IRON, RUTHENIUM, AND OSMIUM

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CONTENTS

Carbonyl, carbonyl phosphine and related complexes

Mononuclear species. The IR spectrum of crystalline $Fe(CO)_5$, obtained[1] by vapour condensation at 200 K, has been measured. The Raman-active A_1' and E'' vibrations, and the totally inactive A_2' mode were observed, presumably because of "site symmetry" activation; a new assignment of the vibrational spectrum was proposed. Ion–molecule reactions involving $Fe(CO)_5$ have been studied[2] by ion cyclotron resonance spectroscopy. The ICR spectral data were in agreement with previous results[3], and the ions $[Fe_2(CO)_4]^+$ and $[Fe_2(CO)_5]^+$ were also detected. In the reaction between $Fe(CO)_5$ and MeF, at the highest methyl fluoride pressures, only one CO group was replaced by MeF in $[Fe(CO)_n]^+$ ($n = 1$–4), and $[Fe(CO)_5]^+$ was inert towards substitution. Other products detected in this reaction were $[MeFe(CO)_4]^+$ and $[MeFe(CO)_5]^+$. The reaction of $Fe(CO)_5$ with H_2O was extensive, and the species $[HFe(CO)_n]^+$ ($n = 4$ or 5), $[Fe(H_2O)(CO)_n]^+$ ($n = 1$–3), $[Fe(H_2O)_2(CO)_n]^+$ ($n = 0$–2) and $[Fe(H_2O)_3(CO)]^+$ were observed. The reaction with NH_3 was generally similar although no hydridic species were discovered. $Fe(CO)_5$ reacted with HCl to give, as major products, $[HFe(CO)_n]^+$ ($n = 4$ or 5), and with benzene to give $[Fe(C_6H_6)(CO)_2]^+$.

The coupling constants $^1J(^{57}Fe{-}^{13}C)$ and $^1J(^{57}Fe{-}^{31}P)$ have been obtained from the appropriate NMR spectra of $Fe(CO)_5$ and $Fe(CO)_4PEt_nPh_{3-n}$ ($n = 1$–3). It was concluded that the CO groups in these compounds underwent intramolecular exchange, since the observation of $^1J(^{57}Fe{-}^{13}C)$ excludes intermolecular exchange.

The ionisation potentials, photoelectron, and mass spectra obtained[5] from $Fe(PF_3)_n(CO)_{5-n}$ ($n = 2$–5) showed that PF_3 is a poorer σ-donor but better π-acceptor (with respect to Fe) than CO.

Reaction of $Fe_2(CO)_9$ with Et_2NPF_2 afforded[6] $Fe(CO)_4(PF_2NEt_2)$ and $Fe(CO)_5$, and with $(Et_2N)_2PF$, $Fe(CO)_4[PF(NEt_2)_2]$ was formed. Treatment of $Fe(CO)_4(PF_2NEt_2)$ with HX (X = Cl or Br) gave $Fe(CO)_4(PF_2X)$, and reaction of $Fe(CO)_4(PF_2Br)$ and $Fe(CO)_4(PFCl_2)$ with AgN_3 or AgNCS afforded $Fe(CO)_4[PF_2(N_3)]$ and $Fe(CO)_4[PF(NCS)_2]$, respectively. Reaction of $Fe_2(CO)_9$ with $E(NMe_2)_3$ (E = P or As) gave[7] $Fe(CO)_4E(NMe_2)_3$.

The reaction between $Fe_2(CO)_9$ and $P(p\text{-}MeC_6H_4)_3$ (L), in which $Fe(CO)_5$, $Fe(CO)_4L$ and $Fe(CO)_3L_2$ were formed, has been studied[8] by IR spectroscopy, and the effect of light, temperature and the presence of CO on the product ratios investigated. It was concluded that $Fe_2(CO)_9$ reacted by two different pathways:

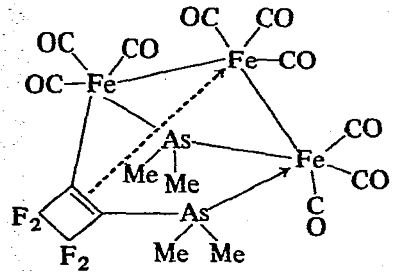
$$\begin{array}{llll}
Fe_2(CO)_9\ (\text{solid}) & \rightleftharpoons & Fe(CO)_5 + Fe(CO)_4 & (\text{slow}) \\
Fe(CO)_4 + L & \rightarrow & Fe(CO)_4L & (\text{very fast}) \\
Fe(CO)_4 + CO & \rightarrow & Fe(CO)_5 & (\text{fast}) \\
Fe(CO)_4 + O_2 & \rightarrow & \text{oxidised product} + CO &
\end{array}$$

The scheme explained previous observations[9] that $Fe_2(CO)_9$ reacted with an excess of $C^{18}O$ to give 10–15% $C^{18}O$ in $Fe(CO)_5$, and that both $Fe(C^{18}O)(CO)_4$ and $Fe(C^{18}O)_2(CO)_3$ were present at the beginning of the reaction; the data did not support the intermediacy of $Fe(CO)_4$ in the formation of $Fe(CO)_3L_2$.

By using the potentially tri- and tetra-dentate ligands $EPh(o\text{-}C_6H_4EPh_2)_2$ [E = P(TP); E = As (TAS)] and $E(o\text{-}C_6H_4EPh_2)_3$ [E = P (QP); E = As (QAS)], the series $Ru(CO)_2(TP)$, $Ru(CO)_2(TAS)$, Ru(CO)(QP) and Ru(CO)(QAS) have been prepared[10]. Halogenation of Ru(CO)(QP) afforded $Ru(QP)X_2$ (X = Cl or I).

Polynuclear species. The IR spectra of UV-irradiated $Fe_2(CO)_9$ in matrices at 20 K revealed[11] the presence of both bridged and non-bridged forms of $Fe_2(CO)_8$. Photolysis in nitrogen matrices provided some evidence for $(CO)_4Fe(\mu\text{-}CO)Fe(CO)_3(N_2)$ and $(CO)_3Fe(\mu\text{-}N_2)(\mu\text{-}CO)Fe(CO)_3$. There were strong similarities between frozen-gas (A or N_2) and solution IR spectra[12] of $M_3(CO)_{12}$ (M = Ru or Os) and $Ru_3(CO)_{10}(NO)_2$, and it appeared that for $M_3(CO)_{12}$ the isolated molecules were somewhat distorted from idealised D_{3h} symmetry. The matrix spectrum of $Fe_3(CO)_{12}$ was completely different to that in solution and indicated that the molecular structure in this situation and in the solid state[13] were identical.

An atmospheric pressure synthesis of $Ru_3(CO)_{12}$, from $RuCl_3{\cdot}nH_2O$, $EtOCH_2CH_2OH$, Zn and CO, has been described[14], and a detailed mass spectral study of the carbonyl reported[15].



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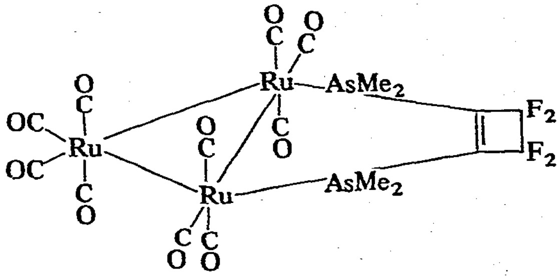

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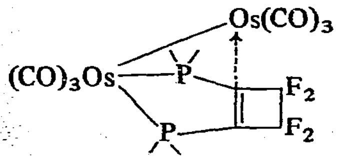

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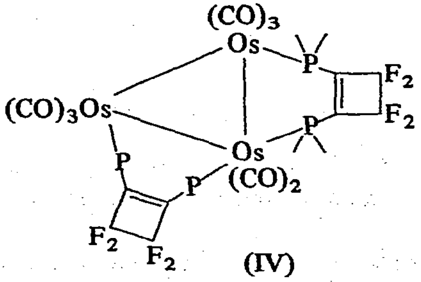

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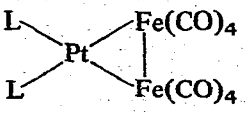

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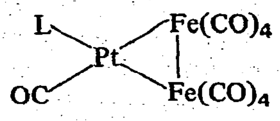
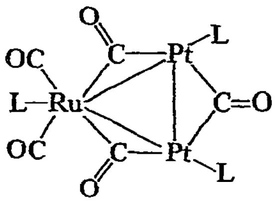


(VI)

The crystal structure determination of $Fe_3(CO)_9(PMe_2Ph)_3$ revealed[16] that the three phosphine ligands were coplanar with the Fe_3-triangle; the structure was otherwise similar to $Fe_3(CO)_{12}$[13] with Fe—Fe distances of 2.69 and 2.54 Å. One of the products of the reaction between $Fe_3(CO)_{12}$ and $(Me_2As)_2C_4F_4$ ($f_4$fars) contained[17] a rearranged arsine ligand (I). The three $Fe(CO)_3$ groups and the $AsMe_2$ moiety are linked together at the corners of a tetrahedrally-distorted square plane. There was a long Fe—Fe bond (2.92 Å) involving the Fe atom bonded to the two As atoms, whereas the shorter Fe—Fe contact (2.67 Å) was associated with the Fe atom bonded to one As atom. The structure of $Ru_3(CO)_{10}[(Me_2As)_2C_4F_4]$, II, in which the diarsine is coplanar with the Ru_3-triangle and bridges two metal atoms, has also been determined[18].

$Os_3(CO)_{12}$ is much less reactive[19] towards $(Ph_2P)_2C_4F_4$($f_4$fos) and $(Ph_2P)_2C_6F_8$($f_8$fos) than either $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$, although $Os_3(CO)_{11}$($f_4$fos), $Os_3(CO)_{10}$($f_4$fos) (analogous to II), $Os_2(CO)_6$($f_4$fos), III, $Os_3(CO)_8$($f_4$fos), IV, and $Os_3(CO)_{11}$($f_8$fos) were isolated; no arsenic analogues of these or related[20] Fe and Ru compounds could be obtained.



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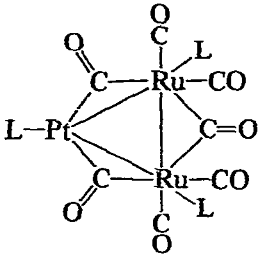

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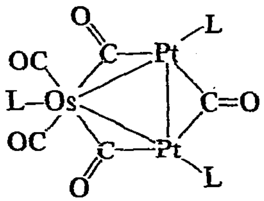

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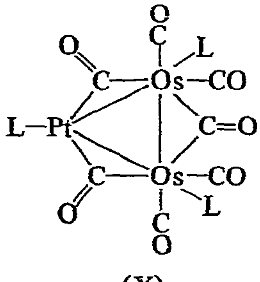
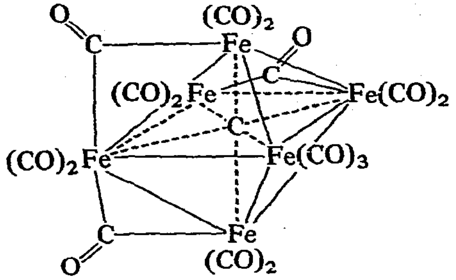


(X)

Tentative assignments of the fundamental CO stretching frequency modes, obtained from solution and polycrystalline samples, and using IR and Raman spectra, have been proposed[21] for $Mn_2Fe(CO)_{14}$, $Re_2Fe(CO)_{14}$ and $MnReFe(CO)_{14}$. Reaction of $Fe_2(CO)_9$ with PtL_4 or $PtL_2(C_2H_4)$ (L = $PMePh_2$, PMe_2Ph, $PPh(OMe)_2$, $P(OPh)_3$, $AsPh_3$, or $Ph_2PCH_2CH_2PPh_2$) afforded[22] $PtFe_2(CO)_8L_2$, V, or $PtFe_2(CO)_9L$, VI. With $Ru_3(CO)_{12}$, VII and VIII were formed, whereas $Os(CO)_4H_2$ reacted with $PtL_2(C_2H_4)$ (L = $PMePh_2$ or PPh_3) giving IX and X. Other products isolated from these reactions included $M_3(CO)_{12-n}L$ (n = 1-3). None of the Pt-containing clusters obeyed the "rare-gas rule".

A second product formed[23] in the reaction between $Fe(CO)_5$ and $[Mn(CO)_5]^-$ in diglyme (the first was[24] $[MnFe_2(CO)_{12}]^-$) has been identified as $[Fe_6(CO)_{16}C]^{2-}$, XI. The hexanuclear cluster contains 13 terminal and 3 bridging CO groups, and a central "carbide" atom; it may be compared with $Fe_5(CO)_{15}C$[25]. Reaction of OsO_4 with CO in xylene at moderate temperatures and pressures afforded[26] $Os_3(CO)_{12}$, $Os_4O_4(CO)_{12}$



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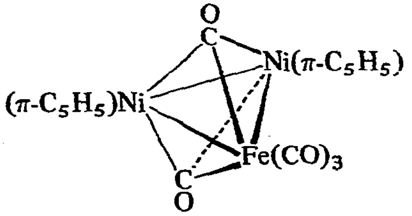

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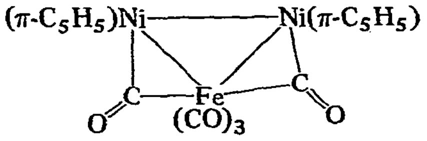

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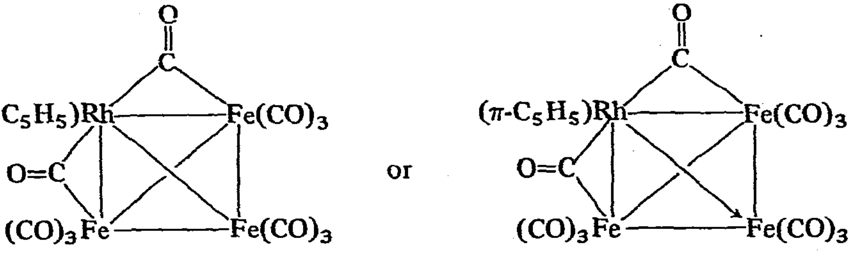

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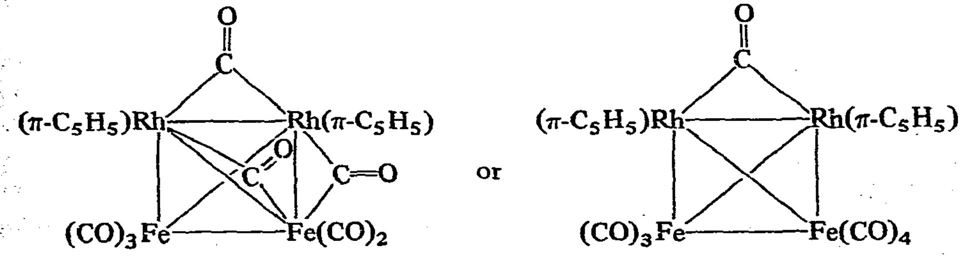
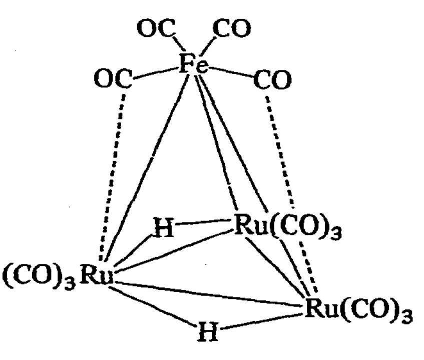


(XV)

and $Os_6O_6(CO)_{16}$. The last compound may contain an octahedral Os_6 unit, has no Os=O group and has only terminal CO groups.

$Fe_2(CO)_9$ reacted[27] with $[(\pi\text{-}C_5H_5)Ni(CO)]_2$ to give $(\pi\text{-}C_5H_5)_2Ni_2Fe(CO)_5$, XII; there may be isomerism between XII and XIII in solution. In the reaction between $Ru_3(CO)_{12}$ and $[(\pi\text{-}C_5H_5)Ni(CO)]_2$, only $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ was identified. The structure of $(\pi\text{-}C_5H_5)RhFe_3(CO)_{11}$[28], XIV, and $(\pi\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$[29], XV, have been determined crystallographically. In the former, the Rh–Fe distances were 2.57-2.62 Å, and the Fe–Fe distances 2.55-2.59 Å; because of the crowding of the ligands around the surface of the $RhFe_3$ tetrahedron, there were additional metal-carbonyl contacts which has the appearance of bridges. In the latter, the Rh–Fe and Fe–Fe distances were in the range 2.57–2.60 and 2.54 Å, respectively. There were two asymmetric CO bridges but the actual structure, within which no metal atom appears to obey the "rare-gas rule", lay between those idealised in XV. It would appear that the structure observed resulted from a compromise between the interligand (stereochemical) repulsions and the electronic requirements of each metal atom.

The molecular structure determination[30] of $H_2FeRu_3(CO)_{13}$, XVI, confirmed the expected[31] $FeRu_3$ tetrahedral cluster, and revealed the existence of asymmetric CO bridges; the Fe–Ru and Ru–Ru distances were in the ranges 2.63-2.70 and 2.78-2.92 Å, respectively. When H_2 was passed through an octane solution of $Ru_3(CO)_{12}$ at 90°, $H_4Ru_4(CO)_{12}$ was formed[32]. This compound has an IR spectrum different to that of $\alpha\text{-}H_4Ru_4(CO)_{12}$[33]. An attempt to repeat the synthesis of $\beta\text{-}H_4Ru_4(CO)_{12}$ afforded the new $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$[33]. Treatment of $Ru_2Fe(CO)_{12}$ with H_2 in refluxing hexane gave $H_4Ru_4(CO)_{12}$. Similar treatment of $Os_3(CO)_{12}$, with H_2 at 110°, afforded $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$. $H_2Ru_4(CO)_{13}$ rapidly reacted with H_2 in boiling hexane to give $H_4Ru_4(CO)_{12}$, and with D_2, $H_2D_2Ru_4(CO)_{12}$ was formed. Hydrogenation of $H_2FeRu_3(CO)_{13}$ gave the unstable $H_4FeRu_3(CO)_{12}$ which readily rearranged to $H_4Ru_4(CO)_{12}$. A series of trimethylphosphite derivatives of $H_4Ru_4(CO)_{12}$, $H_4Ru_4(CO)_{12-n}[P(OMe)_3]_n$ ($n = 0\text{–}4$) was prepared[34]; only one CO group on each Ru atom was displaced. From the H NMR spectrum, it was apparent that each substituted species was prepared as only one (pure) isomer, and the molecules underwent an intramolecular rearrangement whereby $^{1}H\text{–}^{31}P$ coupling was averaged. Reaction of $Ru_3(CO)_{12}$ with CO and H_2 under pressure gave[35] $Ru(CO)_5$ and $H_4Ru_4(CO)_{12}$, identical to that



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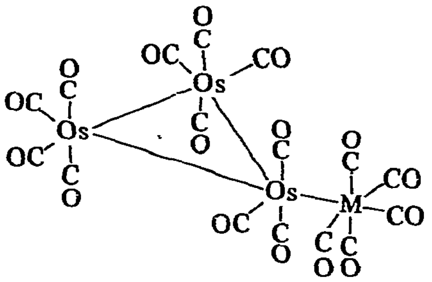

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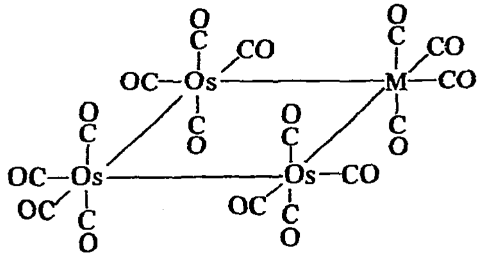

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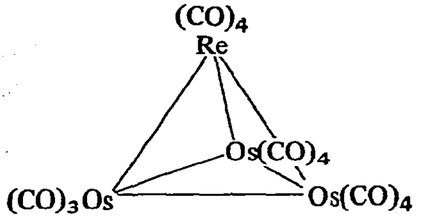

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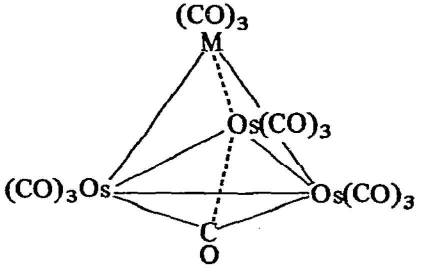
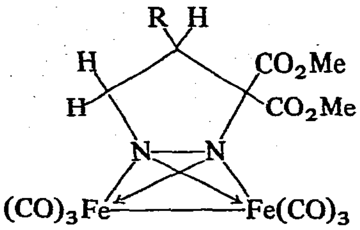


(XX)

described earlier[33]. Treatment of the hydride with PR_3 (R = n-Bu or Ph) under a variety of conditions afforded $H_4Ru_4(CO)_n(PR_3)_{12-n}$ ($n = 8$–11).

Treatment of $Os_3(CO)_{12}$ with $[M(CO)_5]^-$ (M = Mn or Re) afforded[36] first $[Os_2M(CO)_{12}]^-$ which, on acidification, gave the polynuclear hydrides $HMnOs_2(CO)_{12}$, $HMOs_3(CO)_{16}$ (proposed structures XVII or XVIII), $HReOs_3(CO)_{15}$ (proposed structure XIX) and $H_3MOs_3(CO)_{13}$ (proposed structure XX). The structure of $H_2Ru_6(CO)_{18}$ has been elucidated[37]; each Ru atom within the octahedron had three terminal CO groups and the two H atoms triply-bridged three Ru atoms on opposite (mutually *trans*) faces of the octahedron. There were six "long" (2.95 Å) and six "short" (2.87 Å) Ru–Ru distances.

Species containing bridging N, P or As atoms. UV irradiation of $Fe(CO)_5$ with 1-pyrazolines gave[38] XXI (R = Ph or i-Pr) whereas treatment of $Fe_2(CO)_9$ with 2,3-diazabicyclo[2.2.1]hept-2-ene afforded[39] XXII. Dialkylcarbodiimides reacted[40] with $Fe(CO)_5$ to give the species XXIII. The spectral information obtained from this compound was consistent with the formulation of the nitrogen ligand as a dehydrotrialkylguanidine moiety. Reaction with PPh_3 resulted in replacement of only one CO group, giving $Fe_2(CO)_2(PPh_3)[C(NR)_3]$. The mechanism of formation of the compound is depicted in Scheme 1; indeed, the generation of CNR was confirmed by the isolation



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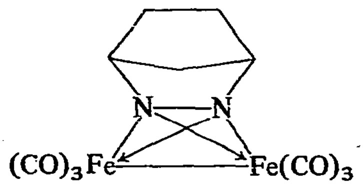
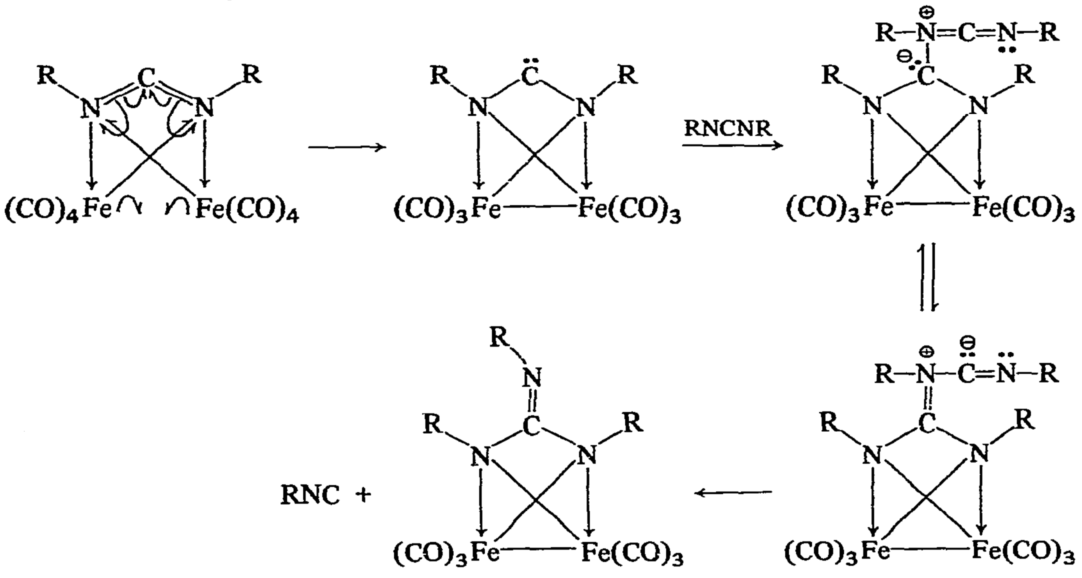


(XXII)

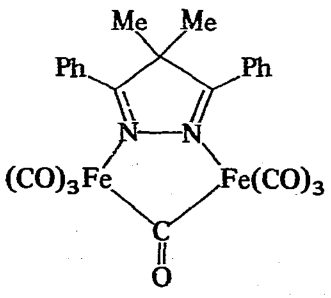
of $Fe(CO)_4(CNC_6H_{11})$. The diazapentadiene complex, XXIV, was obtained[41] by reaction of the free ligand with $Fe_2(CO)_9$.



(XXIII)

Scheme 1

The crystal structure determination of $Fe_2(CO)_6(RNO)_2$, where R = 3-chloro-2-methylnitrosobenzene, revealed[42] that the compound could be described as either XXV or XXVI. The molecule was centrosymmetric with the two Fe and two N atoms



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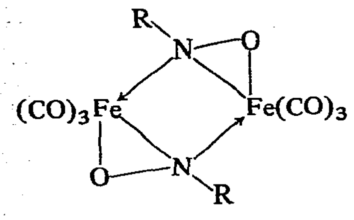

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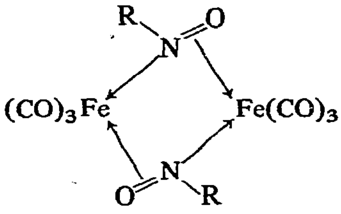
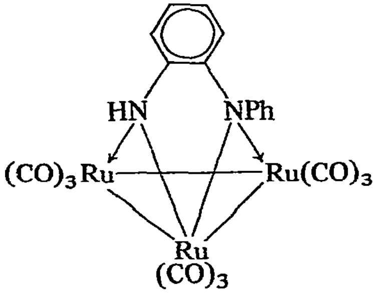


(XXVI)

coplanar; the O atoms lay on either side of this plane in positions such that each was bonded to one Fe atom only. The complex could best be regarded as an N-bridged species, and was unusual in that no other such compound involves a planar Fe_2N_2 ring; all previously determined[43] Fe_2N_2 systems had Fe–Fe distances shorter, by 0.7-0.8 Å, than that reported here (3.13 Å, regarded as bonding).

Reaction of azobenzene (azbH) with $Ru_3(CO)_{12}$ afforded[44] XXVII, XXVIII and XXIX; reduction of the last with $LiAlH_4$ afforded azobenzene, and oxidation with bromine gave $[Ru(CO)_2(azb)Br]_2$. $Ru_3(CO)_{12}$ and *o*-semidine ($semH_2$) reacted together to give a series of complexes which were separated by chromatography. These included $Ru_2(CO)_4(semH_2)$, XXX and possibly XXXI.



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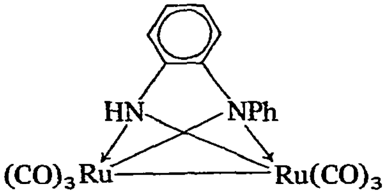

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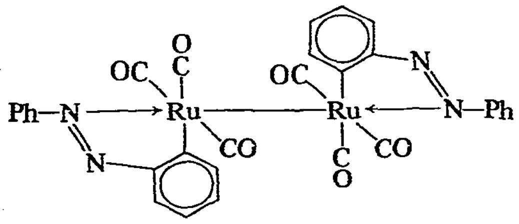

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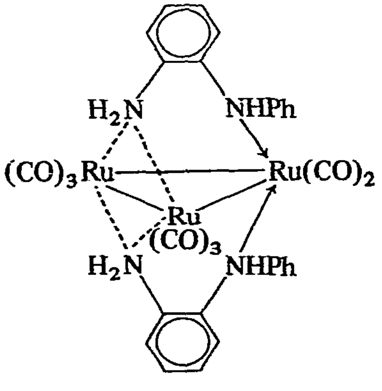

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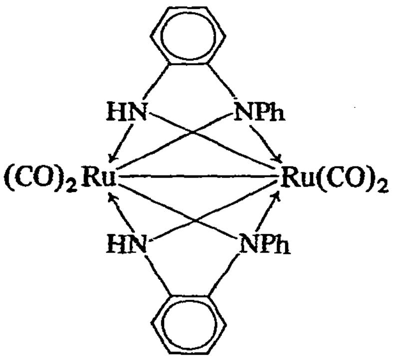
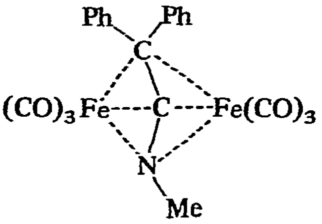


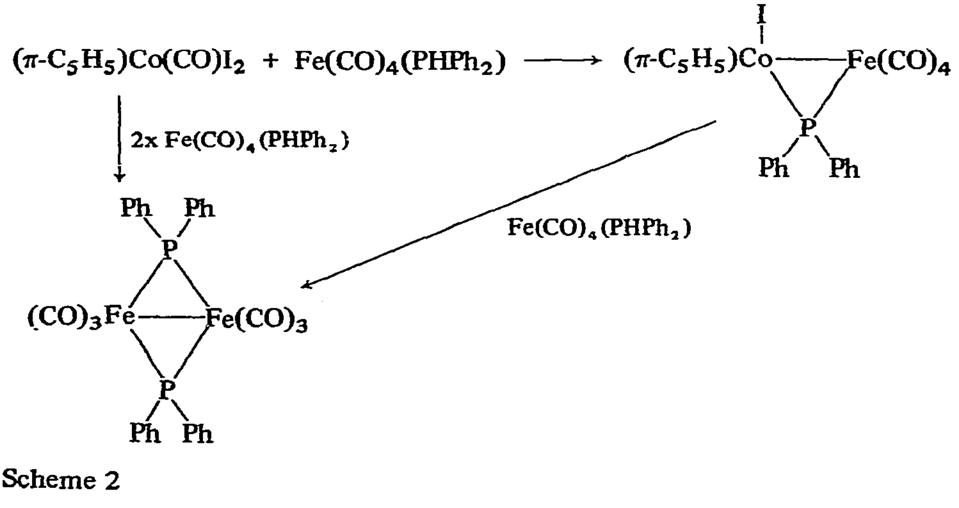
(XXXI)

Treatment of $Fe(CO)_4I_2$ with $LiN{=}CR^1R^2$ ($R^1 = R^2 = Ph$ or p-MeC_6H_4; $R^1 = Ph$ and R^2 = t-Bu) afforded[45] $[Fe(CO)_3N{=}CR^1R^2]_2$ and $Fe_2(CO)_6I(N{=}CR^1R^2)$; the Mössbauer spectra of these complexes were obtained. The C–C (1.38 Å) and C–N



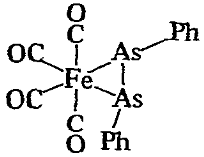
(XXXII)

(1.36 Å) distances in XXXII were longer[46] than those for uncoordinated C=C and C=N bonds, but were shorter than the C–C distances in the μ-allylic species[47] $Fe_2(CO)_5(PPh_3)(H_2C{=}C{=}CH_2)$; the Fe–Fe distance in XXXII was 2.54 Å.



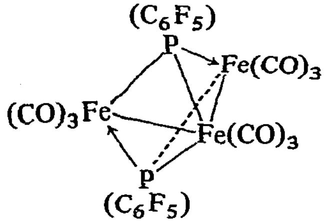
Scheme 2

Elimination of HX (X = halogen) occurred[48] in the presence of $NHEt_2$ in the reaction between $Fe(CO)_4(PHPh_2)$ and $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ or $(\pi\text{-}C_5H_5)Ni(CO)I$, the products being $(\pi\text{-}C_5H_5)(CO)_2Fe(\mu\text{-}PPh_2)Fe(CO)_4$ or $(\pi\text{-}C_5H_5)(CO)Ni(\mu\text{-}PPh_2)Fe(CO)_4$. UV irradiation or heating of these compounds gave the μ-carbonyl metal-metal bonded species $(\pi\text{-}C_5H_5)(CO)Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3$, or $(\pi\text{-}C_5H_5)Ni(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3$. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ with $Ni(CO)_3(PHPh_2)$ afforded $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot(\mu\text{-}PPh_2)Ni(CO)_3$ and eventually $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}CO)(\mu\text{-}PPh_2)Ni(CO)_2$. Treatment of $Mn(CO)_5Br$ or of $(\pi\text{-}C_3H_5)Mn(CO)_4$ with $Fe(CO)_4(PHPh_2)$ gave only $(CO)_4Fe(\mu\text{-}PPh_2)\text{-}Mn(CO)_4$, in which there is a Fe–Mn bond. The reactions of $(\pi\text{-}C_5H_5)Co(CO)I_2$ with $Fe(CO)_4(PHPh_2)$ are outlined in Scheme 2, and $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ was the only product formed in the reaction between $Fe(CO)_4(PHPh_2)$ and $(\pi\text{-}C_5H_5)Ru(CO)_2Cl$, $(\pi\text{-}C_5H_5)Cr(NO)_2Cl$, $(\pi\text{-}C_5H_5)_2TiCl_2$, $M(PPh_3)_2Cl_2$ (M = Ni or Pd) or $M'(PPh_3)_2MeI$ (M' = Pd or Pt).

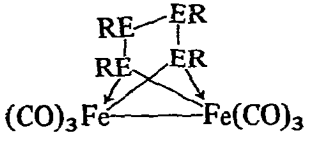


(XXXIII)

Reactions of $Fe(CO)_5$ with $(AsC_6F_5)_4$ afforded[49] $Fe(CO)_4(AsC_6F_5)_2$, XXXIII; the As–As distance (2.39 Å) was significantly shorter than that in $(AsMe)_5$ or $(AsPh)_6$ (2.43-2.46 Å) but longer than the As–As "double bond" (2.27 Å) in $As_2Co_2(CO)_5\text{-}(PPh_3)$[50]. Treatment of $Fe(CO)_5$ with $(PC_6F_5)_4$ gave $Fe_3(CO)_9(PC_6F_5)_2$, XXXIV, and $Fe_2(CO)_6(PC_6F_5)_4$ (XXXV, E = P). $Fe(CO)_5$ reacted[49] with $(AsR)_n$ ($n = 5$, R = Me or Et; $n = 6$, R = Ph) giving XXXV (E = As); with $(AsPh)_6$, $Fe_2(CO)_6(AsPh_2)_2$ was also obtained.

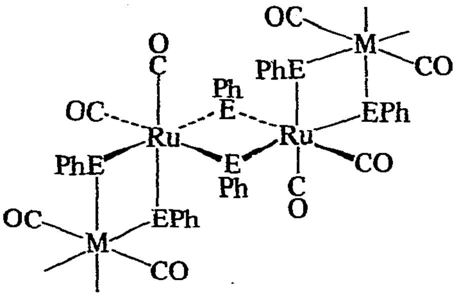


(XXXIV)



(XXXV)

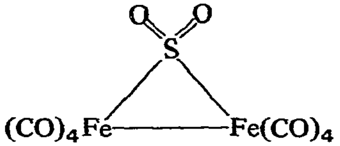
Species containing bridging S, Se or Te atoms. Reaction of $Fe_2(CO)_6(\mu\text{-}SR)_2$ (R = Me, Et, t-Bu or Ph) with L (PR'_3, R' = Et, Ph, OMe; $AsPh_3$ or $SbPh_3$) afforded[51] $Fe_2(CO)_5L(\mu\text{-}SR)_2$ and $[Fe(CO)_2L(\mu\text{-}SR)]_2$. With the bidentate ligands L–L (Ph_2PQPPh_2, Q = $(CH_2)_n$, $n = 1$ or 2; NEt; or C_2H_2; $Ph_2As(CH_2)_nAsPh_2$, $n = 1$ or 2) $[\{Fe(CO)_2(\mu\text{-}SR)\}_2\text{-}(L\text{–}L)]$, in which L–L bridged the two metal atoms, and $[(CO)_3Fe(\mu\text{-}SR)_2Fe(CO)(L\text{–}L)]$, were formed. Mössbauer and IR spectra were used to elucidate the structures of these compounds. The *syn-anti* equilibrium in $[Fe(CO)_3(\mu\text{-}SR)]_2$ (R = Me, Et, n-Bu, Ph, C_6Cl_5 or C_6F_5) has been studied[52]. The two isomers of $[Fe(CO)_3(\mu\text{-}SR)]_2$ (R = alkyl) reacted[52] at different rates with PR'_3 giving the corresponding isomers of $Fe_2(CO)_5(PR'_3)(\mu\text{-}SR)_2$. The mixed isomers of $[Fe(CO)_3(\mu\text{-}SMe)]_2$ reacted[53] with L—L ($f_4$fos or $f_8$fos) under mild conditions giving $(CO)_3Fe(\mu\text{-}SMe)_2Fe(CO)(L\text{—}L)$, whereas, at higher temperatures with L—L = $f_4$fos or $f_4$fars, $[\{Fe(CO)_2(\mu\text{-}SMe)\}_2(L\text{—}L)]$ could be obtained. The polymeric $[Ru(CO)_2EPh]_n$, E = Se or Te, was obtained[54] by reaction of $Ru_3(CO)_{12}$ with E_2Ph_2, together with small amounts of $[Ru(CO)_3EPh]_2$. The polymers, XXXVI, existed in low molecular weight (n = 6–7) and high molecular weight (n = 12–14) forms.



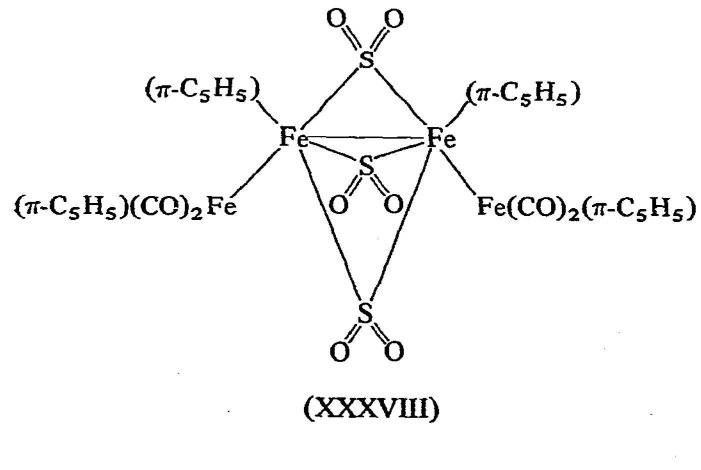
(XXXVI)

Treatment of $Fe(CO)_5$ with $S_2C_2(CF_3)_2$ afforded[55] $Fe(CO)_3[S_2C_2(CF_3)_2]$ which, on reaction with EPh_3 (E = P, As or Sb), gave $Fe(CO)_n(EPh_3)_{3-n}[S_2C_2(CF_3)_2]$; $Fe(Ph_2PCH_2CH_2PPh_2)[P(OMe)_2Ph][S_2C_2(CF_3)_2]$ and $Fe[P(OMe)_2Ph]_3[S_2C_2(CF_3)_2]$ were also isolated. Similar ruthenium complexes, $Ru(CO)(EPh_3)_2[S_2C_2(CF_3)_2]$, (E = P or As), $Ru[P(OMe)_2Ph]_3[S_2C_2(CF_3)_2]$ and $Ru[P(OMe)_3]_3[S_2C_2(CF_3)_2]$ were obtained by treating $Ru_3(CO)_{12}$ with $S_2C_2(CF_3)_2$ and allowing the product to react with the appropriate phosphine, arsine or phosphite.

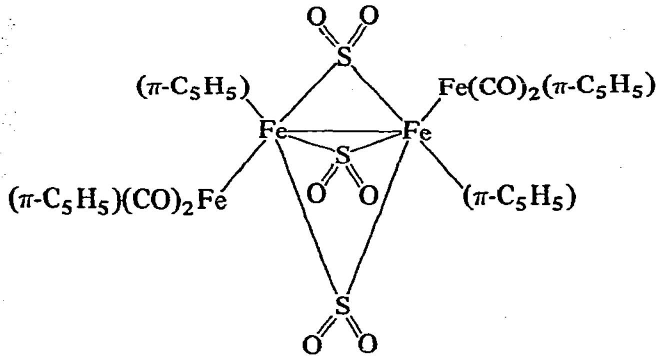
Reaction of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with SO_2 gave[56] $Fe_2(CO)_8(SO_2)$, XXXVII, whereas, with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, XXXVIII and XXXIX were obtained.



(XXXVII)



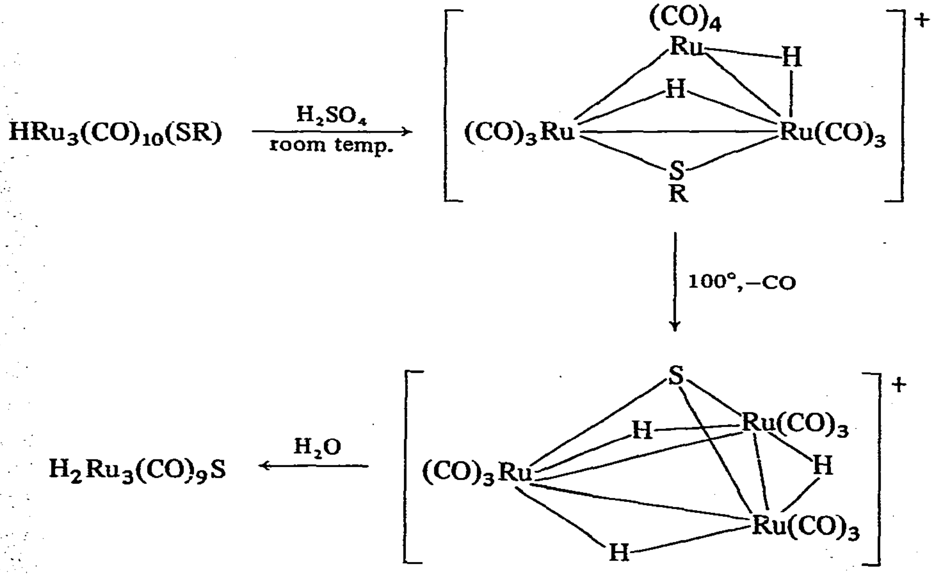
(XXXVIII)



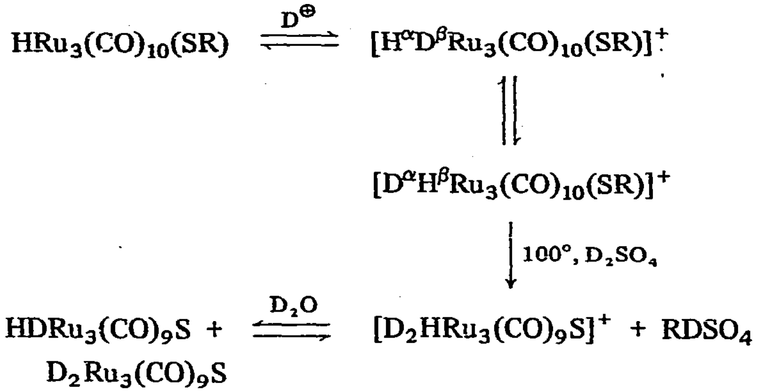
(XXXIX)

The molecular structures of $FeCo_2(CO)_9S$[57], $FeCo_2(CO)_9Se$[58] and $FeCo_2(CO)_9Te$[58] have been discussed and compared with those of $Co_3(CO)_9S$ and $Co_3(CO)_9Se$. These molecules contain a basic M_3E (E = S, Se or Te) tetrahedral unit, and all CO groups are terminal. The removal of one electron from the Co_3E unit, by replacement of one Co atom by an Fe atom, resulted in a large decrease of the M–M distances (by 0.083 Å in the sulfide and 0.039 Å in the selenide). $FeCo_2(CO)_9E$ (E = Se or Te) was prepared[58] by heating together, under CO pressure, $Co_2(CO)_8$ and $Fe_3(CO)_{12}$ with H_2Se or $TeEt_2$, respectively.

The preparation of $H_2Ru_3(CO)_9S$, by heating $HRu_3(CO)_{10}(\mu\text{-SEt})$ in sulphuric acid, has been described[59] in detail. However, the reaction would appear to proceed[60] in stages (Scheme 3). Studies in D_2SO_4 indicated that neither $HRu_3(CO)_{10}(\mu\text{-SEt})$ nor



Scheme 3

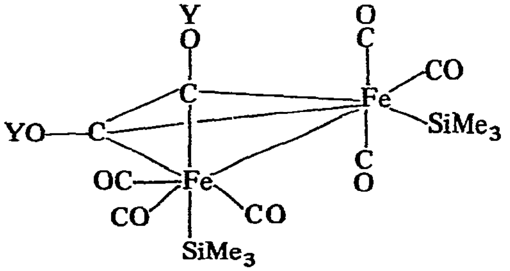


Scheme 4

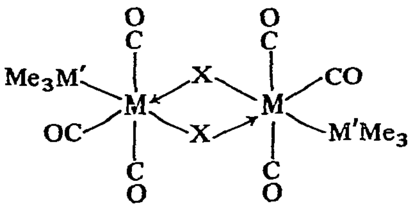
$[H_3Ru_3(CO)_9S]^+$ underwent proton exchange in concentrated acid, but did so in more dilute solution (Scheme 4).

Species containing Si, Ge or Sn atoms. UV irradiation of $Fe(CO)_5$ and $(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2SiCl_3$ with $SiHCl_3$ afforded[61] *cis*-$Fe(CO)_4H(SiCl_3)$ and $(\pi\text{-}C_5H_5)Fe(CO)H\text{-}(SiCl_3)_2$, respectively; with $SiHPh_3$, *cis*-$Fe(CO)_4H(SiPh_3)$ was obtained. Reaction of $Fe(CO)_4H(SiCl_3)$ with C_2F_4 gave $[Fe(CO)_4(SiCl_3)]_2$, and $[Fe(CO)_2(SiCl_2)]_2$ was obtained from this on heating *in vacuo*. Deprotonation of $Fe(CO)_4H(SiR_3)$ R = Cl or Ph) in the presence of $[Et_4N]^+$ led[62] to the isolation of $[Et_4N]$ $[Fe(CO)_4(SiR_3)]$. IR spectral studies of the reaction $[Fe(CO)_4(SiPh_3)]^-$ + $Fe(CO)_4H(SiCl_3)$ $\rightleftharpoons$ $Fe(CO)_4H(SiPh_3)$ + $[Fe(CO)_4(SiCl_3)]^-$ showed that the equilibrium was well to the right and that $Fe(CO)_4H(SiCl_3)$ was quantitatively the stronger acid. With $SiCl_4$, $[Fe(CO)_4(SiCl_3)]^-$ afforded small amounts of $Fe(CO)_4(SiCl_3)_2$ which did not revert to the monosilyl anion in basic media. With $SnCl_4$, however, *cis*-$Fe(CO)_4(SiCl_3)(SnCl_3)$ was obtained and this reacted with further $[Fe(CO)_4(SiCl_3)]^-$ to give $[(Cl_3Si)(CO)_4Fe]_2SnCl_2$.

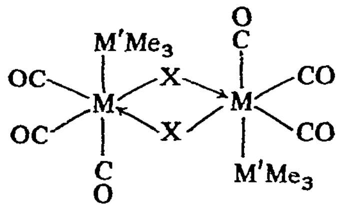
Reaction of $SiMe_3I$ with $Na_2Fe(CO)_4$ afforded[63] XL (Y = $SiMe_3$) which, on hydrolysis with HCl, gave apparently the desilylated product XL (Y = H). Treatment of $Fe(CO)_5$ with $(SiMe_2H)_2$ provided[64] $(CO)_3Fe(\mu\text{-}CO)(\mu\text{-}SiMe_2)_2Fe(CO)_3$, which was stereochemically non-rigid. Halogenation of $[M(CO)_4(SiMe_3)]_2$ (M = Ru or Os) or $[Ru(CO)_4(GeMe_3)]_2$



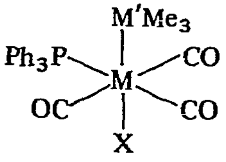
(XL)



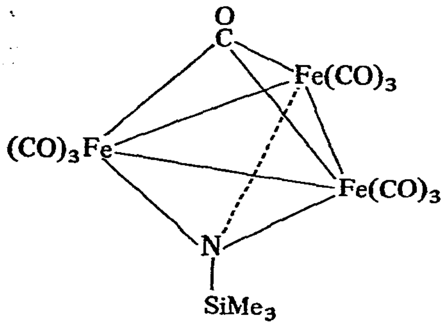
(XLI)



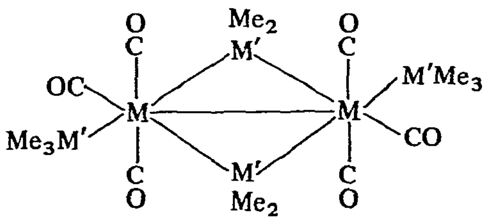
(XLII)



(XLIII)



(XLIV)

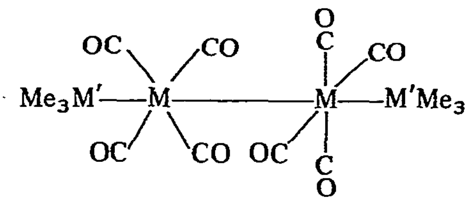


(XLV) (M' = Si or Ge)

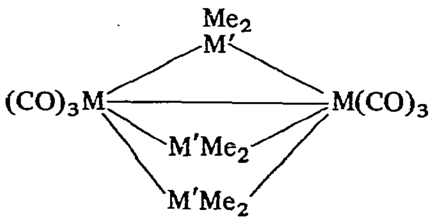
gave[65] $M(CO)_4(SiMe_3)X$ or $Ru(CO)_4(GeMe_3)X$ (X = Br or I). Several of these compounds, and the corresponding Sn complexes, could also be obtained by selective halogen cleavage of the Group IVA-transition metal bonds in $M(CO)_4(M'Me_3)_2$ (M' = Si, Ge or Sn). Decarbonylation of the halides afforded isomers of $[M(CO)_3(M'Me_3)X]_2$, with X-bridges, XLI and XLII, which reacted with PPh_3 giving $M(CO)_3(PPh_3)(M'Me_3)X$, XLIII. Treatment of $Ru(CO)_4(SiMe_3)I$ with $NaRe(CO)_5$ afforded $Me_3Si(CO)_4RuRe(CO)_5$.

Reaction of $Fe_2(CO)_9$ with Me_3SiN_3 at room temperature gave[66] $Fe_3(CO)_{10}NSiMe_3$, XLIV; the Fe—Fe distances were 2.54 Å. Treatment of $M_3(CO)_{12}$ with Si_2HMe_5, or of $M(CO)_4(SiMe_3)_2$ with Si_2HMe_5, afforded[67] $[M(CO)_3(SiMe_3)(\mu\text{-}SiMe_2)]_2$, XLV (M = Ru or Os). However, reaction of $(SiHMe_2)_2$ with $[Ru(CO)_4(M'Me_3)]_2$, XLVI, (M' = Si or Ge) gave $Ru_2(CO)_6(\mu\text{-}SiMe_2)_3$, XLVII; with $Os(CO)_4H_2$ the cyclic $[Os(CO)_3(\mu\text{-}SiMe_2)]_3$, XLVIII, was produced.

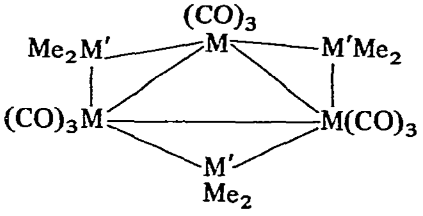
The vibrational spectrum of *cis*-$Fe(CO)_4(GeH_3)_2$, obtained[68] by reaction of $Na_2Fe(CO)_4$ with GeH_3Br, has been reported. With an excess of $GeHMe_3$, $Ru_3(CO)_{12}$, at 80–100° in hexane, formed[69] *cis*-$Ru(CO)_4(GeMe_3)_2$ and $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$, whereas with a slight excess of the germane, and using UV light, only $Ru(CO)_4(GeMe_3)_2$



(XLVI) (M′ = Si or Ge)



(XLVII) (M′ = Si or Ge)



(XLVIII) (M′ = Si or Ge)

was produced. $Os_3(CO)_{12}$ was less reactive, but at 150° gave $Os(CO)_4(GeMe_3)_2$, $[Os(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ and low yields of $Os(CO)_4H(GeMe_3)$. Using UV irradiation, the same products were obtained but there was no evidence for $[Os(CO)_4(GeMe_3)]_2$. By heating $M(CO)_4(GeMe_3)_2$ (M = Ru or Os) at 160°, $[M(CO)_3(\mu\text{-}GeMe_2)]_3$ (whose structure, XLVIII, M = Ru, has been determined[70]; Ru–Ru distances 2.93 Å) and $M_2(CO)_6(\mu\text{-}GeMe_2)_3$ were obtained. Sodium amalgam reduction of $Ru(CO)_4(GeMe_3)_2$ afforded $[Ru(CO)_4(GeMe_3)]^-$ which, on treatment with XCl, where X = $SnMe_3$, $AuPPh_3$ or $Re(CO)_5$, afforded *cis*-$Ru(CO)_4X(GeMe_3)$ (the Re complex was *trans*). Reaction of $[Ru(CO)_4(GeMe_3)]^-$ with $(\pi\text{-}C_5H_5)Fe(CO)_2I$ afforded only $Hg[Ru(CO)_4(GeMe_3)]_2$, the mercury having originated from traces of amalgam present in the reaction mixture. $Ru_3(CO)_{12}$ reacted with $GeHCl_3$ giving *cis*-$Ru(CO)_4(GeCl_3)_2$.

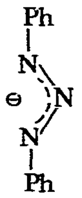
Species containing Zn, Cd or Hg atoms. IR spectral examination[71,72] of $MFe(CO)_4$ (M = Cd or Hg) showed that the M atoms were linked to the $Fe(CO)_4$ group in a zig-zag chain, being attached to the Fe at mutually *cis*-positions. The Fe atoms were octahedrally coordinated and Mössbauer and IR spectral data indicated that the M–Fe bonds were covalent. The reaction between Zn^{2+} and $[Fe(CO)_4]^{2-}$ was studied potentiometrically[73], and species such as $ZnFe(CO)_4$, $[ZnHFe(CO)_4]^+$, $[Zn_2Fe(CO)_4]^{2+}$ and $[HOZnFe(CO)_4]^{2+}$ were detected. The pK_a values for $Fe(CO)_4H_2$ in 1*M* aqueous $NaClO_4$ was 4.00 ± 0.01, and for $[HFe(CO)_4]^-$ 12.68 ± 0.04. The IR and Mössbauer spectral data obtained[72] from $Fe(CO)_4ML_2$ (M = Zn or Cd, L = *N*-donor ligand) indicated that these species also were di- or poly-meric, and that the Fe atom was octahedrally coordinated. Insertion[74] of Hg, Zn or Cd into the Fe–Fe bond in $[Fe_2(CO)_8]^{2-}$, giving $[(CO)_4Fe\text{–}M\text{–}Fe(CO)_4]^{2-}$, occurred over a long time at temperatures greater than 100°.

Carbonyl, phosphine and related hydride and halide complexes of Fe^{II}, Ru^{II} and Os^{II}. Displacement of N_2 by CO in $Fe(PEtPh_2)_3(N_2)H_2$ gave[75] $Fe(CO)(PEtPh_2)_3H_2$. Treatment of $Ru(CO)(PPh_3)HCl$ with $PHPh_2$ afforded[76] $[Ru(CO)(PHPh_2)_4H]^+$, in which the hydride ligand was *trans* to CO. It has been shown[77] that there is a relationship between the ^1H NMR chemical shift of the hydride resonance and the stereochemistry of $Ru(CO)(PPh_3)_3HX$. Reaction of K_2OsCl_6 with $P(C_6H_{11})_3$ in alcohols afforded[78] the five-coordinate $Os(CO)[P(C_6H_{11})_3]_2HCl$ as a mixture of isomers.

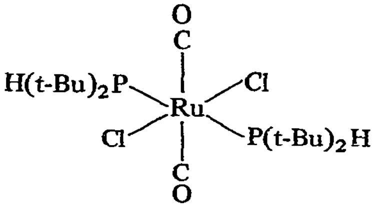
Reaction of $M(CO)(PPh_3)_3HCl$ (M = Ru or Os) and $Ru(CO)(PPh_3)_3H_2$ with 1,3-di-*p*-tolyltriazenide (dtt) or 1,3-diphenyltriazenide (dpt, XLIX) gave[79] $Ru(CO)(PPh_3)_2(dtt)Cl$ and $M(CO)(PPh_3)_2(dpt)H$. ^1H NMR spectra indicated that the triazenide ligand was mono- or bi-dentate, and did not bridge two metal atoms.

Reduction ($NaBH_4$ or $LiAlH_4$) of *mer*-$Os(CO)(PR_3)_2X_3$ (X = Cl or Br; PR_3 = PMe_2Ph or PEt_2Ph) gave[80] *mer*-$Os(CO)(PR_3)_2HX$, and $Os(PR_3)_2H_2Cl_2$ reacted with CO giving $Os(CO)(PR_3)_2Cl_2$.

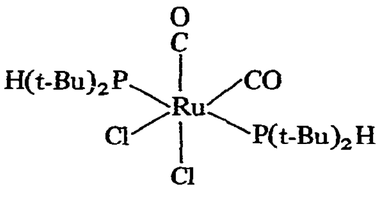
Reductive carbonylation of RuX_3 using HCO_2H in the presence of HX (X = Cl, Br or I) afforded[81], depending on the conditions, a series of carbonyl halide derivatives of Ru^{II} or Ru^{III}. These included $[Ru(CO)X_5]^{2-}$ (X = Cl or Br), $[Ru(CO)(H_2O)Cl_4]^{2-}$, $Ru(CO)Cl_3$, $[Ru(CO)(H_2O)Cl_2]_n$, $[Ru(CO)_2X]_4]^{2-}$, $[Ru(CO)_3X_3]^-$, $[Ru(CO)_2X_2]_n$ (X = Br or I) and, ultimately, $[Ru(CO)_3X_2]_2$.



(XLIX)



(L)

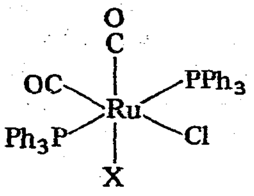


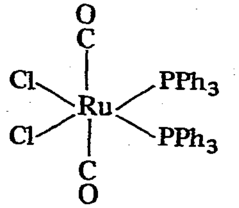
(LI)

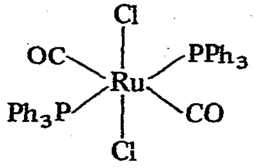
Treatment of $Fe(CO)_4I_2$ with $MeC(CH_2PPh_2)_3$ (triphos) gave[82] $Fe(CO)_2(triphos)I$, in which the phosphine was bidentate. Iodination of this afforded $Fe(CO)_2[(Ph_2PCH_2)_2$-$CMe(CH_2PI_2Ph_2)]I_2$, and similar species were obtained by halogenation of $Fe(CO)_2$ (triphos).

Reaction of $RuCl_3 \cdot nH_2O$ with CO and $PH(t\text{-}Bu)_2$ in 2-methoxyethanol afforded[83] L, which, in boiling ethanol, was converted into LI. The ^{31}P–^{31}P coupling constants were measured.

Reaction of $Ru(PPh_3)_3Cl_2$ with CO and H_2 in dimethylacetamide afforded[84] $Ru(CO)_2(PPh_3)_2HCl$ and $Ru(CO)_2(PPh_3)_2$, LII. Carbonylation in DMF gave an isomer of LII, viz. LIII, whereas in acetamide LIII and a further isomer, LIV, were obtained. Treatment of $Ru(AsPh_3)_3Cl_2$ with O_2 gave[85] $Ru(AsPh_3)_3Cl_2(O_2)$ which reacted with CO giving $Ru(CO)_2(AsPh_3)_2Cl_2$. Solutions containing the arsine complex and maleic acid activated oxygen and catalytically reduced maleic to succinic acid in the presence of hydrogen. $Ru(PhSCH_2CH_2SPh)_2X_2$ (X = Cl or Br) reacted[86] with CO in refluxing 2-methoxyethanol giving *cis*-$Ru(CO)_2(PhSCH_2CH_2SPh)X_2$. The corresponding complex

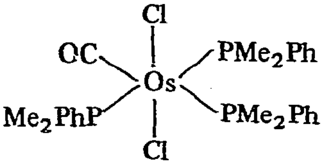

(LII)
(X = H or Cl)

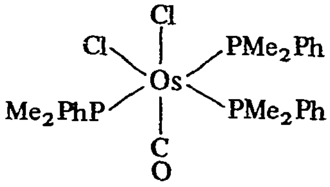

(LIII)


(LIV)

containing $EtSCH_2CH_2SEt$ did not react with CO, and neither sulfur complexes reacted with PhC≡CPh. In refluxing DMF, $Ru[(EtSCH_2)_3CMe]Cl_2$ gave $Ru(CO)[(EtSCH_2)_3CMe]Cl_2$ (the dibromide was obtained from this using LiBr), but in refluxing 2-methoxyethanol in the presence of CO the seven coordinate $Ru(CO)_2[(EtSCH_2)_3CMe]Cl_2$ was formed. Reduction of these compounds with $LiAlH_4$ did not apparently produce hydride complexes.

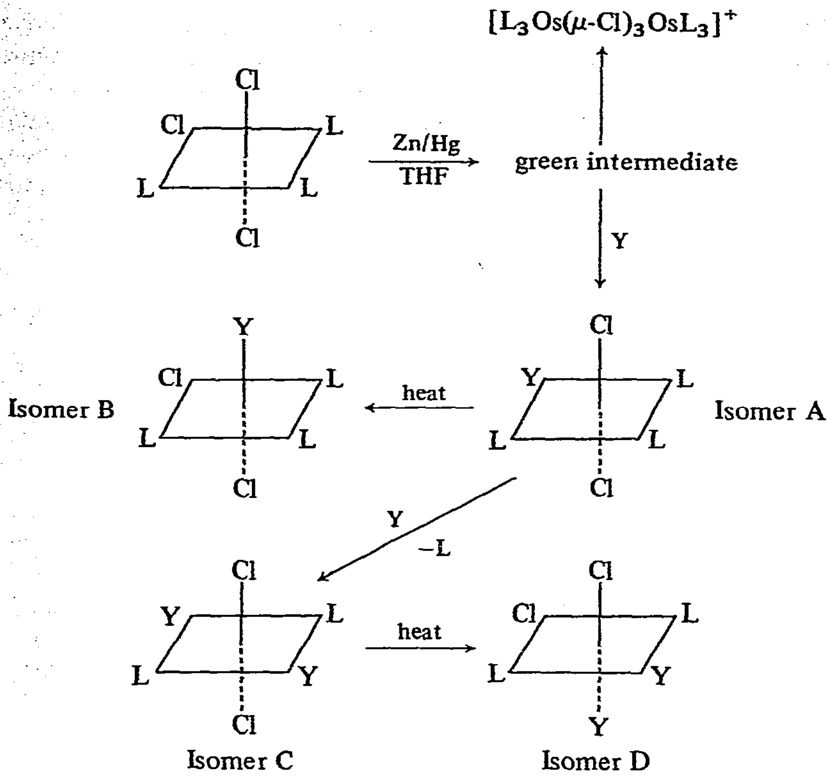
Zinc amalgam reduction[87] of $Os(PMe_2Ph)_3Cl_3$ in THF gave $Os(CO)(PMe_2Ph)_3Cl_2$, LV, and at its melting point it isomerised to LVI. Zinc reduction of OsL_3X_3 (X = Cl or


(LV)


(LVI)

Br, L = tertiary phosphine or $AsMe_2Ph$) in the presence of Y (Y = CO, MeNC, PhNC, MeCN or PhCN) gave[88] $OsL_3(Y)X_2$, $OsL_2(Y)_2X_2$ and $[Os_2L_6X_3]^+$ (Scheme 5). Reaction with NO ($L = PMe_2Ph$) gave $OsL_2(NO)Cl_2(NO_2)$ and $[OsL_3(NO)Cl(NO_2)]^+$ and oxidation of $Os(CNMe)L_3Cl_2$ with Cl_2 provided the paramagnetic $[Os(CNMe)L_3Cl_2]^+$. Reaction of $OsL_3(N_2)Cl_2$ ($L = PMe_2Ph$; isomer B) with CO in toluene at 70° gave $Os(CO)L_3Cl_2$ (75%; B) and $OsL_3(N_2)Cl_2$ (25%; B), but reaction of $OsL_2(CO)_2Cl_2$ ($L = P(n\text{-}Pr)_2Ph$; C) with L and CO in toluene gave $Os(CO)L_3Cl_2$ (B). Small amounts of $Os(CNMe)L_3Cl_2$ ($L = PEt_3$) were obtained when $Os(CNMe)_2L_2Cl_2$ was treated with L, but $Os(CNMe)L_3Cl_2$ ($L = PMe_2Ph$) readily afforded $Os(CO)L_3Cl$ when treated with CO. The integrated intensities of the stretching frequency (IR) of L in $OsL(PR_2Ph)_3X_2$ (L = CO or N_2; R = Me, Et or OMe; X = Cl or Br) were used to show[89] that CO is a better σ-donor and π-acceptor than N_2.

Oxidative addition of *o*-quinones ($C_6X_4O_2$; X = Cl or Br; 1,2-naphthaquinone) afforded[90] *cis*-dicarbonyl species, $Ru(CO)_2(PPh_3)_2O_2C_6X_4$, and these were also obtained from $Ru(CO)_2(PPh_3)_2Cl_2$ and $C_6X_4(OH)_2$ in the presence of base. Addition of SO_2 to $Ru(CO)_3(PPh_3)_2$ gave[91] $Ru(CO)_2(PPh_3)_2(SO_2)$ which reacted with O_2 to give $Ru(CO)_2(PPh_3)_2(O_2SO_2)$, also obtained from the parent carbonyl with H_2SO_4.



Scheme 5

Oxygenation of $Ru(CO)_3(PPh_3)_2$ afforded $Ru(CO)_2(PPh_3)_2(O_2CO)$ from which $Ru(CO)_2(PPh_3)_2Cl_2$ was obtained on treatment with HCl.

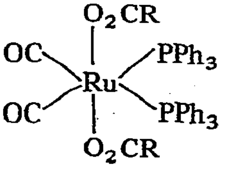
Other carbonyl species. Metathetical displacement of NaCl from $CoCl_2$ and $Na_3[Fe(CO)(CN)_5]$ (ν(CO) = 2040 cm^{-1}) afforded[92], in water, $Co_3[Fe(CO)(CN)_5]\cdot 5\text{-}7H_2O$ (ν(CO) = 1950 cm^{-1}); the drop in ν(CO) was interpreted in terms of a Fe—C=O→Co interaction. Manganese and nickel salts were obtained similarly.

Mesoporphyrin(IX) dimethylester and tetraphenylporphine(II) reacted[93,94] with $Ru_3(CO)_{12}$ giving ruthenium(II) monocarbonyl porphyrin complexes. The ^{1}H NMR spectra of the imidazole adducts of these were initially interpreted[93] in terms of a "shuttling" between the two N atoms of the heterocycle, but may in fact be explained[94] by a relatively rapid exchange between free and bound imidazole.

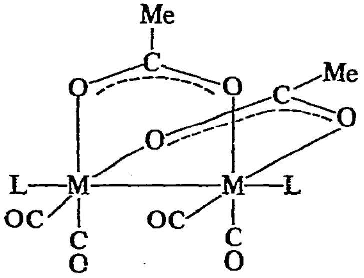
Oxidative addition of $S_2C_2(CF_3)_2$ to $Ru(CO)(S_2CNR_2)_2$ (R = Me or Et) gave[95] the diamagnetic, stereochemically non-rigid $Ru[S_2C_2(CF_3)_2](S_2CNR_2)_2$.

Carboxylic acids reacted[96] with $Ru(CO)_4(PPh_3)$ or $Ru_3(CO)_9(PPh_3)_3$ giving $Ru_2(CO)_4(PPh_3)_2(O_2CR)_2$ (R = H, Me or Et). $Ru(CO)_3(PPh_3)_2$ reacted with RCO_2H giving $Ru(CO)_2(PPh_3)_2(O_2CR)_2$, LVII. The structures of $Ru_2(CO)_4(pyridine)_2(O_2CMe)_2$ and $Os_2(CO)_6(O_2CMe)_2$ are similar (LVIII), the latter having[97] C_{2v} symmetry. The

Ru–Ru distance was 2.68 Å whereas the Os–Os distance was 2.73 Å, significantly shorter than that in $Os_3(CO)_{12}$[98], and equivalent to a single bond. The axial CO groups were not colinear with the Os–Os bond but were tilted along a mirror plane towards the acetate groups, and were weakly bonded (M–CO(axial) 1.96 Å; M–CO(equatorial) 1.79 Å) and more easily replaced. The interactions between the CO groups of LVIII, particularly intermolecular coupling, and coupling between CO groups bonded to different metal atoms, were described[99] as being due principally to dipole-dipole forces. This force field approach allowed a consistent interpretation of the solution and solid state spectra for LVIII and for $[(\pi\text{-}C_5H_5)M(CO)_2]_2$ (M = Fe or Ru) to be made.



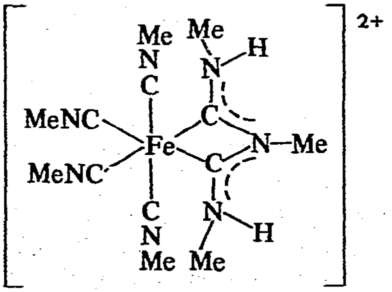
(LVII)



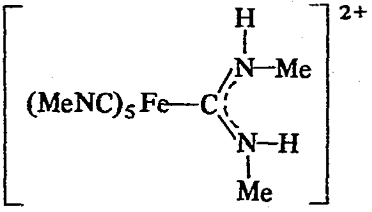
(LVIII)
(M = Ru, L = pyridine; M = Os, L = CO)

Isocyanide complexes

Octahedral complexes $Fe(CNR)_4(CNBX_3)_2$ (R = H, Me or Et; X = halogen) were obtained[100] in the reaction between $Fe(CNR)_4(CN)_2$ and BX_3. The signs of the ^{57}Fe quadrupole splittings in the Mössbauer spectra of *trans*-Fe(*p*-$MeOC_6H_4NC)_4Cl_2$ (positive), its *cis*-isomer (negative) and *trans*-$Fe(CNEt)_4(CN)_2$ (negative) have been determined[101]. Ethyl isocyanide reacted[102] with $Ru(EPh_3)_nX_2$ (E = P or Sb; X = Cl or Br; n = 3 or 4) or $Ru(AsPh_3)_2(MeOH)X_3$ giving *trans*-$Ru(CNEt)_2(EPh_3)_2X_2$, which was converted to the *cis*-isomer by heating at 240° or refluxing in 2-methoxyethanol. These complexes reacted[103] with $SnCl_2$ giving *cis*-$Ru(CNEt)_2(EPh_3)_2(SnCl_3)Cl$. *trans*-$Ru(CNEt)_4Cl_2$ formed *trans*-$Ru(CNEt)_4(SnCl_3)_2$ and $Ru(CNEt)_4Cl_2 \cdot HgCl_2$ when



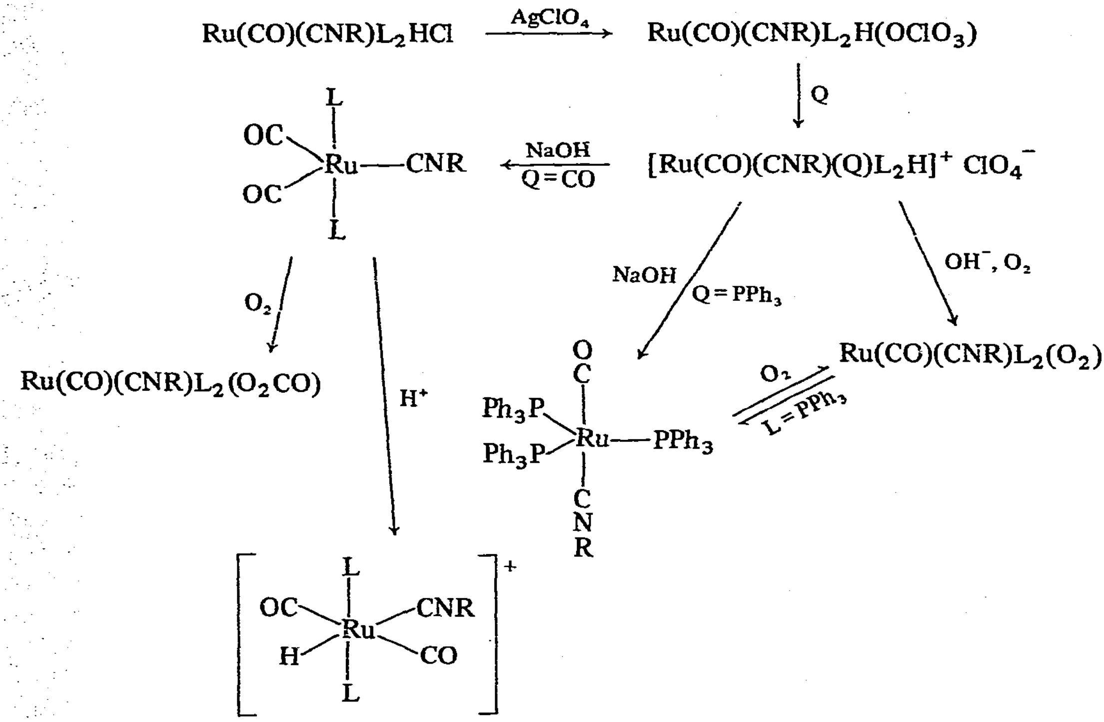
(LIX)



(LX)

treated[104] with $SnCl_2$ or $HgCl_2$; the latter formed $[Ru(CNEt)_4(MeNO_2)Cl]^+[HgCl_3]^-$ when dissolved in nitromethane.

Isocyanides reacted[105] with $Ru(CO)L_3HCl$ ($L = PPh_3$) giving $Ru(CO)(CNR)L_2HCl$, whose reactions are summarised in Scheme 6. Protonation of $Ru(CO)_2(CNR)(PPh_3)_2$ occurred specifically *trans* to CNR and not to CO, and $Ru(CO)(CNR)(PPh_3)_3$ was a catalyst for the oxidation of PPh_3.

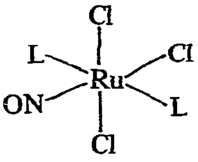


Scheme 6

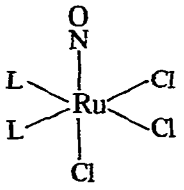
Addition of methylamine to $[Fe(CNMe)_6][HSO_4]_2$ afforded[106] LIX, and it was suggested that $MeNH_2$ addition occurred in a stepwise fashion via LX.

Nitrosyl complexes

A series of potentially bidentate ligands (L–L = $Me_2AsC(CF_3)=C(CF_3)AsMe_2$, $f_4$fos, $f_6$fos or $f_8$fos[107], o-$C_6H_4(AsMe_2)_2$[108]) reacted with $Fe(NO)_2(CO)_2$ to give $Fe(NO)_2$(L–L). With $Ph_2PCH_2CH_2AsPh_2$, both $Fe(NO)_2(CO)$(L–L) (monodentate L–L) and $Fe(NO)_2$(L–L) were obtained[107], but complexes with $Me_2AsCH{=}CHAsMe_2$ were too unstable to isolate[108]. $Fe(NO)_2(f_6fos)$ had a distorted tetrahedral structure[109] and there was evidence for considerable $Fe \rightarrow NO$ donation. The Mössbauer spectra of $Fe(NO)_2(CO)L$ ($L = PPh_3$, $PMePh_2$, $AsPh_3$, $P(OPh)_3$, CO) and of $Fe(NO)_2L_2$, were measured[107] and an order of π-acceptor strengths of L and L—L constructed. The weak ESR spectra of $[Fe(NO)_2X]_2$ (X = Br or I) in CCl_4 were consistent with the formation of $Fe(NO)_2X(CCl_4)$. Reaction of $[Fe(NO)_2Br]_2$ with NaO_2CCH_2NHR (R = H or Me) afforded[110] $Fe(NO)_2(O_2CCH_2NHR)$ which could be reduced by sodium amalgam to $Na^+[Fe(NO)_2(O_2CCH_2NHR)]^-$; $Fe(NO)_2(O_2CCHRNH_2)$ (R = Me, i-Pr or Ph) and $Fe(NO)_2[OC_6H_4C(R){=}NOH]$ (R = H or Me) were also prepared.



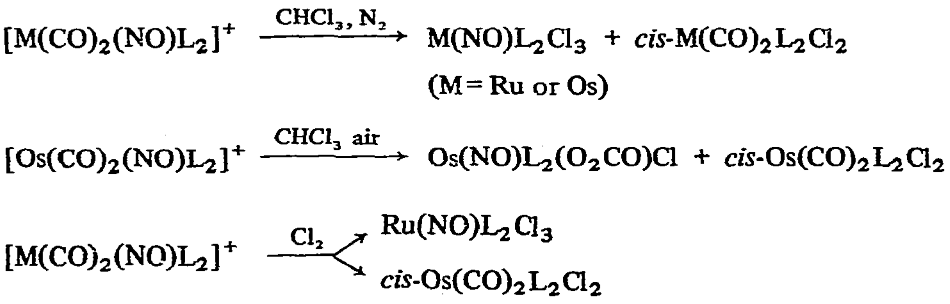
(LXI)



(LXII)

The crystal structure determinations of $Ru(NO)(PPh_3)_3H$ and $[Ru(NO)(Ph_2PCH_2CH_2PPh_2)_2]^+$ have established[111] the linearity of the Ru—N—O bond systems. Reaction of $Ru(NO)Cl_3$ with L (L = $P(n\text{-}Bu)_3$, PPh_3, PMe_2Ph or $AsMe_2Ph$) in ethanol or 2-methoxyethanol afforded[112] two isomers of $Ru(NO)L_2Cl_3$ (LXI and LXII), and there was evidence for $[Ru(NO)L_3Cl_2]^+$. Treatment of $Ru(NO)Cl_3$ with $o\text{-}C_6H_4(AsMe_2)_2$ (diars) in ethanol gave[113] $Ru(NO)(diars)Cl_3$, but on refluxing, *trans*-$[Ru(NO)(diars_2Cl]Cl_2$ was formed. Similar products were obtained with *cis*-$Me_2AsCH{=}CHAsMe_2$. Hydrazine reduction of $[Ru(NO)(diars)_2Cl]^+$ afforded $Ru(diars)_2(N_3)Cl$, and reaction with $PhNHNH_2$ gave $Ru(diars)_2[N(O){=}NNHPh]Cl$. Reaction of $Ru(diars)_2(N_3)Cl$ with NO^+ gave the starting material together with $Ru(diars)_2(N_3)Cl$ and $[Ru(NO)(diars)_2Cl]^{2+}$.

trans-$Fe(CO)_3(PPh_3)_2$ reacted[114] with NOX (X = BF_4 or PF_6) in methanol giving $[Fe(CO)_2(NO)(PPh_3)_2]X$. The corresponding Ru and Os complexes did not behave similarly, affording instead $[M(CO)_3(PPh_3)_2H]^+$. However, $[M(CO)_2(NO)(PPh_3)_2]^+$ (M = Ru or Os) were obtained by reacting $Ru_3(CO)_9(PPh_3)_3$ with NO^+ in methanol, or $Os(CO)(NO)(PPh_3)_2Cl$ with CO and $NaBPh_4$. Methoxide ion attack on $[M(CO)_2(NO)(PPh_3)_2]^+$ (M = Fe or Os) afforded $M(CO)(NO)(PPh_3)_2(CO_2Me)$, and the starting material was regenerated when this was treated with HPF_6; the reaction when M = Ru was complex



$$[M(CO)_2(NO)L_2]^+ \xrightarrow{CHCl_3,\ N_2} M(NO)L_2Cl_3 + cis\text{-}M(CO)_2L_2Cl_2 \quad (M = Ru \text{ or } Os)$$

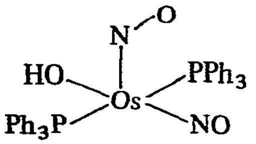
$$[Os(CO)_2(NO)L_2]^+ \xrightarrow{CHCl_3\ air} Os(NO)L_2(O_2CO)Cl + cis\text{-}Os(CO)_2L_2Cl_2$$

$$[M(CO)_2(NO)L_2]^+ \xrightarrow{Cl_2} Ru(NO)L_2Cl_3,\ cis\text{-}Os(CO)_2L_2Cl_2$$

Scheme 7 (L = PPh_3)

and did not give stable products. Other reactions of these complexes are summarised in Scheme 7. IR spectral data suggested that the M–CO bond in the Ru cations is weaker than those in the corresponding Fe and Os species.

$Ru(PPh_3)_3HCl$ reacted with $[ArN_2][BF_4]$ (Ar = p-MeC_6H_4 and p-$MeOC_6H_4$) giving[115] $[Ru(N_2Ar)_2(PPh_3)_2Cl][BF_4]$. Chlorination of these afforded $Ru(N_2Ar)(PPh_3)_2Cl_3$ and sodium amalgam reduction in ethanol afforded some $ArNH_2$. Reaction of $Ru(PPh_3)_3Cl_2$ with $[ArN_2][BF_4]$ gave $\{[Ru(N_2Ar)(PPh_3)_2Cl_2][BF_4]\}_n$, which may be dimeric with Cl bridges. The crystal structure determination of $[Os(NO)_2(PPh_3)_2(OH)]^+$ has shown[116] that the molecule was square pyramidal, LXIII, and that while the equatorial Os–N–O bond angle was essentially 180°, the axial bond angle was 127.5°. This may be compared with the similar $[Ru(NO)_2(PPh_3)_2Cl]^+$, where the axial bond angle was 136° [117].



(LXIII)

Reaction of $[Fe(CO)_3(NO)]^-$ with $GeX_2(Ph_2)$ (X = Cl or Br) gave[118] $[Fe(CO)_3(NO)]_2$-$GePh_2$, and $[(\pi$-$C_5H_5)Fe(CO)_2]_2$ afforded $(\pi$-$C_5H_5)Fe(CO)_2X$ and $[(\pi$-$C_5H_5)Fe(CO)_2]_2$-$GePh_2$. Sodium amalgam reduction of $Hg[Fe(CO)_2L(NO)]_2$ (L = CO, PPh_3, $P(OPh)_3$ or $AsEt_2Ph$) afforded[119,120] $[Fe(CO)_2L(NO)]^-$ which reacted with a variety of alkyl and phenyl Group IVA halides giving $Fe(CO)_2L(NO)(MR_3)$ (M = Ge, Sn, or Pb; R = Me, Et, n-Bu, Ph, Cl or Br), and $[Fe(CO)_2L(NO)]_2MPh_2$ (M = Sn or Pb). Reaction of $Na[Fe(CO)_3(NO)]$ with $SnPhCl_3$ or $SnCl_4$ afforded[120] $[Fe(CO)_3(NO)]_3SnPh$ or $[Fe(CO)_3(NO)]_4Sn$, respectively. From IR spectral data it was suggested that these compounds have trigonal bipyramidal structures with a linear L–Fe–M arrangement. When the Group IVA fragment was $SnPh_3Cl$ or $SnPhCl_3$, or L = $AsEt_2Ph$, isomerism owing to restricted rotation about the Fe–Sn or Fe–As bond, was observed. In acetonitrile, $Fe(CO)_2L(NO)(MPh_3)$ and $[Fe(CO)_2L(NO)]_2MPh_2$ dissociated reversibly giving $[Fe(CO)_2L(NO)]^-$. Displacement of CO by L′ (PPh_3, $P(OPh)_3$, or $AsEt_2Ph$) from $Fe(CO)_3(NO)AuL$ (L = alkyl, aryl phosphine or phosphite) afforded[121] $Fe(CO)_2L'(NO)AuL$. The compounds were isostructural with $Co(CO)_4AuPPh_3$ and had an approximately linear L′–Fe–Au–L system with trigonal bipyramidal coordination about the Fe. The complexes dissociated in donor solvents giving $[Fe(CO)_2L'(NO)]^-$.

π-Cyclopentadienyl and related carborane complexes

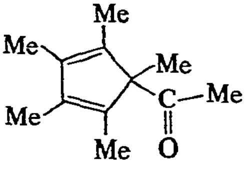
Simple binuclear species. Szilard-Chalmers reactions in $[(\pi$-$C_5H_5)Fe(CO)_2]_2$ gave[122] the radioactive dimer, as well as radioactive $(\pi$-$C_5H_5)_2Fe$ and $Fe(CO)_5$. No proton resonance shifts were detected[123] in the ^1H NMR spectra of $(\pi$-$C_5H_5)Fe(CO)_2X$ (X = Br, I, NCS or Me) when treated with $Eu(fod)_3$*, but they were observed when X = Cl, N_3 or

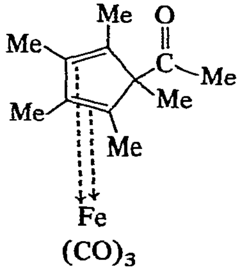
---

* fod = 1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyl-4,6-octanedionate.

CN, and in the spectra of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. Considerable spectral simplification of $(\pi\text{-}C_5H_5)Fe(CO)[P(n\text{-}Bu)_3](COMe)$ was achieved with $Eu(fod)_3$ enabling identification of the ^{31}P—^1H coupling in the $\pi\text{-}C_5H_5$ protons. It would appear that suitable bridging groups (*e.g.* CO, CN) are necessary before interaction with the Eu atom is possible.

Protonation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ in liquid HCl afforded[124] the known[125] $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2H]^+$, but in the presence of NOCl or Cl_2, $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ was formed. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, Br or I) with BCl_3 in liquid HCl gave the known[126] $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2Cl]^+$, and chlorination of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ in HCl produced low yields of $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+Cl^-$, which was converted to the BCl_4^- salt by addition, in HCl, of BCl_3.


(LXIV)


(LXV)

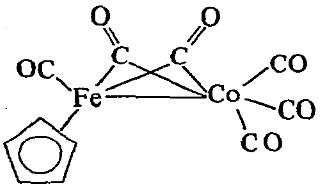
Hexamethyl-Dewar-benzene reacted[127] with K_2PtCl_4 in acid conditions to give $Pt(C_5HMe_5)Cl_2$ which, on treatment with $Fe_3(CO)_{12}$, afforded the diene $Fe(C_5HMe_5)(CO)_3$ and $[(\pi\text{-}C_5Me_5)Fe(CO)_2]_2$. The latter could also be prepared[128] from LXIV and $Fe(CO)_5$ or $Fe_2(CO)_9$, but LXV and $(\pi\text{-}C_5Me_5)Fe(CO)_2COMe$ were also formed; the reaction is summarised in Scheme 8. Also prepared were $(\pi\text{-}C_5Me_5)Fe(CO)_2Br$ and $(\pi\text{-}C_5H_5)Fe(CO)_2C_6F_5$.

$$\begin{tikzcd}
\text{LXIV} \arrow[r, "Fe_x(CO)_y"] & \text{LXV} \arrow[r, "-CO"] & (\pi\text{-}C_5Me_5)Fe(CO)_2COMe \arrow[d, "-CO"] \\
(\pi\text{-}C_5Me_5)Fe(CO)_2^{\bullet} \arrow[d] & & (\pi\text{-}C_5Me_5)Fe(CO)_2Me \arrow[ll, "-Me"'] \\
{[(\pi\text{-}C_5Me_5)Fe(CO)_2]_2} & &
\end{tikzcd}$$

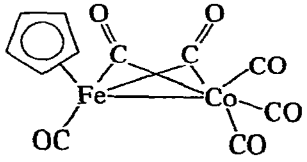
Scheme 8

Reaction of $SiMe_3(C_5H_5)$ with $Fe(CO)_5$ gave[129] $[(\pi\text{-}Me_3SiC_5H_5)Fe(CO)_2]_2$, but treatment of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with the silane produced ferrocene-type derivatives, CO and possibly H_2. Tetraphenyldiazocyclopentadiene reacted[130] with $Fe_2(CO)_9$ giving $[(\pi\text{-}C_5HPh_4)Fe(CO)_2]_2$.

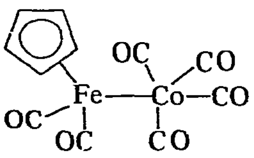
IR spectral studies of $(\pi\text{-dienyl})FeCo(CO)_6$ (dienyl = C_5H_5, C_5H_4Me or indenyl) revealed[131] the existence of two bridged (LXVI, LXVII), and one non-bridged (LXVIII), isomers. The proportion of non-bridged isomer present in polar solvents depended on temperature and the nature of the dienyl ring. Only the non-bridged isomer of $(\pi\text{-}C_5H_5)RuCo(CO)_6$ was observed. The IR spectrum of $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}CO)_2Ni(\pi\text{-}C_5H_5)$ was independent[132] of solvent, and consistent with an almost planar $Fe(\mu\text{-}CO)_2Ni$ bridging system.



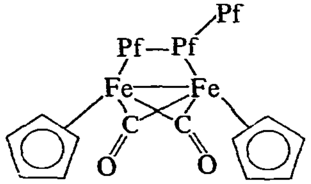
(LXVI)



(LXVII)



(LXVIII)



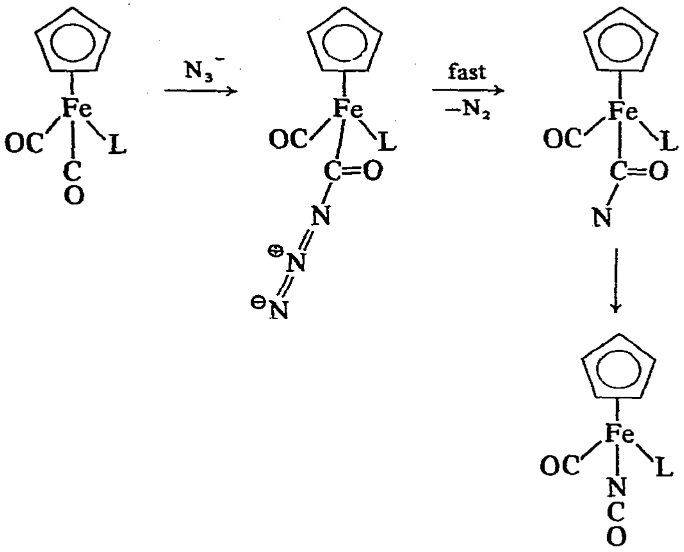
(LXIX)

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $PhP(CH_2CH_2PPh_2)_2$ (Pf-Pf-Pf) gave[133] $[(\pi\text{-}C_5H_5)Fe(CO)]_2$Pf-Pf-Pf (LXIX) and $Fe_2(CO)_9$ afforded $Fe(CO)_4$(Pf-Pf-Pf) in which the triphosphine was monodentate. In boiling acetonitrile, $(\pi\text{-}C_5H_5)Fe(CO)_2Me$ reacted with Pf-Pf-Pf giving $(\pi\text{-}C_5H_5)Fe(CO)$(Pf-Pf-Pf)(COMe) in which the phosphine was again monodentate, but UV irradiation of $(\pi\text{-}C_5H_5)Fe(CO)_2Br$ with the phosphine in benzene afforded $[(\pi\text{-}C_5H_5)Fe(\text{Pf-Pf-Pf})]^+$ where the ligand was tridentate. Reaction of $(Ph_2PCH_2CH_2PPhCH_2)_2$ (Pf-Pf-Pf-Pf) with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, $(\pi\text{-}C_5H_5)Fe(CO)_2Me$ and $(\pi\text{-}C_5H_5)Fe(CO)_2I$ gave[134] $[(\pi\text{-}C_5H_5)_2Fe_2(CO)_2]_2$(Pf-Pf-Pf-Pf), $(\pi\text{-}C_5H_5)Fe(CO)$-(Pf-Pf-Pf-Pf)(COMe) (phosphine monodentate) and $[(\pi\text{-}C_5H_5)Fe(\text{Pf-Pf-Pf-Pf})]^+$ (phosphine tridentate). Treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ with $P(CH_2CH_2PPh_2)_3$ $(P\text{-}Pf_3)$ afforded $[(\pi\text{-}C_5H_5)Fe\{P(Pf_3)\}]^+$.

Cationic species. Oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $Fe(ClO_4)_3$ in acetonitrile or acetone gave[135] $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ (L = MeCN or Me_2CO). Replacement of L by X (Cl, Br, I, NCS, SCN or ONO_2) led to $(\pi\text{-}C_5H_5)Fe(CO)_2X$, and L′ (pyridine, CO, SEt_2 or PPh_3) gave $[(\pi\text{-}C_5H_5)Fe(CO)_2L']^+$. Slow addition of $Ph_2PCH_2CH_2PPh_2$(diphos to the species with L = acetone gave[136] $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{diphos})]^+$, which, on UV irradiation, afforded $[(\pi\text{-}C_5H_5)Fe(CO)(\text{diphos})]^+$ (phosphine bidentate) and which, on treatment with further acetone adduct, gave $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(\text{diphos})]^{2+}$. Similar complexes could be obtained with pyrazine and $MeSCH_2CH_2SMe$.

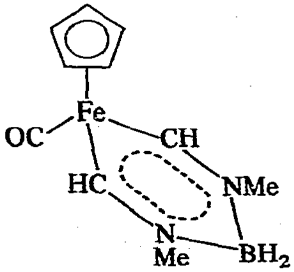
Mössbauer spectral data obtained from $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ (L = CS, CO or PPh_3) and $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = CN, NCO, NCS or Br) indicated[137] that the electron density on the Fe atom decreased in the order CS > CO > CN > PPh_3 > NCO > NCS > Br.

Nucleophilic attack by N_2H_4 or N_3^- on $[(\pi\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+$ gave[138] $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)NCO$. The kinetics of this reaction, and those involving the related $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$, L = CO or C_2H_4, indicated that an acyl azide was formed as an intermediate by attack of N_3^- on CO (Scheme 9). The reaction between $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ and $N^{14}CO$ gave[139] $(\pi\text{-}C_5H_5)Fe(CO)_2NCO$ and ^{14}CO, $(\pi\text{-}C_5H_5)Fe(CO)_2N^{14}CO$ and CO, and small amounts of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. The results showed clearly that the greatest percentage of ^{14}C was in $(\pi\text{-}C_5H_5)Fe(CO)_2NCO$, so that the reaction was thought to proceed via displacement of a CO group from the metal.

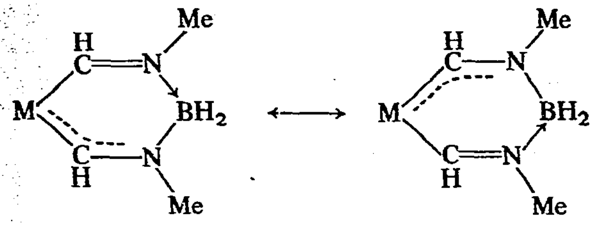


Scheme 9

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2(CS)]^+$ with N_3^- or N_2H_4 gave[140] $(\pi\text{-}C_5H_5)Fe(CO)_2NCS$ where as NCO^- or NCS^- afforded $(\pi\text{-}C_5H_5)Fe(CO)_2CN$. However, with OR^- or NH_2R (R = Me or Et), the thiocarbonyl cation formed $(\pi\text{-}C_5H_5)Fe(CO)_2C(=S)OR$ or $(\pi\text{-}C_5H_5)Fe(CO)_2C(=S)NHR$; both of these compounds reformed the precursor on treatment with acid (HCl).

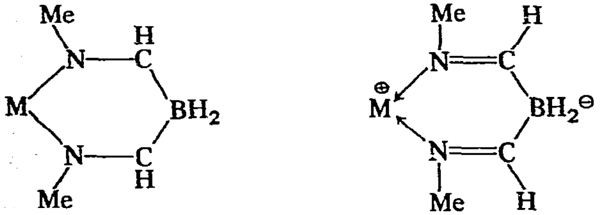


(LXX)

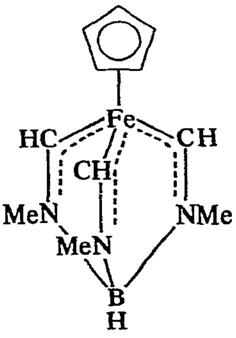


(a) (b)

(LXXI)



(c) (d)

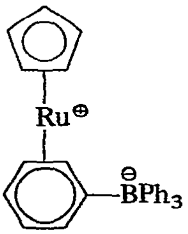


(LXXII)

Treatment of $[(\pi\text{-}C_5H_5)Fe(CO)(CNMe)_2]^+$ with BH_4^- gave[141] LXX and small amounts of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNMe)$, $(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(CNMe)_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. Similar reactions with $[(\pi\text{-}C_5H_5)Fe(CO)_2(CNMe)]^+$ gave $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNMe)$ and only very small amounts of LXX (L = CO). The bonding within the unusual amino-borane ring system could be represented by two canonical forms, LXXIa and LXXIb, although two other structures, LXXIc and LXXId, are possible. Reaction of $[(\pi\text{-}C_5H_5)Fe(CNMe)_3]^+$ with BH_4^- gave LXXII, and interaction of LXXI with $Ph_3C^+BF_4^-$ afforded $(\pi\text{-}C_5H_5)Fe(CO)[(CHNMe)_2BF_2]$.

Halide and related complexes. The metal-carbonyl bending vibrations in $(\pi\text{-}C_5H_4R)Fe(CO)_2X$ (R = H or Me; X = Cl, Br, I, $SnCl_3$, $SnBr_3$, HgCl, HgBr or HgI) were assigned[142] in CS_2 solution.

Halogenation of $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ in toluene, in the presence of BPh_4^- or PF_6^-, gave[143] the appropriate salts of $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]^+$ (X = Cl, Br or I); at low temperatures (−80°) the species isolated were green, but these were yellow at room temperature. The compounds where X = Cl or Br were particularly susceptible to nucleophilic attack, *viz.* $\{[(\pi\text{-}C_5H_5)Ru(CO)_2]_2\}X^+ + Y^- \rightarrow (\pi\text{-}C_5H_5)Ru(CO)_2X + (\pi\text{-}C_5H_5)Ru(CO)_2Y$ (Y = Cl, Br, I, CN, SCN or N_3), and with BPh_4^-, $(\pi\text{-}C_5H_5)Ru(CO)_2X$ and $(\pi\text{-}C_5H_5)Ru(CO)_2Ph$ were formed. The reaction with $[BBu_4]^-$ was similar, but with $[BPh_3(CN)]^-$, $(\pi\text{-}C_5H_5)Ru(CO)_2X$ and $(\pi\text{-}C_5H_5)Ru(CO)_2CN$ were the products. However, treatment of $(\pi\text{-}C_5H_5)Ru(CO)_2Cl$ with $NaBPh_4$ in refluxing methanol gave $(\pi\text{-}C_5H_5)Ru(CO)_2Ph$, in contrast to the reaction with $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cl$, where $(\pi\text{-}C_5H_5)Ru(\pi\text{-}C_6H_5BPh_3)$, LXXIII, was formed.



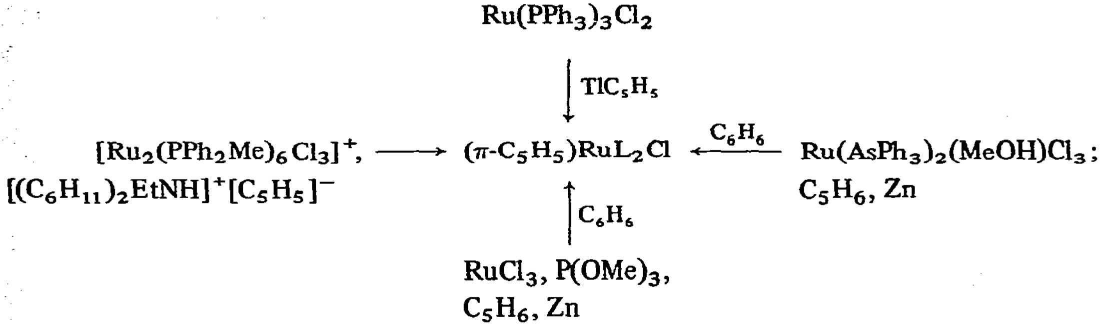
(LXXIII)

Complexes containing P, As or Sb donor ligands. Treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ with $P(OR)_3$ (R = Me, Et, n-Bu or C_3H_5) gave[144] $(\pi\text{-}C_5H_5)Fe(CO)[P(OR)_3]Cl$, $[(\pi\text{-}C_5H_5)Fe(CO)_2\{P(OR)_3\}]^+Cl^-$, $(\pi\text{-}C_5H_5)Fe(CO)_2[P(=O)(OR)_2]$ and $(\pi\text{-}C_5H_5)Fe(CO)[P(OR)_3][P(=O)(OR)_2]$; reaction with $P(OC_3H_5)_2Ph$ or $P(OC_3H_5)Ph_2$ afforded similar compounds in which the P–C bond remained intact. The phosphonite complexes were formed via the phosphite adduct in a form of the Michaelis-Arbuzov rearrangement. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ with $P(OR)_3$, however, gave only $(\pi\text{-}C_5H_5)Fe(CO)[P(OR)_3]I$. With PR_3 (R = Et or n-Bu), $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl or I) formed $(\pi\text{-}C_5H_5)Fe(CO)(PR_3)X$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2(PR_3)]^+Cl^-$.

With an excess of $P(OPh)_3$, $(\pi\text{-}C_5H_5)Fe[P(OPh)_3]_2I$ formed[145] $[(\pi\text{-}C_5H_5)\text{–}Fe\{P(OPh)_3\}_3]^+$ whereas the iodide, in the presence of a slight excess of $AgPF_6$ and L, gave $[(\pi\text{-}C_5H_5)Fe\{P(OPh)_3\}_2L]^+$ where L = RCN (R = Me, CH_2Cl, NMe_2, CH_2CONH_2, CH_2CO_2H or Et), C_2H_4, SO_2, $P(OPh)_3$, PEt_3 or CO. Borohydride or LiPh reduction of the triphosphite cation afforded $(C_5H_5R)Fe[P(OPh)_3]_3$ (R = H or Ph, respectively), but borohydride reduction of the ethylene complex (L = C_2H_4) gave the corresponding ethyl, $(\pi\text{-}C_5H_5)Fe[P(OPh)_3]_2Et$. UV irradiation of $(\pi\text{-}C_5H_5)Fe[P(OPh)_3]_2I$ in the presence of diphos afforded $(\pi\text{-}C_5H_5)Fe(diphos)I$ which, when treated with Ag^+ and CO, gave $[(\pi\text{-}C_5H_5)Fe(diphos)(CO)]^+$. Treatment of $(\pi\text{-}C_5H_5)Fe(dmpe)I$ (dmpe = $Me_2PCH_2CH_2PMe_2$) in acetone under N_2 at 0° with $TlBF_4$ gave[146] $[\{(\pi\text{-}C_5H_5)Fe(dmpe)\}_2N_2](BF_4)_2\cdot 2H_2O$, but if the reaction was carried out under argon, the product was $[(\pi\text{-}C_5H_5)Fe(dmpe)(acetone)]^+$; reaction of this acetone adduct with N_2 gave the binuclear nitrogen complex, but reaction of either of these with CO afforded

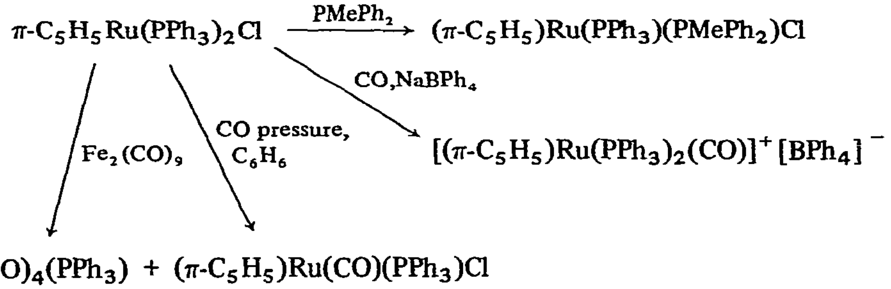
$[(\pi\text{-}C_5H_5)Fe(dmpe)(CO)]^+$. Reduction of $(\pi\text{-}C_5H_5)Fe(dmpe)I$ or $[\{(\pi\text{-}C_5H_5)Fe(dmpe)\}_2N_2]^{2+}$ with $LiAlH_4$ afforded only $(\pi\text{-}C_5H_5)Fe(dmpe)H$, and no NH_3.

A series of π-cyclopentadienylruthenium-phosphine, -arsine and -phosphite complexes have been prepared[147] (Scheme 10). Reaction of $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cl$ with LiMe,



Scheme 10

MeMgI, LiC_6F_5 and $SnCl_2$ gave $(\pi\text{-}C_5H_5)Ru(PPh_3)_2X$ (X = Me, I, C_6F_5 or $SnCl_3$ respectively). With $NaBH_4$, the phosphine chloride afforded $(\pi\text{-}C_5H_5)Ru(PPh_3)_2(H_2BH_2)$, in contrast to $(\pi\text{-}C_5H_5)Ru(CO)_2Cl$ which gave the corresponding hydride[148]. However, the phosphine hydride (X = H) was obtained from the chloride using $LiAlH_4$. Further reactions of $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Cl$ are summarised in Scheme 11. In acetonitrile, the phosphine chloride gave $[(\pi\text{-}C_5H_5)Ru(PPh_3)_2(NCMe)]^+$, and if this was carried out in the presence of $ZnCl_2$ or $HgCl_2$, the cation so formed was stabilised by the anions $[Zn_2Cl_6]^{2-}$ or $[HgCl_3]^-$.



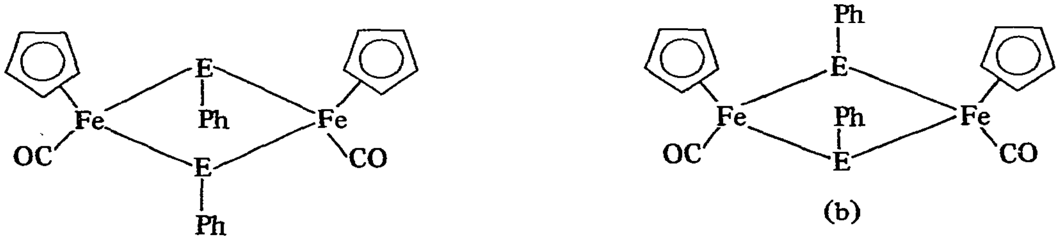
Scheme 11

When PPh_2Cl was treated with $NaFe(CO)_2(\pi\text{-}C_5H_5)$, $(\pi\text{-}C_5H_5)Fe(CO)_2PPh_2$ was formed[149]. This reacted with $Fe_2(CO)_9$ giving $(\pi\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}PPh_2)Fe(CO)_4$ which has been described elsewhere[48], and can also be obtained from the reaction between $NaFe(CO)_2(\pi\text{-}C_5H_5)$ and $Fe(CO)_4(PPh_2Cl)$. As mentioned previously, UV irradiation of the μ-phosphide afforded $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe(CO)_3$. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2(PPh_2)$ with $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ gave $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(PPh_2)]^+Cl^-$.

Treatment of the μ-phosphido-μ-carbonyl species with PR_3 or $P(OR)_3$ (L) gave three types of products: (i) (π-C_5H_5)$Fe_2(CO)_4L(PPh_2)$ (L = PR_3, R = Et or Ph; L = $P(OR)_3$, R = Me, Et, s-Bu, Ph) which had bridging and terminal CO groups; (ii) (π-C_5H_5)-$Fe_2(CO)_5L(PPh_2)$ (L = PEt_3; L = $P(OR)_3$, R as before), and (iii) (π-C_5H_5)$Fe_2(CO)_4L_2$-(PPh_2) (L as for (ii)). Groups (ii) and (iii) had only terminal CO groups and were derivatives of (π-C_5H_5)$Fe(CO)_2$(μ-PPh_2)$Fe(CO)_4$. There was some evidence for the existence of (π-C_5H_5)$Fe(CO)_2$(μ-SR)$Fe(CO)_4$, obtained[149] by treating (π-C_5H_5)$Fe(CO)_2SR$ (R = Me, t-Bu or Ph) with $Fe_2(CO)_9$, but the μ-mercaptides could not be isolated. However, UV irradiation of the reaction mixture when R = t-Bu afforded (π-C_5H_5)Fe(CO)-(μ-SR)(μ-CO)$Fe(CO)_3$; when R = Me or Ph, only $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $Fe_2(CO)_6(SR)_2$ were produced.

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with AsX_3 (X = Cl or Br) in dichloromethane afforded[150] salts of $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2AsCl_2]^-$, and also ($\pi$-$C_5H_5$)$Fe(CO)_2AsX_2$. Similar derivatives could be obtained using SbX_3, but by changing solvents, neutral species only, *e.g.* (π-C_5H_5)$Fe(CO)_2SbX_2$ or $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SbX$ (X = Cl, Br or I), could be prepared; $SbBr_3$, under forcing conditions in acetone, afforded $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_3$-SbBr] $[(SbBr_6)(Me)_2CO]$. With BiX_3 (X = Cl or Br), only (π-C_5H_5)$Fe(CO)_2BiX_2$ could be isolated, and with $Sb(CF_3)_2I$, $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2Sb(CF_3)_2]$ $[Sb(CF_3)_2I_2]$ was formed.

Complexes containing S, Se or Te donor ligands. Silver ion or iodine oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)SPh]_2$ afforded[151] the corresponding cation (cyclopentadienyl, CO and Ph groups mutually *cis*) whose Fe—Fe distance (2.93 Å) was shorter than in the neutral precursor (3.39 Å[152]). In the neutral species the Fe—Fe distance was regarded as essentially non-bonding, whereas, in the cation, it corresponded to a one-electron metal-metal bond. The bridging Fe—S—Fe angle was distorted from 98° in the neutral species to 82° in the cation. Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with E_2Ph_2 (E = Se or Te) afforded[153] (π-C_5H_5)$Fe(CO)_2EPh$ and $[(\pi\text{-}C_5H_5)Fe(CO)EPh]_2$; two isomers of the latter, LXXIVa and LXXIVb, were obtained and isolated with E = Se.

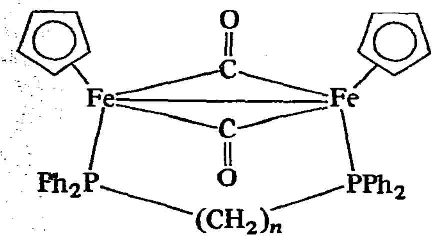


(a)

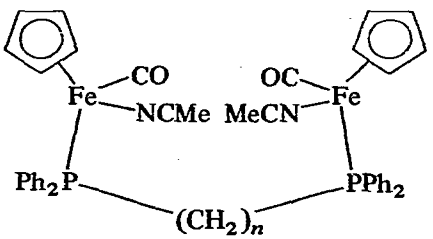
(b)

(LXXIV)

Electrochemical studies. Electrochemical oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ occurred[154] in a two-electron process and could be achieved in acetonitrile, acetone or dichloromethane, using a C or Pt electrode, and a variety of base electrolytes. The products were



(LXXV) (n = 1,2 or 3)



(LXXVI)

$[(\pi\text{-}C_5H_5)Fe(CO)_2(NCMe)]^+$ (using MeCN and NH_4PF_6), $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (using Et_4NCl instead of NH_4PF_6) and $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{acetone})]^+$ (using acetone instead of MeCN). If, after electrolysis in acetone, and using PF_6^- as base electrolyte, SEt_2 was added to the solution, $[(\pi\text{-}C_5H_5)Fe(CO)_2(SEt_2)][PF_6]$ was isolated.

Cyclic voltammograms of LXXV revealed[155] that the one-electron oxidation of these complexes was reversible; the cation, $[LXXV]^+$, was stable in dichloromethane, but disproportionated in MeCN giving $[LXXV]^0$ and $[\{(\pi\text{-}C_5H_5)Fe(CO)(CNMe)\}_2(Ph_2P(CH_2)_nPPh_2]^{2+}$ (LXXVI). $[LXXV]^0$ could be oxidised further giving $[LXXV]^{2+}$ but this decomposed giving $[LXXV]^+$ and $[LXXVI]^{2+}$. The appearance of multiple oxidation processes in these dimeric phosphine complexes, but not in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, is apparently a consequence of the phosphine bridges.

Anodic oxidation of $[(\pi\text{-}C_5H_5)FeS]_4$ afforded[156] solutions of $[(\pi\text{-}C_5H_5)FeS]_4{}^{+,\,2+}$; the monocation was paramagnetic ($S = \frac{1}{2}; g = 1.980$) and the dication was diamagnetic. Cyclic voltammograms of $[(\pi\text{-}C_5H_5)FeS]_4{}^{2+}$ revealed four waves corresponding to the generation of an electrochemical series:

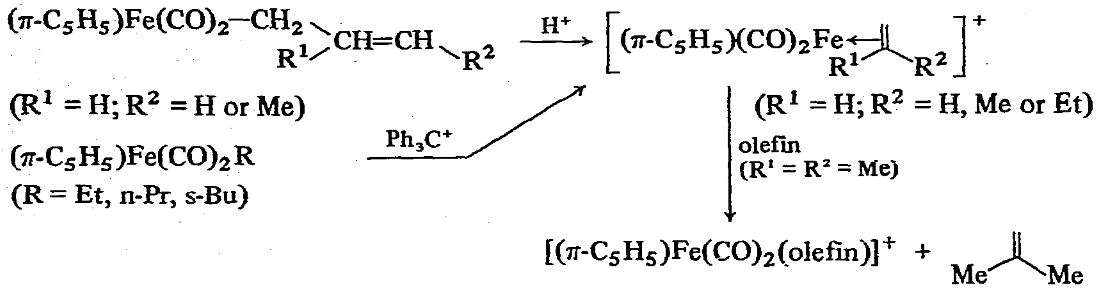
$$[(\pi\text{-}C_5H_5)FeS]_4{}^{3+} \rightleftharpoons [(\pi\text{-}C_5H_5)FeS]_4{}^{2+} \rightleftharpoons [(\pi\text{-}C_5H_5)FeS]_4{}^{+} \rightleftharpoons [(\pi\text{-}C_5H_5)FeS]_4{}^{0} \rightleftharpoons [(\pi\text{-}C_5H_5)FeS]_4{}^{-}$$

Attempts to prepare $[(\pi\text{-}C_5H_5)FeS]_4{}^{3+,-}$ were unsuccessful. The related carbonyl cluster, $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ also existed in an electrochemical series:

$$[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^{2+} \rightleftharpoons [(\pi\text{-}C_5H_5)Fe(CO)]_4{}^{+} \rightleftharpoons [(\pi\text{-}C_5H_5)Fe(CO)]_4{}^{0} \rightleftharpoons [(\pi\text{-}C_5H_5)Fe(CO)]_4{}^{-}.$$

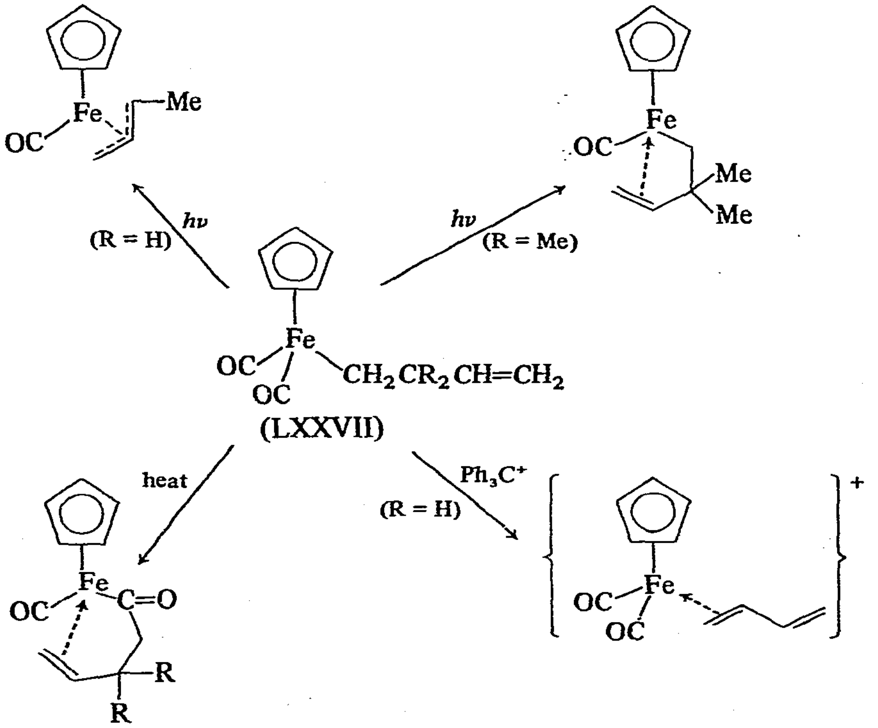
Controlled potential electrolyses of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ afforded the paramagnetic ($S = \frac{1}{2}$) $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^+$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^-$ ($g = 2.013$). Attempts to prepare the dication by electrolysis in MeCN afforded only small amounts of $[(\pi\text{-}C_5H_5)Fe(CO)_2(CNMe)]^+$.

Alkyl, olefin and related species. Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with $H_2C{=}C(Me)CH_2Cl$ gave[157] $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C(Me){=}CH_2$, which, on protonation with HBF_4 in acetic anhydride, afforded the olefin complex $[(\pi\text{-}C_5H_5)Fe(CO)_2\{H_2C{=}CMe_2\}]^+$. Borohydride reduction of this gave $(\pi\text{-}C_5H_5)Fe(CO)_2CMe_3$ and $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2CHMe_2$. A general route to olefin complexes has been developed[158]



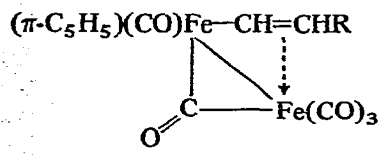
Scheme 12

(Scheme 12); the exchange reaction has been best effected via the isobutene complex cation ($R^1 = R^2 = Me$) using ethylene, cyclohexene, heptene or octene, cyclohexadienes or norbornadiene). With cycloocta-1,5-diene (COD), both $[(\pi\text{-}C_5H_5)Fe(CO)_2(COD)]^+$ and $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(COD)]^{2+}$ were obtained. Reaction of the isobutene complex cation with PPh_3 afforded $[(\pi\text{-}C_5H_5)Fe(CO)_2PPh_3]^+$. These olefin complexes could be obtained in lower yields by oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $AgPF_6$ in dichloromethane in the presence of the olefin. It was possible that $[(\pi\text{-}C_5H_5)Fe(CO)_2]^+$ was an intermediate in these reactions, but oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ in the absence of olefin gave $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$, and in THF, $[(\pi\text{-}C_5H_5)Fe(CO)_2(THF)]^+$ could be isolated from the reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ with $AgBF_4$.

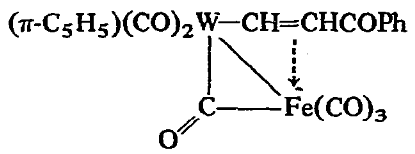


Scheme 13

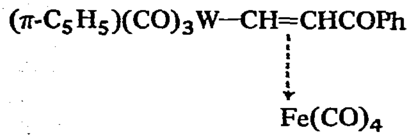
Treatment of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with $H_2C{=}CHCR_2CH_2X$ (R = H or Me: X = Cl or $p\text{-}MeC_6H_4$) or with $p\text{-}MeC_6H_4OSO_2CH_2CHMe_2$ gave[159] $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2CR_2CH{=}CH_2$ (LXXVII) or $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2CHMe_2$; reactions of LXXVII are summarised in Scheme 13. Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with $RCOCH{=}CHCl$ (R = Me or Ph) or $RCH{=}CHCOCl$ (R = H or Ph) gave[160] *trans*-$(\pi\text{-}C_5H_5)Fe(CO)_2CH{=}CHCOR$ and $(\pi\text{-}C_5H_5)Fe(CO)_2COCH{=}CHR$. UV irradiation of the latter gave $(\pi\text{-}C_5H_5)Fe(CO)_2CH{=}CHR$ which reacted with $Fe_2(CO)_9$ giving LXXVIII (where R = *trans*-MeCO, PhCO, H or Ph).



(LXXVIII)

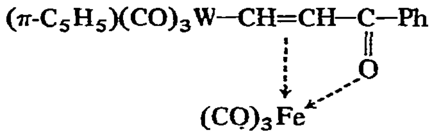


(LXXIX)

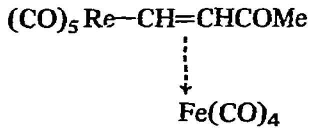


$(\pi\text{-}C_5H_5)(CO)_3W{-}CH{=}CHCOPh \rightarrow Fe(CO)_4$

(LXXX)



(LXXXI)



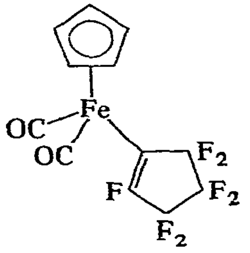
$(CO)_5Re{-}CH{=}CHCOMe \rightarrow Fe(CO)_4$

(LXXXII)

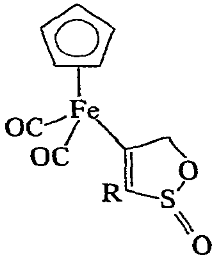
Treatment of $(\pi\text{-}C_5H_5)W(CO)_3CH{=}CHCOPh$ with $Fe_2(CO)_9$ afforded LXXIX, LXXX and LXXXI, and with $Re(CO)_5CH{=}CHCOMe$, LXXXII was obtained. The formation of a metal–iron bond depended on the presence of a double bond adjacent to M. Thus, reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2COCH{=}CHR$ (R = H or Ph) with $Fe_2(CO)_9$ gave the $(\pi\text{-}C_5H_5)Fe(CO)_2$-analog of LXXX, but at 60° in benzene (R = Ph) this was decarbonylated giving LXXVIII (R = Ph). However, UV irradiation of the $(\pi\text{-}C_5H_5)Fe(CO)_2$-analog of LXXX afforded the corresponding analog of LXXXI. The ^1H NMR spectral degeneracy of the butadienyl protons in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2C_4H_4$ could be removed[161] by recording the spectrum in C_6D_6 or in $C_6D_5CD_3$, and at 100 MHz the $AA'BB'$ resonances could be clearly observed confirming the static nature of the complex.

In acetonitrile, $(\pi\text{-}C_5H_5)Fe(CO)_2R$ (R = Me, Et or i-Pr) reacted[162] with PR'_3 giving $(\pi\text{-}C_5H_5)Fe(CO)(PR'_3)COR$. The ^1H NMR spectral studies provided evidence for diastereotopic shielding by an asymmetric iron atom and the kinetic measurements of acyl formation were interpreted in terms of an intermediate which was not specifically solvated, in contrast to previous suggestions[163]. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2R$ (R = Et or i-Pr) with L (PPh_3 or $PPhMe_2$) in the presence of Ph_3C^+ gave $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$.

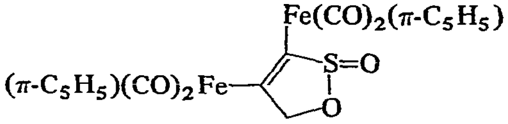
There was no evidence for β-abstraction of H^-. Treatment of $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)Me$ with $P(OR)_3$ (R = Me, n-Bu or Ph) afforded[164] $(\pi\text{-}C_5H_5)Fe(CO)[P(OR)_3]Me$ which gave, in liquid SO_2, $(\pi\text{-}C_5H_5)Fe(CO)[P(OR)_3]SO_2Me$. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2Me$ with PPh_3 in refluxing hydrocarbon solvents gave $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ and $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)Me$ (via decarbonylation of the acyl) but in refluxing dioxane only the acyl was formed. Similar products were obtained with $(\pi\text{-}C_5H_5)Fe(CO)_2Et$. UV irradiation of $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)COR$ (R = Me or Et) gave the corresponding alkyls in good yield contrary to previous reports[165].



(LXXXIII)



(LXXXIV)



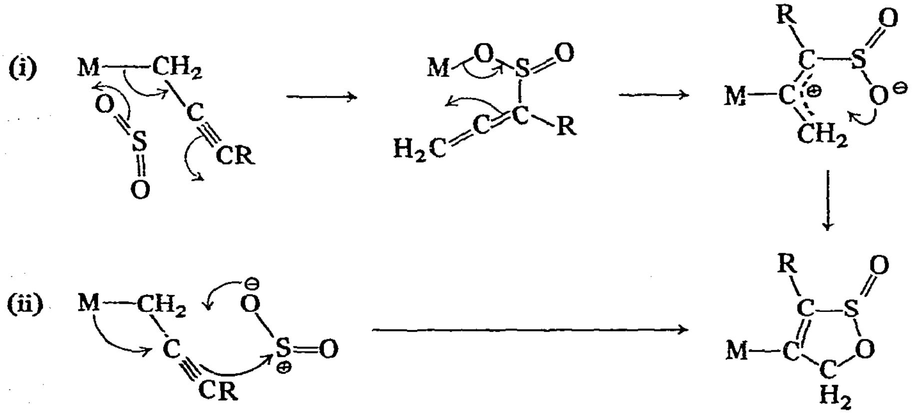
(LXXXV)

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with perfluorocyclopentene gave[166] LXXXIII and treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2(m\text{-}BrC_6F_4)$ with Li(n-Bu) produced[167] $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}(m\text{-}LiC_6F_4)$. Addition to the last of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ afforded $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}[\{m\text{-}(\pi\text{-}C_5H_5Fe(CO)_2\}C_6F_4]$, which was also obtained in the reaction between $1,3\text{-}C_6F_4Br_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$.

The reaction between $(\pi\text{-}C_5H_5)Fe(CO)_2R$ (R = Me, CH_2Ph, $p\text{-}MeC_6H_4$) and SO_2 (as solvent) occurred[168] in two stages; complex + SO_2 → intermediate → $(\pi\text{-}C_5H_5)Fe(CO)_2S(=O)_2R$, and treatment of the product with an excess of KI afforded $K^+O_2SR^-$. This, together with ^1H NMR data, implied that the intermediate contained the Fe–OS(=O)R, rather than the Fe–S(=O)(OR), group. The X-ray crystallographic determination of $(\pi\text{-}C_5Me_5)Fe(CO)_2S(=O)_2CH_2CH{=}CHPh$ confirmed[169] that it had the anticipated structure.

The *erythro* and *threo* isomers of $(\pi\text{-}C_5H_5)Fe(CO)_2CHDCHDCMe_3$ had[170] distinct ^1H NMR spectra. The *threo* complex reacted with SO_2 at –50° giving $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}S(=O)_2CHDCHDCMe_3$ with 80% inversion of configuration. Reaction of the same isomer with $HgCl_2$ at 40° afforded $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and $Me_3CCHDCHDHgCl$ with 90% retention of configuration in the organomercurial, whereas bromination afforded $(\pi\text{-}C_5H_5)Fe(CO)_2Br$ and $Me_3CCHDCHDBr$ with greater than 90% inversion. The reaction with $HgCl_2$ gave a result expected for frontside electrophilic attack of $HgCl_2$ on the Fe–C bond. Treatment of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with (–)Ph(Me)CHCOCl afforded[171] (–)-$(\pi\text{-}C_5H_5)Fe(CO)_2COCH(Me)Ph$ with retention of configuration, and reaction of this with $Rh(PPh_3)_3Cl$ gave (+)-$(\pi\text{-}C_5H_5)Fe(CO)_2CH(Me)Ph$. Insertion of SO_2 gave optically active $(\pi\text{-}C_5H_5)Fe(CO)_2S(=O)_2CH(Me)Ph$ but it was not known whether this occurred with retention or inversion of configuration. Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with SO_2 and optically active PhCH(Me)Br gave the insertion product which was optically inactive.

Sulfur dioxide reacted with $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C{\equiv}CR$ (R = Me or Ph) giving[172] complexes containing sultine rings, $(\pi\text{-}C_5H_5)Fe(CO)_2(C_3H_2RSO_2)$, LXXXIV. With $[(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C]_2$ the closely related LXXXV was formed. Thermolysis of LXXXIV (R = Me) gave the starting material and reaction with HCl afforded $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$, presumably via the starting material. The structure of LXXXIV was confirmed[173] crystallographically. The species $(\pi\text{-}C_5H_5)Fe(CO)_2R$, $R = CH_2CH_2C{\equiv}CMe$, reacted with SO_2 giving the complex with $R = S({=}O)_2CH_2CH_2C{\equiv}CMe$, whereas when $R = C{\equiv}CMe$ no reaction with SO_2 occurred and when $R = CH{=}C{=}CH_2$, $CH{=}C{=}CHMe$ or $CH{=}CH_2$, no tractable compounds could be isolated. It was concluded that sultine formation was a kinetic rather than a thermodynamic effect since $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}S({=}O)_2CH_2C{\equiv}CMe$, obtained from the reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ SO_2 and $MeC{\equiv}CCH_2Br$, did not rearrange to the isomeric sultine (the sulphonate could not be obtained from the reaction of the corresponding propynyl complex and SO_2). It was apparent that the product of reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C{\equiv}CPh$ was the sultine species LXXXIV (R = Ph) and not $(\pi\text{-}C_5H_5)Fe(CO)_2[OS({=}O)C(Ph){=}C{=}CH_2]$[174]. The site for electrophilic attack would appear to be the electron-rich $C{\equiv}C$ bond and two reaction pathways were proposed (Scheme 14)[172,173]; the second was preferred[173]. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2R$ (R = Me or Ph) with SO_3 afforded[175] the sultone species LXXXVI.

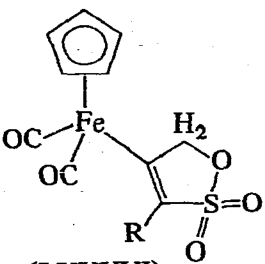


$(M = (\pi\text{-}C_5H_5)Fe(CO)_2)$

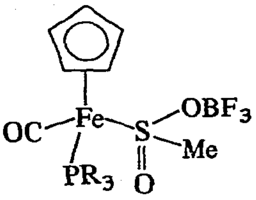
Scheme 14

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$, or of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $C_6F_5SO_2Cl$ afforded[176] $(\pi\text{-}C_5H_5)Fe(CO)_2S({=}O)_2C_6F_5$, and $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$, and a 1/1 product, LXXXVII, was obtained[177] when BF_3 was added to $(\pi\text{-}C_5H_5)Fe(CO)(PR_3)(SO_2Me)$ (R = n-Bu or Ph).

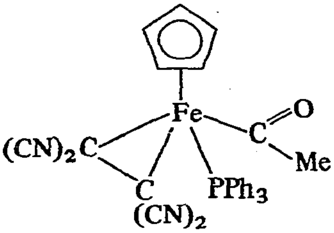
Addition of tetracyanoethylene to $(\pi\text{-}C_5H_5)Fe(CO)LR$ gave[178] $(\pi\text{-}C_5H_5)FeL\text{-}[C_2(CN)_4]COR$, LXXXVIII ($L = PPh_3, PBu_3, P(OPh)_3$; R = Me, Et, n-Pr) but $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2Ph$ afforded $(\pi\text{-}C_5H_5)Fe(CO)L[N{=}C{=}C(CN)C(CN)_2CH_2Ph]$;



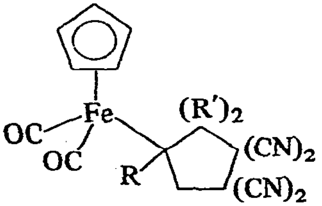
(LXXXVI)



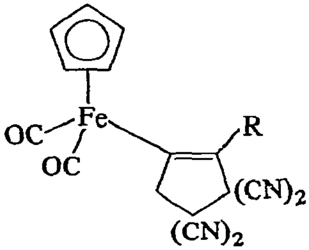
(LXXXVII)



(LXXXVIII)



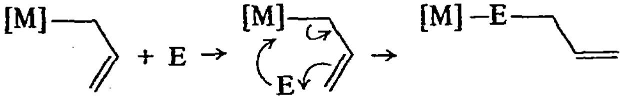
(LXXXIX)



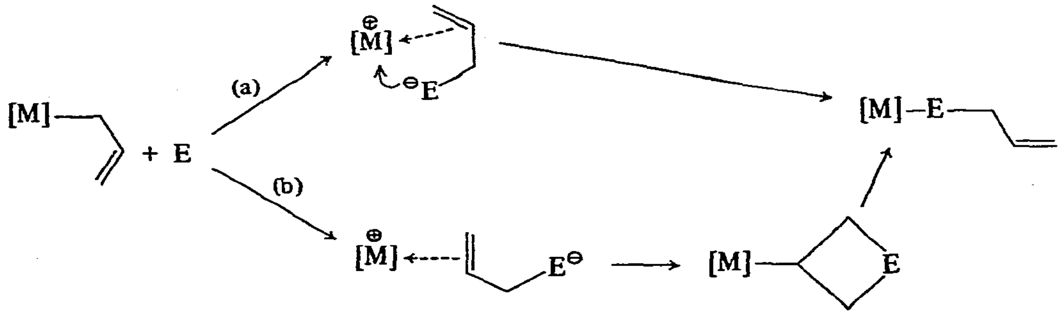
(XC)

similar compounds were obtained on heating LXXXVIII (R = Et). With (π-C_5H_5)-$Fe(CO)_2CH_2CR{=}CR'_2$ (R = Me; R′ = H; R = H, R′ = Me) tetracyanoethylene gave LXXXIX, and (π-C_5H_5)$Fe(CO)_2CH_2C{\equiv}CR$ (R = Me or $CH_2Fe(CO)_2$(π-C_5H_5)) afforded XC.

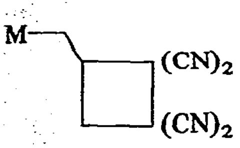
The problem of metal-assisted cycloaddition reactions, involving electrophilic attack by SO_2 or $C_2(CN)_4$ on metal-carbon compounds, has been generalised[179]. The insertion of electrophiles, E, into Fe—C bonds could be either a concerted process:



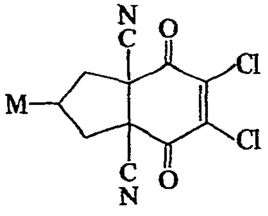
or a stepwise process:



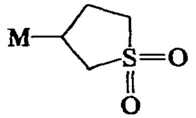
Route (b) in the second process is uncommon in SO_2-insertion reactions, but addition of $C_2(CN)_4$ to (π-C_5H_5)$Fe(CO)_2CH_2CH{=}CH_2$ afforded LXXXIX (R = R′ = H). The possibility that the adducts were derived by 2 + 2 addition, *e.g.* XCI, was excluded spectroscopically. Addition of 2,3-dicyano-5,6-dichloro-*p*-quinone afforded XCII, but no products were obtained with *p*-quinone itself, or with tetrachloro-*p*-quinone.



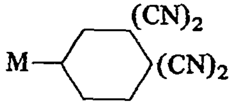
(XCI) (M = $Fe(CO)_2(\pi\text{-}C_5H_5)$)



(XCII)

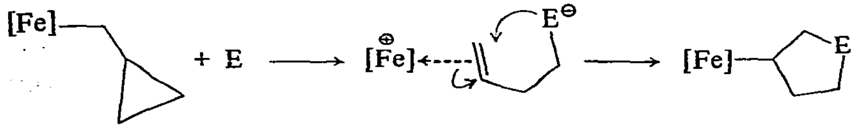


(XCIII)



(XCIV)

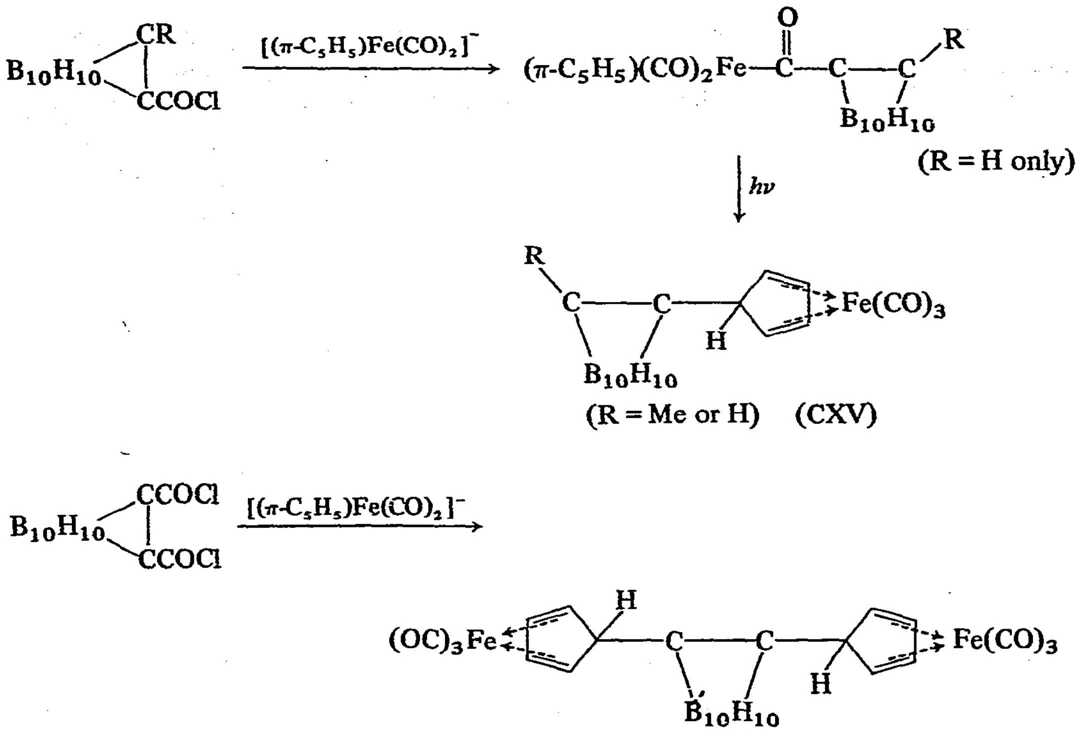
Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with $CH_2CH_2CHCH_2SO_2Ph$ afforded $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2CHCH_2CH_2$, and insertion of SO_2 or $C_2(CN)_4$ into this complex gave XCIII or XCIV; thermolysis of XCIII afforded $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2CH_2CH{=}CH_2$.



Each adduct could be accounted for in terms of a metal-assisted electrophilic attack on the cyclopropyl ring and subsequent collapse of this species by nucleophilic addition to the coordinated olefinic bond.

Complexes containing Group IIIB elements. Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with *o*-carborane carboxylic acid chlorides has afforded[180] a series of cyclopentadiene iron complexes CXV (Scheme 15). Iodination of these compounds released the cyclopentadienyl-substituted *o*-carborane, FeI_2 and CO. Using *m*-carborane carboxylic acid chlorides in place of their *ortho* analogs, species such as $(\pi\text{-}C_5H_5)Fe(CO)_2C({=}O)(m\text{-}B_{10}H_{10}CH)$ were formed, and decarbonylation was effected thermally. Treatment of $o\text{-}B_{10}H_{10}$-$(MeCCCH_2COCl)$ with $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ afforded XCVI, which was decarbonylated (UV) to give XCVII. Some reactions of XCV (R = Me) and related compounds are summarised in Scheme 16.

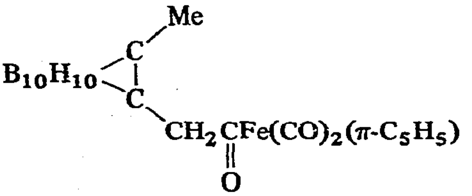
Treatment of $Ru_3(CO)_{12}$ with potassium tripyrazolylborate, followed by halogenation, afforded[181] $[HB(pyz)_3]Ru(CO)_2X$ (pyz = pyrazolyl; X = Cl, Br or I). The species with X = Cl was also obtained by reaction of $[Ru(CO)_3Cl_2]_2$ with $TlHB(pyz)_3$. When $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe(CO)_4I_2$, $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ or $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ reacted with



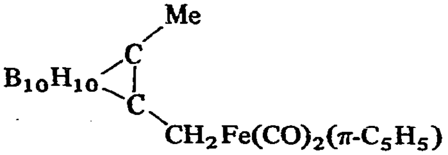
Scheme 15

$KHB(pyz)_3$, the only product of importance was $[HB(pyz)_3]_2Fe$. However, reaction of $Fe(CO)_5$ with $KHB(pyz)_3$ and MeI afforded very small yields of $[HB(pyz)_3]Fe(CO)_2Me$.

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ with 1-Li-10-Me-1,10-$B_8C_2H_8$ gave[182] XCVIII (R = Me) whereas with 1,10-Li_2-1,10-$B_8C_2H_8$, XCVIII (R = H) and XCVIII

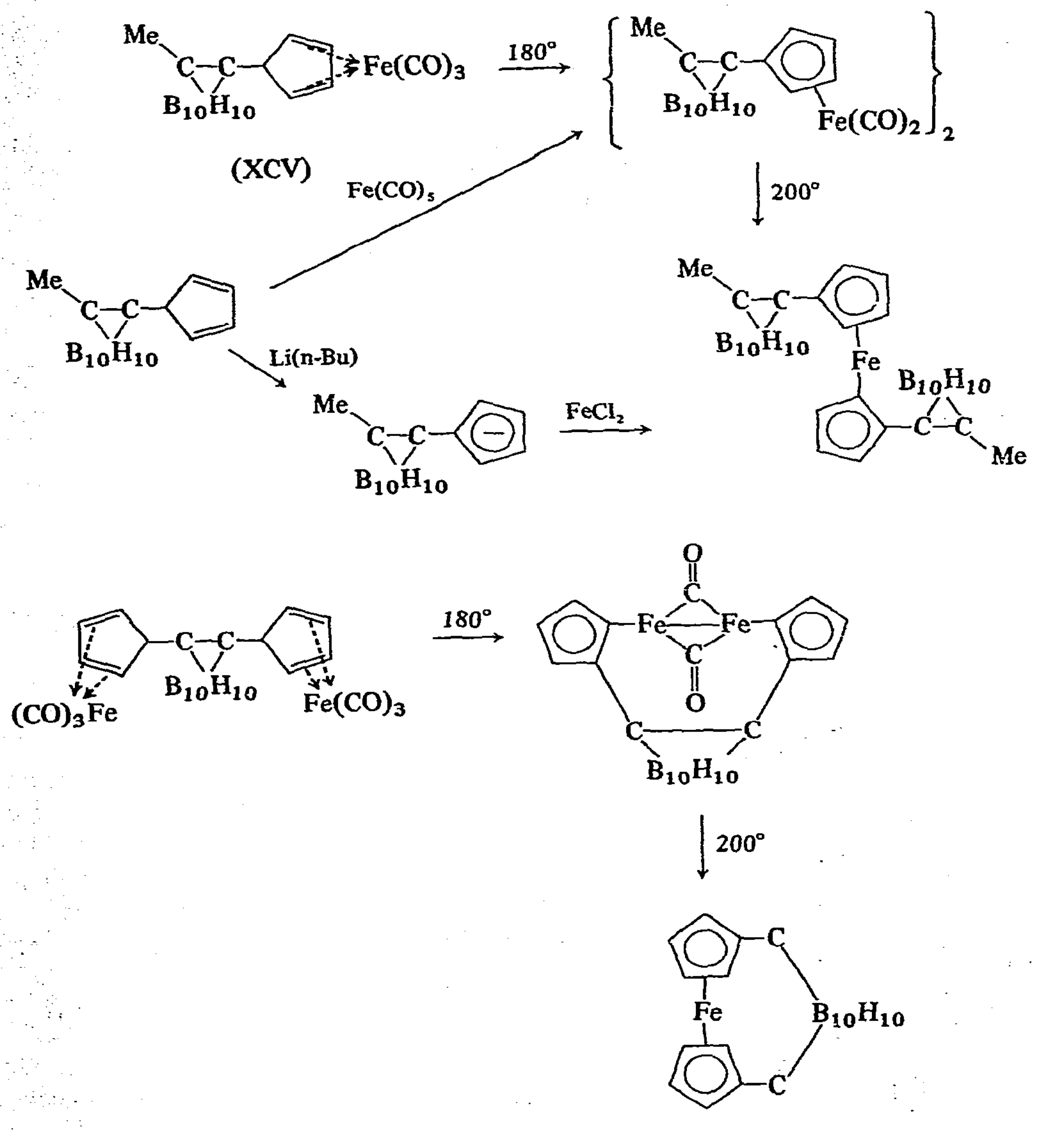


(XCVI)



(XCVII)

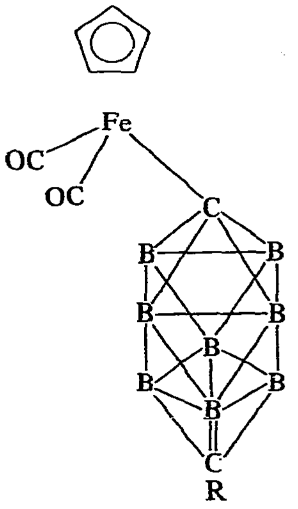
(R = $Fe(CO)_2(\pi\text{-}C_5H_5)$) were produced; treatment of the last with PPh_3 caused replacement of only one CO group. With 1-Li-2-R-1,2-$B_{10}C_2H_{10}$ (R = Me or Ph) $(\pi\text{-}C_5H_5)Fe(CO)_2I$ afforded 1-$[(\pi\text{-}C_5H_5)Fe(CO)_2]$-2-R-1,2-(o-$B_{10}C_2H_{10}$). Reaction of $FeCl_2$ with $[B_{10}H_{12}CH]^-$, and Li(n-Bu) gave[183] $[Fe(B_{10}H_{10}CH)_2]^{3-}$ which could be oxidised or reduced polarographically in a one-electron process. Treatment of $B_{10}H_{12}CNH_3$ with Li(n-Bu) and $FeCl_2$ afforded $Fe(B_{10}H_{10}CNH_3)_2$. Addition of CS_2



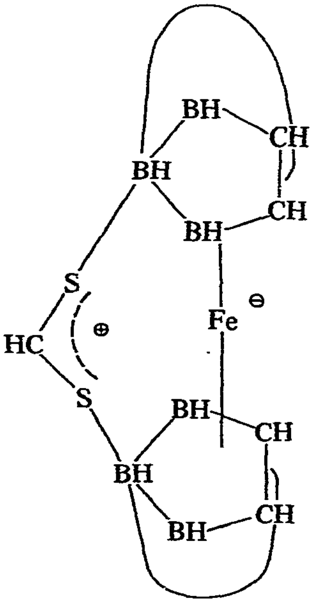
Scheme 16

to $[Fe(1,2\text{-}B_9C_2H_{11})_2]^-$ gave[184] XCIX. By heating $Fe(CO)_5$ with $B_4C_2H_6$, $\pi\text{-}C_2B_4H_6Fe(CO)_3$, C, and $\pi\text{-}C_2B_3H_7Fe(CO)_3$, CI, were formed[185]; C was less stable thermally than CI.

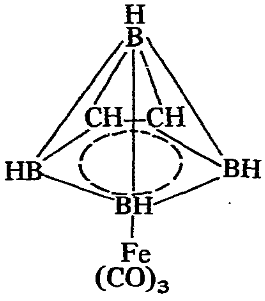
Adducts of $[(\pi\text{-}C_5H_5)M(CO)_2]_2$ (M = Fe or Ru) with $Al(i\text{-}Bu)_3$ were formed[186] in heptane solution. The nature of the products was elucidated by IR spectroscopy and the spectral data were interpreted as in Scheme 17. It was suggested that the formation of the *O*-coordinated bridging CO served as a driving force for the isomerisation of the non-bridged to the bridged compounds.



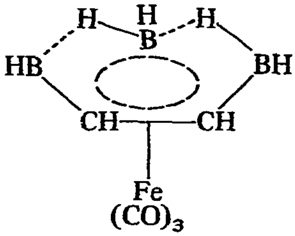
(XCVIII)



(XCIX)

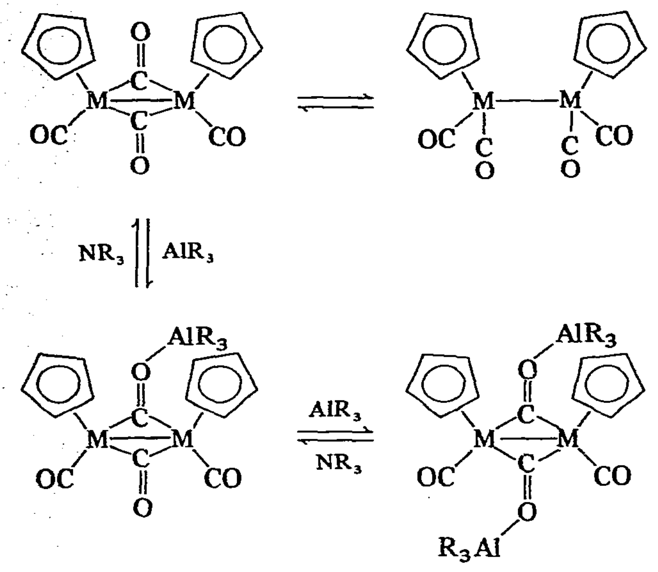


(C)



(CI)

The trimetallic species $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2InX$ was obtained[187] either by direct insertion of InX (X = Cl or Br) into $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ or by treatment of Hg $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with the indium(I) halide.



Scheme 17

Compounds containing Si, Ge or Sn atoms. Reaction of $SiHCl_3$ with $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2]_2$ afforded[188] $(\pi\text{-}C_5H_5)Fe(CO)_2SiCl_3$, $(\pi\text{-}C_5H_5)Fe(CO)H(SiCl_3)_2$, $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ $[(\pi\text{-}C_5H_5)Fe(CO)(SiCl_3)_2]^-$ and $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+[FeCl_4]^-$. The relative yields of these products were dependent on reaction temperature. The hydride was an acid in MeCN (pK_a ca. 2.6) and was stronger in that solvent than $HClO_4$; $[(\pi\text{-}C_5H_5)Fe(CO)(SiCl_3)_2]^-$ was the anion derived from the acidic hydride. Treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2SiCl_3$ with $AgBF_4$ or $AgPF_6$ afforded[189] $(\pi\text{-}C_5H_5)Fe(CO)_2SiF_3$. Polarographic reduction of the $(\pi\text{-}C_5H_5)Fe(CO)_2SiCl_3$ in acetonitrile occurred[190] in two steps, and the processes appeared to correspond to stripping of the Cl^- ions from the Si atom; $(\pi\text{-}C_5H_5)Fe(CO)H(SiCl_3)_2$ could also be polarographically reduced.

Photo-decarbonylation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2GePh_2$ afforded[191] $(\pi\text{-}C_5H_5)Fe(CO)\text{-}(\mu\text{-}CO)(\mu\text{-}GePh_2)Fe(CO)(\pi\text{-}C_5H_5)$, and a similar product was obtained with the diphenylsilyl derivative. The compounds existed as *cis* or *trans* isomers (with respect to the C_5H_5 ring), and these did not rapidly interconvert in solution. It was shown[192] by ^1H NMR spectroscopy that the $\pi\text{-}C_5H_5$ rings in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Ge(C_5H_5)_2$ were stereochemically rigid and did not exchange with the other rings attached to the Ge atom, although these were fluxional.

In exchange reactions between $(\pi\text{-}C_5H_5)Fe(CO)_2SnMe_3$ and $SnMe_3(CF_3)$, the starting materials, $(\pi\text{-}C_5H_5)Fe(CO)_2SnMe_2(CF_3)$, and $SnMe_4$ were recovered[193]. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$ (R = Me, Ph or Cl) with L under UV light gave[194] $(\pi\text{-}C_5H_5)Fe(CO)L(SnR_3)$ (L = PPh_3, $AsPh_3$, $SbPh_3$, f_6fos, $PMePh_2$, PMe_2Ph, $P(CF_3)Ph_2$, $As(CF_3)Ph_2$) and $(\pi\text{-}C_5H_5)FeL_2(SnR_3)$ (R = Me or Ph, L = $PMePh_2$, PMe_2Ph, or $SbPh_3$). The Mössbauer isomer shift for both Fe and Sn became more positive on introduction of L. The IR spectra indicated the presence of rotational isomers in some species. The X-ray crystal structure determination[195] of $(\pi\text{-}C_5H_5)Fe(CO)(f_6fos)SnMe_3$ revealed that there was no significant shortening of the Fe–Sn bond relative to the dicarbonyl analog.

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with $SnPh_nCl_{3-n}$ afforded[196] $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_nCl_{3-n}$ $(n = 1, 2$ or $3)$. The sign of the Mössbauer quadrupole coupling constant for ^{119}Sn in $(\pi\text{-}C_5H_5)Fe(CO)_2SnX_3$ (X = Cl or n-Bu) and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnX_2$ (X = Cl or NCS) was positive[197] except when X = n-Bu when it had a small negative value, and the sign for Fe was positive in all cases. The Mössbauer spectra of the products of insertion reaction of SnX_2 (X = Cl, Br, I, NCS, formate, acetate) with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ were compared[198] with those obtained by the replacement of Cl from $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ and $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$.

Insertion of SO_2 into the Sn–C bond in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnPh_2$ afforded[199] $[(\pi\text{-}C_5H_5)Fe(CO)_2Sn(OSOPh)_2$, also obtained from $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ and $NaSO_2Ph$. Similarly, $(\pi\text{-}C_5H_5)Fe(CO)_2[SnPh(OSOPh)_2]$ was obtained from the $SnPh_3$ derivative or by reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2SnPhCl_2$ with $NaSO_2Ph$ (in the latter reaction $(\pi\text{-}C_5H_5)Fe(CO)_2[SnPh(OH)(OSOPh)]$ was also formed). Treatment of the disulphinate with ethanol gave $(\pi\text{-}C_5H_5)Fe(CO)_2[SnPh(OH)(OSOPh)]$ which further reacted with HCl yielding $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$. It was established[200] that the hydroxo complex was binuclear in the solid state, with a $Sn(OH)_2Sn$ bridging system. While $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2$ did not react with SO_2, the corresponding $SnMe_2$ complex afforded $(\pi\text{-}C_5H_5)Fe(CO)_2SO_2Me$.

Compounds containing Hg atoms. Treating $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ with $Hg(C_6F_5)Br$ afforded[201] $(\pi\text{-}C_5H_5)Fe(CO)_2Hg(C_6F_5)$. This compound was also obtained[202] by reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2HgCl$ with LiC_6F_5. However, in solution, the equilibrium:

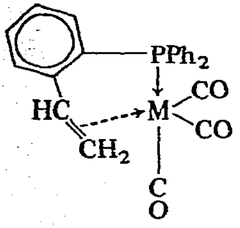
$$Hg[Fe(CO)_2(\pi\text{-}C_5H_5)]_2 + HgX_2 \rightleftharpoons 2\,(\pi\text{-}C_5H_5)Fe(CO)_2HgX$$

lay far to the right when X = halogen, but far to the left when X = organo group. Thus, treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2HgCl$ with Li(n-Bu) afforded $Hg[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$, $Hg(n\text{-}Bu)_2$ and LiCl. It would appear that in this reaction $Li^+[(\pi\text{-}C_5H_5)Fe(CO)_2Hg(n\text{-}Bu)_2]^-$ and $LiFe(CO)_2(\pi\text{-}C_5H_5)$ were formed, and indeed treatment of the latter with $SnPh_3Cl$ afforded $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$.

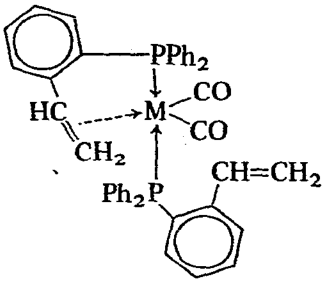
Olefin complexes

Monoolefin species. Photolysis of $Fe(CO)_5$ and C_2H_4 in an argon matrix gave[203] $(C_2H_4)Fe(CO)_4$. With acetylene, an iron complex containing $H_2C{=}CHC{\equiv}CH$ was formed. Reaction of $Fe_2(CO)_9$ with $PhCH(Me)N{=}CHCO_2Et$, Q, afforded[204] low yields of $QFe(CO)_4$ (bonding via C=N system) and $Fe(CO)_5$. Tetramethoxyethylene reacted[205] with $Fe_2(CO)_9$ giving $[C_2(OMe)_4]Fe(CO)_4$.

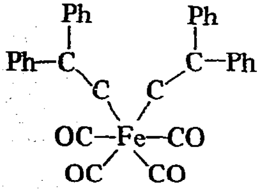
The vinylic tertiary phosphine, $o\text{-}C_6H_4(CH{=}CH_2)(PPh_2)$, SP, reacted with $M_3(CO)_{12}$ (M = Fe or Ru) giving[206] $M(CO)_3SP$, CII, and $M(CO)_2(SP)_2$, CIII. The molecular structure of CIII (M = Fe) was determined crystallographically and the C=C distance (1.45 Å) was significantly longer than that in an uncoordinated vinyl group (1.33 Å).



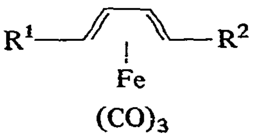
(CII)



(CIII)



(CIV)

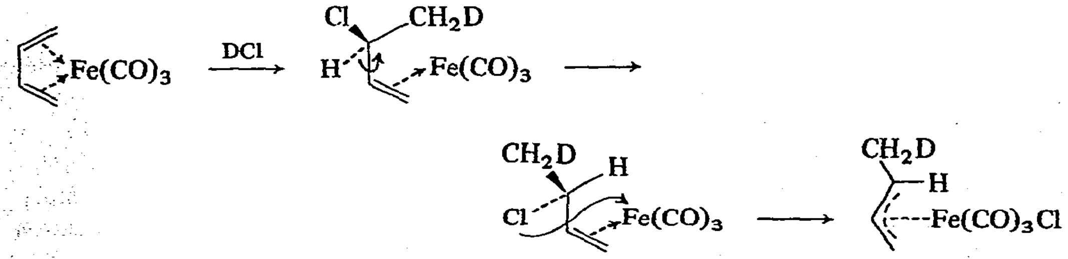


(CV)

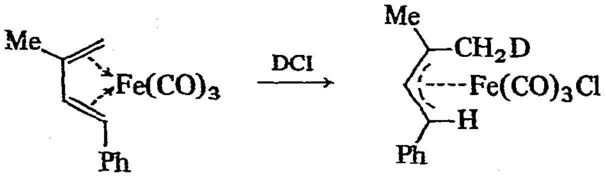
The crystal structure determination[207] of $(Ph_2C{=}C{=}C{=}CPh_2)Fe(CO)_4$, CIV, revealed that the $Ph_2C{-}C{-}C$ bond angle was 151°, that the hydrocarbon chain lay in the equatorial plane of a trigonal bipyramidal molecule, and that the three "C=C" distances were equal (1.34 Å).

Non-cyclic diene complexes. Iron tricarbonyl complexes of a series of optically active monoolefinic acids and diolefinic aldehydes and acids have been resolved[208] and the CD spectra of the complexes compared with those of the free ligands. The pK_a values of CV (R^1 = Me, $R^2 = CO_2H$; R^1 = H, R^2 = p-$NH_2C_6H_4$) have been compared[209] with those of the free olefins and it was established that the $Fe(CO)_3$ group somewhat reduced the electron-withdrawing properties of the diene moiety.

Reaction of diene-$Fe(CO)_3$ with HCl afforded (π-allylic)$Fe(CO)_3Cl$ complexes. It has been proposed[210] that incorporation of the proton (deuteron) occurs at the *syn* methyl group exclusively (Scheme 18). However, it has been shown[211] (Scheme 19) that

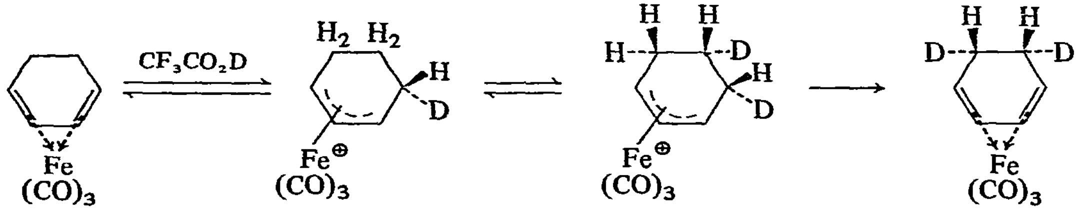


Scheme 18



Scheme 19

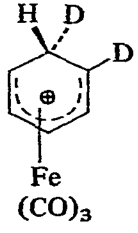
deuteriation occurs exclusively at the *anti*-methyl group. Deuteriation of $C_6H_8Fe(CO)_3$ in CF_3CO_2D afforded a dideuteriated product which was apparently formed reversibly but stereospecifically (Scheme 20). Deprotonation of the dideuteride gave CVI which



(CVI)

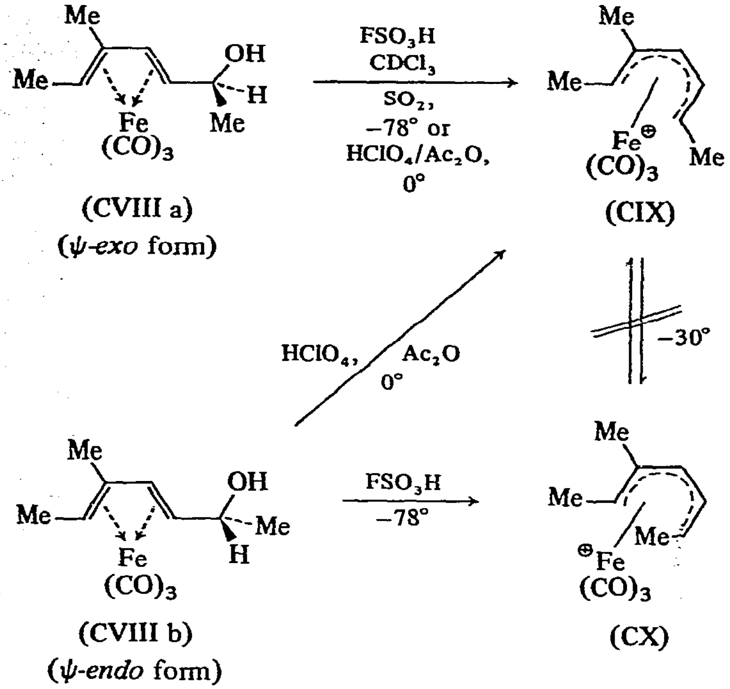
Scheme 20

afforded CVII (Scheme 20) on reaction with Ph_3C^+. These experiments showed that H^- abstraction and H^+ addition occurred from opposite sides of the hydrocarbon ligand, and that protonation was *endo* with respect to the $Fe(CO)_3$ group.



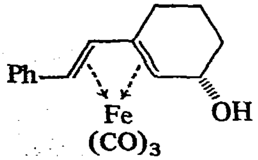
(CVII)

The behaviour of the complexes CVIIIa and CVIIIb in acid media, where π-pentadienyl cations are formed[212,213] is summarised in Scheme 21. There was no interconversion of CIX and CX at –30°, but this occurred at 0°, and quenching either CIX or CX with aqueous $NaHCO_3$ gave only CVIIIa. The solvolysis of CXI gave the *trans* cation, CXII. It would appear that solvolysis of these alcohols CVIII occurs[213] primarily via the *trans*-pentadienyl cation, CXIIIa or b. Protonation of CXIV afforded initially the *trans* cation CXV which isomerised to the *cis* form, CXVI; the equilibrium constant for the CXV $\rightleftharpoons$ CXVI conversion was 3.0 ± 0.3 at 50°, clearly favoring the *trans* isomer. It was

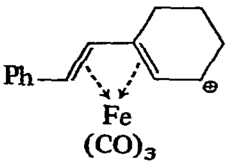


Scheme 21

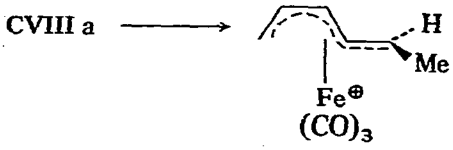
suggested[214] that the solvolyses of CVII and CVIII, and their ester, were very similar to those of the corresponding ferrocenyl derivatives and proceeded via cations which were stabilised by Fe–C hyperconjugation. Nucleophilic attack by primary amines on the pentadienyl cation CXVII afforded[215] the diene complexes CXVIII or CXIX. It was concluded that strongly basic amines (pK_b ca. 3–6) gave products determined by kinetic



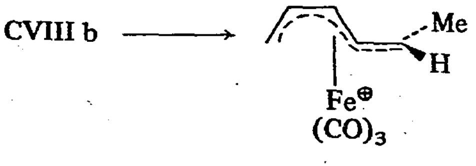
(CXI)



(CXII)

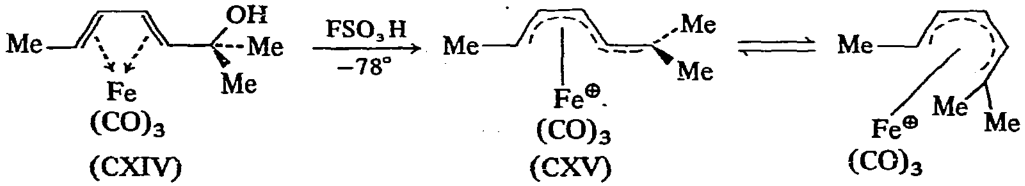


(CXIII a)

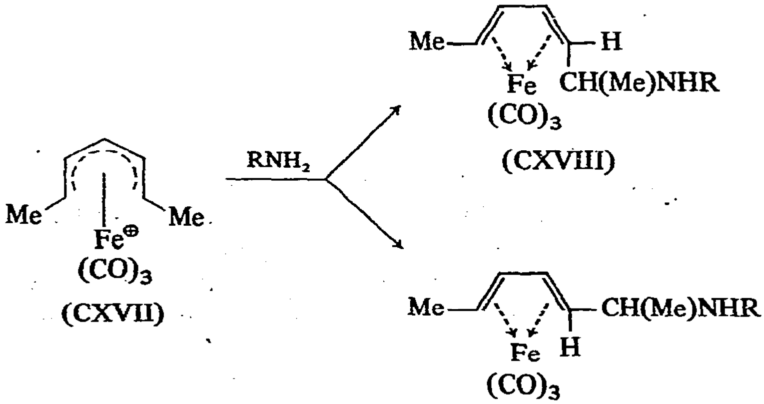


(CXIII b)

control (*e.g.* CXVIII) whereas the weakly basic amines (pK_b 10) gave products determined by thermodynamic control (*e.g.* CXIX); *p*-toluidine (pK_b 8.9) exhibited intermediate behaviour.



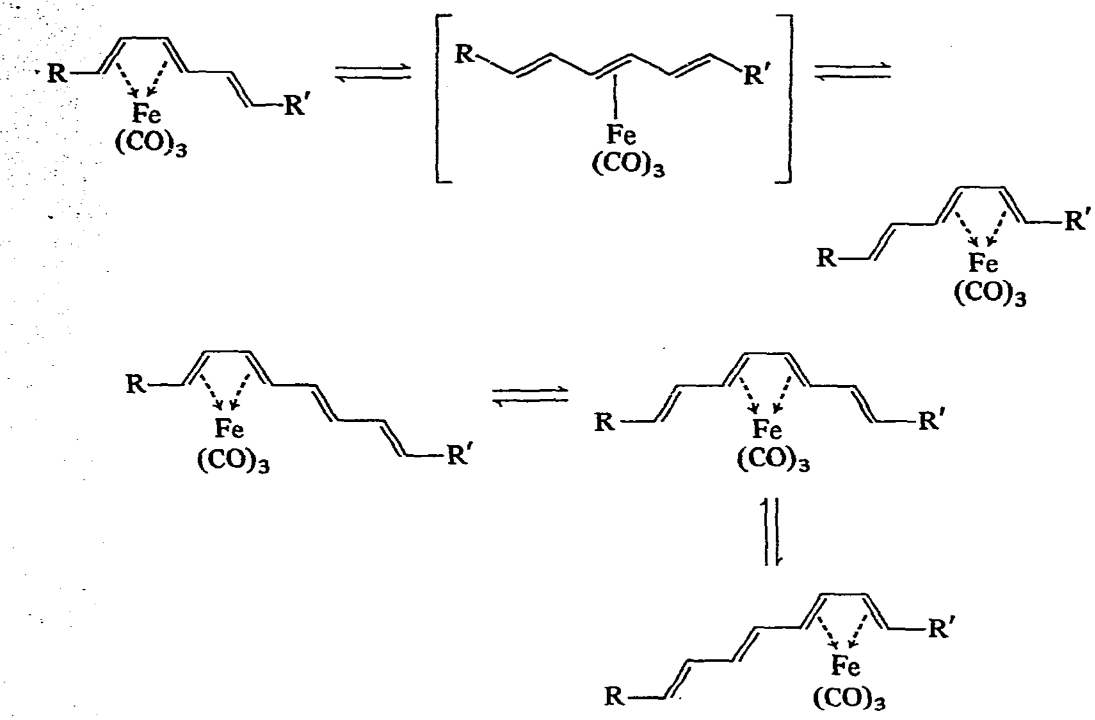
(CXIV) (CXV) (CXVI)



(CXVII) (CXVIII) (CXIX)

In a study of the mechanism of interconversion of shift isomers of iron tricarbonyl complexes of 1,6-disubstituted hexatrienes and 1,8-disubstituted octatetraenes, it was established[216] that the substituents had a relatively small electronic effect on the position of equilibrium (Scheme 22), that the substituents exhibited a somewhat greater effect on the rate of interconversion of isomers, and that, contrary to previous suggestions[217], the movement of $Fe(CO)_3$ from one end to the other of the polyene could occur without obligatory formation of intermediate species.

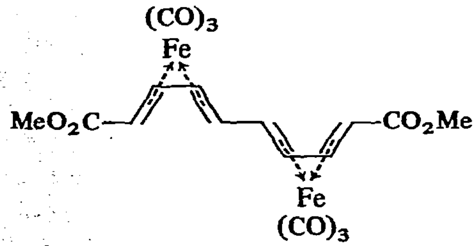
The synthesis and interconversion of CXX and CXXI has been studied[218]. Heating of these caused loss of optical activity by a first order concentration independent process; the rate constants for both isomers were similar. Formation of the *meso* complex was



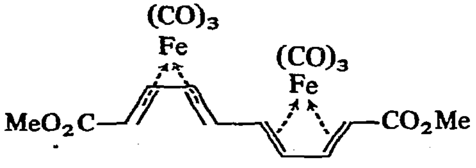
Scheme 22

the major, if not only, pathway to racemisation; the proposed mechanism is shown in Scheme 23.

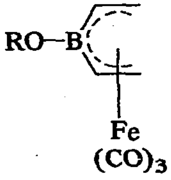
Reaction of $B(OR)(CH{=}CH_2)_2$ with $Fe_2(CO)_9$ afforded[219] initially $B(OR)(CH{=}CH_2)_2$-$Fe(CO)_4$ which, on UV irradiation, rearranged to give CXXII.



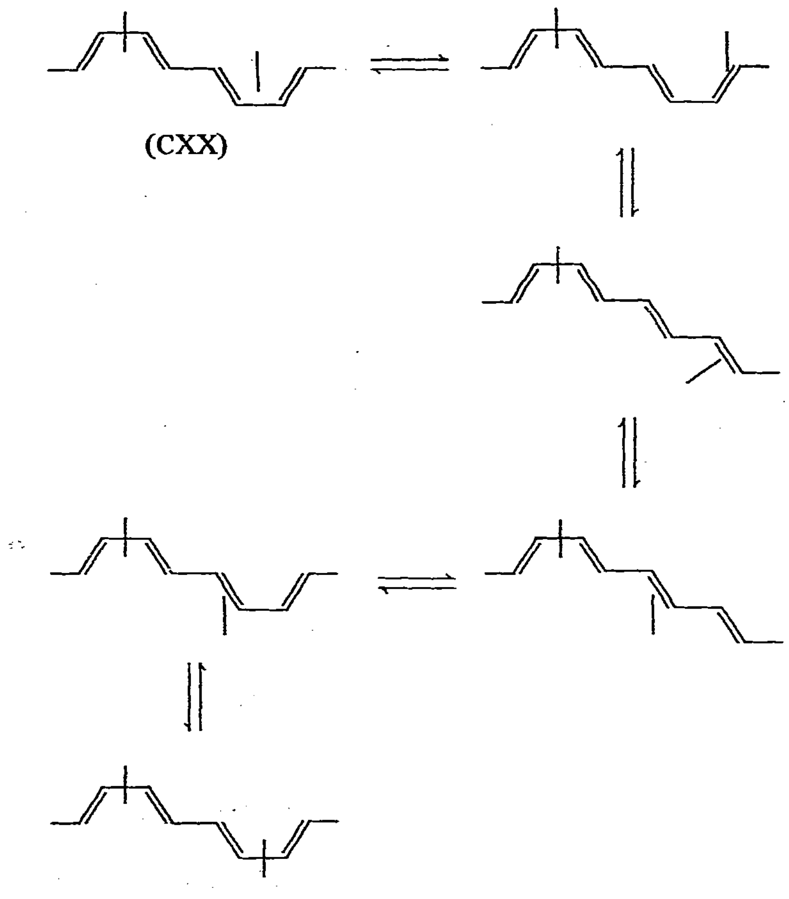
(CXX)



(CXXI)



(CXXII)



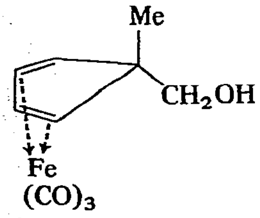
(CXX)

(CXXI)

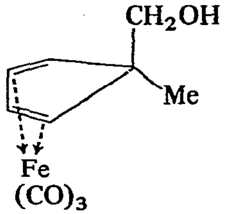
(Fe(CO)$_3$ and CO$_2$Me omitted for clarity)

Scheme 23

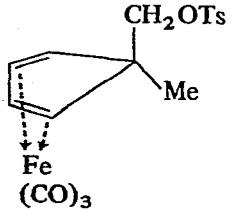
Cyclic diene complexes. Treatment of Fe$_2$(CO)$_9$ with C$_5$H$_4$(Me)CH$_2$OH afforded[220] CXXIII and CXXIV whereas with C$_5$H$_4$(Me)CO$_2$Et only the *endo* carboxylate ester (analogous to CXXIII) was formed. Ring expansion of CXXV, giving CXXVI, occurred[221] when the former was treated with acetic anhydride, HBF$_4$ and water, but the *endo*-tosylate decomposed under similar conditions. The synthesis of (7-norbornadienone)-Fe(CO)$_3$[222], CXXVII, and some of its reactions, are summarised in Scheme 24. CXXVII underwent relatively normal organic reactions associated with the keto group, in which the Fe(CO)$_3$ moiety was retained. Reaction of CXXVIII with Fe$_2$(CO)$_9$ afforded[223] CXXIX. Dechlorination of CXXX by Fe$_2$(CO)$_9$ did not give CXXIX, and only CXXXI was isolated. Reaction of CXXXII with iron carbonyls afforded[224] CXXXIII; one Fe(CO)$_3$ group (adjacent to the ether ring) could be selectively removed under mild Ce^{4+} oxidation, but under more stringent conditions all Fe could be eliminated.



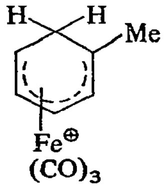
(CXXIII)



(CXXIV)



(CXXV)



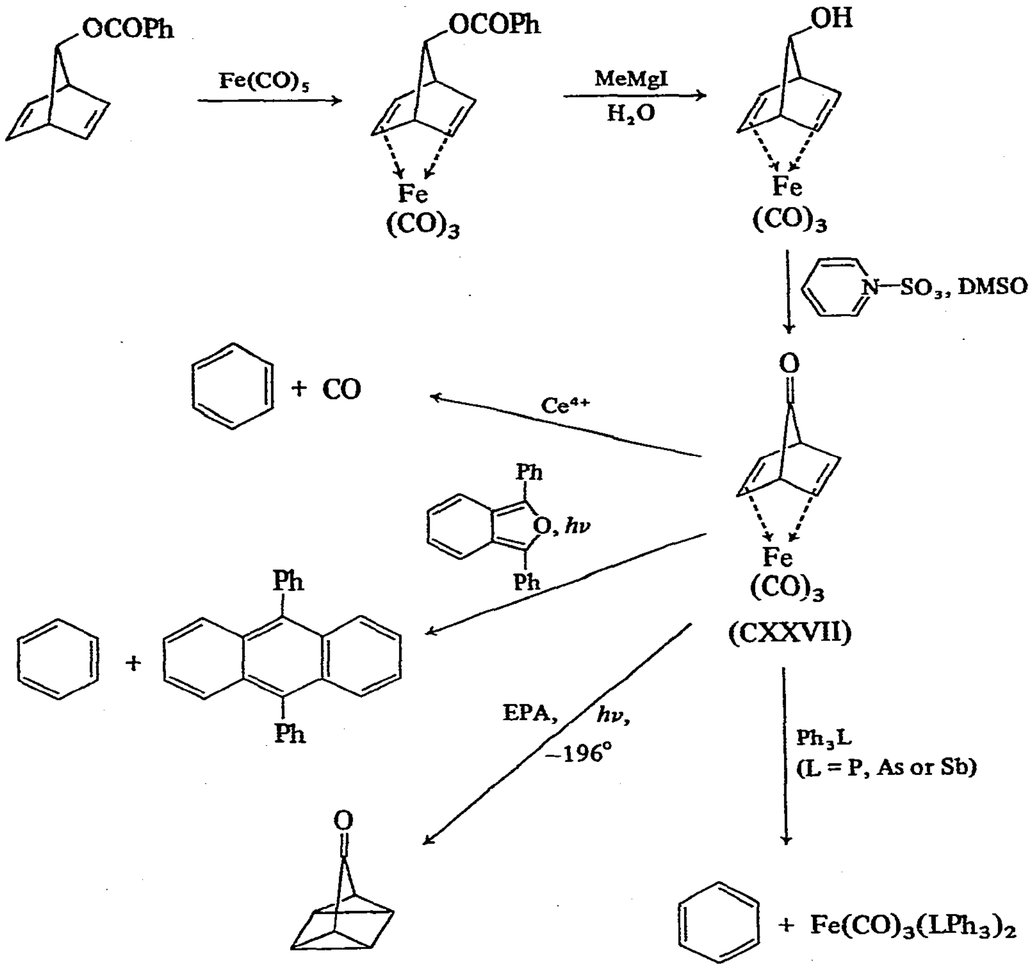
(CXXVI)

Reaction of $[Ru(CO)(C_7H_8)Cl_2]_2$ (C_7H_8 = norbornadiene) with HCl in acetone in the presence of $[PPh_3(CH_2Ph)]^+$ afforded[225] $[Ru(CO)(C_7H_8)Cl_3]^-$ whereas, with $[AsPh_4]^+$ and Cl^-, *cis*-$[Ru(CO)_2Cl_4]^{2-}$ was precipitated. Similar treatment of $[Ru(CS)(PPh_3)_2Cl_2]_2$ gave $[Ru(CS)(PPh_3)_2Cl_3]^-$.

Cyclic tri- and tetra-ene complexes. Use of Eu^{III} shift reagents with $Fe(CO)_3$ complexes of cyclohepta-dienone and -trienone, and with CXXXIV, confirmed[226] their ^1H NMR spectra assignments.

Cycloocta-1,3-diene (C_8H_{12}) reacted[227] over 8 hours with $Ru_3(CO)_{12}$ to form $C_8H_{12}Ru(CO)_3$ and the three isomers of C_8H_{12}, but after 10 hours a second isomer of $C_8H_{12}Ru(CO)_3$, containing a Ru–C σ-bond and a π-allylic group, was isolated. It has been reported[227] that the 1,5-diene gave $C_8H_{12}Ru_3(CO)_n$ (n = 9 or 10). UV irradiation of 1,3-C_8H_{12} with $Os_3(CO)_{12}$ resulted in the formation of pure (1,3-C_8H_{12})$Os(CO)_3$ whereas the 1,5-diene produced a mixture of 1,5- and 1,3-diene complexes. Some reactions of these compounds and their iron analogs are shown in Scheme 25. Hydride abstraction of (1,5-C_8H_{12})$Ru(CO)_3$ afforded[228] a cation which underwent nucleophilic attack by CN^- giving CXXXV. The ring in this complex was extensively folded to permit the four C-atom attachment, and the CN group location implied that nucleophilic attack on the intermediary cation occurred from the *exo* direction.

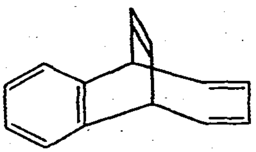
Reaction of cyclooctatetraene oxide, C_8H_8O with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ afforded[229] $C_8H_8OFe_2(CO)_6$ and $(C_7H_8CHO)Fe(CO)_3$. The ^1H NMR spectrum of the former was temperature independent and the compound could be represented as CXXXVIa or b. Its thermolysis, under conditions in which the free epoxide was inert, afforded $C_8H_8Fe(CO)_3$, *trans*-$C_8H_8Fe_2(CO)_6$ and $C_8H_8Fe_2(CO)_5$. The crystal



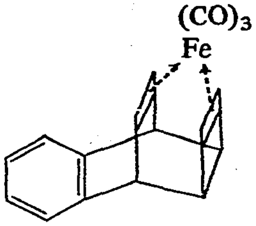
Scheme 24

structure determination[230] of (3-acetyl-1-H-azepine)iron tricarbonyl revealed that the dihedral plane between the *cis*-dienoidal $Fe(CO)_3$ fragment and the remaining NC group was 141°.

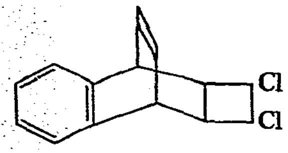
It has been suggested that protonation of $C_8H_8Fe(CO)_3$ afforded initially the cyclooctatrienylium cation stabilised by $Fe(CO)_3$, and that this subsequently underwent



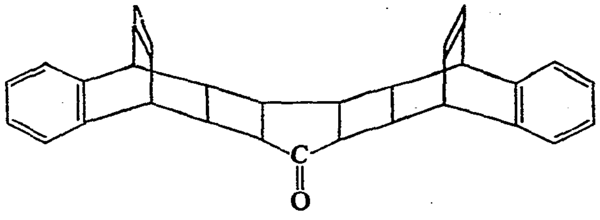
(CXXVIII)



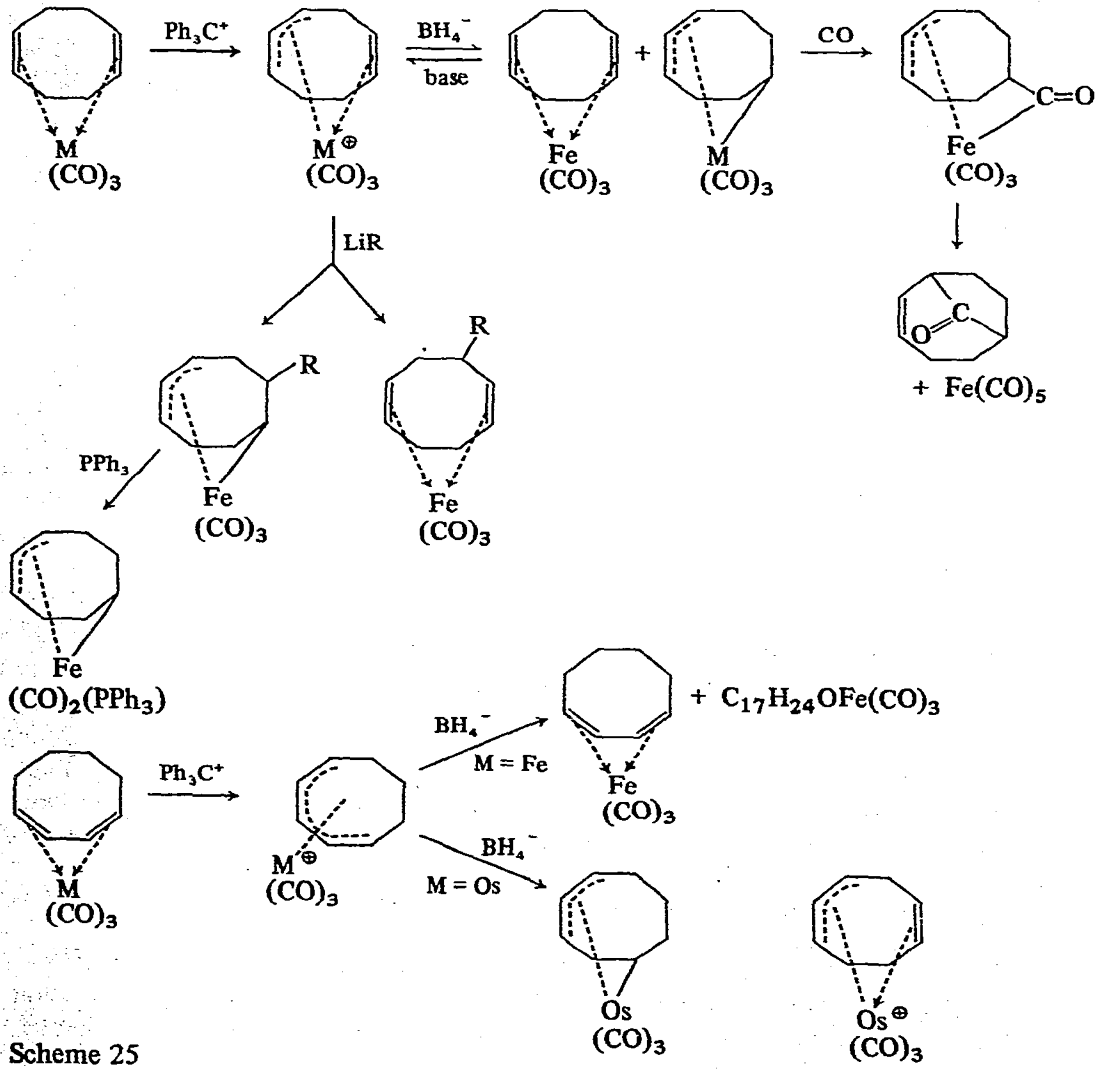
(CXXIX)



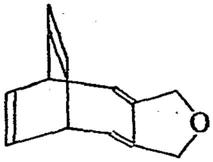
(CXXX)



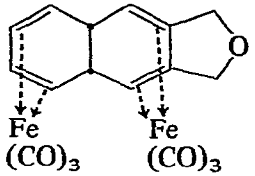
(CXXXI)



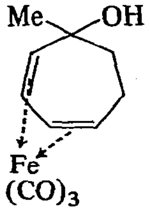
Scheme 25



(CXXXII)

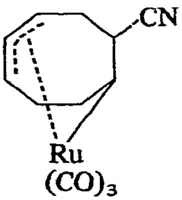


(CXXXIII)

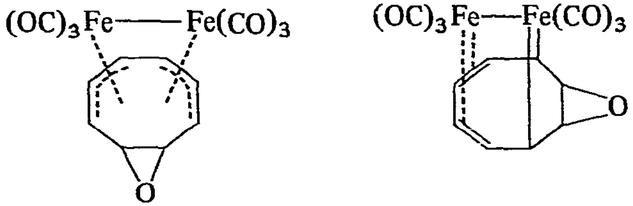


(CXXXIV)

ring closure to give bicyclo[5.1.0] octadienium irontricarbonyl cation. The related Ru and Os complexes behaved differently[231], the initially formed bicyclic cation, CXXXVII, undergoing ring opening (Scheme 26) giving CXXXVIII. In ether/water mixtures, CXXXVII isomerised to CXXXVIII. However, protonation in HBF/acetic anhydride led to the formation of both CXXXVII, and a new isomer, CXXXIX. Treatment of CXXXVIII or CXXXIX with CN$^-$, or $[CH_2NO_2]^-$ afforded CXL. Protonation of $C_8H_8Os(CO)_3$ (α-form) gave two isomers of $[C_8H_9Os(CO)_3]^+$, one of which was isostructural with CXXXVIII/CXXXIX, and the other with CXXXVII. The iron complex did not behave similarly.



(CXXXV)

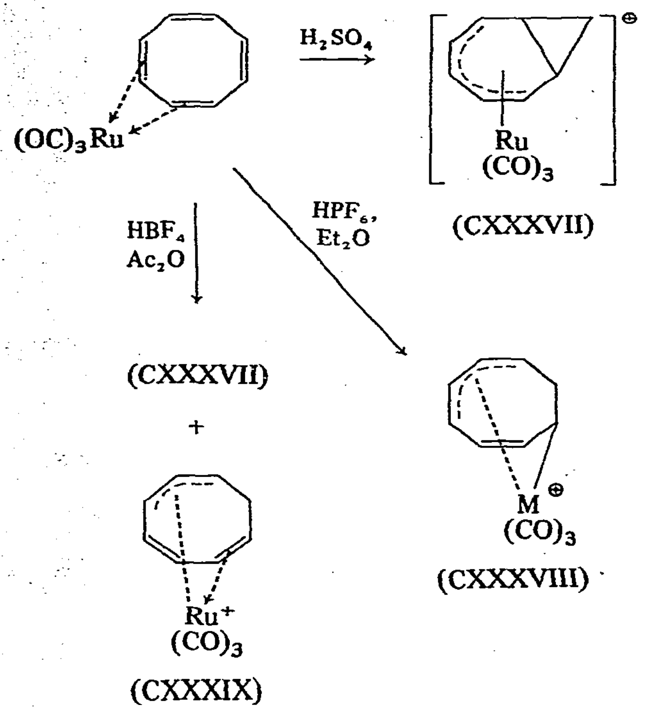


(a) (b)

(CXXXVI)

The electrophilic substitution and addition reactions of $C_8H_8Fe(CO)_3$ are summarised[232] in Scheme 27. The formylation reaction, giving $(C_8H_7CHO)Fe(CO)_3$, would appear to be one of electrophilic substitution whereas acetylation, giving CXLI and CXLII, would appear to be electrophilic addition, which probably reflects the differences in mechanisms of reaction for the two processes. The preference of a metal-stabilised homotropylium intermediate (CXLI) over a cyclooctatrienium species, CXLII, was rationalised in terms of a maximisation of the overlap of the $p\pi$ orbitals in the C_5 fragment and a removal of steric strain in the uncoordinated double bound of the hypothetical CXLIII by re-arrangement. This type of ring closure was a first order process and was regarded[233] as an electrocyclic reaction.

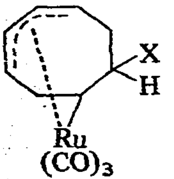
Wideline ^1H NMR spectra studies of $C_8H_8Fe(CO)_3$ in the solid state revealed[234] that molecular motion, involving apparently simultaneous distortion and reorientation of the hydrocarbon ring, occurred. Similar studies of $C_8H_8Fe_2(CO)_5$ revealed that it was rigid in the solid state, as in solution.



Scheme 26

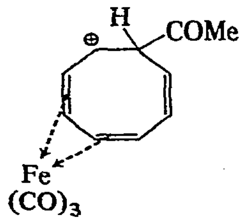
The synthesis of heptafulvene irontricarbonyl, and its monodeuterio analog, has been achieved[235] (Scheme 28). The compound dimerised slowly at room temperature, gave a 1/1 adduct with $MeO_2CC{\equiv}CCO_2Me$, and was protonated in CF_3CO_2H. Alkyl and aryl heptafulvene complexes have also been prepared[236] (Scheme 28). In the species where $R^1 = H$, $R^2 = Ph$, two isomers, determined by the position of the Ph group with respect to the $Fe(CO)_3$ moiety, were detected.

Displacement of cyclooctatetraene from $C_8H_8Fe(CO)_3$ by terpyridyl (terpy) or $MeC(CH_2PPh_2)_3$(triphos) afforded[237] $Fe(CO)_2$(terpy) and $Fe(CO)_2$(triphos), but at lower temperatures, $Fe(CO)_3$(triphos), in which one PPh_2 group was uncoordinated, was obtained. The reactions of $C_8H_8Ru(CO)_3$ with PR_3 were interpreted[238] in terms of a

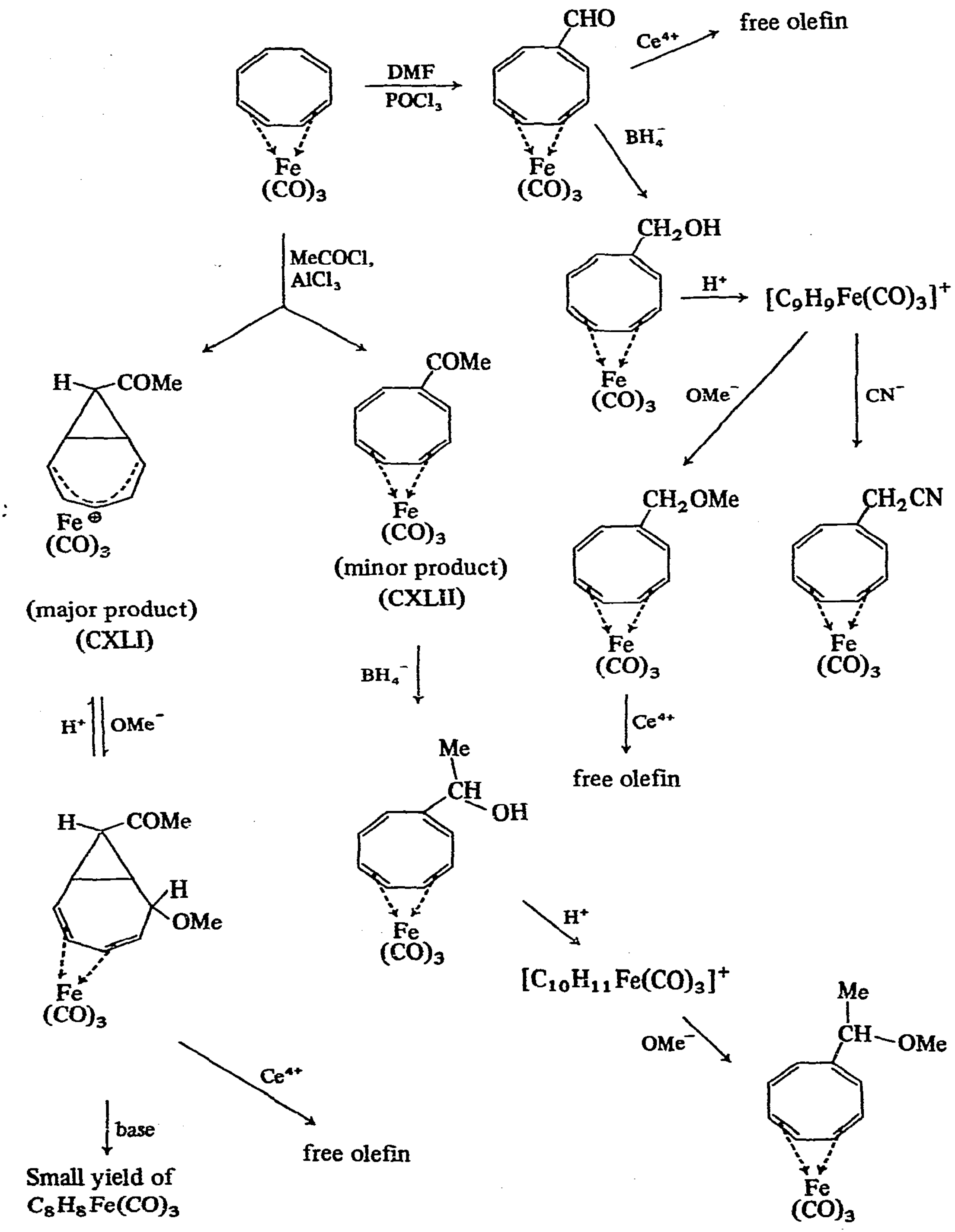


(X = CN or CH_2NO_2)

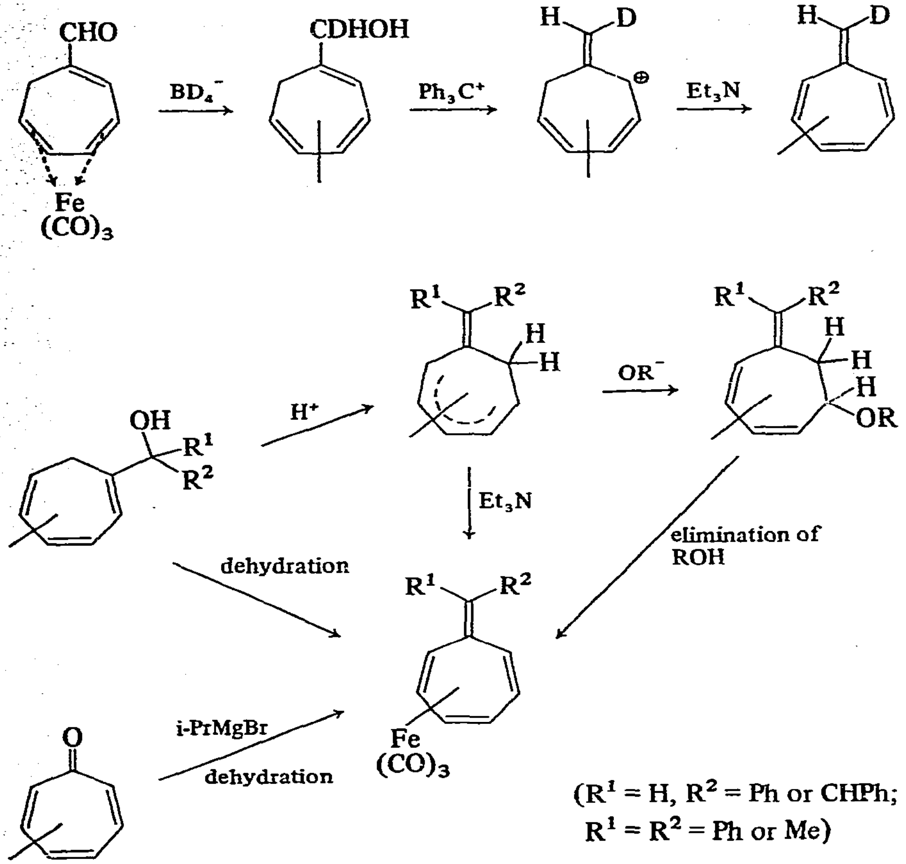
(CXL)



(CXLIII)


CHO
DMF
POCl3
Ce4+
free olefin
BH4-
Fe
(CO)3
MeCOCl,
AlCl3
CH2OH
H+
[C9H9Fe(CO)3]+
OMe-
CN-
H
COMe
Fe⊕
(major product)
(CXLI)
(minor product)
(CXLII)
CH2OMe
CH2CN
BH4-
H+
OMe-
Me
CH
OH
OMe
[C10H11Fe(CO)3]+
free olefin
base
Small yield of C8H8Fe(CO)3

Scheme 27



(R^1 = H, R^2 = Ph or CHPh;
$R^1 = R^2$ = Ph or Me)

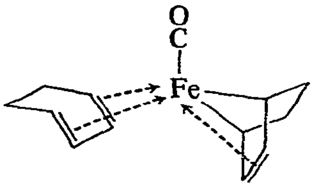
($Fe(CO)_3$ omitted for clarity)

Scheme 28

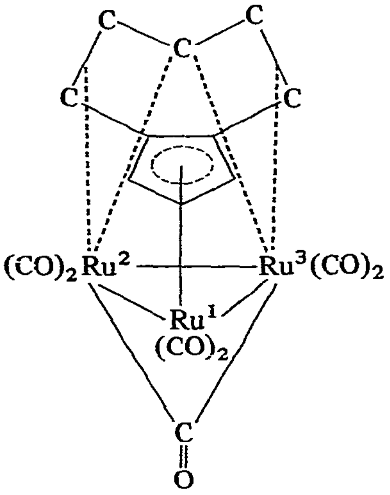
mechanism involving bimolecular attack of PR_3 on the substrate, *e.g.* $C_8H_8Ru(CO)_3 + PR_3 \rightarrow C_8H_8Ru(CO)_3(PR_3) \xrightarrow{+PR_3,\ fast}$ *trans*-$Ru(CO)_3(PR_3)_2 + C_8H_8$.

Bis-olefin complexes. Photolysis of $Fe(CO)_5$ gave $Fe(CO)_4$ which reacted[239] with *trans*-buta-1,3-diene giving (*trans*-C_4H_6)$Fe(CO)_3$, and (*cis*-C_4H_6)$Fe(CO)_3$; with further C_4H_6, eventually $(C_4H_6)_2Fe(CO)$ was formed. Similar products were obtained[240] with isoprene and cyclohexa-1,3-diene. These complexes catalysed the trimerisation of C_4H_6, and, in the presence of PR_3, the formation of cyclooctadiene and vinylcyclohexene. The molecular structure determination of $(C_6H_8)_2Fe(CO)$ revealed[241] that the two rings differed in conformation and in their bonding to Fe by amounts too large to be accounted for by experimental errors. It was suggested that the bonding could be represented as in CXLIV. $(C_4H_6)_2Fe(CO)$ and $(C_4H_6)(C_8H_8)Fe(CO)$ could be prepared[242] by mild carbonylation of the catalytic solution used for butadiene oligomerisation ($FeCl_3$, i-PrMgCl, Et_2O and C_4H_6); $(C_8H_8)_2Fe$ reacted with C_4H_6 and CO to give $(C_4H_6)(C_8H_8)Fe(CO)$.

Azulene and acetylenic derivatives. Azulene reacted with $Ru_3(CO)_{12}$ giving[243] $C_{10}H_8Ru_3(CO)_7$, CXLV, which was unlike $C_{10}H_5Me_3Ru_4(CO)_9$[244]. The azulene ligand had "slipped along the triangular Ru_3 bonding face towards Ru^1", and the bonding of Ru^2 and Ru^3 to the large ring could seem to involve two individual olefin bonds and a three-center MO involving one C atom and Ru^2 and Ru^3. It was suggested that this structure was an intermediate in the formation of $C_{10}H_8R_3Ru_4(CO)_{10}$, the reaction proceeding via displacement of the bridging CO by $Ru(CO)_3$ or a related fragment, with concomitant rearrangement of the Ru–Ru bonds.



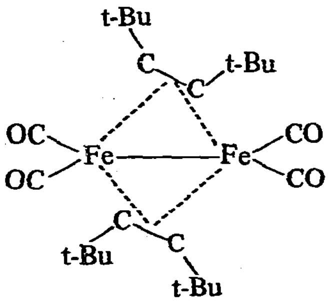
(CXLIV)



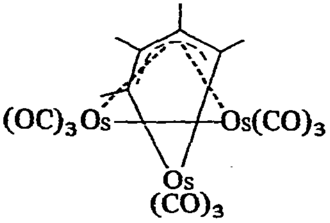
(Ru^2–Ru^1 = Ru^3–Ru^1 = 2.94 Å; Ru^2–Ru^3 = 2.74 Å)

(CXLV)

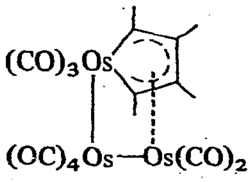
Reaction of $Fe_3(CO)_{12}$ with t-BuC≡C-t-Bu afforded[245] $(C_{10}H_{18})_2Fe_2(CO)_4$, CXLVI. The two Fe atoms and 4 CO groups were in the same basal plane and the two acetylenes



(CXLVI)



(CXLVII)

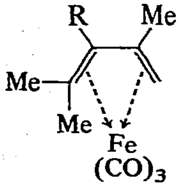


(CXLVIII)

formed a plane normal to this. The Fe-Fe distance was very short (2.22 Å) and the C—C—t-Bu bond angle was 143°. The bonding was consistent with the sharing of two electron pairs, donated by the acetylenes, with each Fe atom. Treatment of $(Ph_2C_2)_2Os_3(CO)_8$ with CO gave[246] $(Ph_2C_2)_2Os_3(CO)_9$ formulated as either CXLVII and CXLVIII. This compound reacted with halogens giving $(Ph_2C_2)_2Os_2(CO)_5X_2$ (X = Cl, Br or I) in which all CO groups were terminal.

Allyl, dienyl, and trimethylenemethane complexes

Allylic complexes. Treatment of the allene compound, $(Me_2C{=}C{=}CMe_2)Fe(CO)_4$ with HBF_4 afforded[247] the π-allylic species $[(\pi\text{-}C_3HMe_4)Fe(CO)_4]^+$. Friedel-Crafts acylation or benzoylation of the allene compound afforded $[\{\pi\text{-}C_3Me_4(COR)\}Fe(CO)_4]^+$ (R = Me or Ph). Deprotonation and loss of a CO group occurred on warming these cations, and CXLIX was formed. The kinetics of substitution of $(\pi\text{-}C_3H_5)Fe(CO)_2(NO)$ by PR_3 (phosphine or phosphite), which afforded $(\pi\text{-}C_3H_5)Fe(CO)(PR_3)(NO)$, have been studied[248], and the rates of substitution were little affected by solvent polarity or by basicity or polarisibility of PR_3, but were altered by steric bulk.



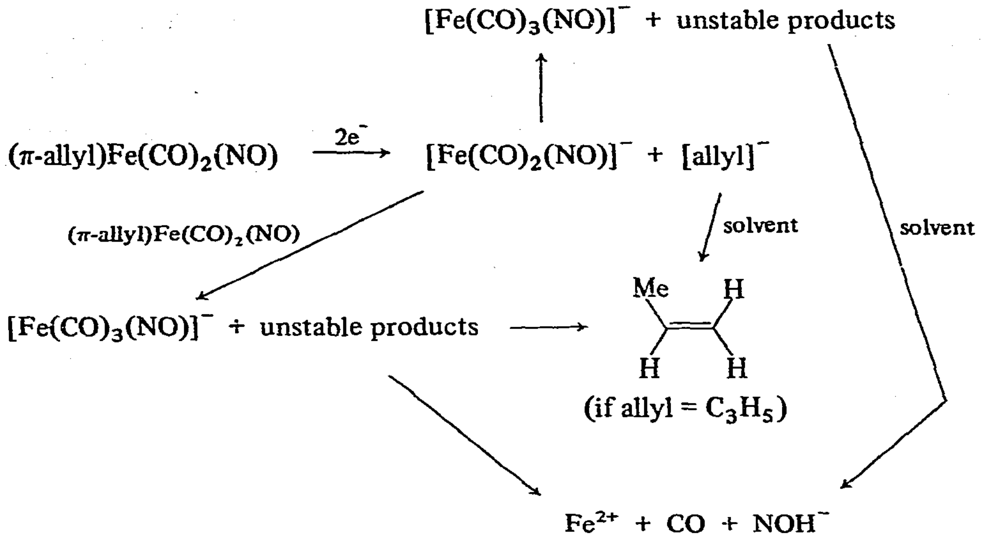
(CXLIX)

(R = H, OCMe or OCPh)

The mass spectral fragmentation pattern of $(\pi\text{-}C_3H_4R)Fe(CO)_3X$ (X = halogen or NO_3) indicated[249] that decomposition proceeded via rupture of Fe—CO and Fe—X bonds primarily, and the ratio of intensities of peaks characterising ions formed in the processes depended on the nature of R and X. In acetonitrile $(\pi\text{-}C_3H_4R)Fe(CO)_2(NO)$ (R = 1- or 2-Me, 1- or 2-Cl, 2-Br or H) exhibited[250] two polarographic reduction waves whose *E*-values depended on the nature and position of R. The principal products of electrochemical reduction were $[Fe(CO)_3(NO)]^-$ and an olefin derived from the allylic group (see Scheme 29). Borohydride reduction of (π-allyl)$Fe(CO)_3(NO)$ also gave $[Fe(CO)_3(NO)]^-$.

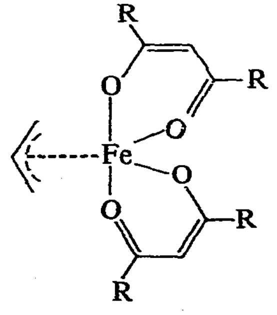
Treatment of $(\pi\text{-}C_3H_5)Fe(CO)_3I$ with β-diketones in the presence of $NHEt_2$ afforded[251] (π-allylic)Fe(β-diketonate)$_2$, CL (R = Me, Ph or thienyl-CF_3). Similar reactions with $[(\pi\text{-}C_5H_5)_2Fe]^+$ and $[(\pi\text{-}C_5H_5)(\pi\text{-}C_6H_6)Fe]^+$ produced $(\pi\text{-}C_5H_5)$Fe(β-diketonate)$_2$ and Fe(β-diketonate)$_3$.

Reaction of $(\pi\text{-}C_4H_7)_2Ru(C_8H_{12})$ (C_8H_{12} = cycloocta-1,5-diene) with L (phosphite or $Me_2PCH_2CH_2PMe_2$) gave[252] $(\pi\text{-}C_4H_7)_2RuL_2$. The ^1H NMR spectra showed that the allylic groups were asymmetrically bound to Ru and that the species probably have structures CLIa or b. Reaction of $(\pi\text{-}C_4H_7)_2RuL_2$ with CO gave $Ru(CO)_3L_2$ (L = $P(OMe)_3$ or $P(OEt)_3$). However, sodium amalgam reduction of $(\pi\text{-}C_4H_7)Ru(CO)_3Br$

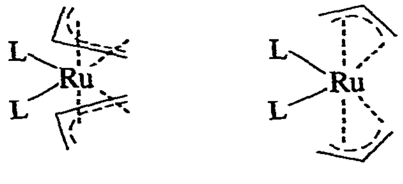


Scheme 29

in the presence of allyl bromide afforded $(\pi\text{-}C_4H_7)_2Ru(CO)_2$, and this could also be obtained[253] by treatment of $[Ru(CO)_3Br_2]_2$ with $SnMe_3(CH_2CH{=}CH_2)$. The behaviour of the ^1H NMR spectrum of this compound over a temperature range indicated that, in addition to a *syn–anti* proton exchange at high temperatures, the allyl groups engaged in a rapid intramolecular rearrangement at room temperature which could be rationalised on the basis of a "twist" mechanism.



(CL)

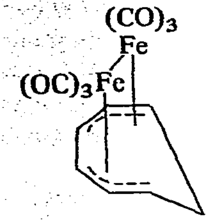


(a) (b)

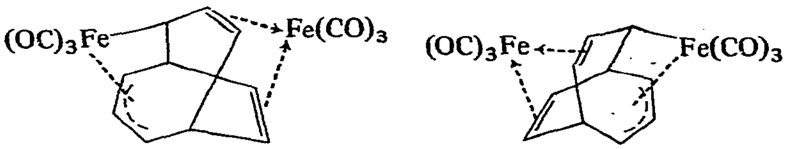
(CLI)

The molecular structure determination[254] of $C_7H_8Fe_2(CO)_6$, CLII, confirmed earlier predictions[255] that it contained two π-allylic groups. The Fe–Fe distance (2.87 Å) was longer than in any similar hydrocarbon $Fe_2(CO)_x$ species. The structure contrasted with those of $C_8H_8Ru_2(CO)_6$ and $C_8H_{10}Fe_2(CO)_6$ where the M–M axes were turned nearly 90° towards the direction of a possible mirror plane analogous to that in $C_7H_8Fe_2(CO)_6$.

Reaction of bullvalene with $Fe_2(CO)_9$ gave[256] CLIIIa and its enantiomer, b, together with $C_4H_4Fe_2(CO)_6$ and six isomers of $C_{10}H_{10}Fe_2(CO)_6$. One of these isomers

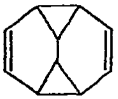


(CLII)

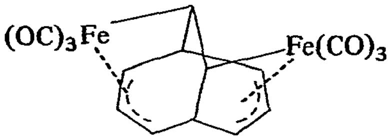


(a) (b)

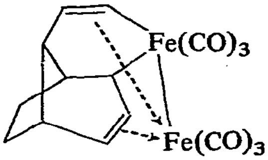
(CLIII)



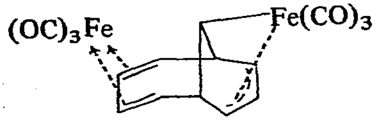
(CLV)



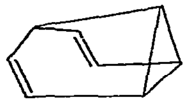
(CLVI)



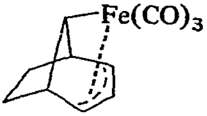
(CLIV)



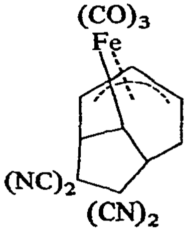
(CLVII)



(CLVIII)



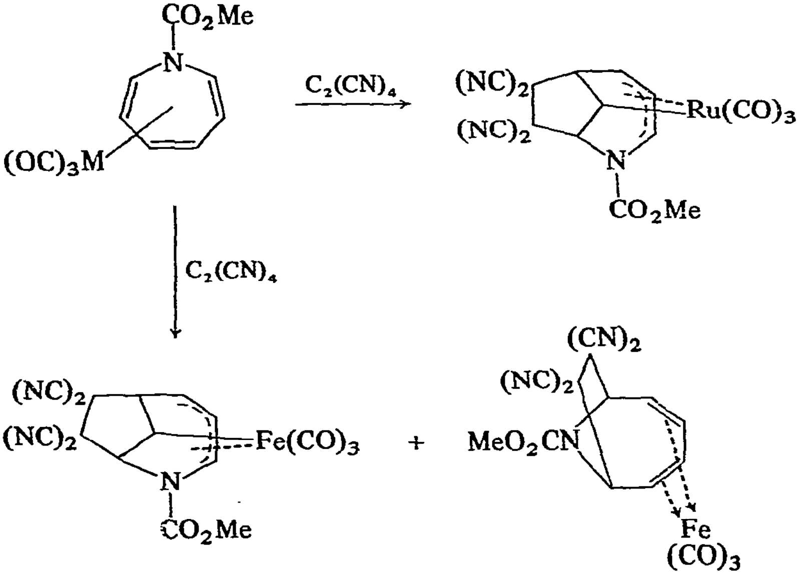
(CLIX)



(CLX)

proved[257] to be CLIV and its enantiomer which mutually interconverted as indicated by ^{1}H NMR spectral studies. The diene, CLV, which has been proposed as an intermediate in the thermally induced conversion of bullvalene into naphthalene, afforded[258] with $Fe_2(CO)_9$ CLVI and its enantiomer (similar to CLIIIb); ^{1}H NMR spectral studies showed that these enantiomers mutually interconverted above 0°. By heating CLVI at 120°, CLVII was formed[259], but this molecule was not an intermediate in the thermally induced isomerisation of (bicyclo[4.2.2] deca-2,4,7,9-tetraene)$[Fe(CO)_3]_2$ to (9,10-dihydronaphthalene)$[Fe(CO)_3]_2$. Treatment of CLVIII with $Fe_2(CO)_9$ gave[260] CLIX.

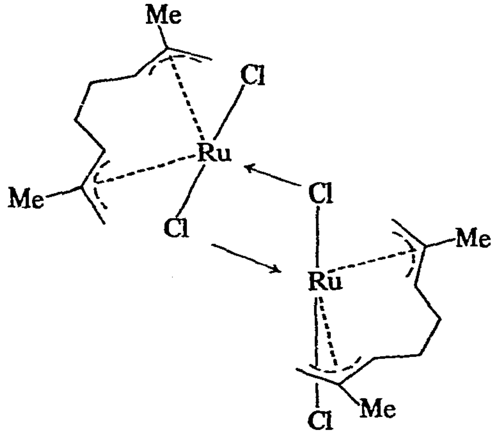
Reaction of $(CF_3)_2CO$, $(NC)_2C{=}C(CF_3)_2$ or $(F_3C)(NC)C{=}C(CN)(CF_3)$ with cycloheptatriene irontricarbonyl gave[261] 1/1 adducts, and the structure of the tetracyanoethylene adduct, CLX, has been determined[262]. Similar 1,3 addition products were obtained with azepine iron- or ruthenium-carbonyls, but with the Fe species a 1,6 addition product was also discovered (Scheme 30).



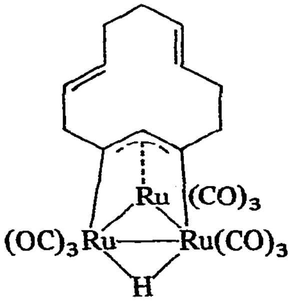
(minor) (major)

Scheme 30

The crystal structure elucidation of the complex formed by reaction[263] of $RuCl_3$ with isoprene revealed[264] that the molecule, CLXI, was dimeric, with chlorine bridges.



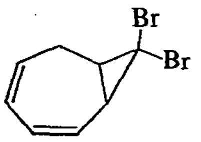
(CLXI)



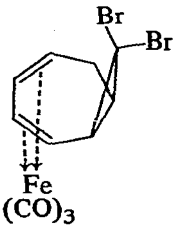
(CLXII)

The coordination geometry around the metal atoms was trigonal bipyramidal and two equatorial positions were occupied by the terminal allylic groups. Reaction of $Ru_3(CO)_{12}$ with cyclododecatriene afforded[265] four complexes, one of which was identified crystallographically[266] as CLXII, $Ru_3(CO)_9H(C_{12}H_{15})$; the non-bridged Ru–Ru distances were 2.78 Å and the hydride-bridged Ru–Ru bond length was 2.93 Å.

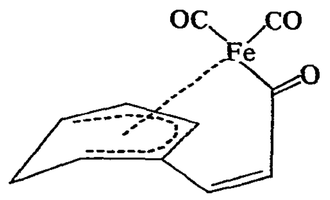
Dienyl complexes. Reaction of the diene CLXIII with $Fe_3(CO)_{12}$ gave[267] CLXIV which reacted with LiMe giving CLXV. Kinetic studies have been made[268] of the reactions between cationic cyclic dienyl complexes of Fe and Os carbonyl derivatives and β-diketones, in which the neutral diene species were formed. There appeared to be a rapid pre-equilibrium dissociation of the β-diketone to yield a reactive carbanion which then attacked directly the coordinated dienyl group in a rapid, rate-determining, step. The order of reactivity towards the β-diketone (acetylacetone or dimedone) was (most reactive first)



(CLXIII)



(CLXIV)



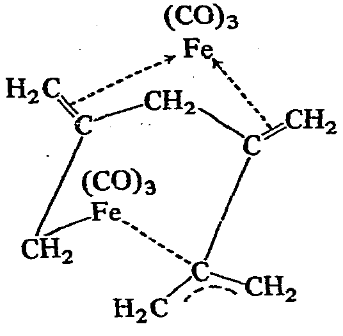
(CLXV)

$$\begin{aligned}&[C_6H_7Os(CO)_3]^+ \geqslant [C_6H_7Fe(CO)_3]^+ > [C_6H_7Fe(CO)_2(PPh_3)]^+\\&\quad > [C_7H_9Fe(CO)_3]^+ > [(C_6H_6OMe)Fe(CO)_3]^+\\&\quad \ggg C_7H_9Fe(CO)_2I,\ C_7H_9Fe(CO)_2CN,\ (C_6H_6OMe)Fe(CO)_2I.\end{aligned}$$

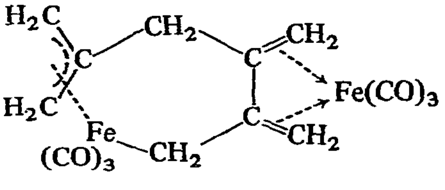
The similarities in rates for the Fe and Os complexes argued against a common mechanism in which the metal was directly involved in the rate-controlling process. There was a two-fold decrease in rate on replacing CO by PPh_3 which was consistent with the increased electron-donating properties of PPh_3 relative to CO and the consequential reduction of the residual positive charge on the dienyl ring (it was therefore less susceptible to nucleophilic attack). Addition at the cycloheptadienyl ring was slower than at the cyclohexadienyl ring, possibly because of steric factors associated with methylene groups. The neutral dienyl complexes were hardly attacked indicating that the positive charge was essential for reactivity.

The ^1H NMR spectral behaviour of $[C_7H_7Fe(CO)_3]^+$ indicated[269] that the molecule was fluxional at $-50 \pm 10°$. Treatment of cycloheptatriene irontricarbonyl with Li(n-Bu) afforded[270] the non-rigid anion $[C_7H_7Fe(CO)_3]^-$ which is isoelectronic with $C_7H_7Co(CO)_3$[271].

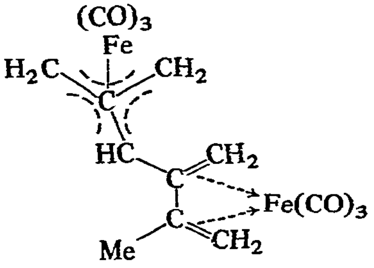
Allene complexes. Allene treated at 85-90° with $Fe_3(CO)_{12}$ afforded[272] CLXVI, $C_9H_{12}Fe_2(CO)_6$, which could also be obtained from the allene dimer complex, $C_6H_8Fe_2(CO)_6$ and allene. At 120° the reaction afforded CLXVII which could be obtained from CLXVI by thermal isomerisation and has been described previously[273].



(CLXVI)



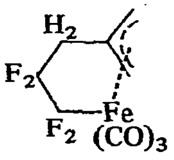
(CLXVII)



(CLXVIII)

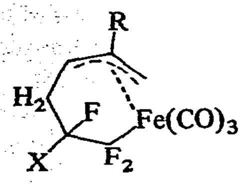
The third complex, CLXVIII was obtained by a thermal isomerisation of CLXVI or CLXVII. The structure of CLXVII was determined crystallographically[272].

Trimethylenemethane complexes. UV irradiation of trimethylenemethane irontricarbonyl with C_2F_4 afforded[274] CLXIX. With C_2F_3X (X = F or CF_3), $C_4H_5RFe(CO)_3$ (R = H or Me) gave CLXX. Cinnamaldehyde complexes of $Fe(CO)_3$ or $Fe(CO)_4$ reacted

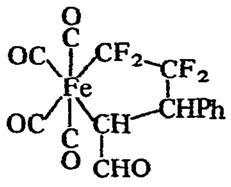


(CLXIX)

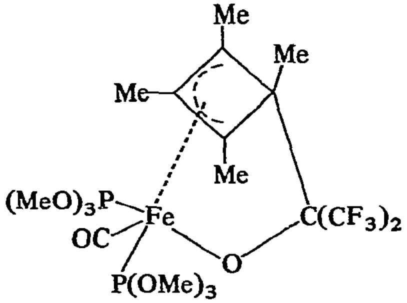
with C_2F_4 giving CLXXI and $(\pi\text{-}C_4Me_4)Fe(CO)_2OC(CF_3)_2$ gave with $P(OMe)_3$ CLXXII. In the last case, the action of $P(OMe)_3$ led to a linking of a C atom of the coordinated $(CF_3)_2CO$ to the C_4 ring.



(CLXX)



(CLXXI)



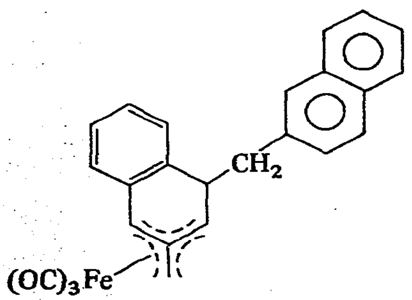
(CLXXII)

Reaction of 1- or 2-bromomethylnaphthalene with $Fe_2(CO)_9$ gave[275] CLXXIII and CLXXIV.

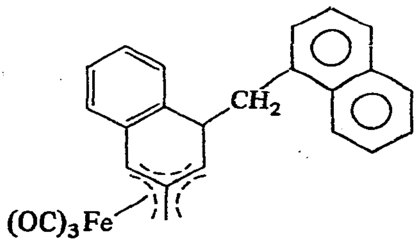
Arene and related complexes

Treatment of bis-π-indenyl iron with BF_3OEt_2 gave[276] CLXXV which could be hydrogenated to give CLXXVI. The latter could be prepared also by treatment of $(\pi\text{-}C_5H_3C_6H_8)_2Fe$ with $AlCl_3$ and indane.

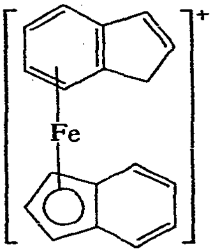
Improved syntheses of $[(\pi\text{-}C_6H_6)_2Fe]^{2+}$ and related species have been developed[277]. Reduction of these complexes with LiR afforded[278] initially, for example, $[(\pi\text{-}C_6H_6)(C_6H_6R)Fe]^+$, and $(C_6H_6R)_2Fe$. From these complexes, aromatic hydrocarbons were recovered on oxidation with $KMnO_4$ or Ce^{4+}, or on heating (Scheme 31).



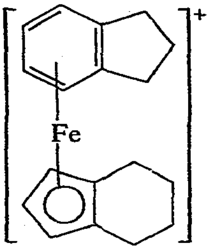
(CLXXIII)



(CLXXIV)

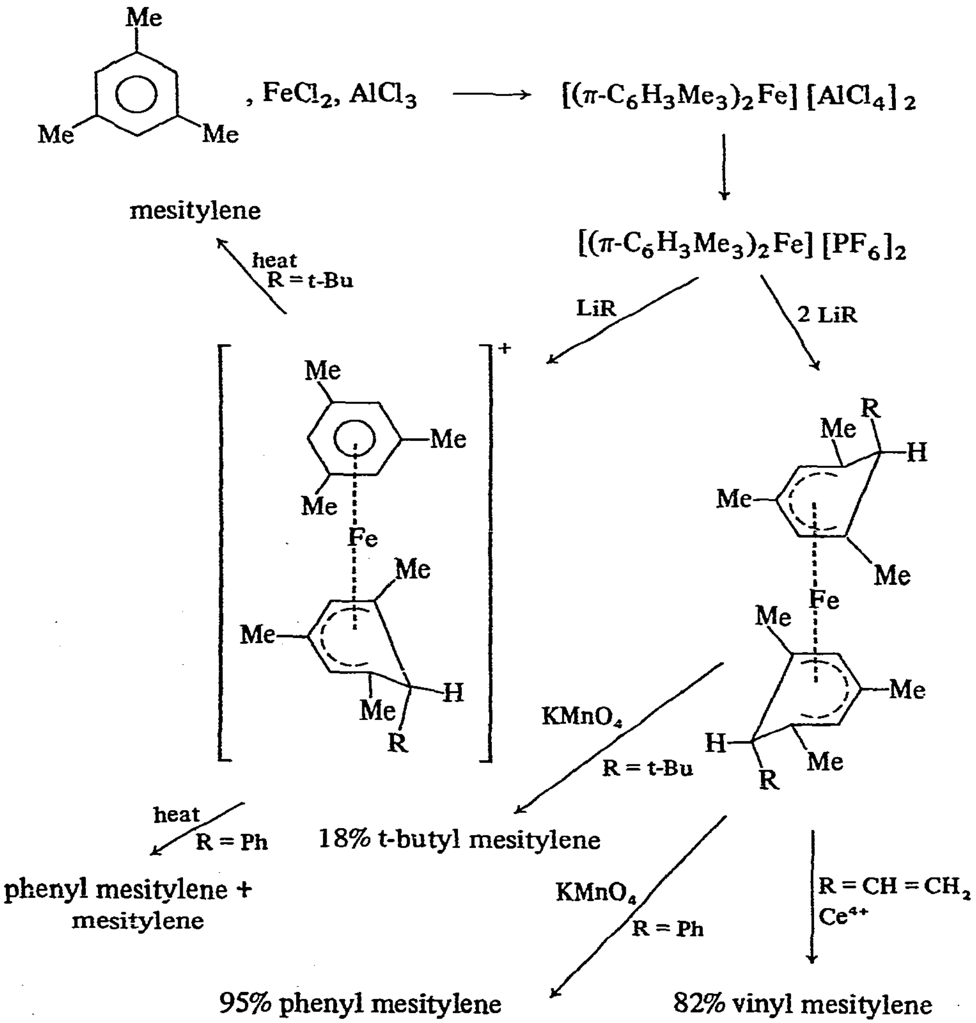


(CLXXV)



(CLXXVI)

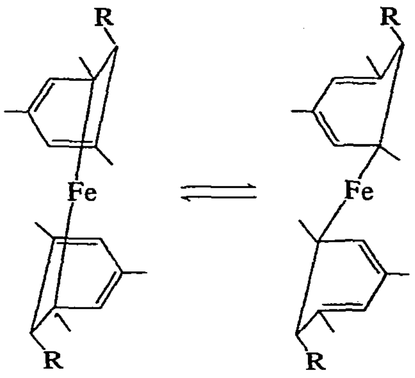
Thus, the synthesis of substituted aromatic hydrocarbons could be achieved via Fe complexes, *viz.* arene → $[(\pi\text{-arene})_2\text{Fe}]^{2+}$ → $(\pi\text{-areneR})_2\text{Fe}$ → R-substituted arene.



Scheme 31

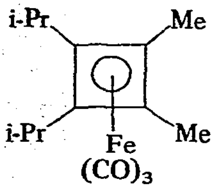
It has been shown[279] that the ^{1}H NMR spectra of $(C_6H_3Me_3R)_2Fe$ are temperature dependent and can be interpreted in terms of the equilibrium CLXXVIIa ⇌ CLXXVIIb.

The molecular structure determination of $(\pi\text{-}C_6Me_6)_2Ru$ showed[280] that one ring was planar whereas the other was essentially dienoidal, with a free double bond whose plane formed a dihedral angle with the C_4 plane of 42.8°.

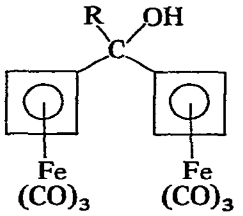


(a) (b)

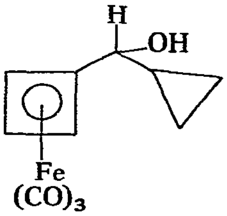
(CLXXVII)



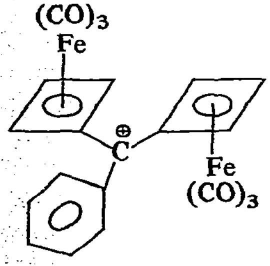
(CLXXVIII)



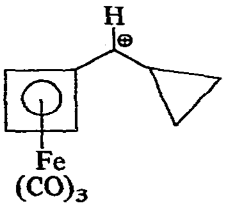
(CLXXIX)
(R = H, Me or Ph)



(CLXXX)

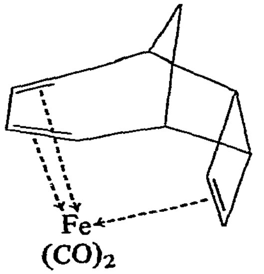


(CLXXXI)

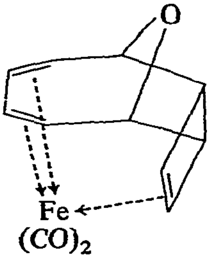


(CLXXXII)

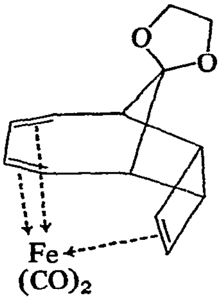
Cyclobutadiene complexes. The mixed isomers of $C_4Me_2(i\text{-}Pr)_2Cl_2$ and of $C_4Me_3(i\text{-}Pr)Cl_2$ reacted[281] with $Fe_2(CO)_9$ giving CLXXVIII and $[\pi\text{-}C_4Me_4(i\text{-}Pr)]Fe(CO)_3$. Whereas $[(\pi\text{-}C_4R_4)PdX_2]_2$ ($R = Ph, p\text{-}ClC_6H_4, p\text{-}MeC_6H_4$ or $p\text{-}MeOC_6H_4$) reacted[282] with $(\pi\text{-}C_5H_5)Fe(CO)_2Br$ giving $[(\pi\text{-}C_4R_4)(\pi\text{-}C_5H_5)Pd]^+$, reaction with $Ru_3(CO)_{12}$ afforded $(\pi\text{-}C_4Ph_4)Ru(CO)_3$. Treatment of $[(\pi\text{-}C_4R_4)NiX_2]_2$ with $Fe(CO)_5$ afforded the corresponding $(\pi\text{-}C_4R_4)Fe(CO)_3$. An IR spectral study of $(\pi\text{-}C_4RR^1R^2R^3)Fe(CO)_3$ revealed[283] that ν(CO) reflected the inductive effects of the groups R, R^1, R^2 and R^3. An analysis[284] of the ^1H NMR spectrum of $(\pi\text{-}C_4Ph_2H_2)Fe(CO)_3$ excluded a rectangular geometry for the hydrocarbon ligand.



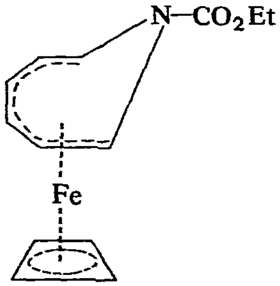
(CLXXXIII)



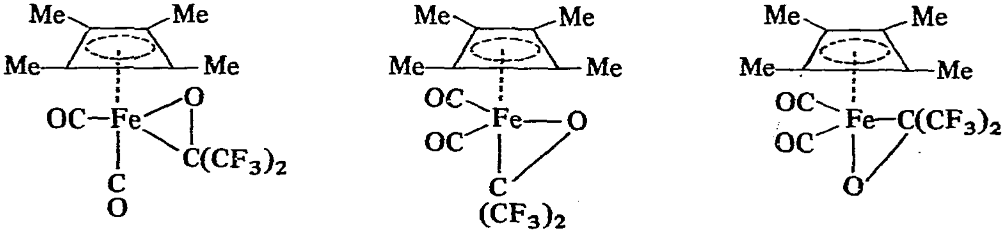
(CLXXXIV)



(CLXXXV)

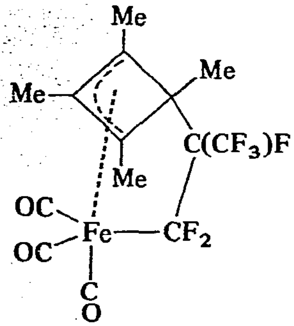


(CLXXXVI)

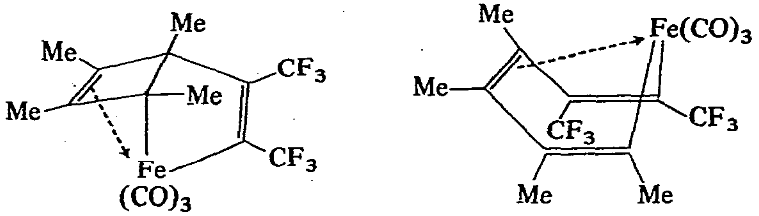


(a) (b) (c)

(CLXXXVII)



(CLXXXVIII)



(a)

(b)

(CLXXXIX)

Dehydration of the alcohols CLXXIX and CLXXX afforded[285] the extremely stable cationic species CLXXXI and CLXXXII. The molecular structure determination of CLXXXI revealed that the C_4 rings were essentially coplanar with a plane incorporating the exocyclic C atom and hence the main source of stabilisation of the carbonium ion arose from the $C_4H_4Fe(CO)_3$ groups rather than the phenyl ring. There was no evidence for long-range Fe–exocyclic C atom interaction and the C–C distances within the C_4 rings were essentially equal.

Cycloheptatriene reacted[286] with $(\pi\text{-}C_4H_4)Fe(CO)_3$ under UV light giving CLXXXIII, possibly via the intermediate $(\pi\text{-}C_4H_4)Fe(CO)_2(C_7H_8)$. Related products CLXXXIV and CLXXXV were obtained from the appropriate olefins, but reaction of *N*-carboxyethylazepine with $(\pi\text{-}C_4H_4)Fe(CO)_3$ gave instead CLXXXVI. Degradation of CLXXXV with Ce^{4+} afforded the free olefin which, on UV irradiation in ether, followed by hydrolysis, gave homopentaprismanone.

UV irradation of $(\pi\text{-}C_4Me_4)Fe(CO)_3$ with $(CF_3)_2CO$ gave[287] CLXXXVIIa, b and c, whereas with fluoroolefins, *e.g.* $(F_3C)CF{=}CF_2$, and with $F_3CC{\equiv}CCF_3$, CLXXXVIII and CLXXXIXa or b are formed.

Metal alkyl, aryl, and related species

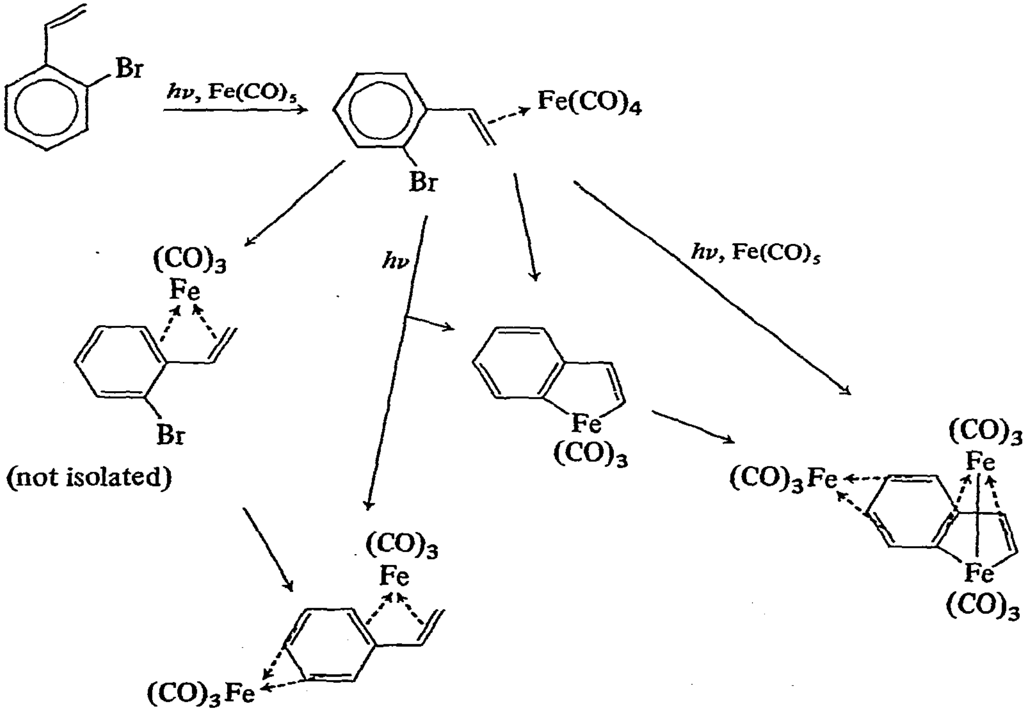
Sodium amalgam reduction of Fe(salen) (salen = *N,N'*-ethylenebis(salicylideneiminato) gave[288] Na[Fe(salen)] which, on treatment with $PhCH_2Cl$ at −60° afforded the paramagnetic ($S = 5/2$) $Fe(CH_2Ph)$(salen). Some reactions of this compound are summarised in Scheme 32. Treatment of Fe(salen) with acetic anhydride gave Fe(COMe)(salen) and acetate ion, but attempts to form this using MeCOCl, or the corresponding methyl via MeI, were unsuccessful. Fe(salen) reacted with $C_6H_{11}NC$ giving $Fe(CNC_6H_{11})$(salen). Addition of MeI to *trans*-$Fe(CO)_3(PMe_3)_2$ afforded[289] $Fe(CO)_2(PMe_3)_2(COMe)I$ which could be decarbonylated to give $Fe(CO)_2(PMe_3)_2MeI$. Carbonylation of the last afforded the precursor acyl and it was confirmed by IR spectroscopy that methyl migration to the nearest coordinate CO group occurred. The related propionyl bromides and iodides were detected spectroscopically and it was suggested that the reactivity of $Fe(CO)_3L_2$ towards oxidative acylation depended on the negative charge associated with the CO

$$\begin{tikzcd}
{[PhCH_2]_2 + Fe(salen)} & Fe(CH_2Ph)(salen) \arrow[l, "60^\circ"'] \arrow[r, "L"] \arrow[dl, "PhCH_2Cl"'] \arrow[dr, "I_2"] & \begin{array}{c} FeL(salen) + [PhCH_2]_2 \\ (L = \text{Lewis base}) \end{array} \\
{[PhCH_2]_2 + Fe(salen)Cl} & & Fe(salen)I + PhCH_2I \arrow[d, "PhMgBr"] \\
 & {[Ph{-}Ph] + [Fe(salen)]_2O} & Fe(Ph)(salen) \arrow[l, "O_2"']
\end{tikzcd}$$

Scheme 32

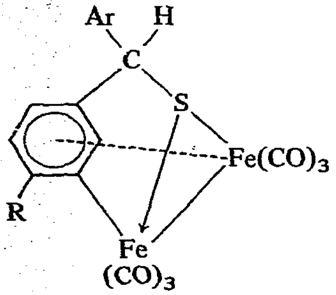
ligands and the bulkiness of the L groups; no reaction occurred when L = CO, $P(OMe)_3$, PPh_3 or PEt_3.

UV irradiation of $Fe(CO)_5$ in the presence of *o*-bromostyrene gave[290] a series of complexes as shown in Scheme 33. Reaction of $Fe_2(CO)_9$ with thiobenzophenone

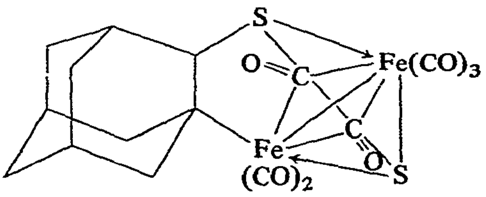


Scheme 33

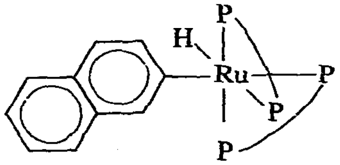
afforded[291] CXC ($R = Ph, p\text{-}MeOC_6H_4$ or $p\text{-}Me_2NC_6H_4$) and with adamantanethione CXCI was formed. The dimer of adamantanethione did not react with $Fe_2(CO)_9$, indicating that CXCI did not result via initial dimerisation of the thioketone and that the extra S atom arose via an intermolecular process.



(CXC)



(CXCI)



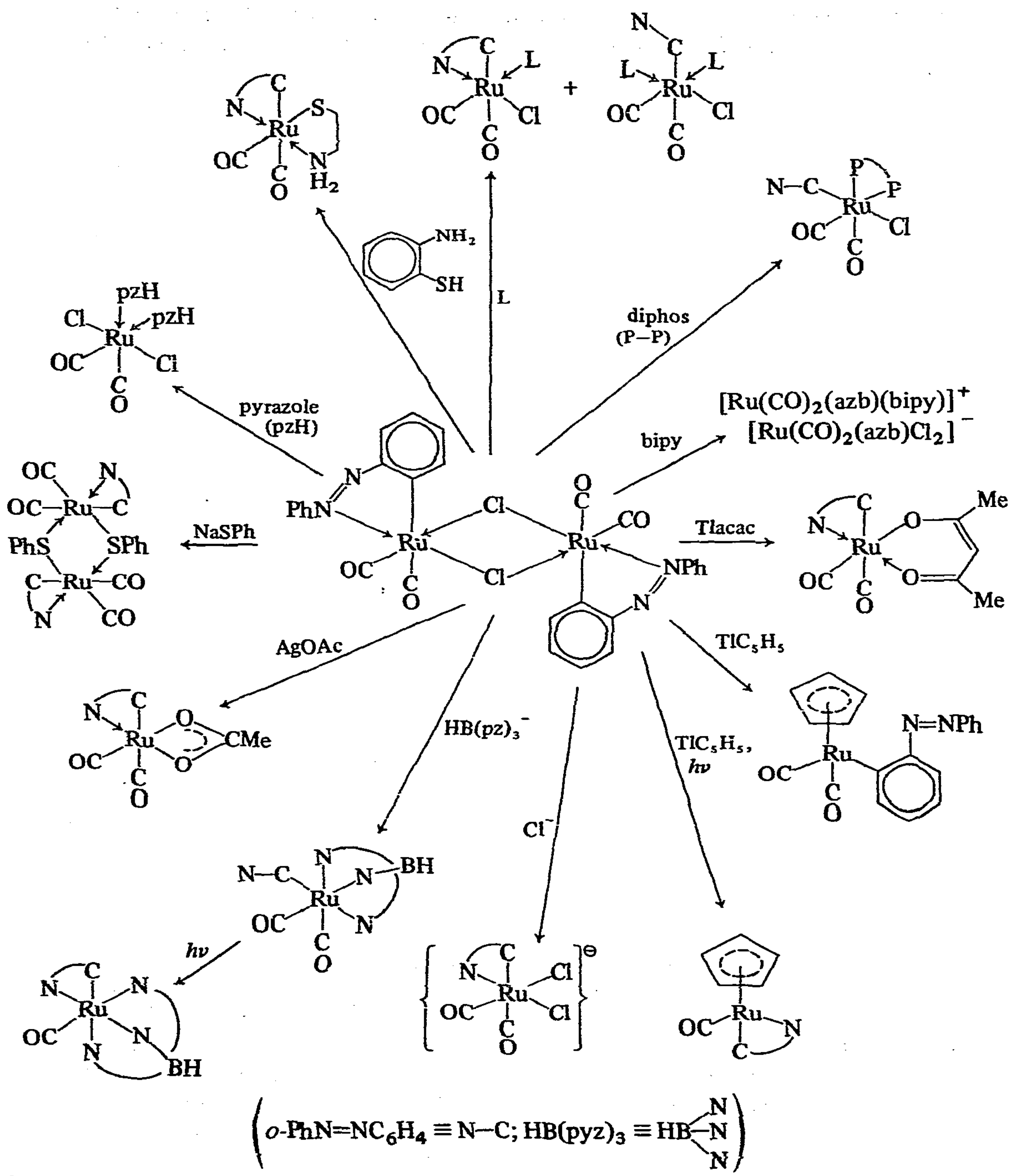
(CXCII)

Some reactions of $[azbRu(CO)_3Cl]_2$ (azbH = azobenzene) are summarised[292] in Scheme 34. The structure, in the solid state, of the naphthyl complex $Ru(Me_2PCH_2CH_2PMe_2)_2H(C_{10}H_7)$, CXCII, has been determined[293]. In solution this system involved the equilibrium:

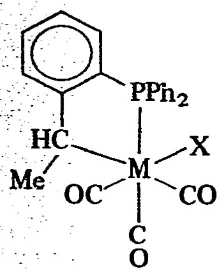
$$Ru(diphosphine)_2(C_{10}H_8) \rightleftharpoons Ru(diphosphine)_2H(C_{10}H_7)$$

but the latter form was present in the crystal. The Ru–C bond length is somewhat longer than that expected for a Ru-aryl distance. On heating the complex to 150°, naphthalene was lost and the system $Ru(Me_2PCH_2CH_2PMe_2)_2 \rightleftharpoons [Ru(Me_2PCH_2CH_2PMe_2)H\{CH_2(Me)PCH_2CH_2PMe_2\}]$ was generated (the latter would not accept $C_{10}H_8$ to regenerate the naphthalene complex). In a brief mechanistic discussion it was stated as unlikely that the rearrangement of the σ-naphthyl to the naphthalene complex would occur via a π-arene intermediate. However, a small shift of the naphthyl ring could bring one of the aromatic C–C bonds into a coordinating position while the hydride atom could shift onto the ring.

Addition of HX to $M(CO)_3(SP)$ ($SP = o\text{-}C_6H_4(CH{=}CH_2)(PPh_2)$) (M = Fe or Ru) afforded[294] the M^{II} complexes, CXCIII, whose structure was confirmed crystallographically

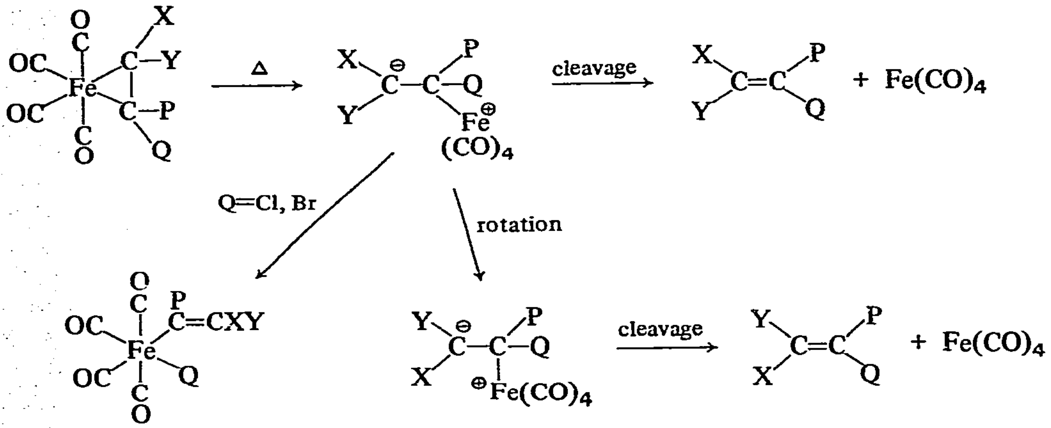

NH₂
SH
L
diphos
(P—P)
pyrazole
(pzH)
bipy
[Ru(CO)₂(azb)(bipy)]⁺
[Ru(CO)₂(azb)Cl₂]⁻
NaSPh
Tlacac
AgOAc
HB(pz)₃⁻
Cl⁻
TlC₅H₅
TlC₅H₅, hν
hν
(o-PhN=NC₆H₄ ≡ N—C; HB(pyz)₃ ≡ HB(N)₃)

Scheme 34

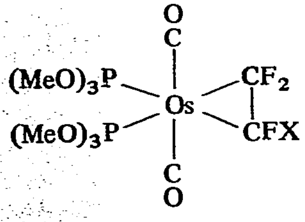


(CXCIII)

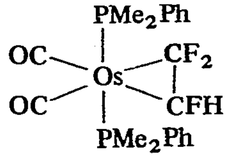
An improved route for the preparation of (fluoroolefin)$Fe(CO)_4$ has been developed[295] using $Fe_2(CO)_9$. Thermal decomposition led, in many cases, to recovery of the original olefin, but also to the formation of other products (Scheme 35). *trans*-$Os(CO)_3[P(OMe)_3]_2$ reacted with $F_2C{=}CFX$ (X = F, H or Cl) on UV irradiation giving[296] CXCIV, whereas *trans*-$Os(CO)_3(PMe_2Ph)_2$ gave CXCV. Iodination of the phosphine complex gave $[Os(CO)_3(PMe_2Ph)_2I]^+I^-$, and with $(CF_3)_2CO$, CXCVI was formed. Treatment of $Os(CO)_2[P(OMe)_3]_2(F_3CC{\equiv}CCF_3)$ with HCl gave $Os(CO)_2[P(OMe)_3]_2[C(CF_3){=}C(CF_3)H]Cl$ (see Scheme 36 for proposed mechanism). UV irradiation of $Fe(CO)_5$ with



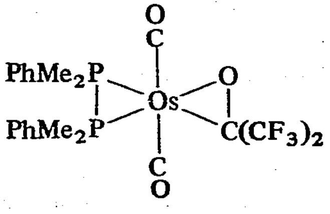
Scheme 35



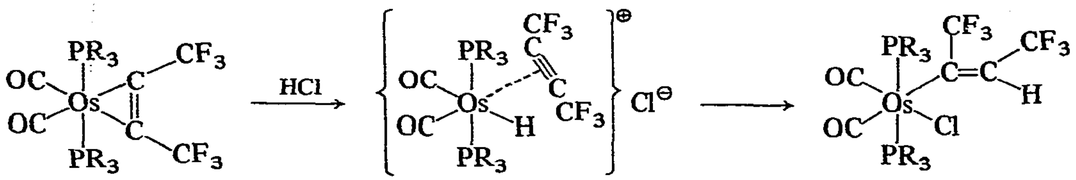
(CXCIV)



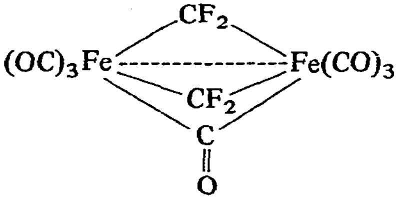
(CXCV)

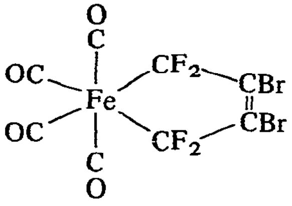


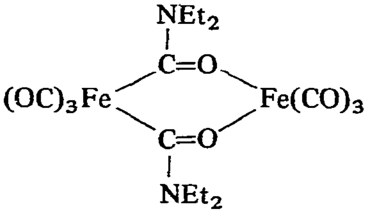
(CXCVI)


Scheme 36

CF_2Br_2 afforded[297] CXCVII, but with BrF_2CCF_2Br, $Fe(CO)_4Br(CF_2CF_2Br)$, $Fe_2(CO)_9$, $FeBr_2$, CO and C_2F_4 were obtained. Reaction with $Br_2C{=}CF_2$ afforded CXCVIII and $Fe(CO)_4(F_2CCBr_2)$.


(CXCVII)


(CXCVIII)


(CXCIX)

Carbene complexes. Treatment of $Fe(CO)_5$ with $LiNEt_2$ afforded[298] $Fe(CO)_4$-$[C(OLi)NEt_2]$ which gave, with Ph_3CCl, $Fe_2(CO)_6(CONEt_2)_2$, CXCIX. CO was displaced from this by $NHEt_2$, giving $Fe_2(CO)_5(NHEt_2)(CONEt_2)_2$. Reaction of $(\pi\text{-}C_5H_5)M(CO)_2Me$ (M = Fe or Ru) with PR_3 gave[299] $(\pi\text{-}C_5H_5)M(CO)(PR_3)COMe$ and protonation (using HCl or HBF_4) or alkylation ($R_3O^+BF_4^-$) afforded $(\pi\text{-}C_5H_5)M(CO)(PR_3)[C(OR')Me]$ (R' = H, Me or Et). Borohydride reduction of $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)[C(OEt)Me]$ provided $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)[CH(OEt)Me]$, and treatment with LiMe gave $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$, propane and propene.

Synthetic and catalytic processes

The byproducts which are produced in the hydroformylation of olefins to alcohols may be completely suppressed[300] using a mixture of $Co_2(CO)_8$, $Fe(CO)_5$ and *N*-methylpyrrolidine as catalyst. This mixture strongly favoured hydrogenation of the aldehyde intermediates to alcohols so that side reactions of the aldehydes (*e.g.* aldol condensations) were avoided.

The mechanism of ligand exchange, hydrogenation and isomerisation of olefins catalysed by (diene)$Fe(CO)_3$ or (monoene)$Fe(CO)_4$ has been elucidated[301] using methyl sorbate as a model system. The mechanism (Scheme 37) was based on the concept of coordinative unsaturation and provided a common metal complex intermediate to all three processes.

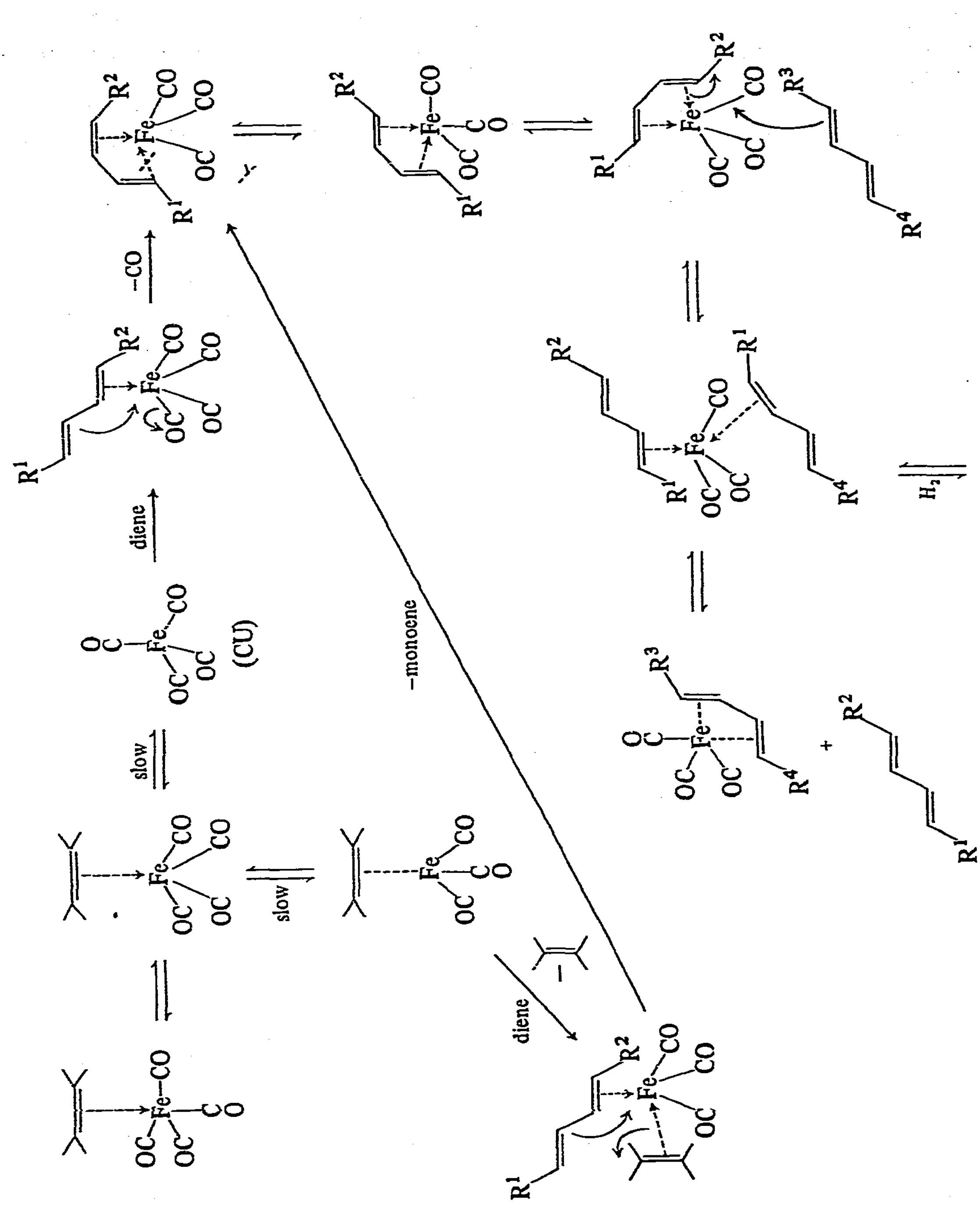
Ethoxycarboxylation of ethyl-acrylate, -crotonate, -3-butenoate, or styrene and α-olefins at 40–70° under CO was effected[302] using $KHFe(CO)_4$ or $K_2Fe(CO)_4$ and an I_2/EtOH reagent system. The general reactions are summarised in Scheme 38, and a number of differences between this general scheme and that involving cobalt carbonyls were noted. Reduction of acyl halides to aldehydes in high yields using $Na_2Fe(CO)_4$ occurred[303] via the intermediacy of $Na[Fe(CO)_4COR]$ (R = Ph, *p*-ClC_6H_4, *o*-ClC_6H_4, n-Bu or i-Bu).

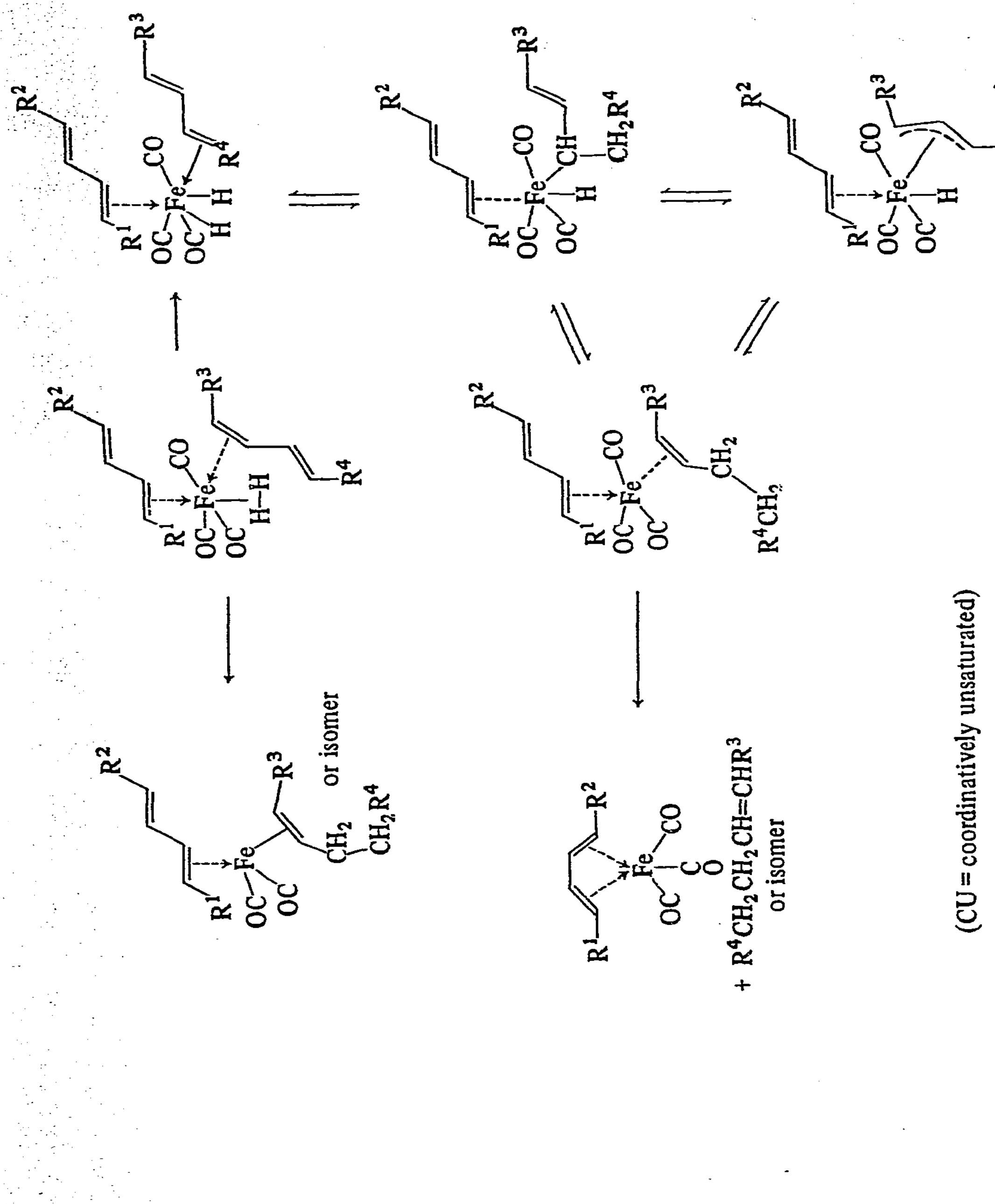
Metal complexes such as $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, $Fe_2(CO)_9$, anhydrous $FeCl_3$, $Ru(EtOH)_3Cl_3$, $Ru(CO)_3(PPh_3)_2$, or $Ru(PPh_3)_3Cl_2$ catalysed[304] the electrocylic ring opening of hexamethyl-Dewar-benzene, although these catalysts were not as effective as those derived from Rh, Ir, Pd or Pt. Treatment of α,α'-dibromoketones with $Fe_2(CO)_9$, $C_4H_6Fe(CO)_3$ (best) or $Fe(CO)_5$ in the presence of 1,3-dienes afforded[305] a useful route to troponoid compounds (Scheme 39).

The kinetics and mechanism of the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$-catalysed positional isomerism of dichlorobutenes has been investigated[306], and a π-allylic intermediate proposed. Small amounts of hydroperoxides greatly accelerated the $Ru(PPh_3)_3Cl_2$-catalysed isomerism of olefins and it seemed likely that $Ru(CO)(PPh_3)_2(\text{diolefin})Cl_2$ was formed as a result of peroxide action, and that this may have been the active species. This carbonyl complex was an isomerisation catalyst in its own right in the absence of O_2 or ROOH, whereas $Ru(PPh_3)_3Cl_2$ was essentially inactive unless these reagents were present.

Metathesis of alkyl Grignard reagents with Fe^{II} or Fe^{III} chlorides occurred[308] readily in THF, and the alkyliron intermediate afforded a reduced form of soluble iron, together with alkane and alkene. The reaction between RMgX and R'X was catalysed by the soluble iron intermediate and alkyl radicals were formed in a step involving oxidative addition to the reduced iron species (Scheme 40). Reaction of $Fe(CH_2CD_2CH_2CH_2Ph)_3$-(solvent)$_x$ with allylbenzene afforded[309] $PhCH_2CH_2CD{=}CH_2$, $PhCH_2CHDCH_2D$ and $PhC(H/D){=}C(H/D)CH_2(H/D)$ in a reaction in which intermolecular β-, H- or D-transfer from the alkyl to the metal and thence to the olefin must have occurred; α-H/D-transfer also occurred.

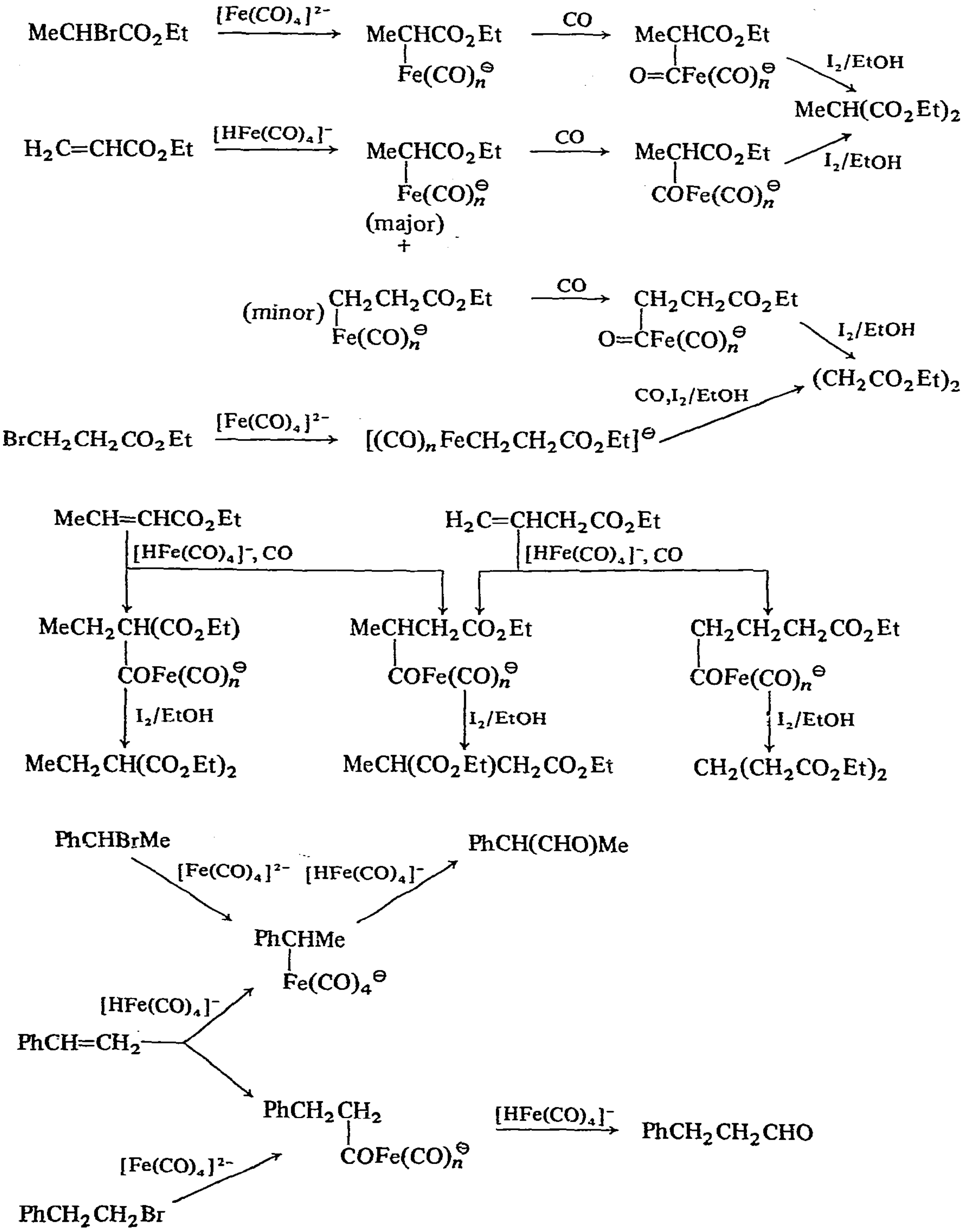
It has been shown[310] that the system $Fe(PPh_3)_2Cl_2$/i-PrMgCl formed a nitrogen complex with N_2 in ether at low temperatures. With HCl this complex effected[311] a ca. 10% conversion of the N_2 to N_2H_4 and with CO, $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$ were produced. The complex was believed to contain the Fe—N_2—Fe group. Reaction of cyclic or acyclic higher olefins with CO, H_2 and secondary amines afforded[312] the corresponding aminomethyl cycloalkanes or non-cyclic-alkanes in 90% yields in a process catalysed by $Fe(CO)_5/Rh_2O_3$.


slow
(CU)
diene
−CO
−monoene
slow
diene
H2

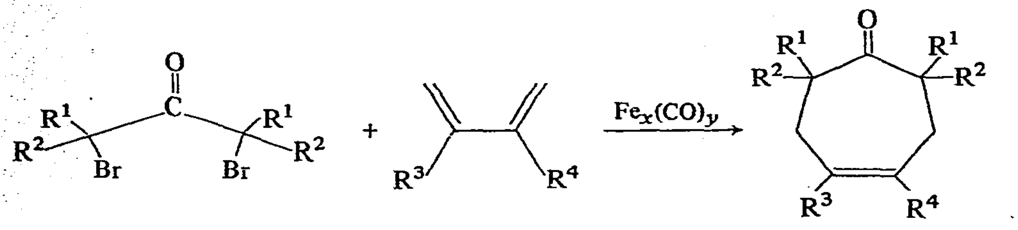


(CU = coordinatively unsaturated)

Scheme 37


MeCHBrCO2Et
[Fe(CO)4]2-
MeCHCO2Et
Fe(CO)n⊖
CO
MeCHCO2Et
O=CFe(CO)n⊖
I2/EtOH
MeCH(CO2Et)2
H2C=CHCO2Et
[HFe(CO)4]-
MeCHCO2Et
Fe(CO)n⊖
(major)
+
CO
MeCHCO2Et
COFe(CO)n⊖
I2/EtOH
(minor) CH2CH2CO2Et
Fe(CO)n⊖
CO
CH2CH2CO2Et
O=CFe(CO)n⊖
I2/EtOH
(CH2CO2Et)2
CO,I2/EtOH
BrCH2CH2CO2Et
[Fe(CO)4]2-
[(CO)nFeCH2CH2CO2Et]⊖
MeCH=CHCO2Et
[HFe(CO)4]-, CO
H2C=CHCH2CO2Et
[HFe(CO)4]-, CO
MeCH2CH(CO2Et)
COFe(CO)n⊖
I2/EtOH
MeCH2CH(CO2Et)2
MeCHCH2CO2Et
COFe(CO)n⊖
I2/EtOH
MeCH(CO2Et)CH2CO2Et
CH2CH2CH2CO2Et
COFe(CO)n⊖
I2/EtOH
CH2(CH2CO2Et)2
PhCHBrMe
[Fe(CO)4]2-
[HFe(CO)4]-
PhCH(CHO)Me
PhCHMe
Fe(CO)4⊖
[HFe(CO)4]-
PhCH=CH2
PhCH2CH2
COFe(CO)n⊖
[HFe(CO)4]-
PhCH2CH2CHO
[Fe(CO)4]2-
PhCH2CH2Br

Scheme 38



($R^1 = R^2 = Me$; $R^1 = R^2 = H$; $R^1 =$ i-Pr, $R^2 = H$)

Scheme 39

$$\begin{aligned}
R'Br + Fe^0 &\longrightarrow R'\cdot + FeBr\\
R'\cdot + Fe^0 &\longrightarrow R'Fe\\
RMgBr + FeBr &\longrightarrow RFe + MgBr_2\\
RFe/R'Fe &\longrightarrow RH, R'H + (R{-}H), (R'{-}H) + 2Fe \longrightarrow \text{etc.}
\end{aligned}$$

Scheme 40

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