ORGANIC REACTIONS OF SELECTED π-COMPLEXES
ANNUAL SURVEY COVERING THE YEAR 1971

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CONTENTS

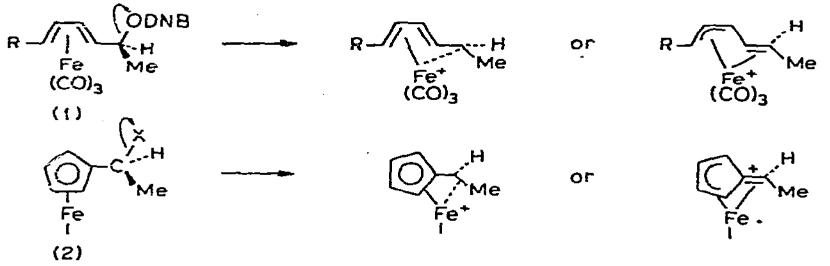
I. RESULTS OF GENERAL INTEREST

A comparison[1] of hydrogen isotope exchange rates in methyl ketones, and pK_a values in the related carboxylic acids, enabled various organometallic groups to be arranged in a series of increasing electron donor power:

	M				
	Fc	Ph	(π-C_5H_4)Mn$(CO)_3$	(π-C_6H_5)Cr$(CO)_3$	(π-C_5H_4)Re$(CO)_3$
[M] COMe (exchange)	1	45	65	145	515
[M] CO_2H (pK_a)	7.66	5.70	4.99	4.80	4.73

The relative Raman intensities for (π-C_6H_6)Cr$(CO)_3$ and (π-C_5H_5)Mn$(CO)_3$ ν(CO) modes differ, and an explanation has been advanced[2].

Protonation of certain organometallic ketones has produced species which are excellent NMR models for metal-stabilised cations. The latter have been shown[3] to be intermediates in the solvolysis of complexed dienyl esters (1) or ferrocenylcarbinyl esters (2). Detailed



DNB = dinitrobenzoate

NMR studies of these two systems, and of the uncomplexed dienones, favour a conjugative mechanism for the stabilisation of these cations by a metal atom, which is formally in the β position, rather than by any neighbouring group participation by iron.

Of the systems mentioned in last year's report[★], no new relevant results were reported for $(\pi\text{-}C_5H_5)V(CO)_4$, $(\pi\text{-}C_5H_5)Cr(CO)_2(NO)$, ruthenocene, osmocene, or nickelocene, during 1971. Most interest centred on the π-diene–$Fe(CO)_3$ complexes, and related π-dienyl–$Fe(CO)_3$ cations.

II. INDIVIDUAL SYSTEMS

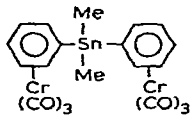
(i). $(\pi\text{-}C_6H_6)Cr(CO)_3$ (benchrotrene)

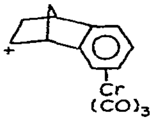
Infrared spectra of several ring- and phosphine-substituted derivatives in the 2100–1850 and 700–225 cm^{-1} regions have been assigned[4], and ^{13}C NMR spectra have been reported[5] for $LM(CO)_3$ (L = mesitylene, durene, cycloheptatriene; M = Cr, Mo, W). In the mass spectra of $LCr(CO)_3$ (L = PhMe, $PhCO_2Me$, mesitylene), binuclear ions, e.g. $[(arene)_2Cr_2(CO)_n]^+$, formed by ion–molecule reactions, are found[6]. In all cases, the most intense ions were $[(arene)Cr_2(CO)_2]^+$.

The synthesis of triphenylene–$Cr(CO)_3$ is described by Sato and coworkers[7]; the NMR spectrum indicates that the $Cr(CO)_3$ group is π-bonded to a peripheral ring. The application of GC methods to the analysis of thirteen derivatives of the parent compound is reported[8]; the NMR spectra are listed, and the mass spectrum of $(\pi\text{-PhBu-n})Cr(CO)_3$ is illustrated. Conformational equilibria between eclipsed and non-eclipsed forms were studied by NMR; the results support the idea of a conformational exchange (see AS70; 103) by variable temperature studies. The NMR spectra of substituted aniline–$Cr(CO)_3$ complexes have been investigated[9]; chemical shifts vs. Hammett σ and σ^- values give straight-line plots, showing direct interaction between the substituents and the amino group. Consequently, the transmission of resonance effects in complexed and uncomplexed benzene rings occurs via similar routes. However, the electron density at nitrogen in the $Cr(CO)_3$ complexes is less sensitive to changes caused by substituents. This results from the presence of the strongly electron-withdrawing $Cr(CO)_3$ group.

[★] See *Organometal. Chem. Rev. B*, 9 (1972) 99.

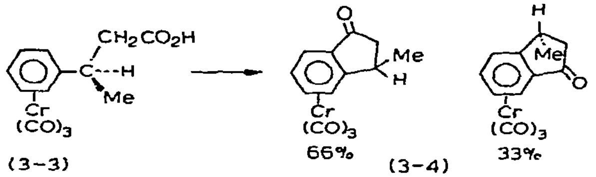
A comprehensive study by NMR, IR, Raman, ^{119m}Sn-Mössbauer, and mass spectroscopic methods of the phenyltin complexes reported last year (AS70; 101) has been described[10] Of interest is $Me_2Sn[C_6H_5Cr(CO)_3]_2$ (3-1), which shows the largest deviations from the expected properties. This is ascribed to a significant distortion from tetrahedral geometry about the tin atom, towards a *trans*-planar structure. A feature of interest in the mass spectra of these complexes is the occurrence of the $[SnCr]^+$ ion, of greatest relative intensity in the spectrum of (3-1).


(3-1)


(3-2)

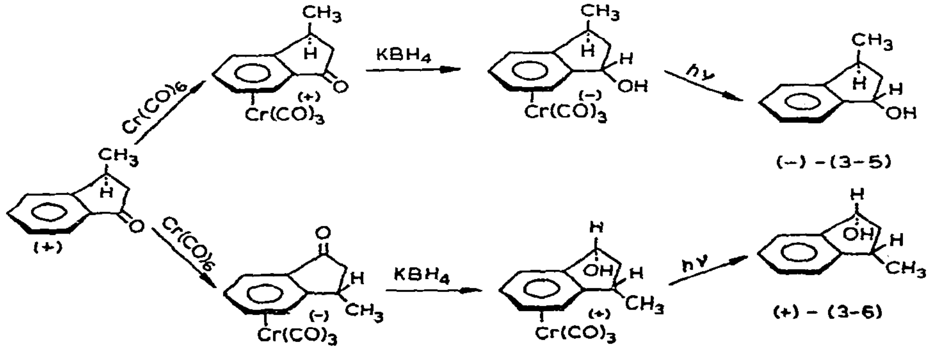
Two accounts [11,12] of the solvolysis of 2-benzonorbornenyl–$Cr(CO)_3$ methane- and *p*-bromobenzenesulphonates show that the rate enhancement at the 3-position relative to that at the 2-position (266–280-fold) indicates that an *endo*-$Cr(CO)_3$ group provides an additional driving force. This probably arises by interaction of the metal with the positive charge. A final conclusion concerning the structure of this intermediate (3-2) was not offered.

Jaouen and Dabard[13] found that polyphosphoric acid cyclisation of (3-3) afforded two ketones (3-4) (33% *endo*, 66% *exo*), showing some stereoselectivity in the reaction.



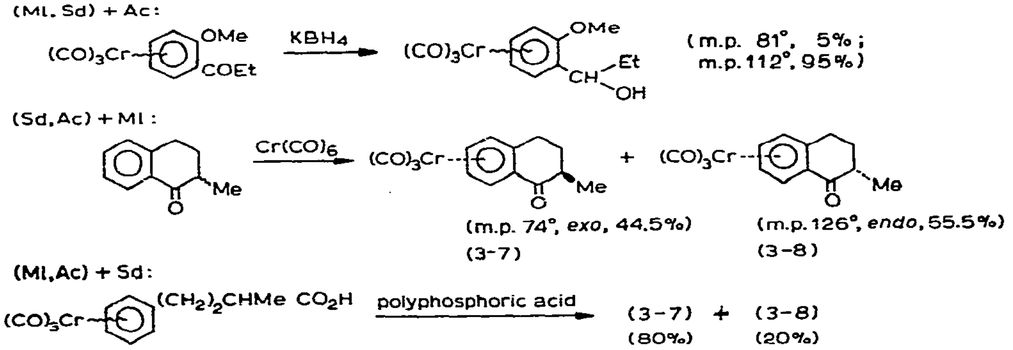
(3-3) (3-4)

Reduction with KBH_4 proceeded exclusively by *exo* attack. These complexes have been used as intermediates in the synthesis of aromatic compounds, e.g. the optically active methoxyindanols (3-5) and (3-6). Removal of the $Cr(CO)_3$ group is achieved by simple irradiation[14].



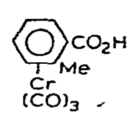
(−) −(3-5)
(+) − (3-6)

The problems associated with asymmetric induction in the benchrotrene series have been studied[15] in the context of three structural elements, termed Ml, Sd and Ac. These are, respectively, the asymmetry caused by complexation of the $Cr(CO)_3$ group to one side of the aromatic ring; by disymmetric disubstitution on the ring; and by the presence of an asymmetric carbon in a side chain. Generally, two of these elements are present in the initial substrate, the third appearing during the reaction. The three combinations used in stereochemical syntheses are thus (Ml, Sd) + Ac, (Sd, Ac) + Ml, and (Ml, Ac) + Sd, and can be illustrated by the following syntheses:

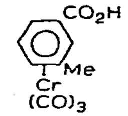


It is established that the reaction sequences (Ml, Sd) + Ac are highly stereoselective, whereas (Sd, Ac) + Ml afford mixtures of diastereomers in approximately equal amount. The sequence (Ml, Ac) + Sd affords the thermodynamically controlled mixture, and shows differences from analogous reactions in the ferrocene series. This is interpreted by electronic interactions, particularly with the electron density at the $Cr(CO)_3$ group.

Chemical correlations of (3-9) and (3-10), whose absolute configurations have been established by X-ray methods, with several *o*- and *m*-disubstituted benchrotrenes, have been reported[16]. Combination of these results with others previously reported enables absolute configurations of some sixty complexes to be established.

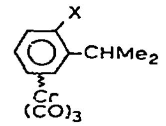


(+)-(3-9)



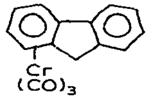
(−)-(3-10)

Chemical shift non-equivalence has been found in (3-11; X = NH_2, NMe_2, OMe) as a result of the presence of diastereomers. The difference in chemical shifts from the *gem*-dimethyl group is ca. 0.1 ppm[17].

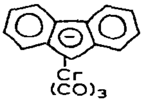


(3-11)

The isomerisation of (π-$PhCH_2SCN$)$Cr(CO)_3$ (prepared from the benzyl chloride complex with NH_4SCN) to isothiocyanate proceeds at a rate comparable to those of benzhydryl thiocyanates[18]. The mechanism probably involves a rate-determining ionisation, and a value of $2.5 \cdot 10^4$ represents the lower limit of the ability of the $Cr(CO)_3$ group to stabilise this transition state. A novel form of valence tautomerism occurs in fluorene–$Cr(CO)_3$ (3-12) and its anion (3-13). Evidence for the migration of the $Cr(CO)_3$ group from the six- to the five-membered ring is provided by the proton NMR spectra of both species[19]. The anion can be prepared by treatment of (3-12) with KOBu-t.



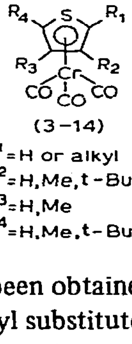
(3–12)



(3–13)

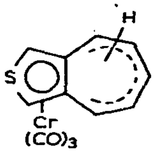
The use of arene–$Cr(CO)_3$ complexes in the stereospecific hydrogenation of dienes[20], and for the synthesis of particular glycerides[21], has been reported. Complexes of chromium, molybdenum and tungsten have also been used as homogeneous catalysts in Friedel–Crafts-type reactions, e.g. alkylation, acylation, sulphonylation, dehydrohalogenation, and polymerisation; some advantages over $AlCl_3$ are claimed[22].

A series of substituted thiophene–$Cr(CO)_3$ complexes (3-14) have been obtained by direct reaction of the thiophene with $Cr(CO)_3(MeCN)_3$ or $Cr(CO)_6$ [23,24]. Complexes have also been obtained from cyclohepta[*c*]- and -[*b*]thiophenes, together with optically active methyl substituted derivatives[24]. The complexes from 2- or 3-phenylthiophene contain the $Cr(CO)_3$ group bonded to the C_6-ring, as shown by their NMR spectra. With the fused 5–7 ring derivatives (3-15) and (3-16), spectroscopic results showed that the $Cr(CO)_3$ group was attached to the thiophene ring in the former, and to the cycloheptatriene ring in the latter. The structure of (3-16) has been determined, and confirms the proposed structure[25]. Treatment of the 5,7-dimethyl derivative with $Et_3O^+BF_4^-$ afforded the thiophenotropylium complex (3-17).

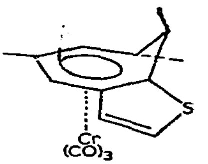


(3–14)

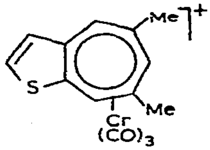
R^1=H or alkyl
R^2=H,Me,t-Bu
R^3=H,Me
R^4=H,Me,t-Bu,OMe



(3–15)

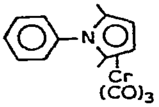


(3–16)

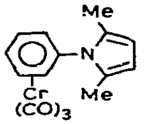


(3–17)

Complexed heterocycles have also been obtained from reactions between pyrrole, and some *N*-substituted derivatives, with $Cr(CO)_6$ or $Cr(CO)_3(MeCN)_3$ [26]. Using 1-phenyl-2,5-dimethylpyrrole and the latter reagent, complex (3-18) was formed; at higher temperatures, or with $Cr(CO)_6$, mixtures of (3-18) with the phenyl—$Cr(CO)_3$ complex (3-19) were obtained. 1-Phenylpyrrole afforded only a complex analogous to (3-19). In refluxing



(3-18)

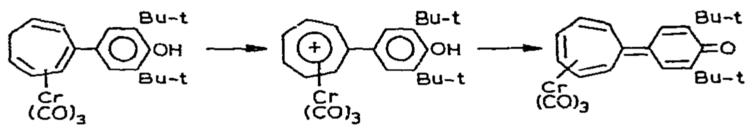


(3-19)

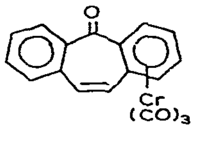
cyclohexane, the π-pyrrole complexes undergo ligand exchange reactions, e.g. with benzene.

(ii). [(π-C_7H_7)Cr(CO)$_3$]$^+$ (tropylium–Cr(CO)$_3$ cation) and derived complexes

During studies of tropylidene quinones, Pauson and coworkers[27] synthesised (5-1), from which the cation (5-2) was formed by hydride abstraction. Further reaction with triethylamine converted (5-2) to the quinone derivative (5-3). The complex with dibenzotropone contains the $Cr(CO)_3$ group bonded to the benzene ring (5-4).



(5-1) (5-2) (5-3)



(5-4)

(iii). (π-C_6H_6)$_2$Cr

The production of 99.98% pure (π-PhEt)$_2$Cr is described by Umilin and coworkers[28] Further studies into the thermal decomposition of bis-arene π complexes of chromium and molybdenum have been reported[29,30]. Such compounds are used for the preparation of pure chromium, microcircuits, and photo templates. The thermal stabilities increase in the order $C_6H_6 < MePh < EtPh <$ mesitylene[31]. Thermal decomposition affords the arene and chromium metal. The Cr^I derivatives [C(arene)$_2$]X decompose by disproportionation to Cr(arene)$_2$ and CrX_2; here the stabilities increase $Br < Cl < I$ [32]. Oxidation of [Cr(π-C_6H_6)$_2$]BPh_4 with CCl_4 affords a variety of products, including C_6H_6, PhCl, $PhCCl_3$, $PhBCl_2$, Ph_2BCl, BCl_3, and inorganic chromium(III). In the presence of cyclohexene, some dichloronorcarane is also formed, suggesting the intermediacy of dichlorocarbene[33]. Oxidation of bis-arene complexes in the presence of water forms hydrogen peroxide; using dithionite a catalytic process can be constructed[34]. The solubilities of several [(π-arene)$_2$Cr] I complexes in water have been reported[35].

One of the products of thermal decomposition of [Cr(π-arene)$_2$]BPh_4 is $CrBPh_4$. While the structure of this compound is at present unknown, it may be related to that proposed for the zwitterionic (π-C_5H_5)Ru(BPh_4), in which one of the B—phenyl groups is π-bonded to the metal[36]. Some reactions of the chromium derivative have been described; mercury(II) chloride affords PhHgCl and BPh_3, together with inorganic chromium(III), while CCl_4 or $CHCl_3$ react to give products derived from chlorocarbenes[37].

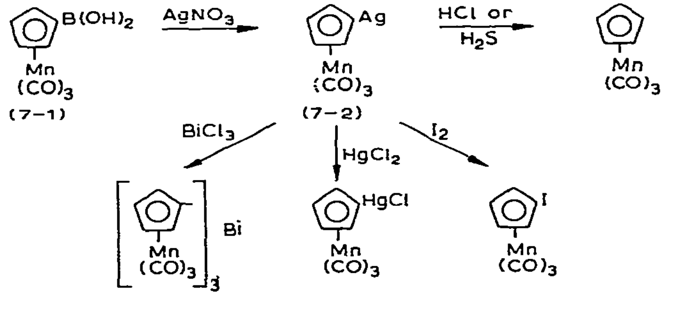
Other papers have described the ESR spectra of Cr(π-arene)$_2$ [38], and several contributions to the vibrational analyses of $Cr(C_6H_6)_2$ and $Cr(C_6D_6)_2$, including normal coordinate analyses[39], and a description of the Raman spectra[40].

(iv). (π-C_5H_5)Mn(CO)$_3$ (cymantrene)

The ^{55}Mn NQR spectra of some fifteen ring-substituted cymantrene derivatives have been reported, together with correlations with π-electron density variations[41]. These results agree with IR, NMR and UV data. Ready substitution of ring-substituted cymantrenes by phosphines to give (π-C_5H_4R)Mn(CO)$_2$(PR'$_3$) derivatives occurs on irradiation; treatment of the chloro or bromo compounds with acid results in protodehalogenation[42]. Hydrogen—deuterium exchange rates have been measured as a function of the phosphine, and increase as the electron-donor power of the phosphine increases[43]. This is paralleled by a decrease in the ν(CO) frequencies. The main contribution to the effect of the R' group is determined by the inductive rather than the conjugative effect.

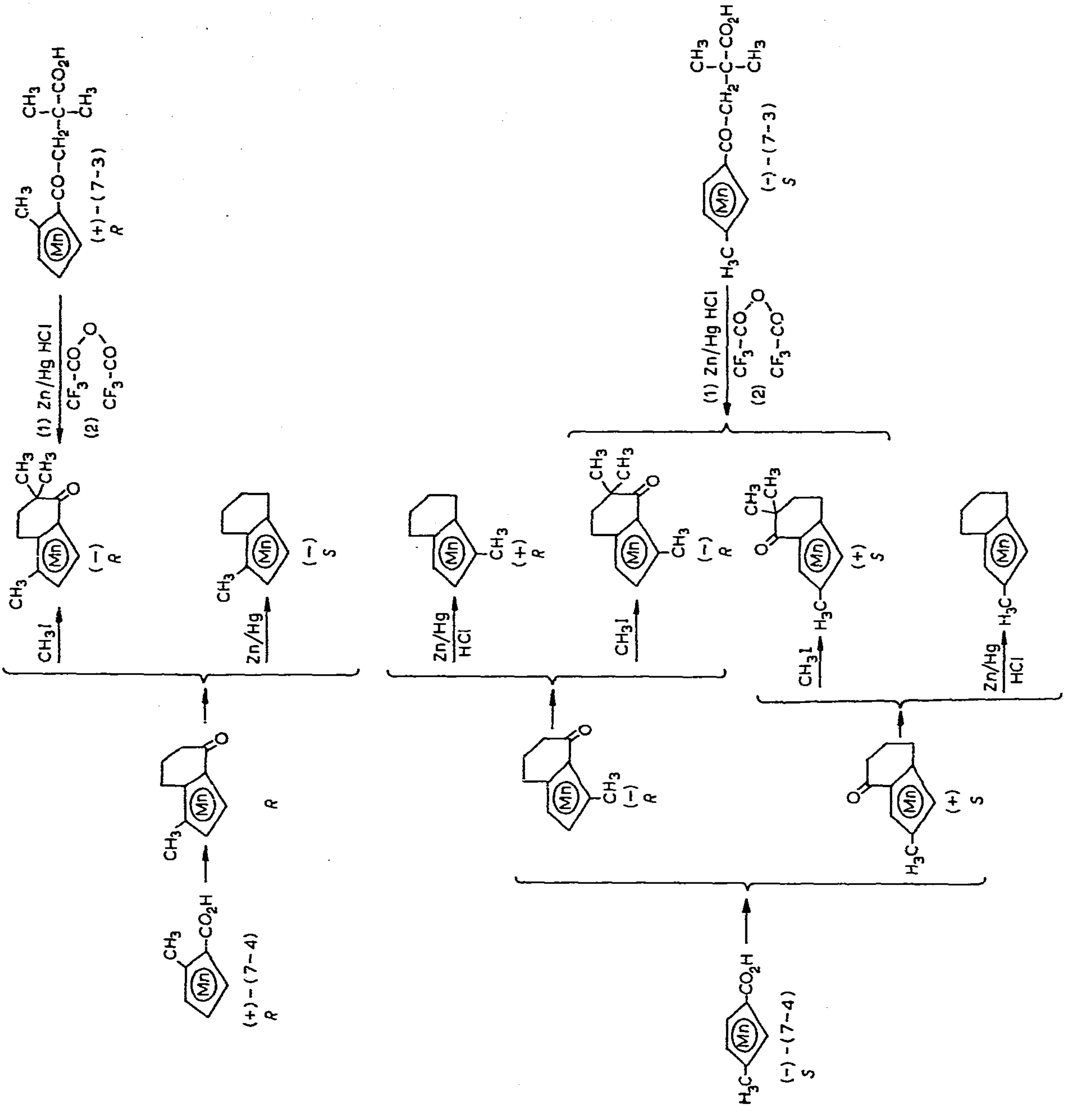
Neutron irradiation of cymantrenes results in transfer of the ring substituent to manganese, e.g. $HMn(CO)_5$ and $MeMn(CO)_5$ are found in irradiated (π-C_5H_5)Mn(CO)$_3$ and (π-C_5H_4Me)Mn(CO)$_3$, respectively[44].

Exchange reactions between $Hg(GeEt_3)_2$ and Hg[Mn(CO)$_3$(π-C_5H_4)]$_2$ afford triethylgermylcymantrenes[45]. Reactions of the boronic acid (7-1) with copper salts[46] gave halocymantrenes with CuX_2 (X = Cl, Br); with copper(II) acetate, a mixture of 88% cymantrene and 10% bicymantrenyl was obtained. The interesting silver derivative (7-2), prepared from (7-1) and silver nitrate in 32—40% yield, undergoes the reactions shown[47].

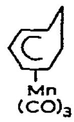


The configurations of the optically active derivatives (7-3) have been determined[48] by chemical methods, relating these acids to the oxotetramethylene compounds, and thus to the carboxylic acid (7-4).

Reactions of the acyclic 5π system in cycloheptadienyl—Mn(CO)$_3$ have been described by Pauson and coworkers[49]. The parent complex (7-5) was obtained from cyclohepta-1,3-


(+)-(7-4)
R
R
CH$_3$I
Zn/Hg
(−) R
(−) S
(1) Zn/Hg HCl
(2) CF$_3$-CO-O-CO-CF$_3$
(+)-(7-3) R
(−)-(7-4) S
(−) R
(+) S
Zn/Hg HCl
(+) R
(−) R
(+) S
(−)-(7-3) S
Mn

diene and $Mn_2(CO)_{10}$; hydride abstraction afforded the cation (7-6), which could be converted into the 6-*exo*-cycloheptadienyl complexes (7-7; X = OR, NMe_2, CN, Me or Ph). The ether (7-8) was obtained from (7-6) and NaOH. With iodide, (7-6) loses hydrocarbon, and $[Mn(CO)_4I]_2$ is isolated. Although (7-5) undergoes ready electrophilic substitution, e.g. with AcCl, to give unstable salts of (7-9), subsequent attempts to eliminate H^+ resulted in



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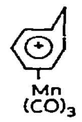

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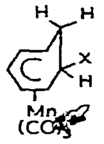
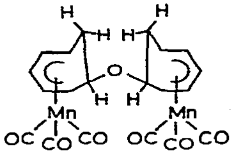


(7-7)



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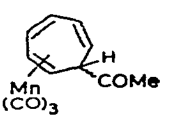


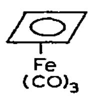
(7-9)

isolation of the metal-free 1-acetylcyclohepta-1,3-diene. The stereochemistry of the products is supported by their proton NMR spectra, which show that the substituent X is in a pseudo-equatorial position[50].

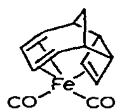
(v). $(\pi\text{-}C_4H_4)Fe(CO)_3$

Full instructions for the preparation of the parent complex (10-1) have been published in *Organic Syntheses*[51]. The procedure starts from $Fe_2(CO)_9$ and *cis*-3,4-dichlorocyclobutene in benzene, and gives a 45% yield on a 14—45 g scale. The complex has been used as a source of cyclobutadiene, and cycloaddition reactions with other organic molecules have been described[52]. Thus, irradiation of (10-1) with cycloheptatriene affords (10-2), with oxepin (10-3), and with tropone ethylene ketal (10-4). Only polymeric material was obtained from reactions using tropone itself. Degradation of (10-4) afforded the ligand, which could be converted to homopentaprismanone (10-5). In contrast, the reaction with *N*-carbethoxyazepin affords the carbonyl-free (10-6). Complex (10-1) has also been used as a key precursor in the synthesis of the $(CH)_{10}$ isomer hypostrophene (10-7), as shown in the Scheme[53].

Addition of fluoroolefins and fluoroacetylenes to cyclobutadiene—$Fe(CO)_3$ complexes gives new types of complexes, e.g., (10-8) in which a metal—carbon σ bond has been created[54].



(10-1)



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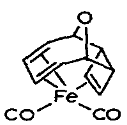

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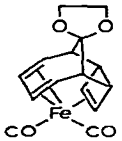

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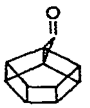

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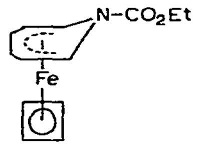
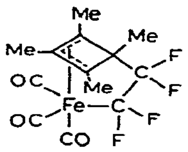


(10-6)

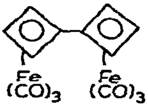
(10-7)



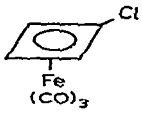
(10-8)

These reactions are thought to proceed via initial coordination of the fluorocarbon derivative to the metal, and such a complex has been obtained using hexafluoroacetone.

The synthesis of (10-1) by halogen elimination reactions with $Fe_2(CO)_9$ has been extended to the synthesis of (10-9) from 3,4-dichloro-1-bromocyclobutene[55]; this contrasts with the formation of (10-10) when the trichlorocyclobutene was used (AS70; 112). This group has extensively discussed[56,57] the proton NMR spectra of a variety of substituted cyclobutadiene–$Fe(CO)_3$ complexes, including the determination of available ^{13}C–H coupling constants within the C_4 ring. These analyses invariably rule out a rectangular ring; nearly uniform bond orders were found for all four C–C bonds.



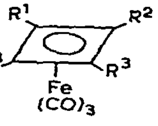
(10-9)



(10-10)

Syntheses of substituted complexes have been developed, using acetylenic precursors, e.g. nona-2,6-diyne affords (10-11), deca-3,7-diyne gives (10-12), 2,9-dimethyldeca-3,7-diyne gives (10-13), and 8-methylnona-2,6-diyne affords (10-14)[58,59]. The effect of alkyl substituents on the ν(CO) frequencies manifests itself in a progressive decrease in the values for both bands with increasing number of substituent groups and carbon atoms[60].

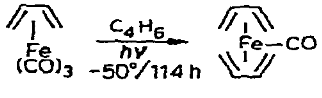
	R^1	R^2	R^3	R^4
(10-11)	Me	Me	Me	Et
(10-12)	Me	Me	Et	Et
(10-13)	Me	Me	i-Pr	i-Pr
(10-14)	Me	Me	Me	i-Pr



The synthesis of the tetraphenyl complex by ligand exchange reactions has been reported for $[(\pi\text{-}C_4Ph_4)PtI_2]_2$ and $Fe(CO)_5$ [61], and from $[(\pi\text{-}C_4Ph_4)MBr_2]_2$ (M = Pd or Ni), the latter in 78% yield[62]. The iron complex reacts with $PdCl_2(PhCN)_2$ affording $[(\pi\text{-}C_4Ph_4)Pd_3Cl_6]_2$. Improved conditions for the direct synthesis of the iron complex from $Fe(CO)_5$ and diphenylacetylene have been described[63].

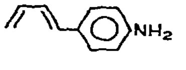
(vi). (Acyclic π-diene)Fe(CO)₃ complexes

Butadiene–$Fe(CO)_3$ (11-1) has been prepared in 65% yield by irradiating a four-fold excess of butadiene with $Fe(CO)_5$ at room temperature for two days[64,65]. Further irradiation of (11-1) with a sevenfold excess of the diene at –50° for 114 h afforded $(\pi\text{-}C_4H_6)_2Fe(CO)$ (11-2) in 21% yield.



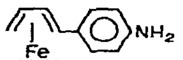
(11-1) (11-2)

The electronic effect of the $Fe(CO)_3$ group complexed to a 1,3-diene has been determined[66] via measurements of apparent pK_a values (in aqueous ethanol) of the compounds (11-3) and (11-4). The $Fe(CO)_3$ group has an electron-donor capacity similar



pK_a (app.) 3.81

(11-3)



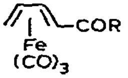
3.90

(11-4)

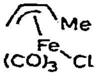
to that of phenyl in this system, i.e. complexation reduces the electron-withdrawing effect of the diene group.

Acylation of (11-1) with acetic anhydride–$AlCl_3$ in dichloromethane affords a 72% yield of (11-5); using acetyl chloride, varying amounts of the adduct (11-6) are also formed[67]. Benzoyl chloride gave the 1-benzoyl derivative. Degradation with lithium aluminium hydride gave 2-hexanol and 1-phenyl-1-pentanol, respectively. Competitive experiments showed an order of reactivity (11-1) ~ ferrocene > cymantrene > benzene. Substitution in the 1-position agrees with theoretical calculations of excess electron density at this position over that in the 2-position. Using the all valence electron SCF MO* method, the charge distribution corresponds to a mixture of excited states of the free molecule, with some negative charge on the iron atom. All butadiene orbitals are perturbed by bonding to iron, which involves both σ and π contributions[68].

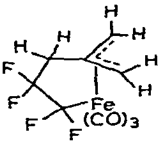
An unusual type of reaction involving diene–$Fe(CO)_3$ complexes consists in the formation of π-allylic complexes (11-7) when (11-1) or its derivatives are treated with fluoroolefins[69].



(11-5) R = Me

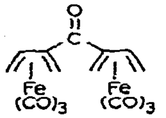


(11-6)



(11-7)

Reactions between 2-bromobutadiene and iron carbonyls have given a number of diene–$Fe(CO)_3$ complexes[70]. The major product is a carbonyl-insertion product (11-8). In more polar solvents, the carboxylic acid (11-9) is formed; several polynuclear complexes, e.g. (11-10) and (11-11) have also been obtained.



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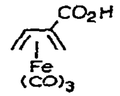

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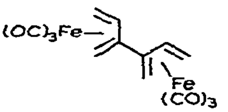
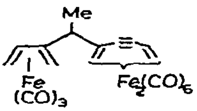


(11-10)



(11-11)

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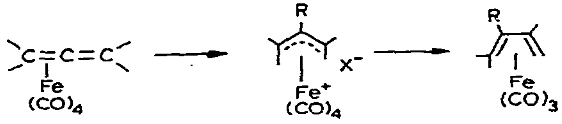
*SCF MO = self consistent field molecular orbital.

Several optically active diene–$Fe(CO)_3$ derivatives have been reported[71], including the (+)- and (–)-*trans,trans*-2,4-hexadienoic acid, aldehyde and ketone complexes. Resolution of the acid was achieved via the *S*-α-phenylethylamine salt.

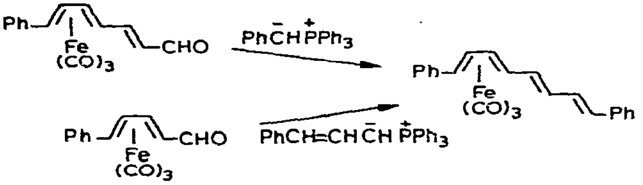
A new route to 2-substituted complexes is electrophilic substitution of the tetramethylallene–$Fe(CO)_4$ complex (11-12), followed by deprotonation (simply by warming in acetone) and loss of CO. Yields are moderate to good, e.g. (11-13; R = Ac or Bz), 60%[72].

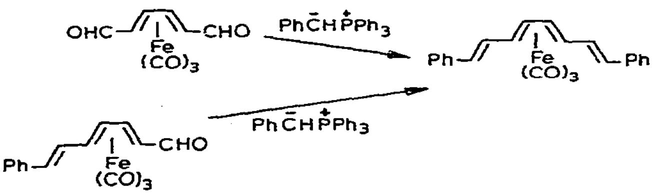


(11–12) (11–13)

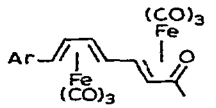
The hydrogenation of methyl sorbate, catalysed by substituted-diene–$Fe(CO)_3$ complexes, is accompanied by ligand exchange reactions[73]. A mechanism has been proposed involving a common metal complex intermediate for the various observed processes. This intermediate would be four-coordinate, and undergoes oxidative-addition or ligand-replacement reactions.

The preparation of a number of isomers of polyene–$Fe(CO)_3$ complexes during a study of their interconversion is described by Whitlock and coworkers[74]. The equilibrium position is little affected by the substituents, although rates of interconversion are influenced by electronic factors. The complexes were readily synthesised by stereoselective Wittig reactions with aldehyde–$Fe(CO)_3$ complexes as illustrated, which introduces *trans* double bonds:

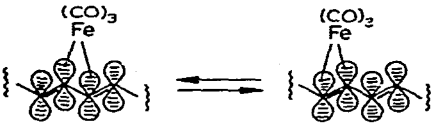




The bis-$Fe(CO)_3$ derivative (11-14) could be isolated from reactions with the heptatrienals. The pure isomer of the tetraene complex may be converted to the equilibrium mixture by heating, and consequently reactions between 1,8-diphenyl-octa-1,3,5,7-tetraene and $Fe_3(CO)_{12}$ afford the equilibrium mixture as shown. Kinetic results suggest isomerisation via the formation of a monoene–$Fe(CO)_3$ intermediate (11-14a). In the case of the

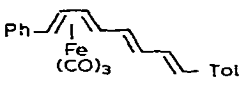


(11–14)

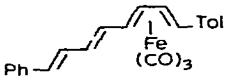


(11–14a)

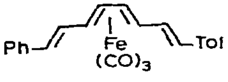
asymmetric octatetraene isomers (11-15) and (11-16), the data suggest that (11-17) is not necessarily involved, and that migration of the $Fe(CO)_3$ group along the polyene is competitive with *trans–cis* isomerisation of two adjacent double bonds, followed by formation of the diene–$Fe(CO)_3$ complex.



(11-15)

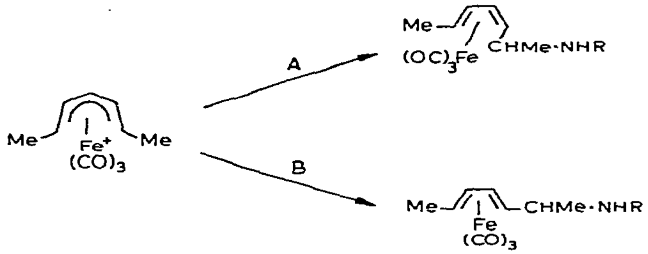


(11-16)

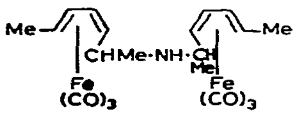


(11-17)

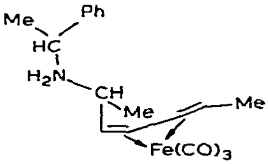
Addition of strongly basic amines to *syn,syn*-1,5-dimethylpentadienyl–$Fe(CO)_3$ salts proceeds via *exo* attack of the nucleophile on the coordinated dienyl group to give *cis,trans*-dienylamine–$Fe(CO)_3$ [75]. With amines which are only weak bases, the *trans,trans* isomer is formed with geometrical inversion. Thus path A is favoured if R = Et, i-Pr, benzyl, i.e. with amines of pK_a 3–6; path B when R = p-BrC_6H_4, m-$NO_2C_6H_4$, i.e. with pK_a 10–13. Amines of intermediate pK_a value (8–9) show both types of behaviour.



Using ammonia, route A is followed, but accompanied by further reaction to afford two diastereomers of (11-18) (racemic and *meso* forms). The two types of behaviour can be rationalised on the basis of kinetic (path A) or thermodynamic (path B) control. The stereochemistry of the products was initially determined from their proton NMR spectra, and confirmed by an X-ray determination of the structure of the (–)-2-(*S*)-α-methylbenzylammonium-*cis,trans*-heptadienyl complex (11-19) [76].



(11-18)

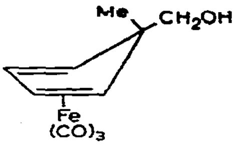


(11-19)

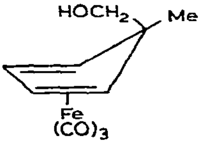
(vii). (Cyclic diene)–Fe(CO)$_3$ complexes

(a) C$_5$ systems. Geometrical isomerism in the cyclopentadiene–$Fe(CO)_3$ series was observed in the products of the reaction between 5-hydroxymethyl-5-methylcyclopentadiene with $Fe_2(CO)_9$, when (11-20) and (11-21) were obtained in a 4/1 ratio[77]. The

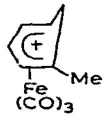
5-carboethoxy complex was obtained in one form only, corresponding to (11-20). The stereochemistry was determined from the proton NMR spectra; in particular the *exo* and *endo* methyl groups resonated at ca. τ 9.3–9.4 and 8.7–8.8 respectively. Heterolysis of the *exo*-tosyl derivative of (11-21) with HBF_4/Ac_2O affords the 1-methylcyclohexadienyl–$Fe(CO)_3$ cation (11-22) via a ring expansion reaction, facilitated by neighbouring group participation[78]. The *endo* isomer does not rearrange under these conditions; instead decomposition to CO and inorganic Fe^{II} occurs.



(11-20)

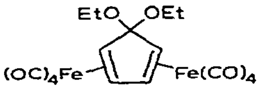


(11-21)



(11-22)

Reactions between $Fe_2(CO)_9$ and cyclopentadienone ketals give three complexes, (11-23), (11-24) and (11-25)[79]. The formation of the latter two from (11-23) on heating was demonstrated. Further pyrolysis of (11-24) affords the 1,1′-dialkoxyferrocene.



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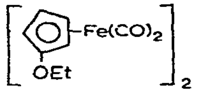
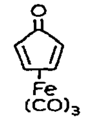
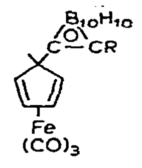


(11-24)



(11-25)

A novel rearrangement reaction affording cyclopentadiene–$Fe(CO)_3$ derivatives was found[80] in the reactions between *o*-carboranecarboxylic acid chlorides with the anion $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$, when the complexes (11-26; R = Me or Ph) or (11-27) were obtained. This rearrangement appears to be peculiar to the *o*-carboranyl series. On heating to 180° (refluxing decalin), the substituted π-cyclopentadienyl complexes are formed, and at 200°, conversion to the ferrocenes occurs.



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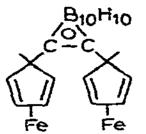
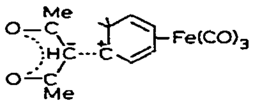


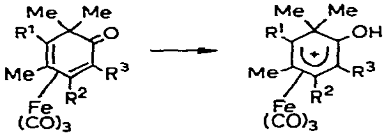
(11-27)

(b) C_6 systems. The nucleophilic addition of β-diketones to cyclic dienyl–$Fe(CO)_3$ has been examined kinetically[81]; the reaction gives substituted diene complexes. The influence of the dienyl group, the metal, and of other ligands was investigated, as well as of the diketone. The results indicate a direct attack on the organic moiety, with a possible transition state of the form shown (11-28). Similar rate constants are found for the iron and osmium compounds, suggesting that the metal is not involved. Comparison with the cycloheptadienyl complex, which reacts several times slower, suggests that steric effects are important.



(11-28)

Several complexes of type (11-29) were prepared from methylated cyclohexadienones, and converted to hydroxypolymethylbenzenonium–Fe(CO)$_3$ cations (11-30)[82].



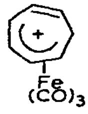
(11-29) (11-30)

R = H or Me(CD$_3$)

Complexation reduces the tendency toward rearrangement of the free ion. The action of concentrated sulphuric acid on 1- or 2-methoxycyclohexa-1,3-diene–Fe(CO)$_3$ complexes converts them to dienyl–Fe(CO)$_3$ cations. The products are independent of the position of unsaturation; some methylated derivatives can be isomerised[83].

In HBF$_4$/HOAc/Ac$_2$O, equilibration does not occur. Loss of OMe from the allylic position is preferred, with the methyl group on an "inner" complexed carbon atom. Generally, equilibration of the complex system tends to move the diene system towards the methyl group, and away from the methoxy substituent.

(c) C$_7$ systems. The fluxional behaviour of the cycloheptatrienyl–Fe(CO)$_3$ cation (11-31) has been compared with that of the isoelectronic neutral manganese derivative[84]. Coalescence of the signals in (11-31) occurs at –50°, compared with 27° for the manganese complex, i.e. increase in charge, and hence decrease in back-bonding, results in a slower rate of tautomerism. Exchange (H–D) in the neutral complex (11-32) occurs rapidly in NaOMe–MeOD, whereas cycloheptatriene does not exchange under these conditions. The *exo*-7-D derivative is formed[85]. Exchange may occur via proton abstraction to form an anionic species. Evidence for the formation of this anion comes from the reaction of (11-32) with LiBu-n at –78°, which affords a viscous red oil. The proton NMR spectrum of this material is consistent with a fluxional anion $[(C_7H_7)Fe(CO)_3]^-$, isoelectronic with the known $C_7H_7Co(CO)_3$.



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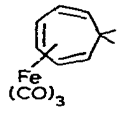
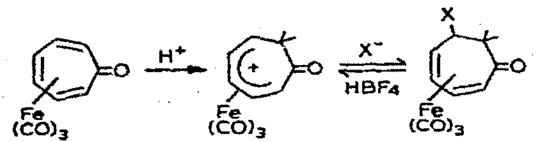


(11-32)

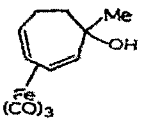
Tropone–Fe(CO)$_3$ (11-33), obtained from tropone and Fe$_2$(CO)$_9$, is protonated in concentrated sulphuric acid to form (11-34) rather than a hydroxy species[86]. Quenching in methanol affords (11-35), which with HBF$_4$/Ac$_2$O gives the tetrafluoroborate of (11-34). Azide reacts with (11-34) to give (11-36). Deuteration studies in D$_2$SO$_4$ suggest a 1,2-shift of the dienyl–Fe(CO)$_3$ system around the ring, via a keto–enol mechanism.



(11-33) (11-34) (11-35) X = OMe
(11-36) X = N_3

The effect of a lanthanide shift reagent, tris(2,2,6,6-tetramethylheptanedionate)europium, on the proton NMR spectra of a number of diene–$Fe(CO)_3$ complexes, particularly those containing cyclic 7-membered rings has been reported[87]. The maximum shift for the OH proton in (11-37) was 57.5 Hz.

A series of $Fe(CO)_3$ and $Ru(CO)_3$ complexes of 1H-1,2-diazepines has been prepared, e.g. (11-38), and a detailed discussion of their mass, Mössbauer and proton NMR spectra given[88]. Comparison with the related azepine–$Fe(CO)_3$ complexes indicate that similar geometries obtain for both types of complex.



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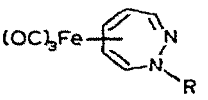
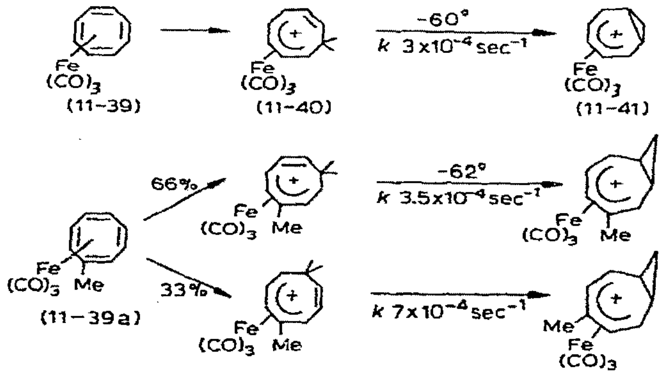


(11-38)

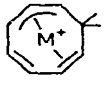
(d). C_8-systems. Wide-line NMR spectra of some cyclooctatetraene–$Fe(CO)_3$ complexes are temperature dependent, showing that distortion and reorientation of the ring occurs in the solid state[89]. Low temperature protonation (FSO_3H–SO_2F_2, −120°) of (11-39) affords the cyclooctatrienyl complex (11-40), which undergoes a first-order electrocyclic ring closure at −60° to the bicyclo[5.1.0]octadienyl complex (11-41)[90]. Similar experiments with the methylcyclooctatetraene complex (11-39a) demonstrate the formation of a 2/1 mixture of isomeric complexes (11-42) which rearrange to the bicyclic derivatives (11-43)[91]. These results are only consistent with protonation at the internal positions of the free diene moiety.



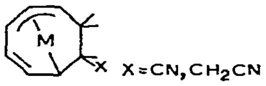
(11-39) (11-40) (11-41)

(11-39a) (11-42) (11-43)

The analogous ruthenium and osmium systems behave differently. Initially a bicyclic cation is formed, which then undergoes a ring-opening reaction to give a new type of cationic C_8H_9 complex. Thus (11-44) isomerises in HBF_4–Ac_2O to (11-45) in which the metal is bonded via a π-allyl and π-ene system. In CD_3CN the reaction is reversed over long periods of time. The cation reacts with CN^- or CH_2CN^- to give the products expected from nucleophilic attack on the coordinated olefin (11-46). This contrasts with addition to π-allylic systems coordinated to Co^I, Rh^I or Ir^I. The osmium system forms two isomeric cations on protonation, analogous to (11-44) and (11-45).

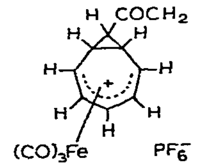


(11-44)

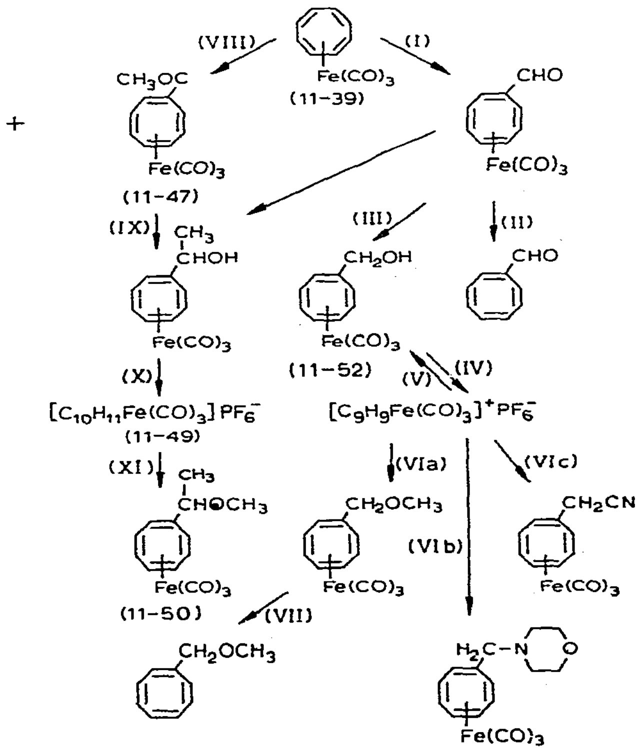


(11-45)

Cyclooctatetraene–$Fe(CO)_3$ can be acylated under Friedel–Crafts conditions to give (11-47; R = Ac), and a bicyclic cation (11-48). Other products of electrophilic substitution and addition have been isolated (see Scheme)[93]. Treatment with Ce^{IV} results in cleavage of the ring–metal bond, and provides a route to substituted cyclooctatetraenes. Evidence for the structures of these complexes was obtained from their proton NMR spectra, together with protonation experiments. The cations resulting from protonation, e.g. (11-49), react with methoxide, affording (11-50). Transformation of the acetyl complex

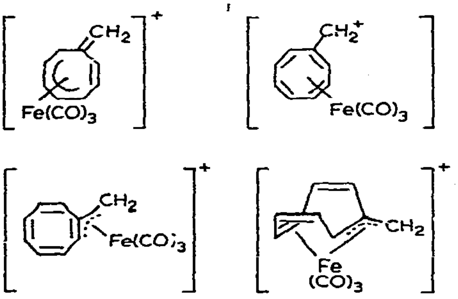


(11-48)



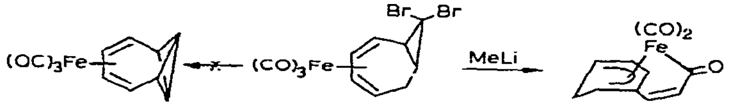
Reagents:
i, DMF–$POCl_3$
ii, $Ce(NO_3)_4 \cdot 2NH_4NO_3$
iii, $NaBH_4$
iv, 64% aqueous HPF_6
v, H_2O
vi, a, MeOH, b, morpholine, c, NaCN
vii, $Ce(NO_3)_4 \cdot 2NH_4NO_3$
viii, MeCOCl–$AlCl_3$
ix, $NaBH_4$; 64% aqueous HPF_6
x, HPF_6
xi, MeOH

to the methoxymethyl derivative is described, followed by conversion to a carbonium ion, the structure of which is discussed. No definite conclusion concerning this cation, for which four structures may be written (11-51), was reached. The formyl derivative was also prepared, and undergoes several conventional organic reactions, e.g. conversion to the alcohol (11-52).



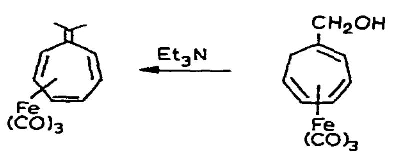
(11–51)

The unusual cyclohexadienyl complex (11-53), whose structure was confirmed by an X-ray determination[44], was obtained by the action of methyllithium on complex (11-54); the anticipated tricyclo$[5.1.0.0^{2,8}]$octa-3,5-diene complex (11-53a) was not formed.

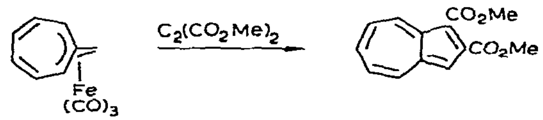


(11–53a) (11–54) (11–53)

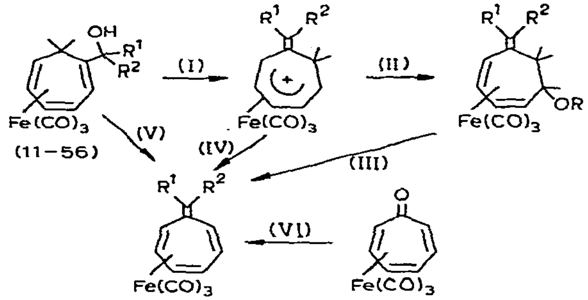
(e). Other diene–Fe(CO)$_3$ complexes. Three groups have described syntheses of complexed heptafulvene derivatives. Thus Ehntholt and Kerber[95] obtained (11-55) in 25% yield from a reaction between 7-hydroxymethylcycloheptatriene and $Fe_2(CO)_9$; their interpretation of the proton NMR spectrum suggested a trimethylenemethane type structure. With $C_2(CO_2Me)_2$, the azulene derivative (11-55a) was formed. Lewis and coworkers[96] found that alcohols (11-56) readily eliminate ROH to give derivatives of heptafulvene complexes. However, attempted dehydration of the hydroxymethylcycloheptatriene complex afforded only the dimer, $C_{16}H_{16}Fe_2(CO)_6$. The proton NMR spectra of these derivatives were interpreted on the basis of a diene–Fe(CO)$_3$ structure. A complex isomeric with (11-55) has been obtained[97] by reaction of triethylamine with the complex (11-57), and is formulated as the parent complex, containing a diene–Fe(CO)$_3$ system (11-57a). The complex slowly (20 h/78°) dimerises. It can also be protonated by strong acids, and forms an adduct with $C_2(CO_2Me)_2$.



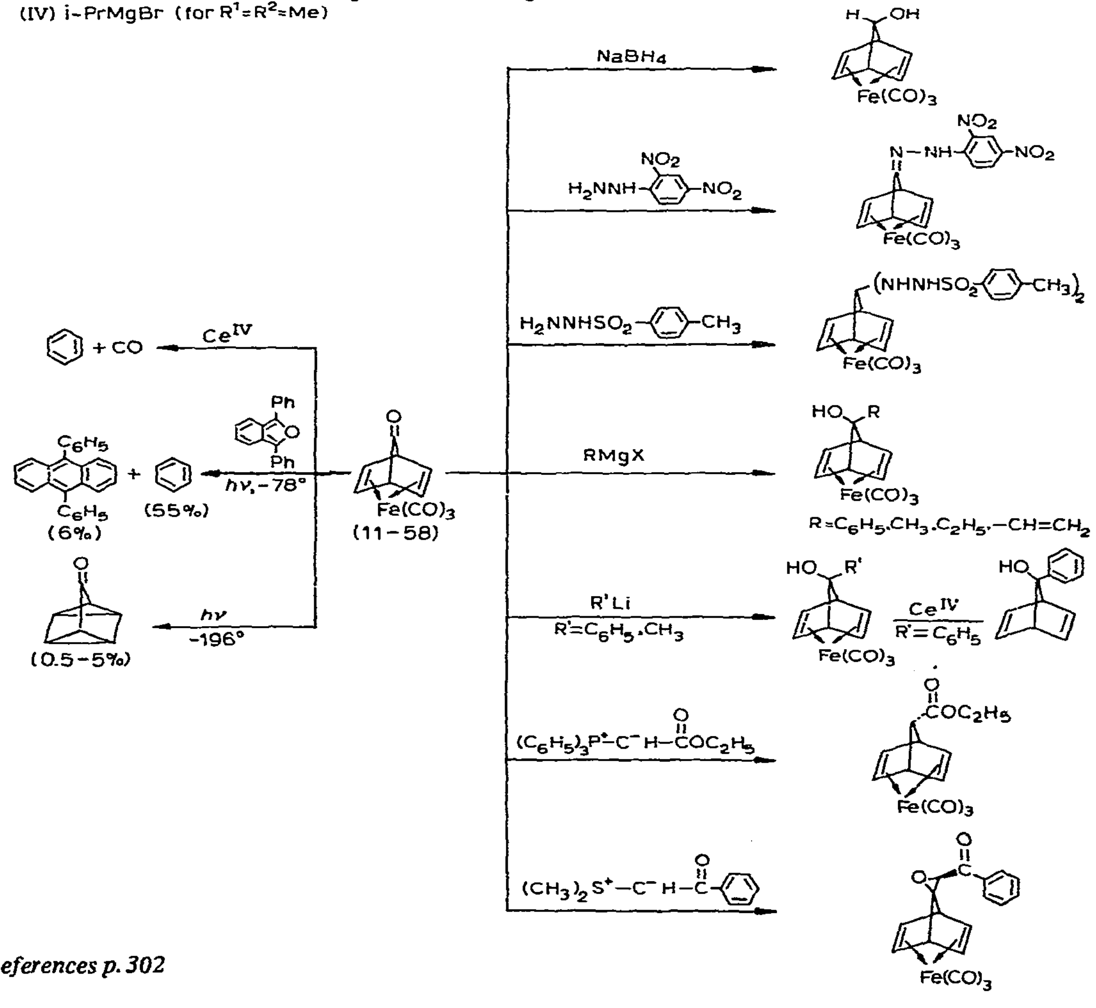
(11–57a) (11–57)



(11−55) (11−55a)

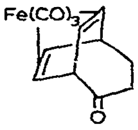


$R^1 = H; R^2 = Ph, PhCH;$ $R^1 = R^2 = Ph;$
(I) Addition of H^+; (II) Addition of OR^- ($R = H, Me$);
(III) Elimination of ROH; (IV) Et_3N; (V) Loss of H_2O
(IV) i-PrMgBr (for $R^1 = R^2 = Me$)

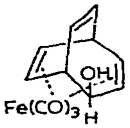


7-Norbornadienone–Fe(CO)$_3$ (11-58) has been synthesised by oxidation of the alcohol with pyridine–SO$_3$ in dimethyl sulphoxide, and the organic chemistry has been investigated (see Scheme)^{98}. In addition, the photochemical behaviour has been explored as a possible route to the unknown 7-norbornadienone. At −196°, irradiation afforded quadricyclanone (11-59); in the presence of trapping reagents, only benzene and 9,10-diphenylanthracene (with 1,3-diphenylisobenzofuran) were found. These results support the existence of 7-norbornadienone as a highly unstable short-lived intermediate.

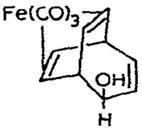
A new route to bicyclo[3.2.2] nonadienyl–Fe(CO)$_3$ derivatives involves reaction of bicyclo[3.2.2]nona-2,6,8-trien-4-ol with Fe$_2$(CO)$_9$ ^{99}. Protonation of either complex (11-60a or b) formed in this reaction leads to (11-61). A third complex (11-60c) from the initial reaction gave (11-62) on treatment with concentrated sulphuric acid. A tricyclic hydrocarbon forms the expected complex (11-63) with Fe$_2$(CO)$_9$; with Fe(CO)$_5$ the dimeric ketone (11-64) was also obtained^{100}. The prebullvalene ether (11-65) reacts with Fe$_2$(CO)$_9$ affording the bis-Fe(CO)$_3$ complex (11-66) in low yield. With Ce^{IV}, selective removal of one Fe(CO)$_3$ group occurs to give (11-67)^{101}.



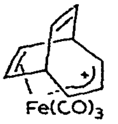
(11-60a)



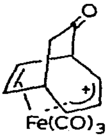
(11-60b)



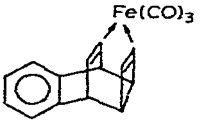
(11-60c)



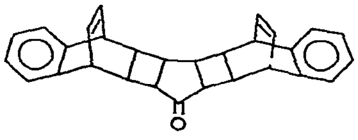
(11-61)



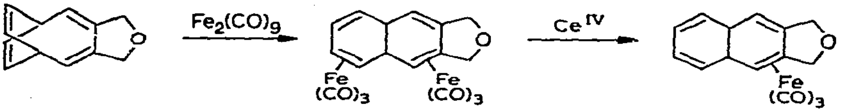
(11-62)



(11-63)



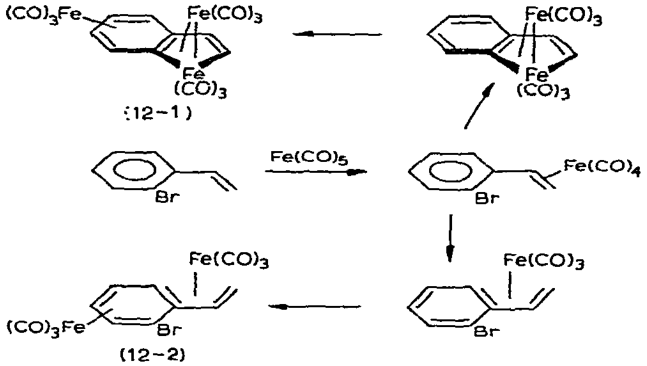
(11-64)



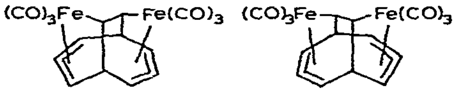
(11-65) (11-66) (11-67)

(viii). *Ferraindene and related complexes*

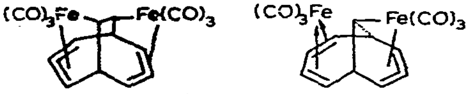
The stabilisation of metallocycles containing iron by π-bonding to a second $Fe(CO)_3$ group has been known for well over ten years[102]. The photolysis of *o*-bromostyrene with $Fe(CO)_5$ has given further examples of complexes of this type, in addition to diene–$Fe(CO)_3$ complexes derived from the organic compound[103]. The formation of complexes (12-1) and (12-2) indicates that the aromaticity of the benzene ring is readily destroyed.



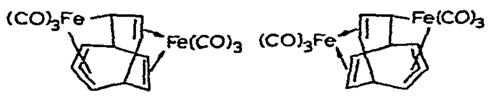
Chromatographic separation of the products from reactions between bullvalene and $Fe_2(CO)_9$ affords six isomeric complexes of formula $C_{10}H_{10}Fe_2(CO)_6$, and one complex $C_4H_4Fe_2(CO)_6$. The major product is (12-3), m.p. 133–134°, the enantiomeric forms of which are configurationally stable on the NMR time-scale. A second isomer, m.p. 172°, has been assigned structure (12-4), and also exists in enantiomeric forms which interconvert above 45°. Complex (12-4) may be formed from an intermediate, tetracyclo$[4.4.0.0^{5,7}.0^{2,10}]$-deca-3,8-diene, also thought to be involved in the thermal decomposition of bullvalene to naphthalene via 9,10-dihydronaphthalene. Above 120°, complex (12-4) rearranges to (12-5), formally a derivative of isobullvalene, via a 1,2-rearrangement of the carbon skeleton. A fourth isomer, m.p. 89°, is derived from tricyclo$[5.3.0.0^{4,8}]$deca-3,7,9-triene, and has structure (12-6). This complex also exhibits rapid valence tautomerism, as shown by its NMR spectrum[104–106].



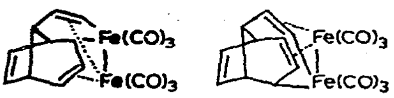
(12-4)



(12-5)



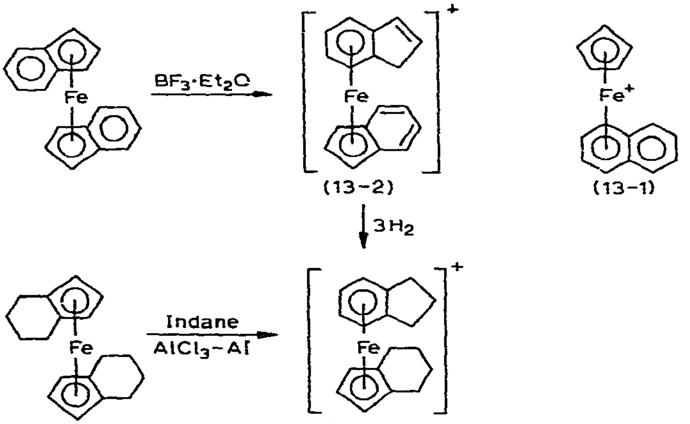
(12-3)



(12-6)

(ix). [(π-C_5H_5)Fe(π-C_6H_6)]$^+$ cation

The naphthalene complex (13-1) can exchange $C_{10}H_8$ for C_6H_6 or CO in a reducing medium, e.g. sodium amalgam in tetrahydrofuran. The latter reagent affords an intense violet colour, perhaps due to the unstable (π-C_5H_5)Fe(π-$C_{10}H_8$) neutral complex. Astruc and Dabard[108] have described the preparation and proton NMR spectra of a number of alkylbenzene derivatives, and by using substituted ferrocenes, they have also prepared some complexes containing substituted cyclopentadienyl groups. The proposed mechanism of formation of these complexes involves formation of hydrocarbon—$AlCl_3$ complexes, and cleavage of the metal—ring bond, followed by recombination to give the favourable arenecyclopentadienyliron cation. Mössbauer studies of [(π-C_5H_5)Fe(π-C_6H_5F)]PF_6 confirm a phase transition at 215 K, ascribed to a reorientation of the complex cation[109].



(13-2)

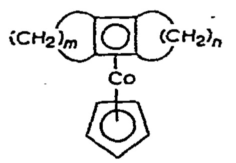
(13-1)

(13-3)

Treatment of bis-indenyliron with $BF_3 \cdot Et_2O$ and addition of ammonium hexafluorophosphate afforded (13-2) in good yield, which could be hydrogenated to (13-3). The latter was synthesised independently from bis(tetrahydroindenyl)iron, indane, and $AlCl_3$ [110]. The formation of (13-2) occurs via an intramolecular shift.

(x). (π-C_4H_4)Co(π-C_5H_5)

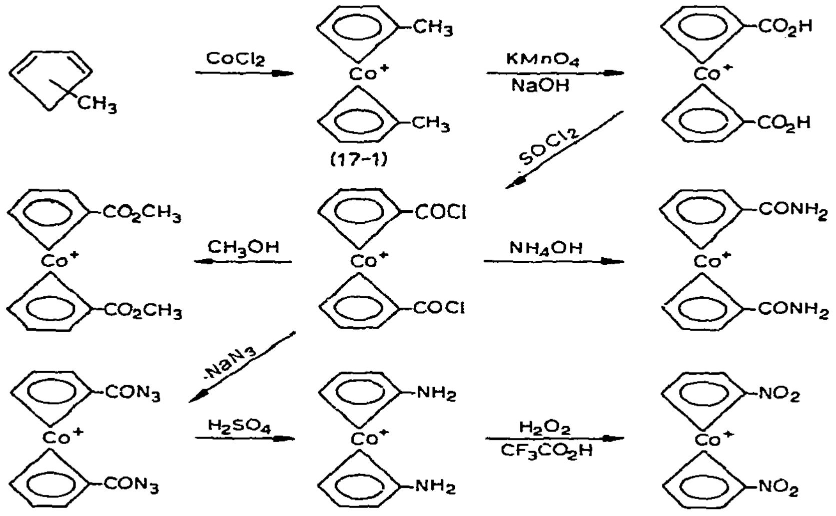
The only examples of this system reported since last year's survey are the complexes (16-1) and (16-2), prepared from (π-C_5H_5)-Co(CO)$_2$ or (π-C_5H_5)Co(π-C_8H_{12}) and the cyclic diacetylenes, cyclotrideca-1,7-diyne and cyclotetradeca-1,8-diyne, respectively. The formation of the cyclobutadiene ring occurs via an intramolecular transannular cyclisation[111].



(16-1) $m=4, n=5$
(16-2) $m=n=5$

(xi). $(\pi\text{-}C_5H_5)_2Co$ and derived $(\pi\text{-}C_5H_5)Co(\pi\text{-diene})$ complexes

The ^{13}C NMR parameters for $Co(\pi\text{-}C_5H_5)_2$ have been reported[112]. Polarographic reduction of this complex shows a reversible one-electron step; at negative potentials, the reduction to $Co(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_6)$ is irreversible. The calculated ionisation potential is 5.88 V[113]. Several ring-substituted cobalticinium salts were synthesised by El Murr and Dabard[114] (see Scheme). Polarographic reduction gave two waves, the first corresponding to the formation of the neutral cobaltocene derivative. The nature of the second reduction wave could not be determined. The key intermediate in these syntheses was the 1,1′-dimethylcobalticinium cation (17-1), which could be converted by conventional organic reactions to (17-2; R = CO_2H, CO_2Me, COCl, CON_3, $CONH_2$, NO_2 or NH_2) (cf. AS70; 125).



Syntheses of complexes (17–2)

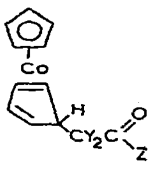
The disproportionation of dihalogeno-π-cyclopentadienylcobalt complexes in polar solvents to form cobalticinium salts has been reported by Roe and Maitlis[115]. The diiodide, probably halogen-bridged, undergoes transfer of one C_5-ring as shown:

e.g. X = I

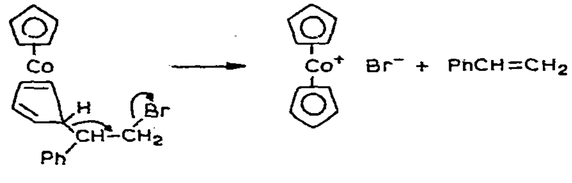
The syntheses of some homologues of the cobalticinium cation, from reactions between $[Co(NH_3)_6]Cl_2$ and the corresponding sodium cyclopentadienide, afforded the ethyl and t-butyl compounds, isolated as tribromide or hexachloroplatinate salts[116]. A new synthesis of azulene from the cobalticinium cation has been described[117].

5-*exo*-(2-Oxoalkyl) derivatives (18-1) are formed from cobaltocene and α-halocarboxylic esters or α-haloketones[118]. These products readily undergo heterolysis to form

$[Co(\pi\text{-}C_5H_5)_2]^+$ and the ketone fragment, for example, in methanol. Dibromostyrene affords (18-2), which fragments into olefin and $[Co(\pi\text{-}C_5H_5)_2]Br$. Other halogenated compounds, e.g. C_2Cl_6 or $CHBr_2CH_2Br$, also eliminate halide to form olefins in this reaction.

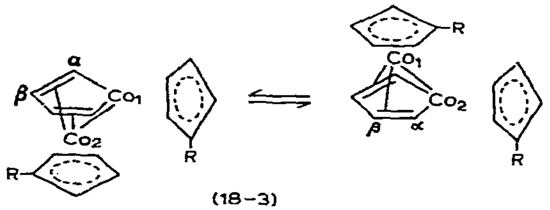


Y = H or Cl
Z = OMe or OPh
(18-1)



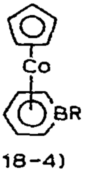
(18-2)

A novel form of fluxional behaviour is found in the complex $Co_2C_{14}H_{14}$ (18-3; R = H), obtained from $(\pi\text{-}C_5H_5)Co(CO)_2$ and photo-α-pyrone. The C_4H_4 unit exchanges σ and π bonds between the two metal atoms, resulting in the appearance of two inequivalent C_5H_5 groups. A study of the proton NMR spectrum of the carbomethoxy derivative (18-3; R = CO_2Me), prepared via the substituted cobalticinium salt as eventual precursor, indicates that the rearrangement is a reversible process; activation parameters have been determined.

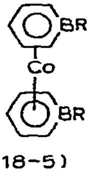


(18-3)

Reactions between organoboron dihalides or boron trihalides and cobaltocene afford an immediate precipitate of cobalticinium halide, and the soluble fraction contains mainly (18-4), together with some (18-5)[120]. The bis-borabenzene derivative (18-5; R = Br) can be obtained from cobaltocene and excess BBr_3. These complexes are paramagnetic, and have low ionisation potentials (6.2–7.2 eV).



(18-4)



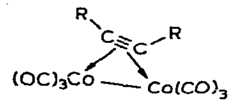
(18-5)

R = Me, Ph, Br, OH, OMe

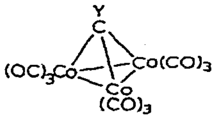
(xii). Cobalt–carbon cluster compounds

Seyferth[121] has reviewed his recent work with systems (19) and (20) at the 23rd IUPAC Congress in Boston.

Methylidenetricobalt nonacarbonyl, $HCCo_3(CO)_9$, reacts with $Hg(CH_2I)_2$ or $Hg(CH_2Br)_2$ to give $MeCCo_3(CO)_9$, via a formal CH_2-insertion into the C–H bond[122]. The complexes $CH_2DCo_3(CO)_9$ and $CHD_2Co_3(CO)_9$ could be obtained using $DCCo_3(CO)_9$, and $Hg(CD_2I)_2$, respectively. Other organomercury carbene transfer reagents, e.g. $PhHgCCl_2Br$, did not cause methylenation; only $PhCCo_3(CO)_9$ could be isolated.

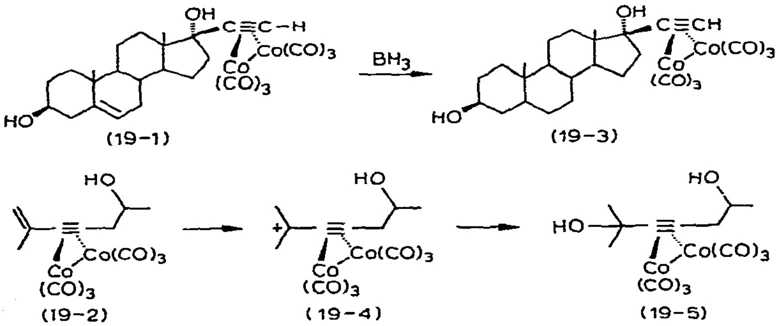


(19)



(20)

The use of $Co_2(CO)_6$ as an alkyne-protecting group has been suggested[123]. These derivatives are readily prepared from the alkyne and $Co_2(CO)_8$, e.g. (19-1) and (19-2). Reduction of isolated double bonds can then be achieved with diimide or BH_3/HOAc, e.g. (19-1) gives (19-3). Several other examples include the formation of alcohols from olefins by reaction with BH_3 followed by oxygen, e.g. the vinylacetylene (19-2) with HBF_4/HOAc formed the diol (19-5) in 91% yield, probably via the metal-stabilised carbonium ion (19-4). In contrast, the free ene-yne-ol gives only an intractable product mixture. Recovery of the alkyne from the complex is simply effected by oxidative degradation with ethanolic iron(III) nitrate.



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