN; $R^1 = R^2$ = CN) [320]. The effect of alkyl substitution on the mass spectrometric fragmentation of nickelocene has been examined. Among the compounds studied were the 1,1'-disubstituted complexes (20.8; R = Et, Pr, Me_2CH, Bu, Me_3C) [321].

The effects of nickelocene on the thermal decomposition of solid propellants based on ammonium perchlorate and carboxyl-terminated polybutadiene have been investigated. At atmospheric pressure the rate of decomposition of the propellant was increased but at elevated pressure the rate of decomposition was suppressed [322]. Nickelocene has been used to prepare nickel-zeolite catalysts, containing 3% nickel, for the hydromethylation of toluene [323, 324].

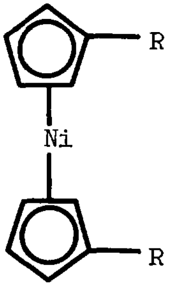


20.6

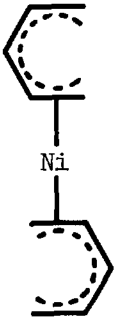


20.7

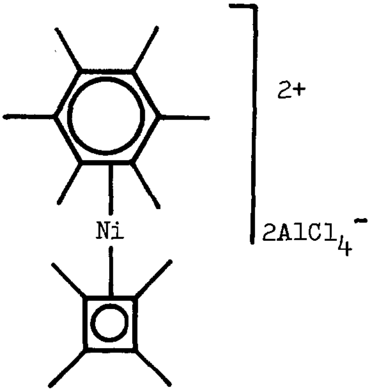
The "open-chain sandwich" complex bis(η-pentadienyl)nickel (20.9) has been the subject of a theoretical investigation using a semiempirical INDO approach. The magnitude of reorganisation effects, Koopmans' defects, in the photoelectron spectrum of the complex were calculated. The dependence of the reorganisation energies on the resonance integral and on the two-centre electron-electron interaction integral has been examined in detail [325].



20.8



20.9



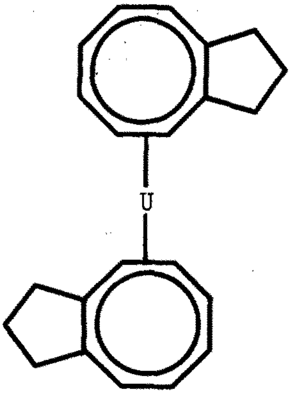
20.10

Cyclodimerization of 2-butyne in the presence of aluminium chloride gave the tetramethylcyclobutadiene complex, Me_4C_4-$AlCl_3$ which combined with tetracarbonylnickel in dichloromethane to form (η-tetramethylcyclobutadiene)nickeldichloride. Under similar conditions the (η-hexamethylbenzene)nickel complex (20.10) was obtained [326].

21. $(\eta\text{-}C_8H_8)_2U$

A method has been described for the synthesis of uranocene from uranium and cyclooctatetraene [327]. 1,1'-Dimethyluranocene has been prepared in high yield by treating the methylcyclooctatetraenyl dianion with uranium(IV) chloride [328]. Three diannulated uranocenes, dicyclopenteno-, bisdimethylcyclopenteno- dicyclohexeno-uranocene have been prepared from the appropriate cyclooctatetraene dianions and uranium(IV) chloride. The crystal and molecular structures of dicyclobuteno- and dicyclopenteno-uranocene have been determined by X-ray crystallography. The energy barriers to ring rotation in 1,1',3,3'- and 1,1'4,4'-tetra-t-butyluranocene have been determined by ^1H NMR spectroscopy as 13.1 and 8.24 kcal mol^{-1} respectively. Alkyl substitution has been found to have little effect on the electronic and magnetic properties of uranocene [329].

Isopropyltris(η^5-cyclopentadienyl)uranium(IV) underwent photolytic decomposition by homolytic cleavage of the uranium-carbon σ-bond and not by β-hydride elimination [330]. The



21.1

electronic structure of 1,1'-disubstituted uranocenes has been studied by He(I) and He(II) photoelectron spectroscopy. Changes in the electron donor-acceptor properties of the substituents had little effect on the spectra. The results were taken as evidence of comparable involvement of uranium 5f and 6d orbitals in the metal-ligand bonding. The values associated with ionizations of ligand centred π-molecular orbitals did not depend upon the nature of the substituent. This suggested that the uranium atom had the ability to restore electronic charge variation induced on the ligand [331]. Dicyclopentenouranocene (21.1) has been synthesized and characterized by X-ray crystallography. The significance of annulation in determining the physical properties of the complex was discussed [332]. The photochemistry of the actinide complexes, $Th(\eta\text{-}C_5H_5)_3R$ and $U(\eta\text{-}C_5H_5)R$, where R = CH_3, $(CH_3)_2CH$, C_4H_9, has been the subject of a mechanistic investigation. The thorium complexes gave alkenes, alkanes and $Th(\eta\text{-}C_5H_5)_3$ as the major products while the uranium complexes underwent hydrogen atom abstraction from the cyclopentadienyl groups [333].

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