IRON, RUTHENIUM AND OSMIUM

ANNUAL SURVEY COVERING THE YEAR 1974

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Contents

Iron, Ruthenium and Osmium, Annual Survey covering the year 1973 see J. Organometal. Chem., 89 (1975) 273—379.

Metal carbonyls

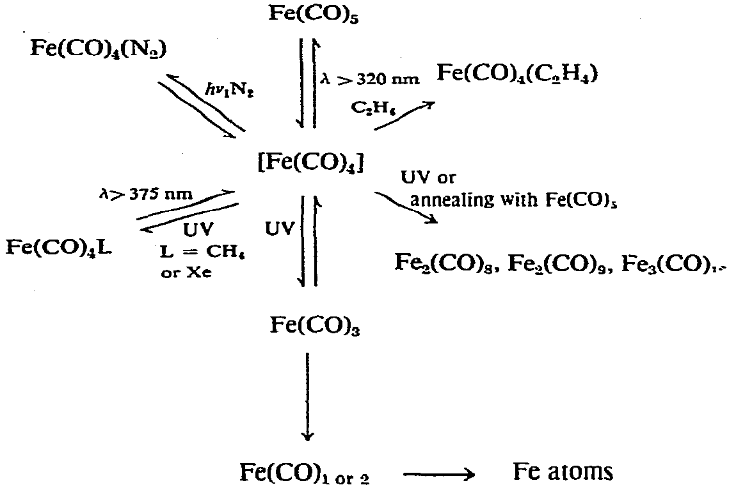
Simple carbonyls and carbonylate anions

The vapour pressure of $Fe(CO)_5$ has been measured [1] and the heat of vaporisation of liquid $Fe(CO)_5$ calculated to be 9.588 ± 0.12 kcal mol^{-1}. The structure of $Fe(CO)_4$ has been re-evaluated [2] using a combination of gas-phase electron diffraction and IR spectroscopy. This has confirmed earlier work in that the equatorial Fe—C bonds are longer than the axial ones. An analysis of the ^{13}C NMR chemical shift tensor in $Fe(CO)_5$ has been made in relation to CO and $Ni(CO)_4$, and the extent of π-back-donation estimated [3].

The synthesis of $M_2Fe(CO)_4$ (M = Na or K) has been described [4]. The optimum conditions require the use of Na/K alloy and an electron-accepting solvent, such as benzophenone or THF; the preparations are carried out at atmospheric pressure. A review of the uses of $Na_2Fe(CO)_4$ as an organic reagent has been published [5].

UV photolysis of $Fe(CO)_5$ in SF_6 or Ar matrices at 20 K followed by IR spectroscopic studies showed [6] that $Fe(CO)_4$ has C_{2v} symmetry. Photolysis in N_2 matrices afforded $Fe(CO)_4$ which reacts reversibly with the matrix forming $Fe(CO)_4(N_2)$. Analogous experiments in CH_4 or Xe matrices afforded two species, one of which is $Fe(CO)_4$ with a structure similar to those found in SF_6 and Ar matrices, and the other for which there is strong circumstantial evidence for the formulation $Fe(CO)_4L$ (L = CH_4 or Xe). $Os(CO)_5$ behaves similarly, but at

SCHEME 1



high $Fe(CO)_5$ concentrations photolysis results in the production of significant amounts of $Fe_2(CO)_8$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. The principal reactions of matrix isolated $Fe(CO)_4$ are summarised in Scheme 1. Prolonged UV photolysis of $Fe(CO)_5$ in the matrices previously mentioned led [7] to the production of $Fe(CO)_3$ which has a pyramidal (C_{3v}) structure. Further photolysis of this resulted in the formation of $Fe(CO)_x$ ($x = 1$ or 2).

The photodissociation of the ions $[Fe(CO)_4]^-$ and $[Fe(CO)_3]^-$ in the gas phase has been studied [8] by ion cyclotron resonance techniques. Dissociation of the tetracarbonyl ion affords $[Fe(CO)_3]^-$, but this tricarbonyl is not formed from $[Fe_2(CO)_6]^-$ on photolysis. However, $[Fe(CO)_3]^-$ condenses with $Fe(CO)_5$ to give $[Fe_2(CO)_6]^-$, which photodissociates into $[Fe_2(CO)_5]^-$ and $[Fe_2(CO)_4]^-$. In the presence of SF_6, the usual photodissociation curves of $[Fe(CO)_4]^-$ were observed, but $[Fe(CO)_3]^-$ was not detected. After irradiation, however, the ions $[Fe(CO)F_2]^-$, $[Fe(CO)_2F]^-$ and $[Fe(CO)_2F_2]^-$ were detected.

Monomeric species containing Group V donor atoms

In THF, $Fe_2(CO)_9$ formed a reactive intermediate which, on treatment with L (pyridine or pyrazine) gave the otherwise inaccessible compounds $Fe(CO)_4L$. In the solid state and in solution these species are trigonal bipyramidal with axial L, but the equatorial and axial CO groups undergo site exchange (^{13}C NMR spectral studies). Under 1 atm CO gas, $Fe_2(CO)_9$ reacts with THF giving $Fe(CO)_4$(THF) and $Fe(CO)_5$; the former trimerises under CO to give $Fe_3(CO)_{12}$.

By a combination of UV irradiation and heat treatment, high yields of $Fe(CO)_4L$ [L = Ph_3M (M = P, As or Sb), (*o*- or *p*-tolyl)$_3$P, Me_2PhP, $(PhO)_3P$, $(MeO)Ph_2P$, $(MeO)_3P$, $(n\text{-}Bu)_3P$] have been obtained [10]. The reaction appears to involve prior formation of $Fe_2(CO)_9$, $Fe(CO)_4L$ and $Fe(CO)_3L_2$. The first reacts with L giving $Fe(CO)_4L$ and $Fe(CO)_3L_2$, and the disubstituted species reacts with $Fe(CO)_5$ affording more $Fe(CO)_4L$. It was noted that $Fe_2(CO)_9$ is soluble in $Fe(CO)_5$.

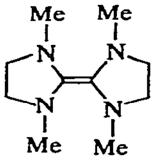
An analysis has been made [11] of the CO stretching vibrations in axially and equatorially substituted iron carbonyls. The ligands included tertiary phosphines and phosphites, carbenes and monosubstituted complexes having equatorial olefinic ligands. For axially substituted $Fe(CO)_4L$, $f(CO)$ for the ligand *trans* to L was greater than those *cis* to L by ca 0.50 mdyn A^{-1}. For equatorially substituted $Fe(CO)_4$(olefin), the two CO groups *trans* to the olefin have somewhat larger values of $f(CO)$ when compared to those of the two mutually *trans* CO groups. Furthermore, $f(CO)$ for $Fe(CO)_4$(olefin) was significantly larger than any corresponding value for axially substituted $Fe(CO)_4L$.

$Fe(CO)_5$ reacted with Me_2PNMe_2 to give [12] phosphorus-bonded $Fe(CO)_4(PMe_2NMe_2)$, and with $(PPh)_3$ in THF to give [13] $Fe(CO)_4(PPh)_3$, in which the P_3 ring remained intact. The ^{13}C NMR spectra of $Fe(CO)_{5-x}(PF_3)_x$ (x = 0—4) have been studied over the temperature range +25 to —100°, and the coupling constants $J(CP)$ and $J(CF)$ evaluated[14]; IR spectral investigations of these compounds were also made.

Treatment of $Fe(CO)_4(PF_2Br)$ with Ag_2O, $AgMnO_4$ or Cu_2O afforded [15] $(OC)_4FePF_2OPF_2Fe(CO)_4$. The structures of $Fe(CO)_4SbPh_3$ [16] and $Fe(CO)_3\{P(OMe)_3\}_2$ [17] have been reported. The antimony ligand occupies the axial site in the former while the phosphite ligands in the latter are mutually *trans* and axial.

Carbene and related acylate complexes

Reaction of $Fe(CO)_4$ with the electron-rich olefin **1** (L) gave [18] the carbene complex $Fe(CO)_4L$. Similar compounds were obtained [19] when **2** was photolysed with $Fe(CO)_5$, the sulphur being extracted as $Fe_3S_2(CO)_9$. This reaction has been extended [20] to afford carbene complexes of $Fe(CO)_4$ from **3** and its analogues, **4** and **5**, and oxygenation by O_2 readily affords the species **A**. Reaction



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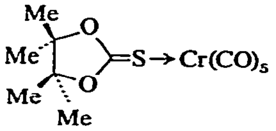

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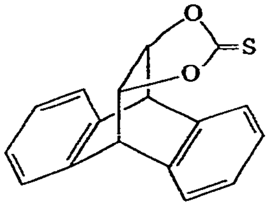

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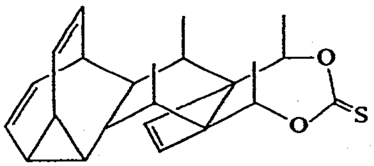

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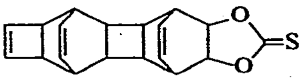

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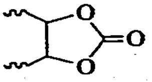
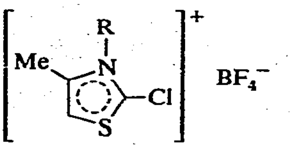
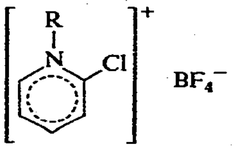


(A)



(R = Me or Et)
(6)



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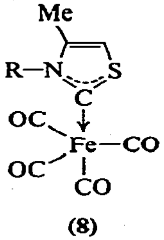

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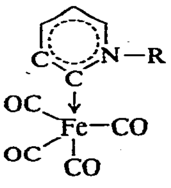
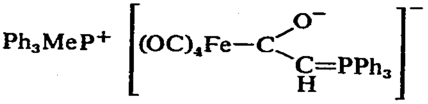


(9)

of the salts 6 and 7 with $[Fe(CO)_4]^{2-}$ gave [21] the carbene complexes 8 and 9.

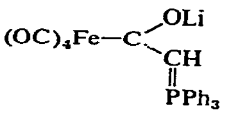
Mass spectral studies have been made [22] of the heterocyclic carbene complexes $Fe(CO)_4L$. The degradation of the metal carbene fragments, formed by successive decarbonylation of the parent ions, depends on the structure of the carbene group.

Reaction of $Fe_2(CO)_9$ with $(Ph_3P)_2C$ afforded [23] a dark brown insoluble product with the loss of one CO group. With Ph_3PCH_2, $Fe(CO)_5$ afforded the salt **10**, and with $2\text{-}Ph_3PCH_2LiBr$, the phosphonium salt $[Ph_3PMe]Br$ and **11**



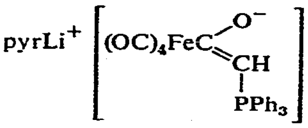
$Ph_3MeP^+\left[(OC)_4Fe{-}C\begin{smallmatrix}O^-\\ \underset{H}{C}{=}PPh_3\end{smallmatrix}\right]^-$

(10)



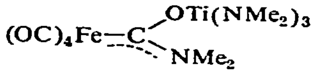
$(OC)_4Fe{-}C\begin{smallmatrix}OLi\\ CH\\ \| \\ PPh_3\end{smallmatrix}$

(11)



$pyrLi^+\left[(OC)_4FeC\begin{smallmatrix}O^-\\ CH\\ | \\ PPh_3\end{smallmatrix}\right]$

(12)



$(OC)_4Fe{-}C\begin{smallmatrix}OTi(NMe_2)_3\\ NMe_2\end{smallmatrix}$

(13)

were formed. Treatment of **11** with pyridine afforded **12**.

The alkylation of *trans*-$Fe(CO)_3L\{C(O^-Li^+)R\}$ (L = CO, PPh_3, $P(n\text{-}Bu)_3$, $P(OMe)_3$, $P(OPh)_3$; R = Ph, Me or CH_2Ph) using MeI, $MeOSO_3F$, $[THF \cdot Me][SO_3F]$ or $[Et_3O][BF_4]$ has been investigated [24]. Alkyl oxonium salts reacted exclusively at the acyl oxygen atom giving the appropriate carbene complex, whereas MeI and $MeOSO_3F$ afforded ketones and products derived from $Fe(CO)_3L$. The rate of reaction of MeI with $Fe(CO)_3L\{C(O^-Li^+)R\}$ depended on the ligand L such that it decreased in the order $L = P(n\text{-}Bu)_3 > PPh_3 > P(OPh)_3$. The formation of ketones with MeI via acylcarbonylferrates occurred at a rate too slow to suggest the intermediacy of a metal carbene species. The acylate ligand, as well as the related alkoxycarbene moiety, labilised the ligand to which it is *trans*. Thus reaction 1 occurred with facility. A kinetic study has been made

[25] of the exchange of PPh_3 in $Fe(CO)_3(PPh_3)\{C(OEt)Me\}$ by $P(n\text{-}Bu)_3$,

$$Fe(CO)_3L\{C(OX)R\} + L' \rightarrow Fe(CO)_3L'\{C(OX)R\} + L \qquad (1)$$

$(X = Li \text{ or } R)$

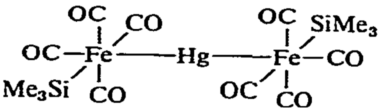
$P(OPh)_3$ and $P(C_6H_{11})_3$. The rates of reaction were independent of the nature and concentration of L′ but did depend on the nature of the carbene or acylate group. It appears that the intermediate $Fe(CO)_3\{C(OEt)R\}$ reacted with L′ at different rates, and showed a preference for more nucleophilic reagents.

Reaction of $Fe(CO)_5$ with $Ti(NMe_2)_4$ afforded [26] the complex **13**.

Complexes with Group IV ligands

Treatment of $Fe_2(CO)_9$ with KCN in acetonitrile, followed by $[(Ph_3P)_2N]Cl$, afforded [27] $[(Ph_3P)_2N][Fe(CO)_4(CN)]$. A crystallographic examination of this salt established the overall trigonal bipyramidal (C_{3v}) symmetry of the ion, in which the cyanide ligand is axial.

UV irradiation of $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe(CO)_4Br_2$ with $Hg(SiMe_3)_2$ afforded [28] *cis*-$Fe(CO)_4(SiMe_3)_2$ and $Hg[Fe(CO)_4(SiMe_3)]_2$ (**14**). It appears that the reaction could be regarded as the insertion of $Fe(CO)_4$ into the Hg—Si bond, or the oxidative addition of Hg—Si to the coordinatively unsaturated $Fe(CO)_4$ intermediate (Scheme 2). An alternative mechanism for the formation of *cis*-$Fe(CO)_4(SiMe_3)_2$ could involve the elimination of mercury from $Me_3SiHgFe(CO)_4SiMe_3$. $Fe(CO)_4(SiMe_3)_2$ is thermally stable at 120°C and does not afford $Fe_2(CO)_6(Me_3SiOC)_4$. Hence the disilyl species is not an intermediate in forming the binuclear species in the course of the reaction of $[Fe(CO)_4]^{2-}$ with $SiXMe_3$ [29].



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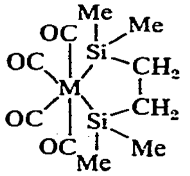


(15)

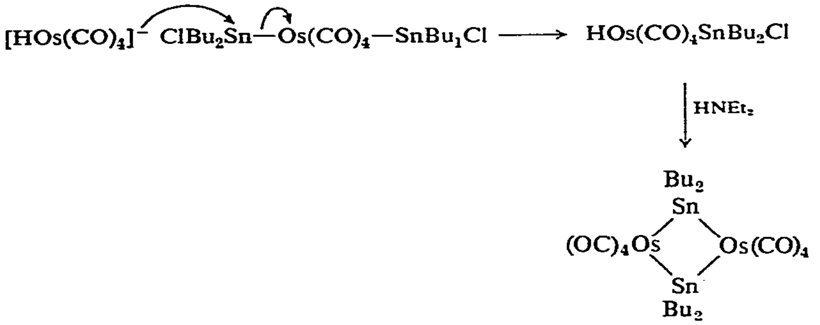
SCHEME 2

$$\begin{tikzcd}
Hg(SiMe_3)_2 + \text{“}Fe(CO)_4\text{”} \arrow[r] & Me_3Si{-}Hg{-}Fe(CO)_4SiMe_3 \arrow[d, "\text{“}Fe(CO)_4\text{”}"] \\
2\,Hg + Fe(CO)_4(SiMe_3)_2 & Hg[Fe(CO)_4SiMe_3]_2 \arrow[l, "Hg(SiMe_3)_2"']
\end{tikzcd}$$

Reaction of $Fe(CO)_5$ or $M_3(CO)_{12}$ (M = Ru or Os) with $HMe_2SiCH_2CH_2SiMe_2H$ afforded [30] the cyclic disilyl complex **15**.

Treatment of $Na_2Os(CO)_4$ with $SnXR_3$ (R = Ph or n-Bu) afforded [31] *trans*-$Os(CO)_4(SnR_3)_2$. The structure of the complex with R = Ph has been confirmed crystallographically (Sn—Os = 2.71 Å). An improved preparation of $Os(CO)_4H_2$, by treatment of $Na_2Os(CO)_4$ with H_3PO_4, has been described, and the reaction of this with $SnQR_3$ ($Q = \frac{1}{2}O$, OR' or NR'_2), in which *trans*-$Os(CO)_4(SnR_3)_2$ is formed, reported. Treatment of the dihydride with base B (Et_2NH or pyridine) afforded initially $[BH][Os(CO)_4H]$ which subsequently reacted with $SnClPh_3$ giving *trans*-$Os(CO)_4(SnPh_3)_2$. However, acidification of $Na_2Os(CO)_4$ with acetic acid, which gave $Na[Os(CO)_4H]$, followed by addition of $SnClPh_3$, afforded not only the *trans*-ditin complex, but also *cis*-$Os(CO)_4H(SnPh_3)$. Reaction of $Na_2Os(CO)_4$ with $SnCl_2R_2$ (R = n-Bu or Ph) gave $[Os(CO)_4(\mu\text{-}SnR_2)]_2$. *trans*-$Os(CO)_4(SnPh_3)_2$ reacted at $-15°$ with HCl giving *trans*-$Os(CO)_4(SnCl_2Ph)_2$, but HBr afforded *trans*-$Os(CO)_4(SnBr_3)_2$. However, direct chlorination resulted in Os—Sn bond cleavage and formation of *trans*-$Os(CO)_4Cl_2$. It was established that the *cis*-dichloride form is the thermodynamically more stable isomer. Mixtures of products were obtained with Br_2 and $HgCl_2$. Treatment of *trans*-$Os(CO)_4(SnBu_2Ph)_2$ with HCl afforded *trans*-$Os(CO)_4(SnBu_2Cl)_2$ which subsequently reacted with $HRe(CO)_5$ in the presence of Et_2NH to give $Os(CO)_4\{Bu_2SnRe(CO)_5\}_2$ as a viscous liquid. Reaction of $Os(CO)_4H_2$ with *trans*-$Os(CO)_4(SnBu_2Cl)_2$ in the presence of Et_2NH gave $[Os(CO)_4(\mu\text{-}SnBu_2)]_2$, possibly via the mechanism outlined in Scheme 3.

SCHEME 3

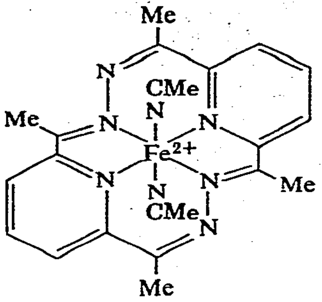


Metal nitrogen compounds and complexes containing chelating or cyclic nitrogen ligands

Carbonylation of $RuCl_3$ in boiling ethanol in the presence of NCS^- ion afforded [32] the green $[Ru_2(CO)_4(NCS)_6]^{2-}$ and the purple $[Ru(CO)_2(NCS)_4]^{2-}$, isolated as Et_4N^+ salts. The vibrational spectra of $[M(NH_3)_5L]^{2+}$ (M = Ru or Os; L = CO or N_2) have been analysed [33] by low-frequency Raman and far IR spectroscopy, and the M—L solid state vibrational modes assigned. Metal-to-ligand charge transfer transitions have been assigned [34] in the electronic spectra of the species $Fe(CO)(DMGH)_2(pyr)$ (DMGH = dimethylglyoximate ion). In these compounds the Mössbauer chemical shift can be correlated with the pK values of the pyridine ligands, and the quadrupole splitting with the CO stretching frequency.

Reaction of the complex **16** with CO in the presence of NH_4PF_6 in CF_3CH_2OH gave [35] $[Fe(CO)(NCMe)(C_{18}H_8N_6)][PF_6]_2$ ($C_{18}H_{18}N_6$ = macrocycle derived from 2,6-diacetylpyridine and hydrazine). However, carbonylation in the presence of LiCl and NH_4PF_6 in methanol afforded $[Fe(CO)Cl(C_{18}H_{18}N_6)][PF_6]$. The species **16** would not react with CO even at 2 atm in acetonitrile.

The six-coordinate low-spin phthalocyanin complexes FeL_2Pc (L = imidazole,



(16)

pyridine, piperidine or 2-methylimidazole) reversibly bind CO in toluene via a dissociative mechanism [36]. The equilibrium constant for reaction 2 decreases

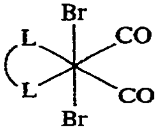
$$FeL_2Pc + CO \rightleftharpoons FeL(CO)Pc + L \tag{2}$$

in the order 2-methylimidazole > piperidine > pyridine > imidazole, and the limiting first-order rate constants for the prior dissociation of L parallel the equilibrium constant. There is a possible correlation between the reactivity of these complexes and related iron(II) porphyrin and glyoxime complexes and the stereochemistry of the proposed five-coordinate intermediates.

The octaethylporphyrin (OEP) complex $Os(O)_2(OEP)$ reacted [37] with hydrazine hydrate in THF to give $Os(N_2)(THF)(OEP)$. This species autooxidised to $Os(O)_2(OEP)$, but with CO gave Os(CO)(THF)(OEP). Reaction of OsO_4 with octaethylporphyrin in diethyleneglycolmonomethylether at about 200°C gave [38] a carbonyl species which, on treatment with L, afforded Os(CO)L(OEP) (L = MeOH, EtOH, THF, pyr, PPh_3, $AsPh_3$). With $P(OMe)_3$, the carbonyl gave $Os\{P(OMe)_3\}_2(OEP)$. The ligand L exerts a *trans* effect on CO, and IR spectral data revealed that back-bonding to the CO ligand increased in porphinato metal carbonyls M(CO)L(PORPH) in the order M = Fe < Ru < Os.

Halide, hydride and other complexes of M^{II}

Detailed syntheses for the series of compounds $M(CO)L_3HCl$, $M(CO)L_3H_2$, $M(NO)L_2Cl_3$, $Ru(CO)_3L_2$, $Ru(NO)_2L_2$, $Os(CO)_2L_2H_2$ and OsL_3H_4 (L = PPh_3, M = Ru or Os) have been reported [39]. The complex $Ru(CO)(PPh_3)_3Cl_2$ may also be obtained [40] from $Ru(PPh_3)_3Cl_2$ and CO_2 in the presence of $SiH(OEt)_3$. The polymeric $[Ru(CO)_2X_2]_n$ reacted with the ditertiary phosphines and arsines $Ph_2Q(CH_2)_nQPh_2$ (Q = P or As, n = 2 or 4; L—L) giving [41] $M(CO)_2(L—L)X_2$. When X = Cl, the complex had an all-*cis* configuration, while the bromide existed as a mixture of all-*cis* form and 17; no definite structural assignments could be made for the iodide.



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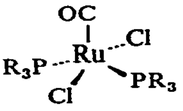

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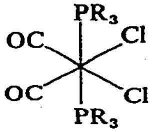
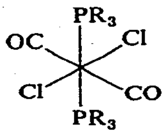


(19)

In refluxing 2-methoxyethanol, $RuCl_3$ reacted with $P(C_6H_{11})_3$ giving [42] $Ru(CO)\{P(C_6H_{11})_3\}_2Cl_2$, **18** and $Ru(CO)\{P(C_6H_{11})_3\}_2HCl$. Treatment of the former with CO afforded, in benzene, $Ru(CO)_2\{P(C_6H_{11})_3\}_2Cl_2$ (**19**) while in the solid state, **20** was produced. Carbonylation of $Os(CO)\{P(C_6H_{11})_3\}_2HX$



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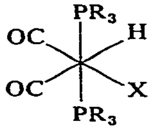
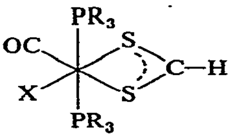


(21)

(X = Cl or Br) gave $Os(CO)_2\{P(C_6H_{11})_3\}_2HX$ (**21**). A mixture of *cis*- and *trans*-dicarbonyl complexes was obtained by treating $RuCl_3 \cdot 3H_2O$ with CO in 2-methoxyethanol and $P(C_6H_{11})_3$ under more vigorous conditions. Carbon disulphide inserted into the M—H bonds in $M(CO)\{P(C_6H_{11})_3\}_2HX$ (M = Ru, X = Cl; M = Os, X = Br) giving $M(CO)\{P(C_6H_{11})_3\}_2X(HCS_2)$ (**22** or **23**).



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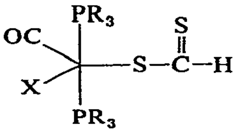
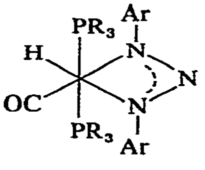


(23)

Ferrous halides reacted with $N(CH_2CH_2PPh_3)_3$ or $P(CH_2CH_2PPh_3)_3$(L) in ethanol in the presence of $NaBPh_4$ to give [43] $[FeLX][BPh_4]$ (X = Cl, Br, I). Borohydride attack on this under argon afforded $[FeLH][BPh_4]$ but similar treatment under CO produced $[FeL(CO)H][BPh_4]$.

Reaction of $M(CO)(PPh_3)_3H_2$, $Ru(CO)_3(PPh_3)_2$ or $M(CO)(PPh_3)_3HCl$ (M = Ru or Os) with diaryltriazenes afforded [44] $M(CO)(PPh_3)_2H(ArN_3Ar)$ (**24**) (Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$, p-ClC_6H_4). Under mild conditions, however, $Ru(CO)(PPh_3)_3HCl$ reacted with $(p\text{-}MeC_6H_4)_2N_3H$ to give $Ru(CO)(PPh_3)_3Cl(ArN_3Ar)$ (same configuration as **24** with H replaced by Cl).



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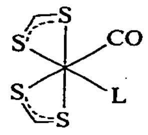
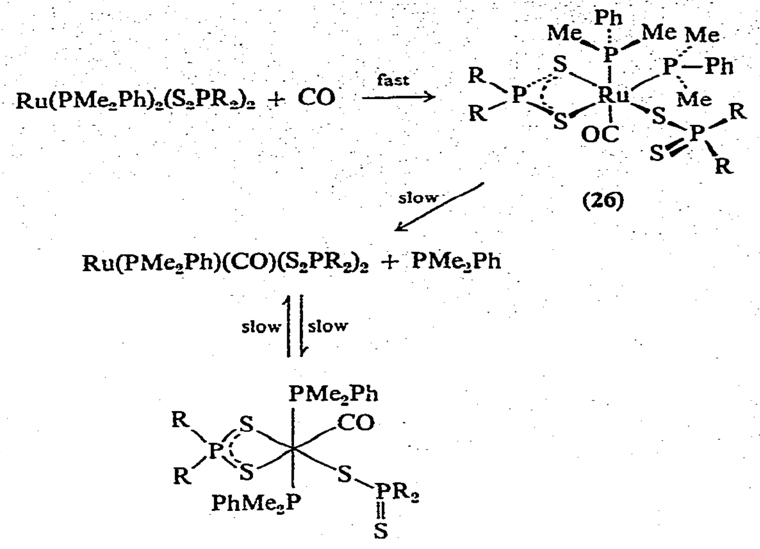


(25)

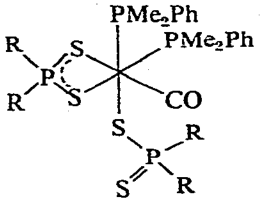
Treatment of the dithiophosphinato complexes $RuL_2(S_2PR_2)$ (L = tertiary aryl or mixed allyl/aryl phosphine, $P(OPh)_3$, etc; R = Me, Et or Ph) with CO gave [45] $Ru(CO)L(S_2PR_2)$ (**25**). Reaction of $Cs_2[Ru(CO)_2Cl_4]$ with NaS_2PMe_2, or of $Ru_3(CO)_{12}$ with HS_2PPh_2, afforded *cis*-$Ru(CO)_2(S_2PR_2)_2$, and with PR'_3, this compound afforded $Ru(CO)(PR'_3)(S_2PR_2)_2$. Prolonged carbonylation of $Ru(PMe_2Ph)_2(S_2PR_2)$ resulted in the formation of $Ru(CO)(PMe_2Ph(S_2PR_2)_2$ and $Ru(CO)(PMe_2Ph)_2(S_2PR_2)_2$. The mechanism whereby these PMe_2Ph complexes are formed is summarised in Scheme 4. There are four possible isomers

SCHEME 4



(27)

for Ru(CO)(PMe$_2$Ph)$_2$(S$_2$PR$_2$) (26—29) and the possible structures of the intermediates in Scheme 4 are indicated. The stereochemical pathway whereby 26 and 27 are interconverted is illustrated in Scheme 5. The rate constants and associated activation parameters for the optical isomerism of Ru(CO)(PPh$_3$)-



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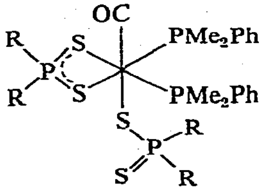
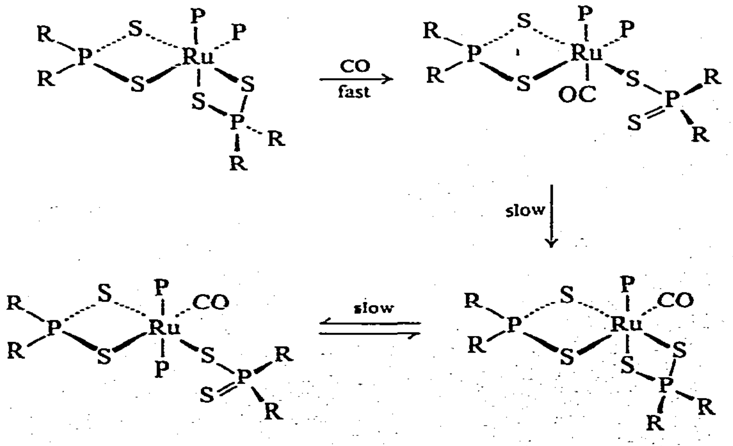
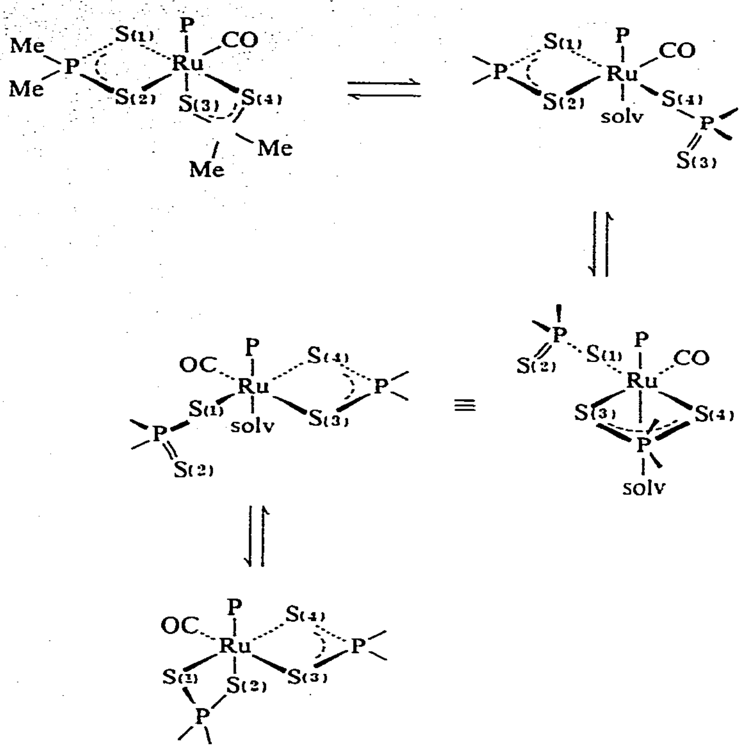


(29)

SCHEME 5

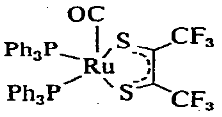


SCHEME 6



$(S_2PMe_2)_2$ has been determined by a line-shape analysis of the temperature dependent NMR spectra of this species. From a detailed consideration of various bond-rupture and twist mechanisms for the optical inversion, it was suggested [46] that only one process could be compatible with the spectral data: a solvent-assisted cleavage of a Ru—S bond *trans* to L (Scheme 6).

The structure of the orange isomer of $Ru(CO)(PPh_3)_2\{S_2C_2(CF_3)_2\}$ (30) has been determined [47] and compared with that of the violet isomer 31.



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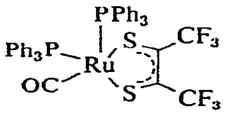


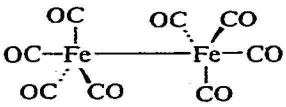
(31)

Bimetallic species

An accurate determination has been made [48] of the structure of $Fe_2(CO)_9$, first studied by Powell and Evans [49]. The Fe—Fe distance of 2.52 Å was confirmed, and the bridge angle Fe—C(O)—Fe (77.6°) was 3° smaller than the average found in other carbonyl-bridged di-iron species.

The structure of $[(Ph_3P)_2N][Fe_2(CO)_8]$ (32) consists [50] of two trigonal bipyramidal iron atoms formed by a metal—metal bond (2.79 Å), in which the two sets of CO groups are staggered and slightly bent towards each other. In the isoelectronic $[(Ph_3P)_2N][FeCo(CO)_8]$ (33) however, the $Fe(CO)_4$ and

$Co(CO)_3$ groups were connected by a metal—metal bond (2.59 Å) and an asymmetric bridging CO group (Fe—C(bridge) 2.21 Å, Co—C(bridge) 1.77 Å).



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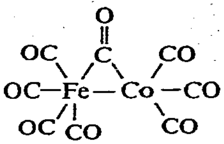

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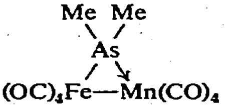


(34)

Reaction of $(OC)_4Fe(\mu\text{-}AsMe_2)Mn(CO)_4$ (34) with L (PPh_3, PMe_2Ph, $P(OMe)_3$, $P(NMe_2)_3$) gave [51] $(OC)_4Fe(AsMe_2)Mn(CO)_4L$, which could also be obtained from $Fe(CO)_4AsMe_2Cl$ and $NaMn(CO)_4L$, or from the reaction of $(OC)_4Fe(AsMe_2)Mn(CO)_4$ with L ($L = PPh_3$). These species contain a linear Fe—As—Mn system. The related $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3$ reacted with L giving $(OC)_4Fe(AsMe_2)Co(CO)_2L$. Hydrolysis of $Fe(CO)_4AsMe_2Cl$ afforded $(OC)_4Fe(Me_2As{-}O{-}AsMe_2)Fe(CO)_4$.

Thermolysis of $Os(CO)_4H_2$ (above 125°) afforded [52] $Os_2(CO)_8H_2$, $Os_3(CO)_{12}$ and $Os_4(CO)_{12}H_4$. The last two are secondary products, produced by heating $Os_2(CO)_8H_2$. Thermolysis of $Os(CO)_4D_2$ afforded the products already described, as well as a mixture of HD, H_2 and D_2, indicating that a bimolecular mechanism was operating. When thermolysis of $Os(CO)_4H_2$ was carried out under D_2, the main product was H_2 with a very small amount of HD. From kinetic studies, the mechanism may be that summarised in Scheme 7, and it was suggested that

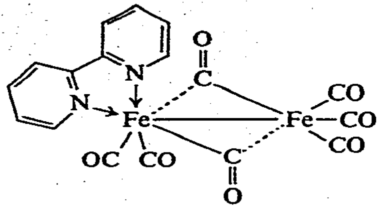
SCHEME 7

$$\begin{aligned}
&Os(CO)_4H_2 \longrightarrow Os(CO)_3H_2 + CO \quad \text{(rate determining step)}\\
&Os(CO)_3H_2 + Os(CO)_4H_2 \longrightarrow Os_2(CO)_7H_2 + H_2 \quad \text{(fast)}\\
&Os_2(CO)_7H_2 + CO \longrightarrow Os_2(CO)_8H_2 \quad \text{(fast)}
\end{aligned}$$

the empty coordination site in $Os(CO)_3H_2$ may allow formation of hydride bridges in the dimerisation step. It is unusual that $H_2Os(CO)_4$ competes successfully for CO with $Os(CO)_3H_2$, and decomposition occurs faster than CO exchange. However, $Os_2(CO)_8H_2$, unlike its monomeric precursor, undergoes rapid CO exchange under the reaction conditions, which indicates that in the thermolysis, reductive elimination of H_2 does not occur.

Bipyridyl reacted [53] with $Fe_2(CO)_9$ in THF to give $Fe_2(CO)_7(bipyr)$ (35). From crystallographic studies it is clear that the molecule contains a "semibridging" CO group and it would appear that the iron bound to bipyridine is electron rich, and forms a weak $d \rightarrow \pi^*$ dative bond with a CO group. It was suggested that the semibridging CO group provides a mechanism for a metal atom otherwise tending to become excessively negatively charged, to transfer surplus electron density to a CO group on a less negatively charged metal atom. It was observed that similar bonding situations occur in 36, [54] $(\eta^5\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$ [55] and $\alpha\text{-}Ru_4(CO)_{13}H_2$ [56].

Treatment of $[Et_4N][Fe(CO)_4SiCl_3]$ with $AlCl_3$ afforded [57] $[Fe(CO)_4SiCl_2]_3$ which may have structure 37 or 38. In the gas phase there was evidence that this trimer dissociated into $[Fe(CO)_4SiCl_2]_2$ and $Fe(CO)_4SiCl_2$. $Fe_2(CO)_9$ reacted [58]



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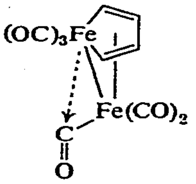

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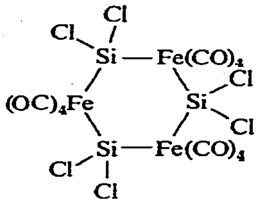

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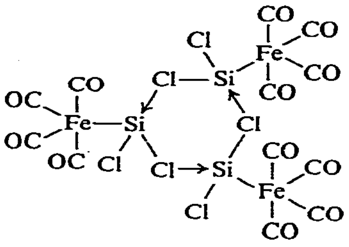
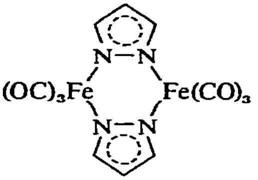


(38)

with SnX_2 (X = Cl, Br, C_5H_5, C_5H_4Me, β-diketonate) giving $[Fe(CO)_4(\mu\text{-}SnX_2)]_2$, which afforded, with pyridine, $Fe(CO)_4(SnX_2pyr)$. With $Sn\{OC(Ph)CHC(Me)O\}_2$, the species $Fe_2(CO)_8SnX_2$ was also formed, but no characterisable products could be obtained from the reaction of $Fe(CO)_5$ with SnX_2. $Na_2Fe(CO)_4$ reacted [59] with $Sn(CH{=}CH_2)_2(O_2CCF_3)_2$ giving $[Fe(CO)_4\{\mu\text{-}Sn(CH{=}CH_2)_2\}]_2$.

Pyrazole, and its 3,5-dimethyl derivative, reacted [60] with $Fe_3(CO)_{12}$ giving



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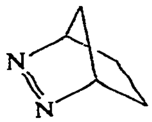
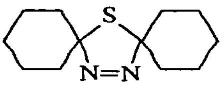
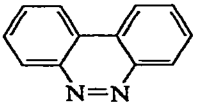


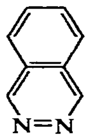
(40a)



(40b)



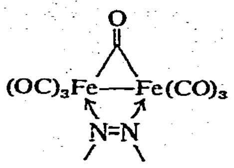
(40c)



(40d)

(40e)

39, and the cyclic azo or diazine compounds 40a—e (L) reacted with $Fe_2(CO)_9$ affording [61] $Fe_2(CO)_7L$ (41), probably via the intermediate $Fe(CO)_4L$. Decarbonylation of $Fe_2(CO)_7L$ afforded $Fe_2(CO)_6L$ (42) only when 41 contained 40a—c. The complex $Fe_2(CO)_6L$, derived from 40c, can also be obtained [62] from $Fe(CO)_5$, it reacts with PPh_3 to give $Fe_2(CO)_5(PPh_3)L$ and acts as a polymerisation initiator for styrene. The reactions of $Fe_2(CO)_6L$ (including the species derived from 40a, 40c and 43) with tertiary phosphines, phosphites or $AsPh_3$ occur [63] via an associative mechanism, leading eventually to $Fe_2(CO)_5$-QL (Q = incoming ligand). The influence of the steric properties of the ligands L is consistent with an activated intermediate whose structure is an octahedral



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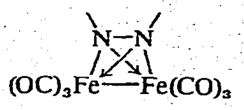
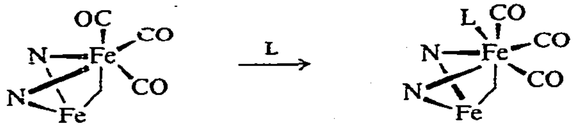


(42)

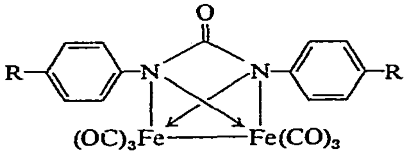
wedge. The entering and leaving groups occupy an edge which is parallel to the edge defined by the two bridging atoms (eq. 3). It may be noted that the



(3)

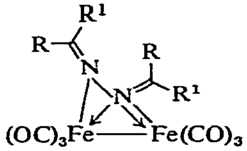
aliphatic rings in the complex derived from **40a** extend over the Fe octahedron, thereby inhibiting approach by Q [64].

Treatment of $Fe(CO)_4I_2$ with LiN=CRR′ (R = R′ = Ph, p-MeC_6H_4; R = Ph, R′ = t-Bu) afforded [65] $[Fe(CO)_3(\mu\text{-}NCR'R)]_2$ (**44**) and, when R = R′ = Ph,



(R = H, OMe)

(43)



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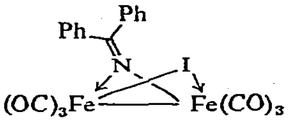

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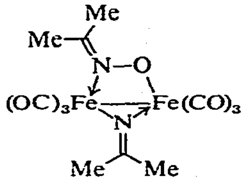


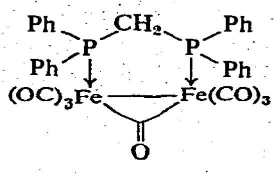
(46)

small amounts of $Fe_2(CO)_5(\mu\text{-}I)(\mu\text{-}NCPh_2)$ (**45**). Reaction of $Na_2Fe(CO)_4$ with $Me_2C(NO)Br$ gave [66] $[Fe(CO)_3(\mu\text{-}NCMe_2)]_2$ (**44**), and **46**.

The Mössbauer spectra of the dehydro-*N*,*N*′,*N*″-trialkylguanido and urea complexes $Fe_2(CO)_6\{C(NR)_3\}$, $Fe_2(CO)_5(PPh_3)\{C(NC_6H_{11})_3\}$ (R = C_6H_{11} or n-Pr) and $Fe_2(CO)_6\{CO(NPh)_2\}$ have been measured [67].

In THF, $Fe_2(CO)_9$ reacted with $Ph_2PCH_2PPh_2$ giving [68] $Fe_2(CO)_7(Ph_2PCH_2PPh_2)$ (**47**). The unique CO groups forms a symmetrical bridge, and the geometry about each Fe atom is roughly trigonal bipyramidal. The two halves of the molecule (at Fe) are not exactly eclipsed, and the Fe—Fe bond is 2.71 Å. In solution the molecule is fluxional, the bridging and terminal CO groups presumably exchanging sites via a triply-bridged intermediate (**48**).

Phenyldiphenylphosphinoacetylene reacted with $Fe_2(CO)_9$ giving [69]



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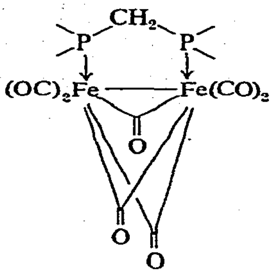
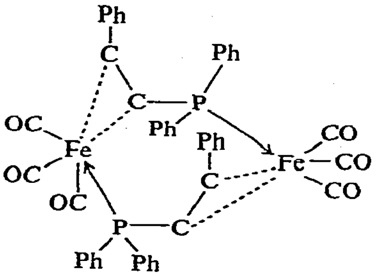


(48)

$Fe_2(CO)_6(C{\equiv}CPh)(PPh_2)$, the structure of which has been determined [70], and $Fe_2(CO)_6(Ph_2PC_2Ph)_2$ (49). The C≡C bond length in the former is 1.23 and in the latter 1.26 Å [69].

A vibrational spectroscopic analysis has been made [71] of $Fe_2(CO)_6S_2$ and



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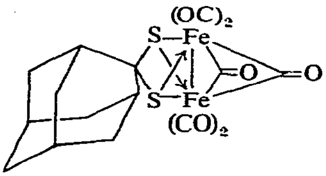

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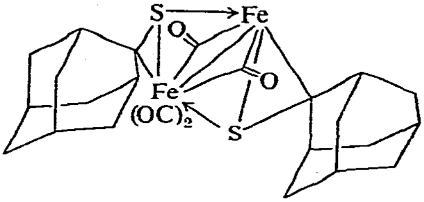

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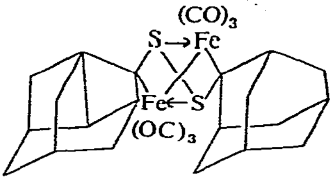

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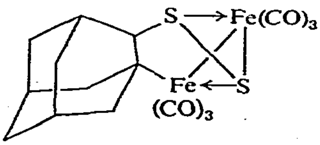

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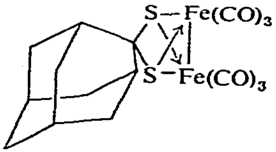
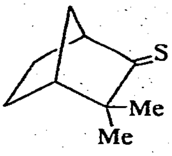


(54)

the *syn*- and *anti*-isomers of $Fe_2(CO)_6(SMe)_2$. The Fe—Fe stretching force constants were consistent with an Fe—Fe bond-order of one.

$Fe_2(CO)_9$ reacted [72] with adamantanethione giving **50** as the major product, together with **51**—**53**. Aerial oxidation of **50** gave **54** which further oxidised to adamantanone. Reduction of **50** with $LiAlH_4$ also provided adamantanone, as well as **53**, and $LiAlH_4$ reduction of the latter afforded diadamantyldisulfide.



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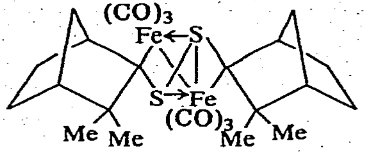

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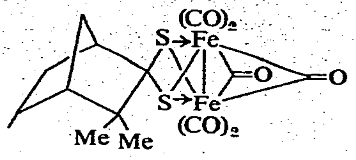

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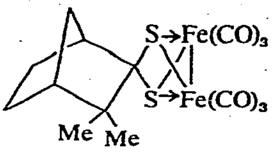

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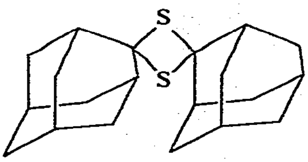
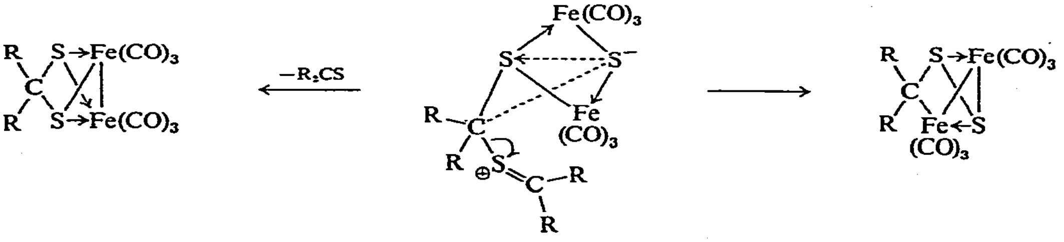


(59)

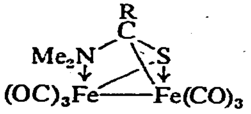
At room temperature in CCl_4, **51** rearranged to **52**. Thiocamphenilone (**55**) reacted with $Fe_2(CO)_9$ to give **56** and **57**, and the latter rapidly rearranged to **58**. Thiofenchone reacted with $Fe_2(CO)_9$ to afford only $Fe_2(CO)_6S_2$ and $Fe_3(CO)_9S_2$ and the latter did not react with adamantanethione. There was no reaction between $Fe_2(CO)_9$ and **59**. A possible mechanism for the formation of these species is outlined in Scheme 8.

SCHEME 8



The thiourea and thioamides $RC(=S)NMe_2$ ($R = Me_2N$, Me or Ph) reacted [73] with $Fe_2(CO)_9$ giving S-bonded $Fe(CO)_4(RC(=S)NMe_2)$, **60** and $Fe_3(CO)_9S_2$. The tetracarbonyl reacted with $P(n\text{-}Bu)_3$ effecting the release of the sulfur ligand and production of $Fe(CO)_4(PBu_3)$ and $Fe(CO)_3(PBu_3)_2$. However, there was no reaction between $Fe(CO)_4(PPh_3)$ and $RC(=S)NMe_2$. The reaction of $Fe_2(CO)_9$ with $ArNHC(=S)NR_2$ ($Ar = Ph$, $p\text{-}MeC_6H_4$ or $p\text{-}MeOC_6H_4$; $R = Me$ or $p\text{-}MeC_6H_4$) gave S-bonded $Fe(CO)_4\{ArNHC(=S)NR_2\}$, **61**, **62** and $Fe_3(CO)_9S_2$.

Mercaptobenzthiazole (BTSH) (**63**) reacted [74] with $Ru_3(CO)_{12}$, in a mixture of pyridine and methanol, giving the octahedral $Ru(CO)_2(pyr)_2(BTS)_2$, in which the thiazole is bonded via the extracyclic S atom, and $Ru_2(CO)_4(pyr)_2$-



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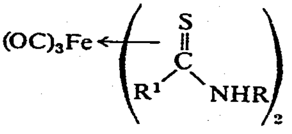

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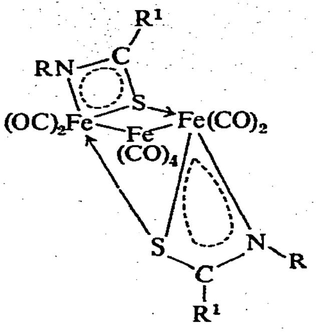
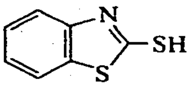


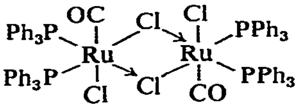
(62)



(63)

$(BTS)_2$, in which the sulphur ligand bridges the two Ru atoms, the metal atoms having octahedral geometry (the sixth site is comprised of a Ru—Ru bond).

When $Ru(CO)(PPh_3)_2(DMF)Cl_2$ was refluxed in CH_2Cl_2, the dimer 64 was formed [75], but when treated with $Ru(PPh_3)_3Cl_2$, the triply-bridged species 65 was produced. Similar bromo complexes were prepared, and mixed halide dimers could be obtained from $Ru(CO)(PPh_3)_2(DMF)X_2$ and $Ru(PPh_3)_3Y_2$. Mixed phosphine complexes could also be prepared by reaction 4. When $Ru(PPh_3)_3Cl_2$ was refluxed in CS_2 under nitrogen, $[Ru(\eta^2\text{-}CS_2)(PPh_3)_2Cl]Cl$ and $[Ru(CS)(PPh_3)_2Cl_2]_2$ were formed [76]. The latter was isolated as a purple-red precipitate, which probably has the structure 66 or 67. This compound reacted with HCl and $[Ph_4As]Cl$ giving $[Ph_4As][Ru(CS)(PPh_3)_2Cl_3]$, of configuration 68 or



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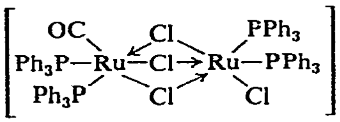
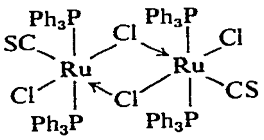
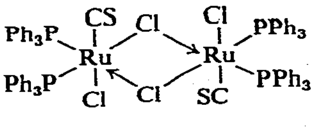


(65)

$$Ru(CO)(PEt_2Ph)_2(DMF)Cl_2 + Ru(PPh_3)_3Cl_2 \rightarrow (PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(CO)(PEt_2Ph)_2 \qquad (4)$$



(66)



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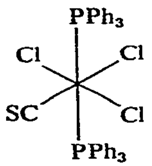
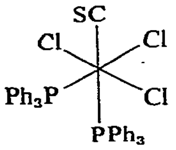
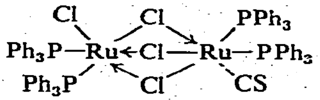


(68)



(69)

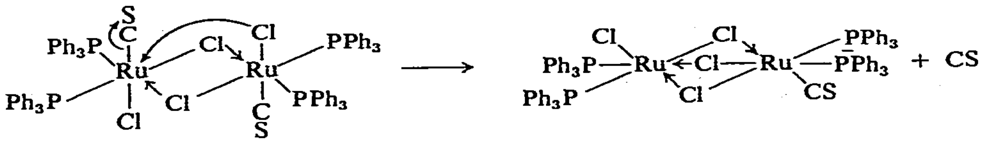
69. An ether extraction of the original reaction mixture afforded another red complex identified crystallographically [77] as **70**, the structure of which is



(70)

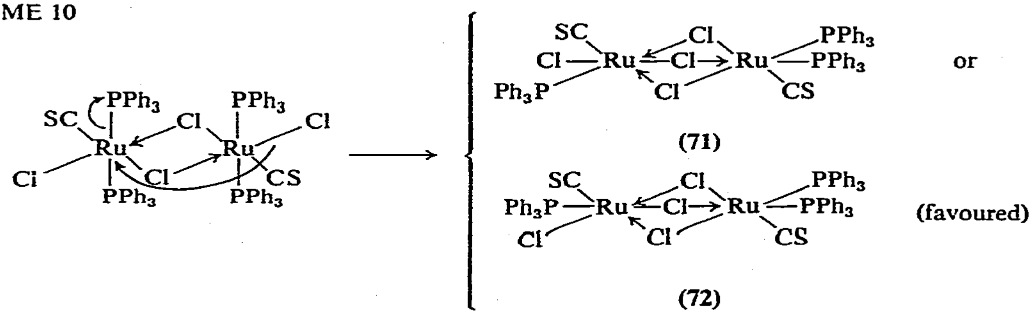
analogous to that of $(PPhEt_2)_3Ru(\mu\text{-}Cl)_3Ru(PPhEt_2)Cl$ [78]. This compound did not react with Cl^- to give $[Ru(CS)(PPh_3)_2Cl_3]^-$, but its mechanism of formation from $[Ru(CS)(PPh_3)_2Cl_2]_2$ may be depicted as in Scheme 9. It reacted

SCHEME 9



slowly with concentrated HCl to give the paramagnetic $(Ph_3P)Cl_2Ru(\mu\text{-}Cl)_3Ru(CS)(PPh_3)_2$ (μ = 2.00 B.M. per dimer). It was thought that $[Ru(CS)(PPh_3)_2Cl_2]_2$ and **70** were formed by competing reactions from $Ru(PPh_3)_3Cl_2$ or $[Ru(\eta^2\text{-}CS_2)(PPh_3)_2Cl]Cl$. In acetone, $[Ru(CS)(PPh_3)_2Cl_2]_2$ rearranged to $(PPh_3)(CS)ClRu(\mu\text{-}Cl)_3Ru(CS)(PPh_3)_2$ (**71** or **72**) perhaps as in Scheme 10.

SCHEME 10



(71)

(72)

Trimetallic and other metal atom cluster compounds

The molecular structure of $Fe_3(CO)_{12}$ has been further refined [79], the overall configuration suggested by Wei and Dahl [80] being confirmed. The nonbridged metal—metal distances are 2.68 Å, but the CO-bridged Fe—Fe bond length is 2.56 Å. This may be compared with 2.52 Å in $Fe_2(CO)_9$. The double CO bridge is asymmetric (Fig. 1) and this is thought to be of significance in relation to the fluxional behaviour of the species in solution (Fig. 2). The temperature dependent ^{13}C NMR spectrum of $Fe_3(CO)_{12}$ is consistent with bridge-terminal CO group exchange. In a comparative study of the IR and ^{13}C NMR spectral data obtained from $Fe_3(CO)_{12}$, $Fe_3(CO)_{11}(PPh_3)$, $Fe_3(CO)_9(PMe_2Ph)_3$ and $Fe_3(CO)_8(SC_4H_8)_2$ it was shown [81] that the $Fe(\mu\text{-}CO)_2Fe$ bridging system can vary, in different molecules in the crystalline phase, from essentially

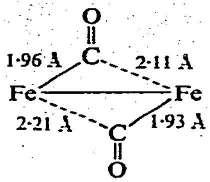


Fig. 1. The asymmetric double carbonyl bridge in $Fe_3(CO)_{12}$.

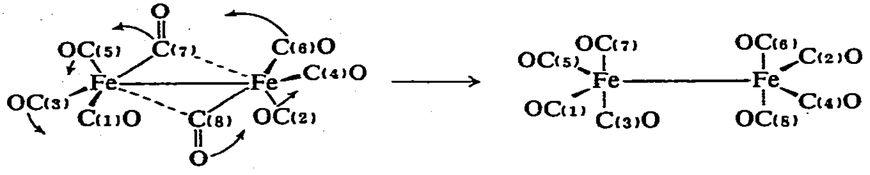
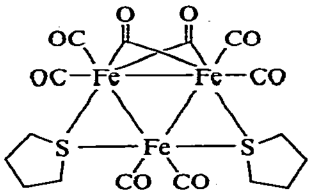


Fig. 2. The fluxional nature of $Fe_3(CO)_{12}$.

symmetric to essentially asymmetric. The data suggest that the energy of the molecules varies only slightly over an entire range of structural variations from practically non-bridged to symmetrically bridged species; this is clearly of significance in the CO ligand scrambling among the three Fe atoms via a bridged-non-bridge mechanism. $Fe_3(CO)_{12}$ is stereochemically non-rigid in $CCl_2F_2/CHCl_2F$ mixtures even at —150° (implying an activation energy $\leqslant 5$ kcal mol^{-1}) and its IR spectrum is neither consistent with a non-bridged (D_{3h}) or bridged (C_{2v}) structure. Rather, the structure of the molecule will vary with the solvent, being a continuum from D_{3h} to C_{2v} symmetry, although in argon matrices it is close to the bridged structure. It was suggested that the broad unresolved band in the IR spectrum of $Fe_3(CO)_{12}$ between 2000 and 2100 cm^{-1} may be regarded as a convolution of many spectral bands due to a wide range of structures with varying degrees of bridging. An increase in the polarity of the solvent apparently causes an increase in the bridged species.



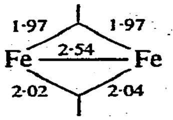
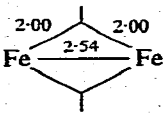
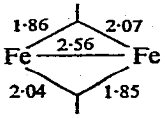
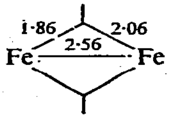
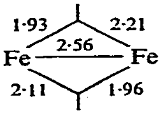
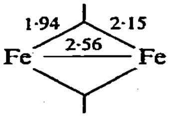
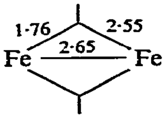
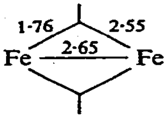
(73)

The tetrahydrothiophene complex $Fe_2(CO)_8(SC_4H_8)_2$ (73) was obtained [82] from the reaction between $Fe_2(CO)_9$ and SC_4H_8 under argon. In addition to two tetrahydrothiphen bridges (Fe—Fe 2.61 Å), the molecule has two very unsymmetrical CO bridges (Fe—C 1.76 Å, Fe—C' 2.55 Å, Fe—Fe 2.65 Å). A comparison of the structural parameters in the bridging system of several tri-iron carbonyl complexes is summarised in Table 1. It was noted that the shortest Fe—Fe distance is accompanied by the most symmetrical bridges.

The preparations of $Ru_3(CO)_{12}$ and its osmium analog have been patented [83], and some useful details given. The vapour pressure, heats and entropies of evaporation and sublimation of $Os_3(CO)_{12}$ have been measured [84] and

TABLE 1

STRUCTURAL PARAMETERS FOR THE BRIDGING SYSTEM IN TRI-IRON CARBONYL CLUSTERS

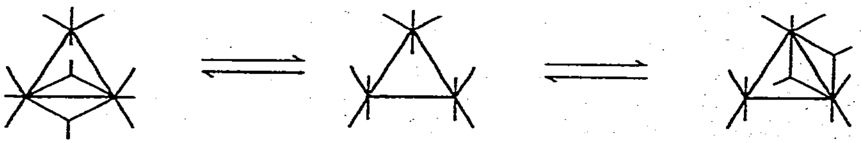
Compound	Actual distances (Å)	Idealised distances in C_2 symmetry (Å)
$Fe_3(CO)_9(PMe_2Ph)_3$		
$Fe_3(CO)_{11}(PPh_3)$ [a]		
$Fe_3(CO)_{12}$		
$Fe_3(CO)_8(THT)_2$ [b]		

[a] Fe atom carrying PPh_3 not involved in bridge bonding. [b] THT ≡ tetrahydrothiophene; complex 73.

calculated. The kinetics of decomposition of this carbonyl have also been determined [85]. From a study of the electronic structure and nature of the metal—metal bonds in $Os_3(CO)_{12}$, it has been calculated [86] that the Os—Os bond energy is 55 kcal mol^{-1}.

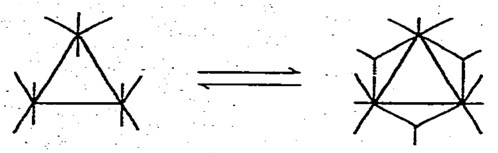
Like $Fe_3(CO)_{12}$, the species $Fe_2Ru(CO)_{12}$, $Ru_3(CO)_{12}$ and $[MnFe_2(CO)_{12}]^-$ are fluxional over a very wide temperature range [87], the CO groups readily exchanging their environments even at —160°. However, $Os_3(CO)_{12}$ has a rigid structure below 10°, which is consistent with D_{3h} symmetry, as established by

SCHEME 11



(CO groups and metal atoms omitted for clarity)

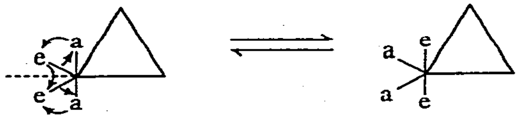
IR spectroscopy. On the basis of IR spectral studies, $Fe_2Ru(CO)_{12}$ and $[MnFe_2(CO)_{12}]^-$ have structures similar to $Fe_3(CO)_{12}$, and the CO site exchange mechanism probably occurs via pair-wise bridge-terminal ligand exchange [88] (Scheme 11). Although, in the solid state, $M_3(CO)_{12}$ (M = Ru or Os) has no



(5)

(CO groups and M atoms omitted for clarity)

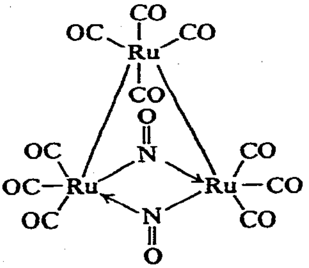
bridging CO groups, CO site exchange could occur via Scheme 11 or by eq. 5, or even by an interconversion of axial and equatorial CO groups on the same metal (eq. 6). This last mechanism does not involve transfer of CO groups



(6)

(CO groups and M atoms omitted for clarity)

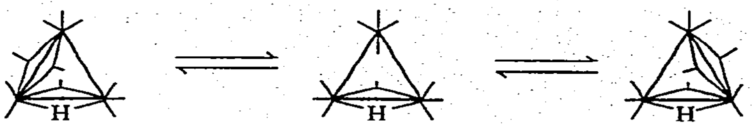
between metal atoms, but occurs by bending the equatorial—metal—equatorial CO group angle to 180°, decreasing the axial—metal—axial group angle to 120° and rotating the $M(CO)_4$ unit by 90°. Scrambling of CO groups between two metal atoms is likely in $Fe_3(CO)_{12}$ and $Fe_2Ru(CO)_{12}$, especially since in the latter, localised site exchange on individual metal atoms would not lead to a completely time-averaged ^{13}C NMR spectrum which is actually observed. In $Ru_3(CO)_{10}(\mu\text{-}NO)_2$ (74) however, a twist mechanism is likely, since the $Ru(CO)_3$



(74)

groups are rigid and the possibility of CO-bridged intermediates is ruled out. The making equivalent of the axial and equatorial CO groups associated with the $Ru(CO)_4$ unit can only occur via a twisting process. It was noted that the CO groups in $Fe(CO)_4(AuPPh_3)_2$ underwent site exchange although $Fe(CO)_4Br_2$ is rigid. Two fluxional processes were observed in the ^{13}C NMR spectrum of $[Fe_3(CO)_{11}H]^-$ over a temperature range; the low temperature maintains the orginal $Fe(\mu\text{-}H)(\mu\text{-}CO)Fe$ bridge intact (Scheme 12) while the high temperature

SCHEME 12

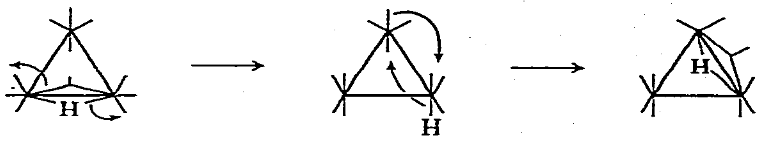


(CO groups and M atoms omitted for clarity)

process permits all groups to interchange (Scheme 13).

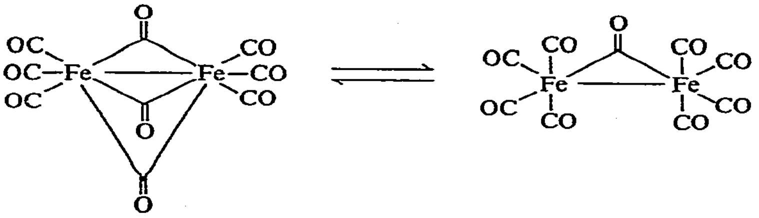
Alkali metal and/or electrochemical reduction of metal carbonyl species has been achieved [89] in air-free, dry ethereal solvents. The solutions of the radical

SCHEME 13



(CO groups and M atoms omitted for clarity)

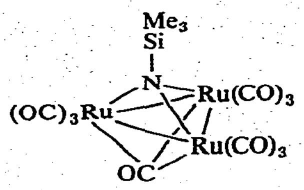
anions produced were, for the most part, stable, the species obtained from the heavy metal compounds being most robust. Among the radical anions produced were $[Fe(CO)_5]^-$, $[Fe_2(CO)_9]^-$, $[Fe_3(CO)_{12}]^-$, $[Fe_3(CO)_{11}\{P(OPh)_3\}]^-$, $[Fe_2Ru(CO)_{12}]^-$, $[Pt\{P(OPh)_3\}_2Fe_3(CO)_8]^-$, $[Ru_3(CO)_{12}]^-$, $[Os_3(CO)_{12}]^-$ and $[Ru_6C(CO)_{17}]^-$. The spectra of these species were temperature dependent, presumably because of the stereochemical non-rigidity of the CO groups. The species $[Fe_2(CO)_9]^-$ was soluble, and its ESR spectrum could be interpreted in terms of the equilibrium shown in eq. 7.



(7)

The kinetics of CO exchange with $Fe_3(CO)_9(NR)(NR')$ (R, R' = H, Me, Et or Ph) have been measured [90]. The reaction rates are independent of CO concentration, all CO groups in the substrate being equivalent. Reaction of $Ru_3(CO)_{12}$ with Me_3SiN_3 gave 75 [91].

$Fe_3(CO)_{12}$ reacted with $Ph_2PC{\equiv}CCF_3$ to give several compounds [92], including 76, in which the acetylene has dimerised to form a *trans*-butadiene unit. Other species produced include $Fe_3(CO)_{11}(Ph_2PC{\equiv}CCF_3)$, $Fe_3(CO)_{10}(Ph_2PC{\equiv}CCF_3)_2$ $Fe(CO)_3(Ph_2PC{\equiv}CCF_3)_2$, and $Fe_3(CO)_8(Ph_2P)\{Ph_2PC_4(CF_3)_2\}$, 77 [93], as well as 78 and 79. The structure of 76 has been established [92] crystallographically, the Fe(2)—Fe(3) distance being 2.51 Å and the C=C distances in the butadiene fragment 1.39 Å. By warming $Fe_3(CO)_{10}\{Ph_2PC{\equiv}CCF_3\}_2$, 76 and 77 were produc-



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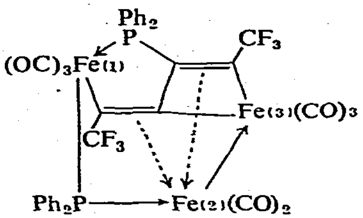

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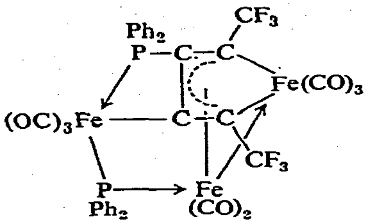

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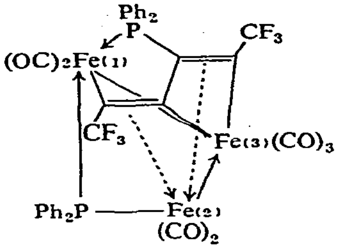

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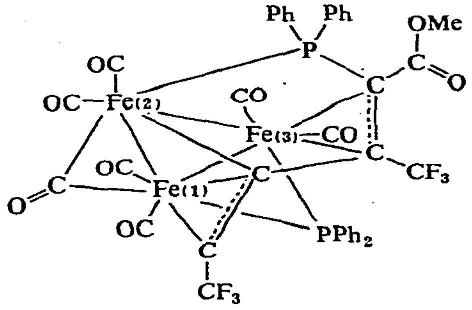
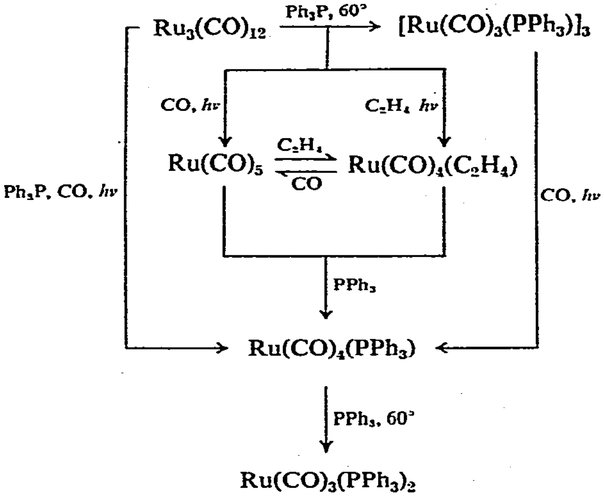


(79)

ed, and heating 76 gave 78, the structure of which has also been determined crystallographically [94]. In 78, the Fe(1)—Fe(2) distance is 2.67 Å (compared with 4.59 Å in 76), and the Fe(2)—Fe(3) bond length is 2.53 Å. The Fe(1)—P—Fe(2) angle decreases from 98° in 76 to 73.3° in 78, and the C=C bond lengths in the latter are 1.32 and 1.24 Å. The methoxy groups found in 79 are thought [95] to arise from methanol used as a stabiliser for $Fe_3(CO)_{12}$. The Fe(1)—Fe(3) and Fe(2)—Fe(3) distances of 2.68 Å are comparable to the metal—metal bond lengths in $Fe_3(CO)_{12}$, $Fe_3(CO)_{11}(PPh_3)$ and $Fe_3(CO)_9(PPhMe_2)_3$. The Fe(1)—Fe(2) distance is 2.54 Å and the metal atoms are also bridged asymmetrically by CO (Fe(1)—C, 1.87 Å; Fe(2)—C, 2.17 Å); this, too, is comparable with $Fe_3(CO)_{12}$ and $Fe_3(CO)_{11}(PPh_3)$. The distances between Fe(1)—C(9) and Fe(2)—C(10) strongly suggest predominantly σ-bonding, whereas the Fe(3) distances to C(11) and C(12) are much shorter than Fe(3)—C(10) (2.04 and 2.08 compared to 2.21 Å), indicating that the butadienoidal fragment is bonded to Fe(3) via two weak σ-bonds or an asymmetric η^3-allyl linkage. It may be noted that P—C bond cleavage has occurred.

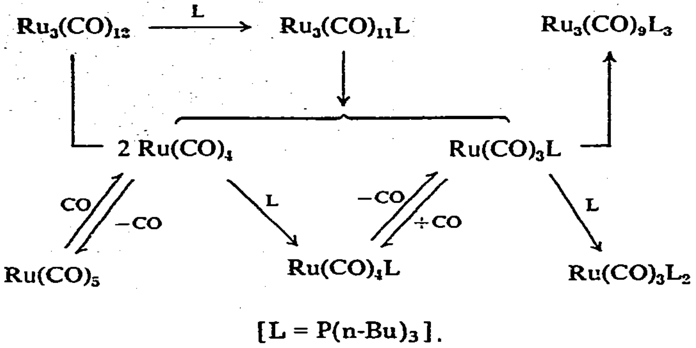
UV irradiation of $Ru_3(CO)_{12}$ in heptane solution under CO gave [96] $Ru(CO)_5$, identified by IR spectroscopy. Under C_2H_4, $Ru(CO)_4(C_2H_4)$ was formed, while PPh_3 gave a mixture of $Ru(CO)_3(PPh_3)_2$ and $Ru(CO)_4(PPh_3)$ (1 : 2 ratio). Under CO in the presence of PPh_3, the main product was $Ru(CO)_4(PPh_3)$, together with small amounts of $Ru(CO)_3(PPh_3)_2$ and $Ru(CO)_5$. $Ru(CO)_3(PPh_3)_2$ does not react with CO under UV irradiation. It would appear that there are two processes operating; one producing only $Ru(CO)_3(PPh_3)_2$ and the other involving CO dissociation of $Ru_3(CO)_{12}$, with formation of $Ru(CO)_4(PPh_3)$ which readily reacts further to give $Ru(CO)_3(PPh_3)_2$. Irradiation of $[Ru(CO)_3(PPh_3)]_3$ with CO gave $Ru(CO)_4(PPh_3)$. It was suggested that the photolysis of Ru_3 clusters might involve an electronically excited state, possibly produced in a $\sigma \rightarrow \sigma^*$ transition associated with the Ru—Ru bonds. The interrelationships of the various species produced are given in Scheme 14.

SCHEME 14



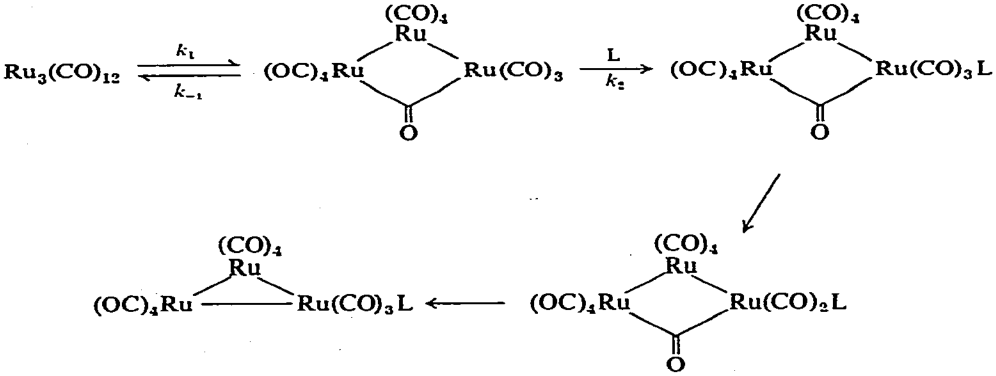
The kinetics and mechanism of the reaction between $Ru_3(CO)_{12}$ and $P(n\text{-}Bu)_3$ (L) have been studied [97]. The products were $Ru_3(CO)_9L_3$, $Ru(CO)_4L$ and *trans*-$Ru(CO)_3L_2$, the ratios of each produced being dependent on the relative initial concentration of $Ru_3(CO)_{12}$ and L. High values of the complex : L ratio led to a predominance of trinuclear products, while low values favoured mononuclear species. The data suggested that production of mononuclear species occurs mainly after $Ru_3(CO)_{11}L$ was formed, and that the $Ru(CO)_4$ and $Ru(CO)_3L$ fragments of this fission showed a stronger tendency to retrimerise than to react further with L. Substitution reactions of L with $Ru(CO)_4L$ proceeded via a dissociative pathway at a rate much faster than that of $Fe(CO)_4(PPh_3)$. When the reactions were carried out under CO (1 atm), it was established that carbon monoxide was about six times more nucleophilic towards $Ru(CO)_3L$ than L itself. The reaction is shown in Scheme 15. In a more extensive report of the details of the method of studying and interpreting the reactions of $Ru_3(CO)_{12}$ with tertiary phosphines and $AsPh_3$, it was observed [98] that reactions with the

SCHEME 15



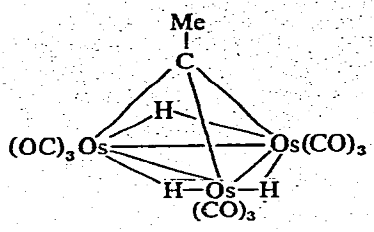
carbonyl involved an exceptionally high degree of bond-making. While PPh_3 reacted with $Ru_3(CO)_{12}$ giving predominantly $Ru_3(CO)_9(PPh_3)_3$, the absence of detectable amounts of mono- and di-substituted trimers revealed that these species react with PPh_3 more rapidly than $Ru_3(CO)_{12}$. On the other hand, $AsPh_3$ reacted to give $Ru_3(CO)_{10}(AsPh_3)_2$, which subsequently afforded other products. With the phosphites $P(OPh)_3$ and $P(OCH_2)_3CMe$, successive formation of $Ru_3(CO)_{11}L$, $Ru_3(CO)_{10}L_2$ and $Ru_3(CO)_9L_3$ was demonstrated, but with $P(OEt)_3$, such successive product formation was not found. Instead, $Ru(CO)_3\{P(OEt)_3\}_2$ was detected, and this type of complex was also rapidly obtained with $Ph_2PCH_2CH_2PPh_2$ and $P(C_6H_{11})_3$. From the kinetic data it was established that the first order pathway was dissociative, while the second order pathway occurred as in Scheme 16 (where $k_{-1} >> k_2$).

SCHEME 16

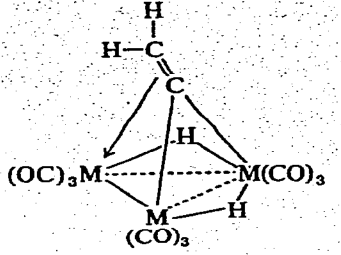


The structure of $Os_3(CO)_9H_3(CMe)$ (80) was established [99] by a combination of nematic phase ^1H NMR spectroscopy and X-ray powder photography. The compound is, as expected, isostructural with $Ru(CO)_9H_3(CMe)$ [100], and the Os—H distance is 1.82 Å, the Os—H—Os bridge angle being 103°.

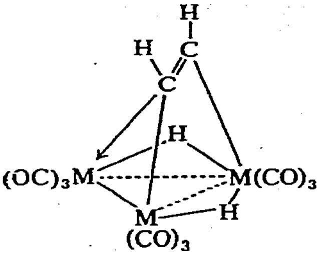
Ethylene reacted with $M_3(CO)_{12}$ (M = Ru or Os) giving [101,102] $M_3(CO)_9H_2(C{=}CH_2)$ (81) and $M_3(CO)_9H_2(CH{=}CH)$ (82). The structure of 81 has been confirmed crystallographically. Protonation of 81 by CF_3CO_2H in SO_2 or $CDCl_3$ gave $[Os_3(CO)_9H_3(C{=}CH_2)]^+$, of probable structure 83, but in neat CF_3CO_2H a



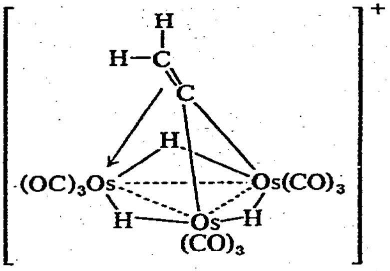
(80)



(81)

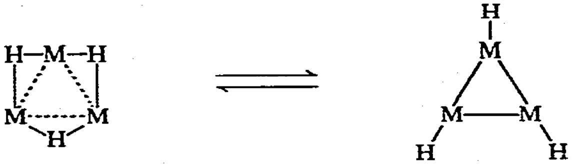


(82)



(83)

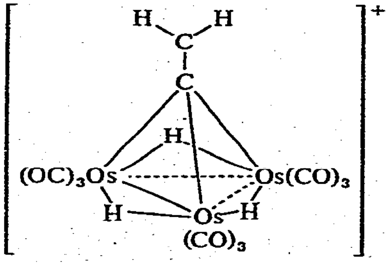
different, but uncharacterised, trihydride is formed; proton abstraction by base effected regeneration of **81**. Deuteriation of **81** afforded $[Os_3(CO)_9DH_2(C{=}CH_2)]^+$ and exchange of the hydridic ligands with the solvent and with the olefinic protons was very slow. The temperature dependence of the ^1H NMR spectrum of $[M_3(CO)_9H_3(C{=}CH_2)]^+$ could be explained via the mechanism shown in eq. 8, or by postulating an intermediate such as **84**. Protonation of



(8)

(ancillary ligands omitted for clarity)

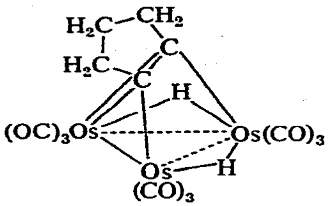
82 could not be studied, but the corresponding cyclooctadiene derivatives $M_3(CO)_9H_2(C_8H_{10})$ afforded $[M_3(CO)_9H_2X(C_8H_{10})]^+$ (X = H or D) whose ^1H NMR spectral behaviour over a temperature range was similar to that of protonat-



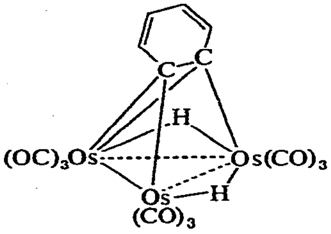
(84)

ed **81**. This behaviour could be interpreted in terms of proton exchange via a more symmetrical arrangement of atoms involving terminal M—H bonds, or by rotation of the olefin about the M_3 cluster. From the crystallographic data obtained from **81**, it was established [102] that the hydrogen-bridged Os—Os bonds were 2.92 and 2.88 Å, while the unbridged intermetallic distance was 2.80 Å. The C—C distance was 1.38 Å and the Os—CH_2 distance was 2.35 Å, while the distance from the apical C atom to the same Os atom was 2.17 Å; the other apical C—Os bond lengths were 2.04 and 2.05 Å.

Cyclopentene and benzene reacted with $Os_3(CO)_{12}$ undergoing 1,2-hydrogen elimination, to give **85** and **86** respectively [102]. Acetylene reacted with

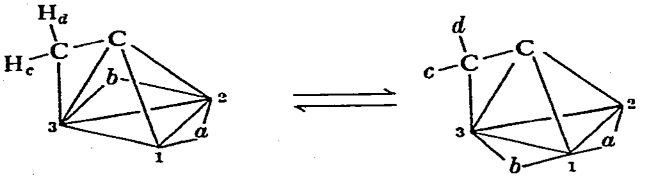


(85)



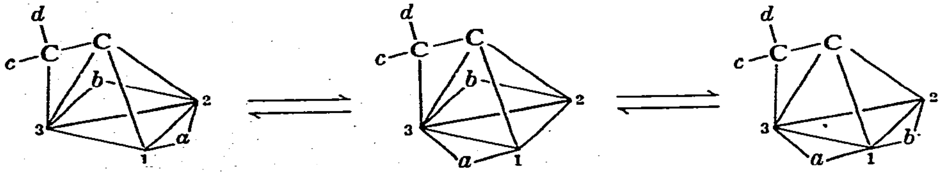
(86)

$Os_3(CO)_{10}H_2$ giving initially $Os_3(CO)_{10}H(CH{=}CH_2)$ which on heating afforded **81**. The intermediate monohydride may be involved in the formation of **81** from ethylene via a 1,2-addition across the Os_3 cluster, followed by H migration from one carbon to the other. The rate of exchange of the "methylene" protons in **81** is faster than hydride exchange, and a mechanism which permits this is shown in eq. 9. Here migration of *b* to the vacant bridge site would exchange *c* with *d* but not *a* with *b*. At higher temperatures, however, hydride signal broadening would be consistent with a slower exchange mechanism (Scheme 17). Here,



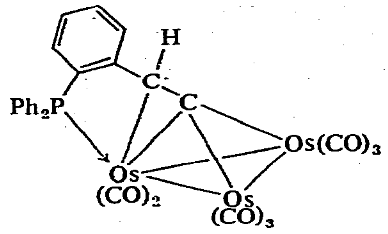
(9)

SCHEME 17

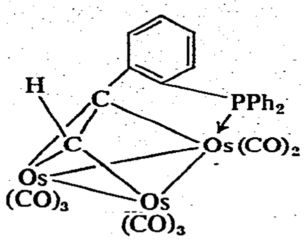


migration of *a* to the vacant bridge site, followed by migration of *a* or *b* back to the vacated site between Os_1 and Os_2 would lead to simultaneous exchange of *a* with *b* and *c* with *d*.

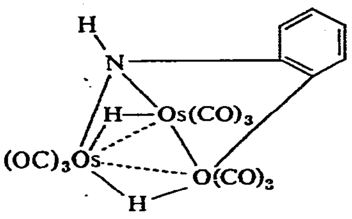
Reaction of *o*-styryldiphenylphosphine with $Os_3(CO)_{12}$ gave a compound formulated [102] as either **87** or **88**. In refluxing aniline, $Os_3(CO)_{12}$ afforded [103] $Os_3(CO)_8H_2(NHC_6H_4)(NH_2Ph)$ which reacted successively with CO to give $Os_3(CO)_9H_2(NHC_6H_4)$ (**89**) (the precursor is probably a CO substituted aniline product of this) and then $Os_3(CO)_{10}H(NHPh)$ (**90**), which is depicted as being similar to $Os_3(CO)_{10}H(SR)$ and $Os_3(CO)_{10}H(OR)$ [104]. Isomerisation of **90** to $Os_3(CO)_9H_2(NPh)$ (**91**) occurred in refluxing nonane, and **91** was the main product obtained after heating a hydrocarbon solution of **90** in a sealed tube. The substituted anilines *p*-$RC_6H_4NH_2$ (R = F or Me) afforded similar products. The interrelationship of the various compounds is shown in Scheme 18.



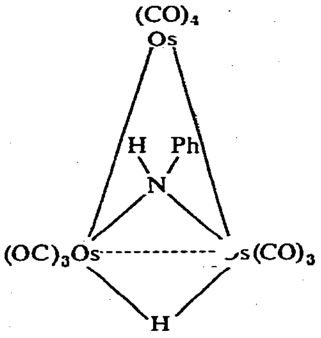
(87)
(2 H atoms omitted; positions unknown)



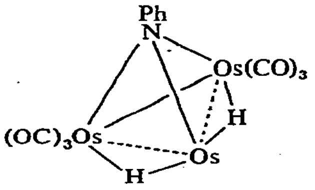
(88)
(2 H atoms omitted; positions unknown)



(89)



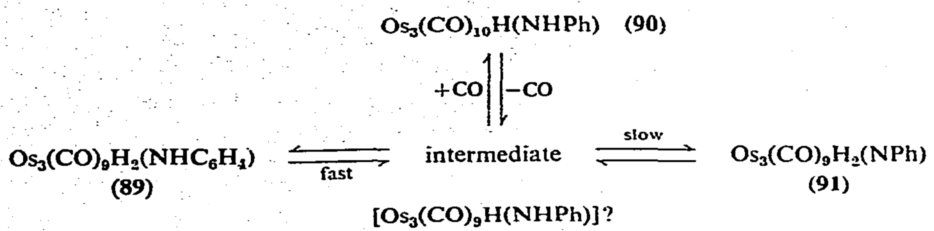
(90)



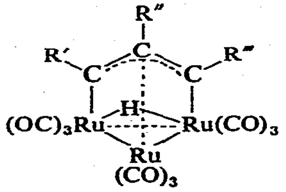
(91)

Reaction of 1,4-*trans,trans*-diphenyl-1,3-butadiene with $Ru_3(CO)_{12}$ gave [105] $Ru_3(CO)_9C_4H_4Ph_2$ (**92**; R′ = Ph, R″ = H, R‴ = CH$_2$Ph), $Ru_2(CO)_6C_4H_2Ph_2$ (**93**; R = R‴ = Ph, R′ = R″ = H), $Ru(CO)_3(C_4H_4Ph_2)$ (**94**; R = R‴ = Ph, R′ = R″ = H) and $Ru_3(CO)_8C_4H_2Ph_2$, which is probably analogous to $Ru_3(CO)_8C_4Ph_4$ [106]. The species **92** are probably similar to $Ru_3(CO)_9H(C_6H_9)$, the structure of which is known [107]. Hexadiene isomers reacted with $Ru_3(CO)_{12}$ giving two

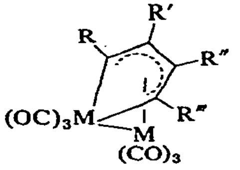
SCHEME 18



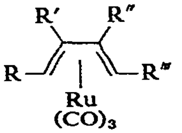
isomers of $Ru_3(CO)_9H(C_6H_9)$, 92 (R′ = Me, R″ = H, R‴ = CH_2Me) and 95 or 96 (hydride position not known) and $Ru(CO)_3(C_6H_{10})$ (94; R, R′, R″, R‴ = H, Me). Conversion of 95 or 96 into 92 occurs on heating. Isoprene reacted with



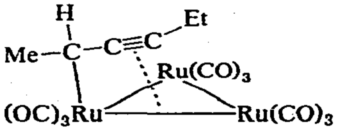
(92)



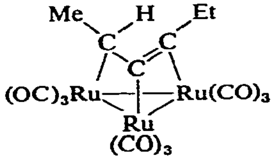
(93)



(94)



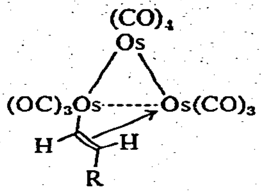
(95)

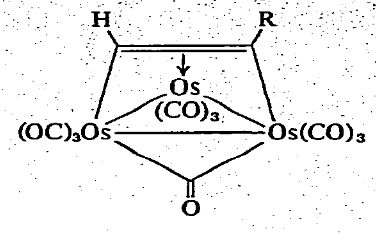


(96)

$Ru_3(CO)_{12}$ giving $Ru_3(CO)_9H(C_5H_7)$ (92; R′ = H, R″ = R‴ = Me) and $Ru_2(CO)_6$-(C_5H_6) which may be analogous to **93**, although this has not been confirmed. With 2,3-dimethylbutadiene, $Ru_3(CO)_{12}$ afforded $Ru_2(CO)_6C_6H_8$ (93; R = R‴ = H, R′ = R″ = Me), $Ru(CO)_3C_6H_{10}$ (94; R = R‴ = H, R′ = R″ = Me) and a low yield of $Ru_3(CO)_8C_6H_8$, while butadiene afforded $Ru_3(CO)_9H(C_4H_5)$ (92; R′ = R″ = H, R‴ = Me). In all of these reactions it seemed necessary that there was at least one H atom in the position α to the double bond in order to permit rearrangements to give complexes of the type $Ru_3(CO)_9H(L{-}H)$ (L = hydrocarbon). This is substantiated by the observation that 2,3-dimethylbutadiene does not afford compounds of the type **92**.

Acetylenes (RC≡CH) reacted [108] with $Os_3(CO)_{10}H_2$ giving $Os_3(CO)_{10}H$-(CH=CHR) (97; R = H or Me) and $Os_3(CO)_{10}(HC_2R)$ (98). Decarbonylation of the former (R = Me) gave **99** and **100**, and, when R = H, **81**. Decarbonylation of **98** gave $Os_3(CO)_9H(C_2R)$, whereas $Os_3(CO)_{10}(MeC_2Me)$ (analogous to **98**, obtained from MeC≡CMe), afforded the Os analog of **92** (R′ = Me, R″ = R‴ = H). With $Os_3(CO)_{12}$, however, acetylenes reacted in a more complicated way [109] (Scheme 19). The species $Os_3(CO)_{10}L$ (L = HC_2Ph) was thought to have the structure **98** or **101**. Preliminary X-ray crystallographic results have established that $Os_3(CO)_{10}L_2$ is a cluster. $Os_3(CO)_9L$ exists as isomers, perhaps isostructural with $Fe_3(CO)_9C_2Ph_2$ (one isomer) (e.g. **102a**) [110] or $Ru_3(CO)_9H(C_2$-t-Bu) (the other isomer) (e.g. **102b**) [111]. However, one isomer of $Os_3(CO)_9$-


(97)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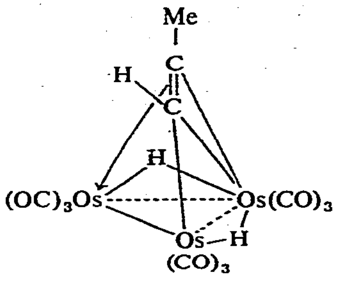
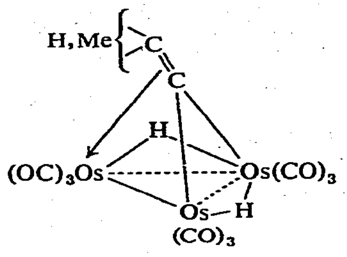
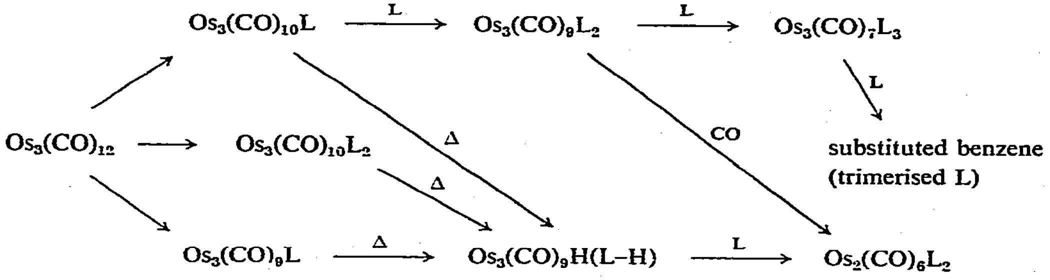

(99)

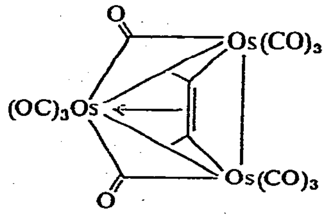

(100)

(MeC_2Ph) contains the group $OsCH_2C{\equiv}CPh$ with the acetylenic group π-bonded to another metal, as in **95** or **96**. The system $Os_3(CO)_9L_2$ is probably isostructural with $Os_3(CO)_9C_4Ph_4$ **(103)** [112], while $Os_2(CO)_6L_2$ probably has an osmacyclopentadienyl group, analogous to **93** [112,113]. However, $Os_3(CO)_8(MeC_2Ph)_2$ may be formulated as being analogous to $Os_3(CO)_8H(C_2PhC_6H_4)(C_2Ph_2)$, while the complexes $Os_3(CO)_7L_3$ are probably analogous to $Os_3(CO)_7(C_2Ph_2)$-

SCHEME 19



(L = PhC≡CH, PhC≡CMe, MeC≡CH, MeC≡CMe)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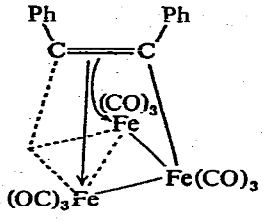
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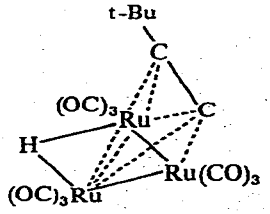
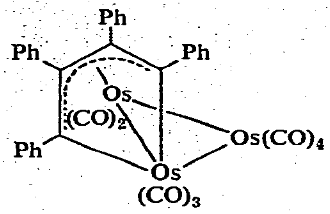
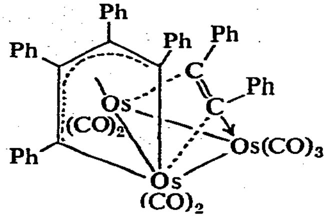

(102b)



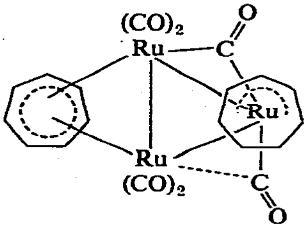
(103)



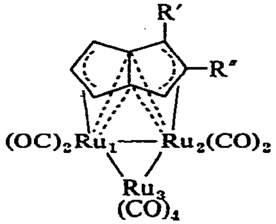
(104)

(C_4Ph_4) (**104**) [114]. The Os—Os distances in $Os_3(CO)_9(C_4Ph_4)$ (**103**) are 2.73—2.74 Å [Os(1)—Os(2) and Os(1)—Os(3)] and 2.89—2.92 Å [Os(2)—Os(3)].

The complex **105** exhibits [115] three fluxional modes: *(i)* rapid rotation of the C_7H_7 ring; *(ii)* slower rotation of the C_7H_9 ring; and *(iii)* corresponding exchange of "bridging" CO groups. The rotation of the C_7H_9 and the potentially coupled exchange of bridging and semibridging CO groups is illustrated in Fig. 3.



(105)



(**106 a**: R′ = R″ = H;
b: R′ = Me or Ph, R″ = H;
R′ = H, R″ = Me or Ph)

Cyclooctatetraenes, C_8H_7R (R = H, Me or Ph) reacted with $Ru_3(CO)_{12}$ in refluxing heptane or octane to give [116] $Ru_3(CO)_8C_8H_5R$. The structure of $Ru_3(CO)_8C_8H_6$ (**106a**) was determined crystallographically [117], and the Ru(1)—Ru(3) and Ru(2)—Ru(3) distances are 2.81 while the Ru(1)—Ru(2) bond length is 2.94 Å, 0.10 Å shorter than the comparable distance in $Ru_2(CO)_4(C_8H_6)(GeMe_3)_2$. The metal triangle makes an angle of 50° with the mean pentalene plane. This compound may also be obtained [118] from $[Ru(CO)_4SiMe_3]_2$, and this dimer, like $Ru_3(CO)_{12}$, afforded the isomers **106b** when reacted with C_8H_7R (R = Me or Ph). Apparently during the dehydrogenative ring

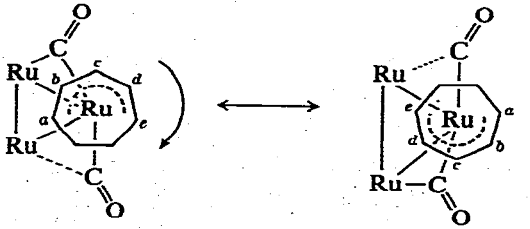


Fig. 3. Rotation of C_7H_9 ring and coupled exchange of carbonyl groups in 15.

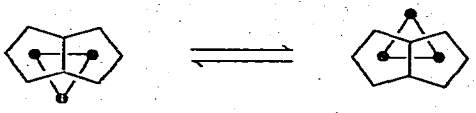
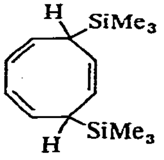


Fig. 4. The fluxional nature of $Ru_3(CO)_8(C_8H_5R)$ (R = H, 2-Me or 2-Ph).

closure of C_8H_7R, the position of the central σ-bond in the bicyclic ring is not greatly influenced by R. The complexes $Ru_3(CO)_8(C_8H_5R)$ (R = H, 2-Me or 2-Ph) are fluxional (Fig. 4) with a free energy of activation essentially independent of R ($E_a = 12.8 \pm 0.3$ kcal mol^{-1}). Fluxionality of this kin for 1-substituted derivatives is impossible since the two components of the fluxional oscillation would be non-degenerate.

Reaction of the cycloheptatriene **107** with $Ru_3(CO)_{12}$ or $[Ru(CO)_4SiMe_3]_2$ gave the stereochemically rigid **108**, whose structure, similar to that of **106**



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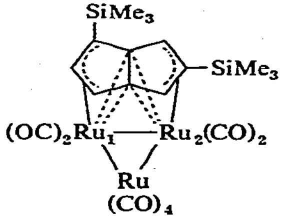

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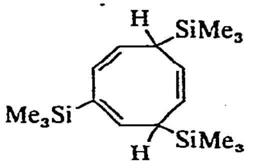

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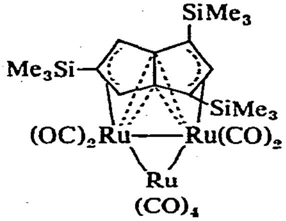
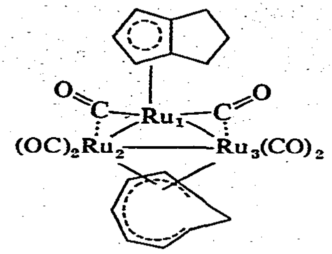


(110)

[116], has been confirmed crystallographically [119]. The Ru(1)—Ru(3) and Ru(2)—Ru(3) distances are 2.81 Å, while the Ru(1)—Ru(2) bond length is 2.93 Å, and the angle between the trimetallic unit and the pentalene ring is 50°. Reaction of **109** with $Ru_3(CO)_{12}$ afforded the fluxional **110**, for which $E_a = 9.2 \pm 0.2$ kcal mol^{-1}. This reduction in activation energy for the ring "flipping" motion may imply weaker coordination of the trisubstituted pentalene when compared to C_8H_6.

In addition to the formation of "simple" pentalene complexes, C_8H_8 reacted with $Ru_3(CO)_{12}$ giving [120] $Ru_3(CO)_6(C_8H_9)(C_8H_9)$ (**111**). In this the monocyclic C_8H_9 ligand is non-planar, coordinating to Ru(2) and Ru(3) by "wrapping" itself around the Ru(2)—Ru(3) edge of the metal triangle. The two CO groups bonded to Ru(3) are asymmetrically bridging with respect to Ru(2) and Ru(3), and the Ru(1)—Ru(2) and Ru(1)—Ru(3) bond distances are 2.84 Å, while that of Ru(2)—Ru(3) is 2.85 Å.



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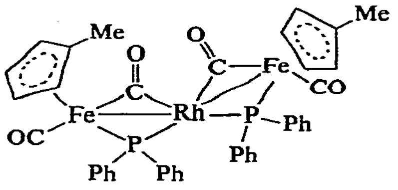
Treatment of $[FeCo_3(CO)_{12}]^-$ and $[MnFe_2(CO)_{12}]^-$ with L (PPh_3, $PMePh_2$, $P\{O(i\text{-}Pr)\}_3$) afforded [121] $[FeCo_3(CO)_{11}L]^-$ and $[MnFe_2(CO)_{11}L]^-$, and $Ph_2PCH_2CH_2PPh_2$ gave $[FeCo_3(CO)_{10}(diphos)]^-$. Protonation of the cobalt complex produced $FeCo_3(CO)_{11}LH$ in better yield than the corresponding preparation of $FeCo_3(CO)_{12}H$. Although the Mn complex reacted with CF_3CO_2H, no characteriseable product could be detected. Diphenylacetylene reacted with $[FeCo_3(CO)_{12}]^-$ giving $[FeCo_3(CO)_{10}(C_2Ph_2)]^-$ whose structure is thought to be different to that of $Co_4(CO)_{10}C_2Ph_2$ [122]. Protonation of this acetylene species afforded $FeCo_2(CO)_8(C_2Ph_2)_2$ which is isoelectronic with $Fe_3(CO)_9C_2Ph_2$ (102a) [110]. Treatment of $FeCo_3(CO)_{12}H$ with $PhC{\equiv}CPh$ also afforded $FeCo_2(CO)_8(C_2Ph)_2$ together with $Co_2(CO)_6(C_2Ph_2)$. It was observed that the polynuclear anions were more difficult to substitute than the related neutral complexes, but were attached more readily than mononuclear anions. The negative charge appeared to strengthen the M—C and M—M bonds in comparison to those in the neutral clusters.

The structure of $[Rh\{(\eta^5\text{-}C_5H_4Me)Fe(CO)_2PPh_2\}_2]PF_6$ (112) has been determined crystallographically [123]. The "closed" structure which necessitates two Rh—Fe and an Fe—Fe bonds, predicted on the grounds of the EAN rule, may be unstable with respect to an open structure because of the substitution of CO by the more basic μ-PPh_2 groups. The Rh—Fe bond distances are 2.66—2.67 Å.



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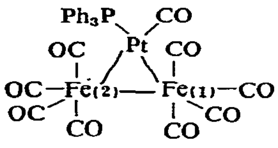

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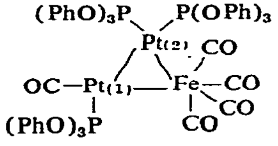
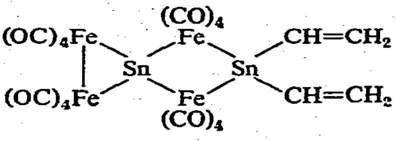


(114)

The structure of $Pt(PPh_3)(CO)\{Fe_2(CO)_8\}$ (113) has been determined crystallographically [124]. The Pt—Fe(1) and Pt—Fe(2) distances are 2.60 and 2.53 Å, respectively, while the Fe—Fe bond length is 2.76 Å. The differences in the Pt—Fe distances are consistent with the *trans* influence of the ligands on Pt. The reason why the intermetallic distances are relatively short may be related to the electron-deficiency of the cluster (it does not have 48 valence electrons) rather than because of M—M' multiple bonding. A similar situation may pertain in $FePt_2(CO)_5\{P(OPh)_3\}_3$ (114), where the M—M' distances appear

[125] to have bond-orders between 1 and 2. Thus the Pt—Pt distance is 2.63 Å, while the Pt(1)—Fe and Pt(2)—Fe bond lengths are 2.55 and 2.58 Å, respectively.

The complex **115** was obtained [126] as a by-product of the reaction between $Na_2Fe(CO)_4$ and $Sn(CH{=}CH_2)_2(O_2CCF_3)_2$, the main product being $[Fe(CO)_4\{Sn(CH{=}CH_2)_2\}]_2$.



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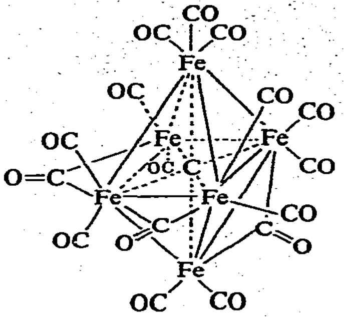
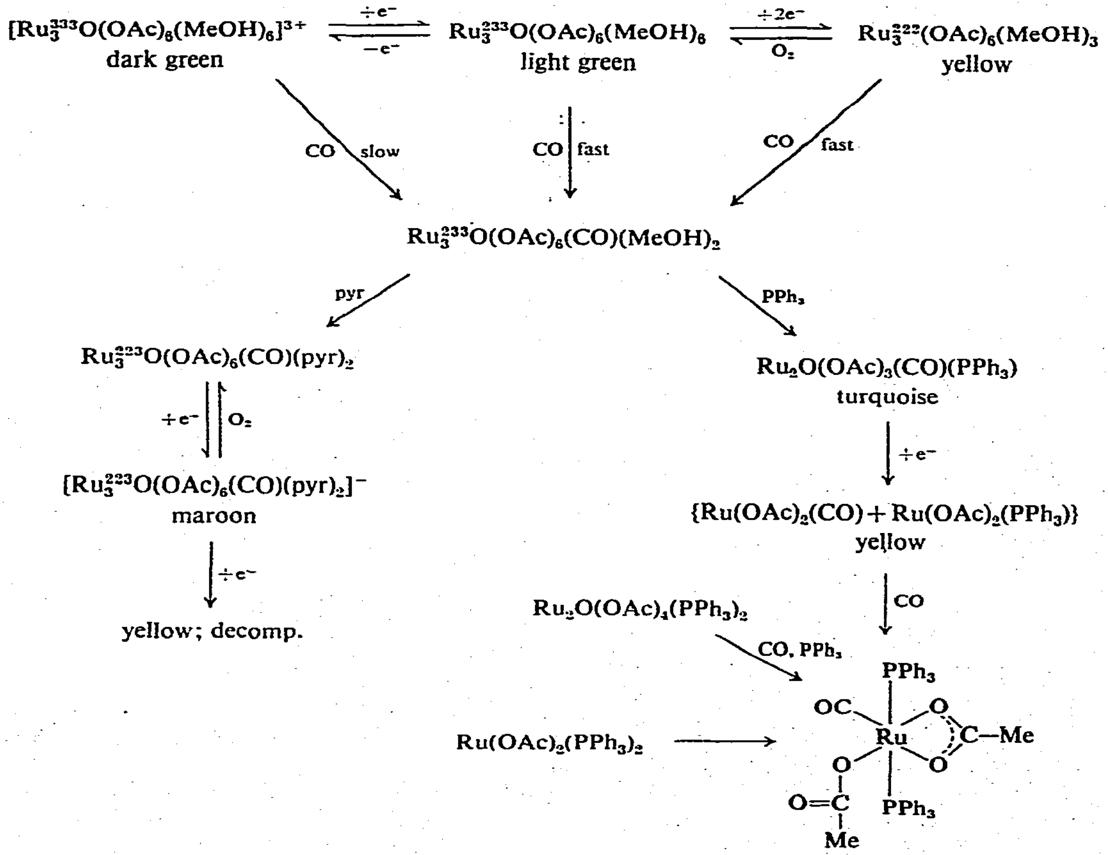


(116)

SCHEME 20



(Ru^{333} refers to formal oxidation state of each Ru atom; Ru(III))

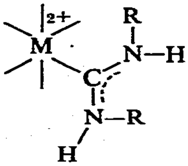
The crystal structure determination of $[Me_4N]_2[Fe_6(CO)_{16}C]$ (116) has been described [127]. The encapsulated C atom has octahedral "coordination" and the non-bridged Fe—Fe bonds range from 2.65 to 2.74 Å, while the bridged Fe—Fe distances are 2.55—2.63 Å; the Fe—C distances being in the range 1.81—1.97 Å.

The μ_3-oxo triruthenium carboxylates $[Ru_3O(O_2CR)_6(MeOH)_3]^+$ and their oxidised derivatives reacted with CO affording [128] monocarbonyl species (Scheme 20). From these reactions $Ru(CO)(PPh_3)_2(OAc)_2$ (see Scheme 20) was obtained, which could also be produced by carbonylation of $Ru(PPh_3)_2(OAc)_2$ or $Ru_2O(PPh_3)_2(OAc)_4$. Reaction of $Ru(PPh_3)_2(OAc)_2$ with MeNC afforded $Ru(CNMe)_2(PPh_3)_2(OAc)_2$ and similar treatment of $Ru_3O(OAc)_6(MeOH)_3$ gave a mixture of $Ru_3O(CNMe)_2(OAc)_6(MeOH)_2$ and $Ru_3O(CNMe)_3(OAc)_6$. With pyridine, $Ru_3O(CNMe)_2(OAc)_6L$ ($L = H_2O$ or MeOH), $Ru_3O(CNMe)_2(OAc)_6(pyr)$ was formed. Carbonyl sulfide reacted with $[Ru_3O(OAc)_6(MeOH)_3]^+$ giving $Ru_3O(CO)(OAc)_6(MeOH)_2$, while NO afforded, in the presence of PPh_3, $Ru_3O(NO)(PPh_3)_2(OAc)_6$.

Metal isocyanides

Cis- and *trans*-isomers of $Fe(CNR)_4X_2$ ($R = o$- and p-MeC_6H_4) have been isolated, and their IR and Mössbauer spectra recorded [129]. In a rapid reaction, the phthalocyanin complex $Fe(CNR)_2Pc$ ($R = CH_2Ph$) reacted with L (piperidine, pyridine, methylimidazole) giving [130] Fe(CNR)LPc. The rate of dissociation of CNR from $Fe(CNR)_2Pc$ was slow in the dark, but increased by a factor of 10^3 in the light. The rate of dissociation of CNR from Fe(CNR)LPc was about 10^3 times slower than the corresponding rate for dissociation of CO from Fe(CO)LPc.

The complexes $[Fe(CNR)_2\{PPh(OEt)_2\}_3Cl][ClO_4]$ ($R = Ph$, p-Me-, p-MeO-, p-$NO_2C_6H_4$ or o-MeC_6H_4, 2,6-$Me_2C_6H_3$), $[Fe\{CN(p\text{-}MeC_6H_4\}_3(PPh_3)_2Cl]X$ (X =



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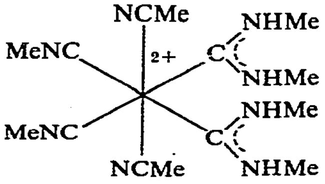

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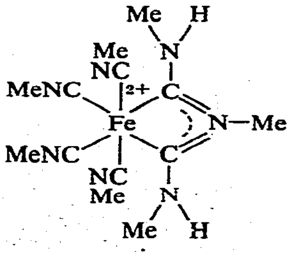


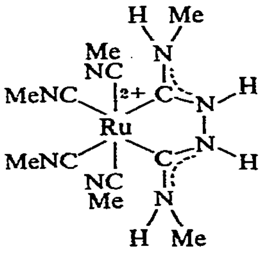
(120)

$FeCl_4$, ClO_4 or BPh_4) and $[Fe(CNC_6H_{11})_3\{PPh(OEt)_2\}_3][ClO_4]_2$ have been prepared [131].

Alkylation by Me_2SO_4 of $[Ru(CN)_6]^{4-}$ and $Fe(o\text{-}phen)_2(CN)_2$ afforded [132] $[Ru(CNMe)_6]^{2+}$ and $[Fe(o\text{-}phen)_2(CNMe)_2]^{2+}$. Voltammetric data obtained from these complexes and from $[Fe(CNMe)_6]^{2+}$ showed that CNMe stabilised M^{II} against oxidation to M^{III}, and that M^{III} species are relatively unimportant in this system.

Carbene species derived from isocyanide complexes

Treatment of $[M(CNMe)_6]^{2+}$ with RNH_2 in refluxing methanol gave [132], after 15 min, **117** (*amphi* configuration), but after 12 h, **118** (*cis* isomer). With ammonia, $[Fe(CNMe)_6]^{2+}$ afforded **119** (*amphi* configuration), and with $MeNH_2$ **120** was produced. The formation of the latter could arise because of steric effects, and it was suggested that a carbene intermediate like **117** might be formed, but that the carbene so produced would function as a nucleophile towards an adjacent CNMe group. Hence ring closure could occur. Indeed, such ring closure appeared to be inhibited in the ruthenium species perhaps because of the larger radius of Ru^{2+}. No carbene species could be obtained from $[Fe(o\text{-}phen)_2(CNMe)_2]^{2+}$. However, $[Ru(CNMe)_6]^{2+}$ and $[Fe(o\text{-}phen)_2(CNMe)_2]^{2+}$ both reacted with hydrazine, affording **121** and **122**. The pK_a value of the "dicarbene" ligand is similar to that in the analogous Fe complex. Treatment of $[M(CNMe)_6]^{2+}$ with acetamidine afforded either **123** or **124**, the former being preferred; 2-aminopyridine did not react with $[M(CNMe)_6]^{2+}$.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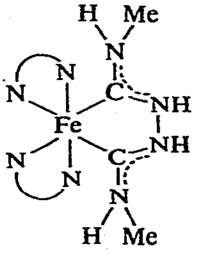
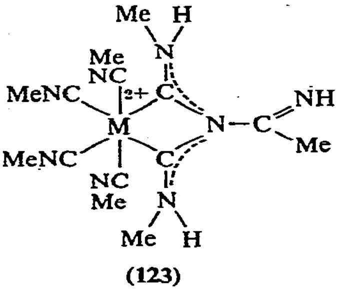

(122)
(N—N≡o-phen)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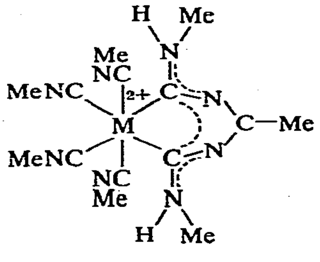
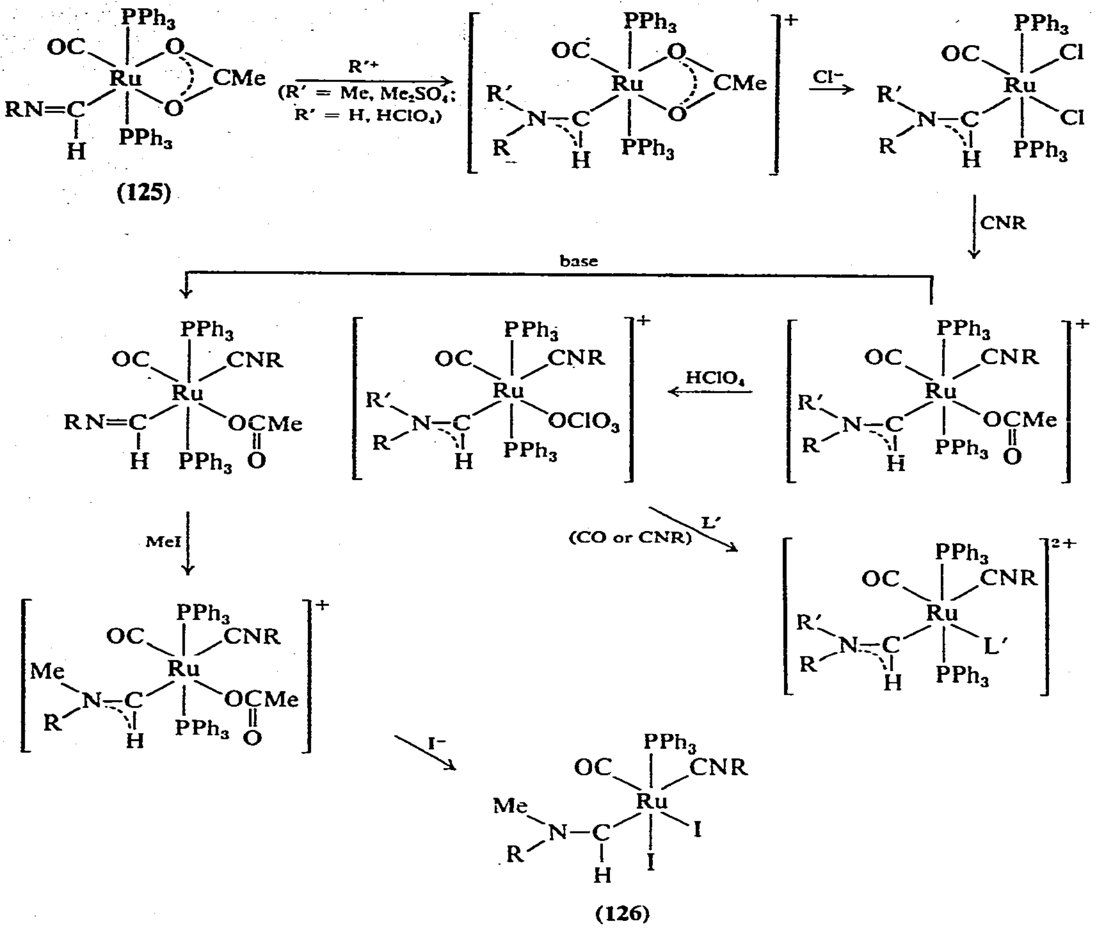

(124)

Reaction of $Ru(PPh_3)_4H_2$ with CNR (R = $p\text{-}MeC_6H_4$) gave [133] $Ru(CNR)(PPh_3)_3H_2$ which, on treatment with acetic acid, afforded $Ru(CNR)(PPh_3)_2H(OAc)$. Carbonylation of this gave rise to $Ru\{CH{=}NR\}(CO)(PPh_3)_2(OAc)$ (**125**)

SCHEME 21



(126)

a complex regarded as containing a coordinated secondary carbene ligand. The reactions of **125** are outlined in Scheme 21, and it was noted that all of the secondary carbene species exhibited a high value of ν(CN)(carbene) suggesting a particularly high bond-order within that ligand. This was confirmed by a crystallographic study [134] of **126**, obtained from $Ru(CO)(CNR)(PPh_3)_2(CH{=}NR)(OAc)$ as shown in Scheme 21. The C—N(carbene) distance of 1.28 Å is significantly shorter than that in other carbene complexes [135] (1.31—1.38 Å), but is longer than that in **125** [136]. The Ru—C(carbene) distance is 2.05 Å, shorter than the Ru—C bond length in related ruthenium(II) imidazol-ylidine complexes [137], and this suggests some degree of Ru—C(carbene) multiple bonding.

Metal nitrosyl and aryldiazo complexes

Mononitrosyl compounds

Dehydrocyanation of $[pyrH]_2[Fe(NO)(CN)_5]$ afforded [138] $Fe(NO)(pyr)_2(CN)_3$, and a similar process afforded [139] the γ-picoline analogue. The latter reacted with 2,2'-bipyridyl affording $Fe(NO)(bipyr)(CN)_3$.

It has been suggested [140] that $[Fe(NO)(CN)_5]^{2-}$ reacted with N_3^- and NH_2OH to give $[Fe(CN)_5(H_2O)]^{3-}$ via intermediates containing the group $\{Fe{-}N(=O)N_3\}^-$ and $\{Fe{-}N(=O)NHOH\}^-$.

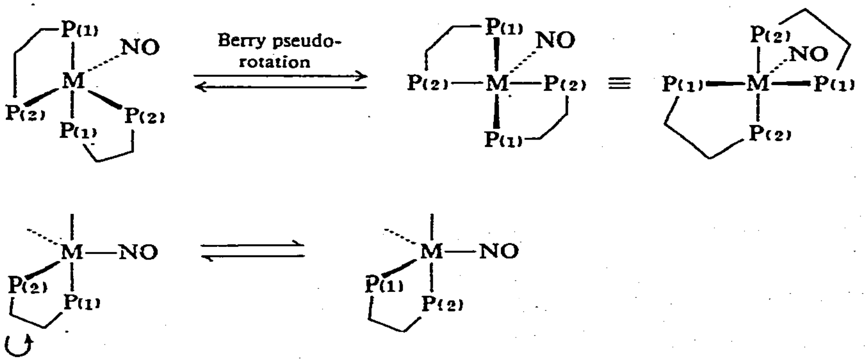
The crystal structure of the tetraphenylporphinato complex Fe(NO)L(TPP) (L = 1-methylimidazole) has been determined [141]. The Fe—N(O) distance (1.74 Å) was longer than that in $[Fe(NO)(CN)_5]^{2-}$ (1.63 Å) [142], the Fe—N—O bond angle was 142.1°, and the metal atom was displaced by 0.07 Å out of the plane of the 4 porphyrin N atoms towards the NO. From self-consistent charge-extended Hückel molecular orbital calculations, it was predicted [143] that CO forms stronger bonds than NO to the iron in haemoglobins.

The kinetics of the attack of NO on $[Ru(NH_3)_6]^{2+}$ in water, which leads to the formation of $[Ru(NO)(NH_3)_5]^{3+}$ at pH values below 7, and $[Ru(N_2)(NH_3)_5]^{2+}$ at pH values above 8.3, have been investigated [144]. From labelling experiments in alkaline solution, it was concluded that NO attacks the ammine ligand, possibly after NO coordinates to the metal. Reaction of *trans*-$[Ru(NO)(NH_3)_4(OH)]Cl_2$ with KSCN in aqueous HCl afforded [145] N-bonded *trans*-$[Ru(NO)(NH_3)_4(NCS)][NCS]_2$. The structures of $[Ru(NO)(NH_3)_5]Cl_3 \cdot H_2O$ and *trans*-$[Ru(NO)(NH_3)_4(OH)]Cl_2$ have been re-examined [146]. In both, as expected, the Ru—N—O bond angle is essentially linear, and the Ru—N(O) distance in the former is 1.77 Å and in the latter 1.74 Å. In the ion $[Ru(NO)(NH_3)_4(OH)]^{2+}$, the Ru—O distance is somewhat shorter than that expected from covalent radii considerations, but is close to that found in *trans*-$Na_2[Ru(NO)(NO_2)_4(OH)]$ [147]. A crystallographic study of $[pyrH]_2[Ru(NO)Cl_5]$ confirmed [148] the expected octahedral geometry of the complex.

Reaction of $[Ru(NO)(bipyr)_2X]^{2+}$ with C_6H_5NRR' (either neat or in MeCN) afforded $[Ru\{N(=O)C_6H_4NRR'\}(bipyr)_2X]^+$ (X = Cl, or NO_2, R, R' = H, Me) [149]. Using coordinated ^{15}NO, formation of the labelled nitroso—arene was confirmed. Reaction of $[Ru(bipyr)_2(solvent)Cl]^+$ with p-$Me_2NC_6H_4NO$ also gave $[Ru\{N(=O)C_6H_4NMe_2\}(bipyr)_2Cl]^+$. The mixed nitrosyl nitroso—arene complex $[Ru(NO)\{N(=O)C_6H_4NMe_2\}(bipyr)_2]^{3+}$, obtained by acidification of $[Ru\{N(=O)C_6H_4NMe_2\}(bipyr)_2(NO_2)]^+$, reacted further with $PhNMe_2$ giving $[Ru\{N(=O)C_6H_4NMe_2\}_2(bipyr)_2]^{2+}$.

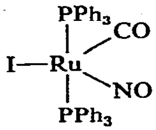
The complexes $[M(NO)(diphos)_2]^+$ (M = Fe or Ru) are fluxional. Their ^1H NMR spectral behaviour over a temperature range could be interpreted [150] in terms of two mechanisms (Scheme 22). From ^{31}P NMR spectral studies, it

SCHEME 22



was established that the Berry pseudo-rotational pathway was the preferred route for rearrangement.

Because of possible disorder in the crystal, it was possible only to suggest [151] that both the Ru—C—O and Ru—N—O bond angles in the molecular structure of $Ru(NO)(CO)(PPh_3)_2I$ (127) were about 159°. Both $Ru(NO)(PPh_3)_2(SO_4)Cl$ (128) [152] and $Ru(NO)(PMePh_2)_2Cl_3$ (129) [153] adopt octahedral geometries. In a comparison of the Ru—N distances of 129 with that of $Ru\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2Cl_3$, [154] it was suggested the NO ligand is a stronger π-acceptor than ArN_2.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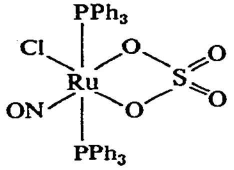
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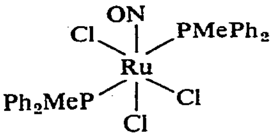
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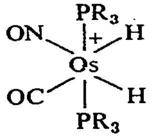

(130)

Treatment of $Os(NO)(CO)L_2Cl$ ($L = PPh_3$ or $P(C_6H_{11})_3$) with $AgPF_6$ and H_2 gave [155] the fluxional $[Os(NO)(CO)L_2H_2]^+$ (130). It was observed that intramolecular rearrangement could not occur via a single hydride migration from one face of a distorted (tetrahedral) intermediate to another, by a mechanism similar to that proposed for FeH_2L_4 [156] (L = tertiary phosphine, phosphite, etc.), but it was suggested that some residual H···H interaction might be retained in the molecule and that rotation of H···H about the ON—Os—CO plane, in a manner similar to olefin rotation in $[Os(NO)(CO)(C_2H_4)(PPh_3)_2]^+$, [157] could occur. Treatment of 130 with CO afforded $[Os(NO)(CO)_2L_2]^+$ and, while $[Os(NO)(CO)(PPh_3)_2H_2]^+$ gave, with PPh_3, $[Os(NO)(CO)(PPh_3)_3]^+$, a similar reaction with $P(C_6H_{11})_3$ gave $[Os(NO)(CO)\{P(C_6H_{11})_3\}_2H]^+$.

A theoretical justification for the value of the M—N—O bond angle in, and overall molecular geometry of, a series of five-coordinate nitrosyl complexes have been made [158]. Among the species considered were $Fe(NO)(S_2CNR_2)_2$, $[Fe(NO)\{S_2C_2(CN)_2\}_2]^{2-}$, $[Ru(NO)_2(PPh_3)_2Cl]^+$, $[Ru(NO)(diphos)_2]^+$, $Ru(NO)(PPh_3)_3H$, $[Os(NO)(CO)_2(PPh_3)_2]^+$ and $[Os(NO)_2(PPh_3)_2(OH)]^+$. A series of "ground rules" was established:

(*a*) the better the σ- or π-donor ability of the basal ligands, the more likely is the M—N—O group to bend in a square pyramidal system;

(*b*) in compounds of the type $[M(NO)L_2L'_2]^z$, L being *trans* to L′, the NO group should bend in the plane containing the poorer donor ligands;

(*c*) in a compound of the type $M(NO)L_2DA$ (D = π-donor, A = π-acceptor, D *trans* to A), if the NO group bends in the D—M—A plane, then it should bend towards A;

(*d*) the NO group is less likely to bend in an equatorial position of a trigonal bipyramid than in the apical site of a square pyramid;
(*e*) if NO bends in an equatorial position of a trigonal bipyramid, then it would prefer to do so in the axial plane than in the equatorial plane;
(*f*) NO groups in axial positions in trigonal bipyramids and basal sites in square pyramids prefer to be linearly coordinated;
(*g*) in the species $M(NO)L_4$, if L is a strong π-acceptor, a trigonal bipyramidal structure with equatorial NO will be preferred, but if L is a strong π-donor, a range of geometries is possible, from a strongly bent NO group in a square pyramid to a less bent equatorial NO in a trigonal bipyramid;
(*h*) a bent NO group will have the N atom displaced from the principal coordination axis in the direction of π-coordination.

Dinitrosyl complexes

The helium(I) photoelectron spectra of $Fe(NO)_2(CO)_2$, $Co(NO)(CO)_3$ and $Ni(CO)_4$ were measured [159] and interpreted by ab initio SCF molecular orbital calculations. The ionisation potentials calculated using Koopman's theorem did not provide a satisfactory interpretation of the spectra of the nitrosyls.

The structures of $Fe(NO)_2(CO)(PPh_3)$ and $Fe(NO)_2(PPh_3)_2$ have been determined crystallographically [160]. Both have distorted tetrahedral geometries and some pertinent bond lengths and angles are given, together with comparable data from related nitrosyls, in Table 2. The structure of $Ru(NO)_2(PPh_3)_2 \cdot \frac{1}{2} C_6H_6$ has also been described [161], the nitric oxide ligands being described as coordinated NO^+. Treatment of $Ru(NO)_2(PPh_3)_2$ with $Ru(PPh_3)_3Cl_2$ in dry benzene in the presence of zinc dust afforded good yields of $Ru(NO)(PPh_3)_2Cl$, a better synthesis of this coordinatively unsaturated species than that reported previously [162].

Reaction of $M(NO)_2(PPh_3)_2$ (M = Ru or Os) with CO at 100 atm. over 24 h or under UV light gave [163] $M(CO)_4(PPh_3)$, and presumably CO_2 and N_2O,

TABLE 2

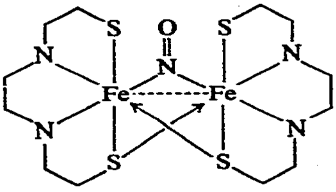
STRUCTURAL PARAMETERS FOR FOUR-COORDINATE IRON, RUTHENIUM AND RELATED NITROSYL COMPOUNDS

Compound	M—N (Å)	M—N—O (°)	N(C)—M—N(C) (°)	P—M—P (°)
$Fe(NO)_2(CO)(PPh_3)$	1.71	178	104	104
$Fe(NO)_2(PPh_3)_2$	1.65	178	124	112
$Fe(NO)_2(f^6\text{-phos})$ [a]	1.65	178	125	87
	1.66	177		
$Ru(NO)_2(PPh_3)_2$ [b]	1.76	171	139	104
	1.78	178		
$Co(NO)(CO)(PPh_3)_2$ [c]	1.71	178	121	114
	1.73	179		
	1.76	179		
$Ir(NO)(CO)(PPh_3)_2$	1.79	174	129	104
$[Ir(NO)_2(PPh_3)_2]^+$ [d]	1.77	164	154	116

[a] f^6-phos ≡ $Ph_2PC{=}C(PPh_2)CF_2CF_2CF_2$. [b] Benzene solvated complex [161]. [c] Disordered crystal. [d] ClO_4^- salt.

although this was not directly confirmed. Similar treatment of $Fe(NO)_2(PPh_3)_2$, however, afforded $Fe(NO)_2(CO)(PPh_3)$ and $Fe(NO)_2(CO)_2$, but no CO_2 or N_2O. From a kinetic study of ^{15}NO exchange with $Fe(NO)_2LI$ (L = PPh_3 or $AsPh_3$) it was established [164] that reaction occurred via a second-order process, perhaps involving a five-coordinate intermediate. Dimerisation of buta-1,3-diene to 4-vinylcyclohex-1-ene was achieved catalytically [165] using a mixture of $[Fe(NO)_2Cl]_n$ and $LiAlH_4$, $NaBH_4$ or $AlEt_2Cl$.

Treatment of the dimeric iron(II) complex of *N,N'*-dimethyl-*N,N'*-bis(β-mercaptoethyl)ethylenediamine with NO^+ gave **131** [166]. The Fe—Fe distance is 2.47 Å. This may be compared with the metal—metal separation in the



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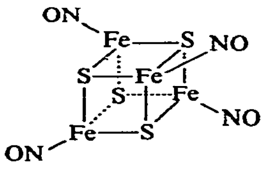

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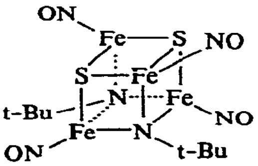


(133)

unnitrosylated species, viz. 3.21 Å, which is non-bonding [167]. Cyclic voltammetry indicated that the species could be reduced, but treatment with $[Et_4N][BH_4]$ failed to provide an anionic species.

In refluxing toluene, $Hg\{Fe(NO)(CO)_3\}_2$ gave [168] the diamagnetic $Fe_4(NO)_4(\mu_3\text{-}S)_4$ (**132**), while treatment with $\{(t\text{-}Bu)N\}_2S$ afforded $Fe_4(NO)_4(\mu\text{-}S)_2(\mu_3\text{-}N\text{-}t\text{-}Bu)_2$ (**133**)· The former has idealised T_d symmetry in which the Fe_4 unit forms a completely bonding tetrahedron. The latter has idealised C_{2v} symmetry and may be regarded as an Fe_2S_2 fragment fused with an Fe_2N_2 fragment via two Fe—S, two Fe—N and four Fe—Fe bonds, thereby forming four chemically equivalent Fe_2SN fragments. The Fe—Fe bond lengths in these and related Fe_4S_4 clusters are summarised in Table 3. Cyclic voltammetric studies indicated that **132** could be oxidised and reduced in one electron processes, whereas **133** could be reduced in four one-electron steps.

TABLE 3

METAL—METAL DISTANCES IN Fe_4 CLUSTERS

	$Fe_4(NO)_4S_4$	$Fe_4(NO)_4S_2(N\text{-}t\text{-}Bu)_2$	$(\eta^5\text{-}C_5H_5)_4Fe_4(\mu_3\text{-}S)_4$	$[Fe_4(SCH_2Ph)_4(\mu_3\text{-}S)_4]^{2-}$
Fe—Fe distance (Å)	2.63	2.64	2.65	2.78
		2.56	(3.36)	2.73
		2.496		

Aryldiazo complexes

From ^{19}F NMR spectral measurements of $Fe(NO(N_2Ar)(CO)(PPh_3)$ and $[Fe(N_2Ar)(CO)_2(PPh_3)_2]^+$ (Ar = Ph, *m*- or *p*-FC_6H_4), it was established [169] that ArN_2 was a poorer π-acceptor than NO. Using ^{15}N labelling experiments, ν(NN) was identified.

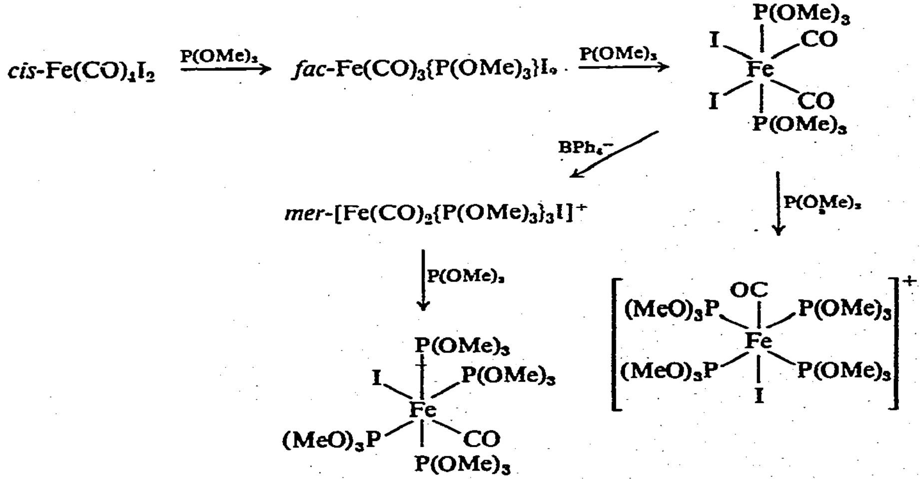
Reaction of $Fe(CO)_3(PPh_3)_2$, $[Fe\{S_2C_2(CN)_2\}_2]_2^{2-}$, $[Fe\{SCH_2CH(NH_3)CO_2\}_2]^{2+}$ and $Fe(CO)_2\{SCH_2CH(NH_2)CO_2\}_2$ with ArN_2^+ (Ar = C_6H_5, *p*-F-, Br-, NO_2-, NEt_2-, Me-, OMe-, CF_3-, SO_3H) failed to provide aryldiazo complexes [170]. Instead, ligand abstraction occurred leading to the formation of $[ArN_2PPh_3]^+$, $ArN_2SCH_2CH(NH_2)CO_2H$ and ArSC(CN)=C(CN)SAr. However, similar treatment of $Ru(CO)_3(PPh_3)_2$ gave [171] $[Ru(N_2Ar)(CO)_2(PPh_3)_2]^+$, which could be protonated by HBF_4 affording $[Ru(NH{=}NAr)(CO)_2(PPh_3)_2]^{2+}$.

Metal trialkylphosphite complexes

Reduction of $Fe\{P(OMe)_3\}_3Cl_2$ by sodium amalgam in the presence of $P(OMe)_3$ afforded [172] the trigonal bipyramidal $Fe\{P(OMe)_3\}_5$. Oxygenation of this gave $(MeO)_3PO$, but CF_3CO_2H or NH_4PF_6 afforded $[Fe\{P(OMe)_3\}_5H]^+$, and prolonged contact with CF_3CO_2H led to the formation of $[Fe\{P(OMe)_3\}_5]^{2+}$. There was some evidence that $Fe\{P(OMe)_3\}_5$ reacted with MeI giving $[Fe\{P(OMe)_3\}_5Me]^+$, but with EtI, although an ethyl complex may have been formed initially, the products were C_2H_4 and $[Fe\{P(OMe)_3\}_5H]^+$ (β-elimination?). While allyl halides reacted to give $[(\eta^3\text{-}C_3H_5)Fe\{P(OMe)_3\}_4]^+$, benzyliodide afforded only $Fe\{P(OMe)_3\}_3I_2$ and dibenzyl. There was no fast exchange of $P(OMe)_3$ with $Fe\{P(OMe)_3\}_5$, and while no substitution by CO occurred in benzene, in ether or methanol both $Fe(CO)\{P(OMe)_3\}_4$ and $Fe(CO)_2\{P(OMe)_3\}_3$ were produced. PF_3 reacted to give $Fe\{P(OMe)_3\}_3(PF_3)_2$.

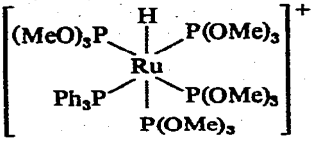
It has been observed that in iron(II) complexes, $P(OMe)_3$ closely resembles isocyanide ligands, being a strong σ-donor and strong π-acceptor. Reaction of $Fe(CO)_2\{P(OMe)_3\}_2I_2$ with $P(OMe)_3$ gave [173] $[Fe(CO)_2\{P(OMe)_3\}_3I]^+$ and

SCHEME 23



$[Fe(CO)\{P(OMe)_3\}_4I]^+$; the relationship of these to other carbonylphosphite complexes is illustrated in Scheme 23. The complexes $[Fe\{P(OMe)_3\}_6]^{2+}$ and $Fe\{P(OMe)_3\}_4Cl(SnCl_3)$ were also described.

Treatment of $[Ru(C_7H_8)Cl_2]_n$ (C_7H_8 = norbornadiene) with $P(OR)_3$ (R = Me or Et) afforded $[Ru\{P(OR)_3\}_5Cl]^+$ and $[Ru\{P(OR)_3\}_6]^{2+}$, while the corresponding bromide gave [174] $[Ru\{P(OR)_3\}_5Br]^+$ and $[Ru_2\{P(OEt)_3\}_6(\mu_2\text{-}Br)_3]^+$. With $Ru(PPh_3)_3HCl$, $[Ru\{P(OR)_3\}_5H]^+$ and $[Ru\{P(OR)_3\}_4(PPh_3)H]^+$ (134) were formed. In ethanol, $Os(PPh_3)_3Br_2$ reacted with $P(OEt)_3$ to give $[Os\{P(OEt)_3\}_5\text{-}Br]^+$, while in acetonitrile, $[Os\{P(OEt)_3\}_6]^{2+}$ was produced. Treatment of $RuCl_3 \cdot 3H_2O$ with $P(OEt)_3$ and $NaBH_4$ gave [175] initially $Ru\{P(OEt)_3\}_4Cl_2$, and then the air sensitive $Ru\{P(OEt)_3\}_4H_2$.



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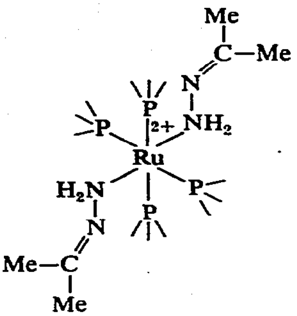

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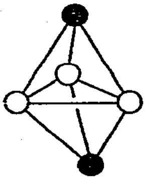

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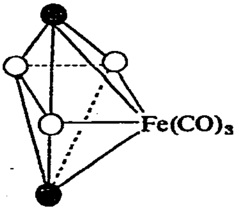
● ≡CH ○ ≡BH



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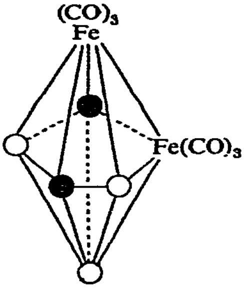

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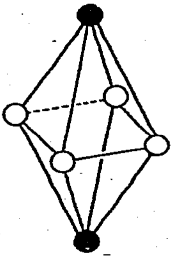

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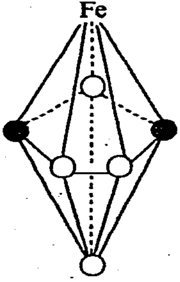


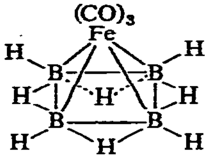
(140)

Reaction of $[Ru(C_8H_{12})(N_2H_4)_4][BPh_4]_2$ with L($P(OMe)_3$, $P(OEt)_3$, $P(OMe)_2Ph$, $P(OEt)_2Ph$) in actone gave [176] $[RuL_4(NH_2N{=}CMe_2)_2][BPh_4]_2$ (135).

Metallo-borane and -carborane complexes

Reaction of an excess of $Fe(CO)_5$ with 1,5-$C_2B_3H_5$ (136) gave [177] $Fe(C_2B_3H_5)(CO)_3$ (137) and $Fe_2(C_2B_3H_5)(CO)_6$ (138), and 137 was converted into 138 by $Fe(CO)_5$. $Fe(CO)_5$ reacted with 1,6-$C_2B_4H_6$ (139) giving $Fe(C_2B_4H_6)(CO)_3$ (140), while 2,4-$C_2B_5H_7$ afforded 1,2,4-$Fe(C_2B_4H_6)(CO)_3$ and 3,1,7-$Fe(C_2B_5H_7)(CO)_3$, which has been reported previously [178].

Pentaborane-9 reacted with $Fe(CO)_5$ to give [179] $Fe(B_4H_8)(CO)_3$ (141), also obtainable from tetraborane-10 and $Fe_2(CO)_9$ (together with μ-$Fe(CO)_4B_6H_{10}$). The compound 141 is a member of the series including B_5H_9, $C_4H_4Fe(CO)_3$ and $Fe_5(CO)_{15}C$. It was noted that B_5H_9 reacted with $Fe(CO)_3$ by loss of BH, whereas *nido*-$C_2B_4H_8$ reacted by loss of two bridge hydrogen atoms to give *closo*-$Fe(C_2B_4H_8)(CO)_3$ [180]. Hexaborane-10 reacted with $Fe_2(CO)_9$ to give $Fe(CO)_5$ and μ-$Fe(CO)_4B_6H_{10}$ (142) [181]. Treatment of this latter species with KH gave $K[\mu\text{-}Fe(CO)_4B_6H_9]$ which could be isolated as the Bu_4N^+ salt. Treatment of this anion with BH_3 gave [182] $[Bu_4N][\mu\text{-}Fe(CO)_4B_7H_{12}]$ (143) which afforded, on protonation at low temperature, the unstable $Fe(B_7H_{11})(CO)_3$.



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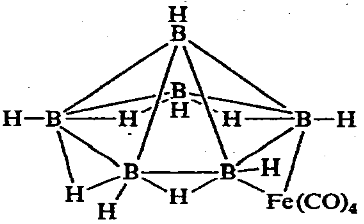

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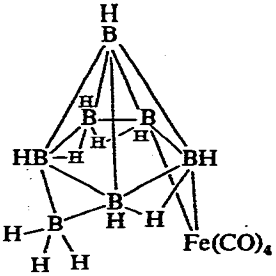


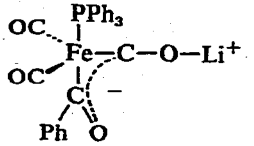
(143)

Complexes containing metal—carbon σ-bonds

Metal carbonyl complexes

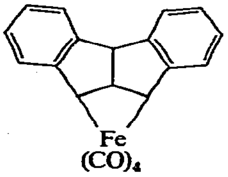
Benzylbromide reacted with $Fe_2(CO)_9$ in hexane giving [183] dibenzylketone in good yield. The related ketones $(RCH_2)_2CO$ (R = 3,5-$Me_2C_6H_3$, 1- or 2-naphthyl, 2- or 4-bromo-1-naphthyl) were prepared similarly. It seems likely that $Fe(CO)_4(CH_2R)_2$ is an intermediate in this reaction, since $Fe_2(CO)_9$ reacted with $C_6F_5CH_2Br$ giving the unstable $Fe(CO)_4(CH_2C_6F_5)_2$, which decomposed on heating to afford $(C_6F_5CH_2)_2CO$. The related bis{(heptafluoro-2-naphthyl)-methyl}iron tetracarbonyl was also prepared, but $Fe_2(CO)_9$ reacted with $(CF_3)_3CI$ in hexane giving only $(CF_3)_3CH$ and $Fe(CO)_4I_2$.

There is direct IR spectral evidence [184] for the interaction of Li^+ with *trans*-$[Fe(CO)_3(PPh_3)(COPh)]^-$ in ether. The ion pair interaction (B) is disrupted by the addition of small amounts of a solvent of higher dielectric constant, e.g. THF or DMF. An even stronger ion pair interaction is observed with $MgCl^+$.



(B)

Dibenzosemibullvalene reacted with $Fe_2(CO)_9$ giving [185] 144 and 145, and the structure of the former was confirmed [186] by X-ray crystallography (the Fe has octahedral geometry and the 4-membered ferretane ring is planar). Quadricyclane reacted with $Fe(CO)_5$ under UV light to give 146, 147 and 148, and 149 could be obtained [187], together with an unidentified complex, in a similar reaction with quadricyclanone.



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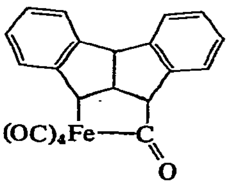

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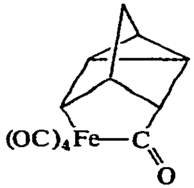

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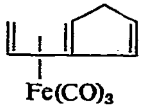

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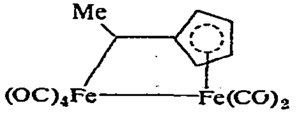

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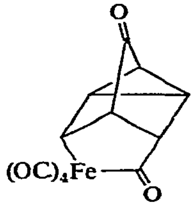
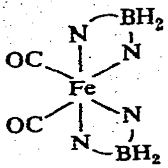


(149)

Reaction of $(\eta^3\text{-}C_3H_5)Fe(CO)_3I$ with $K[H_2B(pyz)_2]$ (pyzH = pyrazole) afforded $Fe(CO)_2\{H_2B(pyz)_2\}_2$ (150), but with $K[HB(pyz)_3]$, a mixture of complexes, viz. $Fe\{HB(pyz)_3\}_2$, $[Fe(CO)_3(pyz)]_2$ (151), $Fe(CO)_3(C_3H_5N_2C_3H_3)$ (152), *trans*-$Fe(CO)_2\{HB(pyz)_3\}CH{=}CHMe$ (153) and $Fe(CO)_2\{HB(pyz)_3\}COCH{=}CHMe$, (154). The proposed mechanism whereby the various species are produced is outlined in Scheme 24. Treatment of $Fe_2(CO)_9$ with *N*-allylpyrazole also afforded 152, and reaction of $Fe_2(CO)_9$ with $K[HB(3,5\text{-}Me_2C_3HN_2)_3]$ gave $Fe\{HB(3,5\text{-}Me_2C_3HN_2)_3\}_2$ and the 3,5-ring methylated analog of 152. The bis(pyrazolyl-



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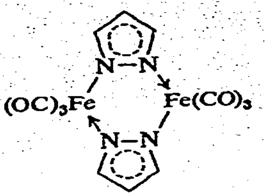
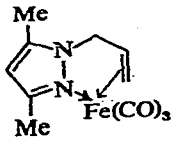


(151)

$N{-}BH_2{-}N \equiv H_2B(pyr)_2$



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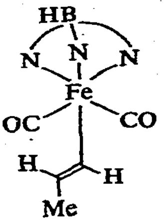

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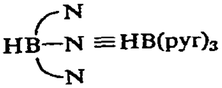
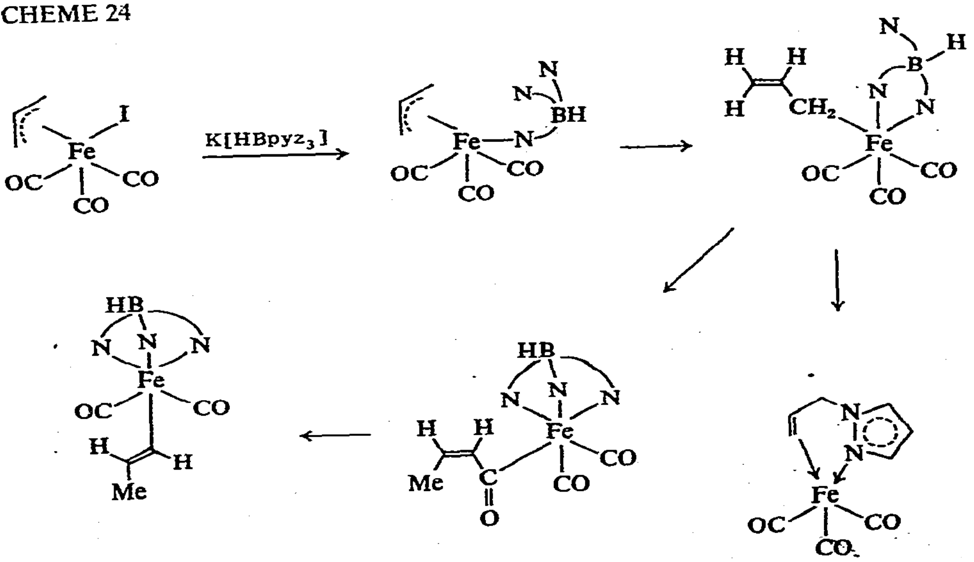
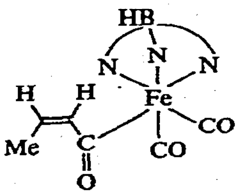


$HB(N)_3 \equiv HB(pyr)_3$

SCHEME 24



borate), $K[H_2B(pyz)_2]$, reacted with $Fe(CO)_4(C_3F_7)I$ giving [189] *fac-* and *mer*-isomers of $Fe(CO)_3\{H_2B(pyz)_2\}(C_3F_7)$ (155 and 156). With $K[HB(pyz)_3]$, however, the octahedral $Fe(CO)_2\{HB(pyz)_3\}(C_3F_7)$ is obtained.



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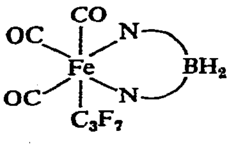

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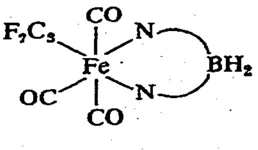
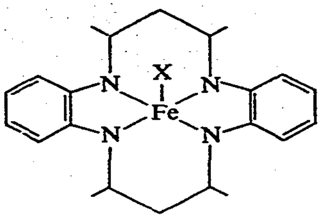


(156)

Macrocyclic ring complexes

Alkylation of the complex **157** (X = NCS) giving the paramagnetic **157** (X = Me, Et or Ph) (μ = 2.21 B.M; X = Me) was achieved [190] using methyl-, ethyl- or phenyl-hydrazine. The five-coordinate structure was confirmed crystallographically. It was found that the Fe—N distances (1.90—1.91 Å) were shorter than those observed [191] for low-spin tetraphenylporphyriniron(III) complexes. The Fe—C(alkyl) bond length, 1.93 Å, was significantly shorter than the Co—C distances in the analogous cobalt(III) complexes.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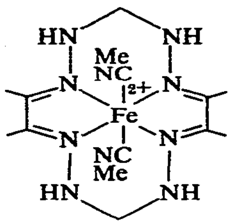
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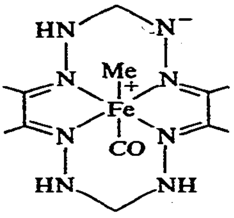
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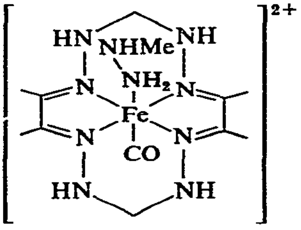
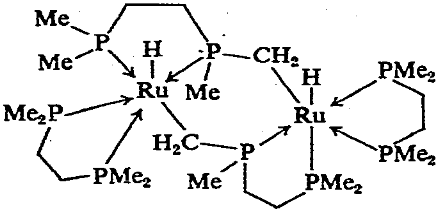

(160)

Treatment of **158** with $MeNHNH_2$, KO-t-Bu and CO (1 atm.) in acetonitrile gave [192] **159**, but in CF_3CH_2OH, **160** was formed. The structure of **159** was investigated crystallographically. It was found that the Fe—C(methyl) distance, 2.08 Å, was markedly longer than expected [190] (see above). This bond lengthening could be attributed to the powerful *trans* influence of the CO group. The Fe—N distances are a little shorter than in related compounds, although they are comparable to dimethylglyoximato derivatives. With acid, **159** afforded methane, and with Hg^{2+} in dimethylsulphoxide, $MeHg^+$ salts were rapidly formed.

Phosphine complexes

Reaction of $Fe(acac)_3$ with $Ph_2PCH_2CH_2PPh_2$(diphos) and $AlMe_2(OEt)$ afforded [193] $Fe(diphos)_2Me_2$, which produced methane when treated with H_2SO_4. With iodide, $Fe(diphos)_2I_2$, CH_4 and C_2H_6 (the last two in the ratio 1 : 2.5) were produced, while reaction with D_2 gave $Fe(diphos)_2D_2$ (isolated as a benzene solvate) and CH_3D. Thermolysis of the dimethyl complex at 130—135° afforded CH_4, C_2H_6 and C_2H_4 in the ratio 75 : 20 : 5, while decomposition in dichloromethane at room temperature gave the same hydrocarbons in a different ratio, viz. 50 : 24 : 26. In deuteriodichloromethane, CH_4, C_2H_6, C_2H_4, $CD_2{=}CH_2$ and C_2D_4 were produced in the ratio 50 : 24 : 8 : 14 : 4, and there was no evidence for the formation of *cis*- or *trans*-CHD=CHD or CH_3D (the metallic product was, of course, $Fe(diphos)_2Cl_2$). These results were thought to suggest the intermediacy of "carbene" species, viz. $\{Fe{=}CH_2\}$ or $\{Fe{=}CD_2\}$. Decomposition in basic solvents, such as pyridine or ethylamine, afforded only CH_4, and no C_2H_4 was produced in dichloromethane in the presence of oxygen. The ethyl, n-propyl and i-butyl analogs of $Fe(diphos)_2Me_2$ were markedly less stable than the dimethyl. Thus, replacement of $AlMe_2(OEt)$ by $AlEt_2(OEt)$ led to the formation of $Fe(diphos)_2(C_2H_4)$, while AlR_3 (R = n-Pr or i-Bu) gave only $Fe(diphos)_2H_2$.

The structure of the compound **161**, obtained [194] by thermolysis of

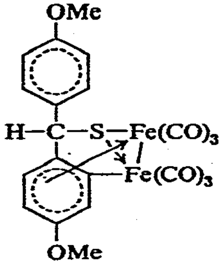


(161)

$Ru(Me_2PCH_2CH_2PMe_2)_2$(naphthalene), has been determined [195]. The dimeric compound appears to be formed by oxidative addition of $H{-}CH_2{-}$ to ruthenium(0), thereby forming octahedral ruthenium(II), in which the hydride ligand occupies the most sterically hindered position at the metal.

o-Metallation reactions

Thiobenzophenones reacted with $Fe_2(CO)_9$ giving [196], inter alia, **162**, which, on treatment with PPh_3 in benzene at room temperature, afforded **163**. Heating either **162** or **163** in benzene in the presence of amines gave the demetallated product, **164**.



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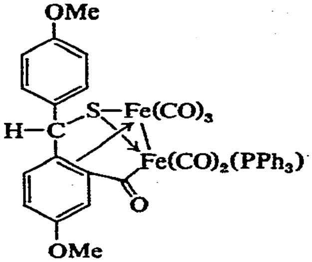

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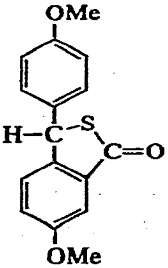

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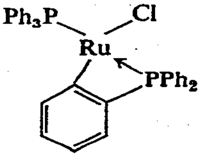
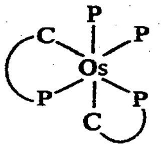


(165)

Reaction of $Ru(PPh_3)_3HCl$ with RCH=CHR in vacuo gave [197] **165**, together with PPh_3 and RCH_2CH_2R. The *o*-metallated compound **165**, was thought to react with H_2 giving a dihydrido ruthenium(IV) intermediate which subsequently dehydrogenated to $Ru(PPh_3)_2HCl$, and reformed the starting material with PPh_3. Treatment of **165** with HCl afforded $Ru(PPh_3)_2Cl_2$ and eventually $Ru(PPh_3)_3Cl_2$, and with CO, $Ru(CO)(PPh_3)(o\text{-}C_6H_4PPh_2)Cl$ was produced.

In boiling decalin, a series of osmiumtriphenylphosphine hydride complexes reacted with $P(OPh)_3$ to afford [198] a series of *o*-metallated and non-metallated phosphite compounds. Thus, $Os(PPh_3)_3H_4$ gave **166**, while $Os(CO)(PPh_3)_3HCl$ (**167**) gave $Os(CO)(PPh_3)_2\{P(OPh)_3\}HCl$ (**168**) and then $Os(CO)(PPh_3)\{P(OPh)_3\}_2HCl$ (**169**). The related $Os(CO)(AsPh_3)_3HCl$ reacted with $P(OPh)_3$ giving $Os(CO)(AsPh_3)_2\{P(OPh)_3\}HCl$, with a configuration identical to **168**. Treatment of **169** with $P(OPh)_3$ in decalin afforded **170** and **171**, and the latter eventually gave **172**. With $Os(CO)(PPh_3)_3H_2$ (**173**) triphenylphosphite reacted according to Scheme 25 to give a series of *o*-metallated complexes different to those obtained from $Os(PPh_3)_4H_4$ or $Os(CO)(PPh_3)_3HCl$.



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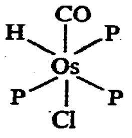

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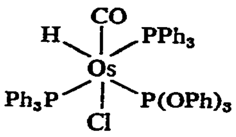

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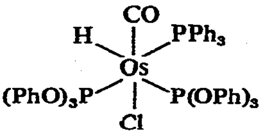

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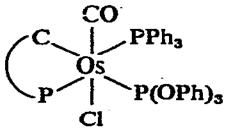

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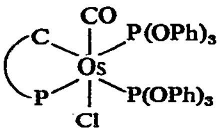

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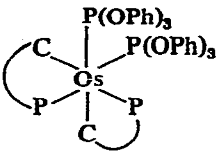

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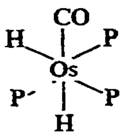


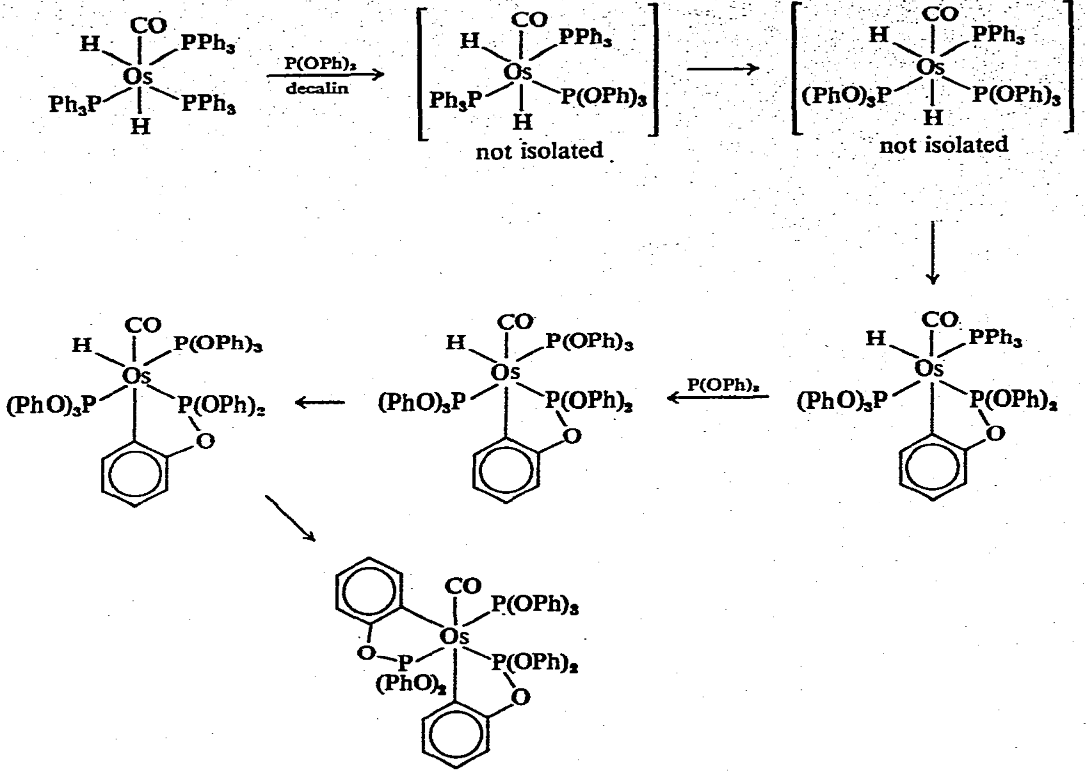
(173)

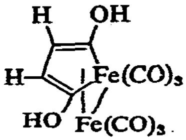
Ferrole complexes

Reaction of **174** with $CF_3C{\equiv}CCF_3$ gave [199] **175**. An earlier report that the diyne **176** reacted with iron carbonyl giving **177** [200] rather than **178** [201] has been investigated [202] using model compounds. Thus, treatment of the benzocyclobutadiene complex **179** with $Fe_3(CO)_{12}$ at 120° gave **180** and **181**, the latter having been prepared by other routes [203]. The structures of the compounds were confirmed crystallographically and it was shown that they did not interconvert at 120°. It was therfore suggested that **176** afforded **177** via an intermediary cyclobutadiene complex, **182**.

The inequivalence of the two Fe atoms in the ferrole complexes **183**, **184** and

SCHEME 25

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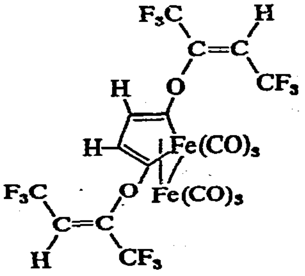
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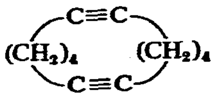
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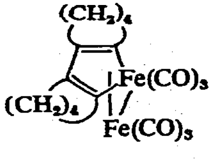
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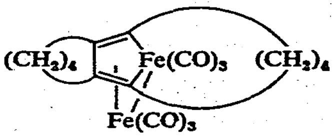
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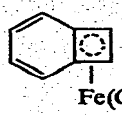

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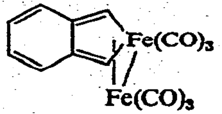
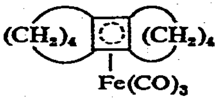


(180)

(181)



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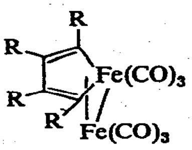

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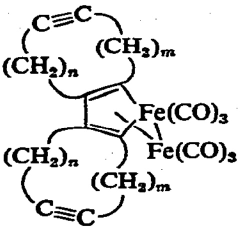

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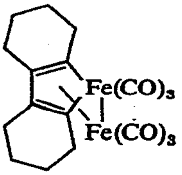
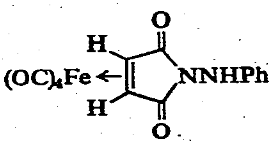


(185)

185, has been resolved [204] by Mössbauer spectroscopy in glassy n-butylbenzene at 85 ± 3 K. This inequivalence could not be resolved in the solid state at the same temperature.

Mono-olefin complexes

Reaction of $Fe_2(CO)_9$ with 1,2-dihaloethylenes gave [205] $Fe(CO)_4L$ (L = *trans*-RCH=CHR′; R, R′ = F, Cl, Br or I; CH_2=CHBr and CH_2=CCl_2). From IR spectral studies it was established that the olefin occupied an equatorial site in the trigonal bipyramidal molecule.



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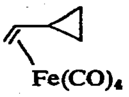

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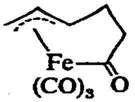

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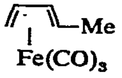

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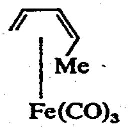

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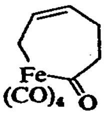

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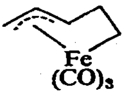


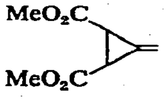
(192)

Treatment of $Fe(CO)_4(PhCOCH{=}CHCl)$ with $PhNHNH_2$ gave [206] 1,3-diphenylpyrazole (30%), while reaction of $Fe(CO)_4$(*cis*-$PhCOCH{=}CHCOPh$) with N_2H_4 in acetic acid gave 2,6-diphenylpyrazine (70%). In acetic anhydride, $Fe(CO)_4(PhNHNHCOCH{=}CHCO_2H)$ rearranged to give **186**, and the organic ligand could be displaced using $FeCl_3$. With $RNHNH_2$, $Fe(CO)_4$(maleic anhydride) reacted to give $Fe(CO)_4(RNHNHCOCH{=}CHCO_2H)$ (R = Ph, MeCO, $\{(COCH{=}CHCO_2H)Fe(CO)_4\}$) in high yields.

The vibrational spectra of $Fe(CO)_4$(maleic anhydride) and its *N*-methylmaleimide analog have been fully assigned [207].

Vinylcyclopropane reacted with $Fe(CO)_5$ under UV light at −50° to give [208] **187** and **188**. Above 0°, **187** decomposed to give $Fe_3(CO)_{12}$ and vinylcyclopropane, but at 50°, the dieneiron tricarbonyl complexes **189** and **190** were also formed. Carbonylation of **188** afforded **191**, while decarbonylation produced **192**; decomposition led to the formation of 2-cyclohexenone.

Cis- and *trans*-Feist's ester (**193**) reacted with $Fe_2(CO)_9$ giving [209] *cis*- or



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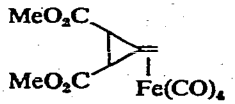
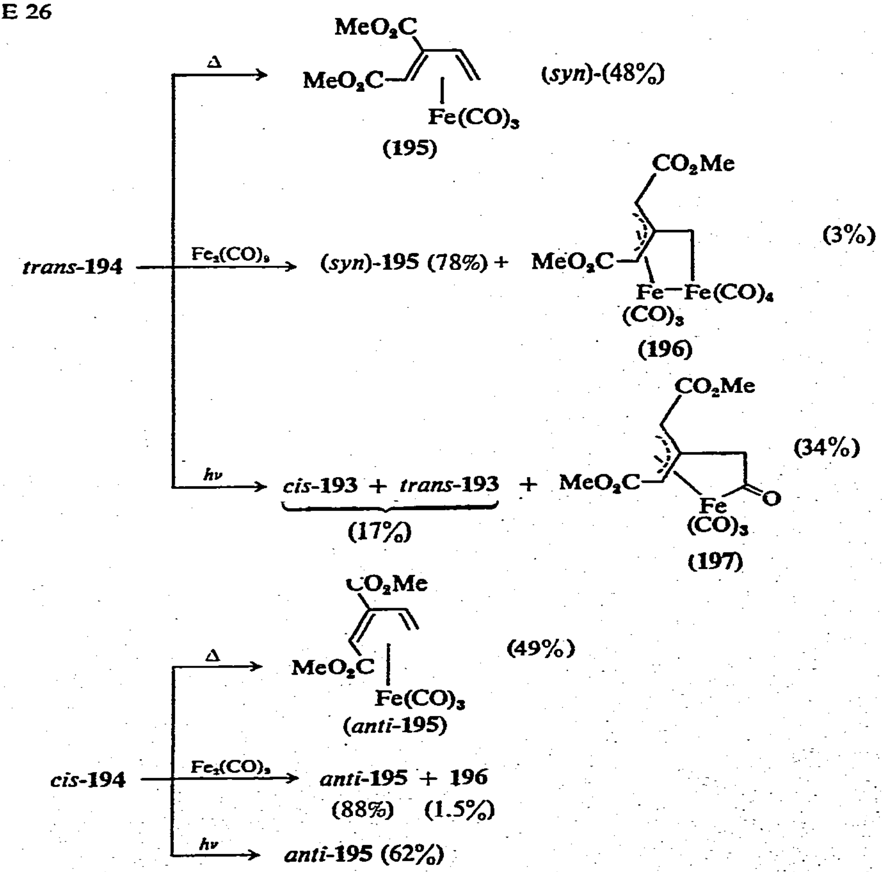


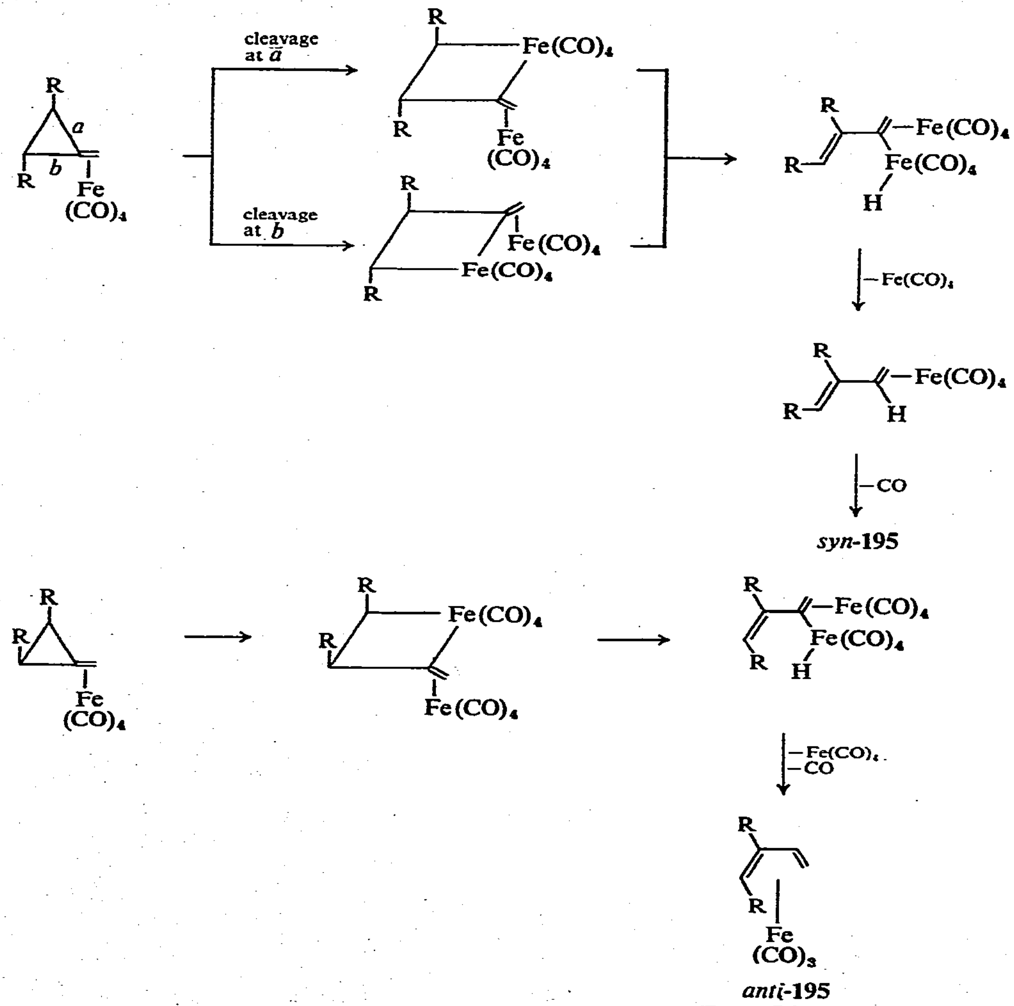
(194)

SCHEME 26



trans-**194**. In subsequent thermal reactions (Scheme 26) cleavage of the strained sp^2—sp^3-hybridised three-membered ring occurred predominantly, this cleavage being followed by a series of stereospecific reactions leading eventually to $Fe(CO)_3$ complexes of *cis*- and *trans*-1,3-butadiene-1,2-dimethylcarboxylates (**195**). A minor reaction pathway involved cleavage of the sp^3—sp^3 C—C bond of the ring to give di-iron species, viz. **196**. In a series of photochemical reactions, *cis*-**194** gave products parallel to those produced thermally, viz. *anti*-**195** and **196**, while *trans*-**194** gave the starting material, **193** together with an allyl-acyl species **197**. The reactions of principal importance involved the stereospecific rearrangements of *cis*-**194** and *trans*-**194** to *anti*-**195** and *syn*-**195**, respectively, and possible mechanisms for these transformations are shown in Scheme 27.

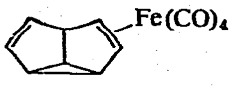
SCHEME 27



(R = CO_2Me)

The structure of *cis*-**194** has been determined [210] crystallographically. It was shown that the Fe atom is located in the same side of the three-membered ring as the ester groups. The intramolecular distances suggested substantial steric congestion between the ester carbonyl groups and the $Fe(CO)_4$ unit. Considerable rehybridisation had occurred at the olefinic linkage of the three-membered ring, and the geometry at the Fe atom was between trigonal bipyramidal and octahedral.

Semibullvalene reacted [211] with $Fe(CO)_5$ (1 : 3 mole ratio) under UV light at —50° to give **198** and **199** (2 : 1 ratio). Under the reaction conditions there was slow interconversion of **198** and **199**, and **198** was fluxional (Fig. 5). By heating **198** at 45°C in benzene, semibullvalene and **200** were formed.



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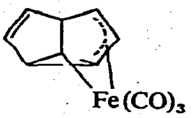
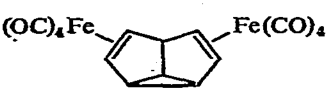


(199)

Semibullvalene reacted with $Fe(CO)_5$ under UV light at 25°C to give **198** and **201**. It was thought that **199** was formed in the process outlined in Scheme 28.



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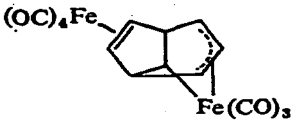
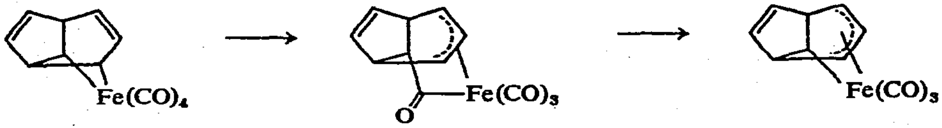


(201)

Reaction of $Fe(CO)_3(PhCH{=}CHCOR)$ (R = H, Me or Ph) with L (PMe_2Ph or $P(OMe)_3$) gave [212] $Fe(CO)_3L(PhCH{=}CHCOR)$.

SCHEME 28



Protonation of **202** in HBF_4/acetic anhydride gave [213] **203**. By using CF_3CO_2D, it was shown that deuterium was incorporated in the *anti*-methyl group. Thus the *S-cis* conformation of the 2-methylbutadiene ligand in the dieneiron tetracarbonyl complex was unequivocally demonstrated. Similar treatment of **204** and **205** gave **206**, demonstrating the *S-trans* configuration of the olefin in $Fe(CO)_4$(diene). It seemed likely that the preferred conformation of the diene in these compounds is *S-trans*, which should lead to the *syn*-1-methyl cation rather than the *anti*-isomer upon protonation.

It has been established [214], using a combination of ^1H and ^{13}C NMR studies

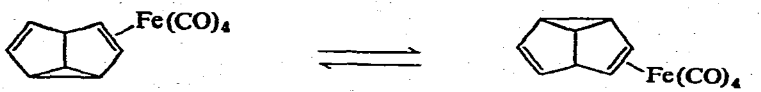
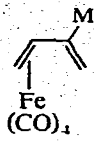
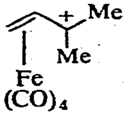


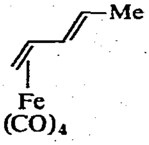
Fig. 5. The fluxional nature of 198.



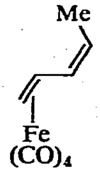
(202)



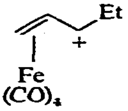
(203)



(204)



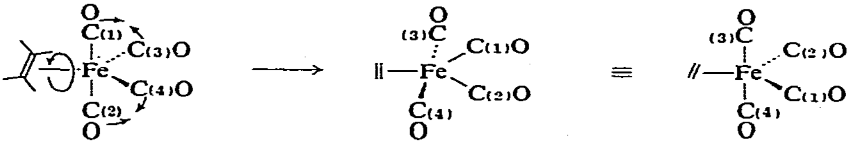
(205)



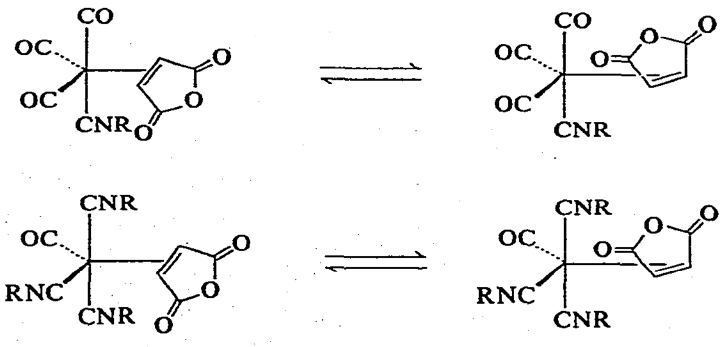
(206)

over a temperature range, that in Fe(CO)$_4$(olefin) (olefin = $CH_2{=}CHR$, R = CO_2Et, CN, Ph; PhCH=CHCOMe, *cis*- and *trans*-$RO_2CCH{=}CHCO_2R$, R = Me or Et; $CF_2{=}CFCl$ and $CCl_2{=}CF_2$) olefin rotation does not occur independently of CO site exchange. Rotation occurs in a process coupled to Berry pseudorotation of the five-coordinate complex (Scheme 29). The rate of rearrangement decreases in the order olefin = styrene > ethylacylate > benzalacetone > diethyl maleate > diethyl fumarate > trifluorochloroethylene. An alternative mechanism could involve intramolecular exchange of olefin with axial CO, the barrier to CO site exchange increasing with increasing π-acceptor strength of the olefin. This mechanism could be discounted by studying the fluxionality of Fe(CO)$_{4-n}$-($CNCH_2Ph$)$_n$(maleic anhydride) (prepared from Fe(CO)$_4$(maleic anhydride) and $PhCH_2NC$). In the equilibration illustrated in Scheme 29, no exchange of olefin with axial CO could be established, and from the equilibration outline in Scheme 30 it was shown that equatorial and axial isocyanide did not exchange at 0°C,

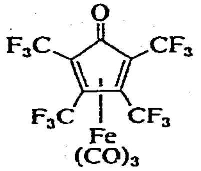
SCHEME 29



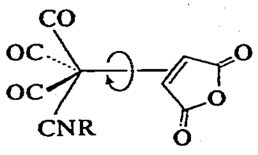
SCHEME 30



but did so above 60°C. Thus, the process of olefin rotation and CO site exchange could be a concerted process involving coupling of Berry rotation with $\mathrm{Fe}-\overset{\mathrm{C}}{\underset{\mathrm{C}}{\|}}$ rotation, or a non-concerted process involving a square pyramidal intermediate (C). The species so illustrated would not represent a transition state, but would be an intermediate of sufficient lifetime during which the rate determining olefin rotation could occur. It was further shown that the preference for equatorial sites in $Fe(CO)_3(CNCH_2Ph)$(olefin) was olefin > CO > $PhCH_2NC$, and that in $Fe(CO)_4(CNCH_2Ph)$, carbonyl and isocyanide site exchange was very fast. Similar fluxional behavious was observed [215] with $Ru(CO)_4$(olefin) (olefin = ethylacrylate or diethyl fumarate), obtained by photolysis of $Ru_3(CO)_{12}$ with the olefin. However, in 207, diene rotation did not occur. At 50°C, $Ru(CO)_4$-



(207)

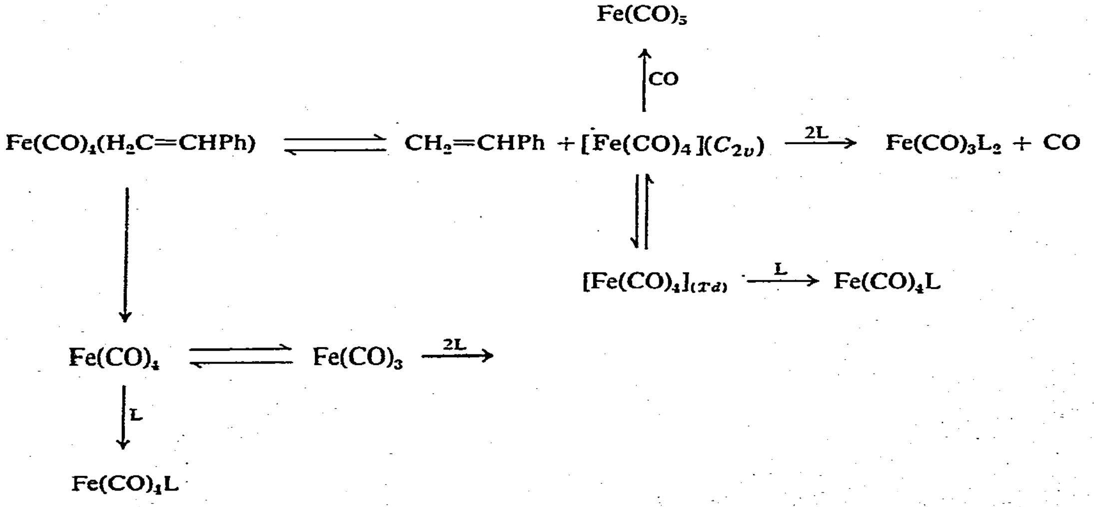


(C)

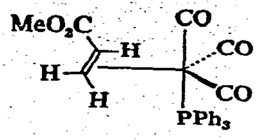
(diethyl maleate) was isomarised to the corresponding fumarate complex, and similar conversion of the $Fe(CO)_4$ derivatives could be achieved photochemically.

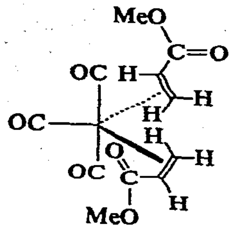
Displacement of styrene from $Fe(CO)_4(PhCH{=}CH_2)$ by L (pyridine, QPh_3, Q = P, As or Sb) was studied [216] kinetically in toluene and other solvents. Two mechanisms, both involving the intermediacy of $Fe(CO)_4$, were proposed, neither of which could be distinguished. When the reaction with PPh_3 was studied under CO pressure, it was further established that $Fe(CO)_3(PPh_3)_2$ was formed by reaction of PPh_3 with $Fe(CO)_3$, produced by CO dissociation from $Fe(CO)_4$ (Scheme 31).

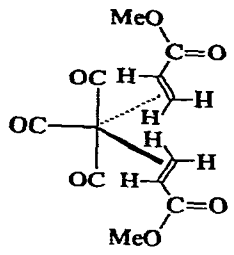
SCHEME 31

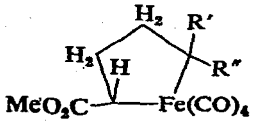


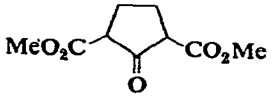
Photolysis of $Fe(CO)_4(CH_2{=}CHCO_2Me)$ (208), the structure of which has been confirmed crystallographically, in the presence of $H_2C{=}CHCO_2Me$ afforded [217] $Fe(CO)_3(CH_2{=}CHCO_2Me)_2$ (**209**) and (**210**) whose reactions are shown in Scheme 32. Methyl acrylate reacted with $Fe(CO)_4$(maleic anhydride)

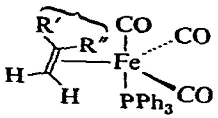

(208)


(209)

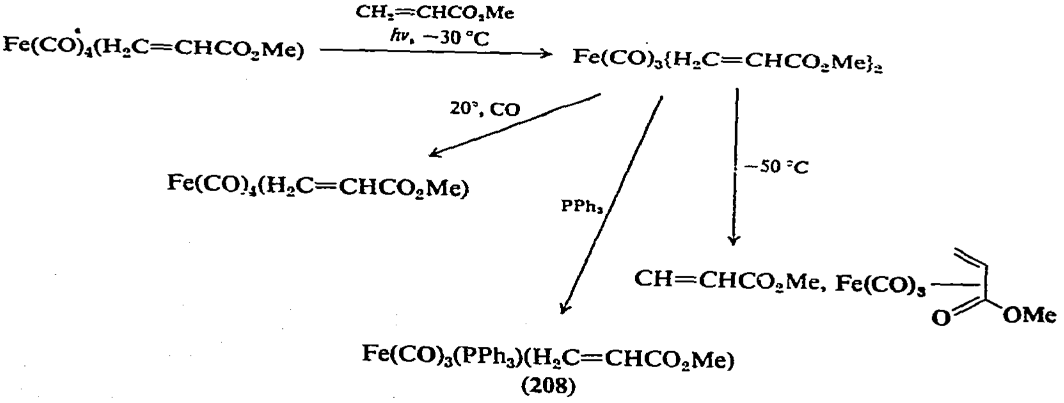

(210)


(211)


(212)


(213)

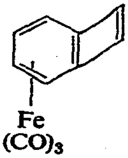
SCHEME 32



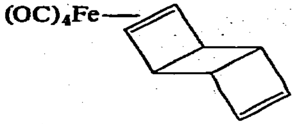
under UV light at 20°C giving some **211** ($R' = CO_2Me$, $R'' = H$ or $R' = H$, $R'' = CO_2Me$) which, on treatment with CO or PPh_3 under normal conditions afforded **212**, but gave with PPh_3 under UV light, **213**.

Syn-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene reacted with $Fe_2(CO)_9$ giving [218] **214**, which, in refluxing hexane afforded (by loss of CO in a reversible reaction)

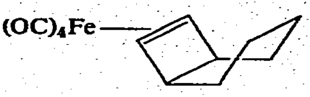

(214)


(215)

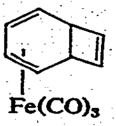
the corresponding tricarbonyl. The latter rearranged to **215** via a concerted disrotatory ring opening pathway. The complexes **216** and **217** similarly rearranged to give **218** and **219**. It was noted that the complexed bicylic triene in **215** and **218** was much more stable than the free ligand which readily undergoes a Cope rearrangement to give cyclooctatetraene; neither of the complexes behaved in this way on heating.



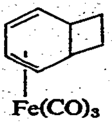
(216)



(217)

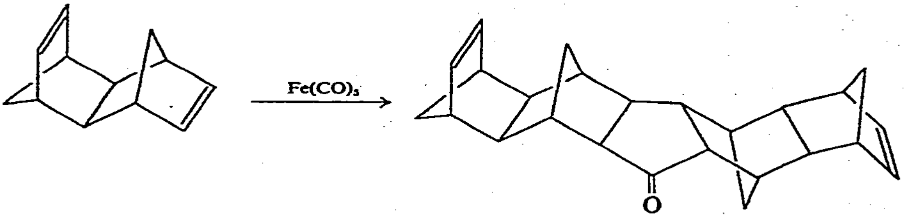


(218)



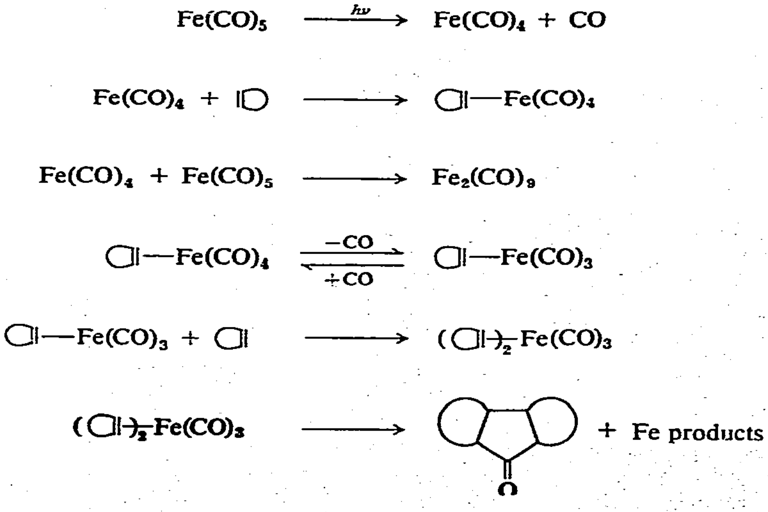
(219)

In the presence of $Fe(CO)_5$ under thermal or photolytic conditions, strained olefins couple and incorporate CO to give [219] with up to 77% yields of polycyclic ketones, viz. eq. 10. A mechanism for the photolytic coupling (Scheme 33) has been proposed, and a key intermediate (not shown in Scheme 33) may be **220**. Benzonorbornadienes (**221**; X = CH_2, C = CMe or O) similarly couple

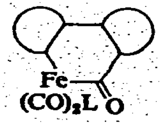


(10)

SCHEME 33

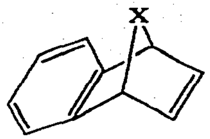


[220], without CO incorporation, in the presence of $Fe(CO)_2(NO)_2$, and benzonorbornadiene (**221**, X = CH_2) reacted at 100°C with $Fe(CO)_5$ to give a mixture

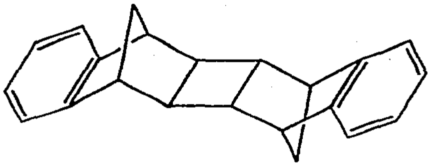


(220)

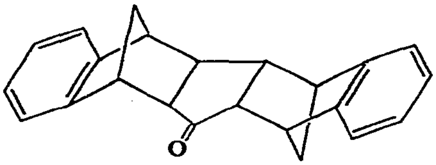
of 222 and 223, while the latter was produced exclusively using $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. With $Fe(CO)_5$ under UV light, or with $Fe_2(CO)_9$, 221 (X = O) afforded 224 which decomposed slowly to naphthalene with loss of iron carbonyl fragments via either 225 or 226.



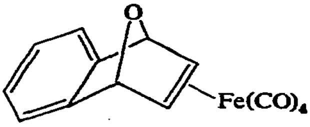
(221)



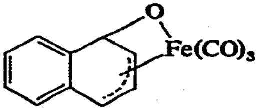
(222)



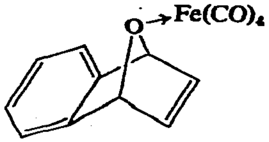
(223)



(224)



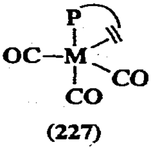
(225)



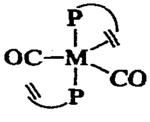
(226)

Complexes of combined olefin-phosphine or arsine ligands

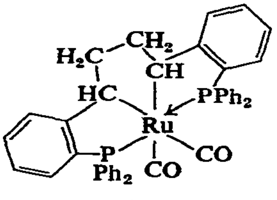
Reaction of *o*-styryldiphenylphosphine (SP) with $M_3(CO)_{12}$ (M = Fe or Ru) gave [221] $M(CO)_3(SP)$, (227) and $M(CO)_2(SP)_2$ (228). The structure of 228



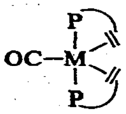
(227)



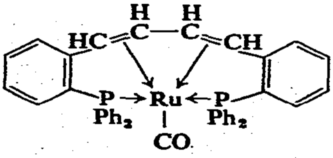
(228)



(229)



(230)

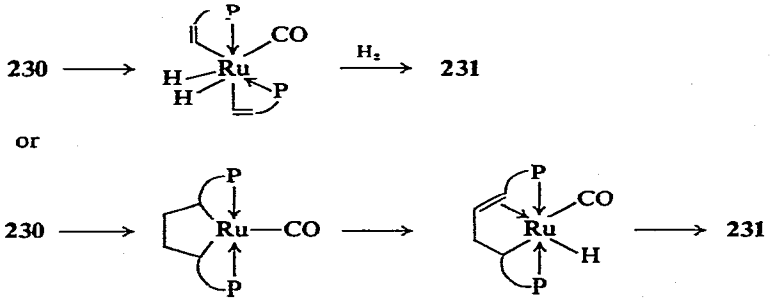


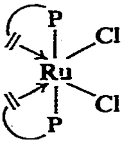
(231)

Fig. 6. Isomers of Ru(CO)ligand(X_2) (X = Cl or Br).

was confirmed crystallographically [222], and the coordinated vinyl group subtends an angle of 6° with the equatorial plane of the trigonal bipyramidal complex. In refluxing n-nonane, $Ru_3(CO)_{12}$ reacted initially with SP to give **228** and then afforded **229** together with **230** (which existed as three isomers according to the particular orientation of the coordinated SP ligands) and **231**. It appeared that **230** was derived from **228** by replacement of one CO group by the free vinyl group, and that **231** was derived from **230** by dehydrogenation followed by coupling of the vinyl groups to give the tetradentate ligand. It seemed probable that **228** and **229** are in equilibrium in a solution of refluxing n-nonane, and that **230** is formed from **228** rather than **229**. The structure of **229** is analogous to the intermediate proposed for tungsten-catalysed olefin metathesis and for rhodium-catalysed rearrangements of strained hydrocarbon rings.Reaction of two moles of HX (X = Cl or Br) with **231** afforded two isomers of Ru(CO)(ligand)X_2 (Fig. 6) which represent rare examples of stable mono-olefin complexes of ruthenium(II). The rearrangement of **230** to **231** may proceed via oxidative addition of β-vinyl CH_2 bonds to the metal, thereby affording a seven-coordinate dihydrido intermediate either in a concerted or stepwise fashion (Scheme 34). Reaction of *o*-styryldiphenylphosphine or its arsenic analog (SA) with $RuCl_3$ in alcohols gave [223] the oxidatively and thermally stable RuL_2X_2 (L = SP or SA). There are three isomers of $Ru(SP)_2Cl_2$, one of which is probably **232** and the other two may be **233** and **234**. However, the last

SCHEME 34





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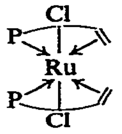

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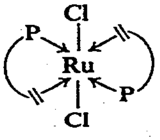
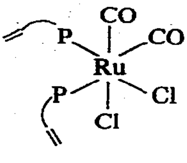
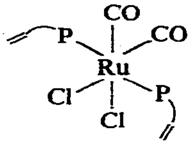


(234)

two may not be favoured sterically and isomerism could arise as a result of different orientations of the two vinyl groups which, however, must remain equivalent in each isomer. Carbonylation (by CO) of $Ru(SP)_2Cl_2$ gave two isomers of $Ru(CO)_2(SP)_2Cl_2$ (235 and 236); the former is concerted to the latter



(235)



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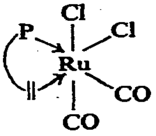
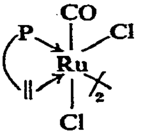
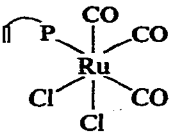


(237)



(238)

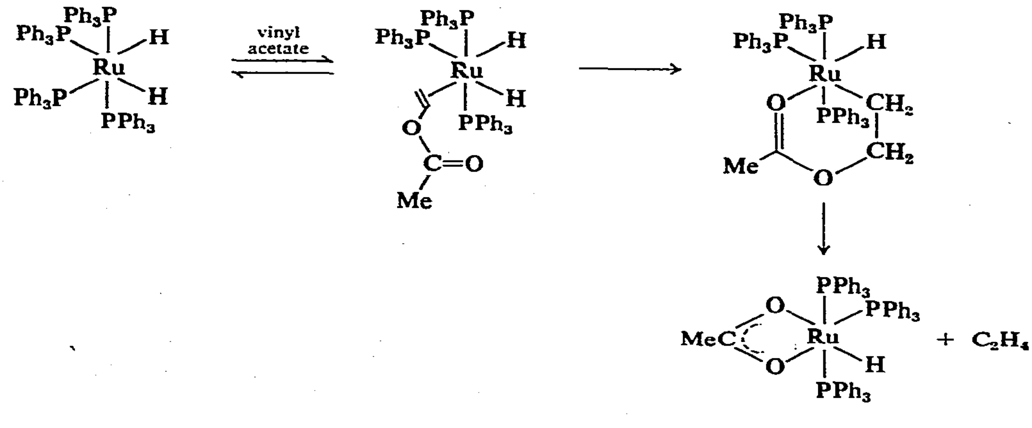


(239)

in dichloromethane. Reaction of $RuCi_3 \cdot 3H_2O$ with 1.5 to 2 moles of SP per g atom of Ru, in 2-methoxyethanol, afforded $Ru(CO)_2(SP)Cl_2$ (237) which, on heating in the solvent in the absence of CO gave $[Ru(CO)(SP)Cl_2]_2$ (possibly 238) which existed as two isomers (238a and 238b); 238a slowly converted to 238b in solution. Reaction of $[Ru(CO)_3Cl_2]_2$ with SP in refluxing benzene gave $Ru(CO)_3(SP)Cl_2$ in which the SP ligand is monodentate (239). In refluxing 2-methoxyethanol this produced 238 which absorbed CO to give 237; with additional SP, 238 afforded 236. It was also observed that $Ru(SA)_2Br_2$ reacted with CO to give $Ru(CO)_2(SA)_2Br_2$.

Cleavage of C—O bonds in alkenyl carboxylates is promoted by iron and ruthenium hydrides [224]. Thus, $Ru(PPh_3)_4H_2$ reacted with vinyl acetate to give ethylene with release of PPh_3. Allyl acetate and vinyl propionate were similarly converted into propylene and ethylene, respectively. There was no reaction with ethyl acetate, or with $Ru(PPh_2H)_4H_2$ or $Ru(PMePh_2)_4H_2$, but C—O bond

SCHEME 35



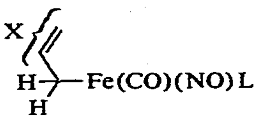
cleavage could be effected by $Fe(PEtPh_2)_3(N_2)H_2$ and $Ru(PPh_3)_3HCl$. A possible mechanism (Scheme 35) involves the intermediacy of a vinyl acetate complex prior to olefin insertion into an M—H bond.

Allyl complexes

Mono-allylic species

A review of π-allyl metal complexes has been published [225]. IR spectral studies have been made [226] of $(\eta^3\text{-}C_3H_5)Fe(CO)_3I$ and isomers of $(\eta^3\text{-}C_3H_4Me)Fe(CO)_3X$ (X = Cl or O_2CCF_3). A correlation was made between ν(CO) and Taft's σ-constants for the allyl group substituents. Mössbauer and IR spectral studies of $(\eta^3\text{-}C_3H_4R)Fe(CO)_2(NO)$ (R = H, 1- or 2-Me or 1-Cl) indicated [227] that the CO and NO groups absorbed the inductive effects of the allyl group substituents, leaving the iron *s*-electron density relatively unaffected.

Reaction of $(\eta^3\text{-}C_3H_4R)Fe(CO)_2(NO)$ (R = H; 1-Me, -Cl, -CN, -Ph; 2-Me, -Cl, -Br) with L (tertiary alkyl, aryl or mixed alkyl/aryl phosphine; $P(OR)_3$, R = alkyl) afforded [228] the intermediate $(\eta^1\text{-}C_3H_4R)Fe(CO)_2L(NO)$; this rearranged to give $(C_3H_4R)Fe(CO)L(NO)$ which existed in the equilibrium **240** $\rightleftharpoons$ **241**. Complexes derived from 2-substituted η^3-allyl complexes were stabilised at the intermediate stage, i.e. giving $H_2C{=}C(R)CH_2Fe(CO)_2L(NO)$ [1-substituted species gave only the transient $RHC{=}CHCH_2Fe(CO)_2L(NO)$] but when R = H, Me or Ph, this intermediate could not be detected, possibly because the subsequent chelation reaction was too rapid. With $P(OR)_3$, the species $(\eta^1\text{-}C_3H_4R)Fe(CO)_2\{P(OR)_3\}(NO)$ rearranged to **240**/**241** and **242**, while with $Ph_2PCH_2CH_2PPh_2$(diphos), $H_2C{=}CHCH_2COFe(CO)(diphos)(NO)$ was produced exclusively. From a kinetic study of these reactions it was established [229] that $(\eta^3\text{-}C_3H_4R)Fe(CO)_2(NO)$ (R = 1-Me or -Ph, 2-Me) and L (PPh_3 or $P(OEt)_3$)) reacted via a 2nd-order associative process to give **240**/**241** but when R = 2-Me and L = PPh_3, a parallel 1st-order dissociative process also occurred. In the species where R = 1-Cl, -CN, 2-Cl or -Br, the intermediate five-coordinate species $(\eta^1\text{-}C_3H_4R)Fe(CO)_2L(NO)$ were formed by a 2nd-order associative process when L = PPh_3, $P(n\text{-}Bu)_3$, $PEtPh_2$, $P(OEt)_3$ or $P(OCH_2)_3CEt$. The rearrangement of this species to $(C_3H_4R)Fe(CO)L(NO)$, i.e. **240**/**241** occurred via a 1st-order formation associative intramolecular chelate, with loss of CO. However, when L = $P(OEt)_3$, a parallel 2nd-order pathway with ligand disubstitution, via CO insertion between the metal atom and the η^1-allyl group, gave **242**.



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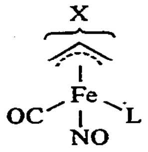

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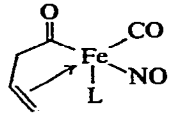
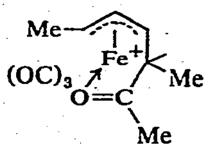


(242)

The reactions of C_3H_5Br and $1\text{-}MeC_3H_4Br$ with Grignard reagents [230] were catalysed by π-allyl- and π-crotyl-ironcarbonyl halides. In a stoichiometric reaction, $(\eta^3\text{-}C_3H_5)Fe(CO)_3Br$ and MeMgI afforded propylene (15%), methane (42%), ethane (16%), $MeCH_2CH{=}CH_2$ (11%) and 1,5-hexadiene (26%). Similar reactions between (η^3-C_3H_5)Fe(CO)$_3$Br and n-BuMgBr and i-PrMgBr were investigated.

Treatment of *trans,trans*-hexa-2,4-dieneiron tricarbonyl with $CH_3COCl/AlCl_3$ afforded [231] 243, in a reaction similar to that described earlier [232] for $C_4H_6Fe(CO)_3$. The stereochemistry of acylation parallels that of protonation and corresponds to *endo* attack.



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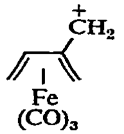

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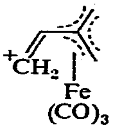

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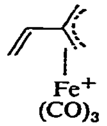
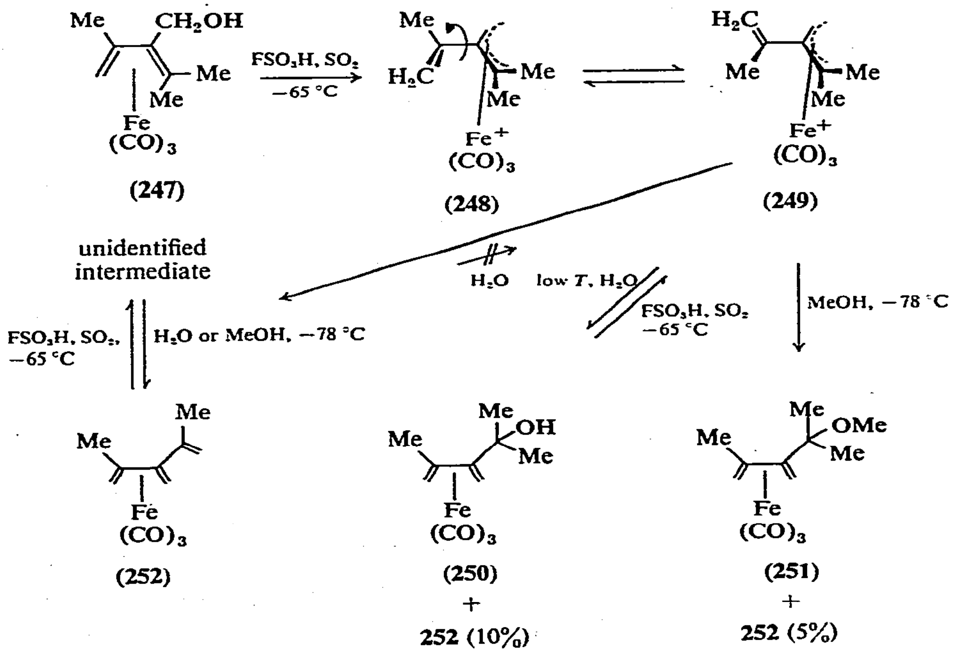


(246)

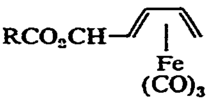
The cross-conjugated pentadienyliron tricarbonyl cations could have three structures, 244, 245 or 246, the metal atoms in the first two having an 18-electron configuration, while that in the last has a 16-electron configuration. It was observed [233] that 246 was preferred on the basis of theoretical calculations. A suitable pentadienyliron carbonyl cation was generated from 247 and FSO_3H. Its reaction with nucleophiles are shown in Scheme 36. The intermediate 248

SCHEME 36



could readily equilibrate giving 249, which subsequently reacted with water or methanol giving 250 and 251, respectively, together with 252; the latter was also obtained via another unidentified intermediate, as shown in Scheme 36. The isomerisation of 247 to give 250 and 251 could not occur via the intermediates 244 or 245, since rotation about the C—C bond in an allylic intermediate, e.g. 248, is necessary to give the desired products. Furthermore, isomerisation would not occur in a species such as $[(\eta^3\text{-}C_5H_5)Fe(CO)_3(OSO_2F)]^+$ (cf. 246), since similar isomerisation data were obtained from studies with SbF_5/FSO_3H in liquid SO_2, which is a system of extremely low nucleophilicity. Thus the prediction that the lowest unoccupied molecular orbital in the cation generated from species such as 247 would be equivalent to a coordinatively unsaturated allyl cation, viz. 246, was justified.

Treatment of 253, where R = styrene polymer, with HBF_4 under CO gave [234] the polymer-bound π-allyl species 254, which would be isolated. With



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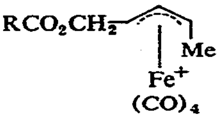


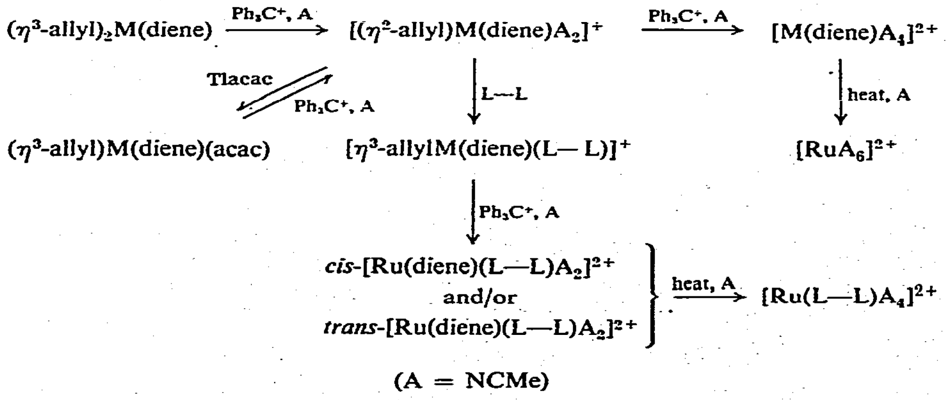
(254)

PPh_3 this afforded an iron—free polyphosphonium salt, and the anion of ethyl acetoacetate attacked both ends of the allylic group, the site furthest removed from the polymer backbone being most favoured.

Bis- and tris-allyl complexes

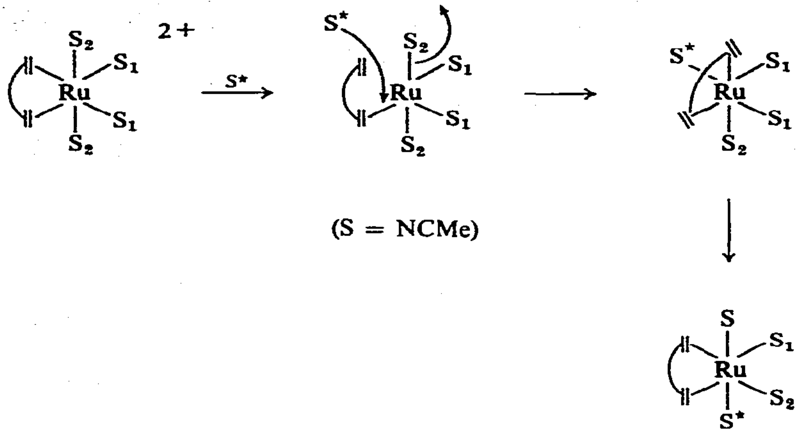
The preparation of a series of bis-π-allyl complexes $(\eta^3\text{-allyl})_2Ru(\text{diene})$, where allyl = C_3H_5, 1- or 2-MeC_3H_4 and diene = norbornadiene (C_7H_8) or 7-phenylnorbornadiene, cycloocta-1,5-diene (C_8H_{12}) or cyclooctatetraene, from $[Ru(\text{diene})Cl_2]_n$ and allylmagnesium halides, has been described [235]. Similar treatment of $[Os(C_8H_{12})Cl_2]_n$ gave $(\eta^3\text{-}C_3H_5)_2Os(C_8H_{12})$ and $(\eta^3\text{-2-}MeC_3H_4)_2Os(C_8H_{12})$. Treatment of $(\eta^3\text{-}C_3H_5)_2Ru(C_7H_8)$ with $[Ph_3C][BF_4]$ in acetonitrile afforded $[(\eta^3\text{-}C_3H_5)Ru(C_7H_8)(NCMe)_2][BF_4]$. The reactions of this and its Os

SCHEME 37



analog, and of $[(\eta^3\text{-2-MeC}_3H_4)\text{Ru(diene)(NCMe)}_2]^+$ are summarised in Scheme 37. Using NMR spectroscopy, a mechanism for the observed stereospecific exchange of acetonitrile in the cations $[\text{Ru(diene)(NCMe)}_4]^{2+}$ was deduced (Scheme 38). Based on similar exchange rate data obtained from the species [Ru(L—L)-

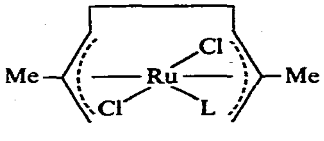
SCHEME 38



(S = NCMe)

$(\text{NCMe})_4]^{2+}$, it was possible to make a kinetic *trans*-effect series for the exchange of acetonitrile *trans* to L—L, viz. L—L = diars > C_7H_8 > C_8H_{12} > bipy > *o*-phen > $(\text{NCMe})_2$.

Reaction of isoprene with $RuCl_3$ afforded [236] dichloro(2,6-dimethylocta-2,6-diene-1,8-diyl)ruthenium which, on treatment with L (CO, PF_3, PPh_3, PF_2NMe_2, PCl_2CF_3, $P(OCH_2)_3CPh$) gave 255. With an excess of PF_3, after further addition of PPh_3, *cis*-$Ru(PF_3)_2(PPh_3)_2Cl_2$ (256) was formed.



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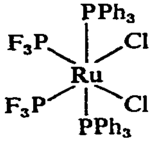
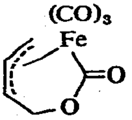


(256)

Treatment of $FeCl_3$ with pentenylmagnesium chloride afforded [237] tris-(π-pentenyl)iron.

π-Allyl complexes incorporating a metal—C σ-bond

Reaction of *N*-phenyl-3,6-dihydro-1,2-oxazine with $Fe_2(CO)_9$ in wet benzene gave [238] 257 which, on treatment with RNH_2 (R = Me or Ph) afforded 258.



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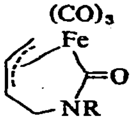

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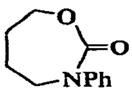
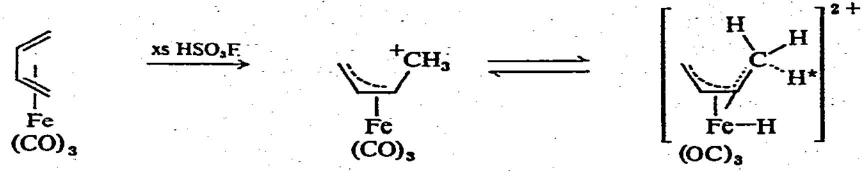


(259)

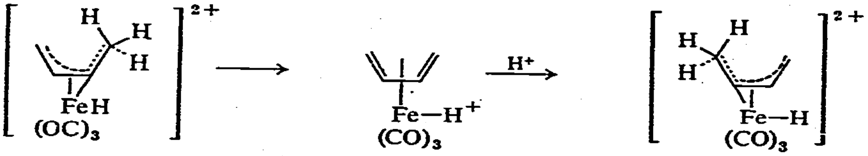
Under anhydrous conditions, $Fe_2(CO)_9$ reacted with *N*-phenyltetrahydro-1,2-oxazine giving only **259**.

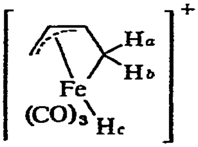
It had been suggested [239] that in strong acid, $C_4H_6Fe(CO)_3$ afforded a mono- and di-protonated species (Scheme 39), and that the labelled proton (H^*) was in equilibrium with solvent acid. Further, it was proposed that the scrambling process, Scheme 40, also occurred in this system. However, a better formulation of the diprotonated species **260** has been proposed [240]. It was further indicated that this would be in equilibrium with **261**, thereby permitting easy permutation of H_a, H_b and H_c. The relatively slower exchange of the other protons in this species could be explained in terms of equilibration via σ,π-rearrangements (Scheme 40) coupled with the faster three proton scrambling. The protonation of $Fe(CO)_3(C_7H_8)$ (C_7H_8 = norbornadiene) could be explained in terms of the intermediate **262** or by the species **263** and **264** in equilibrium. Intermediates of the last type may be important in the mechanism of 1,4-hydrogen shifts and D-exchange in $[(\eta^3\text{-}C_3H_5)Fe(CO)_4]^+$ [241].

SCHEME 39



SCHEME 40





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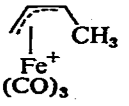

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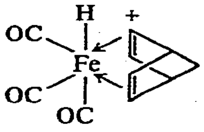

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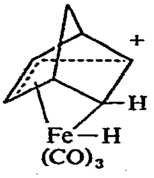

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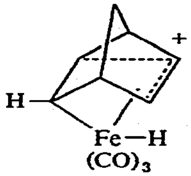

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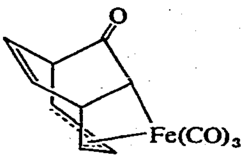
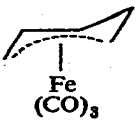


(265)

A minor product of the reaction between $Fe_2(CO)_9$ and impure bicyclo[2.6.0]-deca-2,4,6-triene [242], in which the major impurity was cyclooctatetraene, was identified crystallographically [243] as an iron carbonyl derivative of barbarolone (265). This species could also be obtained [244] directly from barbarolone and $Fe_2(CO)_9$. It was suggested, without proof, that the progenitor of this diene might be C_8H_8. Although it had been suggested that the metal—ring interaction in 265 could be regarded as a homobutadiene system (D) there was no broad crystallographic evidence for this. Carbonylation, at 20 atm, of 266 gave 267.



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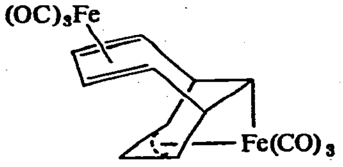

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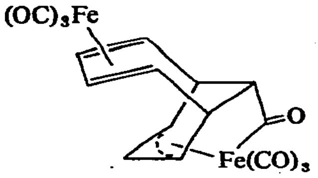
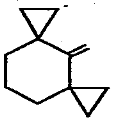


(267)

Photolysis of 268 in the presence of $Fe(CO)_5$ gave [245] initially 269 and 270, and 269 reacted further with $Fe(CO)_5$ giving 271. Conversion of 270 into 271 proved impossible. Photolysis of 272 with $Fe(CO)_5$ gave, as a minor product, 273, and 274 which could either react further with $Fe(CO)_5$ giving



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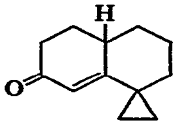

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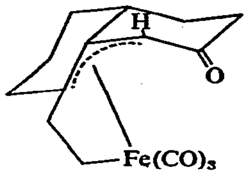

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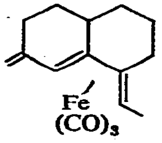

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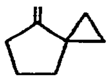

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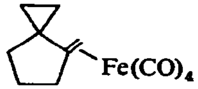

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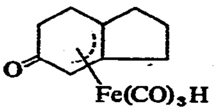

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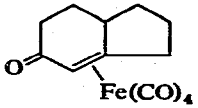

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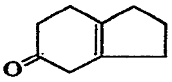

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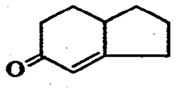

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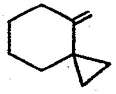

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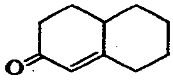
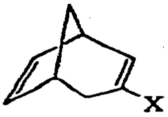


(279)

275, the major reaction product, or undergo demetallation affording 276 or 277. Reaction of 278 with $Fe(CO)_5$ under UV light gave only 279, but in high yield.

Reaction of bicyclo[3.2.1]octa-2,6-diene (280, X = H) with $Ru_3(CO)_{12}$ in refluxing benzene gave [246] 281 (X = H) and 282 (a possible structure not confirmed). Using the labelled species 280 (X = D), the deuterated complex 281 (X = D) was obtained, possibly via a mechanism involving hydride transfer.



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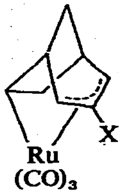

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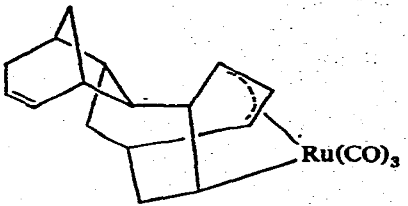

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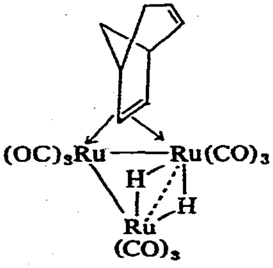

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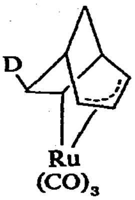

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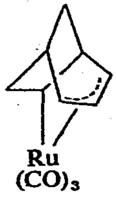

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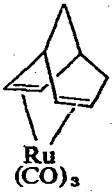
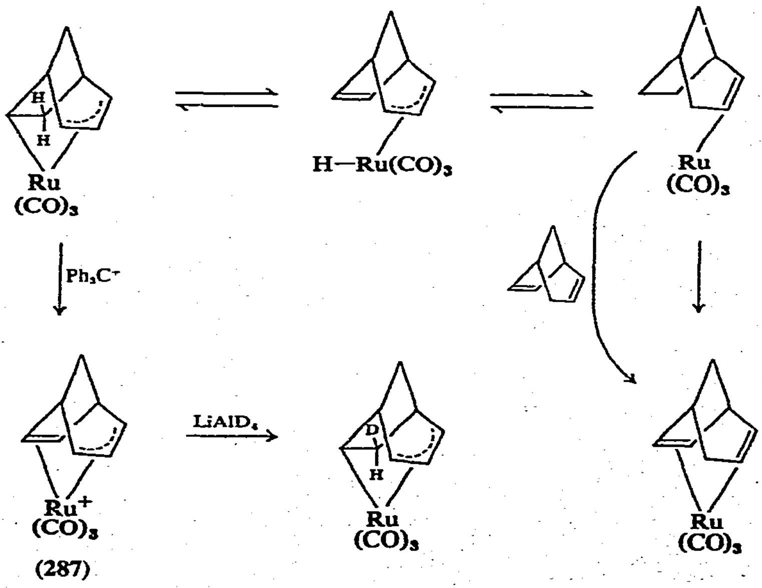


(286)

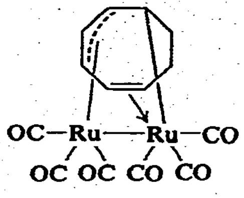
Careful study of this reaction revealed that an important intermediate was the known species 283 [247]. In refluxing benzene, 283 remained unaffected, but when treated with 280 (X = D), readily produced 281 (X = D). An IR spectral

SCHEME 41



study of the reaction between 284 and 280 (X = H) showed that 285 and 286 were formed. The proposed mechanism of these interconversions is outlined in Scheme 41. It was shown that reaction of 285 with Ph_3C^+ gave 287 which, on subsequent treatment with $LiAlD_4$, afforded 284.

An isomeric mixture of cycloocta-1,3,5- and 1,3,6-trienes (C_8H_{10}) reacted with $Ru(CO)_4(SiMe_3)_2$ and $[Ru(CO)_4(SiMe_3)]_2$ giving [248] $Ru_2(CO)_6(C_8H_{10})$ (288) $Ru(CO)_3(C_8H_{10})$ (289) and 290; 288 and 289 could also be obtained from



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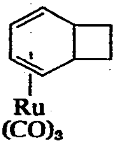

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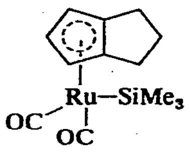

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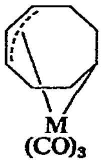
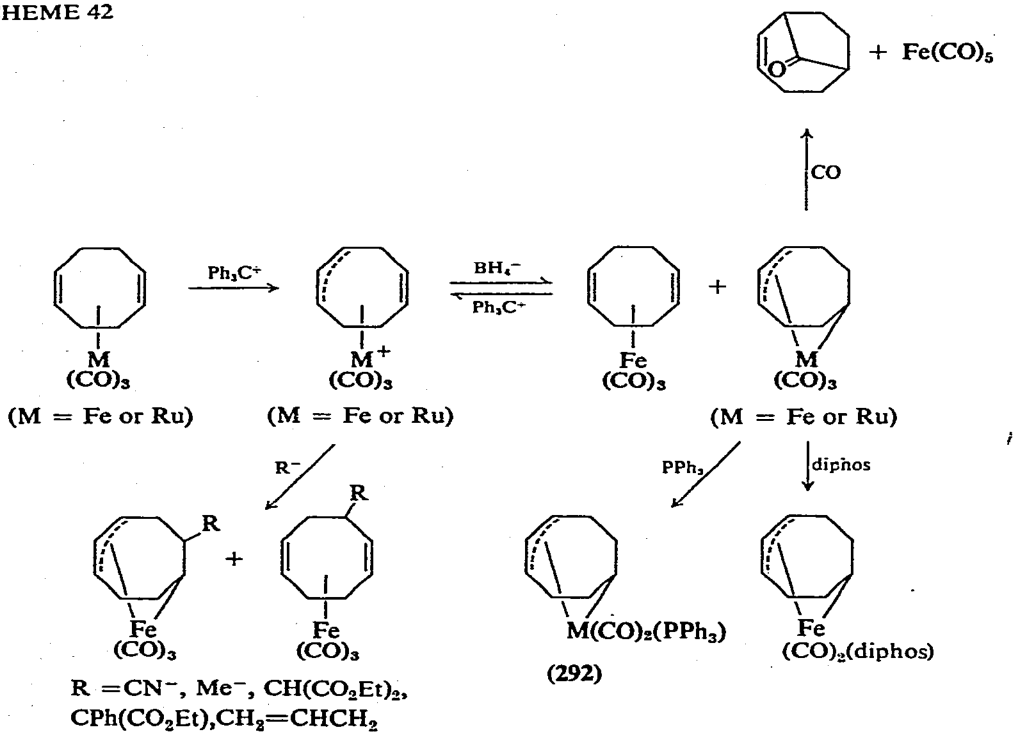


(291)

SCHEME 42



$Ru_3(CO)_{12}$ and C_8H_{10}. The analogous rutheniumtrimethylgermyl carbonyls reacted with C_8H_{10} giving mainly $Ru_2(CO)_4(C_8H_9)(\mu\text{-}GeMe_2)_2(GeMe_3)$. The species 288 is fluxional (see Fig. 7).

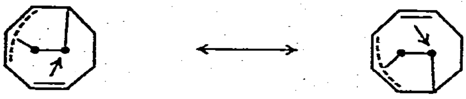


Fig. 7. The fluxional nature of 288.

Under UV light, $Fe(CO)_5$ reacted [249] with 1,3- and 1,5-cyclooctadiene giving $Fe(CO)_3(1,5\text{-}C_8H_{12})$ and $Fe(CO)_3(1,3\text{-}C_8H_{12})$, together with some other minor product, including $Fe(CO)_4(1,5\text{-}C_8H_{12})$ (photolysis of this gave the corresponding tricarbonyl). While $Ru_3(CO)_{12}$ reacted with 1,5-cyclooctadiene in refluxing benzene to give $Ru(CO)_3(1,5\text{-}C_8H_{12})$ [this slowly isomerised to 291 (M = Ru)], 1,3-cyclooctadiene afforded only Ru_3- and Ru_4-cluster compounds. $Os_3(CO)_{12}$ reacted with 1,3-cyclooctadiene in refluxing benzene to give $Os_3(CO)_9C_8H_{12}$ which should perhaps be formulated as $Os_3(CO)_9H_2(C_8H_{10})$. Under UV light, $Os_3(CO)_{12}$ reacted with either diene giving $Os(CO)_3(1,3\text{-}C_8H_{12})$ and $Os(CO)_3(1,5\text{-}C_8H_{12})$ (only from the 1,5-diene) [which slowly isomerised to 291 (M = Os)], and some other unidentified species. Reactions of $M(CO)_3(1,5\text{-}C_8H_{12})$ (M = Fe or Ru) are summarised in Scheme 42, and those of $C_8H_{12}Fe(CO)_2(PPh_3)$ (292) in Scheme 43. The distribution of products of nucleophilic attack upon the cation 293, viz. 294 and 295, are summarised in Table 4. Treatment of $M(CO)_3(1,3\text{-}C_8H_{12})$ (M = Fe or Os) with Ph_3C^+ afforded the octadienyl cation

SCHEME 43

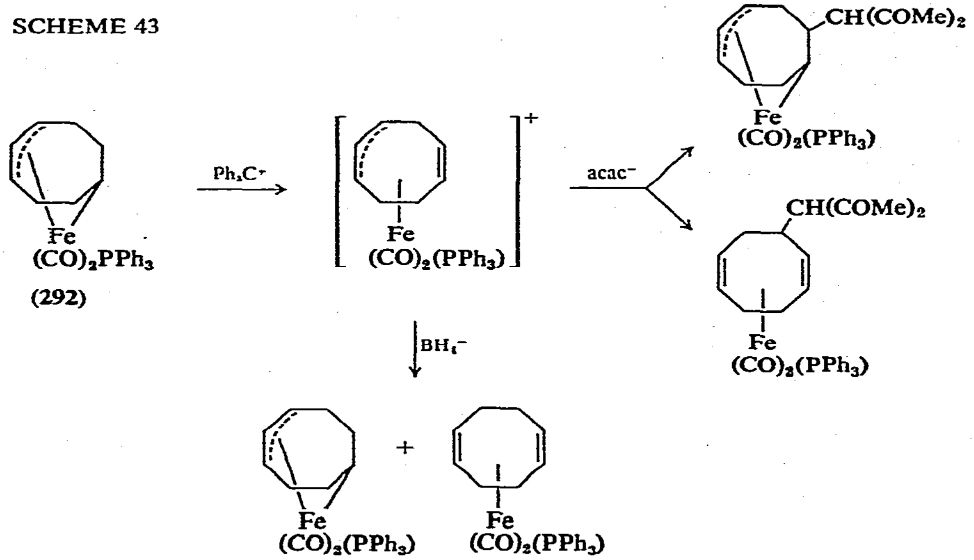
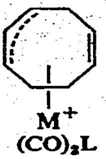


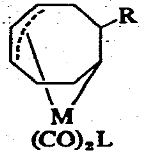
TABLE 4

PRODUCT DISTRIBUTION AFTER NUCLEOPHILIC ATTACK ON IRON AND RUTHENIUM DIENYL CATIONS (293 → 294 + 295)

293		Nucleophilic reagent (R^-)	Products (%)	
M	L		294	295
Ru	CO	BH_4^-	100 (R = H)	0
Fe	CO	BH_4^-	90 (R = H)	10 (R = H)
Fe	CO	CN^-	70	30
Fe	CO	acac⁻	50	50
Fe	CO	$CH(CO_2Et)_2^-$	60	40
Fe	CO	$CPh(CO_2Et)_2^-$	60	40
Fe	PPh_3	BH_4^-	92 (R = H)	8 (R = H)
Fe	PPh_3	acac⁻	55	45



(293)



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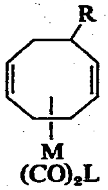
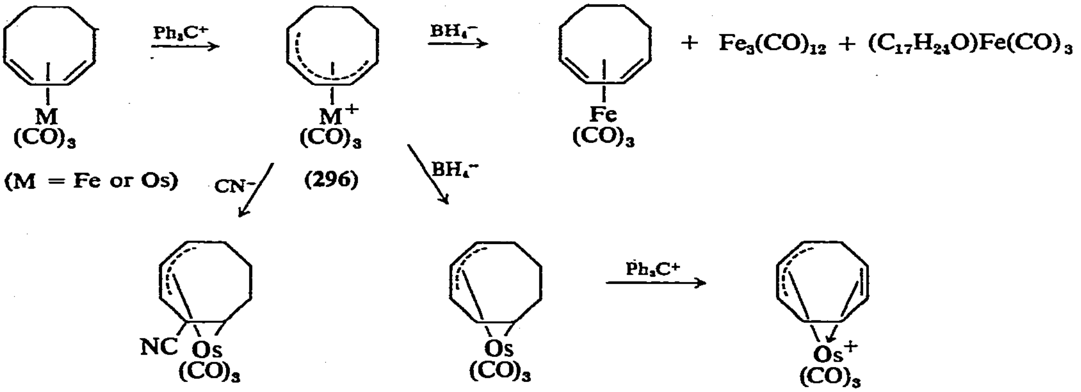


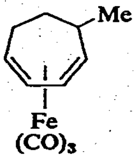
(295)

296, the reactions of which are illustrated in Scheme 44. During the preparation of $Ru(CO)_3(1,5\text{-}C_8H_{12})$ there was considerable isomerisation of the excess of the 1,5-diene to the 1,3-isomer via 1,4-cyclooctadiene as an intermediate.

SCHEME 44



$Ru(CO)_3(1,5\text{-}C_8H_{12})$ itself catalysed the isomerisation of the 1,5-diene, and was itself converted into 291 (M = Ru) which, likewise, was a catalyst in this system. The overall isomerisation is summarised in Scheme 45. The iron complex $Fe(CO)_3(1,5\text{-}C_8H_{12})$ behaved differently, isomerising on heating or on photolysis to give the corresponding 1,3-diene complex; spectroscopic studies established that 291 (M = Fe) was not an intermediate in this process. On heating, 291 (M = Fe) was converted into 297 or 298, and ring collapse with iron is obviously a favoured pathway since 291 (M = Fe) reacted with Ph_3C^+ giving 299. Similar reactions occurred with 292 (M = Fe), although the reaction temperatures had to be higher. Both $Fe(CO)_3(1,5\text{-}C_8H_{12})$ and $Fe(CO)_3(1,3\text{-}C_8H_{12})$ reacted with PPh_3 giving $Fe(CO)_3(PPh_3)_2$, while 291 (M = Fe) afforded 292 (M = Fe). Similar reactions occurred with 291 (M = Ru). In both the Fe and Ru systems it was



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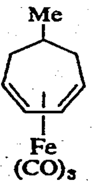

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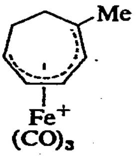

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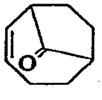
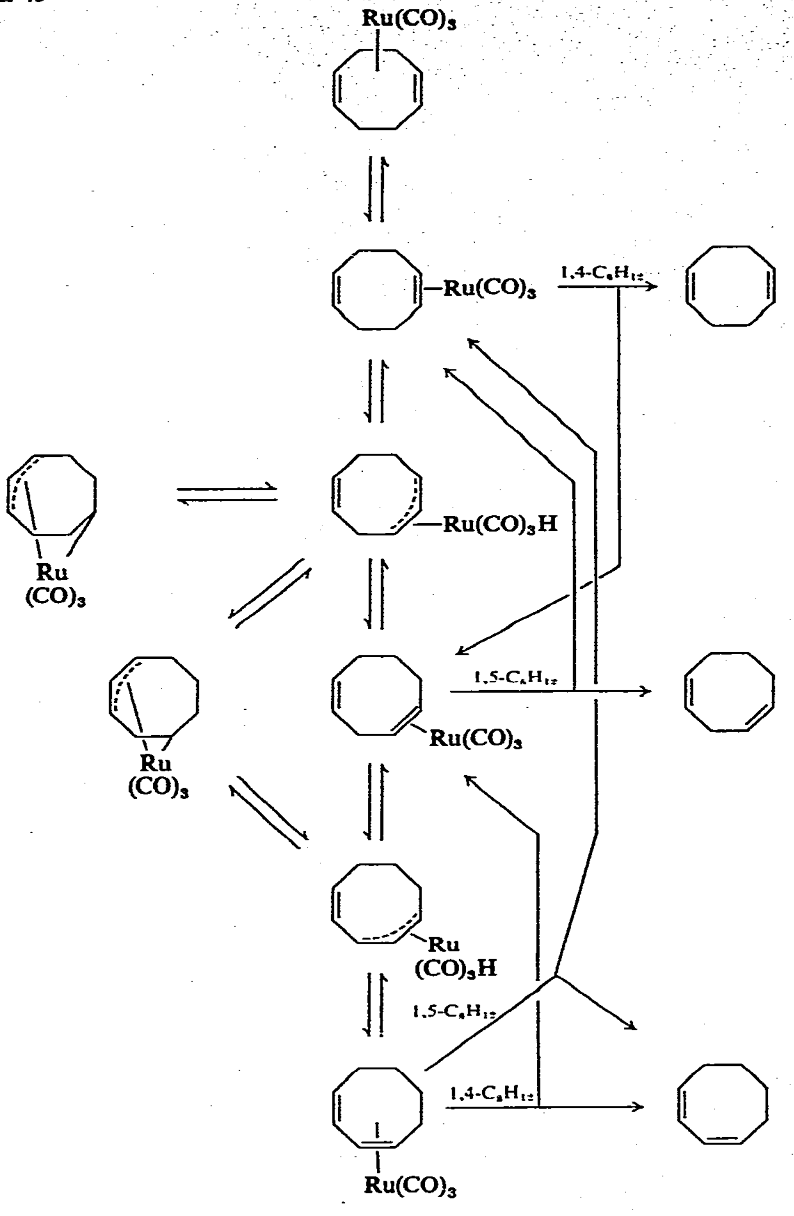


(300)

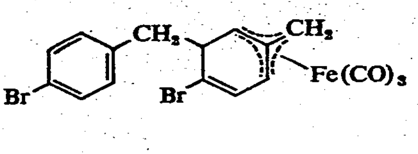
SCHEME 45



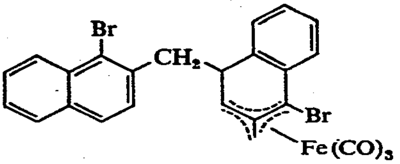
established that the CO group *trans* to the M—C σ-bond was the one which was displaced. In related reactions with $Ph_2PCH_2CH_2PPh_2$, only one CO group could be substituted. In a kinetic study [250] of the reactions of **291** (M = Fe or Ru) with PPh_3 and with $P(OPh)_3$, the product **292** (M = Fe or Ru) and its triphenylphosphite analog were produced via a dissociative reaction. Loss of CO from the ruthenium complex occurred at a rate (at 40°C) nearly 40 times faster than that from the iron compound. Using more nucleophilic reagents, e.g. $P(OEt)_3$, the ketone **300** and $M(CO)_3\{P(OEt)_3\}_2$ were formed.

Trimethylenemethane complexes

Reaction of p-$BrC_6H_4CH_2Br$ with $Fe_2(CO)_9$ at 45°C gave [251] **301** (4%) together with (p-$BrC_6H_4CH_2)_2$ (33%), $FeBr_2$, $Fe(CO)_5$ and CO. Reaction of 1-bromo-2(bromomethyl)naphthalene with $Fe_2(CO)_9$ afforded **302**, the structure of which was confirmed crystallographically [252].



(301)

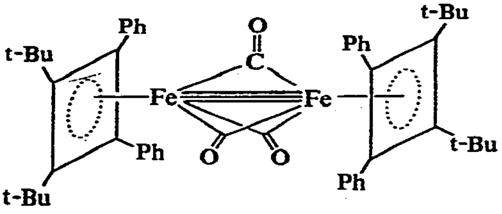


(302)

Cyclobutadiene complexes

A study has been made of the effect of vibrational averaging on the geometry of (η^4-C_4H_4)$Fe(CO)_3$ as derived from ^1H NMR spectra in nematic solvents [253]. It was concluded that the ring has less than four-fold symmetry. However, ^1H NMR spectral studies of (η^4-C_4H_3R)$Fe(CO)_3$ (R = Cl, Br or Me) indicated [254] that the C—C distances had almost uniform bond orders. A normal coordinate analysis has been made [255] of (η^4-C_4H_4)$Fe(CO)_3$. From microwave spectral investigations it was shown [256] that the molecule could be described essentially as a "symmetrical top".

Photolysis of {η^4-C_4(t-Bu)$_2Ph_2$}$Fe(CO)_3$ afforded [257] the dimer **303**, the structure of which has been confirmed crystallographically. The Fe—Fe distance, 1.77 Å, is much shorter than that in $Fe_2(CO)_9$ (2.52 Å) [48] and $Fe_2(CO)_4${(t-Bu)C≡C(t-Bu)}$_2$ (2.21 Å) [258]; the bond orders in the latter two are regarded as 1 and 2, respectively, and so in **303** the species is described as having an iron—iron triple bond (this is also consitent with the 18-electron rule). At 80°C under CO pressure (140 atm), **303** reverts to the monomeric precursor.



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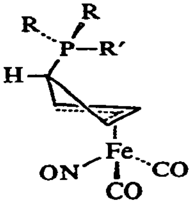


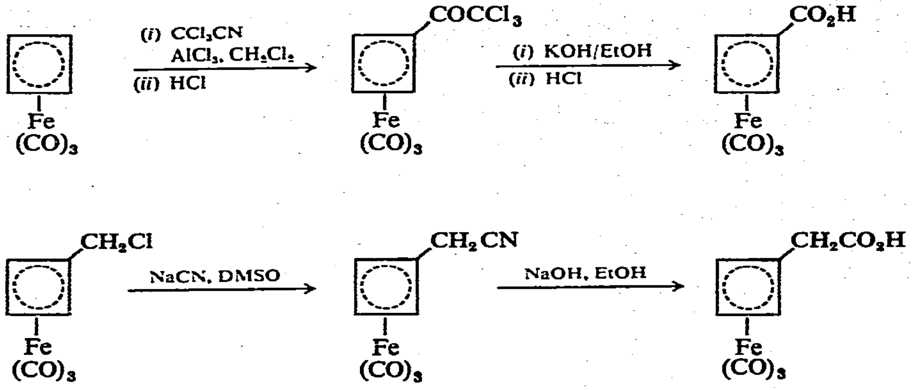
(304)

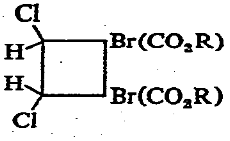
Reaction of (η^4-C_4H_4)$Fe(CO)_3$ with $NOPF_6$ in acetonitrile afforded [259] [(η^4-C_4H_4)$Fe(CO)_2(NO)]^+$; the related η^4-C_4Me_4 and η^4-C_4Ph_4 complexes were prepared similarly. Reaction with L gave [(η^4-C_4R_4)Fe(CO)L(NO)]$^+$ (R = H, L = PPh_3, $AsPh_3$ or $SbPh_3$; R = Ph, L = PPh_3 or $AsPh_3$). With $P(OPh)_3$, [(η^4-C_4Ph_4)-Fe{$P(OPh)_3$}$_2$(NO)]$^+$ was formed. With alkyl or mixed alkyl/aryl phosphines, [(η^4-C_4H_4)$Fe(CO)_2(NO)]^+$ underwent nucleophilic addition in acetone to give

[260] 304; using PPh_3, this species was probably formed but rapidly rearranged to give $[(\eta^4\text{-}C_4H_4)Fe(CO)(PPh_3)(NO)]^+$.

Vinylcyclobutadieneiron carbonyl complexes $(\eta^4\text{-}C_4H_3C{=}CRR')Fe(CO)_3$ were prepared [261] by carrying out a Wittig reaction between $(\eta^4\text{-}C_4H_3CHO)Fe(CO)_3$ and Ph_3PCRR' ($R = R' = H$; $R = H$, $R' = Ph$, CO_2Et or Me; $R = R' = Me$). Carboxylic acid derivatives of cyclobutadieneiron tricarbonyl were prepared as shown in Scheme 46. From a determination of the pK_a values of these acids it appeared that $(\eta^4\text{-}C_4H_3)Fe(CO)_3$ is electron-withdrawing by induction and electron-releasing by resonance (Fig. 8). Photolysis of a mixture of 3-carbomethoxy-2-pyrone and $Fe(CO)_5$ afforded [263] $(\eta^4\text{-}C_4H_3CO_2Me)Fe(CO)_3$. Reaction of **305** with $Fe_2(CO)_9$ gave [264] **306** which could readily be converted to **307**, **308** and **309**. Reductive dimerisation of $(\eta^4\text{-}C_4H_3COMe)Fe(CO)_3$ afforded [265] the diol QCMe(OH)C(OH)(Me)Q $\{Q = (\eta^4\text{-}C_4H_3)Fe(CO)_3\}$ which underwent a pinacol rearrangement and then dehydration, giving Q_2C-(Me)C(=O)Me and $CH_2{=}CQCQ{=}CH_2$, respectively. Treatment of $(\eta^4\text{-}C_4H_3COMe)$-$Fe(CO)_3$ with base gave QC(Me)=CHC(=O)Q, while reaction with diborane afforded $(\eta^4\text{-}C_4H_3Et)Fe(CO)_3$. The latter could be further acylated giving a mixture of *o*- and *p*-$\{\eta^4\text{-}C_4H_2(COMe)Et\}Fe(CO)_3$ (45 : 55 molar ratio).

SCHEME 46





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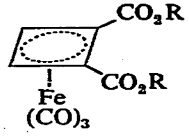

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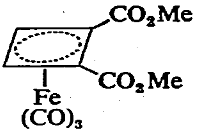

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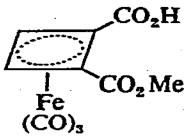

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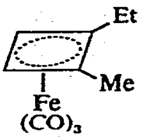

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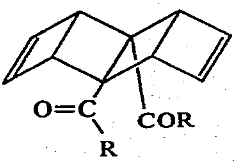

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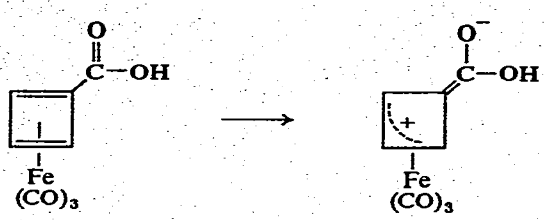
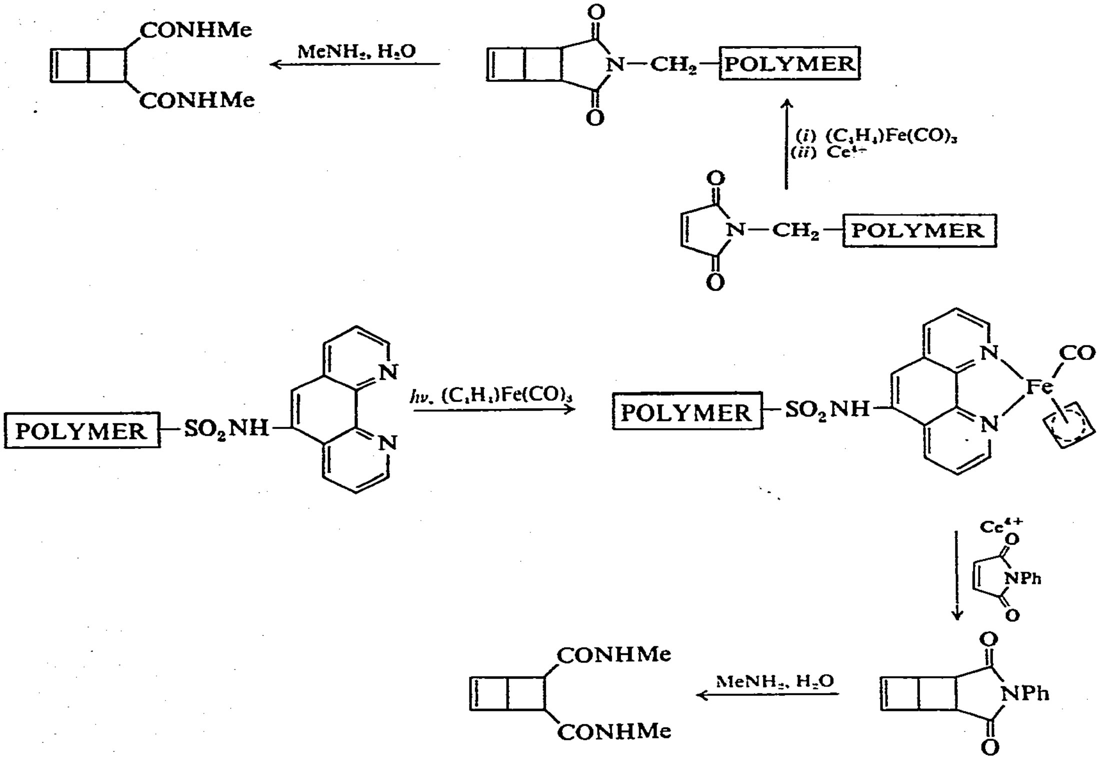


Fig. 8. The electron-releasing and -withdrawing nature of (η^4-C_4H_3)Fe(CO)$_3$.

The utility of (η^4-C_4H_4)Fe(CO)$_3$ and related complexes in organic synthesis has been reviewed.[266]. Oxidation by Ce^{4+} in acetone of a mixture of RCOC≡CCOR (R = Ph or Me) and two equivalents of (η^4-C_4H_4)Fe(CO)$_3$ afforded **310**. In the study of reactions outlined in Scheme 47, it was observed [267] that the

SCHEME 47

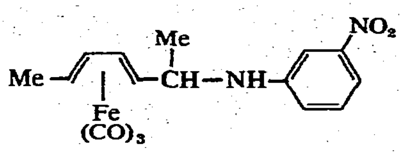


isolation of fused cyclobutene adducts provided additional evidence that C_4H_4 is free of Fe(CO)$_3$ when (η^4-C_4H_4)Fe(CO)$_3$ is oxidised by Ce^{4+}.

Diene and related olefin complexes

Conjugated non-cyclic diene complexes

The structures of *syn* and *anti* substituted 1,3-butadieneiron tricarbonyl complexes have been determined crystallographically [269]. In **311**, the *anti*-H atom



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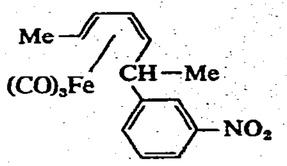
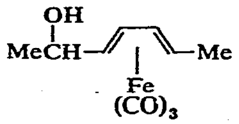


(312)



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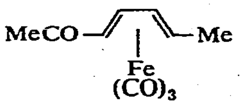
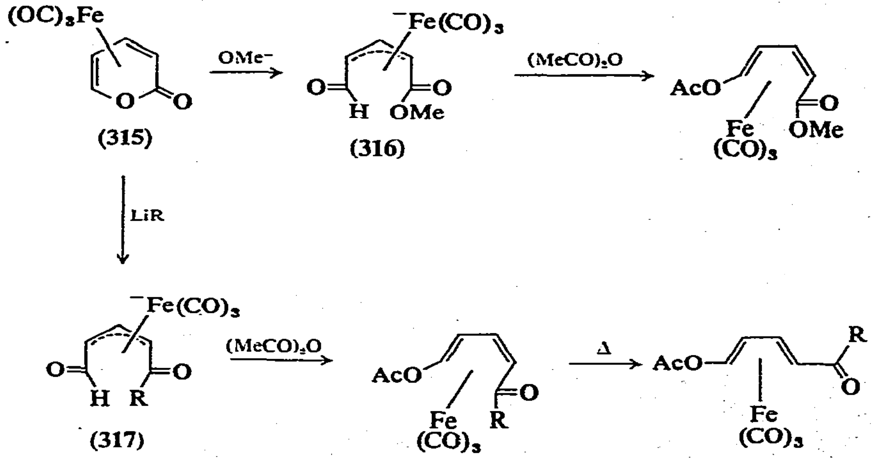


(314)

deviates by 30° from the diene plane, away from the metal, while in **312** the *syn*-H atom deviates by 20° towards the metal. Measurements of the ^{13}C NMR spectra of $Fe(CO)_3(C_4H_6)$, **313** and **314** have been reported [270]. Over a temperature range, it was established that $Fe(CO)_3(C_4H_6)$ is fluxional (Fig. 9). The behaviour of the CO groups was interpreted by assuming that the molecule had a square-pyramidal geometry and the mechanism proposed is similar to that suggested [271] for PF_3-substituted dieneiron tricarbonyl complexes. The fluxional properties are general for other diene complexes, and the rate of rearrangement increases most significantly for non-conjugated diene species.

SCHEME 48



Reaction of α-pyrone with $Fe_2(CO)_9$ in benzene gave [273] **315**, the reactions of the latter with OMe^- and RLi, followed by treatment with acetic anhydride, are outlined in Scheme 48. The anions **316**, **317** and **318** (derived by deprotona-

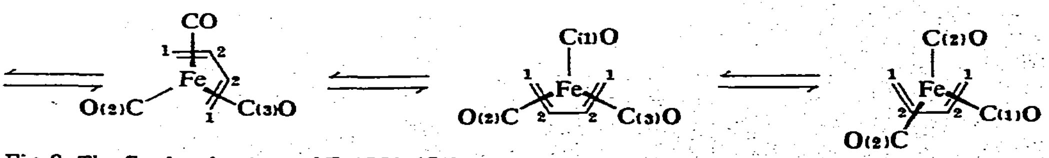
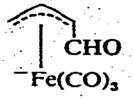
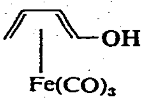


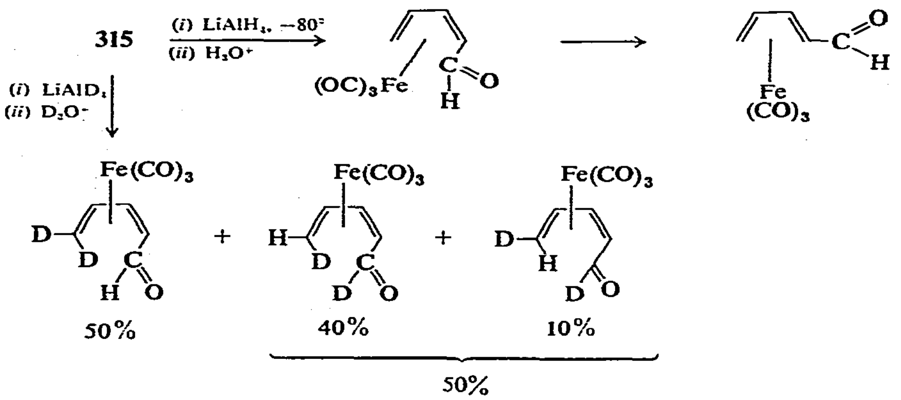
Fig. 9. The fluxional nature of $Fe(CO)_3(C_4H_6)$.

tion of **319**) are highly coloured and stable, the pK_a values of **317** (R = Me) and **318** being 8.60 and 9.68, respectively. Further reactions of **315** with LiAlD$_4$, LiAlH$_4$ and H$_3$O$^+$, are shown in Scheme 49, and a mechanism for the formation of the deuteriated aldehyde complex **320** in Scheme 50. The anionic inter-

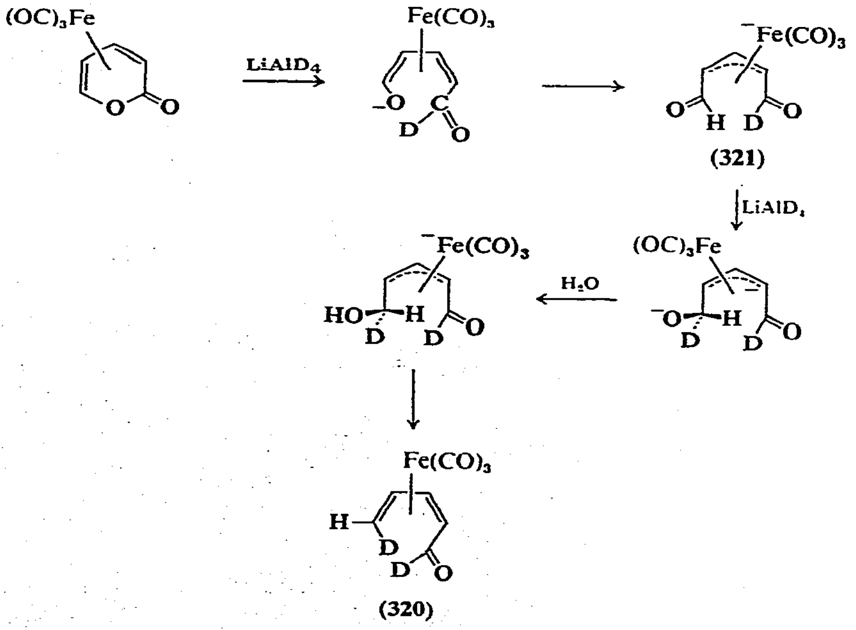

(318)


(319)

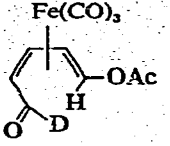
SCHEME 49



SCHEME 50



mediate **321** was trapped by extraction into base, followed by acetylation (with acetic anhydride); the products **322** and **323** were formed in equal amounts.



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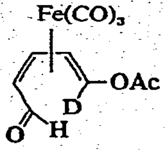

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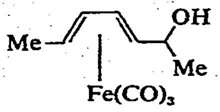

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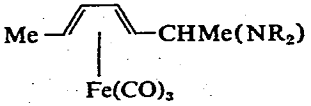
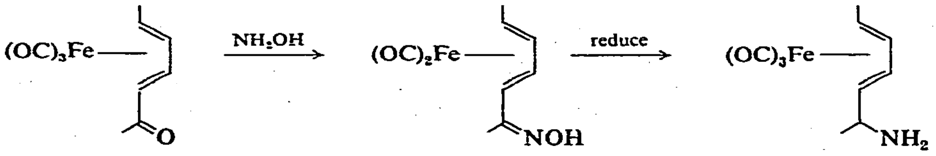


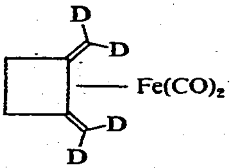
(325)

Reaction of the *endo*-hydroxy species **324** with $MeSO_2Cl$ and Me_3N in dichloromethane, followed by addition of RNH_2 (R = H or Me) gave [274] **325**; **325** (R = H) could also be prepared as outlined in Scheme 51.

SCHEME 51



Vapour-phase pyrolysis of **326** resulted [275] in H/D scrambling; the possible intermediate **327** would permit H/D exchange while the mechanism in Scheme 52 would effect methylene group exchange. Treatment of $C_6H_4(o\text{-}CH_2Br)_2$ with



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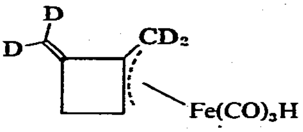


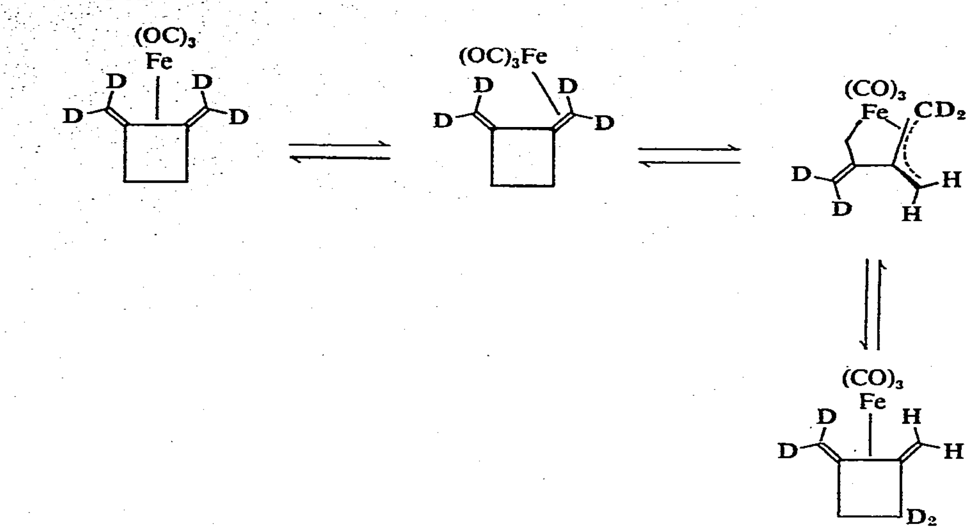
(327)

$Na_2Fe(CO)_4$ afforded [276] **328** which reacted with MeCOCl at 0°C to give **329**. Reaction of **329** with $AlCl_3$ gave 5-acetyl-2-indanone, but **330**, on treatment with $AlCl_3$, afforded **331**. Photolysis [277] of **328** in the presence of $Fe(CO)_5$ gave **332** (*trans*-$Fe(CO)_3$ groups), **333** (*cis*-$Fe(CO)_3$ groups) and **334**.

Radical-initiated polymerisation of 2,4-hexadien-1-ylacrylateiron tricarbonyl afforded [278] a high molecular weight homopolymer, and copolymerisation was effected with acrylonitrile, vinyl acetate, styrene and methylacrylate. These polymers decomposed thermally to give Fe_2O_3 and insoluble polymeric material.

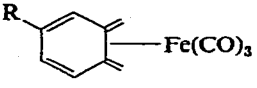
Cathodic reduction of $Fe(acac)_3$ in the presence of butadiene or isoprene and

SCHEME 52



PPh$_3$, in methanol at −15°C gave [279] Fe(PPh$_3$)(diene)$_2$, species which have been fully characterised spectroscopically. The diene complexes could also be obtained from aromatic *o*-hydroxy and *o*-aminoaldehyde complexes, from Schiff base or polyamine compounds.

Complexes of the type Fe$_2$(CO)$_6$(butatriene), obtained by reaction of Fe$_3$(CO)$_{12}$ with cumulenes, have been briefly reported [280].



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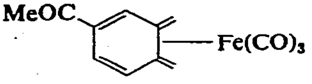

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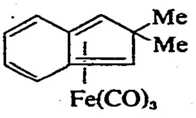

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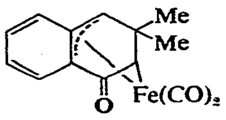

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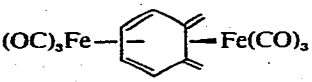

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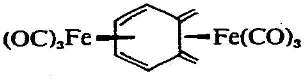

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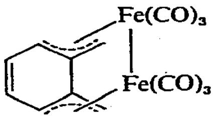
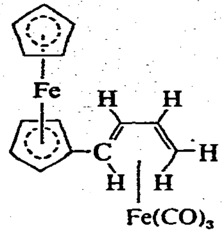


(334)

Ferrocenyldiene complexes

Reaction of FcCH=CHCH(OH)Me (Fc = (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$)) with Fe$_2$(CO)$_9$ in the presence of CuSO$_4$ gave [281] low yields of **335** and FcCH$_2$CH$_2$COMe. With FcC(Me)(OH)CH=CH$_2$, **336** was produced, and a series of fluorophenyl-substituted dieneiron tricarbonyl complexes **337** and **338**, were also obtained in low yield by reaction of the appropriate diene with Fe$_3$(CO)$_{12}$.



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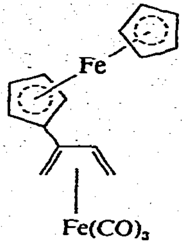

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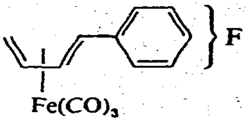

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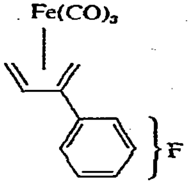

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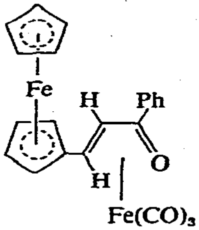

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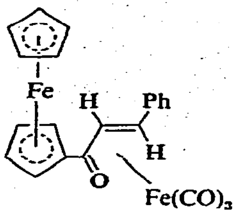

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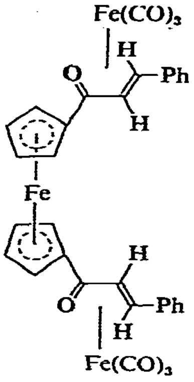

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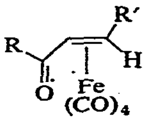

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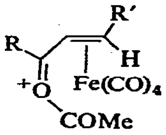

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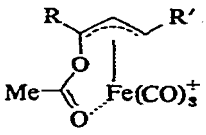

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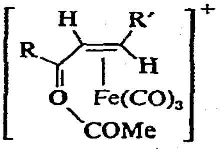

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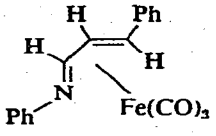

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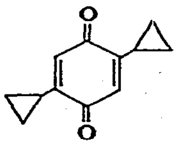

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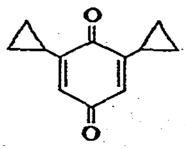

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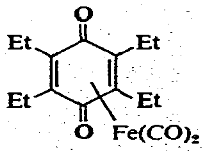


(349)

Treatment of $FcCH{=}CHCMe(OH)CH_2CN$ with $Fe_3(CO)_{12}$ in benzene, in the presence of $CuSO_4 \cdot 5H_2O$ gave [282] $FcCH{=}CHCOMe$ (52%), $FcCH{=}CHCMe{=}CHCN$ (21%) and two isomers of $(FcCH{=}CHCMe{=}CHCN)Fe(CO)_3$. Reaction of β-benzoylferrocene with $Fe_2(CO)_9$ afforded [283] $(FcCH{=}CHCOPh)Fe(CO)_4$; cinnamoylferrocene similarly gave $(FcCOCH{=}CHPh)Fe(CO)_4$. Prolonged heating of these species afforded the heterodiene isomers **339** and **340**. Treatment of 1,1′-dicinnamoylferrocene with $Fe_3(CO)_{12}$ afforded **341**.

Heterodiene complexes

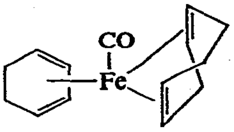
Treatment of **342** with $[MeCO][BF_4]$ gave [289] **343** which decarbonylated to give either **344** or **345**; the latter two reverted to **342** in methanol. Treatment of **344** with $R''OH$ gave **342** and $MeCO_2R''$, and reaction of the former with $PhNH_2$ gave **346** and $PhNH_3^+$.

Cyclic non-conjugated diene complexes

UV irradiation of cyclopropylacetylene in the presence of $Fe(CO)_5$ afforded [285] uncharacterised organometallic products which, on oxidative degradation afforded **347** and **348**. Phenyl- and butyl-acetylenes behaved similarly and diethylacetylene afforded **349**, as well as the free *p*-quinone and some other uncharacterised organoiron carbonyls.

Evaporation of metallic iron into a 10% solution of cycloocta-1,5-diene in methylcyclohexane at −120°C gave [286] brown crystals of $Fe(C_8H_{12})_2$. This gave a green solution in pentane, which rapidly decomposed into metallic Fe above 20° and reacted with α,α'-bipyridyl in ether at −30°C, in the presence of NH_4PF_6 to give $[Fe(bipy)_3][PF_6]_2$. With PF_3 at −30°C in hexane, $Fe(PF_3)_3(C_8H_{12})$ was formed, and with cyclooctatetraene, $Fe(C_8H_8)_2$ was produced. It was suggested that the complex was paramagnetic and so possibly had a tetrahedral geometry.

Irradiation of $[(C_7H_9)Fe(CO)_3]^+$ in the presence of cyclohexa-1,3-diene (C_6H_8) gave $[(C_7H_8)Fe(CO)(C_6H_8)]^+$ which, on treatment with $NaBH_4$, afforded **350**



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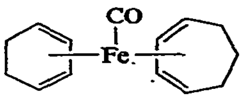

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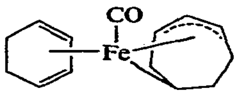

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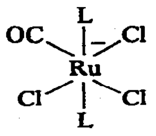

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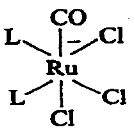

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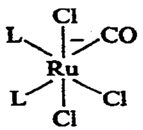

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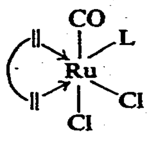

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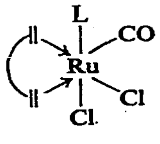
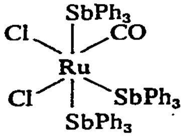


(357)

[287]. This reaction provided a relatively rare example of nucleophilic addition to the C(3) position in a dienyl system thereby giving an unstable diene. On warming, **350** rearranged to **351** which existed in equilibrium with **352**, but only **351** could be isolated. Under 80 atm of CO at 60°C, **351** afforded $Fe(CO)_3(C_6H_8)$ which could also be obtained from **350** at 1 atm and 20°C.

Treatment of $[Ph_3(PhCH_2)P][Ru(CO)(C_7H_8)Cl_3]$ (C_7H_8 = norbornadiene) with Lewis bases (L = Me_2S, DMSO, $CH_2{=}CHCN$) gave [288] $[Ru(CO)L_2Cl_3]^-$, mainly as **353** or **354**, with minor amounts of **355**. When L = $AsPh_3$, $SbPh_3$ or pyridine, $[Ru(CO)L_2Cl_3]^-$ and $Ru(CO)L(C_7H_8)Cl_2$, either **356** or **357**, were formed. Treatment of $[Ru(CO)(C_7H_8)Cl_3]^-$ with an excess of $SbPh_3$ led to the formation of $[Ru(CO)(SbPh_3)_2Cl_3]^-$, $Ru(CO)(SbPh_3)(C_7H_8)Cl_2$ and $Ru(CO)(SbPh_3)_3Cl_2$ (**358**). When $[Ru(CO)(C_7H_8)Cl_3]^-$ was treated with PPh_3 (1 : 2 ratio), $[Ru(CO)(PPh_3)_2Cl_2]_2$ was formed, and with an excess of PPh_3, a species formulated as $Ru(CO)(PPh_3)_3Cl_2$, which was a mixture of isomers analogous to **358**, and



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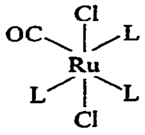

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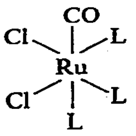

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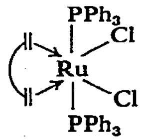
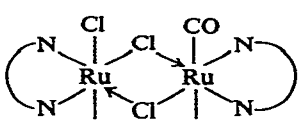


(361)

359 and **360** were produced. Treatment of $[Ru(CO)(C_7H_8)Cl_3]^-$ with PMe_2Ph afforded $Ru(PMe_2Ph)_2(C_7H_8)Cl_2$ (**361**), and the corresponding bromide was obtained by reaction of $[Ru(CO)(C_7H_8)Br_3]^-$ with PMe_2Ph, or of treatment of $Ru(PMe_2Ph)_3X_3$ with C_7H_8 (X = Cl or Br). With $PMePh_2$, $[Ru(CO)(C_7H_8)Cl_3]^-$ afforded $Ru(PMePh_2)_2(C_7H_8)Cl_2$ and $Ru(CO)(PMePh_2)_3Cl_2$. The carbonyl anion reacted with *α,α'*-bipyridyl or *o*-phenanthroline (N—N) giving $[Ru(CO)(N{-}N)Cl_2]_n$ and $[Ru(CO)(N{-}N)Cl_3]^-$. The former was tentatively formulated as a dimer (**362** or **363**) and the latter as **364**. With an excess of bipyridyl, $[Ru(CO)(bipy)Cl_2]_n$ (probably **365**) was produced (this may be a mixture of two isomers having *trans*-CO groups). The mechanism whereby these Lewis base adducts may be formed is outlined in Scheme 53. If L is small and is a strong nucleophile, step *ii* is favored, but if the nucleophile is bulky, reactions *iii* and *iv* will be faster. Thus with Me_2S, DMSO and acrylonitrile, reaction *ii* occurred, but with



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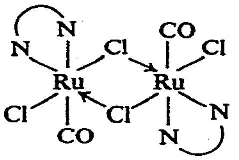

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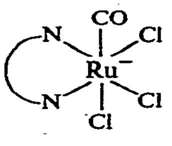

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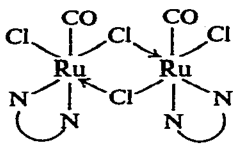
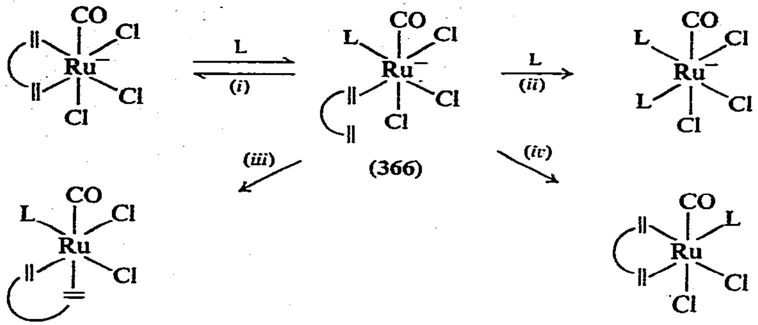


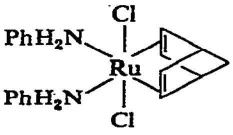
(365)

SCHEME 53



$AsPh_3$ and $SbPh_3$, steps *ii*, *iii* and *iv* were observed. The solvent also had a significant effect on the reaction; in dichloromethane or methanol, when L = $AsPh_3$, pathway *ii* was followed (in addition to *iii* and *iv*), but in benzene, only *iii* and *iv* were important. The mechanistic proposals hinged on the existence of the intermediate **366**.

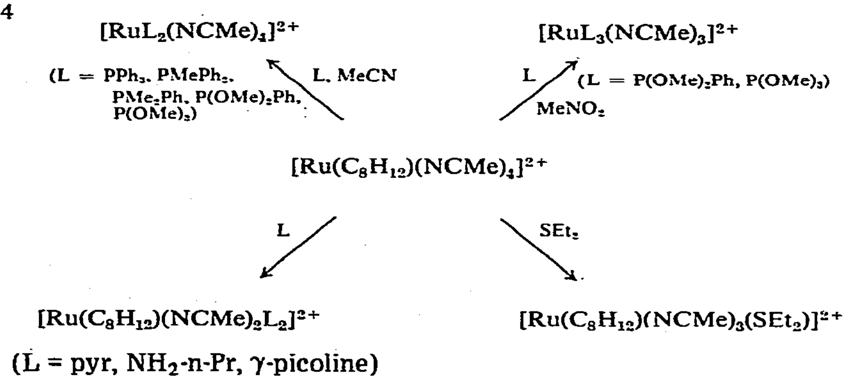
Treatment of $[Ru(diene)Cl_2]_n$ with amine hydrochlorides afforded [289] $RuL_2(diene)HCl$ (diene = cycloocta-1,5-diene, L = Me_2NH, cyclohexylamine, pyridine or piperidine; diene = norbornadiene, L = pyridine). An X-ray crystallographic study of $Ru(NH_2Ph)_2(C_7H_8)Cl_2$ established [290] that the compound had a distorted octahedral geometry (**367**).



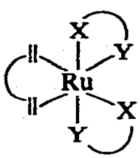
(367)

In refluxing acetonitrile, $[Ru(C_8H_{12})Cl_2]_n$ (C_8H_{12} = cycloocta-1,5-diene) was converted [291] into $[Ru(C_8H_{12})(NCMe)_3Cl]^+$, and treatment of this with $AgPF_6$ in acetonitrile gave $[Ru(C_8H_{12})(NCMe)_4]^{2+}$. Reactions of this dication are summarised in Scheme 54. In refluxing acetonitrile, $[Ru(C_8H_{12})(NCMe)_3Cl]^+$ reacted with L (PPh_3, $PMePh_2$ or PMe_2Ph) to give $[RuL_2(NCMe)_3Cl]^+$; with $AgPF_6$ in methanol, $[Ru(C_8H_{12})(NCMe)_3(MeOH)]^{2+}$ was formed.

SCHEME 54



Treatment of $[Ru(C_8H_{12})Cl_2]_n$ with acetylacetone, benzoylacetone, salicylaldehyde, 2-mercaptopyridine, 8-hydroxyquinoline or 2-mercaptobenzthiazole (chelH) gave [292] $Ru(C_8H_{12})(chel)_2$. Two isomers of the benzoylacetonate complex were obtained, one of which was identified as **368**. The complexes $Ru(diene)(S_2CNR_2)_2$ (diene = C_7H_8 or C_8H_{12}) were also described.



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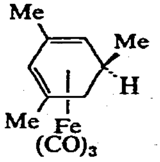

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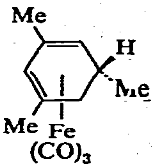

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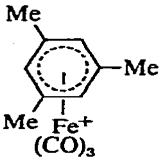

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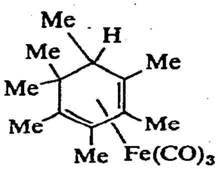

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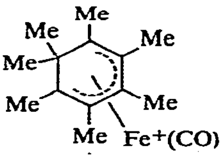

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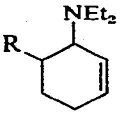

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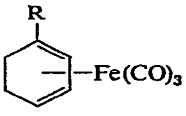


(375)

Cyclic conjugated diene complexes

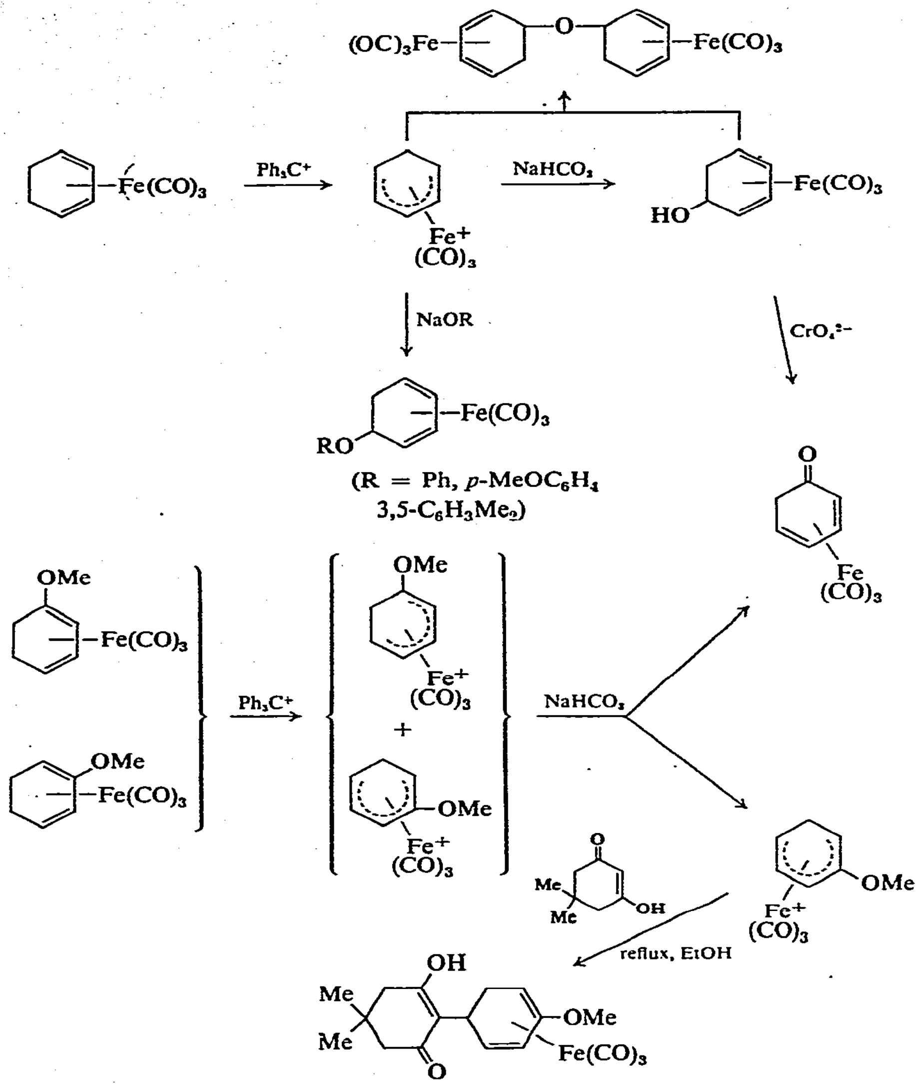
Reaction of 1,3,5-trimethylcyclohexa-1,4-diene with $Fe_2(CO)_9$ afforded [293] a mixture of **369** and **370** (4 : 1), and treatment of this mixture with Ph_3C^+ afforded **371**. Reaction of 1-methylene-2,3,4,4,5,6-hexamethylcyclohexa-2,5-diene with $Fe(CO)_5$ resulted [294] in rearrangement of the olefin and formation of **372**; treatment of this with Ph_3C^+ afforded **373**.

Diethylaminobutadiene reacted with $RCH{=}CH_2$ (R = CHO or COMe) giving **374** which, after treatment with $Fe_3(CO)_{12}$, afforded **375** [295]. The syntheses of 2,4-cyclohexadienone and cyclohexadiene(ether)iron tricarbonyl complexes, and some of their related dienyl precursors, are illustrated [296] in Scheme 55. Reduction of 2,4-cyclohexadienoneiron tricarbonyl with zinc in the presence of ethylbromoacetate afforded, after acid hydrolysis, **376**.

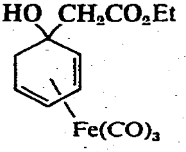
Reaction of **377** with **378** afforded [297] selectively and specifically, **379**, the pure diene being liberated with Ce^{4+}. A similar reaction involving **381**, **382** and **383** (in the ratio 10 : 5 : 1, with an overall yield of 50%); oxidation of **381** by Ce^{4+} liberated the diene. Only small yields of **379** could be obtained after heating **378** with $Fe_2(CO)_9$ or photolysing it in the presence of $Fe(CO)_5$. A similar treatment of **380** gave mainly **383**, and no **381**.

A study has been made [298] of the electron-impact fragmentation of 30

SCHEME 55



substituted {styrene$Fe_2(CO)_6$} complexes. The mass spectra are uniformly characterised by sequential loss of CO to give $[(\text{styrene})Fe_2]^+$, and the formation of $[\text{styreneFe}]^+$. The breakup of this ion was studied in detail and four



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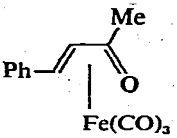

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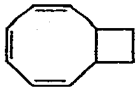

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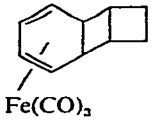

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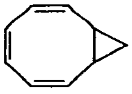

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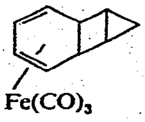

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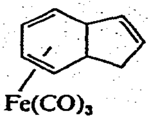

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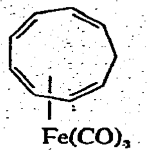
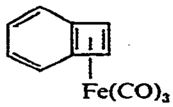


(383)

general disintegration pathways recognised. Nine new {styrene$Fe_2(CO)_6$} complexes were reported.

Photolysis of 384 in the presence of $Fe(CO)_5$ afforded [299] mainly 385, but also 386—389, as well as two other minor, but uncharacterised, products.



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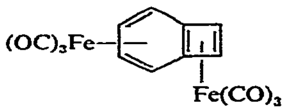

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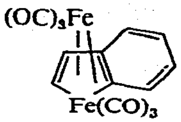

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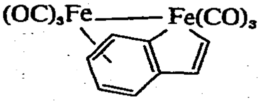

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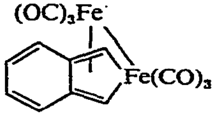

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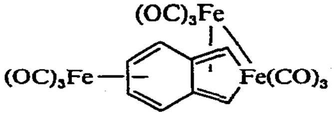

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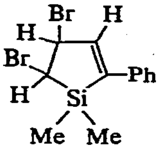

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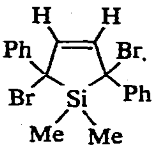

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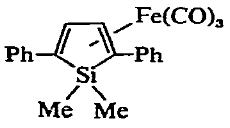

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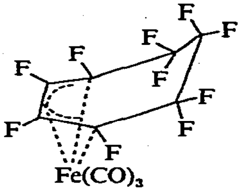


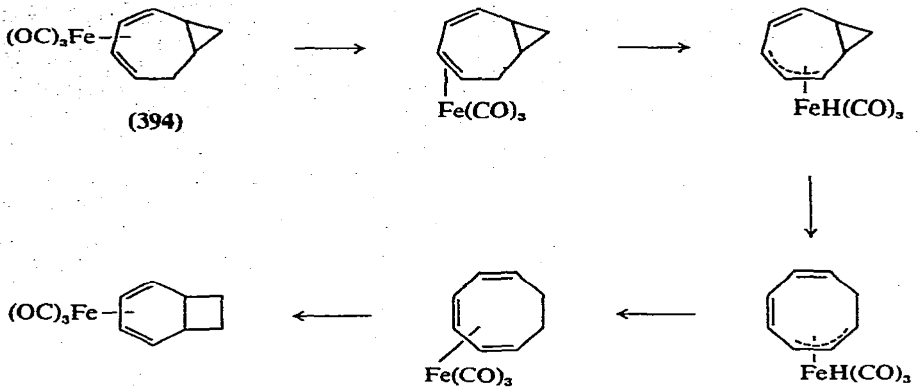
(393)

Treatment of a mixture of 390 and 391 (obtained by bromination of 1,1-dimethyl-2,5-diphenylsilacyclopentadiene) with $Fe_2(CO)_9$ afforded [300] 392. The Rh—Fe stretching mode in $(OC)_3FeC_7H_7Rh(CO)_2$ (which has an inter-metallic distance of 2.76 Å) has been observed [301] by resonance Raman spectroscopy.

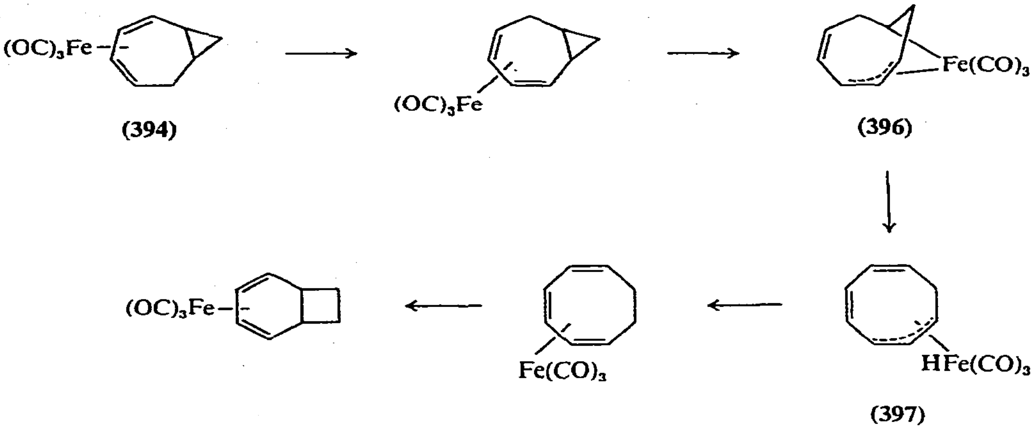
An X-ray crystallographic examination [302] of 393, prepared by reaction [303] of C_7H_8 with $Fe_3(CO)_{12}$, revealed that there was a significant contribution from σ—π interactions between the diene fragment and the metal. Thus, the C—C distances within this fragment had the values 1.43, 1.40 and 1.43 Å, respectively. Prolysis of 393 at 440°C afforded [303] C_6F_6.

Two plausible mechanisms have been proposed [304] for the thermal rearrange-

SCHEME 56

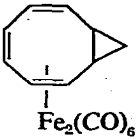


SCHEME 57

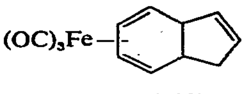


ment of **394** to **395**. In both (Schemes 56 and 57), 1,3,5-cyclooctatrieneiron tricarbonyl was proposed as an intermediate, but the second mechanism (Scheme 57) contains steps which have some precedent, viz. β-hydride elimination from **396** to give **397**.

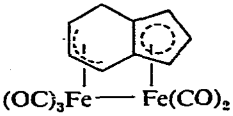
Thermolysis of **398** afforded [305], as the major product **399**, together with **400**, **401** and **402**. While the structure proposed for **402** is tentative, that for



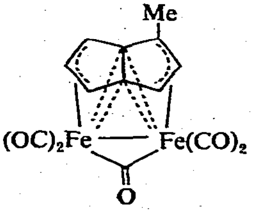
(398)



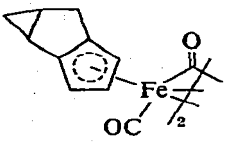
(399)



(400)



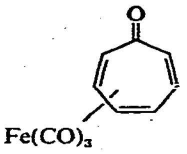
(401)



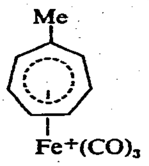
(402)

401 is based on the known structure [306] of $Ru_2(CO)_4(C_8H_6)(GeMe_3)_2$ (C_8H_6 = pentalene). In boiling xylene, $Fe_2(CO)_9$ reacted with *cis*-8,9-dihydroindene giving **399** and **400**; **399** reacted with $Fe_2(CO)_9$ to give **400**. It is possible that **398** rearranged initially on heating to give **383**, which subsequently underwent ring closure to afford **399**.

A variety of methods have been devised [307] for the preparation of heptafulveneiron tricarbonyl **403**, but the compound is usually isolated as a dimer.



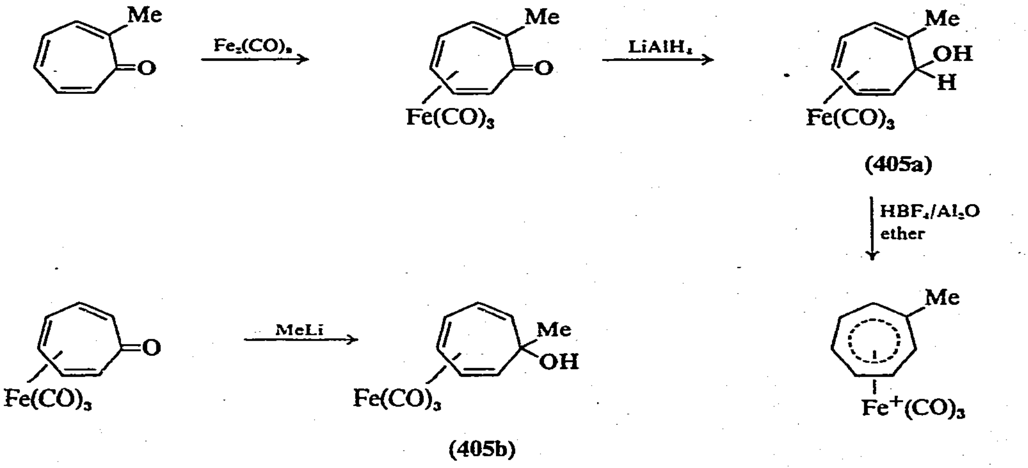
(403)



(404)

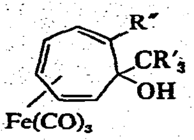
Starting from tropone, a new route to a convenient precursor of heptafulvene-iron tricarbonyl (**404**) has been developed [308], (Scheme 58). It may be noted

SCHEME 58



that there is a single preparation of **403** from two isomeric alcohols **405a** and **b**, indicating that the species is fluxional. Treatment of **406** with HBF_4 in acetic anhydride, followed by NEt_3, afforded the dimer **407**, and an X-ray crystallographic examination of the species with R′ = H revealed that the eight-membered ring had a slightly distorted crown-like conformation and it was suggested that the head-to-head dimerisation could have occurred via a radical process.

Photolysis [309] of cycloheptatrieneiron tricarbonyl at 0°C in the presence of $MeO_2CC{\equiv}CCO_2Me$ gave **408** (10%), and similar treatment of **409** gave **410**. Reaction of $Fe(CO)_3(C_7H_8)$ with $PhC{\equiv}CPh$ gave the free ligand adduct **411**, while photolysis of $Fe(CO)_3(C_8H_{12})$ (C_8H_{12} = 1,3-cyclooctadiene) and $Fe(CO)_3(C_8H_8)$ gave **412** and **413**, respectively. These mild reactions were regarded as being examples of $2\pi + 6\pi$ cycloadditions, and their proposed mechanism is shown in Scheme 59 (no $2\pi + 4\pi$ addition of C_7H_8 and $PhC{\equiv}CPh$ occurred in benzene



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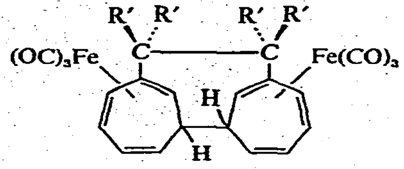

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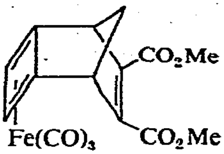

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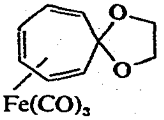

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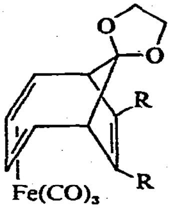

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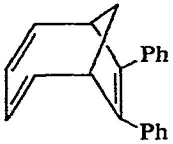

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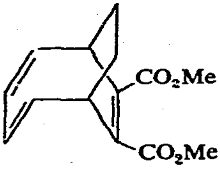

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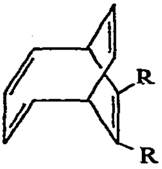

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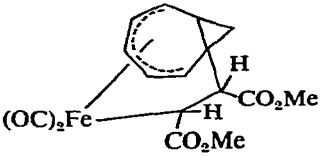
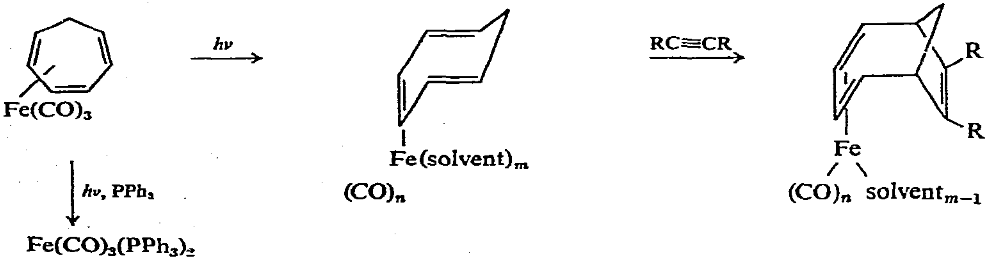


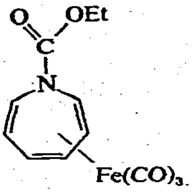
(414)

SCHEME 59



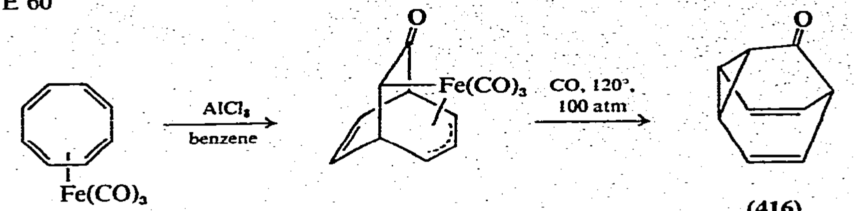
at room temperature over three weeks). Photolysis of $Fe(CO)_3(C_7H_8)$ with *cis*-$C_2H_2(CO_2Me)_2$ at −78°C afforded 414.

An X-ray structural examination of 415 established [310] that the ring has



(415)

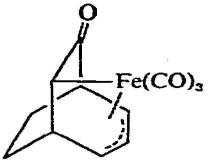
SCHEME 60



(416)

two nearly planar groups of C atoms: those associated with the diene—Fe(CO)$_3$ interaction, and the others, the dihedral angle between them being 138°.

In a two stage synthesis [311] (Scheme 60), barbaralone (**416**) could be synthesed from Fe(CO)$_3$(C$_8$H$_8$) (the intermediate complex has been obtained from barbaralone and Fe$_2$(CO)$_9$). Treatment of cyclooctatreieniron tricarbonyl with AlCl$_3$ and carbon monoxide afforded an uncharacterised species $C_9H_{10}OFe(CO)_3$ (possibly **417**) while norbornadieneiron tricarbonyl gave **418** and



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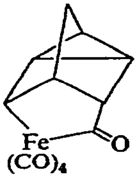

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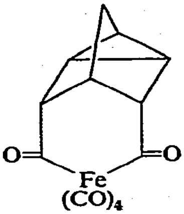
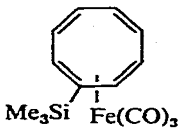


(419)

419. An alternative preparation of the latter from quadricyclane and Fe$_2$(CO)$_9$ was also reported. Cycloheptatrieneiron tricarbonyl did not react under the conditions used for the preparation of **416**—**419**.

In a series of ring-closure reactions, the substituted cyclooctatetraene complexes **420**, **421** and **422** have been converted [312] thermally into **423** (R =



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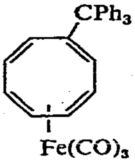

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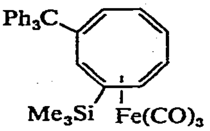

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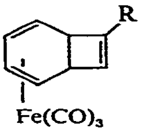

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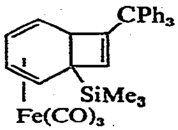

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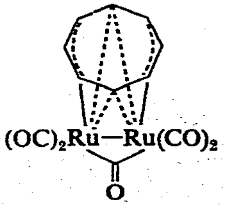

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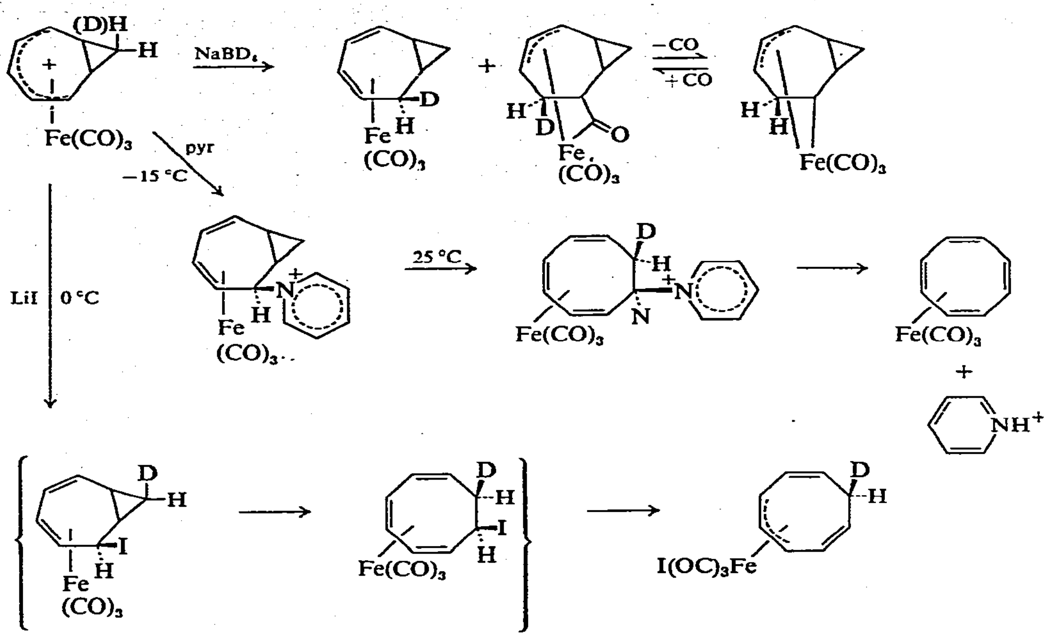
SCHEME 61



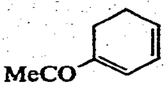
$SiMe_3$ or CPh_3) and **424**. The structure of the latter was confirmed crystallographically. Thermolysis of the ruthenium analog of **420** afforded **425**.

A study has been made [313] of nucleophilic attack on the bicyclo[5.1.0 octadienyl]iron tricarbonyl cation (**426**, Scheme 61). Depending on the type of nucleophile, addition occurred either at C(2), giving conjugated diene complexes, at C(3) giving non-conjugated π-allyl—σ-alkyl type complexes, or at C(1), with opening of the cyclopropane ring to give cyclooctatriene complexes. The latter could be transformed into complexes of cyclooctatetraene, and addition of iodide ion eventually afforded an iodoiron compound. All of the reactions investigated were highly regio- and stereo-specific.

In the presence of triethylaluminium, $Fe(acac)_3$ reacted with C_8H_8 giving $Fe(C_8H_8)_2$ [314].

Dienyl metal complexes

A group of complexes containing coordinated *trans*-pentadienyl carbonium ions, which cannot rearrange via simple bond rotation to their *cis*-analogs, have been prepared [315]. Thus reaction of **427** with $Fe(CO)_5$ under UV light gave **428**, and treatment of the latter with borohydride ion afforded a mixture of **429** and **430** (9 : 1). Reaction of **428** with LiMe gave **431**. At —120°C, **429** was protonated by FSO_3H/SO_2ClF to give **432** which, on warming, rearranged to give **433**. The latter was also prepared by protonation of **429** in FSO_4H at —78°C or in concentrated H_2SO_4 at 0°C. The rearrangement is an acid catalysed, pseudo-first-order process. Coupling between **432** and **430** afforded **434** which, on hydrolysis, produced a mixture of the ethers **435** and **436**. Treatment of



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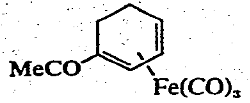

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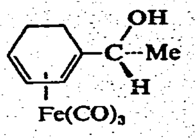

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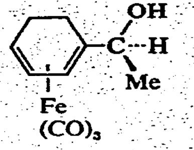

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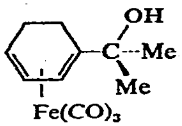

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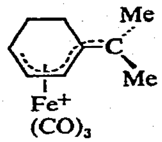

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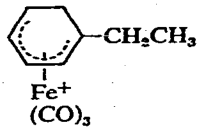

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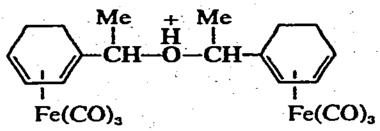

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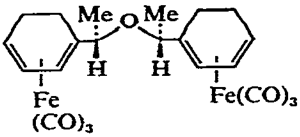

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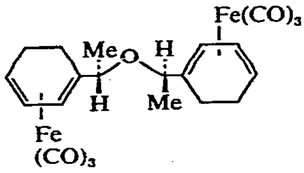

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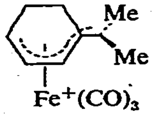

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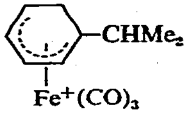
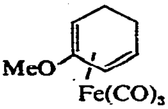


(438)

431 with FSO_3H/SO_2ClF at −120°C gave **437** which rearranged on warming to the thermodynamically more stable **438**. The rate of rearrangement of **432**→**433** was much faster than that of **437** → **438**, indicating that there is a substantial amount of residual positive charge on the exocyclic C atoms in these complexes of *trans*-pentadienyl carbonium ions.

Treatment of 2-methoxycyclohexa-1,3-diene with $Fe(CO)_5$ afforded [316] the isomers **439** and **440**, and reaction of the former gave the dienyl cation,



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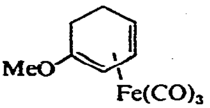

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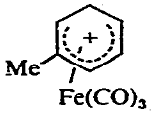

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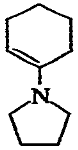

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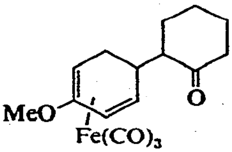
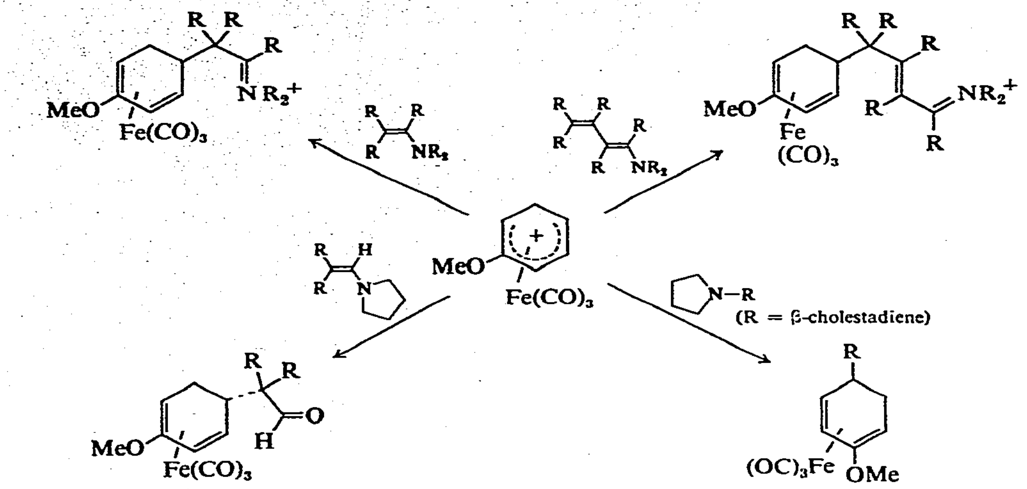


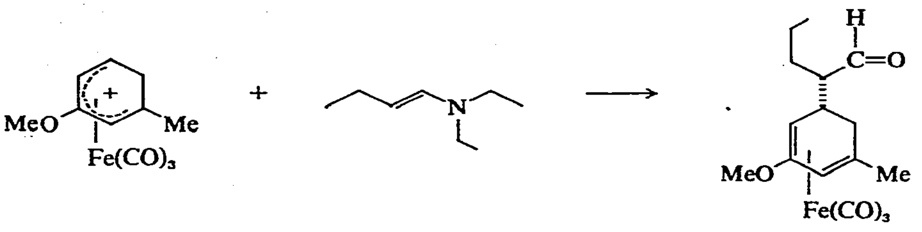
(443)

441. Addition of **442** to the latter gave the species **443** whose structure was confirmed crystallographically. Other reactions of **439** with enamines are out-

SCHEME 62



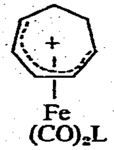
lined in Scheme 62, and 444 was prepared as shown in eq. 11. Cyclohexadienyliron tricarbonyl cation reacted with aromatic compounds (RH) to give [317] $Fe(CO)_3(C_6H_7R)$, the rate of reaction decreasing in the order RH = pyrrole > indole > furan > 1,3,5-trimethoxybenzene > 1,3-dimethoxybenzene > thiophene. Reactions of methoxycyclohexadienyliron tricarbonyl cation with trialkylalkynylborates [318] are summarised in Scheme 63. Attack by borates proceeded in a regio- and stereo-specific manner. It was reported that $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ and $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]^+$ also underwent attack by $R'_3BC{\equiv}CR''$.



(11)

(444)

Nucleophilic attack on $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ gave [319,320] only cyclohexadiene derivatives, and $[(\eta^5\text{-}C_6H_7)Fe(CO)_2(PPh_3)]^+$ behaved similarly. Treatment of $(\eta^5\text{-}C_7H_9)Fe(CO)_2I$ with $AgPF_6$ in acetone afforded $[(\eta^5\text{-}C_7H_9)Fe(CO)_2(acetone)][PF_6]$ which, on treatment with Lewis bases afforded $[(\eta^5\text{-}C_7H_9)Fe(CO)_2L]^+$ (445; L = PPh_3, $AsPh_3$, $SbPh_3$, pyr, MeCN, NH_3, $CH_2{=}CHCN$). The latter (L = PPh_3) could also be obtained [321] from $Fe(CO)_2(PPh_3)(C_7H_{10})$ and Ph_3C^+. The weakest σ-donor Lewis bases, e.g. MeCN, remained inert to displacement by other σ-donor/π-acceptors, e.g. PPh_3. However, attack upon 445 (L = PPh_3 or $AsPh_3$) by H^- or CN^- afforded only 446, while addition of H^-, OMe^- or CN^- to 445 (L = pyr, MeCN, NH_3 or $CH_2{=}CHCN$) resulted in decomposition, probably via ring attack. This behaviour was in marked contrast to that reported by Aumann [322], for $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]^+$, so reactions of this with nucleo-



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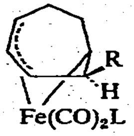

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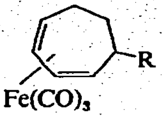

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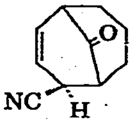

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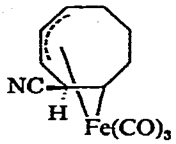

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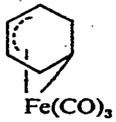
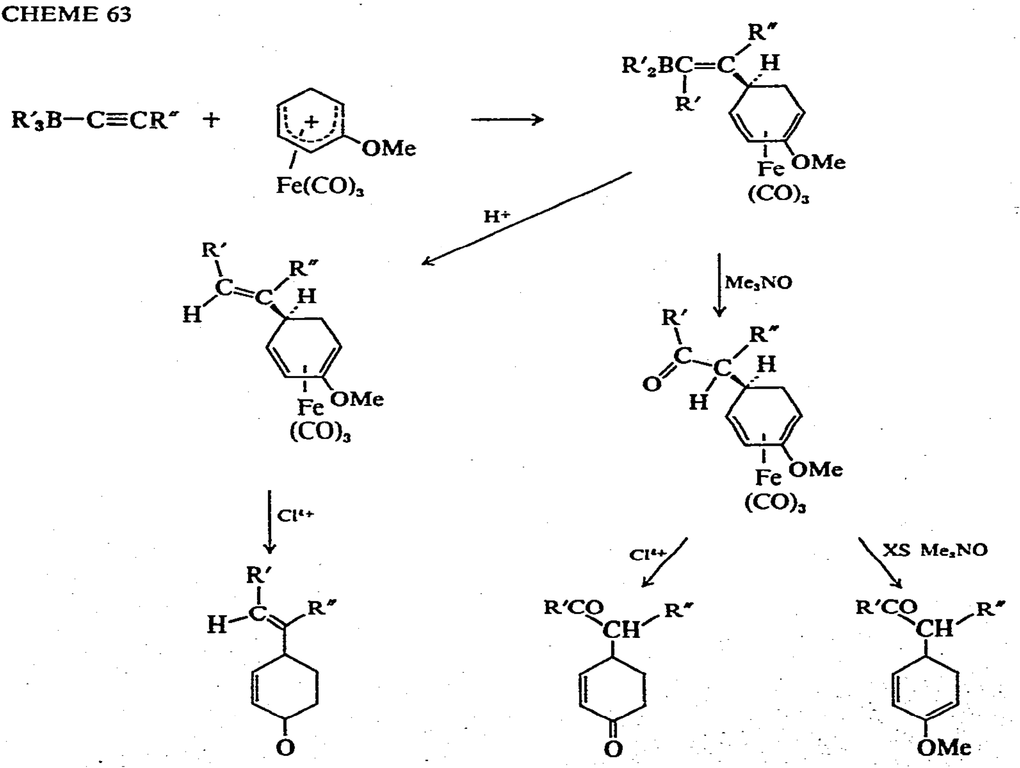


(450)

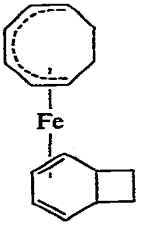
philes were reinvestigated. The products obtained were **446** (L = CO) and **447** in the ratio 2.3 : 1; changes of solvent caused a shift in the ratio of these products. Reaction of the mixture of **446** (L = CO) and **447** with Ph_3C^+ effected the regeneration of $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]^+$. Treatment of the cyclooctadienyl cation $[(\eta^5\text{-}C_8H_{11})Fe(CO)_3]^+$ with CN^- under CO afforded the ketone **448**, possibly via the unstable intermediate **449**; under N_2, CN^--attack afforded only $(C_8H_{11})_2$ as the organic product. It was observed that nucleophilic attack on the cyclohexadienyl cations would be unlikely to produce the unstable species **450**, whereas π-allyl-

SCHEME 63



σ-alkyl derivatives such as 434 are relatively stable. Thus, nucleophilic attack on C_7-cationic species is likely to occur at C(1) or C(2) (see 445), and a similar situation will occur in C_8 species; there was no evidence for attack at C(3). Substitution of one CO group in $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ by PPh_3 caused a decrease in the rate of nucleophilic attack, probably because of the poorer π-acceptor properties of PPh_3. It was suggested also that PPh_3 might exert a *trans*-effect on the ring, causing a deactivation at the C(3) position (see 445). Hydride attack on $[(\eta^5\text{-}C_7H_9)Ru(CO)_3]^+$ afforded the ruthenium analogs of 446 (L = CO, R = H) and 447 (L = CO, R = H) in the ratio 3 : 1, but similar treatment of $[(\eta^5\text{-}C_7H_9)Os(CO)_3]^+$ gave only the Os analog of 446 (L = CO, R = H).

The structure of $Fe(C_8H_{10})_2$, obtained [323] by reaction of $FeCl_3$ with (i-Pr)-MgBr and C_8H_{10} under UV light, was established crystallographically [324] as 451.



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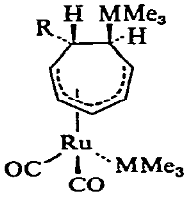

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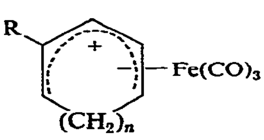

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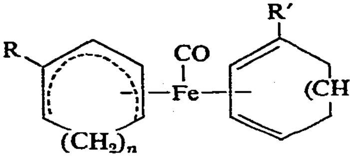

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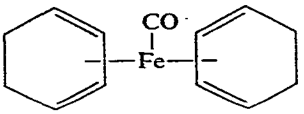
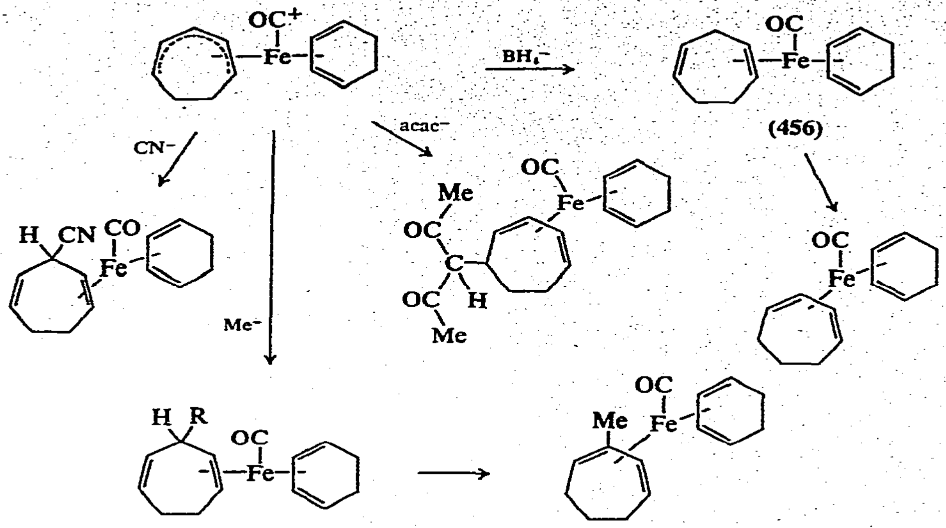


(455)

In refluxing heptane, $Ru(CO)_4(MMe_3)_2$ (M = Si or Ge) reacted [325] with cycloheptatriene and with $7\text{-}C_6F_5C_7H_7$ producing 452 (M = Si or Ge, R = H) and 452 (M = Si, R = C_6F_5). The quantitative formation of these complexes suggested that the MMe_3 group migration from metal to ring occurred intramolecularly, so that the MMe_3 group would be expected to occupy a position on the ring *endo* with respect to the metal, and not *exo* as observed. Equimolar mixtures of $Ru(CO)_4(SiMe_3)_2$ and $Ru(CO)_4(GeMe_3)_2$ with C_7H_8 gave mainly 452 (M = Si and Ge, R = H), small amounts of $(\eta^5\text{-}C_7H_9)Ru(CO)_2(MMe_3)$ and a species tentatively identified as $(\eta^5\text{-}C_7H_8SiMe_3)Ru(CO)_2(GeMe_3)$.

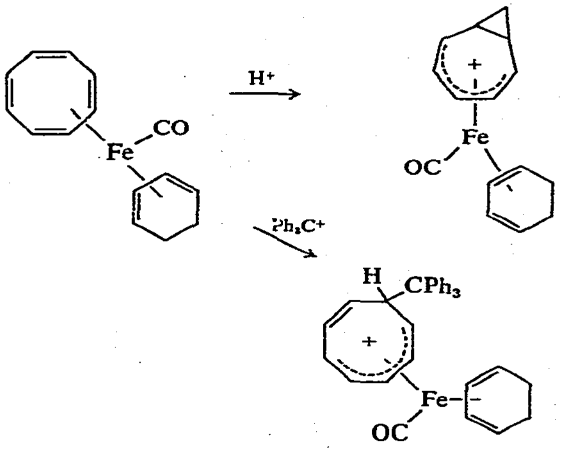
Photolysis of the dienyl cations 453 in the presence of cyclic 1,3-dienes afforded [326] 454, but the reactions of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ and $[(\eta^5\text{-}C_7H_9)\text{-}Fe(CO)_3]^+$ with cycloocta-1,3- and -1,5-diene or with cyclooctatetraene followed different courses. Thus, the former underwent disproportionation, giving C_6H_6 and $Fe(CO)_3(C_6H_8)$, while the latter was converted into 454 ($n = 2$, $m = 3$, R = R′ = H). The new cations 454 underwent nucleophilic attack, and some of their reactions are summarised in Scheme 64. However, treatment of $[(\eta^5\text{-}C_8H_{11})Fe\text{-}(CO)(C_6H_8)]^+$ (454; $n = 3$, $m = 2$, R = R′ = H) with BH_4^- resulted in its rearrange-

SCHEME 64

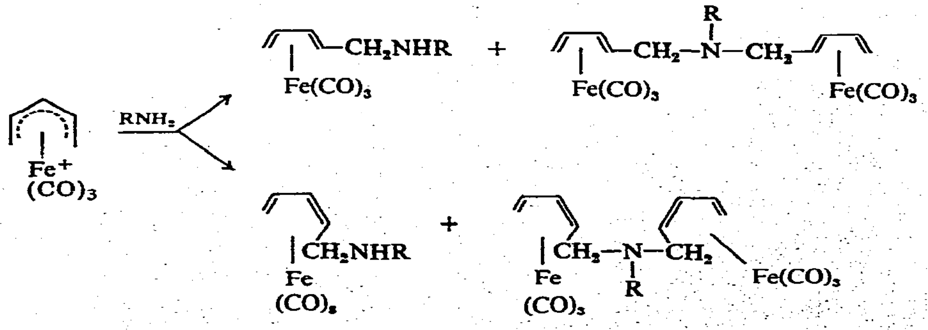


ment to 455. Cycloheptadiene could be readily displaced from 456 by either PPh$_3$ or C$_8$H$_8$, and some reactions of Fe(CO)(C$_6$H$_8$)(C$_8$H$_8$) are summarised in Scheme 65.

SCHEME 65



SCHEME 66



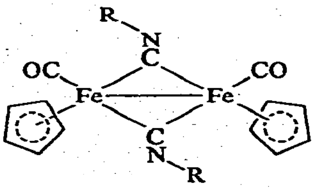
Non-cyclic pentadienyl complexes

Attack of amines on pentadienyliron tricarbonyl cation led to the formation [327] of *cis,trans* or *trans, trans* diene adducts, (Scheme 66); the actual products depended on the basicity of the amines. Further reaction between the dienyl cation and the newly formed dieneamine resulted in dimerisation.

Cyclopentadienyl metal complexes

Binuclear cyclopentadienyl compounds

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with CNMe afforded [328] three compounds, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNMe)$, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNMe)_2$ and $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)(CNMe)_3$; there was no evidence for $[(\eta^5\text{-}C_5H_5)Fe(CNMe)_2]_2$. The structure of one isomer of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(CNMe)_2$ (457) was determined [329] crystallographically, and other isomers of the other complexes were detected [330] in solution by ^{1}H NMR spectroscopy. It was noted that the average Fe—Fe distance in the isomers of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was 2.53 Å, and in 457 and the related



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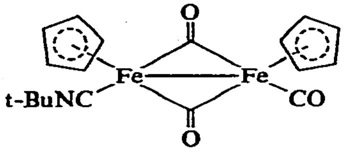

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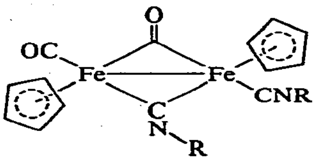

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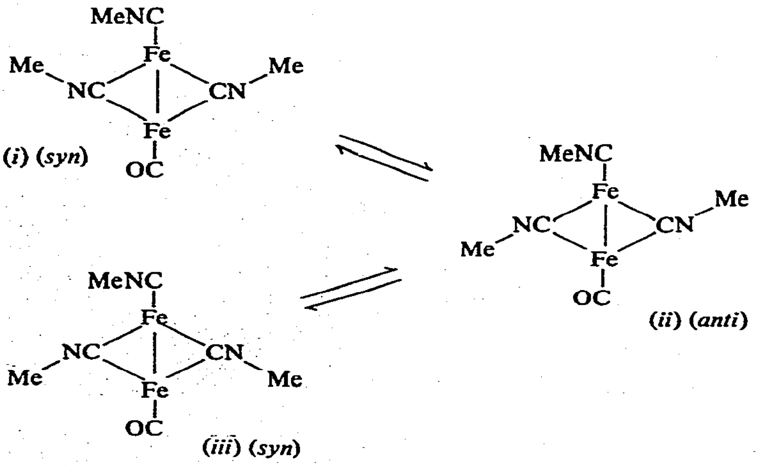
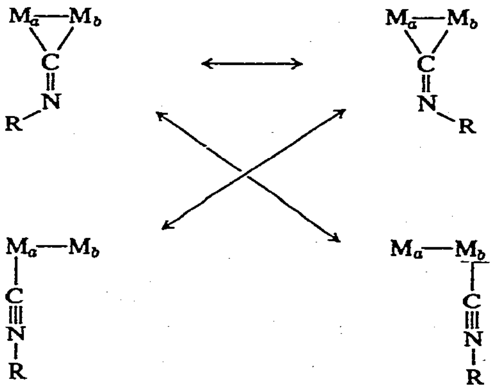


Fig. 10. The fluxional nature of $(\eta^5\text{-}C_5H_5)_2Fe(CO)(CNMe)_3$.

(η^5-C_5H_5)$_2$$Fe_2(CO)_3${CN(t-Bu)} (458) [331] were 2.54 and 2.52 Å, respectively. In a comparison of the structures of 457 and 458, it was noted that the t-BuNC analog of 457 would be significantly sterically strained and this could explain the absence of detectable amounts of this isomer in solutions of 458 (see below).

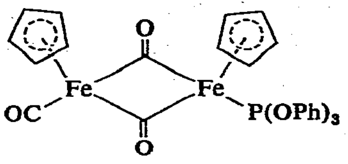
The fluxional behaviour of (η^5-C_5H_5)$_2$$Fe_2$(CO)(CNMe)$_3$, and ($\eta^5$-$C_5H_5$)$_2$$Fe_2(CO)_2$(CNMe)$_2$ were examined [330] by ^{1}H NMR spectroscopy over a wide temperature range. The former species exists in solution in entirely one tautomeric form, having either *cis*- or *trans*-cyclopentadienyl groups with two bridging isocyanide ligands. Three interconverting isomers could be present (Fig. 10) and there was spectral evidence that two of these interconverted. The *anti* isomer *ii* was definitely detected but only a very small amount of isomer *iii* was detected. The spectral changes observed could not result from bridge-terminal ligand exchange and it was concluded that inversion at nitrogen was occurring independently at each isocyanide ligand. The spectra of (η^5-C_5H_5)$_2$$Fe_2(CO)_2$(CNMe)$_2$ provided evidence for two isomers, 457 (*syn* and *anti* forms) and 459. These isomers interconverted via a bridge-terminal ligand-exchange process, probably involving a transition state having a linear bridging RNC group. A reversal of configuration at nitrogen is an essential step in the overall rearrangement (Scheme 67) whereby an isocyanide ligand passes from one metal to the other. The mechanism for ligand exchange in (η^5-C_5H_5)$_2$$Fe_2(CO)_3${CN(t-Bu)} (458) [331] is shown in Scheme 68. *Cis-trans* isomerism of the species having terminal isocyanide is very rapid even at —120°C ($\Delta G^{\neq} < 7.0$ kcal mol^{-1}), whereas exchange of isocyanide between metals is slower (because of the unfavourable bridged intermediate necessary to effect this) ($\Delta G^{\neq}$ 14.4 ± 0.7 kcal mol^{-1}).

SCHEME 67



Reduction of [(η^5-C_5H_5)Fe(CO)(CNMe)]$_2$ with sodium amalgam probably gave [332] the anion Na[Fe(CO)(CNMe)(η^5-C_5H_5)], which very readily afforded the hydride (η^5-C_5H_5)Fe(CO)(CNMe)H. Reaction of the anion with Group IVB halides led to the formation of (η^5-C_5H_5)Fe(CO)$_2$R (R = CH_2CN) $GeMe_2Cl$ and $SnMe_3$; Hg[Fe(CO)(CNMe)(η^5-C_5H_5)]$_2$ was also prepared.

The structure of *cis*-(η^5-C_5H_5)$_2$$Fe_2(CO)_3${P(OPh)$_3$} (460) has been determined crystallographically [333]. The Fe—Fe distance (2.54—2.55 Å) is comparable to that in [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ (2.53 Å). In solution the molecule is fluxional



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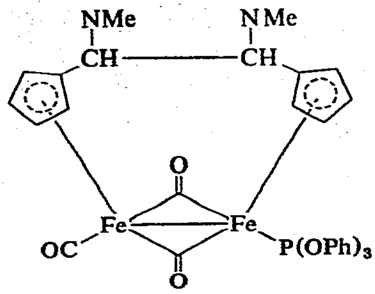

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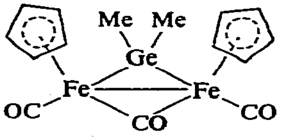
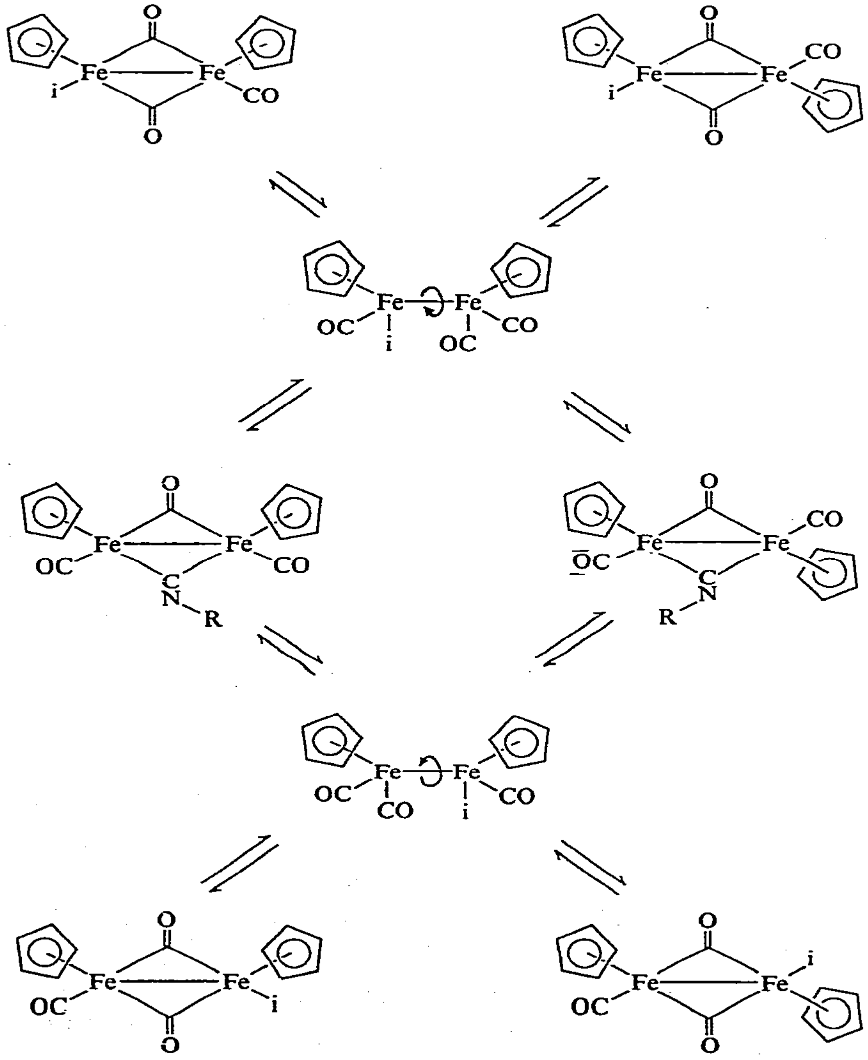


(462)

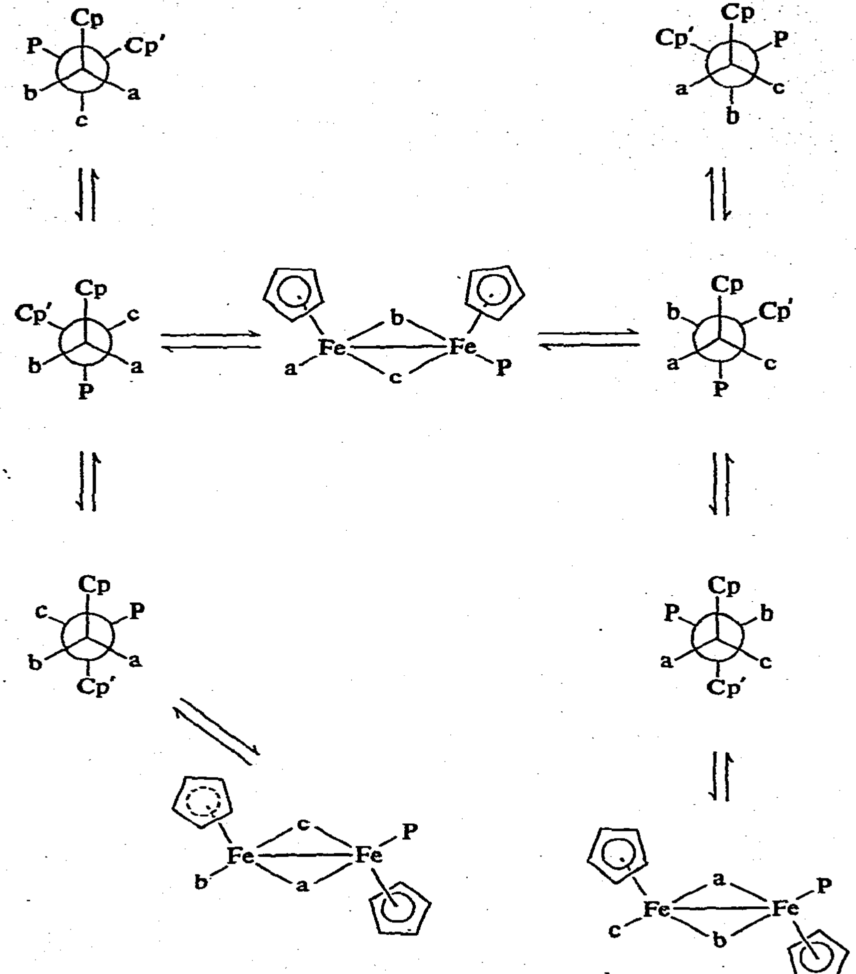
SCHEME 68



(i = *t*-BuNC)

[334], undergoing *cis/trans* isomerisation of the cyclopentadienyl ligands and scrambling of the linear and terminal CO groups. Both processes have the same rate at the various temperatures studied, and have the same activation energies (within experimental error). Previous proposals for such species are applicable to this system, and the mechanisms are outlined in Scheme 69. Similar data were

SCHEME 69

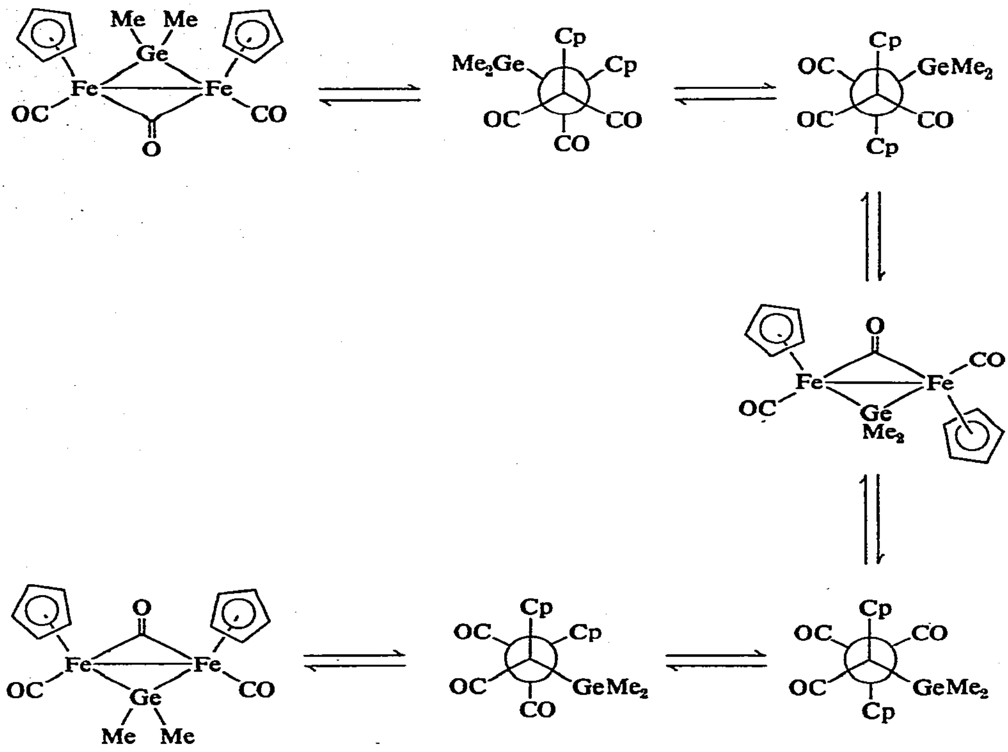


(P = P(OPh)$_3$; a, b, c≡CO; cp, cp' = η^5-C_5H_5)

obtained [335] from a study of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3\{P(OEt)_3\}$, and it was observed that in both cases the phosphite ligand was not involved in bridge exchange reactions. From an IR study of 461, prepared from the corresponding tetracarbonyl and $P(OPh)_3$, it was deduced that $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3\{P(OPh)_3\}$ existed predominantly as the *cis* isomer in solution. The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(\mu_2\text{-}CO)_2Ni(\eta^5\text{-}C_5H_5)$ and $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ also underwent rapid bridge/terminal CO ligand exchange in solution.

The molecular structure of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(GeMe_2)$ (462) has been determined crystallographically [336]; The bridges are symmetrical and the Fe—Fe distance is 2.63 Å. In solution there is an approximately 8 : 1 *cis* : *trans* mixture of isomers, but these interconvert [336] too slowly to influence either ^1H or ^{13}C NMR spectral line shapes at low and room temperatures. However, between 90° and 160°C (decomposition point), 462 exhibits fluxionality, and the spectral behaviour has been explained by a process outlined in Scheme 70.

SCHEME 70

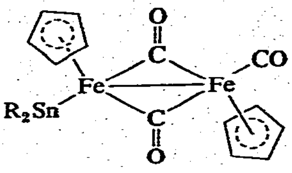


The activation energy for the combined ring site exchange and CO ligand scrambling process (ca 21 kcal mol^{-1}) is higher than that for the previously mentioned species and for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and this was attributed to the relative instability of the intermediates having a terminal dimethylgermylene ligand. However, treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with SnR_2 ($R = CH\{SiMe_3\}_2$) afforded [337] 463, whose stability may be due, in part, to steric effects.

The structure of 464, prepared by King et al. [338], has been determined crystallographically [339]. The Fe—Fe distance is 2.51 Å and the dicyanamylidene ligand is planar and forms a symmetrical bridge between the two Fe atoms.

Photolysis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in the presence of PhC≡CPh gave [340] $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(C_2Ph_2)$ (465) but photolysis of the dicarbonyl dimer on its own [341] afforded $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^{\bullet}$; which formed an adduct with ArNO of presumed structure 466.

Reaction of 1-acetyl-pentamethylcyclopenta-2,4-diene with $Fe_2(CO)_9$ afforded



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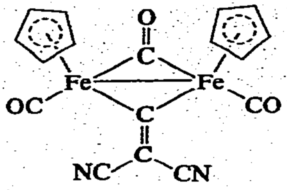

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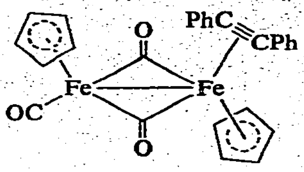

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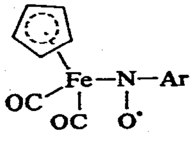

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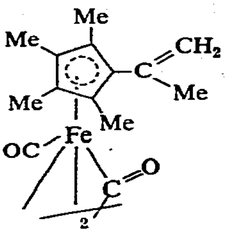

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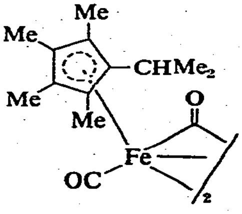
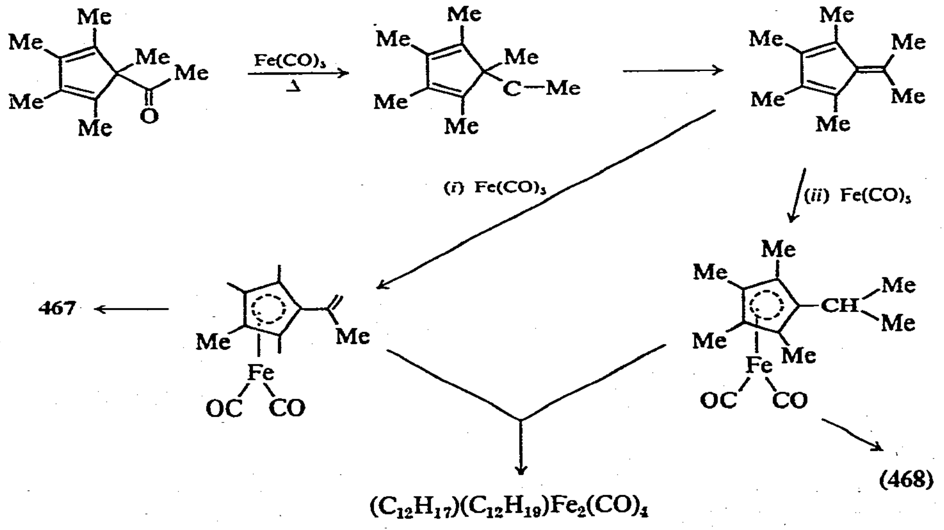


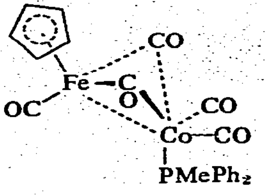
(468)

[342] $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ but in boiling 2,2,5-trimethylhexane in the presence of $Fe(CO)_5$, the pentadiene gave **467** and **468**. A mechanism for the formation of these compounds is given in Scheme 71 and the pathway (*ii*) has precedent [343]. Reduction of $[(\eta^5\text{-}C_5Me_4R)Fe(CO)_2]_2$ (R = Me or CMe=CH_2) with sodium amalgam afforded $Na[Fe(CO)_2(\eta^5\text{-}C_5Me_4R)]$ which, on treatment with R′X (R′ = Me, MeCO or $SnPh_3$) gave $(\eta^5\text{-}C_5Me_4R)Fe(CO)_2R'$. Oxidation of $[(\eta^5\text{-}C_5Me_4R)\text{-}Fe(CO)_2]_2$ with $FeCl_3$, $HgBr_2$ or I_2 afforded $(\eta^5\text{-}C_5Me_4R)Fe(CO)_2X$ (R = Me, X = Br; R = CMe=CH_2, X = Cl or I).

SCHEME 71



The structure of $(\eta^5\text{-}C_5H_5)Fe(CO)(\mu_2\text{-}CO)_2Co(CO)_2(PMePh_2)$ (**469**) has been determined crystallographically [344]. The Fe—CO distance is 2.54 Å, and the $Fe(\mu_2\text{-}CO)_2Co$ ring is non-planar, the cyclopentadienyl ligand being *trans* to the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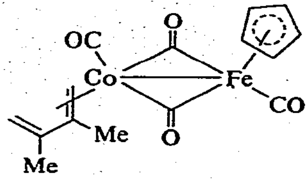
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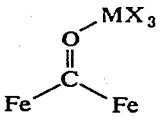
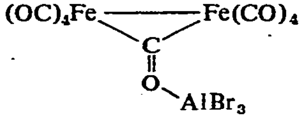

(E)

PMePh$_2$ ligand. The Fe—C and Co—C distances in the bridges are not equal. Similar non-planarity of the bridging system in (η^5-C$_9$H$_7$)Fe(CO)(μ_2-CO)$_2$Co(CO)$_3$ was revealed by X-ray crystallographic studies [345], and again the metal—carbon bond lengths were irregular; the Fe—Co distance is 2.55 Å. In (η^5-C$_5$H$_5$)Fe(CO)(μ_2-CO)$_2$Co(CO)(C$_4$H$_4$Me$_2$) (470) however, the Fe(μ_2-CO)$_2$Co system was almost planar [346], although some asymmetry occurred in the M—C distances; the Fe—Co bond length is 2.55 Å.

Group IIIA halides reacted with [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$ and [(η^5-C$_5$H$_5$)Fe(CO)]$_4$ giving [347] the species [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$BX$_3$ (X = F or Br) and [(η^5-C$_5$H$_5$)Fe(CO)]$_4x$BF$_3$ (x = 1, 2 or 4), [(η^5-C$_5$H$_5$)Fe(CO)]$_4x$BX$_3$ (x = 1 or 2, X = Cl or Br) and [(η^5-C$_5$H$_5$)Fe(CO)]$_4x$AlBr$_3$ (x = 1, 2, 3 or 4). In all of these species, bonding of the Lewis acid to the iron complex occurs via a bridging CO group (E). AlBr$_3$ reacted with Fe$_2$(CO)$_9$, Fe$_3$(CO)$_{12}$ and Ru$_3$(CO)$_{12}$ giving 1 : 1 adducts, the structure of the first being probably 471, whereas the species obtained from Fe$_3$(CO)$_{12}$ could be either 472 or 473, the former being more likely. The structure of Ru$_3$(CO)$_{12}$ ··AlBr$_3$ may involve a bridging CO group, but structures analogous to 472 or 473 could not be detected.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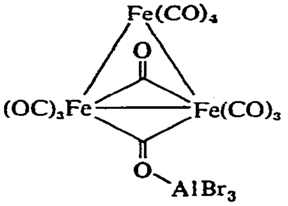
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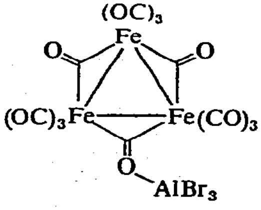
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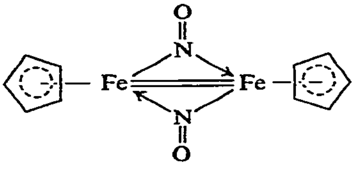

(474)

From Mössbauer spectral studies of [(η^5-C$_5$H$_5$)Fe(CO)]$_4^z$ (z = 0 or +1) it was suggested [348] that the unpaired electron in the monocation was in a delocalised molecular orbital which was at least partly and perhaps largely metal—metal bonding in character.

The structure of [(η^5-C$_5$H$_5$)Fe(μ_2-NO)]$_2$ (474) has been determined [349] crystallographically. The bridges are symmetrical, and the shortness of the Fe—Fe bond (2.33 Å) is consistent with a bond-order of 2 (Fe—Fe single bonds occur in the range 2.50—2.70 Å).

Cationic species

Mössbauer ,^{13}C NMR and IR spectral studies have been made [350] on $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$ (L = CO, MeCN, C_2H_4, PPh_3, pyridine). The Mössbauer spectral data indicated that the σ-donor/π-acceptor ability of L in this system increased in the order L = MeCN $\leqslant$ C_2H_4 < pyr < PPh_3 < CO. From ^{13}C NMR spectral studies of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$ (L = CS, CO, PPh_3 or NH_3) it was established [351] that the CS ligand is a significantly better π-acceptor than CO. Mössbauer spectral studies have been made [352] on $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$ (L = SR_2, R = Me, Et, n-Pr, n-Bu; PPh_3) and of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_2Me$. The broadness of the spectral lines in the latter suggested hindered rotation about the Fe—Si bond.

Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ with concentrated H_2SO_4 or $AgPF_6$ afforded [353] $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2X]^+$ (X = halide). The Fe atoms were equivalent according to the Mössbauer spectra of these compounds. When the species with X = Cl or Br were heated, $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ was formed, but when X = I, $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ was also produced.

In acetonitrile, $[(\eta^5\text{-}C_5H_5)Fe(CO)(CN)_2]^-$ was alkylated [354] by RX or $R_3O^+BF_4^-$ (R = Me, Et or CH_2Ph) affording $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNR)_2]^+$. In less polar solvents (e.g. THF, dichloromethane or ethanol) the yield of this cation was decreased, and that of $(\eta^5\text{-}C_5H_5)Fe(CO)(CNR)(CN)$ correspondingly increased. The species $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CNMe)]^+$ was prepared from $(\eta^5\text{-}C_5H_5)Fe(CO)_2CN$ and MeI in acetonitrile. Photolysis in dioxan of $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNMe)_2]I$ afforded $[(\eta^5\text{-}C_5H_5)Fe(CNMe)_3]I$, even in the presence of KCN. The relative rates of reactions of coordinated CO and CNR with NH_2Me in the species $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNMe)L]^+$ (L = CO, CNMe or PPh_3) have been investigated [355]. Like $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CNMe)]^+$ afforded $(\eta^5\text{-}C_5H_5)Fe(CO)(CNMe)\{C(=O)NHMe\}$ in a readily reversible reaction. However, $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNMe)_2]^+$ gave the carbene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNMe)\{C(NHMe)_2\}]^+$. In a slow reaction, $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNMe)(PPh_3)]^+$ afforded $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(NHMe)_2\}]^+$. In general, the reactions of NH_2Me with coordinated CO appeared more rapid than those with coordinated CNR, a factor reflected in the electron density at the respective C atoms. This electron density may be related to ν(CO) and to the CO stretching force constant, low values of *f*(CO) indicating relatively high electron density at the carbon atom, and vice versa. The data obtained from these species are summarised in Table 5. It appeared that amine attack occurred preferentially at CO with a high *f*(CO) value because of a higher rate of reaction and the possibly higher thermodynamic stability of the product. As *f*(CO) decreased, addition of NH_2R to CO became thermodynamically less favorable and attack of the amine on CNR predominated. Thus, even when CO is unreactive, addition to CNMe still occurred.

Treatment of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ with propylene oxide in THF, followed by HBF_4, afforded [356] the known $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2{=}CHMe)]^+$, which reacted with NaI releasing propene and forming $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$. Treatment

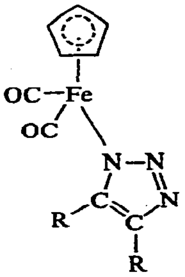
TABLE 5

CORRELATION OF FORCE CONSTANTS AND REACTIVITY OF IRON CARBONYL CATIONS TOWARDS AMINES

Compound	f(CO) (mdyn Å^{-1})	Reactions towards $MeNH_2$
$[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$	17.6	Carbamoyl [a] complex readily formed in solution [b]
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CNMe)]^+$	17.1	Carbamoyl [a] complex readily formed in solution [b]
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+$	16.9	Carbamoyl [a] complex readily formed in solution [b]
$[(\eta^5\text{-}C_5H_5)Fe(CO)(CNMe)_2]^+$	16.6	Reacted reversibly but attack at CNMe may be due to equilibrium favouring this
$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CNMe)]^+$	16.1	CO unreactive, so CNMe attacked

[a] Fe CNHMe species formed. [b] Product isolated if insoluble.

of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_2H_4)]^+$ with NaN_3 gave [357] $(\eta^5\text{-}C_5H_5)Fe(CO)_2N_3$ and not $(\eta^5\text{-}C_5H_5)Fe(CO)(C_2H_4)(NCO)$ as previously reported [358]. The azide was also obtained in low yield by metathesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and NaN_3. Photolysis of the azide gave, in low yield, the corresponding *N*-cyanate, while, with $MeO_2CC{\equiv}CCO_2Me$, 475 was formed.



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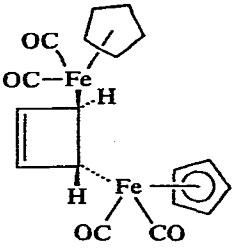

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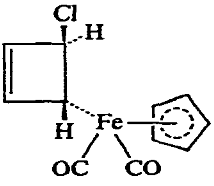

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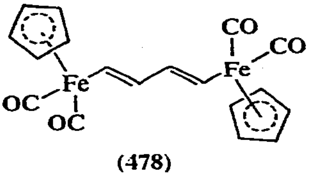

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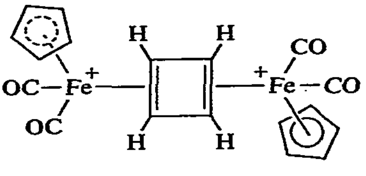

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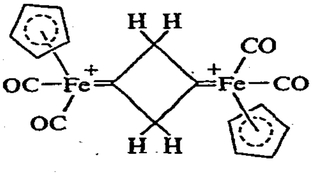

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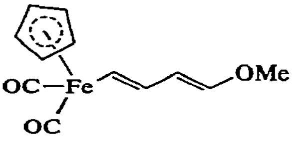
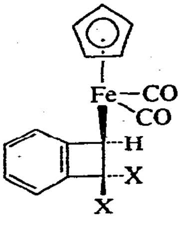


(481)

Reaction of Na[Fe(CO)$_2$(η^5-C$_5$H$_5$)] with *cis*-1,2-dichlorocyclobutene gave [359] at −78°C, **476** and **477**. The former was readily converted on warming into the known [360] **478**. Treatment of **476** with Ag$^+$ or Ph$_3$C$^+$ gave the binuclear dication **479** which, on reduction with LiAlH$_4$ or [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$^-$, regenerated **476**. From spectroscopic studies it was established that **479** could not be regarded as a dicarbene, viz. **480**, and treatment of **479** with NaHCO$_3$ in methanol gave **481**.



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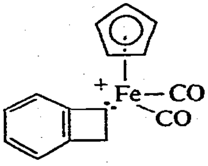
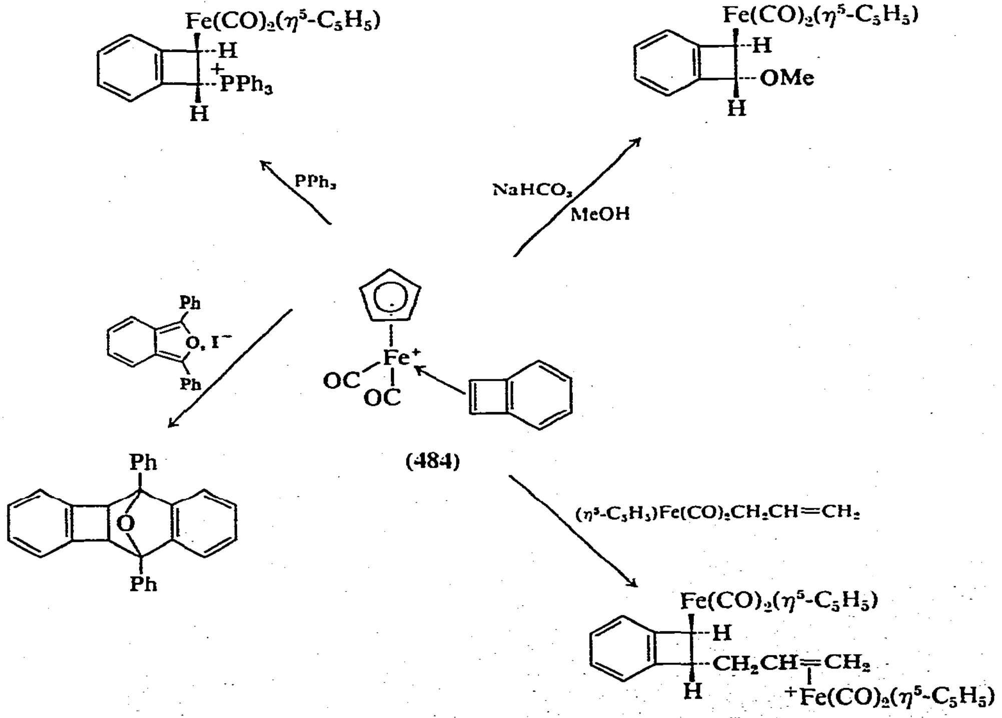
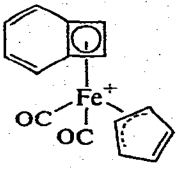


(483)

Treatment of 482 (X = H) with Ph$_3$C$^+$ afforded [361] 483, but 482 (X = Fe(CO)$_2$(η^5-C$_5$H$_5$)) afforded, at −78°C, 484, some reactions of which are shown in Scheme 72. While these reactions are typical of a derivative of the type [(η^5-C$_5$H$_5$)Fe(CO)$_2$(olefin)]$^+$, where the olefin is benzocyclobutadiene, the formulation of the species as 485 cannot be discounted. Reaction of 483 with (η^5-C$_5$H$_5$)Fe(CO)$_2$C$_3$H$_5$ (C$_3$H$_5$ = cyclopropyl) gave [362] [(η^5-C$_5$H$_5$)Fe(CO)$_2$-

SCHEME 72





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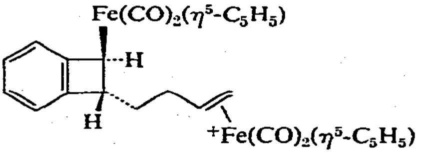
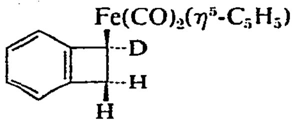


(486)

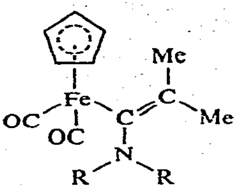


(487)

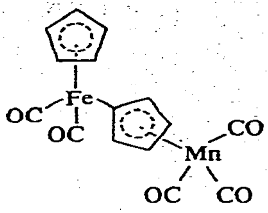
$(H_2C{=}C{=}CH_2)]^+$ (the product of hydride ion abstraction), $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CHMe)]^+$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ and 482 (X = H). However, treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_3H_5$ with Ph_3C^+ gave only the addition product $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CHCH_2CPh_3)]^+$. Similar treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2C_3H_5$ with 483 gave $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-}H_2C{=}CHCHCH_2)]^+$ and 482 (X = H) but no 486, whereas with Ph_3C^+, the addition product $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CHCH_2CH_2CPh_3)]^+$, an unidentified cation and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CHCH_2CH_3)]^+$ were formed. Thus, 483 is a hydride ion abstracting agent far more specific than Ph_3C^+. The formation of the allene complex from $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_3H_5)$, and butadiene species from $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2C_3H_5$, was envisaged as α- and γ-hydride ion abstraction, respectively, by 483 concomitant with the opening of the three-membered cyclopropyl rings. However, with σ-allyl species there is no distinction between the reactivity of 483 and Ph_3C^+, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CR'{=}CR''R'''$ being converted smoothly into $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CR'CR''R'''Q)]^+$ (where Q = 483 or CPh_3). It was suggested that the differences in reactivity between 483 and Ph_3C^+ might be interpreted in terms of a greater shielding of the positive carbon atom in 483 than in Ph_3C^+, and possibly also to the possibility of H^- addition to the aromatic rings in the trityl cation, which cannot occur in 483. However, treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH(CD_3)_2$ with the two reagents afforded, respectively, 487 and Ph_3CD, there being no evidence for the deuteriation of either the cyclopentadienyl or phenyl rings. Thus, the fact that 483 has a greater propensity for hydride ion abstraction than Ph_3C^+ may be related to steric factors.

Complexes containing M—C σ-bonds

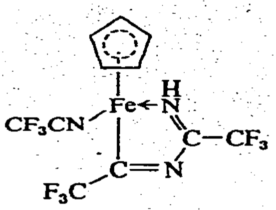
Reaction of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2I][BF_4]$ with RMgX (R = Me, CH_2Ph, Ph or C_5H_5) afforded [363] $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$. Treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ with $PhCH_2Cl$ and polymer bound $C_6H_4CH_2Cl$ afforded [364] $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Ph$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2C_6H_4$—(polymer) (the polymer was either linear polystyrene or styrene—divinylbenzene copolymer). Thermolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Ph$ at 140°C, on its own in benzene or decane, resulted in first-order Fe—C bond homolysis and formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2Ph)Fe_2(CO)_4$, dibenzyl and tar. Thermal decomposition of the polymer-bound metallic species on its own was slow at 140°C, but in solution rapidly gave $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2C_6H_4$—polymer)$Fe_2(CO)_4$. Studies of the ^{13}C NMR spectral parameters obtained from $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = CH_2Ph, CHMePh or CH_2CH_2Ph) indicated [365] that the phenyl ring substituent did not interact with the ring via an inductive effect, but that the σ-electrons of the Fe—CH_2 bond were conjugated with the π-electrons of the phenyl ring. In the species where R = CH_2CH_2Ph, there was no appreciable



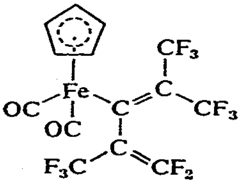
(488)



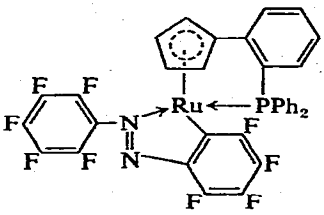
(489)



(490)



(491)



(492)

H/D exchange at the phenyl ring, but when R = CH_2Ph or CHMePh, exchange of the ring hydrogen atoms occurred at comparable rates.

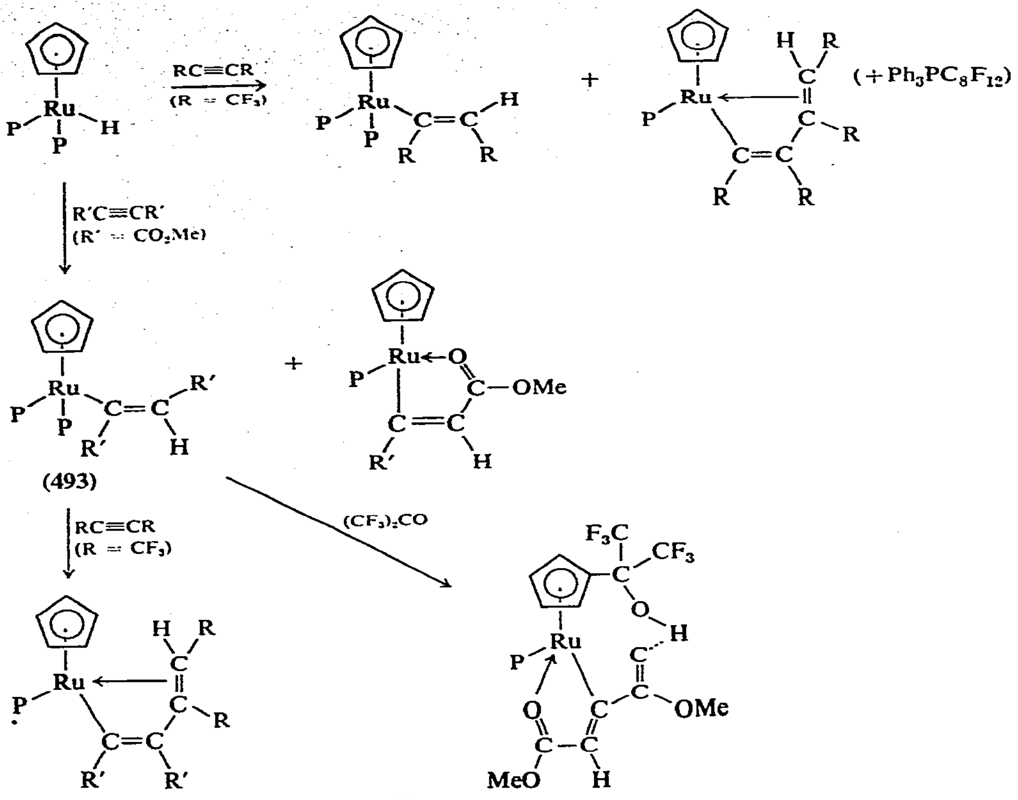
Reaction of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ with $Me_2C{=}C(NR_2)Cl$ gave [366] 488, while treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with ArCOCH=CHI afforded [367] a mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH{=}CHCOPh$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$. An X-ray crystallographic study of $(\eta^5\text{-}C_5H_5)Fe(CO)_2C{\equiv}CPh$ established [368] that the Fe—C≡C—Ph system was essentially linear.

At —70°C, $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ reacted with $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4Li)$ giving [369] $(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_4Fe(CO)_2(\eta^5\text{-}C_5H_5)\}$, whereas treatment of $(\eta^5\text{-}C_5H_5)\text{-}Fe(\eta^5\text{-}C_5H_4COCl)$ with $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ afforded [370] $(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_4COFe(CO)_2(\eta^5\text{-}C_5H_5)\}$. Attack by $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ upon $(\eta^5\text{-}C_5H_5)Fe\text{-}(\eta^5\text{-}C_5H_4COCH_2Cl)$ resulted in the formation of $(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_4COCH_2Fe\text{-}(CO)_2(\eta^5\text{-}C_5H_5)\}$. Reaction of this species with $LiAlH_4$ or $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ gave $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4COMe)$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, while iodination afforded $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4COCH_2I)$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$. With LiPh, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4COMe)$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Ph$ were produced, whereas $(\eta^5\text{-}C_5H_4Li)Mn(CO)_3$ afforded 489, also obtained by reaction of $(\eta^5\text{-}C_5H_5)Fe\text{-}(CO)_2I$ with $(\eta^5\text{-}C_5H_4Li)Mn(CO)_3$.

A species obtained by reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with CF_3CN formulated [371] as $(\eta^5\text{-}C_5H_5)Fe(NCCF_3)\{C(CF_3){=}NH\}_2$, may in fact be **490** [372]. At —70°C, $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ reacted [373] with $(CF_3)_2C{=}C{=}C(CF_3)_2$ giving 491. Treatment of *sym*-trichlorotrifluorobenzene with $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ gave [374] *sym*-$(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6F_3Cl_2$. Lithiation afforded $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}C_6F_3ClLi$, hydrolysis and carbonylation with CO_2 followed by hydrolysis, gave $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6F_3ClH$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2C_6F_3Cl(CO_2H)$, respectively. Reaction of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Me$ with $C_6F_5N{=}NC_6F_5$ gave [375], at 100°C, 492.

Insertion of the acetylene into the Ru—H bond occurred [376] when $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2H$ was treated with either $CF_3C{\equiv}CCF_3$ or $MeO_2CC{\equiv}CCO_2Me$; the reactions of the hydride with these acetylenes and with $(CF_3)_2CO$ are shown

SCHEME 73



$(P = PPh_3)$

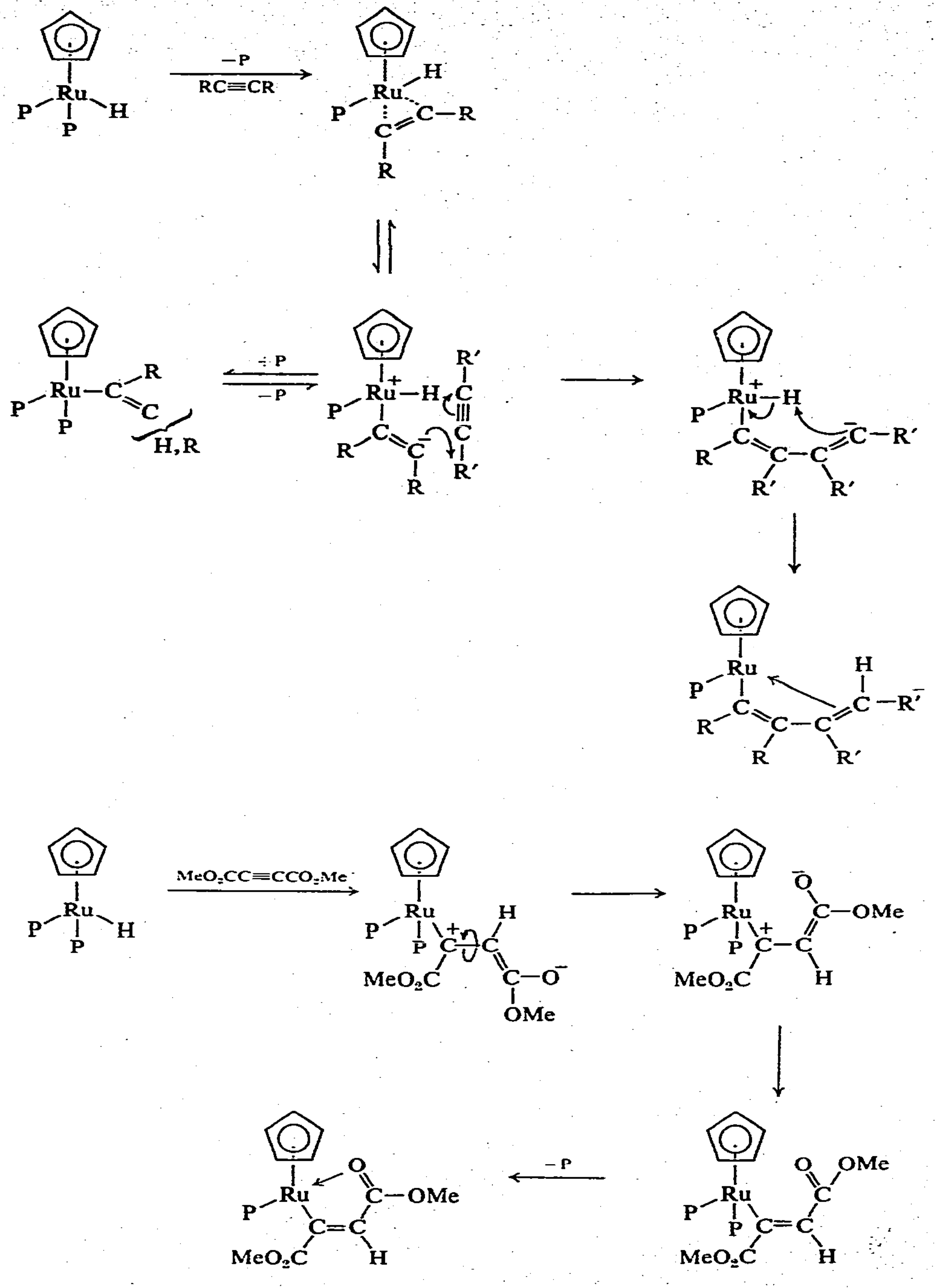
in Scheme 73. The mechanisms of the reactions are outlined in Scheme 74 but, mechanistically, *cis* addition of the metal complex to the C≡C bond does not explain the possible formation of the *trans* isomer 493. Reaction of the hydride with $(CF_3)_2C{=}C(CN)_2$ afforded $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2\{C(CN)_2C(CF_3)_2H\}$.

Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_4(CNR)X$ (R = C_6H_{11}, t-Bu or $PhCH_2$; X = Cl or I) with $p\text{-}YC_6H_4CH_2MgCl$ (Y = H or Cl) gave $(\eta^5\text{-}C_5H_5)Fe(CO)(CNR)(CH_2C_6H_4Y)$, but with other Grignard reagents, decomposition resulted [377]. However, reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(CNR)X$ with RMgX (X = Cl, Br or I; R′ = Me, i-Pr, Ph or $p\text{-}ClC_6H_4$), in the presence of CO, afforded $(\eta^5\text{-}C_5H_5)Fe(CO)(CNR)COR'$. However, when R′ = $p\text{-}YC_6H_4CH_2$, both the σ-alkyl and σ-acyl products were obtained. Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)(CNR)R'$ with CO gave preferentially $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CR'{=}NR)$ [R = C_6H_{11} or CH_2Ph; R′ = $p\text{-}YC_6H_4CH_2$ (Y = H or Cl) or $p\text{-}ClC_6H_4$]. A possible mechanism for the formation of the acyl complexes is shown in Scheme 75.

Optically-active metal alkyl complexes

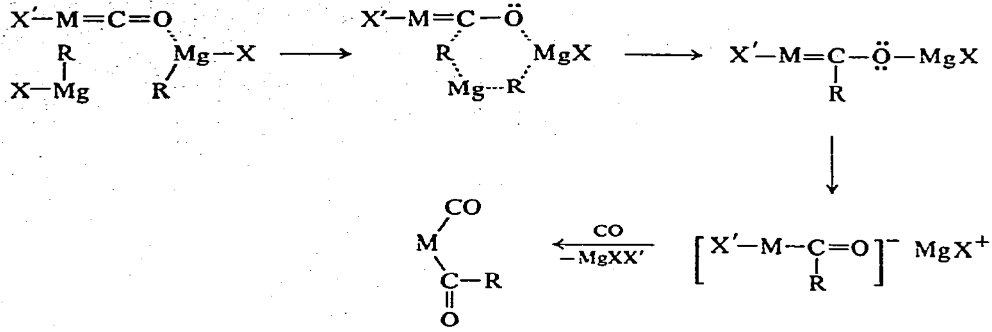
Reaction of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ with PhMeCHCl gave [378] 494. The ^{13}C NMR spectrum of this species revealed the inequivalence of the CO groups arising from the chiral nature of the C atom. The IR and NMR spectral data obtained [379] from $(\eta^5\text{-}C_5H_5)Fe(CO)LCH_2R$ (L = PPh_3, $P(OMe)_3$ or $PMePh_2$;

SCHEME 74

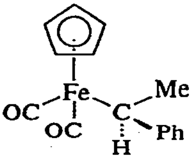


(P = PPh$_3$

SCHEME 75

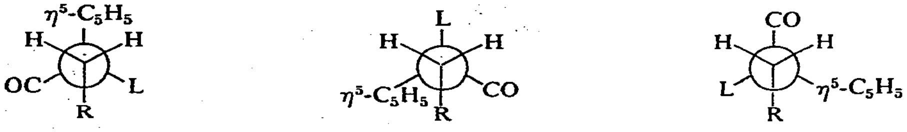


R = $SiMe_3$ or Ph) revealed that the species existed as three rotamers (Fig. 11) the most stable being those, *i* and *iii*, having both methylene hydrogen atoms *gauche* to the cyclopentadienyl ring. It was shown that *i* was the most stable conformer because of its low-energy conformation.



(494)

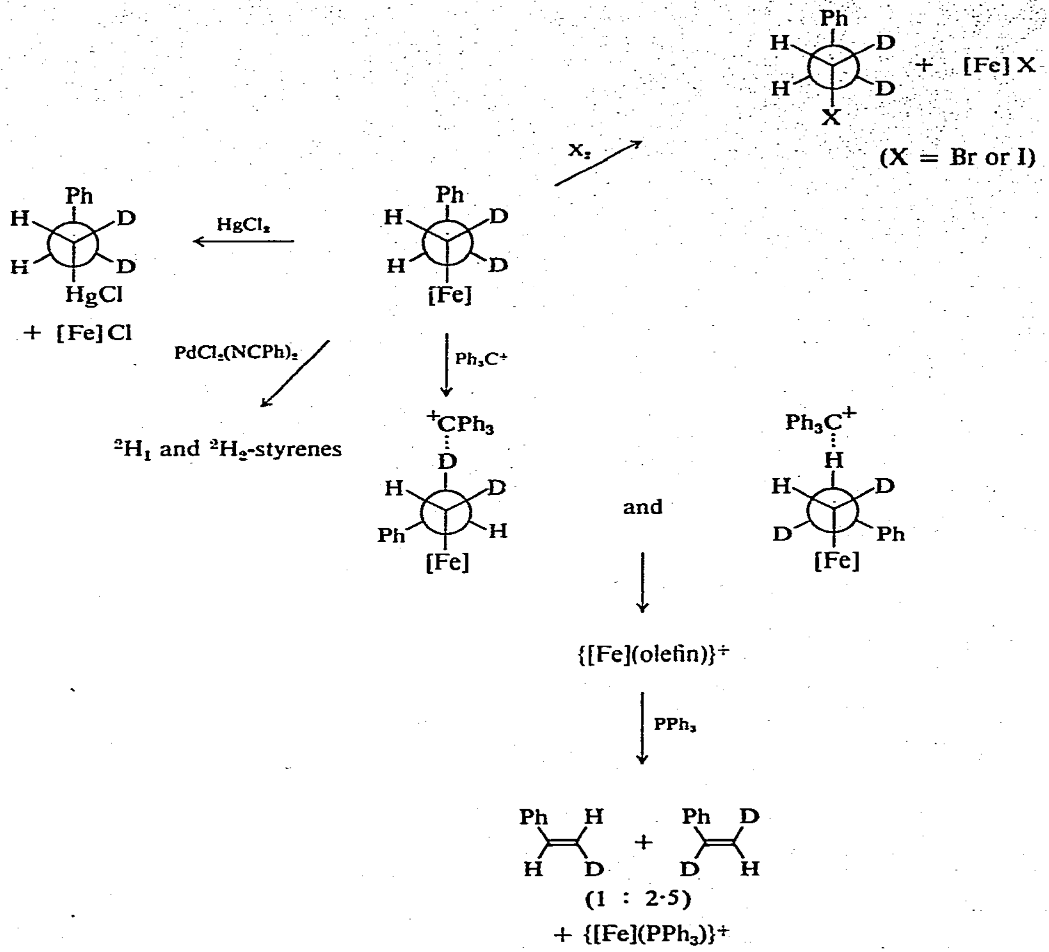
Cleavage of the Fe—C bond of *threo*-PhCHDCHDFe$(CO)_2(\eta^5$-$C_5H_5)$ by Br_2, I_2 or $HgCl_2$ proceeded [380] with retention of the configuration of the alkyl ligand. However, hydride abstraction via Ph_3C^+ occurred mainly via *trans* elimination, whereas reaction with $Pd(NCPh)_2Cl_2$ afforded a phenylethyl-palladium intermediate which eliminated deuteriated styrenes with complete loss of stereospecificity. These reactions are summarised in Scheme 76; the Fe—C cleavage by $HgCl_2$ was thought to occur via an S_E2 (cyclic) process. Reaction of *p*-bromobenzenesulfonate esters of *threo*- and *erythro*-3,3-dimethylbutan-1-ol-1,2-d_2 with salts of $[(\eta^5$-$C_5H_5)Fe(CO)_2]^-$ gave [381] *erythro* or *threo* complexes (Scheme 77). The reactions of the *erythro* complex are illustrated in Scheme 78. Fe—C bond cleavage by Br_2 in pentane, chlorinated hydrocarbons, CS_2 or DMF, and by I_2 in CS_2 resulted in 95% inversion of the configuration at the C atom of the alkylhalide so produced. However, reaction with $HgCl_2$, PPh_3, (t-Bu)NC, Cl_2 in $CHCl_3$, Br_2 in methanol, O_2 or Cl^{4+} afforded 4,4-dimethylpentanoic-2,3-d_2



(*i*) (*ii*) (*iii*)

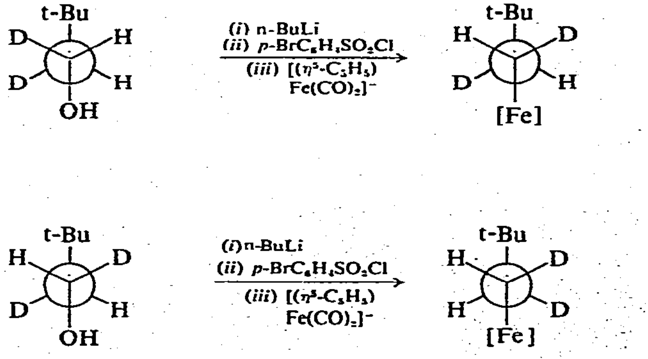
Fig. 11. The rotational conformers of $(\eta^5$-$C_5H_5)Fe(CO)LCH_2R$ (L = PPh_3, $P(OMe)_3$ or $PMePh_2$; R = $SiMe_3$ or Ph).

SCHEME 76



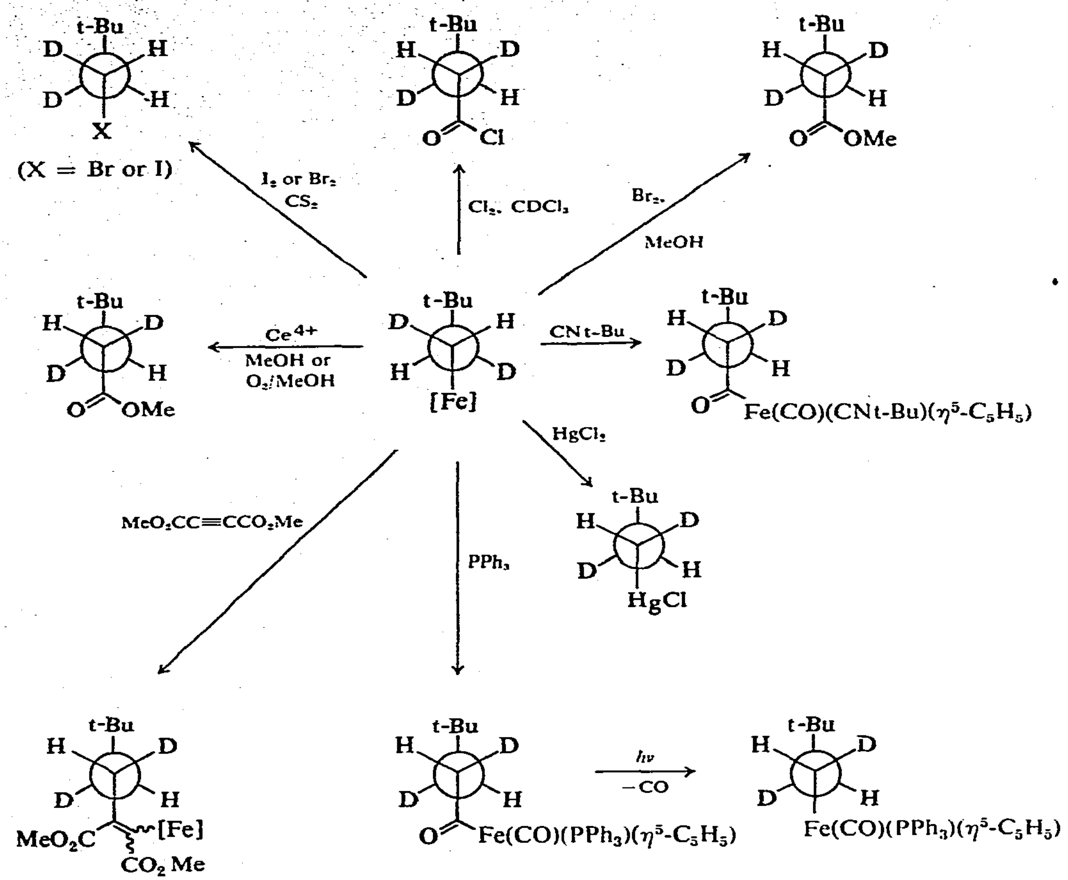
([Fe] ≡ η^5-$C_5H_5Fe(CO)_2$)

SCHEME 77



([Fe] ≡ (η^5-C_5H_5)$Fe(CO)_2$)

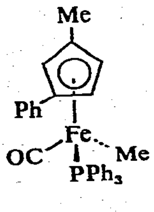
SCHEME 78



([Fe] ≡ (η^5-C_5H_5)Fe(CO)$_2$)

acid with greater than 90% retention of configuration. Reaction with SO_2, giving (η^5-C_5H_5)Fe(CO)$_2$$SO_2$CHDCHD(t-Bu) occurred with greater than 95% inversion, whereas insertion of $MeO_2CC{\equiv}CCO_2Me$ took place with greater than 80% retention of configuration. Thermal decomposition of (η^5-C_5H_5)Fe(CO)$_2$-CHDCHD(t-Bu) gave a range of isotopically substituted derivatives of 3,3-dimethylbut-1-ene.

Reaction of diastereoisomers of (η^5-C_5H_3MePh)Fe(CO)(PPh_3)Me (495) with HI, I_2 or HgI_2 gave [382] (η^5-C_5H_3MePh)Fe(CO)(PPh_3)I and unreacted 495.



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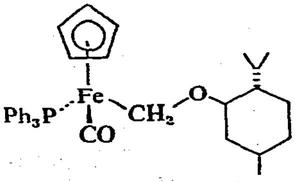

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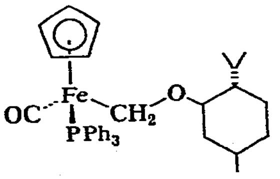

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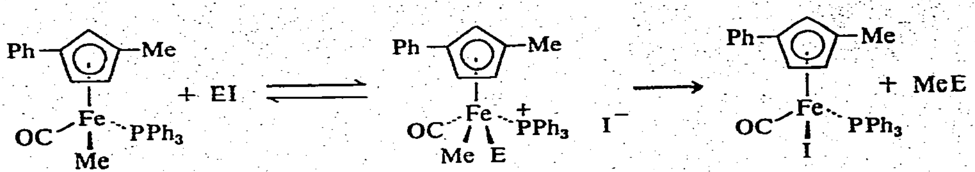


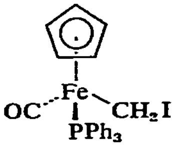
(12)

This recovered species, however, had undergone partial epimerisation and this could be accounted for by the formation of an intermediate as shown in eq. 12. This intermediate, formed by oxidation of EI, is probably fluxional, like $(\eta^5\text{-}C_5H_5)Mo(CO)_2LX$ and its analogs [383], and rapid configurational changes, resulting in epimerisation, could occur.

Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2OMe$ with PPh_3 under UV light gave [384] $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2COMe$. Reaction of this with HCl afforded $(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)(PPh_3)CH_2Cl$ from which the diastereomeric pair (+)- and (—)-$(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)(PPh_3)CH_2OC_{10}H_{19}$ (**496** and **497**) were obtained after treatment with the appropriate enantiomer of sodium mentholate. The absolute stereochemistry of these two complexes was assigned on the basis of their CD spectra by comparison with the CD spectrum of the structurally characterised $[(\eta^5\text{-}C_5H_5)Fe(CO)\text{-}(PPh_3)\{C(=NHCHMePh)Me\}][BF_4]$ [385]. Reaction of **496** with HBF_4 in the presence of *trans*-PhCH=CHMe gave, stereospecifically, **498** (26% e.e), while similar treatment of **497** gave **499** (38.5% e.e.). Reaction of **497** with HI gave the relatively optically pure **500**.

(498)

(499)



(500)

Acyl complexes, CO insertion and decarbonylation reactions

Reaction of **501** with $Fe_2(CO)_9$ in boiling ether gave [386] **502** and **503**, the structure of the former having been confirmed crystallographically. In ether at room temperature, the same reaction afforded **504**, while in benzene **505**, of unknown configuration, was produced. Reaction of **506** with $Fe_2(CO)_9$ in boiling benzene gave **507**. The fact that the cyclohexadiene group in this compound is not complexed indicated that its complexation is not a necessary prerequisite for the opening of the cyclopropyl ring.

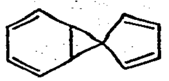
The rates of the reactions 13 and 14 and the overall rate of conversion of the

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2R + DMSO \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)(DMSO)(COR) \qquad (13)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)(DMSO)(COR) + PPh_3 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COR) \qquad (14)$$

$(R = C_6H_{11}$ or $CH_2C_6H_{11})$

alkyl dicarbonyl to the acyl phosphine carbonyl, showed [387] no specific acceleration in DMSO, and no specific correlation with solvent donor properties. The results were in accord with a two step reaction involving the coordinatively unsaturated intermediate $(\eta^5\text{-}C_5H_5)Fe(CO)(COR)$. It was thought that there was



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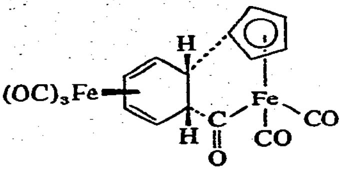

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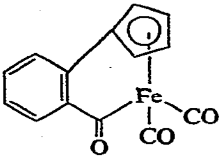

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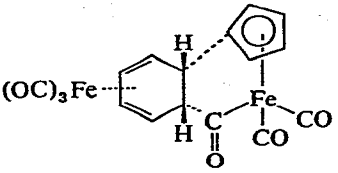

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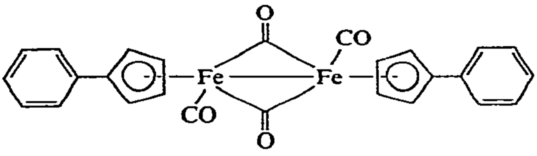

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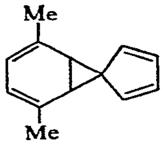

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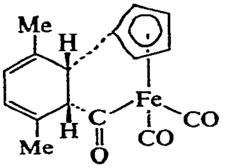
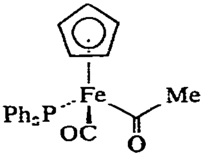


(507)

little charge separation in the transition state for the formation of this intermediate.

Chiral complexes have been used [388] in studying the decarbonylation of (η^5-C_5H_5)Fe(CO)(PPh_3)COEt. Thus, treatment of (+)-*R*-**508** with [Et_3O][BF_4]



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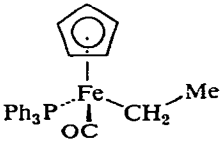

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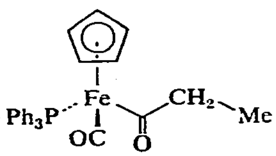

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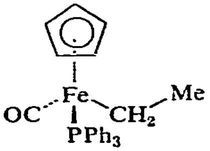
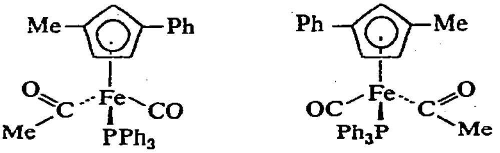


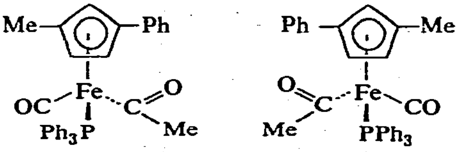
(511)

gave (+)-(*R*)-[(η^5-C_5H_5)Fe(CO)(PPh_3){C(OEt)Me}]$^+$ which, on reduction with $NaBH_4$, afforded (+)-(*R*)-**509**. However, photolysis of (+)-(*R*)-**510** resulted in inversion to give (—)-(*S*)-**511**; **509** and **511** are enantiomeric. Photolysis of (+)-(*R*)-**509** gave initially (—)-(*S*)-(η^5-C_5H_5)Fe(CO)(PPh_3)Me, but continuing exposure to UV light caused racemisation. The high degree of stereoselectivity in the inversion reaction could be explained by migration of the alkyl group into the site vacated by the leaving CO group. Iodination of (+)-(η^5-C_5H_5)Fe(CO)-(PPh_3)COMe gave [389] the racemised (η^5-C_5H_5)Fe(CO)(PPh_3)I, while reaction of (—)-(η^5-C_5H_5)Fe(CO)(PPh_3)$_4$$CO_2C_{10}H_{19}$ ($C_{10}H_{19}$ = menthyl) with I_2 gave [(η^5-C_5H_5)Fe$(CO)_2$(PPh_3)]I and optically inactive (η^5-C_5H_5)Fe(CO)(PPh_3)I. Thermal decomposition of (—)-(η^5-C_5H_5)Fe(CO)(PPh_3)COMe, and photolysis of the (+)-isomer in hexane both gave racemic (η^5-C_5H_5)Fe(CO)(PPh_3)Me, although short irradiation periods resulted in the formation of some (—)-(η^5-C_5H_5)Fe(CO)(PPh_3)Me as found by others. It was concluded that configurational inversion at iron occurred upon decarbonylation. Reaction of $Fe_2(CO)_9$ with 1-methyl-3-phenylcyclopenta-2,4-diene gave [η^5-C_5H_3MePh)Fe$(CO)_2]_2$ from which (η^5-C_5H_3MePh)Fe$(CO)_2$Me was prepared by reaction with Na/Hg in THF followed by addition of methyl iodide [390]. Treatment of this methyl derivative with PPh_3 afforded (η^5-C_5H_3MePh)Fe(CO)(PPh_3)(COMe) as two pairs of diastereomerically related enantiomers, **512a** or **b** and **513a** or **b**. These were separated by chromatography, and on photolysis in benzene underwent decarbonylation



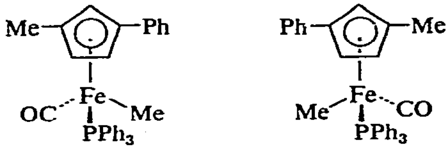
a b

(512)



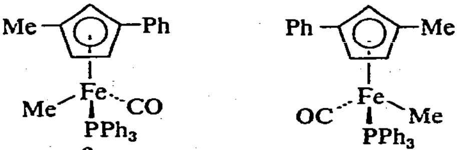
a b

(513)



a b

(514)



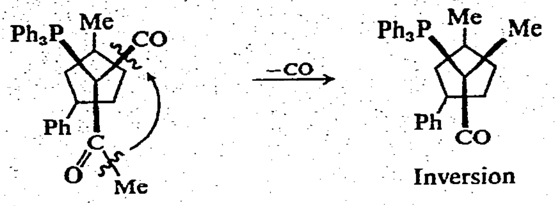
a b

(515)

to give **514a** or **b** and **515a** or **b**. The conversion of **512/513** into **514/515** was highly stereospecific and may have occurred with 100% specificity rather than the 84% actually observed. The decarbonylation and epimerisation reactions were carried out under identical conditions and the sequence of reactions could be represented as:

$$\mathbf{512a/513a} \rightarrow \mathbf{514a/515a} \rightleftharpoons \mathbf{514b/515b} \leftarrow \mathbf{512b/513b}$$

The decarbonylation reaction could proceed in a concerted fashion (eq. 15) with the displaced CO ligand being replaced by the methyl group. This would result in inversion at iron, as preferred by Davison [388] and Brunner [389]. However the Fe—CO bond could break prior to migration of the methyl group, giving (η^5-C_5H_5)Fe(PPh_3)(COMe) (eq. 16), and methyl migration could proceed with either retention or inversion of configuration at iron. While it was not possible to differentiate between the two mechanisms, that depicted in eq. 15, i.e. inversion, was preferred. Other substituted cyclopentadienyl complexes were prepared (Scheme 79), and these included also (η^5-C_5H_5)Fe(CO){PMePh-(β-$C_{10}H_7$)}Me, (η^5-C_5H_5)Fe(CO){(+)-(*S*)-P(CH_2CHPhEt)Ph_2}R (R = Me or COMe) and (η^5-C_5H_5)Fe(CO)(PPh_3)R (R = $COCH_2$CHMePh or CH_2CHMePh). The de-



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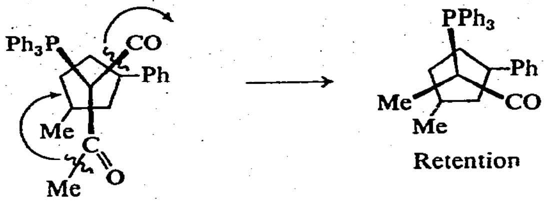
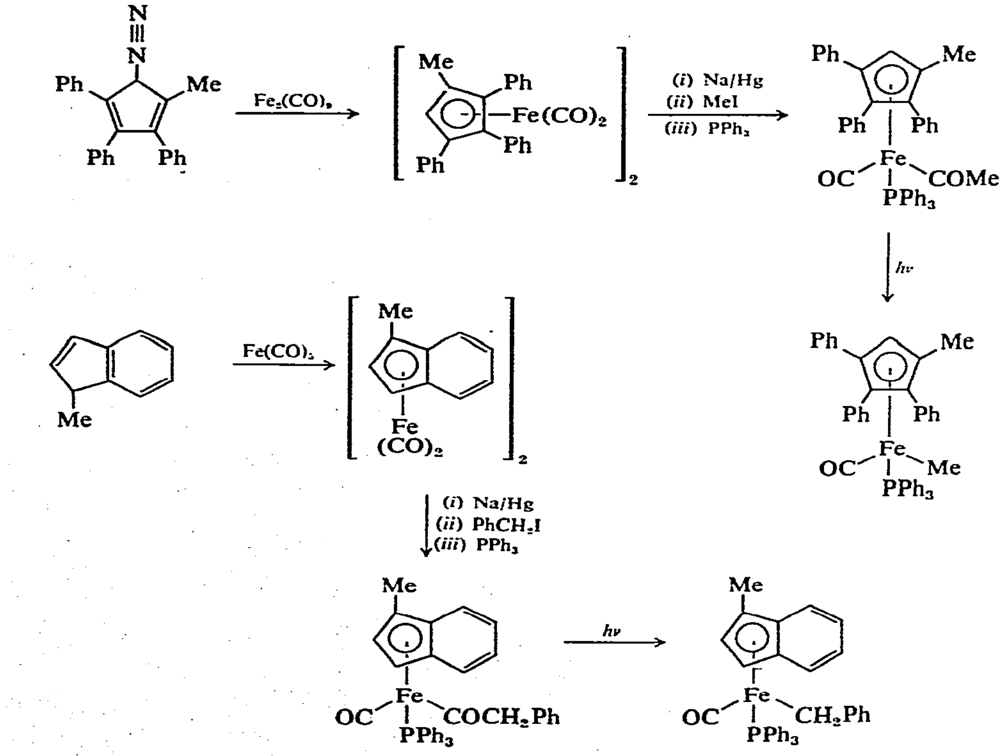


(16)

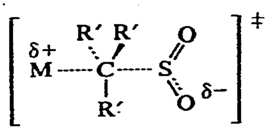
carbonylation of the acyl to the alkyl complexes occurred in a way entirely similar to that of their more simple analogues, and no further mechanistic information could be deduced. Although insertion of SO_2 into the metal—alkyl bond in (η^5-C_5H_5)Fe(CO)(PPh_3)$CH_2CHMePh$ also occurred stereospecifically [391], it was not possible to establish whether this took place with retention or inversion of configuration (see below).

SCHEME 79



Insertion reactions at M—C bonds

The kinetics of insertion of SO_2 into the Fe—C bond in (η^5-dienyl)$Fe(CO)_2R$ [dienyl = C_5H_5, C_5H_4Me, C_5Me_5 or C_9H_7; R = Me, CH_2Ph, CH_2(i-Pr), CH_2(t-Bu), CH_2CH_2(t-Bu), t-Bu, XC_6H_4 (X = H, *p*- or *m*-Me, *p*-MeO)] have been investigated [392] as a function of the dienyl ring, R and solvent. These insertion reactions have a characteristically large and negative $\Delta S^{\neq}$ and the strong dependence of rate upon R indicated that Fe—C bond cleavage was an electrophilic process. It was initially suggested that backside attack of SO_2 on the α-carbon atom of the alkyl group led to heterolysis of the iron—alkyl bond (F) and formation of a contact ion pair. However, studies of the effect of solvent polarity on the rates of this reaction led [393] to the proposal that an associative mechanism operated which incorporated a polar contrained transition state (G). This was thought to rearrange to the contact ion pair {[(η^5-dienyl)$Fe(CO)_2]^+[O_2SCRR'R'']^-$} which afforded ($\eta^5$-dienyl)$Fe(CO)_2OS(=O)CRR'R''$ and/or (η^5-dienyl)$Fe(CO)_2$-$S(=O)_2CRR'R''$, the O-bonded sulfinate being readily isomerised to the S-bonded species. That the proposed contact ion pair must have high configurational stability was established [382] by studying the stereoselectivity of reactions of SO_2 with the diastereoisomers of (η^5-C_5H_3MePh)Fe(CO)(PPh_3)Me. It was not possible with this system to determine whether insertion occurred with retention or inversion of configuration, although earlier studies [394] of SO_2 insertion into (—)-(η^5-C_5H_5)Fe(CO)(PPh_3){$CH_2C(=)OC_{10}H_{19}$} and the work mentioned above, indicated that there was greater than 90% retention of configuration at the iron atom. A radical mechanism could be discounted [392], since a mixture of (η^5-C_5H_5)$Fe(CO)_2CH_2Ph$ and (η^5-C_5H_5)$Mo(CO)_3Me$ in SO_2 gave exclusively (η^5-C_5H_5)$Fe(CO)_2S(=O)CH_2Ph$ and (η^5-C_5H_5)$Mo(CO)_3S(=O)_2Me$. Furthermore, in reactions involving η^5-indenyl complexes, intermediates of the type **516** could be dismissed since insertion of SO_2 into the Fe—benzyl bonds in (η^5-C_9H_7)$Fe(CO)_2CH_2Ph$ and (η^5-C_5H_5)$Fe(CO)_2CH_2Ph$ proceeded at similar rates.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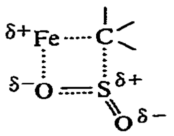
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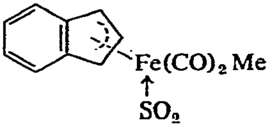
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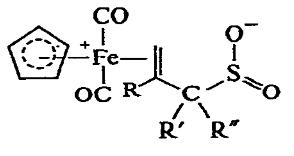
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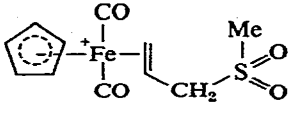
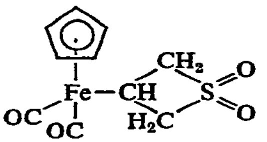

(518)

The rates of cleavage of the M—C bonds in (η^5-C_5H_5)$Cr(NO)_2R$, (η^5-C_5H_5)M-$(CO)_3R$ (M = Mo or W), (η^5-C_5H_5)$M(CO)_2R$ (M = Fe or Ru) and $M(CO)_5R$ (M = Mn or Re) have been investigated [395] in liquid SO_2 at low temperatures. In general, methyl compounds (R = Me) undergo SO_2 insertion more rapidly than their benzyl counterparts (R = CH_2Ph). Iron compounds generally react faster than their ruthenium counterparts and CO insertion reactions apparently follow similar trends. However, when R = CH_2Ph or Ph, SO_2 attack occurs more rapidly with $(\eta^5\text{-}C_5H_5)Cr(NO)_2R$ than with the isoelectronic $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$, possibly because the Cr complex was regarded as being in a lower formal oxidation state than the Fe species. Although $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$ undergoes CO insertion at 25° and 51°C at a rate, in THF, faster than the comparable iron complex, the rate of SO_2 insertion is reversed at -18°C, a probable reflection of differences in the mechanism of reaction.

It has been proposed [396] that in reaction 17, olefinic species, e.g. 517

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2CRR'CR''{=}CH_2 + SO_2 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2S({=}O)_2CRR'CR''{=}CH_2 \tag{17}$$

(R,R′ = H, Me), are formed as intermediates. This suggestion was supported by several observations. Thus, when $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH{=}CH_2$ was dissolved in liquid SO_2 at low temperature and treated rapidly with $MeOSO_2F$ or HCl gas, the cationic propene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CHMe)]^+$ was produced. A similar reaction using $[Me_3O][BF_4]$ afforded the salt 518. Reaction with Ph_3CCl in the presence of NH_4PF_6 resulted in the formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2C{=}CHCH_2S({=}O)CPh_3][PF_6]$. Rapid removal of SO_2 from solutions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CRR'CR''{=}CH_2$ (R′ or R″ = Me) in that solvent, however, afforded only $(\eta^5\text{-}C_5H_5)Fe(CO)_2S({=}O)_2CRR'CR''{=}CH_2$, but similar treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH{=}CH_2$ not only afforded the insertion product (R = R′ = R″ = H), but also afforded the cycloaddition product 519. The latter polymerised after forming relatively soluble dimers or trimers. It was proposed that, in common with SO_2, $(NC)_2C{=}C(CN)_2$, $ClSO_2NCO$ and $(CF_3)_2CO$ probably formed olefinic intermediates during their reactions with σ-allyl complexes of iron. It was also observed that the rate of rearrangement of these iron—olefinic intermediates to insertion or cycloaddition products tended to increase with the increasing extent of alkyl group substitution at the olefin. This is consistent with a weakening of Fe—olefin interaction as substitution increases, thereby rendering the olefin more susceptible to S_N1 or S_N2 displacement. The least substituted Zwitterionic product, viz. 517 (R = R′ = R″ = H) was the slowest to dissociate to give $(\eta^5\text{-}C_5H_5)Fe(CO)_2S({=}O)_2CH_2CH{=}CH_2$ and it was also the only intermediate which rearranged via cycloaddition. This probably occurred because the metal bonds this unsubstituted olefin most strongly thereby activating it best towards nucleophilic attack by sulfinate O or S atoms.



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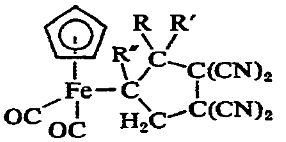

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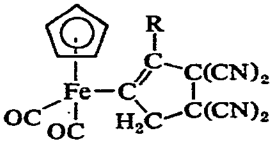
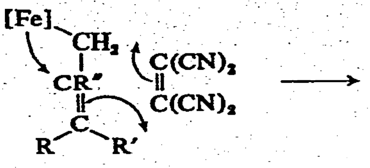


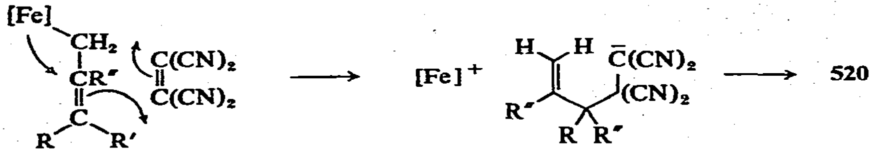
(521)

When $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CR''{=}CRR'$ reacted with $(NC)_2C{=}C(CN)_2$ 3- and 2-cycloaddition occurred [397] with 1,2-metal migration giving 520, the struc-



(18)

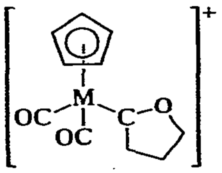
([Fe] ≡ (η^5-C_5H_5)Fe$(CO)_2$)



(19)

([Fe] ≡ (η^5-C_5H_5)Fe$(CO)_2$)

ture of the species with R,R′ = H and R″ = Me being confirmed crystallographically. In related reactions, (η^5-C_5H_5)Fe$(CO)_2CH_2C{=}CR$ (R = Me or Fe$(CO)_2$(η^5-C_5H_5) afforded **521**. Two mechanisms for the formation of **520** were advanced (eq. 18 and 19). The second one was favoured since it was observed that the rate of reaction of (η^5-C_5H_5)Fe$(CO)_2CH_2C{\equiv}CMe$ with $(NC)_2C{=}C(CN)_2$ was accelerated by increasing the polarity of the solvent, thereby lending support to the existence of a Zwitterionic olefinic intermediate analogous to **517**.



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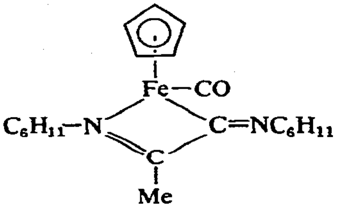

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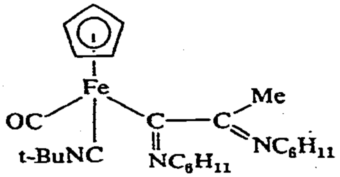

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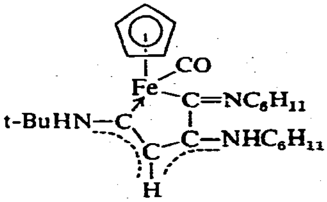

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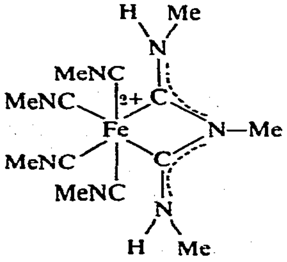


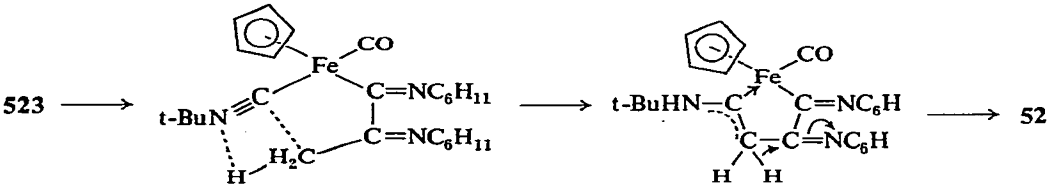
(526)

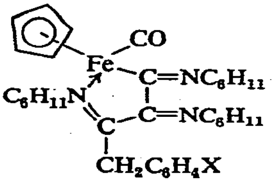
Metal carbene complexes

Reactions of $[(\eta^5\text{-}C_5H_5)M(CO)_2]^-$ (M = Fe or Ru) with $ClCOCH_2CH_2CH_2Cl$ afforded [398] $(\eta^5\text{-}C_5H_5)M(CO)_2C(=O)CH_2CH_2CH_2Cl$. Treatment of this species with $AgPF_6$ gave the 2-oxacyclopentylidene complexes **522**. Addition to this species (M = Fe) of halide ion resulted in the regeneration of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}C(=O)CH_2CH_2CH_2X$; the complexes **522** were regarded as metal-stabilised carbonium ions.

Photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)(CNC_6H_{11})COMe$ or a mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ and CNC_6H_{11} afforded [399] the species **523** which reacted further with t-BuNC to give **524** and then, in boiling benzene, **525**. The structure of **525** was determined crystallographically. It was found that the Fe—C(carbene) and Fe—C(iminoacyl) distances, 1.93 and 1.97 Å, respectively, were significantly shorter than the Fe—C(carbene) bond lengths in **526** [400]. A tentative mechanism is outlined in Scheme 80 which represented an apparent insertion of isonitrile into a C—H bond. These reactions, and the identification of the products, prompted a re-examination of the "triple insertion" product obtained from the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2(p\text{-}XC_6H_4)$ (X = H or Cl) with $C_6H_{11}NC$, which had been described as **527**. This species has now been reformulated as **528** which may be prepared by reacting $(\eta^5\text{-}C_5H_5)Fe(CO)(CNC_6H_{11})\{CH_2(p\text{-}XC_6H_4)\}$ with CNC_6H_{11}. However, photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)(CNC_6H_{11})\text{-}\{CO(p\text{-}ClC_6H_4)\}$ afforded $(\eta^5\text{-}C_5H_5)Fe(CO)(CNC_6H_{11})(p\text{-}ClC_6H_4)$ which reacted with CNC_6H_{11} giving **529**.

SCHEME 80

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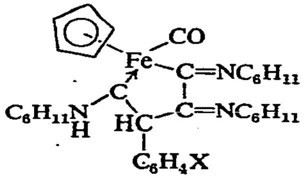
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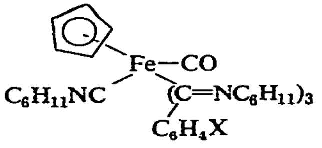
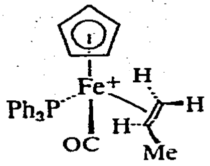

(529)

π-Allyl complexes

At 40°C, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_2CH{=}CH_2)$ underwent [401] a clean first-order associative reaction to give $(\eta^5\text{-}C_5H_5)Fe(CO)(\eta^3\text{-}C_3H_5)$ and PPh_3 at a rate virtually independent of solvent. Protonation of the σ-allyl derivative afforded two diastereoisomers of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(H_2C{=}CHMe)]^+$ (**530** and **531**).

Only one isomer of $(\eta^5\text{-}C_5H_5)M(CO)(\eta^3\text{-}C_3H_4R)$ (M = Fe or Ru) and its indenyl



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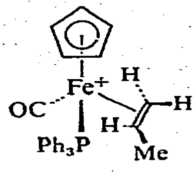

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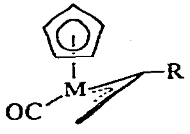

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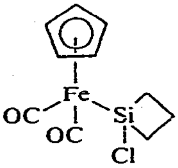


(533)

analog could be detected [402], even after prolonged observations in solution. This species was assigned the configuration **532**.

Complexes containing Group IVB elements

Reaction of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ with $SiRR'R''X$ ($X = Cl$ or Br) afforded [403] $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiRR'R''$ ($R = R' = R'' = Me$; $R = R' = Me$, $R'' = Cl$; $R = R' = Cl$, $R'' = H$ or Me; $R = H$, $R' = Me$, $R'' = Cl$). Treatment of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ with $Cl_2SiCH_2CH_2CH_2$ gave [404] **533**, while reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiHCl_2$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMeHCl$ with carbon tetrachloride produced $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMeCl_2$, respectively. Treatment of $SiR_2(CH{=}CH_2)Cl$ ($R = Me$ or Cl) with $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ gave [405] $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiR_2(CH{=}CH_2)$ which, on reaction with $AgBF_4$ (when $R = Cl$) afforded $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiF_2(CH{=}CH_2)$. Further treatment of this with $AgBF_4$ led to the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiF_3$. Attack by HX ($X = F, Cl, Br, I, O_2CCF_3$ or O_2CCl_3) upon $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiR_2(CH{=}CH_2)$ led to disruption of the vinyl complex and formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ (the species where $X = F$ and O_2CCl_3 are new compounds) and loss of $SiHMe_2(CH{=}CH_2)$. However, treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_2(CH{=}CH_2)$ with HBr and with $HF/BF_3 \cdot OEt_2$ gave, respectively, $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_2CH_2CH_2Br$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiF_3$. Fluorination of other organochlorosilyliron complexes may be achieved by $AgBF_4$, or HPF_6 [406]. Thus the following reactions have been carried out:

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_{3-x}Cl_x + AgBF_4 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_{3-x}F_x$$

($x = 1, 2$ or 3)

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiHMeCl + AgBF_4 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2SiHMeF$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiHCl_2 + AgBF_4 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2SiHF_2$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_3 + AgBF_4 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2SiF_3$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2Si(OMe)_3 + HPF_6 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2SiF_3$$

TABLE 6

REACTIONS OF $(\eta^5\text{-}C_5H_5)Fe(CO)_2MMe_3$ WITH HALOGENS, HX AND CF_3I

M	Reagent	Products
Si, Ge, Sn	Cl_2	$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, Me_3MCl
Si, Ge, Sn	HCl	$(\eta^5\text{-}C_5H_5)Fe(CO)_2H$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, Me_3MCl
Sn	I_2	$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, Me_3SnI
Si, Ge, Sn	ICl	$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, Me_3MCl, Me_3MI (M = Ge or Sn)
Si	CF_3I	$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, Me_3SiF
Ge, Sn	CF_3I	$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CF_3$, Me_3MI, Me_3MF

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnCl_3$ with AgF afforded $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnF_3$.

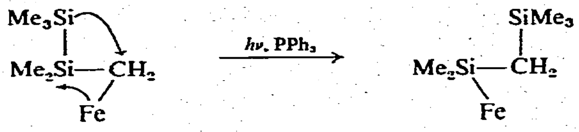
Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiF_3$ with $Me_3P{=}C(SiMe_3)_2$ afforded [407] $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$ and $Me_3P{=}C(SiF_3)(SiMe_3)$, while a mixture of $(\eta^5\text{-}C_5H_5)$-$Fe(CO)_2SiMe_2F$ with $Me_3P{=}CH_2$ led to the formation of $Me_3P{=}CH(SiMe_2F)$ and possibly $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$.

In benzene or pure amine, $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_3$ reacted [408] with NHRR' (R = H, R' = alkyl or Ph; R = R' = alkyl) to give $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_{3-x}(NRR')_c$ (x = 1, 2 or 3). The value of x depended on the basicity and steric requirements of the amine.

The reactions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2MMe_3$(M = Si, Ge or Sn) with halogens, HX and CF_3I [409] are summarised in Table 6. The species $(\eta^5\text{-}C_5H_5)Fe(CO)L$-$(SnPh_3)$ (L = CO, PEt_3, PPh_3 or $P(OPh)_3$) reacted with HCl or HBr giving $(\eta^5\text{-}C_5H_5)Fe(CO)L(SnPh_2X)$. In general, it was found that HCl or HBr reacted with organotiniron complexes causing partial or complete cleavage of the organo groups on the tin atom, but that all other reactions resulted in fission of the Sn—Fe bond.

Reaction of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ with methylated di-, tri-, or tetra-silyl halides has afforded [410] a variety of polysilyliron compounds. Thus, treatment of the carbonylate ion with Si_2Me_5X (X = Cl or Br), Si_3Me_7Cl, Si_4Me_9Cl and $Si(SiMe_2Cl)_4$ gave, respectively, $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_nMe_{2n+1}$ (n = 2, 3 or 4) and $\{(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2\}_4Si$. Reaction with $Si_2Me_4X_2$ (X = Cl or Br) led to the formation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_2Me_4X$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2SiMe_2Fe(CO)_2$-$(\eta^5\text{-}C_5H_5)$; treatment of the monohalide with $AgBF_4$ afforded the corresponding fluoride. Reaction $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_2Me_4Cl$ with $Me_3P{=}CHSiMe_3$ and with $Me_2S({=}O){=}CH_2$ afforded $[Me_3PCH_2SiMe_3][Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ and $(\eta^5\text{-}C_5H_5)Fe$-$(CO)_2SiMe_2SiMe_2CH{=}S({=}O)Me_2$, respectively.

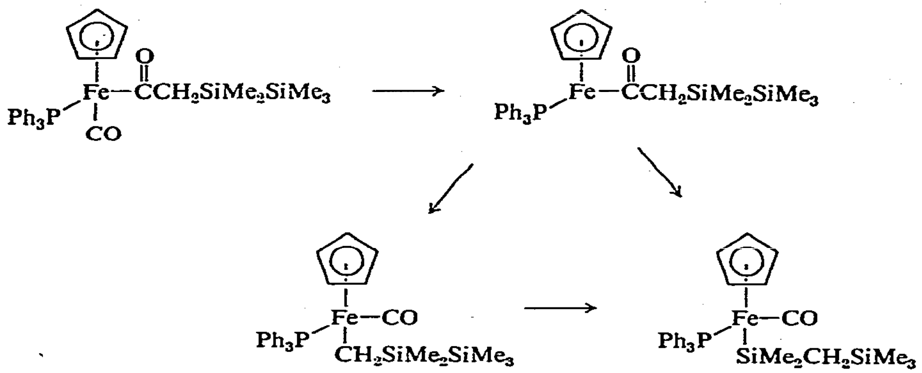
Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2SiMe_2SiMe_3$ with PPh_3 and with SO_2 gave [411] the expected "insertion" products, viz. $(\eta^6\text{-}C_5H_5)Fe(CO)(PPh_3)C({=}O)$-$CH_2Si_2Me_5$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2S({=}O)_2CH_2Si_2Me_5$. However, photolysis of the pentamethyldisilylmethyl complex in the presence and absence of PPh_3 gave $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)SiMe_2CH_2SiMe_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2CH_2SiMe_3$; the latter could be converted into the former photolytically in the presence of PPh_3. These rearrangements appeared to be related to the thermal reorganisation of pentamethyldisilylmethylacetate and may be represented as in eq. 20. Thermal decarbonylation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2SiMe_2SiMe_3$ afforded two products: that which was kinetically controlled, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2Si_2Me$, and that which was thermodynamically controlled, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)SiMe_2$-



(20)

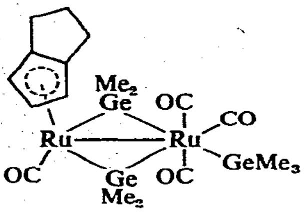
CH_2SiMe_3. The latter was presumably formed via the unstable (η^5-C_5H_5)Fe(CO)-(PPh_3)$CH_2Si_2Me_5$ (Scheme 81). It seemed clear that replacement of CO by PPh_3 increased the tendency of the disilylmethyl group to rearrange, possibly due to an increase of electron density on the metal atom and to the greater ability of silicon to accept this surplus charge.

SCHEME 81



The relative strengths of Fe—C and Fe—Si bonds in a series of complexes containing (η^5-C_5H_5)Fe$(CO)_2$ have been investigated [412]. Thus, reaction of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$ with $ClCH_2SiMe_{3-n}Cl_n$ afforded, under carefully controlled conditions, (η^5-C_5H_5)Fe$(CO)_2SiMe_{2-n}(CH_2Cl)Cl_n$ ($n = 0$, 1 or 2). At 100°C, the species where $n = 0$ or 1 rearranged to (η^5-C_5H_5)Fe$(CO)_2CH_2SiMe_{2-x}Cl_{n+1}$ ($n = 0$ or 1) but when $n = 2$, this reorganisation took place only when catalysed by $AlCl_3$ in dichloromethane and even then only in low yield. The rearrangements when $n = 0$ or 1 were in direct contradiction to intuitive predictions and to expectations based on reported M—C and M—Si bond energies [413]. It was estimated that in (η^5-C_5H_5)Fe$(CO)_2SiMe_2(CH_2Cl)$, the Fe—Si bond could be no more than 9—11 kcal mol^{-1} stronger than the Fe—C bond in (η^5-C_5H_5)Fe$(CO)_2$-CH_2SiMe_2Cl. From a study of the rearrangement of the analogous bromide, it was estimated that the Fe—Si bond was no more than 5—7 kcal mol^{-1} stronger than the Fe—C bond. Hence, it is possible that the Fe—Si bond could, in some situations, be weaker than the Fe—C bond.

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ with $GePh_nCl_{4-n}$ ($n = 1$ or 2) gave [414] (η^5-C_5H_5)Fe$(CO)_2FePh_{3-n}Cl_n$ ($n = 1$ or 2). With $GePhCl_3$, however, a mixture of (η^5-C_5H_5)Fe$(CO)_2GePhCl_2$, $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2GePhCl$ and (η^5-C_5H_5)Fe$(CO)_2Cl$ was formed. Photolysis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in the presence of $GeHCl_3$ or of $SiHPh_{3-n}X_n$ ($n = 1$ or 2; X = Cl or C_6F_5) afforded (η^5-C_5H_5)Fe$(CO)_2GeCl_3$ or (η^5-C_5H_5)Fe$(CO)_2SiPh_{3-n}X_n$. Treatment of (η^5-C_5H_5)Fe$(CO)_2MPh_{3-n}X_n$ (X = Cl or Br; $n = 1$, 2 or 3; M = Sn but $n = 3$ for Si or Ge) with LiC_6F_5 led to the formation of (η^5-C_5H_5)Fe$(CO)_2MPh_{3-n}(C_6F_5)_n$.



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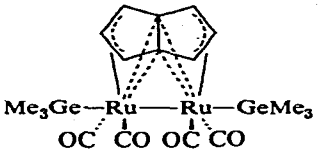

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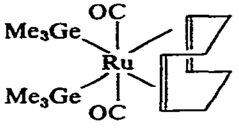

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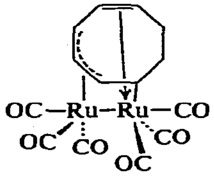

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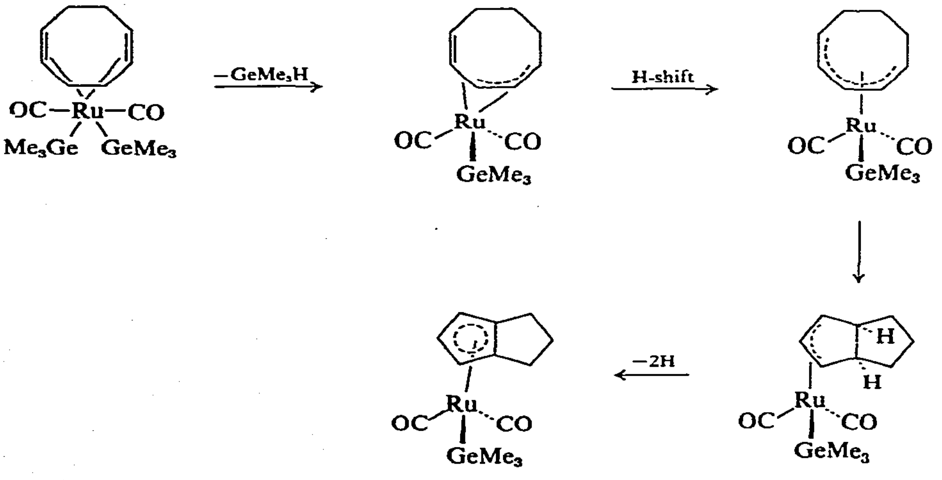
Trans-cyclododeca-1,5,9-triene reacted [415] with *cis*-$Ru(CO)_4(GeMe_3)_2$ or $[Ru(CO)_4GeMe_3]_2$ giving **290** (germyl analog) **534** and **535**. The first two could also be produced as minor by-products of the reaction between cycloocta-1,5-diene and $Ru(CO)_4(GeMe_3)_2$, the major product being $Ru(CO)_2(C_8H_{12})(GeMe_3)_2$ (**536**). $Ru(CO)_4(SiMe_3)_2$ reacted with cyclododecatriene giving **290** and **537**. A solvent was necessary for these reactions, since in its absence species not containing Ge or Si are also formed [416], viz. $Ru_2(CO)_6(C_8H_{10})$, $Ru(CO)_3$-(C_8H_{12}) and $Ru_4(CO)_{12}(C_8H_{10})$. When **536** was heated, **290** (germyl analog) and **534** were produced together with $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$, indicating that **536** is a possible precursor in the formation of **290** (germyl analog) and **534** from cyclododecatriene. A mechanism for the ring contraction of the cyclooctadiene complex is outlined in Scheme 82.

Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ with $SnCl_2$ in refluxing methanol/THF mixtures afforded [417] $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnMe_2Cl$ and only traces of $(\eta^5$-

SCHEME 82

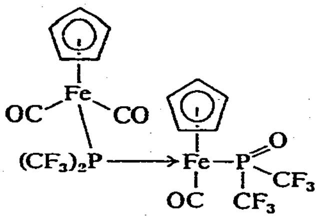


$C_5H_5)Fe(CO)_2SnCl_3$. A similar reaction with $(\eta^5\text{-}C_5H_5)Fe(CO)_2Et$, however, afforded $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnCl_3$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ and only traces of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnEtCl_2$. With $SnBr_2$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnBr_3$ were formed. Attack of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ on $Sn(CH_2I)Me_3$ afforded [418] a mixture of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnMe_3$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$, while treatment of the latter with $Sn\{N(SiMe_3)_2\}_2$ gave [419] $(\eta^5\text{-}C_5H_5)Fe(CO)_2Sn\{N(SiMe_3)_2Me\}$.

Complexes containing Group VB donor atoms

Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ with an excess of X_2 (X = Cl, Br or I) led [420] to the quantitative formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(CF_3)_2X\}]X_3$, but when X = Cl or Br, decomposition afforded $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ and $P(CF_3)_2X$. With iodine monochloride, the phosphide complex gave $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(CF_3)_2Cl\}]Cl_3$. Protonation of the phosphido species afforded $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(CF_3)_2H\}]^+$, while similar treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(=E)(CF_3)_2\}$ led to the formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(EH)(CF_3)_2\}]^+$ (E = O, S or Se). An X-ray crystallographic examination led to the observation [421] that, on oxidation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ to $(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(=O)(CF_3)_2\}$, the Fe—P distance decreased from 2.27 to 2.19 Å while the Fe—CO bond lengths increase was relatively insignificant (ca. 0.01 Å).

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with $\{(CF_3)_2P\}_2O$ gave [422] 538 as the major product, together with $(\eta^5\text{-}C_5H_5)Fe(CO)_2P(CF_3)_2$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(=O)(CF_3)_2\}$; 538 could not be obtained from mixtures of the latter two.



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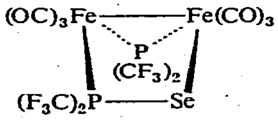

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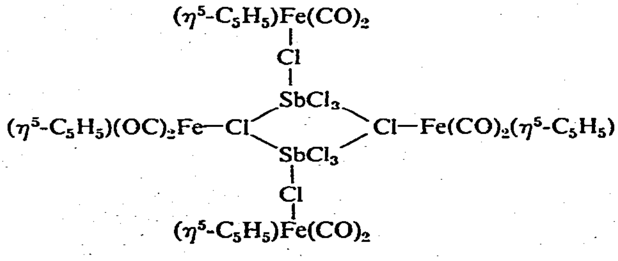

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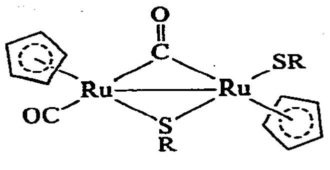
Reaction of the dicarbonyl dimer with $\{(CF_3)_2P\}_2E$ (E = S or Se) led only to analogs of the latter two species. Treatment of $Fe(CO)_2(NO)_2$ with $\{(CF_3)_2P\}_2E$ (E = O, S or Se) afforded $Fe(CO)(NO)_2\{(CF_3)_2PEP(CF_3)_2\}$ and $Fe(CO)_4\{(CF_3)_2PEP(CF_3)_2\}$ (X = O or S only), while $Fe_2(CO)_9$ reacted with the selenophosphine giving 539.

Reaction of Na[Fe(CO)$_2$(η^5-C$_5$H$_5$)] or (η^5-C$_5$H$_5$)Fe(CO)$_2$SiMe$_3$ with AsMe$_2$Cl gave [423] (η^5-C$_5$H$_5$)Fe(CO)$_2$AsMe$_2$, and apparently quaternisation of the arsenic led to the formation of [(η^5-C$_5$H$_5$)Fe(CO)$_2$(AsMe$_2$R)]$^+$X$^-$.

Treatment of Na[Fe(CO)$_2$(η^5-C$_5$H$_5$)] with SbMe$_2$Br gave [424] (η^5-C$_5$H$_5$)Fe(CO)$_2$SbMe$_2$, which reacted with (η^5-C$_5$H$_5$)Fe(CO)$_2$Br affording [425] {[(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_2$SbMe$_2$}Br. Exchange of bromide by [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$^-$ occurred when [(η^5-C$_5$H$_5$)Fe(CO)$_2$SbMe$_3$]$^+$Br was treated with Na[Fe(CO)$_2$(η^5-C$_5$H$_5$)]. In THF, Sb(CH$_2$CH=CH$_2$)RR′ (R = allyl, R′ = Me or Ph; R = R′ = Me, Ph or allyl) reacted with (η^5-C$_5$H$_5$)Fe(CO)$_2$Cl giving [426] [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_2$SbRR′]$^+$. From ^{57}Fe and ^{121}Sb Mössbauer spectral studies it was established [427] that in the compounds [{(η^5-C$_5$H$_5$)Fe(CO)$_2$}$_n$SbR$_{4-n}$]$^+$ (R = Cl, Br, I, CF$_3$, Ph, n-Bu; n = 1, 2 or 3) Fe—Sb π-bonding was more significant than Fe—Sn π-bonding in comparable systems. From a crystallographic study, it was established that [(η^5-C$_5$H$_5$)Fe(CO)$_2$]$_4$Sb$_2$Cl$_{10}$ (540) consisted of two SbCl$_3$ groups and two (η^5-C$_5$H$_5$)Fe(CO)$_2$Cl units linked about a centre of symmetry by weak Sb····Cl bridges. In the SbCl$_3$ fragments, the distorted octahedron about the antimony atom is completed by interactions from Cl atoms associated with three surrounding (η^5-C$_5$H$_5$)Fe(CO)$_2$Cl groups, as shown.

Compounds containing sulfur

Photolysis of (η^5-C$_5$H$_5$)Ru(CO)$_2$SC$_6$F$_5$ gave [429] 541 and 542, while treatment of (η^5-C$_5$H$_5$)Ru(CO)$_2$Cl with [Et$_3$NH][SMe] gave (η^5-C$_5$H$_5$)Ru(CO)$_2$SMe. On heating the methyl mercaptide derivative this afforded [(η^5-C$_5$H$_5$)Ru(CO)SMe]$_2$ as *syn* and *anti* isomers (with respect to the conformation of the SMe groups) analogous to [(η^5-C$_5$H$_5$)Fe(CO)SMe]$_2$. Photolysis of (η^5-C$_5$H$_5$)Ru(CO)$_2$SMe gave only traces of [(η^5-C$_5$H$_5$)Ru(CO)SMe]$_2$ but mainly 543.



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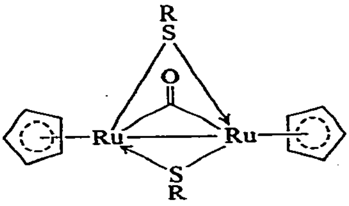

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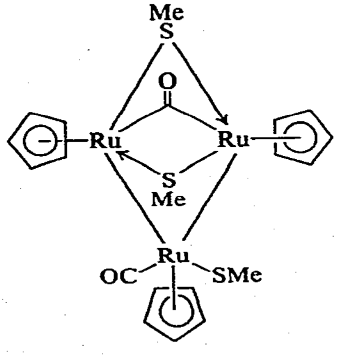

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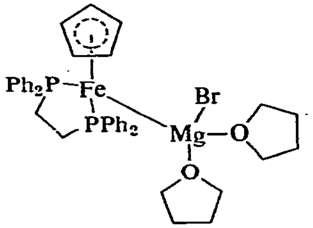


(544)

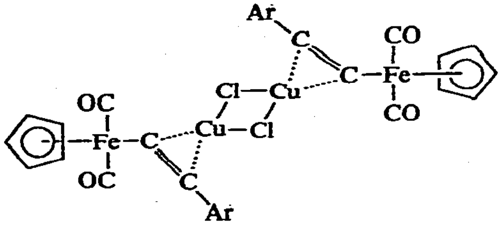
The structure of $(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2C_6F_5$ has been determined crystallographically [430], and the species is an *S*-sulphinato derivative.

Complexes containing magnesium, thallium or copper

Reaction of $(\eta^5\text{-}C_5H_5)Fe(diphos)Br$ (diphos = $Ph_2PCH_2CH_2PPh_2$) with $BrCH_2CH_2Br$ and magnesium in dry THF led [431] to the formation of $(\eta^5\text{-}C_5H_5)Fe(diphos)MgBr \cdot 3THF$ (544). The structure of this "inorganic Grignard reagent" was determined crystallographically, the Fe—Mg distance (2.59 Å) indicating strong covalent character in this bond.

Reaction of a thallium(I) salt with $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$, $[Fe(CO)_4R]^-$ (R = CH_2CN, COPh or $SnPh_3$) or $[Fe(CO)_3(NO)]^-$ gave [432] the species $Tl\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_3$, $Tl\{Fe(CO)_4R\}$ or $Tl\{Fe(CO)_3(NO)\}$. From the preparative details and the behaviour of these thallium compounds, it was suggested that weakly basic iron carbonylate ions reacted with Tl^+ giving predominantly ionic and stable salts with only weak Tl—Fe covalency. However, strongly basic carbonylate ions reacted with Tl^+ giving, initially, thallium(I) species which then readily disproportionated to thallium(III) compounds and Tl metal.

Treatment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl or Br) with CuC_2R (R = Ph, $p\text{-}MeC_6H_4$, $p\text{-}FC_6H_4$ or C_6H_5) gave [433] $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_2R)CuX]_2$ (545) whose structure has been confirmed crystallographically [434]. Reaction of this species with $Fe_2(CO)_9$ led to the formation of $(\eta^5\text{-}C_5H_5)Fe_3(C_2R)(CO)_7$, possibly 546a or b. The iron acetylides $(\eta^5\text{-}C_6H_5)Fe(CO)_2C{\equiv}CR$ (R = Me or Ph) were obtained



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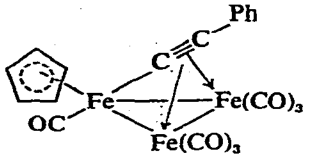

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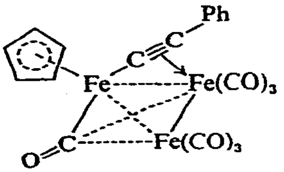

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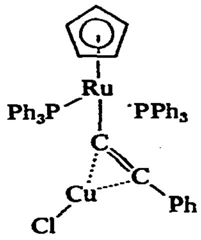

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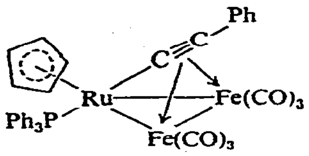

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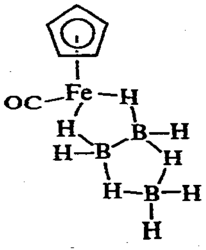


(549)

by reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ with RC_2MgX; the phenyl derivative reacted with aqueous HCl giving $(\eta^5\text{-}C_5H_5)Fe(CO)_2COCH_2Ph$. The complex $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(C_2Ph)CuCl$ (547) was obtained [435] from $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ and CuC_2Ph, and on treatment with $Fe_2(CO)_9$; the former afforded 548.

Compounds containing boron, boron hydrides or carboranes

The structure of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CNBPh_3$ was determined crystallographically [436], and it was shown that the Fe—C—N—B system was essentially linear.

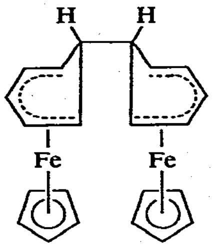
In dichloromethane under UV light, $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ reacted with $[Me_4N][B_3H_8]$ giving [437] the stereochemically rigid complex $(\eta^5\text{-}C_5H_5)Fe(CO)B_3H_8$ (549).

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_{10})]^+$ (C_6H_{10} = cyclohexene) with $[1,2\text{-}GeCHB_{10}H_{10}]^-$ gave [438] $(\eta^5\text{-}C_5H_5)Fe(CO)_2GeCHB_{10}H_{10}$. The analogous complexes containing $[7,8\text{-}PCHB_9H_{10}]^-$, $[7,8\text{-}As_2B_9H_{10}]^-$, $[PB_{10}H_{12}]^-$ and $[AsB_{10}H_{12}]^-$ were prepared similarly. It was proposed that in each species, the iron was bound to the boron cage via the heteroatom.

Arene complexes

Complexes containing aromatic hydrocarbons

The paramagnetic species $(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)$ exhibited [439] polarographically a reversible anodic wave corresponding to the formation of $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]^+$, and an irreversible cathodic wave. The neutral species dimerised [440] in 75% yield after 15 h in pentane to give 550. Oxidation of this species with oxygen, *N*-bromosuccinimide or iodine afforded the known $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]^+$. Reaction of ferrocene with a selection of bi-, tri- and tetra-cyclic arenes in the presence of aluminium and $AlCl_3$ gave [441] a series of dicationic arene complexes (551—564); 559 was not fluxional.



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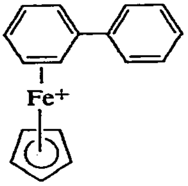

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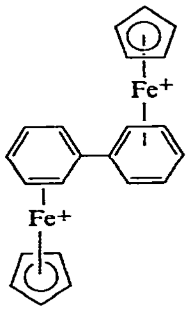

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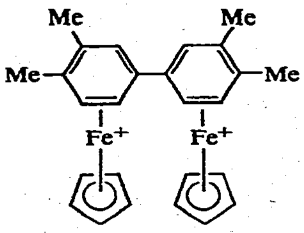

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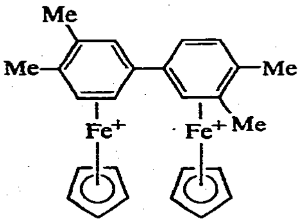

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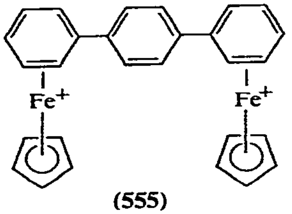

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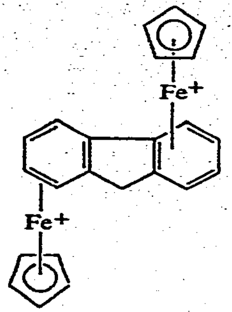
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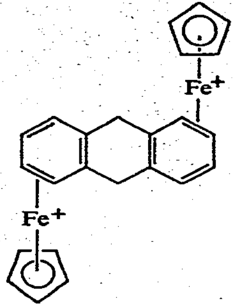
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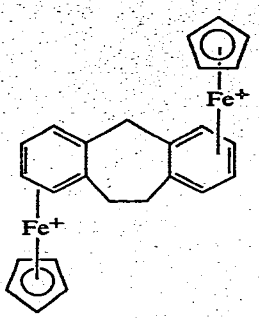
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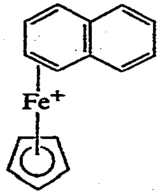
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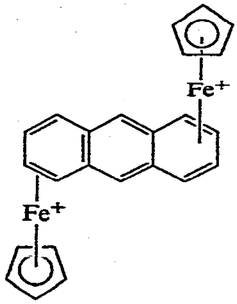
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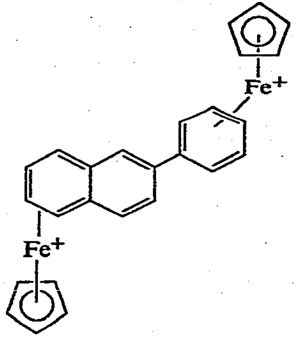
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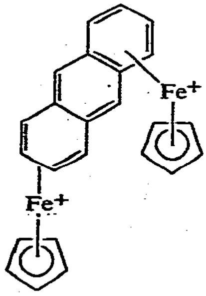
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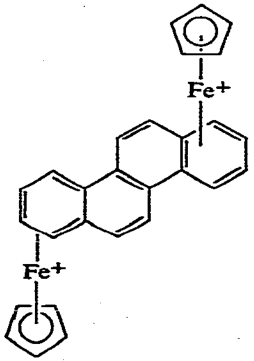
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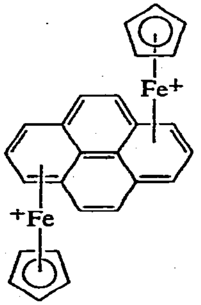
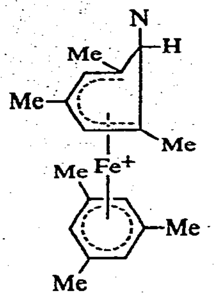
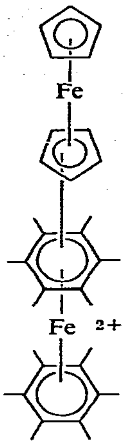

(564)

Attack by CN^-, $(CH_2NO_2)^-$, $[CHMe(NO)_2]^-$ or $[CH_2CO_2(t\text{-}Bu)]^-$ upon $[(\eta^6\text{-}C_6H_3Me_3)_2Fe]^{2+}$ afforded [442] the arene—cyclohexadienyl cations 565 (R = anionic nucleophile). Oxidation of this species with Ce^{4+} caused liberation of mesitylene and substituted mesitylene. However, treatment of the arene dication with NH_2^-, NMe_2^-, $[N(SiMe_3)_2]^-$, OMe^- or $[O(t\text{-}Bu)]^-$ led to proton abstraction and the sequence of reactions shown in Scheme 83. In D_2O, $[(\eta^6\text{-}C_6Me_6)_2\text{-}Fe]Br_2$ underwent rapid H/D exchange catalysed by triethylenediamine. This indicated α-proton abstraction at the methyl groups, a reaction which hexamethylbenzene would not undergo in the absence of the metal.

Electron-rich aromatic molecules formed [443] highly coloured charge-transfer compounds with $[(\eta^6\text{-arene})_2Fe]^{2+}$ (arene = C_6Me_6 or durene). Adducts were also formed with ferrocene, e.g. 566, and the charge-transfer complex forma-



(565) (N = nucleophilic agent)

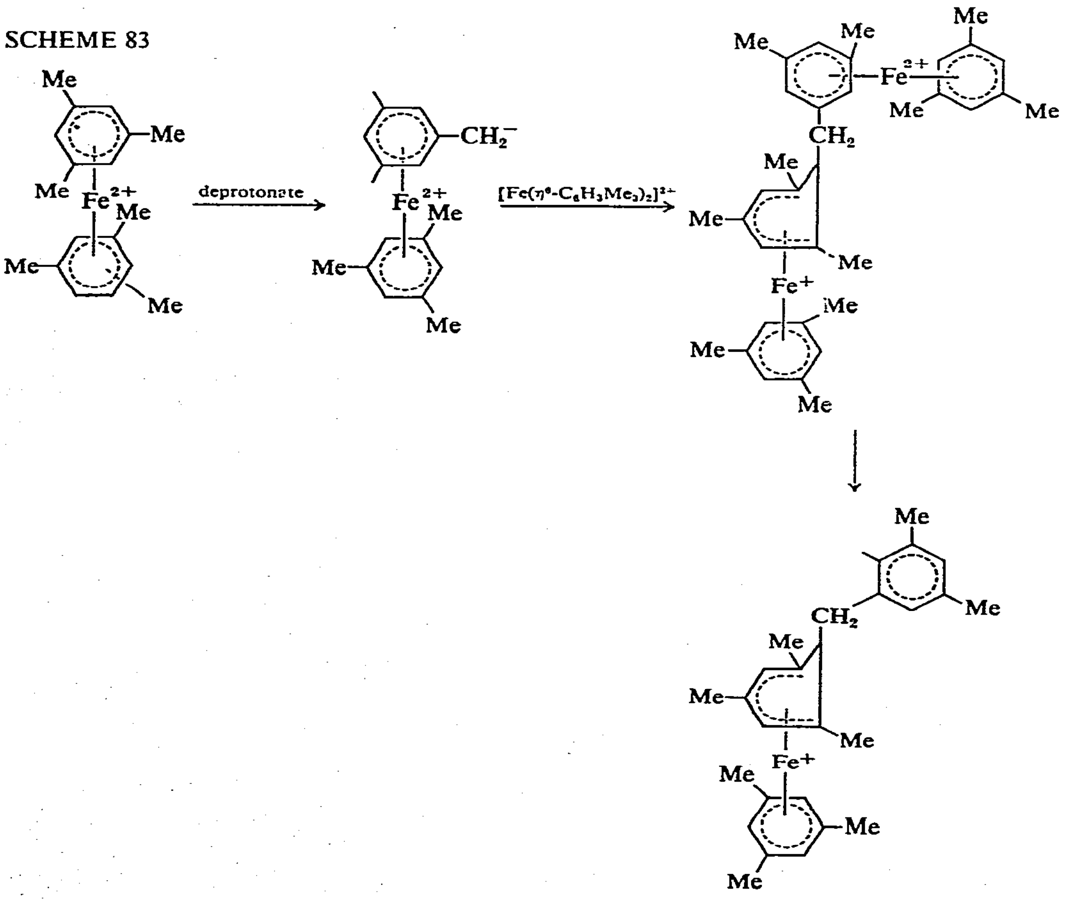


(566)

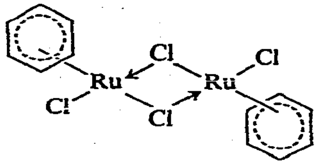
tion could be used to separate phenanthrene from anthracene and *N*-dimethylaniline from 1,3-dimethylaniline.

Suitable cyclohexa-1,3- or 1,4-dienes reacted [444] with $RuCl_3$ in ethanol

SCHEME 83



giving $[(\eta^6\text{-arene})RuCl_2]_2$ (567). Treatment of this with tertiary phosphines, arsines or pyridine (L) afforded $(\eta^6\text{-arene})RuCl_2L$, and treatment of this with LiMe, MeMgX, $HgMe_2$ or $SnMe_4$ gave $(\eta^6\text{-arene})RuClMeL$ and $(\eta^6\text{-arene})RuMe_2L$; analogous bromides and iodides were also prepared. In hot water containing PF_6, 567 afforded $[(\eta^6\text{-arene})_2Ru_2Cl_3][PF_6]$ (568) but when treated with Ag^+ in acetonitrile gave $[(\eta^6\text{-arene})Ru(NCMe)_3]^{2+}$. The complexes $(\eta^6\text{-arene})RuCl_2L$ ($L = P(n\text{-}Bu)_3$ or PPh_3) underwent partial or complete arene group exchange on heating or UV irradiation in an aromatic solvent, providing that this did not contain electron-withdrawing substituents in the ring.



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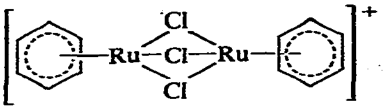

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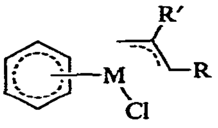

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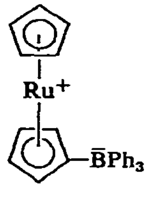

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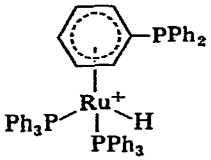

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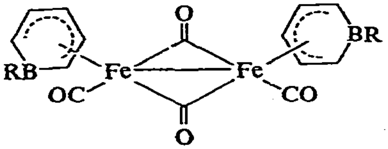

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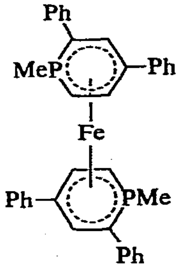

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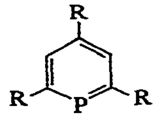


(573)

Reaction of $[(\eta^6\text{-}C_6H_6)MCl_2]_2$ (M = Ru or Os) with $Hg(CH_2CR'{=}CHR)Cl$ afforded [445] the species $(\eta^6\text{-}C_6H_6)M(\eta^3\text{-}CH_2CR'CHR)Cl$ (569; R = H, Me, Ph, COMe; R′ = H, Me or Ph).

Treatment of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ with $NaBPh_4$ in methanol afforded [446] $(\eta^5\text{-}C_5H_5)Ru(\eta^6\text{-}C_6H_5BPh_3)$ (570) the structure of which was confirmed crystallographically. The species $[Ru(PPh_3)_3H]^+$ (571), obtained either by treatment of $Ru(PPh_3)_3H(OAc)$ with HBF_4 in methanol [447], or by dissociation of phosphine from $[Ru(PPh_3)_4H]^+$ in solution [448], has been examined [449] crystallographically. The Ru—H distance may be ca. 1.7 Å, and, as might be expected, the species is catalytically inactive towards the hydrogenation of alkenes.

Complexes containing heterocyclic aromatics

Reaction of $(C_5H_5BR)_2Co$ (R = Ph or Me) with $Fe(CO)_5$ or $Fe_2(CO)_9$ readily afforded [450] $[(C_5H_5BR)Fe(CO)_2]_2$ (572) which, on thermolysis, afforded $(C_5H_5BR)_2Fe$. The crystal and molecular structure of $[(C_5Me_5BMe)Fe(CO)_2]_2$ (572, R = Me) has been determined [451]. The Fe—Fe distance, 2.57 Å, was only slightly longer than that in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.

Treatment of 573 with LiR′ afforded [452] $(C_5H_2R_3PR')^-$ (R = Ph, R′ = Me or Ph) which reacted with $FeCl_2$ giving 574.

Organic reactions catalysed or promoted by iron or ruthenium complexes

Hydrogenation

Under CO pressure $[Fe(CO)_4H]^-$ catalysed [453] the hydrogenation of the C=C double bond in methylvinylketone, methylacrylate, ethylmethacrylate, methylcrotonate and acrylonitrile.

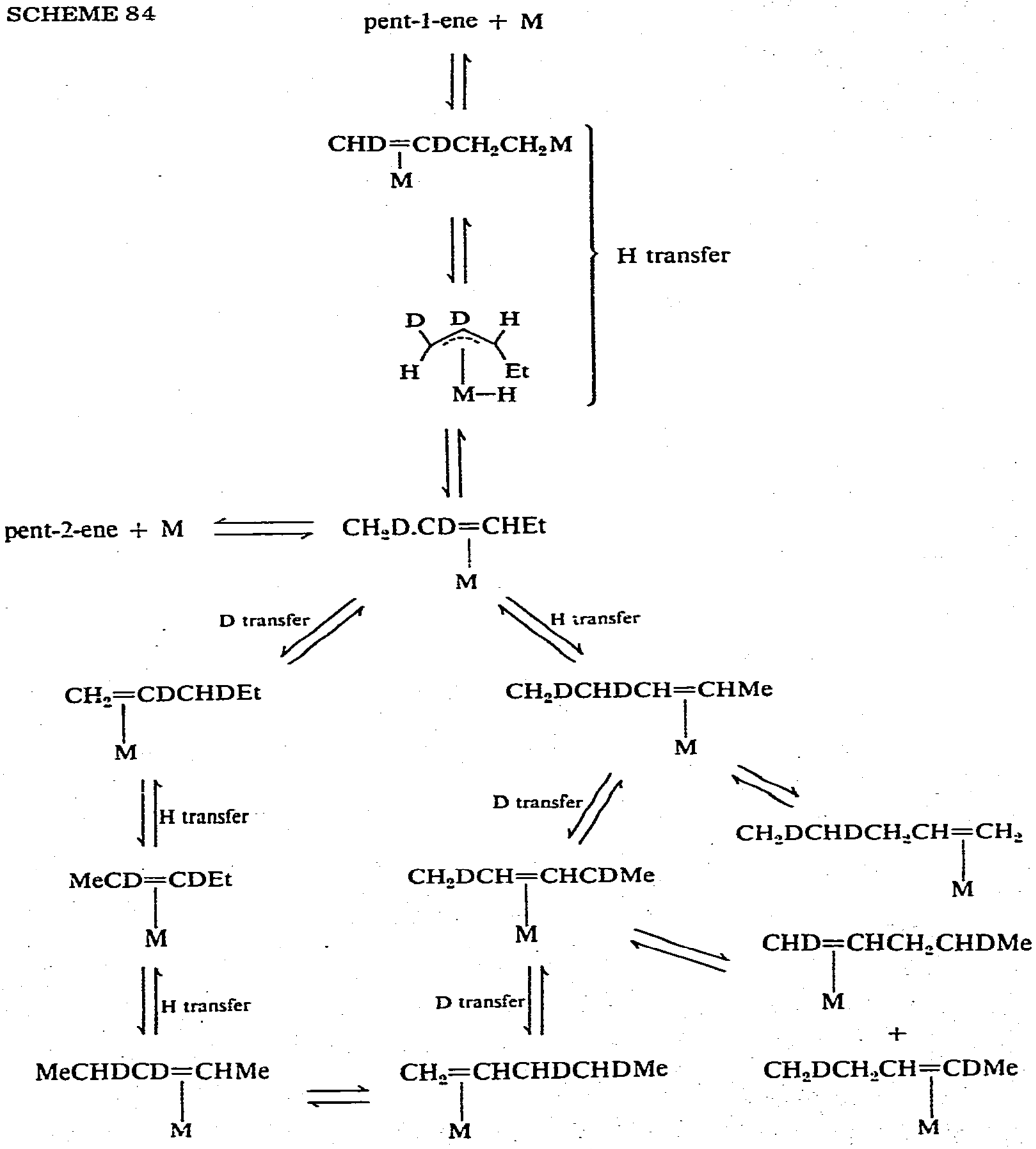
Addition of hydrogen to methyl sorbate was catalysed [454] by $Ru(PPh_3)_3Cl_2$, the products being *trans* $Me(CH_2)_2CH{=}CHCO_2Me$ (39%) and *cis*-$MeCH_2CH{=}CH\text{-}CH_2CO_2Me$ (52%). A tritium labelling study showed [455] that hydrogenation of *trans*-penta-1,3-dienes catalysed by $Ru(PPh_3)_3HCl$ occurred via 1,4-addition of hydrogen. The diene was coordinated in a cisoid manner to the metal. Hydrogenation of *cis*-penta-1,3-diene occurred by 1,2- and 1,4-addition. Hydrogenation of cyclododeca-1,5,9-triene in the presence of $Ru(CO)_3(PPh_3)_2$ gave [456] cyclododecane (2.7%), cyclododecene (94.6%), cyclododecadiene (2.3%) and unreacted triene (0.4%). Similar results were obtained with $Ru_3(CO)_{12}$, but ruthenium deposited on carbon gave the same products in different yields, viz. 39.7, 33.0 12.1 and 15.2% respectively. Other ruthenium catalysts including $Ru(CO)_2(PPh_3)_2Cl_2$, $Ru(CO)(PPh_3)_3H_2$, $Ru(PPh_3)_3Cl_2$ and $Ru(PPh_3)_2(MeOH)Cl_3$ were utilised [457] in the hydrogenation of cyclododecatriene, cycloocta-1,5-diene and norbornadiene. Improved selectivity in the formation of monoenes occurred in the presence of ligand-forming solvents such as diethylamine, or in the presence of $AsPh_3$ or $P(n\text{-}Bu)_3$ in excess of the molar requirements for catalyst formation from $RuCl_3$. The π-arene complexes $[(\eta^6\text{-arene})RuCl_2]_n[RuCl_2]_m$ (Arene = C_6H_6, 1,3,5-$C_6H_3R_3$; R = Me or Ph) can also catalyse [458] the hydrogenation of olefins. Species containing 1,3,5-$C_6H_3Ph_3$ exhibited the greatest activity, which was enhanced in the presence of small amounts of pyrrolidine.

Olefin isomerisation and oligomerisation

In the presence of $Fe(CO)_5$, castor oil was isomerised [459] to octadecadienoic acid. The isomerisation of pent-1-ene has been catalysed homogeneously [460] by $Ru(PPh_3)_3HCl$ and $Ru(CO)(PPh_3)_3HCl$. In benzene, preferential formation of the *cis*-pent-2-ene occurred at high catalyst concentrations, but a change to preferential formation of the *trans* isomer occurred as the catalyst concentration was reduced. This change in selectivity, which was not accompanied by a change in reaction mechanism, was attributed to a progressive "decongestion" of the catalytically active site occasioned by a gradual increase in the extent of dissociation of PPh_3 from the catalyst. Isomerisation of pent-1-ene was also effected [461] by solutions of $Fe(CO)_{12}$ in benzene. *Trans*-pent-2-ene was formed preferentially, and selective deuterium-labelling experiments indicated that reaction proceeded via intramolecular transfer of H and D atoms, π-allylic intermediates being involved (Scheme 84). It was observed [462] that N_2 has a strongly inhibiting effect on the isomerisation of pent-1-ene by $Ru(PPh_3)_3H_2$, since the nitrogen competes with the olefin for coordination to the metal.

In a benzene slurry, $Ru_3(CO)_{12}$ reacted [463] with Al_2O_3 and then with PH_3 at 250—300°C to give a ruthenium phosphide species dispersed on the aluminia. A similar iron species was obtained in vacuo using $Fe(CO)_5$. Under hydrogen

SCHEME 84

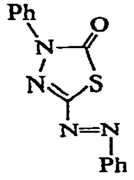


the ruthenium phosphide isomerised but-1-ene to *cis*- and *trans*-but-2-ene, without reduction of the olefin to butane. An analogous ruthenium antimonide behaved similarly, while ruthenium metal dispersed on Al_2O_3 effected mainly hydrogenation. The iron and ruthenium phosphides caused dimerisation of isobutylene in modest yields, while the ruthenium species selectively reduced acetylene to ethylene. However, ethylene and hydrogen reacted exothermally to give ethane.

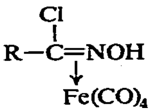
Cocondensation of iron atoms with butadiene and a cocatalyst, e.g. $AlEt_2Cl$, in toluene afforded [464] polybutadiene in very high yields. Fe atoms in benzene effected 90% conversion of butadiene into linear trimers (63%), *cis,trans,trans*-cyclododecatriene (30%) and *cis,cis*-cycloocta-1,5-diene (7%).

Synthesis and reactions of aldehydes, ketones and related oxygenated compounds

In aprotic solvents, α,β-unsaturated carboxylic esters underwent [465] insertion into the metal—hydride bond of $[Fe(CO)_4H]^-$ giving iron—alkyl compounds. On treatment with alkyl iodide, these species afforded hydroacylated products. In the presence of $M[Fe(CO)_4H]$ (M = Na or K), indole reacted with RCHO (R = H, Me, n-Pr, Ph, *p*-ClC_6H_4 or *p*-MeC_6H_4) giving [466] 3-alkyl or 3-aryl substituted indoles. The catalytic species involved in the hydroxymethylation of propylene in the presence of $Fe(CO)_5$ and tertiary amines was identified [467] as $[Fe(CO)_4H]^-$. Reaction of PhCOCl with $Na_2Fe(CO)_4$ afforded [468] benzaldehyde in 55% yield. Treatment of dehydrodithizone with $Fe(CO)_5$ gave [469] 575.

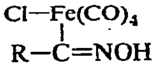


(575)



$R-\overset{\overset{Cl}{|}}{\underset{\underset{Fe(CO)_4}{\downarrow}}{C}}=NOH$

(576)



$R-\overset{\overset{Cl-Fe(CO)_4}{|}}{C}=NOH$

(577)

Reactions of amines

The catalytic carbonylation of secondary amines exclusively to *N*-formyl derivatives was achieved [470] homogeneously using $[Ru(CO)_2(OAc)]_n$, $Ru_3(CO)_{12}$ and a complex tentatively formulated as $[Ru(CO)_3H]_n$. The acetate compound dissolved in amines to give $[Ru(CO)_2(amine)_2(OAc)]_2$. Kinetic studies of the carbonylation of piperidine using the acetate catalyst in neat amine, or using $[Ru(CO)_3H]_n$, indicated that a monomeric tricarbonyl species was involved in the mechanism in each case.

In the presence of $M[Fe(CO)_4H]$ (M = Na or K) in ethanol, NHRR′ (R = Ph, *o*- or *p*-MeC_6H_4, $PhCH_2$, C_6H_{11} or n-$C_{12}H_{25}$, R′ = H; R,R′ = $(CH_2)_4$) reacted with R″CHO (R″ = H, Me, n-Pr or Ph) giving [471] at least 80% yields of $NRR'(CH_2R'')$. When primary amines were employed as starting materials, mono- or di-alkyl derivatives were obtained [472], depending on the molar ratios of amine, aldehyde and carbonylate ion. The reaction could also be catalysed by $Fe(CO)_5$ in the presence of amine [473] (the active species presumably being $[Fe(CO)_4H]^-$). Cyclohexanone reacted with cyclohexylamine giving $NH(C_6H_{11})_2$, while formaldehyde reacted with aniline affording NHMePh (91%).

Other reactions

Benzohydroxamoyl chlorides (RC(Cl)=NOH) were converted [474] to nitriles using $Fe(CO)_5$ or $[Fe(CO)_{11}H]^-$, possible intermediates in the reaction being 576 and 577.

In the absence of $Fe(CO)_5$ there was no reaction between n-BuSH and CCl_4, but in the presence of the carbonyl, $CHCl_3$ was produced [475]. In the presence of $Ru(PPh_3)_3Cl_2$, 1-olefins reacted [476] with $CRCl_3$ (R = H or Cl) giving products such as $RCl_2CCH_2CHCl(CH_2)_nMe$ ($n = 3 \rightarrow 6$) or $PhCHClCH_2CCl_3$. $Fe(CO)_5$ catalysed [477] the addition of C_2HCl_5 to allyl alcohol, the products being $(n\text{-}Pr)_2O$ and $HCCl_2CCl_2CH_2CHClCH_2OH$.

Tertiary amine oxides caused [478] the decomposition of dieneiron carbonyls with the quantitative liberation of the diene and production of CO_2 and NR_3.

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