IRON, RUTHENIUM AND OSMIUM
ANNUAL SURVEY COVERING THE YEAR 1972

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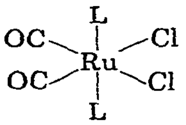
Contents

Simple carbonyl complexes

Phosphine, arsine and stibine complexes of M^0

Detailed studies of the mass spectral fragmentation of $Fe(CO)_3[P(NMe_2)_3]_2$ have been reported [1]; ionisation and appearance potentials were measured. The ions $[Fe(CO)_3\{P(NMe_2)_3\}_2]^+$ and $[Fe(CO)_2\{P(NMe_2)_3\}_2]^+$ both lost two CO groups in one fragmentation step. UV irradiation of $Fe(CO)_5$ and $As(MMe_3)_3$ (M = Ge or Sn) gave [2] $Fe(CO)_4[As(MMe_3)_3]$. The Mössbauer spectra ([2] Sb and ^{57}Fe) of $Fe(CO)_4(SbPh_3)$ and $Fe(CO)_3(SbPh_3)_2$ have been measured [3]; the isomer shift for ^{57}Fe increased on going from the mono- to the bis-substituted species, and the quadrupole splittings were apparently among the largest for low-spin Fe compounds.

Reaction of $Fe(CO)_5$ with $PMe_2(CH_2Ph)$ gave [4] impure $Fe(CO)_4$-$[PMe_2(CH_2Ph)]$ and *trans*-$Fe(CO)_3[PMe_2(CH_2Ph)]_2$, whereas the corresponding arsine gave only $Fe(CO)_4[AsMe_2(CH_2Ph)]$. In refluxing cyclohexane, $Ru_3(CO)_{12}$ afforded $Ru_3(CO)_9[QMe_2(CH_2Ph)]_3$ (Q = P or As), and in boiling chloroform, $Ru(CO)_3[PMe_2(CH_2Ph)]Cl_2$ and $Ru(CO)_2[AsMe_2(CH_2Ph)]_2Cl_2$, I (L = $AsMe_2(CH_2Ph)$), were formed. The formation of the phosphine halide indicated that in $Ru_3(CO)_9[PMe_2(CH_2Ph)]_3$ only one phosphine ligand was coordinated to each Ru atom. With $[Ru(CO)_3Cl_2]_2$, the phosphine afforded I (L = $PMe_2(CH_2Ph)$), whereas the arsine gave both I (L = $AsMe_2(CH_2Ph)$ and II. $RuCl_3$ reacted with $PMe_2(CH_2Ph)$ producing $Ru[PMe_2(CH_2Ph)]_4Cl_2$ which could be carbonylated giving $Ru(CO)[PMe_2(CH_2Ph)]_3Cl_2$, III. Hydrogenation of $Ru[PMe_2(CH_2Ph)]_4Cl_2$ in dimethylacetamide afforded a carbonyl hydride adduct which was converted to I (L = $PMe_2(CH_2Ph)$) in chloroform under CO.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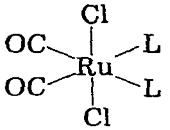
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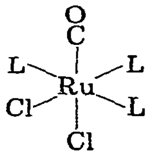
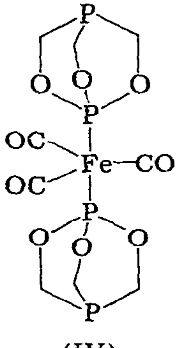
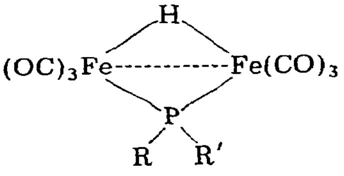

(III)

Iron carbonyls reacted [5] with $Ph_3P{=}CH(p\text{-}XC_6H_4)$ (X = H, Me or OMe) giving $Fe(CO)_4(PPh_3)$, Ph_3PO, reasonable yields of the appropriate stilbenes, and unstable and uncharacterised organometallic species. Corresponding alkyl ylides behaved similarly. Irradiation of $Fe(CO)_5$ in the presence of $P(OCH_2)_3P$ gave [6] $Fe(CO)_4[P(OCH_2)_3P]$, $Fe(CO)_4[P(CH_2O)_3P]$, $(OC)_4Fe[P(OCH_2)_3P]$-$Fe(CO)_4$ and $Fe(CO)_3[P(OCH_2)_3P]_2$, IV. The structure of the last was established by ^{31}P NMR spectroscopy.


(IV)

Reaction of $Fe_2(CO)_9$ with PRH_2 and $PRR'H$ (R, R' = Me, Et, Ph or p-MeC_6H_4; or mixtures of these) afforded [7] $Fe(CO)_4(PRH_2)$ or $Fe(CO)_4$-$(PRR''H)$. Small amounts of $Fe_2(CO)_6(\mu\text{-}PRR')_2$, usually accompanied the formation of $Fe(CO)_4(PRR'H)$. The binuclear $Fe_2(CO)_6(PRR')H$, V, was also obtained by reaction of $Fe_2(CO)_9$ with $PRR'H$, or by addition of $Fe_2(CO)_9$ to $Fe(CO)_4(PRR'Li)$. The last was produced by treatment of $Fe(CO)_4(PRR'H)$ with LiBu-n. At higher temperatures, $Fe(CO)_4$ reacted with $PPhH_2$ giving $Fe_3(CO)_9(PPh)_2$ which gave, with $P(OMe)_3$, $Fe_3(CO)_{9-n}(PPh)_2[P(OMe)_3]_n$ (n = 1, 2 or 3). As mentioned previously $Fe(CO)_4(PPh_2H)$ could be deprotonated using LiBu-n, thereby giving $Fe(CO)_4(PPh_2Li)$; $Fe(CO)_4(PPhMeH)$ similarly afforded [8] $Fe(CO)_4(PPhMeLi)$. Alkylation of these with methylating agents gave $Fe(CO)_4(PPhRMe)$ (R = Ph or Me). Lithiation of $Fe_2(CO)_6(\mu\text{-}PPhH)_2$ gave $Fe_2(CO)_6(\mu\text{-}PPhLi)_2$ which, on methylation with MeI, gave two isomers of $Fe_2(CO)_6(\mu\text{-}PPhMe)_2$, VI. With $BrCH_2CH_2CH_2Br$, the dilithio complex afforded $Fe_2(CO)_6(PhPCH_2CH_2CH_2PPh)$.



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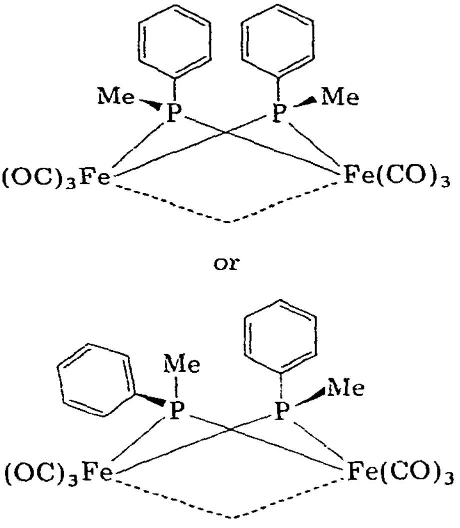
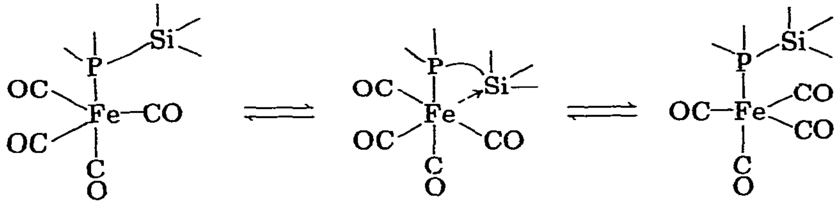


(VI)

$Fe(CO)_5$ and $Fe_2(CO)_9$ reacted with $Me_2PCH_2CH_2SiX_3$ (X = F or Me) giving [9] $Fe(CO)_4(Me_2PCH_2CH_2SiX_3)$ and $Fe(CO)_3(Me_2PCH_2CH_2SiX_3)_2$. Analogous reactions with $Me_2Si(CH_2CH_2PMe_2)_2$ afforded high molecular weight species containing $Fe(CO)_4$ and $Fe(CO)_3$ groups. The species $Fe(CO)_4(Me_2PCH_2$-$CH_2SiF_3)$ was stereochemically non-rigid and there was some evidence to suggest Fe → Si π-bonding (Scheme 1).

The potentially bidentate $(R_2Sb)_2CH_2$ (R = Me or Ph) reacted [10] with $Fe(CO)_5$ giving only $Fe(CO)_4(Ph_2SbCH_2SbPh_2)$ and $(OC)_4Fe(Me_2SbCH_2SbMe_2)$-$Fe(CO)_4$. The X-ray structural determination of $Fe(CO)_4[Ph_2\overline{PC{=}C(AsMe_2)CF_2CF_2}]$ established [11] that the phosphinoarsine was monodentate and bonded to the iron via the P atom. In the complex $Fe(CO)_3(Me_2PCH_2CH_2PMe_2)$ [12] the phosphine ligand occupied an axial and an equatorial site in the trigonal bipyramid; ^{13}C NMR spectral studies revealed that the compound was stereochemically non-rigid, even at −80°.

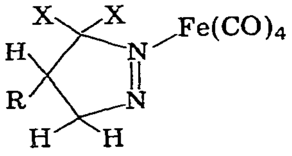


Scheme 1

($>P{-}Si\lessgtr \equiv Me_2PCH_2CH_2SiF_3$)

Complexes containing N and P bridges

Treatment of $Fe_2(CO)_9$ with 1-pyrazolines afforded [13] VII which reacted with an excess of $Fe_2(CO)_9$ giving VIII (R = Ph, X = CO_2Me). The structure of one of the products of reaction between 2,3-diazabicyclo[2.2.1]hept-2-ene [14] and iron carbonyls has been established crystallographically [15] as IX. $Fe_2(CO)_9$ reacted [16] with the diazepine X giving $C_{23}H_{18}N_2Fe\ (CO)_6$, the structure of which is known [17] to be XI. The Fe—Fe distance is 2.39 Å, and from Mössbauerspectral studies is was suggested that the Fe_2N_2 bonding system was represented as



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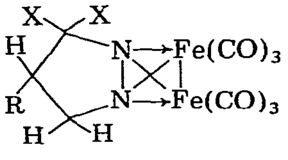

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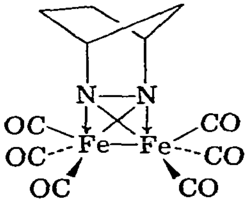

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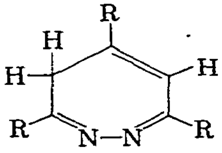

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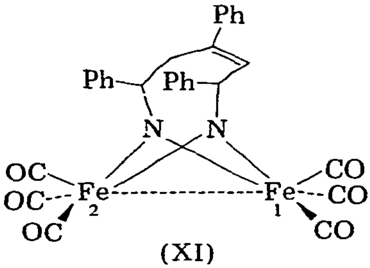

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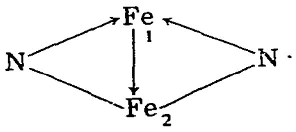
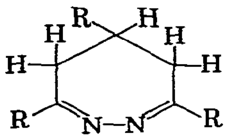


The reduced diazepine XII also reacted with $Fe_2(CO)_9$ giving the same type of complex, viz. $C_{23}H_{20}N_2Fe_2(CO)_6$ whose structure may be slightly distorted relative to that of XI because of a more puckered NC_5N ring in XII relative to



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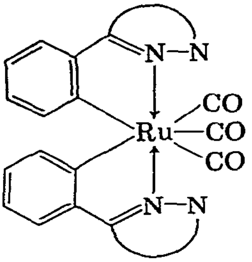

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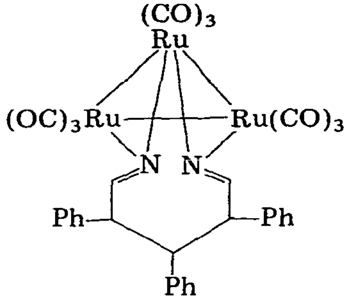
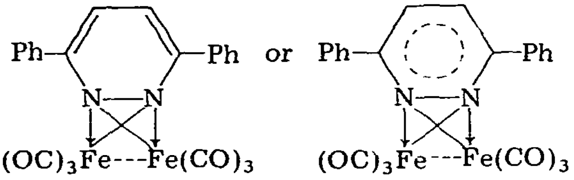


(XIV)

that in X. $Ru_3(CO)_{12}$ reacted with X giving [16] $(C_{23}H_{18}N_2)_2Ru(CO)_3$, which did not react with $PPhEt_2$ and may have the structure XIII. With XII, $Ru_3(CO)_{12}$ gave $(C_{23}H_{20}N_2)Ru_3(CO)_9$, which, on the basis of spectroscopic studies, may have the structure XIV. 3,6-Diphenylpyridazine reacted with $Fe_2(CO)_9$ giving XV which, in turn, treated with maleic anhydride afforded XVI. The X-ray structural examination of the latter revealed an Fe—Fe separation of 2.60 Å which is longer than those in other N-bridged binuclear iron carbonyls. While XV reacted with PhC≡CPh, giving the free pyridazine and $Fe_2(CO)_7(PhC_2Ph)_2$, $MeO_2CC{\equiv}CCO_2Me$ and its ethyl analogue afforded 1/1 adducts similar to XVI; Mössbauer spectral studies of the latter products showed that the Fe atoms were inequivalent.



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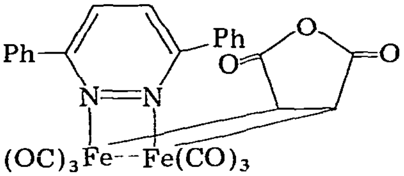

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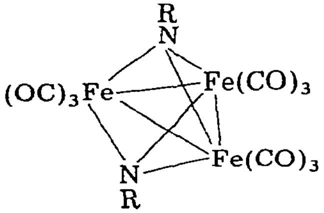

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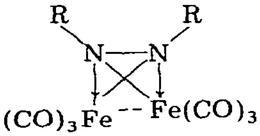

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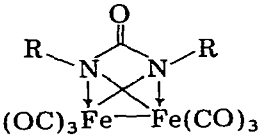

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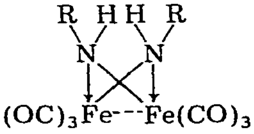
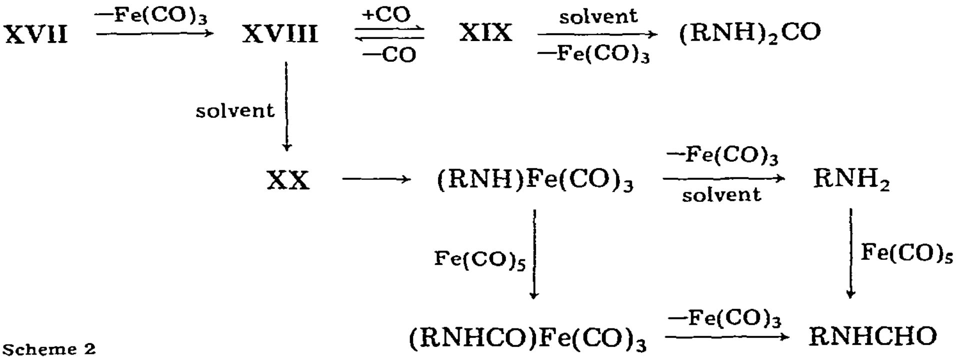


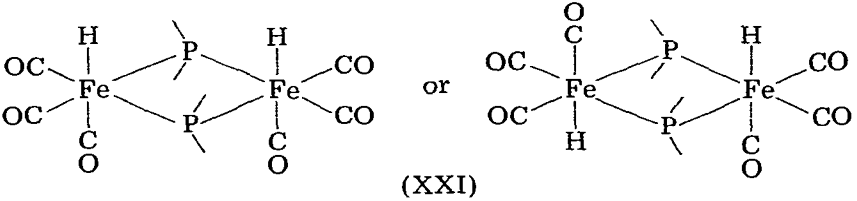
(XX)

Non-aromatic nitro compounds reacted [19] with $Fe(CO)_5$ or $Fe_2(CO)_9$ in refluxing diglyme giving RNHCHO and $(RNH)_2CO$ (R = n-Pr or i-Pr, c-C_6H_{11}, t-Bu or 1-adamantyl). Under milder conditions, XVII, XVIII, XIX and XX could be obtained; on heating these four compounds decomposed into RNHCHO and $(RNH)_2CO$, perhaps via Scheme 2. α,β-Unsaturated nitro compounds did not react with $Fe(CO)_5$ in diglyme.



Scheme 2

Treatment of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with $P(CF_3)_2H$ gave [20], at 80-90°, both $Fe_2(CO)_6[\mu\text{-}P(CF_3)_2]_2$ and $Fe_2(CO)_6[\mu\text{-}P(CF_3)_2]_2H_2$ which exists as *cis-* and *trans*-isomers, XXI. Using $P(CF_3)_2D$, the corresponding deuteride was formed. At 20°, $Fe_2(CO)_9$ afforded initially $Fe(CO)_4[P(CF_3)_2H]$ which, on heating, decomposed into XXI. Iron carbonyls reacted with $[P(CF_3)_2]_2$ giving $Fe_2(CO)_6[\mu\text{-}P(CF_3)_2]_2$, and $Fe(CO)_2(NO)_2$ afforded $Fe_2(NO)_4[\mu\text{-}P(CF_3)_2]_2$, XXII. Treatment of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $P(CF_3)_2H$ gave $(\pi\text{-}C_5H_5)$-$Fe(CO)_2P(CF_3)_2$.



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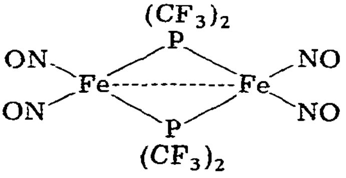

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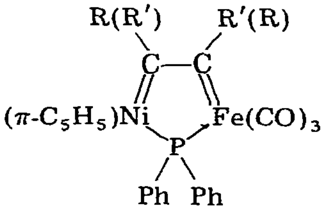


(XXIII)

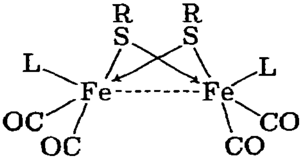
Debromination of $Fe(CO)_4\{PF_2Br\}$ by $Ni(CO)_4$ afforded [21] $Fe_2(CO)_6$-$(\mu\text{-}PF_2)_2$. Reaction of $(\pi\text{-}C_5H_5)Ni(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3$ with RC≡CR' (R = R' = Ph, CO_2Me; R = Ph, R' = H, Me, CO_2Me; R = Me, R' = H, CO_2Me) giving [22] a species formulated as XXIII; when R ≠ R' two isomers were obtained.

Complexes containing O, Se, S and Te donor atoms

UV irradiation of $Fe(CO)_5$ with 9,10-phenanthrenequinone (Quon), in THF, gave [23] $Fe(Quon)_3$, but in the presence of pyridine or α,α'-bipyridyl, $Fe(Quon)_2(Py)$ and $Fe(Quon)_2(Bipy)$ were formed.

$Fe_3(CO)_{12}$ reacted with Se_2R_2 (R = Me, Et, CF_3 or C_2F_5) giving [24] $[Fe(CO)_3(\mu\text{-SeR})_2]_2$; $i\text{-}C_3F_7SeH$ afforded $[Fe(CO)_3\{\mu\text{-Se}(i\text{-}C_3F_7)\}]_2$. However, while Se_2R_2 (R = Me or Et) afforded with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)(\mu\text{-SeR})]_2$, where as with R = CF_3, C_2F_5 or C_3F_7, only the monomer $(\pi\text{-}C_5H_5)Fe(CO)_2SeR$ was formed.

$[Fe(CO)_3(\mu\text{-SBu-t})]_2$ reacted [25] with tertiary phosphine or phosphites, L (PEt_3, PPh_3, $P(OMe)_3$ or $P(OPh)_3$) giving $Fe_2(CO)_5L(\mu\text{-SBu-t})_2$ or $[Fe(CO)_2L(\mu\text{-SBu-t})]_2$, depending on reaction conditions. With the exception of L = PEt_3, the latter compounds occurred as a single isomer in solution, viz. XXIV. With *cis*-$Ph_2PCH{=}CHPPh_2$, XXV was formed, whereas with $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2), XXVI was produced. $[Fe(CO)_3(\mu\text{-SPh})]_2$ behaved similarly with $Ph_2P(CH_2)_nPPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$ or $Ph_2PN(Et)\text{-}PPh_2$, giving [26] XXVI and XXV. The thiophenate also reacted with PEt_3, PPh_3, $SbPh_3$ or $P(OPh)_3$ giving XXIV, XXVII and XXVIII. With the chelating diphosphines, $Fe_2(CO)_5(Ph_2PCH_2PPh_2)(\mu\text{-SPh})_2$ and XXVII were formed, in which one phosphine ligand was monodentate. The complexes $Fe(CO)_2(Diphos)(SPh)_2$ (Diphos = $Ph_2PCH_2CH_2PPh_2$ or *cis*-$Ph_2PCH{=}CHPPh_2$), XXIX, were also obtained.



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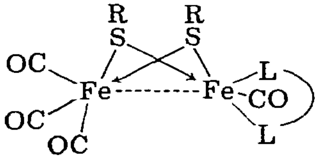

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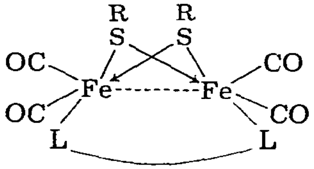

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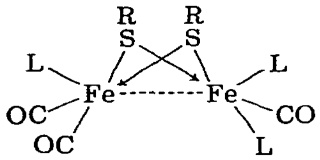

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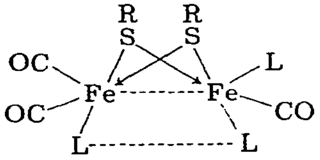

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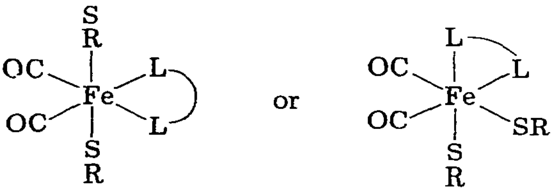
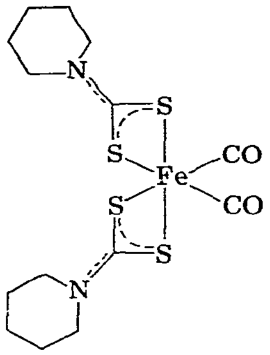


(XXIX)

Treatment of $Fe(S_2CNR_2)_2$ (R = Me or Et) with CO gave [27] *cis*-$Fe(CO)_2\text{-}(S_2CNR_2)_2$, and the structure of *cis*-$Fe(CO)_2[S_2CN\overline{CH(CH_2)_3C}H_2]_2$, XXX, obtained by reaction of the thiuram disulphide with $Fe(CO)_5$, has been determined crystallographically [28].

Reaction of $Fe_2(CO)_9$ with $S_2C_2(CF_3)_2$ under mild conditions afforded $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_n$; in solution, $n = 1$ but in the solid state $n = 2$, XXXI. With phosphines and isocyanides $Fe(CO)_{3-n}L_n[S_2C_2(CF_3)_2]$ (L = (PPh_3, $P(OEt)_3$,



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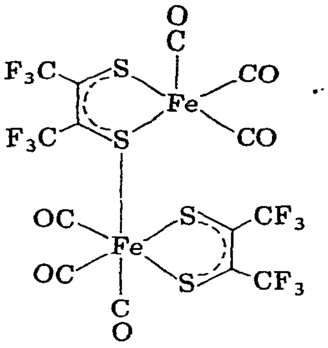

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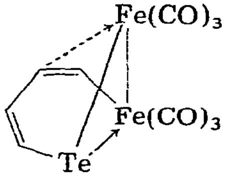


(XXXII)

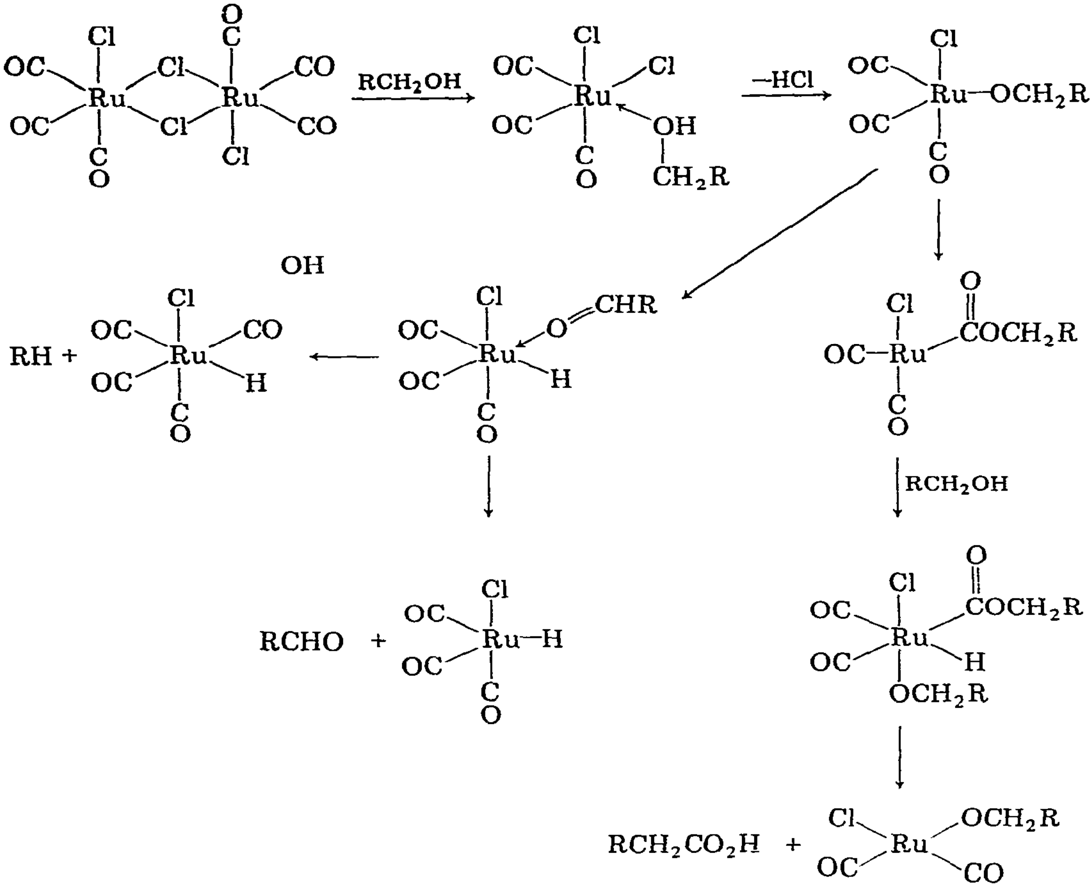
CNBu-t, $CN(p\text{-}ClC_6H_4)$) was formed and with the diphosphines $Ph_2PCH_2CH_2PPh_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$, $Fe(CO)(diphos)[S_2C_2(CF_3)]$ was produced. Treatment of the diphosphine complexes with $NOPF_6$ afforded the diamagnetic $[Fe(NO)(diphos)\{S_2C_2(CF_3)_2\}][PF_6]$, which could be readily reduced, chemically or voltammetrically, to the paramagnetic ($S = \frac{1}{2}$) Fe(NO)(diphos)-$[S_2C_2(CF_3)_2]$. These monomeric species probably have square pyramidal structures. Reaction of $[Fe(CO)_3\{S_2C_2(CF_3)_2\}]_2$ with H_2S was reported [30] to provide an inorganic model for reduced 2Fe—S* iron sulphur proteins.

Tellurophene reacted [31] with $Fe_3(CO)_{12}$ giving $Fe_3(CO)_9Te_2$, a ferrocyclopentadiene complex, $C_4H_4Fe_2(CO)_6$ and XXXII. The last, on heating afforded $C_4H_4Fe_2(CO)_6$.

Carbonyl halides

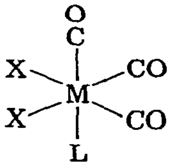
Approximate molecular orbital calculations have been used to describe [32] the electronic structure of *cis*-$Fe(CO)_4X_2$ (X = Cl, Br or I). These calculations were used to comment on the factors influencing the CO stretching force constants, and it was shown that X could affect $f(CO)$ by direct donation of electron density from the halogen's σ-bonding orbital to the π-orbital on *cis*-carbonyl groups.

When the red solution obtained by passing CO into $RuCl_3$ in refluxing ethanol was treated [33] with Et_4NI, two compounds, one $[Et_4N]_2[Ru_2(CO)_4I_6]$, were formed. This dimer reacted with pyridine, PPh_3 or $AsPh_3$ (L) giving $Ru(CO)_2L_2I_2$, and with $SbPh_3$ giving $Ru(CO)(SbPh_3)_3I_2$.



Scheme 3

The IR spectrum of $[Ru(CO)_3X_2]_2$ (X = Cl or Br) has been studied [34] in various solvents and changes of the spectra with time in $CHCl_3$ have been interpreted in terms of reactions involving ethanol stabiliser in the chloroform (Scheme 3).



(XXXIII)

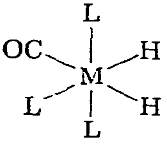
The halide reacted [34] with pyridine or nitriles giving XXXIII and with PPh_3 giving *cis*-$Ru(CO)_2(PPh_3)_2X_2$. Bromoform solutions of $[Ru(CO)_3X_2]_2$ reacted with CO under pressure forming *cis*-$Ru(CO)_4X_2$.

Complexes of M^{II} containing Group VA donor atoms

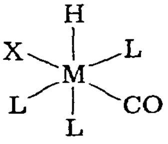
The heats of binding of CO and CNMe (L) in $[Ru(NH_3)_5L]^{2+}$ were calculated [35], on the basis of the reaction with Ce^{4+}, to be − 84.5 ± 0.5 and − 13.5 ± 0.5 kcal/mole. Free CO does not react with Ce^{4+} in solution, but when coordinated to Ru^{II} is released as CO_2.

$Ru_3(CO)_{12}$ reacted [36] with mesotetraphenylporphine (Porph) in ethanol to give *trans*-$Ru(CO)_2$(Porph), and not Ru(CO)(EtOH)(Porph) as previously thought [37]. The etiophorphyrin iodine (EporphI) complex Ru(CO)(Py)(EporphI), and its octaethylporphyrin analog, on UV irradiation, gave [38] the dimer (Py)(EporphI)Ru=Ru(EporphI)(Py). Inter- and intra-molecular site exchange of coordinate *N*-bases (pyridines, pyridazines and a pyrazole) in Ru(CO)(base)(Porph) (Porph = tetra(isopropylphenyl)porphyrin) has been studied [39] by total line shape analysis of the variable temperature ^1H NMR spectra of the complexes. All compounds underwent intermolecular ligand exchange, with rates of ca. 0.09 to 2 × 10^4 sec^{-1}, which was independent of the concentration of the base; the rate-determining step was dissociative. The rates for intramolecular site exchange were 20 to 85 times faster than those for intermolecular exchange, but there was apparently no intramolecular ligand exchange involving 3,5-dimethylpyrazole complexes.

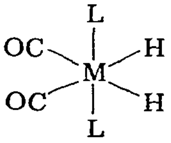
Carbonylation of $Fe(PPh_2Me)_4H_2$ gave [40] $Fe(CO)(PPh_2Me)_3H_2$, and this complex, like its ethyl analog and $Ru(CO)(PPh_2Me)_3H_2$, had the structure XXXIV at −50°; above this temperature the complexes were stereochemically non-rigid. Mössbauer spectral studies of $[Fe(L)(Et_2PCH_2CH_2PEt_2)_2H]^+$ indicated [41] that the σ-donor and π-acceptor ability of the ligand L increased in the order L = MeCN < PhCN ~ N_2 < $P(OPh)_3$ ~ $P(OMe)_3$ < CNBu-t < *p*-MeC_6H_4NC < CO. The data established that N_2 is a poorer σ-donor and π-acceptor than CO, but that N_2 is a better π-acceptor but poorer σ-donor than RNC. The ruthenium and osmium hydrides and chlorides *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$ (*cis*-CO), $Os(CO)(PPh_3)_3HCl$ (XXXV), $Os(CO)(PPh_3)_3H_2$ (XXXIV) and $Os(CO)_2(PPh_3)_2H_2$ (XXXVI) were prepared [42] by treating $RuCl_3$, $OsCl_3$ or $OsCl_6{}^{3-}$ with ethanolic KOH or Et_3N and PPh_3. In 2-methoxyethanol, $RuCl_3$ and PR_3 (R = Ph, *p*-MeC_6H_4 or *p*-$MeOC_6H_4$) afforded $Ru(CO)_3(PR_3)_2$. If the reactions designed to give $Ru(CO)_2(PPh_3)_2H_2$ were carried out in the presence of *p*-$MeC_6H_4SO_2N(Me)NO$, $Ru(NO)_2(PPh_3)_2$ was formed. Reaction of $Ru(PPh_3)_3HCl$, or its $P(p\text{-}MeC_6H_4)_3$ analog, with $AlEt_3$ under N_2 in ether afforded [43] $Ru(PPh_3)_3(N_2)H_2$; the N_2 was easily displaced by CO giving $Ru(CO)(PPh_3)_3H_2$ (XXXIV).



(XXXIV)

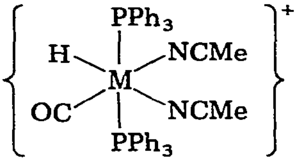


(XXXV)



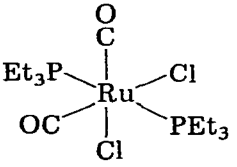
(XXXVI)

Abstraction of chloride from $M(CO)(PPh_3)_2HCl$ (M = Ru or Os) in MeCN using Ag^+ gave [44] $[M(CO)(PPh_3)_2(NCMe)_2H]^+$, XXXVII. Carbonylation of this, followed by addition of PF_6^-, gave $[M(CO)_2(PPh_3)_3H]^+$, different isomers being obtained by changing the order of ligand addition. Deprotonation of the dicarbonyl by OMe^- or $OBu\text{-}t^-$ gave *trans*-$M(CO)_2(PPh_3)_3$, whereas, with OEt^-, $M(CO)(PPh_3)_3H_2$ was the major product. The latter may have been formed via acetaldehyde elimination from $M(CO)(PPh_3)_3H(OEt)$. The species $Ru(CO)_2(PPh_3)_3$ apparently rapidly dissociated in solution giving $Ru(CO)_2(PPh_3)_2$, and this reacted with H_2, C_2H_4, PhC≡CPh and O_2 giving, respectively, $Ru(CO)_2(PPh_3)_2H_2$, $Ru(CO)_2(C_2H_4)(PPh_3)_2$, $Ru(CO)_2(PhC_2Ph)(PPh_3)_2$ and $Ru(CO)_2(PPh_3)_2(O_2)$. $Os(CO)_2(PPh_3)_3$ dissociated less readily and $Os(CO)_2(PPh_3)_2(O_2)$ was formed more slowly than its Ru analog.



(XXXVII)

^{13}C NMR spectral studies of $Ru(CO)_2(PhC_2Ph)(PPh_3)_2$ and $Ru(CO)_2$-structure as XXXVIII. The red solution produced by carbonylation of $RuCl_3$ in ethanol reacted [46] with $P(CH_2SiMe_3)_3$ giving $Ru(CO)_2[P(CH_2SiMe_3)_3]_2Cl_2$ XXXIX. However, treatment of $[Ru(CO)_2Cl_2]_n$ with the silylphosphine also resulted in the formation of $Ru(CO)_2[P(CH_2SiMe_3)_2Me]_2Cl_2$, (XXXIX). The carbonylation of $RuCl_3$ in boiling 2-methoxyethanol afforded [47] with L (PEt_3, PPr_2Ph or PPh_3) $Ru(CO)_2L_2Cl_2$, XXXVIII, but under similar conditions $P(p\text{-}MeC_6H_4)Bu\text{-}t_2$, L′, gave $Ru_2(CO)_4L'_2Cl_2$, XL. The Ru—Ru distance (2.63 Å) was much shorter than that found in other binuclear Ru^0 and Ru^I complexes. The Ru_2Cl_2 bridge had a dihedral angle of 92°, but the bridge conformation did not reflect steric effects and the remaining $Ru(CO)_2Cl_2$ groups were planar. Chlorination of XL in CCl_4 gave $[Ru(CO)_2L'Cl_2]_2$, XLI, which, on treatment with pyridine or $PPhMe_2$ (Q) gave $Ru(CO)_2L'QCl_2$, XLII. Heating XLI alone in 2-methoxyethanol, or with L′, gave XL which reacted with AgOCOMe giving $[Ru(CO)_2L'(O_2CMe)]_2$, XLIII. It was suggested that L′ was too bulky to permit the formation of the normal six-coordinate Ru^{II} complexes, $Ru(CO)_2L'_2Cl_2$.



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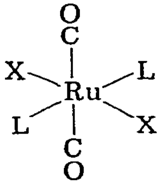
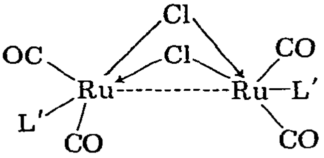
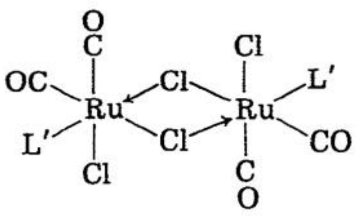


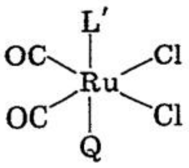
(XXXIX)



(XL)

In contrast to previous reports [48], $Ru(CO)_3(PPh_3)_2$ did not react with MeI in benzene at room temperature, or even on refluxing. There was no


(XLI)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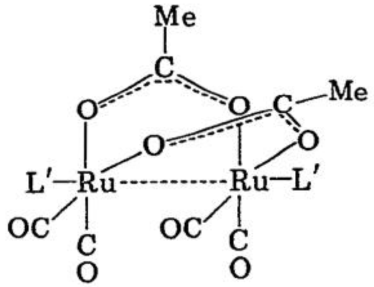
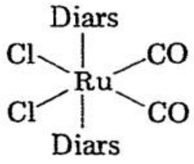
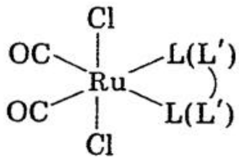
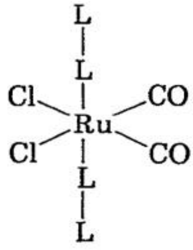
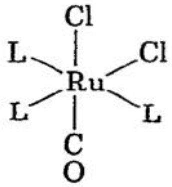

(XLIII)

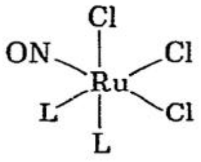
reaction either with THF at room temperature, but on refluxing, $[PPh_3Me]$-$[Ru(CO)_2(PPh_3)I_3]$ was formed [49]; this anion was also obtained by action of MeI on $Ru(CO)_2(PPh_3)_2I_2$, itself produced by treatment of $Ru(CO)_2(PPh_3)_2Cl_2$ with KI. $[PPh_3Me][Ru(CO)_2(PPh_3)I_3]$ reacted with PPh_3 giving $Ru(CO)_2$-$(PPh_3)_2I_2$. The *cis*- and *trans*-isomers of the latter (XXXVIII and XXXIX) could be interconverted by UV irradiation or heating; the analogous $Ru(CO)_2$-$(PPh_2Me)_2I_2$ was also prepared. $RuCl_3$ reacted [50] with $Ph_2AsCH_2CH_2AsMe_2$ (Diars) giving $Ru(Diars)_3Cl_2$ in which the diarsine ligands were both mono- and bi-dentate; carbonylation of this compound gave $Ru(CO)_2(Diars)_2Cl_2$, XLIV, also obtained by reaction of $RuCl_3$ with CO and diars in ethanol. Under similar conditions, using $Ph_2PCH_2PPh_2$ and *cis*-$Ph_2AsCH{=}CHAsPh_2$ (L—L), $Ru(CO)_2(L{-}L)_2Cl_2$, XLVI, was prepared. Carbonylation of $Ru(Ph_2PCH_2PPh_2)_2Cl_2$ gave *trans*-$[Ru(CO)(Ph_2PCH_2PPh_2)_2Cl]Cl$ and oxidation with $NOBF_4$ afforded $[Ru(Ph_2PCH_2PPh_2)_2Cl_2][BF_4]$. Reaction of NO or RONO with the latter afforded $[Ru(NO)(Ph_2PCH_2PPh_2)_2Cl][BF_4]_2$. Treatment of $RuCl_3$ in ethanol with CO and *trans*-β-styryldiphenylphosphine or arsine (L) gave $Ru(CO)L_3Cl_2$, XLVII, and further reaction with CO provided *cis*-$Ru(CO)_2L_2Cl_2$, XLV. With *cis*-β-styryldiphenylphosphine (L′), only *cis*-$Ru(CO)_2L'_2Cl_2$ was formed. $Ru(NO)Cl_3$ reacted with the styryl phosphines and arsine giving $Ru(NO)L_2Cl_3$, XLVIII.


(XLIV)


(XLV)


(XLVI)

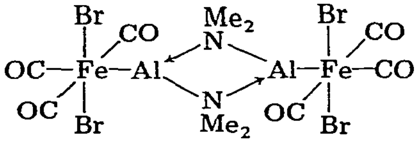

(XLVII)


(XLVIII)

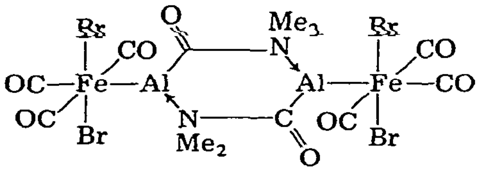
Reaction of $Ru(CO)(PPh_3)_3H_2$, $Ru(CO)(PPh_3)_3HCl$ and $Ru(NO)(PPh_3)_2(OCOCF_3)_3$ with RCO_2H (R = alkyl or aryl) afforded [51] $Ru(CO)(PPh_3)_2X(O_2CR)$ (R = alkyl or aryl; X = H or Cl). With CF_3CO_2H in benzene $Os(CO)(PPh_3)_2(OCOCF_3)_2$, $Os(CO)(PPh_3)_3Cl(OCOCF_3)$ and $Os(CO)_2(PPh_3)_2(OCOCF_3)_2$. $Ru(NO)_2(PPh_3)_2$ reacted with CF_3CO_2H giving $Ru(NO)(PPh_3)_3(OCOCF_3)_3$ which was carbonylated by KOH and ethanol afforded $Ru(CO)(PPh_3)_2(OCOCF_3)_2$. The trifluoroacetate group in the Os complexes could be exchanged metathetically with NaOCOR (R = alkyl or aryl). In the species $M(CO)(PPh_3)_2(OCOMe)_2$, both mono- and bi-dentate acetate groups were present, and there was ^1H NMR spectral evidence for exchange between mono- and bi-dentate coordination.

Complexes containing σ-bonded Group IIB, IIIB and IVB elements

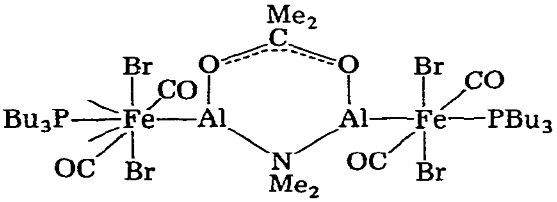
Reaction of $Fe(CO)_3[P(OMe)_3]_2$ with HgX_2 (X = Cl, Br or I) gave [52] $Fe(CO)_3[P(OMe)_3]_2(HgX_2)$, and 1/4 ($HgCl_2$) and 1/2 ($HgBr_2$ or HgI_2) adducts were also obtained. The last two species dissociated in nitrobenzene giving $[Fe(CO)_3\{P(OMe)_3\}_2HgX]^+[HgX_3]^-$; similar species were obtained with $Fe(CO)_3[(PMe_3)_2]_2$.



(XLIX)

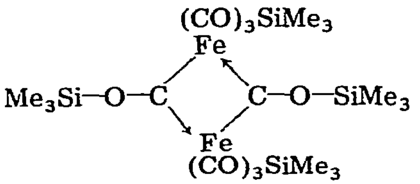


(L)

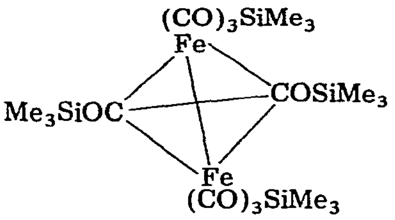


(LI)

Treatment of $Fe_2(CO)_9$ with B_6H_{10} afforded [53] μ-$(OC)_4FeB_6H_{10}$, in which the Fe atom is probably bridging a basal edge of a pentagonal pyramid of B_6 atoms. Reaction of $Fe_3(CO)_{12}$ with $[Me_2NAlBr_2]_2$ gave [54] XLIX, which on treatment with PBu_3 and CO_2 gave, respectively, L and LI.

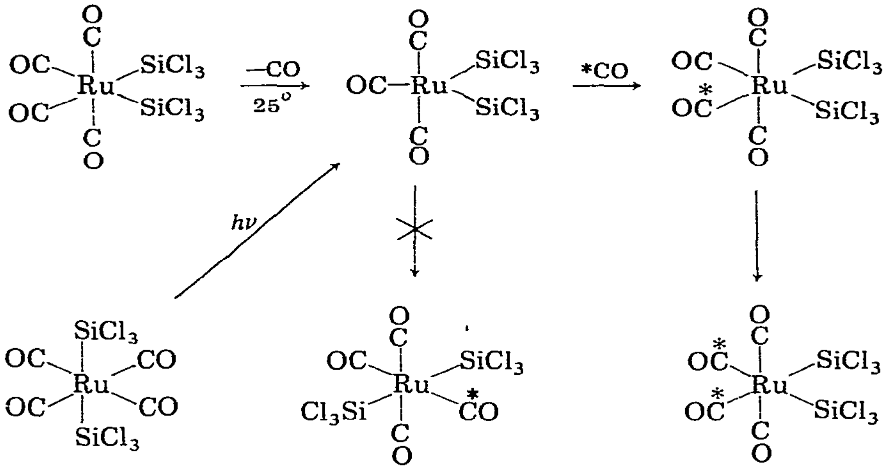


(LII)



(LIII)

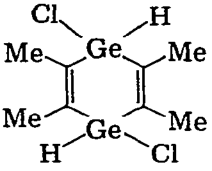
When $SiMe_3I$ was added to $Na_2Fe(CO)_4$, $[Fe(CO)_4(SiMe_3)_2]_2$ was formed [55]; this may have the structure LII or LIII. Addition of HCl afforded $[Fe(CO)_3(COH)(SiMe_3)]_2$, and the original tetracarbonyl could be regenerated from this by addition of $SiMe_3Cl$ and NMe_3. Exchange of two CO groups in *cis*-$Ru(CO)_4(SiCl_3)_2$ occurred [56] at 25° specifically at the equatorial sites, the axial CO groups not undergoing exchange at all. It was also shown that *cis*- and *trans*-isomers of the chlorosilyl complex did not interconvert in solution or in the solid state. Thus, *trans*-$Ru(CO)_4(SiCl_3)_2$ was converted into the



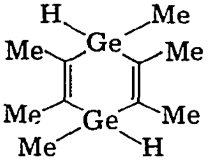
Scheme 4

enriched CO form without proceeding via the unenriched *cis*-isomer. The mechanism of CO exchange (Scheme 4) is perhaps understood in terms of a five-coordinate bipyramidal intermediate which has equatorial $SiCl_3$ groups. Stereospecificity is maintained as this intermediate accepts a second CO group establishing that the initially axial and equatorial sets of CO groups are distinguished at all times in the intermediate. The behaviour of *cis*-$Ru(CO)_4(GeCl_3)_2$ was similar, but $Fe(CO)_4(SiCl_3)_2$ did not undergo absolutely stereospecific CO exchange. The compounds $Ru(CO)_4(SiMe_3)_2$, $Os(CO)_4(SiMe_3)_2$, $Os(CO)_4(SiMe_2Cl)_2$ and $Os(CO)_4(SnMe_3)_2$ were stereochemically non-rigid [57], as established by ^1H NMR spectral studies. It seems likely that *cis/trans*-isomerism proceeds via a non-dissociative mechanism, perhaps involving silyl or stannyl group migration through an acyl intermediate. Reaction of $Na_2Fe(CO)_4$

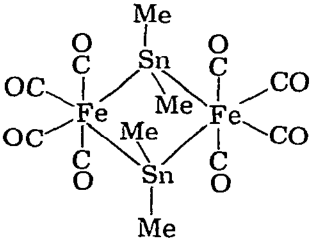
and $Fe_2(CO)_9$ with LIV and LV afforded [58] organometallic oils which could not be adequately characterised but contained Fe and Ge. The structures of the *cis*- and *trans*-isomers of $Ru(CO)_4(GeCl_3)_2$ have been elucidated crystallographically [59]; the Ru—Ge distances in both complexes were 2.48 Å, and from the Ru—C distances it was apparent that the $GeCl_3$ group had an unusual π-bonding capability.



(LIV)



(LV)

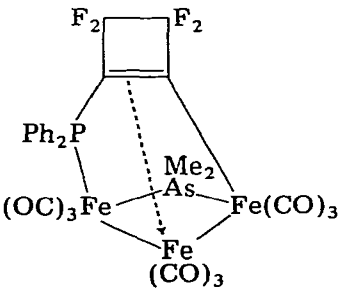


(LVI)

The crystal structure determination of $[Fe(CO)_4SnMe_2]_2$, LVI, established [60] that the Fe—Sn distances (2.65 Å) corresponded to the sum of covalent radii of Fe^{II} and Sn^{IV}; the Sn—Fe—Sn angle was 77°, and the Fe—Fe separation 4.14 Å.

Metal carbonyl clusters

The two Fe—Fe distances in LVII, 2.68 and 2.87 Å, were determined [61] by X-ray crystallography. $Fe(CO)_5$ reacted with $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$ in diglyme giving [62] $[Fe_5(CO)_{14}C]^{2-}$, LVIII, isolated as the Me_4N^+ salt. This anion could also be obtained [63], together with $[Fe_6(CO)_{16}C]^{2-}$, from the reaction



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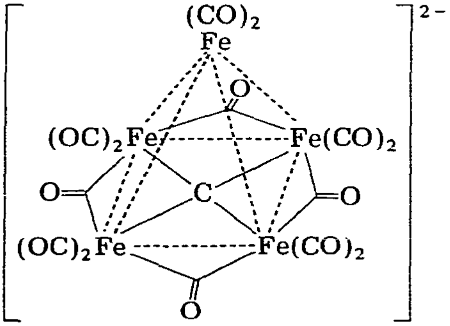
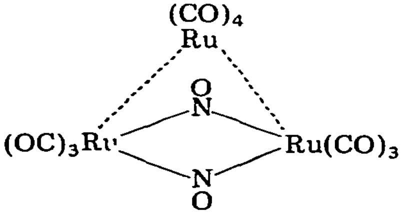


(LVIII)

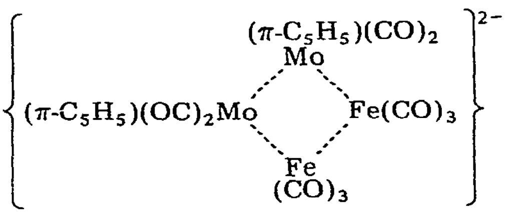


(LIX)

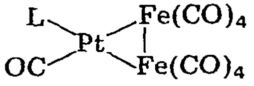
of $Fe(CO)_5$ with $[Mn(CO)_5]^-$. The pentanuclear species may be related to $Fe_5(CO)_{15}C$ [64].

The X-ray crystallographic structural determination of α-$Ru_4(CO)_{13}H_2$ revealed [65] that eleven of the CO groups were terminally bound, and the other two formed asymmetric bridges between two Ru atoms each. There were two different metal—metal distances, two Ru—Ru separations being 2.93 Å and four being 2.78 Å; it was suggested that the H atoms bridged the two long Ru—Ru bonds. Reaction of $Ru_3(CO)_{12}$ with NO in benzene at 80° gave [66] $Ru_3(CO)_{10}(NO)_2$, and this further reacted with NO giving $[Ru(CO)_{1.3}(NO_2)_{1.6}]_n$, $Ru_4C_{12}N_2O_{13}$ and perhaps also $Ru_4(CO)_{12}(N_2O)$. $Os_3(CO)_{12}$ also reacted with NO giving $Os_3(CO)_{10}(NO)_2$. The structure of the ruthenium nitrosyl, LIX, has been elucidated; the direct Ru—Ru bond distances were 2.87 Å, and the $Ru(\mu\text{-}NO)_2$—Ru separations were 3.15 Å; $Os_3(CO)_{10}(NO)_2$ was isostructural. Pyrolysis of $Ru_3(CO)_{12}$ in a sealed tube at ca. 150° gave $Ru_6(CO)_{17}C$ and undecomposed dodecarbonyl [67]. However, similar treatment of $Os_3(CO)_{12}$ at 195–200° afforded, in addition to starting material, $Os_4(CO)_{13}$, $Os_5(CO)_{16}$), $Os_6(CO)_{18}$ (which is probably an octahedral cluster of $Os(CO)_3$ groups), $Os_7(CO)_{21}$, $Os_8(CO)_{23}$, and $Os_5(CO)_{15}C$; $Os_6(CO)_{17}C$ was not detected.

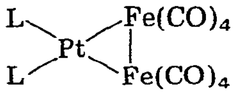
Reaction of $Fe_2(CO)_9$ with $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$ at room temperature gave [68] $[Fe_2(\pi\text{-}C_5H_5Mo)_2(CO)_{10}]^{2-}$, LX.



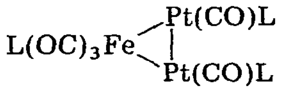
(LX)



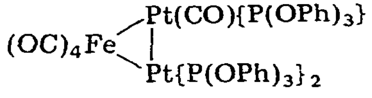
(LXI)



(LXII)

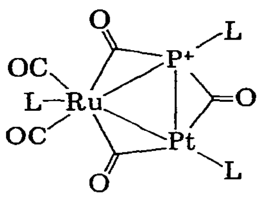


(LXIII)

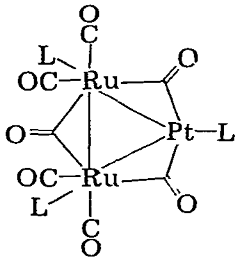


(LXIV)

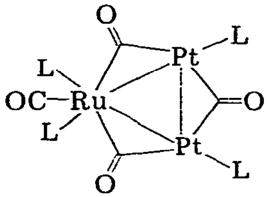
$Fe_2(CO)_9$ reacted with PtL_4, PtL_3 or PtL_2(stilbene) (L = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3 or $AsPh_3$) giving [69] LXI, LXII (also obtained where L = $PPh(OMe)_2$, $P(OPh)_3$ or $Ph_2QCH_2CH_2QPh_2$, Q = P or As), and LXIII. Some of these compounds could also be obtained [70] using $Fe_3(CO)_{12}$, and the structures of $Fe_2(CO)_8[Pt(CO)(PPh_3)]$ [70] (see LX) and $Fe(CO)_4$-$[Pt_2(CO)\{P(OPh)_3\}_3]$ [71], LXIV, have been determined. In the former the two independent Pt—Fe bond distances were significantly different, reflecting, perhaps, the high *trans* influence of PPh_3 relative to CO. The general stereochemistry of the cluster suggested that the bonding involved $[Pt(CO)(PPh_3)]^{2+}$ and two $[Fe(CO)_4]^-$ groups. In the latter, the metal—metal bonds were shorter than expected for electron-pair bonds, suggesting Fe—Pt bond multiplicity (the compound does not obey the rare gas rule).



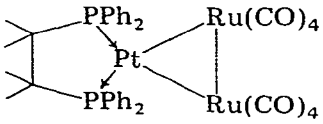
(LXV)



(LXVI)

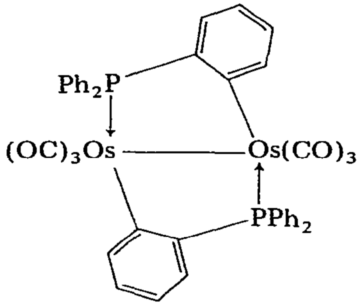


(LXVII)

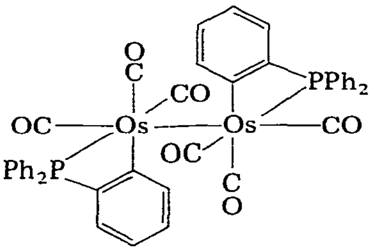


(LXVIII)

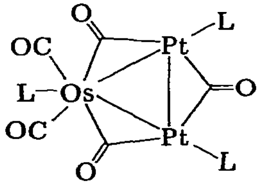
$Ru_3(CO)_{12}$ also reacted [72] with PtL_4, PtL_3 or PtL_2(stilbene) giving $Ru_3(CO)_{12-n}L_n$ ($n = 1$, 2 or 3) and LXV (L = PPh_3, PPh_2Me, $PPhMe_2$, $PPh(OMe)_2$ or $AsPh_3$), LXVI (L = $PPhMe_2$), LXVII (L = $PPh(OMe)_2$ or $P(OPh)_3$) and LXVIII. Reaction of $Os_3(CO)_{12}$ with $Pt(PPh_2Me)_4$ gave $Os_3(CO)_8(PPh_2Me)_4$ and with $Pt(PPh_3)_2$(stilbene), $Os_3(CO)_{12-n}(PPh_3)_n$ ($n = 1$, 2 or 3). With $Os(CO)_4H_2$, these Pt compounds afforded $OsPt_2(CO)_5L_3$



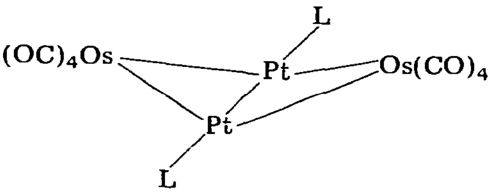
(LXIX)



(LXX)



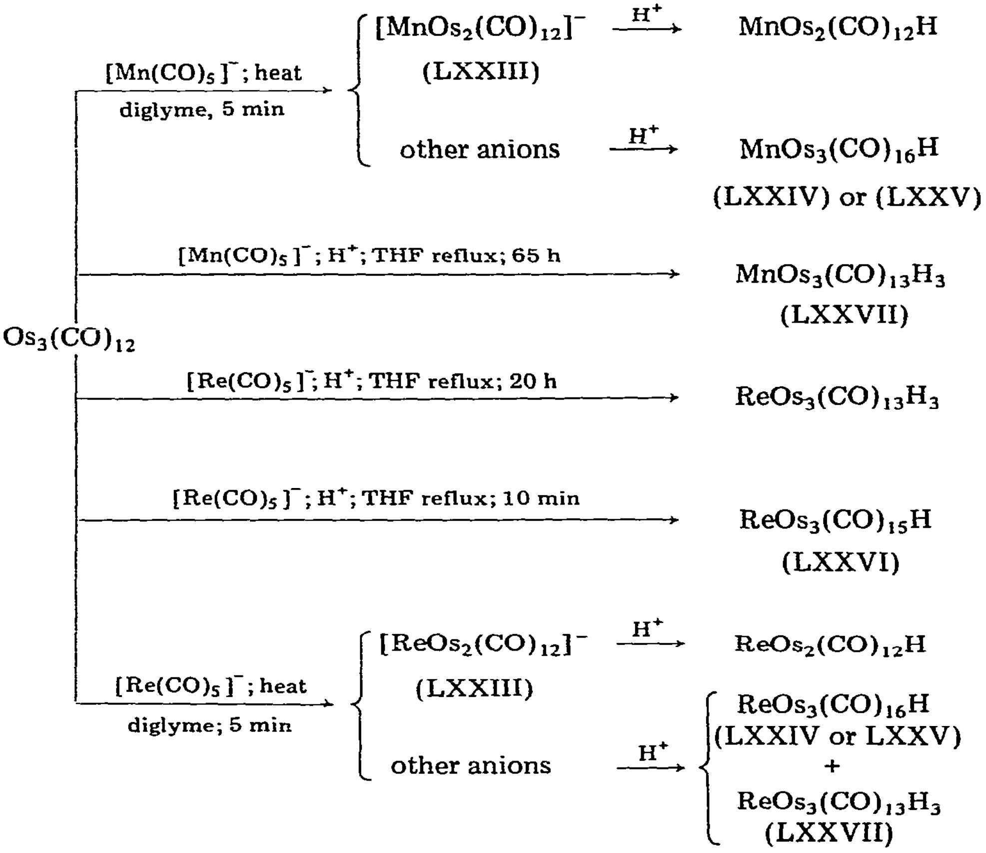
(LXXI)



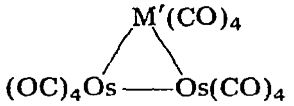
(LXXII)

(L = PPh_3 or PPh_2Me) and $Os_2Pt(CO)_7(PPh_2Me)_3$. Minor products of the reaction between $Os_3(CO)_{12}$ and $Pt(PPh_3)_2$(stilbene) were $Os_2(CO)_6[(C_6H_4)$-$PPh_2]_2$, with structure either LXIX or LXX, and $Os(CO)_x(PPh_3)_y(PPh_2)$ ($x = 6$ or 5; $y = 1$ or 2). Treatment of $Os(CO)_4H_2$ with $Pt(PPh_3)_2(C_2H_4)$ gave $Os(CO)_3(PPh_3)H_2$, $OsPt_2(CO)_5(PPh_3)_3$, LXXI and $[OsPt(CO)_4(PPh_3)H]_2$, LXXII. In the last, the H atoms may either bridge the two Pt atoms or may be bonded terminally to each of them. All of the reactions occurred via oxidative addition in which the Pt moiety was inserted into Ru—Ru as Os—Os bonds. This was then probably followed by disproportionation and elimination of an $M(CO)_4$ (M = Ru or Os) group. The formation of Pt_2M clusters was envisaged as a second series of insertion and disproportionation reactions.

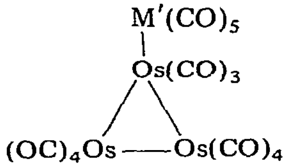
The reactions between $M_3(CO)_{12}$ (M = Ru or Os) and $[M'(CO)_5]^-$ (M' = Mn or Re) were complex [73] and the nature of the products was dependent on the solvent and temperature of the reactions. The behaviour of $Os_3(CO)_{12}$ with $[M'(CO)_5]^-$ is summarised in Scheme 5. The structure of LXXIII is analogous to that of $FeOs_2(CO)_{12}$ [74], and the overall symmetry of $MnOs_2(CO)_{12}H$ was low, the structural assignment being impossible. There are two possible structures



Scheme 5

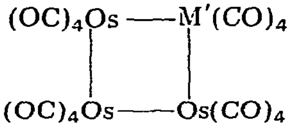


(LXXIII)

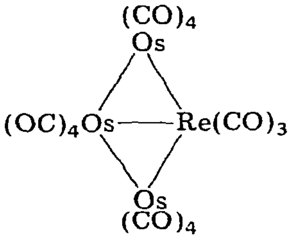


(LXXIV)

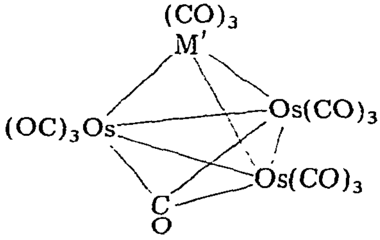
or



(LXXV)

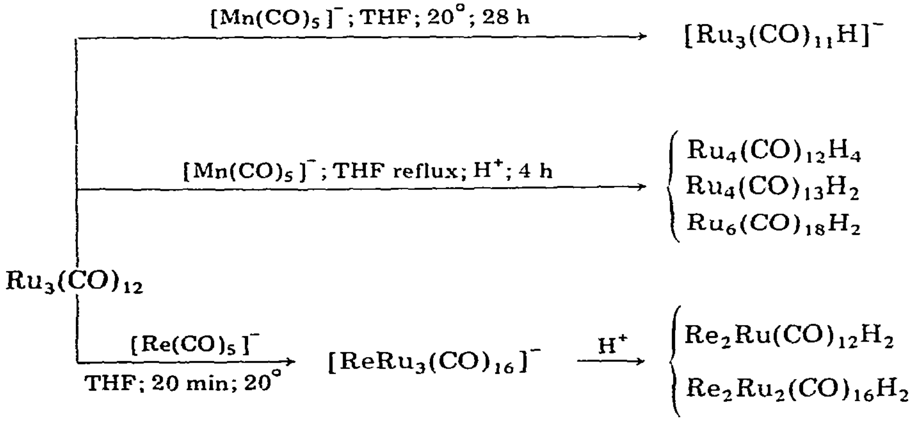


(LXXVI)



(LXXVII)

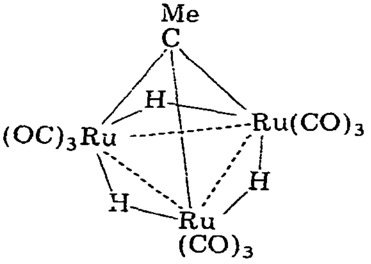
for $M'Os_3(CO)_{16}H$, LXXIV and LXXV. $ReOs_3(CO)_{15}H$, LXXVI, is probably electronically similar to $[Re_4(CO)_{16}]^{2-}$ [75], and so may contain a double triangulated $ReOs_3$ nucleus; the Mn analogue could not be prepared. In $M'Os_3(CO)_{13}$, LXXVII, both terminal and bridging CO groups are present—the compound may be analogous to $[Fe_4(CO)_{13}]^{2-}$ [76]. The H atoms may be located around the edges of the basal Os_3 triangle or in the three faces of the tetrahedron linking M' to the Os atoms. The reactions of $Ru_3(CO)_{12}$ with $[M'(CO)_5]^-$ are summarised in Scheme 6. This carbonyl was much more readily



Scheme 6

attacked than its Os analog. $[Ru_3(CO)_{11}H]^-$ is probably similar to $[Fe_3(CO)_{11}H]^-$ and, on acidification, gave an unstable compound (dihydride?) which decomposed to $Ru_3(CO)_{12}$. $Ru_6(CO)_{18}H_2$ is an octahedral cluster with six $Ru(CO)_3$ groups, and in which the H atoms bridge three metal atoms in or above opposite faces of the octahedron [77]; $[ReRu_3(CO)_{16}]^-$ is probably closely related to $M'Os_3(CO)_{16}H$, LXXIV or LXXV.

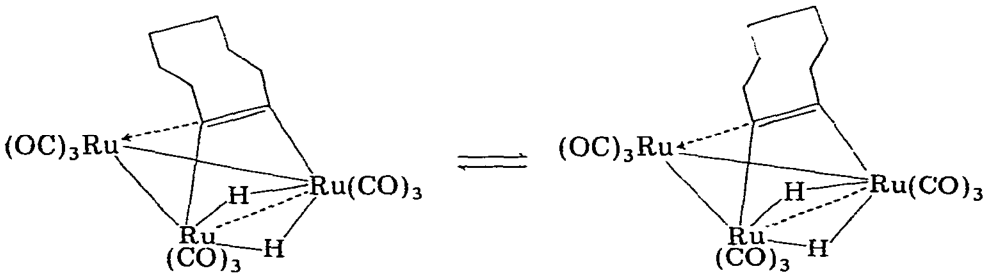
Ethylene reacted with α-$Ru_4(CO)_{12}H_4$ giving [78] α-$Ru_4(CO)_{13}H$ and $Ru_3(CO)_9(CMe)H_3$, LXXIX. The α-hydrides $Ru_4(CO)_{12}H_4$ and $Ru_4(CO)_{13}H_2$



(LXXIX)

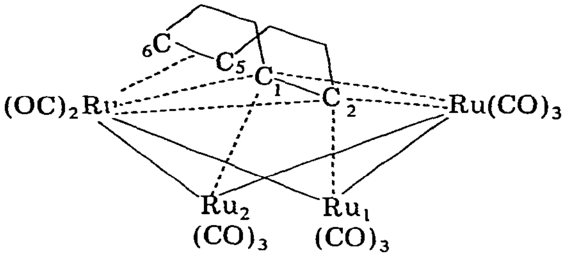
reacted with 1,5-cyclooctadiene (C_8H_{12}) giving [79] $Ru_3(CO)_9(C_8H_{12})H_2$, LXXX, $Ru_3(CO)_9(C_8H_{11})H$, $Ru_4(CO)_{11}(C_8H_{10})$, LXXXI, $Ru_4(CO)_{12}(C_8H_{12})$, $Ru_4(CO)_{12}(C_8H_{10})$, unreacted dodecarbonyl, 1,3-C_8H_{12} and C_8H_{14}. The structure of LXXXI has been determined [80] and bears similarities to $Co_4(CO)_{10}(EtC_2Et)$ [81]. Thus the four Ru atoms have a butterfly conformation, and the C_1—C_2 bond is "acetylenic", forming two Ru—C "σ-bonds", Ru_1—C_2 and Ru_2—C_1 (2.16 Å) and two "μ-bonds" involving Ru_3 and Ru_4 (2.21 Å). The Ru—Ru distances averaged 2.74 Å except that of Ru_1—Ru_2 which is 2.82 Å; the dihedral angle between the two trimetal planes is 112°. By heating $M_3(CO)_{12}$ (M = Ru or Os) with cyclooctene, $M_3(CO)_9(C_8H_{12})H_2$ (LXXX, M = Ru) was obtained, and $Ru_3(CO)_9(C_8H_{11})H$, when heated under 1 atm. of H_2, also gave LXXX. The compound LXXX was stereochemically non-rigid (Scheme 7). Treatment of $Ru_3(CO)_{12}$ with bicyclo[3.2.1]-octa-2,6-diene gave [82] the stereochemically non-rigid LXXXII.

With RC≡CH, $Ru_3(CO)_{12}$ gave [83] LXXXIII (R = t-Bu or Ph), which is similar to $Fe_3(CO)_9C_2Ph_2$ [84]. With PhC≡CPh, in alkaline solution, $Ru_3(CO)_{12}$

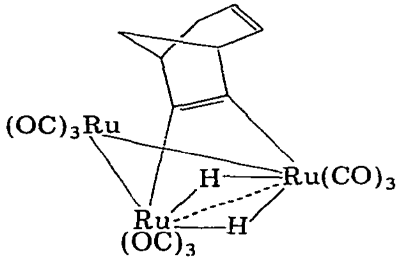


(LXXX)

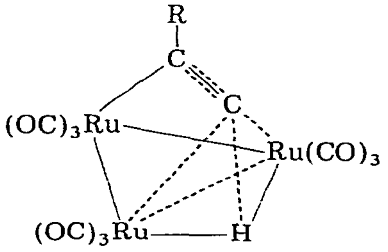
Scheme 7



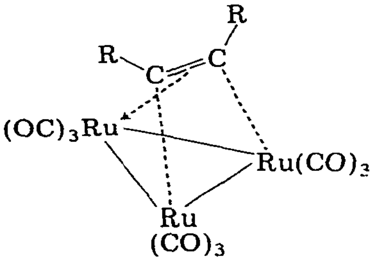
(LXXXI)



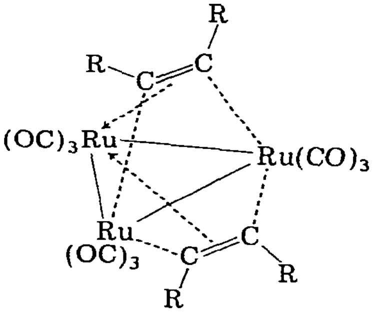
(LXXXII)



(LXXXIII)

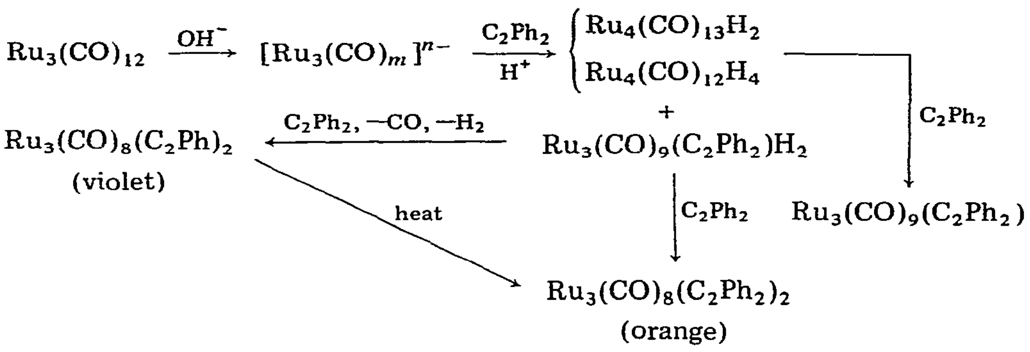


(LXXXIV)
(H omitted)



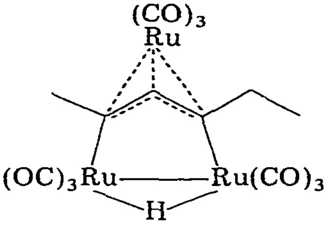
(LXXXV)

afforded [85] $Ru_3(CO)_9(C_2Ph_2)H$, probably LXXXIV, and further reaction of this with PhC≡CPh gave LXXXV (proposed structure). The general reactions are summarised in Scheme 8. $Ru_3(CO)_{12}$ also reacted with di- or tetra-phenylbuta-1,3-diene giving [86] orange isomers of $Ru_3(CO)_8L_2$ ($L = C_2Ph_2$ or C_2HPh); such species may also have been produced in the reactions of $Ru_3(CO)_{12}$ with PhC≡CPh [87]. Also obtained from the reactions of the arylbutadienes were $Ru_3(CO)_9(C_7H_{12})$, $Ru_3(CO)_9(C_6H_{10})Ru_4(CO)_{12}H_4$, $Ru_4(CO)_{13}H_2$ and $Ru_3(CO)_9C_4H_4Ph_2$. All CO groups in these compounds are terminal. The ^1H and NMR spectra of $Ru_3(CO)_9(C_6H_{10})$ were consistent [88] with the presence of a Ru—H bond and a π-1,3-methylethylallyl group coordinated, as in LXXXVI, so that the compound must be reformulated as $Ru_3(CO)_9(C_6H_9)H$. The

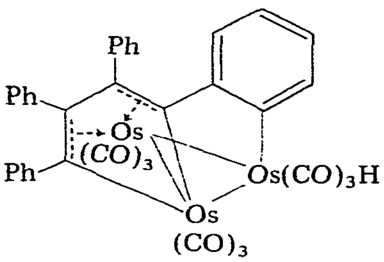


Scheme 8

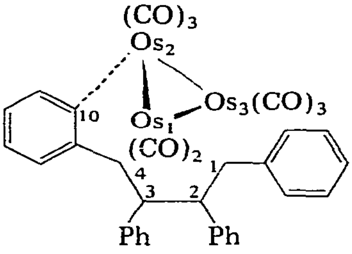
compound LXXXVI was also obtained from *cis,trans-* or *trans,trans*-hexa-2,4-diene and $Ru_3(CO)_{12}$, and its structure has been confirmed crystallographically; it is comparable with $Ru_3(CO)_9(C_{12}H_{15})H$ [89].



(LXXXVI)



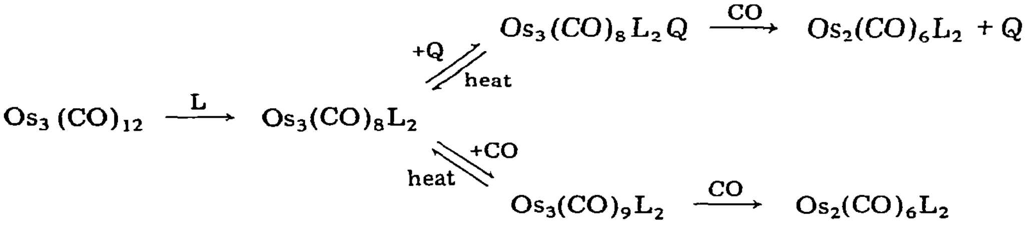
(LXXXVII)



(LXXXVIII)

Arylacetylenes also reacted [90] with $Os_3(CO)_{12}$ giving $Os_3(CO)_8L_2$ ($L = C_2Ph_2$, $C_2(p\text{-}ClC_4H_4)_2$ or $C_2(p\text{-}MeC_6H_4)$. These compounds contained an Os—H bond and the structure LXXXVII was proposed. However, crystallographic studies indicated [91] that the molecule had an overall structure LXXXVIII in which the Os_1—Os_3 and C_1—C_2—C_3—C_4 bonds were mutually perpendicular. There was indication of a bond between Os_2 and the phenyl ring A (C_{10}) (Os_2—C_1 2.18 Å). The Os_1—C_1 or C_4, Os_3—C_1 or C_4, C_1—C_2 and C_3—C_4 distances were consistent with single bonds while C_2—C_3 appeared to be a double bond. It was implied that there was a μ-bond involving C_2—C_3

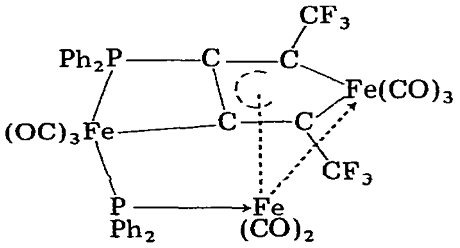
and Os_1 and Os_3. The intermetallic distances were: Os_1—Os_2 2.87 Å, Os_1—Os_3 2.75 Å and Os_2—Os_3 2.94 Å. The complexes $Os_3(CO)_8L_2$ reacted further with CO, PF_3, PPh_3, $AsPh_3$ or $SbPh_3$(Q) affording $Os_3(CO)_8L_2Q$ (Scheme 9).



L = Ph_2C_2; $(p\text{-}ClC_6H_4)_2C_2$; $(p\text{-}MeC_6H_4)_2C_2$
Q = PF_3, PPh_3, $AsPh_3$, S_6Ph_3, CO

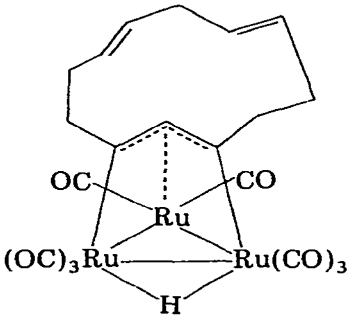
Scheme 9

Reaction of $Fe_3(CO)_{12}$ with $Ph_2MC{\equiv}CCF_3$ (M = P or As) gave LXXXIX which afforded [92], with $P(OR)_3$ (R = Me or Et) $Fe_3(CO)_x[Ph_2PC_2(CF_3)]_2$-$[P(OR)_3]$. The Fe_3—C (1.96 Å) and C—C (1.43 Å) distances within the ferrocyclopentadiene ring were similar to those found in $Fe_2(CO)_6[C_4Me_2(OH)_2]$

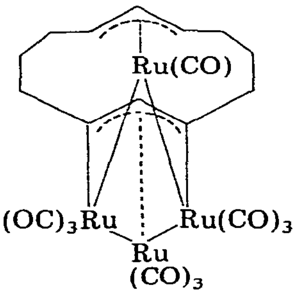


(LXXXIX)

and $Fe_3(CO)_6(C_2Ph_2)$ [93]. The Fe_2—Fe_3, Fe_1—Fe_2 and Fe_1—Fe_3 distances were 2.55, 3.50 and 4.98 Å, respectively. The molecule was two electrons short of the rare gas configuration.

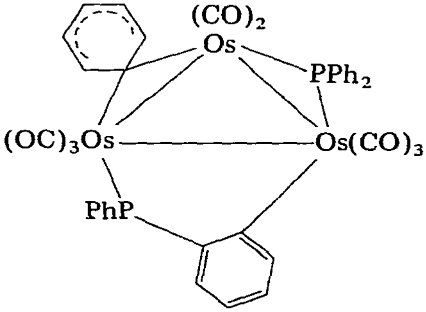


(XC)

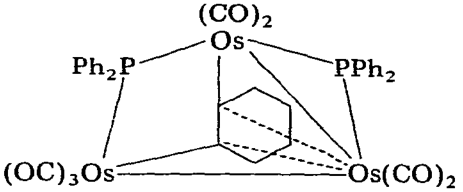


(XCI)

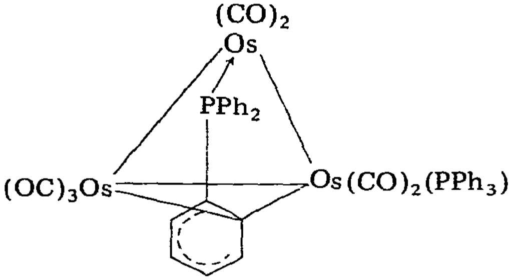
Treatment of $Ru_3(CO)_{12}$ with cyclododeca-1,5,9-triene isomers afforded [94] $Ru_3(CO)_8(C_{12}H_{15})H$, XC, $Ru_3(CO)_9(C_{12}H_{17})H$, $Ru_2(CO)_{17}(C_{12}H_n)H$ (n probably 17) and $Ru_4(CO)_{10}(C_{12}H_{16})$, XCI. XC reacted with $Ru_3(CO)_{12}$ giving XCI, but did not react with $Fe_2(CO)_9$. XC also reacted with L($P(OMe)_3$, $PPhMe_2$ or $P(OCH_2)_3CEt$) giving $Ru_3(CO)_{9-n}L_n(C_{12}H_{15})H$ (n = 1, 2 or 3).



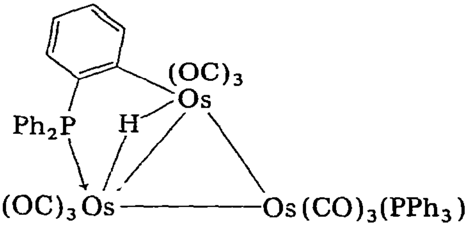
(XCII)



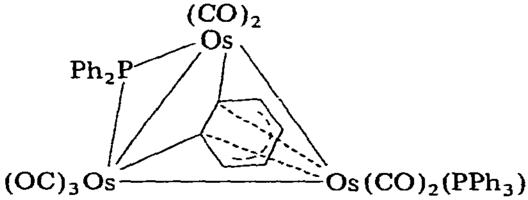
(XCIII)



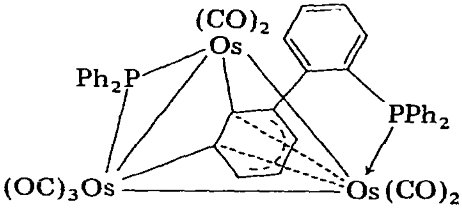
(XCIV)



(XCV)



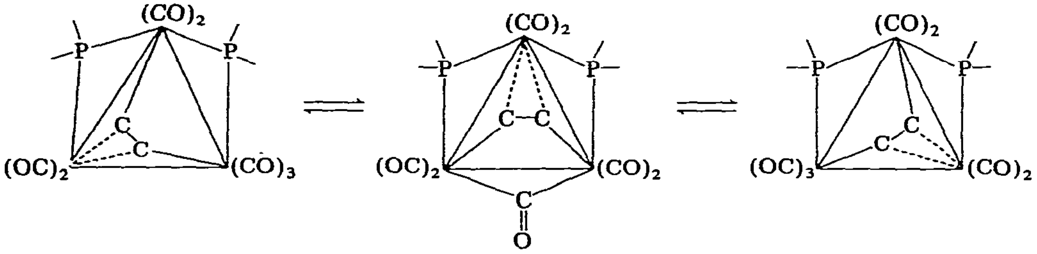
(XCVI)



(XCVII)

Reaction of $Os_3(CO)_{12}$ with PPh_3 in a molar ratio of 1/2 [95] gave a mixture of nine compounds, $Os_3(CO)_8(PPh_2)(C_6H_5)(PPhC_6H_4)$, XCII, $Os_3(CO)_7(PPh_2)_2$-(C_6H_4), XCIII, $Os_3(CO)_8''(PPh_3)(PPh_2)''$, $Os_3(CO)_8''(PPh_3)_2''H$, XCIV, $Os_3(CO)_9$-$(PPh_3)(PPh_2C_6H_4)H$, XCV, $Os_3(CO)_9''(PPh_3)_2''H$, XCVI and $Os_3(CO)_{12-n}(PPh_3)_n$ (n = 1, 2 or 3); also described were $Os_3(CO)_8[P(C_6H_4Me)_3]_2(C_6H_4Me)$-$[P(C_6H_4Me)(C_6H_3Me)]$, $Os_3(CO)_7(AsPh_2)_2(C_6H_4)$, probably similar to XCIII, and $Os_3(CO)_9(PPh_3)_3H^+$. Thermal decomposition of $Os_3(CO)_{10}(PPh_3)_2$ gave

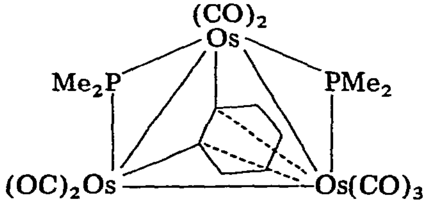
$Os_3(CO)_7(PPh_2)[PPh_2(C_6H_4C_6H_3)]$, XCVII. The structures of those numbered compounds have been determined crystallographically [95, 96], and all contain Os_3 triangles. The coordination of the benzyne ligands in XCIII and XCVI is very similar; XCVII may be regarded as being formed by intracluster oxidative addition of benzyne to a β-CH bond of terminal PPh_3 in XCVI. The mean C—C bond length in the coordinated benzyne ligands in XCII, XCVI and XCVII is 1.42 Å, and the dihedral angle between the Os_3 plane and the aryne ligand plane is 69 ± 3°. XCIV exhibits metallation of a β-CH bond in PPh_3 by two adjacent Os atoms, and, as such, may be regarded as a precursor of XCII, XCIII and XCV. The Os—C—Os bond angle (74°) was smaller than that observed in XCII. In XCVI and XCVII, the H atom may be terminally bound to the "top" Os atom, whereas in XCIV it presumably bridges the "bottom" Os atoms.



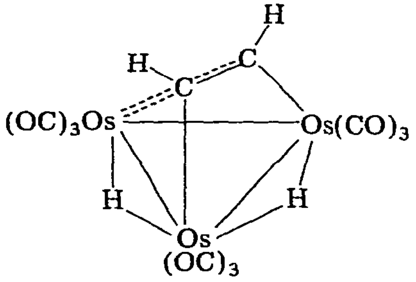
Me groups, Os atoms
and part of C_6H_4 ring
omitted for clarity

Scheme 10

$Os_3(CO)_{12}$ reacted with $PPhMe_2$ in refluxing toluene [97] giving $Os_3(CO)_{12-n}(PPhMe_2)_n$ (n = 1, 2 or 3). Heating these in refluxing n-nonane gave $Os_3(CO)_9(PMe_2)(C_6H_4)H$ and $Os_3(CO)_7(PMe_2)_2(C_6H_4)$, XCVIII. The latter has a structure analogous to XCIII, and is stereochemically non-rigid (Scheme 10); the former behaves similarly. Reaction between o-vinylphenyldiphenylphosphine (L) and $Os_3(CO)_{12}$ gave [98] $Os_3(CO)_8L_2$ and no $Os(CO)_3L$. The former was shown, by ^1H NMR spectroscopy, to be $Os_3(CO)_8(Ph_2PC_6H_4C_2H)H$, the vinyl group having been dehydrogenated to give an acetylenic ligand bridging the three Os atoms. $Os_3(CO)_{12}$ reacted with



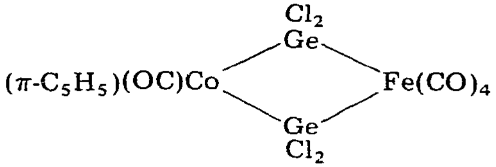
(XCVIII)



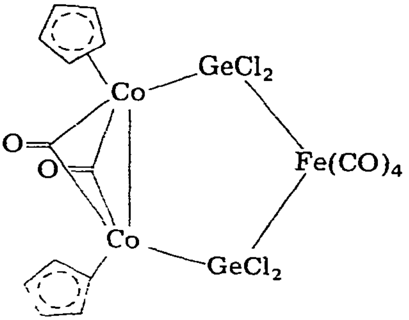
(XCIX)

C_2H_4 in n-octane at 125° giving $Os_3(CO)_9(C_2H_2)H_2$, possibly XCIX, and with benzene at 180° giving $Os_3(CO)_9(C_6H_4)H_2$ (this may contain *o*-phenylene bonded to an Os_3 triangle via two C atoms). Reaction with H_2S in *n*-octane at 125° gave $Os_3(CO)_9(S)H_2$.

The structure proposed [99] for $[(\pi\text{-}C_5H_5)Co(CO)]_2(\mu\text{-}GeCl_2)_2Fe(CO)_4$, C, has been shown crystallographically to be CI [100].



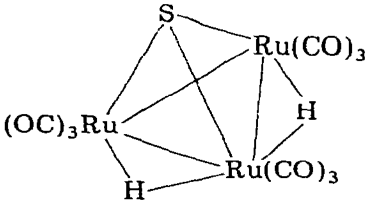
(C)



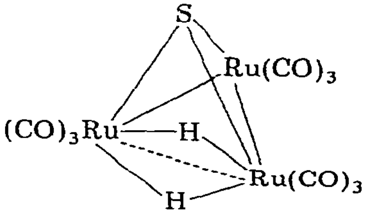
(CI)

The reaction of $Fe_3(CO)_9XY$ (X, Y = S, Se or Te; X ≠ Y) with L ($P(OPh)_3$ or $AsPh_3$) obeyed [101] a two-term rate law for substitution. Iron carbonyls reacted [102] with $Co_2(CO)_6(SR)_2$ (R = C_6F_5 or C_6Cl_5) giving $FeCo_2(CO)_9S$,, also obtained [103] in the reaction of $Fe_2(CO)_6S_2$ with $Co_2(CO)_8$. However, reaction of $Co_2(CO)_8$ with $Fe_2(CO)_6(SR)_2$ gave only $Co_4(CO)_{12}$. $Fe_3(CO)_{12}$ reacted with $Co_6(CO)_{11}(SEt)_4S$ and $Co_3(CO)_4(SEt)_5$ giving, under UV irradiation, $FeCo_2(CO)_9S$ and *syn*- and *anti*-$Fe_2(CO)_o(\mu\text{-}SR)_2$.

$Ru_3(CO)_{12}$ reacted [104] with XO_3^- (X = S, Se or Te) in alkaline solution giving an anion which, on acidification, gave $Ru_3(CO)_9(X)H_2$, either CII or CIII. When $Ru_3(CO)_{12}$ was refluxed in CS_2, $[Ru(CO)_3(CS)]_n$ was formed, and with cyclohexene sulphide, $[Ru(CO)_3(C_6H_{10})S]_n$ was produced.



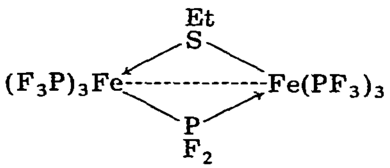
(CII)



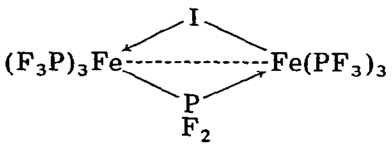
(CIII)

Metal trifluorophosphine complexes

$Fe(PF_3)_5$ reacted with PF_3 and H_2 under UV irradiation giving [105, 106] the thermally and oxidatively stable $Fe(PF_3)_4H_2$. The compound was stereochemically non-rigid, existing as octahedral *cis*- and *trans*-isomers at low temperatures. Deprotonation by KOBu-t gave $K[Fe(PF_3)_4H]$ and $K_2[Fe(PF_3)_4]$;



(CIV)



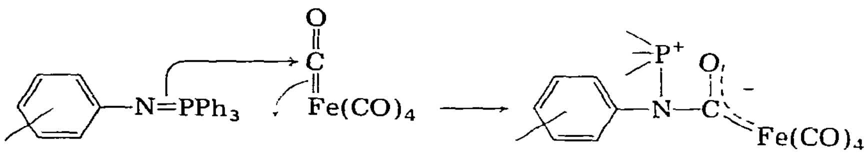
(CV)

the former species, and its analogs $[M(PF_3)_4H]^-$ [107], M = Ru or Os, was also stereochemically non-rigid having distorted trigonal bipyramidal structures at low temperatures. $Fe(PF_3)_4H_2$ reacted with EtSH and I_2 giving [105] CIV and CV, respectively; under UV irradiation, it reacted with isoprene giving the diene complex $Fe(C_5H_8)(PF_3)_3$.

$Ru_3(CO)_{12}$ reacted with PF_3 at high pressures giving [108] the stereochemically non-rigid $Ru(PF_3)_x(CO)_{5-x}$ (x = 5, 4 or 3), and traces of $Ru(CO)_3(PF_3)_2$ and $Ru(CO)_4(PF_3)$. At high CO pressures and moderate PF_3 pressures, $Ru_3(CO)_{12-y}(PF_3)_y$ (y = 0–6) was produced.

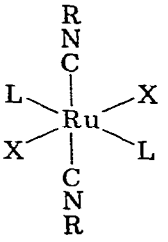
Metal isocyanide complexes

Deoxygenation of a CO group in $Fe(CO)_5$ by $Ph_3P{=}NC_6H_4Me$ gave [109] $Fe(CO)_4[CN(C_6H_4Me)]$, $Fe(CO)_3[CN(C_6H_4Me)]_2$ and Ph_3PO; the proposed mechanism of reaction is summarised in Scheme 11. With $Fe_2(CO)_9$, the phosphineimine gave the same isocyanides together with urea, oxamide and hydrazobenzene derivatives. Fe, Ru and Os^{II} hexacyanides reacted [110] with acetone and $[Et_3O][BF_4]$ giving $[M\{C{\equiv}NCMe_2CH_2COMe\}_6][BF_4]$ and similar species were obtained with methylethylketone, cyclohexanone and acetophenone (the latter formed only $[Fe\{C{\equiv}NCMePhCN_2COPh\}_5(CN)][BF_4]$.

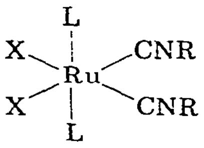


Scheme 11

Addition of CNEt to RuL_nX_2 (L = PPh_3 or $SbPh_3$; n = 3 or 4; X = Cl or Br) and to $Ru(AsPh_3)_2(MeOH)X_3$ (X = Cl or Br) gave [111] *trans*-$Ru(CNEt)_2L_2X_2$, CVI. The *trans*-isomer was converted to the *cis*-form, CVII, by heating.

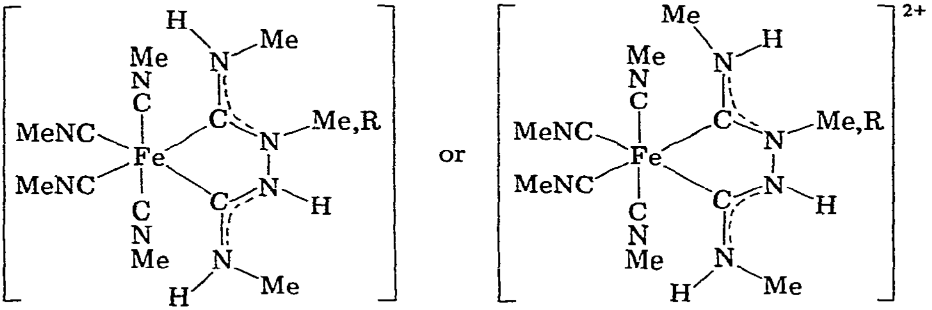


(CXI)

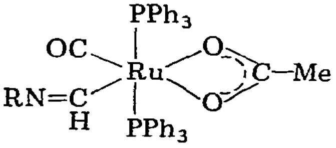


(CVII)

Correlation has been made [112] of isomer shift and quadrupole splittings obtained from the Mössbauer spectra of $[Fe(CNAr)_5(SnCl_3)]^+$, *trans*-Fe[CN-(*p*-MeC_6H_4)]$_4Cl_2$, its $SnCl_3$ derivative and [Fe{CN(*p*-MeC_6H_4)}$_5(SnCl_3)]^+$ and their electronic spectra and Fe 2*p* and 3*p* core electron binding energies [113].



(CVIII)



(CIX)

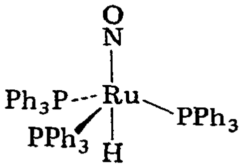
Reactions of $[Fe(CNMe)_6]^{2+}$ with the hydrazines RNHNHR (R = H, Me or Ph) gave [114] CVIII (the two most probable configurations are shown). Addition of ethanol to $Ru(CO)(CNR)(PPh_3)_2(O_2)$ (R = *p*-MeC_6H_4) gave [115] CIX which, on treatment with HCl gave $Ru(CO)[CH(NHR)](PPh_3)_2Cl(O_2CMe)$ which contained a coordinated carbene ligand. Reaction of CIX with NaS_2CNEt_2 gave $Ru(CO)(PPh_3)_2[CH(=NR)](S_2CNEt_2)$, analogous to CIX with acetate replaced by dithiocarbamate. This same compound could be obtained by addition of NaS_2CNEt_2 to $Ru(CO)(CNR)(PPh_3)_2(OClO_3)$.

Metal nitrosyl complexes

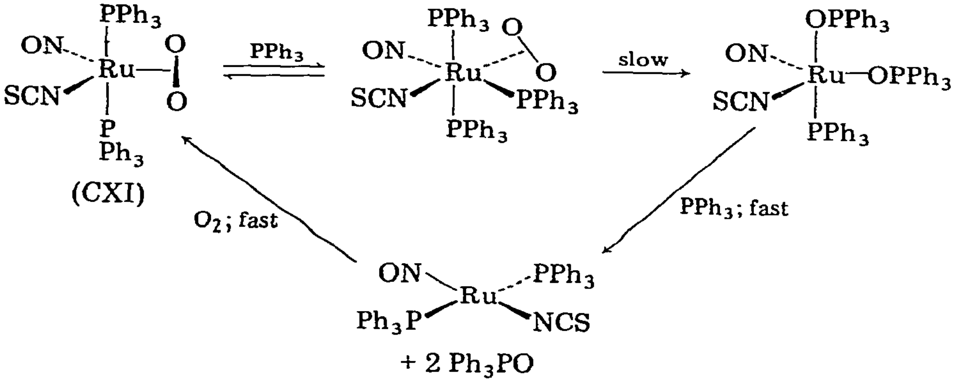
An excellent review of transition metal nitrosyls, their structures, spectral properties and reactions, has recently been published [116].

Addition of $NOPF_6$ to $Fe(CO)_3L_2$ (L = PPh_3, PPh_2Me, $PPhMe_2$, PEt_3, P(c-$C_6H_{11})_3$, $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$, $P(OMe)_3$ or $P(OPh)_3$) gave [117] $[Fe(CO)_2(NO)L_2]^+$ which reacted further with L ($P(OMe)_3$, PPh_2Me or $PPhMe_2$) and with $Ph_2PCH_2CH_2PPh_2$ giving $[Fe(CO)(NO)L_3]^+$ and $[Fe(NO)(Ph_2PCH_2CH_2PPh_2)_2]^+$, respectively. The latter was also obtained by reaction of $Fe(Ph_2PCH_2CH_2PPh_2)_2HCl$ and *p*-$MeC_6H_4SO_2N(Me)NO$ in the presence of $NaBH_4$. Addition of OMe^- to $[Fe(CO)_2(NO)(PPh_3)_2]^+$ or its diphos analog gave $Fe(CO)(NO)(PPh_3)_2(CO_2Me)$ and $Fe(CO)(NO)(Ph_2PCH_2CH_2PPh_2)(CO_2Me)$; there was no evidence for methoxide attack upon coordinated NO.

The structure of $Ru(NO)(PPh_3)_3H$, CX, has been determined crystallographically [118]. The Ru atom was displaced by 0.55 Å out of the trigonal plane of the PPh_3 groups towards the NO; the Ru—N—O bond angle was 176°. Molecular oxygen reacted with $Ru(CO)(NO)(PPh_3)_2NCS$ giving [119] $Ru(NO)(PPh_3)_2(O_2)NCS$, CXI, and may be displaced and replaced by CO. The carbonyl and its analog $Ru(NO)(PPh_3)_2(O_2)NCS$, were efficient catalysts for the homogeneous oxidation of PPh_3 to Ph_3PO, the rate being proportional to the increase of the PPh_3 concentration. The rate also depended on the partial pressure of O_2 for the carbonyl but not for CXI. The proposed mechanism is summarised in Scheme 12.

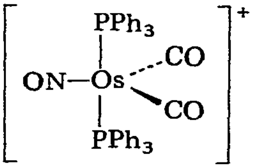


(CX)



Scheme 12

Borohydride reduction of $Os(CO)(NO)(PPh_3)_2Cl$ gave [120] $Os(CO)(NO)(PPh_3)_2H$, which reacted with HX (X is non-coordinating) in the presence of CO giving $[Os(CO)_2(NO)(PPh_3)_2]X$, CXII. Addition of L (PPh_3, PPh_2Me, $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$ or p-MeC_6H_4NC) to CXII afforded $[Os(CO)(NO)(PPh_3)_2L]^+$ and addition of excess of RNC in the presence of O_2 gave $[Os(CO)(CNR)_2(PPh_3)_2(NO_2)]^+$. Treatment of CXII with X^- (coordinating) gave $Os(CO)(NO)(PPh_3)_2X$ and $Os(CO)_2(PPh_3)_2X_2$. The structure of CXII has been determined, and the Os—N—O and Os—C—O bond angles were essentially linear. The Os—NO bond length (1.89 Å) was quite long, linear M—NO groups usually having shorter M—N bond distances.



(CXII)

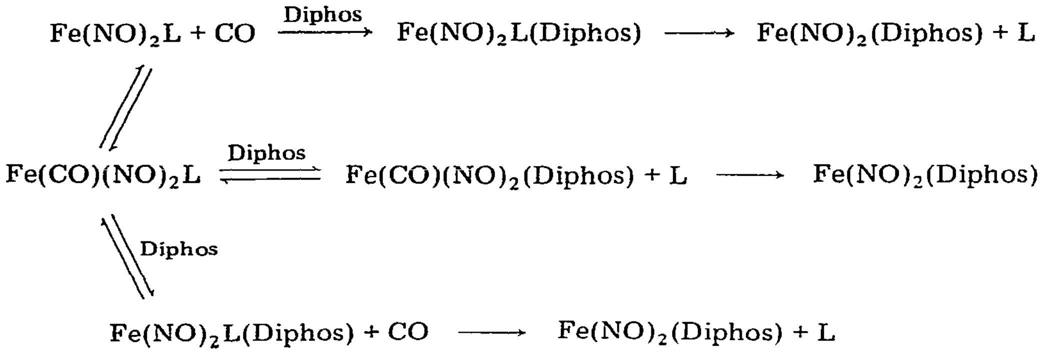
The crystal and molecular structures of $[NH_4]_2[Ru(NO)Cl_5]$ [121] and its K^+ analog [122], established that the $[Ru(NO)Cl_5]^{2-}$ was a slightly distorted octahedron. The Ru—N—O group was essentially linear (ca. 177°) and the Ru—N(NO) distance was 1.74-1.75 Å. It was suggested that the nitrosyl group was bonded as NO^+. The Ru—Cl bond length *trans* to NO was shorter than the others in the ion. The electronic and magnetic circular dichroism spectra of $[Ru(NO)(NH_3)_4L]X$ (L = Cl, Br, NCO, N_3, OH, NH_3 or OCOMe) have been assigned [123] and interpreted. It was suggested that the compounds contain the $\{Ru^{III}—NO^0\}$ group rather than $\{Ru^{II}—NO^+\}$. The complex $[Ru(NO)(Bipy)_2X]^{2+}$ (X = Cl or NO_2) reacted [124] with N_3^- in the presence of solvent, S, giving $[Ru(Bipy)_2X(S)]^+$, N_2 and N_2O.

The halides $M(NO)(QR_3)_2X_3$ (M = Ru or Os; X = Cl or Br; Q = P or As; R = alkyl, aryl or mixed species) were conveniently prepared [125] by reaction of MX_3 with p-$MeC_6H_4SO_2N(Me)NO$ or pentyl nitrite with a solution of QR_3 in boiling alcohols. Addition of an excess of LiI to these mixtures afforded $M(NO)(QR_3)_2I_3$. The paramagnetic $Ru(NO)(PPh_3)_2Cl_2$ was also detected as a minor product during the formation of $Ru(NO)(PPh_3)_2Cl_3$. Reaction of azide ion with *trans*-$[Ru(NO)(Diars)_2Cl]Cl_2$ (Diars = *o*-phenylenebis(dimethylarsine)) afforded [126] *trans*-$[Ru(Diars)_2(N_3)Cl]$ together with N_2 and N_2O. The complex containing ^{15}NO eliminated nitrous oxide as $^{14}N_2O$ and $^{15}N_2O$ in equal amounts. The IR spectra of *trans*-$[Ru(NO)(Diars)_2X]^{2+}$ (X = Cl or I), *trans*-$[Ru(N_2)(Diars)_2Cl]^+$ and *trans*-$[Ru(CO)(Diars)_2Cl]^+$ were compared [127] and it was indicated that NO was a better π-acceptor in these complexes than CO or N_2. The magnetic susceptibilities, ESR and Mössbauer spectra of *trans*-$[Fe(NO)(Diars)_2X]^+$ (X = halide) have been measured [128]. The compound had one unpaired electron and ESR spectral parameters indicated that the Fe^{III} ion existed in a rhombic field.

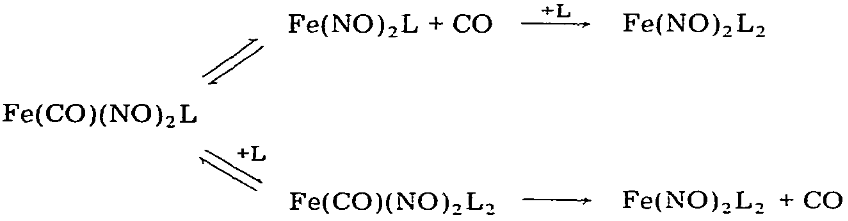
Reaction of $Fe(NO)(S_2CNEt_2)_2$ with impure NO (containing ca. 3% NO_2) or pure NO_2 gave [129] $Fe(NO)(S_2CNEt_2)_2(NO_2)$; with pure NO no reaction was observed. Oxidation of $Fe(NO)(S_2CNEt_2)_2$ by halogen afforded $Fe(NO)(S_2CNEt_2)_2X$ (X = Br or I) in which the NO and X groups were mutually *cis* (also when X = NO_2). Improved syntheses of *cis*-$Fe(CO)_2(S_2CNR_2)_2$ (R = Me or Et) were also reported, and reaction of $[Fe(CO)_3(\mu\text{-}SMe)]_2$ with NaS_2CNEt_2 in the presence of some I_2 afforded one isomer (precise structure unknown) of $[Fe(CO)_2(S_2CNEt_2)(\mu\text{-}SMe)]_2$; the last had *cis*-CO and bidentate dithiocarbamate groups.

Phosphines, $Ph_2PCH_2CH_2PPh_2$ and $AsPh_3$ displaced [130] CO from $Fe(CO)(NO)_2L$ (L = tertiary phosphine) by an associative mechanism, the order of reactivity being $CO > AsPh_3 \gg P(OPh)_3 > P(OBu)_3 > PPh_3 > PBu_3$. The mechanistic pathways are illustrated in Schemes 13 and 14; the former relates to reaction of diphos when L = PPh_3 or PBu_3, the latter to all other ligands.

The complexes $Fe(NO)_2(Bipy)$, $Fe(NO)_2(o\text{-phen})$ and CXIII were polarographically oxidised [131] in one step giving $[Fe(NO)_2(N—N)]^+$ (N—N = heterocyclic ligand) and reduced in two steps giving mono- and di-anions. It was suggested that the unpaired electron in $[Fe(NO)_2(N—N)]^-$ was located in an orbital of π^* (N—N) character, whereas in the monocation it was localised in an orbital of σ-character. The Ru^{II} carbonyl mesoporphyrin (IX) dimethylester (Porph) reacted with NO affording $Ru(NO)_2(Porph)$.

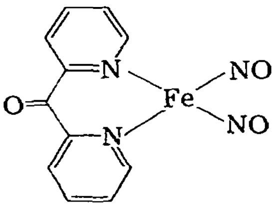


Scheme 13

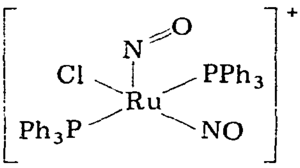


Scheme 14

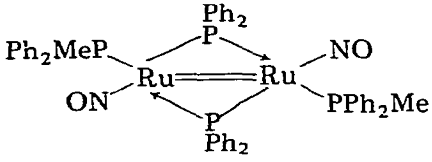
The crystal and molecular structure of $[Ru(NO)_2(PPh_3)_2Cl][PF_6]$, CXIV, has been determined [133]. The molecule was essentially square pyramidal, the apical Ru—N—O bond angle being 138°, the Ru—N and N—O bond distances 1.85 and 1.17 Å. The basal Ru—NO group was essentially linear (178°), and the Ru—N and N—O distances 1.74 and 1.16 Å. During recrystallisation of $Ru(NO)(PPh_2Me)_3H$ [134], the dimer $[Ru(NO)(PPh_2Me)(PPh_2)]_2$, CXV, was formed [135]. CXV was also obtained in the reaction between $Ru(NO)(PPh_2Me)_2Cl_3$ and PPh_2H with Zn/Cu couple, together with the tetranuclear CXVI. In the former the Ru—Ru distance was short (2.63 Å), indicating a bond order of nearly 2, and the Ru—N distance, 1.70 Å, was shorter than those observed for most other linear Ru—NO systems. In the latter, the bonded Ru—Ru distances were 2.79 Å (bond order 1) and the non-bonded separations 3.67 Å; the Ru—N distances were 1.78 Å.



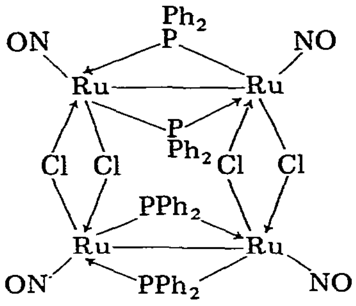
(CXIII)



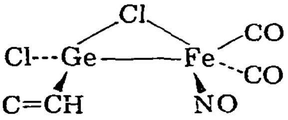
(CXIV)



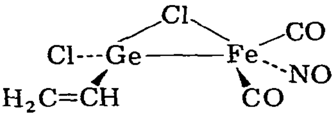
(CXV)



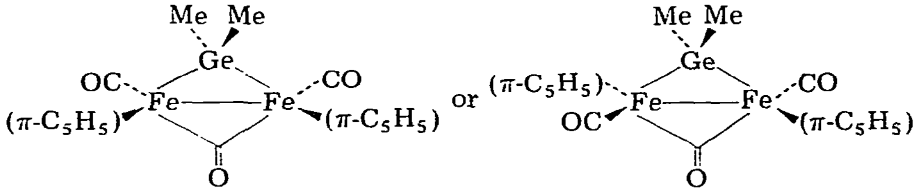
(CXVI)



(CXVII)



(CXVIII)



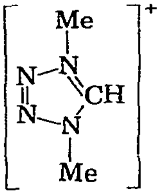
(CXIX)

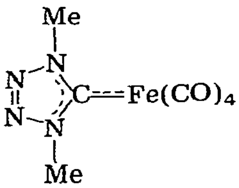
$Ge(CH{=}CH_2)Cl_3$ reacted [136] with $Na[Fe(CO)_3(NO)]$ giving CXVII, and $GeMe_2Cl_2$ afforded CXVIII (isomers of CXVII were identified). UV irradiation of $(\pi\text{-}C_5H_5)Fe(CO)_2GeMe_2Cl$ afforded a 4/1 mixture of the *cis*- and *trans*-isomers of CXIX.

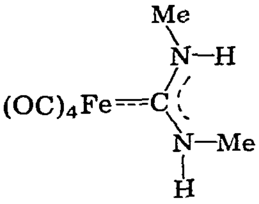
Metal carbene complexes

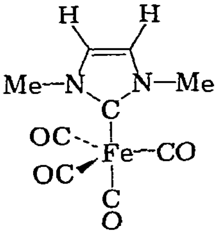
UV irradiation of the carbene complex $(\pi\text{-}C_5H_5)Mo(CO)(NO)[CRPh]$ (R = OMe, OEt or NMe_2) in the presence of $Fe(CO)_5$ afforded [137] $Fe(CO)_4[CRPh]$ and $(\pi\text{-}C_5H_5)Mo(CO)_2(NO)$. The complexes $Fe(CO)_4[C(OEt)R]$ (R = C_6F_5, C_6Cl_5, NMe_2 or NEt_2) were prepared by treating $Fe(CO)_4[C(OLi)R]$ with $[Et_3O][BF_4]$. Addition of 1,4-dimethyltetrazolium salts (CXX) to $Na[Fe(CO)_4H]$ afforded [138] the carbene species CXXI and CXXII, probably via the mechanism shown in Scheme 15. The isocyanide complexes were isolated and characterised. The structure of CXXIII has been established crystallographically; the Fe—C (carbene) distance was 2.01 Å [139].

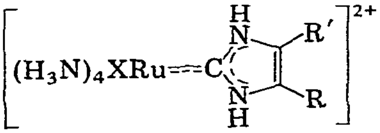
The imidazole complex $[Ru(NH_3)_5(imide)]^{2+}$ (N-bonded imide) reacted [140] with acid, HX, giving $[Ru(NH_3)_5(H_2O)]^{2+}$ and $[Ru(NH_3)_4(imide)X]^{2+}$ in which the imidazole ligand was C-bound (CXXIV). $[Ru(NH_3)_5(H_2O)]^{2+}$ afforded a similar species when treated with 4,5-dimethylimidazole in acid at pH 5.5.

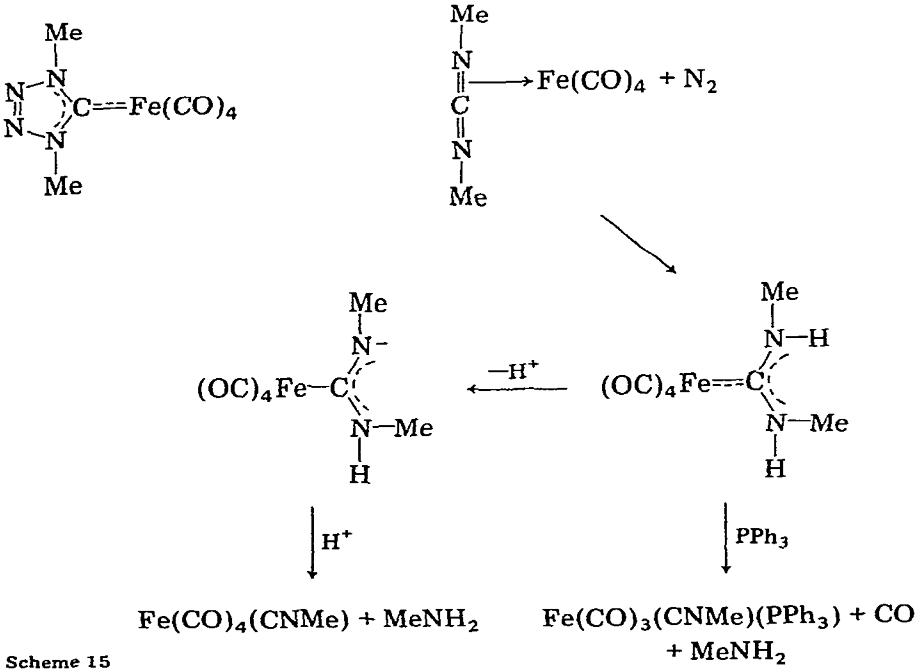

(CXX)


(CXXI)


(CXXII)


(CXXIII)

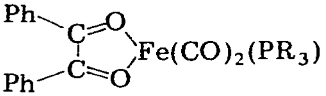

(CXXIV)



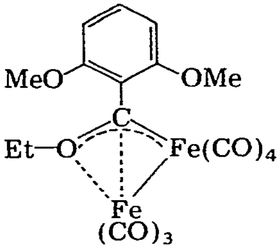
Scheme 15

Reaction of $Fe(CO)_2(NO)_2$ or $Fe(CO)(NO)(PPh_3)$ with LiR (R = NHMe, NMe_2, NEt_2, or Ph) gave [141] $Fe(CO)(NO)_2[C(OLi)R]$ and $Fe(NO)_2(PPh_3)$-$[C(OLi)R]$. Treatment of these with $[Et_3O][BF_4]$ afforded $Fe(CO)(NO)_2$-$[C(OEt)R]$ and $Fe(NO)_2(PPh_3)[C(OEt)R]$.

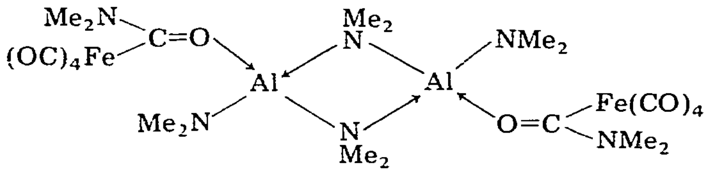
Addition of L (NH_3, $NHEt_2$, $PhNHNH_2$ or pyridines) to $Fe_2(CO)_6(\mu\text{-}COR)_2$ (R = Me or Ph) afforded [142] $Fe_2(CO)_5(L)(\mu\text{-}COR)_2$, and with EtSH or PhSeH, $Fe_2(CO)_6(\mu\text{-}SEt)_2$ and $Fe_2(CO)_6(\mu\text{-}SePh)_2$ were isolated. Reaction with PPh_3 or $PPr\text{-}i_3$ gave CXXV and $Fe(CO)_3(PR_3)_2$.



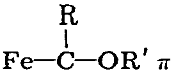
(CXXV)



(CXXVI)



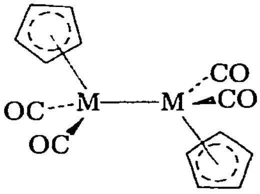
(CXXVII)

Treatment of $Fe(CO)_5$ with $LiC_6H_3(OMe)_2$, followed by $[Et_3O][BF_4]$, afforded [143] CXXVI whose molecular structure has been determined [144]. The compound was described as containing the system  $Fe{-}\overset{R}{\overset{|}{C}}{-}OR'$ π-bonded to an $Fe(CO)_3$ group. Reaction of $Fe(CO)_5$ with $[Al(NMe_2)_3]_2$ gave [145] the binuclear aluminoxycarbene CXXVII.

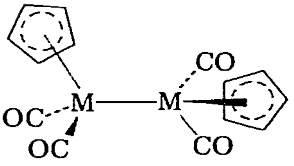
π-Cyclopentadienyl complexes

Neutral bi- and tetra-nuclear carbonyl complexes

In solution, the existence of four isomers of $[(\pi\text{-}C_5H_5M(CO)_2]_2$ (M = Fe or Ru), the *cis-* and *trans-*forms, and two non-bridged forms, CXXVIII and CXXIX, were detected by ^1H NMR spectral studies [146]. The measured



(CXXVIII)

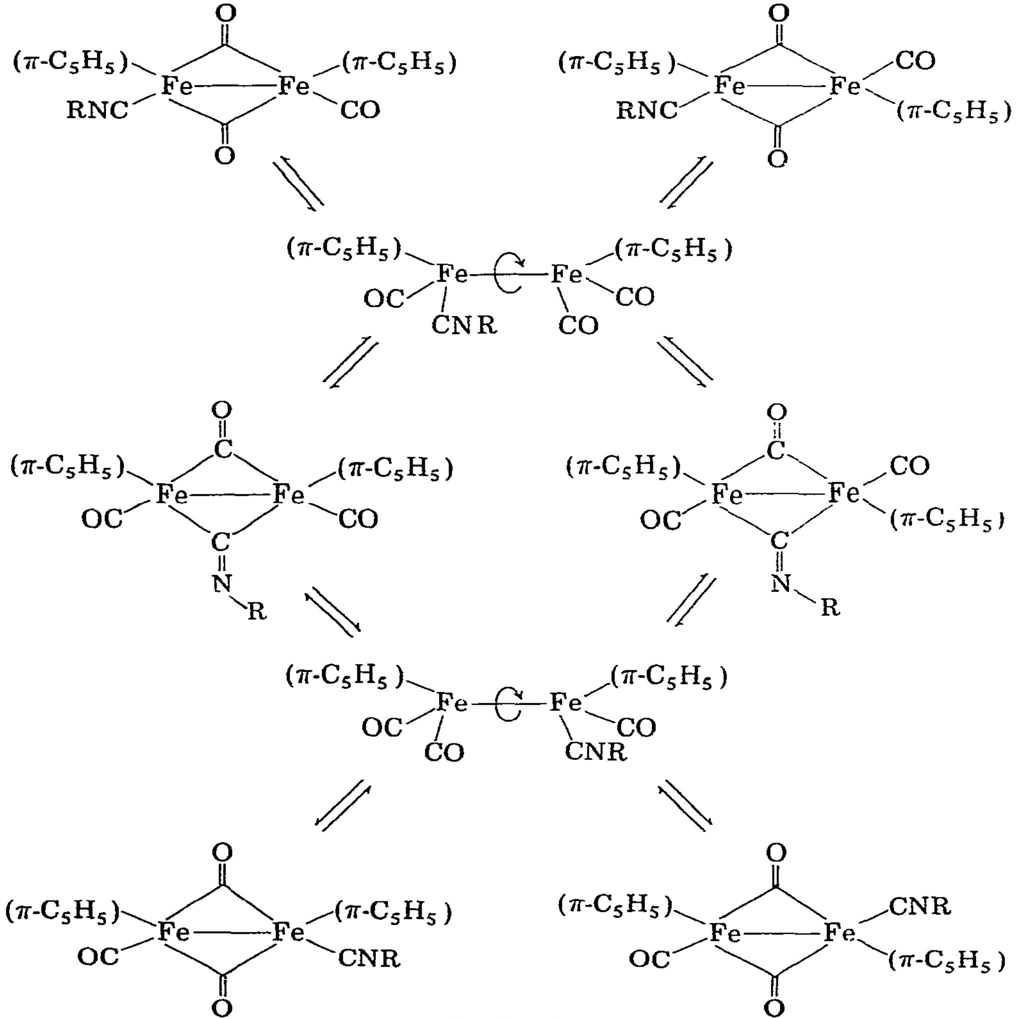


(CXXIX)

thermodynamic and kinetic data could be interpreted in terms of non-bridged isomers as intermediates in the *cis–trans* bridged isomer interconversion. By using ^{13}C NMR spectroscopy, with $Cr(Acac)_3$ as a shiftless relaxation agent, it was shown [147] that both *cis*- and *trans*-forms of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ interconverted their terminal and bridging CO groups. No evidence for non-bridged isomers could be detected by this spectral method. $Fe_3(CO)_{12}$ was also shown to be stereochemically non-rigid.

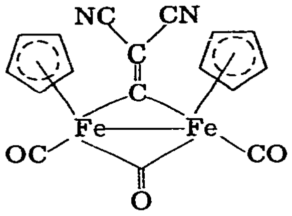
The species $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNBu\text{-}t)$ was non-rigid, the isocyanide ligand being exchanged [148] between the two Fe atoms via bridged and non-bridged intermediates (Scheme 16).

Reaction of $Na[Fe(CO)_2(\pi\text{-}C_5H_5)]$ with $(NC)_2C{=}CCl_2$ gave $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2]_2$, and two isomers of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3\{C{=}C(CN)_2\}$, CXXX [149].

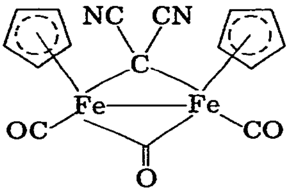


(R = Bu-t)

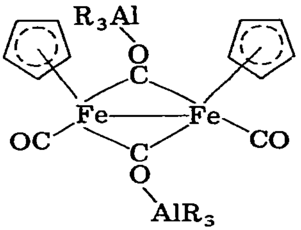
Scheme 16



(CXXX)

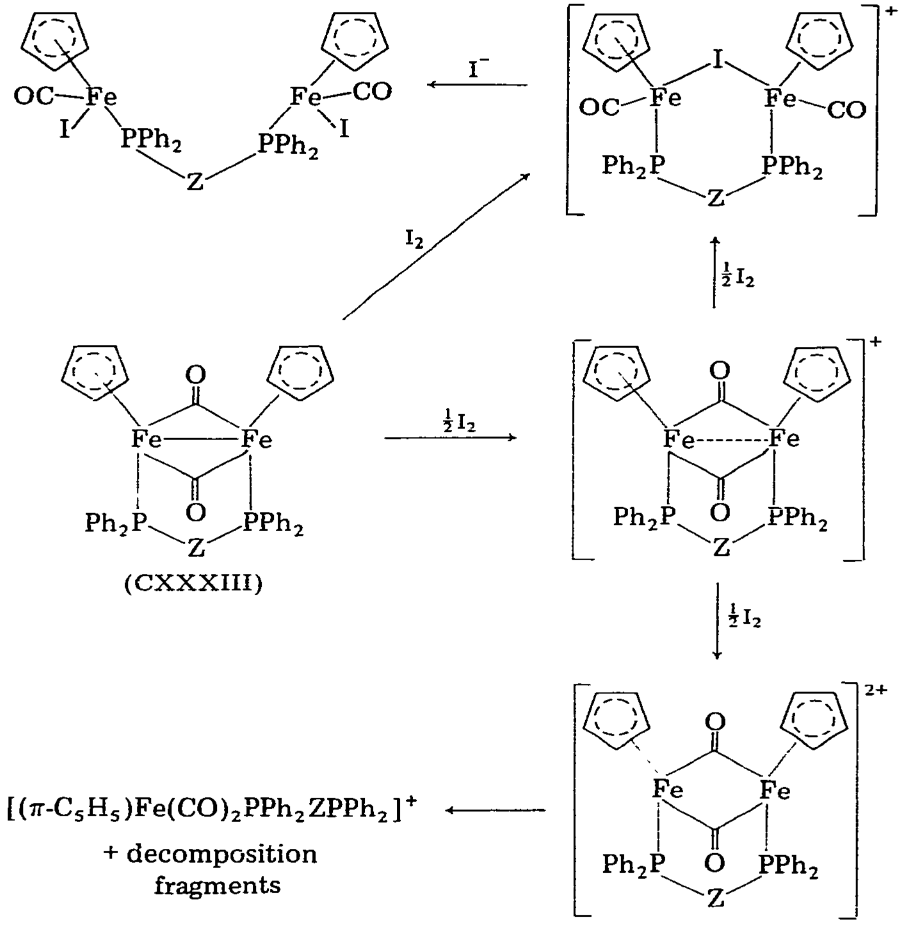


(CXXXI)

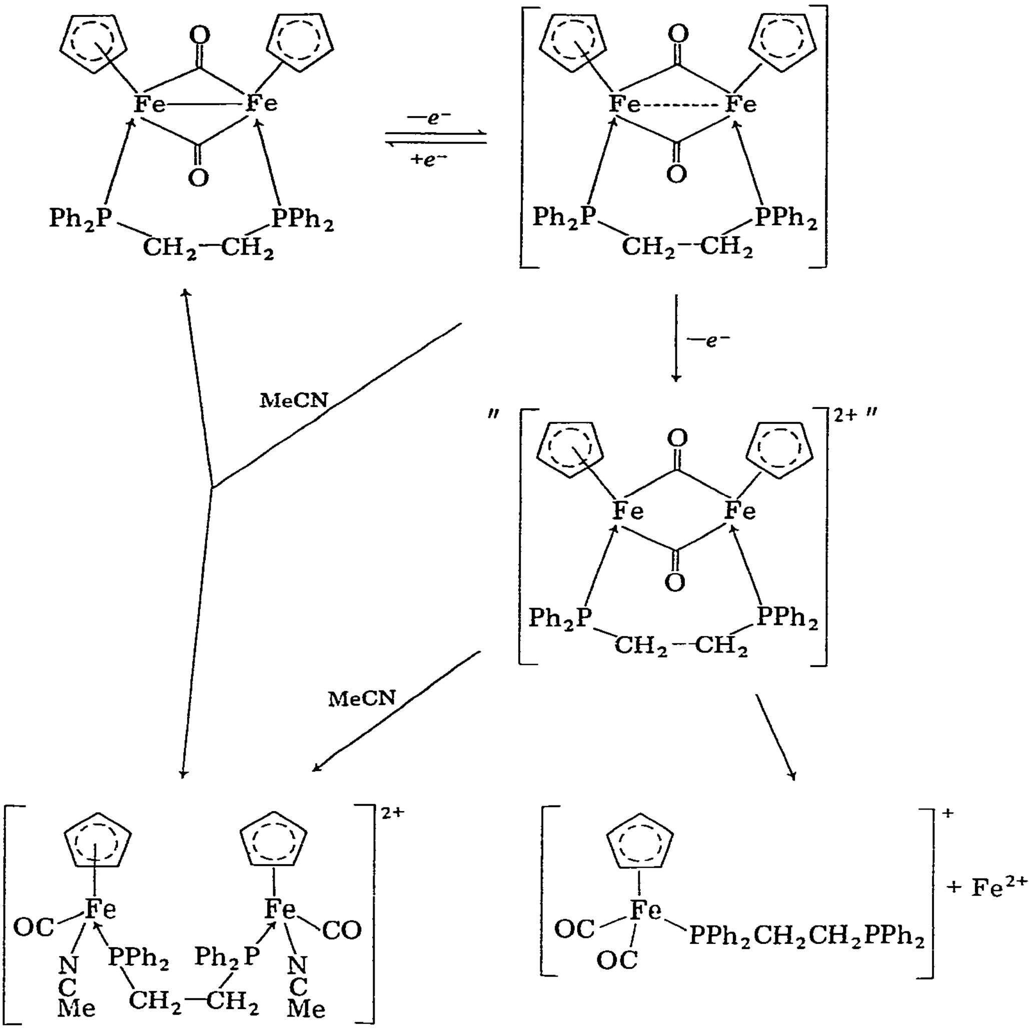


(CXXXII)

The carbonylate anion also reacted with $C(CN)_2Br_2$ giving the dicarbonyl dimer, $(\pi\text{-}C_5H_5)Fe(CO)_2Br$, $(\pi\text{-}C_5H_5)Fe(CO)_2[C(CN)_2H]$ (this last was also produced in the reaction between $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ and $CH(CN)_2Br$), and $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3[C(CN)_2]$, CXXXI.



Scheme 17



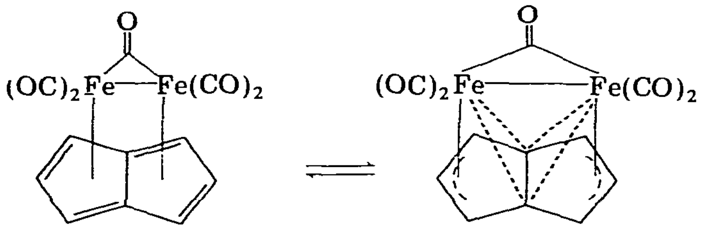
Scheme 18

Solution IR spectral studies of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ in the presence of AlR_3 (R = Et or i-Bu) revealed that 1/1 and 1/2 adducts, CXXXII, were formed [15]. The AlR_3 was removed by Et_3N, and the rate of *cis* ⇌ *trans* isomerisation of the dimer was slowed by AlR_3, suggesting that the isomerism involved non-bridged intermediates. $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ behaved similarly and caused rapid isomerisation of the non-bridged form to the *cis*- and *trans*-AlR_3 adducts. The tetramer $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ also formed AlR_3 adducts. With $Sm(C_5H_4Me)_3$ and $Sm(C_5H_5)_3$, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ afforded [151] 1/1 and 1/2 addition compounds similar to those already described for AlR_3; $Fe(CO)_2(NO)_2$ apparently did not afford these adducts [150, 152].

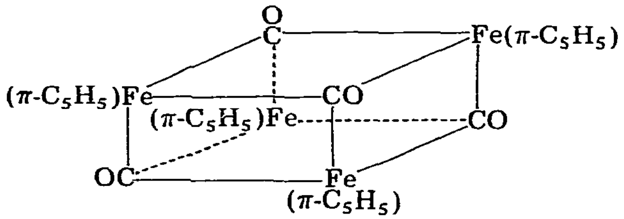
Careful treatment [153] of $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PZPPh_2)$ (Z = CH_2, C_2H_2, C_2H_4, C_3H_6 or NEt), CXXXIII, with iodine or Ag^+ gave $[\{(\pi\text{-}C_5H_5)\text{-}Fe(CO)\}_2(Ph_2PZPPh_2)]^+$. Reduction of this cation to CXXXIII (Z = CH_2) was achieved using hydrazine or I^-. With excess I_2, CXXXIII (Z = CH_2) afforded $[\{(\pi\text{-}C_5H_5)Fe(CO)]_2I(Ph_2PZPPh_2)]^+$ which contained bridging iodine as well as bridging diphosphine, but similar treatment of CXXXIII (Z = C_2H_4) gave only $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (the diphosphine is monodentate); $[(\pi\text{-}C_5H_5)Fe(CO)I]_2(Ph_2PCH_2CH_2PPh_2)$ was also obtained. These reaction, and the proposed structures, are outlined in Scheme 17. Electrochemical oxidation of CXXXIII (Z = C_2H_4) in a variety of solvents occurred [154] in two one-electron steps, affording, initially $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_2(Ph_2PCH_2CH_2\text{-}PPh_2)]^+$. It was suggested that this cation was isostructural with CXXXIII but had a "one-electron Fe—Fe bond". In MeCN, the cation disproportionated giving CXXXIII and $[\{(\pi\text{-}C_5H_5)Fe(CO)(NCMe)\}_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$. Removal of the second electron from CXXXIII (Z = C_2H_4) caused decomposition by two pathways (Scheme 18).

Pentalenes reacted with $Fe(CO)_5$ giving bimetallic complexes, CXXXIV [155].

The tetrameric species $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^n$ (n = 0) could be electrochemically oxidised or reduced giving [156] the species n = —1, +1 or +2. The monoanion (g = 2.013) was characterised spectroscopically in solution whereas the monocation (μ = 2.46 B.M.) was isolated. Attempts to isolate $[(\pi\text{-}C_5H_5)Fe(CO)]_4{}^{2+}$ resulted in its decomposition to Fe^{2+} and $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2S]^+$ (S = solvent, MeCN or BuCN). The molecular structure determination of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$, CXXXV, established [157] that it had a cubane-like architecture with triply bridging CO groups; the Fe—Fe distances averaged 2.50 Å. The monocation, $[(\pi\text{-}C_5H_5)Fe(CO)]_4[PF_6]$, had essentially the same



(CXXXIV)



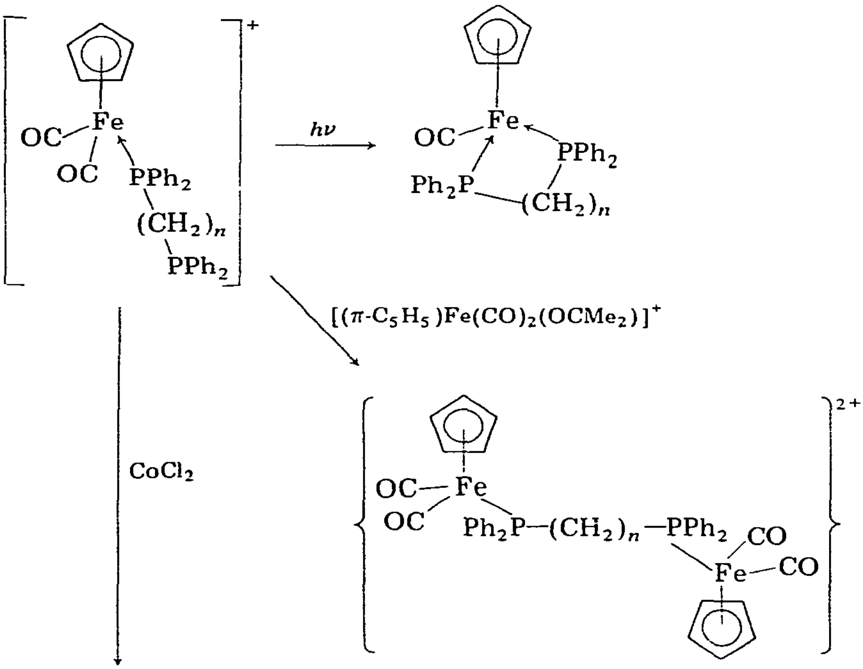
(CXXXV)

structure [158]; the major differences arose from a decrease in Fe—Fe distances to 2.48 Å. The average C—O bond length (1.19 Å) was ca. 0.02 Å shorter than that in CXXXV whereas the Fe—CO bond distances in both species were virtually identical. A molecular orbital description of these clusters suggested that oxidation of CXXXV should lead to electron loss from an orbital weakly antibonding with respect to the Fe_4 cluster, and hence contraction of the Fe—Fe bond lengths would be expected. It was predicted that reduction should lead to a large increase in the Fe—Fe distances.

Cationic complexes

Addition of NO^+ to $(\pi\text{-}C_5H_5)Fe(CO)_2I$ and $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}SMe)_2$ in MeCN afforded [159] $[(\pi\text{-}C_5H_5)Fe(CO)_2(NCMe)]^+$ and $[\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}SMe)]_2{}^+$, respectively. Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2(OCMe_2)]^+$ with $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, 2 or 3) gave [160] $[(\pi\text{-}C_5H_5)Fe(CO)_2\{Ph_2P(CH_2)_nPPh_2\}]^+$ in which the diphosphine was monodentate. These complexes behaved as ligands towards $[(\pi\text{-}C_5H_5)Fe(CO)_2(OCMe_2)]^+$ and $CoCl_2$ (Scheme 19), and were decarbonylated by UV radiation. The complexes $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(MeSCH_2CH_2SMe)](ClO_4)_2$ and $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2(pyrazine)](ClO_4)_2$ were also isolated.

The CO stretching force constant in $[(\pi\text{-}C_5H_5)M(CO)_2L]^+$ (M = Fe or Ru, L = CO or PPh_3) have been correlated [161] with the ease of reaction of the CO groups with amines giving coordinated carboxamides. Thus those species



$\{[(\pi\text{-}C_5H_5)Fe(CO)_2Ph_2P(CH_2)_nPPh_2]_2CoCl_2\}^{2+}$

Scheme 19

with ν(CO) less than 2000 cm^{-1} did not form carboxamides. Such adducts were readily formed with $[(\pi\text{-}C_5H_5)M(CO)_3]^+$ and although $[(\pi\text{-}C_5H_5)Fe(CO)_2(PPh_3)]$ should have given an equilibrium mixture of cation and carboxamide, only the latter was obtained because of its insolubility.

The cations $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ (L = CO, PEt_3 or PPh_3) reacted [162] with liquid NH_3 giving $(\pi\text{-}C_5H_5)Fe(CO)L(CONH_2)$; the related $[(\pi\text{-}C_5H_4CH_2Ph)\text{-}Fe(CO)_2L]^+$ and $[(\pi\text{-}C_7H_8CPh_3)Fe(CO)_3]^+$ behaved similarly. Oxidative degradation of the carboxamido complexes with iodine afforded isocyanato complexes, whereas reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2(CONH_2)$ with HCl or HI gave $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+X^-$ (X = Cl or I). Bromination of $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}(CONHMe)$ afforded [163] $(\pi\text{-}C_5H_5)Fe(CO)_2Br$, $[(\pi\text{-}C_5H_5)Fe(CO)_3]Br$, MeNCO and $[MeNH_3]Br$. Iodination or chlorination of the cyclohexyl carboxamide gave similar compounds but MeI and C_3F_7I did not react. With $HgCl_2$, $(\pi\text{-}C_5H_5)Fe(CO)_2HgCl$, $[\pi\text{-}C_5H_5)Fe(CO)_3]Cl$, $C_6H_{11}NCO$ and $[C_6H_{11}NH_3]Cl$ were formed.

Reaction of LiMe with $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ gave [164] only traces of $(\pi\text{-}C_5H_5)Fe(CO)_2(COMe)$ and mainly $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, but with LiPh both $(\pi\text{-}C_5H_5)Fe(CO)_2(COPh)$ (80%) and the dimer were obtained. Action of $PhCH_2MgCl$ on the cation afforded *exo*-$(5\text{-}PhCH_2C_5H_5)Fe(CO)_3$, and $[(\pi\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+$ behaved similarly. Treatment of $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2(CS)]^+$ with LiMe gave the dicarbonyl dimer and other unidentified products.

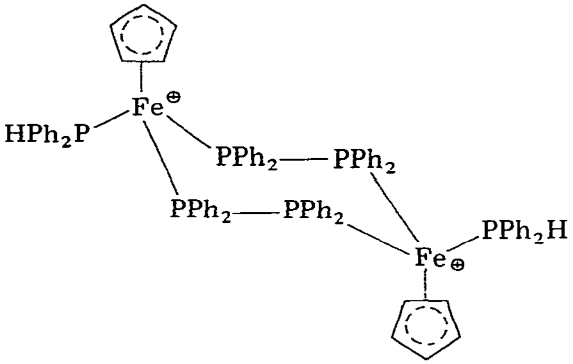
Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Br or I) with $PPhH_2$ and PPh_2H (L) gave [165] $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ and $(\pi\text{-}C_5H_5)Fe(CO)LX$. Treatment of $[(\pi\text{-}C_5H_5)Fe(CO)_2(PPhH_2)]$ with LiMe gave $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}PPhH)]_2$, but with LiBu at low temperatures an unidentified, possibly lithiated, species was formed: addition of MeI to this at low temperature afforded $[(\pi\text{-}C_5H_5)Fe(CO)_2(PPhMe_2)]^+$ and at room temperature $(\pi\text{-}C_5H_5)Fe(CO)_2Me$. Addition of methoxide ion to $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2(PPh_2H)]^+$ gave *cis*- and *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}PPh_2)]_2$, and treatment of the cation with OMe^- and MeI afforded $[(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}(PPh_2Me)]^+$. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)(PPh_2H)Br$ with LiBu gave *cis*-$[(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}PPh_2)]_2$, and similar treatment of $Fe(CO)_4(PPh_2H)$ under UV light gave $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$. UV irradiation of $[(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}(PPh_2H)]^+$ afforded CXXXVI.

Complexes containing P and S bridges

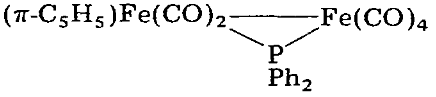
Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $(F_3C)_2PP(CF_3)_2$ gave $(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2[P(CF_3)_2]$ which, on heating or UV irradiation, afforded [166] $[(\pi\text{-}C_5H_5)Fe(CO)\{\mu\text{-}P(CF_3)\}]_2$. While the latter did not react with NO, the former gave $(\pi\text{-}C_5H_5)Fe(CO)_2[P(=O)(CF_3)_2]$ apparently without prior coordination of the NO to the metal. UV irradiation of this phosphonite afforded $[(\pi\text{-}C_5H_5)Fe(CO)\{\mu\text{-}P(CF_3)_2\}]_2$ and the paramagnetic $(\pi\text{-}C_5H_5)_2Fe_3\text{-}(CO)_2[P(=O)(CF_3)_2]_4$ (μ = 4.5-4.6 B.M.). Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}[P(CF_3)_2]$ with S_8 gave $(\pi\text{-}C_5H_5)Fe(CO)_2[P(=S)(CF_3)_2]$ which, on irradiation, produced $(\pi\text{-}C_5H_5)Fe(CO)_2SP(=S)(CF_3)_2$.

Treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2(PPh_2)$ with $Fe_2(CO)_9$, or of $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2]^-$ with $Fe(CO)_4(PPh_2Cl)$, afforded [167] $(\pi\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}PPh_2)\text{-}$

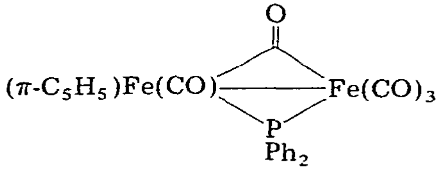
$Fe(CO)_4$, CXXXVII, and this, on UV irradiation, gave $(\pi\text{-}C_5H_5)Fe(CO)$-$(\mu\text{-}PPh_2(\mu\text{-}CO)Fe(CO)_3$, CXXXVIII. Reaction of CXXXVIII with phosphines or phosphites, L, gave $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe(CO)_2L$ or its isomer $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}PPh_2)Fe(CO)_3L$ and $(\pi\text{-}C_5H_5)Fe_2(CO)_3(\mu\text{-}PPh_2)L_2$. With $Ph_2PCH_2CH_2PPh_2$, CXXXVIII afforded CXXXIX. $(\pi\text{-}C_5H_5)Fe(CO)_2SMe$ reacted with $Fe_2(CO)_9$ giving $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}SR)Fe(CO)_4$ (R = Me or Ph) and $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}SR)(\mu\text{-}CO)Fe(CO)_3$, analogs of CXXXVII and CXXXVIII.



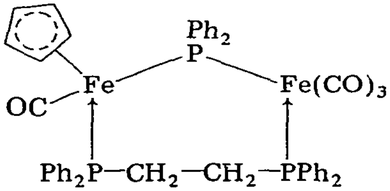
(CXXXVI)



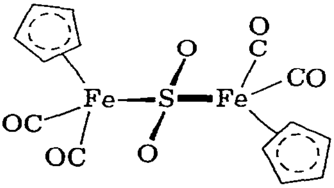
(CXXXVII)



(CXXXVIII)



(CXXXIX)



(CXL)

Excess of SO_2 in THF at low temperatures reacted [168] with $Na[Fe(CO)_2(\pi\text{-}C_5H_5)]$ giving $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, heat and light sensitive $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SO_2$, CXL, and traces of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$. The X-ray structural determination of CXL revealed that the central S atom had a distorted geometry and that the Fe—S distance (2.28 Å) was between that in $(\pi\text{-}C_5Me_5)Fe(CO)_2SO_2CH_2CH{-}CHPh$ (2.22 Å) [169] and that expected for an Fe—S bond of unit order. CXL reacted with MeI giving $(\pi\text{-}C_5H_5)Fe(CO)_2$-$SO_2Me$ and $(\pi\text{-}C_5H_5)Fe(CO)_2I$.

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2SMe$ with $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ afforded [170] $[(\pi\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}SMe)Fe(CO)_2(\pi\text{-}C_5H_5)]^+$, and treatment of the chloride with $(\pi\text{-}C_5H_5)Mn(CO)_2[MeSSnMe_3]$ and $M(CO)_5[MeSSnMe_3]$ (M = Cr, or W) gave $(\pi\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}SMe)Mn(CO)_2(\pi\text{-}C_5H_5)$ and $(\pi\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}SMe)M(CO)_5$, respectively.

Oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}SMe)]_2$ by O_2 in acidic media gave [171] the monocation, $[(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}SMe)]_2^+$; reduction could be effected using amines or hydrazines in the presence of water. The redox reaction was stereoselective, the *cis*-neutral species affording the *cis*-cation. Excess Br_2 reacted with the neutral species giving $[(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}SMe)]_2^{2+}$ and Mössbauer spectral studies showed that there was an increase in the *s*-electron density at the Fe atoms on oxidation, but that the two Fe atoms remained equivalent.

Halide complexes

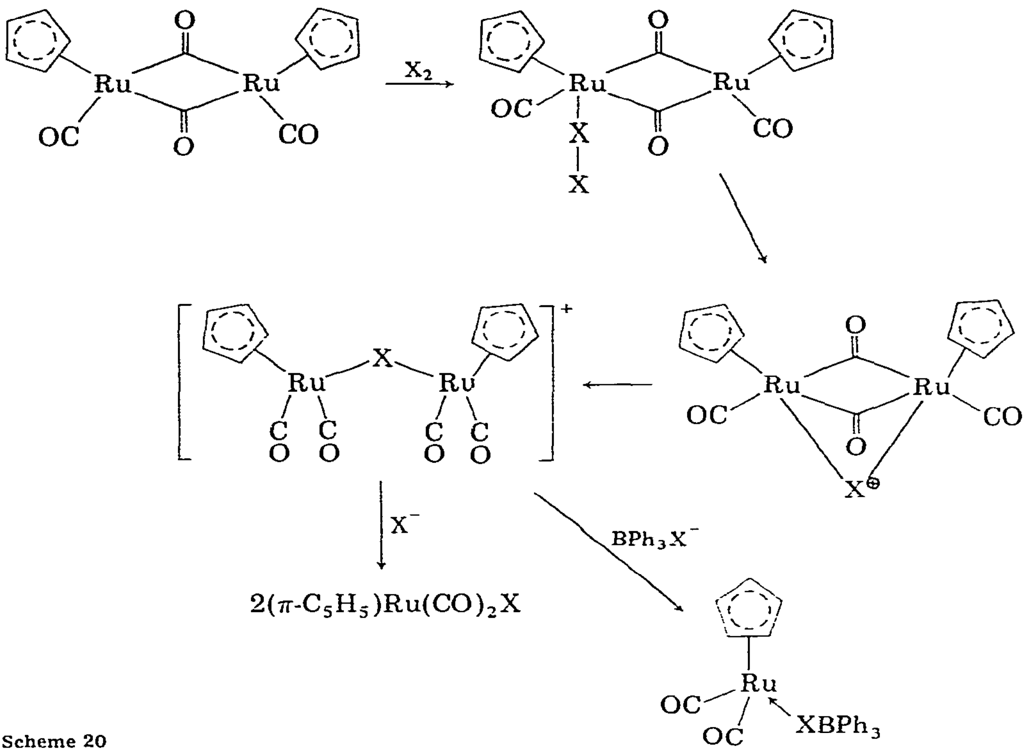
$(\pi\text{-}C_5H_5)Fe(CO)_2I$ reacted [172] with $Hg(C_6Cl_5)Cl$ giving $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$. Addition of AlX_3 or $FeCl_3$ to $(\pi\text{-}C_5H_5)Fe(CO)_2X$ and to $Fe(CO)_2(PMe_3)_2X_2$ (X = Cl, Br or I) gave [173] the adducts $(\pi\text{-}C_5H_5)Fe(CO)_2(X \rightarrow AlX_3)$, $(\pi\text{-}C_5H_5)Fe(CO)_2(X \rightarrow FeCl_3)$ and $Fe(CO)_2(PMe_3)_2(X \rightarrow \text{acceptor})_2$.

The integrated intensities of $\nu(CO)$ in solution have been determined [174] for $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, I, CN, $SnCl_3$, COMe) and $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_2Ph)$, and the results were interpreted in terms of the $\pi\text{-}C_5H_5$ ring acting primarily as a donor in these compounds. The ^{13}C NMR spectra of $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, Br, I, CN, COMe, alkyl, aryl, SiR_3, SnR_3 and $GePh_3$) have been measured [175] and there is a linear dependence of $\nu(CO)$ on the Taft σ_I value for X and on the measured value of $\nu(CO)$. It would appear that $\nu(CO)$ varies according mainly to changes in the paramagnetic screening term.

CO substitution reactions of $(\pi\text{-}C_9H_7)Fe(CO)_2I$ (C_9H_7 = indenyl) proceeded [176] by an S_N1 mechanism and were ca. 600 times faster than those of its $\pi\text{-}C_5H_5$ analog. The acceleration could not be accounted for by steric arguments since the even more crowded tetrahydroindenyl complex reacted at a rate comparable with $(\pi\text{-}C_5H_5)Fe(CO)_2I$. However, the rate enhancement could be due to a lowering in energy of the activated state caused by an interaction between the aromatic six-membered ring and the Fe atom which partly compensated for the loss of bonding to the leaving CO group.

Addition of (+)-α-CNCH(Me)Ph to $(\pi\text{-}C_5H_5)Fe(CO)_2I$ afforded [177] the diastereoisomeric pairs (+)- and (—)-$(\pi\text{-}C_5H_5)Fe(CO)(CNR^*)I$, which were separable. These were conformationally stable in the absence of light, but underwent photoracemisation. Treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ with $Ni(PF_3)_4$ gave [178] $(\pi\text{-}C_5H_5)Fe(CO)(PF_3)I$. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Br or I) with $PF_2(NR_2)$ (R = Me, Et or piperidine) under UV light gave [179] $(\pi\text{-}C_5H_5)Fe(CO)\{PF_2(NR_2)\}X$ and/or $(\pi\text{-}C_5H_5)Fe\{PF_2(NR_2)\}_2X$ depending on the reaction stoichiometries. Reaction of $PF_2(NC_5H_{10})$ with the iodide in the presence of Ag^+ gave $[(\pi\text{-}C_5H_5)Fe(CO)_2\{PF_2(NC_5H_{10})\}]^+$. Treatment of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $PF_2(NEt_2)$ afforded $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3[PF_2(NEt_2)]$ and $(\pi\text{-}C_5H_5)_2Fe_2(CO)_2[PF_2(NEt_2)]_2$, and of $(\pi\text{-}C_5H_5)Fe(CO)_2Me$ with $PF_2(NR_2)$ $(\pi\text{-}C_5H_5)Fe(CO)[PF_2(NR_2)](COMe)$.

Halogenation of $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ gave [180] the white $(\pi\text{-}C_5H_5)Ru(CO)_2X$ (X = Cl, Br or I) in dichloromethane or chloroform, but in benzene,



Scheme 20

in the presence of PF_6^-, $[\{(\pi\text{-}C_5H_5)Ru(CO)_2\}_2X]^+$ was produced. Reaction of this cation with nucleophiles, Y (SCN, CN or X) gave $(\pi\text{-}C_5H_5)Ru(CO)_2X$ and $(\pi\text{-}C_5H_5)Ru(CO)_2Y$. The binuclear cation also reacted with BPh_4^- and BPh_3CN^- giving, in both cases, $(\pi\text{-}C_5H_5)Ru(CO)_2X$ and also $(\pi\text{-}C_5H_5)Ru(CO)_2Ph$ and $(\pi\text{-}C_5H_5)Ru(CO)_2CN$, respectively. The intermediate in the cyanoborate ion reaction was believed to be $(OC)_2(\pi\text{-}C_5H_5)Ru^+CNBPh_3^-$; the mechanism is summarised in Scheme 20.

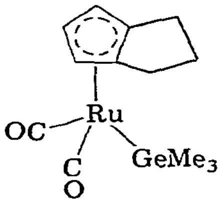
Mixed metal compounds

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with Mg amalgam in a basic solvent B (THF, pyridine or $Me_2NCH_2CH_2NMe_2$) gave [181] $[(\pi\text{-}C_5H_5)Fe(CO)_2]MgB_x$ ($x = 2$ when B is monobasic). The Fe bond was not wholly dissociated in solution and ν(CO) indicated vibronic coupling across the Fe—Mg—Fe bond system. The complex $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Zn$ in methanol was tetrameric [182] with a structure probably similar to $[Zn(OMe)Me]_4$ [183].

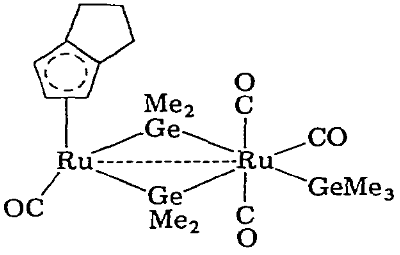
Reaction of $Na[Fe(CO)_2(\pi\text{-}C_5H_5)]$ with $InCl_3$, or $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ or $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Hg$ with InCl in dioxan gave [184] $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2InCl$. However, reaction of $Na[Fe(CO)_2(\pi\text{-}C_5H_5)]$ with InX_3 (X = Cl or Br), or of $(\pi\text{-}C_5H_5)Fe(CO)_2X$ with InX in THF afforded $(\pi\text{-}C_5H_5)Fe(CO)_2InX_2$.

IR spectral studies revealed [185] that $(\pi\text{-}C_5H_5)Fe(CO)_2(SiMeCl_2)$ existed as rotational isomers. Reaction of $Na[Fe(CO)_2(\pi\text{-}C_5H_5)]$ with $XMe_2SiSiMe_2Cl$ (or Br) gave [186] $(\pi\text{-}C_5H_5)Fe(CO)_2SiMe_2SiMe_2X$.

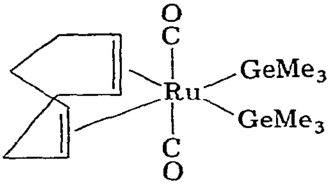
$(\pi\text{-}C_5H_5)Fe(CO)_2(GeX_3)$ (X = Cl, Br or I) was prepared [187] by reaction of GeX_4 with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. *cis*-$Ru(CO)_4(GeMe_3)_2$ caused [188] ring contraction of *trans,trans,trans*-cyclododecatriene giving a mixture of products, among them CXLI and CXLII. These compounds could also be obtained from 1,5-cyclooctadiene and *cis*-$Ru(CO)_4(GeMe_3)_2$, when CXLIII was also formed. Indeed, CXLIII appeared to be a mutual precursor for CXLI and CXLII.



(CXLI)



(CXLII)

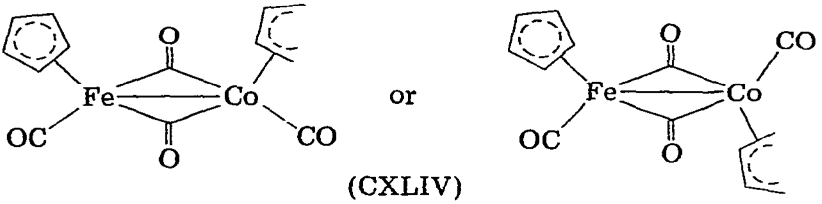


(CXLIII)

Reaction of $[(\pi\text{-dienyl})Fe(CO)_2]_2$ (dienyl = C_5H_5, C_5H_4Me or C_9H_7) with SnX_2 (X = F, Cl, Br or I) gave [189] $(\pi\text{-dienyl})Fe(CO)_2X$, $(\pi\text{-dienyl})Fe(CO)_2SnX_3$, $[(\pi\text{-dienyl})Fe(CO)_2]_2SnX_2$ or $[(\pi\text{-dienyl})Fe(CO)_2]_3SnX$ depending on X, the reaction conditions and stoichiometries. When X = F or Cl, insertion of SnX_2 into the Fe—Fe bond occurred in one step giving $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnX_2$. When X = Br or I, the precursor was first converted into mixtures of $(\pi\text{-dienyl})Fe(CO)_2X$ and $(\pi\text{-dienyl})Fe(CO)_2SnX_3$. The latter reacted further with an excess of $[(\pi\text{-dienyl})Fe(CO)_2]_2$ giving $[(\pi\text{-dienyl})Fe(CO)_2]_2SnX_2$. Reaction of $[(\pi\text{-dienyl})Fe(CO)_2]_2$ with $(\pi\text{-dienyl}')Fe(CO)_2SnX_3$ or $[(\pi\text{-dienyl}')Fe(CO)_2]_2SnX_2$ could be used to prepare $[(\pi\text{-dienyl})Fe(CO)_2][(\pi\text{-dienyl}')Fe(CO)_2]SnX_2$ or $[(\pi\text{-dienyl})Fe(CO)_2]_2[(\pi\text{-dienyl}')Fe(CO)_2]SnX$. SnX_4 also reacted with $[(\pi\text{-dienyl})Fe(CO)_2]_2$ giving similar products.

The ^{119m}Sn Mössbauer spectral parameters for $(\pi\text{-}C_5H_5)Fe(CO)_2SnCl_{3-n}Ph_n$ (n = 0, 1, 2 or 3) have been interpreted [190] in terms of a point charge model and the data showed that the *p*-donor capacity was less than that of Ph or alkyl groups.

The binuclear $(\pi\text{-dienyl})FeCo(CO)_6$ (dienyl = C_5H_5, C_5H_4Me or C_9H_7) reacted [191] with dienes (norbornadiene, cyclohexa-1,3-diene or 2-3-dimethylbuta-1,3-diene) giving $(\pi\text{-dienyl})Fe(CO)(\mu\text{-}CO)_2Co(CO)(\text{diene})$, which existed in the solid state, and in solution, as *cis*- and *trans*-isomers, CXLIV. The relative abundance of the two forms in solution depended on the solvent, its

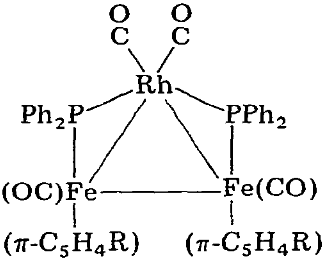


(CXLIV)

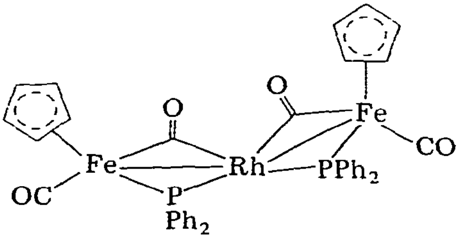
temperature, the diene, and, to a lesser extend, the π-dienyl ligand: the proportion of *cis*-isomers decreased along the series $C_7H_8 > C_6H_8 > C_6H_{10}$. There was no evidence for non-bridged species.

Reaction of $[Rh(C_8H_{12})Cl]_2$, $[Rh(CO)_2Cl]_2$ or $RhCl_3 \cdot nH_2O$ in methanol, or of $[Rh(C_8H_{12})(THF)_2]^+$ in THF, with an excess of $(\pi\text{-}C_5H_4R)Fe(CO)_2(PPh_2)$ (R = H or Me) afforded [192] $[Rh\{Fe(\mu\text{-}PPh_2)(CO)_2(\pi\text{-}C_5H_4R)\}_2]X$ (X = BPh_4, PF_6 or SbF_6). The structure of this compound (R = Me) was predicted, on the basis of the rare gas rule, to be CXLV, but was found crystallographically, to be CXLVI. The Fe—Rh distances were 2.66-2.67 Å, and the Fe—Rh—Fe dihedral angle was 145°. Reaction of the trinuclear species with L ($P(OMe)_3$ or PPh_3) gave $[Rh\{Fe(\mu\text{-}PPh_2)(CO)_2(\pi\text{-}C_5H_4R)\}_2L]BPh_4$, and the complex where L = PPh_3 could be obtained directly from the reaction of $Rh(C_8H_{12})(PPh_3)Cl$ with $(\pi\text{-}C_5H_5)Fe(CO)_2(PPh_2)$ in ethanol in the presence of BPh_4^-. Similar iridium complexes were obtained using $[Ir(C_8H_{12})(THF)_2]^+$, and mercaptide-containing analogs were produced via $(\pi\text{-}C_5H_5)Fe(CO)_2(SR)$ (R = Et or Bu-t).

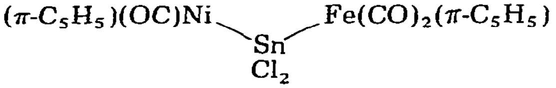
Treatment of $(\pi\text{-}C_5H_5)Ni(PR_3)X$ (PR_3 = PPh_3, PPh_2Me, $PPhMe_2$ or PMe_3) with $Na[Fe(CO)_2(\pi\text{-}C_5H_5)]$ gave [193] eventually $(\pi\text{-}C_5H_5)Ni(\mu\text{-}CO)_2\text{-}Fe(PR_3)(\pi\text{-}C_5H_5)$ via two intermediates (Scheme 21) which were not isolated. However, reaction of $(\pi\text{-}C_5H_5)Ni(\mu\text{-}CO)_2Fe(CO)(\pi\text{-}C_5H_5)$ with PPh_3 gave only $(\pi\text{-}C_5H_5)_2Ni$, $Ni(CO)_2(PPh_3)_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. Reaction of $(\pi\text{-}C_5H_5)Ni(\mu\text{-}CO)_2Fe(CO)(\pi\text{-}C_5H_5)$ with $SnCl_2$ afforded CXLVII.



(CXLV)

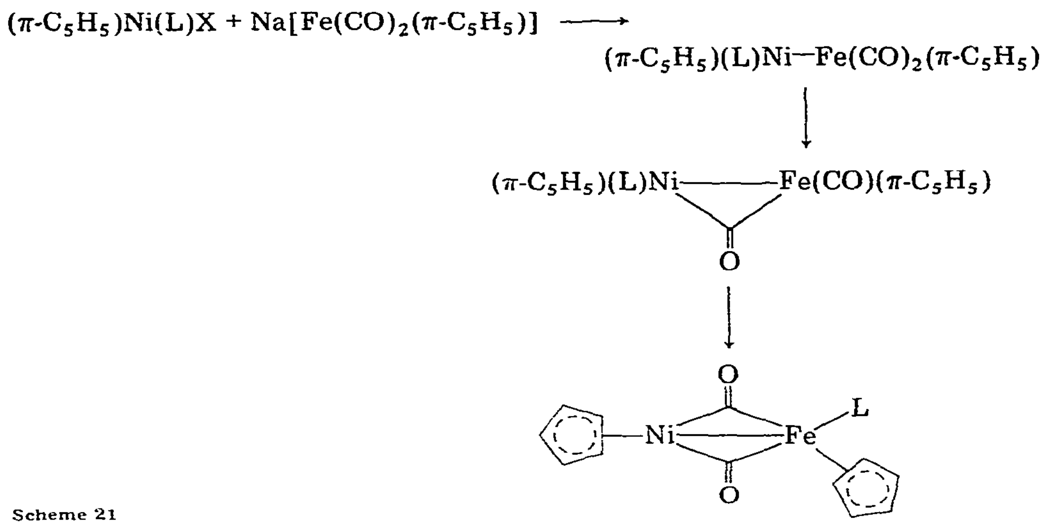


(CXLVI)



$$\underset{Cl_2}{(\pi\text{-}C_5H_5)(OC)Ni{-}Sn{-}Fe(CO)_2(\pi\text{-}C_5H_5)}$$

(CXLVII)

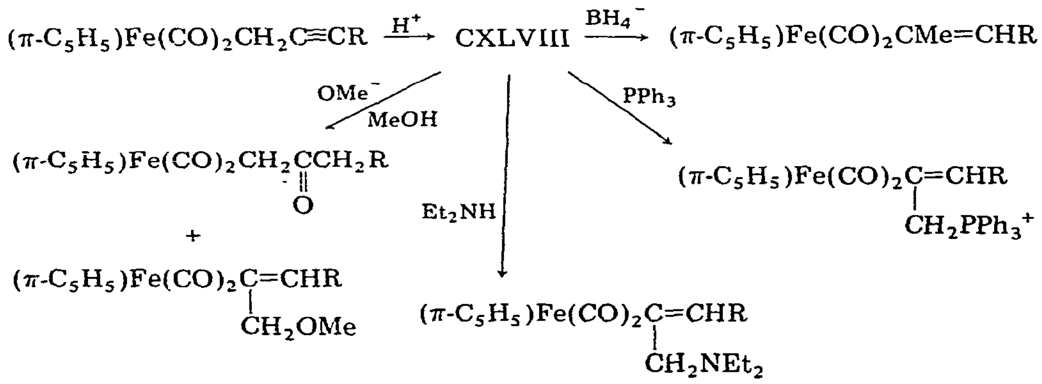


Scheme 21

Metal σ- and π-bonded carbon derivatives

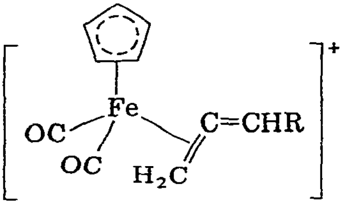
^{1}H NMR spectral studies of (π-C_5H_5)Fe$(CO)_2$X (X = halide, Me, Ph, COMe or CN) and of (π-C_5H_5)Fe(CO)(PPh_3)(p-RC_6H_4) (R = OMe, Me, H, Cl, F or CO_2Et) revealed [194] that the effects of X and R on δ (C_5H_5) were predominantly inductive. On the basis of ^{19}F NMR spectral investigations, the σ inductive and resonance constants of (π-C_5H_5)Fe(CO)L in (π-C_5H_5)Fe(CO)L-(p-FC_6H_4) (L = CO, PPh_3 or P$(OPh)_3$) were determined, and it was shown that an inductive interaction within the Fe—Aryl bond was predominant.

Addition of HBF_4 in acetic anhydride to (π-C_5H_5)Fe$(CO)_2CH_2C{\equiv}CR$ (R = Me or Ph) gave [195] the cationic allene complex CXLVIII. The reactions of this cation with various nucleophiles are summarised in Scheme 22. The observed reactivity towards nucleophiles of the terminal C atom of the coordinated allene added support to the proposed mechanism of cycloaddition reactions of the $FeCH_2C{\equiv}CR$ group. Thus, the formation of CXLIX, where

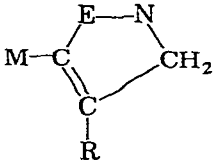


Scheme 22

EN = SO_2, SO_3, $(CF_3)_2CO$ or $ClSO_2NCO$, may proceed via the intermediacy of an allene complex which is generated by attack of the electrophilic part (E) of EN on the C≡C bond. This allene then rearranges to a cyclic product via interaction with the nucleophilic part (N) of EN with the terminal C atom of the coordinated allene.

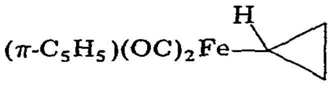


(CXLVIII)

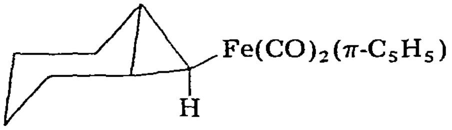


(CXLIX)

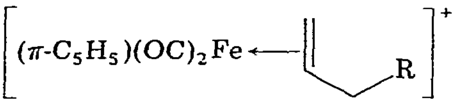
The cyclopropyl complexes CL and CLI were prepared [196] by reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2Br$ with LiC_3H_5, and $Na[Fe(CO)_2(\pi\text{-}C_5H_5)]$ with the appropriate cyclopropyl bromide, respectively. CL reacted with HCl giving $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$, and releasing cyclopropane and propene, but with HBF_4



(CL)

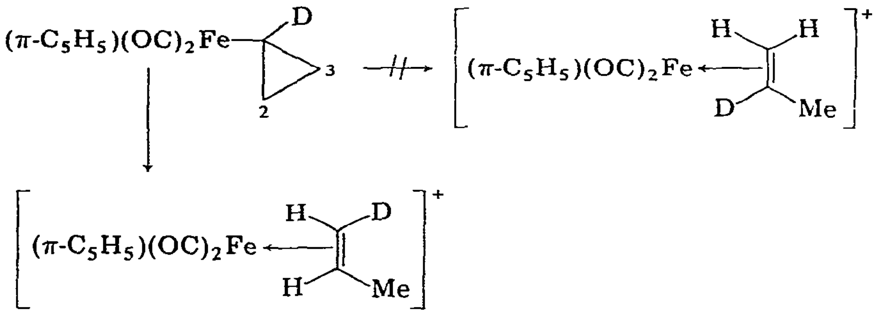


(CLI)



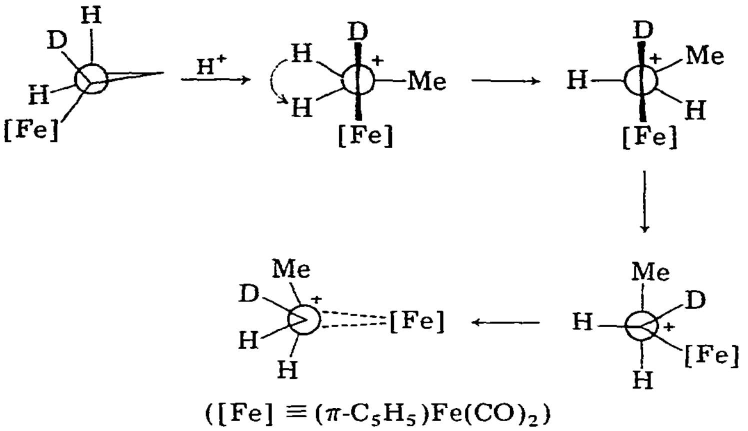
(CLII)

or Ph_3CBF_4, CLII was formed. The formation of the olefinic cation did not proceed via C_2—C_3 cleavage, as shown in Scheme 23. This may be accounted for by initial formation of a cationic carbene complex via cleavage of the C_1—C_2 bond and rapid rearrangement of this ion through minimum energy



Scheme 23

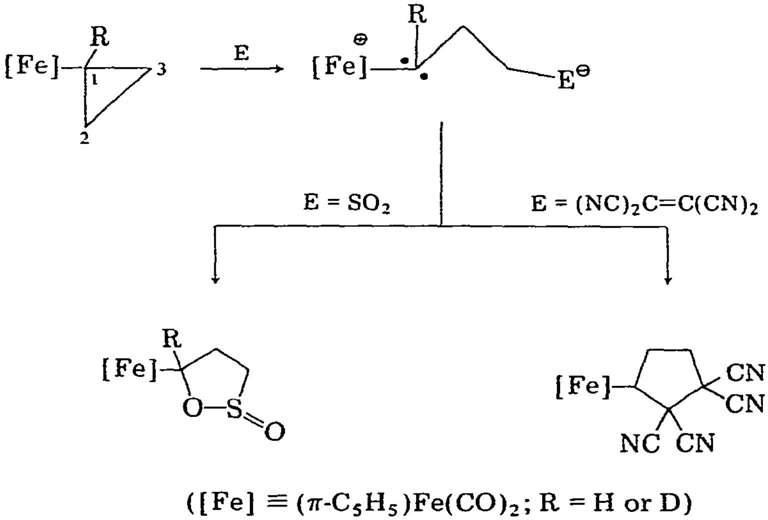
References p. 514



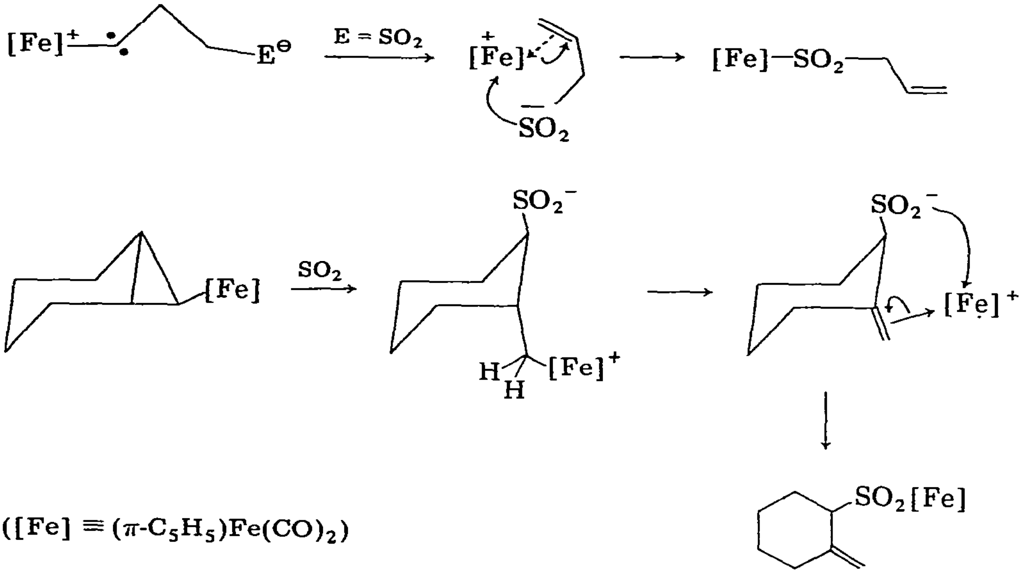
Scheme 24

conformational changes (Scheme 24). The cationic carbene intermediate could be trapped via the reaction of CL with an uncharged electrophile, E, viz. SO_2 or $(NC)_2C{=}C(CN)_2$ (Scheme 25). The products depicted again arose via collapse of the carbene intermediate induced by metal-assisted electrophilic cleavage of the C_1—C_2 bond. Rearrangement of the carbene intermediate is, to a limited extent, also possible, as depicted for SO_2 addition to CL and CLI in Scheme 26.

Reaction of CLIII with R″NCO gave [197] CLIV when R″ = 2,5-$C_6H_2Cl_2$ SO_2Cl, H, p-$MeC_6H_4SO_2$ or $MeOSO_2$, but no reaction was observed when R″ = Et or Ph. Addition of p-$MeC_6H_4SO_2NCO$ to CLV afforded CLVI, and of $MeO_2CN{=}SO_2$.THF to CLIII, CLVII. These reactions probably occurred via a



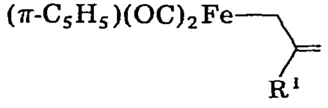
Scheme 25



([Fe] ≡ (π-C_5H_5)$Fe(CO)_2$)

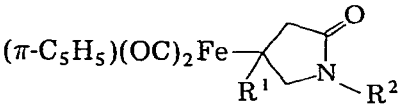
Scheme 26

two-step process (Scheme 27). The cyclic olefinic derivatives CLVIII (n = 2, 3 or 4) were prepared by H^- abstraction from the corresponding cyclic alkyl derivatives, by exchange of the cyclic olefin with isobutylene in $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{isobutylene})]^+$, by treatment of epoxides with $NaFe(CO)_2(\pi\text{-}C_5H_5)$ and then H^+ (ref. 214) or by reaction of 3-chlorocyclopentene with $NaFe(CO)_2(\pi\text{-}C_5H_5)$. Conversion of CLVIII ($n$ = 2 or 3) to CLIX was achieved using Et_3N, and the failure of CLVIII (n = 4) to react was rationalised on steric grounds.



(R^1 = H or Me)

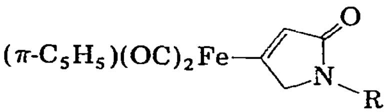
(CLIII)



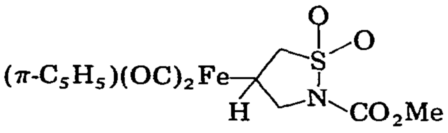
(CLIV)

$(\pi\text{-}C_5H_5)(OC)_2FeCH_2C{\equiv}CMe$

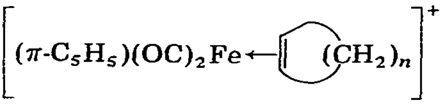
(CLV)



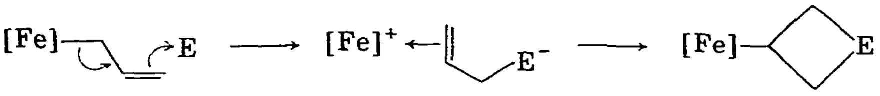
(CLVI) (R = tosylate)



(CLVII)



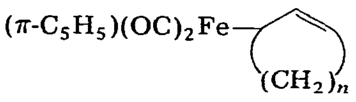
(CLVIII)



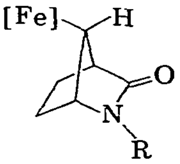
([Fe] ≡ $(\pi\text{-}C_5H_5)Fe(CO)_2$)

Scheme 27

Models indicated that in CLVIII ($n = 4$) the metal function lay *exo* to the ring and no allylic protons *trans* to the metal-olefin bond were available for abstraction. Reaction of CLIX ($n = 2$ or 3) with $p\text{-}MeC_6H_4SO_2NCO$ afforded

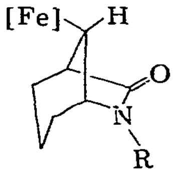


(CLIX)



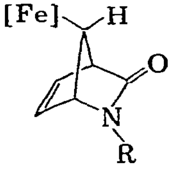
(CLX)

([Fe] = $(\pi\text{-}C_5H_5)Fe(CO)_2$;
R = tosylate)



(CLXI)

([Fe] ≡ $(\pi\text{-}C_5H_5)Fe(CO)_2$;
R = tosylate)

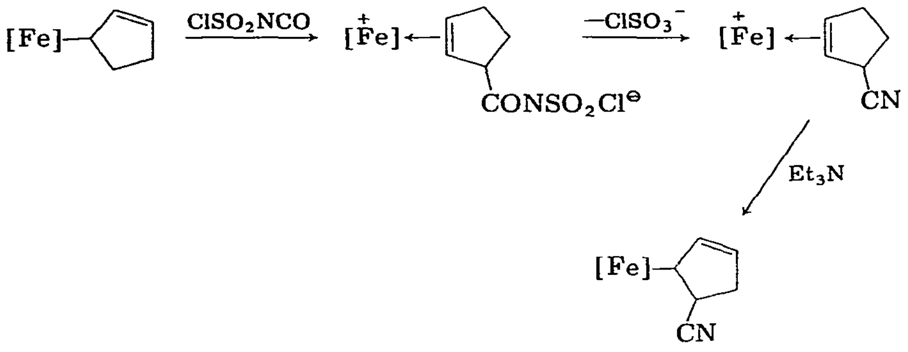


(CLXII)

([Fe] ≡ $(\pi\text{-}C_5H_5)Fe(CO)_2$;
R = tosylate)

CLX and CLXI, respectively, and $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$ gave CLXII; similar products were obtained with $MeOSO_2NCO$. The stereochemistry assigned to these species corresponded to that derived from sterically preferred cycloaddition *trans* to the bulky $(\pi\text{-}C_5H_5)Fe(CO)_2$ group. The behaviour of CLIX ($n = 2$ or 3) with $ClSO_2NCO$ was different to that with the tosyl isocyanate, but only the products when $n = 2$ were characterised (Scheme 28). It would appear that base-assisted deprotonation of π-bonded olefins occurred preferentially *exo* to the metal—olefin bond, in contrast to the behaviour in π-allylic systems, where *endo* proton exchange with the solvent was apparently preferred.

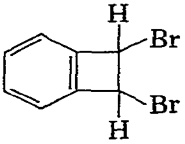
In passing, it may be noted that RNCO (R = Bu-t) reacted [198] with $(\pi\text{-}C_5H_5)Fe(CO)_2H$ giving $(\pi\text{-}C_5H_5)Fe(CO)_2(CONHR)$, $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(CNR)$ (terminal isocyanide) and $(\pi\text{-}C_5H_5)Fe(CO)(CNR)(CONHR)$.



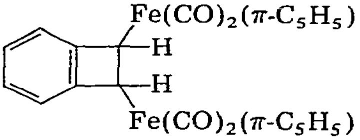
([Fe] ≡ (π-C_5H_5)Fe$(CO)_2$)

Scheme 28

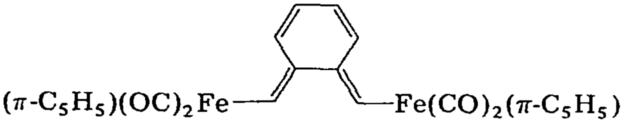
Reaction of Na[Fe$(CO)_2$(π-C_5H_5)] with CLXIII gave [199] CLXIV and not CLXV, in contrast to the reaction with 3,4-dichlorocyclobutene, which afforded [200] CLXVI.



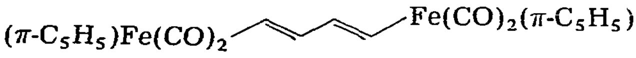
(CLXIII)



(CLXIV)



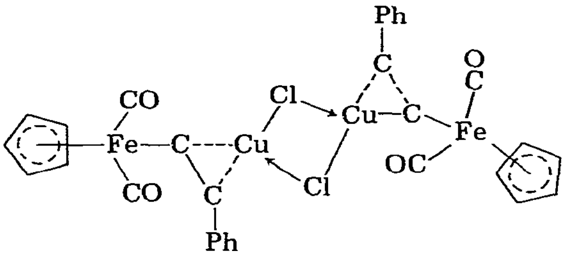
(CLXV)



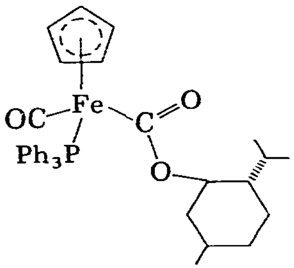
(CLXVI)

^{13}C NMR spectral studies of (π-C_5H_5)Fe$(CO)_2$(σ-C_5H_5) lent [201] further support to the proposal that the σ-bonded ring undergoes a series of 1,2-shifts. Spectral comparisons were made with (π-C_5H_5)Fe$(CO)_2CH_2CH{=}CH_2$, and this helped in assignation of the various δ_C. Wide-line NMR studies of the σ-cyclopentadienide established [202] that it is non-rigid in the solid state, but this occurred via the jumping of the π-bonded C atoms between sites and did not apparently involve the σ-bonded ring.

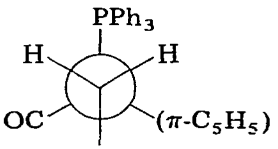
Reaction of (π-C_5H_5)Fe$(CO)_2$Cl with CuC_2Ph afforded CLXVII, whose molecular structure has been determined [203]. The Fe—C distance (1.89 Å) was somewhat shorter than that expected for a σ-bond, and the "acetylenic" C—C distance was 1.27 Å. The structure was somewhat related to that of $[CuC_2Ph]_n$ [204].



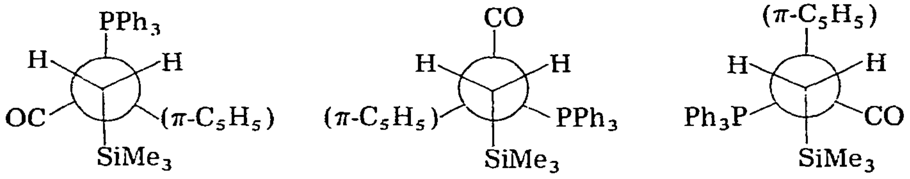
(CLXVII)



(CLXVIII)



(CLXIX)



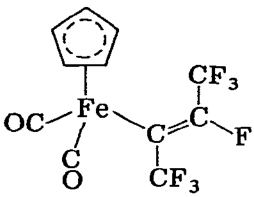
a b c

(CLXX)

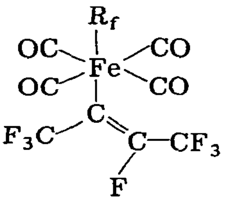
The (+)-mentholate, CLXVIII, reacted [205] with LiMe giving (—)-(π-C_5H_5)Fe(CO)(PPh_3)(COMe), and the (—)-mentholate afforded the (+)-acyl. The preferred conformation of (π-C_5H_5)Fe(CO)(PPh_3)Me was [206] CLXIX, whereas of the three possible conformations for (π-C_5H_5)Fe(CO)(PPh_3)CH_2-$SiMe_3$, CLXX*a*, *b* or *c* would be most likely, and *c* was, in fact, probable.

Treatment of (π-C_5H_5)Fe$(CO)_2$I and of Fe$(CO)_4R_f$I ($R_f = C_2F_5$, C_3F_7 or $(CF_3)_2CF$) with AgC_4F_7 afforded [207] CLXXI and CLXXII, respectively

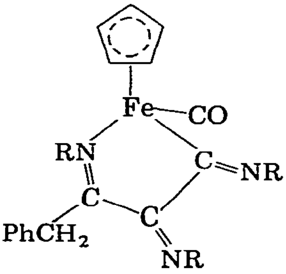
Cyanide addition to (π-C_5H_5)Fe$(CO)_2$R (R = Me or Et) gave [208] $[(\pi\text{-}C_5H_5)Fe(CO)(CN)(COMe)]^-$ which could be methylated giving (π-C_5H_5)-Fe(CO)(CNMe)(COMe). There was no reaction between CNC_6H_{11} and (π-C_5H_5)Fe$(CO)_2$Me at room temperature, but on refluxing in THF, (π-C_5H_5)Fe(CO)[CN(C_6H_{11})](COMe) was formed [209]; (π-C_5H_5)Fe(CO)-(CNBu-t)(CH_2Ph) was formed similarly. With CNC_6H_{11}, the benzyl complex and its CH_2(*p*-ClC_6H_4) analog, in refluxing THF, afforded CLXXIII. The potentially bidentate $(Ph_2AsCH_2CH_2)_2PPh$ reacted [210] with (π-C_5H_5)Fe-$(CO)_2$Me giving CLXXIV.



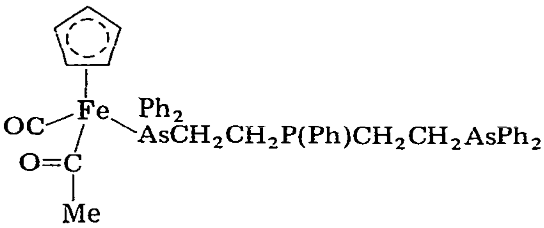
(CLXXI)



(CLXXII)

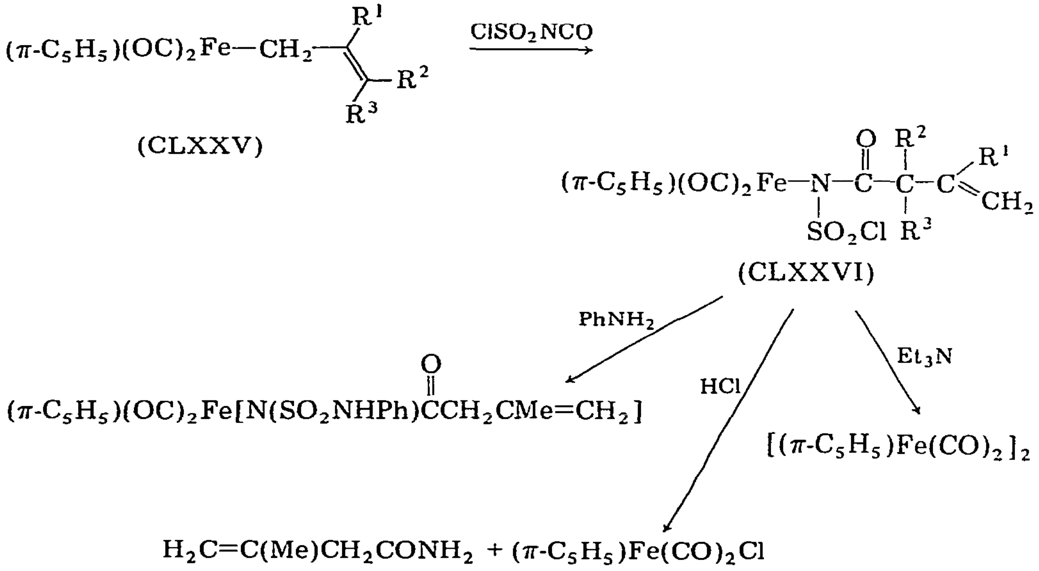


(CLXXIII)



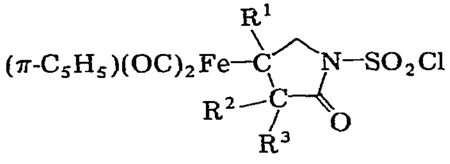
(CLXXIV)

Treatment of CLXXV (R^1 = Me; R^2 = R^3 = H) with $ClSO_2NCO$ afforded [211] CLXXVI, whose reactions with acid and bases are summarised in Scheme 29. It was suggested that initial electrophilic attack of $ClSO_2NCO$ at the C=C bond in CLXXV gave a dipolar olefinic complex which rearranged to CLXXVI via displacement of the coordinated olefin by the N atom. Reaction of CLXXV (R^1 = H; R^2 = R^3 = Me, or R^1 = R^3 = H, R^2 = Ph) gave CLXXVII whose formation was ascribed to the relative stabilities of the respective olefinic



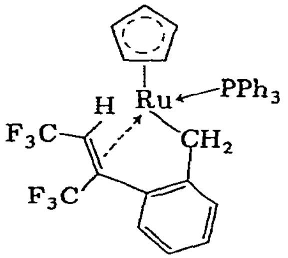
Scheme 29

intermediates, with the least substituted and therefore most stable dipolar olefin intermediate collapsing via attack of the N atom at the terminal C atom rather than at the metal.

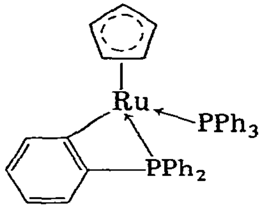


(CLXXVII)

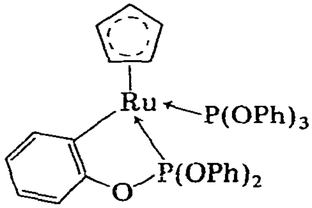
Insertion of $F_3CC{\equiv}CCF_3$ into the Ru—C bond in $(\pi\text{-}C_5H_5)Ru(PPh_3)_2(CH_2Ph)$ gave [212] CLXXVIII, a reaction perhaps occurring via metal activation of the *o*-CH bond of the benzyl group. Heating $(\pi\text{-}C_5H_5)Ru(PPh_3)_2R$ and $(\pi\text{-}C_5H_5)Ru[P(OPh)_3]_2Cl$ in decalin resulted in isolation of CLXXIX and CLXXX, and $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Me$ reacted with azobenzene giving CLXXIX and CLXXXI.



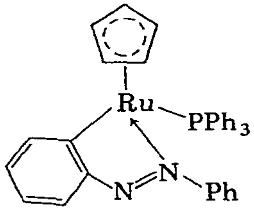
(CLXXVIII)



(CLXXIX)

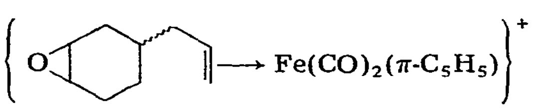


(CLXXX)

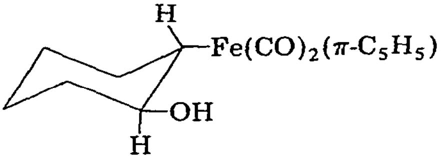


(CLXXXI)

The ^{13}C NMR spectrum of $[(\pi\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CHMe)](OCOCF_3)$ has been reported [213]. Reduction of epoxides by $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ occurred [214] stereospecifically with complete retention of configuration, and in the presence of other potentially reducible groups, e.g. CHO or CO_2R (Scheme 30). With terminal epoxides, reaction took place rapidly whereas degradation of internal epoxides occurred more slowly, thereby facilitating, for example, isolation of CLXXXII from the corresponding di-epoxide. The stereochemical results were accounted for by initial S_N2 opening of the

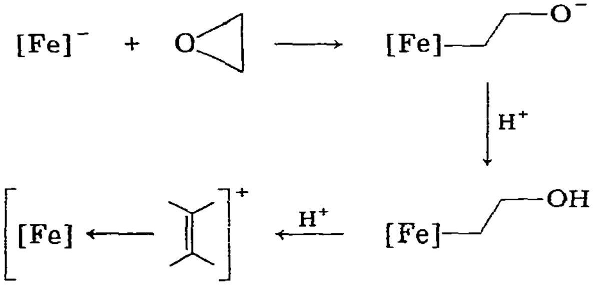


(CLXXXII)



(CLXXXIII)

epoxide by $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$, followed by *trans* migration of $(\pi\text{-}C_5H_5)$-$Fe(CO)_2$ concerted with loss of H_2O from the oxonium ion produced by protonation of the alcohol. The intermediary alcohols could be isolated by quenching the reaction with water, so that CLXXXIII could be produced from cyclohexene oxide.



$([Fe] \equiv (\pi\text{-}C_5H_5)Fe(CO)_2)$

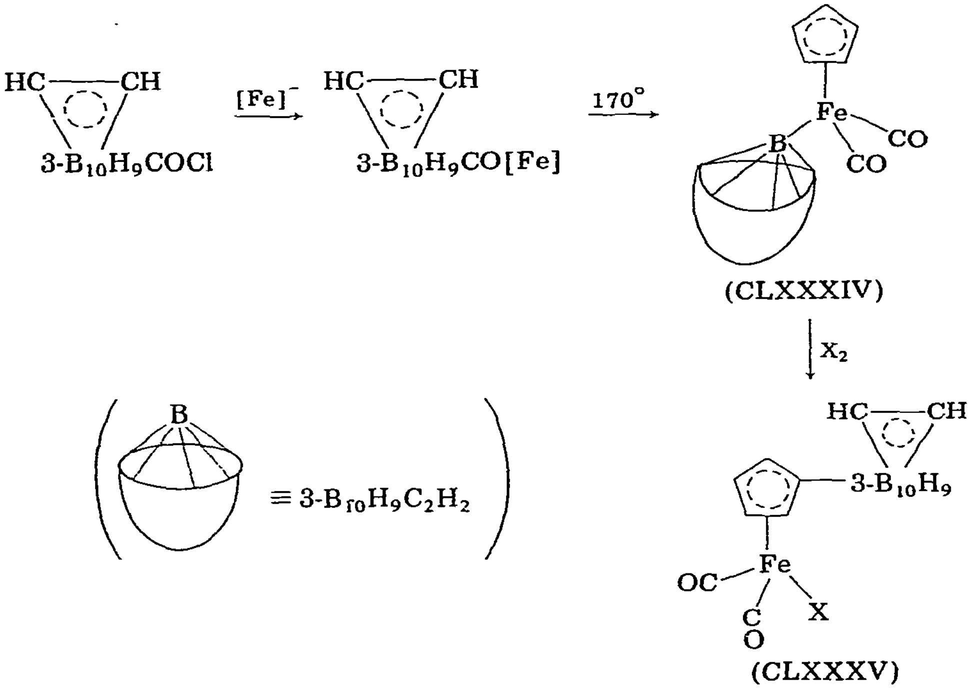
Scheme 30

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(OEt)Me\}][PF_6]$ with NaI afforded [215] $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)(COMe)$; the starting material could be regenerated from the acyl by ethylation. With ethoxide ion, the cation afforded $(\pi\text{-}C_5H_5)$-$Fe(CO)(PPh_3)[C(OEt)CH_2]$ and this was reduced by H_2/PtO or B_2H_6 in ethanol giving $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)\{CH(OEt)Me\}$. This last species was formed as enantiomeric pairs which were detected by ^1H NMR spectroscopy. Methoxide ion attack on this species gave $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)[C(OMe){=}CH_2]$. Borohydride reduction of this methoxyvinyl derivative afforded $(\pi\text{-}C_5H_5)Fe$-$(CO)(PPh_3)[CH(OEt)Me]$ and $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)Et$, whereas BD_4^- produced $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)[CD(OEt)Me]$ and $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)CD_2Me$; $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)[CD(OEt)Me]$ did not react with B_2H_6 with, or without, $NaBH_4$ in ethanol. Reaction of $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)I$ with Ag^+ and C_2H_4 provided $[(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_4)]^+$ and BH_4^- reduction of this gave the corresponding σ-ethyl derivative. These data suggested that the C(OEt)Me ligand in $[(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(OEt)Me\}]^+$ behaved as a carboxonium rather than carbenoid group. Primary amines, and NH_3, attacked the co-ordinated ethylene in $[(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)(C_2H_4)]^+$ giving carbimonium salts, so that *S*(—)-α-phenylethylamine afforded $[(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)$-$\{C[(S)\text{-}NHCHMePh]Me\}]^+$, as *RS* and *SS* isomers, which could be resolved: secondary amines did not react, presumably because of steric problems.

Reduction of $FeCl_3$ by i-PrMgBr in ether in the presence of cycloheptatriene gave [216] dicycloheptadienyliron, $(\pi\text{-}C_7H_9)_2Fe$. The structure of $(\pi\text{-}6\text{-Bu-t-}1,3,5\text{-}Me_3C_6H_2)_2Fe$ [217] has been determined; the bond distances and angles of the ligands were normal for a π-pentadienyl system and the absence of CH stretching frequencies at 2730–2830 cm^{-1} indicated [218] that the H atom attached to the t-BuC atom was *endo*.

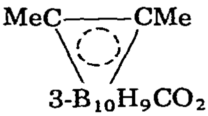
Compounds containing B

Chlorine and bromine effected [219] cleavage of the Fe—B bond in CLXXXIV causing migration of the 3-*o*-carboranyl group to the cyclopentadienyl ring (CLXXXV); an intermediate may have been a cyclopentadiene dihalide complex of iron(II). However, with the σ(1,2-dimethyl-*o*-carboranyl) ligand, the carboranyl group migrated to a coordinated CO ligand, giving eventually CLXXXVI. The general reactions are summarised in Scheme 31. These carboranyl complexes reacted with PPh_3 by replacement of CO giving $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)$(*o*-carboranyl), and with $HgCl_2$ which caused cleavage of the Fe—B bond.

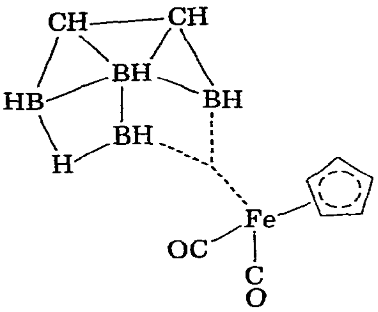


Scheme 31

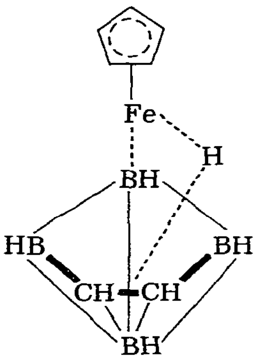
Reaction of $NaB_4C_2H_7$ with $(\pi\text{-}C_5H_5)Fe(CO)_2I$ afforded [220] CLXXXVII. This, on UV irradiation at −20° gave CLXXXVIII and the paramagnetic CLXXXIX. Treatment of $[(1,7\text{-}B_9H_9CHQ)_2Fe]^{2-}$ (Q = P or As) with $M(CO)_6$ (M = Cr, Mo or W) under UV light caused formation [221] of $[\{1,7\text{-}B_9H_9\text{-}CHQ \rightarrow M(CO)_5\}_2Fe]^{2-}$.



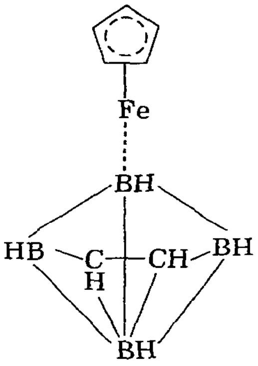
(CLXXXVI)



(CLXXXVII)



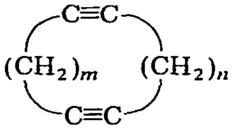
(CLXXXVIII)



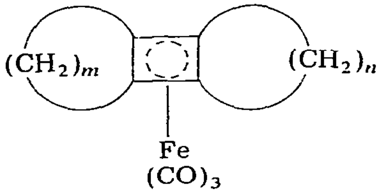
(CLXXXIX)

Metal cyclobutadiene and arene complexes

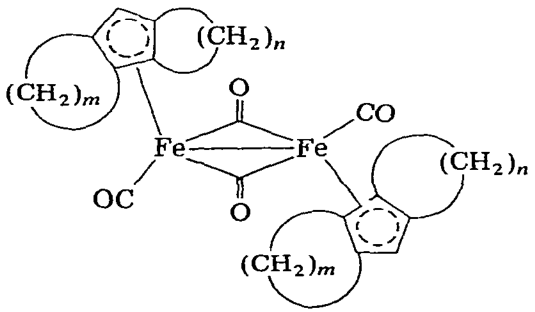
The vibrational spectrum of (π-C_4H_4)Fe$(CO)_3$ has been reported and assigned [222]. Reaction of the cyclic diacetylene, CXX ($m = 4$, $n = 6$) with Fe$(CO)_5$ afforded [223] CXCI ($m = 4$, $n = 6$ but no tricyclic π-cyclopentadienyl derivatives. However, CXC ($m = n = 5$) gave with Fe$(CO)_5$, CXCII ($m = 4$, $n = 5$)



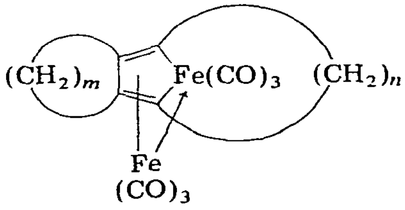
(CXC)



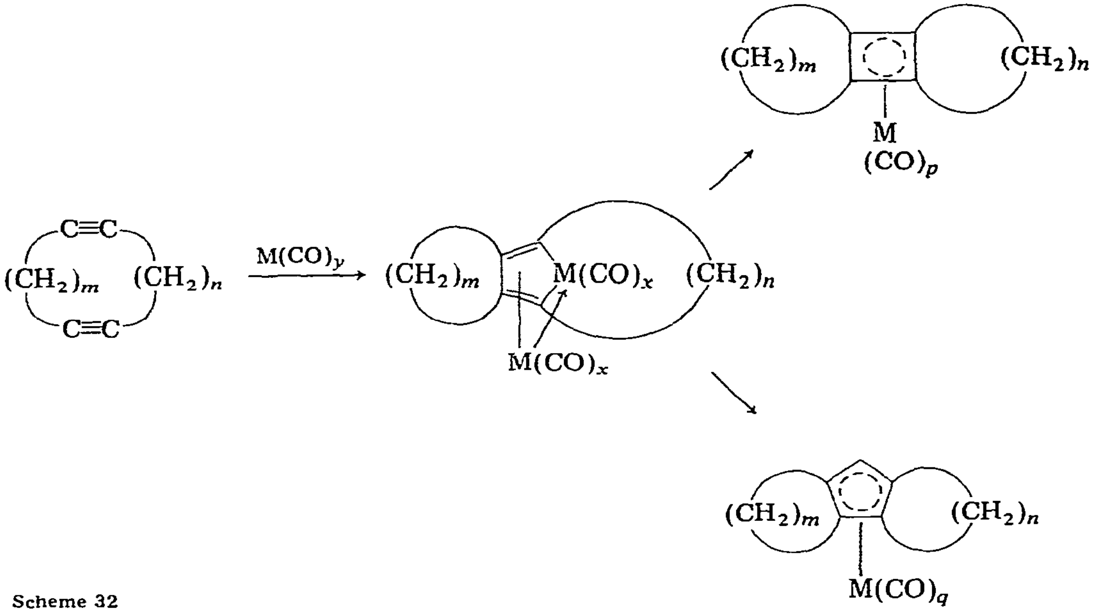
(CXCI)



(CXCII)



(CXCIII)



Scheme 32

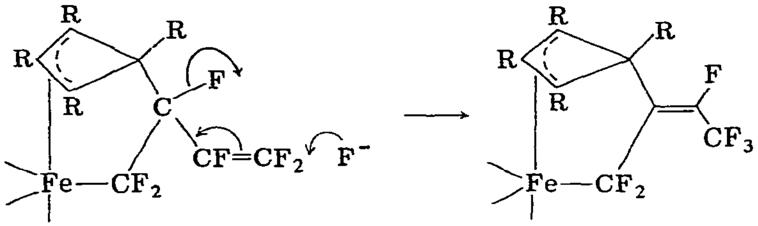
and CXC ($m = n = 4$) afforded CXCIII ($m = n = 4$). While these results indicated that iron carbonyls could form either tricyclic C_4 or C_5 ring systems, the nature of the products was strongly dependent on existing ring sizes in CXC (Scheme 32). Oxidative addition of C_2F_4, under UV light, to $(\pi\text{-}C_4R_4)Fe(CO)_3$ (R = H

a b

(CXCVIII)

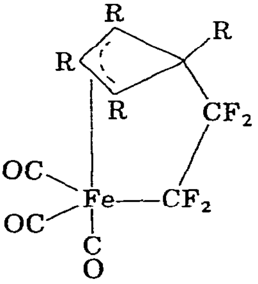
a b

(CIC)

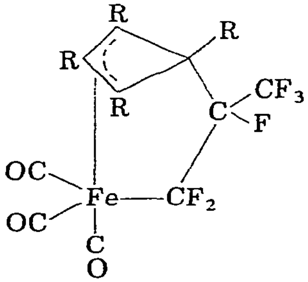


Scheme 33

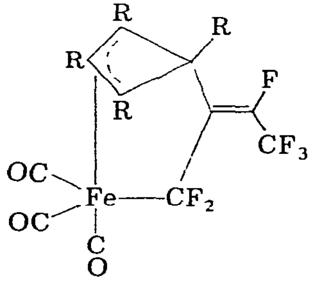
or Me) gave [224] CXCIV, and $F_3CCF{=}CF_2$ afforded CXCV. Hexafluorobutadiene provided CXCVI in a mechanism probably involving a 1,3-fluorine shift (Scheme 33). Reaction of $(\pi\text{-}C_4Me_4)Fe(CO)_3$ with $(CF_3)_2CO$ gave two isomers of CXCVII (of which there are three possibilities, a, b and c). Reaction of XCCVIIa with PEt_3 afforded CXCVIII, which also existed as isomers. Treatment of CXCVII with L = ($P(OMe)_3$ or $P(OEt)_3$) gave CICa and with $PPhMe_2$ CICb.



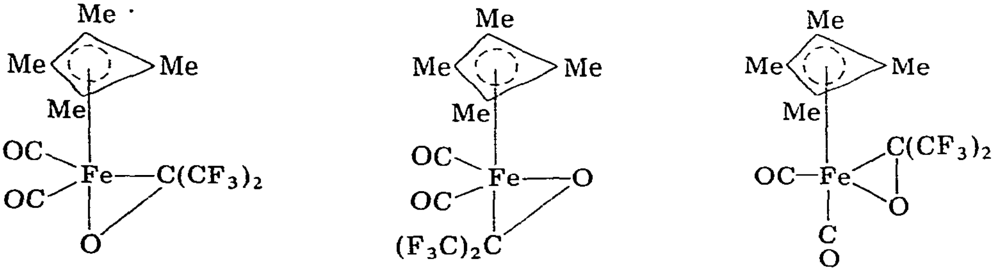
(CXCIV)



(CXCV)



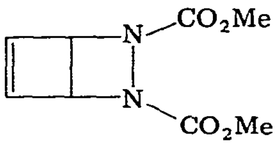
(CXCVI)



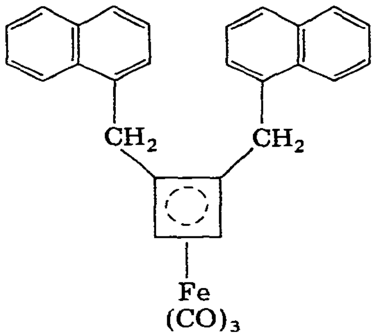
a b c

(CXCVII)

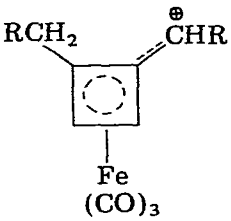
In the presence of Ce^{4+}, $(\pi\text{-}C_4H_4)Fe(CO)_3$ reacted with methyldiazoacetate giving [225] CC. Reduction of $[\pi\text{-}1,2\text{-}C_4H_2(COR)_2]Fe(CO)_3$ (R = 1-naphthyl) with BH_3/BF_3 in THF afforded [226] CCI which, on treatment with Ph_3C^+ gave CCII. Diborane reduction of $[\pi\text{-}1,2\text{-}C_4H_2(CHROH)_2]$-$Fe(CO)_3$, and reaction of CCII with 1,5-diazobicyclo[4.3.0]non-5-ene, or of the dialcohol with HCl gave CCIII. Diborane and acid treatment of $[\pi\text{-}1,2\text{-}C_4H_2(COPh)_2]Fe(CO)_3$, however, gave CCIV. The mechanism of these reactions



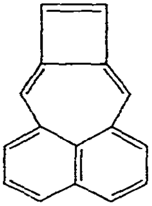
(CC)



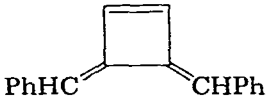
(CCI)



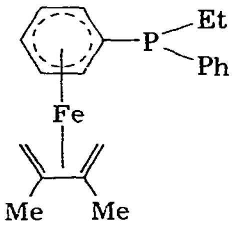
(CCII)



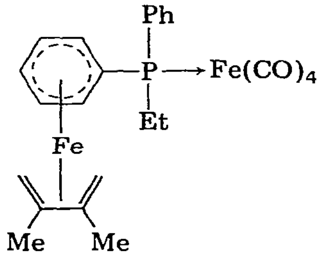
(CCIII)



(CCIV)

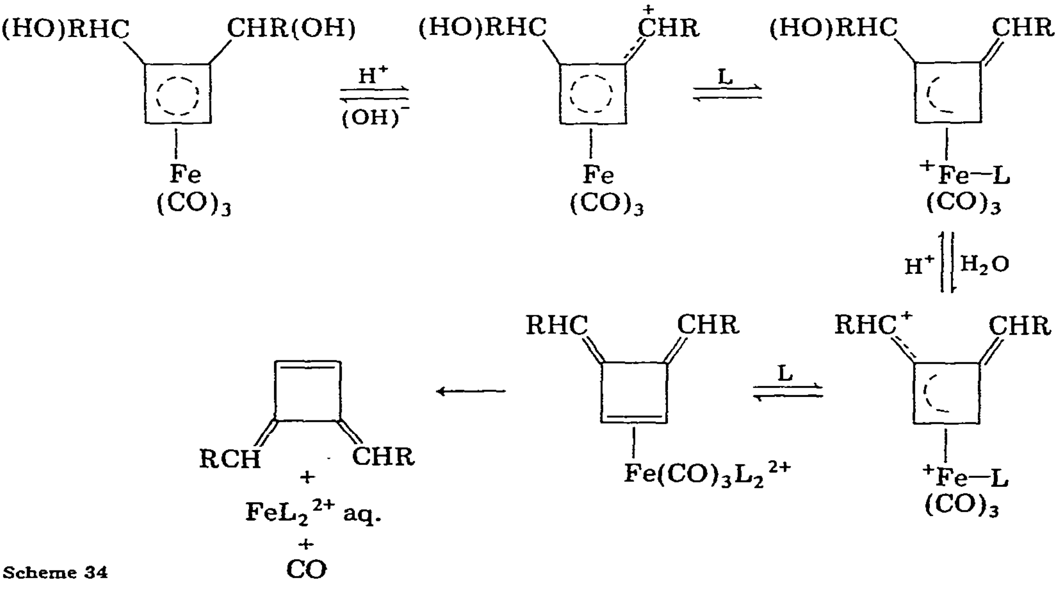


(CCV)



(CCVI)

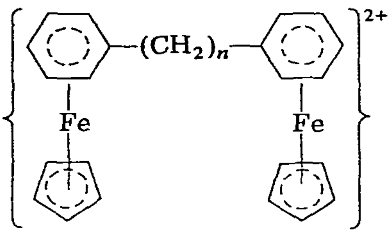
is summarised in Scheme 34. It has been reported [227] that UV irradiation of $Fe(N_2)(PPh_2Et)_3H_2$ gave $Fe(N_2)(PPh_2Et)_2(C_6H_4PPhEt)H$, but if this irradiation was carried out in the presence of 2,3-dimethylbutadiene, 40–50% of 2,3-dimethyl-2-butene, CCV, N_2 and H_2 were produced [228]. It was suggested



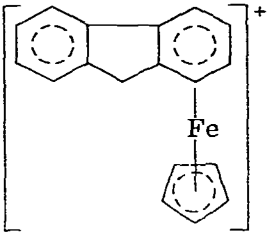
Scheme 34

that electronic excitation of the dinitrogen complex gave $Fe(PPh_2Et)_3H_2$ which functioned as the hydrogenating agent. Treatment of CCV with $Fe(CO)_5$ afforded CCVI.

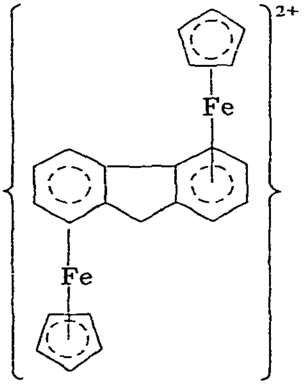
Reaction of $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_5R)]^+$ (R = Ph or CH_2Ph) with ferrocene, Al and $AlCl_3$ in hot decalin gave [229] CCVII (R = Ph, $n = 0$; R = CH_2Ph, $n = 1$). Similar treatment of CCVIII afforded CCIX, and BH_4^- reduction provided appropriate neutral complexes.



(CCVII)



(CCVIII)



(CCIX)

$RuCl_3$ reacted in ethanol with cyclohexa-1,3- or 1,4-diene giving [230, 231] $[(\pi\text{-}C_6H_6)RuCl_2]_n$, and $n = 1$ in solution; toluene, PhOMe, $p\text{-}Me_2C_6H_4$ and $p\text{-}MeC_6H_4CHMe_2$ analogs have also been prepared [231]. Reaction of $[(\pi\text{-}C_6H_6)RuCl_2]_n$ with L (tertiary phosphine or phosphite) afforded $(\pi\text{-}C_6H_6)RuLCl_2$, and the molecular structure determination [231] of $(\pi\text{-}C_6H_6)Ru(PPh_2Me)Cl_2$ and its *p*-cymene analog established that these complexes had geometries similar to $(\pi\text{-}C_6H_6)Cr(CO)_3$. The π-arene and three other ligands were mutually staggered, the arene rings being bent (not tilted) about the C_1—C_4 bond, the dihedral angle being 5° (C_6H_6) and 2° ($p\text{-}MeC_6H_4\text{-}CHMe_2$). It was suggested that the asymmetric ring bonding arose from the *trans* bond weakening effect of PPh_2Me. The coordinated C_6H_6 ring was inert to electrophilic attack [230] (acylation, H/D exchange in acid). However, H/D exchange was catalysed by NaOEt in 1/1 $EtOD/(CD_3)_2SO$, and apparently coordination to the Ru made the arene ring more susceptible to nucleophilic attack. Thus, treatment with CN^- afforded a cyanocyclohexadienyl derivative.

Reduction of $[(\pi\text{-}C_6H_6)RuCl_2]_n$ with BH_4^- gave small amounts of a cyclohexadienyl species, but mainly $Ru(1,3\text{-}C_6H_8)$-containing compounds which decomposed to cyclohexa-1,3- and -1,4-dienes. Treatment of $[(\pi\text{-}C_6H_6)RuCl_2]_n$ with $HgMe_2$ in the presence of PPh_3 gave [232] $(\pi\text{-}C_6H_6)Ru)(PPh_3)Cl_2$ and $(\pi\text{-}C_6H_6)Ru(PPh_3)ClMe$: similar treatment with $HgEt_2$ gave $Ru(PPh_3)_3ClEt$, and with $HgPh_2(\pi\text{-}C_6H_6)Ru(PPh_3)ClPh$. With $Sn(C_3H_5)_4$, $(\pi\text{-}C_6H_6)Ru(\pi\text{-}C_3H_5)Cl$ was formed, and TlC_5H_5 afforded $[(\pi\text{-}C_5H_5)Ru(\pi\text{-}C_6H_6)]Cl$.

The crystal structure determination of $(\pi\text{-}C_6Me_6)_2Ru$ revealed [233] that one ring was planar whereas the other was bent about the C_1—C_4 axis by ca. 43°. In the latter, four C atoms were bonded to the metal as a *cis*-buta-1,3-dienoidal species, the $C_1 \rightarrow C_4$ plane being nearly parallel to that of the other ring. The C—C distance of the uncomplexed fragment was 1.33 Å, whereas the C—C distances of the planar ring were 1.41 Å (those in $(\pi\text{-}C_6Me_6)Cr(CO)_3$ were [234] 1.42 Å).

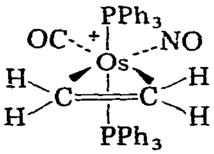
Metal olefin complexes

Non-cyclic species

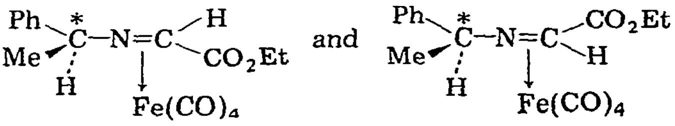
A vibrational spectral analysis has been made of $Fe(C_2H_4)(CO)_4$ [235]. $Ru(PPh_3)_4H_2$ reacted [236] with $CH_2{=}CHR$ (R = H or Ph) giving $Ru(PPh_3)_3$-$(CH_2{=}CHR)$, PPh_3 and C_2H_5R. The styrene complex was unstable in organic solvents, being converted in toluene to some $Ru(PPh_3)_3H_2$ and ethylbenzene. Reaction of the hydride with C_2Cl_4 gave $Ru(PPh_3)_3(C_2Cl_4)$. When $Ru(PPh_3)_3$-(C_2H_4) was heated, C_2H_6 was formed, possibly via a Ru—Et intermediate, the extra H atom being acquired from an *o*-C atom on a Ph ring in PPh_3. Reaction of the ethylene complex with C_2D_4 in benzene afforded $C_2H_nD_{4-n}$ ($n = 0 - 4$), and on oxidation of the metal complex, the Ph_3PO produced also contained D at the *ortho* positions in the phenyl rings.

Treatment of $Os(CO)(NO)(PPh_3)_2Cl$ with Ag^+ in acetone gave [237] $[Os(CO)(NO)(PPh_3)_2(acetone)]^+$ which reacted with C_2H_4 giving CCX. The ethylene ligand was shown, by a combination of ^1H, ^{13}C and ^{31}P NMR spectral methods, to rotate about the Os—olefin axis.

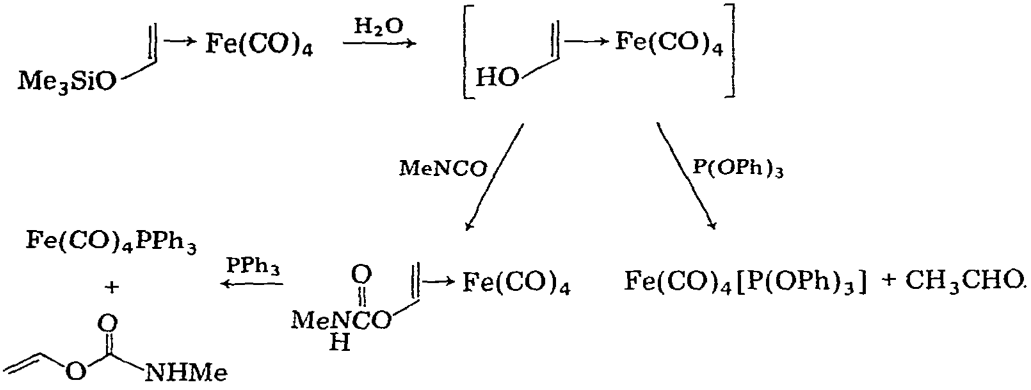
Reaction of $Fe_2(CO)_9$ with $CH_2{=}CHOSiMe_3$ gave [238] CCXI whose reaction are summarised in Scheme 35. The reactivity of the coordinated maleic anhydride in $Fe(C_2H_2C_2O_3)(CO)_4$ resembled [239] that of the free olefin. Each enantiomer of $PhMeCHN{=}CH(CO_2Et)$ reacted [240] with $Fe_2(CO)_9$ giving a mixture of two diastereomeric complexes, CCXII; the *D*(—)-imine species was isolated optically pure. Reaction of *L*(+)-CCXII with $PhCH_2Br$ followed by reduction (H_2/Pt) and base hydrolysis, gave *D*(+)-phenylalanine in 53% yield with 77% optical purity; the *D*(—)-imine



(CCX)



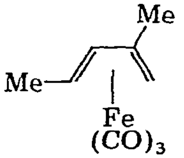
(CCXII)



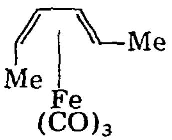
Scheme 35

complex likewise afforded *L*(—)-phenylalanine. Aspartic acid and *o*-methyltyrosine were obtained in yields of ca. 26% with optical purities greater than 78% using EtO_2CCH_2Br and o-$MeC_6H_4CH_2Br$. No significant amounts of alanine could be obtained from CCXII and MeI, but MeCOCl afforded threonine and alanine perhaps via a decarbonylation of an intermediary acyl species.

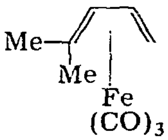
Reaction of 1,1-dimethylbutadiene with $Fe(CO)_5$ afforded [241] CCXIII whereas 1,4-dimethylbutadiene gave CCXIV. The driving force for the



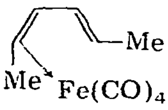
(CCXIII)



(CCXIV)

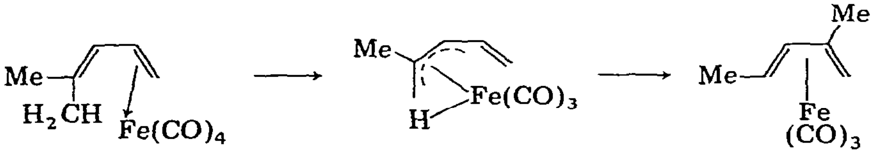


(CCXV)

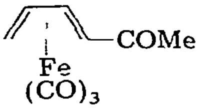


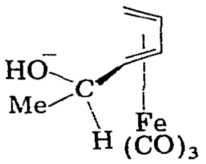
(CCXVI)

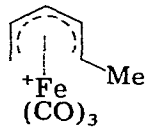
isomerisation was believed to be the relief of ring strain between *anti* methyl substituents of the 1,1-dimethylbutadiene and the Fe atom, and the *anti*-H atom on the other terminal C atom in the proposed intermediate CCXV. The proposed mechanism of isomerism is depicted in Scheme 36. In the formation of CCXIV, the proposed intermediate is CCXVI where the Me substituent of the uncoordinated olefin has a *syn* configuration and so cannot participate in H transfer to the Fe atom. The CO stretching frequencies in *p*-substituted 1-phenylbuta-1,3-diene iron tricarbonyls were linearly related [242] to the Hammett σ_p function for the *p*-substituents (NH_2, NHAc, OMe, Br, CN, OCOMe, H). The effect was related to the extent of d_π—p_π bonding from the metal to the CO groups.

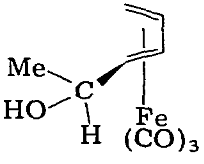


Scheme 36

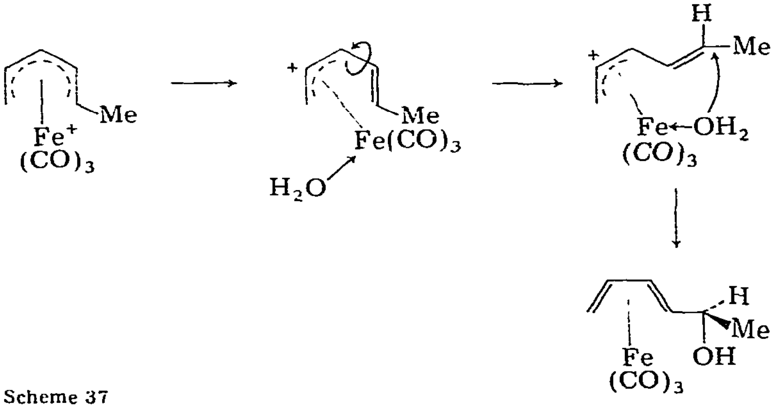

(CCXVII)

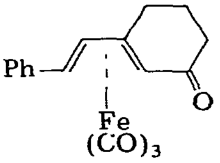

(CCXVIII)

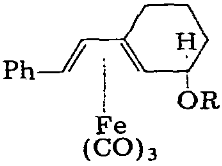

(CCXIX)

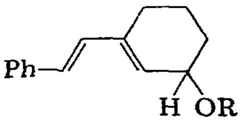

(CCXX)

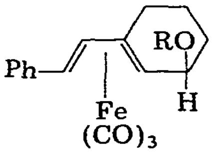
Using the lanthanide shift reagent Eu(Fod)$_3$, the conformations of disymmetric alcohol derivatives of diene iron tricarbonyls obtained by different stereospecific reactions were determined [243]. Thus CCXVII, on borohydride reduction afforded CCXVIII, with a ψ-*exo* configuration, whereas hydrolysis of CCXIX gave CCXX with a ψ-*endo* configuration. The structure of CCXX indicated that hydrolysis of CCXIX led to *RS* and *SR* racemates, rather than *RR* and *SS* forms. The mechanism of these reactions may be as shown in Scheme 37. Reduction by borohydride in methanol of CCXXI gave [244] the *endo* species CCXXII, whereas reaction of CCXXIII with Fe(CO)$_5$ afforded 34% of CCXXII and 38% of the *exo* species CCXXIV. The reactions of CCXXV,

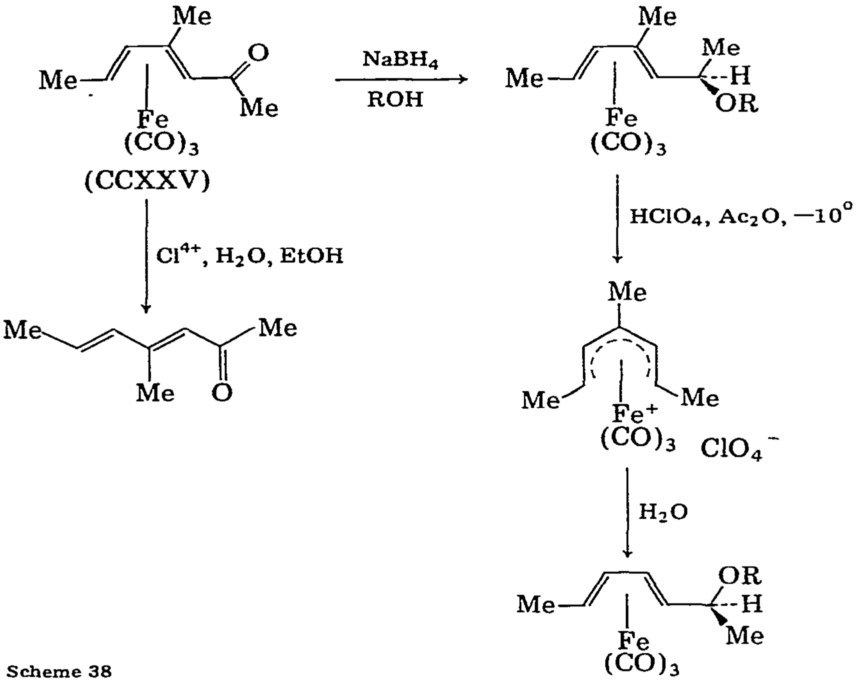

Scheme 37


(CCXXI)


(CCXXII)

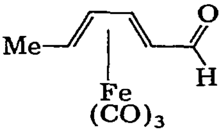

(CCXXIII)


(CCXXIV)

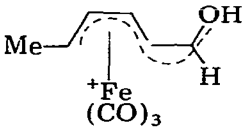


Scheme 38

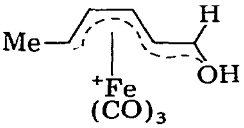
obtained from MeCH=CHC(Me)=CHCOMe and $Fe_2(CO)_9$, are summarised in Scheme 38 (R = H or 3,5-dinitrobenzoyl). All ψ-*exo* esters solvolysed more rapidly than any of their ψ-*endo* analogs, but the low reactivity of CCXXIV could be attributed to steric hindrance. There was conclusive evidence that the leaving group in the solvolysis reactions departed *exo* to the Fe atom. Protonation of CCXXVI gave [245], in equal amounts, CCXXVII and CCXXVIII. The ratio represented the kinetically controlled product distribution and indicated that the unprotonated aldehyde was present in equally populated *S-cis* and *S-trans* forms. Both cations isomerised to CCXXIX.



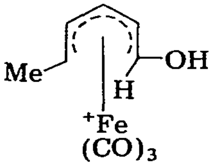
(CCXXVI)



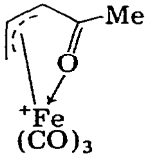
(CCXXVII)



(CCXXVIII)



(CCXXIX)



(CCXXX)

Butadiene iron tricarbonyl was 3800 times more reactive [246] towards Friedel—Crafts acylation than benzene, the initial product being CCXXX. Assuming a partial rate factor for $Fe(C_4H_6)(CO)_3$ of unity, the rates of acylation of related diene complexes are given in Fig. 1.

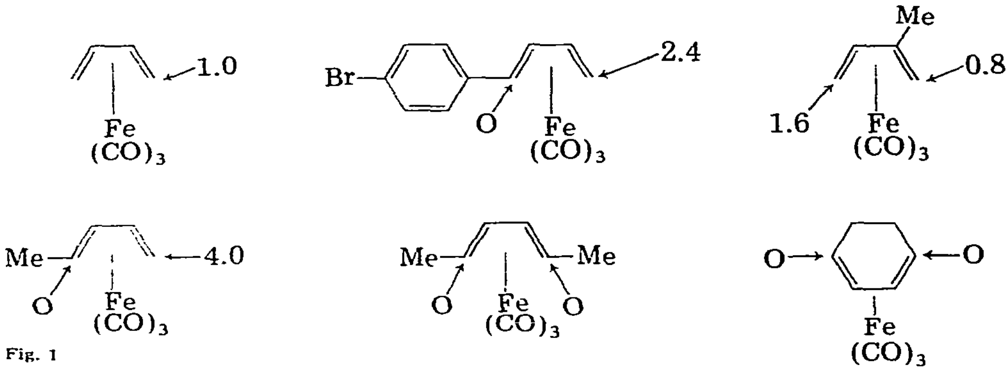
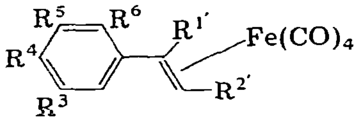
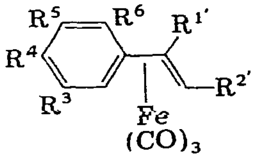


Fig. 1

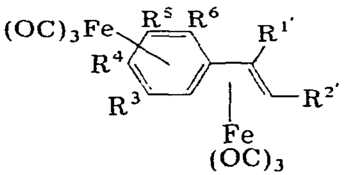
UV irradiation of styrene, and substituted analogs, with $Fe(CO)_5$ gave [247] CCXXXI, CCXXXII and CCXXXIII. Chemical and spectral evidence indicated that in CCXXXII and CCXXXIII, the aromaticity of the benzene ring had been destroyed. This was confirmed by a crystallographic examination of CCXXXIV [248], where the $Fe(CO)_3$ groups were *trans* with respect to the hydrocarbon. The angle between the planes of the two "isoprene" fragments was 37.4°, and the lack of aromatic properties of the benzene ring was thought to be derived from the formation of two isoprene-type complexes appreciably isolated from each other, rather than to bond fixation in the benzene ring. Styrenes with *meta* substituents gave positional isomers for complexes of the type CCXXXIII, but benzene species with α,β unsaturated rings attached did



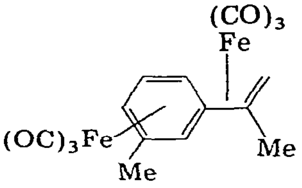
(CCXXXI)



(CCXXXII)

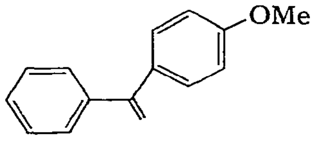


(CCXXXIII)

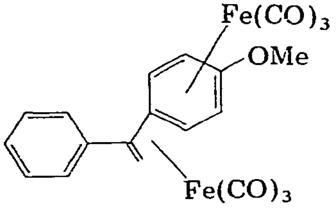


(CCXXXIV)

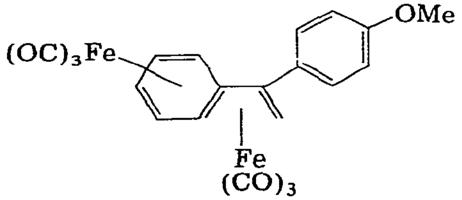
not give complexes analogous to CCXXXI or CCXXXII. Styrene could be converted sequentially to CCXXXI, CCXXXII and CCXXXIII in the dark using $Fe_2(CO)_9$, and CCXXXII was converted to CCXXXIII also in the dark. However, the conversion of CCXXXI to CCXXXII alone would occur only in light. Reaction of CCXXXV with $Fe_2(CO)_9$ afforded CCXXXVI and CCXXXVII.



(CCXXXV)



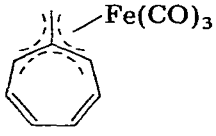
(CCXXXVI)



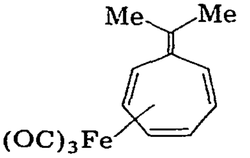
(CCXXXVII)

Reaction of $Fe_2(CO)_9$ with α,β-unsaturated ketones (PhCH=CHCOR, R = Me or Ph; PhMeC=CHCOPh) afforded $Fe(CO)_4$ and $Fe(CO)_3$ complexes [249]. $Fe(PhCH{=}CHCOMe)(CO)_3$ reacted with PPh_3 giving $Fe(CO)_3(PPh_3)_2$ more readily than $Fe(C_4H_6)(CO)_3$ or its cinnemaldehydeanil analog. It also reacted with 8,8-diphenylheptafulvene giving the appropriate Fe(diene)$(CO)_3$ complex. With 7-hydroxymethyl cycloheptatriene and dimethyl-7 cycloheptatrienylmethanol, CCXXXVIII and CCXXXIX were produced. Cinnemaldehydeanil reacted [250] with iron carbonyls giving CCXL. The species CCXLI, CCXLII (R = OH or H) and CCXLIII (R^1, R^2 = H, Cl or OMe) were also prepared and it was shown that charge transfer occurred from essentially non-bonding metal orbitals into π^* orbitals on the ligands. Protonation of CCXL occurred at the N atom, and these species containing hetero-O atoms behaved similarly; ketonic groups lost their characteristic properties on coordination. The molecular structure determinations of $Fe(PhCH{=}CHCHO)(CO)_3$ [251] and $Fe(PhCH{=}CHCH{=}NPh)(CO)_3$ [252] showed that the C=C—C=X (X = O or N) group was coplanar and that the lone pairs on X did not play an important part in bonding.

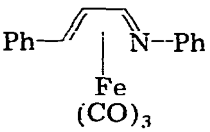
Reduction of $FeCl_3$ with i-PrMgCl in ether in the presence of C_8H_8 or a non-cyclic diolefin, followed by carbonylation at moderate pressures, afforded [253] $Fe(C_4H_6)_2(CO)$, $Fe(C_5H_8)_2(CO)$, (C_5H_8 = isoprene) and its 1,3-pentadiene isomer, $Fe(C_4H_6)(C_8H_8)(CO)$ and $Fe(C_5H_8)(C_8H_8)(CO)$. In the presence of protic acids, those species not containing C_8H_8 induced butadiene polymerisation



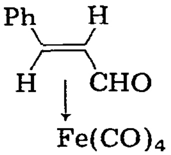
(CCXXXVIII)



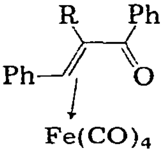
(CCXXXIX)



(CCXL)

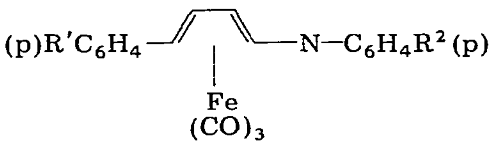


(CCXLI)



(R = H or OH)

(CCXLII)



(CCXLIII)

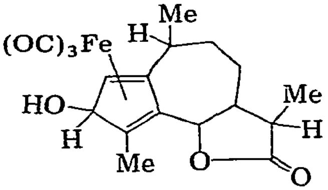
whereas $Fe(C_4H_6)(C_8H_8)(CO)$ reacted with HCl giving $Fe(C_4H_6)(C_8H_9)(CO)Cl$; in the absence of acid $Fe(C_4H_6)(C_8H_8)(CO)$ promoted the oligomerisation of C_4H_6 although the overall activity of these catalysts was lower than that of $Fe(C_8H_8)_2$. The complex $Fe(C_4H_6)_2(CO)$ was prepared [254, 255] by condensation of evaporated Fe atoms with butadiene followed by CO; replacement of CO by PF_3 gave $Fe(C_4H_6)_2(PF_3)$. Reaction of Fe atoms with cyclohexa-1,3-diene gave [255], together with cyclohexene and benzene, $Fe(C_6H_6)(C_6H_8)$, and with toluene and PF_3 or C_4H_6, $Fe(C_6H_5Me)(PF_3)_2$ or $Fe(C_6H_5Me)(C_4H_6)$ respectively. The vibrational spectrum of $Fe(C_4H_6)_2(CO)$ has been assigned [256], and the molecular structure of $Fe(C_4H_6)(C_8H_8)(CO)$ determined [257]. In the latter, the C_8H_8 ring adopted a chair conformation, and the two butadienoidal C_4 fragments had the expected dimensions.

Cyclic olefins

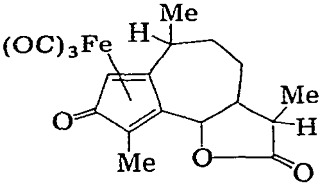
Methane chemical ionisation mass spectrometric studies of cyclobutadiene, norbornadiene, tropone, heptafulvene and cyclooctatetraeneiron tricarbonyls have been reported [258].

UV irradiation of $Fe(PF_3)_5$ with C_5H_6 afforded [259] $Fe(C_5H_6)(PF_3)_3$ which, in the presence of weak bases, gave $(\pi\text{-}C_5H_5)Fe(PF_3)_2H$; the last reacted with KOBu-t affording $K[(\pi\text{-}C_5H_5)Fe(PF_3)_2]$. 1-Acetylpentamethylcyclopentadiene reacted [260] with $Fe(CO)_5$ giving $[(\pi\text{-}C_5Me_5)Fe(CO)_2]_2$ but with $Fe_2(CO)_9$ afforded $Fe[C_5Me_5(COMe)](CO)_3$ and $(\pi\text{-}C_5Me_5)Fe(CO)_2(COMe)$. Thiophen-1,1-dioxides, on UV irradiation with $Fe(CO)_5$, provided $Fe(CO)_3$ complexes [261]. Santonin reacted with $Fe_2(CO)_9$ giving [262] CCXLIV and

CCXLV; the reaction involved the first reported reduction of a ketonic group by $Fe_2(CO)_9$ and the ligand trapped in CCXLV was believed to be the product of UV irradiation of solid santonin.

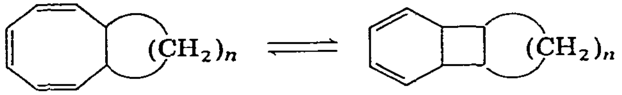


(CCXLIV)

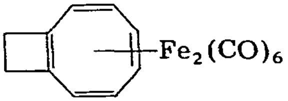


(CCXLV)

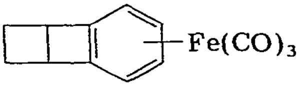
$Fe(C_6H_8)(CO)_3$ reacted with PF_3 giving [263] the stereochemically non-rigid $Fe(C_6H_8)(CO)_{3-x}(PF_3)_x$: when $x = 1$ or 2, two isomers could be detected but not separated. Reaction of CCXLVI with iron carbonyls gave



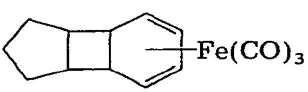
(CCXLVI)



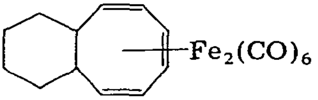
(CCXLVII)



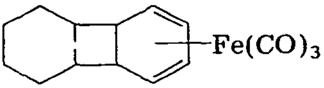
(CCXLVIII)



(CCXLIX)

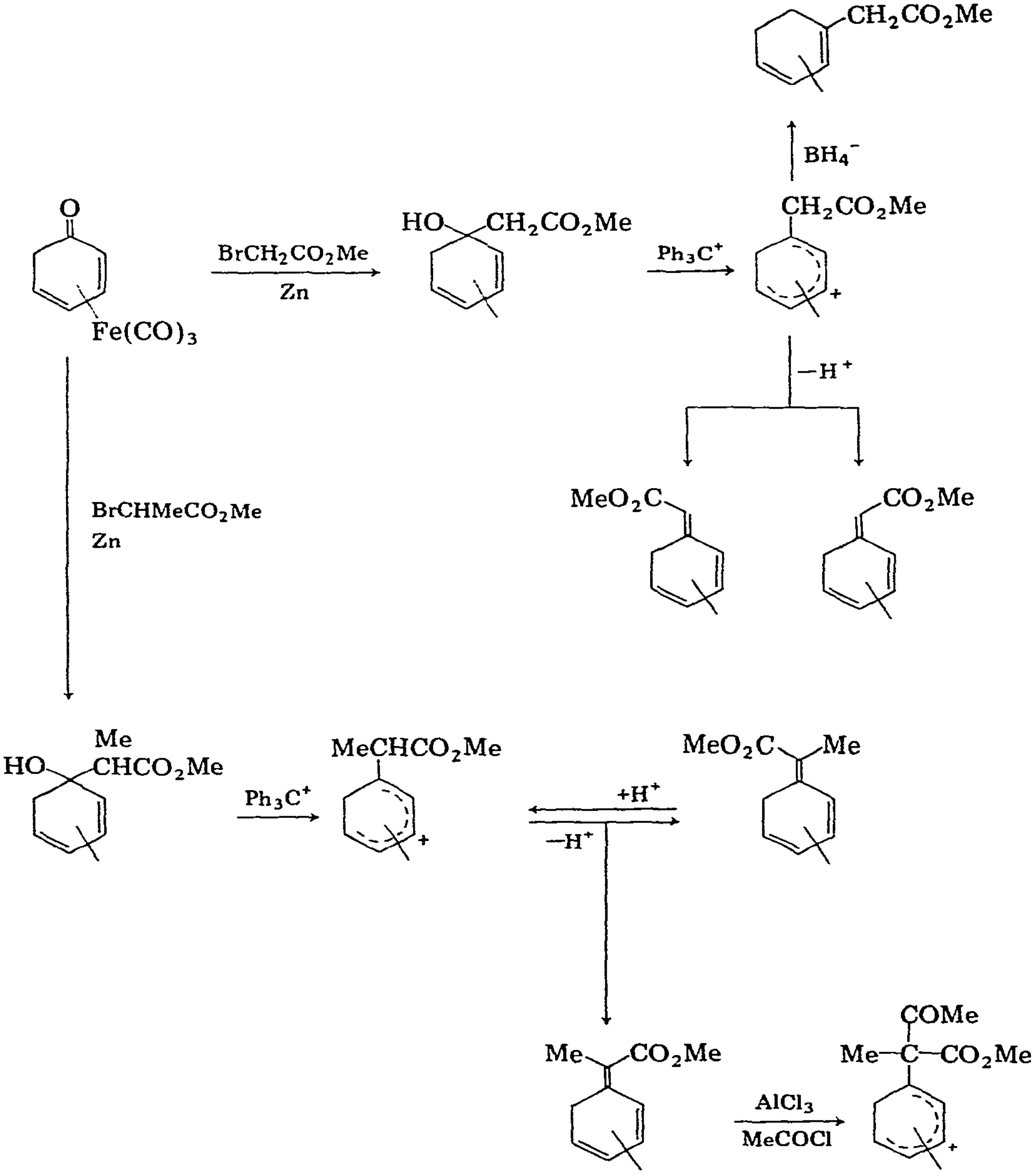


(CCL)



(CCLI)

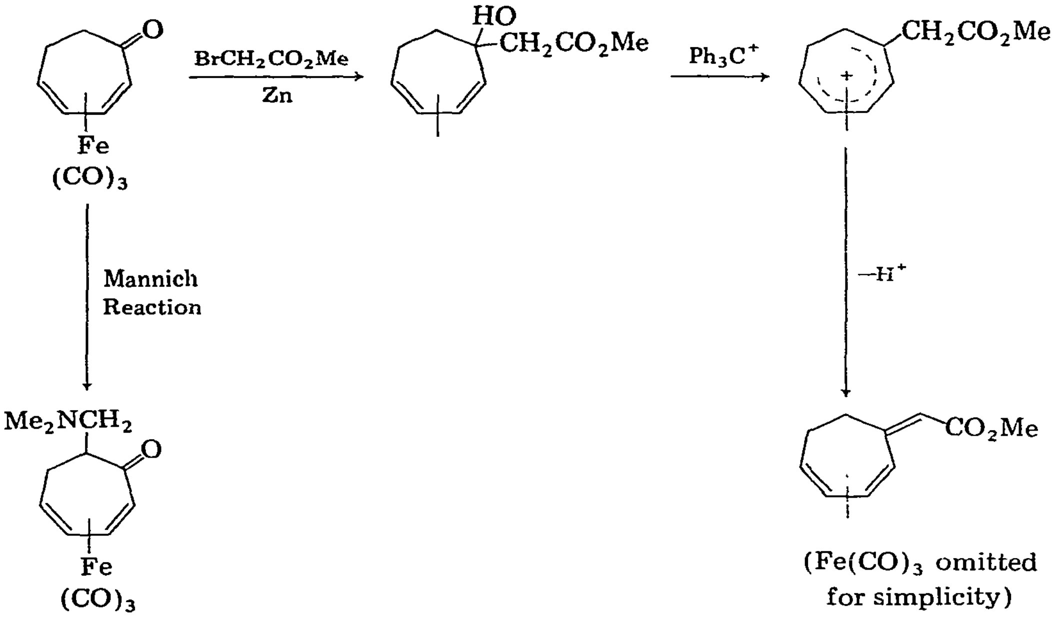
CCXLVII, CCXLVIII, CCXLIX, CCL and CCLI. Both cyclohexadienone- and cycloheptadienoneiron tricarbonyls underwent the Reformatsky reaction with MeO_2CCH_2Br and $MeO_2CCHMeBr$ (Schemes 39 and 40) [265]. Reaction of the hydroxy species so formed with Ph_3C^+ afforded dienyl salts which could be reduced to diene complexes by BH_4^- (Scheme 39) or deprotonated giving



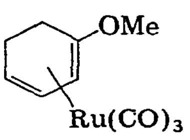
(Fe(CO)$_3$ omitted for clarity)

Scheme 39

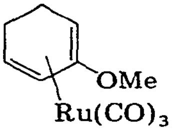
trienes in which there was an *exo*-cyclic double bond. $Ru_3(CO)_{12}$ reacted with 1-methoxycyclohexa-1,3- or -1,4-diene giving some CCLII and mostly CCLIII. Treatment of the last with Ph_3C^+ and then water afforded CCLIV.



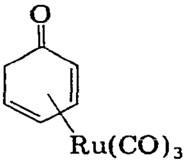
Scheme 40



(CCLII)

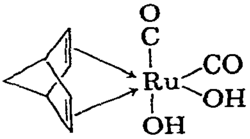


(CCLIII)

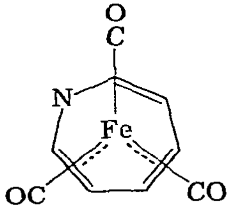


(CCLIV)

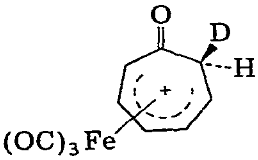
The complexes $[Ru(diene)(N_2H_4)_4][BPh_4]_2$ (diene = cycloocta-1,5-diene, norbornadiene) and $[Ru(C_8H_{12})HL_3][BPh_4]$ ($L = N_2H_4$, NH_2NMe_2) have been prepared [266] and are useful precursors for the syntheses of Ru^{II} compounds. Atmospheric pressure carbonylation of $[Ru(diene)Cl_2]_2$ (diene = norbornadiene or "bidentate" benzene), in the absence of added reducing agent afforded [267] $[Ru(CO)_3Cl_2]_2$, which reacted with ethanol (reversibly) giving $[Ru(CO)_2(EtOH)Cl_2]_n$. In the presence of hydrazine, carbonylation of the diene complexes gave a mixture of $[RuL(NH_3)_5]Cl_2$ ($L = CO$ or N_2). When PPh_3 was added to this system, the ammines were again formed together with *trans*-$Ru(CO)_3(PPh_3)_2$. If the carbonylation was effected in the presence of zinc, variable yields of $Ru_3(CO)_{12}$ were obtained together with CCLV and $Ru_4(CO)_{12}H_4$. Atmospheric pressure carbonylation of $[(\pi\text{-}C_6H_6)RuCl_2]_n$ in ethanol containing LiOCOMe in the presence of Zn gave a ca. 50% yields of $Ru_4(CO)_{13}H_2$.



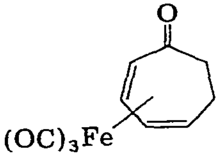
(CCLV)



(CCLVI)

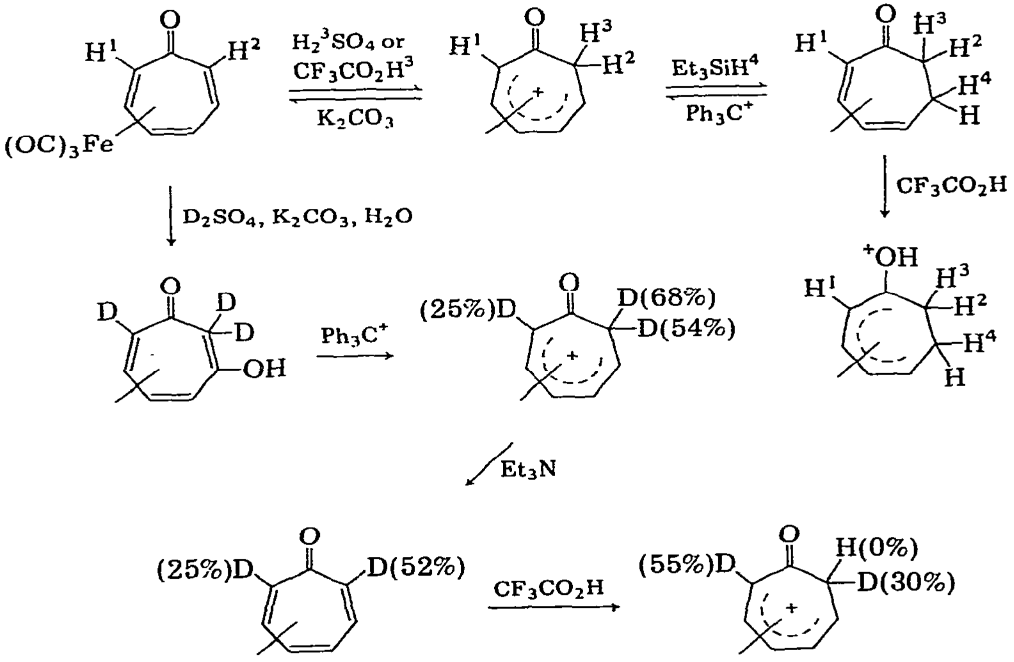


(CCLVII)

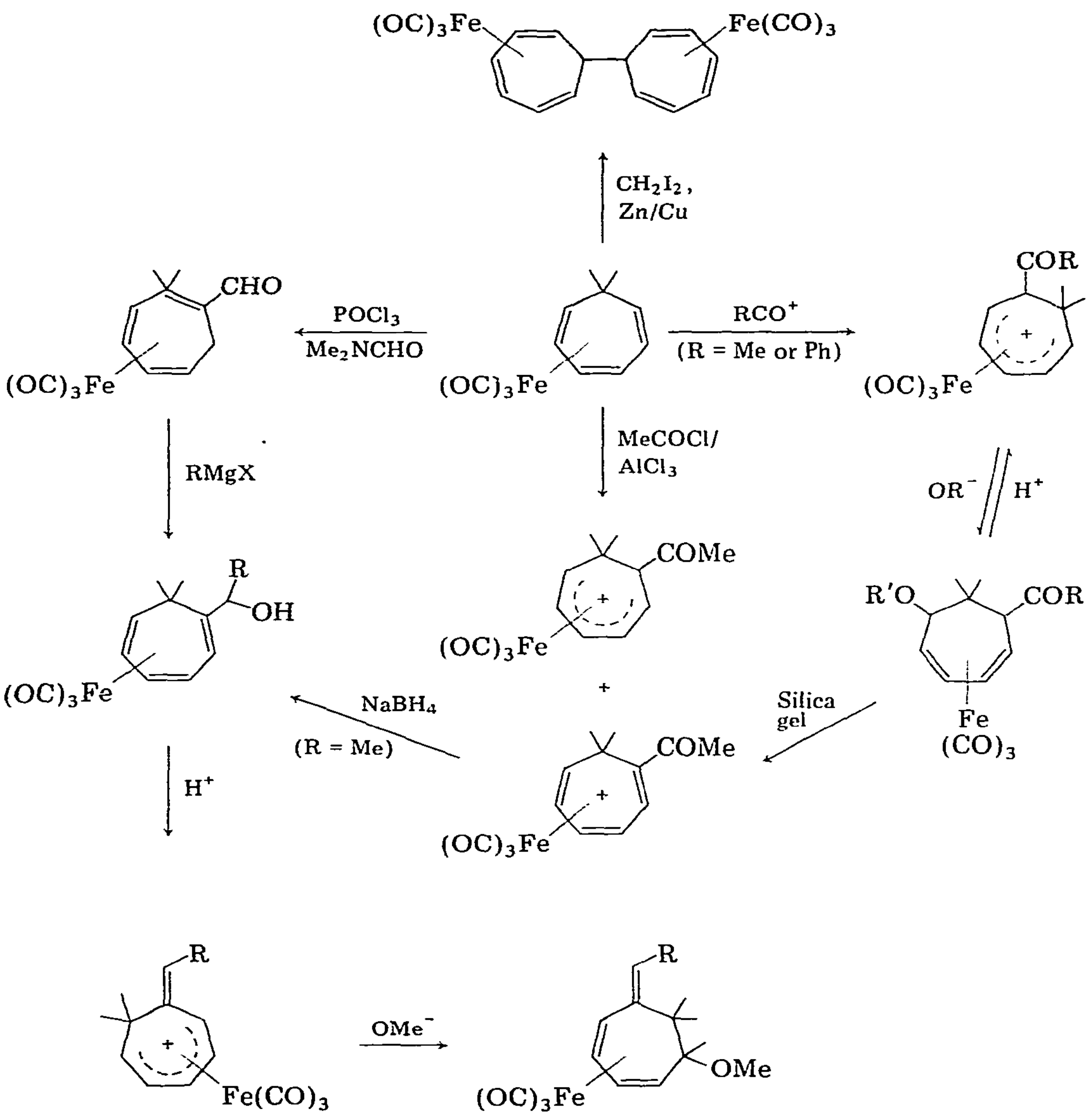


(CCLVIII)

The molecular structure determination of azepine iron tricarbonyl, CCLVI, showed [268] that the uncoordinated N—C=C and C_4 groups were not coplanar. In CF_3CO_2H, protonation of cycloheptatrienoneiron tricarbonyl, giving CCLVII, occurred [269] specifically from the *exo* side of the ring, at a C atom adjacent to the keto group. In H_2SO_4, however, protonation was not stereoselective, occurring probably from either the *endo* or *exo* side of the ring.

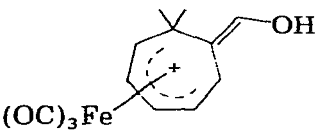


Scheme 41

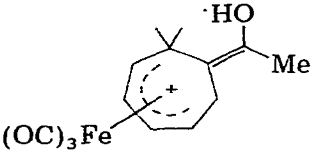


Scheme 42

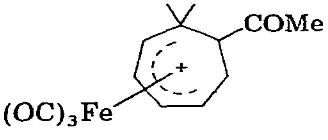
CCLVII could be reduced to CCLVIII using $SiHEt_3$. These reactions, including deuteriation studies. are summarised in Scheme 41. Cycloheptatriene iron tricarbonyl underwent [270] a series of electrophilic attacks depicted in Scheme 42. Acetylation of $Fe(C_7H_8)(CO)_3$ gave $[Fe(C_7H_8OCOMe)(CO)_3]^+$ which could not be deprotonated. However, deprotonation of $[Fe(C_7H_8$-$OCOMe)(CO)_3]^+$ which was produced by protonation of $Fe(C_7H_7OCOMe)$-$(CO)_3$, was readily accomplished. These, and related data [271], served to indicate that the former protonated species had an *exo* acetyl group, whereas the latter had an *endo* acetyl group. Protonation of $Fe(C_7H_7CHO)(CO)_3$ afforded CCLIX and $Fe(C_7H_7COMe)(CO)_3$ gave the unstable CCLX which rearranged to CCLXI.



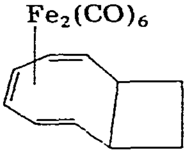
(CCLIX)



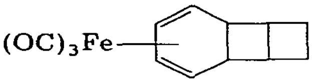
(CCLX)



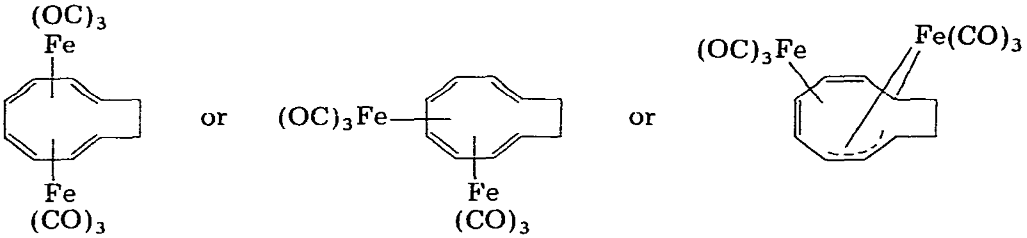
(CCLXI)



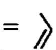
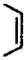
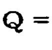
(CCLXII)

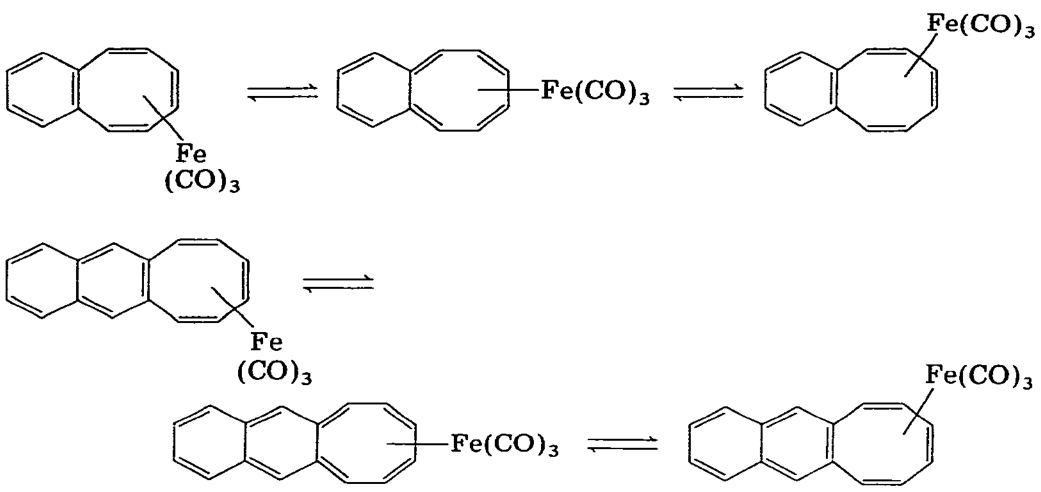


(CCLXIII)

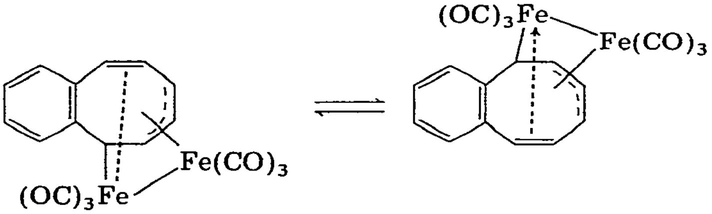


(CCLXIV)

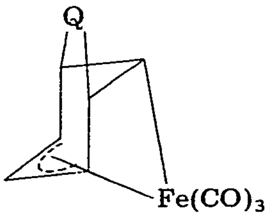
Reaction of *cis*-bicyclo[6.2.0]deca-2,4,6-triene with $Fe_2(CO)_9$ afforded [272], after chromatography, CCLXII, which was not fluxional, CCLXIII and CCLXIV (three possible structures are shown). The fluxional nature of benzo- and naphtho-cyclooctatetraeneiron tricarbonyls is shown in Scheme 43 (the activation energies for the first and second processes were 18.6 and 31 kcal/mole whereas that for $Fe(C_8H_8)(CO)_3$ was 7.2 kcal/mole). The activation energy for the rearrangement of CCLXV was 8.1 kcal/mole; a CO group attached to the allylically bonded Fe atom could be displaced by PPh_3. The complexes CCLXVI, where Q =  or $Fe(CO)_3$, reacted [274] with CO giving CCLXVII, whereas when Q = $Fe(CO)_4$, CO uptake was slow, and at high pressures the $Fe(CO)_4$ group was removed leaving CCLXVI (Q = ). Reaction of CCLXVI (Q =  or $Fe(CO)_3$) with PPh_3 gave CCLXVIII, but when Q = $Fe(CO)_4$, the products were CCLXVI (Q = ) and $Fe(CO)_4(PPh_3)$. Neither CCLXIX nor CCLXX reacted with CO or PPh_3.



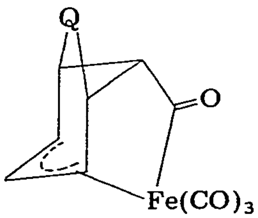
Scheme 43



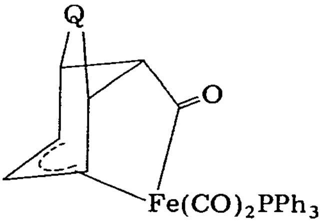
(CCLXV)



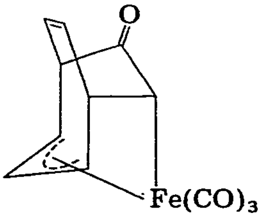
(CCLXVI)



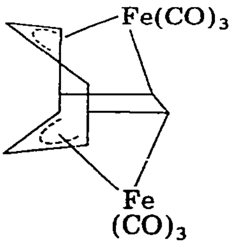
(CCLXVII)



(CCLXVIII)



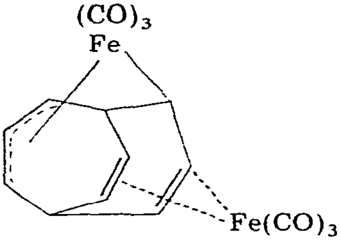
(CCLXIX)



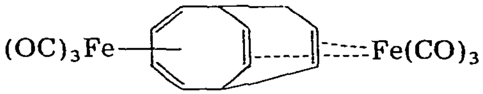
(CCLXX)

Bullvalene reacted with $Fe_2(CO)_9$ giving CCLXXI, whose structure has been determined crystallographically [275], and the known CCLXXII [276].

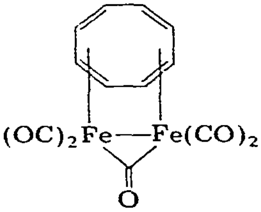
^{13}C NMR spectral studies [277] of $Fe(C_8H_8)(CO)_3$ over a temperature range were in agreement with ^1H NMR spectral investigations. The CO groups also underwent site exchange independent of the ring rearrangements. Broad-line ^1H NMR studies of $Fe(C_8H_8)(CO)_3$ and $Fe_2(C_8H_8)(CO)_5$ showed [278] that, in the solid state, the former was non-rigid whereas the latter was rigid. In the presence of oxygen, no product was obtained [279] when $Fe(C_8H_8)(CO)_3$ was irradiated with UV light, but in the absence of oxygen, CCLXXIII was produced [280], together with C_8H_8 and CO; CCLXXIII was also prepared by irradiation of $Fe_2(C_8H_8)(CO)_6$.



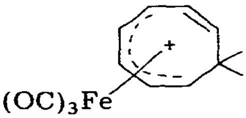
(CCLXXI)



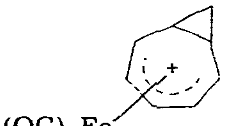
(CCLXXII)



(CCLXXIII)



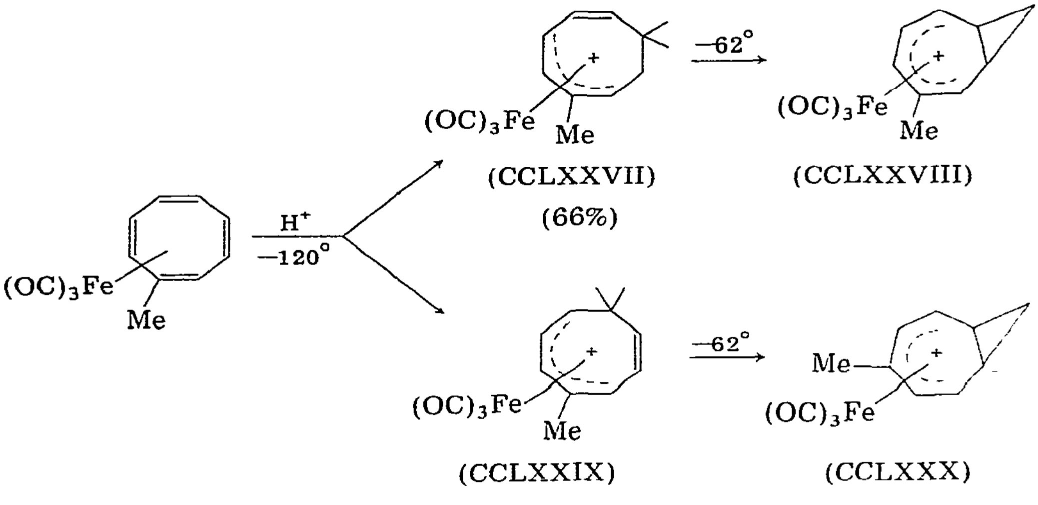
(CCLXXIV)



(CCLXXV)

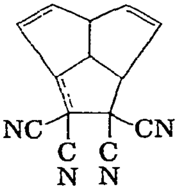
(CCLXXVI)

At −120°, treatment of $Fe(C_8H_8)(CO)_3$ with FSO_3H/SO_2ClF gave [281] CCLXXXIV. On warming this collapsed to CCLXXV which, after 24 h in H_2SO_4 at 35° may have given CCLXXVI. Similar treatment of the methylcyclooctatetraene analog gave CCLXXVII which collapsed to CCLXXVIII, and CCLXXIX which collapsed to CCLXXX (Scheme 44). Collapse of CCLXXVII to CCLXXVIII occurred much more slowly than that of CCLXXIX implying, possibly, that the positive charge at the central γ-C atom in these cationic pentadienyl complexes may be somewhat greater than that at the α-C atom.

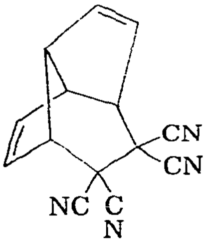


Scheme 44

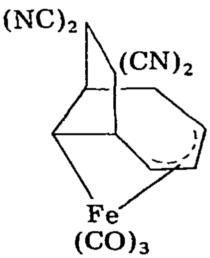
When the adduct of $Fe(C_8H_8)(CO)_3$ and $(NC)_2C{=}C(CN)_2$ was treated [282] with Ce^{4+}, either CCLXXXI or CCLXXXII (probably the former) was formed. $FeCl_3$ oxidative degradation of CCLXXXIII gave CCLXXXIV. In terms of the cycloadditions of $(NC)_2C{=}C(CN)_2$ occurring via electrophilic attack [283], the mechanism of adduct formation with cycloheptatriene and cyclooctatetraene complexes, and their oxidative degradation, may be as depicted in Scheme 45.



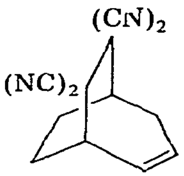
(CCLXXXI)



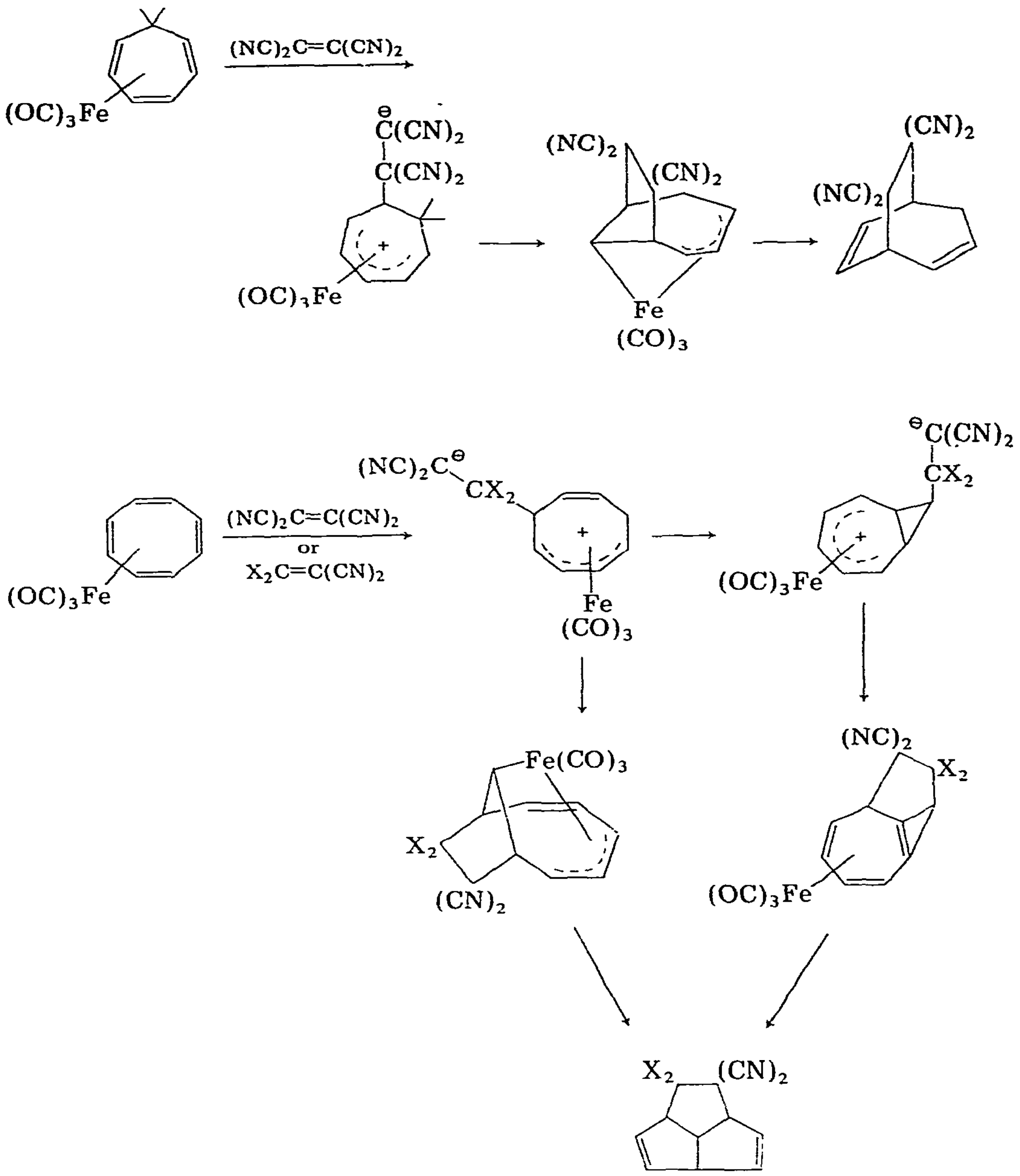
(CCLXXXII)



(CCLXXXIII)

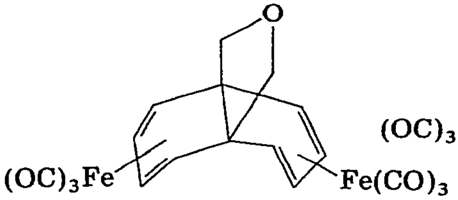


(CCLXXXIV)

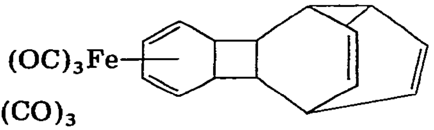


Scheme 45

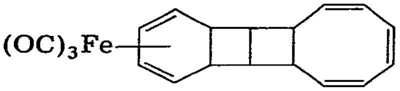
Reaction of 12-oxa[4.4.3]propella-2,4,7,9-tetraene with $Fe_2(CO)_9$ gave CCLXXXV whose structure was established [284] crystallographically. UV irradiation of the iron tricarbonyl complexes of cyclooctatetraene dimers, CCLXXXVI and CCLXXXVII, with more $Fe(CO)_5$ afforded [285] CCLXXXVIII;



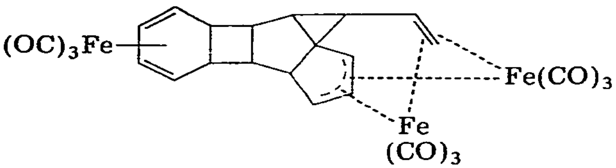
(CCLXXXV)



(CCLXXXVI)



(CCLXXXVII)



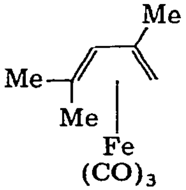
(CCLXXXVIII)

the two Fe atoms were symmetrically positioned with respect to the allyl group. The formation of CCLXXXVIII implied that CCLXXXVII isomerised to CCLXXXVI prior to reaction with $Fe(CO)_5$.

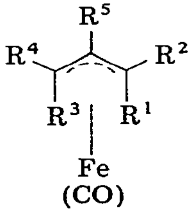
Broad-line ^1H NMR spectral studies of $Ru_3(C_8H_8)_2(CO)_4$ showed [286] that, in the solid state, the rings were undergoing rearrangement via a series of 1,2-shifts.

Allyl and trimethylenemethane complexes

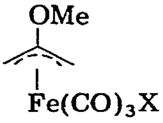
Protonation of butadiene- and isopreneiron tricarbonyls, and CCLXXXVII gave [287] allyl tricarbonyl cations, which, on standing, afforded the π-allyl tetracarbonyl cations, CCLXXXVIII. It appeared that protonation preceded CO transfer. In CF_3CO_2H, CCLXXXVIII [288] (all R = Me) or (R^1 = i-Pr, $R^2 = R^3 = R^4 = H$, R^5 = Me) gave a mixture of both species; in CF_3CO_2D no incorporation of D occurred. CCLXXXVIII ($R^1 = R^2$ = Me, $R^3 = R^4 = R^5$ = H)



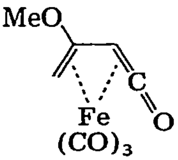
(CCLXXXVII)



(CCLXXXVIII)

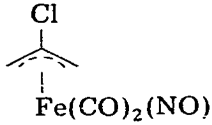


(CCLXXXIX)

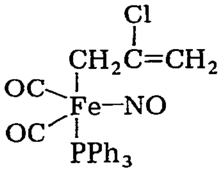


(CCXC)

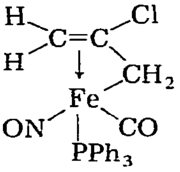
in CF_3CO_2H contained small amounts of ($R^1 = R^5 = Me$, $R^2 = R^3 = R^4 = H$), and in CF_3CO_2D complete deuteration occurred at the *anti*-methyl substituents, and at positions R^3 and R^4 in CCLXXXVIII ($R^1 = R^2 = Me$, $R^3 = R^4 = R^5 = H$) and at R^1 in ($R^1 = R^5 = Me$, $R^2 = R^3 = R^4 = H$). In CCLXXXVIII ($R^1 = Me$, $R^2 = R^3 = R^4 = R^5 = H$), D incorporation occurred at positions R^3 and R^4 as well as at the methyl group, and in ($R^1 = R^3 = Me$, $R^2 = R^4 = R^5 = H$) D was incorporated slowly at the methyl groups only. In CCLXXXVIII ($R^1 = R^3 = R^4 = R^5 = H$, $R^2 = Et$) no D uptake, even over long periods, was observed.



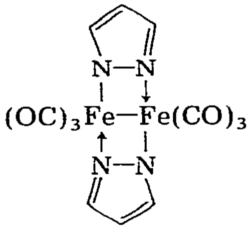
(CCXCI)



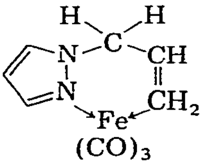
(CCXCII)



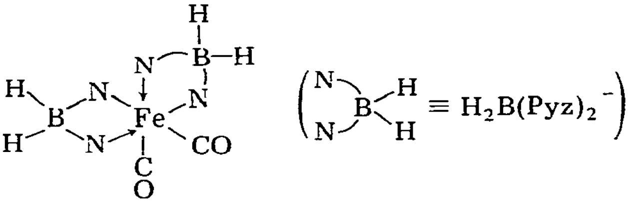
(CCXCIII)



(CCXCIV)

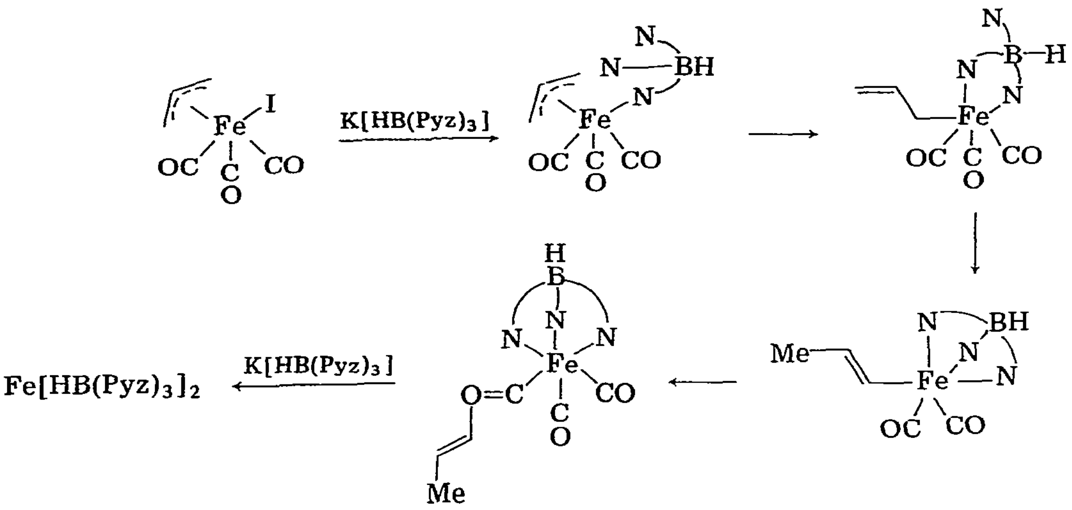


(CCXCV)



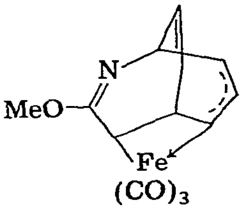
(CCXCVI)

Reaction of $CH_2{=}C(OMe)CH_2X$ ($X = Br$ or I) with $Fe_2(CO)_9$ gave [289] the π-allyl complex CCLXXXIX but when X = Cl, CCXC was formed; CCLXXXIX could also be obtained using $MeC(OMe){=}CHX$. Treatment of XCCI with PPh_3 afforded [290] CCXCII which eventually decarbonylated giving CCXCIII. Reaction of $(\pi\text{-}C_3H_5)Fe(CO)_3I$ with the trispyrazolylborato ion $[HB(Pyz)_3]^-$ gave [291] $Fe[HB(Pyz)_3]_2$ (56%), CCXCIV (2.6%), CCXCV (ca. 1%), $Fe(CO)_2[HB(Pyz)_3](CH{=}CHMe)$ (ca. 1%), and $Fe(CO)_2[HB(Pyz)_3](COCH{=}CHMe)$ (28%). The proposed mechanism is given in Scheme 46. The allyl iodide reacted with $[H_2B(Pyz)_2]^-$ giving CCXCVI.

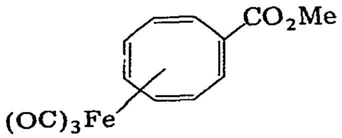


Scheme 46

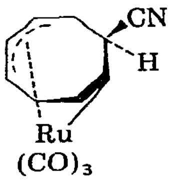
2-Methoxy-azabullvalene reacted with $Fe_2(CO)_9$ giving [292] CCXCVII and CCXCVIII. Hydride abstraction from $Ru(C_8H_{12})(CO)_3(C_8H_{12}$ = cycloocta-1,5-diene) followed by addition of CN^- afforded [293] CCXCIX.



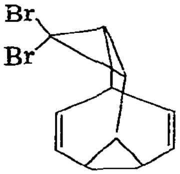
(CCXCVII)



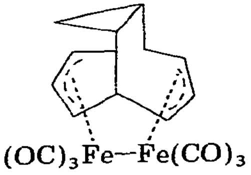
(CCXCVIII)



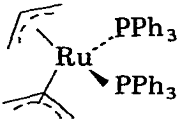
(CCXCIX)



(CCC)

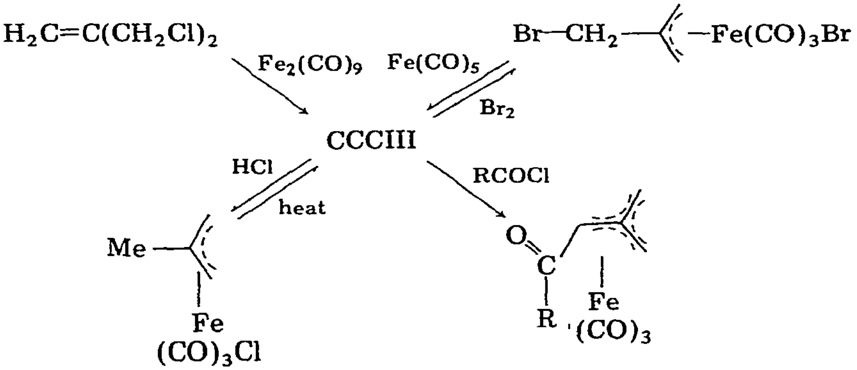


(CCCI)



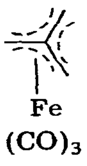
(CCCII)

Treatment of CCC with $Fe_2(CO)_9$ afforded the binuclear bis-π-allyl CCCI [294]. The molecular structure determination of $(\pi\text{-}C_3H_5)_2Ru(PPh_3)_2$, CCCII revealed [295] that the bond angles between the central allylic C atoms, and Ru and P atoms, were all close to tetrahedral. This, together with the shortness of the Ru—central C atom distance (2.13 Å compared with 2.24 Å), suggested that the Ru atom was tetrahedrally coordinated to the central allylic C atom, and that a significant degree of σ-bonding was involved.

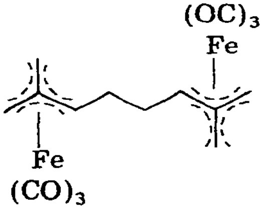


Scheme 47

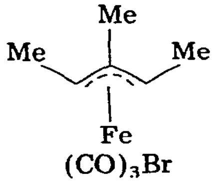
Various trimethylenemethaneiron tricarbonyl complexes, especially CCCIII. have been prepared [296] by either dehalogenation of 3-halo(2-halomethyl)-propenes with $Fe_2(CO)_9$ or by thermal disproportionation of 2-methylallyiron tricarbonyl complexes (Scheme 47). Dehalogenation of tris(bromomethyl)-ethylene using excess of $Fe_2(CO)_9$ afforded CCCIV. Thermolysis of CCCV or CCCVI did not give trimethylenemethane complexes but instead provided dieneiron tricarbonyls; reaction of 1,1,2-trimethylallyl bromide with $Fe_2(CO)_9$ gave only CCCVII. Alane and $AlCl_3$ reduction of CCCVIII gave isopreneiron



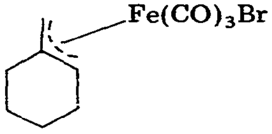
(CCCIII).



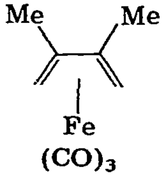
(CCCIV)



(CCCV)

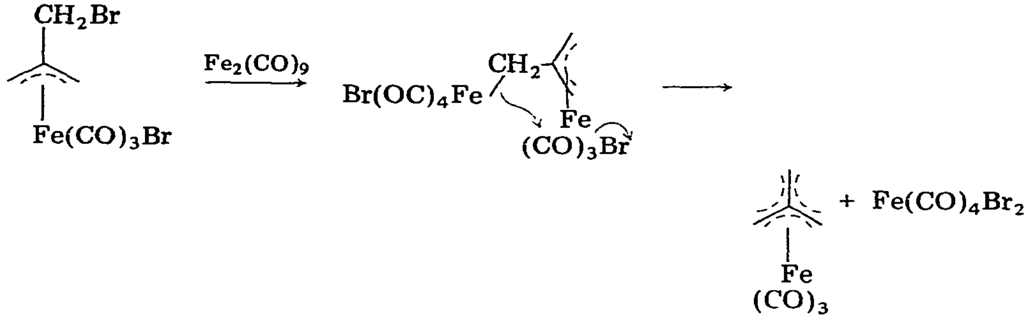


(CCCVI)



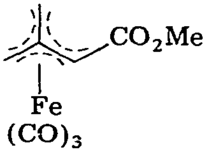
(CCCVII)

tricarbonyl and CCCIX. Benzoyl chloride addition to CCCVIII gave CCCX and, eventually, CCCXI. Acid hydrolysis of CCCIX or its 1,1-dimethyl analog afforded isopreneiron tricarbonyl or CCCVII, respectively. The mechanism of formation of CCCVIII from 3-bromo(3-bromomethyl)propene is depicted in Scheme 48.

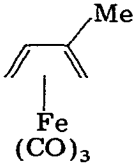


Scheme 48

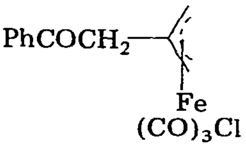
Treatment of CCCXII with $Fe_2(CO)_9$ gave [297] CCCXIII. The vibrational spectrum of CCCXIII has been assigned [298] and CCCXIII reacted with PF_3 giving $Fe[C(CH_2)_3](CO)_{3-x}(PF_3)_x$ ($x = 1$, 2 or 3) [299]. The ^{19}F NMR spectrum of the last indicated that there was hindered rotation of the $Fe(CO)_{3-x}(PF_3)_x$ group relative to the trimethylenemethane ligand.



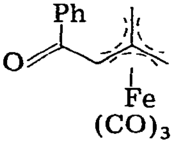
(CCCVIII)



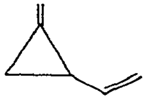
(CCCIX)



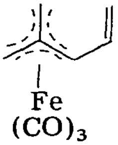
(CCCX)



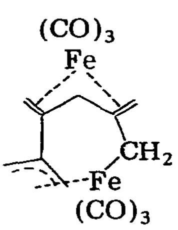
(CCCXI)



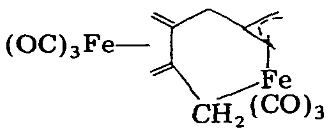
(CCCXII)



(CCCXIII)



(CCCXIV)



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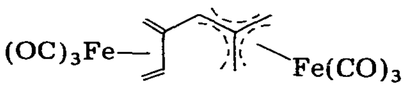
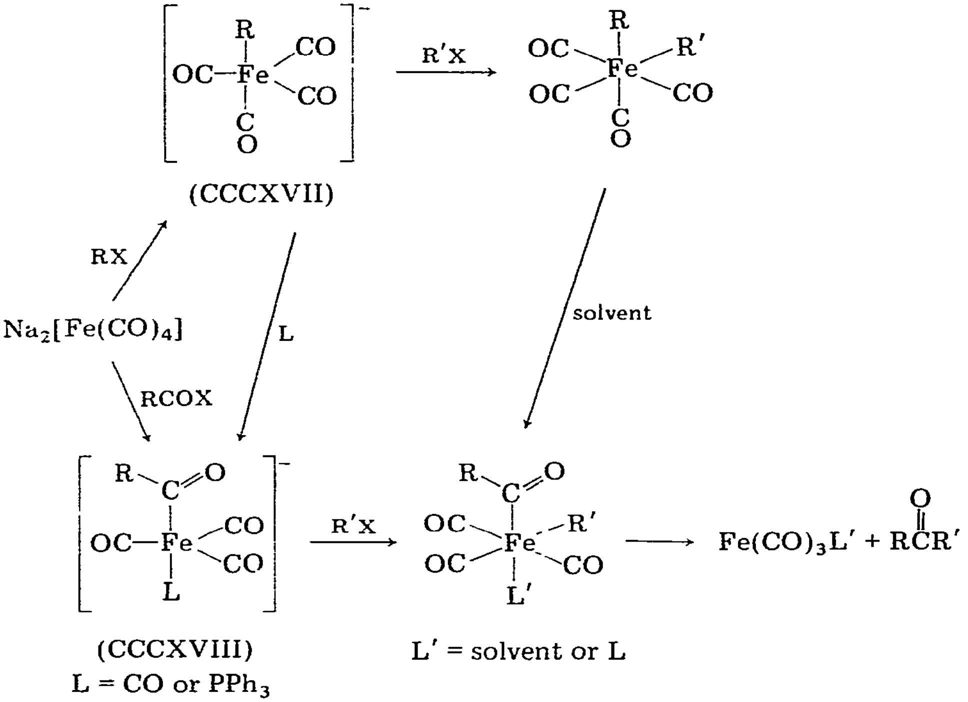


(CCCXVI)

Allene reacted with $Fe_3(CO)_{12}$ giving [300] CCCXIV which isomerised at 100-110° in toluene or *o*-dichlorobenzene afforded CCCXV. Either of these two compounds in refluxing toluene or *o*-dichlorobenzene gave CCCXVI. The structures of all three species have been determined [301]. Polymerisation of the allene occurred when an excess was added to any of these in *n*-hexane.

Alkyl- and aryl-metal complexes

Reaction of $Fe(CO)_5$ with LiR, or of $Na_2[Fe(CO)_4]$ with RCOCl afforded [302] the acyl$[Fe(CO)_4(COR)]^-$, and the closely related alkyls were obtained by reaction of $[Fe(CO)_4]^{2-}$ with RX; these compounds were isolated as $[(Ph_3P)_2N]^+$ salts. Reaction of $[Fe(CO)_4(CH_2Ph)]^-$ with MeI gave $Me(PhCH_2)CO$, and of $[Fe(CO)_4(COCH_2Ph)]^-$ with MeI and with acetic acid afforded $Me(PhCH_2)CO$ and $PhCH_2CHO$, respectively. These reactions have been generalised [303] providing a selective synthesis of aliphatic ketones (Scheme 49). Thus treatment of the intermediates CCCXVII or CCCXVIII with an alkyl halide led to isolation of RR′CO. The nucleophilicity of the carbonylate ions towards attack of RX decreased in the order $[Fe(CO)_4]^{2-} > [Fe(CO)_4R]^- > [Fe(CO)_3(PPh_3)(COR)]^- > [Fe(CO)_4(COR)]^-$. It was suggested that formation of $[Fe(CO)_4R]^-$ occurred with inversion of configuration at R, and carbonylation giving $[Fe(CO)_4(COR)]^-$ apparently occurred with retention

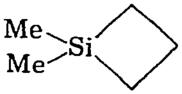


Scheme 49

of configuration. The ion $[Fe(CO)_4]^{2-}$ was apparently unreactive towards some functional groups, e.g. reaction with $Br(CH_2)_4CO_2Et$ and EtI gave $EtCO(CH_2)_4CO_2Et$. The migration of the allyl group to CO, thereby affording an acyl complex, was strongly influenced [304] by the nature of the counter cations associated with $[Fe(CO)_4R]^-$ and $[Fe(CO)_4(COR)]^-$.

Reaction of the cyclic silane CCCXIX with $Fe_2(CO)_9$ afforded [305] CCCXX, also produced by treatment of $ClCH_2CH_2CH_2SiMe_2Cl$ and $[Fe(CO)_4]^{2}$ Hydrolysis of CCCXX gave $MeCH_2CH_2SiMe_2(OH)$ and $(MeCH_2CH_2SiMe_2)_2O$, reaction with PR_3 gave organosilicon polymers, $Fe(CO)_4(PR_3)$ and $Fe(CO)_3(PR_3)_2$, and thermolysis gave $Fe(CO)_5$ and traces of organosilanes.

Treatment of $Fe_2(CO)_6(\mu\text{-}SCF_3)_2$ with $F_3CC{\equiv}CCF_3$ afforded [306] CCCXXI whose molecular structure was determined; the C—C bond length was 1.34 Å, and the Fe—Fe distance 3.27 Å (i.e. non-bonding). the Fe_2S_2 was appreciably non-planar. Reaction of CCCXXII with $Fe_2(CO)_9$ gave [307]



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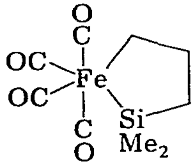

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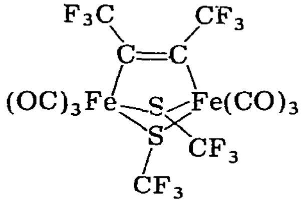

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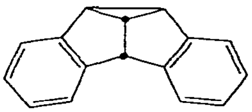

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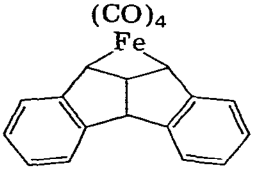
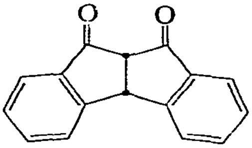


(CCCXXIII)



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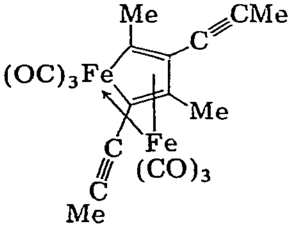

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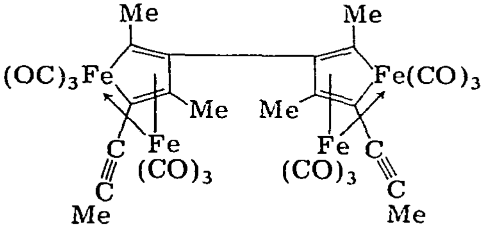
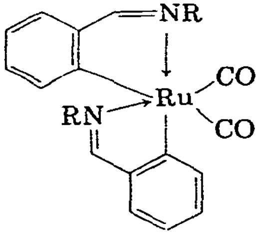


(CCCXXVI)

CCCXXIII. Reaction of the last with $Ph_2PCH_2CH_2PPh_2$ caused displacement of two CO groups and formation of a diphos complex, whereas reaction with Ce^{4+} gave CCCXXIV. The structure determination of CCCXXIII revealed that the molecule was folded about the C—C bond fusing the two indane fragments. $Fe_3(CO)_{12}$ reacted with 2,4-hexadiyne in boiling toluene giving CCCXXV and CCCXXVI; the former was presumably the precursor of the latter [308].

$[Ru(CO)_3Cl_2]_2$ reacted with PhCH=NMe (BzmH) giving [309] $[Ru(CO)_2Cl(Bzm)]_2$, and this Schiff base, or PhCH=NPh, reacted with $Ru_3(CO)_{12}$ giving CCCXXVII. These bases did not react with $(\pi\text{-}C_5H_5)Fe(CO)_2Me$, and with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ afforded only $[(\pi\text{-}C_5H_5)Fe(CO)]_4$.

By heating in decalin $Ru_3(CO)_9[P(OPh)_3]_3$, two isomers of $Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$, $Ru_4(CO)_9[P(OPh)_3]_3H_4$ and $Ru_2(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]H$, CCCXXVIII, were formed [310]. $Ru(CO)_2[P(OC_6H_4)(OPh)_2]_2$ could also be obtained [311] from $Ru(CO)_2[P(OPh)_3]_2Cl_2$. The structure of CCCXXVIII was determined crystallographically and the Ru—Ru distance was 2.89 Å. One *o*-metallated $P(OC_6H_4)(OPh)_2$ group was primarily attached to Ru_1 and the Ru_1—P distance was the shortest yet detected. The other *o*-metallated phosphite was bonded to Ru_2 and Ru_1, the *o*- and *m*-C atoms of the metallated ring being within bonding distance of Ru_1 while Ru_2 was bonded to the *ortho* C atom. It was suggested that the interaction was best described in terms of a four-centre three electron contribution from the bridging aryl group to the two metal atoms. There was thought to be some similarity between this interaction and that involving the "benzyne" ligand and the Os atoms in $Os_3(CO)_{10}(PPh_2)_2(C_6H_4)$ and its analogs [95, 96].



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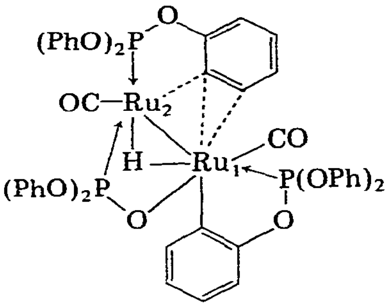

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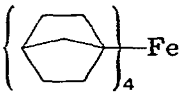


(CCCXXIX)

The diamagnetic norbornyl complex CCCXXIX was obtained [312] by treating LiC_7H_{11} with $FeCl_3$, whereas Li_5FePh_5 was obtained [313] by treating $FeCl_3$ in LiPh under very mild conditions. Hydrolysis of the pentaphenyl gave biphenyl and $Fe(OH)_2$, whereas $HgCl_2$ afforded $FeCl_2$, LiCl, Hg and HgPhCl.

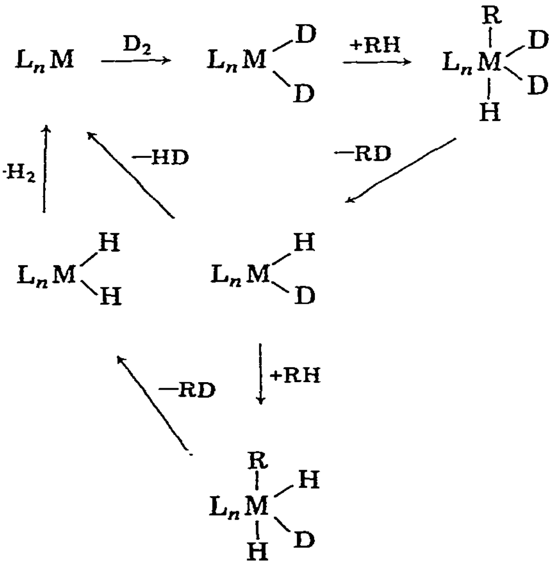
Reaction of $Fe(N_2)(PPh_2Et)_3H_2$ with C_2H_4 in solution gave [314] $Fe(PPh_2Et)_3HEt$, or the solvated (S) species $Fe(PPh_2Et)_2(S)HEt$, probably via the intermediate $Fe(PPh_2Et)_2L(C_2H_4)H$ (L = PPh_2Et or solvent). Reduction of $Fe(Acac)_3$ with PPh_3 and $AlEt_3$ at −30° gave [315] the paramagnetic $Fe(PPh_3)_3Et(Acac)$. This compound initiated polymerisation of styrene, acrylo- and methacrylonitrile. Disproportionation occurred in polar solvents with release of C_2H_6. Reduction using $AlPr_3$ gave $Fe(PPh_3)_3Pr(Acac)$ and with $AlMe_3$ $Fe(PPh_3)_3Me_2$. Thermal decomposition or alcoholysis of the latter gave methane. Alkyl derivatives were not formed when $AlHEt_2$ or $AlMe_2(OEt)$ were used as reducing agents.

Reaction of organoiron phthalocyanin complexes, $[RFePc]^{n-}$ (R = Me or Ph, $n = 0$ or 1) with styrene in the presence of Li_2PdCl_4 afforded [316] PhCH=CHR. Introduction of anhydrous $FeCl_3$ into a THF solution containing Mg metal under nitrogen caused [317] degradation of the THF thereby generating an unsaturated hydrocarbon. This was picked up by the Fe giving uncharacterised σ-bonded species, $C_4H_5FeCl_2Mg(THF)_2 . 6H_2O$ and/or $(C_4H_5)_2FeCl_7Mg_2(THF)_4 . 6H_2O$.

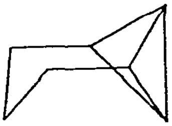
Organometallic complexes in synthesis and catalysis

Selective reduction of RCH=CHCOR′ to RCH_2CH_2COR' was achieved [318] using $Fe(CO)_5$ in slightly wet basic solvents. Phthalazine was reduced [319] to 1,2-dihydrophthalazine and $Fe_2(CO)_6(\mu\text{-}N_2C_8H_8)$ using $Fe_3(CO)_{12}$, and a number of Schiff bases derived from aniline could be reduced similarly.

The complexes $Ru(PPh_3)_3HCl$ and $Ru(PPh_3)_3Cl_2$ caused [320] a random redistribution of D in *trans*-$C_2H_2D_2$, via an ethyl intermediate. The hydride complex was more active than its dichloro analog, and H/D exchange was observed between $C_2H_2D_2$ and the H atom in the *ortho* positions of the PPh_3 ligands in the hydride. H/D isotopic exchange between D_2, and acetic acid, MeOH, EtOH or morpholine was observed [321] in the presence of $Ru(PPh_3)_3Cl_2$ or $Os(PPh_3)_3Br_2$($Fe(PPh_3)_2Cl_2$ was inactive). The proposed mechanism is shown in Scheme 50.



Scheme 50



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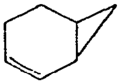

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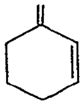

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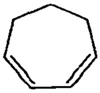
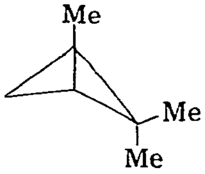
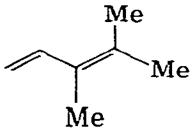


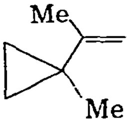
(CCCXXXIII)



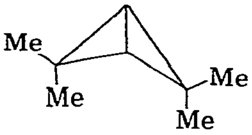
(CCCXXXIV)



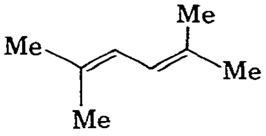
(CCCXXXV)



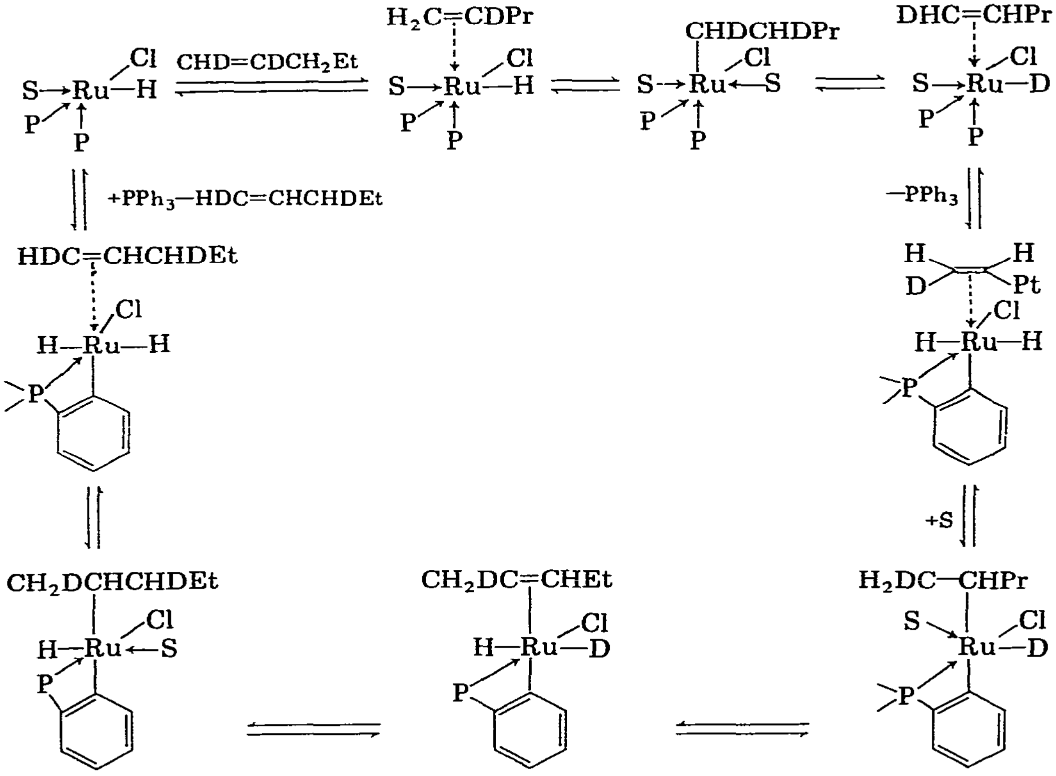
(CCCXXXVI)



(CCCXXXVII)

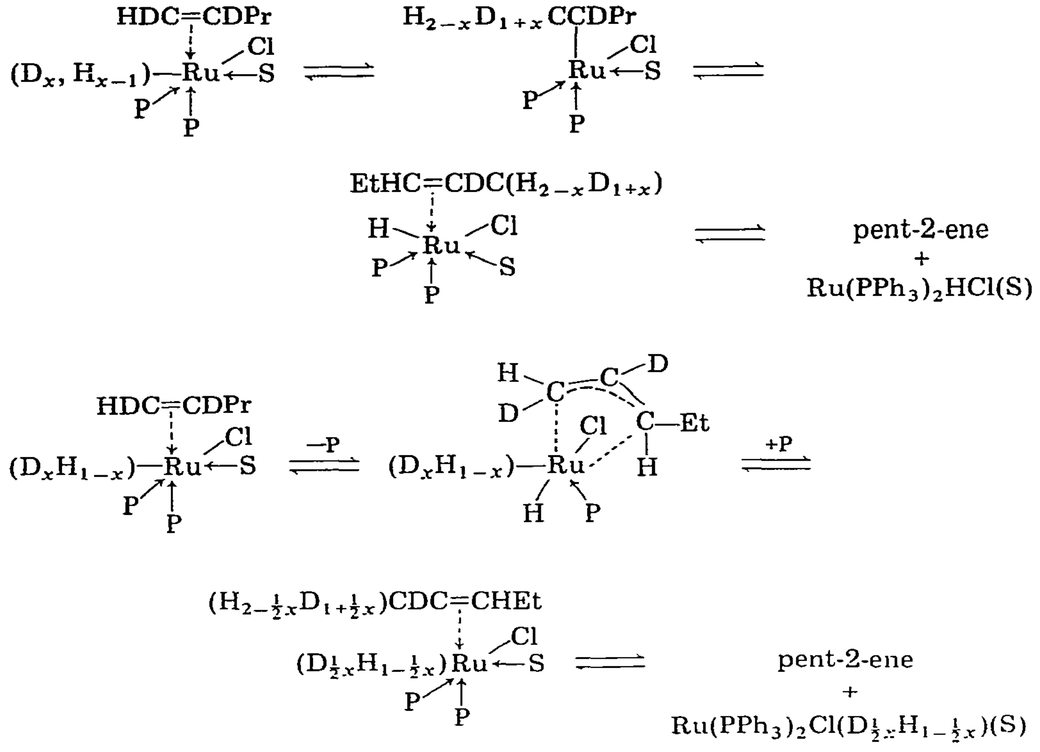


(CCCXXXVIII)



Scheme 51

(P = PPh_3; S = Solvent)

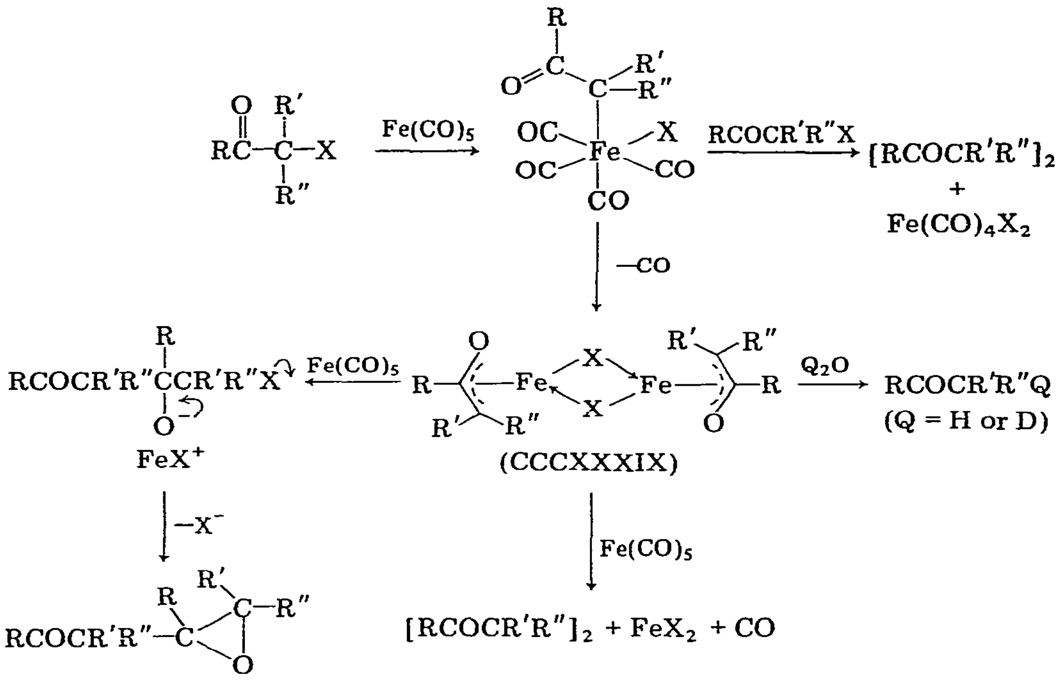


(P = PPh_3; S = solvent)

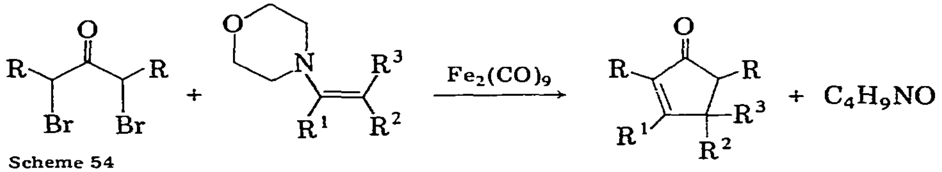
Scheme 52

Rearrangement of CCCXXX to CCCXXXI and CCCXXXII, but not CCCXXXIII, was catalysed [322] by $[Ru(CO)_3Cl_2]_2$. CCCXXXIV was isomerised [323] to CCCXXXV and CCCXXXVI, and CCCXXXVII to CCCXXXVIII by $Ru_3(CO)_{12}$, $[Ru(CO)_3Cl_2]_2$ or $RuCl_3$. Pent-1-ene was isomerised [324] by $Ru(PPh_3)_3HCl$ in benzene to *cis*- (60%) and *trans*-(40%)-pent-2-ene. Both the *cis*- and *trans*-forms could be formed via a mechanism involving a pentyl intermediate (Scheme 51), but the *trans*-isomer could also be produced via a π-allylic intermediate (Scheme 52).

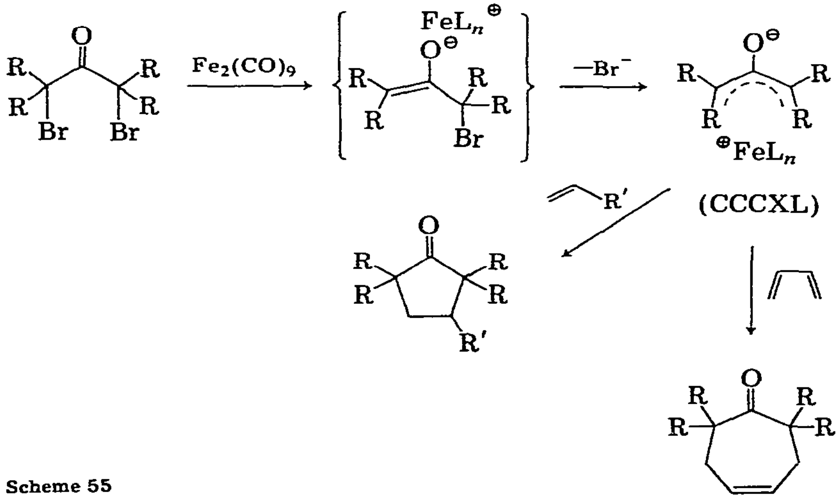
Condensation of RCH_2CH_2OH in the presence of alkoxides giving $RCH_2CH_2CHRCH_2OH$ (90%) was catalysed [325] by a mixture of $RuCl_3 \cdot nH_2O$ and PBu_3 (molar ratio 1/4). Addition of RCHO and PhNCO, giving RCH=NPh (R = MeCH=CH, PhCH=CH or Ph) was catalysed [326] by $Fe(CO)_5$. The pentacarbonyl reacted with a variety of primary, secondary or tertiary alkyl and aryl α-haloketones in refluxing dimethoxyethane giving [327] coupled 1,4-diketones and reduced monoketones (Scheme 53). The intermediate CCCXXXIX may have the π-oxallyl structure or may be a binuclear allyl derivative having halide (X) bridges. Reaction of RSO_2Cl with $Fe(CO)_5$ afforded RSO_2SO_2R and $RSSO_2R$.



Scheme 53



Scheme 54



Scheme 55

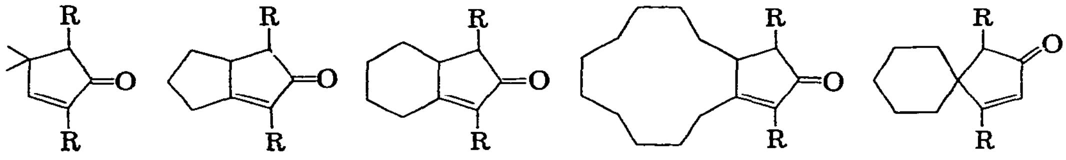
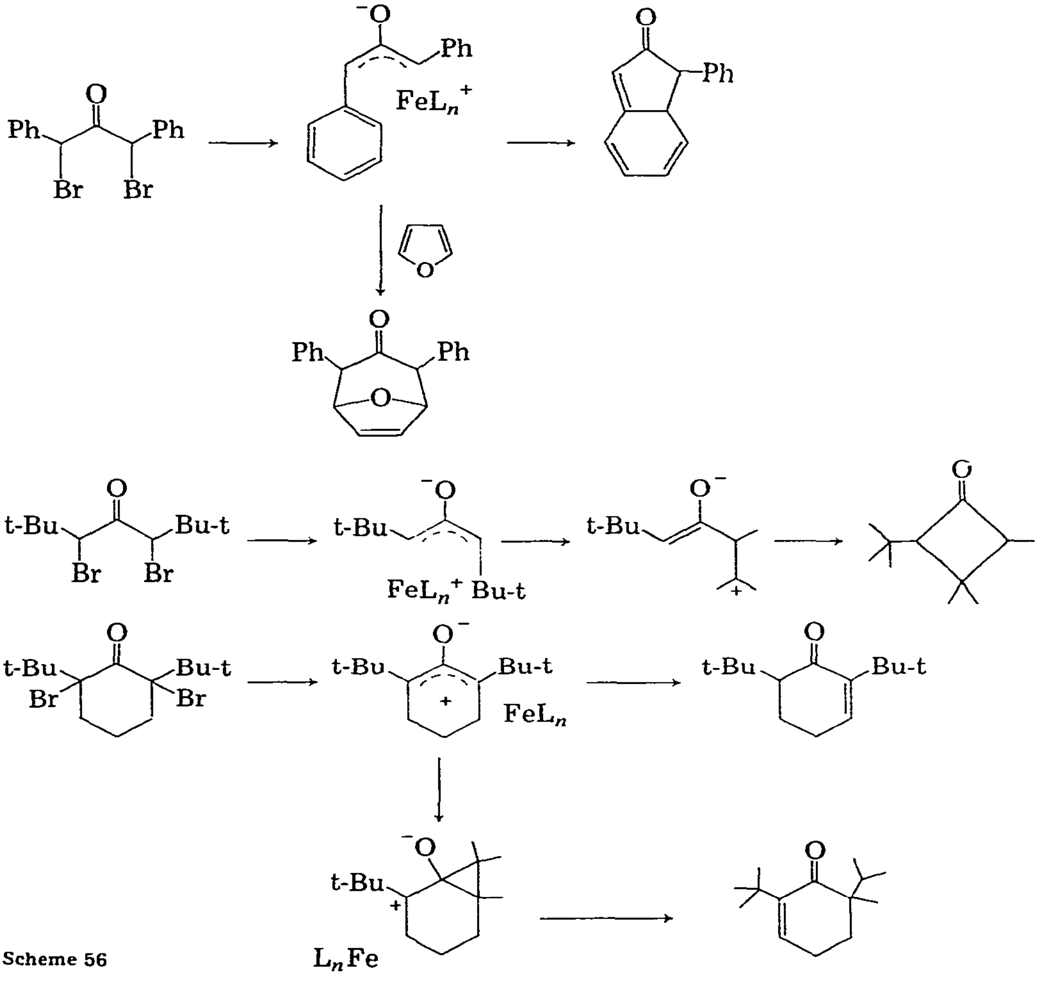


Fig. 2

Reaction of α,α′-dibromoketones with enamines in the presence of $Fe_2(CO)_9$ afforded [328] cyclopentenone (Scheme 54). Species produced by this reaction are illustrated in Fig. 2. The mechanism of reaction of these dibromoketones with $Fe_2(CO)_9$ in the presence of olefins is summarised [329] in Scheme 55. In the absence of olefines, internal reactions occurred, as shown in Scheme 56. It would appear that in all these reactions, the allyl species CCCXL is implicated.



Scheme 56

Irradiation of $Os_3(CO)_{12}$ in the presence of organic halides initiated [330] the polymerisation of methylmethacrylate and acrylonitrile. The species produced by photoexcitation was shown to abstract H atoms from hydrocarbons thereby forming free radicals. Irradiation of $Os_3(CO)_{12}$ in cyclohexane was shown by IR spectroscopy to afford a mixture of $Os_3(CO)_{10}H_2$, $Os_3(CO)_{10}\cdot H(OH)$, $Os_4(CO)_{13}H_2$ and $Os_4(CO)_{12}H_4$.

References

1 F.E. Saalfeld, J.J. De Corpo and M.V. McDowell, J. Organometal. Chem., 44 (1972) 333.
2 H. Schumann, G. Pfeifer and H. Roser, J. Organometal. Chem., 44 (1972) C10.
3 L.H. Bowen, P.E. Garrou and G.G. Long, Inorg. Chem., 11 (1972) 182.
4 R.L. Bennett, M.I. Bruce and F.G.A. Stone, J. Organometal. Chem., 38 (1972) 325.
5 H. Alper and R. A. Partic, J. Organometal. Chem., 44 (1972) 371.
6 D. A. Allison, J. Clardy and J.G. Verkade, Inorg. Chem., 11 (1972) 2804.
7 P.M. Treichel, W.K. Dean and W.M. Douglas, Inorg. Chem., 11 (1972) 1609.
8 P.M. Treichel, W.M. Douglas and W.K. Dean, Inorg. Chem., 11 (1972) 1615.
9 J. Grobe and U. Möller, J. Organometal. Chem., 36 (1972) 335.
10 T. Fukumoto, Y. Matsumura and R. Okawara, J. Organometal. Chem., 37 (1972) 113.
11 F.W.B. Einstein and R.D.G. Jones, J. Chem. Soc. Dalton, (1972) 442.
12 M. Akhtar, P.D. Ellis, A.G. Macdiarmid and J.D. Odom, Inorg. Chem., 11 (1972) 2917.
13 H. Kisch, J. Organometal. Chem., 36 (1972) C19.
14 R.B. Bennett, Inorg. Chem., 9 (1970) 429; M. Herberhold and W. Golla, J. Organometal. Chem., 26 (1971) C27.
15 R.G. Little and R.J. Doedens, Inorg. Chem., 11 (1972) 1392.
16 D.P. Madden, A.J. Carty and T. Birchall, Inorg. Chem., 11 (1972) 1453.
17 A.J. Carty, D.P. Madden, M. Mathew, G.J. Palenik and T. Birchall, Chem. Commun., (1970) 1664.
18 H.A. Patel, A.J. Carty, M. Mathew and G.J. Palenik, Chem. Commun., (1972) 810.
19 H. Alper, Inorg. Chem., 11 (1972) 976.
20 R.C. Dobbie, M.J. Hopkinson and D. Whittaker, J. Chem. Soc. Dalton, (1972) 1030.
21 W.M. Douglas and J.K. Ruff, Inorg. Chem., 11 (1972) 901.
22 K. Yasufuku and H. Yamazaki, J. Organometal. Chem., 35 (1972) 367.
23 C. Floriani, R. Henzi and F. Calderazzo, J. Chem. Soc. Dalton, (1972) 2640.
24 P. Rosenbuch and N. Welcman, J. Chem. Soc. Dalton, (1972) 1963.
25 J.A. de Beer and R.J. Haines, J. Organometal. Chem., 37 (1972) 173.
26 J.A. de Beer and R.J. Haines, J. Organometal. Chem., 36 (1972) 297.
27 H. Buttner and R.D. Feltham, Inorg. Chem., 11 (1972) 971.
28 J.S. Ricci, C.A. Eggers and I. Bernal, Inorg. Chim. Acta, 6 (1972) 97.
29 C.J. Jones, J.A. McCleverty and D.G. Orchard, J. Chem. Soc. Dalton, (1972) 1109.
30 K.A. Rubinson and G. Palmer, J. Amer. Chem. Soc., 94 (1972) 8375.
31 K. Öfele and E. Dotzauer, J. Organometal. Chem., 42 (1972) C87.
32 M.B. Hall and R.F. Fenske, Inorg. Chem., 11 (1972) 1619.
33 J.V. Kingston and G.R. Scollary, J. Inorg. Nucl. Chem., 34 (1972) 227.
34 E. Benedetti, G. Braca, G. Sbrana, F. Salvetti and B. Grassi, J. Organometal. Chem., 37 (1972) 361.
35 G.D. Watt, J. Amer. Chem. Soc., 94 (1972) 7351.
36 D. Cullen, E. Meyer, T.S. Srivastava and M. Tsutsui, Chem. Commun., (1972) 584.
37 M. Tsutsui, D. Ostfeld and L.M. Hoffman, J. Amer. Chem. Soc., 93 (1971) 1820; M. Tsutsui, D. Ostfeld, J.M. Francis and L.M. Hoffman, J. Coord. Chem., 1 (1971) 115.
38 G.W. Sovocool, F.R. Hopf and D.G. Whitten, J. Amer. Chem. Soc., 74 (1972) 4350.
39 S.S. Eaton, G.R. Eaton and R.H. Holm, J. Organometal. Chem., 39 (1972) 179.
40 D.H. Gerlach, W.G. Peet and E.L. Muetterties, J. Amer. Chem. Soc., 94 (1972) 4545.
41 G.M. Bancroft, R.E.B. Garrod, A.G. Maddock, M.J. Mays and B.E. Prater, J. Amer. Chem. Soc., 94 (1972) 647.
42 N. Ahmad, S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton, (1972) 843
43 W.H. Knoth, J. Amer. Soc., 94 (1972) 104.
44 B.E. Cavit, K.R. Grundy and W.R. Roper, Chem. Commun., (1972) 60.
45 B.E. Mann, B.L. Shaw and R.E. Stainbank, Chem. Commun., (1972) 151.
46 A.T.T. Hsieh, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. Dalton, (1972) 1966.
47 R. Mason, K.M. Thomas, D.F. Gill and B.L. Shaw, J. Organometal. Chem., 40 (1972) C67.
48 J.P. Collman and W.R. Roper, J. Amer. Chem. Soc., 87 (1965) 4008; Advan. Organometal. Chem., 7 (1968) 54.
49 J. Jeffery and R.J. Mawby, J. Organometal. Chem., 40 (1972) C42.
50 J.T. Mague and J.P. Mitchener, Inorg. Chem., 11 (1972) 2714.
51 S.D. Robinson and M.F. Uttley, Chem. Commun., (1972) 1047.
52 B. Demerseman, G. Bouquet and M. Bigorgne, J. Organometal. Chem., 35 (1972) 341.
53 A. Davison, D.D. Trafficanto and S.S. Wreford, Chem. Commun., (1972) 1155.

54 W. Petz and G. Schmid, J. Organometal. Chem., 35 (1972) 321.
55 M.A. Nasta, A.G. Macdiarmid and F.E. Saalfeld, J. Amer. Chem. Soc., 94 (1972) 2449.
56 R.K. Pomeroy, R.S. Gay, G.O. Evans and W.A.G. Graham, J. Amer. Chem. Soc., 94 (1972) 272.
57 R.K. Pomeroy and W.A.G. Graham, J. Amer. Chem. Soc., 94 (1972) 274.
58 J.V. Scibelli and M.D. Curtis, J. Organometal. Chem., 40 (1972) 317.
59 R. Ball and M.J. Bennett, Inorg. Chem., 11 (1972) 1806.
60 C.J. Gilmore and P. Woodward, J. Chem. Soc. Dalton, (1972) 1387.
61 F.W.B. Einstein and R.D.G. Jones, J. Chem. Soc. Dalton, (1972) 2563.
62 A.T.T. Hsieh and M.J. Mays, J. Organometal. Chem., 37 (1972) C53.
63 M.R. Churchill, J. Wormald, J. Knight and M.J. Mays, J. Amer. Chem. Soc., 93 (1971) 3073.
64 E.H. Braye, L.F. Dahl, W. Hubel and D.L. Wampler, J. Amer. Chem. Soc., 84 (1962) 4633.
65 D.B.W. Yawney and R.J. Doedens, Inorg. Chem., 11 (1972) 838.
66 J.R. Norton, J.P. Collman, G. Dolcetti and W.T. Robinson, Inorg. Chem., 11 (1972) 382.
67 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 37 (1972) C39.
68 A.T.T. Hsieh and M.J. Mays, J. Organometal. Chem., 39 (1972) 157.
69 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc. Dalton, (1972) 1082.
70 R. Mason, J. Zubieta, A.T.T. Hsieh, J. Knight and M.J. Mays, Chem. Commun., (1972) 200.
71 V.G. Albano, G. Ciani, M.I. Bruce, G. Shaw and F.G.A. Stone, J. Organometal. Chem., 42 (1972) C99.
72 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc. Dalton, (1972) 1781.
73 J. Knight and M.J. Mays, J. Chem. Soc. Dalton, (1972) 1022.
74 W.R. Moss and W.A.G. Graham, J. Organometal. Chem., 23 (1970) C23.
75 M.R. Churchill and R. Bau, Inorg. Chem., 7 (1968) 2606.
76 R.J. Doedens and L.F. Dahl, J. Amer. Chem. Soc., 88 (1966) 4847.
77 M.R. Churchill, J. Wormald, J. Knight and M.J. Mays, Chem. Commun., (1970) 458.
78 A.J. Carty, B.F.G. Johnson, J. Lewis and J.R. Norton, Chem. Commun., (1972) 1331.
79 A.J. Carty, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 43 (1972) C35.
80 R. Mason and K.M. Thomas, J. Organometal. Chem., 43 (1972) C39.
81 L.F. Dahl and D.L. Smith, J. Amer. Chem. Soc., 84 (1962) 2450.
82 A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 36 (1972) C43.
83 E. Sappa, O. Gambino, L. Milone and G. Certini, J. Organometal. Chem., 39 (1972) 169.
84 J.F. Blount, L.F. Dahl, C. Hoogzand and W. Hübel, J. Amer. Chem. Soc., 88 (1966) 292.
85 O. Gambino, E. Sappa and G. Cetini, J. Organometal. Chem., 44 (1972) 185.
86 M. Valle, O. Gambino, L. Milone, G.A. Vaglio and G. Cetini, J. Organometal. Chem., 38 (1972) C46.
87 G. Cetini, O. Gambino, E. Sappa and M. Valle, J. Organometal. Chem., 17 (1969) 437.
88 M. Evans, M. Hursthouse, E.W. Randall, E. Rosenberg, L. Milone and M. Valle, Chem. Commun., (1972) 545.
89 M.I. Bruce, M.A. Cairns, A. Cox, M. Green, M.D.H. Smith and P. Woodward, Chem. Commun., (1970) 735.
90 R.P. Ferrari, G.A. Vaglio, O. Gambino, M. Valle and G. Cetini, J. Chem. Soc. Dalton, (1972) 1998.
91 G. Ferraris and G. Gervasio, J. Chem. Soc. Dalton, (1972) 1057.
92 T. O'Connor, A.J. Carty, M. Mathew and G.J. Palenik, J. Organometal Chem., 38 (1972) C15.
93 A.A. Hock and O.S. Mills, Acta Cryst., 13 (1961) 139: Y. Degreve, J. Meunier-Piret, M. van Meersche and P. Piret, Acta Cryst., 23 (1967) 119.
94 M.I. Bruce, M.A. Cairns and M. Green, J. Chem. Soc. Dalton, (1972) 1293.
95 C.W. Bradford, R.S. Nyholm, G.J. Gainsford, J.M. Guss, P.R. Ireland and R. Mason, Chem. Commun., (1972) 87.
96 G.J. Gainsford, J.M. Guss, P.R. Ireland, R. Mason, C.W. Bradford, and R.S. Nyholm, J. Organometal. Chem., 40 (1972) C70.
97 A.J. Deeming and, R.S. Nyholm and M. Underhill, Chem. Commun., (1972) 224.
98 A.J. Deeming and M. Underhill, J. Organometal. Chem., 42 (1972) C60.
99 R. Kummer and W.A. Graham, Inorg. Chem., 7 (1968) 1208.
100 M. Elder and W.L. Hutcheon, J. Chem. Soc. Dalton, (1972) 175.
101 R. Rossetti, P.L. Stanghellini, O. Gambino and G. Cetini, Inorg. Chim. Acta, 6 (1972) 205.
102 G. Natile and G. Bor, J. Organometal. Chem., 35 (1972) 185.
103 S.A. Khattab, L. Markó, G. Bor and B. Markó, J. Organometal. Chem., 1 (1964) 373.
104 E. Sappa, O. Gambino and G. Cetini, J. Organometal. Chem., 35 (1972) 375.
105 T. Kruck and R. Kobelt, Chem. Ber., 105 (1972) 3765.
106 T. Kruck and R. Kobelt, Chem. Ber., 106 (1972) 3772.
107 R. Meakin, E.L. Muetterties and J.P. Jesson, J. Amer. Chem. Soc., 94 (1972) 5271.
108 C.A. Udovich and R.J. Clark, J. Organometal. Chem., 36 (1972) 355.
109 H. Alper and R.A. Partic, J. Organometal. Chem., 35 (1972) C40.
110 M. Schaal and W. Beck, Angew. Chem. Int. Ed. Engl., 11 (1972) 527.
111 B.E. Prater, J. Organometal. Chem., 34 (1972) 379.
112 G.M. Bancroft and K.D. Butler, J. Chem. Soc. Dalton, (1972) 1209.
113 I. Adams, J. M. Thomas, G.M. Bancroft, K.D. Butler and M. Barber, Chem. Commun., (1972) 751.
114 A.L. Balch and J.L. Miller, J. Amer. Chem. Soc., 94 (1972) 417.
115 D.F. Christian, G.R. Clark, W.R. Roper, J.M. Waters and K.R. Whittle, Chem. Commun., (1972) 458.
116 N.G. Connelly, Inorg. Chim. Acta Rev., 6 (1972) 47.
117 B.F.G. Johnson and J. Segal, J. Chem. Soc. Dalton, (1972) 1268.

118 C.G. Pierpoint and R. Eisenberg, Inorg. Chem., 11 (1972) 1094.
119 B.W. Graham, K.R. Laing, C.J. O'Connor and W.R. Roper, J. Chem. Soc. Dalton, (1972) 1237.
120 G.R. Clark, K.R. Grundy, W.R. Roper, J.M. Waters and K.R. Whittle, Chem. Commun., (1972) 119
121 J.T. Veal and D.J. Hodgson, Inorg. Chem., 11 (1972) 1420.
122 J.T. Veal and D.J. Hodgson, Acta Cryst., B28 (1972) 3525.
123 A.F. Schreiner, S.W. Lin, P.J. Hauser, E.A. Hopcus, D.J. Hamm and J.D. Gunter, Inorg. Chem., 11 (1972) 880.
124 S.A. Adeyemi, F.J. Miller and T.J. Meyer, Inorg. Chem., 11 (1972) 994.
125 S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton, (1972) 1.
126 P.G. Douglas and R.D. Feltham, J. Amer. Chem. Soc., 94 (1972) 5254.
127 M.S. Quinby and R.D. Feltham, Inorg. Chem., 11 (1972) 2468.
128 R.D. Feltham, W. Silverthorn, H. Wickman and W. Wesolowski, Inorg. Chem., 11 (1972) 676.
129 H. Buttner and R.D. Feltham, Inorg. Chem., 11 (1972) 971.
130 G. Cardaci and S.M. Murgia, Inorg. Chim. Acta, 6 (1972) 222.
131 R.E. Dessy, J.C. Charkoudian and A.L. Rheingold, J. Amer. Chem. Soc., 94 (1972) 738.
132 T.S. Srivastava, L. Hoffman and M. Tsutsui, J. Amer. Chem. Soc., 94 (1972) 1385.
133 C.G. Pierpoint and R. Eisenberg, Inorg. Chem., 11 (1972) 1088.
134 S.T. Wilson and J.A. Osborn, J. Amer. Chem. Soc., 93 (1971) 3068.
135 R. Eisenberg, A.P. Gaughan, C.G. Pierpoint, J. Reed and A.J. Schultz, J. Amer. Chem. Soc., 94 (1972) 6240.
136 M.D. Curtis and R.C. Job., J. Amer. Chem. Soc., 94 (1972) 2153.
137 E.O. Fischer, H.-J. Beck, C. Kreiter, J. Lynch, J. Müller and E. Winkler, Chem. Ber., 105 (1972) 162.
138 K. Ofele and C.G. Kreiter, Chem. Ber., 105 (1972) 529.
139 G. Huttner and W. Gartzke, Chem. Ber., 105 (1972) 2714.
140 R.J. Sundberg, R.E. Shepherd and H. Taube, J. Amer. Chem. Soc., 94 (1972) 6558.
141. E.O. Fischer, F.R. Kreibl, E. Winkler and C.G. Kreiter, Chem. Ber., 105 (1972) 588.
142 V. Kiener and E.O. Fischer, J. Organometal. Chem., 42 (1972) 447.
143 E.O. Fischer, E. Winkler, G. Huttner and D. Regler, Angew. Chem. Int. Ed. Engl., 11 (1972) 238.
144 G. Huttner and D. Regler, Chem. Ber., 105 (1972) 2726.
145 W. Petz and G. Schmid, Angew. Chem. Int. Ed. Engl., 11 (1972) 934.
146 J.G. Bullitt, F.A. Cotton and T.J. Marks, Inorg. Chem., 11 (1972) 671.
147 O.A. Gansow, A.R. Burke and W.D. Vernon, J. Amer. Chem. Soc., 94 (1972) 2550.
148 R.D. Adams and F.A. Cotton, J. Amer. Chem. Soc., 94 (1972) 6193.
149 R.B. King and M.S. Saran, J. Amer. Chem. Soc., 94 (1972) 1784.
150 A. Alich, N.J. Nelson, D. Strode and D.F. Shriver, Inorg. Chem., 11 (1972) 2976.
151 A.E. Crease and P. Legzdins, Chem. Commun., (1972) 268.
152 N.J. Nelson, N.E. Kime and D.F. Shriver, J. Amer. Chem. Soc., 91 (1969) 5173.
153 R.J. Haines and A.L. du Preez, Inorg. Chem., 11 (1972) 330.
154 J.A. Ferguson and T.J. Meyer, Inorg. Chem., 11 (1972) 631.
155 D.F. Hunt and J.W. Russell, J. Amer. Chem. Soc., 94 (1972) 7198, J, Organometal. Chem., 46 (1972) C22.
156 J.A. Ferguson and T.J. Meyer, J. Amer. Chem. Soc., 94 (1972) 3409.
157 M.A. Neuman, Trinh-Toan and L.F. Dahl, J. Amer. Chem. Soc., 94 (1972) 3383.
158 Trinh-Toan, W.P. Fehlhammer and L.F. Dahl, J. Amer. Chem. Soc., 94 (1972) 3389.
159 N.G. Connelly and J.D. Davies, J. Organometal Chem., 38 (1972) 385.
160 M.L. Brown, J.L. Cramer, J.A. Ferguson, T.J. Meyer and N. Winterton, J. Amer. Chem. Soc., 94 (1972) 8707.
161 R.J. Angelici and L.C. Black, Inorg. Chem., 11 (1972) 1754.
162 J. Ellermann, H. Behrens and H. Krohberger, J. Organometal. Chem., 46 (1972) 119.
163 W. Jetz and R.J. Angelici, Inorg. Chem., 11 (1972) 1960.
164 M.Y. Darensbourg, J. Organometal. Chem., 38 (1972) 133.
165 P.M. Treichel, W.K. Dean and W.M. Douglas, J. Organometal. Chem., 42 (1972) 145.
166 R.C. Dobbie, P.R. Mason and R.J. Portèr, Chem. Commun., (1972) 612.
167 R.J. Haines and C.R. Nolte, J. Organometal. Chem., 36 (1972) 163.
168 M.R. Churchill, B.G. DeBoer, K.L. Kalra, P. Reich-Rohrwig and A. Wojcicki, Chem. Commun., (1972) 981.
169 M.R. Churchill and J. Wormald, Inorg. Chem., 10 (1971) 572.
170 W. Ehrl and H. Vahrenkamp, Chem. Ber., 105 (1972) 1471.
171 J.A. de Beer, R.J. Haines and R. Greatrex, Chem. Commun., (1972) 1094.
172 G. Wulfsberg and R. West, J. Amer. Chem. Soc., 94 (1972) 6069.
173 M. Pankowski, B. Demerseman, G. Bouquet and M. Bigorgne, J. Organometal. Chem., 35 (1972) 155.
174 D.J. Darensbourg, Inorg. Chem., 11 (1972) 1606.
175 O.A. Gansow, D.A. Schexnayder and B.Y. Kimura, J. Amer. Chem. Soc., 94 (1972) 3406.
176 D.J. Jones and R.J. Mawby, Inorg. Chim. Acta, 6 (1972) 157.
177 H. Brunner and M. Vogel, J. Organometal. Chem., 35 (1972) 169.
178 R.B. King and A. Efraty, J. Amer. Chem. Soc., 94 (1972) 3768.
179 R.B. King, W.C. Zipperer and M. Ishaq, Inorg. Chem., 11 (1972) 1361.
180 R.J. Haines and A.L. du Preez, J. Chem. Soc. Dalton, (1972) 944
181 G.B. McVicker and R.S. Matyas, Chem. Commun., (1972) 972.

182 J.M. Burlitch and S.E. Hayes, J. Organometal. Chem., 42 (1972) C13.
183 H.M.M. Shearer and C.B. Spencer, Chem. Commun, (1966) 194.
184 A.T.T. Hsieh and M.J. Mays, J. Organometal. Chem., 37 (1972) 9.
185 J. Dalton, Inorg. Chem., 11 (1972) 915.
186 W. Malisch, J. Organometal. Chem., 39 (1972) C28.
187 R.C. Edmondson, R. Eisner, M.J. Newlands and L.K. Thompson, J. Organometal. Chem., 35 (1972) 119.
188 S.A.R. Knox, R.P. Phillips and F.G.A. Stone, Chem. Commun., (1972) 1227.
189 P. Hackett and A.R. Manning, J. Chem. Soc. Dalton, (1972) 1487; J. Organometal. Chem., 34 (1972) C15.
190 G.M. Bancroft, K.D. Butler and A.T. Rake, J. Organometal. Chem., 34 (1972) 137; G.M. Bancroft, K.D. Butler, A.T. Rake and B. Dale, J. Chem. Soc. Dalton, (1972) 2025.
191 A.R. Manning, J. Chem. Soc. Dalton, (1972) 821.
192 R.J. Haines, R. Mason, J.A. Zubieta and C.R. Nolte, Chem. Commun., (1972) 990.
193 K. Yasufuku and H. Yamazaki, J. Organometal. Chem., 38 (1972) 367.
194 A.N. Nesmeyanov, I.T. Leshcheva, I.V. Polovyanyuk, Yu.A. Ustynyuk and L.G. Makarova, J. Organometal. Chem., 37 (1972) 159.
195 D.W. Lichtenberg and A. Wojcicki, J. Amer. Chem. Soc., 94 (1972) 8271.
196 A. Cutler, R.W. Fish, W.P. Giering and M. Rosenblum, J. Amer. Chem. Soc., 94 (1972) 4354.
197 W.P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt and R.W. Fish, J. Amer. Chem. Soc., 94 (1972) 8251.
198 W. Jetz and R.J. Angelici, J. Organometal. Chem., 35 (1972) C37.
199. R.B. King, A. Efraty and W.C. Zipperer, J. Organometal. Chem., 38 (1972) 121.
200 M.R. Churchill, J. Wormald, W.P. Giering and G.F. Emerson, Chem. Commun., (1968) 1217; R.E. Davis, Chem. Commun., (1968) 1218; M.R. Churchill and J. Wormald, Inorg. Chem., 8 (1969) 1936.
201 D.J. Ciappenelli, F.A. Cotton and L. Kruczynski, J. Organometal. Chem., 42 (1972) 159.
202 A.J. Campbell, C.A. Fyfe, R.G. Goel, E. Maslowsky and C.V. Senoff, J. Amer. Chem. Soc., 94 (1972) 8387.
203 M.I. Bruce, R. Clark, J. Howard and P. Woodward, J. Organometal. Chem., 42 (1972) C107.
204 P.W.R. Corfield and H.M.M. Shearer, in G.E. Coates, K. Wade and M.L.H. Green, (Eds.), Organometallic Compounds, Methuen, London, Vol 2, 1968, p. 275.
205 H. Brunner and E. Schmidt, J. Organometal. Chem., 36 (1972) C18.
206 J. Thompson, W. Keeney, M.C. Baird and W.F. Reynolds, J. Organometal. Chem., 40 (1972) 205.
207 R.B. King and W.C. Zipperer, Inorg. Chem., 11 (1972) 2119.
208 T. Kruck, M. Höfler and L. Liebig, Chem. Ber., 105 (1972) 1174.
209 Y. Yamamoto and H. Yamazaki, Inorg. Chem., 11 (1972) 211.
210 R.B. King and P.N. Kapoor, Inorg. Chim. Acta, 6 (1972) 791.
211 Y. Yamamoto and A. Wojcicki, Chem. Commun., (1972) 1088.
212 M.I. Bruce, R.C.F. Gardner and F.G.A. Stone, J. Organometal. Chem., 40 (1972) C39
213 K.R. Aris, V. Aris and J.M. Brown, J. Organometal. Chem., 42 (1972) C67.
214 W.P. Giering, M. Rosenblum and J. Tancrede, J. Amer. Chem. Soc., 94 (1972) 7170.
215 A. Davison and D.L. Regler, J. Amer. Chem. Soc., 94 (1972) 9237.
216 J. Müller and B. Mertschenk, Chem. Ber., 105 (1972) 3346.
217 J.F. Helling and D.M. Braitsch, J. Amer. Chem. Soc., 92 (1970) 7207.
218 M. Mathew and G.J. Palenik, Inorg. Chem., 11 (1972) 2809.
219 L.I. Zakharkin, L.V. Orlova, B.V. Loshkin and L.A. Fedorov, J. Organometal. Chem., 40 (1972) 15.
220 L.G. Sneddon and R.N. Grimes, J. Amer. Chem. Soc., 94 (1972) 7161.
221 D.C. Beer and L.J. Todd, J. Organometal. Chem., 36 (1972) 77
222 D.C. Andrews and G. Davidson, J. Organometal. Chem., 36 (1972) 349.
223 R.B. King and I. Haiduc, J. Amer. Chem. Soc., 94 (1972) 4044.
224 A. Bond and M. Green, J. Chem. Soc. Dalton, (1972) 763
225 E.E. Nunn and R.N. Warrener, Chem. Commun., (1972) 818.
226 R.W. Roberts and A. Wissner, J. Amer. Chem. Soc., 94 (1972) 7168.
227 M. Aresta, P. Giannoccaro, M. Rossi and A. Sacco, Inorg. Chim. Acta, 5 (1971) 115.
228 E. Koerner von Gustorf, I. Fischler, J. Leitich and H. Dreeskamp, Angew. Chem. Int. Ed. Engl., 11 (1972) 1088.
229 C.C. Lee, R.G. Sutherland and B.J. Thomson, Chem. Commun., (1972) 907.
230 R.A. Zelonka and M.C. Baird, J. Organometal. Chem., 35 (1972) C43.
231 M.A. Bennett, G.B. Robertson and A.K. Smith, J. Organometal. Chem., 43 (1972) C41.
232 R.A. Zelonka and M.C. Baird, J. Organometal. Chem., 44 (1972) 383.
233 G. Huttner and S. Lange, Acta Cryst., B28 (1972) 2049.
234 M.F. Bailey and L.F. Dahl, Inorg. Chem., 4 (1965) 1298.
235 D.C. Andrews and G. Davidson, J. Organometal. Chem., 35 (1972) 161.
236 S. Komiya, A. Yamamoto and S. Ikeda, J. Organometal. Chem., 42 (1972) C65.
237 B.F.G. Johnson and J.A. Segal, Chem. Commun., (1972) 1312.
238 H. Thyret, Angew. Chem., Int. Ed. Engl., 11 (1972) 520.
239 R.W. Giese and B.L. Vallee, J. Amer. Chem. Soc., 94 (1972) 6199.
240. J.Y. Chenard, D. Commereuc and Y. Chauvin, Chem. Commun., (1972) 750.
241 S.M. Nelson and M. Sloan, Chem. Commun., (1972) 745.
242 J.M. Landesberg and L. Katz, J. Organometal. Chem., 35 (1972) 327.

243 M.I. Foreman, J. Organometal. Chem., 39 (1972) 161.
244 D.E. Kuhn and C.P. Lillya, J. Amer. Chem. Soc., 94 (1972) 1682.
245 M. Brookhart and D.L. Harris, J. Organometal. Chem., 42 (1972) 441.
246 R.E. Graf and C.P. Lillya, J. Amer. Chem. Soc., 94 (1972) 8282.
247 R. Victor, R. Ben-Shoshan and S. Sarel, J. Org. Chem., 37 (1972) 1930.
248 F.H. Herbstein and M.G. Reisner, Chem. Commun., (1972) 1077.
249 J.A.S. Honell, B.F.G. Johnson, P.L. Josty and J. Lewis, J. Organometal. Chem., 39 (1972) 329.
250 A.M. Brodie, B.F.G. Johnson, P.L. Josty and J. Lewis, J. Chem. Soc. Dalton, (1972) 2031.
251 A. de Cian and R. Weiss, Acta Cryst., B28 (1972) 3273.
252 A. de Cian and R. Weiss, Acta Cryst., B28 (1972) 3264.
253 A. Carbonaro and F. Cambisi, J. Organometal. Chem., 44 (1972) 171.
254 E. Koerner von Gustorf, O. Jaenicke and O.E. Polansky, Angew. Chem. Int. Ed. Engl., 11 (1972) 532.
255 D.L. Williams-Smith, L.R. Wolf and P.S. Skell, J. Amer. Chem. Soc., 94 (1972) 4042.
256 G. Davidson and D.A. Duse, J. Organometal. Chem., 44 (1972) 365.
257 I.W. Bassi and R. Scordamaglia, J. Organometal. Chem., 37 (1972) 353.
258 D.F. Hunt, J.W. Russell and R.L. Torian, J. Organometal. Chem., 43 (1972) 175.
259 T.H. Kruck and L. Knoll, Chem. Ber., 105 (1972) 3783.
260 R.B. King and A. Efraty, J. Amer. Chem. Soc., 94 (1972) 3773.
261 Y.L. Chow, J. Fossey and R.A. Perry, Chem. Commun., (1972) 501.
262 H. Alper and E.C.-H. Keung, J. Amer. Chem. Soc., 94 (1972) 2144.
263 J.D. Warren, M.A. Busch and R.J. Clark, Inorg. Chem., 11 (1972) 452.
264 F.A. Cotton and G. Deganello, J. Amer. Chem. Soc., 94 (1972) 2142.
265 R.J.H. Cowles, B.F.G. Johnson, J. Lewis and A.W. Parkins, J. Chem. Soc. Dalton, (1972) 1768.
266 J.J. Hough and E. Singleton, Chem. Commun., (1972) 371.
267 R.B. King and P.N. Kapoor, Inorg. Chem., 11 (1972) 336.
268 A. Gieren and W. Hoppe, Acta Cryst., B28 (1972) 2766.
269 D.F. Hunt, G.C. Farrant and G.T. Rodeheaver, J. Organometal. Chem., 38 (1972) 349.
270 B.F.G. Johnson, J. Lewis, P. McArdle and G.L.P. Randall, J. Chem. Soc. Dalton, (1972) 456.
271 P.L. Pauson, G.H. Smith, J.H. Valentine, J. Chem. Soc., C, (1967) 1061; P.E. Baikie, O.S. Mills, P.L. Pauson, G.H. Smith and J.H. Valentine, Chem. Commun., (1965) 425.
272 F.A. Cotton and G. Deganello, J. Organometal. Chem., 38 (1972) 147.
273 H.W. Whitlock and H. Stucki, J. Amer. Chem. Soc., 94 (1972) 8594.
274 R. Aumann, Angew. Chem. Int. Ed. Engl., 11 (1972) 522.
275 G. Huttner and D. Regler, Chem. Ber., 105 (1972) 3936.
276 G.N. Schrauzer, P. Glockner, K.I.G. Reid and I.C. Paul, J. Amer. Chem. Soc., 92 (1970) 4479.
277 G. Rigatti, G. Boccalon, A. Ceccon and G. Giacometti, Chem. Commun., (1972) 1165.
278 A.J. Campbell, C.A. Fyfe and E. Maslowsky, J. Amer. Chem. Soc., 94 (1972) 2690.
279 T.A. Manuel and F.G.A. Stone, J. Amer. Chem. Soc., 82 (1960) 366; M.D. Rausch and G.N. Schrauz Chem. Ind., (1959) 957.
280 J. Schwartz, Chem. Commun., (1972) 814.
281 M. Brookhart, E.R. Davis and D.L. Harris, J. Amer. Chem. Soc., 94 (1972) 7853.
282 D.J. Ehntholt and R.C. Kerber, J. Organometal. Chem., 38 (1972) 139.
283 M. Green, S. Tolson, J. Weaver, D.C. Wood and P. Woodward, Chem. Commun., (1971) 222; S.R. Su and A. Wojcicki, J. Organometal. Chem., 31 (1971) C34; W.P. Giering and M. Rosenblum, J. Amer. Chem. Soc., 93 (1971) 5299.
284 K.B. Birnbaum, Acta Cryst., B28 (1972) 161.
285 A.H.-J. Wang, I.C. Paul and G.N. Schrauzer, Chem. Commun., (1972) 736.
286 C.E. Cottrell, C.A. Fyfe and C.V. Senoff, J. Organometal. Chem., 43 (1972) 203.
287 D.H. Gibson and R.L. Vonnahme, J. Amer. Chem. Soc., 94 (1972) 5090.
288 D.H. Gibson and R.L. Vonnahme, Chem. Commun., (1972) 1021.
289 A.E. Hill and H.M.R. Hoffmann, Chem. Commun., (1972) 574.
290 G. Cardaci, S.M. Murgia and A. Foffani, J. Organometal. Chem., 37 (1972) C11.
291 R.B. King and A. Bond, J. Organometal. Chem., 46 (1972) C53.
292 Y. Becker, A. Eisenstadt and Y. Shvo, Chem. Commun., (1972) 1156.
293 F.A. Cotton and M.D. LaPrade, J. Organometal. Chem., 39 (1972) 345.
294 R. Aumann and B. Lohmann, J. Organometal. Chem., 44 (1972) C51.
295 A.E. Smith, Inorg. Chem., 11 (1972) 2306.
296 K. Ehrlich and G.F. Emerson, J. Amer. Chem. Soc., 94 (1972) 2464.
297 W.E. Billups, L.-P. Lin and O.A. Gansow, Angew. Chem. Int. Ed. Engl., 11 (1972) 637.
298 D.C. Andrews and G. Davidson, J. Organometal. Chem., 43 (1972) 393.
299 R.J. Clark, M.R. Abraham and M.A. Busch, J. Organometal. Chem., 35 (1972) C33.
300 S. Otsuka, A. Nakamura and K. Tani, J. Chem. Soc., A, (1971) 154.
301 N. Yasuda, Y. Kai, N. Yasuoka, N. Kasai and M. Kakudo, Chem. Commun., (1972) 157.
302 W.O. Siegl and J.P. Collman, J. Amer. Chem. Soc., 94 (1972) 2516.
303 J.P. Collman, S.R. Winter and D.R. Clark, J. Amer. Chem. Soc., 94 (1972) 1788.
304 J.P. Collman, J.N. Cawse and J.I. Brauman, J. Amer. Chem. Soc., 94 (1972) 5905.
305 C.S. Cundy, and M.F. Lappert, Chem. Commun., (1972) 445.
306 J.L. Davidson, W. Harrison, D.W.A. Sharp and G.A. Sim, J. Organometal. Chem., 46 (1973) C47.
307 R.M. Moriarty, K.-N. Chen, C.-L. Yeh, J.L. Flippen and J. Karle, J. Amer. Chem. Soc., 94 (1972) 8944.

308 R.B. King and C.W. Eavenson, J. Organometal. Chem., 42 (1972) C95.
309 R.L. Bennett, M.I. Bruce, B.L. Goodall, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc. Dalton, (1972) 1784.
310 M.I. Bruce, J. Howard, I.W. Nowell, G. Shaw and P. Woodward, Chem. Commun., (1972) 1041.
311 J.J. Levison and S.D. Robinson, J. Chem. Soc., A, (1970) 639.
312 B.K. Bower and H.G. Tennent, J. Amer. Chem. Soc., 94 (1972) 2512.
313 B. Sarry and S. Noll, Z. Anorg. Allg. Chem., 394 (1972) 141.
314 V.D. Bianco, S. Doronzo and M. Aresta, J. Organometal. Chem., 42 (1972) C63.
315 Y. Kubo, A. Yamamoto and S. Ikeda, J. Organometal. Chem., 46 (1972) C50.
316 M.E. Vol'pin, R. Taube, H. Drevs, L.G. Volkova, I.Ya. Levitin and T.N. Ushakova, J. Organometal. Chem., 39 (1972) C79.
317 B. Jezowska-Trzebiatowska and P. Subota, J. Organometal. Chem., 46 (1973) 339.
318 R. Noyori, I. Umeda and T. Ishigami, J. Org. Chem., 37 (1972) 1542.
319 H. Alper, J. Org. Chem., 37 (1972) 3972.
320 B. Hudson, D.E. Webster and P.B. Wells, J. Chem. Soc. Dalton, (1972) 1204.
321 G.G. Eberhardt, M.E. Tadros and L. Vaska, Chem. Commun., (1972) 290.
322 P.G. Gassman and T.J. Atkins, J. Amer. Chem. Soc., 94 (1972) 7748.
323 P.G. Gassman, G.R. Meyer and F.J. Williams, J. Amer. Chem. Soc., 94 (1972) 7741.
324 D.F. Ewing, B. Hudson, D.E. Webster and P.B. Wells, J. Chem. Soc. Dalton, (1972) 1287.
325 G. Gregorio, G.F. Pregaglia and R. Ugo, J. Organometal. Chem., 37 (1972) 385.
326 J. Drapier, A.J. Hubert and Ph. Teyssie, Chem. Commun., (1972) 484.
327 H. Alper and E.C.H. Keung, J. Org. Chem., 37 (1972) 2566.
328 R. Noyori, K. Yokoyama, S. Makino and Y. Hayakawa, J. Amer. Chem. Soc., 94 (1972) 1772.
329 R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R.I. Kobayashi and S. Tsutsumi, J. Amer. Chem. Soc., 94 (1972) 7202.
330 C.H. Bamford and M.U. Mahmud, Chem. Commun., (1972) 762.