IRON, RUTHENIUM AND OSMIUM

ANNUAL SURVEY COVERING THE YEAR 1973

J.A. McCLEVERTY
Chemistry Department, The University, Sheffield S3 7HF (Great Britain)

Contents

Metal carbonyls

Simple carbonyls and carbonylate anions

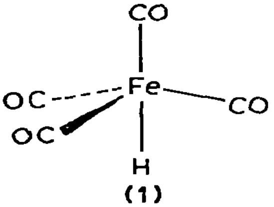
UV photolysis of $Fe(CO)_5$ in an argon matrix at low temperatures gave $Fe(CO)_4$ and CO [1]. Recombination to give $Fe(CO)_5$ occurred if the irradiation time was short but if prolonged, formation of the tetracarbonyl was irreversible since CO diffused through the matrix. The $Fe(CO)_4$ formed had C_{3v} symmetry since there was apparently Jahn—Teller distortion of the idealised tetrahedral geometry. An ion—cyclotron resonance study of ion—molecule reactions of $Fe(CO)_5$ has been carried out [2]. The most abundant primary ion was $[Fe(CO)_4]^-$, although some $[Fe(CO)_3]^-$ was also detected. The major product observed was $[Fe_2(CO)_6]^-$, apparently formed in the reaction 1.

$$[Fe(CO)_3]^- + Fe(CO)_5 \rightarrow [Fe_2(CO)_6]^{2-} + 2CO \qquad (1)$$

$[Fe(CO)_4]^-$ did not appear to undergo any condensation reactions.

By electrolysis of $Fe(acac)_3$ in pyridine or dimethylsulfoxide under CO (1 atm) a series of carbonyls and carbonylate ions was prepared [3]. Thus, in pyridine at low current, $Fe(CO)_5$ and $Fe_3(CO)_{12}$ were produced, whereas at higher currents $[Fe(CO)_4]^{2-}$and $[Fe_4(CO)_{13}]^{2-}$ were formed. In dimethylsulfoxide, $[Fe_2(CO)_8]^{2-}$ and $[Fe_4(CO)_{13}]^{2-}$ were produced.

The structure [4] of $[Fe(CO)_4H]^-$, as the $[(Ph_3P)_2N]^+$ salt, is that of a distorted trigonal bipyramid (1)*, in which the Fe—H distance is 1.57 Å; the



(1)

---

[*] Throughout this article compounds are indicated by bold arabic numerals; references are as usual in square brackets.

angles between the apical and the equatorial CO groups are 96.9, 98.4 and 101.9°. The most stable species present when $Fe(CO)_5$ was dissolved in methanol under CO pressure below 150°, in the presence of water and tertiary amine, was $[Fe(CO)_4H]^-$ [5]. The concentration of this hydride decreased with increasing temperature until the only species at 150° was $Fe(CO)_5$. At 170°, when hydrogen was also present, complete conversion of $Fe(CO)_5$ to $[Fe(CO)_4H]^-$ occurred in 10 hours. The mechanism of reaction appeared to involve prior dissociation of CO, giving $Fe(CO)_4$, which underwent oxidative addition with H_2 giving $Fe(CO)_4H_2$, and, in the presence of NR_3, proton abstraction from this acidic hydride gave $[Fe(CO)_4H]^-$.

Reduction of $Os_3(CO)_{12}$ with sodium in liquid ammonia afforded [6] a cream solid which may have contained $[Os(CO)_4H]^-$. Acidification gave $Os(CO)_4H_2$, and with $[Ni(bipy)_3]^{2+}$, $[Ni(bipy)_3][Os(CO)_4]$ was precipitated. Treatment of the cream solid with RX (R = Me, GeH_3, $SnPh_3$, $Au(PPh_3)$) gave *cis*-$Os(CO)_4X_2$ (X = halide) and only small amounts of $Os(CO)_4HX$; with $SnCl_2Me_2$, $[Os(CO)_4SnMe_2]_2$ was formed.

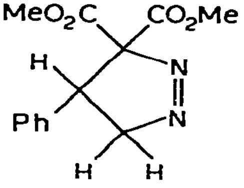
Addition of acetic formic anhydride to $Na_2[Fe(CO)_4]$ in THF at 25° gave [7] $[Fe(CO)_4(CHO)]^-$, isolated as the $[N(PPh_3)_2]^+$ salt. This formyl derivative slowly decarbonylated giving $[Fe(CO)_4H]^-$, but the reverse process, CO insertion into the Fe—H bond, did not occur. Reaction of $[Fe(CO)_4(CHO)]^-$ with acid gave formaldehyde, and with O_2 performic acid may have been formed; with octyliodide, octane and traces of nonanal were produced.

Monomeric species containing Group V donor atoms

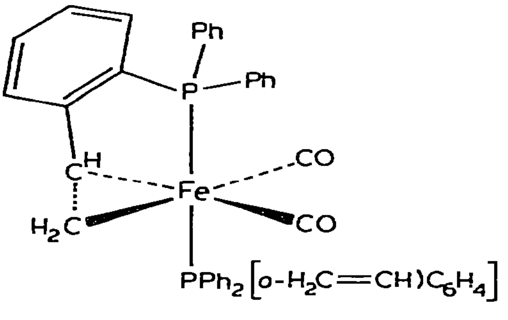
The structure of the compound prepared [8] by treating $Fe_2(CO)_9$ with 3,3-bis(methoxycarbonyl)-4-phenyl-1-pyrazoline (2) has been determined. The N atom adjacent to the di-substituted methylene group was bonded to the metal atom in an apical position.

Reaction of $Na_2[Fe(CO)_4]$ with QPh_2Cl (Q = P or As) afforded [9] $[Fe(CO)_4QPh_2]^-$ (apical Q). Treatment of this with RX (R = Me, Q = P; R = $CH_2C(Me){=}CH_2$, CH_2Ph, CH_2CO_2Et, $CH_2C{\equiv}CH$, $GePh_3$, $Fe(CO)_2(\pi\text{-}C_5H_5)$, Q = As) gave $Fe(CO)_4QPh_2R$, and with $Q'Ph_2Cl$, $Fe(CO)_2Q(Ph_2)Q'Ph_2$ (Fe—Q bonded), was isolated. $Fe(CO)_5$ reacted with $P(CH_2SiMe_3)_3$ (siphos) giving [10] $Fe(CO)_4$(siphos) and *trans*-$Fe(CO)_3$(siphos)$_2$; $Hg[Fe(CO)_3(NO)]_2$ afforded $Hg[Fe(CO)_2(NO)(siphos)]_2$. An X-ray crystallographic structural determination [11] of $Fe(CO)_4[PCl\{(OCH_2)_2CMe_2\}]$ revealed that the dioxaphosphorane ring had a "chair" structure and that the Fe atom was attached to an equatorial position. A similar study of $Fe(CO)_3(Ph_2PCH_2PPh_2)$ established [12] that the coordination geometry was an intermediate between trigonal bipyramidal and square pyramidal. It was observed that this would lead to the expectation of very rapid site exchange of the CO groups on the ^{13}C NMR time scale. The structure of a complex (3) obtained [13] by treating 2-vinylphenyldiphenylphosphine with iron carbonyl has been determined [14]. The molecule has approximate trigonal bipyramidal geometry and the Fe—P distance (2.21 Å) associated with the chelated ligand is significantly shorter than that associated with the unidentate ligand (2.24 Å). The π-bonded vinyl group is symmetrically bonded to the iron atom.

Room temperature Mössbauer spectral parameters for a series of tertiary



(2)

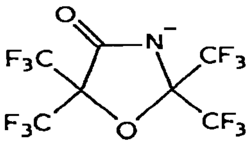


(3)

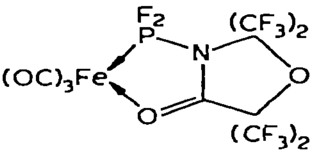
phosphine and phosphite complexes, $Fe(CO)_4L$ and $Fe(CO)_3L_2$, have been measured [15]. The trend in isomer shift values was interpreted in terms of a dominant σ-interaction backed up by π-bonding due to the synergic effect. From a study of Mössbauer spectral measurements of the asymmetry parameter of the electric field gradient and the sign of the ^{57m}Fe quadrupole splitting, it was shown [15] that, in $Fe(CO)_5$, $Fe(CO)_4(PPh_3)$, $Fe(CO)_3(PPh_3)_2$, $Fe_2(CO)_8$·(diphos) and $Fe(CO)_3$(diphos) (diphos = $Ph_2PCH_2CH_2PPh_2$), a lack of axial symmetry could be detected, but no more detailed stereochemical information could be obtained.

Photolysis of $Fe(CO)_3[P(p\text{-}MeC_6H_4)_3]_2$ in the presence of CO, and in a matrix or in solution, led [16] to the formation of $Fe(CO)_4[P(p\text{-}MeC_6H_4)_3]$. In the absence of CO, the reaction was reversible. Similar treatment of $(\pi\text{-}C_4H_4)Fe(CO)_3$, in the absence of CO, led only to the formation of $(\pi\text{-}C_4H_4)$-$Fe(CO)_2$, and there was no evidence for the release of cyclobutadiene.

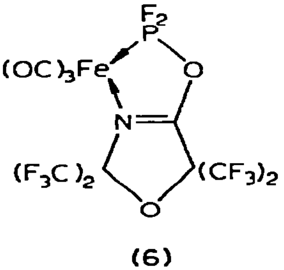
Treatment of $Fe(CO)_4(PF_2Br)$ with 4 gave [17] 5 but no 6, and with $Na[OC(CF_3)_2(CN)]$ the volatile $Fe(CO)_4[PF_2\{O(CF_3)_2(CN)\}]$ was formed. With an excess of $Na[OC(CF_3)_2(CN)]$ the last afforded 7.



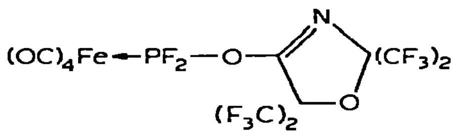
(4)



(5)



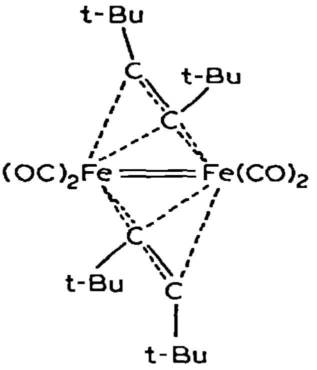
(6)



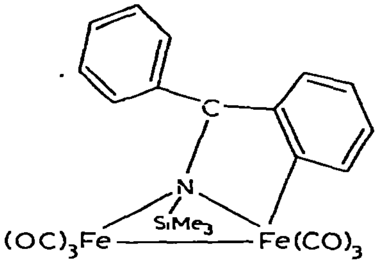
(7)

Bimetallic species

Treatment of $Fe_2(CO)_9$ with $Na_2[Cr(CO)_5]$ gave [18] $Na_2[(OC)_5CrFe$-



(8)

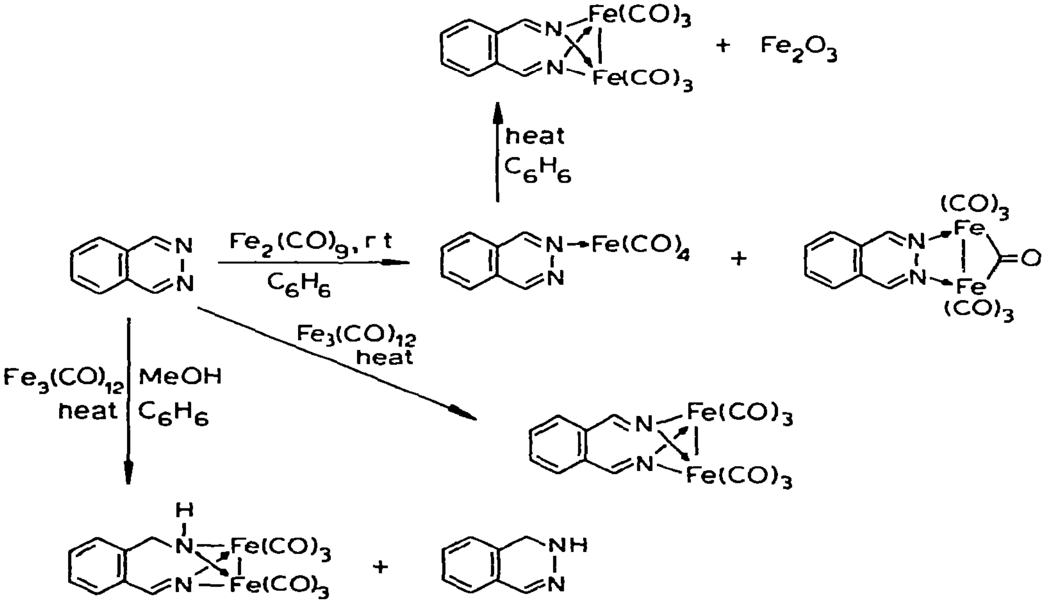


(9)

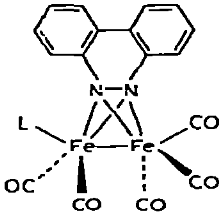
(CO)$_4$]. A resonance Raman spectral study of $Fe_2(CO)_4(C_2\text{-t-}Bu_2)_2$ (8) afforded [19] the stretching force constant for the Fe—Fe bond (3.0 ± 0.4 mdyn /Å) which was roughly twice that expected for an Fe—Fe single bond.

Reaction of $Fe_2(CO)_9$ with *N*-trimethylsilyl-benzophenonimine gave [20] 9, in which the inequivalence of the iron atoms could be detected by Mössbauer spectroscopy. Phthalazine reacted with iron carbonyls giving [21] a series of binuclear phthalazine-containing species, as indicated in Scheme 1.

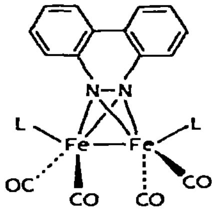
SCHEME 1



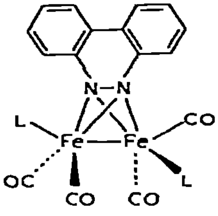
Displacement of CO occurred when $Fe_2(CO)_6(C_{12}H_8N_2)$ ($C_{12}H_8N_2$ = benzo[*c*]-cinnoline) was treated [22] with tertiary phosphines, $AsPh_3$, phosphites, or CNC_6H_{11}, and $Fe_2(CO)_5L(C_{12}H_8N_2)$ and $Fe_2(CO)_4L_2(C_{12}H_8N_2)$ were formed. Spectral studies indicated that substitution occurred preferentially at a site or sites *trans* to the Fe—Fe bond, viz. **10** and **11**, although, occasionally, another



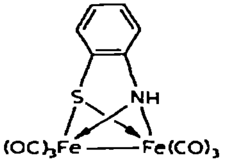
(10)



(11)

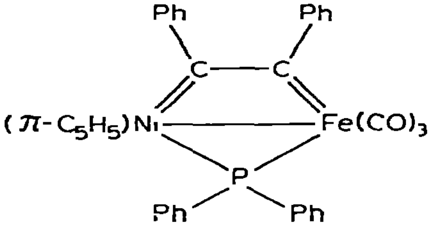


(12)

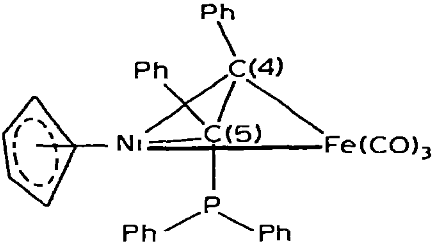


(13)

isomer, possibly 12, was detected. This behaviour was very similar to that of $Fe_2(CO)_6(SR)_2$. The Fe—Fe distance in $Fe_2(CO)_6[S(NH)C_6H_4]$ (13), determined crystallographically [23], is 2.41 Å.

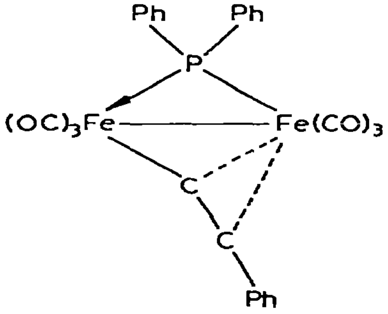


(14)

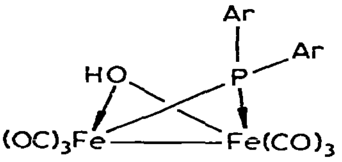


(15)

The species obtained by treating $(\pi\text{-}C_5H_5)Ni(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3$ with PhC≡CPh, originally formulated [24] as 14, has been shown by X-ray crystallography [25], to be 15. The iron atom has a distorted octahedral geometry and the Ni—Fe distance is 2.44 Å, in good agreement with that found in $(OC)_3Fe(MeC_2Me)_2Ni(\pi\text{-}C_4Me_4)$ [26]. The P atom interacts only with the iron atom, and is attached to "C(5)" which is effectively inserted into the original Ni—P bond. The Ni—Fe bond is bridged asymmetrically by C(4) and the important bond distances are Ni—C(4) 1.90, Ni—C(5) 2.00, Fe—C(4) 2.00, Ni—P 2.78 (non-bridging), Fe—P 2.20 and C(4)—C(5) 1.45 Å. Reaction of $Ph_2PC\equiv CPh$ with $Fe_2(CO)_9$ afforded [27] $Fe_2(CO)_6(Ph_2PC_2Ph)$ (16). The acetylide group functions as a one-electron donor to one iron atom via a σ-bond (Fe—C 1.89 Å) and as a two-electron donor to the other via a π-bond (Fe—C 2.13 and 2.30 Å). The Fe—Fe and C—C (acetylide) distances are 2.58 and 1.23 Å, respectively (C≡C is 1.20 Å). Reaction of $C_7H_8Fe(CO)_3$ with $Ph_2PC\equiv CCF_3$(L) gave $Fe(CO)_4L$ and $Fe(CO)_3L_2$.

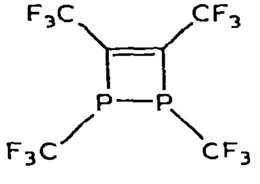


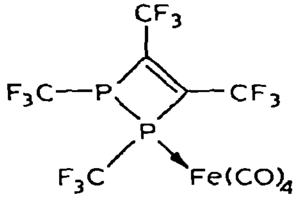
(16)

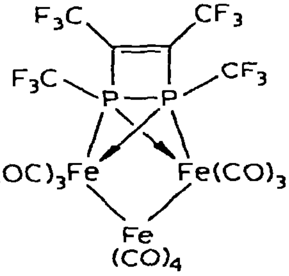


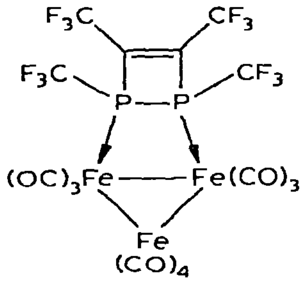
(17)

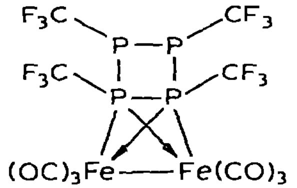
Reaction of $Fe(CO)_4[P(p\text{-}MeC_6H_4)_2H]$ with Li-n-Bu in THF then with $Fe_2(CO)_9$ gave, inter alia, a species initially formulated [28] as $Fe_2(CO)_6$-$[P(p\text{-}MeC_6H_4)_2]H$. X-ray crystallographic studies [29], however, have established that this species contains a bridging OH group, viz. 17; the Fe—Fe distance is 2.51 Å. Treatment of $Fe_2(CO)_9$ with the cyclic diphosphine 18 gave [30] 19 and 20 (an alternative formulation of the latter is 21). With $[P(CF_3)_2]_4$, however, $Fe_2(CO)_9$ gave only 22.

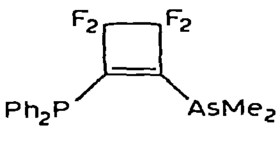

(18)

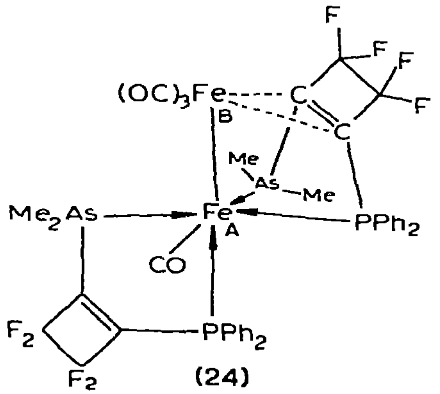

(19)


(20)

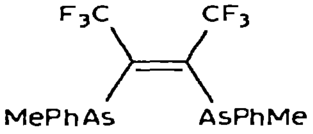

(21)


(22)

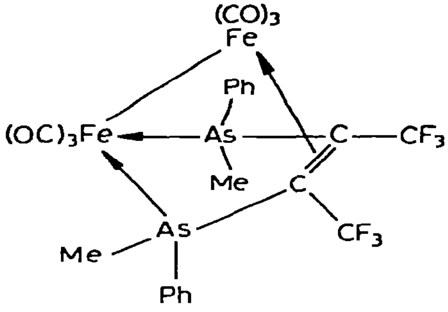

(23)


(24)

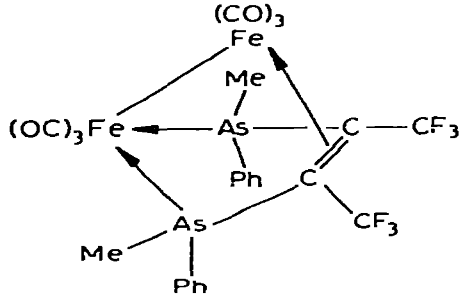
UV irradiation of $Fe_2(CO)_6(f_4asp)$ (f_4asp = 23) gave $Fe_2(CO)_4(f_4asp)_2$, the structure of which, 24, has been determined [31]. One iron atom (Fe_A), has an approximate distorted octahedral geometry while the other is in an approximately trigonal bipyramidal environment; the Fe_A—Fe_B distance is 2.87 Å. The two diastereomers of 25 (L—L) reacted [32] with $Fe(CO)_5$ giv-



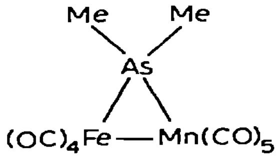
(25)



(26)



(27)



(28)

ing Fe(CO)$_3$(L—L) and Fe$_2$(CO)$_6$(L—L). Two of the three possible geometric isomers of the latter were obtained, and their properties permitted an assignment of the configuration of (L—L). These isomers are probably 26 and 27. Minor amounts of symmetric and asymmetric forms of [Fe(CO)$_3$AsMePh]$_2$ were also detected.

UV irradiation of (OC)$_4$Fe(μ-AsMe$_2$)Mn(CO)$_5$ afforded 28 [33], in which each metal atom has an octahedral geometry and the Fe—Mn distance is 2.85 Å

Thiocyanogen reacted with Fe(CO)$_5$ giving [34] the polymeric [Fe(CO)$_2$-(SCN)$_2$]$_n$. The kinetics and mechanism of CO substitution by tertiary phosphine, phosphite or AsPh$_3$ in Fe$_2$(CO)$_6$(S$_2$C$_6$H$_3$Me) and Fe$_2$(CO)$_6$(S$_2$C$_2$H$_4$) have been studied [35]. In these species, the bridging sulfur atoms are held in a rigid organic framework, and the reactions obeyed a second order rate law, being first order in each reagent and independent of CO concentration. With the species Fe$_2$(CO)$_6$(SR)$_2$ (where the SR groups are not joined) *syn*—*anti* isomerism (with respect to the orientation of the Fe(μ-SR)$_2$Fe system) is possible, and *syn*- and *anti*-isomers interconverted at rate comparable to those of the CO substitution reactions. These geometric isomers underwent CO substitution at different rates while obeying the same basic rate law. It

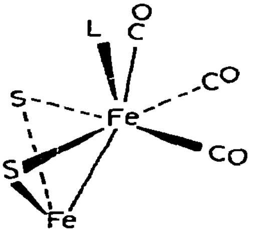


Fig. 1.

TABLE 1

METAL—METAL BOND LENGTHS AND METAL—BRIDGE—METAL BOND ANGLES IN IRON AND OSMIUM CARBONYL AND RELATED COMPLEXES

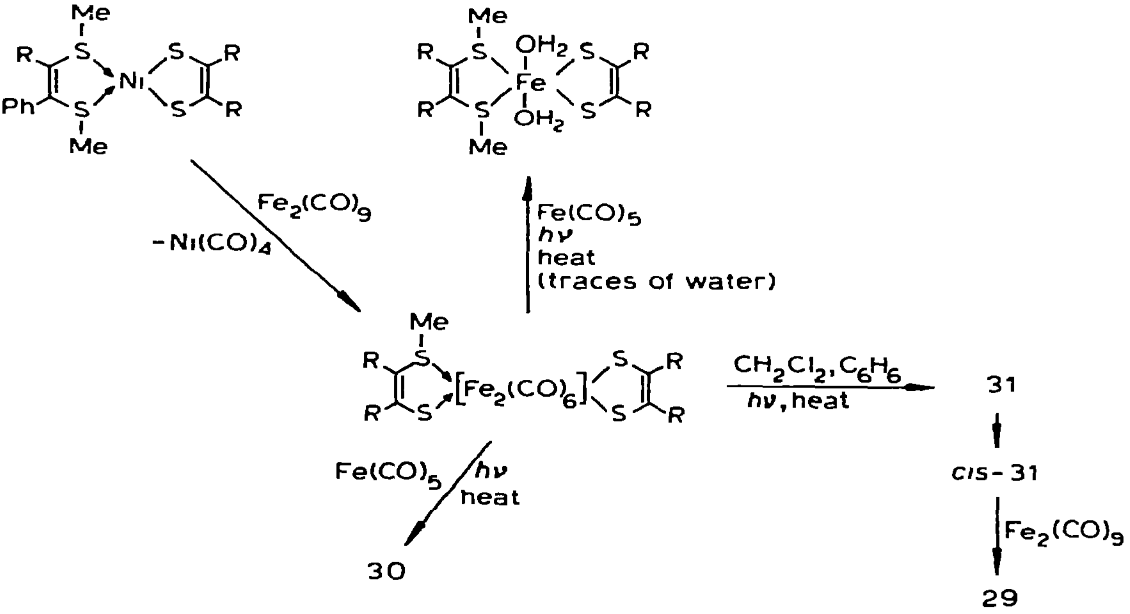
Compound	M—M′ (Å)	M—X—M′ (°)	Nature of bridge
$Fe_2(CO)_6(SEt)_2$	2.54	68.0	Fe—S—Fe
$Fe_2(SR)_2(S_2CR)_4$	2.61	72.3	Fe—S—Fe
$Fe_2(NO)_4(SEt)_2$	2.72	74.0	Fe—S—Fe
$[(\pi\text{-}C_5H_5)Fe(CO)SMe]_2^+$	2.93	82 0	Fe—S—Fe
$[(\pi\text{-}C_5H_5)Fe(CO)SPh]_2$	3.39	98.0	Fe—S—Fe
$[Fe(CO)_4PdCl(PPh_2)]_2$	2.59	72.3	Fe—P—Pd
$Fe_2(CO)_6(PMe_2)_2I_2$	3.59	102.4	Fe—P—Fe
$Os_3(CO)_8(PPh_2)Ph(PPhC_6H_4)$	3.10	84.1	Os—C—Os
$Os_3(CO)_7(PPh_2)_2(C_6H_4)$	2.80 2.99	73.5 76.5	Os—P—Os
$HOs_3(CO)_7(PPh_3)(PPh_2)(C_6H_4)$	2.89	75.0	
$Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$	3.11	82.8	

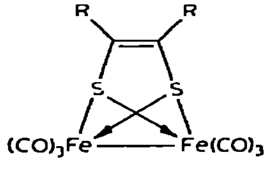
was proposed that substitution occurred via an S_N2 or I_a process, via a 7-coordinate activated intermediate (Fig. 1).

The geometries and bonding of bi- and tri-nuclear iron and osmium carbonyl species containing bridging mercaptide, phosphide and benzyne ligands have been discussed [36]. A list of intermetallic bond distances and M—X—M′ bond angles (X = bridging group) is collected in Table 1. For closely related bridged species with the same formal bond order, the metal—metal distance is very dependent on the nature of the bridging group. Thus, the M—M distance decreases as the electronegativity of the bridging group also decreases.

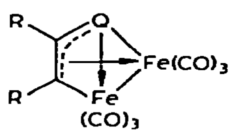
UV irradiation of a mixture of the 1,2-dithiolato-1,2-dithioether complex $Ni[(MeS)_2C_2R_2][S_2C_2R_2]$ (R = Ph or p-$MeOC_6H_4$) and $Fe(CO)_5$ afforded

SCHEME 2

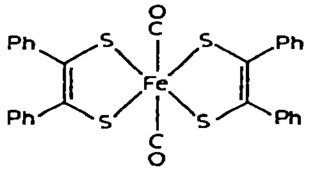




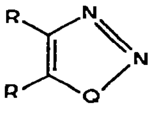
(29)



(30)



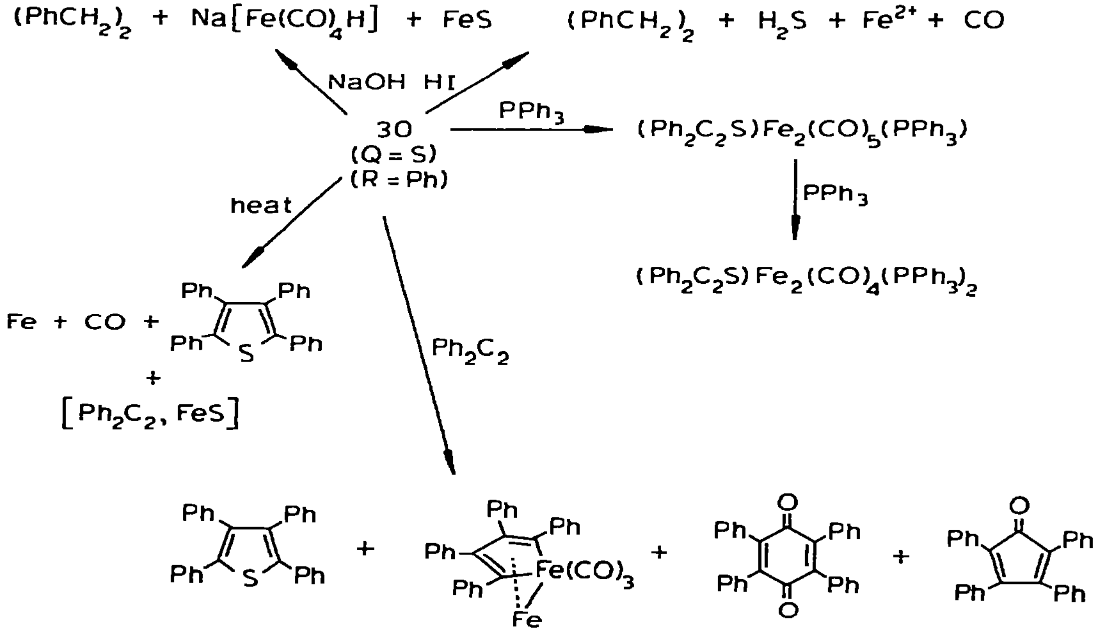
(31)



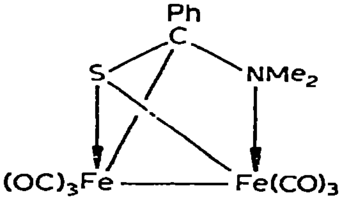
(32)

[37] free $(MeS)_2C_2R_2$, 29 and 30 (Q = S). The last was also produced in low yield by similar treatment of mixtures containing $Ni(L{-}L)(S_2C_2R_2)$ (L—L = diphos or *o*-phen). The mechanistic pathway whereby these various species were thought to be produced is outlined in Scheme 2. The species 31, which contains *trans*-CO groups, was also isolated. Thio- or seleno-keto carbene complexes analogous to 30 (Q = S or Se), could also be obtained by thermolysis or irradiation of 32 (R = H or Ph) in the presence of iron carbonyls. Some reactions of 30 (Q = S) are summarised in Scheme 3.

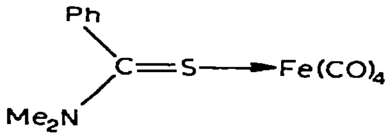
SCHEME 3



When *o*-ethylthiobenzoate reacted [38] with $Fe_2(CO)_9$, a series of organosulfur-containing compounds, together with $Fe_3(CO)_9S_2$, were produced (see

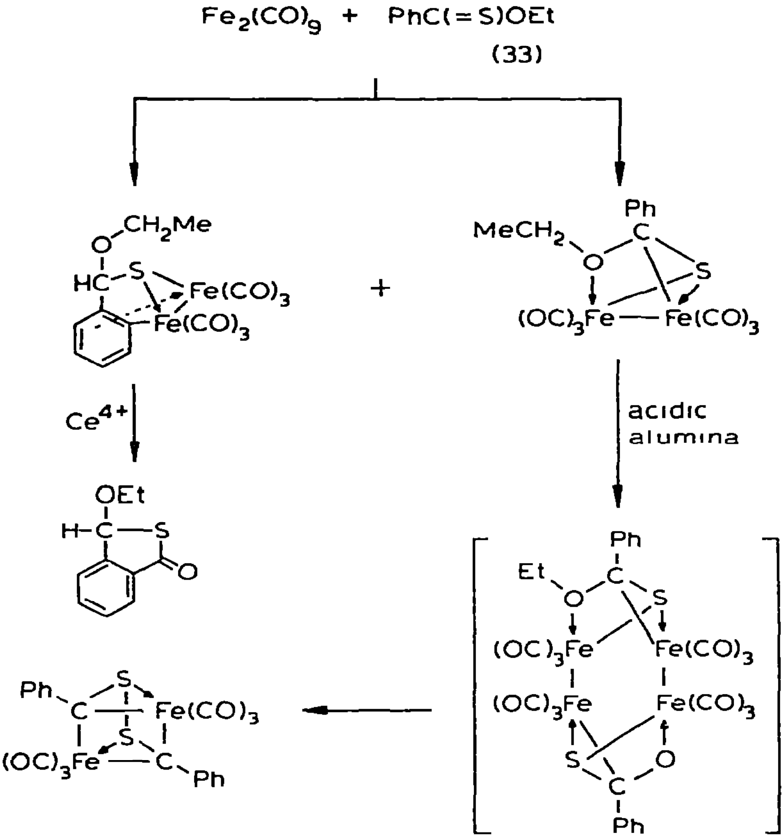


(34)

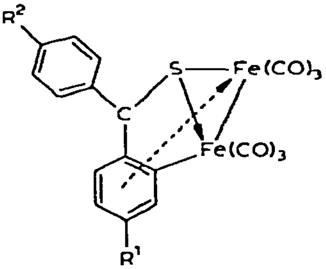


(35)

SCHEME 4

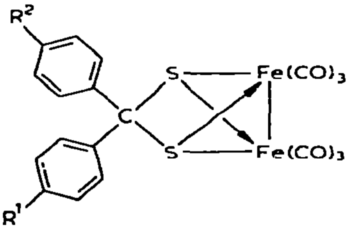


Scheme 4). When the OEt group was replaced by NMe_2, $Fe_3(CO)_9S_2$, 34 and 35 were formed. It would appear that the N atom, being a better donor than the O atom, inhibited benzene ring *ortho*-metallation. However, in turn, the O atom is a more effective donor than the benzene ring itself, and so donor ligand atom complexation predominated over ring metallation. Reaction of thiobenzophenones with $Fe_2(CO)_9$ gave the *o*-metallated product 36, together



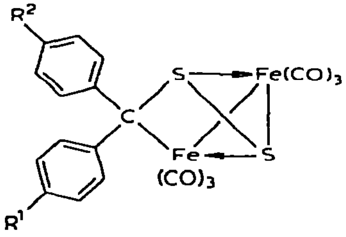
($R^1 = R^2 = H, OMe, NMe_2$,
$R^1 = OMe$, $R^2 = H$;
$R^1 = H$, $R^2 = OMe$;
$R^1 = H$, $R^2 = CF_3$)

(36)



($R^1 = R^2 = H$;
$R^1 = H$, $R^2 = OMe$)

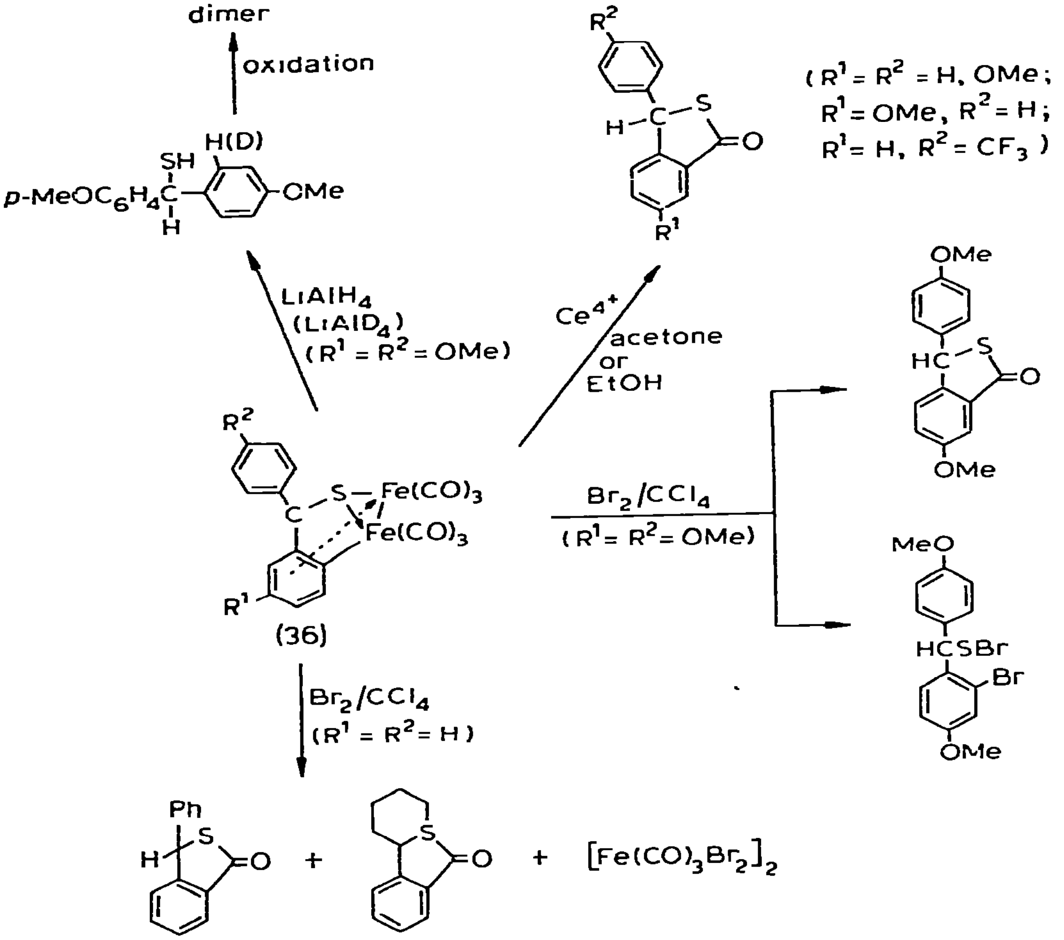
(37)



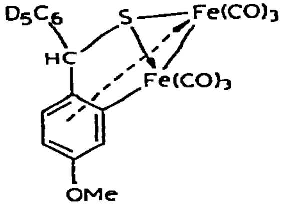
($R^1 = R^2 = H$)

(38)

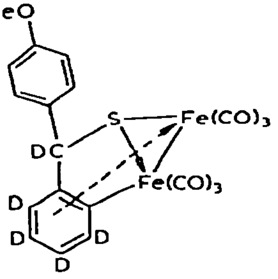
SCHEME 5



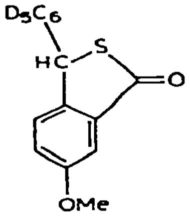
with 37, 38, and $Fe_3(CO)_9S_2$. Some reactions of 36 are given in Scheme 5. Treatment of $C_6D_5C(=S)(p\text{-}MeOC_6H_4)$ with $Fe_2(CO)_9$ gave 39 and 40, and bromination of the former afforded 41 proving that cyclisation occurred onto the ring previously bound to the metal. Reaction of 38 with $LiAlD_4$ gave Ar_2-CD(SH), which subsequently dimerised. However, similar treatment of 42 gave 43. When thiobenzophenones containing blocked aryl groups were used, the



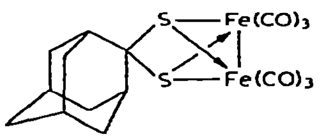
(39)



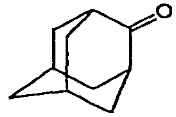
(40)



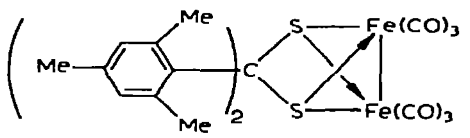
(41)



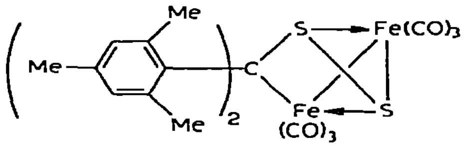
(42)



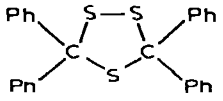
(43)



(44)



(45)

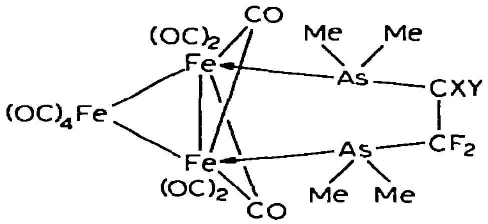


(46)

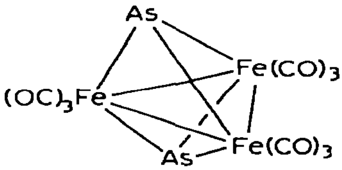
reaction products obtained with $Fe_2(CO)_9$ were different. Thus $(C_6H_2Me_3)_2CS$ gave $Fe_3(CO)_9S_2$, 44 and 45. The compounds $(R^1R^2CS)_2$ did not react with $Fe_2(CO)_9$, but with 46 afforded $Fe_3(CO)_9S_2$, and species of the type 36, 37 and 38. This paper [39] was an extremely useful source of references to *o*-metallation reactions (see also page 366).

Trimetallic and other metal atom cluster compounds

Reaction of $Fe_3(CO)_{12}$ with $Me_2AsCXYCF_2AsMe_2$ (X = Y = H; X = H, Y = F; X = F, Y = CF_3) afforded [40] $Fe(CO)_3(Me_2AsCXYCF_2AsMe_2)$ (X = F, Y = CF_3), $Fe_2(CO)_6(AsMe_2)_2$ and 47. The Mössbauer spectra of these complexes, together with those of $Fe_3(CO)_9$ derivatives of 23, were also reported. $Fe(CO)_5$ reacted with AsF_3 in benzene at 120° to give [41] $Fe_3(CO)_9As_2$ (48). The mean Fe—Fe distance, 2.62 Å compared favorably with that in



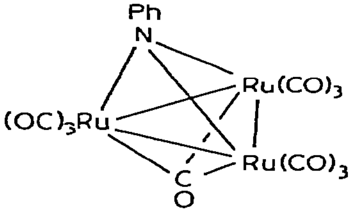
(47)



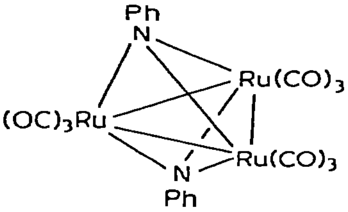
(48)

$Fe_3(CO)_{12}$ (2.63 Å) [42] and $[Fe_3(CO)_{11}H]^-$ (2.62 Å) [43]. Both arsenic atoms were bonded equally to the Fe_3 triangle (Fe—As 2.33 Å). It was suggested that in the paramagnetic $Fe_3(CO)_{11}As_2$ (obtained [44] from $AsCl_3$ and $[Fe(CO)_4]^{2-}$) two additional CO groups might be inserted into either terminal or bridging positions in the $Fe_3(CO)_9As_2$ cluster.

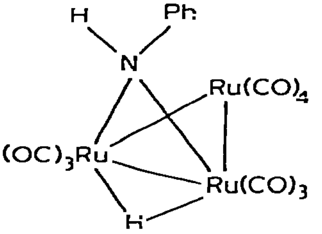
A kinetic study has been made [45] of the reactions of $Ru_3(CO)_{12}$ with QR_3 (Q = P or As) in decalin. From the activation parameters and dependence of the rate constants on the nature of the phosphine and arsine ligands, it was suggested that there was an exceptionally high degree of bond-making in the transition state. The first stage of the reaction involved reversible dissociation of CO, and it was observed that CO competed slightly more successfully for $[Ru_3(CO)_{11}]$ than did $P(OPh)_3$. $Ru_3(CO)_{12}$, when treated with either $PhNO_2$ or $PhNH_2$, af-



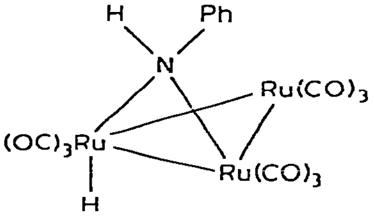
(49)



(50)

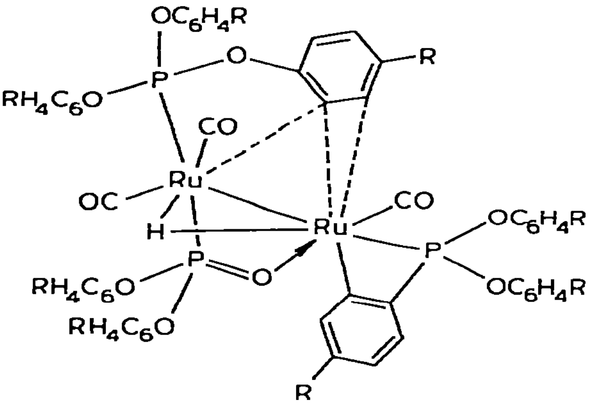


(51)

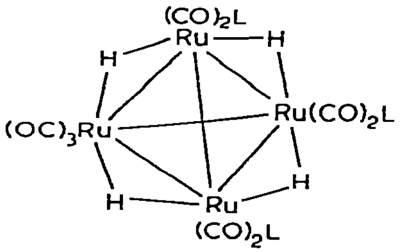


(52)

forded [46] $Ru_3(CO)_{10}(NPh)$ (49), $Ru_3(CO)_9(NPh)_2$ (50), $Ru_3(CO)_{10}H(NHPh)$ (51 or 52), and $Ru_3(CO)_9H_2(NPh)$. With PhNCO, $Ru_3(CO)_{12}$ gave 49 and traces of 50, but with PhNC, rubber-like metal carbonyl species were obtained. Treatment of 49 with an excess of $PhNO_2$ in boiling benzene gave 50 and hydrogenation (20 atm, 85°, benzene) afforded $Ru_3(CO)_9H_2(NPh)$ and $Ru_4(CO)_{12}H_4$. The structure of 49 is analogous to that of $Fe_3(CO)_{10}(NSiMe_3)$ [47] and 50 has homologues containing iron [48]. Of the two alternative structures for $Ru_3(CO)_{10}H(NHPh)$ (51 or 52), the former is analogous to $M_3(CO)_{10}H(SR)$ [49]. It appeared that $Ru_3(CO)_9H_2(NPh)$ could not be obtained directly from $Ru_3(CO)_{12}$ (perhaps it was produced via 49), and may have a structure analogous to $Ru_3(CO)_9H_2Q$ (Q = S, Se or CCH_2 groups) [50]. With triarylphosphites under mild conditions, $Ru_3(CO)_{12}$ afforded [51] $Ru_3(CO)_{12-n}[P(OR)_3]_n$ (R = Ph, n = 2 or 3; R = *p*-tolyl, n = 3), but in refluxing decalin, *o*-metallation of the aryl



(53)



(54)

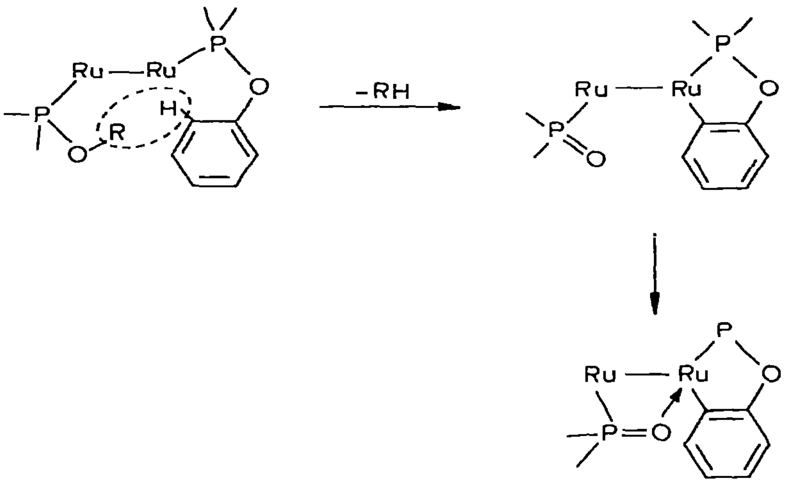
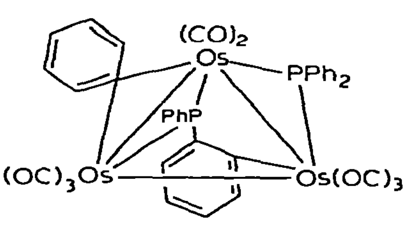


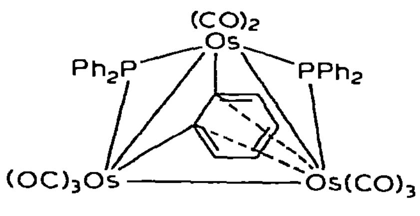
Fig. 2.

rings occurred. Thus $Ru(CO)_2[P(OC_6H_3R)(OC_6H_4R)_2]_2$ (R = H, two isomers; R = Me, one isomer), and $Ru_2(CO)_3H[P(OC_6H_3R)(OC_6H_4R)_2][OP(OC_6H_4R)_2]$ (R = H or Me) (53), together with $Ru_4(CO)_9[P(OPh)_3]_3H_4$ (54, L = $P(OPh)_3$) were produced. The first is probably an octahedral derivative of Ru^{II} with *cis*-CO groups. The structure of 53 has been established crystallographically and a possible mode of formation is outlined in Fig. 2. The mechanism of reaction may involve initial transfer of a $P(OPh)_3$ group from one metal to another in the symmetrical $Ru_3(CO)_9[P(OPh)_3]_3$; such a reaction is known [52] and could give rise to $Ru(CO)_2[P(OC_6H_3R)(OC_6H_4R)_2]_2$ and 53, suggesting that *o*-metallation of $P(OPh)_3$ is concomitant with, or closely related to, the formation of the diarylphosphonate ligand.

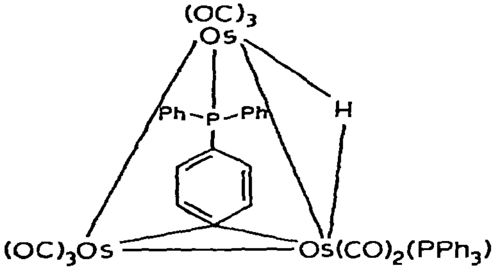
$Os_3(CO)_{12}$ reacted in refluxing xylene with PPh_3 to give [53] $Os_3(CO)_9(PPh_3)_3$, but when heated in the absence of solvent (in a 1/2 molar ratio), $Os_3(CO)_{12-n}(PPh_3)_n$ (n = 1. 2 or 3) and seven other remarkable products, identified crystallographically [54], were produced. These were $Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$ (55), $Os_3(CO)_8(PPh_2)_2(C_6H_4)$ (56), $Os_3(CO)_8$"$(PPh_3)(PPh_2)$", which was somewhat similar to 55 and 56 except that *o*-hydrogen atoms in some of the phenyl rings may have been eliminated, $Os_3(CO)_8(PPh_3)H(PPh_2C_6H_4)$ (57), $Os_3(CO)_9(PPh_3)H(PPh_2C_6H_4)$ (58), $Os_3(CO)_7(PPh_3)H(PPh_2)(C_6H_4)$ (59), and $Os_3(CO)_7H(PPh_2)(PPh_2C_6H_4C_6H_3)$ (60). The presence of hydride ligands was established by ^{1}H NMR spectroscopy, but although tentatively



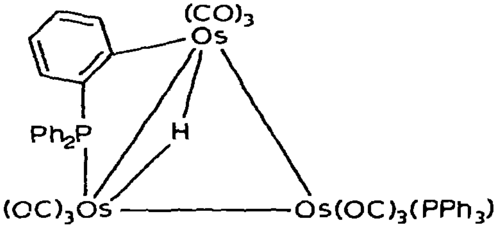
(55)



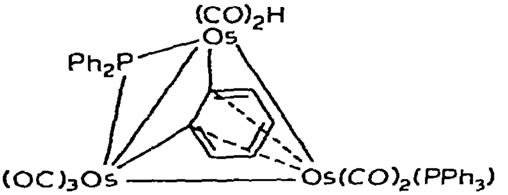
(56)



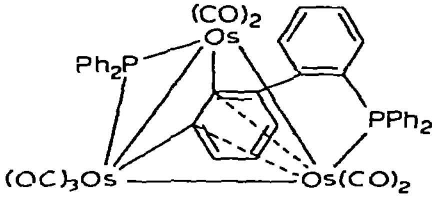
(57)



(58)

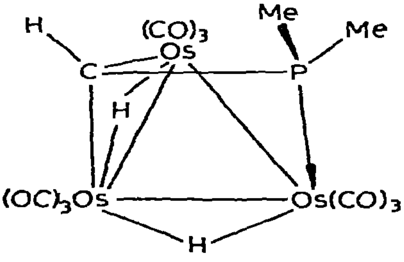


(59)

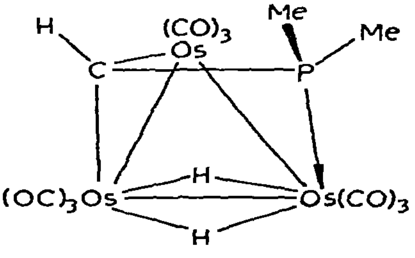


(60)

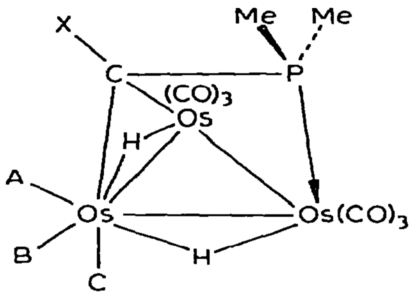
placed as shown in 57, 58 and 59, their exact location is not known with certainty. By heating $Os_3(CO)_{12}$ with $P(p\text{-}MeC_6H_4)_3$, $Os_3(CO)_{12-n}(PR_3)_n$ (n = 1 or 2) and $Os_3(CO)_8[P(C_6H_4Me)_2](C_6H_4Me)[P(C_6H_4Me)(C_6H_3Me)]$ were prepared, and under similar conditions with $AsPh_3$, $Os_3(CO)_7(AsPh)_2(C_6H_4)$ and $Os_3(CO)_{10}(AsPh_3)_2$ were produced. Protonation of $Os_3(CO)_9(PPh_3)_3$ with HBr in refluxing chloroform afforded $[Os_3(CO)_9(PPh_3)_3H]Br$. When the trialkylphosphine complexes $Os_3(CO)_{12-n}(PR_3)_n$ (R = Me or Et, n = 1 or 2) were heated in refluxing n-nonane, the species $Os_3(CO)_9H_2(R_2PCX)$ and $Os_3(CO)_8(PR_3)H_2(R_2PCX)$ (X = H or Me) (63) were formed [55]. The R_2PCX group bridges the three osmium atoms and in the first species there is rapid site exchange between the R and H groups. Of the two possible structures proposed for $Os_3(CO)_9H_2(R_2PCX)$ (viz. 61 and 62), the former is favored, and in the latter species, 63, it seems that the PMe_3 group occupies position A, B or C. The products of the reaction between $Os_3(CO)_{12}$ and $o\text{-}C_6H_4XY$ (X = Y = H; X = Y = $AsMe_2$; X = H, Y = PMe_2 or $AsMe_2$), may be generalised [56] as the "benzyne"-containing species $Os_3(CO)_nXY(C_6H_4)$ (X = Y = H, n = 9; X = Y = $AsMe_2$, n = 7; X = H, Y = PMe_2



(61)

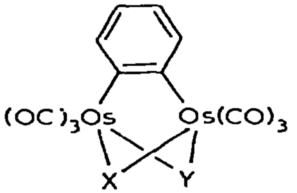


(62)

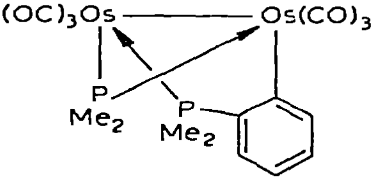


(63)

or $AsMe_2$, *n* = 9). The following observations could also be made: (i) cleavage of both C—H bonds *ortho* to a C—P or C—As bond, and of the C—P or C—As bond occurred, and no species was obtained as a result of C—H cleavage alone (cf. reactions of $Os_3(CO)_{12}$ with PPh_3): it may be noted also that both $Os_3(CO)_9XY(C_6H_4)$, X = H, Y = PMe_2 or $AsMe_2$, and $Os_3(CO)_8(PMe_2Ph)H(PMe_2)(C_6H_4)$ are different to 59, but that $Os_3(CO)_7XY(C_6H_4)$, X = Y = $AsMe_2$, is similar to $Os_3(CO)_7(PPh_2)_2(C_6H_4)$ [53]; (ii) in the thermolysis of $Os_3(CO)_{11}(PMe_2Ph)$ and $Os_3(CO)_{10}(PMe_2Ph)_2$, all of the original P atoms were retained, and only on prolonged heating did $Os_3(CO)_{12}(PMe_2Ph)$ give $Os_3(CO)_7(PMe_2)_2(C_6H_4)$; the corresponding arsine compounds gave significant yields of products with one less arsenic atom per cluster than the starting material; (iii) there was no evidence for the production of dimeric species on the pyrolysis of PMe_2Ph-containing clusters, but complexes containing $AsMe_2Ph$ afforded $Os_2(CO)_6(AsMe_2)_2(C_6H_4)$ and $Os_2(CO)_6H(AsMe_2)(C_6H_4)$ (generalised as $Os_2(CO)_6XY(C_6H_4)$ (64). When $Os_3(CO)_7(PMe_2)_2(C_6H_4)$ was refluxed under CO in n-nonane, $Os_2(CO)_6(PMe_2)(PMe_2C_6H_4)$ (65) was formed. The species $Os_3(CO)_7XY(C_6H_4)$ (X = Y = PMe_2 or $AsMe_2$) were fluxional (Fig. 3). Exchange of the X and Y environments could occur, without C_a/C_b ("benzyne" ring) exchange, via pathway 1, whereas simultaneous X/Y and C_a/C_b exchange could occur via pathway 2; the two processes actually took place and the combination of both led to an effective rotation of the "benzyne" ring about the trimetallic cluster [53].



(64)



(65)

In a structural study of $Ru_3(CO)_9H_3(CMe)$ by nematic-phase NMR spectroscopy it was assumed [57] that the Ru—H—Ru bridges were symmetrical. The Ru—H bond length and Ru—H—Ru bridge angles were calculated to be 1.90 Å and 101° respectively. Reaction of $Os_3(CO)_{12}$ with ethylene afforded [58] $Os_3(CO)_9H_2(CCH_2)$, in which both methylene protons and hydride li-

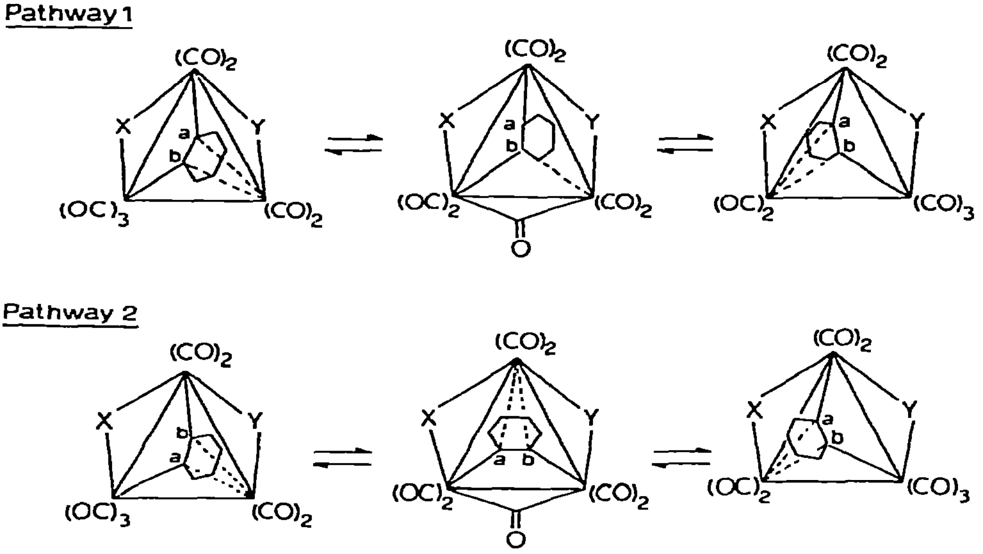
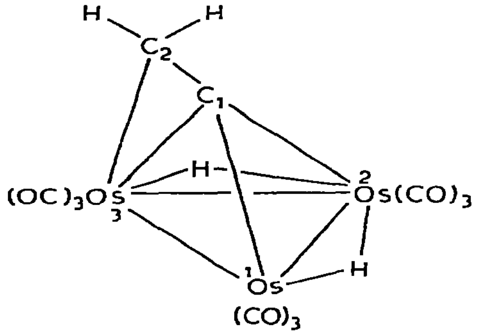
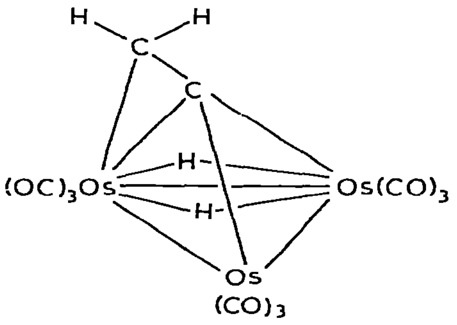


Fig. 3.

gands underwent site exchange. Two possible structures, relating to the location of the H ligands, are possible, viz. 66 and 67; the Os(1)—Os(2), Os(1)—Os(3) and Os(2)—Os(3) bond lengths are 2.89, 2.80 and 2.92 Å, respectively, while

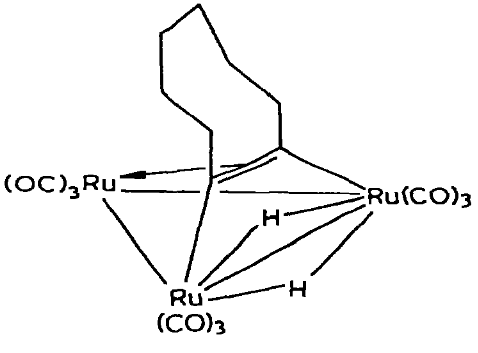


(66)

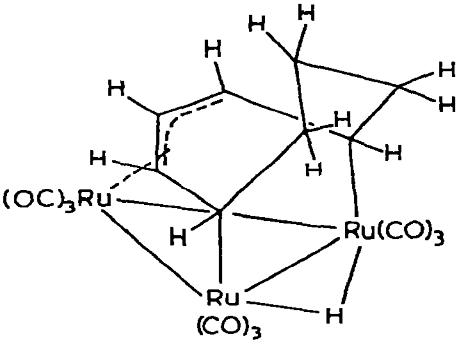


(67)

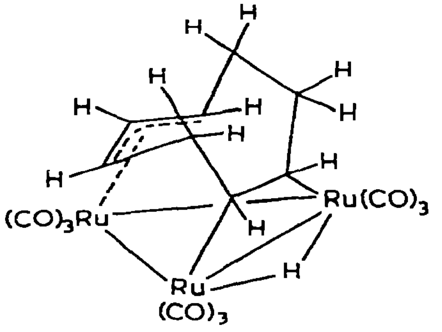
the Os(1)—C(1), Os(2)—C(1) and Os(3)—C(2) distances are 2.05, 2.04 and 2.29 Å, respectively; the C(1)—C(2) distance is 1.33 Å and the bond angles defined by Os(3)—C(2)—C(1) and Os(2)—C(1)—C(2) are 138 and 124°, respectively. The H_c/H_d exchange (E_a = 20.4 kcal/mole) was faster than hydride ligand exchange and it was proposed that, starting with 66, one hydrogen atom could move to an unprotonated metal—metal bond, causing H_c/H_d exchange, without simultaneous hydride ligand exchange. In refluxing heptane, $Os_3(CO)_9H_2(CCH_2)$ reacted with hydrogen giving $Os_3(CO)_9H_3(CMe)$, analogous to its ruthenium counterpart [59]; deuteration afforded $Os_3(CO)_9C_2H_2D_4$ in which D_2 may have been initially incorporated into the methylene group, intermolecular exchange perhaps leading to H/D exchange of the hydridic ligands.



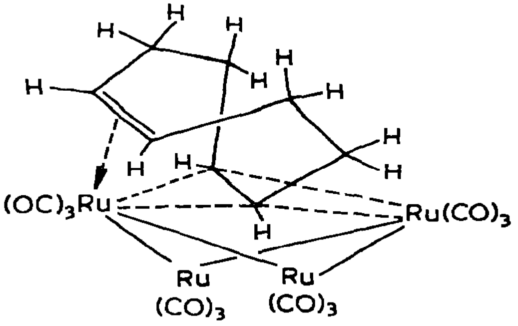
(68)



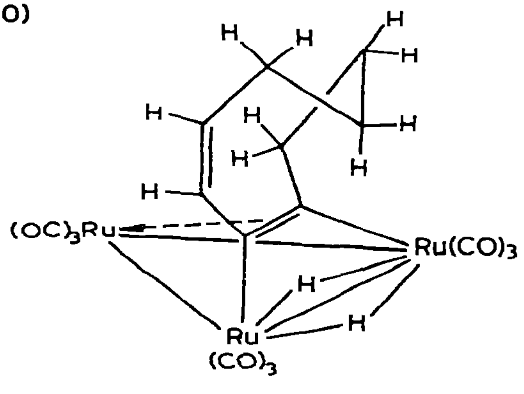
(69)



(70)



(71)



(72)

Reaction of 1,5- or 1,3-cyclooctadiene with α-$Ru_4(CO)_{12}H_4$, or of the 1,5-diene with α-$Ru_4(CO)_{13}H_2$, gave [60] $Ru_3(CO)_9H_2(C_8H_{12})$ (68), $Ru_3(CO)_9H(C_8H_{11})$ (69 or 70), $Ru_4(CO)_{11}(C_8H_{10})$, $Ru_4(CO)_{12}(C_8H_{10})$, $Ru_4(CO)_{12}(C_8H_{12})$ and $Ru(CO)_3(C_8H_{12})$ (from $Ru_4(CO)_{12}H_4$). With cyclooctene, α-$Ru_4(CO)_{12}H_4$ gave 68, $Ru_3(CO)_{12}$ and α-$Ru_4(CO)_{13}H_2$, while $Ru_3(CO)_{12}$ reacted with 1,3-cyclooctadiene affording $Ru_3(CO)_9H_2(C_8H_{10})$ (72), as well as 68-71, $Ru(CO)_3(C_8H_{12})$ and the other above-mentioned Ru_4 species. Reaction of $M_3(CO)_{12}$ (M = Ru or Os) with cyclooctene gave $M_3(CO)_9H_2(C_8H_{12})$, viz. 68. It is highly probable that 68 is similar to $Ru_3(CO)_9H_2(C_8H_8)$ [61] and is fluxional, under-

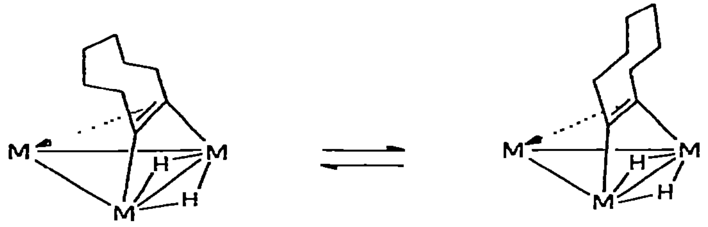
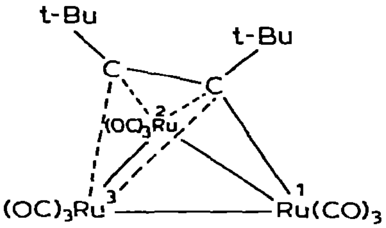


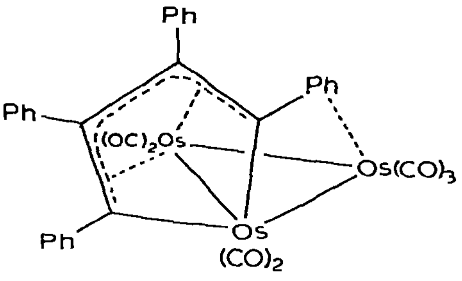
Fig. 4.

going a flipping process, associated with the C_8H_{12} ring, which is independent of the metal (Fig. 4). A second intramolecular process appears to cause rotation of the C_8H_{12} group about the M_3 triangle. The complex $Ru_3(CO)_9H(C_8H_{11})$ may have the structure 69 or 70, and is similar to $Ru_3(CO)_9H(C_{12}H_{15})$ and $Ru_3(CO)_9H$-$(C_{12}H_{17})$ [62]; it reacted with hydrogen at 80-90°C in hexane giving 68. The structure of 71 has been established crystallographically [63] and while the precise geometries of $Ru_4(CO)_{12}(C_8H_{10})$ and $Ru_4(CO)_{12}(C_8H_{12})$ are not known, they are likely to be similar to that of 71, the double bond in the former being uncoordinated. 71 and $Ru_4(CO)_{12}(C_8H_{12})$ reacted with hydrogen at 80-90° in toluene giving 68 and α-$Ru_4(CO)_{12}H_4$, whereas, under identical conditions in hexane, $Ru_4(CO)_{12}(C_8H_{10})$ afforded only the latter hydride. The results of this work were explained in terms of an oxidative addition of the appropriate olefin across the Ru_3 cluster.

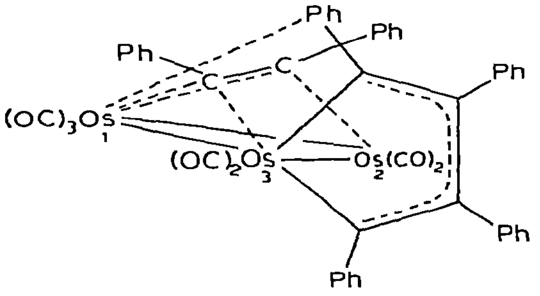
From the structural parameters obtained [64] from 73, it appears that the acetylenic fragment is bonded to the Ru_3 triangle in a way similar to that in $Fe_3(CO)_9(C_2Ph)_2$ [65]. Thus there is a three-centre μ-type bond between Ru(2) and Ru(3) and the (acetylenic) C(10)—C(11) group, and a σ-bond between Ru(1) and C(10). The trimetallic system forms an equilateral triangle (Ru—Ru 2.78-2.79 Å) and the C(10)—C(11) distance is 1.29 Å. The main differences between the Fe and Ru structures are shortenings of the C(10)—M(1) and C(10)—C(11) bonds. Reaction of the osmacyclopentadienyl complex $Os_3(CO)_7(ac)_2$ (74), (ac = Ph_2C_2, $(p\text{-}ClC_6H_4)_2C_2$ or $(p\text{-}MeC_6H_4)_2C_2$) with a further mole of acetylene gave [66] $Os_3(CO)_7(ac)_3$ which, with further ac after 10 h, gave $Os_3(CO)_6(ac)_3$ and a benzene derivative based on cyclisation of the acetylene groups (e.g. $Os_3(CO)_7(C_2Ph_2)_3$ afforded $Os_3(CO)_6(C_2Ph_2)_3$ and C_6Ph_6). After 48 h, the products were $Os_2(CO)_6(ac)_2$, $Os(CO)_3(ac)_2$ and the appropriate benzene. The structure of $Os_3(CO)_7(Ph_2C_2)(Ph_4C_4)$ (75), (derived [66] from 74 (ac = Ph_2C_2) and C_2Ph_2) has been established crystallographically [67]. The three metal atoms form a nearly equilateral triangle (Os(1)—Os(2) 2.68, Os(1)—Os(3) 2.74 and Os(2)—Os(3) 2.81 Å), chelation occurring between the Ph_4C_4 group and the cluster via two σ-bonds to one metal atom (Os(1)) and an interaction between the π-electrons of the osmacyclopentadiene fragment and the adjacent $Os(2)(CO)_3$ group. The additional acetylenic fragment appears to function as a four-electron donor to the whole cluster. There is no apparent interaction between the phenyl group (as illustrated) and the Os(3) atom, unlike the situation in 74 (ac = C_2Ph_2) [68]. The C—C bond of the unique acetylenic group is roughly parallel to the Os(1)—Os(2) bond and its mid-point is nearly above the "centre of gravity" of the Os_3 cluster.



(73)



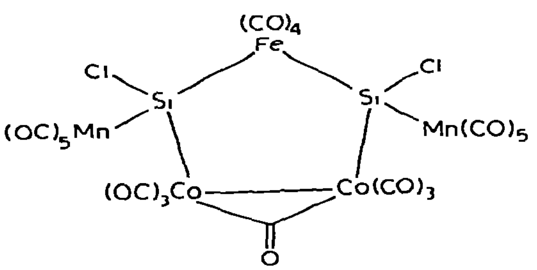
(74)



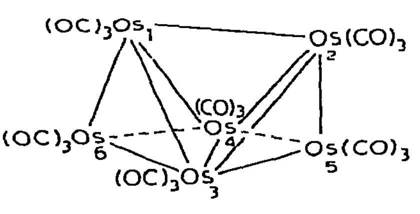
(75)

Reaction of *trans*-PtCl$_2$(py)$_2$ with Na$_2$Fe(CO)$_4$ afforded [69], after refluxing in methanol/THF, *trans*-Fe(CO)$_4$[PtCl(py)$_2$]$_2$, in which there are two Pt—Fe bonds somewhat ionic in character (Pt$^{\delta+}$—Fe$^{\delta-}$). Treatment of Fe$_3$(CO)$_{12}$ with SiHCl[Mn(CO)$_5$][Co(CO)$_4$] gave [70] Fe(CO)$_4$[SiCl{Mn(CO)$_5$}]$_2$[Co$_2$(CO)$_7$] (76).

The products of reaction of M$_3$(CO)$_{12}$ (M = Ru or Os) with water were [71], respectively, α-Ru$_4$(CO)$_{12}$H$_4$ and α-Ru$_4$(CO)$_{13}$H$_2$, and Os$_3$(CO)$_{10}$H(OH), Os$_4$(CO)$_{13}$H$_2$, Os$_4$(CO)$_{12}$H$_4$, Os$_5$(CO)$_{10}$H$_2$, Os$_5$(CO)$_{15}$H$_2$, Os$_6$(CO)$_{18}$H$_2$ and Os$_7$(CO)$_{19}$H$_2$C. From the simplicity of the IR spectra of these species it seemed that molecular symmetries were high. There were no CO groups bridging two metal atoms, but the presence of carbonyl groups bridging three metal atoms could not be excluded. Treatment of α-Ru$_4$(CO)$_{12}$H$_4$ with ethylene (10-12 atm, 130°) gave [72] eight products, including Ru$_5$(CO)$_{15}$C and Ru$_6$(CO)$_{17}$C. The structure of the former, on the basis of IR spectra, is analogous to that of Os$_5$(CO)$_{15}$C (prepared by pyrolysis of Os$_3$(CO)$_{12}$ or Os$_6$(CO)$_{18}$ [73] in vacuo at 255°) and Fe$_5$(CO)$_{15}$C [74]. It seemed quite likely that the ethylene played no part in the formation



(76)



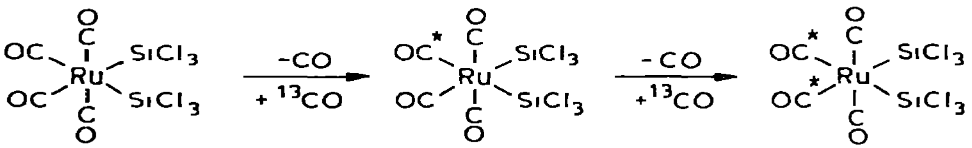
(77)

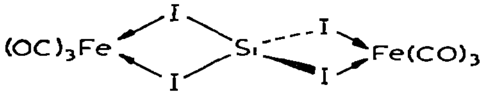
of M$_5$(CO)$_{15}$C, and when M = Os the precursor of the appropriate carbide is probably Os$_6$(CO)$_{18}$. The structure of the hexanuclear species, 77, is derived [75] from a bicapped tetrahedron. The intermetallic distances Os(1)—Os(2) and Os(3)—Os(4) are short (2.73 and 2.76 Å), while Os(1)—Os(3), Os(1)—Os(4) and the comparable bond lengths involving Os(2) and all those connecting Os(5) and Os(6) to the cluster, are in the range 2.78-2.84 Å. The short metal—metal contacts were consistent with distances connecting Os^1 atoms. It was suggested that Os$_7$(CO)$_{21}$ and Os$_8$(CO)$_{23}$ might have capped octahedral structures.

Metal—metal bonded species involving Group IV atoms

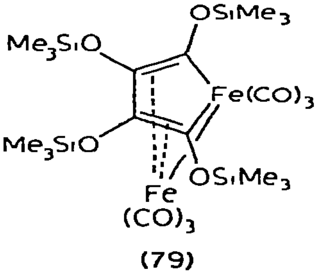
It has been established [76] that a five-coordinate intermediate is involved in the CO-exchange reactions [77] of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ (Scheme 6). By UV irradiation of a mixture of Fe(CO)$_5$ and SiI$_4$, Fe$_2$(CO)$_6$(SiI$_4$) (78), was formed [78]. Reaction of Fe(CO)$_5$ with an excess of Si$_2$Cl$_6$, however, afforded [Fe(CO)$_4$SiCl$_2$]$_2$, perhaps via Fe(CO)$_4$(SiCl$_3$)$_2$ as an intermediate [79]. From kinetic studies of the reaction of [Ru(CO)$_4$(SiMe$_3$)]$_2$ with PPh$_3$, which gave Ru(CO)$_3$(PPh$_3$)$_2$ and Ru(CO)$_2$(PPh$_3$)$_2$(SiMe$_3$)$_2$, it was shown [80] that the initial reaction rate changed steadily from first order towards an order of ½ (in terms of the starting complex) as the concentration of the precursor was increased. Reaction of the silyl complex with CCl$_3$Br afforded initially Ru(CO)$_4$Br(SiMe$_3$), and the results suggested prior homolytic fission of [Ru(CO)$_4$(SiMe$_3$)]$_2$. However, the reaction overall was considerably more complex.

SCHEME 6





(78)



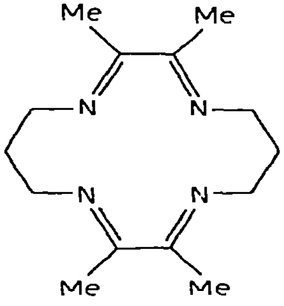
(79)

The species formulated [81] as [Fe(CO)$_4$(SiMe$_3$)$_2$]$_2$, obtained from the reaction of Na$_2$[Fe(CO)$_4$] with SiIMe$_3$, contained anomalous mass spectral features. Thus, the ions [Fe$_2$(CO)$_9$(SiMe$_3$)$_4$]$^+$ and [Fe$_2$(CO)$_{10}$(SiMe$_3$)$_4$]$^+$, were detected [81]. The species has been resynthesised (using SiBrMe$_3$) and has been identified [82] as a ferracyclopentadienyl derivative, 79.

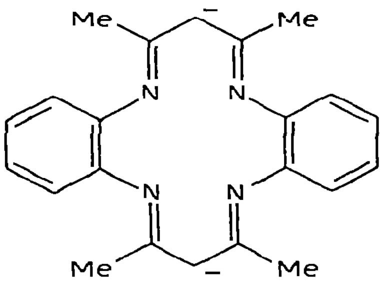
The binuclear species [Fe(CO)$_4$MR$_2$]$_2$ (M = Ge, Sn, Pb; R = Me, Bu, Ph) reacted [83] with relatively weak Lewis bases (L) giving Fe(CO)$_4$MR$_2$L (L = pyridine, acetone, THF or ether). Mössbauer (^{119m}Sn) and X-ray photo-electron spectral studies of Fe(CO)$_4$Sn-t-Bu$_2$(L) (L = pyridine or DMSO) established [84] that the species contained Sn^{IV}. Addition of SnX_4 (X = Cl or Br) to $Fe(CO)_4(QPh_3)$ (Q = P, As or Sb) afforded [85] $Fe(CO)_3(QPh_3)X(SnX_3)$.

Complexes containing cyclic N-donor atom ligands

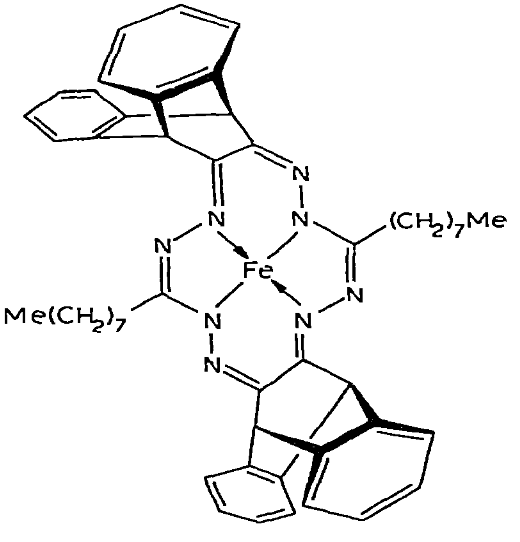
Iron(II) complexes derived the tetracyclic tetradentate ligand TIM (80), $[Fe(NCMe)_2(TIM)][PF_6]_2$ reacted [86] reversibly, in acetonitrile, with CO giving $[Fe(NCMe)(CO)(TIM)][PF_6]_2$. The Mössbauer spectral parameters obtained from this species were consistent with a low-spin Fe^{II} formulation. The dianionic ligand Q (81) reacted [87] with iron(II) amine complexes under CO in the presence of appropriate bases L giving diamagnetic Fe(CO)L(Q) (L = MeCN, pyridine, $4\text{-}MeC_5H_4N$ or N_2H_4). The structure of the hydrazine adduct is represented in Fig. 5. The iron atom is displaced 0.11 Å towards the CO group out of the plane of the four N atoms of Q, and the $Fe{-}N(N_2H_4)$ bond is unusually long (2.12 Å). In DMF at 100°, $Fe(OAc)_2$ reacted [88] with the appropriate ligand giving 82. The benzo substituents provided an open-sided cavity of depth 5 Å (Fig. 6) and the species reacted with CO to give a 1/1 adduct



(80)



(81)



(82)

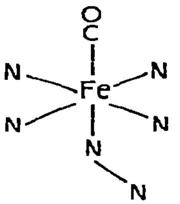


Fig. 5.

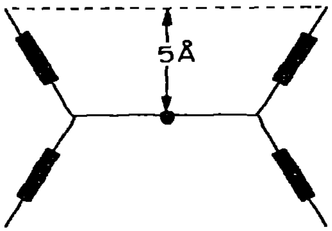
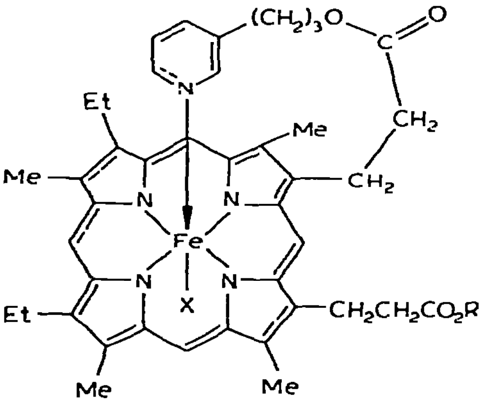
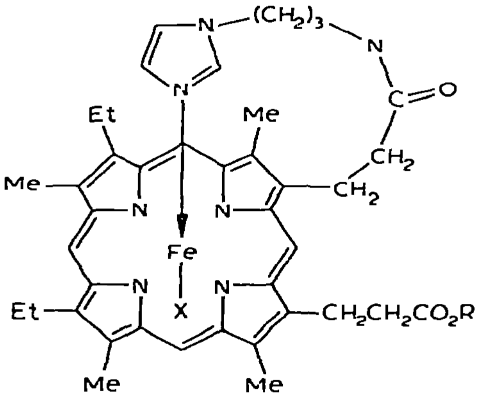


Fig. 6.

The complexes 83 and 84 had an affinity for CO which was apparently influenced [89] by the nature of the group R (whether it could interfere by coordinating in the sixth position at Fe when the X position is initially vacant). The two complexes had similar affinities for CO but differred substantially in their affinities for O_2; 84 preferred O_2 to CO, but 83 in pyridine (X = py) would not bind oxygen. The formation of Fe(CO)(pip)(porph) (pip = piperidine, porph = protoporphyrin-IX or tetraphenylporphyrin) from $Fe(pip)_2(porph)$ has been studied [90] kinetically. The mechanism involved predissociation, giving the five-coordinate Fe(pip)(porph), and the data indicated that the models resembled quite closely the kinetic properties of the active iron site in deoxy-myoblobin and -hemoglobin; iron glyoxime complexes were shown to be poor models for heme protein systems. Nitric oxide reacted [91] with $Fe(pip)_2(porph)$ giving paramagnetic Fe(NO)(pip)(porph), and it was suggested that the Fe—N—O bond system was bent. The ligand exchange reaction Fe(CO)(pip)(porph) + NO $\rightleftharpoons$ Fe(NO)(pip)(porph) + CO (porph = protoporphyrin-IX) has been compared with the analogous one involving the hemoglobin complexes. Both reactions involved six-coordinate diamagnetic carbonyl and paramagnetic nitrosyl species, but in the porphyrin complex, the sixth ligand was piperidine while in the hemoglobin species it was imidazole. Preliminary studies indicated that the enthalpy of formation of the nitrosyl from the carbonyl was comparable in the two cases, so that the differences between equilibrium constants for the two systems lay in entropies of solvation which were clearly different for the porphyrin model in piperidine solution and for hemoglobin in aqueous media. The



(83)



(84)

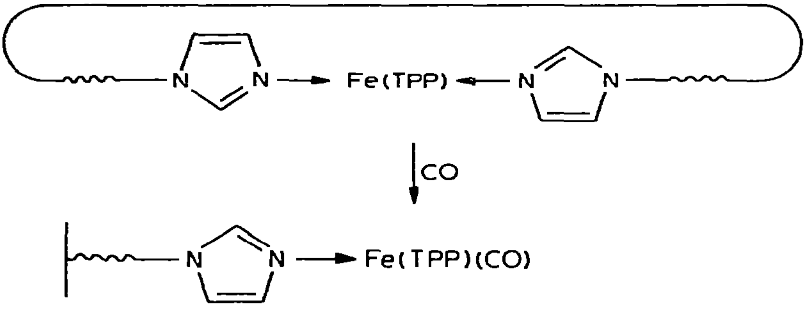


Fig. 7.

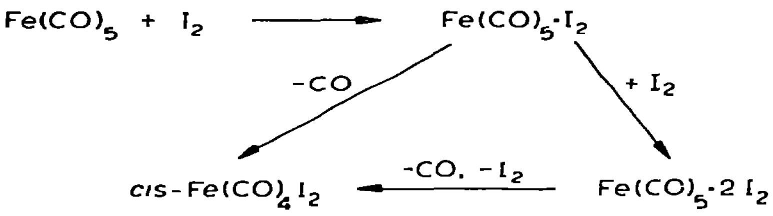
preliminary studies also indicated that in the competition reactions of Fe(pip)$_2$-(porph) for NO and CO, more of the nitrosyl complex was formed initially than was expected from the separate equilibrium constants. On standing, however, the relative amounts of NO and CO adducts reached their equilibrium concentrations. The kinetic measurements again indicated the involvement of five-coordinate intermediates and were in general agreement with the reported kinetics of addition of NO and CO to hemoglobin [92]. When Fe(TPP) (TPP = *meso*-tetraphenylporphyrin) was treated with resin-bound imidazole, a metalloporphyrin-containing resin was produced [93]. Carbonylation of this species afforded a monocarbonyl species still attached to the resin (Fig. 7). Oxidation resulted in the degradation of the complex, with removal of [Fe(TPP)]$_2$O. ^{13}C NMR spectral studies of ^{13}CO incorporated in rabbit hemoglobin revealed [94] that there were three distinct Fe^{II}—^{13}CO coordination sites.

The product obtained by reaction of $Ru_3(CO)_{12}$ with tetraphenylporphine (TPP) followed by recrystallisation from $CHCl_3$/EtOH has been described either as Ru(CO)(TPP) [95] or $Ru(CO)_2$(TPP) [96] (a similar species was reported containing tetra-*p*-isopropylphenylporphine). This reaction has been reexamined [97], and on the basis of chemical, spectral and X-ray crystallographic analysis, the species has been reformulated as Ru(CO)(EtOH)(TPP). The crystallographic study revealed a disorder of the CO and EtOH groups, which may have led to earlier incorrect reports of a bent Ru—C—O bond arrangement; otherwise the structure was as expected, containing a planar arrangement of N atoms, with a Ru—C(O) bond length and R—C—O bond angle of 1.77 Å and 175.8(1.9)° respectively. The structural data obtained [98] from Ru(CO)(py)(TPP) agreed well with those described above for Ru(CO)(EtOH)(TPP). The metal atom is displaced 0.079 Å out of the plane of the four N atoms towards the CO group, the Ru—C(O) and Ru—C—O dimensions being 1.84 Å and 178.4° respectively. The long axial Ru—N distance was attributed to the *trans*-influence of the CO ligand. The porphyrin complexes Ru(CO)(TPP), Ru(CO)(py)(TPP), Ru(CO)-(OEP) (OEP = octaethylporphyrin) and Ru(CO)(etiol) (etiol = etioporphyrin-I) underwent [99], voltammetrically, two one-electron oxidations in dichloromethane. The first oxidation process occurred at the ring, giving π-cation radical species.

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

The mechanism of formation of *cis*-$Fe(CO)_4I_2$ from $Fe(CO)_5$ and I_2 in-

SCHEME 7



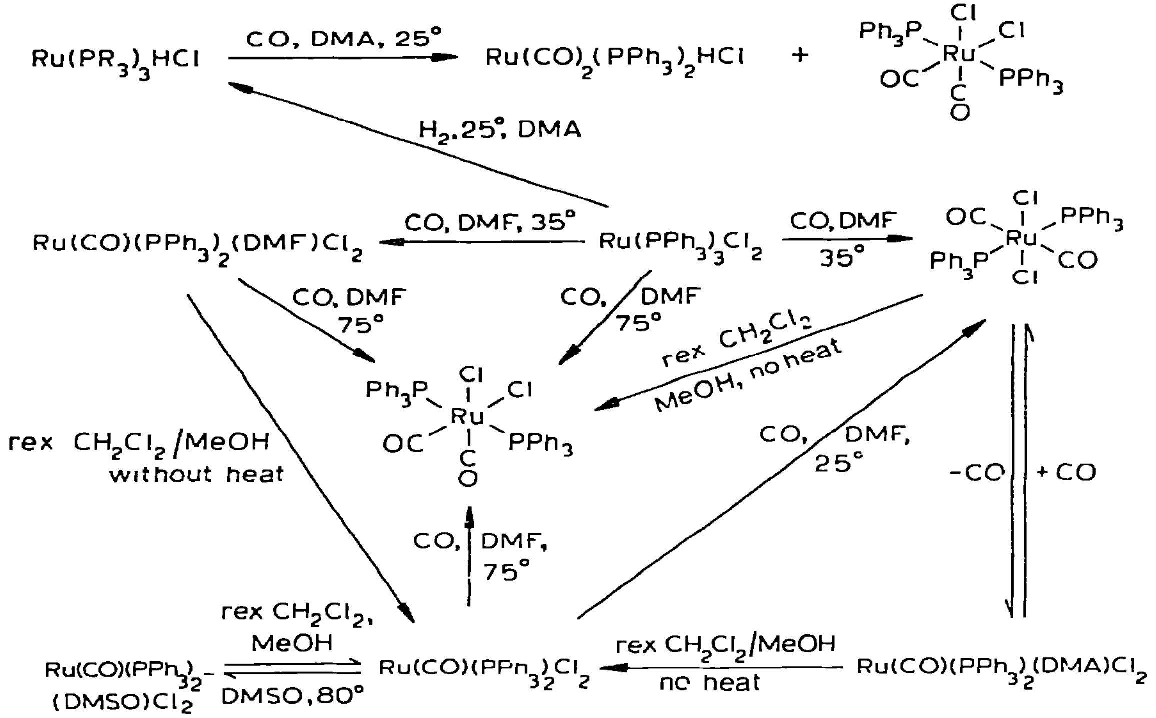
volved [100] (Scheme 7) the successive formation of 1/1 and 1/2 molecular adducts. Mössbauer spectral parameters have been obtained [101] from *cis*-$Fe(CO)_4X_2$ (X = Cl, Br and I); those for $Fe(CO)_4I_2$ differed to those previously reported [102]. It was also noted that there was no Mössbauer spectral evidence for the formation of *trans*-$Fe(CO)_4I_2$ on photolysis of the *cis*-isomer.

Carbonylation (by CO gas) of $RuCl_3 \cdot nH_2O$ dissolved in ethanol is known [103] to give a bright red solution. It has been shown [104] that this solution contains $[Ru(CO)_2Cl_2]_n$ (as evidenced by isolation of salts of $[Ru(CO)_2Cl_4]^{2-}$ upon addition of Cl^-), *fac*-$[Ru(CO)_3Cl_3]^-$ and $Ru(CO)Cl_3$ (addition of Cl^- gave $[Ru(CO)Cl_5]^{2-}$).

Mössbauer spectral data have been obtained [105] for a series of Lewis base complexes of iron(II) carbonyl halides, viz. $Fe(CO)_3LX_2$ (X = I, L = $CN(p\text{-}MeOC_6H_4)$, PPh_2Et, PPh_3, $P(OPh)_3$ or $P(OMe)_3$; X = Br, L = $P(OPh)_3$), $Fe(CO)_2L_2X_2$ (X = Cl, L = PPh_2Me, PPh_2Et, PPh_3 or $P(OPh)_3$; X = Br, L = PPh_2Me, PPh_2Et, PPh_3, $P(OPh)_3$, $P(OMe)_3$ or L_2 = $Ph_2PCH_2CH_2PPh_2$; X = I, L = $CN(p\text{-}MeOC_6H_4)$, PPh_2Me, PPh_2Et, PPh_3, $P(OPh)_3$, $P(OMe)_3$, PMe_3 (*cis*- and *trans*-complexes) and L_2 = $Ph_2PCH_2CH_2PPh_2$). From partial quadrupole and centre shifts, the σ-donor and π-acceptor properties of L were estimated. It was observed that $P(OMe)_3$ was the strongest σ-donor and π-acceptor, being similar in its bonding properties to $CN(p\text{-}MeOC_6H_4)$. From the general correlation between the partial quadrupole and centre shift data, it was suggested that in these complexes σ-bonding of L was dominant in determining the chemical and quadrupole shifts.

Reduction of $RuCl_3 \cdot nH_2O$ by hydrogen, using Adams catalyst in the presence of RCN (R = Me, Et, n-Pr, i-Pr, Ph or CH_2Ph) gave [106] $Ru(NCR)_4Cl_2$. Treatment of this species with $Ph_2PCH_2CH_2PPh_2$ (diphos) afforded $Ru(diphos)(NCR)_2Cl_2$ which reacted with CO giving $Ru(CO)(diphos)(NCR)Cl_2$. Carbonylation of $Ru(NCR)_4Cl_2$ in boiling methanol gave $Ru(CO)(NCR)_3Cl_2$ and, in boiling acetone, $Ru(CO)_2(NCR)_2Cl_2$ (*cis*-CO groups). A series of carbonyl triphenylphosphine complexes of $RuCl_2$ has been synthesised [107] in dimethylacetamide (DMA), DMF or DMSO (Scheme 8). A number of solvent-containing species were isolated in which the solvent molecules were O-bonded. Reaction of $Ru(PPh_3)_3HBr$ with CO in DMA gave $Ru(CO)_2(PPh_3)_2$-HBr (85 or 86). Reduction by hydrogen at 80° of $RuCl_3 \cdot nH_2O$ dissolved in DMF gave brown ruthenium(I) species which, on treatment with acetic acid/sodium acetate mixtures, afforded $[Ru(CO)_2(PPh_3)(OAc)]_2$. Under mild conditions the carbonyl species illustrated in Scheme 8 showed low activity as catalysts for the homogeneous hydrogenation of olefins, and were ineffective as hydroformylation catalysts; $Ru(CO)_2(PPh_3)_2Cl_2$ was an efficient olefin isomerisation catalyst.

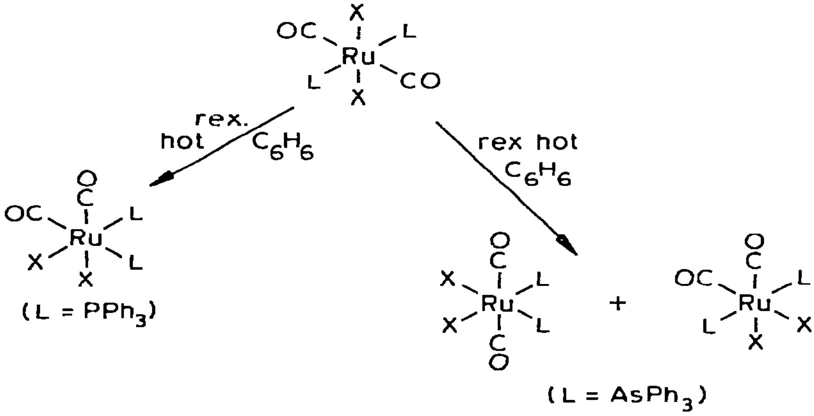
SCHEME 8

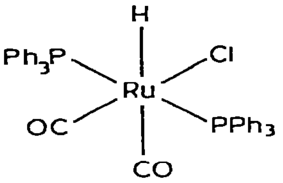


(rex = recrystallisation)

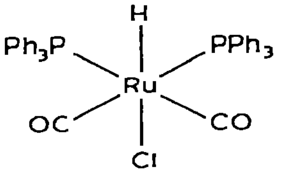
Reaction of $Ru(MeOH)(QPh_3)_2Cl_3$ with CO gave [108] *trans*-$Ru(CO)_2$-$(QPh_3)_2Cl_2$ ($Q = P$ or As), and these species isomerised in hot benzene (Scheme 9). By refluxing $Ru(MeOH)(QPh_3)_2Cl_3$ in CS_2, $Ru(CS_2)(QPh_3)_2Cl_3$ (87) was produced whereas with $Ru(MeOH)(QPh_3)_2Br_3$, mixtures of the bromo-analogue of 87 and $Ru(CS)(QPh_3)_2Br_3$ were formed. The ruthenium(III) complexes also reacted with norbornadiene in refluxing benzene giving $Ru(C_7H_8)$-$(QPh_3)_2X_2$ (88); and $Ru(C_7H_8)(PMe_2Ph)_2Cl_2$ could be prepared by treating

SCHEME 9

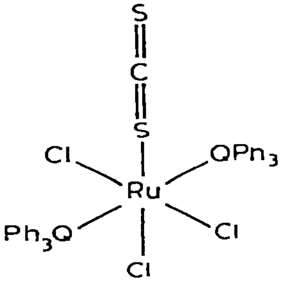




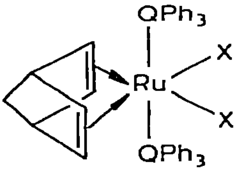
(85)



(86)

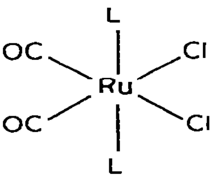


(87)

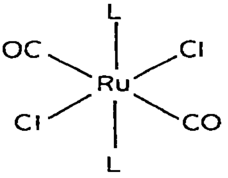


(88)

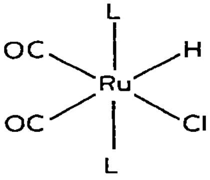
$[Ru(CO)(C_7H_8)Cl_3]^-$ with PMe_2Ph. However the reaction between $Ru(MeOH)(AsPh_3)_2Cl_3$ and 1,5-cyclooctadiene afforded only $[Ru(C_8H_{12})Cl_2]_n$, and with ethylene or $PhC{\equiv}CPh$, $Ru(AsPh_3)_2Cl_3$ alone was isolated. Passage of CO through ethanol solutions containing $RuCl_3 \cdot nH_2O$ and AsR_3 (R = *o*-, *m*- or *p*-MeC_6H_4) gave [109] *cis*-$Ru(CO)_2(AsR_3)_2Cl_2$ and treatment of this with LiBr afforded the corresponding bromides. After boiling a mixture of $RuCl_3$ and $P(t\text{-}Bu)R_2(L)$



(89)

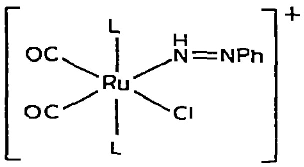


(90)

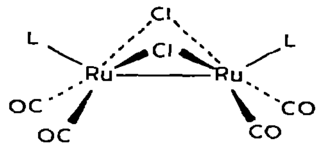


(91)

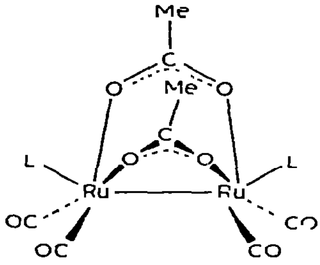
(R = Me, Et, n-Pr, n-Bu, Ph or *p*-MeC_6H_4) in 2-methoxyethanol under CO for 2½ h; a mixture of the *cis*- and *trans*-isomers 89 and 90, was formed [110]. However, after 16 h, only 89 was obtained. There was a linear relationship, obtained from ^{31}P NMR spectral studies, between $\delta(P)$ for free $P(t\text{-}Bu)R_2$ and $\Delta\delta$ for the coordinated phosphines in XC but not in 89, possibly because of conformational effects in the latter. There was also a linear relationship between $\delta(C)$ (^{13}CO) and carbonyl stretching free constants obtained from these complexes. Treatment of *cis*-$Ru(CO)_2[P(n\text{-}Bu)_2(t\text{-}Bu)]_2Cl$ with KOH in 2-methoxyethanol gave $Ru(CO)_2[P(n\text{-}Bu)_2(t\text{-}Bu)]_2HCl$ (91) (L = $P(n\text{-}Pr)_2(t\text{-}Bu)$), which afforded with PhN_2^+, the diimine complex 92. By reaction of the bulky phosphines $P(t\text{-}Bu)_2R$ (R = Ph or *p*-MeC_6H_4) with $RuCl_3 \cdot nH_2O$ in 2-methoxyethanol, the dimeric species $[Ru(CO)_2\{P(t\text{-}Bu)_2R\}\,Cl]_2$ (93), whose structures has elucidated crystallographically [111], was prepared. The Ru—Ru distance in these complexes, 2.63 Å, is quite short. When $[Ru(CO)_2(P(t\text{-}Bu)_2Ph)Cl]_2$ and $[Ru(CO)_2\{P(t\text{-}Bu)_2(p\text{-}MeC_6H_4)\}Cl]_2$ were refluxed together in toluene, the mixed species $[\{P(t\text{-}Bu)_2Ph\}(CO)_2Ru(\mu\text{-}Cl)_2Ru(CO)_2\{P(t\text{-}Bu)_2(p\text{-}MeC_6H_4)\}]$ was formed and the P—P coupling (ca. 80 Hz) observed in the NMR spectrum of the complex was apparently transmitted through the metal—metal bond. Chloride ion could be metathetically displaced from **93** by Br^- or I^-, but with OAc^-, species **94** was produced. In the acetate J(PP) was greater than that in the chloride, possibly due to a release of steric strain occasioned by replacement of Cl by OAc thereby leading to greater linearity of the P—Ru—Ru—P bond system. Similar acetates could be obtained alternatively [112] from $Ru_3(CO)_{12}$, PR_3 and acetic acid. The compounds did not react with NO but, on chlorination, afforded $Ru_2(CO)_4L_2Cl_4$ (L = $P(t\text{-}Bu)_2Ph$ or $P(t\text{-}Bu)_2(p\text{-}MeC_6H_4)$) (**95** or **96**). When $Ru_2(CO)_4(P(t\text{-}Bu)_2Ph)_2Cl_4$ was treated with $P(t\text{-}Bu)_2Ph$ in 2-methoxyethanol, **93** (R = Ph) was regenerated, and with pyridine or PMe_2Ph the monomeric **97** (Q = py or PMe_2Ph). $Ru_3(CO)_{12}$ or $Ru(CO)_3(PPh_3)_2$ treated with 1,1,1-tris(diphenylphosphinomethyl)ethane (TDP), giving [113] $Ru(CO)_2$-(TDP) (**98**). This compound did not react with CO but with halogens formed $[Ru(CO)_2(TDP)X]^+ X^-$ (X = Cl or Br) which, on thermolysis, rearranged to $Ru(CO)(TDP)X_2$. Reaction of $Ru(CO)_2(PPh_3)_2Cl_2$ with TDP, or of $Ru(CO)_2$-(TDP) with O_2 and treatment of the resulting $Ru(CO)(TDP)(O_2CO)$ with HCl, gave $Ru(CO)(TDP)Cl_2$. Some reactions of this last compound are summarised in Scheme 10.



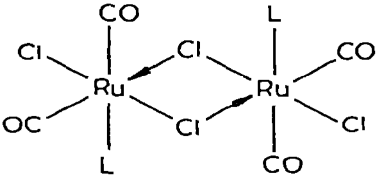
(92)



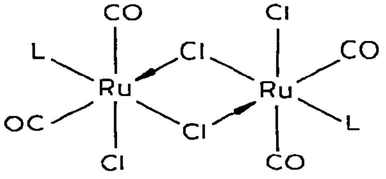
(93)



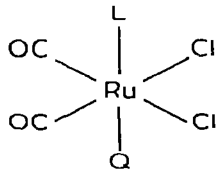
(94)



(95)



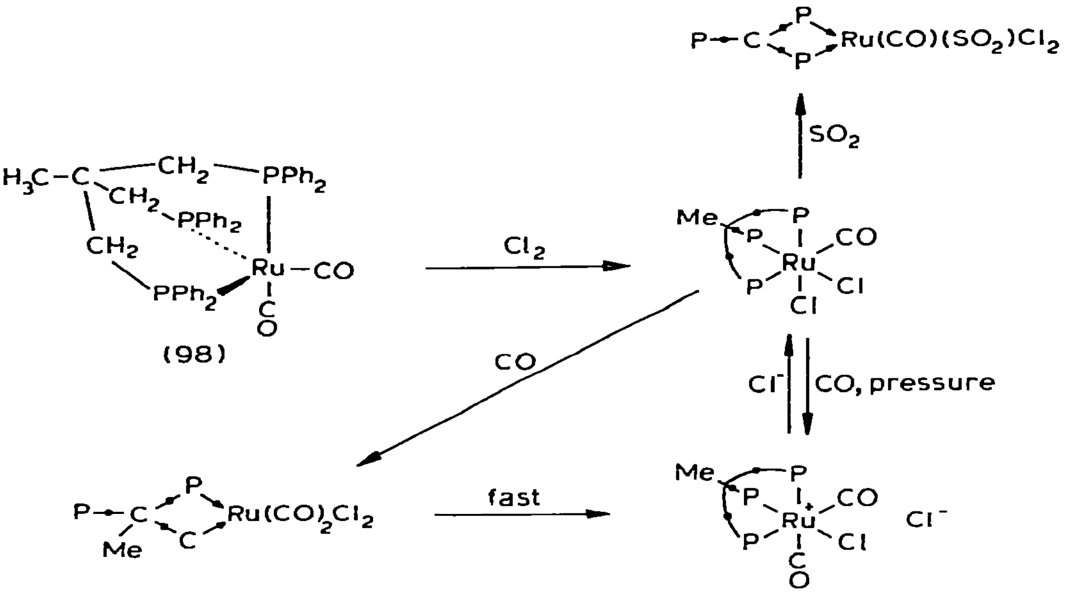
(96)



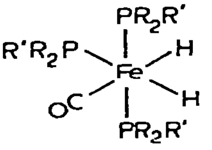
(97)

When $Ru(CO)_4(PPh_3)$ was pressurised with hydrogen in an IR high-pressure cell, $Ru(CO)_3(PPh_3)H_2$ could be identified, and the equilibrium CO + $Ru(CO)_3(PPh_3)H_2 \rightleftharpoons Ru(CO)_4(PPh_3) + H_2$ was confirmed using deuterium isotopic labelling [114]. At low temperatures, $Ru(CO)_5$ reacted with H_2 giving $Ru(CO)_4H_2$ which, at 20°, decomposed into polynuclear products. The temperature dependencies of the ^1H and ^{31}P NMR spectra of $M(CO)L_3H_2$ (M = Fe

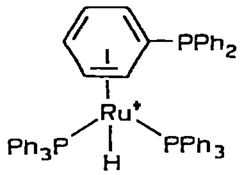
SCHEME 10



or Ru; L = phosphite, phosphine, phosphinite or phosphonite) have been reported [115]. These complexes underwent *cis* ⇌ *trans* rearrangements via an intramolecular "tetrahedral jump" mechanism. When M = Fe and L = PPh_2Me



(99)

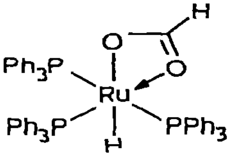


(100)

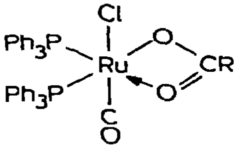
or PPh_2Et, which exist upon formation as the *cis*-isomer, 99, the barrier to interconversion to the *trans* form is ca. 12.5 kcal/mol.

Treatment of $Ru(PPh_3)_4H_2$ with $[Ph_3C][PF_6]$ afforded [116] the coordinatively unsaturated $[Ru(PPh_3)_4H][PF_6]$. This hydride reacted with HCHO, and with p-$MeC_6H_4SO_2N(NO)Me$, giving $Ru(CO)(PPh_3)_3H_2$ and $Ru(NO)_2(PPh_3)_2$, respectively. With norbornadiene or cyclooctadiene, $[Ru(diene)(PPh_3)_3H]^+$ was formed. Dissolution of the red $[Ru(PPh_3)_4H]^+$ gave, after a few hours, a green solution from which a light yellow species, $[Ru(PPh_3)_3H]^+$ (100) was isolated. The same species was also prepared from $[Ru(PPh_3)_4H]^+$ by heating in polar or non-polar solvents. Reduction of 100 with $NaBH_4$ afforded $Ru(PPh_3)_3H_4$.

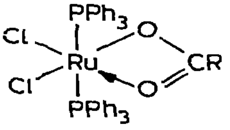
Reaction of $Ru(PPh_3)_4H_2$, $Ru(N_2)(PPh_3)_3H_2$ or $Ru(PPh_3)_3H_4$ with CO_2 gave [117] $Ru(PPh_3)_3H(O_2CH)$ (101), which may exist in an equilibrium with $Ru(PPh_3)_3(CO_2)H_2$. Treatment of the formate with CO gave $Ru(CO)(PPh_3)_3H_2$ and CO_2, and with CS_2, $Ru(PPh_3)_2(S_2CH)_2$ and CO_2 were formed. Reaction of 101 with HX or RX (X = Cl, Br or I; R = allyl) afforded only $Ru(PPh_3)_3HX$. Treatment of $Ru(CO)(PPh_3)_2HCl$ with carboxylic acids (RCO_2H) gave [118]



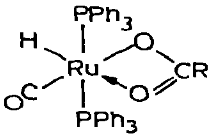
(101)



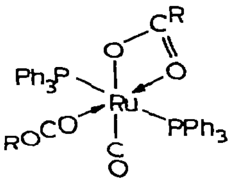
(102)



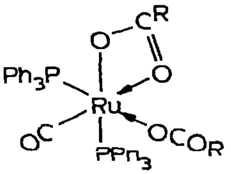
(103)



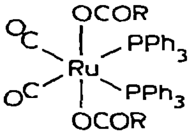
(104)



(105)



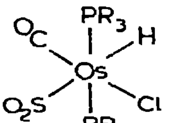
(106)



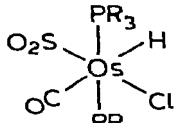
(107)

$Ru(CO)(PPh_3)_2(OCOR)$ (**101**, **102** or **103**). Carboxylic acids with pK_a values greater than ca. 4.2 reacted with $Ru(CO)(PPh_3)_3H_2$ in boiling 2-methoxyethanol giving $Ru(CO)(PPh_3)_2(O_2CR)H$ (**104**), whereas acids having pK_a < 4.2 gave $Ru(CO)(PPh_3)_2(OCOR)(O_2CR)$ (**105**) or, less likely, **106**; **107** was obtained by reaction of RCO_2H with $Ru(CO)_3(PPh_3)_2$. The phenylarsonato complexes, $Ru(CO)_2L_2(O_3AsPh)$ (L = triarylphosphine or arsine) and $Ru(CO)_2(LL)(O_{2.5}AsPh)_2$ (LL = $Ph_2MCH_2CH_2MPh_2$, M = P or As) have been reported [119]; the ligand O_3AsPh is bidentate in these species.

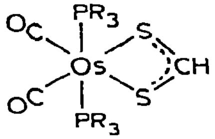
Reaction of $Os(CO)[P(C_6H_{11})_3]_2HCl$ with SO_2 in benzene gave [120] $Os(CO)[P(C_6H_{11})_3]_2(SO_2)HCl$ (**108** or **109**), as a benzene solvate. With CS_2, the hydrido chloride gave **110** or $Os(CO)[P(C_6H_{11})_3]_2(CS_2)HCl$ (**111**). Carbonylation of OsL_3H_4 (L = tertiary phosphine or arsine) with CO produced [121]



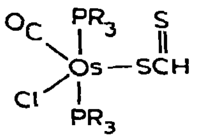
(108)



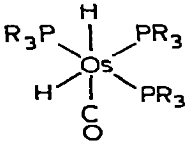
(109)



(110)

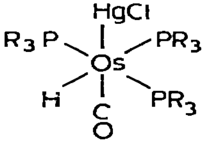


(111)

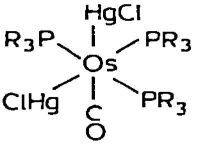


(112)

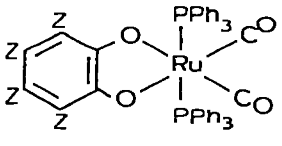
$Os(CO)L_3H_2$ (**112**, L = PR_3), also obtainable by similar treatment of *cis*-OsL_2H_4 in boiling toluene, or by refluxing OsL_3H_4 in 2 methoxyethanol. With $Os(PPh_3)_3H_4$, a mixture of $Os(CO)(PPh_3)_3H_2$ and $Os(CO)_2(PPh_3)_2H_2$ was produced. When treated with four equivalents of 1,5-cyclooctadiene at 100° in ethanol, $Os(PPh_2Et)_3H_4$ gave cyclooctene (50%), unreacted cyclooctadiene and $Os(C_8H_{12})(PPh_3)_3(EtOH)$. With twelve equivalents of the diene various octenes, two equivalents of octane, and the olefin complex, were formed. With PhC≡CPh, 40% reduction to 1,2-diphenylethylene was achieved and an unidentified acetylene-free olefin complex was produced. Isomerisation and hydrogenation of 1-octene was accomplished using *cis*-$Os(PPh_2Et)_4H_2$, and the amount of octane formed indicated the transfer of more than two H atoms per Os complex to the octene. This suggested that hydrogen is made available from the phenyl group of the coordinated phosphine. $Os(CO)(PPh_2Et)_3H_2$ isomerised octenes in boiling toluene without forming octane, and the isomerisation of the 1-ene was faster than the 2-ene. Treatment of $Os(CO)_2(PR_3)_2$ with HCl afforded $Os(CO)(PR_3)_3HCl$ and then $Os(CO)(PR_3)_3Cl_2$, and with $HgCl_2$, both **113** and **114** were produced.



(113)

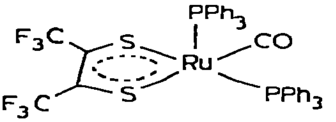


(114)

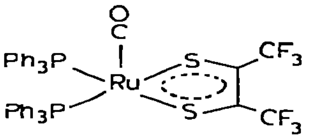


(115)

The dioxylene complexes **115** (Z = Cl or Br) underwent [122] one-electron oxidation affording paramagnetic cations; the unpaired electron was probably located in the π-orbitals of the dioxylene ligand. The structures of the violet and orange forms of $Ru(CO)(PPh_3)_2[S_2C_2(CF_3)_2]$ (**116** and **117**) have been established [122] crystallographically.



(116)

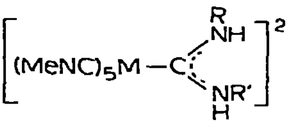


(117)

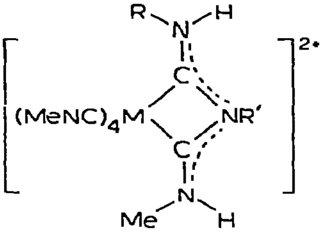
Metal isocyanides

Treatment of $K_3[Fe(CN)_6]$ with $MeOSO_3F$ gave [123] $[Fe(CNMe)_5(CN)][SO_3F]$. In alkaline media both the *cis*- and *trans*-isomers of $Fe(CNMe)_4(CN)_2$ decomposed [124] into Fe^{2+} and free isocyanide in an S_N2 process involving nucleophilic attack by OH^-. UV irradiation facilitated the exchange of CNMe with H_2O. The Mössbauer spectrum of $[Fe\{CN(p\text{-}MeC_6H_4)\}_5I]I_3$ has been reported [125].

Addition of amine to $[M(CNR)_6]^{2+}$ (M = Fe or Ru; R = Me or Et) afforded [126] the "carbene" complexes **118** or **119**, the particular species formed being determined apparently by steric effects. Thus $[Ru(CNMe)_6]^{2+}$ reacted with $MeNH_2$ giving, after 15 min, **118** (R = R′ = Me) but after longer periods [Ru-



(118)

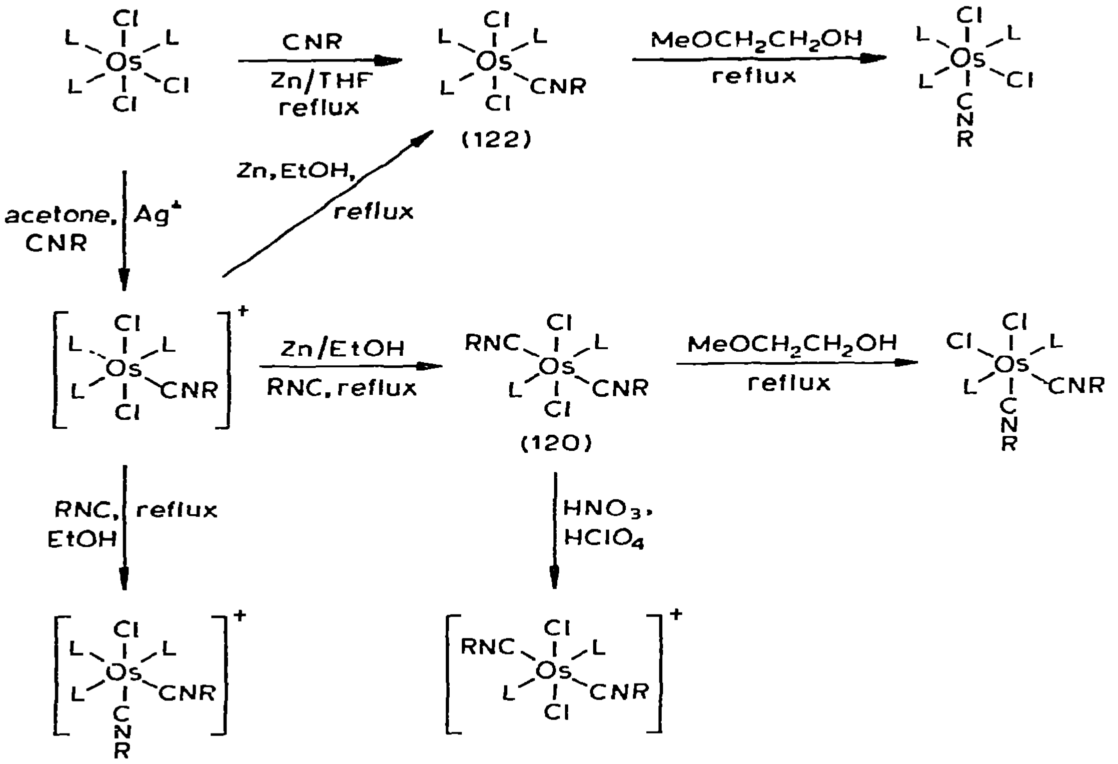


(119)

$(CNMe)_4\{C(NHMe)_2\}_2]^{2+}$ was formed. Ethylamine behaved somewhat similarly giving **118** (R = Me, R' = Et), and **118** (R = Et, R' = Me); the latter existed as two isomers due to steric constraints within the planar carbene ligand. $[Fe(CNMe)_6]^{2+}$ reacted with methylamine affording **119** (R = R' = Me), the structure of which has been confirmed crystallographically [127]. The mechanism of formation possibly involved prior formation of **118** (R = R' = Me), but because of the close proximity of the ligands in these Fe^{II} species, the carbene in the intermediary **118** could behave as a nucleophile towards a second isocyanide ligand, thereby effecting ring closure to give **119**. The hexaisocyanoiron(II) complex also reacted with $EtNH_2$ giving **119** (R = Me, R' = Et) and **119** (R = Et, R' = Me), the latter being isolated as two isomers (vide supra). Ammonia added to $[Fe(CNMe)_6]^{2+}$ giving **118** (R = H, R' = Me). When $[Ru(CNMe)_6]^{2+}$ was treated with CD_3NH_2, a mixture of **118** (R = Me, R' = CD_3) and **118** (R = CD_3, R' = Me) was formed. On heating, the methyl and perdeuteromethyl positions were "scrambled" in a process presumably involving an intermediate like **119**. After heating $[Ru(CNMe)_5\{C(NHEt)(NHMe)\}]^{2+}$ in DMSO for 6 h, $[Ru(CNMe)_4(CNEt)\{C(NHMe)_2\}]^{2+}$ (probably with *trans* geometry) was formed. Reaction of CD_3NH_2 with $[Fe(CNMe)_6]^{2+}$ in refluxing methanol also afforded a perdeuteromethyl-containing species, **119**, in which the majority of CD_3 was located in the chelated "carbene" ring, although some "scrambling" to isocyanide positions occurred.

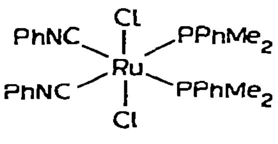
A series of isocyanide complexes of osmium(II) and -(III) has been prepared (Scheme 11) [128]. Reaction of $[NH_4]_2[OsBr_6]$ with an excess of CNMe in ethanol gave *trans*-$Os(CNMe)_4Br_2$, while addition of an excess of CNPh in THF to $Os(CO)_2(PEt_3)_2Cl_2$ (configuration **120**, L = CO) provided $Os(CO)(CNPh)(PEt_3)_2Cl_2$ (also with configuration **120**, one L being CNPh, the other CO). Treatment of *mer*-$Os(PR'_3)_3Cl_3$ with CNR in acetone in the presence of $AgClO_4$ afforded $[Os(CNR)(PR'_3)_3Cl_2][ClO_4]$ and methylation of $K_3[Os(CN)_6]$ by either Me_2SO_4 or $MeOSO_3F$ gave $[Os(CNMe)_6]^{2+}$. The ruthenium complex $Ru(CNPh)_2(PPhMe_2)_2Cl_2$ (**121**) was obtained by the reduction of *mer*-$Ru(PPhMe_2)_3Cl_3$ by zinc in refluxing THF in the presence of CNPh. The uncharged M^{II} isocyano species were inert to attack by ROH, RNH_2, or OEt^-, but $Os(CNPh)(PPhMe_2)_3Cl_2$ (**122**) reacted with BH_4^- giving the hydride **123**. The cationic $[Os(CNR)_2(PR'_3)_3Cl][ClO_4]$ was also inert to amine or alkoxide attack, but primary amines reduced $[Os(CNR)_2(PR'_3)_2Cl_2]^+$ and $[Os(CNR)(PPhMe_2)_3Cl_2]^+$ to neutral Os^{II} compounds. $[Os(CNPh)(PEt_3)_3Cl_2][ClO_4]$ reacted with RNH_2 giving $Os(CNPh)(NH_2R)(PEt_3)_2Cl_2$ (R = Me or Et) (**124**) and $[Os(CNMe)_6][SO_3F]_2$, on treatment with $MeNH_2$ in refluxing methanol, afforded **125** and **126** (in the latter the "carbene" ligands probably had *amphi* configurations).

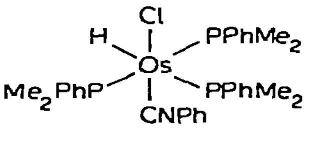
SCHEME 11

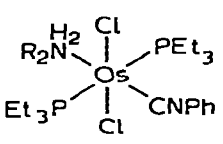


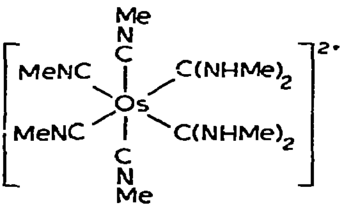
L = PPhMe$_2$, PPhEt$_2$, PPh-n-Bu$_2$, PEt$_3$; R = Me, Ph, p-MeOC$_6$H$_4$, p-O$_2$NC$_6$H$_4$, CO

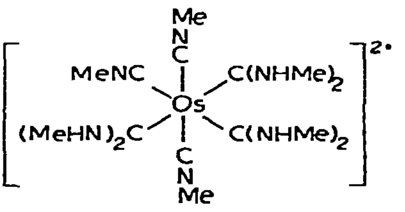
A correlation was drawn up between $\Delta\nu$(RN≡C) (ν(NC)(free ligand) − ν(NC)(coord. ligand)) and the reactivity of the bound CNR towards nucleophilic attack. It appeared that for coordinated CNMe, those species having $\Delta\nu$(NC) greater than 65 cm^{-1} were reactive towards MeNH$_2$, but it was suggested that the appropriate $\Delta\nu$ value for other isocyanides might be lower.


(121)


(123)


(124)


(125)

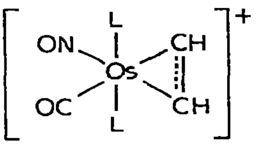

(126)

Metal nitrosyl and aryldiazo complexes

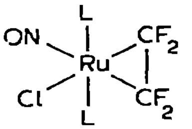
Mononitrosyl compounds

From dipole moment studies it was estimated [129] that the L group in $Fe(CO)_2(NO)L(SnPh_3)$ (L = CO, PPh_3, $AsPh_3$ or $P(OPh)_3$) was *cis* to the axial $SnPh_3$ ligand. This contrasted with the situation in analogous Mn and Co complexes. In $Hg[Fe(CO)_2(NO)\{P(OPh)_3\}]_2$, the phosphite ligands probably occupy equatorial sites in the coordination sphere of each Fe atom.

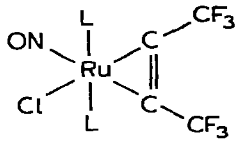
In attempts to prepare species analogous to $[Fe(CO)_2(NO)L_2]^+$ [130], $M(CO)_3(PPh_3)_2$ (M = Ru or Os) was treated [131] with $NOPF_6$ in methanol. The products, however, were $[M(CO)_3(PPh_3)_2H]^+$, in accord with the reaction $NOPF_6 + MeOH \rightarrow HPF_6 + MeONO$. These hydrides could be prepared by protonation of $M(CO)_3(PPh_3)_2$ using HPF_6, $HClO_4$ or HBF_4. A ruthenium nitrosyl, $[Ru(CO)_2(NO)(PPh_3)_2]^+$ was produced by reaction of $NOPF_6$ in methanol with $Ru_3(CO)_9(PPh_3)_3$, but there was no evidence for the formation of $[Ru(CO)_3(NO)(PPh_3)]^+$; the analogous osmium cation could not be obtained by this route. The nitrosyl cations, $[M(CO)_2(NO)(PPh_3)_2]X$, could be conveniently produced by abstraction of Cl^- from $M(CO)(NO)(PPh_3)_2Cl$ using NaX (X = BPh_4 or PF_6) in the presence of CO (complexes containing $P(C_6H_{11})_3$ were also prepared). Displacement of CO from $[M(CO)_2(NO)(PPh_3)_2]^+$ by PPh_3 afforded $[M(CO)(NO)(PPh_3)_3]^+$, and reactions with PPh_2Me and $Ph_2PCH_2CH_2PPh_2$ (diphos) gave $[Os(CO)(NO)(PPh_2Me)_3]^+$, and $[M(CO)(NO)(PPh_3)(diphos)]^+$, respectively. With an excess of diphos and under more vigorous conditions, $[M(NO)(diphos)_2]^+$ was produced. Treatment of $M(CO)(NO)(PPh_3)_2Cl$ with $AgPF_6$ in acetone afforded $[M(CO)(NO)(PPh_3)_2(acetone)]^+$, and the acetone could be displaced by L (L = CO when M = Os or PPh_3 when M = Ru). Chlorination of $[M(CO)_2(NO)L_2]^+$ gave $Ru(NO)L_2Cl_3$ with some *cis*-$Ru(CO)_2L_2Cl_2$, and *cis*-$Os(CO)_2L_2Cl_2$, respectively. With HCl, however, the osmium cation afforded $Os(CO)(HNO)(PPh_3)_2Cl_2$. Addition of halide ion to the cations led to $M(CO)(NO)L_2X$ (X = Cl or I). Oxygenation of $[Os(CO)_2(NO)(PPh_3)_2]^+$ in the presence of Cl^- gave $Os(NO)(PPh_3)_2(CO_3)Cl$, presumably via $Os(CO)(NO)(PPh_3)_2Cl$ as an intermediate. Methoxide addition afforded $Os(CO)(NO)(PPh_3)_2(CO_2Me)$ and borohydride reduction of $[Os(CO)(NO)(PPh_3)_3]^+$ gave the stereochemically non-rigid $Os(CO)(NO)(PPh_3)_2H$. Addition of acetylenes, $RC{\equiv}CR'$ (R = R' = H, Ph or CO_2Me, R = H, R' = Ph) to $[Os(CO)(NO)L_2(acetone)][PF_6]$ (L = PPh_3 or $P(C_6H_{11})_3$) led to the formation of the fluxional $[Os(CO)(NO)L_2(RC_2R')][PF_6]$ (127) [132]. It was suggested that the coordinated acetylene undergoes "propeller-like" rotation.



(127)

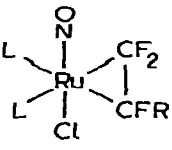


(128)

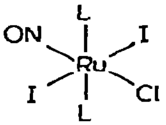


(129)

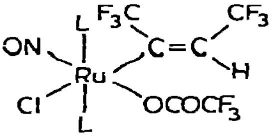
Oxidative addition of C_2F_4 and $CF_3C{\equiv}CCF_3$ to $Ru(NO)L_2Cl$ (L = PPh_3, PPh_2Me, $PPhMe_2$) afforded [133] **128** and **129**. However, $Ru(NO)(PPhMe_2)_2Cl$ reacted with $CF_2{=}CFR$ (R = Cl or CF_3) giving **130** while iodination of $Ru(NO)(PPh_2Me)_2Cl$ gave $Ru(NO)(PPh_2Me)_2ClI_2$ (**131**). Addition of CF_3CO_2H to **129** (L = PPh_3 or PPh_2Me) gave **132**.



(130)



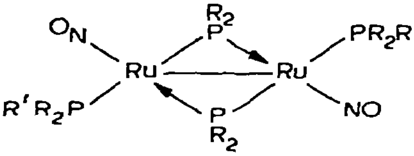
(131)



(132)

A temperature variation study of the ^{31}P NMR spectra of [M(NO)(diphos)$_2$] (M = Fe or Ru) revealed [134] that these complexes underwent a Berry-type pseudo-rotation (Fig. 8). It was suggested that the transition state had a square pyramidal geometry with axial NO, and that bending of the M—N—O bond might accompany pseudo-rotation thereby having an observable influence on the activation energy for the process.

Reduction of Ru(NO)(PPh$_2$Me)$_2$Cl$_3$ with Li metal in THF in the presence of PPh$_3$ gave [135] [Ru(NO)(PPh$_2$Me)(μ-PPh$_2$)]$_2$ (133), and [Ru(NO)(PPh$_3$)(μ-PPh$_2$)]$_2$ could be obtained by an analogous reaction between Ru(NO)Cl$_3$ · 2H$_2$O, Li and PPh$_3$, or by thermolysis of Ru(NO)(PPh$_3$)$_3$H in decalin. The structure of 133 was confirmed crystallographically, and each Ru atom had a distorted octahedral geometry; the Ru—Ru distance (2.63 Å) was short enough to be consistent with a double bond formulation. Treatment of Ru(NO)(PPh$_3$)$_2$Cl with Ph$_2$PCH$_2$CH$_2$PPh$_2$ (diphos) gave [136] Ru(NO)(diphos)$_2$Cl which, with NaBPh$_4$, afforded [Ru(NO)(diphos)$_2$][BPh$_4$]. The trigonal bipyramidal nature of this cation, isolated as an acetone solvate, was confirmed crystallographically; the NO group occupied an equatorial site. The Ru—N—O bond angle was 174° and the complex was regarded as a Ru^0 (d^8) complex containing NO$^+$.



(133)

The tetraphenylporphyriniron(III) complex, Fe(TPP)Cl absorbed nitric oxide giving [137] the paramagnetic Fe(NO)(TPP)Cl (μ = 4.5 BM). The electronic spectrum of this species was similar to that of the CO adduct of the Fe^{II} myoglobin complex and to nitrosyl complexes of ferric peroxidase. On this basis, the porphyrin adduct was described as Fe^{II}(NO$^+$)(TPP)(Cl$^-$), where, effectively, a whole electron was transferred from NO to Fe^{III}. Loss of "NOCl"

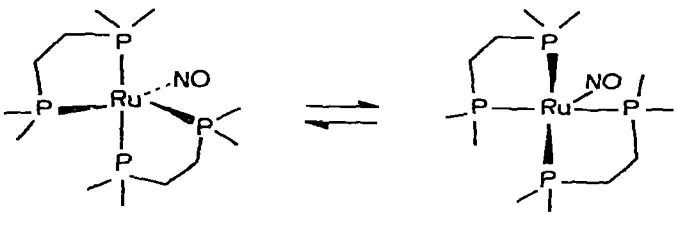


Fig. 8.

occurred in methanol, but the resultant $Fe^{II}(TPP)$ gave a 1/1 adduct with NO which formed, with nitrogenous bases, a series of paramagnetic ($S = 2$) six-coordinate complexes.

By heating $Na_2[Ru(NO)(NO_2)_4(OH)]$ in aqueous HCl the salt $Na_2[Ru(NO)Cl_5]$ was obtained [138]. The K^+ and NH_4^+ salts of $[Ru(NO)X_5]^{2-}$ (X = Br or I) are isostructural with the octahedral $K_2[Ru(NO)Cl_5]$. The product of hydrolysis of $[NH_4]_2[Ru(NO)Cl_5]$ was identified [139] crystallographically as $[NH_4]_2[Ru(NO)(H_2O)Cl_4]$ in which the octahedral Ru atom was coordinated linearly by NO *trans* to H_2O. UV irradiation, or electrolytic or chemical reduction, of $[Fe(NO)(CN)_5]^{2-}$ afforded [140] the paramagnetic $[Fe(NO^{\bullet})(CN)_5]^{2-}$ in which the added electron was located on the NO ligand; this species eventually gave $[Fe(NO)(CN)_5]^{3-}$.

At pH values below 7, $[Ru(NH_3)_6]^{3+}$ reacted [141] with NO giving $[Ru(NH_3)_5(NO)]^{3+}$, but at values above 8.3, NO attacked a coordinated NH_3 giving $[Ru(NH_3)_5(N_2)]^{2+}$. Reduction of $[Ru(NH_3)_5(NO)]^{3+}$ to $[Ru(NH_3)_6]^{2+}$ was achieved [142] using Cr^{2+} in acid media. Nitric oxide reacted with *cis*-$[Ru(NH_3)_4X_2]^{m+}$ (X = H_2O, OH, Cl, Br or I) producing [143] *cis*-$[Ru(NH_3)_4(NO)X]^{n+}$. Preliminary studies of *cis*—*trans*-interconversion indicated that isomerisation did not occur readily in the solid state or in acid solution, but that the *cis*-form was slowly converted to the *trans*-isomer in alkaline solution.

Nitrosylation by NO of $[Os(NH_3)_5I]I_2$ gave [144] $[Os(NH_3)_5(NO)]I_3$ and $[Os(NH_3)_4(NO)I]I_2$; the latter was converted to the former in liquid ammonia. Attack by hydroxide ion on $[Os(NH_3)_5(NO)]X_3$ (X = Cl, Br or I) gave $[Os(NH_3)_4(NH_2)(NO)]X_2$, but under different, more vigorous, conditions, *trans*-$[Os(NH_3)_4(NO)(OH)]X_2$ was formed. When this hydroxide was refluxed with hydrohalic acids, *trans*-$[Os(NH_3)_4(NO)X]X_2$ was produced. Although $[Os(NH_3)_5(NO)]^{3+}$ reacted with refluxing hydrazine to give $[Os(NH_3)_5(N_2)]^{2+}$, none of the other species underwent nucleophilic attack at the nitrosyl ligand.

The likelihood of nucleophilic attack at coordinated NO has been correlated [145] with $\nu(NO)$, and the NO stretching force constant ($f(NO)$), in a series of nitrosyl complexes (Table 1). Thus, species with $\nu(NO) > 1886\ cm^{-1}$ or $f(NO) > 13.8$ mdyn/Å will be attacked at the nitrosyl group by OH^-, hydrazine, hydroxylamine or azide ion.

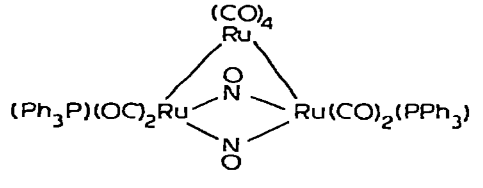
Dinitrosyl complexes

Treatment of $FeCl_2$ in methanol containing NEt_3 or tetramethylethylenediamine with NO gave [146] $[Fe(NO)_2Cl_2]^-$ (isolated as the $NHEt_3^+$ salt), but when PPh_3 was added to the reaction mixture, $Fe(NO)_2(PPh_3)Cl$ and $Fe(NO)_2(PPh_3)_2$ were formed. The synthesis of $[Fe(NO)_2I]_2$, from solid FeI_2 and NO, has been reported [147] in detail.

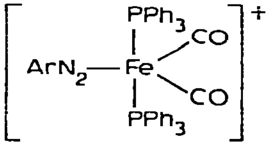
Partial or total displacement of fluoride ion occurred [148] when $Fe(NO)_2(PF_3)_2$ was treated with hydroxide or alkoxide ions, respectively. Thus, in diisopropylamine/water mixtures, OH^- reacted to give $[Fe(NO)_2(PF_2O)_2]^{2-}$ but with $Ba(OH)_2$ in THF, $[Fe(NO)_2(PF_3)(PF_2O)]^-$ was formed. Ethylation of these produced $Fe(NO)_2(PF_3)_{2-n}(PF_2OEt)_n$ ($n = 1$ or 2); with alkoxides, $Fe(NO)_2(PF_3)_2$ afforded $Fe(NO)_2[P(OR)_3]_2$ (R = Me, Et, n-Pr, i-Pr, n-Bu or Ph) directly. The ESR spectrum of $Fe(NO)_2(SbR_3)Br$ (R = Et, Ph or 4-$Me_2NC_6H_4$) has been reported [149]; hyperfine splittings due to Sb and Br were observed.

In a reinvestigation of complexes originally formulated [150] as $[\mathrm{Fe(NO)_2L}]^+\mathrm{X}^-$ (L = thiourea, thioacetamide, thiobenzamide, *o*-aminothiophenol and diphenylthiourea) it was shown [151] that the compounds were non-electrolytes, did not contain bidentate L, and probably had tetrahedral structures. $\mathrm{Ru(NO)_2(PPh_3)_2}$ was prepared [152] by reaction of NO with $\mathrm{Ru(PPh_3)_3H_4}$, while with NOCl, $\mathrm{Ru(NO)(PPh_3)_2Cl_3}$ was produced; CO gave $\mathrm{Ru(CO)(PPh_3)_3H_2}$.

The reaction between $\mathrm{Ru_3(CO)_{10}(\mu\text{-}NO)_2}$ and $\mathrm{PPh_3}$, in which 134 was formed, obeyed [153] first order kinetics. There was no dependence on $\mathrm{PPh_3}$ concentration over a wide range, but with more alkylated phosphines, e.g. $\mathrm{PPh_2Me}$, 134 slowly cleaved to give $\mathrm{Ru(CO)_3L_2}$. However, the rate of primary substitution remained virtually the same and was independent of the nature, as well as of the concentration, of the substrate. The mechanism therefore appeared to involve initial dissociation, giving $\mathrm{Ru_3(CO)_9(\mu\text{-}NO)_2}$. A comparison of the data collected here was made with that obtained from reactions of $\mathrm{Ru_3(CO)_{12}}$ with tertiary phosphines [154]. Both sets of information were consistent with a dissociative mechanism, and it was clear that the bridging NO groups played no important role in the process. It was suggested, however, that after monosubstitution of $\mathrm{Ru_3(CO)_{12}}$, giving $\mathrm{Ru_3(CO)_{11}L}$, some change in reactivity of the Ru atoms occurred, possibly occasioned by the transient formation of labile bridging carbonyl species.



(134)



(135)

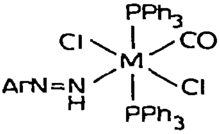
Photolysis of $\mathrm{Os(CO)_5}$ in the presence of NO in an argon matrix at 20 K afforded [155] some $\mathrm{Os(CO)_2(NO)_2}$. Photolysis of $\mathrm{Fe(CO)_2(NO)_2}$ gave only $\mathrm{Fe(CO)_5}$ and NO.

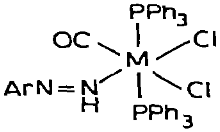
Aryldiazo complexes

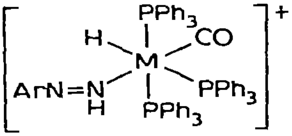
Addition of $[\mathrm{ArN_2}][\mathrm{BF_4}]$ to $\mathrm{Fe(CO)_3(PPh_3)_2}$ and $[\mathrm{Fe(CO)_3(NO)}]^-$ afforded [156] 135 (Ar = *p*-$\mathrm{XC_6H_4}$; X = H, F, Cl, Br, $\mathrm{NO_2}$, OMe, OH, but not $\mathrm{NMe_2}$) and the unstable, tetrahedral $\mathrm{Fe(CO)_2(NO)(N_2Ph)}$, respectively. At −70°, the latter reacted with $\mathrm{PPh_3}$ giving $\mathrm{Fe(CO)(NO)(N_2Ph)(PPh_3)}$; no products were obtained by reaction of aryldiazonium salts with $[(\pi\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2}]^-$ or $[\mathrm{Fe(CO)_4(SnPh_3)}]^-$. It was shown that the aryldiazo group had lower π-acceptor properties than NO, and resisted catalytic hydrogenation. A preliminary X-ray crystallographic study of 135 (X = H) revealed that the Fe—N—N bond angle is ca. 180° while the N—N—Ph angle is ca. 124°; the N—N distance is 1.19 Å.

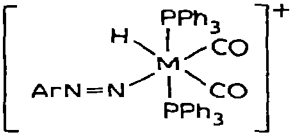
The coordinatively unsaturated $\mathrm{Ru(PPh_3)_3X_2}$ (X = Cl or Br) and $\mathrm{Os(PPh_3)_3Br_2}$ reacted with $[\mathrm{ArN_2}][\mathrm{BF_4}]$ (Ar = *p*-$\mathrm{C_6H_4}$; X = Me, OMe, Cl, $\mathrm{NO_2}$ or H) in the presence of LiX giving [157] $\mathrm{M(N_2Ar)(PPh_3)_2X_3}$ (M = Ru or Os). These species could also be synthesised by treating $\mathrm{MX_3}$ with 1,3-diaryltriazenes in ethanol in the presence of $\mathrm{PPh_3}$; they were resistant to protonation. M(CO)-

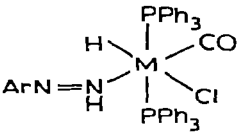
$(PPh_3)_3HCl$ (M = Ru or Os) afforded $[M(CO)(NH{=}NAr)(PPh_3)_2Cl(BF_4)]$ on treatment with $[ArN_2][BF_4]$, and the corresponding osmium perchlorate was produced using $[ArN_2][ClO_4]$. In these species, the BF_4^- or ClO_4^- was believed to be coordinated to the metal. Then treatment with LiCl and with CO led to the isolation of $M(CO)(NH{=}NAr)(PPh_3)_2Cl_2$ (136) and $[M(CO)_2(NH{=}NAr)(PPh_3)_2Cl][BF_4]$, respectively. Recrystallisation of the former (Ar = *p*-MeC_6H_4) caused isomerisation to 137, and treatment of the latter with LiCl gave mixtures of $M(CO)(NH{=}NAr)(PPh_3)_2Cl_2$ and *cis*-$M(CO)_2(PPh_3)_2Cl_2$. Treatment of $M(CO)(PPh_3)_3H_2$ with $[ArN_2][BF_4]$ gave $[M(CO)(NH{=}NAr)(PPh_3)_3H][BF_4]$ (138), and while the osmium complex did not react with CO, the ruthenium compound afforded $[Ru(CO)_2(NH{=}NAr)(PPh_3)_2H][BF_4]$ (139). Reaction of 138

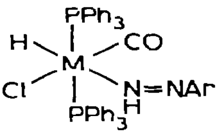

(136)


(137)


(138)

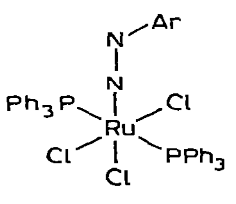

(139)


(140)

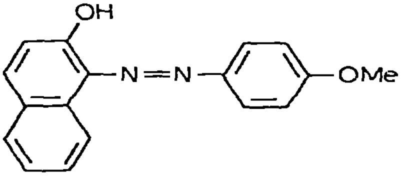

(141)

with LiCl in cold acetone/methanol mixtures gave a mixture of isomers of $Ru(CO)(NH{=}NAr)(PPh_3)_2HCl$ (140 and 141); conversion of the former into the latter was rapid on recrystallisation. In boiling acetone/methanol mixtures, however, $M(CO)(NH{=}NAr)(PPh_3)_2Cl_2$ was formed. The structure of $Ru[N_2$-(*p*-$MeC_6H_4)](PPh_3)_2Cl_3$, inadvertently obtained [158] by reaction of $Ru(PPh_3)_3Cl_2$ with the diazonium salt (addition of LiCl improved yields), has been determined crystallographically. The molecule (142) has an effectively linear Ru—N—N bond system (171.2°), while the N—N—Ar bond angle is 135.9°.

Metal-assisted diazotisation occurred when *cis*-$[Ru(bipy)_2(NO)Cl]^{2+}$ was treated with $ArNH_2$ (Ar = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$) in acetonitrile [159]. The product was *cis*-$[Ru(bipy)(N_2Ar)Cl]^{2+}$ which, on treatment with KI gave, when Ar = *p*-$MeOC_6H_4$, *p*-$MeOC_6H_4I$ and $Ru(bipy)_2I_2$; with β-naphthol and NaOH in ethanol, 143 and $Ru(bipy)_2(OH)Cl$ were produced.


(142)

(Ar = *p*–MeC_6H_4)

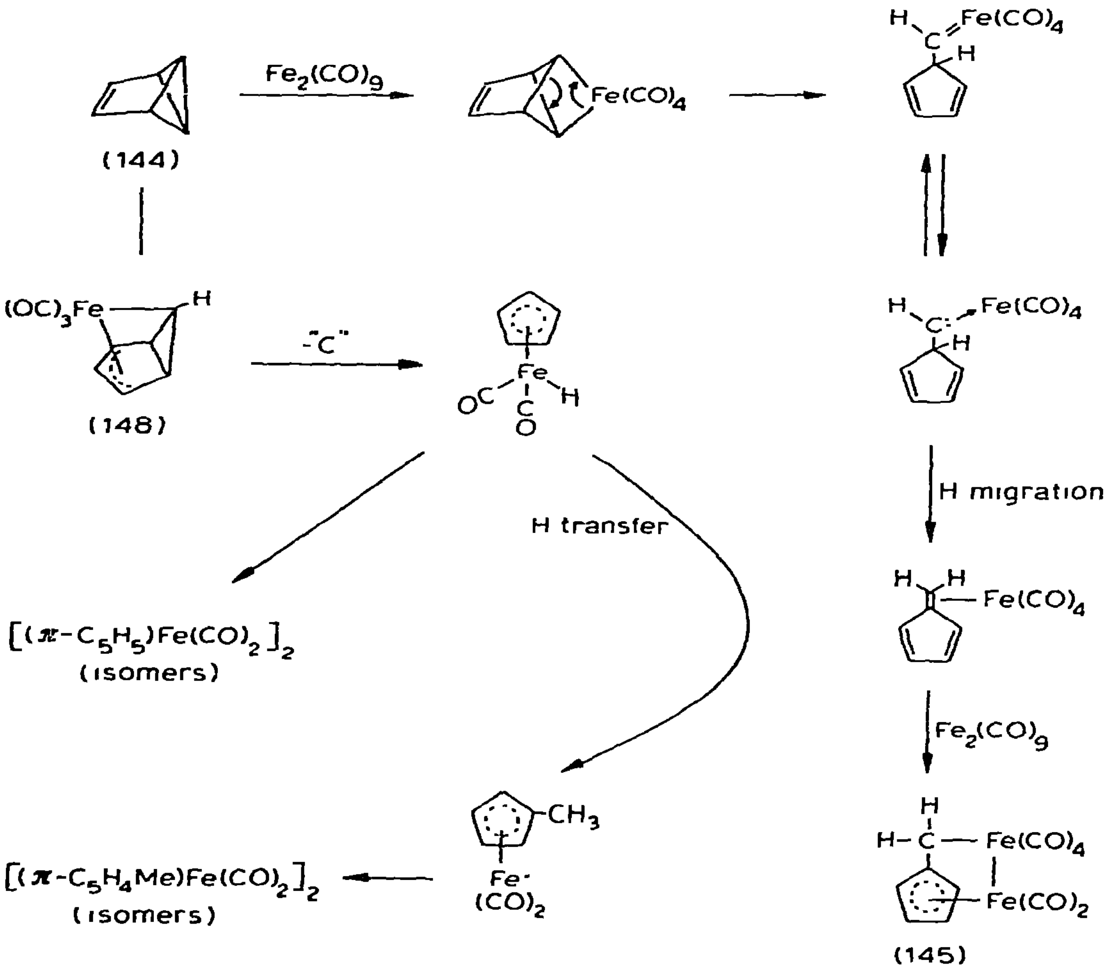

(143)

π-Cyclopentadienyl complexes

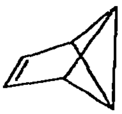
Binuclear cyclopentadienyl compounds

Reaction of $Fe_2(CO)_9$ with benzvalene (144) gave *cis*-[(π-C_5H_4Me)Fe-(CO)$_2$]$_2$, *cis*- and *trans*-[(π-C_5H_5)Fe(CO)$_2$]$_2$ (involving loss of a CH group from a C_6H_6 precursor) and 145 [160]. A mechanism is outlined in Scheme 12. Benzobenzvalene (146) afforded with $Fe_2(CO)_9$ only 147 and no bis-π-indenyl complexes were detected, possibly because a σ—π intermediate, e.g. 148, is impossible for benzobenzvalene. It may be recalled that benzosemibullvalene (149) gave [161] only σ—π complexes with $Fe_2(CO)_9$, viz. 150.

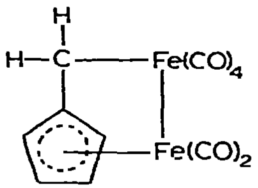
SCHEME 12



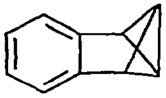
Cyclopentadiene reacted [162] with $Ru_3(CO)_{12}$ giving, as an intermediate, $C_5H_6Ru(CO)_3$. This underwent a hydride shift affording (π-C_5H_5)Ru(CO)$_2$H which very slowly dimerised, with H_2 loss, in refluxing heptane in the absence of air. When air was admitted, 60-70% yields of *trans*-[(π-C_5H_5)Ru(CO)$_2$]$_2$ were obtained. Cyclopentadiene also reacted with $Ru_4(CO)_{12}X_4$ (X = H or D) afford-



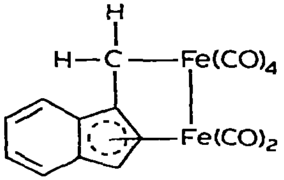
(144)



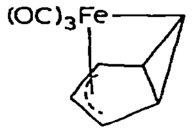
(145)



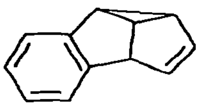
(146)



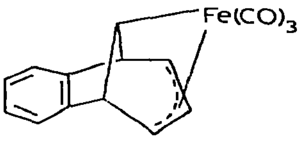
(147)



(148)



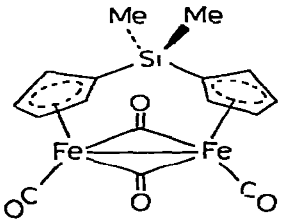
(149)



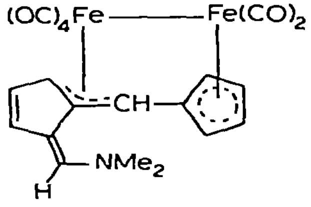
(150)

ing exclusively (π-C_5H_5)Ru(CO)$_2$H proving that the source of hydride ligand was C_5H_6 itself. While Os$_4$(CO)$_{12}$H$_4$ did not react with C_5H_6 in refluxing octane, Os$_3$(CO)$_{12}$ gave a mixture of uncharacterised products, and Os$_3$(CO)$_{10}$H$_2$ afforded small amounts of (π-C_5H_5)Os(CO)$_2$H.

An X-ray crystallographic structure determination of **151** [163], obtained from SiMe$_2$(C_5H_5)$_2$ and Fe(CO)$_5$, revealed that the Fe$_2$(μ-CO)$_2$ ring is non-planar and is folded about the Fe—Fe axis (angle of fold ca. 160°) away from the C_5H_4 rings; the Fe—Fe distance is 2.51 Å. Fe$_2$(CO)$_9$ reacted with 6-dimethylaminofulvene giving **152** whose structure was confirmed crystallographically (Fe—Fe distance 2.74 Å) [164].



(151)

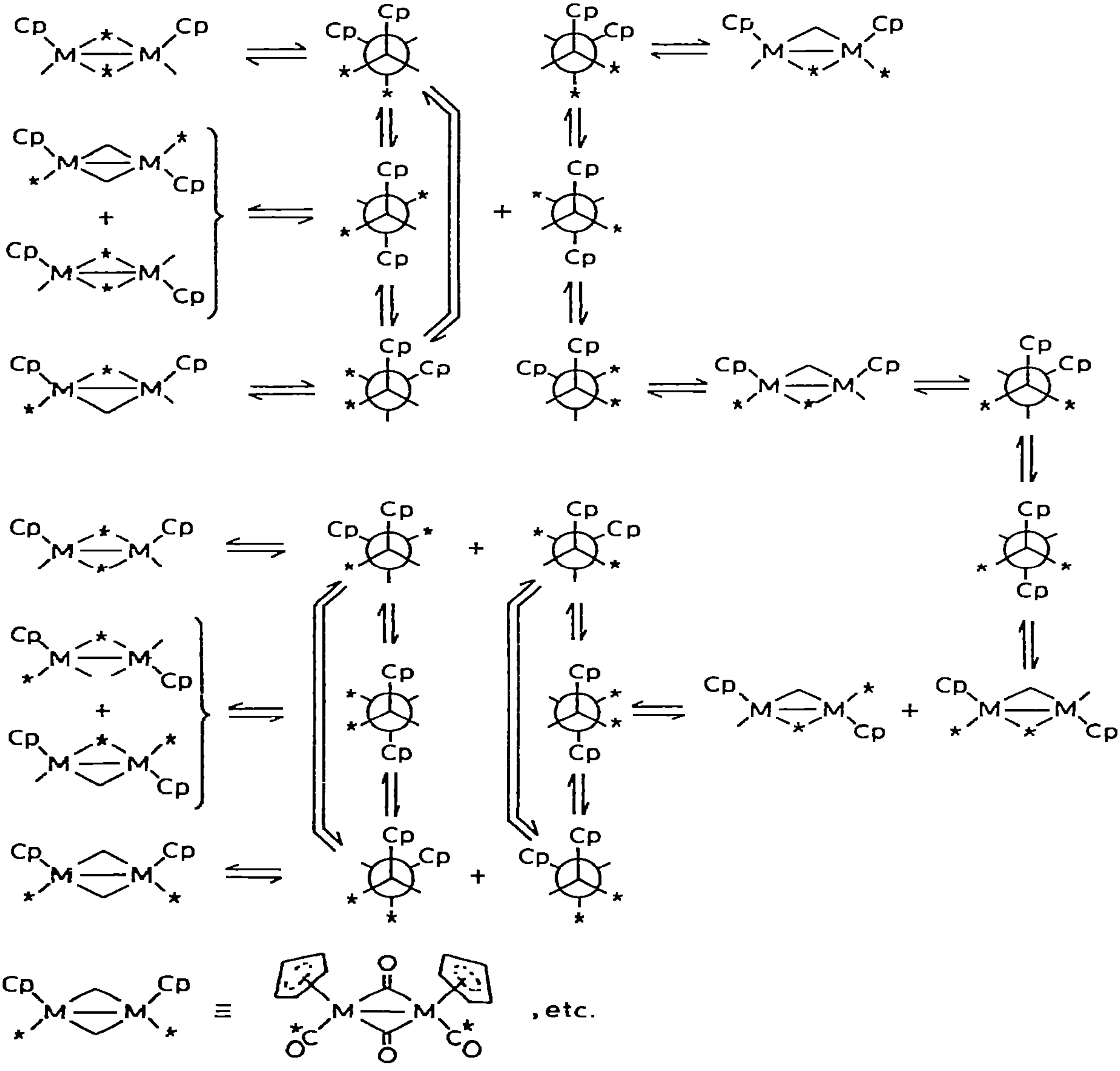


(152)

Carbon monoxide was displaced when isocyanide was added [165] to [(π-dienyl)Fe(CO)$_2$]$_2$ (dienyl = C_5H_5, C_5H_4Me, C_9H_7). The products, (π-dienyl)$_2$-Fe$_2$(CO)$_{4-n}$(CNR)$_n$ (R = Me, Et, i-Bu, t-Bu, CH$_2$Ph or C_6H_{11}) existed in solution as mixtures of *cis*- and *trans*-carbonyl- and isocyanide-bridged tautomers. The incidence of CNR-bridged species decreased as the bulk of the R group increased.

From previous variable temperature NMR spectral data obtained [166] from $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, and from new information relating to $(\pi\text{-}C_5H_5)_2Fe_2(CO)_2(CNMe)_2$, the possible pathways whereby bridging and terminal ligands can be interchanged in such binuclear and other related species have been described [167]. The data can be understood in terms of two main assumptions: (i) that bridges open and close only in pairs; and (ii) that the rotational barriers in unbridged tautomers contribute [168] critically to activation energies when rotations about metal—metal bonds are required. In relation to the first point, one-for-one bridge-terminal site interchanges are not

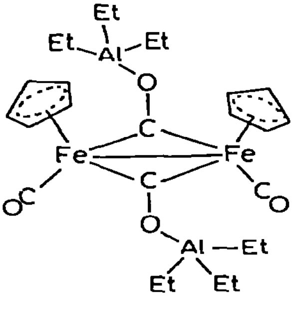
SCHEME 13



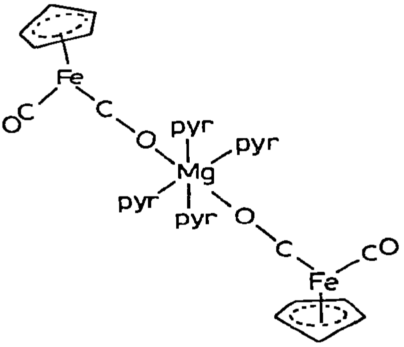
only unnecessary but their occurrence is incompatible with the collected data. The various pathways for bridge-terminal interchange in, for example, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, are illustrated in Scheme 13.

The following points arose from this study: (a) molecules in which the ground state structure had no bridges could effect exchange of ligands between metals via a bridged intermediate; (b) in a molecule having three bridges, two could be opened, the bridging system being reconstituted by ligands previously located in terminal positions; (c) in a molecule with only one bridging group, two terminal ligands could move into bridging positions thereby generating a triply-bridged intermediate, which would then revert to a mono-bridged species incorporating the initial bridging group in a terminal position; and (d) in binuclear systems where bridged and non-bridged species had roughly similar stabilities it was probable that there would be very low activation energies for isomer interconversion and ligand site exchange, since the activation energy for opening and closing bridges, and that for rotation about the M—M bond, would act separately rather than wholly or partially together. In solution $[(\pi\text{-}C_5H_5)Cr(NO)_2]_2$, $[(\pi\text{-}C_5H_5)Mn(CO)(NO)]_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ existed [169] as *cis*- and *trans*-isomers, the ratio of the former to the latter decreasing in the order Fe > Mn > Cr. The activation energies of *cis/trans* interconversion, and of bridge/terminal ligand exchange, decreased in the order Cr > Mn > Fe. For the iron and manganese complexes, the ligand site exchange process was more rapid for the *trans*-isomers than for the *cis*-forms.

From pressure, volume and temperature measurements of the reactions between $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and BF_3 or BBr_3, it was established [170] that 1/1 adducts were formed. Binding of the Lewis acid to the metal complex occurred via the bridging CO groups. Similarly, $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ formed 1/1 and 1/2 adducts with BX_3 (X = F, Cl or Br). The X-ray structure determination of the 1/2 adduct formed between $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $AlEt_3$, 153, confirmed [171] that the aluminum atoms are bonded to bridging CO groups. The Fe—Fe distance is 2.49 Å, and the dihedral angle formed by the two planes of the $Fe(\mu\text{-}CO)_2Fe$ bridging system had increased, relative to that in the uncomplexed dimer, by 3°. It has been suggested [172] by analogy with the known structure of $[Mg(py)_4][(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, that $[Mg(py)_4][(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ contains a Fe—C—O—Mg—O—C—Fe bonding system, viz. 154. Lanthanide tricyclopentadienyl compounds formed [173] adducts with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. Thus, with Sm-



(153)



(154)

$(C_5H_4Me)_3$, a 1/2 adduct, involving bonding between bridging CO groups and the lanthanide element, could be isolated. Adducts were also observed with $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}CO)_2Ni(\pi\text{-}C_5H_5)$ (again utilising CO bridges) and $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl or I), (interaction probably occurred between X and the lanthanide element). No lanthanide complex addition was observed with $Fe(CO)_2(NO)_2$, $(C_8H_8)Fe(CO)_3$, $Fe(NO)_2(PPh_2Me)_2$, $Fe(NO)(S_2CNMe_2)_2$ or $Ru(NO)(PPh_3)_2Cl_3$.

Monomeric cationic species

Oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with molecular oxygen in acetone containing aqueous HBF_4 afforded [174] $[(\pi\text{-}C_5H_5)Fe(CO)_2(H_2O)]^+$ which, on treatment with X^- (Cl, Br, NCO, CN, NO_3, N_3, O_2CH or $O_2C_2Cl_3$) or L (PPh_3, pyridine, hydrazine, $S(n\text{-}Bu)_2$) provided $(\pi\text{-}C_5H_5)Fe(CO)_2X$ or $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ (as the BF_4^- salt). In acetone, AgY (Y = ClO_4, BF_4 or SbF_6) oxidised [175] $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ to $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{acetone})]Y$ and again, with X^- (Cl or Br), or L (CO, $AsPh_3$, $SbPh_3$, MeCN, $PhCH_2CN$, SPhMe or $(\pi\text{-}C_5H_5)Fe(CO)_2I$), the species $(\pi\text{-}C_5H_5)Fe(CO)_2X$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2L]Y$, were formed. However, with AgY (Y = NO_3, O_2CCF_3, SCN, NCO, O_2CPh, $p\text{-}MeC_6H_4SO_2$ or $OP(=O)(OPh)_2$), the dimeric carbonyl afforded $(\pi\text{-}C_5H_5)Fe(CO)_2Y$ directly. The cation $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ could be obtained from $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ using NO_2 as a one-electron oxidant [176]. NO_2, in this respect, is similar to $NOPF_6$ since, in polar solvents, it dimerises to N_2O_4 which behaves as $[NO^+][NO_3^-]$. A crystallographic determination of the structure of $[(\pi\text{-}C_5H_5)Fe(CO)_3][PF_6]$ established [177] that the iron atom has quasi-octahedral geometry and that the C—O distances are shorter than in the isoelectronic $(\pi\text{-}C_5H_5)Mn(CO)_3$.

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)]_4$ with BCl_3 in liquid HCl gave [178] $[\{(\pi\text{-}C_5H_5)Fe(CO)\}_4H_2][BCl_4]_2$. It was believed that the hydrogen atoms occupied two non-adjacent edges of the Fe_4 tetrahedron. The tetramer, an improved preparation of which was described, reacted with PF_5 in liquid HCl to give $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$, in a reaction consistent with previous observations [179].

The kinetics of oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ by $[Ru(bipy)_2Cl_2]^+$, and by $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ in acetonitrile, in which the ultimate product was $[(\pi\text{-}C_5H_5)Fe(CO)_2(NCMe)]^+$, have been investigated [180]. The rate-determining step appeared to involve an outer-sphere electron transfer from the dimer, giving, initially, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^+$. This may then degrade via the reaction:

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^{+} \xrightarrow{-e^-} [(\pi\text{-}C_5H_5)Fe(CO)_2]_2^{2+} \xrightarrow{MeCN} 2\ [(\pi\text{-}C_5H_5)Fe(CO)_2(NCMe)]$$

or via the process:

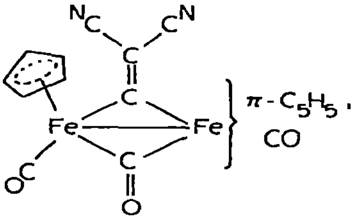
$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^{+} \xrightarrow{NCMe} [(\pi\text{-}C_5H_5)Fe(CO)_2(NCMe)]^{+} + [(\pi\text{-}C_5H_5)Fe(CO)_2]^{\bullet}$$

$$\xrightarrow{-e^-} [(\pi\text{-}C_5H_5)Fe(CO)_2]^{+} \xrightarrow{MeCN} [(\pi\text{-}C_5H_5)Fe(CO)_2(NCMe)]^{+}$$

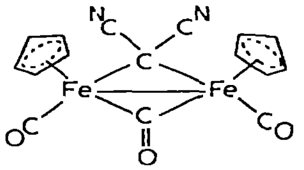
Complexes containing M—C σ-bonds, and carbene species

Reaction of $Na[(\pi\text{-}C_5H_5)Fe(CO)_2]$ with CH_2ClI, and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $PhCOCH{=}CHI$, afforded $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2Cl$ [181] and a mixture [182] of $(\pi\text{-}C_5H_5)Fe(CO)_2CH{=}CHCOPh$ and $(\pi\text{-}C_5H_5)Fe(CO)_2I$, respectively.

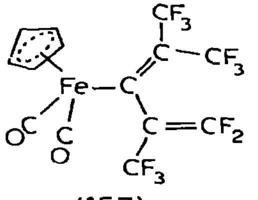
Treatment of Na[(π-C_5H_5)Fe$(CO)_2$] with $(NC)_2C$=CXCl (X = H or Cl) in THF gave [183] (π-C_5H_5)Fe$(CO)_2$[CH=C$(CN)_2$] (X = H), and low yields of *cis*- and *trans*-(π-C_5H_5)$_2$Fe$_2$(CO)$_2$[C=C$(CN)_2$](155) (when X = Cl). Using C$(CN)_2$-Br_2, low yields of (π-C_5H_5)$_2$Fe$_2$(CO)$_3$[C$(CN)_2$] (156), (π-C_5H_5)Fe$(CO)_2$[CH$(CN)_2$] and (π-C_5H_5)Fe$(CO)_2$Br were produced. At −70°, Na[(π-C_5H_5)Fe$(CO)_2$] reacted [184] with $(F_3C)_2C$=C=C$(CF_3)_2$ giving **157**. A series of isomers, (π-C_5H_5)Fe$(CO)_2$(C_6F_4X) (X = 2- or 3-H; 2-, 3- or 4-Br) was prepared [185] either by reaction of $C_6F_4Br_2$ with Li[(π-C_5H_5)Fe$(CO)_2$] or by the reaction of LiC_6F_4Br with (π-C_5H_5)Fe$(CO)_2$I. With n-butyllithium, these complexes underwent Li/Br exchange in preference to Fe—C bond cleavage. Thus, treatment of the appropriate isomers of (π-C_5H_5)Fe$(CO)_2$(C_6F_4Br) with Li-n-Bu afforded (π-C_5H_5)Fe$(CO)_2$(C_6F_4Li) which reacted in turn with (π-C_5H_5)Fe$(CO)_2$I giving **158** and **159**.



(155)

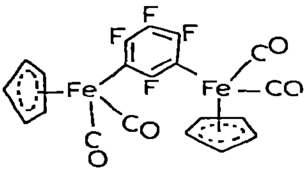


(156)

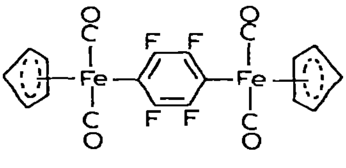


(157)

Reaction of ferrocenyllithium with (π-C_5H_5)Fe$(CO)_2$Br at −70° afforded [186] (π-C_5H_5)Fe[π-C_5H_4Fe$(CO)_2$(π-C_5H_5)], while addition of Na[(π-C_5H_5)Fe$(CO)_2$] to (π-C_5H_5)Fe(π-C_5H_4COCl) gave (π-C_5H_5)Fe[π-C_5H_4COFe$(CO)_2$(π-C_5H_5)]. Bromination of the σ-bonded *o*- and *m*-carboran-1-yl complexes R$CB_{10}H_{10}$CFe$(CO)_2$(π-C_5H_5) gave [187] R$CB_{10}H_9$BrCFe$(CO)_2$(π-C_5H_5) and treatment with an excess of bromine did not lead to Fe—C bond cleavage. Fe—C bond cleavage did occur, however, when these species were treated with $HgCl_2$; (π-C_5H_5)Fe$(CO)_2$Cl was released in these reactions.



(158)

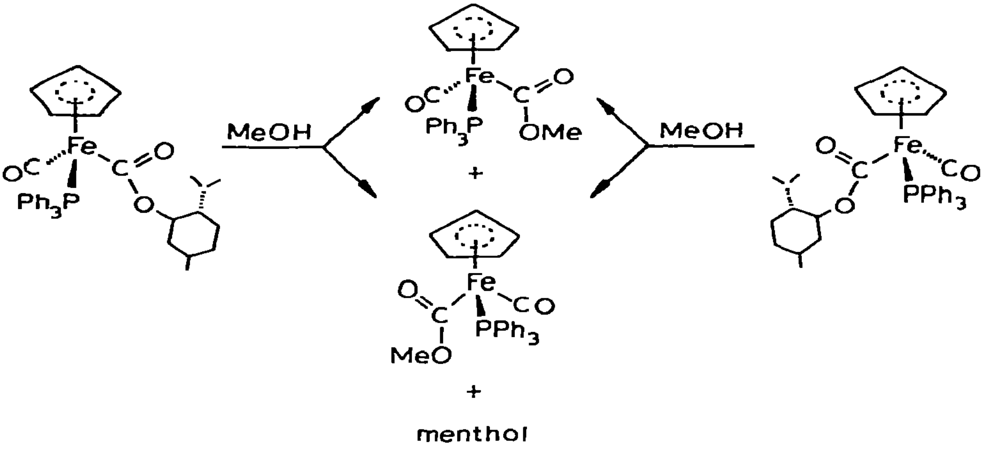


(159)

Treatment of *m*-ClCO$CB_{10}H_{10}$CCOCl with Na[(π-C_5H_5)Fe$(CO)_2$] afforded, initially, *m*-$B_{10}H_{10}C_2$[COFe$(CO)_2$(π-C_5H_5)]$_2$, which was readily decarbonylated to give *m*-$B_{10}H_{10}C_2$[Fe$(CO)_2$(π-C_5H_5)]$_2$. Polarographic reduction of R$CB_{10}H_{10}$-CCH_2Fe$(CO)_2$(π-C_5H_5) resulted in the consumption of two electrons and the formation of [(π-C_5H_5)Fe$(CO)_2$]$^-$, and this anion was also produced when carboranyl species were reduced with sodium amalgam.

Addition of sodium mentholate to [(π-C_5H_5)Fe$(CO)_2$(PPh_3)]$^+$ afforded [188] (+)- and (−)-forms of the diastereoisomeric species **160**. These compounds did not racemise in solution, even at relatively high temperatures. However, the methoxycarbonyl species, produced after transesterification in methanol, were

SCHEME 14



optically inactive (Scheme 14). A series of inversion steps was proposed as a mechanism for racemisation. Using the optically active mentholphosphite, $P(OCH_2CH_2O)(OC_{10}H_{19})$, L, the diastereomeric species $(\pi\text{-}C_5H_5)Fe(CO)L(COMe)$ was also prepared.

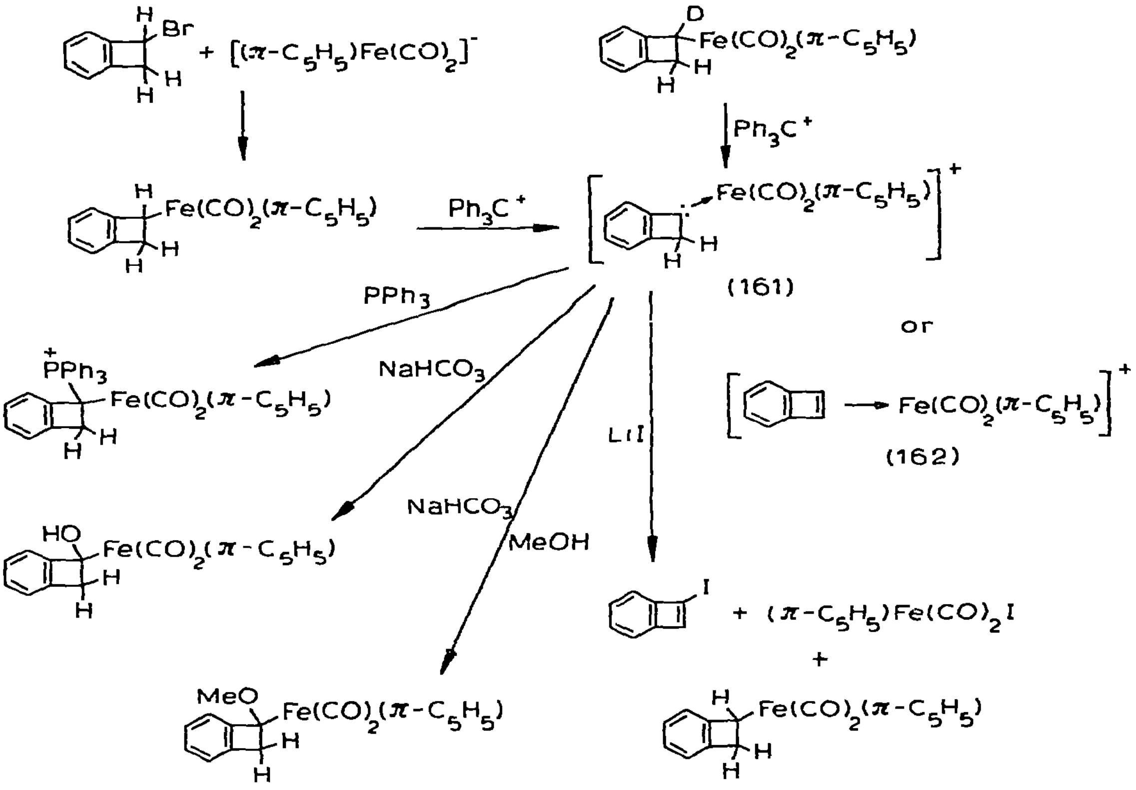
Reaction of $Fe_2(CO)_9$ with the tris(pyrazolyl)borate ligand, $[HB(pyz)_3]^-$, in the presence of methyl iodide, led [189] to the formation of $Fe(CO)_2(COMe)$-$[HB(pyz)_3]$ and $Fe[HB(pyz)_3]_2$. IR spectral studies of the acyl indicated the presence of conformers presumably differing in the rotational orientation of the acetyl group relative to the remainder of the molecule. The iron atom had a slightly distorted octahedral geometry, and the pyrazolylborato ligand was tridentate.

Mössbauer spectral data have been correlated [190] with ν(CO) for the species $(\pi\text{-}C_5H_5)Fe(CO)LQ$ (L = CO or PPh_3; Q = COMe, SO_2Me, CH_2Ph, SO_2-CH_2Ph, $SO_2(p\text{-}FCH_2C_6H_4)$, Me). It was shown that the σ-donor ability of the acetyl group was greater than that of RSO_2^-.

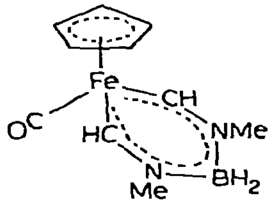
Treatment of $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ with methylfluorosulfonate gave [191] $[(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)\{C(OMe)Me\}]^+$. A complex, 161, obtained by the route outlined in Scheme 15, has been formulated [192] as a metal-coordinated carbene derivative lacking heteroatom stabilisation. The reactions of this unusual compound are also summarised in Scheme 15. Reaction of 161 with cycloheptatriene, and with $(\pi\text{-}C_5H_5)Fe(CO)_2Et$, afforded $[C_7H_7]^+$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2H_4)]^+$, respectively. The formation of 161, which involved α-hydride abstraction, is almost without precedent. Hydride abstraction from $(\pi\text{-}C_5H_5)Fe(CO)_2CDMePh$ using Ph_3C^+ afforded $[(\pi\text{-}C_5H_5)Fe(CO)_2(CH_2{=}CDPh)]^+$, and similar treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2Ph$ gave only Ph_3CCH_2Ph. 161 underwent neither of these processes, and so its alternative formulation, viz. 162, may be dismissed.

The structure of the product 163, obtained [193] by treatment of $[(\pi\text{-}C_5H_5)Fe(CO)(CNMe)_2]^+$ with BH_4^-, has been determined [194] crystallographically. The metal chelate ring system has a "boat" geometry, the molecular dimensions of which are outlined in Fig. 9. The Fe—C distances are identical to the average value for Fe—C(sp^2) bonds and are not significantly different to

SCHEME 15



the Fe—C(CNMe) distances in **119** (M = Fe, R = R′ = Me); in the latter, the Fe—C(carbene) distance is 2.02 Å, however. The C—N distances in **163** are in the range for a double bond, while the B—N (nitrogen regarded as *sp*^{2} hybridised) distance is consistent with a bond order of unity.



(163)

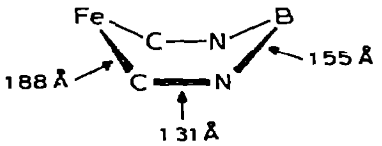


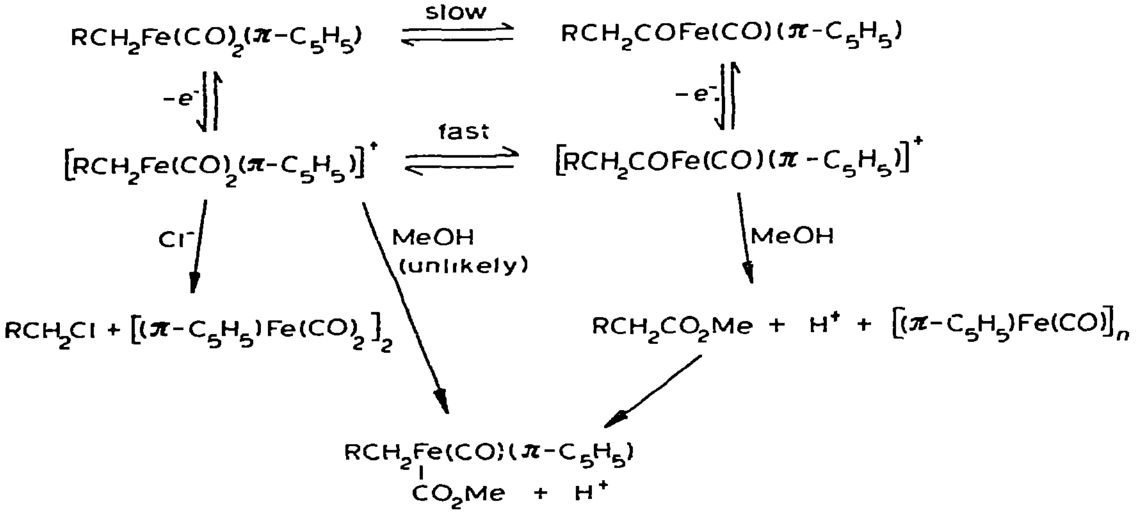
Fig. 9.

Decarbonylation, carbonylation and carboxylation reactions

Photochemical decarbonylation of $(\pi\text{-1-Me-3-PhC}_5H_3)Fe(CO)(PPh_3)COMe$ and of $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CHMePh$ proceeded [195] with high stereospecificity at the iron atom. Modest decarbonylation of $(\pi\text{-}C_5H_5)Fe(CO)_2(COR)$ could be effected [196] by $Rh(PPh_3)_3Cl$. The products were $(\pi\text{-}C_5H_5)Fe(CO)_2R$, $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)COR$ and, of course, $Rh(CO)(PPh_3)_2Cl$. When R = Me, 40 % of the alkyl and 4 % of the acyl were obtained but when R = CHMePh, only the alkyl (54 %) was isolated. Neither alkyl nor acyl was detected in reactions involving R = $CMePh_2$, CPh_3, CH=CHPh, SO_2Me, or SO_2Ph, although in every case substantial amounts of $Rh(CO)(PPh_3)_2Cl$ were formed. There was no reaction when R = CF_3, or with $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)SO_2CH_2Ph$.

Oxidative carboxylation of $(\pi\text{-}C_5H_5)Fe(CO)_2R$ (R = $CH_2C_6H_{11}$, CH_2CH_2Ph or C_6H_{11}), using $CuCl_2$ in the presence of R'OH (R' = Et, i-Pr or t-Bu), gave [197] RCO_2R' without epimerisation. Similar oxidation when R = $CH_2(p\text{-}FC_6H_4)$ or $CH_2CH_2(p\text{-}C_6H_4)$, in methanol using Ce^{4+} in the presence of LiCl, gave [198] RCO_2Me with some RCl and ROMe. A mechanism was formulated for these reactions (Scheme 16).

SCHEME 16



Addition and insertion reactions

The kinetics and mechanism of SO_2 insertions into the Fe—C bond of $(\pi\text{-}C_5H_5)Fe(CO)_2R$ (R = alkyl or aryl) have been investigated [199]. When R = alkyl, the reaction rate decreased with increasing values of Taft's σ^* constant for R, and with increasing values of ν(CO) for the reacting species; the rate decreasing in the order R = Et > Me > CH_2OMe > CH_2CN. The rate also decreased as the bulkiness of R increased, in the order R = Me > i-Pr > $CH_2CH_2CMe_3$ > CH_2CMe_3 > t-Bu. When R = aryl, the rate constant decreased as a function of increasing Taft's constant σ^+, viz. in the order R = $p\text{-}MeOC_6H_4$ > $p\text{-}MeC_6H_4$ > $m\text{-}MeC_6H_4$ ~ Ph. Methylation of the cyclopentadienyl ring (when R = CH_2Ph) caused an increase in the rate of insertion, but when R = aryl, the trend was irregular. These had characteristically large and negative values of $\Delta S^{\ddagger}$, and low values

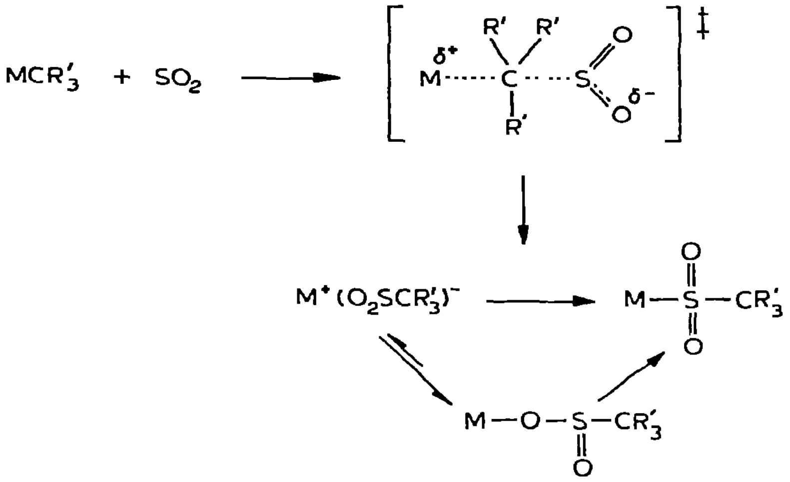
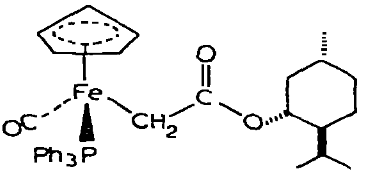
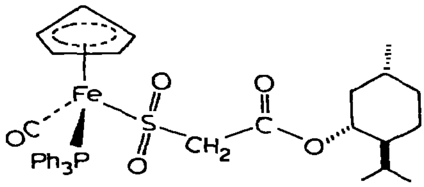


Fig. 10.

of $\Delta H^{\ddagger}$. The observation that the rate of reaction was dependent on the nature of R indicated that cleavage of the Fe—R bond was an electrophilic process. The results were generally consistent with backside attack by SO_2 on the α-carbon atom. This presumably led to heterolysis of the Fe—R bond and formation of a contact ion pair, viz. $[(\pi\text{-dienyl})Fe(CO)_2]^+[O_2SR]^-$ (Fig. 10) These ions appeared to recombine rapidly giving the *O*-sulfinate, $(\pi\text{-}C_5H_5)Fe(CO)_2OS(=O)R$, which subsequently rearranged [200] to the thermodynamically more stable *S*-bonded sulfinate, $(\pi\text{-}C_5H_5)Fe(CO)_2S(=O)_2R$. Although the *O*-sulfinates could be detected spectroscopically, they proved impossible to isolate from reactions in liquid SO_2. Sulfur dioxide insertion into the Fe—C bond in **164** (which was epimeric at Fe), giving **165** occurred [201] with retention of configuration at the metal atom. This result contrasted with previous observations [202].



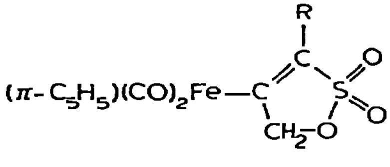
(164)



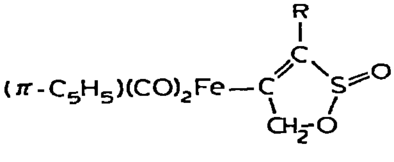
(165)

Addition of SO_3 to the acetylenic bond in $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C{\equiv}CR$ (R = Me or Ph) afforded [203] the sultone derivative **166**; these species were more stable than the corresponding sultines, **167**, and were resistant to attack by HCl.

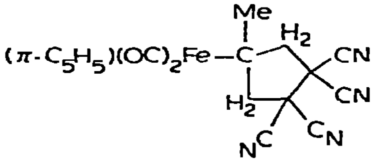
The structure of the product **168**, obtained [204] by addition of TCNE to $(\pi\text{-}C_5H_5)Fe(CO)_2[CH_2C(Me){=}CH_2]$, has been elucidated [205] crystallographically. The Fe—C bond length is 2.10 Å, suggesting that the covalent radius of the iron in this compound is ca. 1.33 Å. The allenyl complexes, $(\pi\text{-}C_5H_5)Fe(CO)_2CH{=}C{=}CHR$ (R = H or Me), were prepared [206] by treating $Na[(\pi\text{-}C_5H_5)\text{-}$



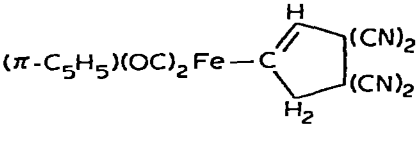
(166)



(167)

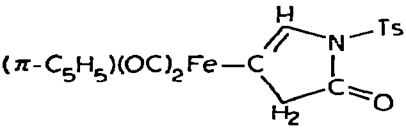


(168)



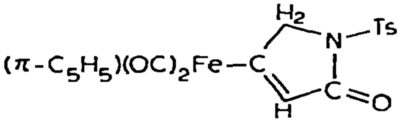
(169)

$Fe(CO)_2]$ with propargyl benzenesulfonate or by displacement of the isobutylene in $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{isobutylene})]^+$ by the appropriate allene. The complex with R = H underwent addition with TCNE, giving **169**; there was evidence for the intermediacy of an acetylene complex in the reaction (Fig. 11). Electrophilic addition to the allenyl species of *p*-toluenesulfonylisocyanate gave **170** but not **171**, while *β*,*β*-dicyano-*o*-chlorostyrene and *N*-carbomethoxysulfonylamine gave **172** and **173**, respectively. However, $(\pi\text{-}C_5H_5)Fe(CO)_2[CH_2C{\equiv}CMe]$

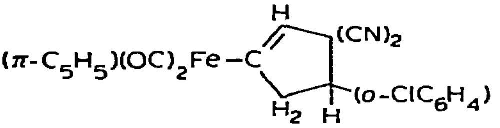


(170)

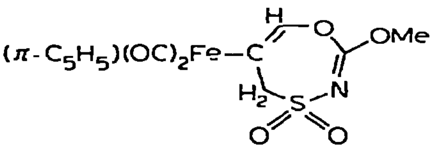
Ts = toluenesulphonyl



(171)



(172)



(173)

reacted with MeO_2CNSO_2 giving **174** in a process apparently involving an allenic intermediate (Fig. 12). The evidence that allenyl derivatives could react via acetylenic intermediates, and that acetylenyl compounds reacted via allenylic der-

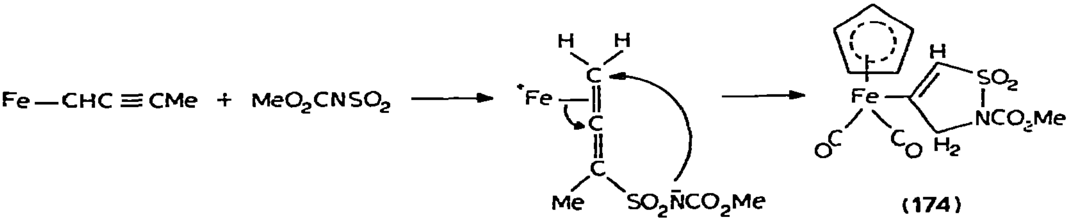


Fig. 11.

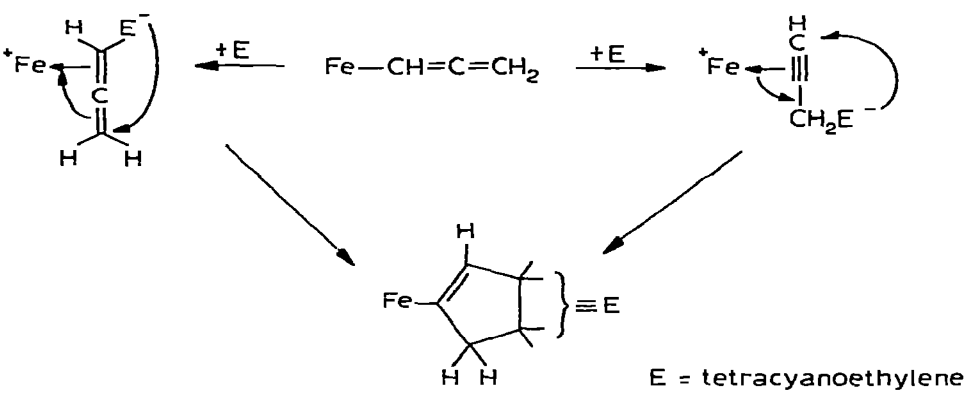


Fig. 12.

ivatives, was as follows: (i) protonation of $(\pi\text{-}C_5H_5)Fe(CO)_2[CH{=}C{=}CH_2]$ gave $[(\pi\text{-}C_5H_5)Fe(CO)_2(HC{\equiv}CMe)]^+$, which reacted with water giving $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2CO_2Me$ and $(\pi\text{-}C_5H_5)Fe(CO)_2COEt$; (ii) protonation of $(\pi\text{-}C_5H_5)Fe(CO)_2[CH_2C{\equiv}CMe]$ gave the cationic allene complex, $[(\pi\text{-}C_5H_5)Fe(CO)_2(H_2C{=}C{=}CHMe)]^+$, as a single stereoisomer (Fig. 13). The formation of this allene species was comparable with the known [207] fluxional behaviour of $(Me_2\text{-}C{=}C{=}CMe_2)Fe(CO)_4$.

A detailed study of the reactions of $(\pi\text{-}C_5H_5)Fe(CO)_2R$ (R = 2-alkenyl or 2-alkynyl), with chlorosulfonyl isocyanate has been made [208]. The 2-alkenyl complexes afforded the pyrrolidone (175) and the *N*-acyl-*N*-(chlorosulfonyl or sulfamoyl)amido species (177), (X = SO_2Cl, H, SO_2NHPh, SO_2NEt_2 or COPh; R, R′ = H, Me, or Ph) depending on whether a methyl group was present or absent at the C(2) atom of the alkenyl group. However, the 2-alkynyl complexes afforded the Δ^3-pyrrolinones (176), (X = SO_2Cl, H, SO_2NHPh, or $SO_2\text{-}NEt_2$; R, R′ = H, Me, Ph or $CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$) exclusively. It was observed

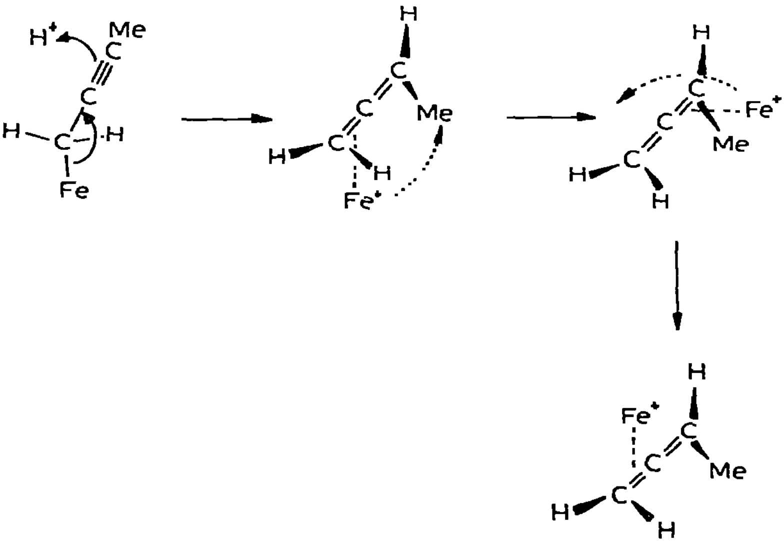
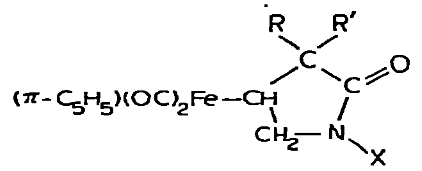
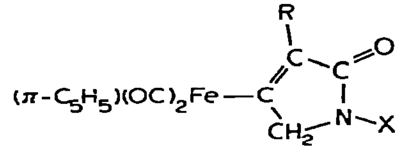


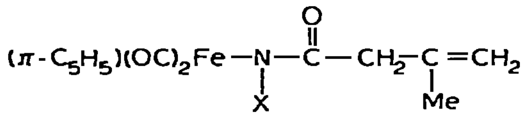
Fig. 13.



(175)

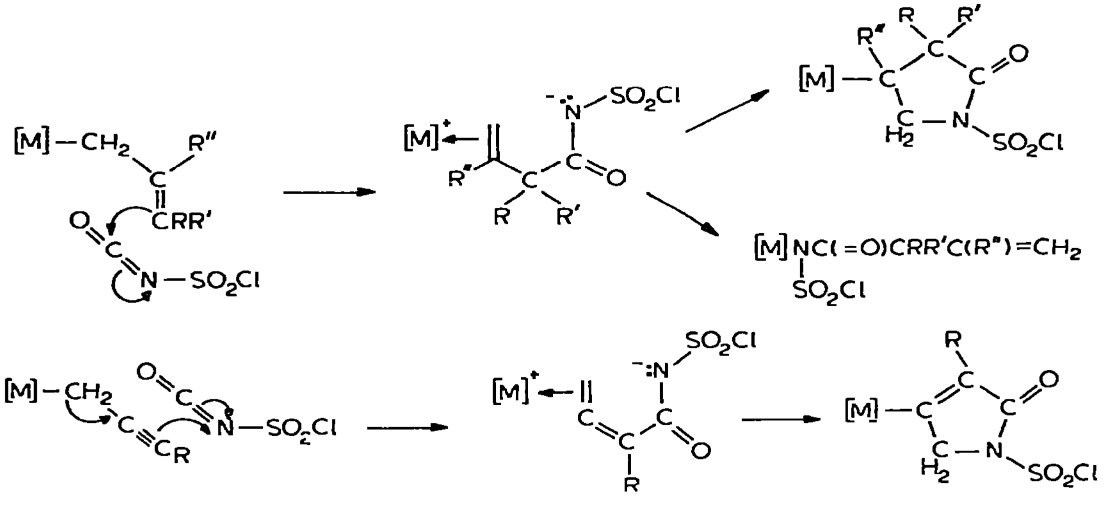


(176)



$(\pi\text{-}C_5H_5)(OC)_2Fe{-}N(X){-}C(=O){-}CH_2{-}C(Me){=}CH_2$

(177)



[M] ≡ $(\pi\text{-}C_5H_5)Fe(CO)_2$

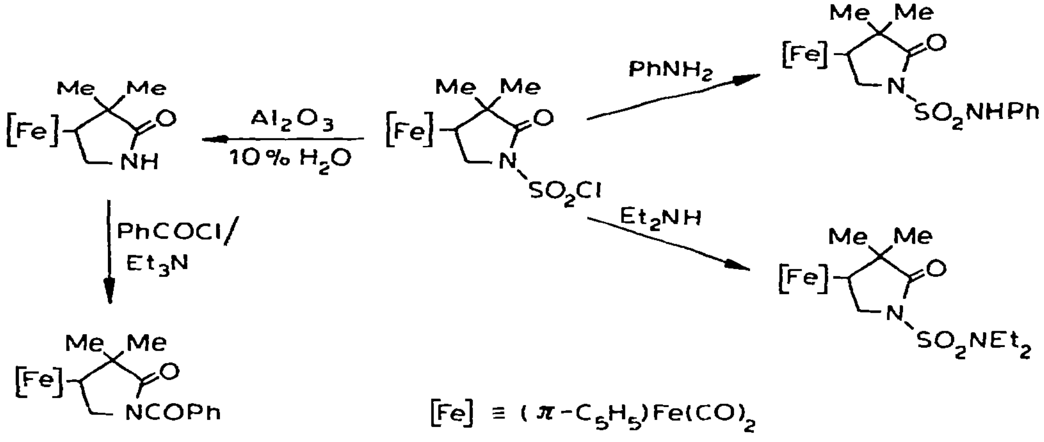
Fig. 14.

that while **175** and **176** were derived by cycloaddition of $ClSO_2NCO$ to the σ-bonded hydrocarbon fragment, and that this was accompanied by 1,2-metal migration, **177** resulted from insertion of $ClSO_2NCO$ into the Fe—C bond. The mechanisms of formation of **175** and **176** are shown in Fig. 14, and some reactions of **175** ($X = SO_2Cl$; $R = R' = Me$) and a species, **178**, closely related to the Δ^3-pyrrolinones, **176**, are summarised in Schemes 17 and 18.

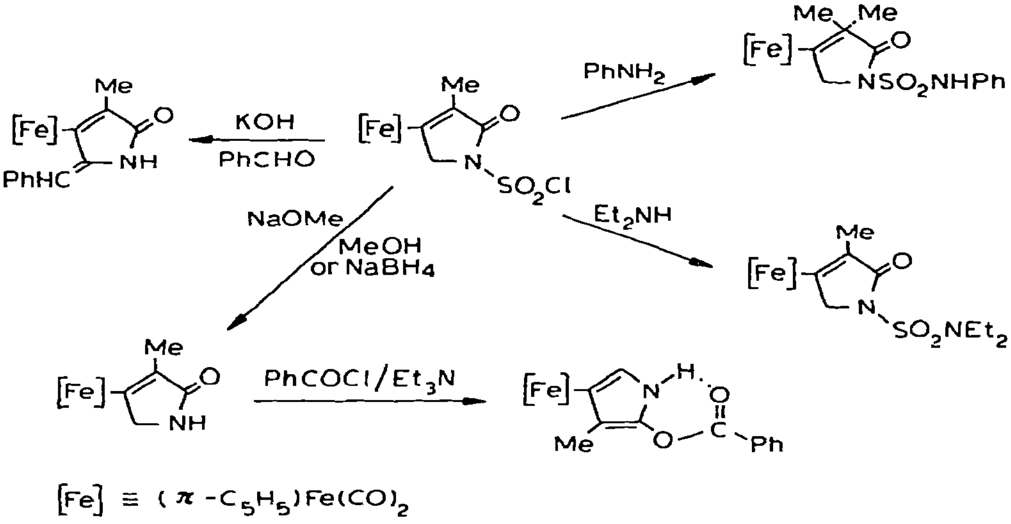
Treatment [209] of the vinylic species **179**, with hexafluoroacetone gave **180**, in which formal insertion of $(CF_3)_2CO$ into a C—H bond of the cyclopentadienyl ring had occurred. On heating **179** lost PPh_3 giving **181**.

Reaction of the cationic complexes $[(\pi\text{-}C_5H_5)Fe(CO)_2(\text{olefin})]^+$ (olefin = C_2H_4, cyclopentene or cyclohexene) with enolate anions ($R = CH(CO_2Et)_2$, $CMe(CO_2Et)_2$, $CH(COMe)(CO_2Et)$) gave [210] the alkyl complexes, $(\pi\text{-}C_5H_5)$-

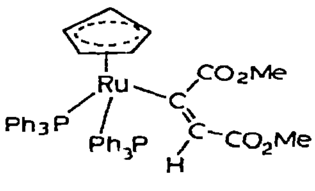
SCHEME 17



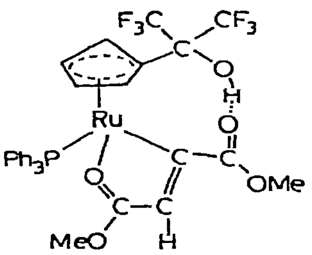
SCHEME 18



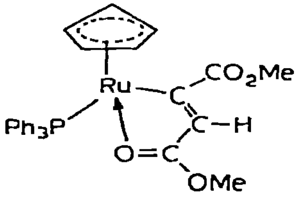
$Fe(CO)_2CH_2CH_2R$ (**182** and **183**). Hydride abstraction from **181** (R = $CH(CO_2Et)_2$) afforded **184**. However, reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2H_4)]^+$ with $(\pi\text{-}C_5H_5)Fe(CO)_2[CH_2CH=CH_2]$ produced **185**, some reactions of which are given



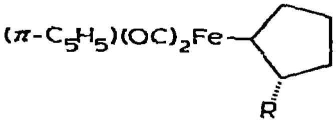
(179)



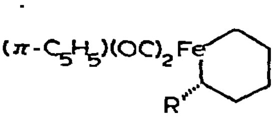
(180)



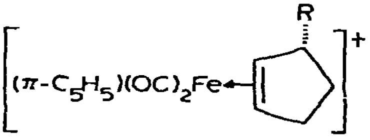
(181)



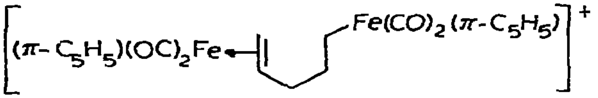
(182)



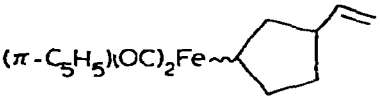
(183)



(184)

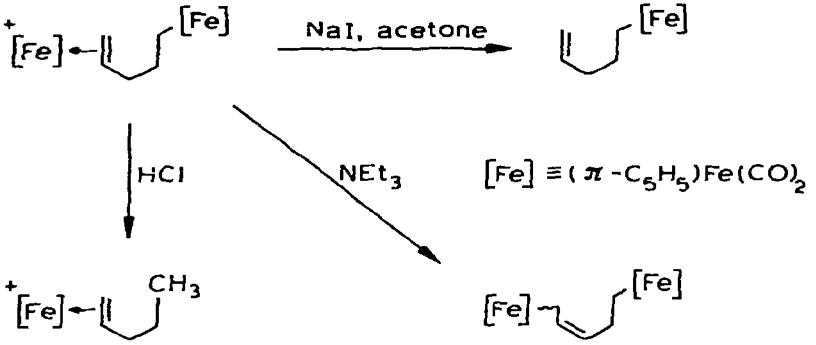


(185)

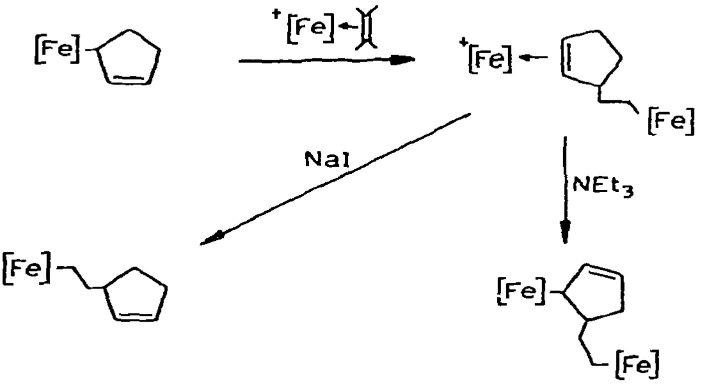


(186)

SCHEME 19

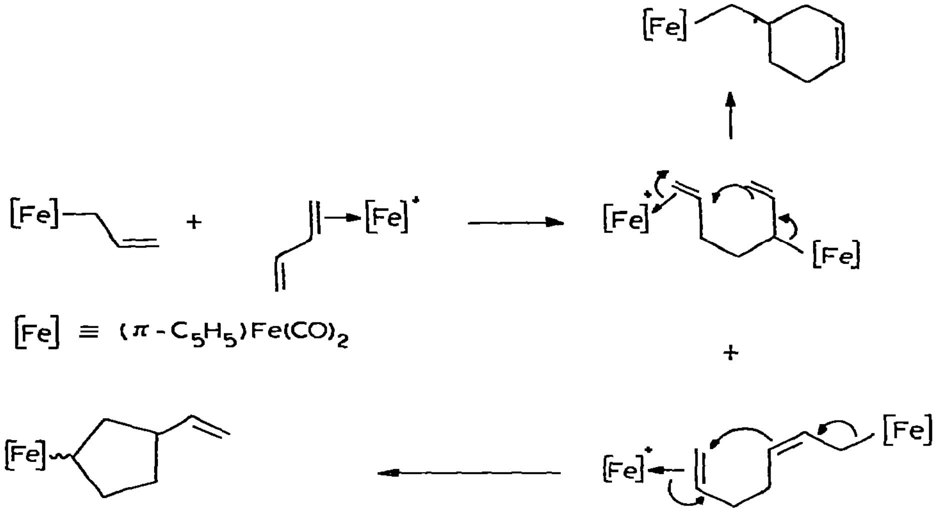


SCHEME 20



[Fe] ≡ $(\pi\text{-}C_5H_5)Fe(CO)_2$

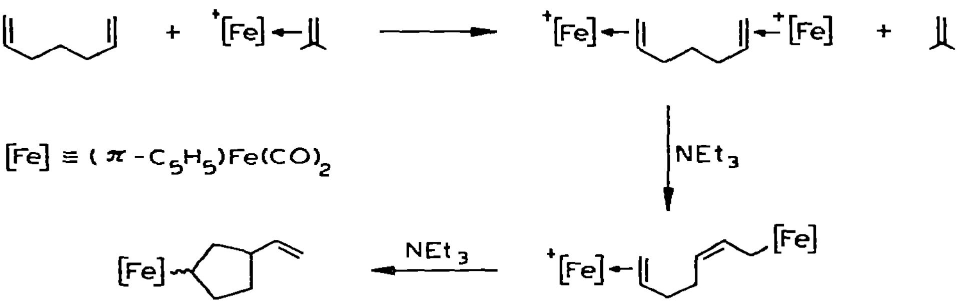
in Scheme 19. Representative reactions of a cyclopentenyl complex are outlined in Scheme 20; the triethylamine abstracts a proton stereoselectively, i.e. *trans* to the Fe—olefin bond. Coupling between $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2CH{=}CH_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_4H_6)]^+$ is demonstrated in Fig. 15, and an alternative route to 186 is shown in Scheme 21.



(186)

Fig. 15.

SCHEME 21



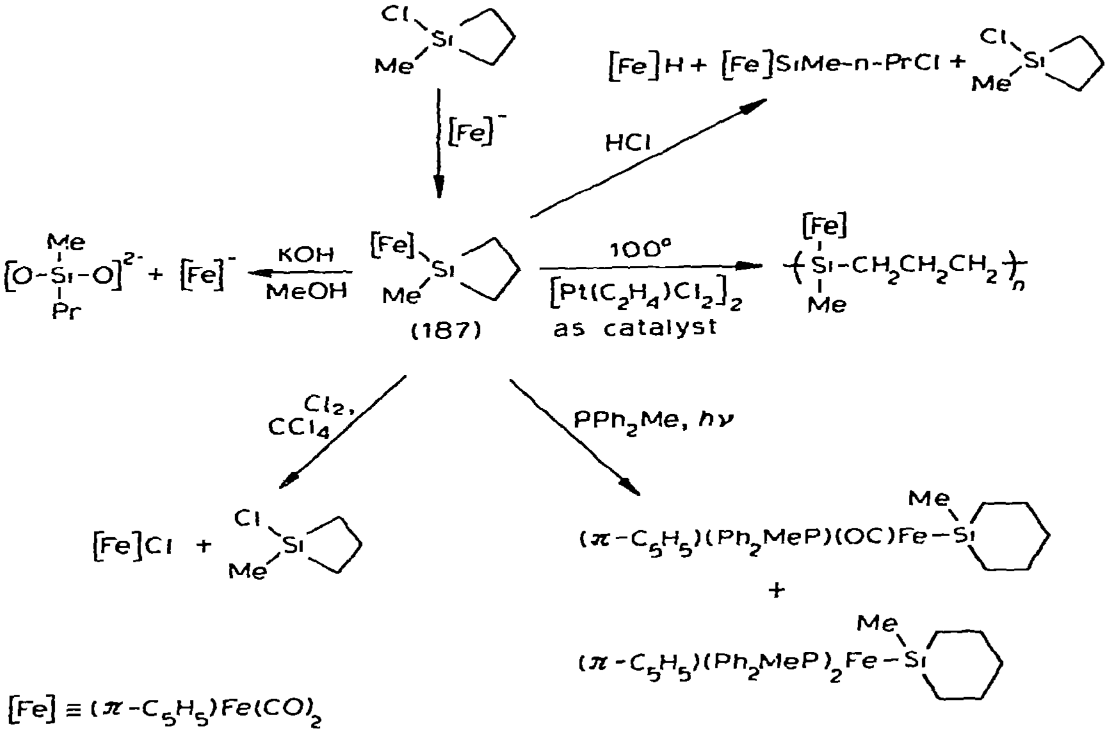
(186)

Complexes containing Group IVB elements and mercury

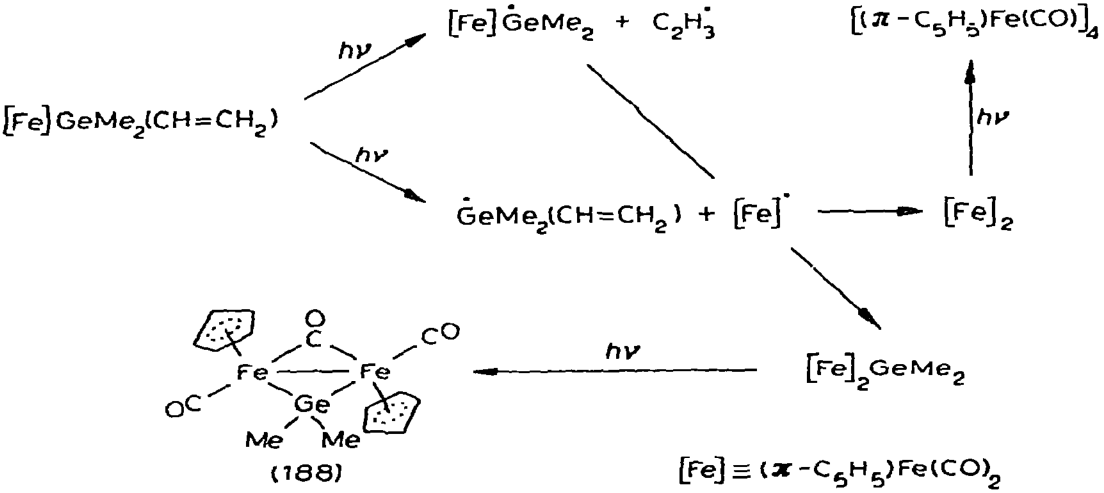
Alcoholysis of $(\pi\text{-}C_5H_5)Fe(CO)_2SiCl_3$ by NaOR in ROH afforded [211] $(\pi\text{-}C_5H_5)Fe(CO)_2[Si(OR)_3]$ (R = Me, Et, i-Pr, n-Pr, t-Bu), but an excess of OR^- caused fission of the Fe—Si bond. The preparation of some organosilyl complexes, $(\pi\text{-}C_5H_5)Fe(CO)_2SiR_3$ ($R_3 \equiv Me_2Ph, MePh_2, Ph_3$, or $Ph_2(CH{=}CH_2)$), including the optically active (—)-$[(\pi\text{-}C_5H_5)Fe(CO)_2\{SiMePh(1\text{-}C_{10}H_7)\}]$, and $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)(SiPh_3)$, has been reported [212]. The 1-methylsilacyclobutadiene complex (187), was obtained [213] by treatment of $Si(CH_2\text{-}CH_2CH_2)MeCl$ with $Na[(\pi\text{-}C_5H_5)Fe(CO)_2]$; some reactions of 187 are outlined in Scheme 22.

The vinyl-substituted germyl complex, $(\pi\text{-}C_5H_5)Fe(CO)_2[GeMe_2(CH{=}CH_2)]$ was obtained [214] by attack of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ on $GeMe_2(CH{=}CH_2)X$ (X = Br or I); and $Fe(CO)_3(NO)[GeMe_2(CH{=}CH_2)]$ was produced similarly using $Na[Fe(CO)_3(NO)]$. Photolysis of the cyclopentadienyl complex afforded 188, the proposed mechanism being illustrated in Scheme 23; 188

SCHEME 22



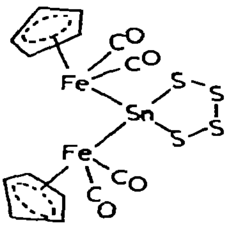
SCHEME 23



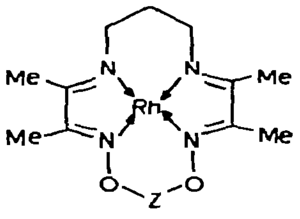
existed as *cis*- and *trans*-isomers with respect to the arrangement of the π-C_5H_5 rings. Photolysis of $GeMe_2[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ also gave [215] *cis*- and *trans*-188, and similar treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2[GeMe_2Cl]$ afforded *cis*-$[(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}GeMe_2)]_2$.

Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $O(SnMe_3)_2$ or $N(SnMe_3)_3$ gave

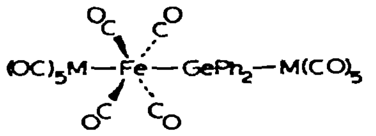
[216] fair yields of $(\pi\text{-}C_5H_5)Fe(CO)_2(SnMe_3)$. Reaction of this compound with iodine afforded [217] $SnMe_3I$ and $(\pi\text{-}C_5H_5)Fe(CO)_2I$, while $SnMe_2[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ gave, initially, $(\pi\text{-}C_5H_5)Fe(CO)_2[SnMe_2I]$, which subsequently broke down into $(\pi\text{-}C_5H_5)Fe(CO)_2I$ and $SnMe_2I_2$ ($SnMe_3I$ was also formed). A 1/1 mixture of $(\pi\text{-}C_5H_5)Fe(CO)_2SnMe_3$ and HgMeCl in DMSO gave, at first $(\pi\text{-}C_5H_5)Fe(CO)_2HgMe$ and $SnMe_3Cl$. This mixture underwent further exchange reactions forming, eventually, $(\pi\text{-}C_5H_5)Fe(CO)_2HgCl$, $Hg[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$, $SnMe_4$ and $HgMe_2$. Similar products were obtained from $SnMe_2[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$, but $SnMe_3Cl$ was obtained in secondary reactions; an excess of HgMeCl also produced $SnMe_2Cl_2$.



(189)



(190)



(191)

Metathetical displacement of Cl^- by S_4^{2-} or S_5^{2-} from $SnCl_2[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ afforded [218] 189. Treatment of $[(\pi\text{-}C_5H_5)Fe\{P(OPh)_3\}_3]BF_4$ with $LiSn_4Me_9$ gave [219] $(\pi\text{-}C_5H_5)Fe[P(OPh)_3]_2[Sn(SnMe_3)_3]$, and halogenation of this (1/3 molar ratio) afforded [220] $(\pi\text{-}C_5H_5)Fe[P(OPh)_3]_2(SnX_3)$ (X = Br or I); an excess of halogen produced $(\pi\text{-}C_5H_5)Fe[P(OPh)_3]_2X$.

The Rh^I complex 190 (Z = H or BF_2), underwent [221] oxidative addition with $(\pi\text{-}C_5H_5)Fe(CO)_2(SnCl_3)$ giving, apparently, an octahedral species having a *trans*-$(\pi\text{-}C_5H_5)Fe(CO)_2(Cl_2Sn)Rh^{III}Cl$ arrangement. However, formulation of this as containing a linear $Fe{-}Rh^{III}{-}SnCl_3$ system could not be dismissed. By heating $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $Mn(CO)_5(SnHPh_2)$, the trimetallic $[(OC)_5Mn(SnPh_2)Fe(CO)_2(\pi\text{-}C_5H_5)]$ was formed [222]. UV irradiation of a mixture of $M(CO)_5(GeHPh_2)$ (M = Mn or Re) and $Fe_2(CO)_9$ afforded 191.

Reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2HgI$ with HCl, and with Na_2SnO_2, gave [223] $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and $(\pi\text{-}C_5H_5)Fe(CO)_2I$, and $Hg[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$, respectively. Treatment of the last with HCl afforded the carbonyl chloride and $(\pi\text{-}C_5H_5)Fe(CO)_2HgCl$.

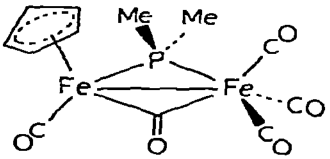
Complexes containing Group VB donor atoms

The monomeric $(\pi\text{-}C_5H_5)Fe(CO)_2[P(CF_3)_2]$ was obtained [224] by reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with $P_2(CF_3)_4$. UV irradiation of this gave *trans*-$[(\pi\text{-}C_5H_5)Fe(CO)\{P(CF_3)_2\}]_2$ while reaction with NO (E = O), S_8 or Se_8 (E = S or Se) afforded $(\pi\text{-}C_5H_5)Fe(CO)_2[P(=E)(CF_3)_2]$. Irradiation of the complex where E = O gave $(\pi\text{-}C_5H_5)_2Fe_3(CO)_2[OP(CF_3)_2]_4$ while similar treatment of those species with E = S or Se afforded $(\pi\text{-}C_5H_5)Fe(CO)_2[EP(CF_3)_2]$. Irradiation of $(\pi\text{-}C_5H_5)Fe(CO)_2[P(=S)(CF_3)_2]$ in the presence of sulfur led to the formation of $(\pi\text{-}C_5H_5)Fe(CO)_2[SP(=S)(CF_3)_2]$.

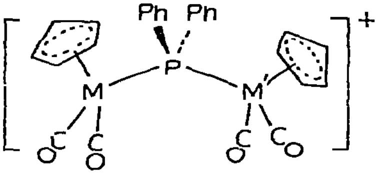
Displacement of chloride from $Fe(CO)_4(PMe_2Cl)$, obtained by reaction of $Fe_2(CO)_9$ with $PMe_2(NMe_2)$ followed by treatment with HCl, by $Na[(\pi\text{-}C_5H_5)$-

$Fe(CO)_2]$ afforded [225] $(\pi\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}PMe_2)Fe(CO)_4$. UV irradiation of this gave $(\pi\text{-}C_5H_5)Fe(CO)(\mu\text{-}PMe_2)(\mu\text{-}CO)Fe(CO)_3$ (192), the structure of which has been confirmed crystallographically (Fe—Fe 2.63 Å), while thermolysis (219°) gave $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $[Fe(CO)_3(\mu\text{-}PMe_2)]_2$. 192 could also be obtained by treatment of $Fe(CO)_4[PMe_2(SiMe_3)]$ with $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$. Chloride displacement from $Ni(CO)_3PMe_2Cl$ by $Na[(\pi\text{-}C_5H_5)Fe(CO)_2]$ afforded $(\pi\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}PMe_2)Ni(CO)_3$, while reaction of $Fe(CO)_4PMe_2Cl$ with $Na[Mn(CO)_5]$ and $Na[Re(CO)_5]$ gave $(OC)_4Fe(PMe_2OPMe_2)Fe(CO)_4$ and $[Re(CO)_4(\mu\text{-}PMe_2)]_2$, respectively. Treatment of $Cr(CO)_5(AsMe_2Cl)$ with $Na[(\pi\text{-}C_5H_5)Fe(CO)_2]$ afforded $(\pi\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}AsMe_2)Cr(CO)_5$, which decomposed on heating.

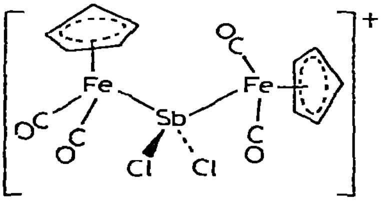
Bridged phosphido complexes containing iron and/or ruthenium, $[(\pi\text{-}C_5H_5)M(CO)_2(\mu\text{-}PPh_2)M'(CO)_2(\pi\text{-}C_5H_5)]^+$ (193), could be obtained [226] by addition of $(\pi\text{-}C_5H_5)M(CO)_2PPh_2$ (M = Fe or Ru) to $(\pi\text{-}C_5H_5)M'(CO)_2Cl$ (M′= Fe or Ru). A mixture of $(\pi\text{-}C_5H_5)Ru(CO)_2(\mu\text{-}PPh_2)Fe(CO)_4$ and $[(\pi\text{-}C_5H_5)Ru(CO)_2]_2$ was obtained by reaction of $(\pi\text{-}C_5H_5)Ru(CO)_2PPh_2$ with $Fe_2(CO)_9$. $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ reacted with $SbCl_3$ in dichloromethane giving [227] $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2SbCl_2][Sb_2Cl_7]$ (194), from which PF_6^- and Reineckate salts could be obtained; the structure of this compound has been determined [228] crystallographically. A similar cation was produced using $SbBr_3$, and with $Sb(CF_3)_2I$, $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2Sb(CF_3)_2][Sb(CF_3)_2I_2]$ was formed. $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ reacted [227] with $SbCl_3$ giving $[\{(\pi\text{-}C_5H_5)Fe(CO)_2Cl\}_2SbCl_3]_2$, probably 195. With $Sb_2(CF_3)_4$, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ may have re-

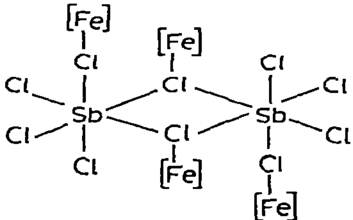


(192)



(193)





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

(194)

(195)

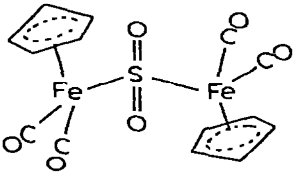
acted to give $(\pi\text{-}C_5H_5)Fe(CO)_2[Sb(CF_3)_2]$. The reactions corresponded formally to an insertion of SbX_2^+ into the Fe—Fe bond of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, and complemented the observations [228] that SbX_3 gave, in THF, $(\pi\text{-}C_5H_5)Fe(CO)_2SbX_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SbX$. Under more rigorous conditions, in refluxing 1,2-dichloroethane, SbX_3 afforded $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_3SbX^+]_n$-

[FeX_4^{n-}] (X = Cl, n = 1; X = Br, n = 2); these compounds were also isolated as BPh_4^- and Reineckate salts. However, reaction with $SbCl_5$ afforded [{(π-C_5H_5)$Fe(CO)_2$}$_2$(μ-Cl)][$SbCl_6$]. Treatment of [(π-C_5H_5)$Fe(CO)_2$]$_2$ with AsX_3 (X = Cl or Br) gave (π-C_5H_5)$Fe(CO)_2AsX_2$ and [{(π-C_5H_5)$Fe(CO)_2$}$_2AsX_2$]-[FeX_4]. The former could be converted into the latter when X = Cl, and with different reaction stoichiometries, [{(π-C_5H_5)$Fe(CO)_2$}$_3AsCl_2$][$FeCl_4$]$_2$ was also formed. The last, on recrystallisation from acetone, afforded [{(π-C_5H_5)-$Fe(CO)_2$}$_2AsCl_2$][$FeCl_4$]. When X = Br, a species formulated as [(π-C_5H_5)Fe-$(CO)_2Br$]$_3$[$AsBr_3$], perhaps analogous to [{(π-C_5H_5)$Fe(CO)_2Cl$}$SbCl_3$]$_2$, was also isolated. Reaction of BiX_3 (X = Cl, Br or I) with [(π-C_5H_5)$Fe(CO)_2$]$_2$ gave only (π-C_5H_5)$Fe(CO)_2BiX_2$.

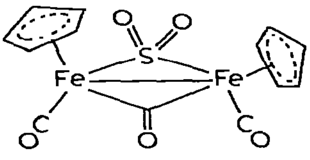
Compounds containing sulfur

UV photolysis of (π-C_5H_5)$Fe(CO)_2(SCF_3)$ gave [229] isomers of [(π-C_5H_5)$Fe(CO)(SCF_3)$]$_2$ similar to other known [230] mercaptide complexes of iron. Treatment of [$Fe(CO)_3(SCF_3)$]$_2$ with PPh_3 afforded $Fe_2(CO)_5(PPh_3)$-$(SCF_3)_2$ and [$Fe(CO)_2(PPh_3)(SCF_3)$]$_2$, while CO displacement by NO provided [$Fe(NO)_2(SCF_3)$]$_2$. Voltammetric oxidation of [(π-C_5H_5)$Fe(CO)(SR)$]$_2$ (R = alkyl or aryl) and [(π-C_5H_5)$Fe(CO)(PPh_2)$]$_2$ occurred [231] in two reversible one-electron steps, giving dimeric mono- and di-cations. The half-wave potentials were dependent on the nature of R, and the oxidations could be achieved chemically. The electron transfer reactions were stereoselective (i.e. *syn*—*syn*$^{n+}$ $\rightleftharpoons$ *syn*—*syn*$^{(n+1)+}$ where *syn* refers to the geometry of the $Fe_2(SR)_2$ system). From Mössbauer spectral studies it was established that electrons were removed from a molecular orbital predominantly metallic in character and associated equally with both metals. Oxidation probably led to a contraction of the Fe—Fe bond lengths.

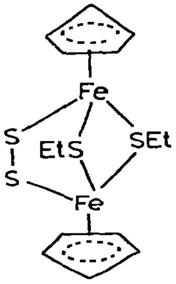
The structures of two SO_2 derivatives of [(π-C_5H_5)$Fe(CO)_2$]$_2$ [232], viz. [(π-C_5H_5)$Fe(CO)_2$]$_2SO_2$ (196) [233], and (π-C_5H_5)$_2Fe_2(CO)_3$(μ-SO_2) (197) [234]



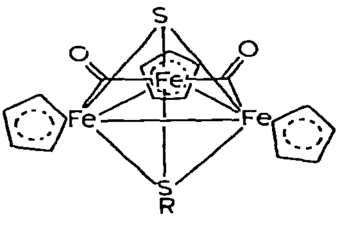
(196)



(197)



(198)



(199)

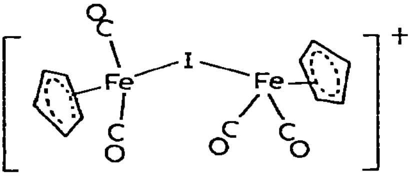
have been determined by X-ray crystallography. In the latter, the Fe—Fe distance is 2.59 Å and the S atom has tetrahedral geometry.

The structure of $[(\pi\text{-}C_5H_5)Fe(SEt)S]_2$ (198), obtained [235] in low yield from a refluxing mixture of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and ethyl polysulfide in methylcyclohexane, has been determined. The Fe—S—S—Fe bridge is planar, the Fe—Fe distance is 3.31 Å, and the S—S distance, 2.02 Å, is shorter than that of an S—S single bond (2.10 Å), corresponding to a π-bond order of ca. $\frac{1}{3}$. Of the various formulations representing the Fe_2S_2 interaction, that of $Fe^{2+}\ {}^{\cdot}S \overset{-}{\cdots} S^{-}\ Fe^{3+}$ was favored. The voltammograms of the compound exhibited one anodic wave, but no cathodic processes were detected. Reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with R_2S_2 gave [236], as expected, $[(\pi\text{-}C_5H_5)Fe(CO)(SR)]_2$ (R = Me, Et, t-Bu or CH_2Ph) and also $(\pi\text{-}C_5H_5)_3Fe_3(CO)_2S(SR)$ (199). Cyclic voltammograms of the latter in dimethoxyethane revealed the existence of a mono- and di-cationic species, and iodination of 199 afforded $[(\pi\text{-}C_5H_5)_3Fe_3(CO)_2S(SR)]^+$ which rapidly decomposed into $[(\pi\text{-}C_5H_5)Fe(CO)(SR)]_2^+$.

Halide, cyanide and other complexes

UV irradiation (λ > 400 nm) of $(\pi\text{-}C_5H_5)Fe(CO)_2X$ in DMSO or pyridine gave [237] $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, C_5H_6 and X^-. When λ > 280 nm, dimeric species, e.g. possibly $(\pi\text{-}C_5H_5)(CO)Fe(\mu\text{-}CO)_2Fe(py)(\pi\text{-}C_5H_5)$, were formed but these could not be isolated. These reactions did not occur in non-polar solvents. Under visible light in pyridine or DMSO, $(\pi\text{-}C_5H_5)Fe(CO)LBr$ afforded [238] $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ when L = $P(OPh)_3$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2(PPh_3)]Br$ when L = PPh_3.

Treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ with $AgBF_4$ gave $[\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2I][BF_4]$ (200), the structure of which has been determined crystallographically [239]. The Fe—I—Fe bond angle was 110.8° and the Fe—Fe separation 4.26 Å (i.e. there was no metal—metal bond).

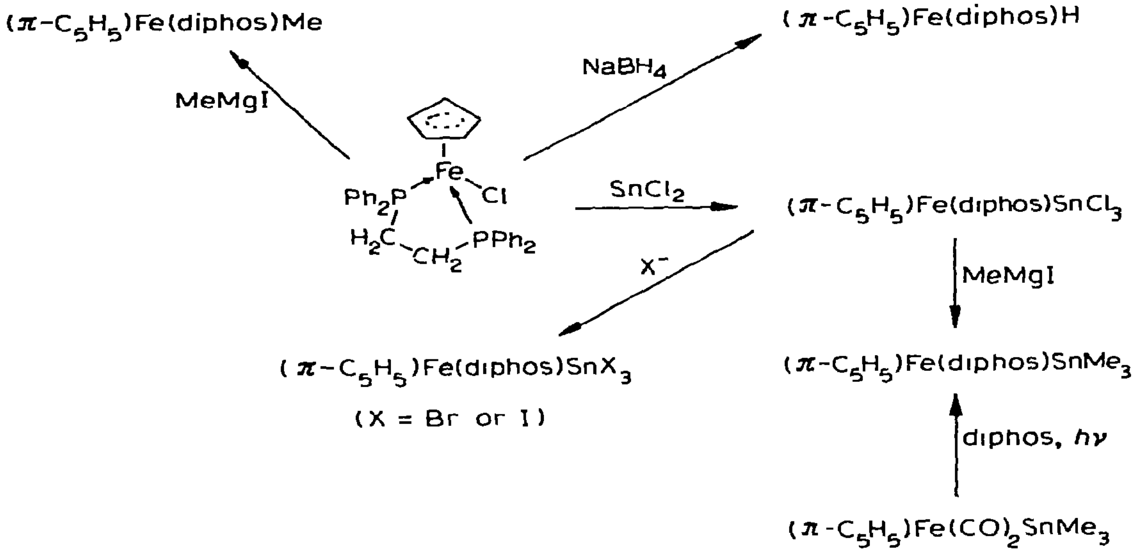


(200)

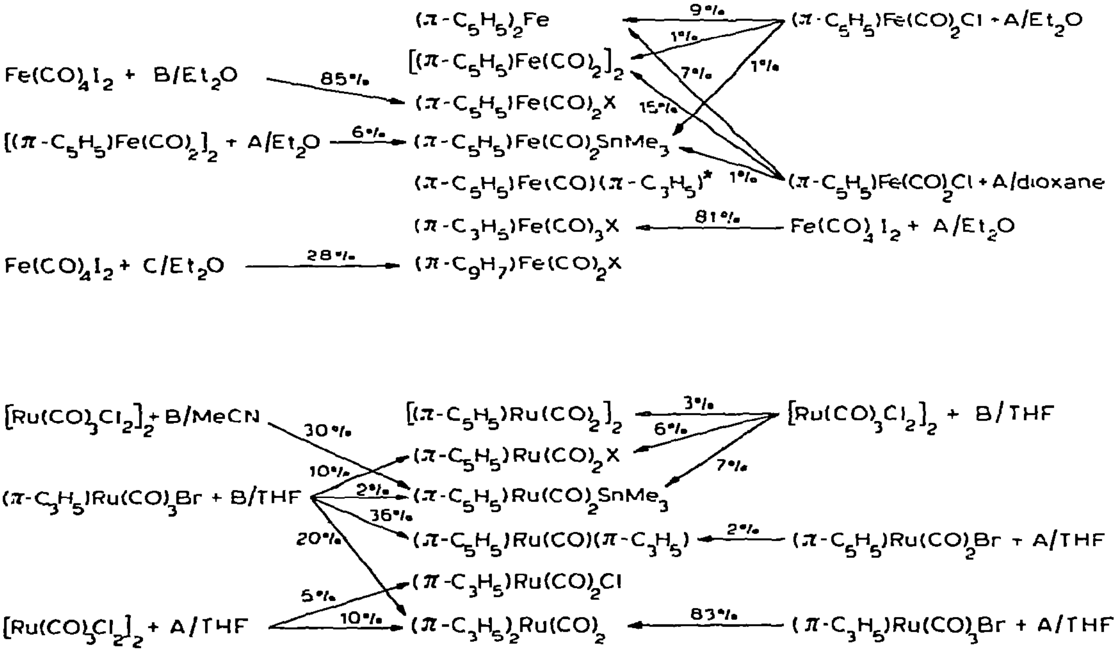
Reaction of $Fe(diphos)_2Cl_2$ with TlC_5H_5 gave $(\pi\text{-}C_5H_5)Fe(diphos)Cl$, some reactions of which are shown in Scheme 24, and ferrocene; ^{57}Fe and ^{119}Sn Mössbauer spectral data were obtained from some of these compounds [240].

The change in asymmetric CO stretching frequencies which occurred [241] upon coordination of a Lewis acid to $(\pi\text{-}C_5H_5)Fe(CO)_2CN$ (giving $(\pi\text{-}C_5H_5)Fe(CO)_2CNL$) provided a convenient measure of the electron-pair acceptor strength of the Lewis acid. Thus, the acceptor properties increased in the order L = $BH_3 < BF_3 < BCl_3 \approx BBr_3$, but decreased in the order L = $BCl_3 > GaCl_3 > AlCl_3$ and $AlMe_3 > BMe_3 \approx GaMe_3$.

SCHEME 24



SCHEME 25



A = $Sn(C_3H_5)Me_3$, B = $Sn(C_5H_5)Me_3$; C = $Sn(C_9H_7)Me_3$

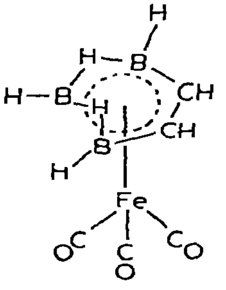
(approx. yields in %)

*This compound is not produced

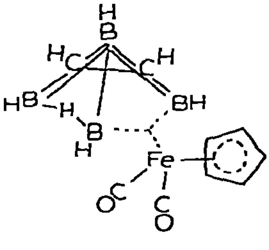
π-Cyclopentadienyl, π-allyl and other carbonyl halides reacted [242] with $Sn(C_3H_5)Me_3$ and $Sn(C_5H_5)Me_3$ affording a series of complexes (Scheme 25). Treatment of $Fe(CO)_4I_2$, and of $(\pi\text{-}C_3H_5)Ru(CO)_3Br$, with $Sn(C_9H_7)Me_3$ gave $(\pi\text{-}C_9H_7)Fe(CO)_2I$ (28%) and $(\pi\text{-}C_9H_7)Ru(CO)(\pi\text{-}C_3H_5)$ (77%), respectively. $Ru(CO)_4(SiMe_3)I$ was converted by $Sn(C_5H_5)Me_3$ into $(\pi\text{-}C_5H_5)Ru(CO)_2(SiMe_3)$ (49%).

Metallo-borane and -carborane cluster compounds

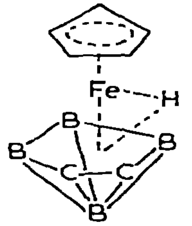
From X-ray crystallographic studies [243] of $(B_3C_2H_7)Fe(CO)_3$ (201) [244], it was established that the carborane skeleton formed a planar ring. Treatment of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ with $NaB_4C_2H_7$ gave [245] $B_4C_2H_7[\mu\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)]$ (202), which, on photolysis afforded $(\pi\text{-}C_5H_5)FeH(\pi\text{-}2,3\text{-}B_4C_2H_6)$ (203) and $(\pi\text{-}C_5H_5)Fe(\pi\text{-}2,3\text{-}B_4C_2H_6)$. The former, an Fe^{II} derivative, could be converted into the latter (a derivative of Fe^{III} with a structure similar to that of 203 without the hydride), and vice versa, in a combination of acid—base and redox reactions. Reduction of 203 with NaH, or of $(\pi\text{-}C_5H_5)Fe(\pi\text{-}2,3\text{-}B_4C_2H_6)$ with sodium amalgam, afforded $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}2,3\text{-}B_4C_2H_6)]$ Treatment of this anion with HCl caused regeneration of 203, but oxidation with air caused reformation of $(\pi\text{-}C_5H_5)Fe(\pi\text{-}2,3\text{-}B_4C_2H_6)$. Reduction of 2,4-$B_5C_2H_7$ with sodium naphthalenide in the presence of $FeCl_2$, NaC_5H_5 and oxygen gave 204 as the major product, together with traces of the 2,4-isomer of 203, viz. $(\pi\text{-}C_5H_5)FeH(6\text{-}R\text{-}\pi\text{-}2,4\text{-}B_4C_2H_5)$ ($R = C_{10}H_7$ or H), and its oxidised counterpart, $(\pi\text{-}C_5H_5)Fe(6\text{-}R\text{-}\pi\text{-}2,4\text{-}B_4C_2H_5)$. Reduction of 204 by sodium amalgam, followed by addition of HCl, gave 205 and the 2,4-isomer of 203, 206. From the gas phase reaction of 2,3-$B_4C_2H_8$ with $Fe(CO)_5$



(201)

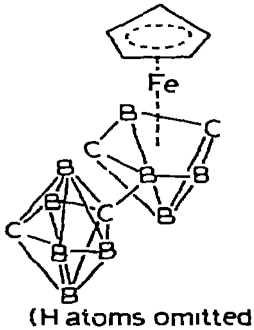


(202)



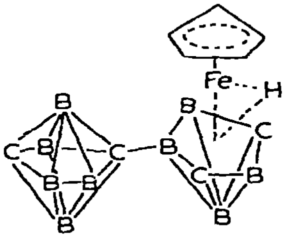
(H atoms omitted for clarity)

(203)



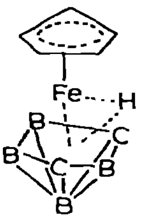
(H atoms omitted for clarity)

(204)



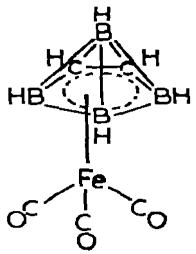
(H atoms omitted for clarity)

(205)



(206)

(H atoms omitted for clarity)

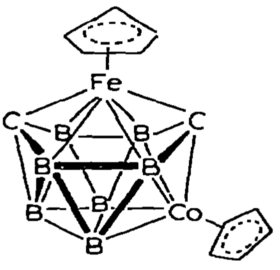


(207)

at 215°, $(\pi\text{-}2,3\text{-}B_4C_2H_6)Fe(CO)_3$ (207), and $(\pi\text{-}2,3\text{-}B_3C_2H_7)Fe(CO)_3$ (201), were obtained; thermolysis of 207 gave 201.

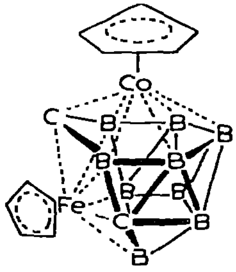
Treatment of $(\pi\text{-}C_5H_5)Co(B_7C_2H_9)$ (a Co^{III} complex), which had been reduced by sodium naphthalenide, with NaC_5H_5 and $FeCl_2$, resulted [246] in the formation of $(\pi\text{-}C_5H_5)Co^{III}[B_7C_2H_9Fe^{III}(\pi\text{-}C_5H_5)]$ (208), which may be reduced to an anion by BH_4^- in acetonitrile. Reduction of $(\pi\text{-}C_5H_5)Co^{III}(B_{10}C_2H_{12})$ by ethanolic KOH in the presence of $FeCl_2$ and C_5H_6 afforded $(\pi\text{-}C_5H_5)Co^{III}[B_9C_2H_{11}Fe^{III}\text{-}(\pi\text{-}C_5H_5)]$ (209). Reduction of 209 with borohydride afforded the corresponding Fe^{II}-containing anion. Photochemical reaction of the K^+ salt of the isomers 7,8- or 7,9-$[B_9H_{10}CHP]^-$ with $Fe(CO)_5$ afforded [247] $[Fe(CO)_4\{7,8\text{-}B_9H_{10}\text{-}CHP\}]^-$. The iron atom had a trigonal bipyramidal geometry with axially bound phosphacarborane, the latter being σ-bonded to the $Fe(CO)_4$ group via the P atom.

In a polyhedral expansion reaction, reduction of 1,7-$B_6C_2H_8$ with sodium, followed by addition of NaC_5H_5 and $FeCl_2$, led [248] to the formation of $(\pi\text{-}C_5H_5)Fe(\pi\text{-}2,3\text{-}B_8C_2H_{10})$ (210), which could be reduced to a monoanion. Reaction of 1,7-$B_6C_2H_8$ with sodium naphthalenide, $FeCl_2$ and NaC_5H_5 afforded isomers of $(\pi\text{-}C_5H_5)Fe(\pi\text{-}B_6C_2H_8)$ (211 and 212). A mixture of $[B_9C_2H_{12}]^-$, $FeCl_2$ and $[C_5H_5]^-$ gave [249] $(\pi\text{-}C_5H_5)Fe(\pi\text{-}B_9C_2H_{11})$ (213) and a similar mixture involving $[B_{10}C_2H_{12}]^{2-}$ afforded [250] $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}B_{10}C_2H_{12})]^-$. The latter anion could be oxidised to its neutral, paramagnetic Fe^{III} counterpart. Reaction of two moles of $[B_{10}C_2H_{12}]^{2-}$ with $FeCl_2$ gave the dianion $[Fe(\pi\text{-}B_{10}C_2\text{-}H_{12})_2]^{2-}$, which could be oxidised, voltammetrically, in a one-electron step to the corresponding monoanion.



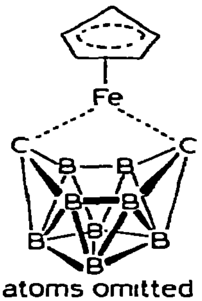
(H atoms omitted for clarity)

(208)



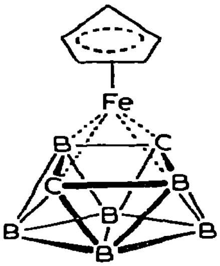
(H atoms omitted for clarity)

(209)



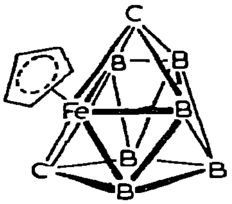
(H atoms omitted for clarity)

(210)



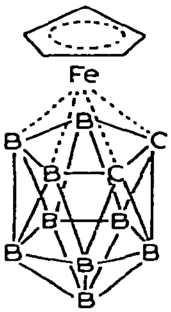
(H atoms omitted for clarity)

(211)



(H atoms omitted for clarity)

(212)



(H atoms omitted for clarity)

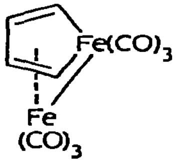
(213)

Cyclobutadiene, trimethylenemethane and arene complexes

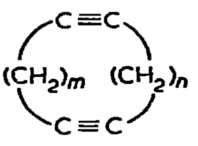
Cyclobutadienemetal compounds

Pressurisation of acetylene-saturated THF solutions of $Fe(CO)_5$ gave [251] (π-C_4H_4)$Fe(CO)_3$ and the metallocyclopentadienyl compound 214 in low yield, together with γ-butyrolactone, quinhydrone and polymeric material.

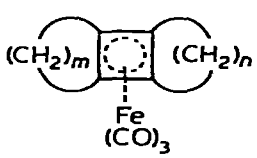
Transannular cyclisation occurred when the diacetylene 215 reacted [252] with $Fe(CO)_5$ or $Fe_3(CO)_{12}$. The products were the substituted cyclobutadiene compounds, 216 ($m = 4, n = 4$, 5 or 6; $m = 5, n = 5$ or 6), metallocyclopentadienyl species, 217 ($m = 4, n = 4$) the structure of which has been confirmed [360] (Fe—Fe distance 2.46 Å) or π-cyclopentadienyl dimers (218) ($m = 4, n = 4$, 5 or possibly 6). A possible mechanistic pathway is outlined in Scheme 26. Also produced in these reactions were $Fe_2(CO)_6$-



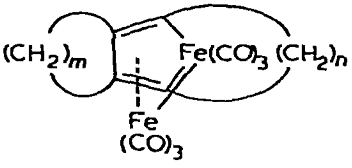
(214)



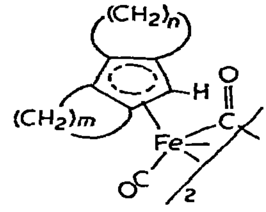
(215)



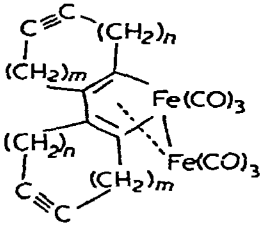
(216)



(217)

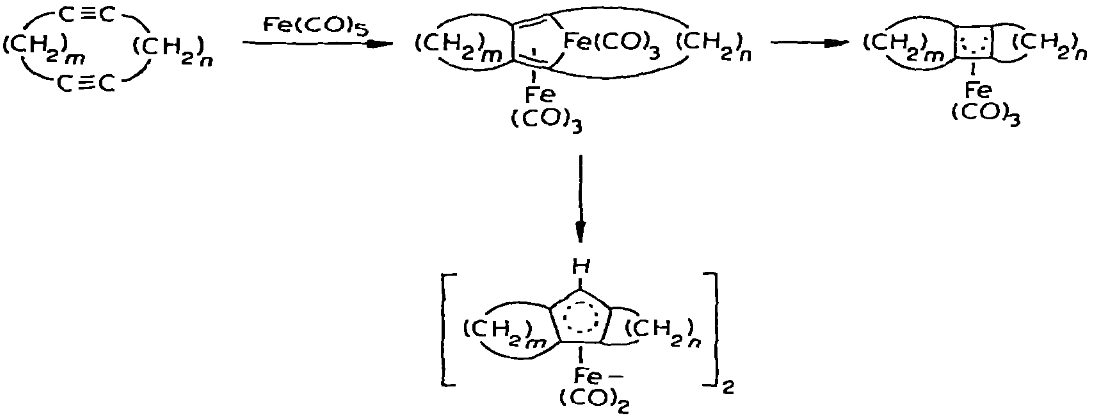


(218)

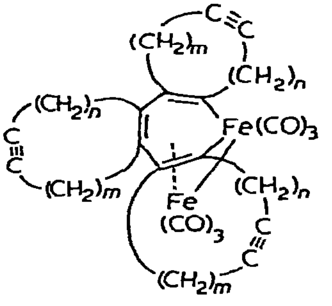


(219)

SCHEME 26

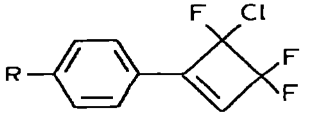


$(C_{13}H_{18})_2$, perhaps **219** (m = 4, n = 5), and $Fe_2(CO)_6(C_{13}H_{18})_3$ (**220**) (m = 4, n = 5). The π-cyclopentadienyl complex **218**, reacted with iodine giving $(\pi\text{-Q})Fe(CO)_2I$ (π-Q = substituted π-cyclopentadienyl ring), and cleavage with sodium amalgam afforded $Na[(\pi\text{-Q})Fe(CO)_2]$. The latter reacted with C_6F_6 and $SnPh_3Cl$ giving $(\pi\text{-Q})Fe(CO)_2C_6F_5$ and $(\pi\text{-Q})Fe(CO)_2SnPh_3$, respectively.

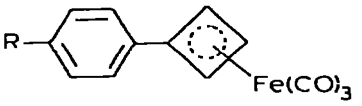


(220)

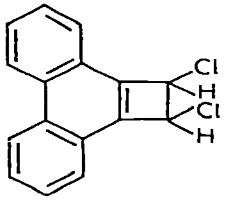
Reaction of **221** (R = Me, F, Cl, Br, OMe, or NMe_2) with $Fe_2(CO)_9$ afforded [253] the substituted π-cyclobutadiene complex **222**. There was no conjugative interaction between the π-electrons of the C_6 and C_4 rings. Dechlorination of **223** by $Fe_2(CO)_9$ afforded [254] **224**.



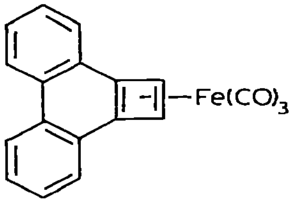
(221)



(222)



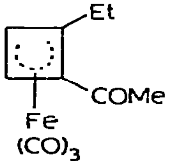
(223)



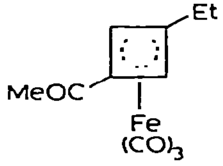
(224)

Photolysis of krypton-matrix-isolated (π-C_4H_4)$Fe(CO)_3$ gave [255], at 8 K, (π-C_4H_4)$Fe(CO)_2$, which, on warming to 35 K, recombined with the CO. Reaction of (π-C_4R_4)$Fe(CO)_3$ (R = H, Me or Ph) with $NOPF_6$ afforded [256] [(π-C_4R_4)$Fe(CO)_2(NO)$][PF_6]. Treatment of this with the appropriate Lewis bases afforded [(π-C_4R_4)Fe(CO)(NO)L]$^+$ (L = PPh_3, $AsPh_3$ or $SbPh_3$) and [(π-C_4R_4)Fe(NO)$\{P(OPh)_3\}_2$]$^+$.

Acylation of (π-C_4H_4)$Fe(CO)_3$ afforded [257] (π-C_4H_3COMe)$Fe(CO)_3$ (or RCOMe where R = π-$C_4H_3Fe(CO)_3$). Reductive dimerisation of this acyl produced RC(OH)Me · C(OH)MeR which could be dehydrated to H_2C=CR=CR=CH_2, or underwent the pinacol rearrangement giving $R_2CMe(COMe)$. Attack by base on RCOMe gave RC(Me)=CHCOR, while reduction by B_2H_6 afforded REt. Acetylation of this ethyl complex led to 225 (45%) and 226 (55%). Condensation of *p*-toluidine with RCOPh in the presence of alumina afforded [258] RC(=NC_6H_4Me)Ph, which was isolated as *syn*- and *anti*-isomers.



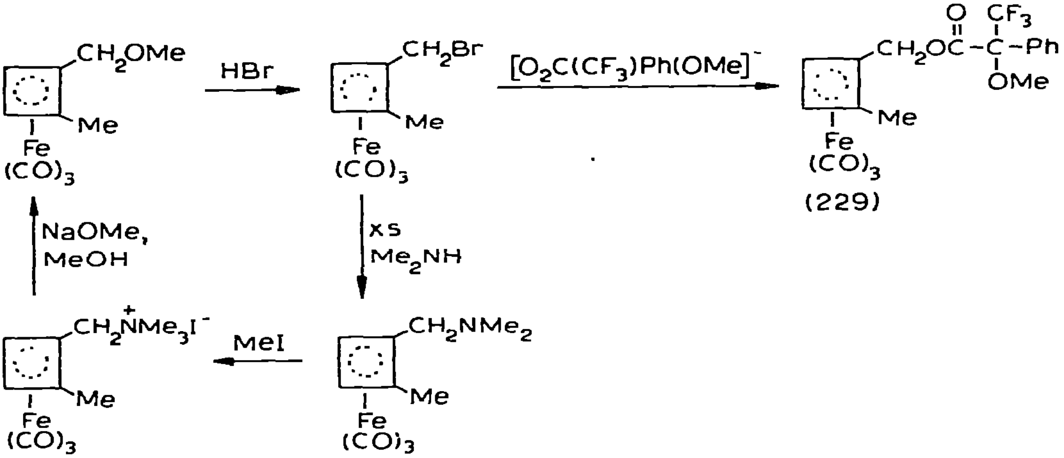
(225)



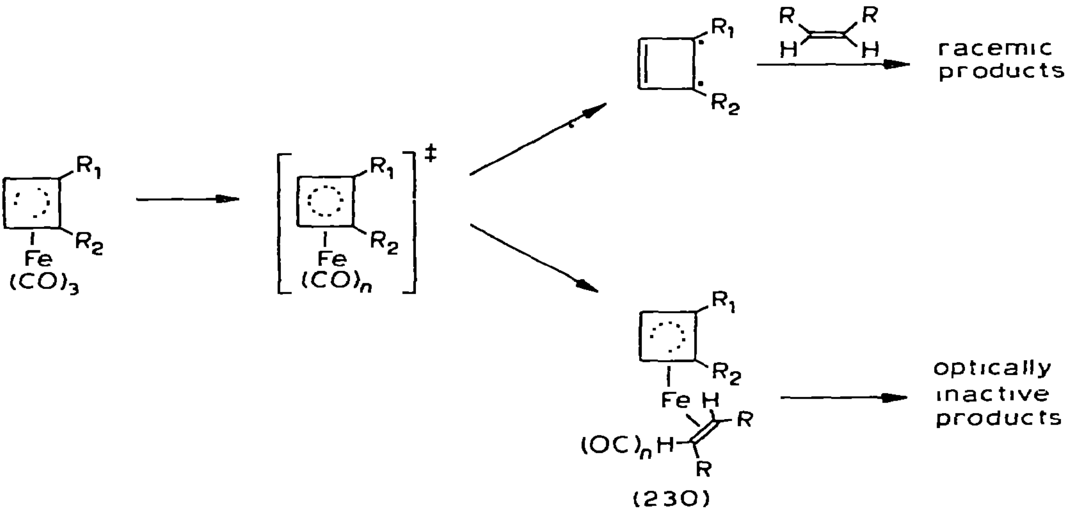
(226)

Reaction of 227 with $Na_2[Fe(CO)_4]$ gave [259] 228. This compound underwent a series of reactions outlined in Scheme 27. The aminomethyl complex was resolved into its diastereoisomers using (+)-camphor-10-sulfonic acid, and 229 was also obtained as a diastereomeric pair. The ^1H NMR spectrum of 229 indicated that less than 5% of racemisation occurred at 120° after 48 h. This contrasted with the behaviour of 5-formyl-2,4-pentadienoateiron tricarbonyl, the racemisation of which had $t_{1/2}$ = 46.5 h at ca. 120°. These results indicated that cyclobutadiene, or its derivatives, must be completely removed from the metal before racemisation can occur. Related to this point is the mechanism of reaction of (π-C_4H_4)$Fe(CO)_3$ with dienophiles in the presence of Ce^{4+}. Various schemes have already been discounted [260], but one pro-

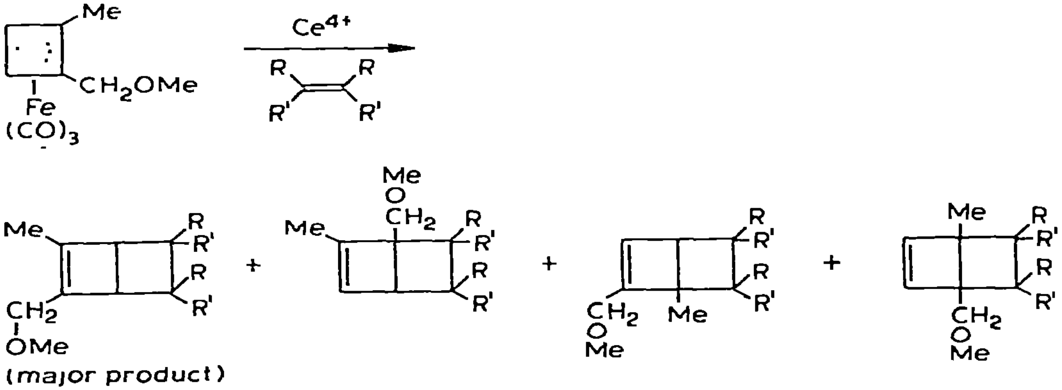
SCHEME 27



SCHEME 28



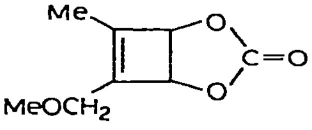
SCHEME 29



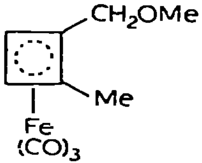
posal seems acceptable (Scheme 28). Thus 228 reacted [261] with TCNE, benzoquinone or *N*-phenylmaleimide in the presence of Ce^{4+} giving the products as shown in Scheme 29. The major product, as shown, was racemic. Reaction of (—)-[(π-2,3-C_4H_2MeEt)Fe$(CO)_3$] with $MeO_2CCH{=}CHCO_2Me$ or TCNE in the presence of Ce^{4+} also afforded [262] racemic products, and these data indicated that greater than 95% of the cyclobutadiene ligand had to react with the dienophile after the ligand had attained a plane of symmetry. Therefore, the metal could not be close enough to the ligand, e.g. as in 230 to alter its symmetry from that of the free ligand, and so could exert little influence on the electronic state, or reactivity, of the ligand.

Trimethylenemethane complexes

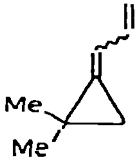
Reaction of 2,2-dimethylallylidene cyclopropane with $Fe_2(CO)_9$ afforded [263] 231, and the isomers 232 and 233; a mechanism for the formation of 234 and 235 is outlined in Scheme 30. Ring opening of Feist's ester by $Fe_2(CO)_9$



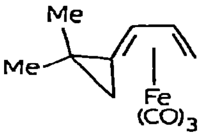
(227)



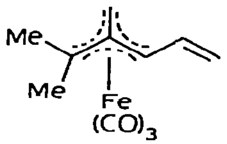
(228)



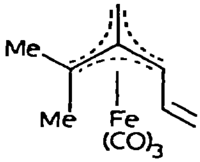
(231)



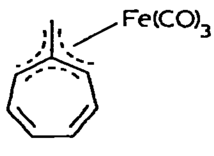
(232)



(233)

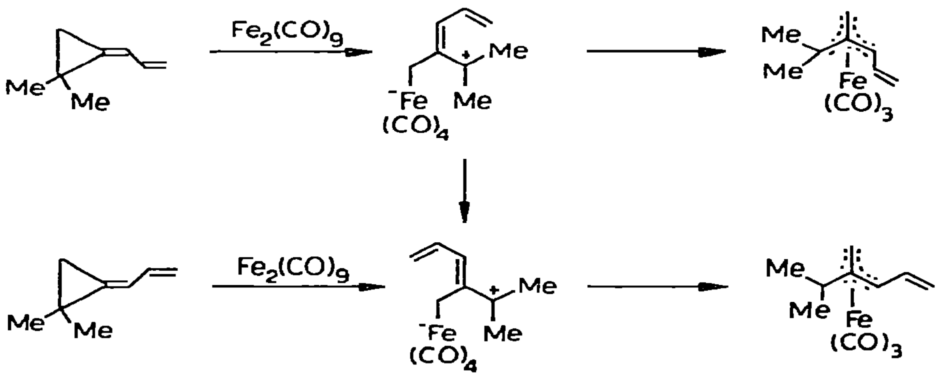


(234)

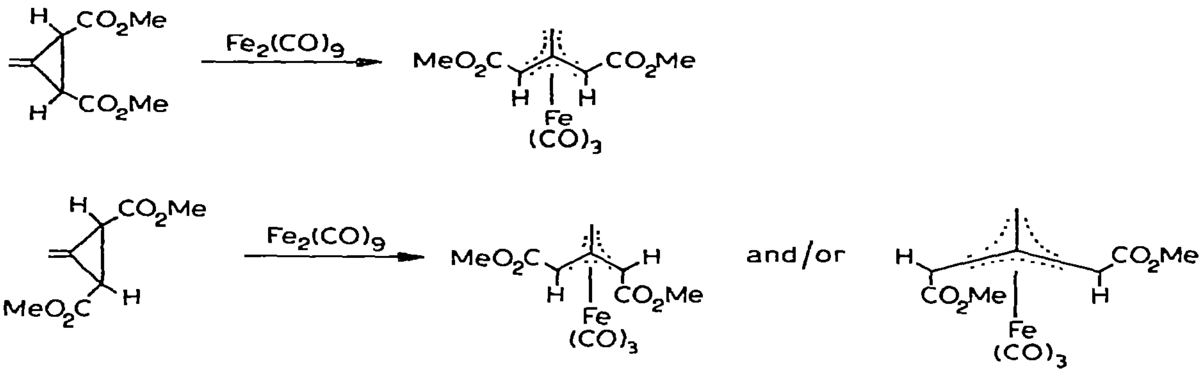


(235)

SCHEME 30



SCHEME 31



(Scheme 31) appeared [264] to be completely stereospecific and to occur in a disrotatory fashion; such a reaction with analogous cyclobutenes were unsuccessful. The structure of a trimethylenemethane species 235, derived [265] from a heptafulvene ring, has been determined [266] crystallographically; the Fe—C distance to the central, and to the peripheral C atoms are 1.95 and 2.12, 2.18 and 2.19 Å, respectively.

Arene complexes

Reduction, by sodium amalgam at −5 to −40°C, of $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_6)]^+$ gave [267] its neutral, paramagnetic counterpart. In the presence of polar solvents, exchange of the $\pi\text{-}C_6H_6$ ring by other ligands, viz. C_5H_5, other arenes, CO or $P(OPh)_3$, could be effected, thereby giving $(\pi\text{-}C_5H_5)_2Fe$, $(\pi\text{-}C_5H_5)Fe(arene)$, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ or even $[(\pi\text{-}C_5H_5)Fe\{P(OPh)_3\}_2]_2$. Among the arene species so obtained were $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_{10}H_8)$ and $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_3Me_3)$, isolated as the more stable monocations.

Iron vapour, PF_3 and benzene condensed [268] at −196° to give $(\pi\text{-}C_6H_6)Fe(PF_3)_2$, whose volatility was similar to that of $(\pi\text{-}C_6H_6)Cr(PF_3)_3$. Reaction of the iron compound with CO (1 atm) gave $Fe(CO)_3(PF_3)_2$.

Treatment of $[(\pi\text{-}C_6H_6)RuCl_2]_2$ with $[BY(pyz)_3]^-$ (pyz = 1-pyrazolyl; Y = H or pyz) gave $[(\pi\text{-}C_6H_6)Ru\{BY(pyz)_3\}]^+$ isolated as the PF_6^- salt. The crystal structure of the species with Y = pyz was determined [270], establishing the pseudo-octahedral geometry of the Ru^{II} atom, and that the $[B(pyz)_4]^-$ ligand was tridentate. Reaction of $[(\pi\text{-}C_6H_6)RuCl_2]_2$ with $CH(pyz)_3$ afforded $[(\pi\text{-}C_6H_6)Ru\{CH(pyz)_3\}]^{2+}$ [269]. Addition of H^- to the tripyrazolylborate gave the fluxional π-cyclohexadienyl complex $(\pi\text{-}C_6H_7)Ru[BH(pyz)_3]$.

Allyl and dienyl complexes

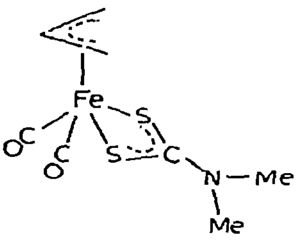
Monoallyl species

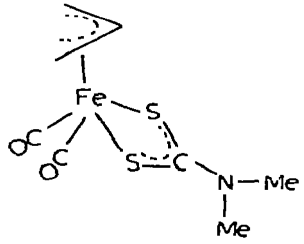
Addition of finely divided Yb, Sm, Y or Mn to THF solutions containing $(\pi\text{-}C_3H_5)Fe(CO)_3I$ afforded [271] an air-sensitive mauve solution which appeared to contain an equilibrium mixture of $(\pi\text{-}C_3H_5)Fe(CO)_3$ and $[(\pi\text{-}C_3H_5)Fe(CO)_3]_2$. Treatment of this mixture with $p\text{-}MeC_6H_4SO_2N(NO)Me$ gave $(\pi\text{-}C_3H_5)Fe(CO)_2(NO)$ (55% yield), but there was no reaction with PPh_3 (thereby eliminating, probably, the existence of an Fe—I bond, since (π-C_3H_5)Fe$(CO)_2$-(PPh_3)I was not isolated). Similar treatment of (π-C_5H_5)Fe$(CO)_2$X (X = Cl or Br) with Yb or Sm gave only [(π-C_5H_5)Fe$(CO)_2$]$_2$.

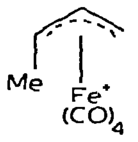
Reaction of (π-C_3H_5)Fe$(CO)_3$I with $Me_3SnS_2CNMe_2$ gave [272] two isomers of (π-C_3H_5)Fe$(CO)_2$(S_2CNMe_2) (236 and 237). The known [273] Fe$(CO)_2$-(S_2CNMe_2)$_2$ could also be obtained from this reaction, although Fe$(CO)_3$I-(S_2CNMe_2) could be conveniently prepared via Fe$(CO)_4I_2$. Treatment of (π-C_5H_5)Fe$(CO)_2$Cl with $Me_3SnS_2CNMe_2$ gave the known [275] (π-C_5H_5)Fe(CO)-(S_2CNMe_2).

UV irradiation of Fe$(PF_3)_5$ with C_3H_5X (X = Br or I) gave [274] (π-C_3H_5)Fe$(PF_3)_2$X, but when X = Cl, the 1,3-hexadiene complex, (C_4H_5Et)Fe$(PF_3)_3$ was produced.

From an X-ray crystallographic study of (π-C_3H_5)Fe$(CO)_2$(PPh_3)I it was established [275] that the metal atom had a quasi-octahedral geometry. ^{13}C


(236)

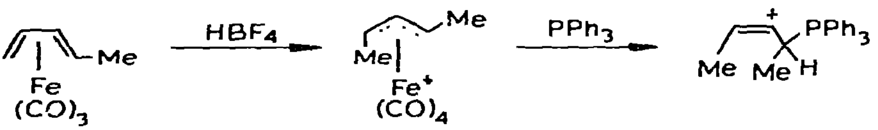

(237)


(238)

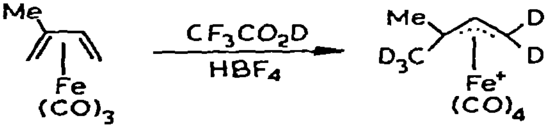
NMR spectral studies of (π-C_3H_5)Fe$(CO)_3$I confirmed [276] the existence of two isomers [277] determined by the orientation of the allyl group. A complete vibrational spectral analysis, in the liquid and solid phases, has been made [278] of (π-C_3X_5)Fe$(CO)_2$(NO) (X = H or D).

Treatment of (C_4H_6)Fe$(CO)_3$ with HBF_4 or CF_3CO_2H in the presence of CO afforded [279] the tetracarbonyl cation 238. The simpler complex, [(π-C_3H_5)Fe$(CO)_4$]$^+$ could be obtained by treating (π-C_3H_5)Fe$(CO)_3$Cl with $AgBF_4$ in the presence of CO. These cationic species were susceptible to nucleophilic attack leading, in some cases, to the release of olefins (e.g. $MeCOCH_2CO_2Me$ gave H_2C=$CHCH_2CH(CO_2Me)COMe$). However, treatment of [(π-C_3H_5)Fe$(CO)_4$]$^+$ with PPh_3 or pyridine (L) gave [(H_2C=$CHCH_2L$)Fe$(CO)_4$]$^+$. When there was a choice between the formation of a *cis* or *trans* double bond in the olefin so formed, *cis*-geometry was favored (e.g. Scheme 32). Stereospecifically labelled

SCHEME 32

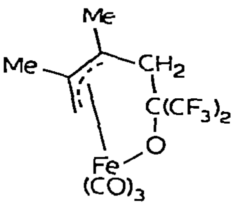


SCHEME 33

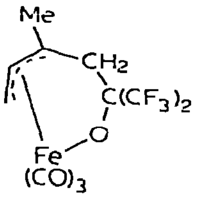


species could be prepared using CF_3CO_2D, viz. Scheme 33, and it was shown that nucleophilic attack occurred preferentially at the unsubstituted terminal π-allyl C atom.

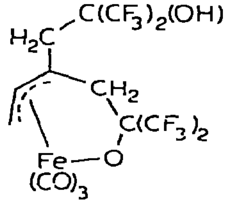
Hexafluoroacetone added [280] to $(2,3\text{-}C_4H_4Me_2)Fe(CO)_3$ and $(2\text{-}C_4H_5Me)Fe(CO)_3$ under UV irradiation, giving **239** and **240**. The latter underwent a rearrangement at 80°, probably involving insertion of $(CF_3)_2CO$ into a CH bond, giving **241** and **242**. Similar photolysis of $(\pi\text{-}C_4Me_4)Fe(CO)_3$ with $CF_2{=}CFH$ afforded [281] **243** and **244**. Carbonylation of the latter at 80° gave **245**, but when heated in hexane, **244** produced $[(\pi\text{-}C_5H_4CF_3)Fe(CO)_2]_2$. It was suggested that this dimer could have been formed via a route involving the migration of hydride from the CF_3CH group to the metal atom, with concomitant ring enlargement via a 1,2-shift, giving $(\pi\text{-}C_5H_4CF_3)Fe(CO)_2H$.



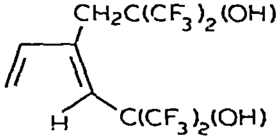
(239)



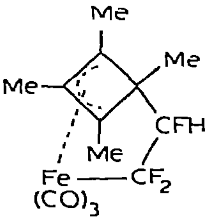
(240)



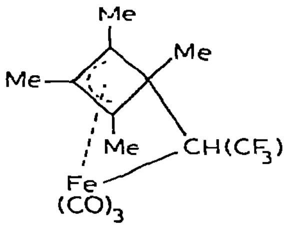
(241)



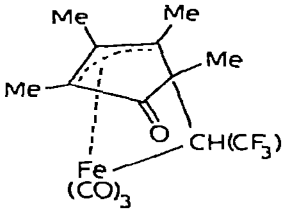
(242)



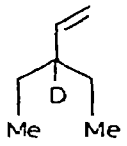
(243)



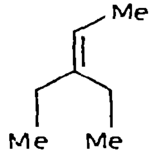
(244)



(245)



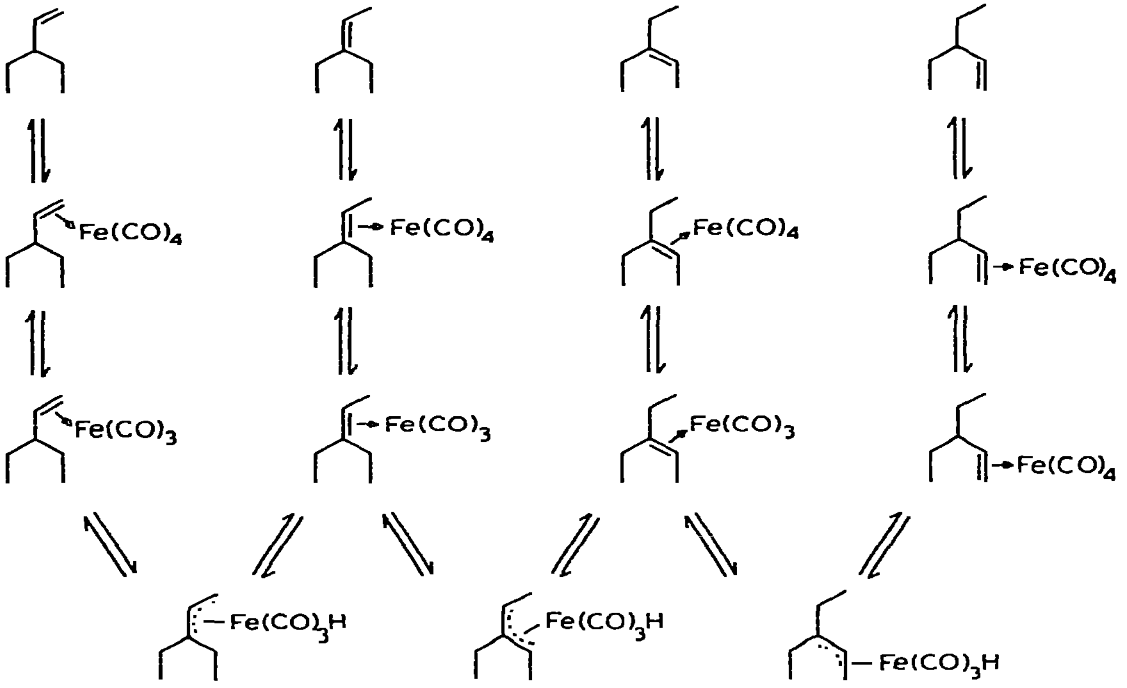
(246)



(247)

The catalytic isomerisation by $Fe_3(CO)_{12}$ of the ethylpentene **246**, gave [282] **247** in which the deuterium label had been randomly distributed in all the methyl groups. It was found that the scrambling of D into the methyl groups and terminal vinylic positions of recovered **246** occurred almost twice as fast as isomerisation. The absence of crossover products from the isomerisation of a mixture of **246** and $Me_2CHCH{=}CH_2$ indicated that olefin isomerisation occurred via an intramolecular hydride shift. No primary deuterium effect was observed when a mixture of 246 and its undeuterated analog were isomerised and so it was suggested that a π-allyl iron hydride was involved as a reaction intermediate. The proposed mechanism, which does not involve an addition/elimination of Fe—H, is outlined in Scheme 34.

SCHEME 34

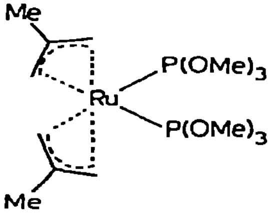


Bis-allyl complexes

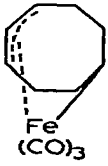
The structure of $(\pi\text{-}C_3H_4Me)_2Ru[P(OMe)_3]_2$ (248) [283] has been determined crystallographically [284]. The bonding of the methallyl groups is asymmetric, the mean Ru—C (*trans* to P) and Ru—C (*trans* to C) bond lengths being 2.38 and 2.18 Å, respectively. The methallyl groups are also non-planar, the methyl group being bent out of the plane of the allyl fragment by ca. 12°.

Monomeric allyl species derived from cyclic olefins

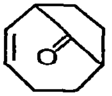
The kinetics of the reaction of the cyclooctadienyl complex 249, to give $(C_8H_{12})Fe(CO)_2L$, and then the transannular ketone 250 and $Fe(CO)_2L_3$ (L =



(248)



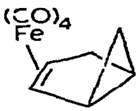
(249)



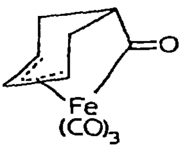
(250)

Lewis base nucleophile) have been studied [285]. Under pseudo-first order conditions with poor nucleophiles (PPh_3 or $P(OPh)_3$), substitution of the CO groups *trans* to the Fe—C σ-bond occurred probably via a CO dissociative pathway. The limiting reaction rate was independent of the nature of L, but the reaction was inhibited by CO. There was no evidence of further reaction of the substituted organometallic to give the ketone **250**. With stronger nucleophiles, e.g. alkyl phosphines or phosphites, the reaction occurred by two paths, one giving the substituted organoiron species, and the other **250**; CO reacted only very slowly with the organoiron species to give the transannular ketone. It seemed likely that a CO group bound to the metal inserted into the Fe—C bond to give **250**.

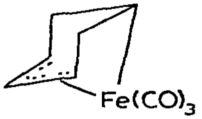
Treatment of bicyclo[3.1.0]hex-2-ene with $Fe_2(CO)_9$ gave [286] **251** and **252** which could be decarbonylated (reversibly) at 130° to give **253** and hence its isomer $(1,3\text{-}C_6H_8)Fe(CO)_3$. Bicyclo[4.1.0]hept-2-ene reacted similarly to give **254** which also decarbonylated (reversibly) to form **255** and so **251**. The last two could also be produced by BH_4^- reduction of **257**.



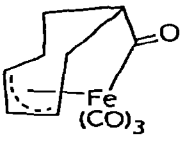
(251)



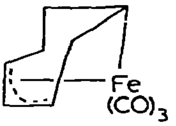
(252)



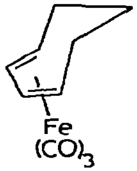
(253)



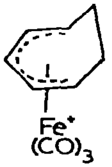
(254)



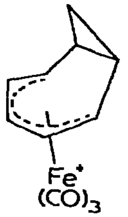
(255)



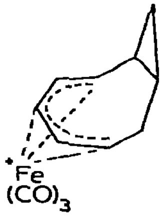
(256)



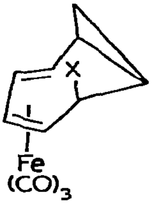
(257)



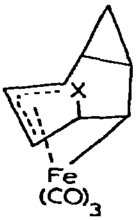
(258)



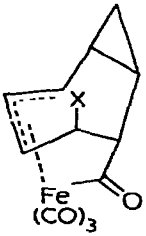
(259)



(260)



(261)



(262)

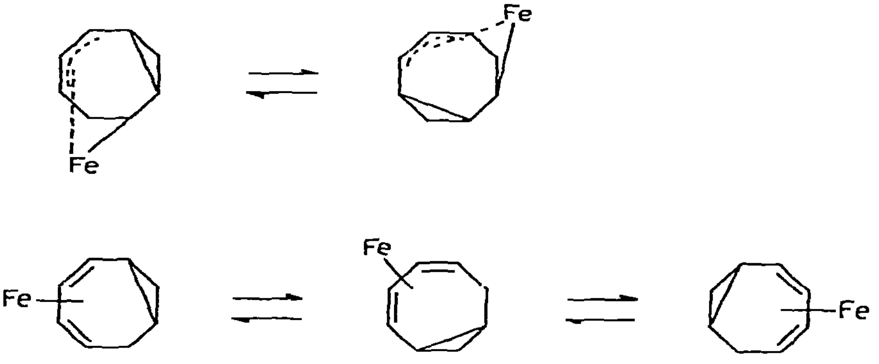
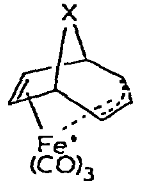
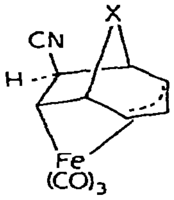


Fig. 16.

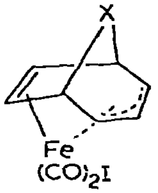
The complex $[(C_8H_9)Fe(CO)_3]^+$, represented as an equilibrium between 258 and 259, was reduced [287] by H^- giving a mixture of 260 (derived from 258) and 261 (derived from 262). Both of these compounds were fluxional (Fig. 16) and the latter underwent (reversible) carbonylation to give 262. Treatment of 263 (X = CH_2, CH=CH or o-C_6H_4) with aqueous CN^- gave [288] 264. With I^- however, 263 afforded 265 which, on treatment with LiMe gave the corresponding metal methyl complex. It was proposed that the lack of conjugation between the unsaturated moieties in 264 was essential for its conversion with CN^- into a π-allylmetal species also containing a Fe—C σ-bond.



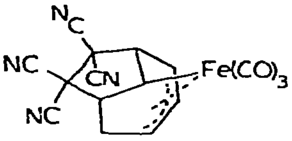
(263)



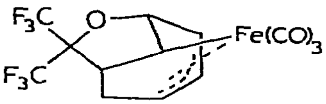
(264)



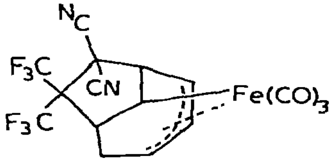
(265)



(266)



(267)



(268)

Reaction of $(C_7H_8)Fe(CO)_3$ (C_7H_8 = cycloheptatriene) with TCNE afforded [289] 266, whose structure has already been established [290]. With

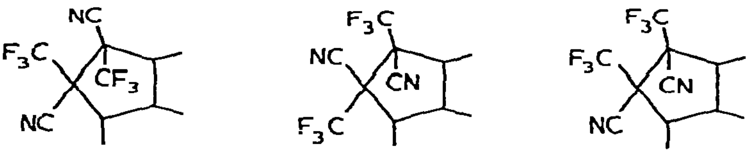


Fig. 17.

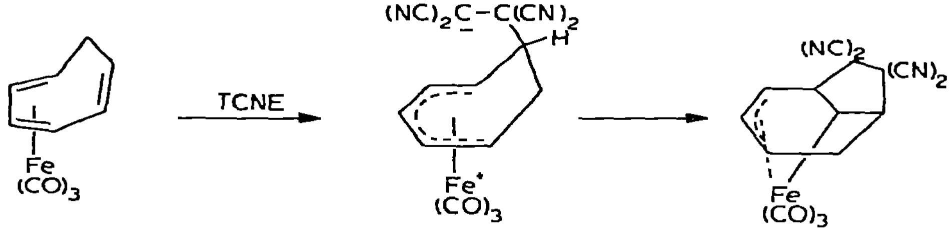
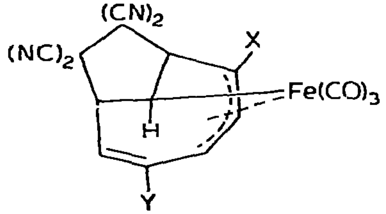


Fig. 18.

$(CF_3)_2CO$ and $(CF_3)_2C{=}C(CN)_2$, 267 and 268 were also produced. With $(CF_3)(NC)C{=}C(CN)(CF_3)$, however, three isomers were formed (Fig. 17.). These reactions involved 1,3-addition of the electrophilic olefin to the coordinated cycloheptatriene (Fig. 18). Reaction of $(C_8H_7R)Fe(CO)_3$ (R = H, Me, Br, Ph or CPh_3) with TCNE gave 269.



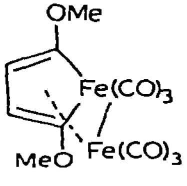
X = Y = H
X = Me, Y = H
X = H, Y = Br
X = H, Y = Ph

(269)

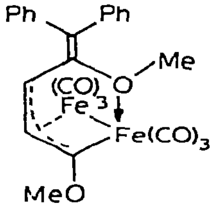
Di- and tri-metallic allyl complexes

Reaction of diphenyldiazomethane with 270 under UV light gave [291] 271, the structure of which was determined crystallographically. The Fe—Fe distance was 2.62 Å and the O→Fe distance 2.07 Å.

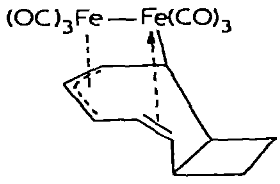
The structure and temperature-dependent ^1H NMR spectrum of the $Fe_2(CO)_6$ adduct of bicyclo[6.2.0]deca-1,3,5-triene (272) has been investigated [292]. The bonding was similar to that encountered [293] in $(C_8H_{10})Fe_2(CO)_6$ and $(C_8H_8)Ru_2(CO)_6$, and while the low temperature (−130°C) NMR spectrum was consistent with the solid state structure (Fe—Fe distance 2.79 Å), that at −70°C indicated a time-averaged plane of symmetry for the system resulting from the fluxionality of the molecule.



(270)



(271)



(272)

While the preparation of 273, from hexadiene and $Ru_3(CO)_{12}$, has been reported previously [294], it may also be produced [295] from 1,3-cyclo-

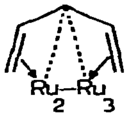
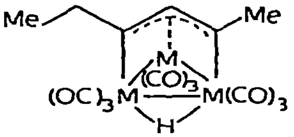
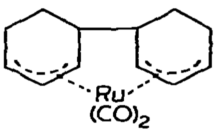


Fig. 19.

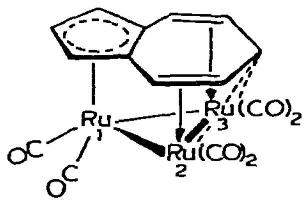
hexadiene (4 mol) and $Ru_3(CO)_{12}$ (1 mol) in refluxing heptane. The reaction involved the catalytic cleavage of an unstrained C—C σ-bond. With a large excess of cyclohexadiene, **273** afforded (1,3-C_6H_8)$Ru(CO)_3$ which is an active catalyst for inter- and intra-molecular hydrogen transfer reactions. (1,4-C_6H_8)-$Ru(CO)_3$ reacted with 1,3-C_6H_8 giving 1,4-C_6H_8, benzene, cyclohexene and **274**. However, no **273** was obtained upon decomposition of (1,3-C_6H_8)$Ru(CO)_3$.



(273)



(274)



(275)

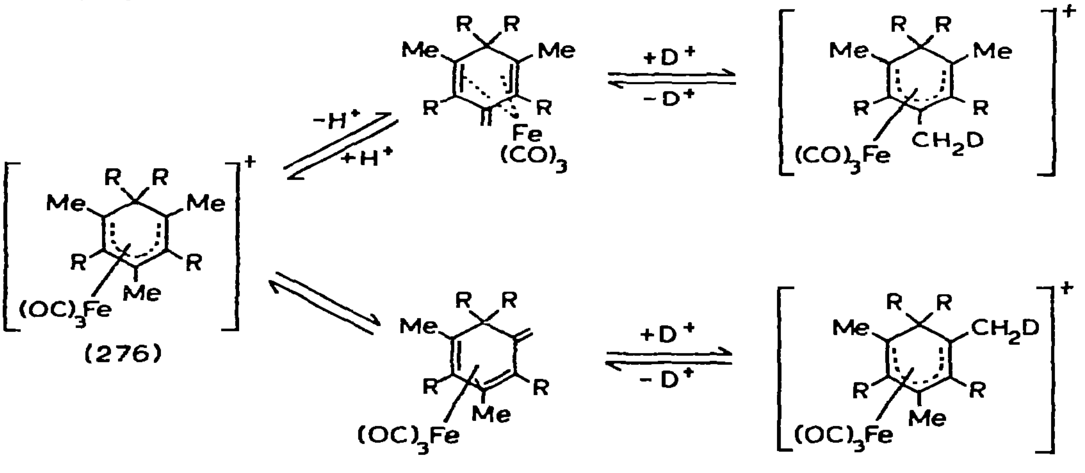
While *cis*-1,3,5-hexatriene cyclised in the presence of $Ru_3(CO)_{12}$ in refluxing heptane to give modest yields of benzene (42%), the *trans*-isomer afforded extremely low yields (1.2%).

Azulene reacted with $Ru_3(CO)_{12}$ giving [296], inter alia, $(C_{10}H_8)Ru_3(CO)_7$ the structure of which (**275**) has been determined crystallographically. The three metal atoms form an isoceles triangle (Ru(1)—Ru(2) = Ru(1)—Ru(3) = 2.94-2.95; Ru(2)—Ru(3) = 2.94 Å); Ru(2) and Ru(3) lie below the 7-membered ring and the bonding could be regarded as in Fig. 19.

Dienyl complexes

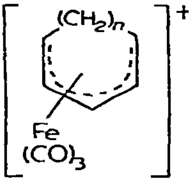
The cyclohexadienyl complexes **276** (R = H or Me) underwent [297] H/D exchange at the methyl groups in dilute deutero acids, as well as D_2O. The proposed mechanisms are outlined in Scheme 35, and the lower path was

SCHEME 35

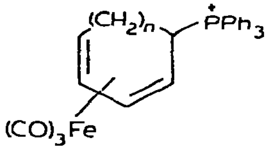


favored. Compounds containing exocyclic methylene groups could be synthesised by proton abstraction using NH_2(t-Bu). Consequently, it was expected, and observed that, in 276 (R = H), H/D exchange occurred exclusively at the methyl groups in the 2 and 6 positions.

Addition of PPh_3 to the dienyl species 277 (*n* = 1 or 2) gave [298] the ring-bonded phosphonium derivative 278. Attempts to abstract a proton from 278 (*n* = 2) using NEt_3 or 1,8-dimethylaminonaphthalene were unsuccessful. Addition of I^- to these dienyl cations afforded (π-dienyl)$Fe(CO)_2I$, and treatment of these with Ag^+ in the presence of PPh_3 gave the metal-bound phosphine cations $[(\pi\text{-dienyl})Fe(CO)_2(PPh_3)]^+$.



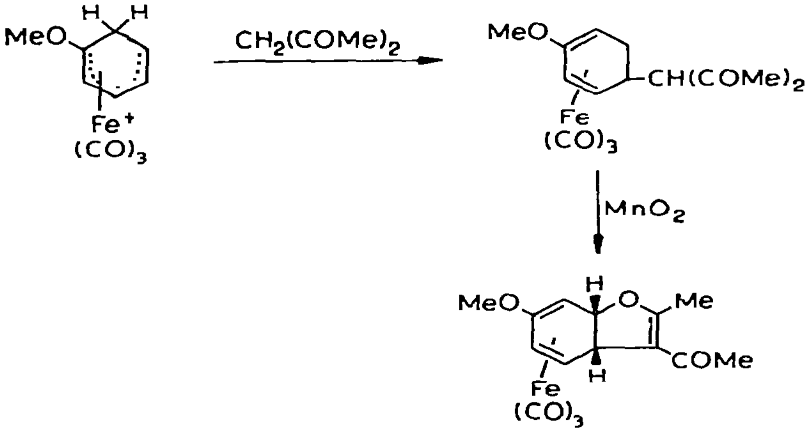
(277)



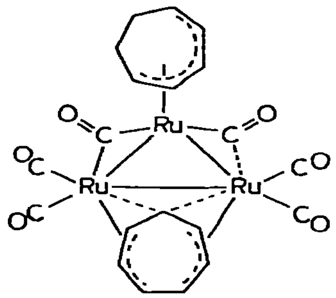
(278)

The formation of C—C bonds was achieved [299] by treating $[(\pi\text{-}C_6H_7)Fe(CO)_3]^+$ with indole, methylindole, pyrrole, furan, thiophen, imidazole or even ferrocene (YH). The products were neutral diene complexes, $(C_6H_7Y)Fe(CO)_3$. Treatment of cyclohexadienyl complexes with β-diketones or β-ketoesters, followed by oxidation of the product of these reactions by MnO_2, afforded [300] dihydrofuran—iron carbonyl complexes (Scheme 36).

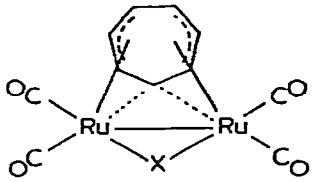
SCHEME 36



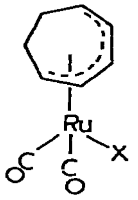
Reaction of cycloheptatriene with $Ru_3(CO)_{12}$ afforded [301] $(C_7H_{10})Ru(CO)_3$ (a derivative of cycloheptadiene), $(C_7H_8)Ru(CO)_3$, $(C_7H_8)Ru(CO)_2$, $(C_7H_8)Ru_2(CO)_6$ (all in low yield) and $(C_7H_9)(C_7H_7)Ru_3(CO)_6$ (279) (in high yield). The structure of 279 has been determined crystallographically; the three ruthenium atoms formed a nearly equilateral triangle (Ru—Ru 2.84-2.86 Å), and there was an asymmetrically bridging CO group. Reaction of 279 with I_2 or CX_4 (X = Cl or Br) afforded the fluxional 280 and 281.



(279)



(280)

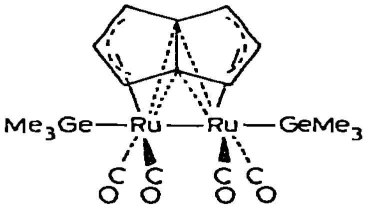


(281)

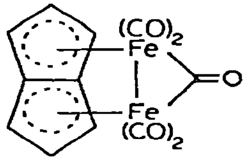
Pentalenyl complexes

In refluxing octane or heptane, *cis*-Ru(CO)$_4$(GeMe$_3$)$_2$ converted [302] C_8H_8 into a metal-stabilised pentalenyl complex 282, the structure of which was confirmed crystallographically. The bonding and configuration of the pentalene ring is illustrated in Fig. 20; the Ru—Ru distance is 3.05 Å and the dihedral angle between the two ring planes is 171°. When the reaction was carried out in refluxing hexane, the fluxional (C_8H_8)Ru(CO)$_2$(GeMe$_3$)$_2$ was produced. Pentalene and its 1,3-dimethyl dimer reacted [303] with Fe$_2$(CO)$_9$ in methylcyclohexane under CO at 50° giving pentalenyl derivatives, e.g. 283, in low yield.

Fig. 20.



(282)



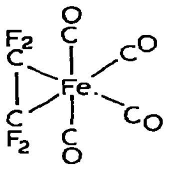
(283)

Olefin complexes

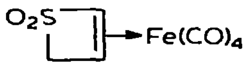
Mono-olefinic compounds

Irradiation of Fe$_2$(CO)$_9$ with Q (Q = *cis*- or *trans*-RCH=CHR′; R, R′ = F, Cl, Br or I; CH$_2$=CHBr or CH$_2$=CCl$_2$; acrylonitrile, methylmethacrylate, methyl-*trans*-croconate, EtOCH=CH$_2$, acenaphthalene, methylfumarate and dimethylmaleate) led to the formation [304] of QFe(CO)$_4$ in which Q occupied an equatorial position in the molecular trigonal bipyramid.

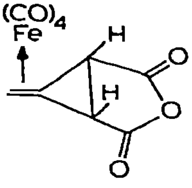
A gas phase electron diffraction study of (C_2F_4)Fe(CO)$_4$ revealed [305]



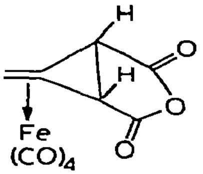
(284)



(285)



(286)

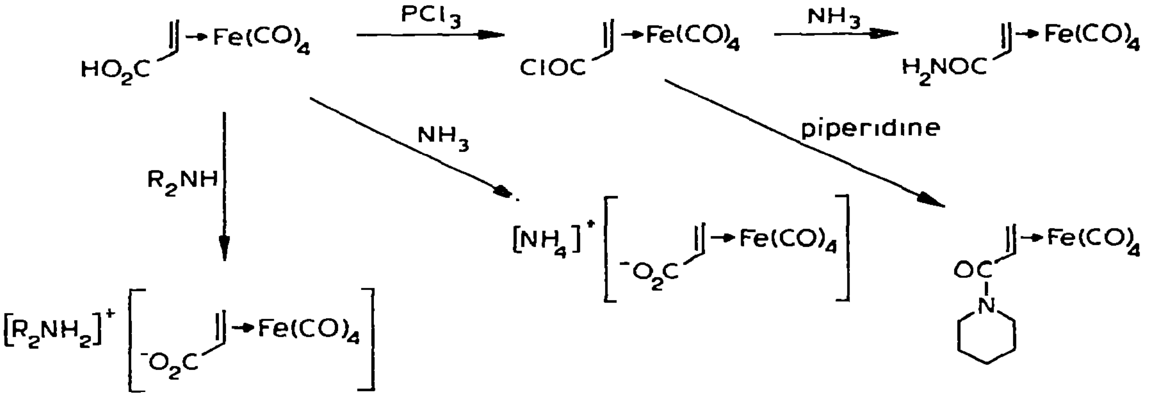


(287)

that the molecule had a distorted octahedral structure (284). The C_2F_4 group resembled a fragment of perfluoropropane rather than $F_2C{=}CF_2$; the Fe—C (CF_2) bond length is 1.99 Å, and the coordinated C—C distance 1.53 Å (ca. 1.34 Å in the free olefin). Thus the compound could be described as a derivative of Fe^{II}.

Reaction of thiacyclobutene-1,1-dioxide with $Fe_2(CO)_9$ gave [306] 285 which, on pyrolysis, afforded $Fe_3(CO)_9S_2$. Treatment of Feist's anhydride with $Fe_2(CO)_9$ gave [307] 286 and 287. Reaction of $(HC_2{=}CHCO_2H)Fe(CO)_4$ with weak Lewis bases and PCl_3 occurred [308] at the carboxylic group (Scheme 37). The pK_a value for the free acid was 4.10 while that for the complexed

SCHEME 37



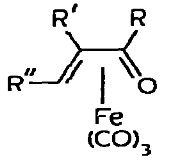
$R = H$, cyclo-C_5H_{10}, cyclo-C_4H_8

species was 5.16, revealing the net electron-withdrawing effect of the $Fe(CO)_4$ group. With stronger Lewis bases L (tertiary phosphines, phosphites or pyridine), $(H_2C{=}CHCO_2H)Fe(CO)_4L$ was formed, probably involving a hydrogen bond between the carboxylate group and L, i.e. $(OC)_4Fe(H_2C{=}CHCO_2 \cdots H \cdots L)$.

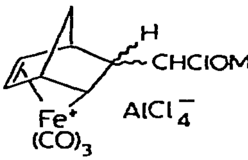
UV irradiation of $Fe(PF_3)_5$ in the presence of *trans*-RHC=CHR′ (R = CN, R′ = H or Me; R = H, R′ = Ph or CO_2Me) afforded [309] *trans*-(RHC=CHR′)-$Fe(PF_3)_4$. Similar treatment with R″HC=CR′COR gave 288 (R = OMe, R′ = Me, R″ = H; R = R′ = H, R″ = Me; R = Me, R′ = R″ = H).

Non-conjugated diene complexes

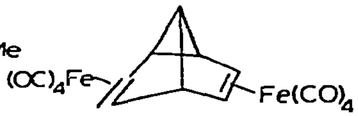
Protonation of the norbornadiene complex $(C_7H_8)Fe(CO)_3$ with HSO_3F gave [310] $[(C_7H_8)Fe(CO)_3H]^+$ (the deuteride was obtained using D_2SO_4) which



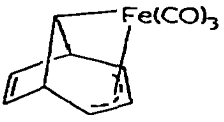
(288)



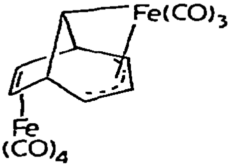
(289)



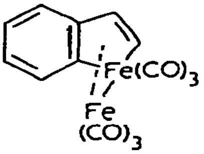
(290)



(291)



(292)

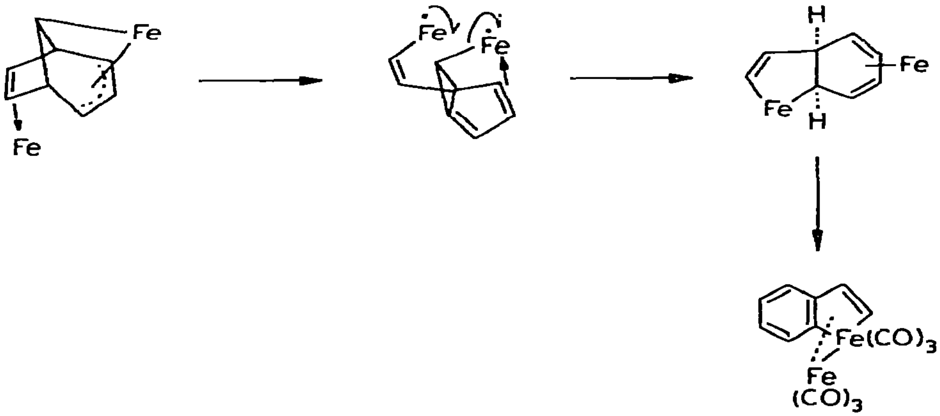


(293)

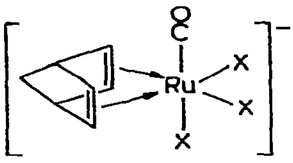
did not undergo H/D exchange. Reaction with $Cl_2HCCOMe$ and $TiCl_4$ in dichloromethane led to the formation of the aldehyde, $(C_7H_7CHO)Fe(CO)_3$ which could be reduced to $(C_7H_7Me)Fe(CO)_3$, also obtainable by reduction of $(C_7H_7CO_2Me)Fe(CO)_3$. Acylation could not be successfully achieved, but the formation of the aldehyde indicated perhaps the existence of intermediary homoallylic ions, e.g. 289.

Semibullvalene reacted [311] with $Fe_2(CO)_9$ giving four complexes, 290, 291, 292 and 293. The last was derived by skeletal rearrangement of 292 (Scheme 38).

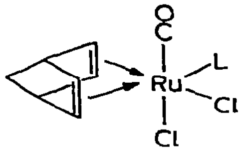
SCHEME 38



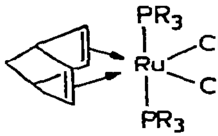
Treatment of $[(C_7H_8)Ru(CO)Cl_2]_n$ with X^- (X = Cl or Br) gave [312] $[(C_7H_8)Ru(CO)X_3]^-$ (294), but reaction with $[Ph_4As][HCl_2]$ afforded only $[Ph_4As]_2[Ru(CO)_2Cl_4]$. $Ru(CO)L_2Cl_3$ was produced [313] on treatment of 294 (X = Cl) when L = Me_2S, Me_2SO or acrylonitrile; it was also formed, together with $(C_7H_8)Ru(CO)LCl_2$ (295), when L = $AsPh_3$, $SbPh_3$ or pyridine. With an excess of $SbPh_3$, only $Ru(CO)(SbPh_3)_3Cl_2$ was formed. With PPh_3 (1/2 molar ratio), $[Ru(CO)(PPh_3)_2Cl_2]_2$ was obtained, while an excess of the phosphine afforded $Ru(CO)(PPh_3)_3Cl_2$. Reaction with $PPhMe_2$ led to the for-



(294)



(295)

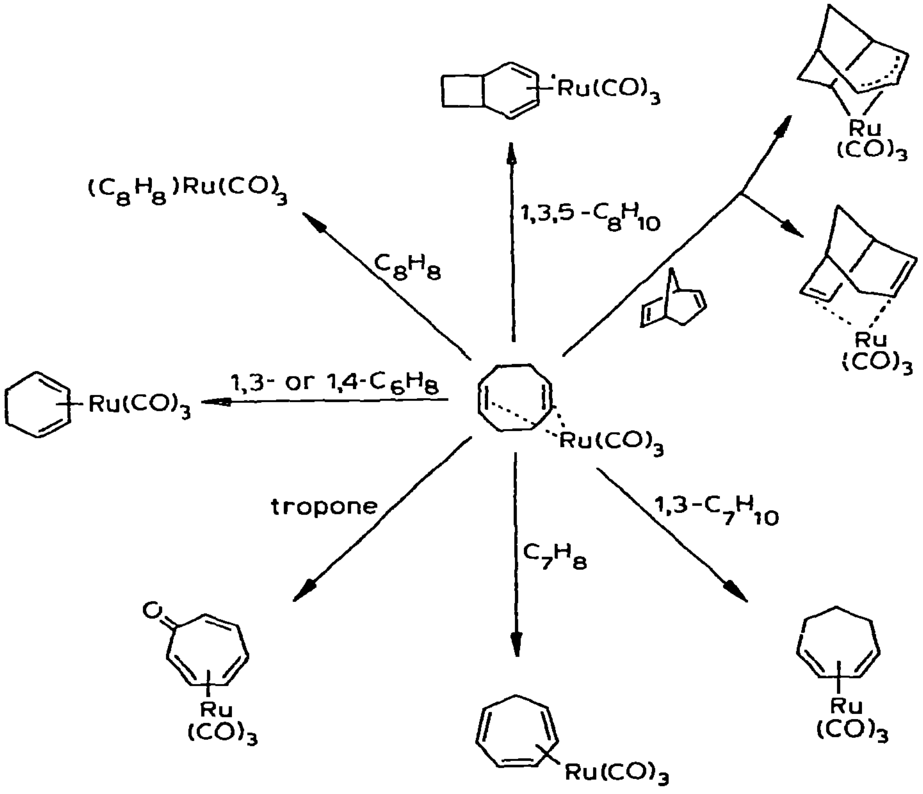


(296)

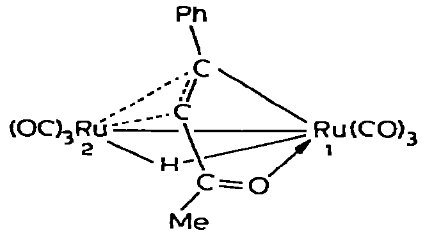
mation of $(C_7H_8)Ru(PPhMe_2)_2Cl_2$ (296), while with bipyridyl or *o*-phenanthroline (N—N) in various reaction stoichiometries, $[Ru(CO)(N{-}N)Cl_3]^+$, $[Ru(CO)(N{-}N)Cl_2]_2$ or $[Ru(CO)(N{-}N)_2Cl]Cl$ were formed.

Some ligand displacement reactions [314] of 1,5-cyclooctadienetricarbonylruthenium are summarised in Scheme 39. Reaction of this compound

SCHEME 39



with benzylideneacetone afforded [315] 297, the structure of which was determined crystallographically. Ru(1) has an approximately octahedral geometry while Ru(2) is approximately trigonal bipyramidal with distortions towards an octahedron. The Ru—Ru distance, 2.86 Å, is identical to that in $(C_8H_8)Ru_2(CO)_6$ [316], and the Ru—H distances are set at 1.85 (Ru(1)) and 164 Å (Ru(2)); the Ru—H—Ru angle is 110°.



(297)

Conjugated non-cyclic diene complexes

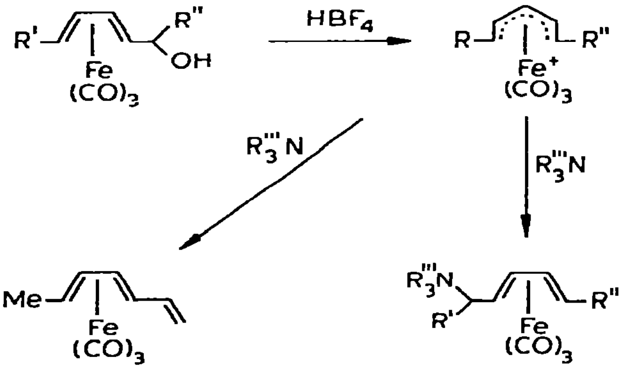
Mixtures of iron tricarbonyl derivatives of dienes and dienones in *m*-xylene and 2,4-dimethylacetophenone could be separated [317], and the ketones determined quantitatively, using high speed liquid—liquid partition chromatography.

By heating $Fe(CO)_5$ with 1-aryl-1-cyclopropylethylenes or 1,1-dicyclopropylethylene, iron tricarbonyl complexes of 2-aryl-1,3-pentadienes or 2-cyclopropyl-1,3-pentadiene and 3-(1-propenyl)cyclohex-2-enone could be produced [318]. The compounds were formed by cyclopropane ring opening followed by hydrogen migration and coordination to iron, and the cyclohexenone species was produced from the cyclopropylpentadiene species by ring opening followed by CO insertion.

Reaction of 1-ferrocenyl-1-buten-3-ol with $Fe_2(CO)_9$ and Cu^{2+} afforded [319] $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4CH{=}CHCH{=}CH_2)$ which reacted further with $Fe_2(CO)_9$ giving 298. UV irradiation of $Fe(PF_3)_5$ in the presence of a variety of butadiene derivatives, as well as 1,3-cyclohexa-, -cyclohepta- and -cycloocta-dienes, afforded [320] $(diene)Fe(PF_3)_3$; norbornadiene, also, gave $(C_7H_8)Fe(PF_3)_3$ without skeletal rearrangement. A crystal structure determination of $(1,4\text{-}C_4H_4Ph_2)$-$Fe(CO)_3$ established [321], as expected, that there was no conjugation between the phenyl rings and the C_4 group.

Reaction of the dienyl cations, obtained [322] by acid dehydration of iron tricarbonyl derivatives of dienols (Scheme 40), with tertiary amines led

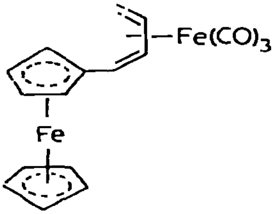
SCHEME 40



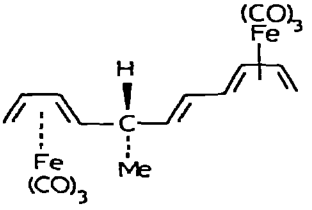
R' = R'' = Me
(299)

R' = H, R'' = Me,
R' = H, R'' = Et
R''' = Me or Et

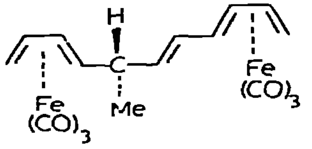
either to addition to the diene fragment, or to proton abstraction, depending on the nature of the dienyl substituents. It was noted that $[(\pi\text{-}C_6H_7)Fe(CO)_3]^+$ was unaffected by water whereas the open-chain dienyl cations were readily hydrolysed. However, the open-chain dienyl species did not undergo CO displacement by I^- to give $(\pi\text{-dienyl})Fe(CO)_2I$. The triene **299** was also produced [323] by treatment of the cationic dienyl precursor with alumina for 1 h,



(298)



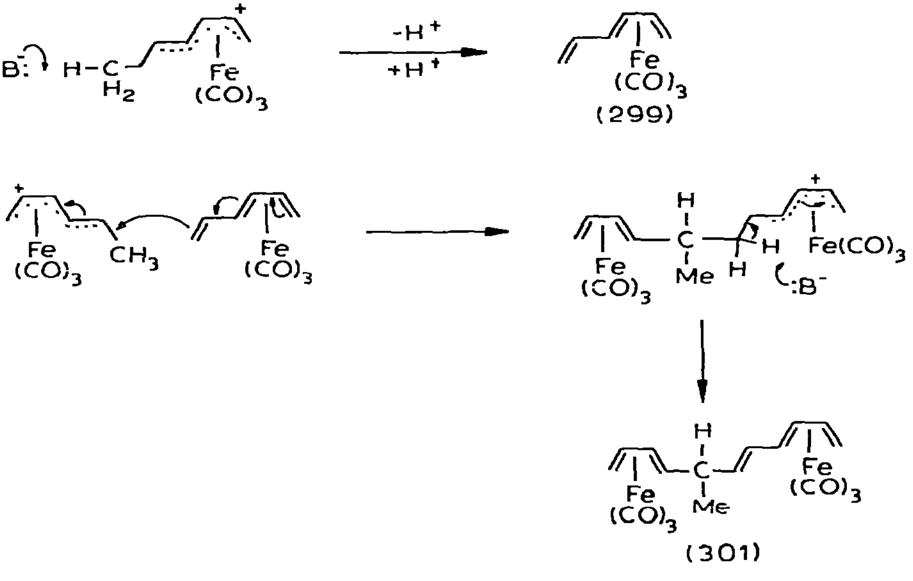
(300)



(301)

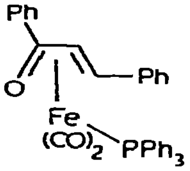
but after 60 h a mixture of isomeric dimers, probably **300** and **301**, was formed. A possible mechanism is outlined in Scheme 41.

SCHEME 41



Non-cyclic heterodiene complexes

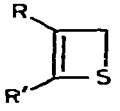
Reaction of the chalcone complex $(PhCOCH{=}CHPh)Fe(CO)_4$ with PPh_3 afforded [324] a mixture of $(olefin)Fe(CO)_3(PPh_3)$ (A), $(olefin)Fe(CO)_2(PPh_3)$ (B), $Fe(CO)_{5-n}(PPh_3)_n$ ($n = 1$ or 2) and $(PhCOCH)_2$, but after one month, a 60% yield of $(PhCOCH{=}CHPh)Fe(CO)_2(PPh_3)$ (**302**) was obtained. Similar treatment of $(PhCOCH{=}CHCOPh)Fe(CO)_4$ and $(PhCOCH{=}CHCO_2Me)Fe(CO)_4$ afforded mixtures of complexes of A and B type. Treatment of ω-phenylpolyene aldehydes with $Fe_3(CO)_{12}$ afforded [325] isomeric mixtures of [Ph-



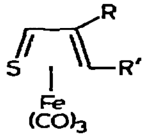
(302)

$(CH{=}CH)_nCHO]\,Fe(CO)_3$ (n = 2-5). The major product was always an isomer with the $Fe(CO)_3$ group bound to the butadiene fragment adjacent to the aldehyde function. UV spectral studies indicated that the $C_4Fe(CO)_3$ unit interrupted considerably the transmission of conjugative effects along the polyene chain.

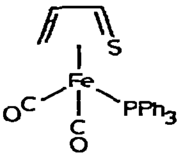
Reaction of the thiacyclobutenes **303** with $Fe_2(CO)_9$ gave [326] **304** which, on treatment with PPh_3 (R = R′ = H) afforded **305**, the structure of



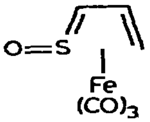
(303)



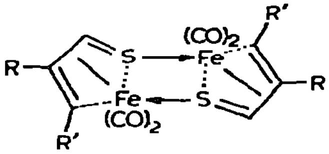
(304)



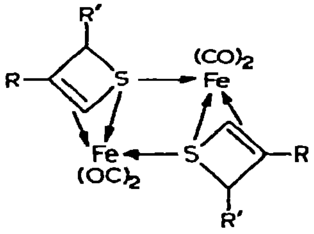
(305)



(306)



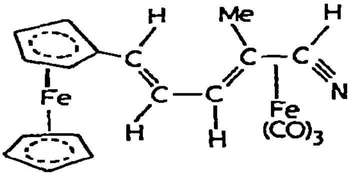
(307)



(308)

which has been elucidated [327] crystallographically. The thioacrolein ligand is essentially planar, the C—C distances being 1.39, 1.33, and the C—S distance 1.79 Å, respectively. Peroxide treatment of **304** (R = R′ = H) gave **306** while thermolysis of the tricarbonyl afforded a dimeric species, represented either as **307** or **308**.

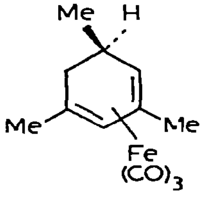
The bimetallic **309** was produced [328] in low yield by reacting (π-C_5H_5)Fe(π-$C_5H_4CH{=}CHCMe(OH)CH_2CN$) with $Fe_3(CO)_{12}$ and Cu^{2+} in benzene.



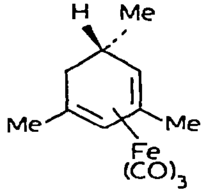
(309)

Conjugated cyclic diene complexes

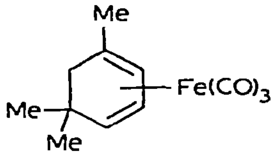
By heating $Fe_2(CO)_9$ in an autoclave with C_5H_6 or C_6H_8 for 10-15 h, the appropriate diene—iron tricarbonyl complexes could be prepared [329]. Treatment of 1,3,5-trimethyl-1,4-cyclohexadiene with $Fe_3(CO)_{12}$ afforded [330] a mixture (4/1) of the *exo*- and *endo*-species 310 and 311. Hydride abstraction from these gave the symmetrical trimethylcyclohexadienyl complex cation. Reaction of $Fe_3(CO)_{12}$ with 1,5,5-trimethyl-3-methylene-cyclohex-1-ene afforded 312.



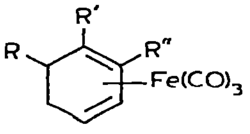
(310)



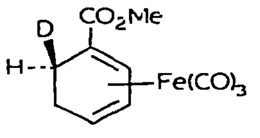
(311)



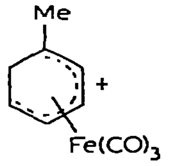
(312)



(313)



(314)

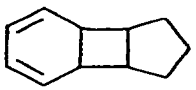


(315)

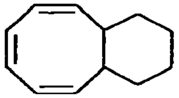
Methylcyclohexadiene carboxylates reacted [331] with $Fe(CO)_5$ giving complexes of the type 313 ($R = R'' = H, R' = CO_2Me$; $R = CO_2Me, R' = R'' = H$; $R'' = CO_2Me, R = R' = H$); hydride abstraction gave the corresponding cyclohexadienyl salts, which were hydrolysed by water giving either hydroxo or dimeric ether complexes. Methoxide treatment of 313 ($R = CO_2Me, R' = R'' = H$ or $R'' = CO_2Me, R = R' = H$) afforded 313 ($R = R'' = H; R' = CO_2Me$), apparently the first reported example of a base-catalysed isomerisation of a cyclohexadiene—iron tricarbonyl system. Deuteration, in acidic methanol, of these carboxylate species afforded, stereospecifically and regardless of the starting material, 314. Saponification, followed by reduction of the carboxylic acid complex, afforded the alcohol $(1\text{-}HOCH_2C_6H_7)Fe(CO)_3$ which, on protonation, gave 315.

1-Methylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene and 2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone reacted [332] with $Fe(CO)_5$ to give tricarbonyliron complexes of the 2,4-cyclohexa-diene or -dienone, respectively. The first reactions at least probably involved a 1,5-hydride shift from the 3- or 5-methyl groups to the exocyclic methylene group, with participation of the iron carbonyl moiety.

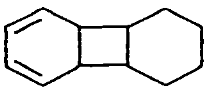
Treatment of 316 with $Fe_2(CO)_9$ afforded [333] the expected iron tricarbonyl complex, the structure of which has been determined [334] crystallographically. The central C_4 ring is essentially square and planar while the cyclopentane ring has an envelope conformation; both ring fusions are *cis* and the 5- and 6-membered rings have an *anti* relationship to the 4-membered ring. The reaction of a mixture of 317 and 318 gave 319 (70%) and 320 (1%).



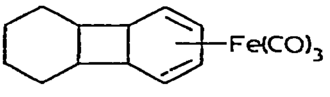
(316)



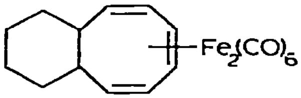
(317)



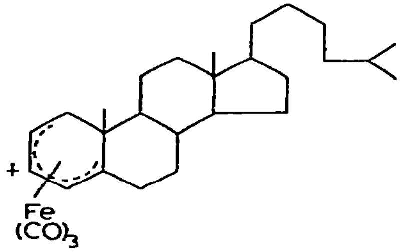
(318)



(319)



(320)



(321)

Cholesta-1,3- and -2,4-diene tricarbonyliron complexes reacted [335] with [Ph$_3$C][BF$_4$] to give the same dienyl cation, 321. Nucleophilic attack (H_2O, OMe^-, CN^- or morpholine) on this species resulted in H^+ elimination (Fig. 21) rather than addition of the nucleophile. Reaction of (π-C_7H_7)Mo(CO)$_2$Q (Q = B(pyz)$_4$, HB(pyz)$_3$, HB(pyzMe$_2$)$_3$ or Et$_2$B(pyz)$_2$; pyz = pyrazolyl, pyzMe$_2$ = 3,5-dimethylpyrazolyl) with Fe(CO)$_5$ under UV irradiation gave [336] the mixed metal complex QMo(CO)$_2$C$_7$H$_7$Fe(CO)$_3$ (322). These species were fluxional even after addition of the Fe(CO)$_3$ group to the C$_7$ ring, although the rates of site exchange were altered from that in the unsubstituted cycloheptatrienyl complex.

A detailed study [337] of the long-range HH coupling constants in butadiene, cyclohexa- and cyclohepta-dieneiron tricarbonyls confirmed that the protons attached to the formal double bonds were coplanar and therefore that the bonding in such complexes is best represented as in 323 rather than in 324. It was suggested [338] that differentiation between *exo*- and *endo*-substituted cyclopentadieneiron tricarbonyl isomers could be made on the basis of an analysis of the mass spectral decomposition pattern emanating

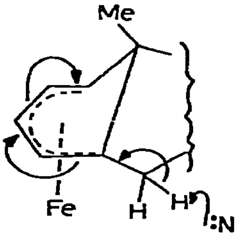
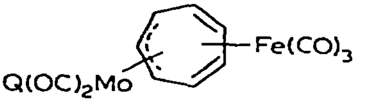
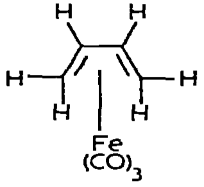


Fig. 21.

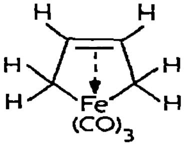
from the molecular ion. Such fragmentation was characterised by radical scission of the *exo*-substituent, viz. Scheme 42, and it was proposed that such a



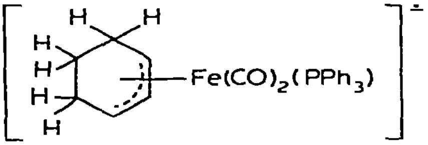
(322)



(323)

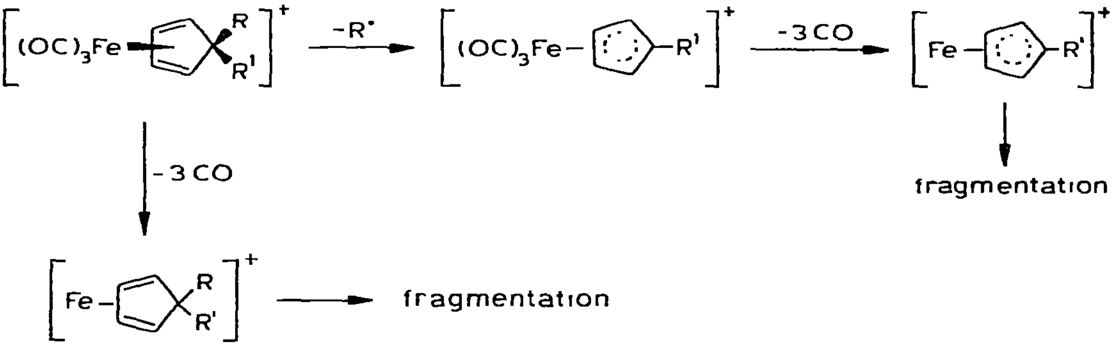


(324)



(325)

SCHEME 42



process would occur generally in isomeric pairs of this type. By γ-irradiation of $(C_6H_8)Fe(CO)_2(PPh_3)$, a radical anion was produced [339] which, at low temperature, reacted with n-BuCl giving, possibly, 325.

Upon irradiation of phenylcyclohexadiene in the presence of $Fe(CO)_5$, the mixture of isomers 326 and 327 (R = H) was formed [340]. An equilibrium between these isomers was established ($t_{1/2}$ = 4 h at 145°C) for which K (326/327) = 3.35 ± 0.1. Two mechanisms were possible for isomerisation (Fig. 22); pathway (i) involved a concerted 1,5-sigmatropic hydrogen shift while pathway (ii) required the formation of an iron hydride intermediate. Pathway (i) required that there should be a considerable isotope effect and might not be restricted to hydrogen migration *cis* to the metal. Pathway (ii), on the other hand, would not necessarily involve hydrogen *cis* to the metal, and would not display an isotope effect provided that the rate-determining step involved the formation of a coordinatively unsaturated intermediate prior to hydrogen abstraction. Accordingly, isomerisations of 326 and 327 (R = D) [341] were studied. Scrambling of deuterium in 326 (R = D) was quite rapid, and from a study of the behaviour of a mixture of 326 (R = H and R = D), it was shown

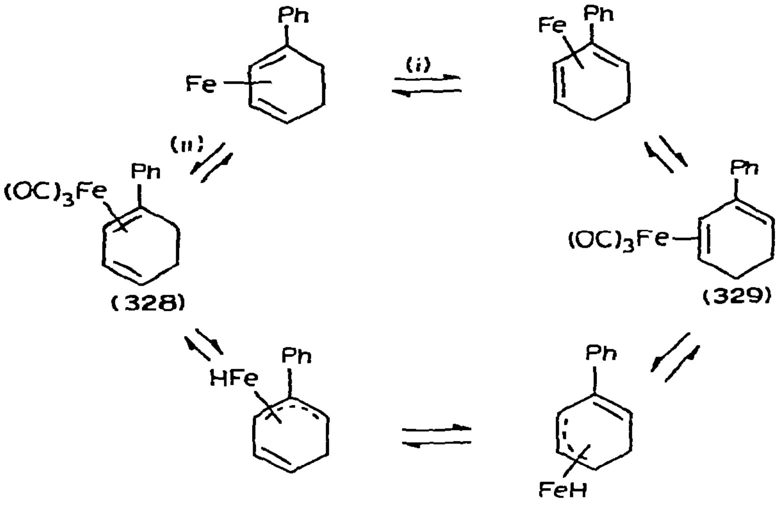
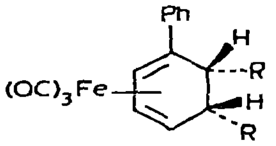
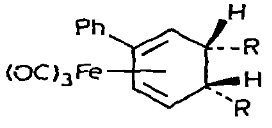


Fig. 22.

that there was a small but significant isotope effect on the rate of conversion of 326 into 327. Furthermore, while 35% isomerisation occurred when 326 was



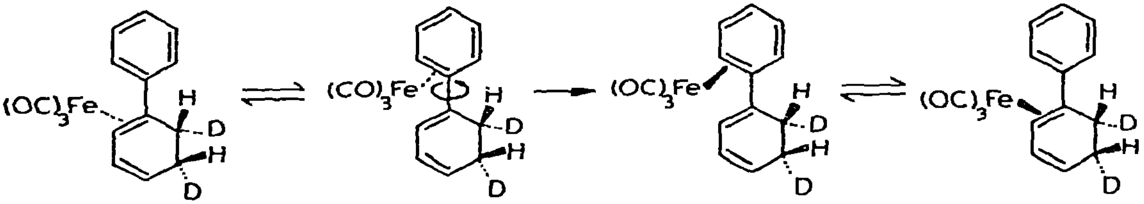
(326)



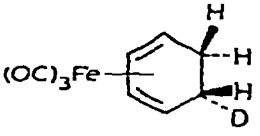
(327)

heated, only 8% of 327 was obtained when PPh_3 was present, the major product (71%) being $Fe(CO)_3(PPh_3)_2$. This result was consistent with the trapping of a coordinatively unsaturated intermediate, e.g. 328 or 329, by the phosphine. That deuterium scrambling could occur only with the assistance of a phenyl ring (Scheme 43) was confirmed by the observation that no D was incorporated

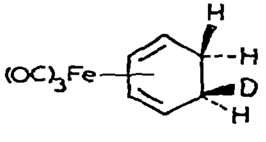
SCHEME 43



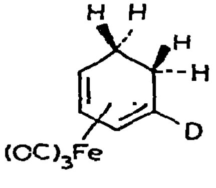
into a vinylic site in 330 while scrambling of deuterium occurred in 331 via the equilibration with 332 (the rate of isomerisation was ca. 125 times faster than the rate of scrambling).



(330)



(331)



(332)

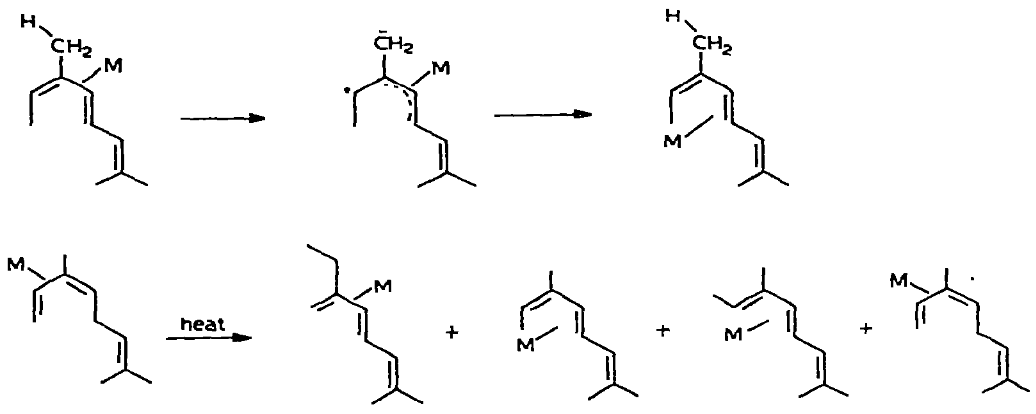
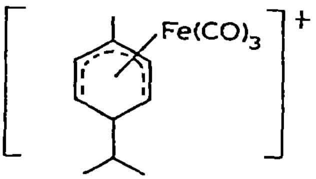


Fig. 23.

Polyene complexes

The monoterpenes, myrcene, *cis*-ocimene, *cis*- and *trans*-alloocimene and α-phellandrene formed [342] tricarbonyliron complexes. The compounds containing ocimene and *cis*-alloocimene isomerised on heating, or after treatment with $[Ph_3C]^+$ followed by BH_4^-, and the possible mechanisms of the thermal reactions are outlined in Fig. 23. The α-phellandrene complex underwent hydride abstraction to give the dienyl salt 333.

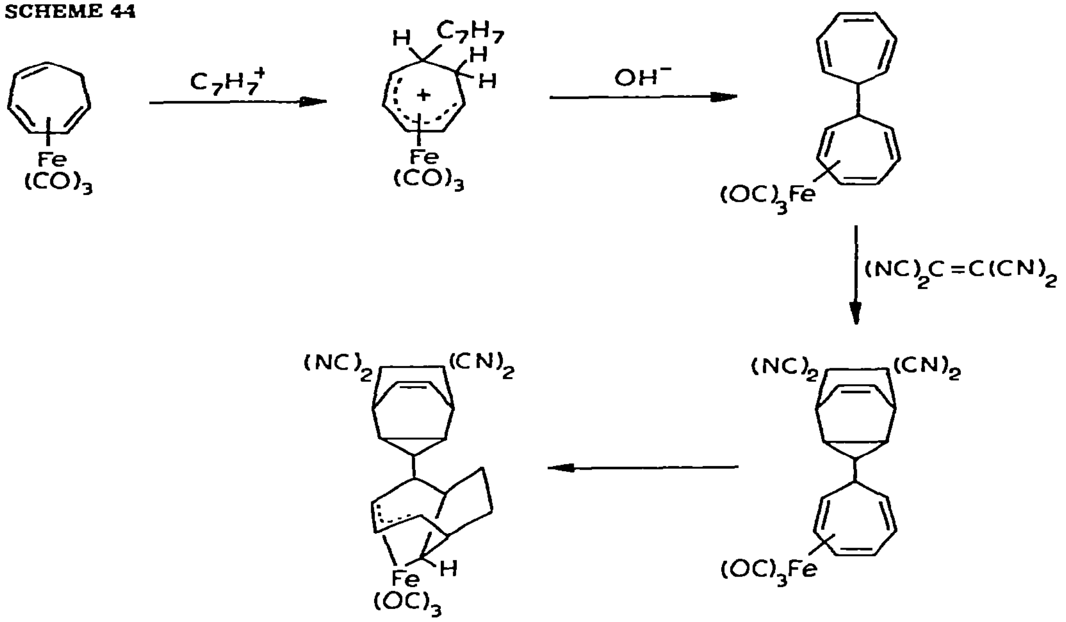


(333)

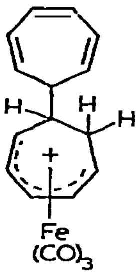
Reaction of $(C_7H_8)Fe(CO)_3$ (C_7H_8 = cycloheptatriene) with $[C_7H_7]^+$ afforded [343] $[(C_7H_7C_7H_8)Fe(CO)_3]^+$ (334). The reactions of this ditropyl complex with TCNE are illustrated in Scheme 44, and it is seen that the uncomplexed olefin underwent 1,4-addition while the complexed moiety underwent 1,3-addition (these modes of addition are observed in the separate components of the compound). There was no evidence for 335. Reaction of the substituted cycloheptatrienes C_7H_7R (R = H, Me, Ph or C_6F_5) with $[Ru(CO)_4(SiMe_3)]_2$ gave [344] 336, together with a minor product (336, R = $SiMe_3$). An X-ray structural examination of the minor product established the overall molecular geometry, and the Ru—Ru distance is 2.94 Å, the silyl group being bent away from the C_7 ring. With the cycloheptatriene substituent R = CN or O(t-Bu) the product of this reaction was 336 (R = H), presumably via loss of $SiMe_3R$.

The ^{13}C NMR spectra of the cyclooctatriene complexes 337 have been measured [345]. From the number of ^{13}CO resonances, it was possible to anticipate fluxional or non-fluxional behaviour for the compounds. Treatment of the diazepine complex 338 (R = CO_2Et, R′ = R″ = H) with NaOH afforded [346] 338 (R = R′ = R″ = H) which existed in tautomeric equilibrium with 339 (R =

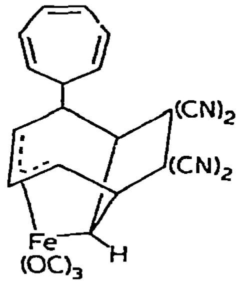
SCHEME 44



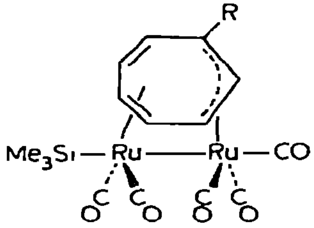
R′ = R″ = H). Reaction of 338 (R = R′ = R″ = H) with NaH/MeCOCl gave 338 (R = COMe, R′ = R″ = H) while Li-n-Bu and $PhCH_2Br$ afforded 339 (R = CH_2Ph, R′ = R″ = H). When R′ = R″ = H but R = Me, only the tautomeric form 339 was observed. The structure of 338 (R = CO_2Me, R′ = R″ = H) was confirmed crystallographically [347].



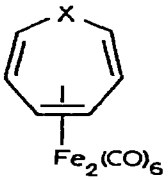
(334)



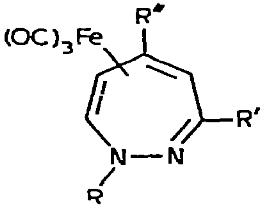
(335)



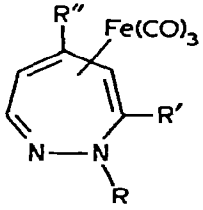
(336)



(337)

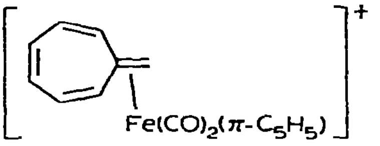


(338)

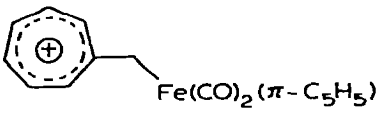


(339)

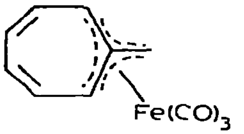
Reaction of $C_7H_7CH_2OSO_2Ph$ with $Na[(\pi\text{-}C_5H_5)Fe(CO)_2]$ gave [348] the σ-bonded cycloheptatriene species $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C_7H_7$. On treatment of this with $[Ph_3C]^+$, a tautomeric equilibrium between **340** and **341** was established in which the positive charge was distributed between the metal atom and the tropylium ring without there being direct bonding between them. This was cited as direct evidence for hyperconjugative or vertical stabilisation of carbonium ion



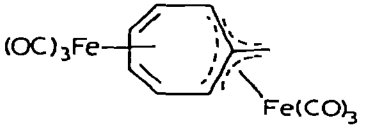
(340)



(341)



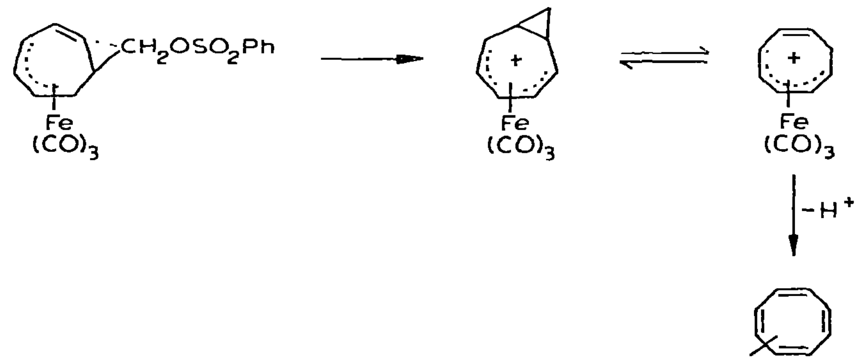
(342)



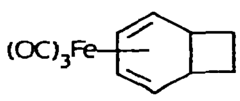
(343)

by a metalloalkyl substituent. When $C_7H_7CH_2OH$ or $C_7H_7CH_2OSO_2Ph$ was treated with simple iron carbonyls, the products were styrene, its $Fe(CO)_4$ complex and $(C_8H_8)Fe(CO)_3$, a proposed mechanism for the formation of the latter being shown in Scheme 45. With an excess of $Fe_2(CO)_9$, $C_7H_7CH_2OH$ afforded the trimethylenemethane derivative **342** (see ref. 266, and page 340), which reacted further with $Fe_2(CO)_9$ to give **343**; **342** did not react with TCNE.

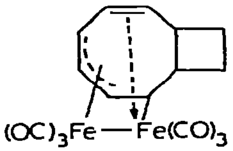
SCHEME 45



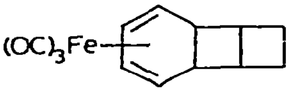
Isomerisation of 1,3,5-cyclooctatrieneiron tricarbonyl to the bicyclooctadiene species **344** occurred [349] in a first order reaction. Less than 1% of the triene complex remained at equilibrium, ($K_{eq} > 100$ and $\Delta F = -3.4$ kcal/mol), while for the free olefin, the triene was favored over the bicyclic diene ($K_{eq} = 0.18$, $\Delta F = 1.1$ kcal/mol). The large shift in equilibrium presumably reflected the relative distortions, and resulting ring strain, introduced into the two olefins by complexing with $Fe(CO)_3$.



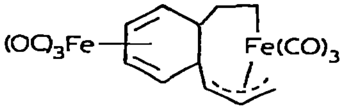
(344)



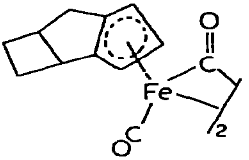
(345)



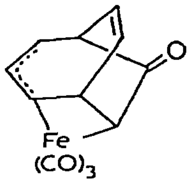
(346)



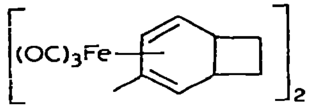
(347)



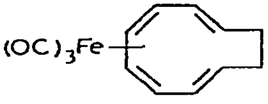
(348)



(349)



(350)

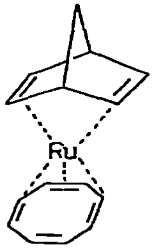


(351)

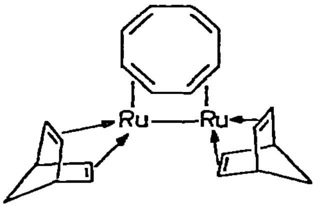
The series of products obtained [350] by treating bicyclo[6.2.0]deca-2,4,6-triene with $Fe_2(CO)_9$ have been identified spectrally and crystallographically as *trans*-$(C_8H_8)[Fe(CO)_3]_2$, $(C_8H_8)Fe_2(CO)_5$, and 345-351.

A detailed mass spectral study has been made [351] of $(C_8H_7R)Fe(CO)_3$ (R = CHO, CH_2OH, CHMeOH and CH_2OMe). Broad-line ^1H NMR spectral studies, over the temperature range −196 to +70°C, of $Fe(C_8H_8)_2$ revealed [352] that the molecule existed in a tautomeric equilibrium in the solid phase.

Treatment of $[(C_7H_8)RuCl_2]_n$ (C_7H_8 = norbornadiene) with $K_2C_8H_8$ in THF gave [353] the fluxional $Ru(C_7H_8)(C_8H_8)$ (352), together with $Ru(C_7H_8)(C_8H_{10})$ and an unidentified complex. The last was also produced together with $Ru_2(C_7H_8)_2(C_8H_8)$ (353), in the reaction between $[Ru(C_7H_8)Cl_2]_n$, K metal, and C_8H_8 in THF. The known [354] $Ru(C_8H_{12})(C_8H_{10})$ was prepared in the reaction of the 1,5-cyclooctadiene complex $[Ru(C_8H_{12})Cl_2]_n$ with $K_2C_8H_8$, and it seemed probable that the C_8H_{12} was bonded to the Ru atom via a π-allyl/σ-C system, as in $(C_8H_{12})Ru(CO)_3$. The osmium analog afforded $Os(C_8H_{12})(C_8H_8)$ and the known [354] $Os(C_8H_{12})(C_8H_{10})$. Treatment of $Ru(PPh_3)_3Cl_2$

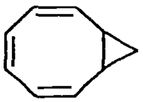


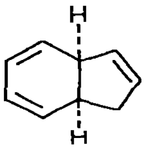
(352)



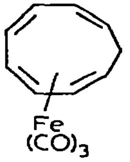
(353)

with $K_2C_8H_8$ gave $Ru(C_8H_8)(PPh_3)_2$, and the analogous $Ru(C_8H_8)(PPhMe_2)_3$ was prepared similarly. In $Ru(C_8H_8)(PPh_3)_2$, $Ru(C_7H_8)(C_8H_8)$ and $Os(C_8H_{12})(C_8H_8)$, only three double bonds of the cyclooctatetraene ring are involved in bonding to the metal. $Ru(C_7H_8)(C_8H_8)$ reacted with $P(OCH_2)_3CEt$ (L) giving $Ru(C_7H_8)L_3$, while with other phosphines (L), a mixture of $Ru(C_7H_8)L_3$ and $Ru(C_8H_8)L_n$ ($n = 2$ or 3) was formed. $Ru(C_7H_8)(C_8H_8)$ and $Ru(C_8H_8)(PPh_3)_2$, but not its $PPhMe_2$ analog, were active catalysts, or catalyst precursors for the hydrogenation of 1-butene, and while C_2H_4 reacted irreversibly with $Ru(C_7H_8)(C_8H_8)$, an unidentified compound, not $Ru(C_7H_8)(C_2H_4)$, was formed.

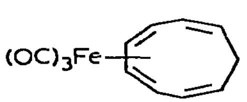

(354)



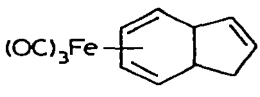
(355)



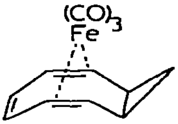
(356)



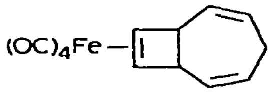
(357)



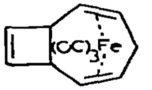
(358)



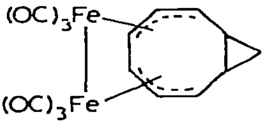
(359)



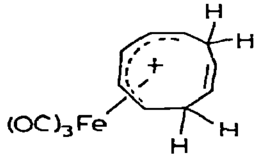
(360)



(361)



(362)



(363)

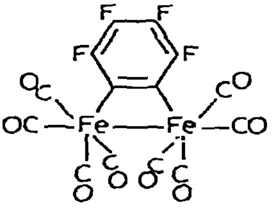
cis-Cyclononatetraene could be stabilised [355] by reaction of either 354 or 355 with $Fe_2(CO)_9$ (or $Fe(CO)_5$ under UV light) giving either 356 or 357. Among the other products of this reaction were 358, 359, either 360 or 361 and 362. Although 356 was stable for several days at room temperature, it underwent an electrocyclic ring closure reaction at 101° giving 358. Protonation of 356 in $FSO_3H—SO_2FCl$ gave 363.

Complexes containing metal—carbon σ-bonds, and carbenes

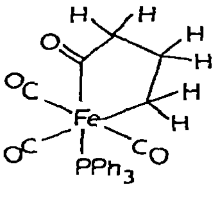
Metal carbonyl complexes

Treatment of $Fe(CO)_5$ with LiC_6F_5 gave [356], initially, $Li[Fe(CO)_4COC_6$-

F_5]. Addition to this of $SiMe_3Cl$ afforded the previously reported [357] $Fe_2(CO)_8(C_6F_4)$ (364), the structure of which was determined. The fluorobenzene



(364)

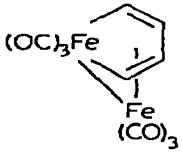


(365)

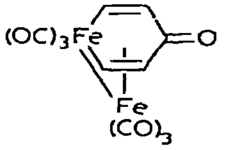
ring is coplanar with the Fe—Fe bond (2.80 Å). Reaction of $Na_2[Fe(CO)_4]$ with 1,3-dibromopropane in the presence of PPh_3 and $PPhMe_2$ gave [358] 365 (L = tertiary phosphine).

Metallocyclopentadienyl complexes

$Fe_3(CO)_{12}$ reacted [359] with PhC≡C(*p*-ClC_6F_4) affording 12 products, including the π-cyclobutadiene species $(PhC_2C_6F_4Cl)_2Fe(CO)_4$, as well as 366 and 367. The complexes 217 ($m = 4$, $n = 4$, 5 or 6; $m = 5$ and $n = 6$) were pre-



(366)

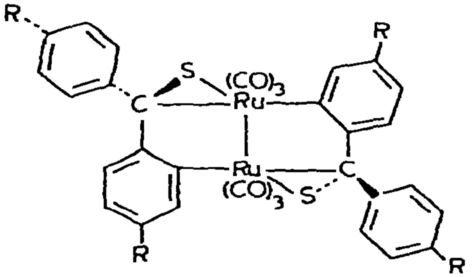


(367)

pared [361] directly from the benzalacetone complex $(PhCH{=}CHCOMe)Fe(CO)_3$ and the appropriate diacetylene 215 (see ref. 252, 360 and page 337).

σ-Metallated compounds

Treatment of $Ru_3(CO)_{12}$ with (*p*-$RC_6H_4)_2CS$ gave [362] 368 (see ref. 38 and 39, page 283). Ruthenium and osmium dodecacarbonyls reacted [363] with



(368)

benzo[*h*]quinoline giving one of the isomers 369, 370 or 371. Reaction of the quinoline with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ afforded only $[(\pi\text{-}C_5H_5)Fe(CO)]_4$.

The 1-naphthylphosphine, $P(C_8H_7)Me_2$ (L), reacted [364] with $RuCl_3{\cdot}nH_2O$ giving RuL_3Cl_2. Treatment of this with CO afforded 372 (M = Ru), and sim-

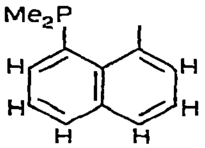
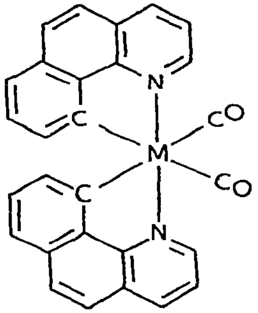
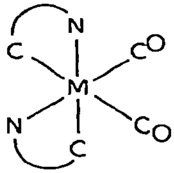


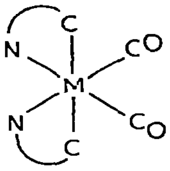
Fig. 24.



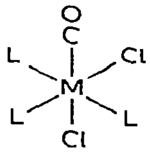
(369)



(370)



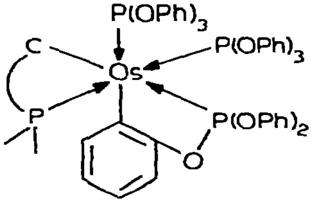
(371)



(372)

ilar, though labile, adducts were obtained with MeCN, MeNC and TCNE. On heating in decalin, RuL_3Cl_2 underwent *o*-metallation, with loss of HCl, giving $Ru(CO)L_2[C—PMe_2]Cl$ ($[C—PMe_2]$, Fig. 24) as a single isomer. Treatment of OsO_4 with L in a mixture of HCl and 2-methoxyethanol gave OsL_3Cl_3 and $OsL_2[C—PMe_2]Cl_2$ (on heating the former at 270°, the latter was formed). Reaction of $OsL_2[C—PMe_2]Cl_2$ with CO in 2-methoxyethanol afforded 372 (M = Os) and treatment with NaOH in the same solvent gave $Os(CO)L[C—PMe_2]_2$.

Reaction of a series of osmium triphenylphosphine hydride complexes with $P(OPh)_3$ afforded [365] a series of *o*-metallated species which were produced via intermediary phosphite complexes. Thus, treatment in boiling decalin of $Os(PPh_3)_3H_4$ with $P(OPh)_3$ gave 373 while $Os(CO)(PPh_3)_3H_2$ and $Os(CO)(PPh_3)_3HCl$ re-



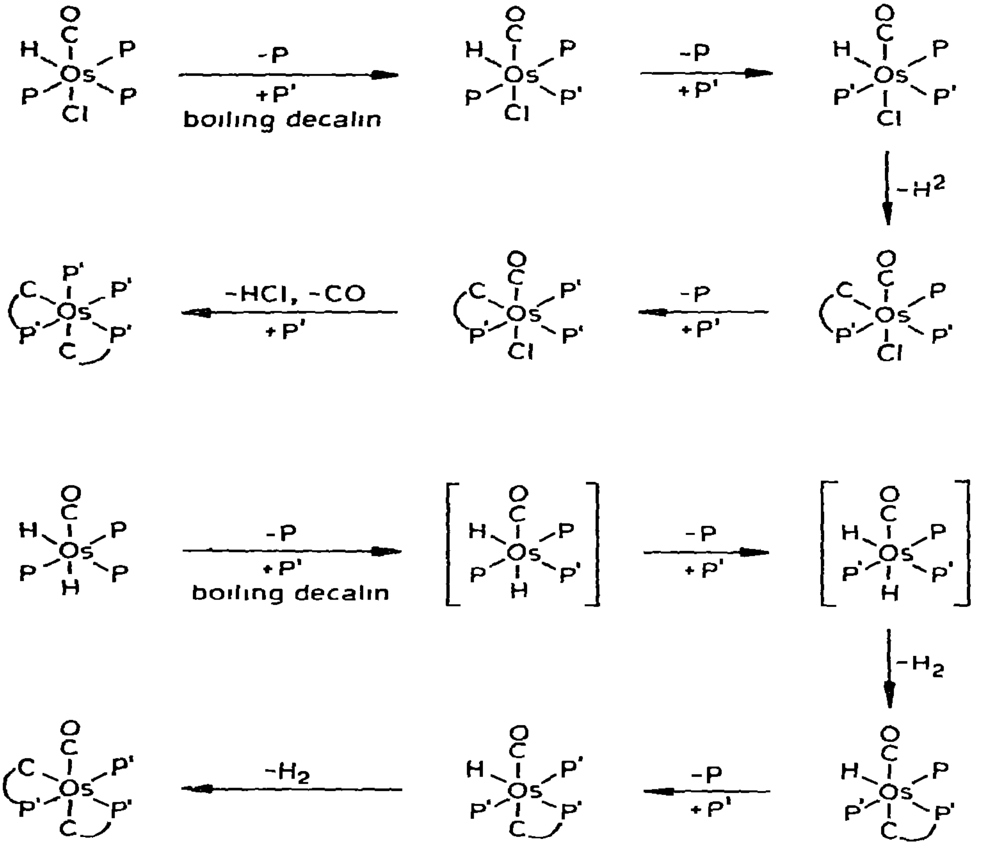
(373)

acted according to Scheme 46. It may be noted that $Os(CO)P(OPh)_3HCl$ was not detected, whereas evidence could be obtained or inferred for all the other species illustrated.

Alkylmetals

At −20°C or lower in ether, anhydrous $FeCl_3$ reacted [366] with LiMe (molar ratio 1/5) to give Li_2FeMe_4. This was formed as a yellow precipitate at −78°, or a red etherate at −30° and could be obtained at, or just below 0°, as

SCHEME 46



(P = PPh_3 ; P' = $P(OPh)_3$)

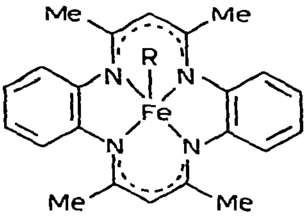
a light yellow dioxane adduct. Attempts to isolate [367] benzyl complexes from the reaction between $FeCl_n$ (n = 2 or 3) and $Mg(CH_2Ph)Cl$ in ether were unsuccessful, but there was some evidence for $FeMeCl_2$, obtained in the reaction between $FeCl_3$ and $ZnMe_2$.

Treatment of $Fe(bipy)R_2$ (R = Me or Et) with AlR'_3 or $AlR'_2(OEt)$ (R' = Me, Et or n-Pr) resulted [368] in decomposition, and elimination mainly of RH. Reaction of 374 (R = NCS) with $R'NHNH_2$ (R' = Me, Et or Ph) gave [369] 374 (R = Me, Et or Ph), and the structure of the species (R = Ph) has been confirmed crystallographically. The Fe atom is displaced by ca. 0.23 Å out of the plane of the 4 nitrogen atoms, towards the aryl group. The iron(II) phthalocyanin (FePc) complex reacted [370] with $LiCH_2SPh$ giving $[FePc(CH_2SPh)]^-$.

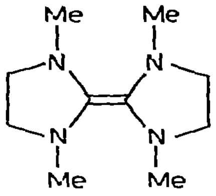
^1H NMR spectral studies of the *o*-phenyl protons in $Ru(Ph_2PCH_2CH_2PPh_2)_2ClMe$ confirmed [371] that the complex had an overall *cis*-geometry.

Carbene complexes

Reaction of $Fe(CO)_5$ with the electron-rich olefin 375 (L_2) afforded [372] $Fe(CO)_4L$. A study has been made [373] of the electronic and steric control



(374)



(375)

exerted by the ligands in the reaction between $Fe(CO)_4L$ (L = tertiary phosphine or phosphite) and $Mg(CH_2Ph)Cl$. Addition of the alkyl group occurred at the CO group *trans* to L, and it was stated that the electronic properties of CO, as measured by the stretching force constant or ν(CO), dominated the reactive site within the molecules and also determined the rate of reaction of the Grignard reagent with the coordinated CO.

Organic reactions catalysed or promoted by iron or ruthenium complexes

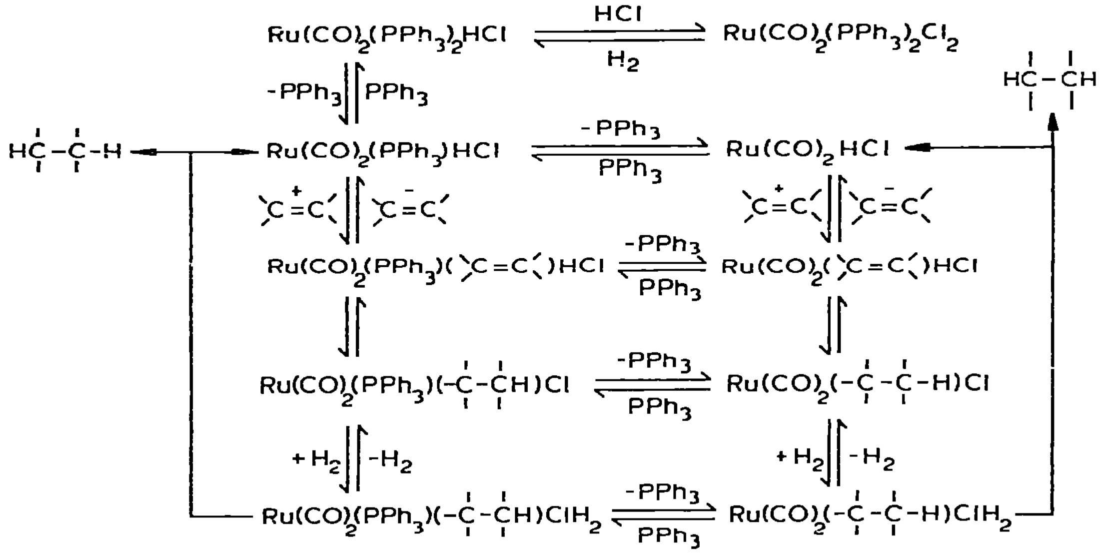
Hydrogenation

The relative rates of homogeneous hydrogenation [374] of olefins by $Ru(CO)_2(PPh_3)_2Cl_2$, in the presence of added PPh_3, decreased in the order conjugated diene > non-conjugated diene > terminal alkene > internal alkene. In general, polyenes were selectively hydrogenated to monoenes, and, for example, 1,5,9-cyclododecatriene could be reduced [375] to cyclododecene. Competitive reactions involved [374] double bond isomerisation, group migration reactions and transannular ring closures. The lower hydrogenation rate for alkenes, in comparison with dienes, was attributed to the equilibrium between the intermediary species $Ru(CO)_2(alkyl)Cl_2$ and $Ru(CO)_2(PPh_3)(alkyl)Cl$ which, in the presence of added PPh_3, formed sterically crowded complexes. It was postulated that such sterically crowded intermediates would readily undergo RuH elimination (β-elimination), while the less overcrowded species would survive long enough to undergo hydrogenolysis. A proposed mechanism is shown in Scheme 47.

Two-electron reduction of $Ru_3O(PPh_3)_3(CO_2Me)_6$ probably gave [376] $Ru(PPh_3)(OAc)_2$ which, in the presence of methanol, PPh_3 and a non-complexing acid afforded an orange-red species which was a catalyst for the hydrogenation of olefins. A similar species could be produced by acidolysis of $Ru(PPh_3)_2H(OAc)$ or $Ru(PPh_3)_4H_2$, and it was suggested that the initial product of these reactions was $[Ru(PPh_3)_3(solvent)_n]^{2+}$. In the presence of olefin, it seemed likely that $[Ru(PPh_3)_2(olefin)(solvent)]^{2+}$ would be formed. On standing, or on treatment with H_2 or CO, in the absence of olefin, this orange-red species afforded the yellow, catalytically (i.e. hydrogenation) inactive $[Ru(PPh_3)_2(OH)(BF_4)]_2$. $Ru(PPh_3)(OAc)_2$ reacted with air giving $Ru_2O(PPh_3)_2(OAc)_4$.

A series of ruthenium(II) arene complexes, formulated as $[Ru(Ar)Cl_2]_n[RuCl_2]_n$ (where Ar = C_6H_6, 1,3,5-$C_6H_3Me_3$, 1,3,5-$C_6H_3Ph_3$), hydrogenated [377, 378] olefins, the best yields being obtained in the presence of traces of pyrrolidine. The compound containing 1,3,5-$C_6H_3Ph_3$ had the greatest activity. It was suggested [377] that the active species might be a hydride complex, possibly $[(\pi\text{-arene})ClRu(\mu\text{-}H)(\mu\text{-}Cl)RuCl(\pi\text{-arene})]$.

SCHEME 47



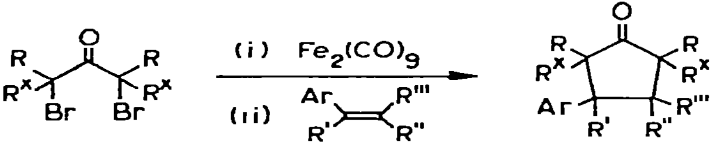
Formation and reactions of ketones and related species

Benzyl bromide was converted [379] by $Fe_2(CO)_9$ into a 60% yield of dibenzylketone over 4 h in hexane, and similar conversions were effected where the aryl group was 3,5-$C_6H_3Me_2$, 1- or 2-naphthyls. Reaction of $Fe_2(CO)_9$ with $C_6F_5CH_2Br$ gave initially the unstable $Fe(CO)_4(CH_2C_6F_5)_2$, together with some $(C_6F_5CH_2)_2CO$, and the former was quantitatively converted to the latter at 80° in benzene. A heptafluoro-2-naphthyl complex, and the corresponding ketone, were prepared similarly, but $(CF_3)_3CFI$ gave only $(CF_3)_3CH$ and $Fe(CO)_4I_2$.

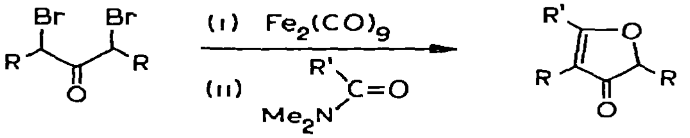
Treatment of $Na_2[Fe(CO)_4]$ with RCOX (R = alkyl, X = halide) gave [380] $Na[Fe(CO)_4COR]$ which, on addition of R'X (R = perfluoralkyl or C_6F_5), afforded the hemifluorinated ketones, RCOR'. These compounds could also be obtained via the "inverse route", viz. $Na[Fe(CO)_4COR'] + RX$, or by treatment of $Na[Fe(CO)_4R]$ with R'COCl. Reaction of $Na[Fe(CO)_4COR]$ (R = alkyl) with halogen and water, or with NaOCl or O_2 followed by aqueous acid, gave [381] the carboxylic acids RCO_2H. Treatment of the carbonylate ion with halogen and R'OH or R'R''NH afforded the esters, RCO_2R', or amides, $RCO_2NR'R''$. In THF, primary aliphatic bromides reacted with $Na_2[Fe(CO)_4]$ at a rate greater than 10^4 times faster than that of the corresponding chlorides, and polar solvents such as hexamethylphosphoramide or *N*-methyl-2-pyrrolidine were used in order to encourage reaction with the less reactive alkyl chlorides. The yields were generally virtually quantitative, and $Br(CH_2)_6Cl$ afforded $Cl(CH_2)_6CO_2H$ in 84% yield.

The reaction of α,α'- dibromoketones with aromatic olefins [382] (Scheme 48) and carboxamides [383] (Scheme 49) was promoted by $Fe_2(CO)_9$. It was

SCHEME 48

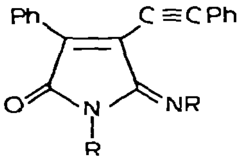


SCHEME 49

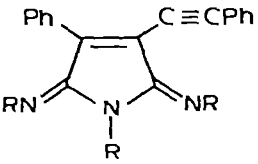


believed that in both cases, a π-oxyallyliron(II) intermediate (Fig. 25) was formed.

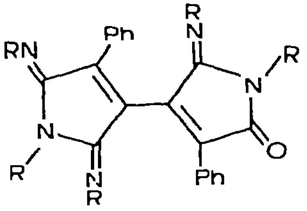
Diphenylbutadiyne reacted [384] with carbodiimides in the presence of Fe(CO)$_5$ at 155-210°C to give 376, 377 and 378. It was thought that aryliso-



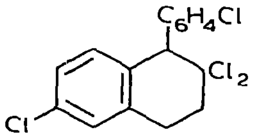
(376)



(377)



(378)



(379)

cyanideiron complexes were intermediates in the formation of the pyrroline rings from the diacetylene and ArN=C=NAr (Scheme 50).

Other reactions

While Fe(CO)$_5$ or $[Fe_3(CO)_{11}H]^-$ denitrogenated [385] RCH=NOH to RCHO, they could also effectively deoxygenate ArClC=NOH or nitrile oxides to ArCN. The addition of ethylene to 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)-ethane, giving 379 was initiated [386], probably in a radical reaction, by Fe(CO)$_5$ under pressure at 140°.

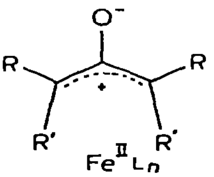
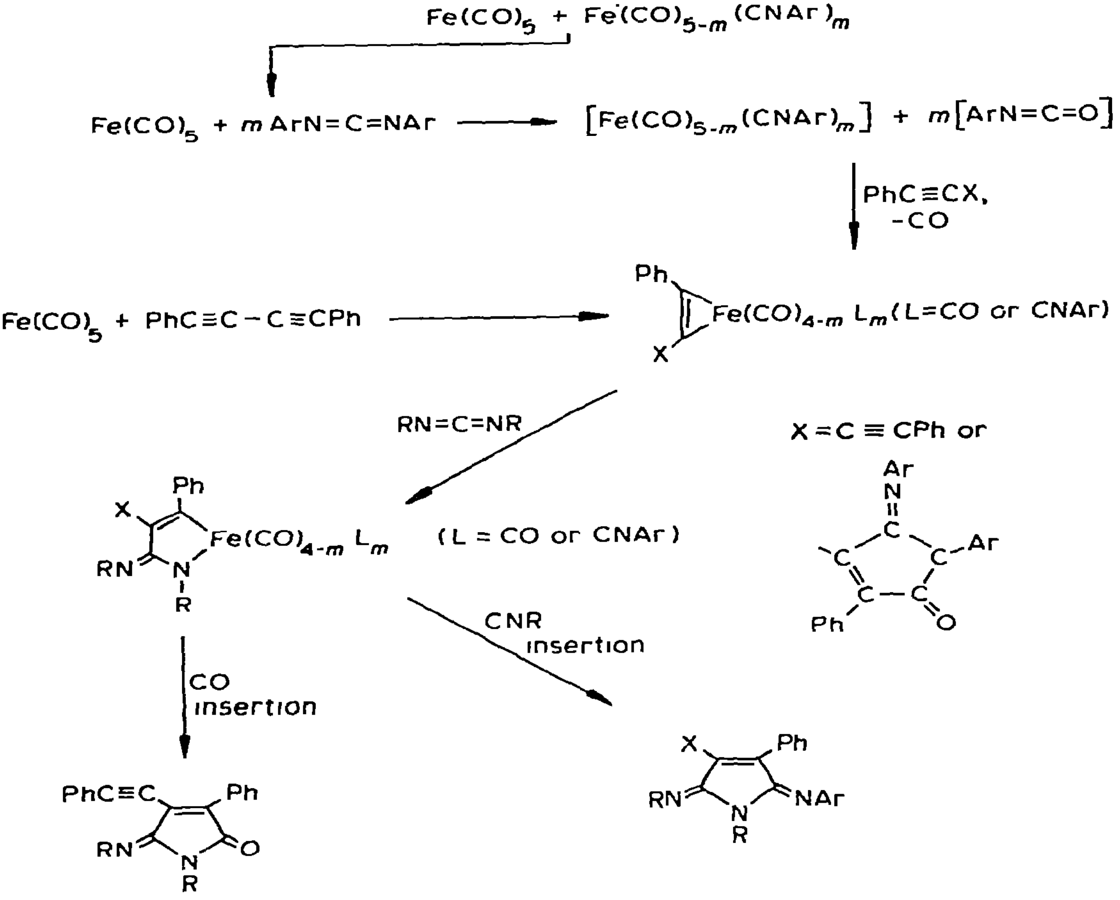


Fig. 25.

SCHEME 50



References

1 M. Poliakoff and J J. Turner, J. Chem. Soc. Dalton, (1973) 1351.
2 R.C. Dunbar, J.F. Ennever and J.P. Fackler, Jr., Inorg. Chem., 12 (1973) 2734.
3 J. Grobe, J. Kaufmann and F. Kober, Z. Naturforsch. B, 28 (1973) 691.
4 M.B. Smith and R. Bau, J. Amer. Chem. Soc., 95 (1973) 2388.
5 F. Wada and T. Matsuda, J. Organometal. Chem., 61 (1973) 365.
6 R.D. George, S.A.R. Knox and F.G.A. Stone, J. Chem. Soc. Dalton, (1973) 972.
7 J.P. Collman and S.R. Winter, J. Amer. Chem. Soc., 95 (1973) 4089
8 H. Kisch, J. Organometal. Chem., 38 (1972) C19; C. Krüger, Chem. Ber., 106 (1973) 3230.
9 J.P. Collman, R.G. Komoto and W.O. Siegl, J. Amer. Chem. Soc., 95 (1973) 2389.
10 A.T.T. Hsieh and G. Wilkinson, J. Chem. Soc. Dalton, (1973) 867.
11 C.B. Bartish and C.S. Kraihanzel, Inorg. Chem., 12 (1973) 391.
12 F.A. Cotton, K.I. Hardcastle and G.A. Rusholme, J. Coordin. Chem., 2 (1973) 217.
13 M.A. Bennett, G.B. Robertson, I.B. Tomkins and P.O. Whimp, J. Chem. Soc. Chem. Commun., (1971) 341.
14 G.B. Robertson and P.O. Whimp, J Chem. Soc. Dalton, (1973) 2454.
15 W.E. Carroll, F.A. Deeney, J.A. Delaney and F.J. Lalor, J. Chem. Soc. Dalton, (1973) 718; M.G. Clark, W.R. Cullen, R.E.B. Garrod, A.G. Maddock and J.R. Sams, Inorg. Chem., 12 (1973) 1045.
16 J.D. Black, M.J. Boylan, P.S. Braterman and W.J. Wallace, J. Organometal. Chem., 63 (1973) C21.
17 D.P. Bauer, W.M. Douglas and J.K. Ruff, J. Organometal. Chem., 57 (1973) C19.
18 E. Lindner, H. Behrens and D. Uhlig, Z. Naturforsch. B, 28 (1973) 276.
19 G.T. Kubas and T.G. Spiro, Inorg. Chem., 12 (1973) 1797.

20 G. Schmid, J. Pebler and L. Weber, J. Organometal. Chem., 61 (1973) 375.

21 H. Alper, J. Organometal. Chem., 50 (1973) 209.

22 P.C. Ellgen and S.L. McMullin, Inorg. Chem., 12 (1973) 2004.

23 G. Le Borgne and D. Grandjean, Acta Crystallogr. B, 29 (1973) 1040.

24 K. Yasufuku and H. Yamazaki, Bull. Chem. Soc. Jap., 42 (1969) 3049 and J. Organometal. Chem., 35 (1972) 367.

25 B.L. Barnett and C. Krüger, Cryst. Struct. Commun., 2 (1973) 347.

26 E.F. Epstein and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970) 502.

27 H.A. Patel, R.G. Fischer, A.J. Carty, D.V. Naik and G. Palenik, J. Organometal. Chem., 60 (1973) C49.

28 P.M. Treichel, W.K. Dean and P.M. Douglas, Inorg. Chem., 11 (1972) 1609 and 1615; J. Organometal. Chem., 42 (1972) 145.

29 P.M. Treichel, W.K. Dean and J.C. Calabrese, Inorg. Chem., 12 (1973) 2908.

30 A.H. Cowley and K.E. Hill, Inorg. Chem., 12 (1973) 1446.

31 F.W.B. Einstein and R.D.G. Jones, Inorg. Chem., 12 (1973) 255.

32 W.R. Cullen and L. Mihichuk, Can. J. Chem., 51 (1973) 936.

33 H. Vahrenkamp, Chem. Ber., 106 (1973) 2570.

34 J. Granifo and H. Müller, J. Chem. Soc. Dalton, (1973) 1891.

35 P.C. Ellgen and J.N. Gerlach, Inorg. Chem., 12 (1973) 2526.

36 R. Mason and D.M.P. Mingos, J. Organometal. Chem., 50 (1973) 53.

37 G.N. Schrauzer and H. Kisch, J. Amer. Chem. Soc., 95 (1973) 2501.

38 H. Alper and A.S.K. Chan, J. Chem. Soc. Chem. Commun., (1973) 724.

39 H. Alper and A.S.K. Chan, J. Amer. Chem. Soc., 95 (1973) 4905.

40 L.S. Chia, W.R. Cullen, J.R. Sams and J.E.H. Ward, Can. J. Chem., 51 (1973) 3223.

41 L.R.J. Delbaere, L.J. Kruczynski and D.W. McBride, J. Chem. Soc. Dalton, (1973) 309.

42 C.H. Wei and L.F. Dahl, J. Amer. Chem. Soc., 91 (1969) 1351.

43 L.F. Dahl and J.F. Blount, Inorg. Chem., 4 (1965) 1373.

44 W. Hieber, J. Gruber and F. Lux, Z. Anorg. Allg. Chem., 300 (1959) 275.

45 A.J. Poe and M.V. Twigg, J. Organometal. Chem., 50 (1973) C39.

46 E. Sappa and L. Milone, J. Organometal. Chem., 61 (1973) 383.

47 B.L. Barnett and C. Kruger, Angew. Chem Int. Ed. Engl., 10 (1971) 910.

48 E. Koerner von Gustorf, M.C. Henry, R.E. Sacher and C. di Pietro, Z. Naturforsch. B, 21 (1966) 1152; T.A. Manuel, Inorg. Chem., 3 (1964) 1703; M.M. Bagga, P.L. Pauson, F.J. Preston and R.I. Reed, Chem. Commun., (1965) 543; W.T Flannigan, G.R. Knox and P.L. Pauson, Chem. Ind. London, (1967) 1094; M. Dekker and G.R. Knox, Chem. Commun., (1967) 1243.

49 B.F.G. Johnson, R.D. Johnston, P.L. Josty, J. Lewis and I.G. Williams, Nature, 213 (1967) 901; B.F.G. Johnson, J. Lewis and P.A. Kilty, J. Chem. Soc. A, (1968) 2859.

50 E. Sappa, O. Gambino and G. Cetini, J. Organometal. Chem., 35 (1972) 375; O. Gambino, E. Sappa and G. Cetini, J. Organometal. Chem., 44 (1972) 185; A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 36 (1972) C43, A.J. Canty, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 43 (1972) C35.

51 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc. Dalton, (1973) 1667; M I Bruce, J. Howard, I.W. Nowell, G. Shaw and P. Woodward, J. Chem. Soc. Chem. Commun., (1972) 1041.

52 M.I. Bruce, C.W. Gibbs and F.G.A. Stone, Z. Naturforsch. B, 23 (1968) 1543.

53 C.W. Bradford and R.S. Nyholm, J. Chem Soc. Dalton, (1973) 529.

54 C.W. Bradford, R.S. Nyholm, G.J. Gainsford, J.M. Guss, P.R. Ireland and R. Mason, J. Chem. Soc. Chem. Commun., (1972) 87; G.J. Gainsford, J.M. Guss, P.R. Ireland, R.Mason, C.W. Bradford and R.S. Nyholm, J. Organometal. Chem., 40 (1972) C70.

55 A.J. Deeming and M. Underhill, J. Chem. Soc. Dalton, (1973) 2727.

56 A.J. Deeming, R.E. Kimber and M. Underhill, J. Chem. Soc. Dalton, (1973) 2589.

57 A.D. Buckingham, J.P. Yesinowski, A.J. Canty and A.J. Rest, J. Amer. Chem. Soc., 95 (1973) 2732.

58 A.J. Deeming and M. Underhill, J. Organometal. Chem., 42 (1972) C60 and J. Chem. Soc. Chem. Commun., (1973) 277.

59 A.J. Canty, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Chem. Comm., (1972) 1331

60 A.J. Canty, A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1973) 2056.

61 A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 36 (1972) C43.

62 M.I. Bruce, M.A. Cairns, A.Cox, M. Green, M.D.H. Smith and P. Woodward, Chem. Commun., (1970) 735; M.I. Bruce, M.A. Cairns and M. Green, J. Chem. Soc. Dalton, (1972) 1293.

63 R. Mason and K.M. Thomas, J. Organometal. Chem., 43 (1972) C39.

64 G. Gervasio and G. Ferraris, Cryst. Struct. Comm., 3 (1973) 447.

65 J.F. Blount, L.F. Dahl, C. Hoogzand and W. Hubel, J. Amer. Chem. Soc., 88 (1966) 292.

66 G.A. Vaglio, O. Gambino, R.P. Ferrari and G. Cetini, Inorg. Chim. Acta, 7 (1973) 193.

67 G. Ferraris and G. Gervasio, J. Chem. Soc. Dalton, (1973) 1933.

68 G. Ferraris and G. Gervasio, J. Chem. Soc. Dalton, (1972) 1057.

69 B. Munchenbach and J. Dehand, Naturwissenschaften, 59 (1972) 647.

70 K.M. Abraham and G. Urry, Inorg. Chem., 12 (1973) 2854.
71 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 57 (1973) C84.
72 C.R. Eady, B.F.G. Johnson, J. Lewis and T. Matheson, J. Organometal. Chem., 57 (1973) C82.
73 C.R. Eady, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 37 (1972) C39.
74 R.D. Stewart, U. Anders and W.A.G. Graham, J. Organometal. Chem., 32 (1971) C49.
75 R. Mason, K.M. Thomas and D.M.P. Mingos, J. Amer. Chem. Soc., 95 (1973) 3802.
76 C.S. Springer, J. Amer. Chem. Soc., 95 (1973) 1459.
77 R.K. Pomeroy, R.S. Gay, G.O. Evans and W.A.G. Graham, J. Amer. Chem. Soc., 94 (1972) 272.
78 G. Schmid and H.-P. Kempny, Angew. Chem. Int. Ed. Engl., 12 (1973) 670.
79 F. Glocking and R.E. Houston, J. Organometal. Chem., 50 (1973) C31.
80 J.P. Fawcett, A.J. Poe and M.V. Twigg, J. Organometal. Chem., 51 (1973) C17.
81 M.A. Nasta and G. MacDiarmid, J. Amer Chem Soc., 93 (1971) 2813 and 94 (1972) 2449.
82 M.J. Bennett, W.A.G. Graham, R.A. Smith and R.P. Stewart, Jr., J. Amer. Chem. Soc., 95 (1973) 1685.
83 T.J. Marks and A.R. Newman, J. Amer. Chem. Soc., 95 (1973) 769.
84 G.W. Grynkewich, B.Y.K. Ho, T.J. Marks, D.L. Tomaja and J.J. Zuckerman, Inorg. Chem., 12 (1973) 2522.
85 T. Takano, Bull. Chem. Soc. Jap., 46 (1973) 522.
86 D.A. Baldwin, R.M. Pfeiffer, D.W. Reichgott and N.J Rose, J. Amer. Chem Soc., 95 (1973) 5152.
87 V.L. Goedken, J. Molin-Case and Y. Whang, J. Chem. Soc. Chem. Commun., (1973) 337.
88 J.E. Baldwin and J. Huff, J. Amer. Chem. Soc., 95 (1973) 5757.
89 C.K. Chang and T.G. Traylor, J. Amer. Chem. Soc., 95 (1973) 8475 and 8477.
90 D V. Stynes and B.R. James, J. Chem. Soc. Chem. Commun., (1973) 325.
91 D.V. Stynes, H.C. Stynes, B.R. James and J.A. Ibers, J. Amer. Chem. Soc., 95 (1973) 4087.
92 Q.H. Gibson and F.J.W. Roughton, J. Physiol. London, 136 (1957) 507.
93 J.P. Collman and C.A. Reed, J Amer Chem Soc , 95 (1973) 2048
94 N.A. Matwiyoff, P.J. Vergamini, T.E. Needham, C.T. Gregg, J.A. Volpe and W.S. Caughey, J. Amer Chem. Soc., 95 (1973) 4429.
95 B.C. Chow and I.A. Cohen, Bioinorg. Chem., 1 (1971) 57; M. Tsutsui, D. Ostfeld and L.M. Hoffman, J. Amer. Chem. Soc., 93 (1971) 1820; M. Tsutsui, D. Ostfeld and J.N. Francis, J. Coordin. Chem., 1 (1971) 115; S.S. Eaton, G.R. Eaton and R.H. Holm, J. Organometal. Chem., 32 (1971) C52 and 39 (1972) 179.
96 D. Cullen, E. Meyer, T.S. Srivastava and M. Tsutsui, J. Chem. Soc. Chem. Commun., (1972) 584.
97 J.J. Bonnet, S.S. Eaton, G.R. Eaton, R.H. Holm and J.A. Ibers, J. Amer. Chem. Soc., 95 (1973) 2141.
98 R.G. Little and J.A. Ibers, J. Amer. Chem. Soc., 95 (1973) 8583.
99 G.M. Brown F.R. Hopf, J A. Ferguson, T.J. Meyer and D.G. Whitten, J. Amer. Chem Soc., 95 (1973) 5939.
100 G.R. Dobson, R.T. Jernigan and P.-T. Chang, J. Organometal. Chem., 54 (1973) C33.
101 P. Vasudev and C.H.W. Jones, Can. J. Chem., 51 (1973) 405.
102 R.H. Herber, R.B. King and G.K. Wertheim, Inorg. Chem., 3 (1964) 101; E. Fluck, W. Kerler and W. Neuwirth, Angew. Chem. Int. Ed. Engl., 2 (1963) 271; R.L. Collins and R. Pettit, J. Chem. Phys., 39 (1963) 3433
103 J. Chatt, B.L. Shaw and A E. Field, J. Chem. Soc., (1964) 3466; J.L. Dawes and J D Holmes, Inorg. Nucl. Chem. Lett., 7 (1971) 847.
104 M.L. Berch and A. Davison, J. Inorg. Nucl. Chem , 35 (1973) 3763.
105 G.M. Bancroft and E.T. Libbey, J. Chem. Soc. Dalton, (1973) 2103.
106 W.E. Newton and J.E. Searles, Inorg. Chim. Acta, 7 (1973) 349.
107 B.R. James, L.D. Markham, B.C. Hui and G.L. Rempel, J. Chem. Soc. Dalton, (1973) 2257.
108 L. Ruiz-Ramirez, T.A. Stephenson and E.S. Switkes, J. Chem. Soc. Dalton, (1973) 1770.
109 D. Negoiu and I. Serban, An. Univ. Bucuresti, Chim., 21 (1972) 37.
110 D.F. Gill, B.E. Mann and B.L. Shaw, J. Chem. Soc. Dalton, (1973) 311.
111 D.F. Gill, R. Mason, B.L. Shaw and K.M. Thomas, J. Organometal. Chem., 40 (1972) C67.
112 G.R. Crooks, B.F.G. Johnson, J. Lewis, I.G. Williams and G.A. Gamlen, J. Chem. Soc. A, (1969) 2761.
113 W.O. Siegl, S.J. Lapporte and J.P. Collman, Inorg. Chem., 12 (1973) 674.
114 R. Whyman, J. Organometal. Chem., 56 (1973) 339.
115 P. Meakin, E.L. Muetterties and J.P. Jesson, J. Amer Chem. Soc , 95 (1973) 75
116 J.R. Sanders, J. Chem. Soc. Dalton, (1973) 743.
117 I.S. Kolomnikov, A.I. Gusev, G.G. Aleksandrov, T.S. Lobeeva, Yu T. Struchkov and M.E. Vol'pin, J. Organometal. Chem., 59 (1973) 349.
118 S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton, (1973) 1912.
119 S.S. Sandhu and A.K. Mehta, Inorg. Nucl. Chem. Lett., 9 (1973) 1197.
120 F.G. Moers, R.W.M. ten Hoedt and J.P. Langhout, Inorg. Chem., 12 (1973) 2196.
121 B. Bell, J. Chatt and G.J. Leigh, J. Chem. Soc. Dalton, (1973) 997.

122 A.L. Balch, J. Amer. Chem. Soc., 95 (1973) 2723, I. Bernal, A. Clearfield, E.F. Epstein, J.S. Ricci, A.L. Balch and J.S. Miller, J. Chem. Soc. Chem. Commun., (1973) 39, J.S. Miller and A.L. Balch, Inorg. Chem., 10 (1971) 1410.

123 C. Eaborn, N. Farrell, J.L. Murphy and A. Pidcock, J. Organometal. Chem., 55 (1973) C68.

124 G. Condorelli, L. Giallongo, A. Giuffrida and G. Romeo, Inorg. Chim. Acta., 7 (1973) 7.

125 J.W. Schwindler, J.R. Luoma and J.P. Cusick, Inorg. Chim. Acta, 7 (1973) 563.

126 D.J. Doonan and A.L. Balch, J. Amer. Chem. Soc., 95 (1973) 4769.

127 J.S. Miller, A L. Balch and J.H. Enemark, J Amer Chem. Soc., 93 (1971) 4613.

128 J. Chatt, R.L. Richards and G.H.D. Royston, J. Chem. Soc. Dalton, (1973) 1433.

129 S. Sorriso, G. Distefano and A. Foffani, J. Organometal. Chem., 47 (1973) 139.

130 B.F.G. Johnson and J.A. Segal, J. Chem. Soc. Dalton, (1972) 1268.

131 B.F.G. Johnson and J.A. Segal, J. Chem. Soc. Dalton, (1973) 478.

132 J. Ashley-Smith, B.F.G. Johnson and J.A. Segal, J. Organometal. Chem., 49 (1973) C38.

133 J. Clemens, M. Green and F.G.A. Stone, J. Chem Soc. Dalton, (1973) 375.

134 P.R. Hoffman, J.S. Miller, C.B. Ungermann and K.G. Caulton, J. Amer. Chem. Soc , 95 (1973) 7902.

135 J. Reed, A.J. Schultz, C.G. Pierpoint and R. Eisenberg, Inorg. Chem., 12 (1973) 2949.

136 C.G. Pierpoint and R. Eisenberg, Inorg. Chem., 12 (1973) 199

137 B.B. Wayland and L.W. Olson, J. Chem. Soc Chem. Commun., (1973) 897; L. Vaska and H. Nakai, J. Amer. Chem. Soc., 95 (1973) 5431.

138 V.S. Psalidas, L.A. Butman, P.M. Sorku and V.M. Sinitsyn, Vestn. Mosk. Univ., Khim., 14 (1973) 44.

139 T.S. Khodashova, M.A. Porai-Koshits, V.S. Sergienko, N.A. Parpiev and G.B. Bokii, Zh. Strukt. Khim. 13 (1972) 1105.

140 M.C.R. Symons, D X. West and J.G. Wilkinson, J. Chem. Soc. Chem. Commun., (1973) 917

141 S.D. Pell and J.N. Armor, J. Amer. Chem. Soc., 95 (1973) 7625

142 J.N. Armor, Inorg. Chem., 12 (1973) 1959.

143 S D. Pell and J.N. Armor, Inorg. Chem., 12 (1973) 873

144 F. Bottomley and S -B Tong, J. Chem. Soc. Dalton, (1973) 217.

145 F. Bottomley, W.V.F. Brooks, S.G. Clarkson and S.-B. Tong, J. Chem. Soc. Chem. Commun., (1973) 919.

146 D. Gwost and K.G. Caulton, J. Chem. Soc. Chem. Commun., (1973) 64, and Inorg. Chem., 12 (1973) 2095.

147 B Haymore and R.D. Feltham, Inorg. Synth., 14 (1973) 14.

148 T. Kruck, J. Waldmann, M. Hofler, G. Birkenhäger and G. Odenbrett, Z. Anorg Allg Chem., 402 (1973) 16

149 J. Schmidt, W L. Dorn and R. Kramolowsky, Inorg. Chim. Acta, 7 (1973) 433.

150 W. Hieber and K. Kaiser, Z. Anorg Allg. Chem., 358 (1968) 271.

151 T. Birchall and K.M Tun, J. Chem. Soc. Dalton, (1973) 2521.

152 R.O. Harris, N.K. Hota, L Sadavoy and J.M.C. Yuen, J. Organometal. Chem., 54 (1973) 259.

153 J.R. Norton and J.P. Collman, Inorg. Chem., 12 (1973) 476.

154 J.P. Candlin and A.C Shortland, J. Organometal. Chem., 16 (1969) 289; G. Cetini, O. Gambino, E. Sappa and G.A. Vaglio, Atti Accad. Sci. Torino Cl. Sci. Fis., Mat. Natur., 101 (1966-67) 855.

155 O. Crichton, M. Poliakoff, A.J. Rest and J.J. Turner, J. Chem. Soc. Dalton, (1973) 1321.

156 W.E. Carroll and F.J. Lalor, J. Organometal. Chem., 54 (1973) C37; D.R. Fisher and D. Sutton, Can. J. Chem., 51 (1973) 1697; W.E. Carroll and F.J. Lalor, J. Chem. Soc. Dalton, (1973) 1754.

157 K.R. Laing, S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton, (1973) 2713 and J. Chem. Soc. Chem. Commun., (1973) 176.

158 J V. McArdle, A J. Schultz, B.J. Corden and R. Eisenberg, Inorg. Chem., 12 (1973) 1676.

159 W.L. Bowden, W.F. Little and T.J. Meyer, J. Amer. Chem. Soc., 95 (1973) 5084.

160 R.M. Moriarty, K.-N. Chen and J.L. Flippen, J. Amer. Chem. Soc., 95 (1973) 6489.

161 R.M. Moriarty, C.-L. Yeh and K.-N. Chen, Tetrahedron Lett., (1972) 5325.

162 A.P. Humphries and S.A.R. Knox, J. Chem. Soc. Chem. Commun., (1973) 326.

163 J. Weaver and P. Woodward, J. Chem. Soc. Dalton, (1973) 1439.

164 U. Behrens and E. Weiss, J. Organometal. Chem., 59 (1973) 335.

165 M.J. Boylan, J. Bellerby, J. Newan and A.R. Manning, J. Organometal. Chem., 47 (1973) C33.

166 J.G. Bullitt, F.A. Cotton and T.J Marks, J. Amer. Chem. Soc., 92 (1970) 3155 and Inorg. Chem., 11 (1972) 671; O.A. Gansow, A.R. Burke and W.D. Vernon, J. Amer. Chem. Soc., 94 (1972) 2550.

167 R.D. Adams and F.A. Cotton, J. Amer. Chem. Soc., 95 (1973) 6589.

168 R.D. Adams and F.A. Cotton, Inorg. Chim. Acta, 7 (1973) 153.

169 R.M. Kirchner, T.J. Marks, J.S. Kristoff and J.A. Ibers, J. Amer. Chem. Soc., 95 (1973) 6602.

170 J.S. Kristoff, N.J. Nelson and D F. Shriver, J. Organometal. Chem., 49 (1973) C82.

171 N.E. Kim, N.J. Nelson and D.F. Shriver, Inorg. Chim. Acta, 7 (1973) 393.

172 S.W. Ulmer, P.M. Skarstad, J.M. Burlitch and R.E. Hughes, J.Amer. Chem. Soc., 95 (1973) 4469.

173 A.E. Crease and P. Legzdins, J. Chem. Soc. Dalton, (1973) 1501.

174 B.D. Dombek and R.J. Angelici, Inorg. Chim. Acta, 7 (1973) 345.
175 W.E. Williams and F.J. Lalor, J. Chem. Soc. Dalton, (1973) 1329.
176 R.H. Reimann and E. Singleton, J. Organometal. Chem., 57 (1973) C75.
177 M.E. Gress and R.A. Jacobson, Inorg. Chem., 12 (1973) 1746.
178 D.A. Symon and T.C. Waddington, J. Chem. Soc. Dalton, (1973) 1879.
179 J.A. Ferguson and T.J. Meyer, Chem. Commun., (1971) 623.
180 J.N. Braddock and T.J. Meyer, Inorg. Chem., 12 (1973) 723.
181 R.B. King and D.M. Braitsch, J. Organometal. Chem., 54 (1973) 9.
182 A.N. Nesmeyanov, M.I. Rybinskaya, V.S. Kaganovich, T.V. Popova and E.A. Petrovskaya, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1973) 2087.
183 R.B. King and M.S. Saran, J. Amer. Chem. Soc., 95 (1973) 1811.
184 A.N. Nesmeyanov, N.E. Kolobova, G.K. Znobina, K.N. Anisimov, I.B. Zlotina and M.D. Bargamova, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1973) 2168.
185 S.C. Cohen, J. Chem. Soc. Dalton, (1973) 553.
186 A.N. Nesmeyanov, L.G. Makarova and V.N. Vinogradov, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1973) 2796.
187 L.I. Zakharkin, L.V. Orlova and L.I. Denisovich, Zh. Obshch. Khim., 42 (1972) 2217.
188 H. Brunner and E. Schmidt, J. Organometal. Chem., 50 (1973) 219.
189 F.A. Cotton, B.A. Frenz and A. Shaver, Inorg. Chim. Acta, 7 (1973) 161.
190 G. Ingletto, E. Tandello, L. di Sipio, G. Carturan and M. Graziani, J. Organometal. Chem., 56 (1973) 335.
191 C.P. Casey, C.R. Cyr and R.A. Boggs, Synth. Inorg. Met. Org. Chem., 3 (1973) 249.
192 A. Sanders, L. Cohen, W.P. Giering, D. Kenedy and C.V. Magatti, J. Amer. Chem. Soc., 95 (1973) 5430.
193 P.M. Treichel, J.P. Stenson and J.J. Benedict, Inorg. Chem., 10 (1971) 1183.
194 W.M. Butler and J.H. Enemark, J. Organometal. Chem., 49 (1973) 233.
195 T.G. Attig, P. Reich-Rohrwig and A. Wojcicki, J. Organometal. Chem., 51 (1973) C21.
196 J.J. Alexander and A. Wojcicki, Inorg. Chem., 12 (1973) 74.
197 K.M. Nicholas and M. Rosenblum, J. Amer. Chem. Soc., 95 (1973) 4449.
198 S.N. Anderson, C.W. Fong and M.D. Johnson, J.Chem. Soc. Chem. Comm., (1973) 1633.
199 S.E. Jacobson and A. Wojcicki, J. Amer. Chem. Soc., 95 (1973) 6962
200 S.E. Jacobson, P. Reich-Rohrwig and A. Wojcicki, Inorg. Chem., 12 (1973) 717.
201 T.C. Flood and D.L. Miles, J. Amer. Chem. Soc., 95 (1973) 6460.
202 G.M. Whitesides and D.J. Boschetto, J. Amer. Chem. Soc., 93 (1971) 1529.
203 D.W. Lichtenberg and A. Wojcicki, J. Organometal. Chem., 7 (1973) 311.
204 S.R. Su and A. Wojcicki, J. Organometal. Chem., 31 (1974) C34; W.P. Giering and M. Rosenblum, J. Amer. Chem. Soc., 93 (1971) 5299.
205 M.R. Churchill and S.W.-Y. Ni Chang, J. Amer. Chem. Soc., 95 (1973) 5931.
206 S. Raghu and M. Rosenblum, J. Amer. Chem. Soc., 95 (1973) 3060.
207 R. Ben-Shoshan and R. Pettit, J. Amer. Chem. Soc., 89 (1967) 233.
208 Y. Yamamoto and A. Wojcicki, Inorg. Chem., 12 (1973) 1779.
209 T. Blackmore, M.I. Bruce, F.G.A. Stone, R.E. Davis and N.V. Raghavan, J. Organometal. Chem., 49 (1973) C35.
210 A. Rosan, M. Rosenblum and J. Tancrede, J. Amer. Chem. Soc., 95 (1973) 3062.
211 M. Höfler and J. Scheuren, J. Organometal. Chem., 55 (1973) 177.
212 R.J.P. Corriu and W.E. Douglas, J. Organometal. Chem., 51 (1973) C3.
213 C.S. Cundy and M.F. Lappert, J. Organometal. Chem., 57 (1973) C72.
214 R.C. Job and M.D. Curtis, Inorg. Chem., 12 (1973) 2510.
215 R.C. Job and M.D. Curtis, Inorg. Chem., 12 (1973) 2514.
216 E.W. Abel and M.O. Dunster, J. Organometal. Chem., 49 (1973) 435.
217 R.M.G. Roberts, J. Organometal. Chem., 47 (1973) 359.
218 C. Ungurenasu, G. Stiubianu and E. Streba, Synth. Inorg. Met. Org. Chem., 3 (1973) 211.
219 W. Kläui and H. Werner, J. Organometal. Chem., 54 (1973) 331.
220 W. Kläui and H. Werner, J. Organometal. Chem., 60 (1973) C19.
221 J.P. Collman, D.W. Murphy and G. Dolcetti, J. Amer. Chem. Soc., 95 (1973) 2687.
222 J.P. Collman, J.K. Hoyano and D.W. Murphy, J. Amer. Chem. Soc., 95 (1973) 3424.
223 A.N. Nesmeyanov, L.G. Makarova and V.N. Vinogradova, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1972) 2798, and (1972) 2605.
224 R.C. Dobbie and P.R. Mason, J. Chem. Soc. Dalton, (1973) 1124.
225 W. Ehrl and H. Vahrenkamp, J. Organometal. Chem., 63 (1973) 389, and Chem. Ber., 106 (1973) 2550; H. Vahrenkamp, J. Organometal. Chem., 63 (1973) 399.
226 R.J. Haines, A.L. du Preez and C.R. Nolte, J. Organometal. Chem., 55 (1973) 199.
227 W.R. Cullen, D.J. Patmore and J.R. Sams, Inorg. Chem., 12 (1973) 867.
228 W.R. Cullen, D.J. Patmore, J.R. Sams, M.J. Newlands and L.K. Thompson, Chem. Commun., (1971) 952; F.W.B. Einstein and R.D.G. Jones, Inorg. Chem., 12 (1973) 1690.

229 J.L. Davidson and D.W.A. Sharp, J. Chem. Soc. Dalton, (1973) 1957.

230 R.Bruce and G.R. Knox, J. Organometal. Chem., 6 (1966) 67; M. Dekker, G.R. Knox and C.G. Robertson, ibid., 18 (1969) 161; E.D. Schermer and W.H. Baddley, ibid., 27 (1971) 83.

231 J.A. de Beer, R.J. Haines, R.Greatrex and J.A. van Wyk, J. Chem. Soc Dalton, (1973) 2341; P.D Frisch, M.K. Lloyd, J.A. McCleverty and D. Seddon, J. Chem. Soc. Dalton, (1973) 2268.

232 M.R. Churchill, B.G. de Boer, K.L. Kalra, P. Reich-Rohrwig and A. Wojcicki, J Chem. Soc. Chem. Commun., (1972) 981.

233 M.R. Churchill, B.G. de Boer and K.L. Kalra, Inorg. Chem., 12 (1973) 1646.

234 M.R. Churchill and K.L. Kalra, Inorg. Chem., 12 (1973) 1650.

235 G.T. Kubas, T.G. Spiro and A. Terzis, J. Amer. Chem. Soc., 95 (1973) 273; A. Terzis and R. Rivest, Inorg. Chem., 12 (1973) 2132.

236 R.J. Haines, J.A. de Beer and R. Greatrex, J. Organometal. Chem., 55 (1973) C30

237 L.H. Ali, A. Cox and T.J. Kemp, J. Chem. Soc. Dalton, (1973) 1475.

238 D.M. Allen, A. Cox, T.J. Kemp and L.H. Ali, J. Chem. Soc. Dalton, (1973) 1899.

239 F.A. Cotton, B.A. Frenz and A.J. White, J. Organometal. Chem., 60 (1973) 147.

240 M.J. Mays and P.L. Sears, J. Chem. Soc. Dalton, (1973) 1873.

241 J.S. Kristoff and D F. Shriver, Inorg. Chem., 12 (1973) 1788.

242 E.W. Abel and S. Moorhouse, J. Chem. Soc. Dalton, (1973) 1706.

243 J.P. Brennan, R.N. Grimes, R. Schaeffer and L.G. Sneddon, Inorg. Chem., 12 (1973) 2266.

244 R.N. Grimes, J. Amer. Chem. Soc., 93 (1971) 261; D.A. Franz, V.R. Miller and R.N. Grimes, J. Amer. Chem. Soc., 94 (1972) 412.

245 L.G. Sneddon, D.C. Beer and R.N. Grimes, J. Amer. Chem. Soc., 95 (1973) 6623.

246 D.F. Dustin, W.J. Evans and M.F. Hawthorne, J. Chem. Soc. Chem. Commun., (1973) 806.

247 D.C. Beer and L.J. Todd, J. Organometal. Chem., 55 (1973) 363.

248 W.J. Evans, G.B. Dunks and M.F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 4565.

249 J Plesek, B. Stibr and S. Hermaner, Synth. Inorg. Met. Org. Chem., 3 (1973) 291.

250 D.F. Dustin, G.B. Dunks and M.F. Hawthorne, J. Amer. Chem. Soc., 95 (1973) 1109.

251 R. Buehler, R. Geist, R. Muednich and H. Plieninger, Tetrahedron Lett., (1973) 1919.

252 R.B. King, I. Haiduc and C.W. Eavenson, J. Amer Chem. Soc , 95 (1973) 2508.

253 H.A. Brune, G. Horlbeck, H. Roettele and U. Tanger, Z. Naturforsch. B, 28 (1973) 68.

254 T.M. Yamamoto, T. Souichi and Y. Odaira, J. Chem Soc. Perkin I, (1973) 138.

255 O.L. Chapman, J. Pacansky and P.W. Wojtkowski, J. Chem. Soc. Chem. Commun., (1973) 681.

256 A. Efraty, R. Bystrek, J. A. Geaman, M.H.A. Huang and R.H. Herber, J. Organometal. Chem., 55 (1973) C33.

257 P. Marcincal, N. Hanoir-Guisez and E. Cuingnet, Trav Soc. Pharm. Montpellier, 33 (1973) 281.

258 R. Damrauer and T.E. Rutledge, J. Org. Chem., 38 (1973) 3330.

259 R.H. Grubbs and R.A. Grey, J. Chem. Soc. Chem. Commun., (1973) 76.

260 P. Reeves, T. Devon and R. Pettit, J. Amer. Chem. Soc., 91 (1969) 5888.

261 R.H. Grubbs and R.A. Grey, J. Amer. Chem. Soc., 95 (1973) 5765.

262 E.K.G. Schmidt, Angew. Chem., 85 (1973) 820.

263 W.E. Billups, L. Plin and B.A. Baker, J. Organometal. Chem , 61 (1973) C55.

264 I.S. Krull, J. Organometal. Chem., 57 (1973) 363.

265 D.J. Ehntholt and R.C. Kerber, Chem. Commun , (1970) 1451.

266 M.R. Churchill and B.G de Boer, Inorg. Chem., 12 (1973) 525.

267 A.N. Nesmeyanov, N.A. Vol'kenau, L.S. Shilovtseva and V.A. Petrakova, J. Organometal. Chem., 61 (1973) 329.

268 R. Middleton, J.R. Hull, S.R. Simpson, C.H. Tomlinson and P.L. Timms, J. Chem. Soc. Dalton, (1973) 120.

269 D J. O'Sullivan and F.J. Lalor, J. Organometal. Chem., 57 (1973) C58.

270 R.J. Restivo and G. Ferguson, J. Chem. Soc. Chem. Commun., (1973) 847.

271 A.E. Crease and P. Legzdins, J. Chem. Soc. Chem. Commun., (1973) 775.

272 E.W. Abel and M.O. Dunster, J. Chem. Soc. Dalton, (1973) 98.

273 F.A. Cotton and J.A. McCleverty, Inorg. Chem., 3 (1964) 1398.

274 T. Kruck and L. Knoll, Z. Naturforsch. B, 28 (1973) 34.

275 M. Minasyants, Yu.T. Struchkov and V.G. Andrianov, Uch. Zap. Erevan Gos. Univ., Estestv Nauki, (1972) 27; Zhur. Khim., (1973) Abstr. No. 7B530.

276 E.W. Randall, E. Rosenberg and L. Milone, J. Chem. Soc. Dalton, (1973) 1672.

277 A.N. Nesmeyanov, Yu.A. Ustynyuk, I.I. Kritskaya and G.A. Schembelov, J. Organometal. Chem., 14 (1968) 395.

278 G. Paliani, A. Poletti, G. Cardaci, S.M. Murgia and R. Cataliotti, J. Organometal. Chem., 60 (1973) 157.

279 T.H. Whitesides, R.W. Arhart and R.W. Slauen, J. Amer. Chem. Soc., 95 (1973) 5792.

280 M. Green and B. Lewis, J. Chem. Soc. Chem. Commun., (1973) 114.

281 A. Bond, M. Green and S.H. Taylor, J. Chem. Soc. Chem. Commun., (1973) 112.
282 C.P. Casey and C R. Cyr, J. Amer. Chem. Soc , 95 (1973) 2248.
283 M. Cooke, R.J. Goodfellow, M. Green and G. Parker, J. Chem. Soc., A, (1971) 16.
284 R.A. Marsh, J. Howard and P. Woodward, J. Chem. Soc. Dalton, (1973) 778.
285 B.F.G. Johnson, J. Lewis and M.V. Twigg, J. Organometal. Chem., 52 (1973) C31.
286 R. Aumann, J. Organometal. Chem., 47 (1973) C29.
287 R. Aumann, Angew. Chem. Int. Ed. Engl., 12 (1973) 574.
288 A. Eisenstadt, J. Organometal. Chem., 60 (1973) 335.
289 M. Green, S. Heathcock and D.C. Wood, J. Chem. Soc. Dalton, (1973) 1564.
290 M. Green, S. Tolson, J. Weaver, D.C. Wood and P. Woodward, Chem. Commun., (1971) 222; J. Weaver and P. Woodward, J. Chem. Soc., A, (1971) 3521.
291 J.A.D. Jeffreys, C.M. Willis, I.C. Robertson, G. Ferguson and J.G. Sime, J. Chem. Soc. Dalton, (1973) 749.
292 F.A. Cotton, B.A. Frenz, G. Deganello and A. Shaver, J. Organometal. Chem., 50 (1973) 227.
293 F.A. Cotton, A. Davison, T J. Marks and A. Musco, J. Amer. Chem. Soc., 91 (1969) 6598; F.A. Cotton and T.J. Marks, J. Organometal. Chem., 19 (1969) 237.
294 M. Evans, M. Hursthouse, E.W. Randall, E. Rosenberg, L. Milone and M. Valle, J. Chem. Soc. Chem. Commun., (1972) 545.
295 T H. Whitesides and R.A. Budnik, J. Chem Soc. Chem. Commun., (1973) 87.
296 M.R. Churchill and J. Wormald, Inorg. Chem., 12 (1973) 191.
297 V.G. Shubin, R.N. Berezina and V.N. Piottukh-Peletski, J. Organometal. Chem., 54 (1973) 239.
298 J. Evans, D.V. Howe, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 61 (1973) C48.
299 L.A.P. Kane-Maguire and C.A. Mansfield, J. Chem. Soc. Chem. Commun., (1973) 540.
300 A.J. Birch, K.B. Chamberlain and D.J. Thompson, J. Chem. Soc. Perkin I, (1973) 1900.
301 R. Bau, J.C. Burt, S.A.R. Knox, R.M. Laine, R P. Philips and F.G.A Stone, J. Chem. Soc. Chem Commun., (1973) 726
302 A. Brookes, J. Howard, S.A.R. Knox, F.G.A. Stone and P. Woodward, J. Chem. Soc. Chem. Commun., (1973) 587.
303 W. Weidemueller and K. Hafner, Angew. Chem., 85 (1973) 958.
304 F.W. Grevels and E. Koerner von Gustorf, Liebigs Ann. Chim., 11 (1973) 1821.
305 B. Beagley, D.G. Schmidling and D.W J. Cruickshank, Acta Crystallogr. B, 29 (1973) 1499.
306 J.E. McCaskie, P.L. Chang, T.R. Nelsen and D.C. Dittmer, J. Org. Chem., 38 (1973) 3963.
307 I.S. Krull, J. Organometal. Chem., 57 (1973) 373.
308 D.J. Darensbourg, J.E. Tappan and B.J. Marwedel, J. Organometal. Chem., 54 (1973) C39
309 T. Kruck and L. Knoll, Chem. Ber., 106 (1973) 3578.
310 R.E. Graf and C.P. Lillya, J. Chem. Soc. Chem. Commun., (1973) 271.
311 D. Ehntholt, A. Rosan and M. Rosenblum, J. Organometal. Chem., 56 (1973) 315.
312 T.A. Stephenson, E.S. Switkes and L. Ruiz-Ramirez, J. Chem. Soc. Dalton, (1973) 2112.
313 L. Ruiz-Ramirez, T.A. Stephenson and E.S. Switkes, J. Organometal. Chem., 49 (1973) C77.
314 A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 49 (1973) C33.
315 A.J.P. Domingos, B.F.G. Johnson, J. Lewis and G.M. Sheldrick, J. Chem. Soc. Chem. Commun., (1973) 913.
316 F.A. Cotton and W T. Edwards, J. Amer. Chem. Soc., 90 (1968) 5412.
317 R.E. Graf and C.P. Lillya, J. Organometal. Chem., 47 (1973) 413.
318 S. Sarel, R. Ben-Shoshan and B. Kirson, Isr. J. Chem., 10 (1972) 787.
319 N.S. Nametkin, A.L. Nekhaev, V.D. Tyurin and V.N. Dontsova, Izv. Akad. Nauk S.S S.R., Ser. Khim., (1973) 959.
320 T. Kruck, L. Knoll and J. Laufenberg, Chem. Ber., 106 (1973) 697.
321 L.G. Kuz'mina, Yu. T. Struchkov and A.I. Nekhaev, Zh. Strukt. Khim., 13 (1972) 1115.
322 P. McArdle and H. Sherlock, J. Organometal. Chem., 52 (1973) C29.
323 M. Anderson, A.D.H. Clague, L.P. Blaauw and P.A. Couperus, J. Organometal. Chem., 56 (1973) 307
324 A.N. Nesmeyanov, L.V. Rybin, N.T. Gubenko, P.V. Petrovskii and M.I. Rybinskaya, Zh. Obshch. Khim., 42 (1972) 2473.
325 A.M. Brodie, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1973) 1997.
326 K. Takahashi, M. Iwanami, A. Tsai, P.L. Chang, R.L. Harlow, L.E. Harris, J.E. McCaskie, C.E. Pfluger and D.C. Dittmer, J. Amer. Chem. Soc., 95 (1973) 6113.
327 R.L. Harlow and C.E. Pfluger, Acta Crystallogr. B, 29 (1973) 2633.
328 N.S. Nametkin, V.D. Tyurin, M.N. El-Laddawi and N.A. Gromasheva, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1973) 2170.
329 N.S. Nametkin, A.I. Nekhaev, V.D. Tyurin and S.P. Gubin, Neftekhimiya, 13 (1973) 130.
330 V.N. Piottukh-Peletskii, R.N. Berezina, A.I. Rezvukhin and V.G. Shubin, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1973) 2083.
331 A.J. Birch and D.H. Williamson, J. Chem. Soc. Perkin I, (1973) 1892.

332 R.N. Berezina, E.P. Yablokova and V.G. Shubin, Izv. Akad. Nauk S.S.S.R., Ser. Khim., (1973) 2273.

333 F.A. Cotton and G. Deganello, J. Amer. Chem. Soc., 95 (1973) 396.

334 F.A. Cotton, V.W. Day, B.A. Frenz, K.I. Hardcastle and J.M. Troup, J. Amer. Chem. Soc., 95 (1973) 4522.

335 H. Alper and C.C. Huang, J. Organometal. Chem., 50 (1973) 213.

336 J.L. Calderon, A. Shaver and F.A. Cotton, J. Organometal. Chem., 57 (1973) 121.

337 P. Crews, J. Amer. Chem. Soc., 95 (1973) 637.

338 J. Müller, G.E. Herberich and H. Müller, J. Organometal. Chem., 55 (1973) 165.

339 O.P. Anderson and M.C.R. Symons, Inorg. Chem., 12 (1973) 1932.

340 T.H. Whitesides and J.P. Neilan, J. Amer. Chem Soc., 95 (1973) 5811.

341 T.H. Whitesides and R.W. Arhart, J. Amer. Chem. Soc., 93 (1971) 5296.

342 D.V. Banthorpe, H. Fitton and J. Lewis, J. Chem. Soc. Perkin I, (1973) 2051.

343 P. McArdle, J Chem. Soc. Chem. Commun., (1973) 482.

344 A. Brookes, J. Howard, S.A.R. Knox, V. Riera, F.G.A. Stone and P. Woodward, J. Chem. Soc. Chem. Commun., (1973) 727.

345 G. Deganello, J. Organometal. Chem., 59 (1973) 329.

346 A.J. Carty, R.F. Hobson, H.A. Patel and V. Snieckus, J. Amer. Chem. Soc , 95 (1973) 6835

347 A. de Cian, P.M. L'Huillier and R. Weiss, Bull Chim. Soc. France, Pt 1 (1973) 457.

348 R.C. Kerber and D.J. Ehntholt, J. Amer. Chem. Soc., 95 (1973) 2927

349 M. Brookhart, N.M. Lippman and E.J. Reardon, Jr., J. Organometal. Chem., 54 (1973) 247.

350 F.A. Cotton and G. Deganello, J. Organometal. Chem., 38 (1972) 147; F.A. Cotton, B.A Frenz, G. Deganello and A. Shaver, ibid , 50 (1973) 227; F.A Cotton, B.A. Frenz, J M. Troup and G. Deganello, ibid., 59 (1973) 317, F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 95 (1973) 3798.

351 J.E. Alsop and R. Davis, J. Chem. Soc. Dalton, (1973) 1686.

352 G. Allegra, A. Colombo and E.R. Mognaschi, Gazz. Chim. Ital., 102 (1972) 1060.

353 R.R. Schrock and J. Lewis, J. Amer. Chem. Soc., 95 (1973) 4102.

354 E.O. Fischer and J. Müller, Chem. Ber., 96 (1963) 3217.

355 G Deganello, H. Maltz and J. Kozarich, J. Organometal. Chem., 60 (1973) 323; E.J. Reardon, Jr. and M. Brookhart, J. Amer. Chem. Soc., 95 (1973) 4311.

356 M.J. Bennett, W.A.G. Graham, R.P. Stewart, Jr. and R.M. Tuggle, Inorg. Chem., 12 (1973) 2944

357 D.M. Roe and A.G. Massey, J. Organometal. Chem., 23 (1970) 547.

358 Y. Watanabe, T. Mitsudo, M. Yamashita, M. Tanaka and Y. Takegami, Chem. Lett., (1973) 475.

359 M.R Wiles and A G. Massey, J Organometal. Chem., 47 (1973) 423.

360 H.B. Chin and R. Bau, J. Amer. Chem. Soc , 95 (1973) 5068.

361 R.B. King and M.N. Ackermann, J. Organometal. Chem., 60 (1973) C57.

362 H. Alper and A.S.K. Chan, J. Organometal. Chem., 61 (1973) C59.

363 M.I. Bruce, B.L. Goodall and F.G.A. Stone, J. Organometal. Chem., 60 (1973) 343

364 P.G. Douglas and B L. Shaw, J. Chem. Soc. Dalton, (1973) 2078

365 E.W. Ainscough, T.A. James, S.D. Robinson and J.N. Wingfield, J. Organometal. Chem., 60 (1973) C63.

366 H.J. Spiegl, G. Groh and H.J. Berthold, Z. Anorg. Allg. Chem., 398 (1973) 225.

367 K. Jacob, I. Wiswedel, T. Zeine and K.-H. Thiele, Z. Anorg. Allg. Chem., 402 (1973) 193.

368 T. Yamamoto and A. Yamamoto, J. Organometal. Chem., 57 (1973) 127.

369 V.L. Goedken, S.-M. Peng and A.Y. Park, J. Amer. Chem. Soc., 96 (1974) 285.

370 R. Taube and D. Steinborn, J. Organometal. Chem., 65 (1974) C9.

371 A.P. Ginsberg and W.E. Lindsell, Inorg. Chem., 12 (1973) 1983.

372 B. Cetinkaya, P. Dixneuf and M.F. Lappert, J. Chem. Soc Chem. Commun., (1973) 206.

373 M.Y. Darensbourg, H.L. Conder, D.J. Darensbourg and C. Hasday, J. Amer. Chem. Soc , 95 (1973) 5919.

374 D.R. Fahey, J. Org. Chem., 38 (1973) 3343.

375 D.R. Fahey, J. Org. Chem., 38 (1973) 80.

376 R.W. Mitchell, A. Spencer and G. Wilkinson, J. Chem. Soc. Dalton, (1973) 846.

377 A.G. Hinze, Rec. Trav. Chim., 92 (1973) 542.

378 R. Iwata and I. Ogata, Tetrahedron, 29 (1973) 2753.

379 A.N. Nesmeyanov, G.P. Zol'nikova, G.M Babakhina, I.I. Kritskaya and G.G. Yakobson, Zh. Obshch. Khim., 43 (1973) 2007.

380 J P. Collman and N.W. Hoffman, J. Amer. Chem. Soc., 95 (1973) 2689.

381 J.P. Collman, S.R. Winter and R.G. Komoto, J. Amer. Chem. Soc., 95 (1973) 249.

382 R. Noyori, K. Yokoyama and Y. Hayakawa, J. Amer. Chem. Soc., 95 (1973) 2722.

383 R. Noyori, Y. Hayakawa, S. Makino, N. Hayakawa and H. Takaya, J Amer. Chem. Soc., 95 (1973) 4103.

384 K. Kinugasa and T. Agawa, J Organometal. Chem., 51 (1973) 329.

385 W.A. Genco, R.A. Partis and H. Alper, J. Org. Chem., 38 (1973) 4365.

386 E.T. Chukovskaya, M.A. Rozhkova and R K. Friedlina, Dokl. Akad Nauk S S S R., 212 (1973) 382.