IRON, RUTHENIUM AND OSMIUM

Annual Survey Covering the Year 1976*

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Contents

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* J. McCleverty, Iron, Ruthenium and Osmium, Annual Survey covering the year 1975, see J. Organometal. Chem., 151 (1978) 1 - 192.

METAL CARBONYLS

Simple carbonyls and carbonylate anions

Iron atoms react (1) with carbon monoxide giving $Fe(CO)_5$, $Fe_3(CO)_{12}$, (in very low yields) and traces of $Fe_2(CO)_9$. However, a study of powdered amorphous iron has been enabled (2) by the glow discharge decomposition of low concentrations of $Fe(CO)_5$ dispersed in neon. A method has been devised (3) for the separation of cobalt carbonyl from liquid mixtures containing $Fe(CO)_5$, $Co_2(CO)_8$ and $Ni(CO)_4$. This involves bubbling ammonia into the liquid mixture, when $[Co(NH_3)_6][Co(CO)_4]_2$ precipitates from the solution. Iron pentacarbonyl behaves as a weak donor towards certain Lewis acids. Thus, species of the type $[FeL_2][SbF_6]_2$, $[CdL_2][AsF_6]_2$ and $[SnL][SbF_6]_2$ have been prepared (4) by reaction of $Fe(CO)_5$ with $Fe[SbF_6]_2$, $Cd[AsF_6]_2$ and $Sn[SbF_6]_2$, respectively. At platinum electrodes in CF_3CO_2H, $Fe(CO)_5$ could be oxidised to the monocation in the presence of $[Bu^n_4N][PF_6]$ as supporting electrolyte (5). The electrode process for generating $[Fe(CO)_5]^+$ is only reversible at very fast cyclic voltammogram scan rates. The species $Fe(CO)_4Br_2$ and $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ can also be oxidised, although irreversibly, and the latter afforded $Fe(\eta^5-C_5H_5)(CO)_2(OCOCF_3)$.

The fluxionality of $Fe(CO)_5$ has been discussed (6). Thus, in the absence of a catalyst, there is no scrambling of $C^{16}O$ and $C^{18}O$ between $Fe(C^{16}O)_5$ and $Fe(C^{18}O)_5$, indicating that fluxional processes are not intermolecular in origin. However, slow intermolecular migration of CO can occur, as established by CO exchange between $Fe(CO)_5$ containing naturally abundant ^{13}CO and $Fe(^{13}CO)_3(PF_3)_2$ (92.5% enriched in ^{13}CO) dissolved in the pentacarbonyl. Studies of the intermolecular exchange of CO between $Fe(^{13}CO)_5$ (92.5% enriched) and $Fe(^{12}CO)_5$ revealed that the rate is extremely low, and confirmed that the scrambling of axial and equatorial CO groups in $Fe(CO)_5$ is intramolecular and probably occurs by a Berry-type process. From a study of partially oriented samples of $Fe(CO)_5$ in solid CO at 20°K, it was shown that in the process

$$Fe(CO)_5 \xrightarrow{h\nu\ ,\ CO} Fe(CO)_4 \ + \ CO \longrightarrow Fe(CO)_5$$

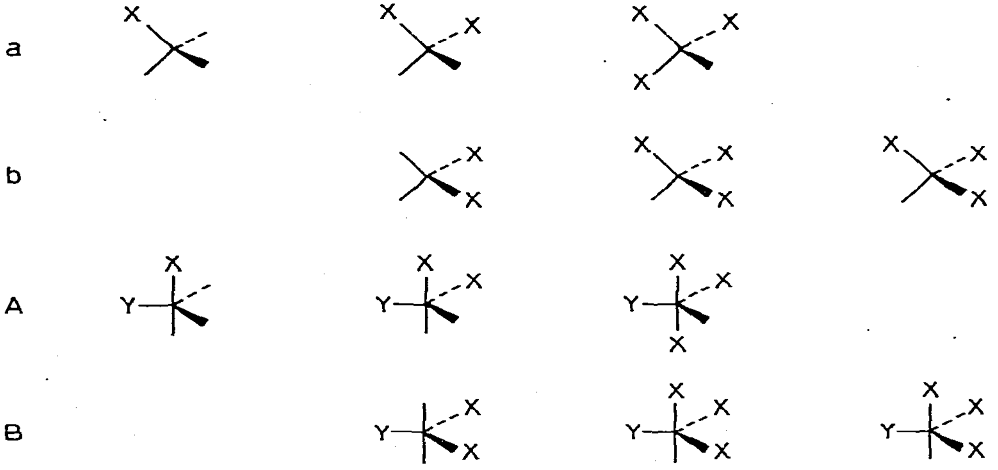
no change took place in the polarisation properties of the isolated carbonyl over several hours (7), indicating that stereochemical rigidity of the $Fe(CO)_5$ prevails in the matrix.

By a combination of matrix isolation techniques and i.r. laser photochemistry, the selective reactions of ^{13}CO-enriched $Fe(CO)_4$ in a methane matrix have been studied (8). The overall processes are summarised as follows:

$$Fe(CO)_5 \xrightarrow[\text{heat, } CH_4]{h\nu} Fe(CO)_4 \ + \ CO; \xrightarrow{h\nu} Fe(CO)_4(CH_4)$$

The different types of ^{13}CO-substituted species obtained in this way are summarised in Scheme 1. Although the mechanism of interconversion of the species is unknown, the following conclusions have been drawn. (i) There is a dramatic increase in intensity of the spectral bands of $Fe(CO)_4$ due either to a or b, but not both, while the other bands due to A or B also increased. This must be due to the reactions a→A or b→B. (ii) These reactions are laser irradiation promoted and are not achieved by warming the matrix. (iii) The selectivity of these reactions is in complete contrast to the unselective reactions caused by broad band radiation from a Nernst glower. (iv) Isotopic selectivity shows that there is not an efficient energy transfer from one isotopic species to another. In other words, the reaction is localised in the matrix cage. (v) The laser has differentiated between molecules with different degrees of isotopic substitution and also between species having different stereochemical arrangements of the ^{13}CO groups. (iv) Such selectivity can only be achieved using an i.r. laser since these molecules have very

Scheme 1



$X = {}^{13}CO$ and $Y = CH_4$

broad u.v. and visible absorption bands which are insensitive to isotopic substitution. It seems unlikely that these reactions involve single photon processes. A theoretical study has been made (9) of the structure and bonding properties of $Fe(CO)_4$ and $Fe_2(CO)_6(C_2R_2)$, using extended Hückel M.O. treatments.

The complex $Os(CO)_2(CS)(PPh_3)_2$ (trans phosphines) has been prepared (10) by borohydride reduction of [1], followed by loss of methanethiol from the product [2].

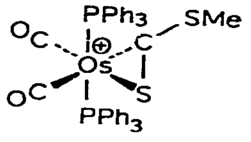
The structure of $Na_2Fe(CO)_4.1.5$ dioxane has been determined (11) crystallographically. In the solid state, the most noteable feature of the structure of the carbonylate anion is its significant distortion from tetrahedral symmetry. Indeed, one of the C-Fe-C bond angles is 129.7°. There are two main types of interaction between Na^+ and $Fe(CO)_4{}^{2-}$: a short-range Na....O interaction at a distance of 2.32Å and a long range Na....C and Na....Fe interaction at distances of 2.95 and 3.09Å, respectively. Two Na^+ and two $Fe(CO)_4{}^{2-}$ ions come together to form a spurious loosely-held cluster in which each Na^+ is associated with a C-Fe-C region of the anions. This interaction is probably responsible for the structural distortions in the solid, and it is thought that similar distortions may occur in $Fe(CO)_4{}^{2-}$ ion-pairs with Na^+ in solution.

A Raman spectral examination of $[Fe_2(CO)_8]^{2-}$ has permitted (12) the identification of the Fe-Fe stretching mode and revealed that the anion exists in a bridged - non-bridged equilibrium mixture in DMF. The presence of bridging CO groups in $[Fe_2(CO)_8H]^-$, [3], suggested by previous i.r. spectral studies (13), was also confirmed. It was further demonstrated that $[Ru(\eta^5\text{-}C_5H_5)(CO)_2]_2$ exists as a mixture of bridged and non-bridged isomers in solution, with the former being favoured at low temperatures.

Complexes with Group IV ligands

Some consideration has been given, using simple M.O. methods (14), to the ligand site preference and intramolecular rearrangements in the complexes $M(CO)_4(SiCl_3)_2$ (M = Fe, Ru and Os), and $M(CO)_4I_2$. In each case, the most stable isomer was determined, and the ligand site preference as a function of d-orbital occupation numbers in d^6 and d^8 systems was used to provide an explanation of some cis $\rightleftharpoons$ trans photochemical isomerisation, e.g. [4] → [5].

A ^{13}C n.m.r. spectral study has been made (15) of $M(CO)_4(EMe_3)_2$ and $M(CO)_4(SiMe_{3-n}Cl_n)_2$ (M = Fe, Ru or Os; E = Si, Ge, Sn or Pb; n = 1, 2 or 3). This has allowed the assignment of the carbonyl signals and has shown that axial-equatorial averaging of the CO signals occurs in the cis-iron complexes at room temperature. From variable temperature (v.t.) n.m.r. spectral studies it was concluded that the barrier to CO site exchange in $M(CO)_4(SiMe_{3-n}Cl_n)_2$ increased with halogen substitution and also from Fe to Ru to Os and, that from the observation of $^{117,119}Sn\text{-}^{13}CO$ coupling in the high temperature limiting spectra of cis-$Fe(CO)_4(SnMe_3)_2$, the fluxional processes were non-dissociative. The pattern of coalescence of signals from cis/trans mixtures suggested that axial-equatorial CO signal averaging proceeded via cis → trans → cis isomerisation processes.



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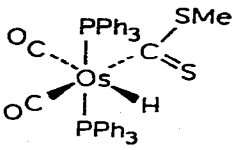

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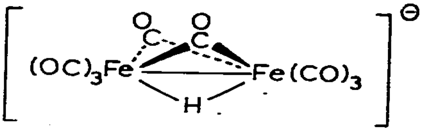

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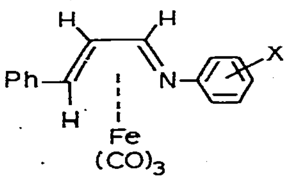
Treatment of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ and $Fe(CO)_2(NO)_2$ with Et_4N^+ or Ph_4As^+ salts of $[SnCl_3]^-$ or $[GeCl_3]^-$ afforded (16) $[Fe(CO)_4(SnCl_3)]^-$ (on heating) and $[Fe(CO)(NO)_2(GeCl_3)]^-$ (under u.v. light), respectively. It was noted that the nucleophilic properties of $[MCl_3]^-$ were unexpectedly small and that $[SnCl_3]^-$ is apparently a weaker base than $[GeCl_3]^-$. Reaction of $Fe(CO)_4(GeH_3)_2$ with $[Mn(CO)_5]^-$ gave (17) $Mn(CO)_5(GeH_3)$ and $[Fe(CO)_4(GeH_3)]^-$, and acidification of the latter afforded $Fe(CO)_4H(GeH_3)$ and some $Fe(CO)_4H_2$. Treatment of $Co(CO)_4(GeH_3)$ with $[Fe(CO)_4]^{2-}$ gave $Fe(CO)_4(GeH_3)_2$.

Complexes with Group V ligands

The reactions of the Schiff bases $PhCH{=}CHCH{=}NC_6H_4X$, A (X = H, p-Cl, -Br, -F, -I, -Me or -OMe, m-Br) and $R^1R^2R^3R^4C_6HCH{=}NC_6H_4(p\text{-}OMe)$, B ($R^1$, R^2, R^3, R^4 = H, Me or OMe) with $Fe_2(CO)_9$ have been reexamined (18). In the first stage of the reactions, the species $Fe(CO)_4L$ were formed, where A and B are attached to the metal via the N atom. However, $Fe(CO)_4A$ subsequently rearranged to give [6], as previously noted (19), whereas $Fe(CO)_4B$, having unsubstituted *ortho* positions on the phenyl rings, rearranged to give complexes of the type $Fe_2(CO)_6L$.

The intramolecular CO exchange processes in several imine and diimine complexes of tricarbonyliron have been examined (20) by v.t. ^{13}C n.m.r. spectroscopy. Those species containing π,π -bonded polar dienes, e.g. [7] or [8], showed the highest barriers to CO scrambling (10-14 kcal/mol) whereas those containing σ,π- or σ,σ-bonded diazadiene ligands, e.g. [9], have lower activation barriers (≤ 9 kcal/mol). These observations are in agreement withthe local C_{3v} symmetry of the $Fe(CO)_3$ moiety in these complexes.



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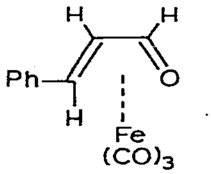

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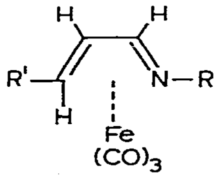

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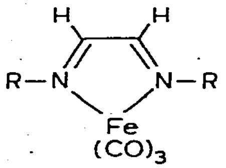

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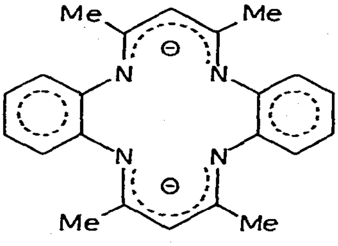
In the complexes Fe(CO)L, Fe(CO)L(pyr) and Fe(CO)L(N_2H_4), where L = [10], crystallographic studies have established (21) that the Fe-C-O group is linear, that the ligands trans to CO have abnormally long Fe-N distances, and that the Fe atom is slightly displaced out of the plane of the N atoms towards the carbonyl group. The reversible addition of CO and NO to Fe(II) phthalocyaninate in concentrated H_2SO_4 has



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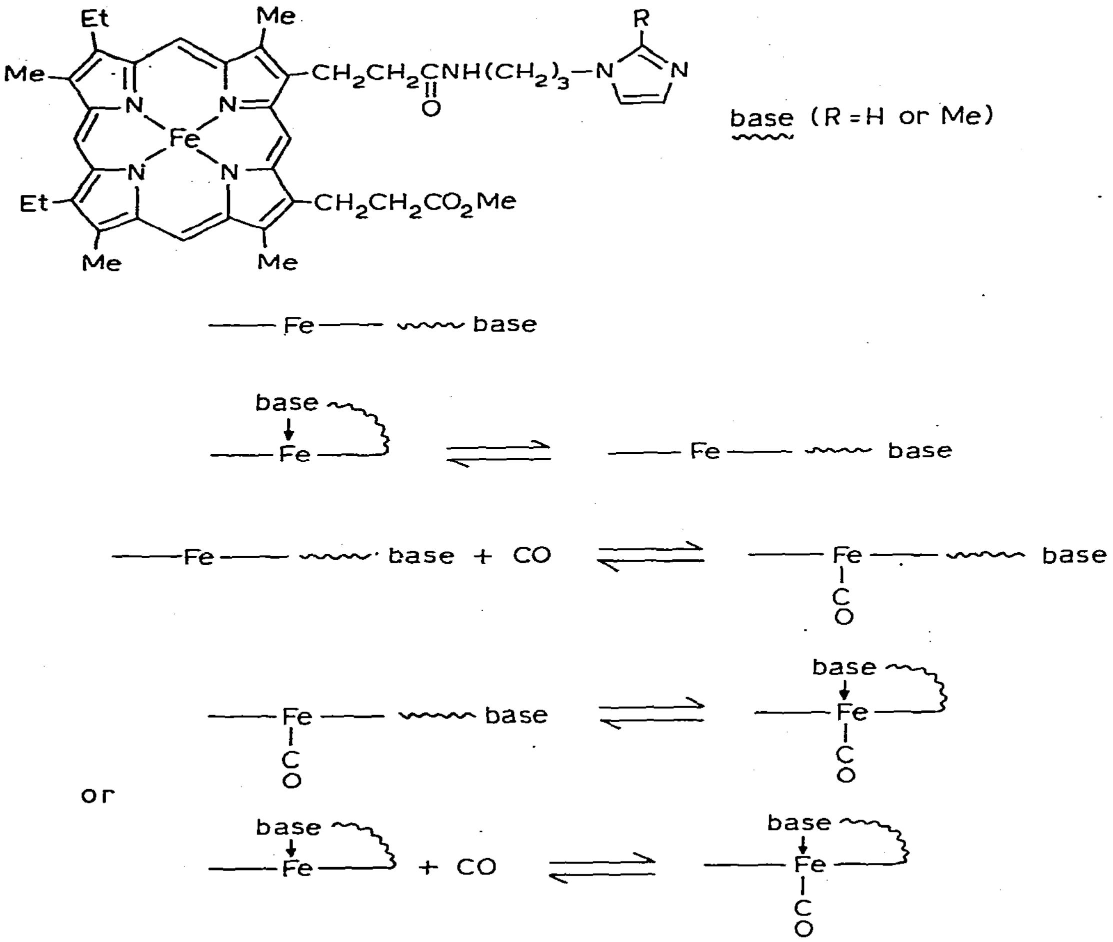
been investigated (22) spectroscopically. Treatment of ferrous acetate with tetraphenylporphyrine ($TPPH_2$) under CO in the presence of pyridine afforded (23) Fe(CO)(TPP)(Pyr). This complex too has a linear Fe-C-O bond system, in apparent contrast to those in related carbonylated hemoproteins derived from biological sources (24). The iron atom is only slightly displaced from the porphyrin N_4 plane. Ab initio calculations have been made (25) of the mode of CO bonding to iron-porphyrin complexes, and it has been concluded that the Fe-C-O bond system should be linear. A series of related complexes derived from meso-tetra(p-anisidyl)-porphyrin (LH_2), viz. Fe(CO)L(L'), where L' = morpholine, pyrrolidine, piperidine, pyridine or imidazole, were obtained (26) by treatment of $FeL(L')_2$ with CO. The i.r. and Mössbauer spectra of these species were examined.

The porphyrin model complexes [11] (R^1, R^2 = $O(CH_2)_4C{\equiv}CC{\equiv}C(CH_2)_4O$ or $O(CH_2)_{12}O$) bind CO (27), giving visible spectra very similar to those observed previously (28). The mode of action of CO with heme protein models has been discussed, and dual pathways, as shown in Scheme 2, advanced (29). The alternative (ii) has been described previously (30).

Resonance Raman spectral studies have been made (31) of a series of carbonyl, nitrosyl, and isocyanide adducts of myoglobin, hemoglobin and some cytochromes. The bonding interactions were discussed and it was shown that Hb(CNEt) (Hb = hemoglobin) dissociated into deoxyhemoglobin and free isonitrile on laser illumination. The temperature and pH dependence of the tetramer-dimer equilibrium of Hb(CO)-A_o has been examined (32), and the origin of the anomalous Soret spectra of carboxycytochrome P-450 discussed (33).

The tetra-arylporphyrin complexes Ru(TAP)XY, [12] (R = p-CF_3, p-Pr^i or p-Me; X = CO, Y = CO or THF or 4-$Bu^tC_5H_4N$; R = p-CF_3, X = Y = $P(OMe)_3$ or Bu^tNC) and their octaethylporphyrin analogue Ru(OEP)(CO)(THF) have been prepared (34), and their ^1H and ^{13}C n.m.r. spectra measured. Meso-porphyrin-IX has been converted into its di-octadecylester (meso-IX-doe), and from this the ruthenium carbonyl complex

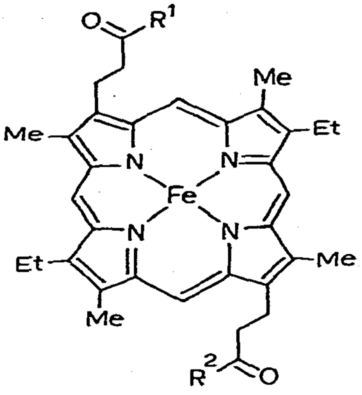
Scheme 2.



Ru(CO)(meso-IX-doe)(pyr) has been prepared (35). This species was used to form stable films in organised monolayer assemblies, whose chemistry is quite different (as summarised in Scheme 3) to that of the complex in solution.

The osmium octaethylporphyrin complexes Os(OEP)XY(X = CO, Y = pyr; X = Y = $P(OMe)_3$) have been synthesised (36). Treatment of the monocarbonyl with $P(OMe)_3$ or pyridine afforded $Os(OEP)Y_2$ (Y = $P(OMe)_3$ or pyr) whereas, with H_2O_2, $Os(OEP)(O_2)$ was formed. Reduction of Os(OEP)(CO)(pyr) using sodium anthracenide, followed by treatment of the product with MeI, afforded (37) [13], whose structure was confirmed crystallographically. The Os atom lies 0.18Å above the porphyrin N_4 plane towards the carbonyl group, and the porphyrin ligand itself has a roof-like geometry, being folded along the methylene-Os-methylene axis by 38.1°. From i.r. spectral data, it is clear that there is an increase in π-bonding between Os and CO, and diminished interaction between the metal and the porphodimethene ring.

Treatment of $Fe(CO)_5$ with $PBu^t_n(EMe_3)_{3-n}$ (E = Si, Ge or Sn; n = $0 \rightarrow 3$) afforded $Fe(CO)_4L$ (38). From extensive spectral studies it was concluded that the phosphine



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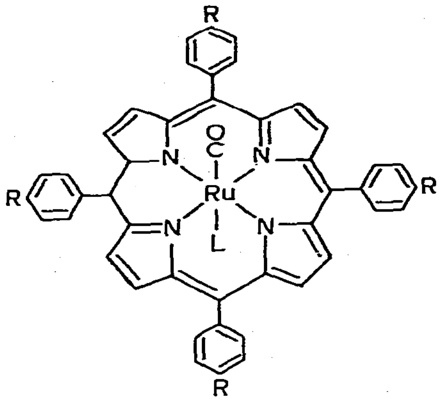

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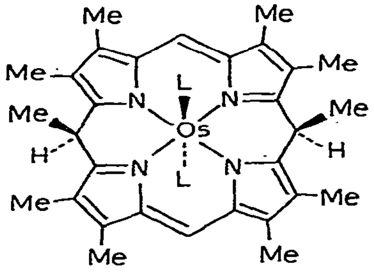

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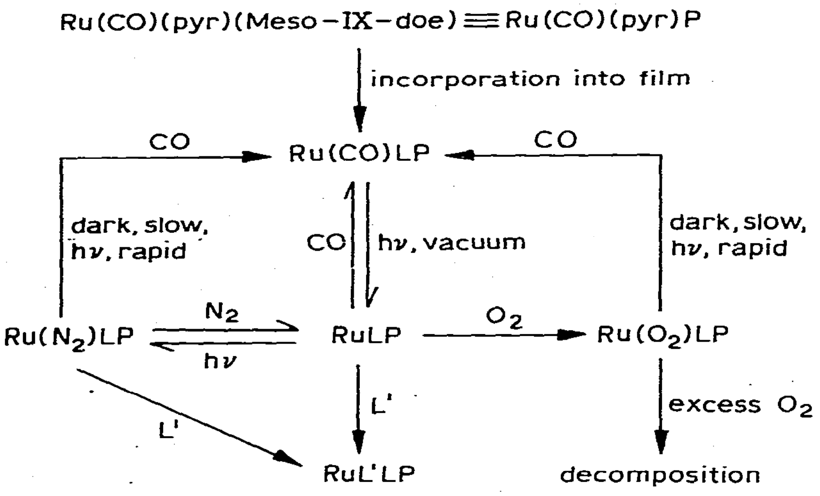
Scheme 3



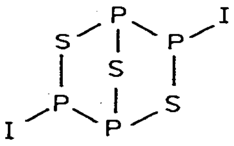
ligands have nearly equal coordinating properties irrespective of the nature of E and n. From X-ray crystallographic studies, it was shown (39) that $Fe(CO)_4PBu^t_3$ has a trigonal bipyramidal structure with axial phosphine (Fe-P 2.36 Å). Reaction of $Fe(CO)_5$ with $P_3S_3I_2$ (L) [14] afforded (40) both $Fe(CO)_4L$ and $Fe(CO)_3L_2$.

Voltammetric oxidation of $Fe(CO)_3L_2$ (L = PPh_3, $PMePh_2$, $P(OPh)_3$ or $P(NMe_2)_3$; L_2 = $Ph_2PCH_2CH_2PPh_2$) afforded (41), reversibly, the monocations $[Fe(CO)_3L_2]^+$. The redox potential is dependent on L and there is a linear correlation between the potential and ν(CO). Reaction of the complexes with $AgPF_6$ also gave $[Fe(CO)_3L_2]^+$, and i.r. and e.s.r. spectral data are consistent with retention of symmetry of $Fe(CO)_3L_2$ (D_{3h}) upon oxidation. On prolonged contact between $Fe(CO)_3L_2$ and $AgPF_6$ in dichloromethane $Fe(CO)_3LCl_2$ was probably formed, and this suggested that oxidative addition of iodine to $Fe(CO)_3L_2$, which gives $Fe(CO)_3LI_2$ (42), may proceed via $[Fe(CO)_3L_2]^+$. However, treatment of $[Fe(CO)_3(PPh_3)_2]^+$ with Cl^- or Br^- (1:1 ration) in dichloromethane showed that $Fe(CO)_3(PPh_3)_2$ is generated in both cases, but with I^-, a 1:1 mixture of $Fe(CO)_3(PPh_3)_2$ and $Fe(CO)_3(PPh_3)I_2$ was produced. This suggests that the carbonyl cation radical oxidised I^- to I_2 which then oxidatively added to $Fe(CO)_3(PPh_3)_2$ via a pathway not involving reversible electron transfer.

M(II) phosphine complexes containing hydrido, halo and other ligands

Reaction of hydridochloro complexes of Ru(II) with $NaBH_4$ and with $NaBH_3(CN)$ afforded (43) $RuH(BH_4)(PPh_3)_3$, [15], $Ru(CO)(PPh_3)_3H(BH_4)$, a mixture of[16] and [17], $Ru(CO)_2[P(C_6H_{11})_3]_2H(BH_4)$, a mixture of two isomers [18] and either [19] or [20], and $Ru(CO)_2(DBP)H[BH_3(CN)]$, where DBP = 5-phenyl-5H-dibenzophosphole. The complex $Rh(PPh_3)_3HCl$ can be generated photochemically (44) from $Ru(CO)(PPh_3)_3HCl$ by irradiaton at 366 nm. It proved impossible to induce photochemical decarbonylation of $Rh(CO)_2(PPh_3)_2HCl$, but this species underwent reversible isomerism as reported earlier (45).

Treatment of $Ru(PPh_3)_4H_2$ and $Ru(CO)(PPh_3)_3H_2$ with di-carboxylic and α-hydroxy-carboxylic acids afforded (46) the species $[RuL(PPh_3)_2H]_2[O_2C(CH_2)_nCO_2]$ (n = 2 4, L = CO or PPh_3), $Ru(PPh_3)_3(O_2CCH_2CO_2H)H$, $Ru(PPh_3)_3H[O_2CH(OH)R]$ (R = H or Ph) and $Ru(CO)(PPh_3)_2H(O_2CCH_2OH)$. In benzene solution, these complexes were efficient catalysts for the hydrogenation of alkenes and also for the isomerisation of alkenes



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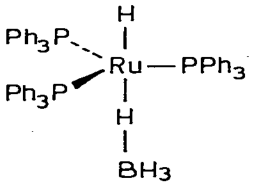

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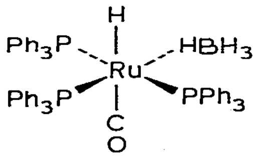

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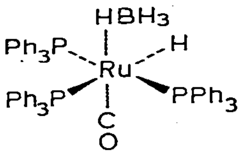

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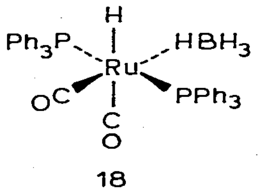

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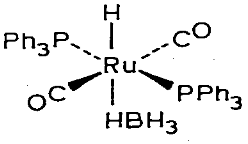

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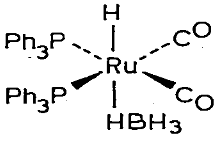

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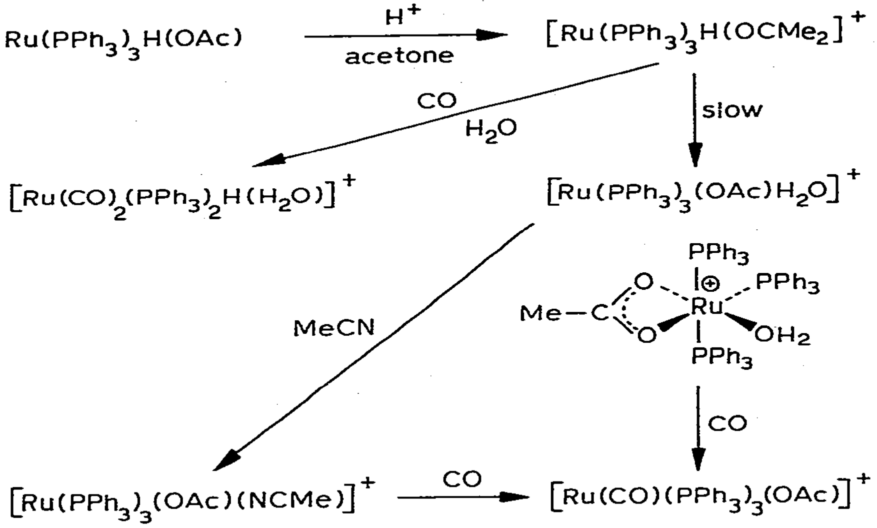
under inert atmospheres. A complex containing (-)-R-phenylglycollic acid was tested as a catalyst for asymmetric induction reactions. However, only products of low optical purity could be isolated from hydrogenation or isomerisation processes.

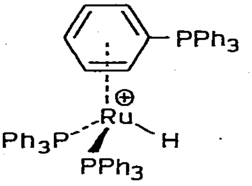
It is known (47) that the species $Ru(PPh_3)_4H_2$, $Ru(PPh_3)_3H(OAc)$ and $Ru(PPh_3)_2(OAc)_2$ react with HBF_4 and other strong non-coordinating acids in methanol giving labile red solutions which, under H_2, become yellow-orange and catalyse the homogeneous hydrogenation of alkenes. Further studies of these species have been made (48) some of which are summarised in Scheme 4. It was noted that in acetone, the ruthenium species were not active as hydrogenation catalysts and that, in contrast to the situation in methanol, the arene species [21] is not formed.

The structure of $Ru(CO)(PPh_3)_2H(RN_3R)$ (R = p-MeC_6H_4) (49) [22] has been determined crystallographically (50).

Scheme 4



The addition complexes $Fe(CO)_2(PMe_3)_2(BrAlBr_3)Br$ and $Fe(CO)_2(PMe_3)_2(BrAlBr_3)_2$ were formed (51) by treatment of the corresponding carbonyl dibromide with $AlBr_3$. Similar 1:1 and 1:2 adducts were formed between $Ru(CO)_2(PMe_3)_2Cl_2$ and $FeCl_3$ while $Fe(CO)_2(PMe_3)_2I_2$ and $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ reacted with iodine giving $Fe(CO)_2(PMe_3)_2(I_3)_2$ and $Fe(\eta^5\text{-}C_5H_5)(CO)_2(I_3)$, respectively. Treatment of $Fe(CO)_3(PMe_3)_2$ with $AlMe_3$



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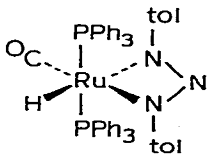


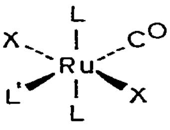
22 (tol = p-MeC_6H_4

afforded $\mathrm{Fe(CO)_2(PMe_3)_2(COAlMe_3)}$, while $\mathrm{Fe(\eta^5\text{-}C_5H_5)(CO)_2X}$ reacted with acceptors Q (X = Cl, Q = $\mathrm{SbCl_3}$, $\mathrm{AlCl_3}$, $\mathrm{FeCl_3}$, $\mathrm{GaCl_3}$, $\mathrm{MoCl_5}$, $\mathrm{NbCl_5}$, $\mathrm{SnCl_4}$, $\mathrm{InCl_3}$, $\mathrm{TiCl_4}$ and $\mathrm{Cl_2}$; X = Br, Q = $\mathrm{AlBr_3}$, $\mathrm{FeBr_3}$ and $\mathrm{Br_2}$; X = I, Q = $\mathrm{AlI_3}$ and $\mathrm{GaI_3}$) giving $\mathrm{Fe(\eta^5\text{-}C_5H_5)(CO)_2\text{-}(XQ)}$.

In acetonitrile or methanol, trans-$\mathrm{Fe(L\text{-}L)_2Cl_2}$ (L-L = $\mathrm{Et_2PCH_2CH_2PEt_2}$ or $\mathrm{Me_2PCH_2\text{-}CH_2PMe_2}$) dissolved (52) giving $\mathrm{[Fe(L\text{-}L)_2ClL']Cl}$ (L' = MeCN or MeOH). Treatment of these salts with CO, $\mathrm{CNBu^t}$, RCN or $\mathrm{P(OMe)_3}$ (L"), afforded $\mathrm{[Fe(L\text{-}L)_2ClL'']^+}$, while with $\mathrm{NO^+}$ and $\mathrm{N_2}$, the complexes $\mathrm{[Fe(NO)(L\text{-}L)Cl]^{2+}}$ and $[\ \mathrm{Fe(L\text{-}L)_2Cl}\ {}_2\mathrm{N_2}]^{2+}$ were formed. A suspension of trans-$\mathrm{[Fe(Et_2PCH_2CH_2PEt_2)_2I_2]}$ in methanol reacted with CO giving a mixture of cis- and trans-$\mathrm{[Fe(CO)(L\text{-}L)_2I]^+}$, but trans-$\mathrm{[Fe(L\text{-}L)_2X_2]}$ (X = NCO or NCS) did not react with CO. The complex $\mathrm{[Ru(CO)L_2Cl][PF_6]}$, where L = 1-(2'-pyridyl)-2-(diphenylphosphino)ethane, has been described (53).

The species cis-$\mathrm{Ru(CO)_2L_2X_2}$ (L = tertiary phosphine or arsine, X = halide) are converted into the corresponding trans-isomers by u.v. irradiation, a process which is reversed on heating. Studies of the thermal rearrangements of the all-trans-$\mathrm{Ru(CO)_2(PMe_2Ph)_2X_2}$ and all-trans-$\mathrm{Ru(CO)_2(PMePh_2)_2X_2}$ showed (54) that they occur by two competing routes: one direct and one by way of a third isomer, the all-cis-species. Evidence was obtained from these studies, and from the stereochemistry of carbonyl substitution reactions of the various isomers of $\mathrm{Ru(CO)_2(PMe_2Ph)_2Cl_2}$, that the mechanism for photochemical and thermal isomerisations must involve prior dissociation of CO. During the isomerisation, partial loss of CO led to the formation of $\mathrm{[Ru(CO)(PMe_2Ph)_2Cl_2]_2}$ as a by-product: these results are summarised in Scheme 5. In related studies (55), four isomers of $\mathrm{Ru(CO)(PMe_2Ph)_2L'Cl_2}$ (L' = $\mathrm{P(OMe)_3}$ or $\mathrm{PPh(OMe)_2}$), [23] - [26], could be identified. Their interconversions are summarised in Scheme 6.

Reaction of $\mathrm{Ru(PPh_3)_3Cl_2}$ with $\mathrm{Ru(CO)(PPh_3)_2(DMF)Cl_2}$ in acetone afforded (56) the binuclear species $\mathrm{(Ph_3P)_2ClRu(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2.2Me_2CO}$, in good yield, a reaction which supports earlier views (57) about the formation of $\mathrm{(Ph_3P_2ClRu(\mu\text{-}Cl)_3Ru(CS)\text{-}(PPh_3)_2}$. This general reaction has been extended to include the formation of $\mathrm{(Ph_3P)_2BrRu(\mu\text{-}BrCl_2)Ru(CO)(PPh_3)_2.Me_2CO}$ and $\mathrm{(Ph_3P)_2ClRu(\mu\text{-}Br_2Cl)Ru(CO)(PPh_3)_2.\text{-}Me_2CO}$. Recrystallisation of $\mathrm{Ru(CO)(PPh_3)_2(DMF)Cl_2}$ from methanol/dichloromethane mixtures afforded $\mathrm{Ru(CO)(PPh_3)_2(MeOH)Cl_2}$, [27] (X = O), which, on refluxing gave $\mathrm{(Ph_3P(CO)ClRu(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2}$, a mixture of isomers (280). Treatment of $\mathrm{[Ru(C_7H_8)(CO)Cl_3]^-}$ with $\mathrm{PPh_3}$ also gave [27] and [28], together with $\mathrm{Ru(CO)(PPh_3)_2Cl_2]}$ Reaction of [28] with $\mathrm{NaBPh_4}$ and $\mathrm{PPh_3}$ afforded $\mathrm{[(Ph_3P)_2(CO)Ru(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2]\text{-}[BPh_4]}$, [29] (X = O), whereas [27](X = O) reacted with $\mathrm{[Ph_4As][HCl_2]}$ in acetone giving $\mathrm{[Ph_4As][Ru(CO)(PPh_3)_2Cl_3].Me_2CO}$. Related thiocarbonyl complexes were describ-



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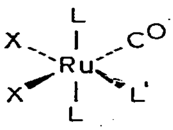

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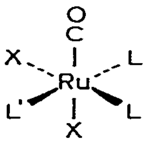

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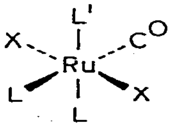

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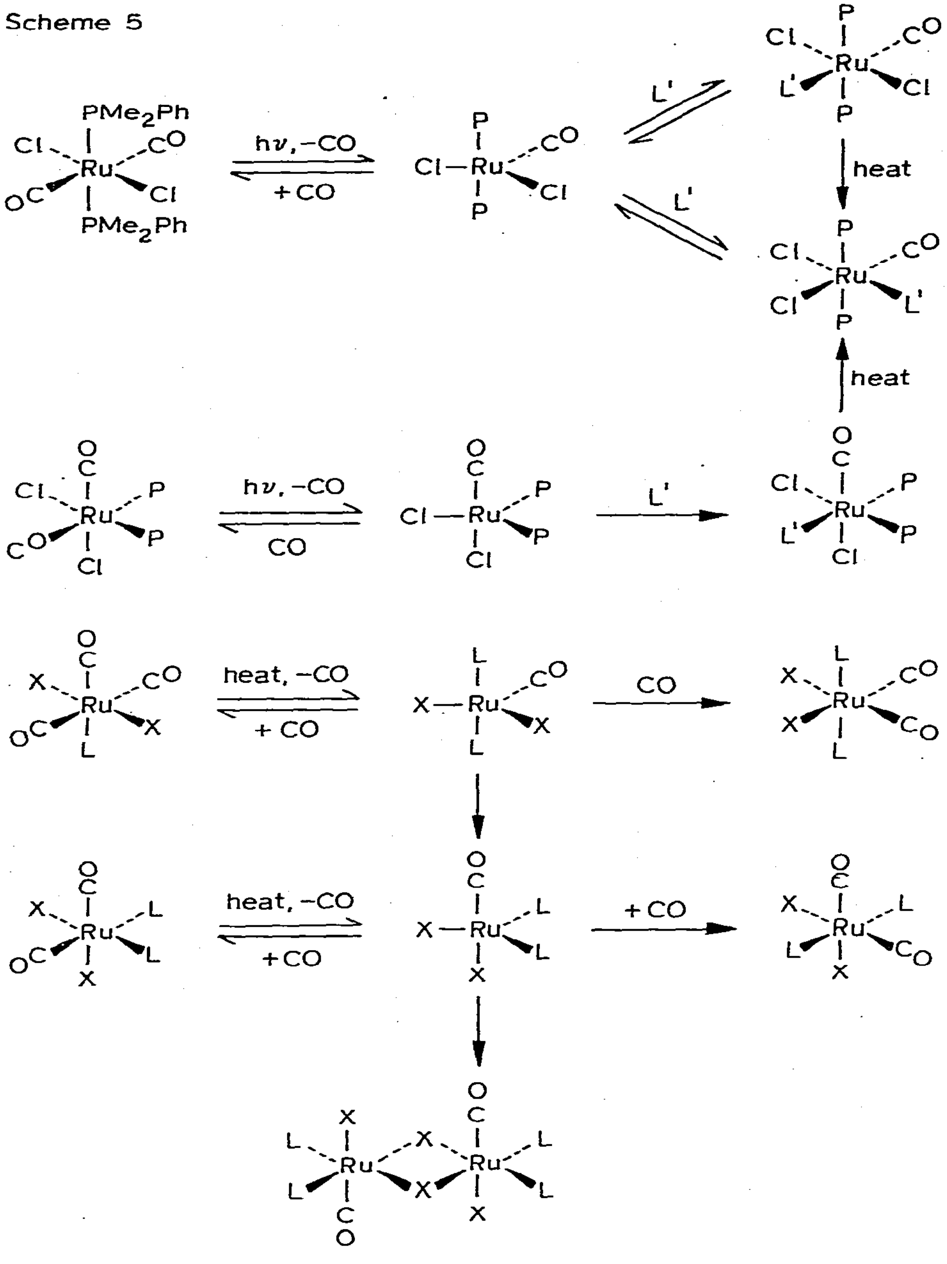
Scheme 5

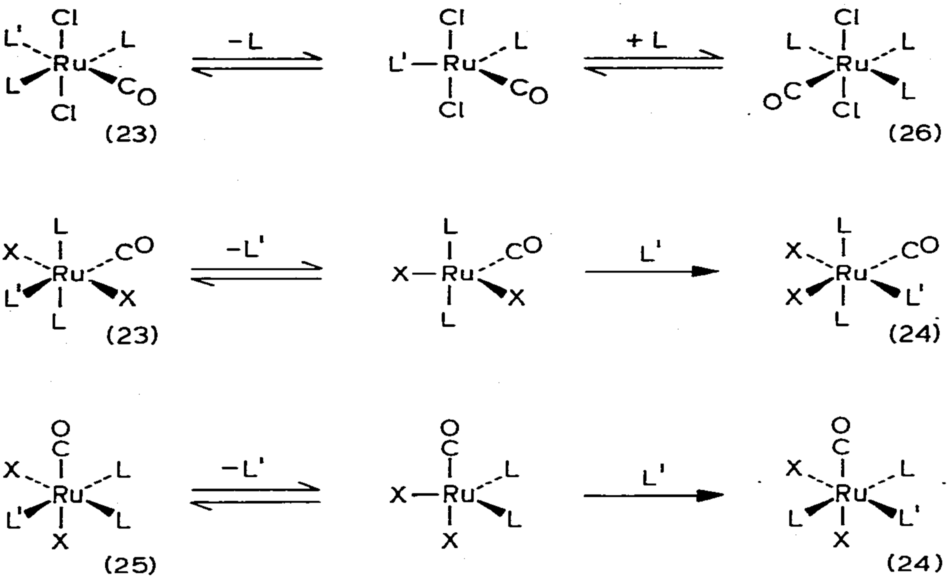


ed and an overall summary of some of these rearrangements is given in Scheme 7.

The complexes $[Os_2(CO)(PPh_3)_5Cl_3]Cl_3$, which contains bridging Cl and is thought to be polymeric, $Os(CO)_3(PPh_3)HCl$, $Os(CO)(PPh_3)_3HCl$, $Os(CO)(L)_2Cl_3$ ($L = Ph_2ECH_2EPh_2$, E = P or As; $Ph_2PCH_2CH_2PPh_2$) and $[Os(CO)_2(AsPh_2)_2Cl_2]Cl_2$, have been prepared (58).

Treatment of $Ru(CO)_3(PPh_3)_2$ with nitric acid afforded (59) $Ru(CO)_2(PPh_3)_2(NO_3)_2$ whereas $M(CO)(PPh_3)_3H_2$ (M = Ru or Os) gave $M(CO)(PPh_3)_2(NO_3)_2$. Carbonylation of the last in boiling ethanol afforded $M(CO)_2(PPh_3)_2(NO_3)_2$ and then $M(CO)(PPh_3)_2H(NO_3)$.

Scheme 6



(23) (26)

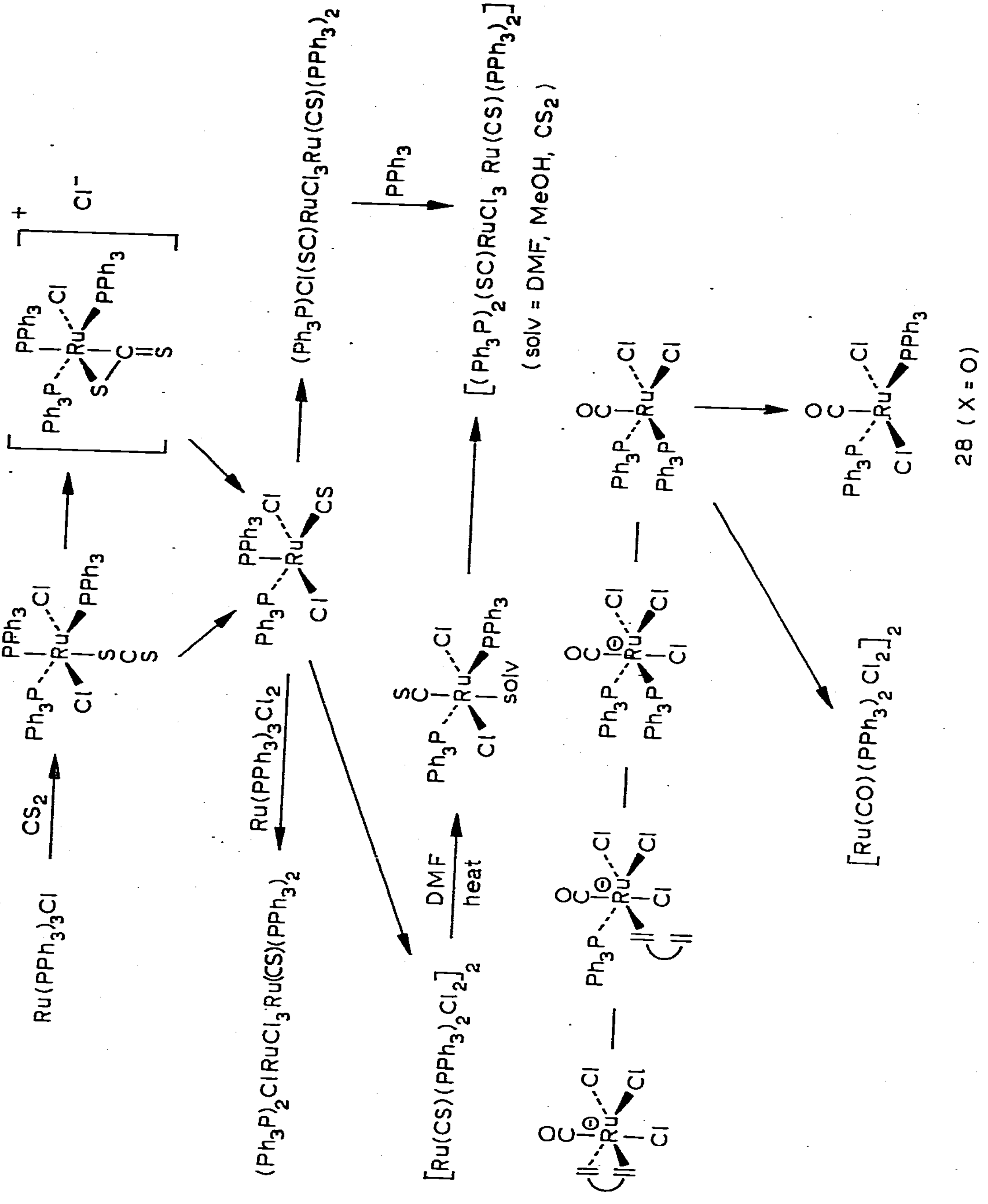
(23) (24)

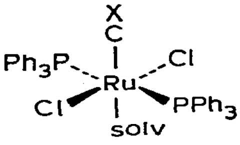
(25) (24)

This latter reaction would seem to involve an alcoholysis followed by β-elimination, and may be the basis of an alcohol dehydrogenation process. Reaction of Os(CO)(PPh$_3$)$_2$H(NO$_3$) with CO gave Os(CO)$_2$(PPh$_3$)$_2$H(NO$_3$). Thiocyanogen reacted (60) with Ru(CO)$_3$(PPh$_3$)$_2$ giving Ru(CO)$_2$(PPh$_3$)$_2$(SCN)$_2$, [30] (X = S), whereas iodine afforded a mixture of [Ru(CO)$_3$(PPh$_3$)$_2$I]I and the corresponding tri-iodide salt. Treatment of [Ru(CO)$_3$(PPh$_3$)$_2$I]I with thiocyanogen merely afforded [Ru(CO)$_3$(PPh$_3$)$_2$I][I(SCN)$_2$]. In an apparently contradictory communication (61), Ru(CO)$_3$(PPh$_3$)$_2$ is said to react with thio- or seleno-cyanogen giving the species [31] (X = S or Se). However, Ru$_3$(CO)$_{12}$ reacted only with thiocyanogen giving the polymeric [Ru(CO)$_2$(CNS)$_2$]$_n$, [32], which breaks up in pyridine giving Ru(CO)$_2$(pyr)$_2$(NCS)$_2$.

Reaction of M(CO)(PPh$_3$)$_3$HX (M = Ru or Os; X = Cl or Br) with RNCS (R = alkyl or aryl) in boiling benzene or toluene afforded (62) a mixture of [33] and [34], and the former can be converted into the latter on heating. Ru(PPh$_3$)$_4$H$_2$ reacts with TNCE giving [35]. Treatment of Ru(CO)$_3$(PPh$_3$)$_2$ with R$_2$P(=S)SH (R = Ph or OPh) afforded (63) the species Ru(CO)$_2$(PPh$_3$)$_2$[SP(=S)R$_2$]$_2$, [36]. However, in refluxing ethanol, Os(PMe$_2$Ph)$_3$Cl$_3$ was converted (64) by [S$_2$PR$_2$]$^-$ (R = Me or Ph) into all-cis-Os(PMe$_2$Ph)$_2$(S$_2$PR$_2$)$_2$. Carbonylation of the species with R = Me in refluxing ethanol in the presence of S$_8$ gave cis-Os(CO)(PMe$_2$Ph)(S$_2$PMe$_2$)$_2$, [37], PMe$_2$PhS and possibly Os(CO)$_2$(PMe$_2$Ph)(S$_2$PMe$_2$)$_2$, [38]. In the presence of CO and PMe$_2$Ph, Os(PMe$_2$Ph)$_2$-(S$_2$PMe$_2$)$_2$ afforded Os(CO)(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)$_2$, [39], while, in the absence of phosphine Os(CO)(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)$_2$, [40], was formed. The interrelationship of these compounds is outlined in Scheme 8.

Scheme 7


Ru(PPh$_3$)$_3$Cl
CS$_2$
Cl$^-$
(Ph$_3$P)Cl(SC)RuCl$_3$Ru(CS)(PPh$_3$)$_2$
PPh$_3$
[(Ph$_3$P)$_2$(SC)RuCl$_3$ Ru(CS)(PPh$_3$)$_2$]$^+$
(solv = DMF, MeOH, CS$_2$)
Ru(PPh$_3$)$_3$Cl$_2$
(Ph$_3$P)$_2$ClRuCl$_3$Ru(CS)(PPh$_3$)$_2$
[Ru(CS)(PPh$_3$)$_2$Cl$_2$]$_2$
DMF
heat
solv
[Ru(CO)(PPh$_3$)$_2$Cl$_2$]$_2$
28 (X = O)



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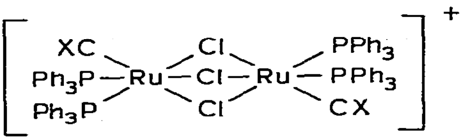

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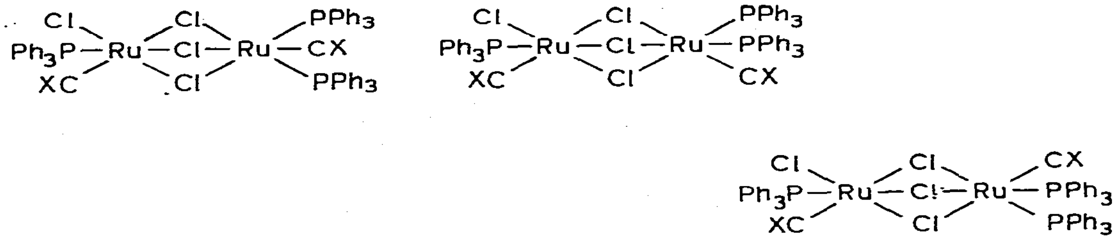

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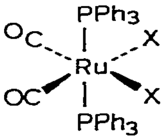

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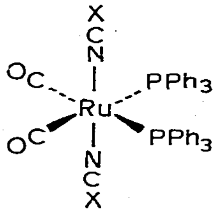

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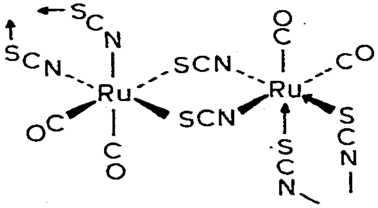

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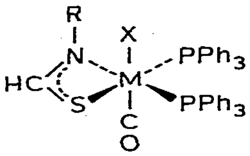

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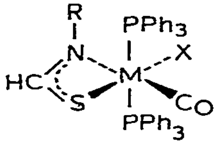

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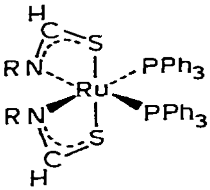

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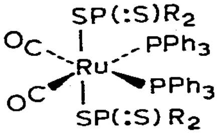
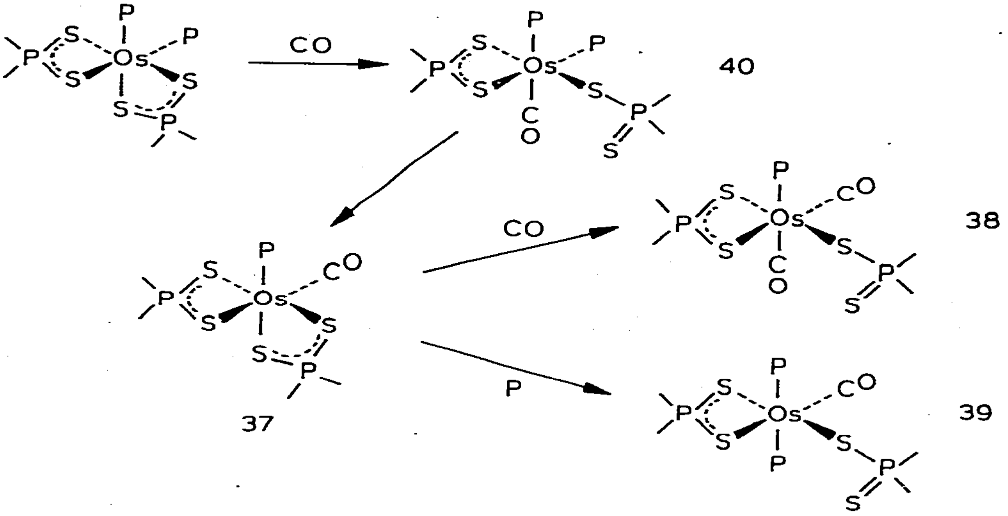


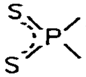
36

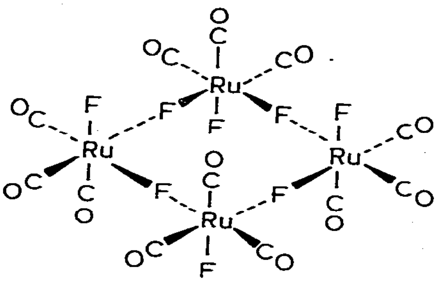
Complexes with sulfur ligands

Reaction of 1,3-dithiane with $Fe_2(CO)_9$ in THF afforded (65) $Fe(CO)_4(S_2C_4H_8)$, in which the dithiane, in the chair conformation, occupies an apical site. Photolysis of $M(S_2CNEt_2)_3$ (M = Fe or Ru) in the presence of CO in acetone, DMF or cyclohexylamine afforded (66) $M(CO)_2(S_2CNEt_2)_2$ and $Ru(CO)(S_2CNEt_2)_2$.

Scheme 8



P = PMe$_2$Ph ;  = S$_2$PR$_2$ (R = Me or Ph)



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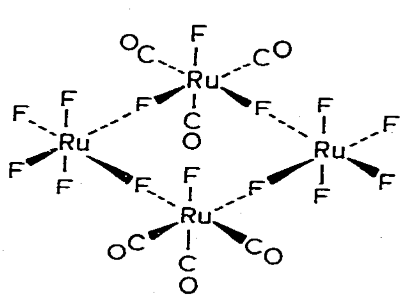

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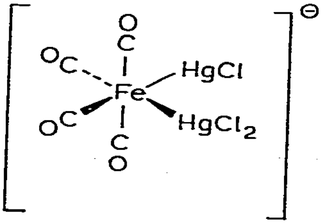

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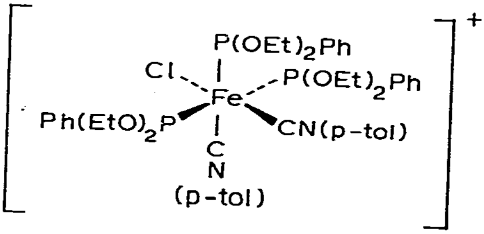

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Carbonyl halide and related complexes

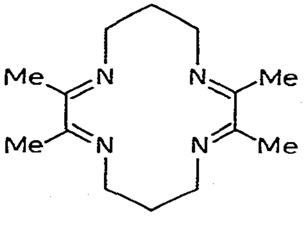
Treatment of $Ru_3(CO)_{12}$ with XeF_2 at room temperature gave (67) $[Ru(CO)_3F_2]_4$, whose structure, [41], has been reported previously (68). With further XeF_2, this tetramer was converted into fac-$Ru(CO)_3F_3$, while $Ru_3(CO)_{12}$ reacted with a large excess of XeF_2 at 100° giving the paramagnetic $[Ru(CO)_3F_2.RuF_5]_2$, [42], ($\mu = 4.45$ B.M. per 2 Ru atoms), which probably contains two Ru(V) atoms. This species may also be obtained from RuF_5 and CO at 200°, and itself reacts further with CO under pressure at 200° to give [41]. Reaction of cis-$[Os(CO)_2X_4]^{2-}$ (X = halide) with CO and 20° gave (69) mer-$[Os(CO)_3X_3]^-$ which isomerised at 171° under CO to give the fac-form. This last was obtained directly from cis-$[Os(CO)_2X_4]^{2-}$ under CO at 171°.

The structure of $[Ph_4As][Fe(CO)_4(HgCl)(HgCl_2)]$, [43], originally prepared (70) from cis-$Fe(CO)_4(HgCl_2)_2$ and $(Ph_4As)Cl$, has been determined crystallographically (71). The Fe-Hg distances are 2.56 and 2.52 Å, and the Hg-Fe-Hg bond angle is 80.3°.

ISOCYANIDE AND CARBENE COMPLEXES

The structure of $[Fe(CNAr)_2\{P(OEt)_2Ph\}_3Cl][ClO_4]$, [44] (Ar = p-$MeC_6H_4$) has been determined (72) cyrstallographically. The Fe-P distances are somewhat longer than usual, while the Fe-C bond lengths indicate some multiple bonding between the metal and the isocyanide ligand. Benzyl isonitrile displaces (73) methyl imidazole (L) from the complexes $FeQL_2{}^z$, where z = 0 and Q = phthalocyaninate, Pc, or $(DMGH)_2$, or z = +2 and Q = TIM, [45], giving either $Fe(CNCH_2Ph)QL^z$, Q = $(DMGH)_2$ or $Fe(CNCH_2Ph)_2Q^z$, Q = Pc, $(DMGH)_2$ or TIM.

Reaction of $[Fe(L-L)_3]^{2+}$ (L-L = bipyridyl or o-phenanthroline) with RNC afforded (74) $[Fe(CNR)_2(L-L)_2]^{2+}$, [46] (R = Me, Pr^i, Bu^t or C_6H_{11}), but attempts to prepare species where R = p-MeC_6H_4 or p-ClC_6H_4 were unsuccessful. In contrast to earlier reports (75), these bis-isonitrile species (R = Me or Pr^i) reacted with $MeNH_2$ (as



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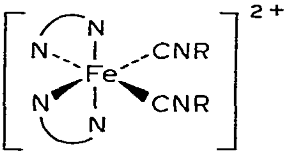

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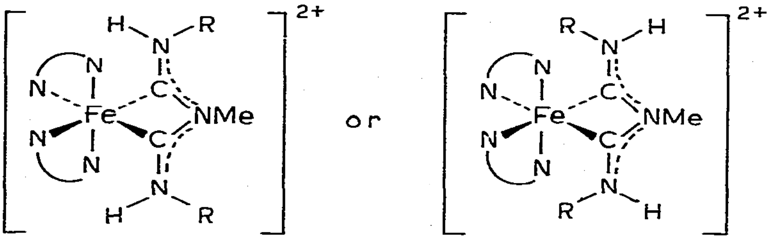

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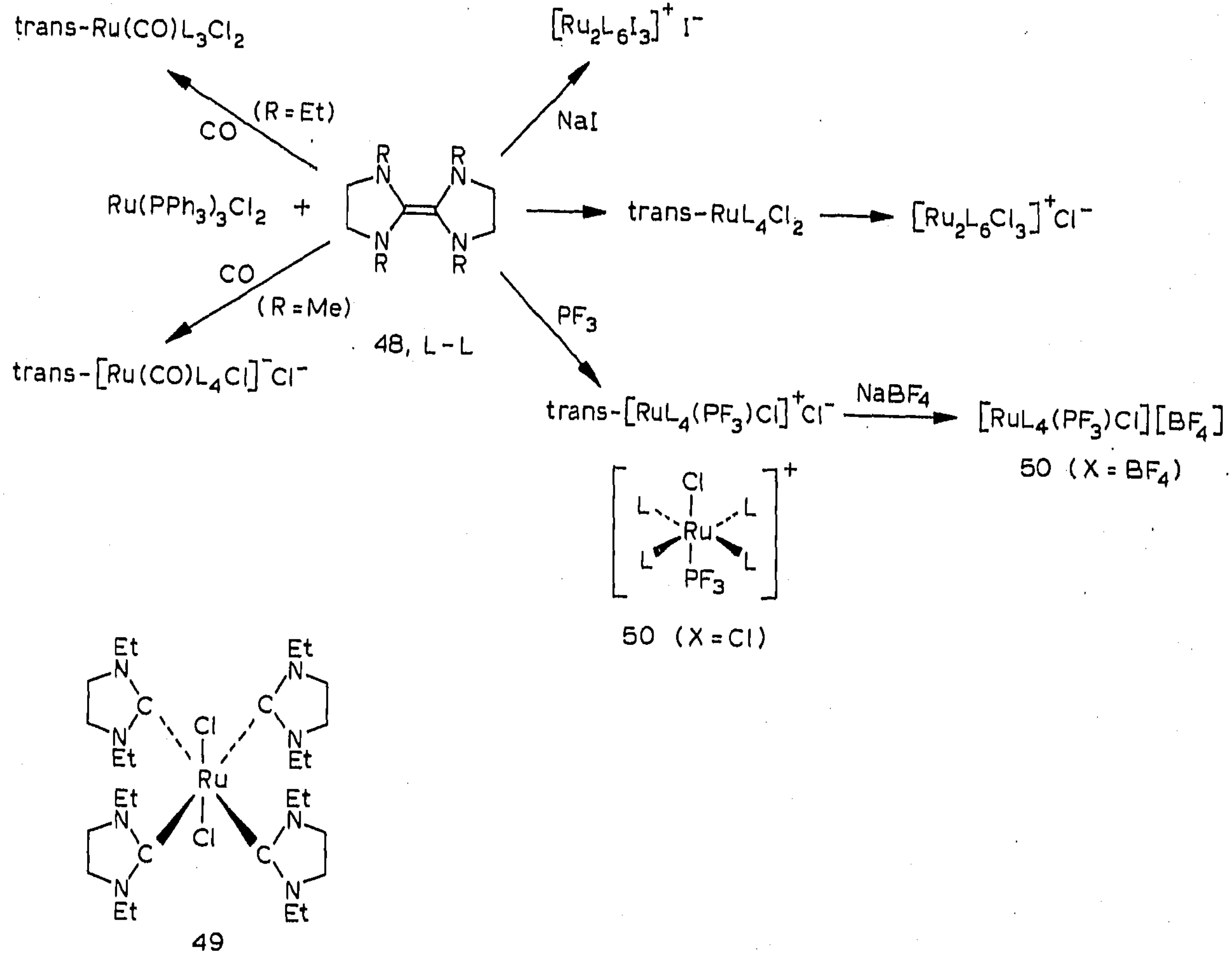
Scheme 9


trans-Ru(CO)L$_3$Cl$_2$
CO
(R = Et)
Ru(PPh$_3$)$_3$Cl$_2$ +
CO
(R = Me)
trans-[Ru(CO)L$_4$Cl]$^-$Cl$^-$
48, L-L
NaI
[Ru$_2$L$_6$I$_3$]$^+$ I$^-$
trans-RuL$_4$Cl$_2$
[Ru$_2$L$_6$Cl$_3$]$^+$Cl$^-$
PF$_3$
trans-[RuL$_4$(PF$_3$)Cl]$^+$Cl$^-$
NaBF$_4$
[RuL$_4$(PF$_3$)Cl][BF$_4$]
50 (X = BF$_4$)
50 (X = Cl)
49

reagent and solvent) giving the chelating bis-carbene species [47]. However, treatment of $[Fe(CNBu^t)_2(dipy)_2]^{2+}$ with methylamine led only to the isolation of $[Fe(bipy)_3]^{2+}$.

The electron-rich olefin [48] reacted (76) with $Ru(PPh_3)_3Cl_2$ according to Scheme 9. From X-ray structural studies of [49], it was established that the four carbene ligands in this complex are arranged in a propeller-like way, and that the Ru-C distances ranged between 1.88 and 2.12 Å. There is a high barrier to rotation about the Ru-C bond, and there is evidence of a direct through-space interaction between one set of NMe protons and an F atom of the PF_3 group in [50] (R = Me, X = Cl or BF_4).

Attack on $[Os(CO)_2(CNR)(PPh_3)_2Cl]^+$, [51] (R = p-$MeC_6H_4$) by methoxide ion afforded (77) $Os(CO)(CNR)(PPh_3)_2Cl(CO_2Me)$, [52], as shown in Scheme 10. However, treatment of [51] with $HOCH_2CH_2Cl$ in the presence of NEt_3 gave the carbene species [53]. With hydrosulfide ion, [51] was converted to [54] which, on protonation or methylation afforded [55]. It is possible that the production of [54] could occur via nucleophilic attack by SH^- on the coordinated isocyanide, giving $L_4Os[C(=S)NHR]$, followed by loss of HCl.

Treatment of $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)$, [56], with $BrCH_2CH_2Br$ afforded (78) $Os(CO)_2(PPh_3)_2Br[C(=S)CH_2CH_2Br]$ and then the carbene species [57]. Similar complexes were obtained using $Os(CO)(CNR)(PPh_3)_2(\eta^2\text{-}CS_2)$ (R = p-MeC_6H_4), its Ru analog, and $Ru(CO)_2(PPh_3)_2(\eta^2\text{-}CSe_2)$. Treatment of [57] and $[Ru(CO)_2(PPh_3)_2Br(\overline{CSeCH_2CH_2Se})]^+$ with Br^- afforded $M(CO)(PPh_3)_2Br_2(\overline{CXCH_2CH_2X})$ (M = Ru, X = Se; M = Os, X = S). With 1,3-dibromopropane, the related carbene species [58] could also be prepared, but attempts to produce carbene species from η^2-RNCS complexes proved unsuccessful.

Reaction of trans-$[Fe(Et_2PCH_2CH_2PEt_2)_2Cl_2]$ with phenylacetylene in methanol in the presence of NaX (X = BPh_4 or PF_6) gave (79) the phenylvinylidene complex [59]. On the basis of Mössbauer spectral data, it was suggested that :C=CHPh is a good σ-donor or a good π-acceptor, comparable with NO^+. There appeared to be no tendency of this species to react with alcohols giving alkoxy-carbene species.

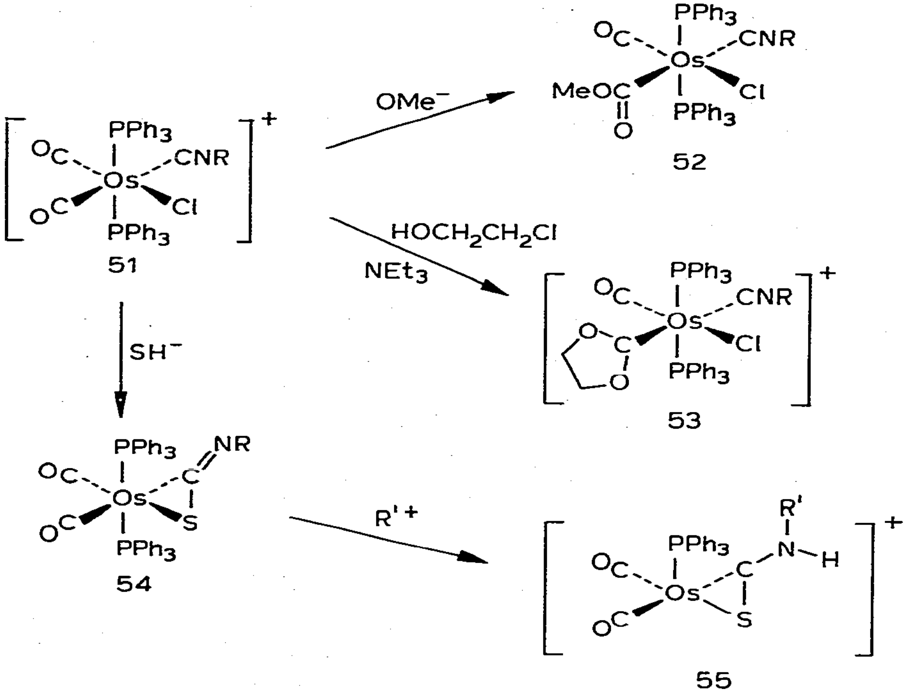
Treatment of $Fe(CO)_5$ with $SnR_3(NR'_2)$ (R = NMe_2, R' = Me; R = R' = Me) gave (80) the monocarbene complex $Fe(CO)_4[C(NMe_2)OSnR'_3]$. However, with two moles of $Fe(CO)_5$, $Sn(NMe_2)_4$ afforded [60], whereas with $SnMe_2(NMe_2)_2$ and $[Sn(NMe_2)_2]_2$, [61] and [62], respectively, were produced.

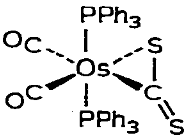
NITROSYL AND ARYLDIAZENATO COMPLEXES

Nitrosyl Complexes

A qualitative study has been made (81) of the reactions of nitric oxide over iron and steel. Nitrogen, N_2O and Fe_3O_4 were produced by vacuum deposition on thin films. There has been some theoretical discussion (82) of the factors which influence the geometry and structure of tetrahedral, planar and related dimeric nitrosyl species such as $M(NO)_2L_2$ (M = Fe, Ru or Os), $[Fe(NO)_2X]_2$ (X = I, $P(CF_3)_2$ or SEt) and $[Ru(NO)(PPh_3)(\mu\text{-}PPh_2)]_2$.

Scheme 10





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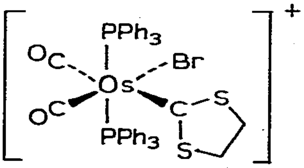

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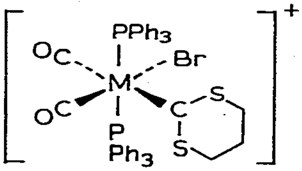

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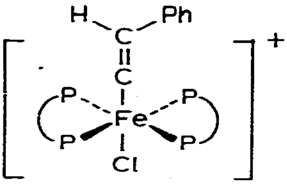

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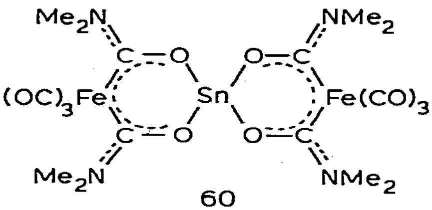

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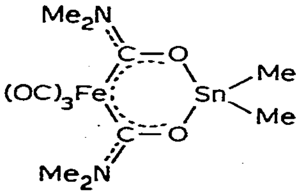

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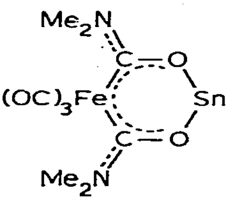
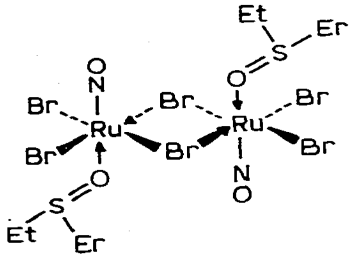


62

Attempted alkylation of $[N(PPh_3)_2][Fe(CO)_3(NO)]$ by RX afforded instead (83) the species $[N(PPh_3)_2][Fe(NO)_2X_2]$ (X = Cl, Br or I). Halogenation of the tricarbonyl(nitrosyl)ferrate gave $[N(PPh_3)_2][Fe(NO)X_3]$ (X = Cl or Br) while treatment with NOCl in dichloromethane led to the formation of $[Fe(NO)_2Cl_2]^-$. Both the nitrosyl halide anions are paramagnetic, $[Fe(NO)_2X_2]^-$ having one unpaired spin, but $[Fe(NO)X_3]^-$ has $\mu = 3.82 - 4.84$ B.M., indicating three unpaired electrons. The species $[Fe(NO)_2X_2]^-$ were also produced (84) by treatment of $Fe(NO)_2(PPh_3)X$ or $[Fe(NO)_2X]_2$ (X = Cl, Br or I) with the carbonylate anions $[V(CO)_6]^-$, $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^-$, $[Mn(CO)_5]^-$, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ or $[Co(CO)_4]^-$. Reaction of $Fe(NO)_2(PF_3)_2$ with $[GeCl_3]^-$ gave (85) $[Fe(NO)_2(PF_3)(GeCl_3)]^-$ while $Fe(PF_3)_5$ reacted with $[SnCl_3]^-$ under u.v. light giving $[Fe(PF_3)_3(SnCl_3)_2]^{2-}$.

The structures of $[Ru(NO)(Et_2SO)Br_3]_2$, [63], obtained (86) from $Ru(NO)L_2Br_3$ (L = dialkyl or aryl-alkyl sulfide or selenide) in diethylsulfoxide, has been determined crystallographically (87). The structure determination of $[Fe(NO)_2\{\mu\text{-}P(CF_3)_2\}]_2$, [64] has also been reported (88), and certain bond lengths and angles in this species have been compared with those in the related complexes $[Fe(NO)_2Q]_2$ (Q = SEt or I), $[Fe(CO)_3Q]_2$ (Q = SEt or $P(CF_3)_2$), and $[Ni(CO)_2(PPh_2)]_2$, Table 1.



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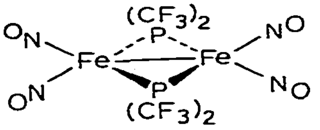


64

TABLE 1

Selected Bond Angles and Lengths in some Bridged Binuclear Nitrosyl and Carbonyl Complexes

Complex	Q	M-Q-M (°)	M-M (Å)
$[Fe(CO)_3Q]_2$	SEt	68	2.54
	$P(CF_3)_2$	80	2.82
$[Fe(NO)_2Q]_2$	SEt	74	2.72
	$P(CF_3)_2$	77	2.75
	I	72,73	3.01, 3.09
$[Ni(CO)_2Q]_2$	PPh_2	70	2.52, 2.51

Treatment of $[Fe(H_2O)_6][BF_4]_2$ with the tripod ligands $E(CH_2CH_2PPh_2)_3$ (E = P or As) in the presence of NO and $NaBPh_4$ gave (89) the diamagnetic species $[Fe(NO)\text{-}\{E(CH_2CH_2PPh_2)_3\}][BPh_4]$. The structure of the compound where E = N was determined crystallographically, and it was found to be similar to that where E = P (90), the complex having a five-coordinate trigonal bipyramidal geometry, with an essentially linear Fe-N-O bond system.

The NO group may be transferred from $Co(NO)(DMGH)_2(MeOH)$, $\underline{A}$, to either ruthenium or iron in a series of reactions described below (91):

(a) $Ru(PPh_3)_3Cl_2 + \underline{A} \longrightarrow Ru(NO)(PPh_3)_2Cl_3 + Ru(NO)(PPh_3)_2(O_2)Cl.$

This reaction differs in stoichiometry from that of $Ru(PPh_3)_3Cl_2$ with NO alone (92):

$$3Ru(PPh_3)_3Cl_2 + 4NO \longrightarrow 2Ru(NO)(PPh_3)_2Cl_3 + Ru(NO)_2(PPh_3)_2 + 3PPh_3.$$

(b) $Ru(PPh_3)_3HCl + \underline{A} \longrightarrow Ru(NO)(PPh_3)_2Cl + PPh_3;\ + \underline{A} \longrightarrow Ru(NO)_2(PPh_3)_2$, or

$Ru(NO)(PPh_3)_3H;\ + \underline{A} \longrightarrow Ru(NO)_2(PPh_3)_2$

The hydrido nitrosyl intermediate appears to react faster with $\underline{A}$ than $Ru(PPh_3)_3HCl$. A side reaction also occurs:

$$Ru(NO)_2(PPh_3)_2 + 3Co(DMGH)_2(PPh_3)Cl,\ \underline{B} \longrightarrow Ru(NO)(PPh_3)_2Cl_3 + Co(NO)(DMGH)_2 + 2Co(DMGH)_2$$

$\underline{B}$ is a by-product of the NO transfer reaction involving A

(c) $Fe(PPh_3)_2Cl_2 + 2\underline{A} + 2PPh_3 \longrightarrow Fe(NO)_2(PPh_3)_2 + 2\underline{B}.$

This reaction may proceed via $Fe(NO)(PPh_3)_2Cl$, and the dinitrosyl product can react further with $\underline{B}$ giving $Co(NO)_2(PPh_3)Cl$.

(d) $[Fe(diphos)_2H(THF)]^+ + \underline{A} \longrightarrow Fe(NO)_2(diphos)$ (diphos = $Ph_2PCH_2CH_2PPh_2$).

(e) $Fe(diphos)_2HCl + PF_6^- + \underline{A} \longrightarrow [Fe(NO)(Diphos)_2][PF_6] + Fe(NO)_2(diphos).$

This reaction may proceed via $Fe(NO)(Diphos)_2H$.

(f) $Fe(diphos)_2Cl_2 + \underline{A} \longrightarrow Fe(NO)_2(diphos) + [Fe(NO)(diphos)_2]^+.$

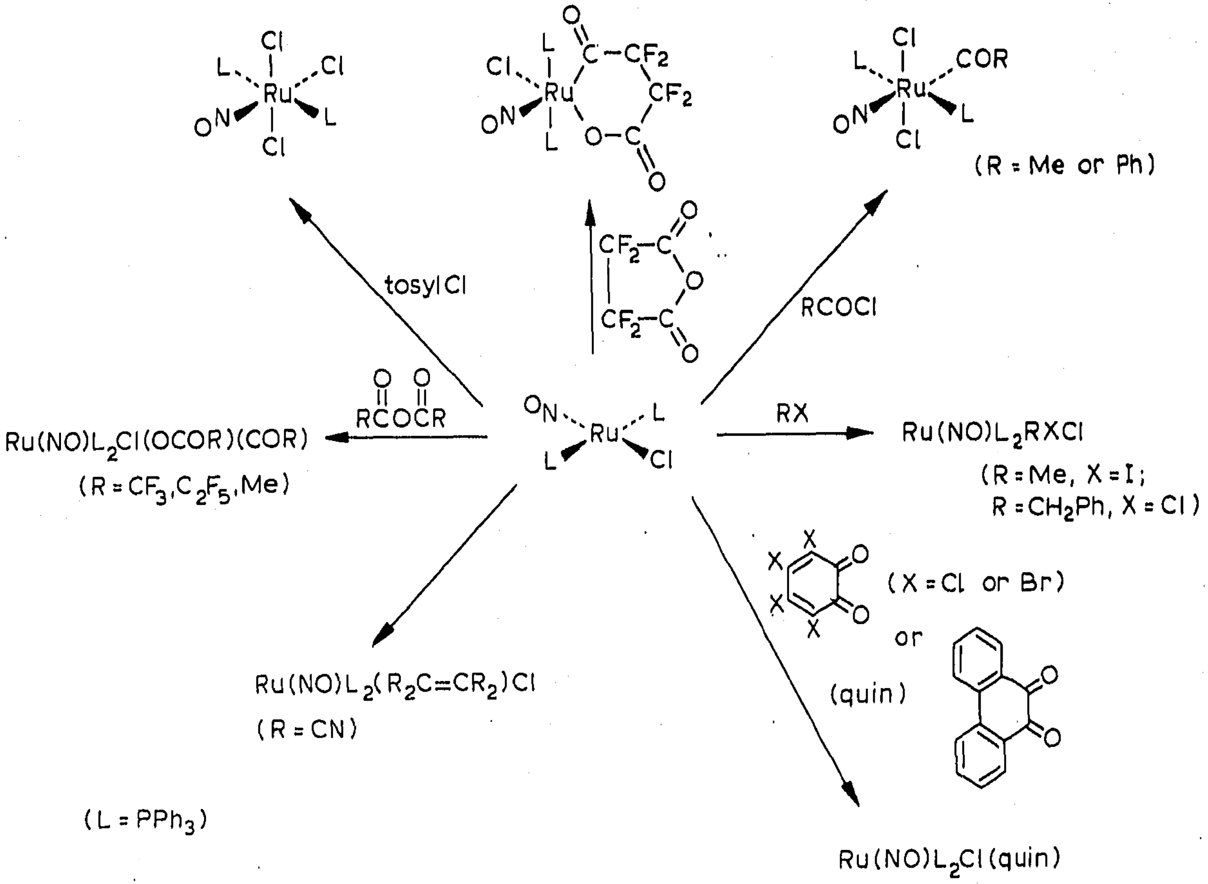
$[Fe(NO)(diphos)_2]Cl + \underline{A} \longrightarrow Fe(NO)_2(diphos)$

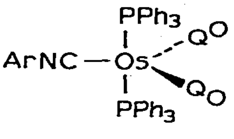
$[Fe(NO)(diphos)_2][PF_6] + \underline{A} \longrightarrow [Co(DMGH)_2(diphos)][PF_6].$

In considering a mechanism for these nitrosyl transfer reactions, it seemed unreasonable to invoke action of free (solvated) NO or NO^-. Instead, binuclear intermediates, attached by NO and/or halide bridges, appeared feasible, a situation which would facilitate both electron and halide transfer. These reactions occurred more readily if the nitrosyl acceptor was coordinatively unsaturated.

The oxidative addition reactions of the coordinatively unsaturated complex $Ru(NO)(PPh_3)_2Cl$ have been investigated (93). These are summarised in Scheme 11. This complex is much more reactive than $M(CO)(PPh_3)_2Cl$ (M = Rh or Ir) with which it is isoelectronic. The structure of $[Os(CO)(CNAr)(NO)(PPh_3)_2][ClO_4]$, [65] (Ar = $p\text{-}MeC_6H_4$) (94), has been determined (95). It proved impossible to differentiate between the NO and CO groups but all three equatorial ligands were bound linearly to the metal.

Scheme 11


tosylCl
RCOCl
RX
RCOCR (with =O over each C)
Ru(NO)L₂Cl(OCOR)(COR)
(R = CF₃, C₂F₅, Me)
Ru(NO)L₂RXCl
(R = Me, X = I;
R = CH₂Ph, X = Cl)
(R = Me or Ph)
(X = Cl or Br)
or
(quin)
Ru(NO)L₂(R₂C=CR₂)Cl
(R = CN)
Ru(NO)L₂Cl(quin)
(L = PPh₃)



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Reduction of RuCl$_3$.nH$_2$O by zinc in the presence of ammonia gave [Ru(NH$_3$)$_6$]Cl$_2$ which, on chlorination, was converted (96) into [Ru(NO)(NH$_3$)$_4$Cl]Cl$_2$. The chloride attached directly to the metal could be metathetically exchanged by acetate or cyanate. Treatment of [Ru(NO)(NH$_3$)$_5$]X$_3$ (X = Cl, Br or I) with hydroxylamine gave (97) [Ru(N$_2$O)(NH$_3$)$_5$]X$_2$ which, on oxidation with Ce^{4+}, afforded dinitrogen oxide. Treatment of Os(NO)(NH$_3$)$_2$(OH)X$_2$ (X = Cl or Br) with dilute HX gave (98) [Os(NO)(NH$_3$)$_2$(H$_2$O)X$_2$]X, while Os(NO)(NH$_3$)$_2$X$_3$ (X = Cl, Br or I) was produced by action of concentrated HX. Reaction of Ru(NO)(NH$_3$)$_2$(OH)(NO$_2$)$_2$ with strong HCl gave isomeric mixtures of Ru(NO)(NH$_3$)$_2$Cl$_3$. Conversion of [OsCl$_6$]$^{2-}$ into trans-[Os(NO)(NO$_2$)$_4$(OH)]$^{2-}$ was achieved (99) using NO$_2^-$, and the nitrosyl nitrite is isostructural with, and more stable in solution than, its ruthenium analog. Treatment of [NH$_4$]$_2$[Os(NO)X$_5$] (X = Cl, Br or I) and Na$_2$[Os(NO)(NO$_2$)$_4$(OH)] with aqueous ammonia afforded (99) Os(NO)(NH$_3$)$_2$(OH)X$_2$ (X = Cl or Br), [Os(NO)(NH$_3$)$_2$(OH)$_2$(H$_2$O)]I and Os(NO)(NH$_3$)$_2$(OH)(NO$_2$)$_2$. The quaternary ammonium salts of [Os(NO)X$_5$]$^{2-}$ were produced (99) by reaction of the [NH$_4$]$^+$ salts with the appropriate amines.

Treatment of Fe(TPP)Cl (RPPH$_2$ = tetraphenylporphyrin) with NO in the presence of 1-methyl imidazole (L) gave (100) Fe(NO)(TPP)L. The X-ray structural determination of this complex revealed that the Fe-N-O bond angle was bent (ca. 140°), and that the Fe-N (imidazole) bond distance was quite long (ca. 2.18 Å). The e.s.r. spectrum of the complex was also discussed. The octaethylporphyrin complex Os(CO)(OEP)(pyr) reacted (101) with NO giving either Os(NO)$_2$(OEP) or Os(NO)(OEP)(OMe) (if methanol was present). It was claimed that the dinitrosyl species contained trans-nitrosyl groups, one bent and the other linear. Treatment of Os(NO)(OEP)(OMe) with HF gave Os(NO)(OEP)F.

Intramolecular exchange of O atoms between coordinated NO and NO$_2$ in cis-[Fe(NO)(NO$_2$)(dtc)$_2$] (dtc = S$_2$CNMe$_2$) has been observed (102). The overall reactions are summarised as follows:

$$\begin{tikzcd}
\text{Fe}(^{15}\text{NO})(\text{dtc})_2 + \text{NO}_2 \arrow[r, "-60^{o}"] & \text{trans-Fe}(^{15}\text{NO})(\text{NO}_2)(\text{dtc})_2 \arrow[d, "5^{o}"] \\
\text{cis-Fe}(^{15}\text{NO}_2)(\text{NO})(\text{dtc})_2] & \text{cis-[Fe}(^{15}\text{NO})(\text{NO}_2)(\text{dtc})_2] \arrow[l]
\end{tikzcd}$$

The rate-determining step in this process requires that there is no direct reaction of cis-[Fe(NO)(NO$_2$)(dtc)$_2$] with either free NO or NO$_2$ which is faster than the above equilibration. The reactions listed below were also investigated, but none occurred faster than the O-transfer depicted above:

$$\underline{\text{cis}}\text{-}[Fe(^{15}NO)(NO_2)(dtc)_2] + NO \longrightarrow \underline{\text{cis}}\text{-}[Fe(NO)(NO_2)(dtc)_2] + {}^{15}NO$$

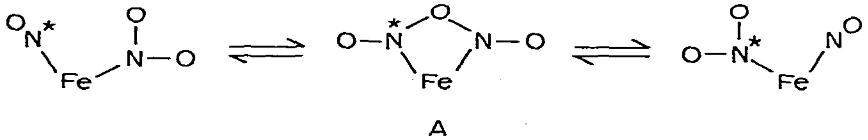
$$\underline{\text{cis}}\text{-}[Fe(NO)(^{15}NO_2)(dtc)_2] + NO \longrightarrow \underline{\text{cis}}\text{-}[Fe(NO)(NO_2)(dtc)_2] + {}^{15}NO$$

$$\underline{\text{cis}}\text{-}[Fe(^{15}NO)(NO_2)(dtc)_2] + NO_2 \longrightarrow \underline{\text{cis}}\text{-}[Fe(NO)(NO_2)(dtc)_2] + {}^{15}NO_2$$

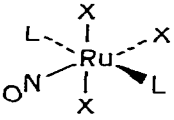
$$\underline{\text{cis}}\text{-}[Fe(NO)(^{15}NO_2)(dtc)_2] + NO_2 \longrightarrow \underline{\text{cis}}\text{-}[Fe(NO)(NO_2)(dtc)_2] + {}^{15}NO_2.$$

These data suggest that O-transfer occurs as shown in Scheme 12. It is possible, however, that the important intermediate A could dissociate, giving N_2O_3 (and hence NO + NO_2) and Fe(dtc)$_2$, with the equilibrium lying well over on the side of A. It was found that trans-Fe(^{15}NO)(NO_2)(dtc)$_2$] reacted with NO giving unlabelled nitrosyl nitrite and ^{15}NO, but there was no observable reaction between trans-[Fe(NO)($^{15}NO_2$)(dtc)$_2$] and NO, which favours the reaction as shown in Scheme 12.

Scheme 12



The Mössbauer spectra of the dithio-oxalato complexes $[R_4N]_2[Fe(NO)(S_2C_2O_2)_2]$ (R = Et or Bu^n) have been recorded (103). Reaction of $[NH_4][Fe_4(NO)_7S_3]$ with $[p\text{-}O_2NC_6H_4N_2][BF_4]$ afforded (104) the paramagnetic $O_2NC_6H_4N_2Fe_4(NO)_4S_3$, and the complexes Ru(NO)L_2X_3, [66] (L = dialkyl or aryl-alkyl sulfides and selenides; X = Cl, Br or I) have been prepared (86).



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Photolysis of aqueous solutions of $[Ru(NO)X_5]^{2-}$ (X = Cl, Br or I), at pH $0\rightarrow14$ with or without O_2, gave (105) $[Ru(H_2O)X_5]^{2-}$ and NO. Treatment of $[Ru(NO)Cl_5]^{2-}$ with barbituric acid (H_2L) afforded (106) $[Ru(NO)(LH)_2Cl_3]^{2-}$ and $[Ru(NO)(LH)_5]^{2-}$, the formation of the latter being assisted by light. No reaction between barbiturate and the coordinated NO group was observed. Nitric oxide reacted with $Ru(AsPh_3)_2(Ph_3AsO)Cl_3$ giving (107) $Ru(NO)(AsPh_3)(Ph_3AsO)Cl_3$, whereas CO afforded $Ru(CO)_2(AsPh_3)(Ph_3AsO)Cl_2$.

The Mössbauer spectra of the series $M[Fe(CO)_2(NO)L]$ (M = $Ph_2P(C_6H_{11})_2$, Na, K, Ph_2Pb, Hg or $Au(PPh_3)$; L = CO, PPh_3, $AsPh_3$, $AsEt_2Ph$ and $AsEt_3$) have been discussed (108) in terms of the dominance of the σ-bonding effects of L in these species.

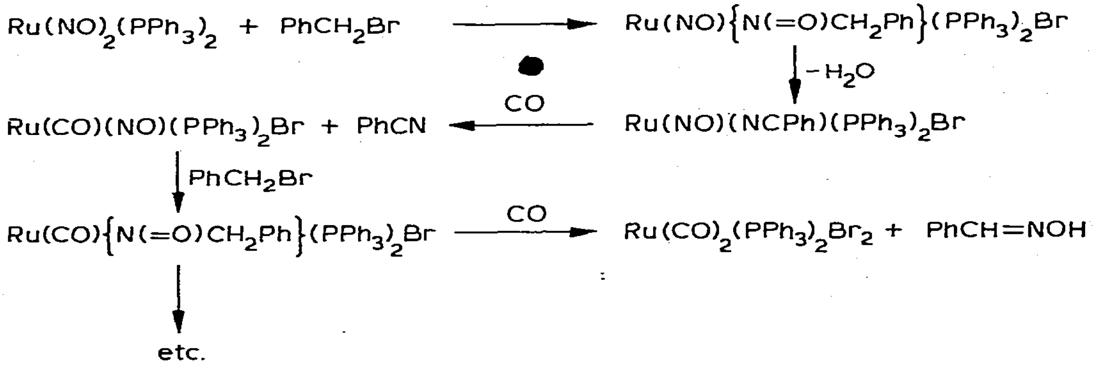
Alkali metal reduction of $[Fe(NO)(CN)_5]^{2-}$ in liquid ammonia has afforded (109) brown $[Fe(NO)(CN)_5]^{3-}$, blue $[Fe(NO)(CN)_4]^{2-}$ (both of which have 1 unpaired electron), brown or dark violet $[Fe(NO)(CN)_4]^{3-}$ (diamagnetic) and dark violet $[Fe(NO)(CN)_3]^{4-}$ (apparently ferromagnetic). The NO stretching frequencies of $[Fe(NO)(CN)_5]^{3-}$ are reported (in the solid state) at 1568 and 1580 cm^{-1}, whereas that in $[Fe(NO)(CN)_3]^{4-}$ is as low as 1300 cm^{-1}. The species $[Fe(CO)_{3-n}(NO)(CN)_n]^{(n+1)-}$ (n = 1 and 2) were also described. E.S.R. spectral examination of the species obtained by γ-irradiation of various salts of $[Fe(NO)(CN)_5]^{2-}$ have been reinterpreted (110) in terms of the presence of $[Fe(NO)(CN)_5]^{3-}$ and $[Fe(NO)(CN)_4]^{2-}$. In the species $[Fe(NO)(CN)_5]^{3-}$ it was suggested that the NO and trans-CN groups were bent off their original axis in the nitroprusside ion. The complex $[Fe(NO)(CN)_4]^{2-}$ was also detected by e.s.r. spectroscopy (111) among the products of thermal reduction of $[Fe(NO)(CN)_5]^{2-}$. Treatment of $Na_4[Fe(NO)(CN)_3]$ in liquid ammonia with PhNC afforded (112) $[Fe(NO)(CNPh)_4]^-$.

Reaction of $[M(CN)_6]^{4-}$ (M = Ru or Os) with nitric acid has given (113) initially $[M(CN)_6]^{3-}$, followed by a species $[M(CN)_5X]^{n-}$ where X is the product of cyanide oxidation. This last species reacted further with HNO_3 giving $[M(NO)(CN)_5]^{2-}$. With more nitric acid under CO_2, the pentacyanonitrosyls were converted into $[M_2(NO)_2(CN)_9]^{3-}$, $[M_2(NO)_2(CN)_8]^{2-}$ and, ultimately, $M(NO)(CN)_3.2H_2O$.

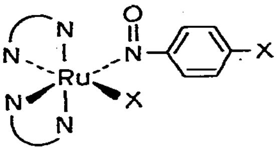
Reactions of coordinated NO

Treatment of $Ru(NO)_2(PPh_3)_2$ with benzyl bromide in boiling toluene under CO afforded (114) $Ru(CO)(NO)(PPh_3)_2Br$, $Ru(CO)_2(PPh_3)_2Br_2$, PhCH=NOH, PhCN, $PhCONH_2$ and traces of PhCHO and $PhCH_2OH$. Under N_2 or ethylene, the reaction of $Ru(NO)_2(PPh_3)_2$ gave $Ru(PPh_3)_2(NCPh)_2Br_2$, $Ru(NO)(PPh_3)_2Br_3$, with some PhCN, and traces of $PhCONH_2$, $(PhCH_2)_2$ and PhCHO. In the absence of the ruthenium complex, NO reacted with $PhCH_2Br$ giving mainly $PhCH_2NO_2$. Other complexes of the type $Ru(NO)_2L_2$ (L = $P(OPh)_3$ or L_2 = diphos) behaved similarly, although the yields of organonitrogen compounds were lower than when L = PPh_3. It was thought that the reaction occurred via benzylation of coordinated NO (Scheme 13) and that PhCH=NOH and PhCN were produced as shown. The formation of $PhCONH_2$ occurred via metal-catalysed rehydration of PhCN.

Scheme 13



Reaction of $[Ru(NO)(bipy)_2X]^{2+}$ (X = Cl or NO_2) with PhNRMe (R = H or Me) afforded (115) $[Ru(bipy)_2\{N(=O)C_6H_4NRMe\}X]^+$, [67], and a similar species could be obtained from phenol. Treatment of $[Ru(NO)(bipy)_2Cl]^{2+}$ with N_3^- in acetone or methanol gave $[Ru(bipy)_2Cl(solvent)]^{2+}$, N_2 and N_2O, and this complex further reacted with nitrosoarenes, p-XC_6H_4NO (X = H, Me or O_2N), giving complexes identical to [67]. The species [67] (X = NO_2) could be converted to $[Ru(NO)(bipy)_2\{N(=O)C_6H_4NRMe\}]^{3+}$ on acidification, and on further treatment with PhNRMe, afforded $[Ru(bipy)_2\{N(=O)C_6H_4NRMe\}_2]^{2+}$. Attack on the coordinated NO group, and its retention in [67], was confirmed using $[Ru(^{15}NO)(bipy)_2X]^{2+}$.

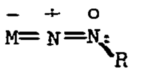


67

Aryldiazenato complexes

Reaction of $Ru(CO)_3(PPh_3)_2$ with $[p\text{-}RC_6H_4N_2]^+$ or $[2,6\text{-}R_2C_6H_3N_2]^+$ has given (116) $[Ru(CO)_2(N_2C_6H_4R)(PPh_3)_2]^+$ (R = H, F, NO_2, OMe or NMe_2) and $[Ru(CO)_2(N_2C_6H_3R_2)(PPh_3)_2]^+$ (R = Cl or Me). Treatment of these complexes with HX (X = BF_4, Cl or I) or LiCl (aqueous) afforded the diazene compounds $[Ru(CO)_2(HN_2C_6H_4R)(PPh_3)_2]^{2+}$, $[Ru(CO)_2(HN_2C_6H_4R)(PPh_3)_2I]^+$ and $Ru(CO)(HN_2C_6H_4R)(PPh_3)_2Cl_2$ (R = F or OMe). These species could be deprotonated to the starting material on treatment with bases. A comparison was made between the chemical properties of these new complexes and their iron analogs. There were few similarities, in fact, and only on treatment with BH_4^- or LiOEt did both the iron and ruthenium aryldiazenates afford $M(CO)_2(PPh_3)_2H_2$ and $M(CO)_2(PPh_3)_3$ (M = Fe or Ru), respectively.

The X-ray photoelectron spectra of $Ru(N_2C_6H_4Me)(PPh_3)_2Cl_3$, $Os(N_2C_6H_4F)(PPh_3)_2Br_3$ and $[M(CO)_2(N_2C_6H_4Me)(PPh_3)_2]^+$ have been measured (117). The N(1s) peaks were identified, and it was noted that the binding energies are among the lowest observed for nitrogen compounds, corresponding closely to that of the N(1s) level in azobenzene. Each compound contains a singly-bent N_2R group and the relative electron densities at the <u>endo</u> and <u>exo</u> N atoms in these, related doubly bent and protonated aryldiazenato species were consistent with the formal charges as shown in



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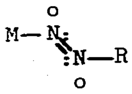

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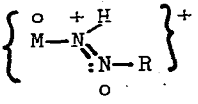


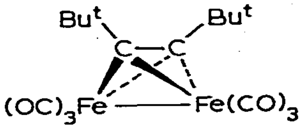
,

respectively.

CLUSTER COMPOUNDS

Binuclear Species (excluding (η^5-C_5H_5) compounds)

Reaction of $Fe_2(CO)_9$ with $Bu^tC_2Bu^t$ gave (118) $Fe(CO)_4(C_2Bu^t{}_2)$ and $Fe_2(CO)_6(C_2Bu^t)_2$,



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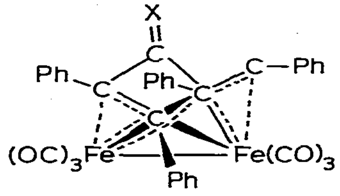
[68]. The structure of the latter was determined crystallographically and is similar to other species described earlier (119). The Fe-Fe distance (2.32 Å) is probably the equivalent of a double bond, and is comparable to those in $Fe_2(CO)_4(C_2Bu^t_2)_2$ (2.22 Å)(120), $Fe_2(CO)_4(C_2R_2)_2$ (2.23 Å)(121)and $[Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$ (2.33 Å)(122). Treatment of $Fe_2(CO)_9$ with PhC_2Ph gave (123) the known $Fe_2(CO)_7(C_2Ph_2)_2$ (119) whose structure, [69] (R = Ph, X = O), was determined crystallographically (Fe-Fe 2.54 Å). This molecule is very similar to [69] (R = Ph, X = CH_2) (124)and [69] (R = Me, X = O)(125)(Fe-Fe 2.53 and 2.51 Å, respectively). The CO groups in these species are fluxional, but it was impossible to say whether CO group scrambling was localised on each Fe atom or whether exchange occurred between the two metal atom sites.

Treatment of the μ-butatriene complexes [70] (L = CO) and [71] with tertiary phosphines and arsines (L) resulted (126) in substitution of a CO group trans to the Fe-Fe bond. Addition of L without CO loss could be demonstrated in some cases, *e.g.* $Fe_2(CO)_6(PBu^n_3)(C_4H_4)$, and kinetic data for the formation of [70] (R = H or Ph; L = PPh_3 or $P(OPh)_3$) and [71] (L = PPh_3 or $P(OPh)_3$) were obtained. The structure of [70] (R = H, L = PPh_3) was confirmed crystallographically (Fe-Fe 2.63 Å).

Reaction of $Fe_2(CO)_9$ with $CH_2{=}C(Me)C{\equiv}CR$ (R = Bu^t or Et) afforded (127) $Fe_2(CO)_6$-$[CH_2C(Me)C_2RO]$, the structures of which [72] were elucidated by X-ray methods. The portion of the ligand represented as $CH_2C(Me)C$ acts as an allylic ligand towards one metal atom and the CC(R)CO moiety serves as a three-electron donor to the other. This last group has character intermediate to that of an allylic and a C=C-CO residue The carbon atom common to both these portions is unusual in that it belongs to two nearly perpendicular three-carbon three-electron donor units while bridging two metal atoms (Fe-Fe 2.74 (R = Bu^t) and 2.76 Å (R = Et)).

Reaction of iron atoms at -196° (128) or of $Fe_3(CO)_{12}$ (129) with thiophenes afforded the ferrole species $Fe_2(CO)_6(C_4R_2R'R'')$ (R = R' = R" = H; R = H, R' = R" = Me; R = R' H, R" = Me) [73]. In the former process, desulfurisation occurred immediately the Fe atoms and thiophenes were co-condensed, and no evidence could be obtained for a thiophene-iron complex. Thus, no ferrocene was produced after the Fe/thiophene co-condensate was treated with cyclopentadiene at -196°, whereas an iron/benzene co-condensate readily afforded $Fe(\eta^5\text{-}C_5H_5)_2$. The addition of 1,3-butadiene, 1,5-cyclooctadiene or PMe_3 to the Fe/thiophene co-condensate, followed by warming, gave red solutions from which it proved impossible to extract products. The structures of [73] (R = R' = R" = H) (129) and [73] (R = R' = R" = Ph)(130)were determined crystallographically (Fe-Fe 2.52 and 2.50 Å, respectively), and the presence of a semi-bridgin

CO group was noted. The fluxional properties of the species [73] (R = R' = R" = H or Ph; R = H, R' = R" = Ph) and the substituted derivatives [74] (L = PBu^n_3 or PPh_3) have also been investigated (131) using v.t. ^{13}C n.m.r. spectroscopy. It was found that the CO groups of the tricarbonylferrole unit were static from -125 to +95°, while those of the π-bonded $Fe(CO)_3$ group were scrambled over this temperature range. A low temperature X-ray structural determination of [74] (L = PPh_3) confirmed that the PPh_3 group was attached to the ferrole iron atom, contrary to previous beliefs (Fe-Fe 2.52 Å).



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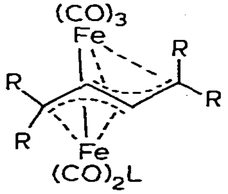

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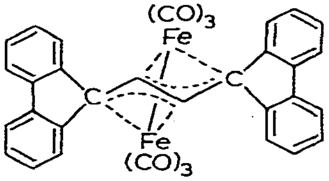

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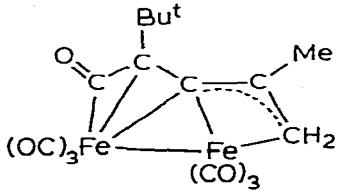

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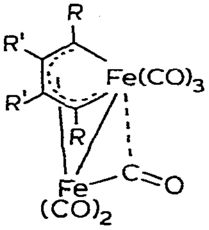

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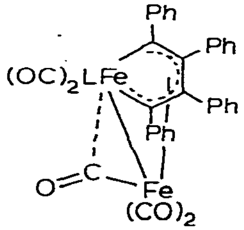

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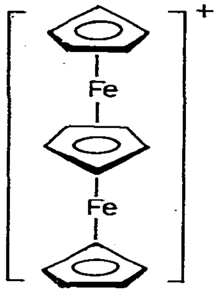
Some theoretical consideration has been given (132) to the bimetallic species $Fe_2(CO)_9$, [75,76 and 77]. Reaction of dihydropentalene with $Fe_2(CO)_9$ afforded (133) five products of which three have been characterised. These are [78] which is analogous to a ruthenium complex (134), [79] and [80]. While [80] remained unchanged on heating, [79] decomposed to a mixture of [78] and [80]. Reaction of $Os(CO)_4(MMe_3)_2$ (M = Si or Ge) or $[Os(CO)_4(SiMe_3)]_2$ with cyclooctatetraene gave (135) $Os(CO)_3(C_8H_9)(MMe_3)$, [81], and small amounts of $Os_2(CO)_6(C_8H_{10})$, [82]. Among the other products were complexes of an unidentified dimer of cyclooctatetraene, viz. $Os(CO)_2(C_{16}H_{16})$ and $Os(CO)_3(C_{16}H_{16})$. This last compound was also obtained from $Os_3(CO)_{12}$ and C_8H_8 on heating. Under u.v. radiation, $[Os(CO)_4(SiMe_3)]_2$ reacted with C_8H_8 giving a moderate yield of $Os(CO)_3(C_8H_8)$. However, $Os(CO)_4Me_2$ afforded a mixture containing, inter alia, $Os_2(CO)_6(C_8H_6)$, [83] (M = Os), which was characterised crystallographically (Os-Os 2.75 Å). Parts of the geometry of this complex are very similar to the compound formed between $Os_3(CO)_{12}$ and 2,3-dimethylbutadiene (136) Minor products of the reaction between $Os(CO)_4Me_2$ and cyclooctatetraene were formulated as $Os(CO)_3(C_{16}H_{16})$ and $Os_2(CO)_6(C_8H_8)$. The n.m.r. spectrum of the tricarbonyl is identical to that of the previously reported [84] (M = Fe)(137). Reaction of



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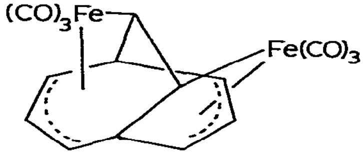

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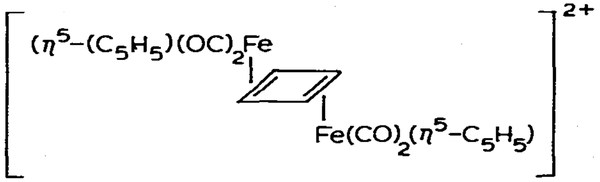

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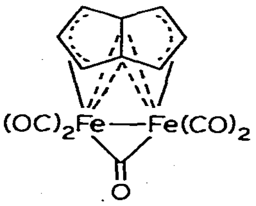

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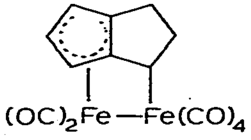

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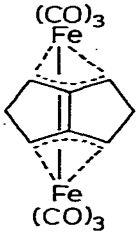

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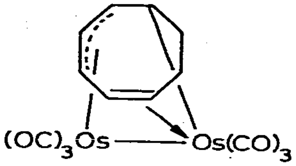
1,4-dibromocyclooctatetraene with either $Fe_2(CO)_9$ at room temperature or $Na_2Fe(CO)_4$ gave [85]. When $C_8H_6Br_2$ was heated with $Fe_2(CO)_9$, however, [83] (M = Fe) was produced, which can also be obtained from the reaction between [85] and $Fe_3(CO)_{12}$ (138). It seems likely, therefore, that [83] (M = Fe) is formed from $C_8H_6Br_2$ and $Fe_2(CO)_9$ via [85]. Reaction of $C_8H_6Br_2$ with $Ru_3(CO)_{12}$ also gave [83] (M = Ru).

Treatment of $SnCl_2MePh$ with $Na_2Fe(CO)_4$ gave (139) $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SnMePh)_2$, [86]. From a v.t. ^1H n.m.r. spectral study of the SnMePh groups, two pathways for the interchange of the Me group site positions, one involving Sn-Fe bond breaking (A) and the other bridge deformation (B), were detected (Scheme 14). The former has a free energy of activation of 11.8±0.06 kcal/mol and the latter 19.2±0.9 kcal/mol (at 289 K). Bridge deformation in the related species $Fe_2(CO)_6(SnBu^n{}_2)_2$ occurred with simultan-



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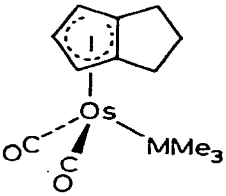

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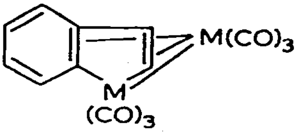

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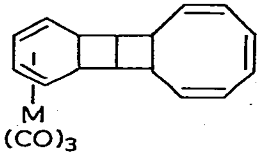

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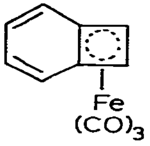

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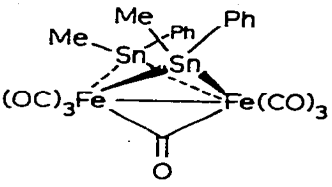

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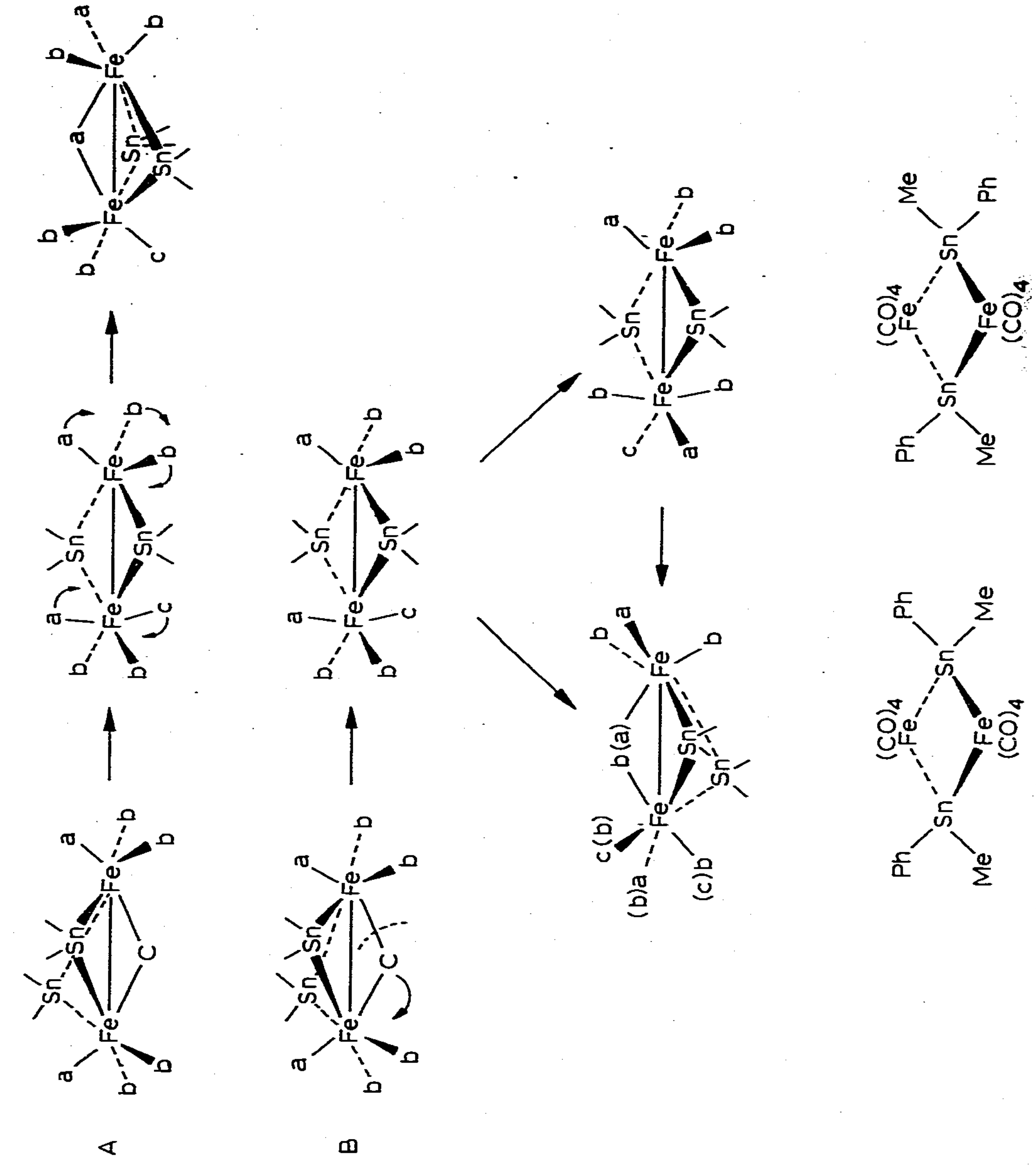
eous stereospecific interchange of bridge and terminal CO ligands (detected by v.t. ^{13}C n.m.r. spectroscopy). The complex $[Fe(CO)_4(\mu\text{-}SnMePh)]_2$,[87], exists as two isomers which interconvert in solution ($\Delta G^{\neq}$ 25.5±0.7 kcal/mol) via Sn-Fe bond cleavage giving a stannylene intermediate $Fe(CO)_4(SnMePh)$. Reaction of $Fe_2(CO)_9$ with $Sn(C_5H_5)_2$ gave (140) a complex $[Fe(CO)_4\{Sn(C_5H_5)_2\}]_2$ analogous to [87], which, on treatment with bases (B), gave $Fe(CO)_4[Sn(C_5H_5)_2B]$. The vibrational spectrum of $Fe(CO)_4\{Sn(C_5H_5)_2\}]_2$ is consistent (141) with two inequivalent η^1-C_5H_5 rings bound to each Sn atom.

Treatment of $Fe_3(CO)_{12}$ with 2-nitropropane afforded (142) several products, including $Fe_2(CO)_6(C_6H_{13}N_2O)$, [88], which was characterised crystallographically (Fe-Fe 2.47 Å, N-N distance 2.66 Å (non-bonding), C=N 1.29 and C-NHPr^i 1.47 Å). The structure of the closely related (143) $Fe_2(CO)_6(C_6H_{12}N_2O)$, [89], has also been established (144) by X-ray methods (Fe-Fe 2.48, C=N 1.29 Å). Reaction of $Fe_2(CO)_9$ with 3,3-pentamethylenediazirine gave (145) two products, [90] and [91]; the structure of the former was confirmed crystallographically. Treatment of $RCH=CHCONR'_2$ (R = H, Me or Ph, R' = Me; R = Ph, R' = Et) with $[Et_3O][BF_4]$ gave (146) $[RCH=CHC(OEt)NR'_2][BF_4]$ which reacted with $Fe_3(CO)_{12}$ affording [92], the structure of one example of which was elucidated (147) by X-ray techniques. The mono-olefin complex $Fe(CO)_4$-$(CH_2=CHCONMe_2)$, on treatment (146) with $[Et_3O]^+$, gave [93] which, in turn, reacted with $Fe_3(CO)_{12}$ giving [94]. However, treatment of this last with $[Et_3O]^+$ and $Fe_3(CO)_{12}$ did not give [92] (R = H). Ethyl-N-α-methylbenzyliminoacetate was dimerised (148) by $Fe_2(CO)_9$ giving two complexes, [95] and [96], and it was shown that [95] reacted with $PhCHMeN=CHCO_2Et$ under u.v. light giving [96]. The structure of both of these compounds was established by X-ray methods (Fe-Fe 2.55 and 2.35 Å, respectively).

Scheme 14



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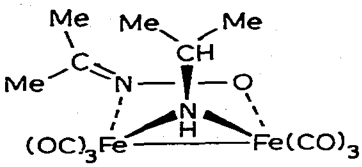

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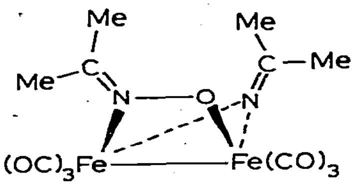

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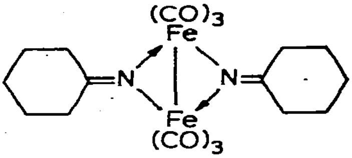

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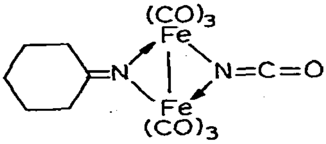

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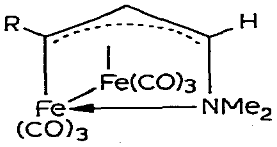

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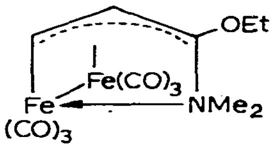

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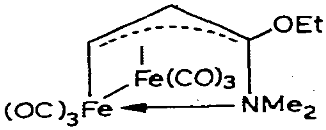
Iron pentacarbonyl reacted (149) with a 1-pyrazoline (R = CO_2Et, R' = Ph) according to Scheme 15. Arylazirine rings (Ar = Ph, p-MeC_6H_4 or p-BrC_6H_4) were opened when reacted (150) with $Fe_2(CO)_9$, the overal mechanism being illustrated in Scheme 16.

Treatment of $Fe_2(CO)_9$ in THF with 1,3-di-t-butyl-2,4-dichlorodiazadiphosphetidine afforded (151) the binuclear species [97]. The full structural details of $[Fe(CO)_3\{\mu\text{-}P(CF_3)_2\}]_2$, [98], have been reported (152). The Fe_2P_2 group is "hinged" about the P_2 group, and a comparison of the "hinge" angle in this species with those of other μ-phosphido complexes was made (Table 2). The substituents on the P atoms are mainly responsible for the variations of this angle, and hence of the alterations in Fe-Fe bond distances (see also Table 1).



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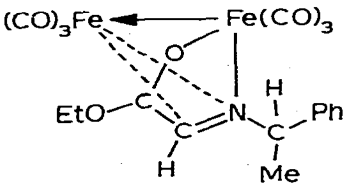

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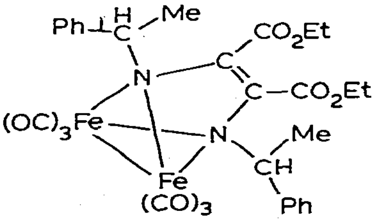

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Scheme 15

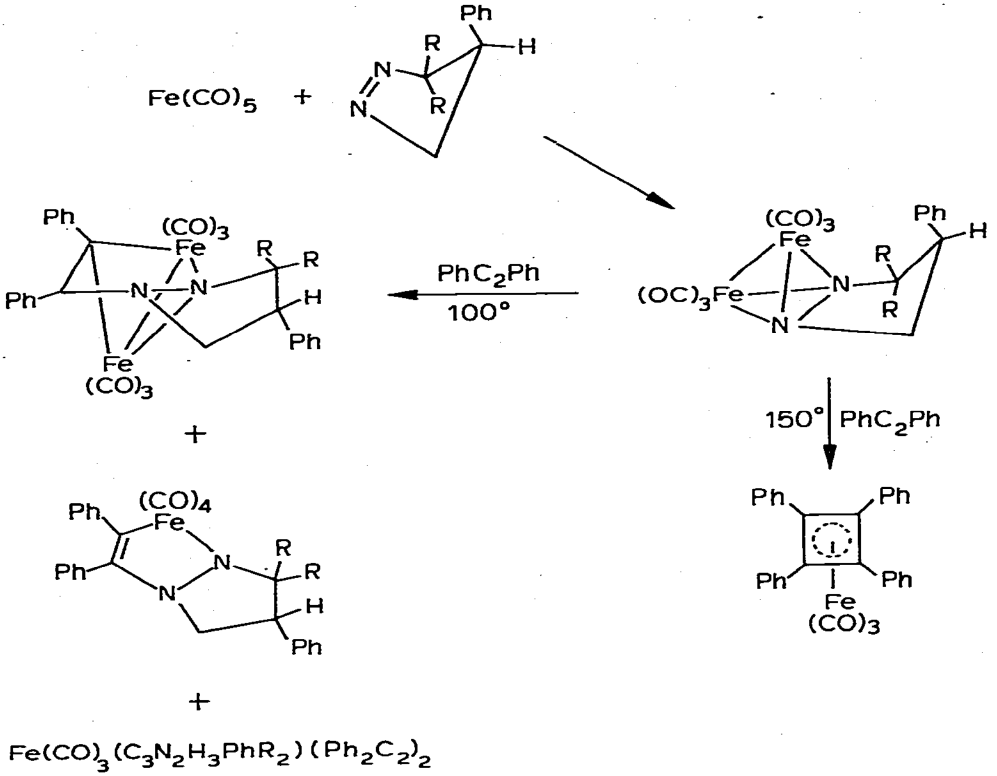


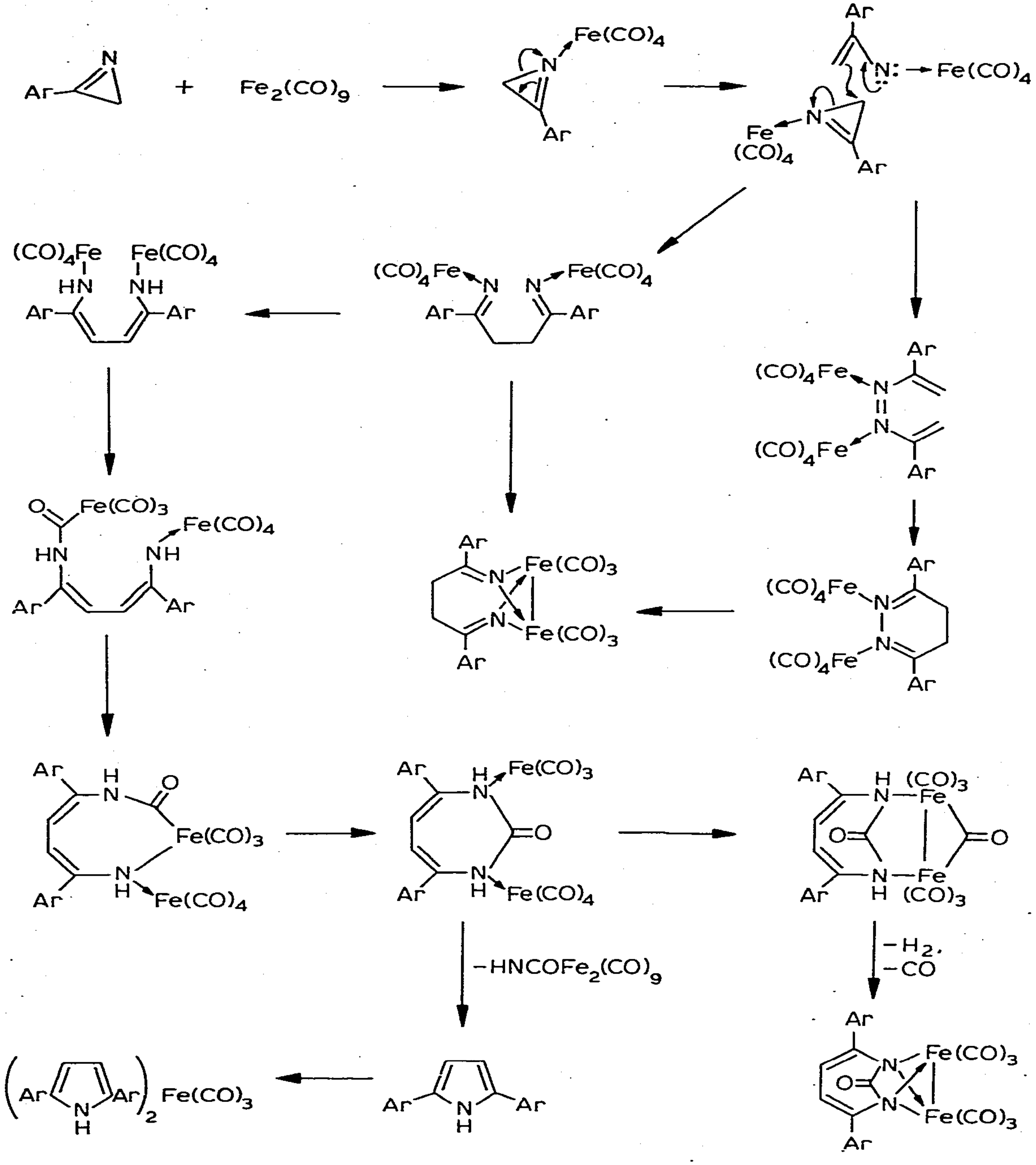
TABLE 2

Metal-metal distances and Fe_2P_2 "hinge" angles as a function of phosphido substituent in $[Fe(CO)_3(\mu\text{-}PRR')]_2$

R	R'	Fe-Fe (Å)	"hinge" angle (°)
Ph	Ph	2.62	100
Ph	Me	2.62	101
Ph	H	2.66	102
Me	H	2.66	101
Me	Me	2.67	107
CF_3	CF_3	2.82	119

The mechanism of substitution of CO by PPh_3, PBu^n_3 or $P(OPh)_3$ (L) in $[Fe(CO)_3(\mu\text{-}PPh_2)]_2$ has been investigated (153). The formation of $Fe_2(CO)_5L(\mu\text{-}PPh_2)_2$ is initiated photochemically and occurs much less readily than the corresponding species $Fe_2(CO)_5L(\mu\text{-}SR)_2$ or $Fe_2(CO)_5L(\mu\text{-}NRR')_2$. The rate-limiting step is the dissociative loss of CO, in contrast to the association of L in the corresponding μ-mercaptides and μ-amido species. However, there is a possibility of the opening of an Fe-

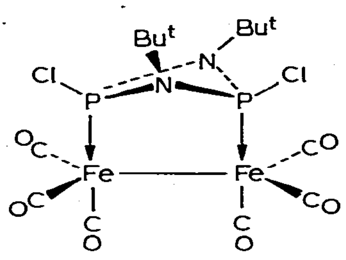
Scheme 16



Ar = p-RC_6H_4 ; R = H, Me or Pr^n

phosphido bridge bond, followed by loss of CO and entry of L, the process being completed by ring closure.

Treatment of the μ-acetylido complex [99] with diethylamine, or on warming [100] in benzene, gave (154) [101] (R = Bu^t, C_6H_{11} or Ph). With triethylamine, however, the species [102] (R = C_6H_{11} or Ph) was formed. An X-ray crystallographic examination of [101] (R = Ph) confirmed the presence of the unique H atom and the tetrahedral geometry of the C atom to which it is attached. It also revealed a very small Fe-C-Fe bond angle, 76° (Fe-Fe 2.55 Å). It was suggested that the $CH(NEt_2)Ph$



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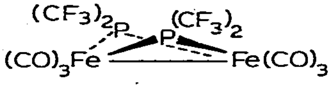

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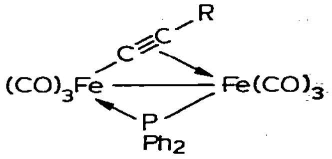

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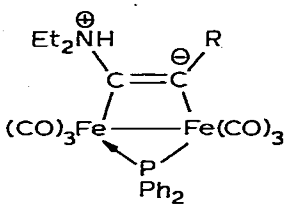

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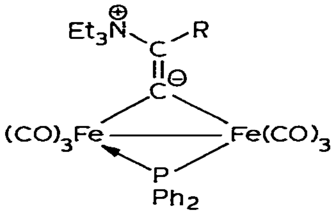

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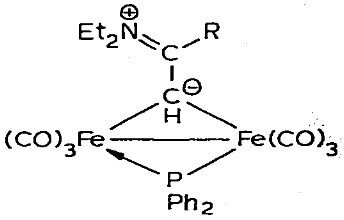

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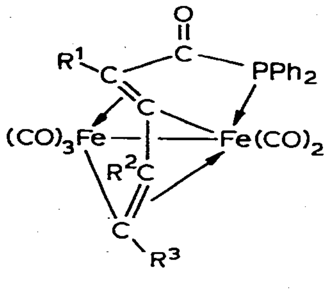
ligand is formed by attack of $NHEt_2$ on the β-C atom of the acetylide group in [99], followed by hydrogen transfer to the α-C atom. This bridging ligand may be regarded formally as analogous to RH$\dot{N}$:, whereas in [102], the bridging ligand is similar to (155) $\dot{R}_2C=N$: and NO. Acetylene-acetylide coupling occurred when [99] was treated with $R'C_2R''$ giving [103] and [104] (R = Bu^t, R' = R'' = CO_2Et, CF_3, Et or Ph; R' = CO_2Et, R'' = Ph). The original α-C atom of the μ-acetylide in [99] remains bound to both iron atoms in the coupled product, contrary to the usual situation in acetylene-acetylide coupling. From the orientation of the substituents in [103] and [104], the lack of isomers and the propensity of [99] to undergo nucleophilic attack by weak nucleophiles on the α-C atom rather than at Fe, it was suggested that an ionic coupling mechanism, perhaps involving [105], is involved in the formation of [103] and [104].

Photolysis of $N(SCF_3)_3$ gave SCF_3 radicals which reacted (156) with $Fe(CO)_5$ affording $Fe(CO)_4SCF_3$ and $[Fe(CO)_3(\mu\text{-}SCF_3)]_2$. The corresponding binuclear selenium



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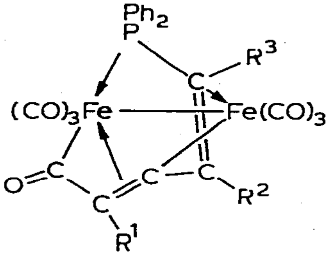

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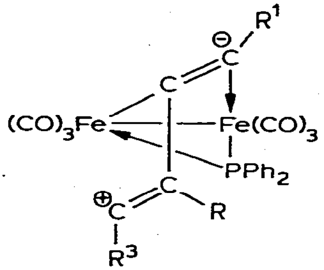

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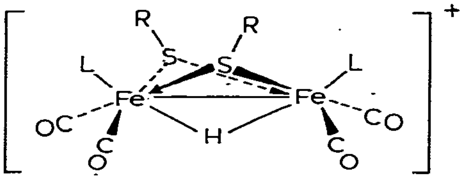

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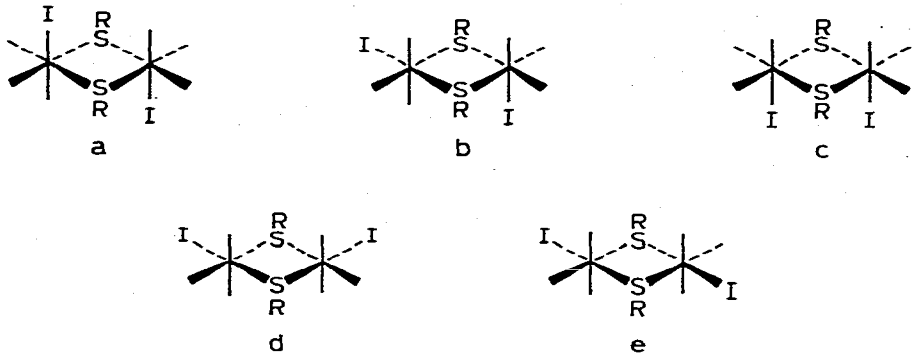
complex was prepared by photolysis of $(SeCF_3)_2$ in the presence of $Fe(CO)_5$. Protonation of $[Fe(CO)_2L(\mu\text{-}SMe)]_2$ (L = PMe_3, PMe_2Ph, $PMePh_2$ and PPh_3) afforded (157) the μ-hydrido cation [106]. An extensive study has been made (158) of the iodination of the μ-mercaptide complexes $[Fe(CO)_3(\mu\text{-}SR)]_2$, and their CO-substituted derivatives. Thus, iodine reacted with $[Fe(CO)_3(\mu\text{-}SR)]_2$ (R = Me, Et, Pr^i or Ph) and with $[Fe(CO)_2(\mu\text{-}SR)]_2[Ph_2PCH_2PPh_2]$ (R = Me, Et or Ph) giving $[Fe(CO)_3I(\mu\text{-}SR)]_2$ and $[Fe(CO)_2I(\mu\text{-}SR)]_2[Ph_2PCH_2PPh_2]$. On the basis of an X-ray structural analysis of $[Fe(CO)_3I(\mu\text{-}PMe_2)]_2$ (159), it was assumed that $[Fe(CO)_3I(\mu\text{-}SR)]_2$ contains a planar Fe_2S_2 bridging system but in the absence of definitive structural data, the precise arrangements of the I atoms and CO groups could not be determined; possible isomers are illustrated by [107] (a, b, c, d, and e). The complexes containing $Ph_2PCH_2PPh_2$ are probably similar. With $Fe_2(CO)_5L(\mu\text{-}SMe)_2$ (L = PPh_3, $AsPh_3$ or $SbPh_3$), $[Fe(CO)_2(PR'_3)(\mu\text{-}SR)]_2$ (R = Me or Ph, R' = Et, Ph, OMe or OPh), $[Fe(CO)_3(\mu\text{-}SR)_2\text{-}\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]$ (R = Me or Bu^t) and $Fe_2(CO)_3[P(OPh)_3]_3(\mu\text{-}SR)_2$ (R = Me or Ph), iodine afforded $[Fe_2(CO)_5I(L)(\mu\text{-}SMe)_2]^+$ (probably [108] with one L replaced by CO), $[\{Fe(CO)_2(PR'_3)(\mu\text{-}SR)\}_2I]^+$ ([108]), $[Fe(CO)_3I(\mu\text{-}SR)_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]^+$ and $[Fe_2(CO)_3I\{P(OPh)_3\}_3(\mu\text{-}SR)_2]^+$ (also analogous to [108] (L = $P(OPh)_3$) with one additional CO group replaced by $P(OPh)_3$). Reaction of the ethanedithiolato complex $Fe_2(CO)_6(\mu\text{-}SCH_2)_2$ with iodine gave $Fe_3(CO)_6I_5(\mu\text{-}SCH_2)_2$, probably [109], although other structures, such as [110] or [111], are possible. The failure to obtain $Fe_2(CO)_6I_2$-



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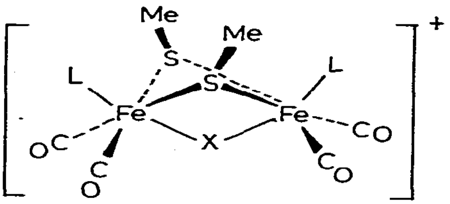
μ-SCH$_2$)$_2$ was attributed to steric factors. The mechanism of halogenation of these metal-metal bonded μ-mercaptide species is thought to involve initial formation of species similar to [108], followed by nucleophilic addition thereto of X$^-$ giving compounds like [107].



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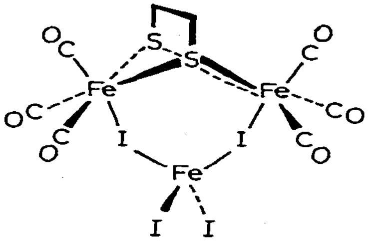

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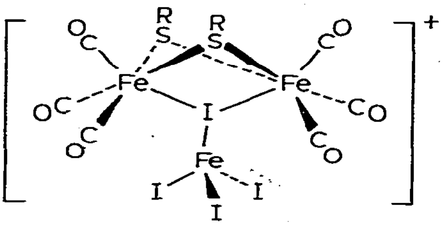

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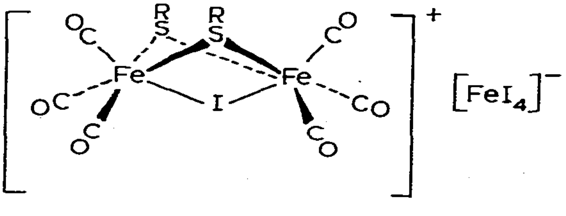
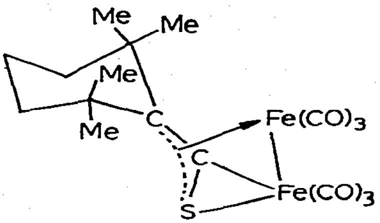


111

Treatment of either Fe$_2$(CO)$_9$ or Fe$_3$(CO)$_{12}$ with 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane gave (160) the bimetallic thioketene complex [112]. A method of phase-transfer catalysed o-metalation of Ar$_2$C=S by Fe$_2$(CO)$_9$, giving [113], has been reported (161). By using benzene, MeOD, [PhEt$_3$N]Cl, NaOD and D$_2$O, it was established that no deuterium was incorporated into [113], indicating that the benzylic H atom therein arose from intramolecular transfer of H from the o-position of the thiobenzophenone rather than from aqueous NaOH.



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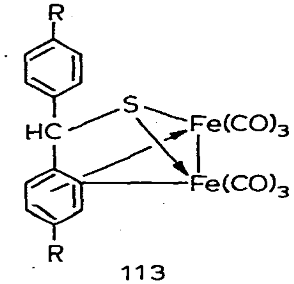

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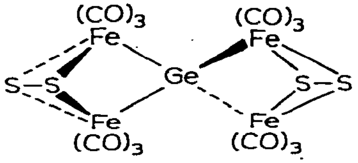

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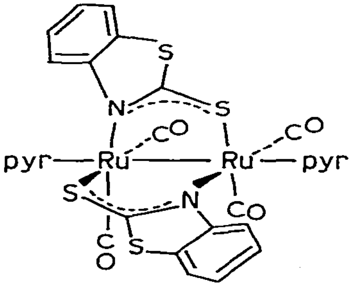
Reaction of $Fe_2(CO)_6S_2$ with $HGeCl_3.2Et_2O$ gave (162) $Fe_2(CO)_6S_2GeCl_2$ and on further treatment of this with $[Et_3NH][GeCl_3]$, [114] was formed. $Ru_3(CO)_{12}$ reacted with 2-mercaptobenzothioazole (BTSH) giving (163) $Ru_2(CO)_6(BTS)_2$ which, on recrystallisation from pyridine, afforded $Ru_2(CO)_2(pyr)_2(BTS)_2$, [115], and $Ru(CO)_2(pyr)_2(BTS)_2$, [116]. The structure of [115] (Ru-Ru 2.76 Å) was established crystallographically.

The thietanones [117] reacted (164) with $Fe_2(CO)_9$ on heating or with $Fe(CO)_5$ under u.v. light giving [118] whose structure was confirmed by X-ray methods (Fe-Fe 2.42 Å).



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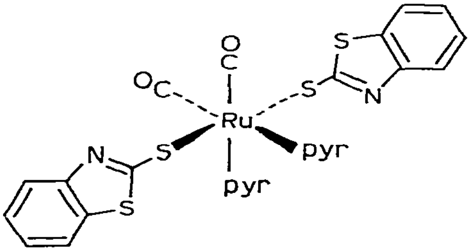

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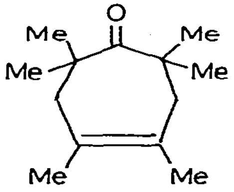

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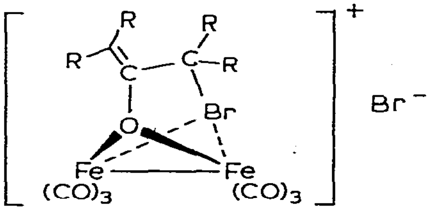

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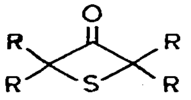

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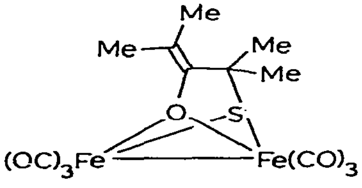

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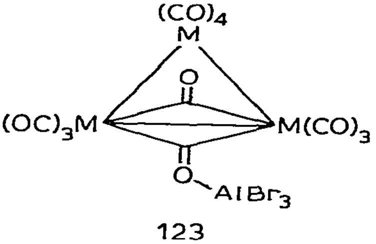
Treatment of [118] with 2,3-dimethylbutadiene afforded the heptenone [119]. This reaction and the structure of [118] may be of relevance to a possible mechanism for the reductive rearrangements by iron carbonyls of α,α'-dibromoketones (165). This view is summarised in Scheme 17, and an important intermediate in this process may be [120] which is very similar to [118]. The binuclear iron complex $(FeL)_2$, [121], reacted with CO or RNC (R = Me or Bu^t) giving (166) $Fe(CO)_2L$ and $Fe(CNR)_2L$, respectively. However a complex derived from [122], similar to [121], did not react with CO, presumably because of steric hindrance.

Trinuclear Species

The decomposition of $M_3(CO)_{12}$ (M = Ru or Os) under argon, nitrogen and air has been investigated (167) thermogravimetrically. Some differences between the two carbonyls were observed, principally that $Os_3(CO)_{12}$ sublimed prior to decomposition to the metal whereas $Ru_3(CO)_{12}$ did not. The structures of $M_3(CO)_{12}$ (M = Fe, Ru and Os) in the solid state have been rationalised (168) using a model based on the polyhedral packing of CO groups where the metal atoms are dispersed as hard spheres within the close-packed matrix of carbonyl groups. This model was extended to explain certain fluxional properties of $M_3(CO)_{12}$, and, in particular, to interpret the behaviour of $Fe_3(CO)_{12}$ in solution (169). In this latter connection, a new isomeric form was proposed which does not contain bridging CO groups, and the stereochemical non-rigidity of $Fe_3(CO)_{12}$ was rationalised in terms of effective rotation of the Fe_3 triangle within the icosahedron of the CO groups. It was suggested that carbonyl scrambling in $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ could also occur by a similar pathway. However this view of metal carbonyl structures and fluxionality has been challenged (170) on the grounds that non-valence interactions of the kind proposed are not the singly most important factor determining the geometries of simple binary metal carbonyls.

The v.t. ^{13}C n.m.r. spectra of $Os_3(CO)_{12-n}(PEt_3)_n$ (n = 1 or 2) have been interpreted (171) in terms of selective CO group exchange along the edges of the Os_3 triangle (Scheme 18); a process involving only six of the 12-n CO groups. Treatment of $M_3(CO)_{12}$ (M = Fe or Ru) with $AlBr_3$ afforded 1:1 adducts (172) where the Al atom is bound to the O atom of a bridging CO group, *viz*. [123] (M = Fe or Ru) or [124]. With $Fe_2(CO)_9$, the species [125] was produced.

V.T. ^1H n.m.r. spectral studies of $[Fe_3(CO)_{11}H]^-$ revealed (173) that this molecule



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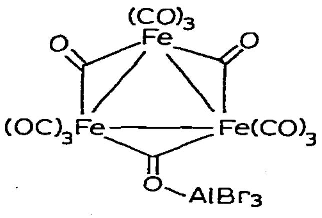

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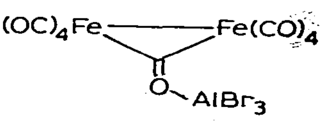

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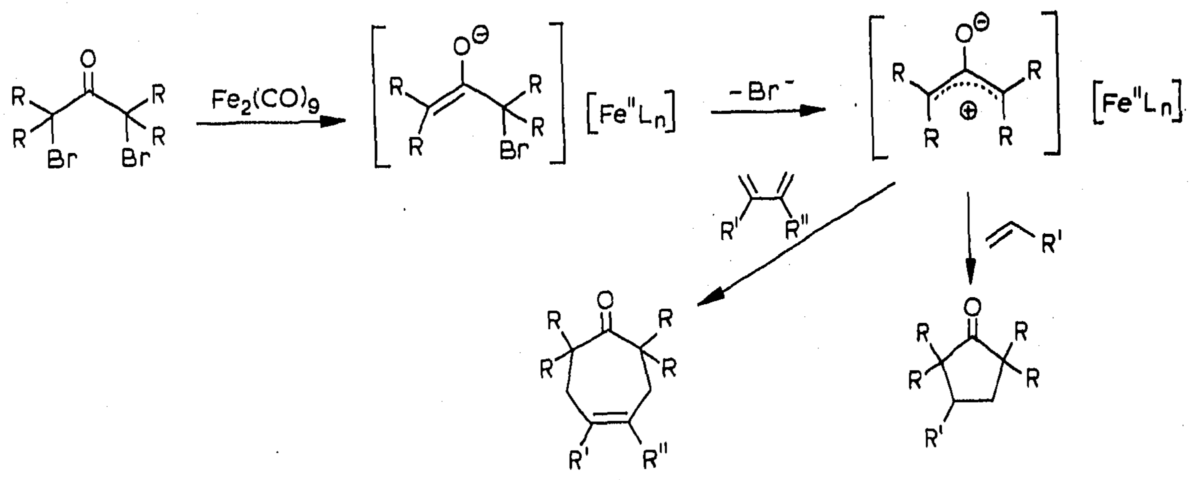
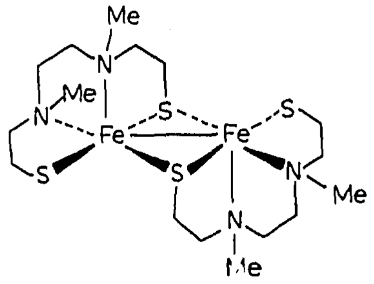
Scheme 17

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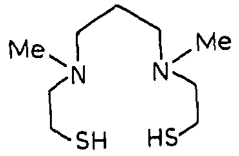
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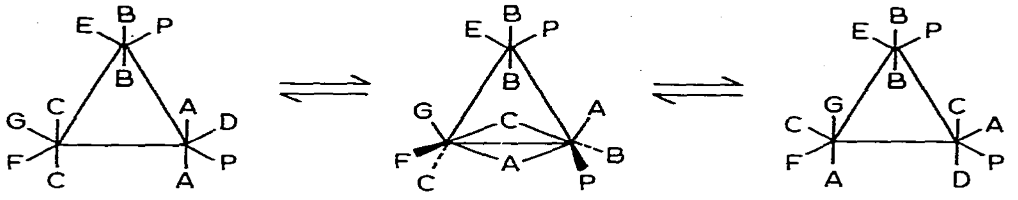
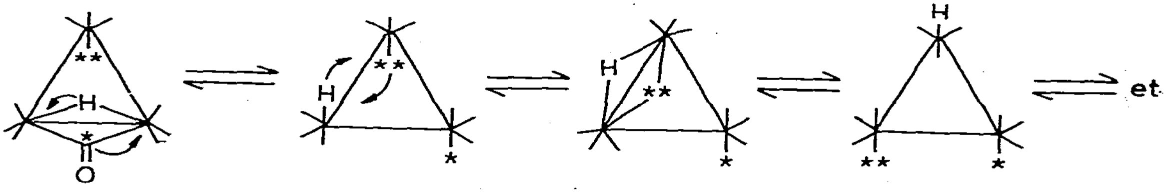
Scheme 18

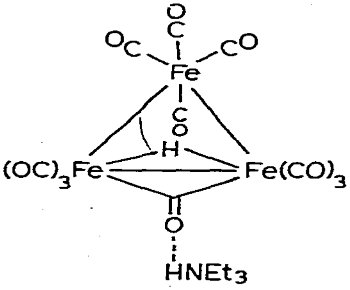


undergoes at least two dynamic processes over the range -107 to +30^0 (Scheme 19). The bridging CO group is very basic and forms acid-base complexes with BF_3 and with $[Et_3NH]^+$, e.g. [126]. These adducts inhibit the fluxional processes at higher temperatures. ^1H n.m.r. spectral studies of $Ru_4(CO)_{12-n}L_nH_4$ (n = 1 to 4) and $Ru_4(CO)_{13-n}L_nH_2$ (n = 1 or 4) (L = tertiary phosphine or phosphite) have revealed (174) that the H atoms are involved in intramolecular tautomerisms which parallel the interstitial nature and mobility established for hydrogen chemisorbed into metallic phases.

Under mild conditions, $Os_3(CO)_{10}H_2$ underwent (175) associative CO substitution reactions giving $Os_3(CO)_{10}LH_2$ (L = CO, PMe_2Ph, PPh_3 or PhCN), [127] (a or b), which slowly released CO giving $Os_3(CO)_9LH_2$. At low temperatures, $Os_3(CO)_{10}H_2$ added CO giving $Os_3(CO)_{11}H_2$, the structure of which was reported earlier (176), and on raising the temperature under CO, this species afforded $Os_3(CO)_{12}$ and hydrogen. In the reactions of $Os_3(CO)_{10}H_2$ with alkenes, simple associative addition of the alkene to the cluster is probably reponsible in part for the facile catalysis by $Os_3(CO)_{10}H_2$ of alkene isomerisation. The kinetics of the catalytic conversion of terminal to

Scheme 19





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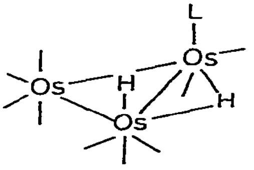

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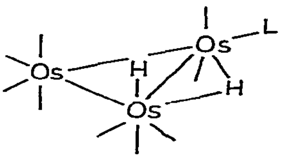
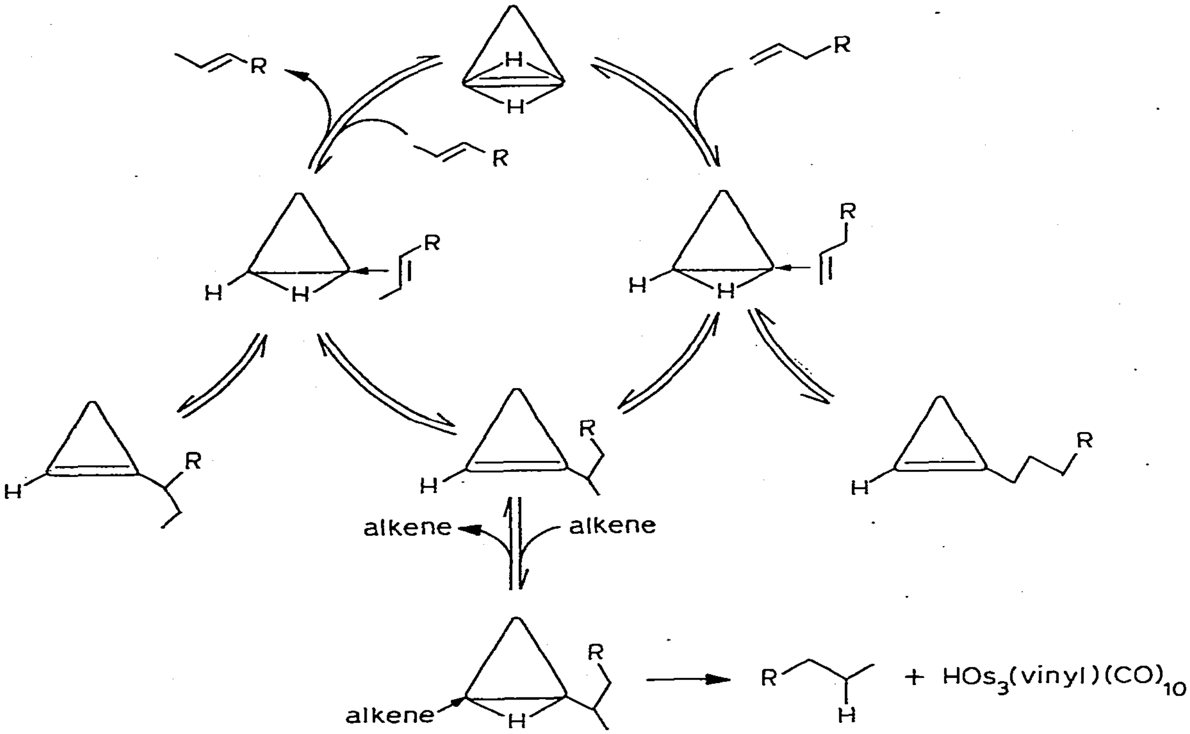


127 b

internal olefins and of the reduction of olefins to alkanes (see also ref. 195) were described and the overall results are summarised in Scheme 20. Allylic halides reacted with $Os_3(CO)_{10}H_2$ giving $Os_3(CO)_{10}HX$ and $Os_3(CO)_{10}X_2$ (X = Cl, Br or I). While the decacarbonyl complies with the 18-electron rule, it may be thought of as having a chemistry broadly similar to that of a coordinatively unsaturated molecule.

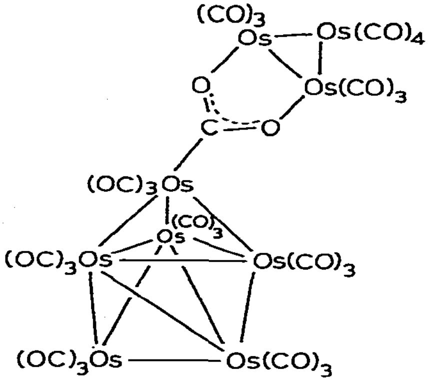
Scheme 20



The production of methane at 140° at 2 atm. from a mixture of hydrogen and CO was slowly catalysed homogeneously (177) by $Os_3(CO)_{12}$. In the presence of D_2, only D_2O and CD_4 were formed, and on substitution of CO in the cluster by $P(OMe)_3$, an increase in the rate of production of methane was observed, although ethane and propane were also formed. A reduction in CO pressure appeared to lead to an increase in the rate of formation of CH_4, which is consistent with the view that the key intermediate in the mechanisms of reduction of CO is a highly coordinatively unsaturated carbonyl cluster possibly containing an η^2-CO ligand. Hydrogenation of $Os_3(CO)_{12}$ under nitrogen gave no ammonia but the methane which was produced relatively quickly was probably formed via a heterogeneous process.

Treatment of $Os_3(CO)_{12}$ with KOH in methanol gave (178) $[Os_3(CO)_{11}H]^-$ which is isostructural with $[Fe_3(CO)_{11}H]^-$ (179). Acidification of this with aqueous H_3PO_4 and with gaseous HCl afforded $Os_3(CO)_{10}H(OH)$ and $Os_3(CO)_{10}H_2$, respectively. The hydrido carbonylate anion reacted with $Os_6(CO)_{18}$ giving $[HOs_3(CO)_{10}O_2COs_6(CO)_{17}]^-$, [128].

The Os-Os distances in the Os_6 fragment (2.78-2.82 Å) are similar to those observed in $Os_6(CO)_{18}$ itself (180), apart from those involving the apical Os atom (2.86-2.90Å). The hydride ligand is probably bound to the Os_3 fragment (Os-Os 2.86-2.90 Å) and the carbon atom of the CO_2 fragment is thought to be of the carbene type (Os-C 1.96 Å). Treatment of [128] with aqueous acid afforded $Os_6(CO)_{18}$ and $Os_3(CO)_{10}H(OH)$.



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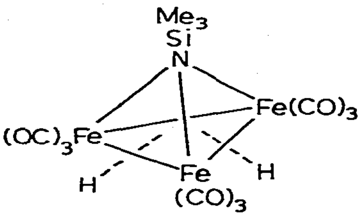
Photolysis of $Fe_3(CO)_{10}(\mu\text{-NSiMe}_3)$ in the presence of hydrogen gave (181) $Fe_3(CO)_9H_2(\mu_3\text{-NSiMe}_3)$, [129]. With PR_3 under u.v. light this gave $Fe_3(CO)_8(PR_3)H_2(\mu_3\text{-NSiMe}_3)$, [130], and $Fe_3(CO)_7(PR_3)_2H_2(\mu_3\text{-NSiMe}_3)$, whereas $Fe_3(CO)_{10}(\mu_3\text{-NSiMe}_3)$ underwent sequential CO substitution on each metal atom, ultimately giving $Fe_3(CO)_7(PR_3)_3(\mu_3\text{-NSiMe}_3)$, [131]. The species [129] acted as a catalyst for the photochemical hydrogenation of olefins and dienes, Scheme 21.



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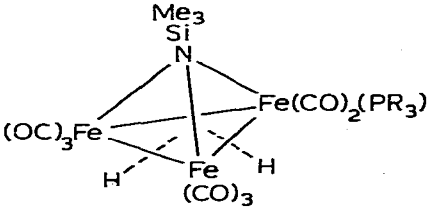

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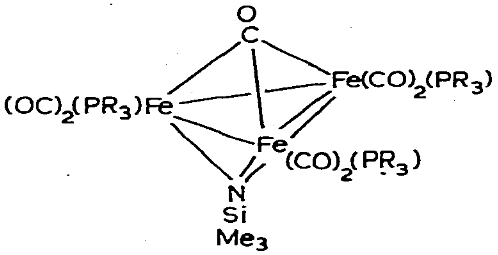

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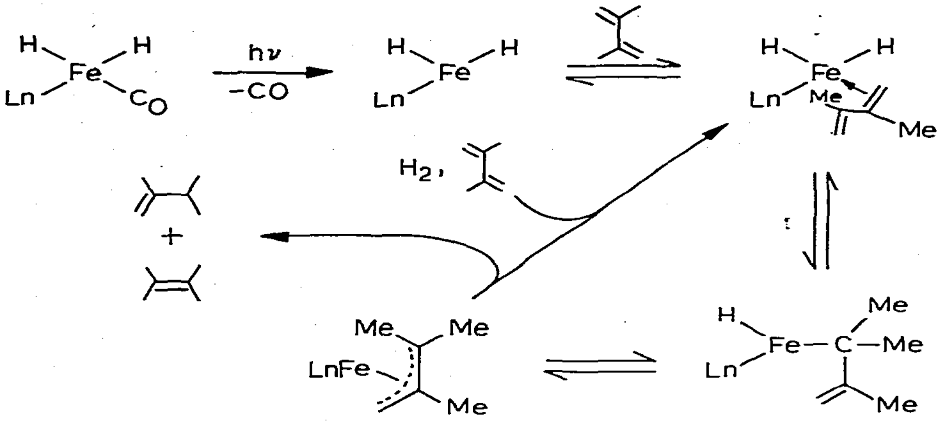
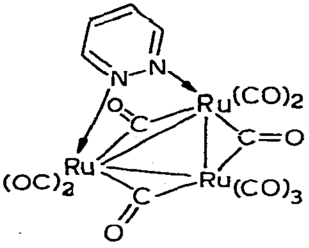
Scheme 21



Reaction of $Ru_3(CO)_{12}$ with 1,2-diazine afforded (182) $Ru_3(CO)_{10}(C_4H_4N_2)$, [132]. The carbonyl bridges are asymmetric, possibly because of packing forces, and the metal distances are 2.74 (diazine bridged) and 2.86 Å. The structure of this species was related to a plausible if as yet undetected pathway for partial CO scrambling on $Ru_3(CO)_{12}$ (<u>Scheme</u> <u>22</u>).



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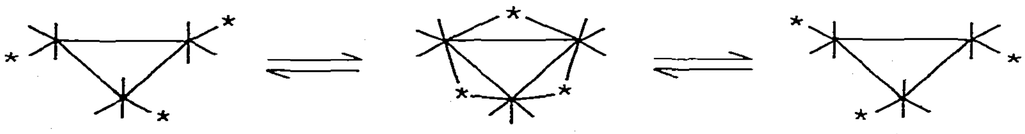
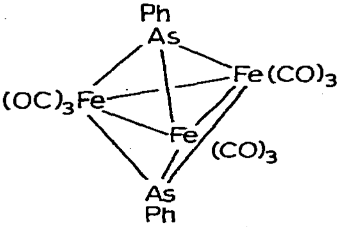
Scheme 22



Treatment of $Na_2Fe(CO)_4$ with $PRCl_2$ (R = Bu^n, Ph or NEt_2) gave (183) $Fe_3(CO)_9(\mu_3$-PR) whereas reaction of $Fe_2(CO)_9$ with $Mn(\eta^5-C_5H_5)(CO)_2(AsPhCl_2)$ afforded (184) $Fe_3(CO)_9(\mu_3-AsPh)_2$, [133]. (This reaction should be compared with those described in refs. 220 and 221). The structure of [133] was determined crystallographically and the Fe-Fe distances were 2.74, 2.79 [(Fe(2)-(3) and Fe(1)-(3); bonding] and 3.70 Å [Fe(1)-(2); non-bonding], respectively. $Fe_3(CO)_{12}$ reacted with 1,2,3-triphenyl-1,2,3-triphosphaindane giving (185) the bimetallic species [134] and [135], and three isomers of formula $Fe_3(CO)_9(C_{24}H_{19}P_3)$, [136], [137] and [138].

Iron carbonyls reacted with $R_2PC\equiv CR'$ giving a series of complexes [139] and [140], (R = R' = Ph), [141], [142] and [143] (R = Ph, R' = CF_3). By heating the last, [141] and [144] were produced, and [141] was further converted to [145]. The structure of [145] was established (186) crystallographically, and the metal-metal bond lengths were 2.66 [Fe(1)-(2)] and 2.53 Å [Fe(2)-(3)], respectively.



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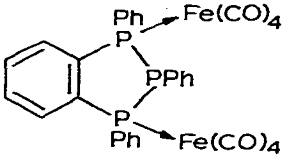

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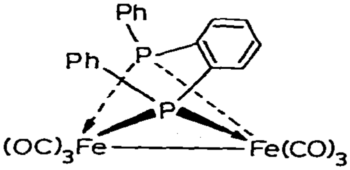

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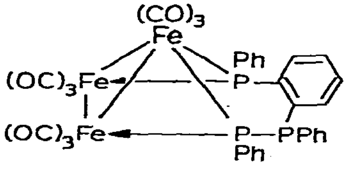

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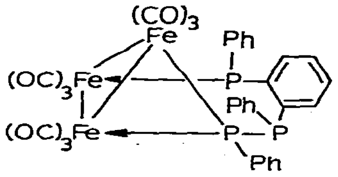

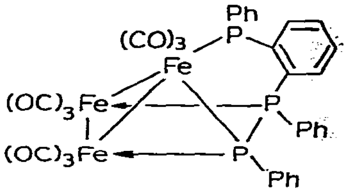

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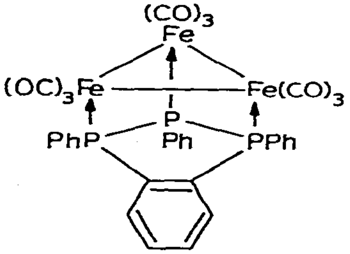

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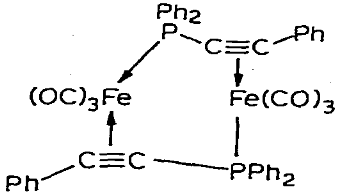

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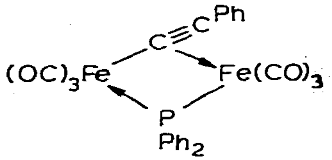

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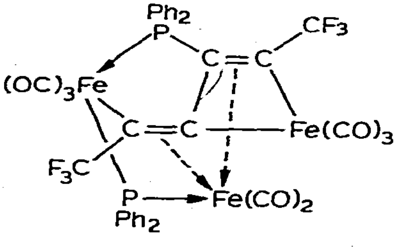

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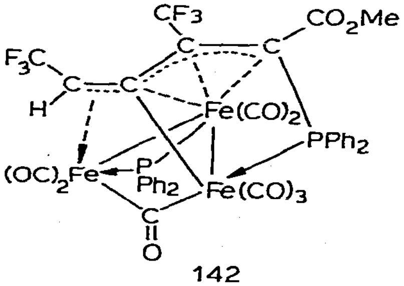

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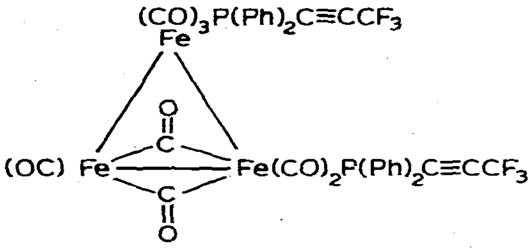

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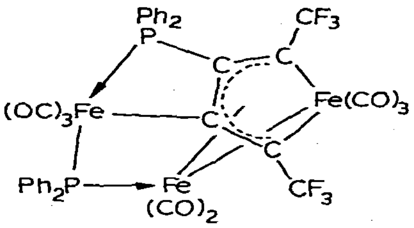

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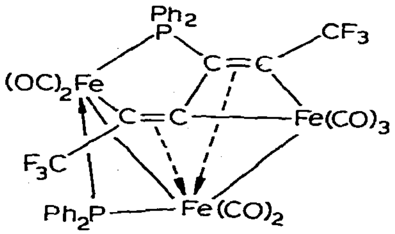

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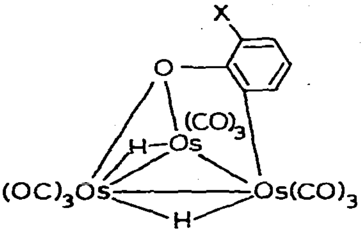
Hydroxy-aryl and -alkyl (ROH) compounds reacted (187) with $Os_3(CO)_{12}$ giving initially $Os_3(CO)_{10}H(OR)$ (R = Ph, β-naphthyl, $CHMe_2$, CHMePh or CMe_2Ph), but on further heating, H transfer occurred giving $Os_3(CO)_9H_2(OQ)$ (Q = monodeprotonated OR). Thus, with phenol and β-naphthol, [146] (X = H) and [147] were formed, whereas α-naphthol gave [148] and [149]. With PhCRMeOH, [150] was formed (R = Me or Ph), whereas catechol afforded [146] (X = OH). Those compounds derived from phenols or naphthols could be protonated, giving $[Os_3(CO)_9H_3(OQ)]^+$ without disruption of the basic structure. With benzyl alcohol, $Os_3(CO)_{12}$ gave (188) $Os_3(CO)_{10}H(OCH_2Ph)$ which, on heating, was decarbonylated reversibly giving a species analogous to [150]. Further dehydrogenation and decarbonylation of this in refluxing xylene gave $Os_3(CO)_9H_2(C_6H_4)$, [151], and the latter reacted with CO in refluxing nonane to give $Os_3(CO)_{12}$ and



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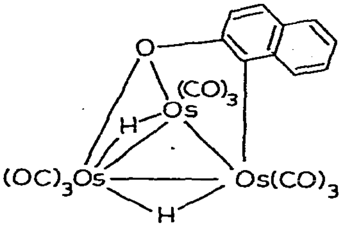

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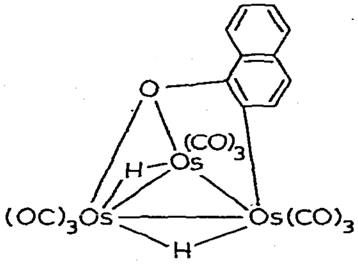

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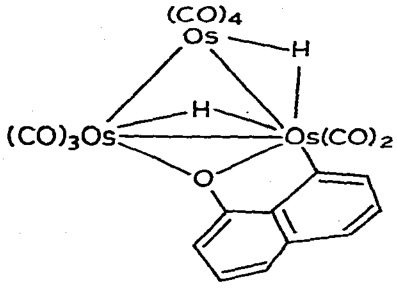

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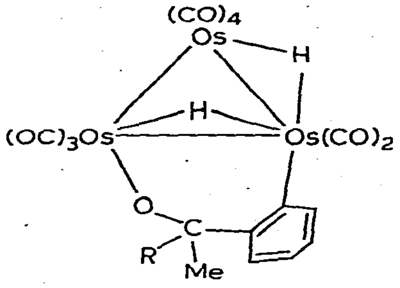

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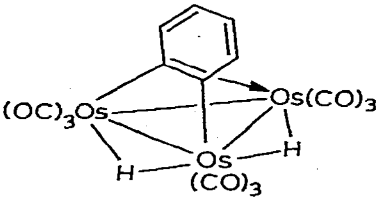
benzene. In refluxing nonane, $Os_3(CO)_{10}H(OCH_2Ph)$ was converted over 23 days into a mixture of $Os_3(CO)_{12}$, $Os_4(CO)_{12}H_4$, PhCHO and benzene, whereas after 60 days, the same metal carbonyl derivatives were detected, but the organic by-products were toluene and p-MeC_6H_4CHO. Thermolysis of $Os_3(CO)_{10}H(OCHMePh)$ in nonane gave mainly MeCOPh, whereas $Os_3(CO)_{10}H($*p*-$OCH_2C_6H_4Me)$, or its *o*-isomer, afforded $Os_3(CO)_9H_2$-(C_6H_3Me), [152]. It was suggested that the conversion of $Os_3(CO)_9H_2(OCH_2C_6H_4)$ to [151] probably involved loss of CO and H_2 rather than of CH_2O since $Os_3(CO)_{10}H$-(OCHMePh) gave MeCOPh rather than benzene which would have required elimination of MeCHO.



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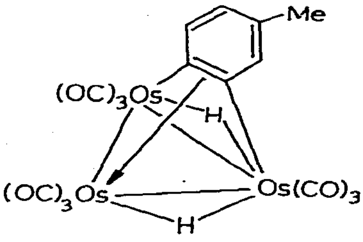

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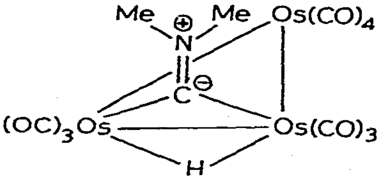

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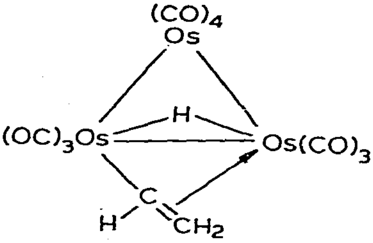
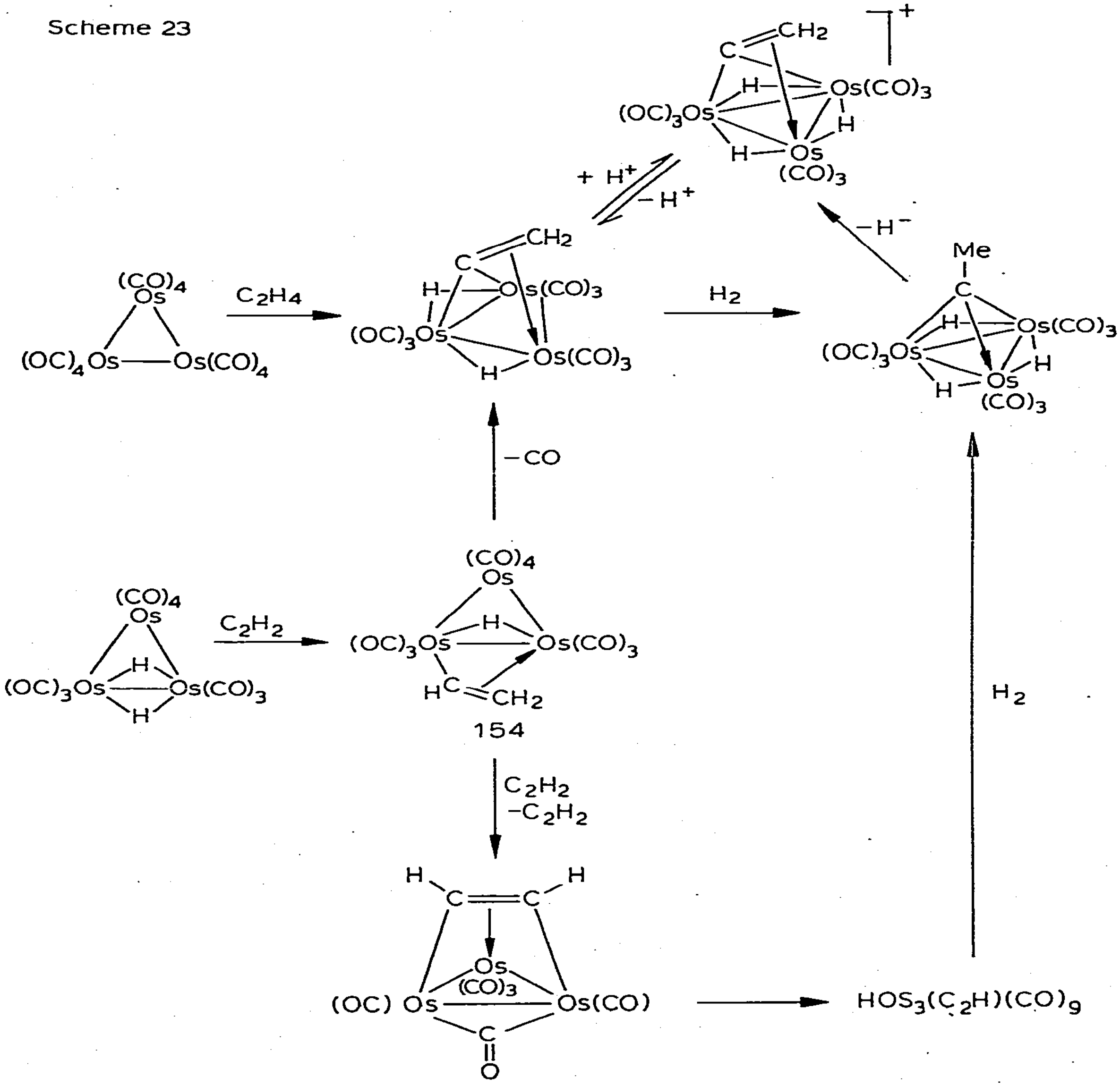


154

V.T. ^{13}C n.m.r. spectral investigations of $M_3(CO)_9H_2(S)$ and $M_3(CO)_9H_3(CMe)$ (M = Ru or Os) revealed (189) that the solid state structure of these species persists in solution. However, in $M_3(CO)_9H_2(S)$ at low temperatures there was hydride ligand scrambling around the M_3 triangle or localised CO group scrambling on each metal, and at higher temperatures there may be a combination of these processes. It was also possible that total CO scrambling occurred around the M_3 triangle via some bridged intermediate. The species $M_3(CO)_9H_3(CMe)$ was non-fluxional whereas the spectrum of $FeCo_2(CO)_9S$ was interpreted in terms of localised CO group exchange about each metal atom.

The complex $Ru_3(CO)_{10}H(C{=}NMe_2)$, [153], obtained in a reaction between $Ru_3(CO)_{12}$ and $SnMe_2CH_2NMe_3$, has been investigated crystallographically (190). The bridged Ru-Ru distance is 2.80 Å while the non-bridged bond lengths are 2.82-2.83 Å. At room temperature, $Os_3(CO)_{10}H_2$ reacted (191) with acetylene giving $Os_3(CO)_{10}H(CH{=}CH_2)$, [154] which, in refluxing octane, was converted into $Cs_3(CO)_{10}H_2(C{=}CH_2)$. These reactions, and others, are summarised in Scheme 23. With disubstituted acetylenes,

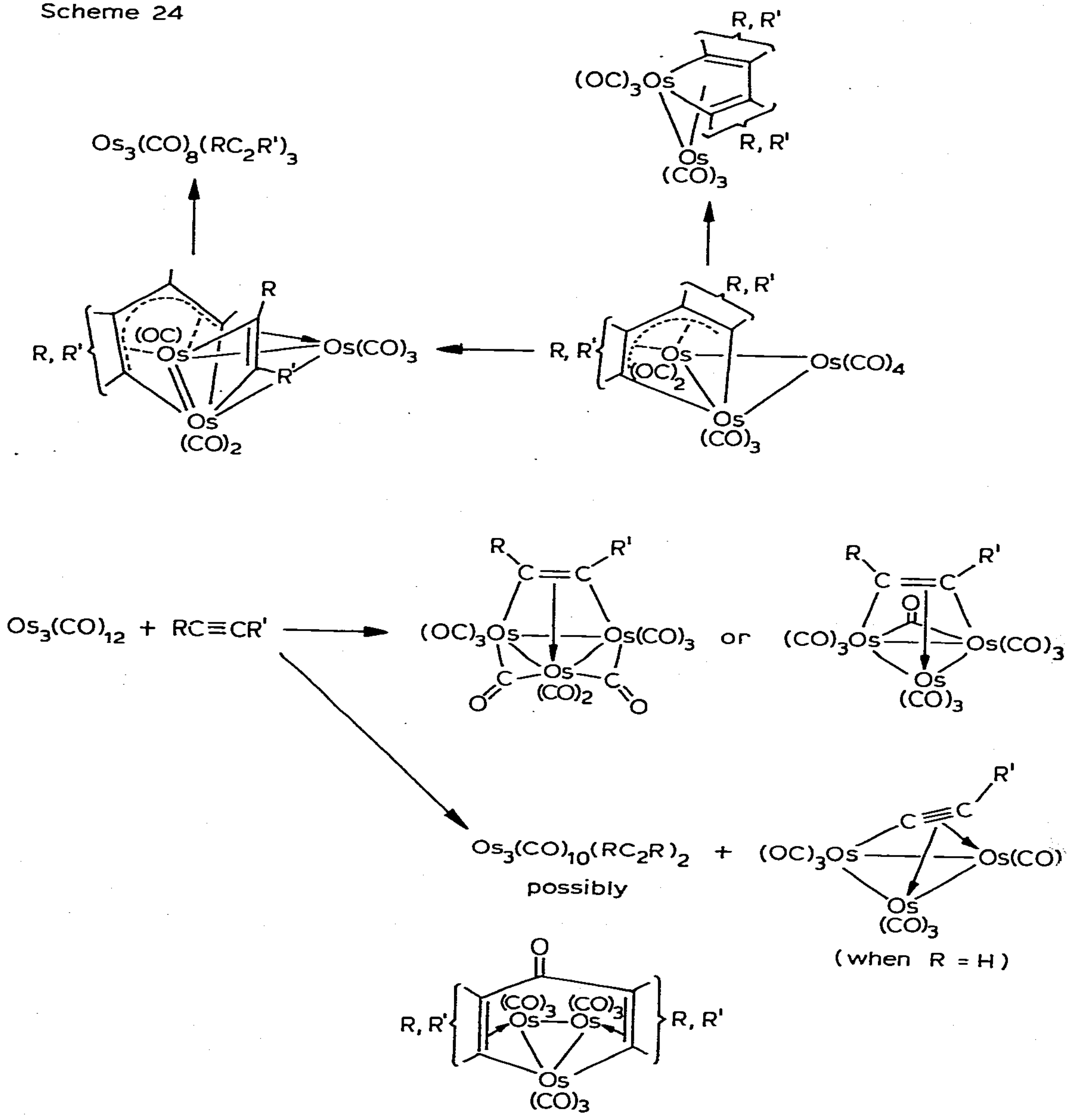
Scheme 23



RC≡CR' (R, R' = Me, Et, Bu^n, H), Os$_3$(CO)$_{12}$ afforded (192) a few compounds analogous to those illustrated in Scheme 23, but others produced by the di- or tri-merisation of the acetylene were also formed (Scheme 24). While M$_3$(CO)$_{12}$ (M = Ru or Os) reacted with Bu^{t}C$_2$H giving (193) M$_3$(CO)$_9$H(C$_2$Bu^t) and M$_3$(CO)$_9$(HC$_2$Bu^t), with RSH (R = CHMeEt or Bu^t), the species Ru$_3$(CO)$_9$H(SR), M$_3$(CO)$_{10}$H(SR) and M$_3$(CO)$_{10}$(HSR) were produced. The structure of Os$_3$(CO)$_{10}$H(CH=CEt), [155], was determined crystallographically (194) [Os(1)-(2) 2.86, Os(1)-(3) 2.92 and Os(2)-(3) 2.83 Å].

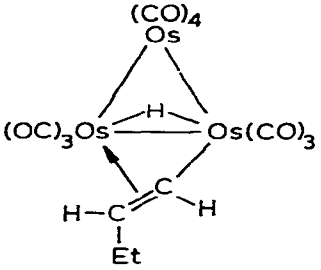
Ethyl acrylate and vinyl acetate reacted (195) faster than ethylene with Os$_3$(CO)$_{10}$H$_2$ whereas propene and isobutene reacted more slowly, and cyclooctene and norbornene

Scheme 24



not at all. The products of these reactions were alkanes and $Os_3(CO)_{10}H(alkenyl)$. With one equivalent of diethyl fumarate or maleate, ethylacrylate, ethyl diazoacetate and maleic anhydride, the complexes [156] (R = Et, R' = CH_2CO_2Et, Me or H) and [157] were formed. These compounds decomposed in solution giving alkanes, and in the absence of other substrates, afforded other Os-containing products. In the presence of olefins, however, decomposition of [156] or [157] gave $Os_3(CO)_{10}H(alkenyl)$ (alkene = C_2H_4, C_3H_6, isobutene or hexene). With styrene, $Os_3(CO)_{10}H(CH{=}CHPh)$ was formed, although styrene does not react directly with $Os_3(CO)_{10}H_2$. While tri-osmium clusters containing 2,2-disubstituted alkenyl groups, e.g. $Os_3(CO)_{10}H(CH{=}CMe_2)$, can be obtained only very slowly from $Os_3(CO)_{10}H_2$, and cannot be produced from this dihydride and alkyne, they are readily formed by reaction of the appropriate olefin with [156]. Diethyl fumarate and ethyl acrylate can be catalytically hydrogenated by $Os_3(CO)_{10}H_2$, although the catalyst is slowly destroyed by side reactions.

Treatment of $Os_3(CO)_{10}H(CH{=}CH_2)$, [154], with PMe_2Ph afforded (196) the zwitterionic species [158]. The structure of this compound was confirmed (197) by X-ray crystallography (bridged Os-Os bond 2.80 Å, others 2.87 Å), and it was noted that similar complexes were produced with PBu^n_3 and $P(OMe)_3$, but not with PPh_3, $AsMe_2Ph$, pyridine, NEt_3 or $NHEt_2$. $Os_3(CO)_{10}H[CHCH_2P(OMe)_3]$ was almost completely dissociated in solution after 8 hours, unlike [158] which remained stable. However, this complex decomposed in refluxing hexane giving $Os_3(CO)_{10}(PMe_2Ph)_2$, ethylene and regenerated [154]. This last was also formed by reaction of [157] with methyl iodide, the byproduct being $[PMe_3Ph]I$. With pyridine, [154] afforded [159]. While $Os_3(CO)_{10}H(C_2Ph)$ reacted with PMe_2Ph giving [160] or [161], $Os_3(CO)_{10}(MeC_2Me)$ did not. The species $Os_3(CO)_9H(MeCCHCH)$, $Os_3(CO)_9H(MeCCCH_2)$, $Os_3(CO)_9H(EtPCH{=}CH_2)$ and $Os_3(CO)_9H_2(C{=}CH_2)$ also reacted with PMe_2Ph giving zwitterionic species.



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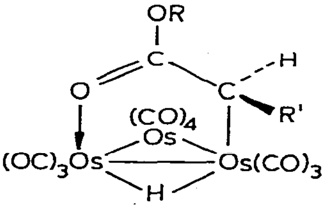

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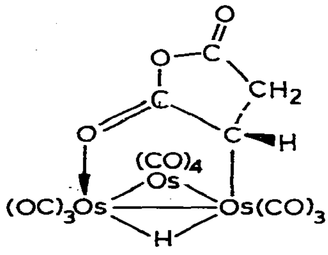

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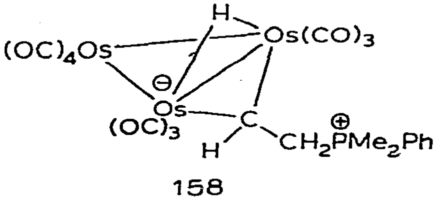

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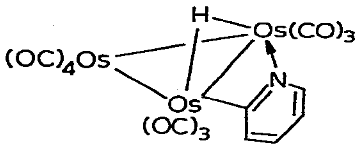

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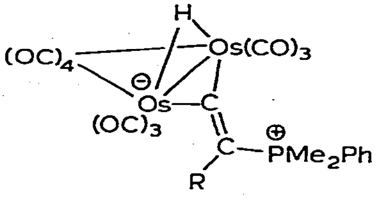

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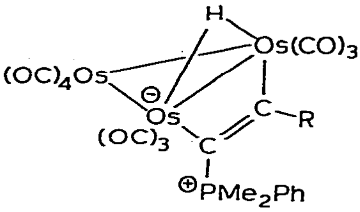

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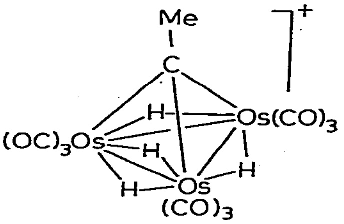
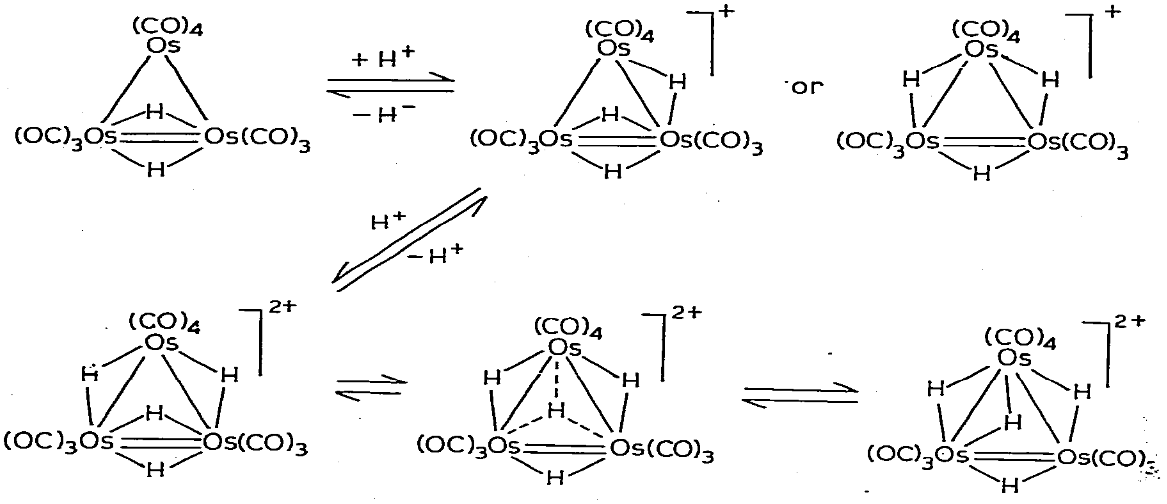
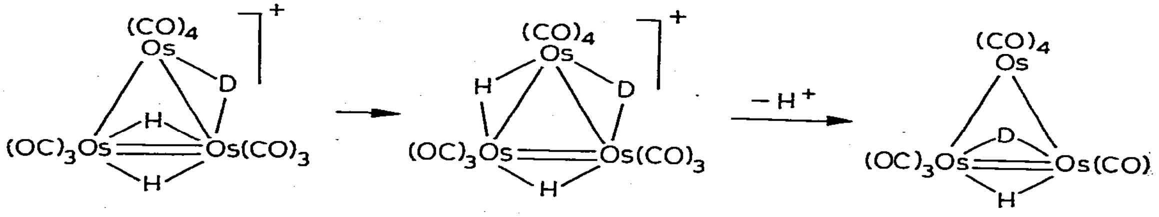


162

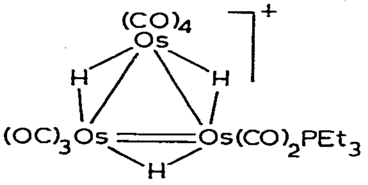
Scheme 25



Scheme 26



The protonation and hydrogen transfer processes of a variety of the alkene and alkyne derivatives of $Os_3(CO)_{12}$ and $Os_3(CO)_{10}H_2$ have been investigated (198). Thus, while $Os_3(CO)_9H_3(CMe)$ is not protonated in CF_3CO_2H, it is in HSO_3F giving [162]. Under similar conditions, $Os_3(CO)_{10}H_2$ afforded $[Os_3(CO)_{10}H_3]^+$ and $[Os_3(CO)_{10}H_4]^{2+}$, the former being stereochemically rigid in contrast to the latter (Scheme 25). Exchange of hydrogen and deuterium is catalysed by $Os_3(CO)_{10}H_2$ (Scheme 26). Protonation of $Os_3(CO)_9LH_2$ (L = Cl, PEt_3, PPh_3 or $AsPh_3$) gave $[Os_3(CO)_9LH_3]^+$, probably [163], while $Os_3(CO)_{10}H(CH{=}CHPh)$ was converted to $[Os_3(CO)_{10}H_2(CH{=}CHPh)]^+$, [164]. $Os_3(CO)_{10}$-(HC_2Me) in acid solution gave a mixture of two isomers, [165] (a and b). It was concluded that (i) the protonation of these Os_3 clusters occurred readily in CF_3CO_2H provided that there was an available Os-Os edge, (ii) disproportionation could occur at an occupied edge but only in strong acid, (iii) in all cases, protonation occurred on a metal or metal-metal bond, and (iv) that in a cluster containing more hydride ligands than polyhedral edges, low-energy fluxional behaviour could occur, indicating



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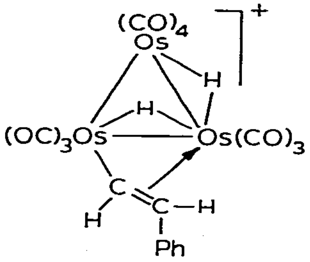

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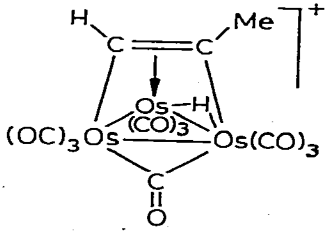

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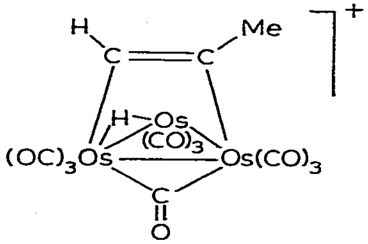

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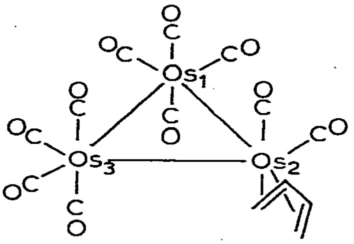

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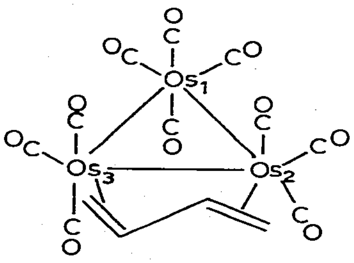

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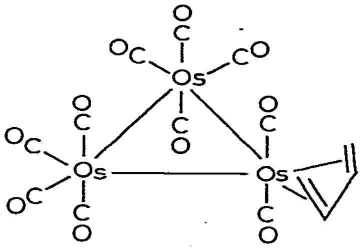


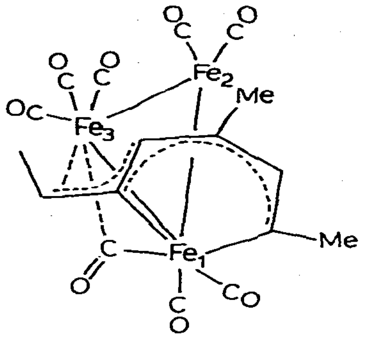
168

that filled edge ⟶ vacant edge H transfer is not the only mechanism for H atom site transfer.

An excess of diene reacted (199) with $Os_3(CO)_{10}H_2$ giving two isomeric species $Os_3(CO)_{10}$(diene), [166] and [167] (diene = 1,3-butadiene or -cyclohexadiene, 2-methyl- and 2,3-dimethyl-1,3-butadiene, and trans, trans-2,4-hexadiene). The structures of these two species were elucidated crystallographically, and for [166] Os(2)-(3) = 2.88 Å while Os(1)-(3) and Os(1)-(2) = 2.86 Å, respectively. For [167], Os(2)-(3) = 2.93 Å while the other distances were 2.86 Å. The ambient ^1H n.m.r. spectrum of [166] (butadiene) was very similar to that of $Fe(CO)_3$(S-cis-butadiene), but a low temperatures, two interconverting, almost equally populated conformers, one symmetrical (possibly [168]) and the other unsymmetrical, were observed. The ^1H n.m.r. spectrum of the other species also exhibited the presence of these conformers.

Reaction of $Fe_3(CO)_{12}$ with MeC_2H gave 14 products, including $Fe_3(CO)_8(C_9H_{12})$, [169], whose structure was determined crystallographically (200). The unsymmetrical Fe_3 triangle is bound to an organic ligand derived by the trimerisation of methylacetylene, Fe(1) being attached by two σ-bonds, Fe(2) by an η^2-C_2 group and Fe(3) by an η^5-fragment. The intermetallic distances are Fe(1)-(2) = 2.59, Fe(1)-(3) = 2.54 and Fe(2)-(3) = 2.71 Å, respectively, and there is an asymmetric carbonyl bridge between Fe(1) and Fe(3). It was suggested that a hydride ligand was located on the Fe(2)-(3) bond, otherwise Fe(2) would have an odd electron configuration, and the molecule would be paramagnetic (which it is not). The structure of $Ru_3(CO)_6(C_{13}H_{20}O)(C_{12}H_{20})$, [170], obtained by reaction of ruthenium carbonyls with Bu^tC_2H, has been established (201) by X-ray techniques. The compound contains an isoceles Ru_3 triangle (Ru(1)-(2) and Ru(1)-(3) = 2.82-2.83 Å, Ru(2)-(3) = 2.67 Å), and one of the hydrocarbon ligands ($C_{13}H_{20}O$) is defined as two molecules of t-butylacetylene joined by CO, whereas the other ligand ($C_{12}H_{20}$) is derived from a head-to-tail attachment of the two alkyne molecules, with a hydrogen shift. The structure of $Os_3(CO)_{10}(PhC_2H)_2$, [171], obtained (202) by reaction of $Os_3(CO)_{12}$ with PhC_2H, has also been determined (203), again revealing the linkage of two acetylene fragments via a CO group.

Isomerisation of pent-1-ene to a mixture of cis- and trans-pent-2-ene was catalysed (204) by $Ru_3(CO)_{12}$. The conversion rate was increased by addition of acid, and it was thought that a π-allylic intermediate was involved in the mechanism. Dehydrogenation of pent-1-ene by $Ru_3(CO)_{12}$ gave an equilibrium mixture of $Ru_3(CO)_9(C_8H_{10})$ (not identified), two isomeric species, [172] and [173] (R = R' = Me), $Ru_4(CO)_{12}H_4$ and $Ru_4(CO)_{13}H_2$. The structural assignments of [172] and [173] were based on previous and recent crystallographic studies (205,206) of the products obtained from $Ru_3(CO)_{12}$ and hexadienes. From kinetic measurements, it was established that the rate determining step in the olefin isomerisation reaction is dissociation of CO from $Ru_3(CO)_{12}$. The acceleration of isomerisation by acid implied the formation of $[Ru_3(CO)_xH_y]^{v+}$ in which the Ru-CO bonds were weakened, but since there was no scrambling between pentene hydrogen atoms and $MeCO_2D$, it was concluded that a metal-hydride + olefin addition-elimination reaction did not occur. As mentioned



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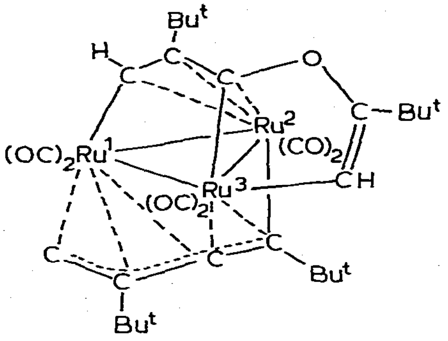

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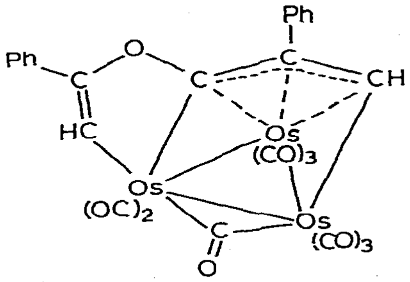

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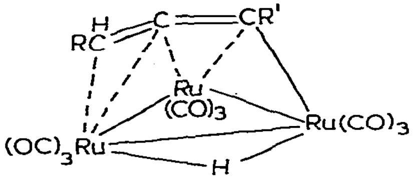

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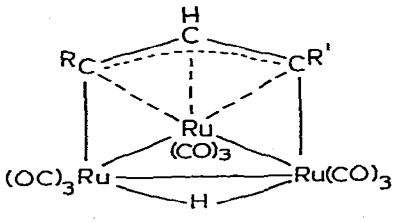

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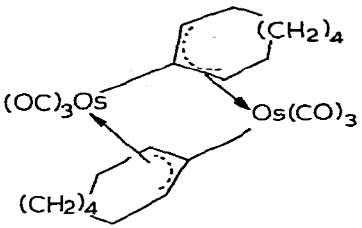

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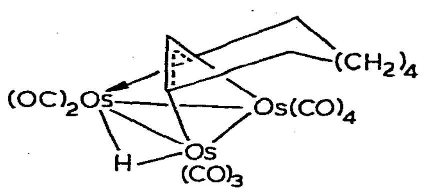
above, the structures of two products obtained from the reaction of $Ru_3(CO)_{12}$ and hexadiene isomers, $Ru_3(CO)_9H(C_6H_9)$, [172] and [173] (R = Me, R' = Et), have been elucidated (205, 206). For [172] (R = Me, R' = Et), Ru(1)-(2) = 2.99 Å while Ru(1)-(3) and Ru(2)-(3) = 2.77 and 2.74 Å, respectively, and the hydrocarbon ligand is regarded as a distorted π-bonded allene.

Cyclonona-1,2-diene reacted (207) with $Os_3(CO)_{10}H_2$ giving $Os_2(CO)_6(C_9H_{14})_2$ and $Os_3(CO)_9H(C_9H_{13})$. The former was identified crystallographically as [174] (Os-Os 3.63 Å; non-bonding) whereas the latter may be either [175] or [176]. The species [174] is distinctly different to its iron isomer [177] which was described earlier (208).



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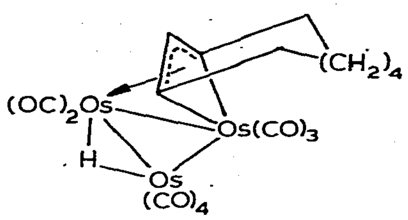

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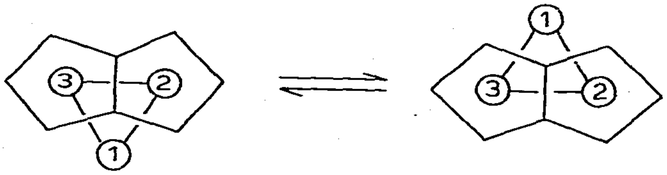
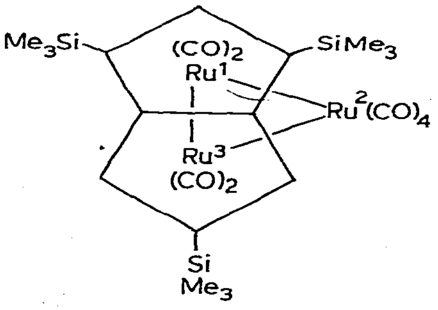
In a previous study, it was shown (209) that $Ru_3(CO)_8(C_8H_6)$ and $Ru_3(CO)_8[1,5\text{-}(Me_3Si)_2C_8H_4]$ contained pentalene ligands directly bound to only two metal atoms of the Ru_3 triangle. The first species was fluxional according, it was proposed, to Scheme 27, whereas the second could not be fluxional because of the unsymmetrical nature of the ligand and the lack of a degenerate rearrangement as shown in Scheme 27.

Scheme 27



However, $Ru_3(CO)_8[1,3,5\text{-}(Me_3Si)_3C_8H_3]$, which does contain a symmetrical pentalene ligand, was obtained (210) as two isomers, [177] (Ru(1)-(3) = 2.93 Å, Ru(1)-(2) = 2.83 and Ru(2)-(3) = 2.81 Å) and [178] (Ru(1)-(2) = 2.79, Ru(1)-(3) = 2.85 and Ru(2)-(3) = 2.86 Å). Both are fluxional and interconvert in solution, and because of this, and in view of the structures of these two species, there has been a major reassessment of the v.t.n.m.r. spectral characteristics of other pentalene Ru_3 species. Hence, by a combination of reversible edge-to-face isomerisation and fluxional oscillation of the Ru_3 triangle, the C_8 ring can move over all faces and edges of the Ru_3 triangle (Scheme 28).



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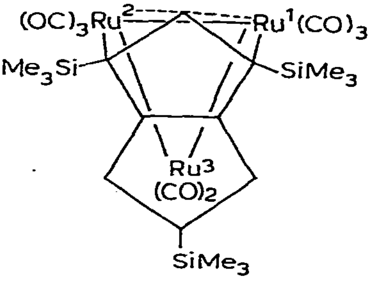

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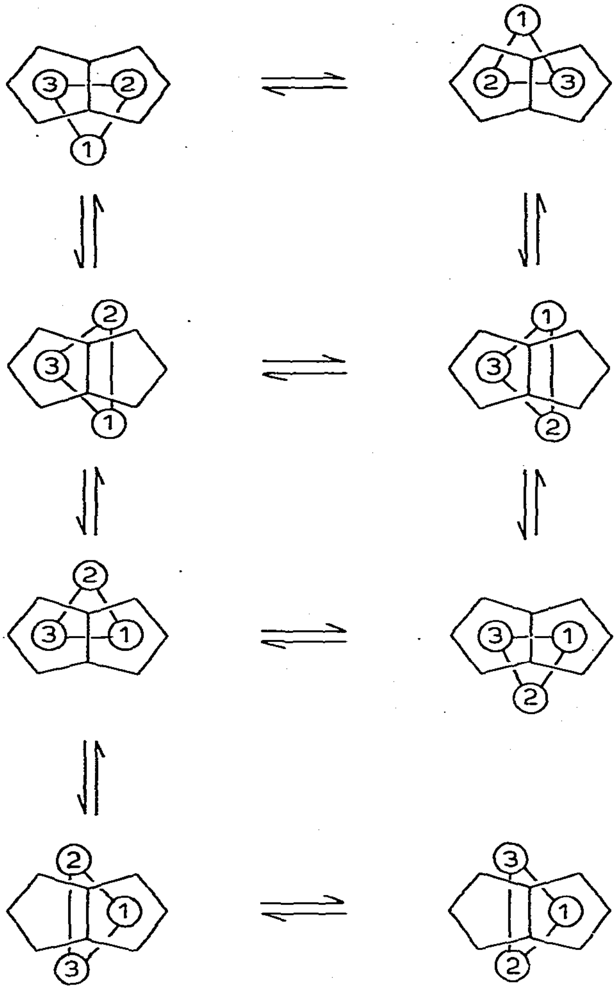
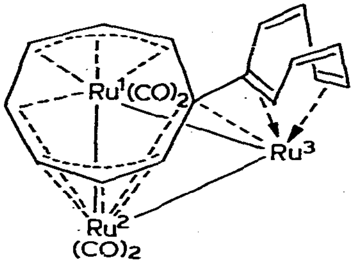
Scheme 28



A minor product of the reaction between $Ru_3(CO)_{12}$ and phenylcyclooctatraene has been characterised crystallographically (211) as [179] (Ru(1)-(2) = 2.99, Ru(2)-(3) = 2.80 and Ru(1)-(3)-2.89 Å). One of the C_8 rings has a bis-η^3-allyl attachment to the Ru(1) and Ru(2) atoms with two formally "bridging" C atoms, one of which is also involved in bonding to Ru(3). The complex can be obtained in higher yield by treating $Ru_3(CO)_{12}$ with bicyclooctatetraenyl, $(C_8H_7)_2$. Reaction of $Fe_2(CO)_9$ with $(C_8H_7)_2$ gave $Fe(CO)_3(C_8H_8)$, $Fe_2(CO)_6(C_8H_8)$ and $Fe(CO)_2(C_{16}H_{14})$, [180] (X-ray structure determined). Treatment of [180] with L (PPh_3 or CO) caused reversible displacement of one olefinic bond and formation of [181], and hydrogenation afforded $Fe(CO)_2(C_{16}H_{18})$, $Fe(CO)_2(C_{16}H_{16})$ and two other unidentified complexes. The related osmium complex $Os(CO)_2(C_{16}H_{14})$ was obtained directly from $Os_3(CO)_{12}$ and $(C_8H_7)_2$. Bicyclooctatetraenyl reacted with $[Ru(CO)_4SiMe_3]_2$ giving the fluxional $Ru_2(CO)_4(C_{16}H_{14})(SiMe_3)_2$, [182].



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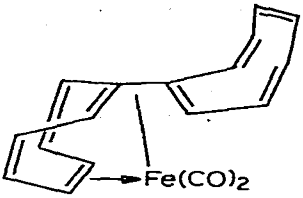

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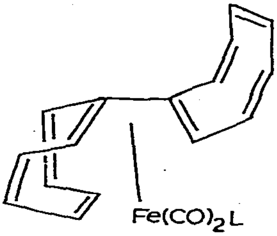

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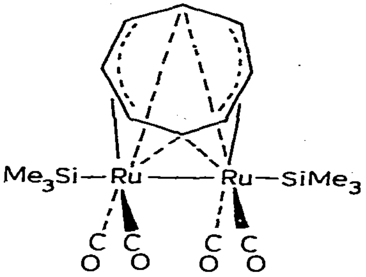

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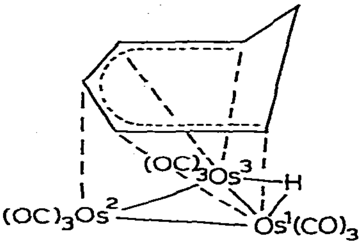
The complexes [183] and [184] (major product) were obtained (212) by treatment of $Os_3(CO)_{10}H_2$ with cyclohexa-1,3-diene. The structure of [183] was elucidated by X-ray methods and it was established that the five C atoms of the pentadienyl fragment are planar and slope away from the Os_3 isoceles by 33° (Os(1)-(3) = 3.05, Os(1)-(2) and Os(2)-(3) = 2.86 Å). It was also noted that the Os(2)-C(3) distance was significantly shorter than the other contacts, and is similar to other Os-C σ-bonds. It was shown that [184], which is presumably similar to [166] or [168] (163), is not an intermediate in the formation of [183]. Treatment of [183] with $[Ph_3C]^+$ afforded the unstable complex [185].



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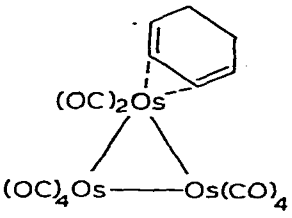

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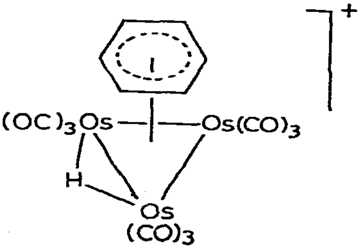
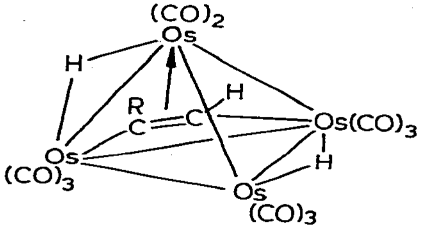


185

Polynuclear clusters

Reaction of $Os_4(CO)_{12}H_4$ with $RCH{=}CH_2$ gave (213) $Os_4(CO)_{11}H_3(RCH{=}CH)$, [186] (R = H, Bu^t or Ph) and $Os_4(CO)_{11}H_2(RC_2H)$ [187]. The latter could also be produced by photolysis of $Os_4(CO)_{12}H_4$ in the presence of alkenes, and on heating it is converted into [186]. On heating [186], however, decomposition occurred and $Os_4(CO)_{12}H_4$ and Os metal were formed.

The structure of $Os_5(CO)_{16}$, [188], obtained by pyrolysis of $Os_3(CO)_{12}$ (214) has been established (215) crystallographically. The metal-metal bond distances range between 2.74 and 2.89 Å, and the bond lengths to the $Os(CO)_4$ group are significantly larger than the other intermetallic distances. This slight distortion towards a capped butterfly arrangement presumably reflects a difference in electron density associated with the $Os(CO)_4$ and $Os(CO)_3$ units.



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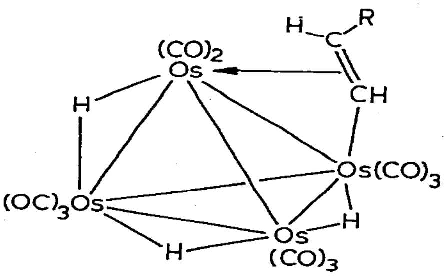

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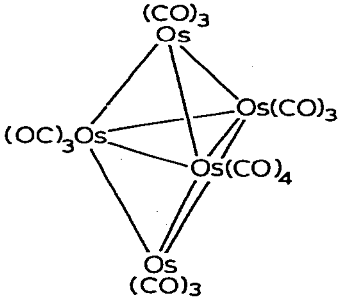

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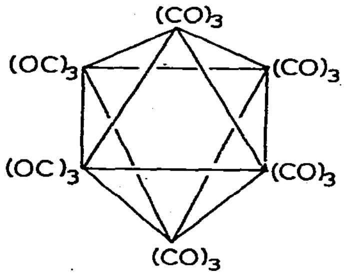
Reduction of $Os_6(CO)_{18}$ by $NaBH_4$ gave (216) $[Os_6(CO)_{18}H]^-$, [189], and with activated zinc, sodium amalgam or $[Bu^n{}_4N]I$, $[Os_6(CO)_{18}]^{2-}$, [190], was formed. On acidification of $[Os_6(CO)_{18}]^{2-}$, the dihydride $Os_6(CO)_{18}H_2$, [191], was produced. The addition of electrons (and protons) to the Os_6 cage resulted in a change from a bicapped tetrahedral geometry (C_{2v}) in $Os_6(CO)_{18}$ to an octahedral structure in [190]. The species [191] has a monocapped square pyramidal structure, unlike that of $Ru_6(CO)_{18}H_2$ (217). In [189], the metal-metal distances range from 2.81 to 2.89 Å, while in [190] they vary from 2.85 to 2.98 Å, the longer distances being associated



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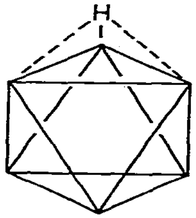

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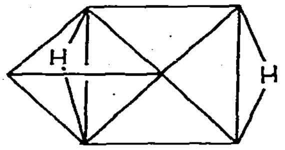
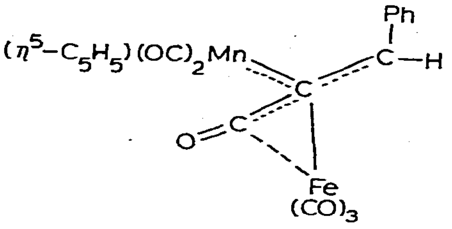


191

with the triangular face carrying a bridging H atom. In [191], the Os-Os distances range from 2.81 to 2.89 Å, and the structural changes incurred on addition of electrons to the Os_6 cage can be rationalised in terms of Wade's theory (218).

Heterometallic clusters

Reaction of $Fe(CO)_4(THF)$ with $PCo_3(CO)_9$ gave (219) $(OC)_4FePCo_3(CO)_9$. Treatment of $Fe_2(CO)_9$ with $Mn(\eta^5-C_5H_5)(CO)_2(C{=}CHPh)$ afforded (220) the heterobimetallic species [192]. Crystallographic studies revealed that the Fe atom is covalently bound to a C atom of the phenylmethylene group, the C atom of a bridging CO ligand, the Mn and central C atoms of the organomanganese ligand. The Fe-Mn distance (2.76 Å) is short in comparison to other Fe-Mn bonds (2.80 - 2.85 Å). Reaction of $Fe_2(CO)_9$ with $Mn(\eta^5-C_5H_5)(CO)_2(PPhCl_2)$ gave (221) [193]. In this, the Mn atom is coplanar with the P atom, the phenyl C atom which attached to it, and Fe(1). The metal-metal distances are relatively long (Fe(1)-(2) 2.74 Å (perhaps non-bonding), Mn-Fe(2) = 2.94 Å). The closely related species [194] has also been described (222).



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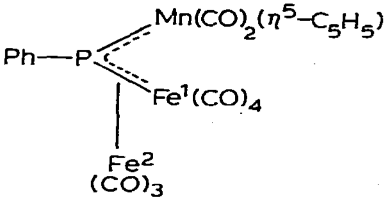

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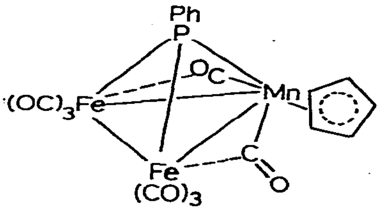


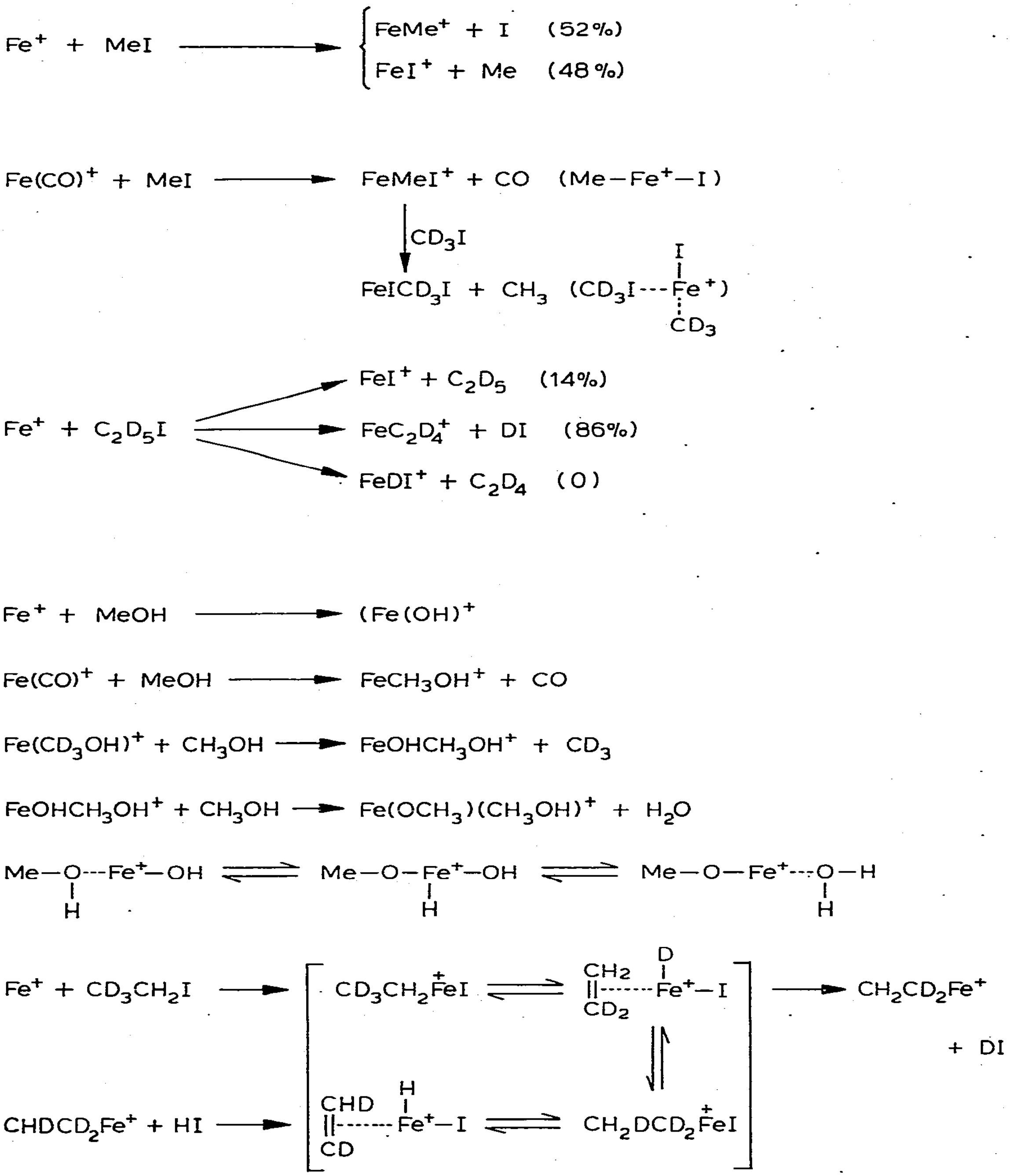
191

METAL-CARBON AND SILICON σ-BONDED SPECIES

Metal alkyl complexes

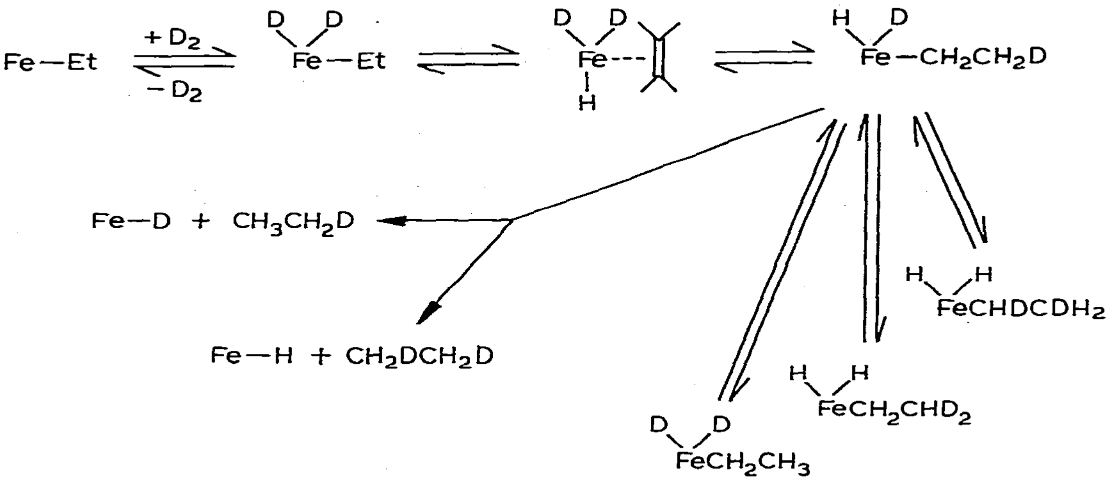
Bimolecular ion-molecule reactions between iron and alkyl halides or alcohols have been extensively investigated (223). The results are summarised in Scheme 29.

Scheme 29

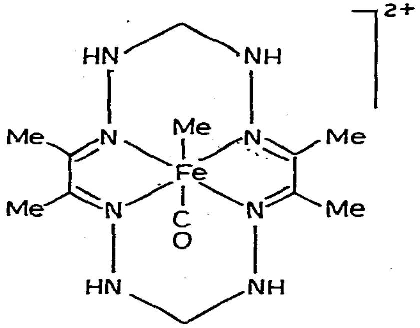


The structure of [195] has been established crystallographically (224) and it was noted that because of the trans influence, the Fe-CH_3 bond length was longer than expected. Reaction of Fe(bipy)$_2$Et$_2$ with deuterium afforded (225) the complete range of ethanes $C_2H_{6-n}D_n$ (n = 0 - 6). It was thought that partial dissociation of bipy was necessary before these exchange processes would occur, the various mechanisms being summarised in Scheme 30. It was also noticed that some H/D exchange occurred in the bipy ligand, but this was absent in the species Fe(bipy)L_4 (L = maleic anhydride) and Fe(bipy)$_2X_2$ (X = Cl or CN).

Scheme 30



Reduction of Fe(acac)$_3$ by AlMe$_2$(OEt) in the presence of diphos ($Ph_2PCH_2CH_2PPh_2$) gave (226) Fe(diphos)$_2$Me$_2$. In solution, this species evolved methane and was converted into [196]. Other reactions of Fe(diphos)$_2$Me$_2$ are given in Scheme 31. It was proposed that the production of deuteriated ethylenes when Fe(diphos)$_2$Me$_2$ was thermally decomposed in CD_2Cl_2 occurred via carbene intermediates (Scheme 32). Reduction of Fe(acac)$_3$ by AlMe$_2$(OEt) in the presence of PMe$_2$Ph afforded Fe(PMe$_2$Ph)-(acac)$_2$Me which reacted with CO giving acetone.



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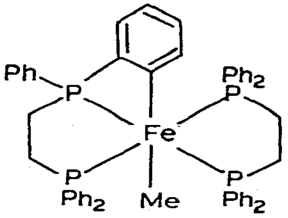

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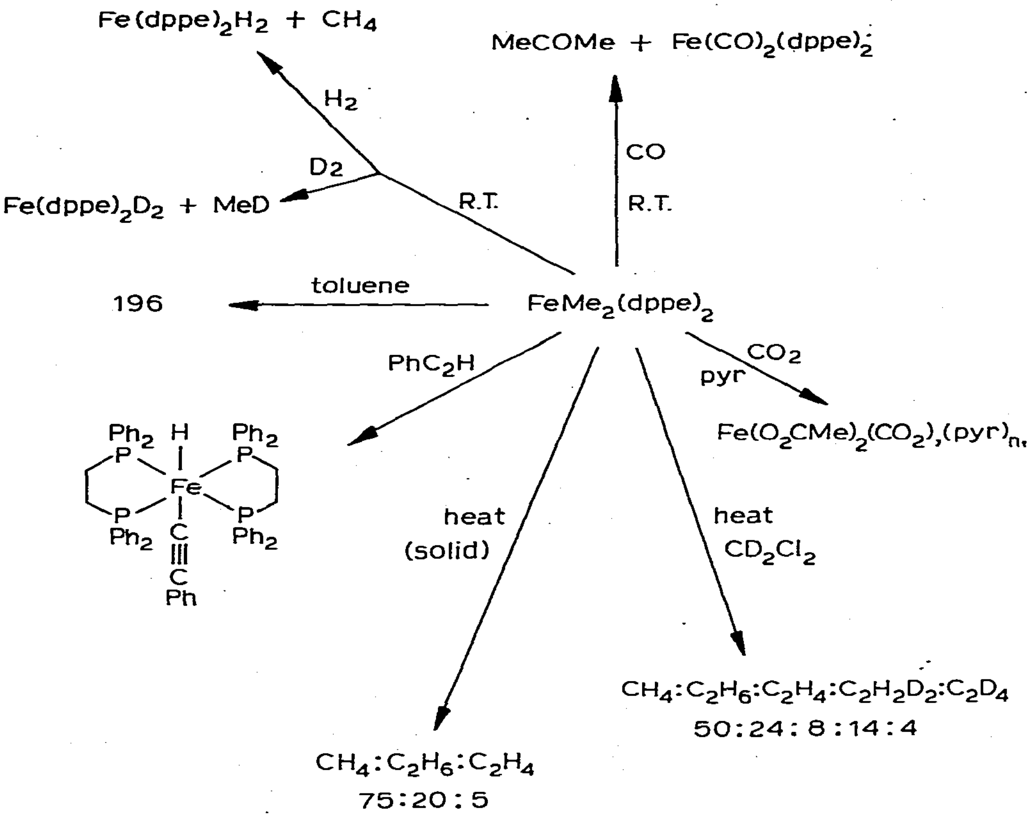
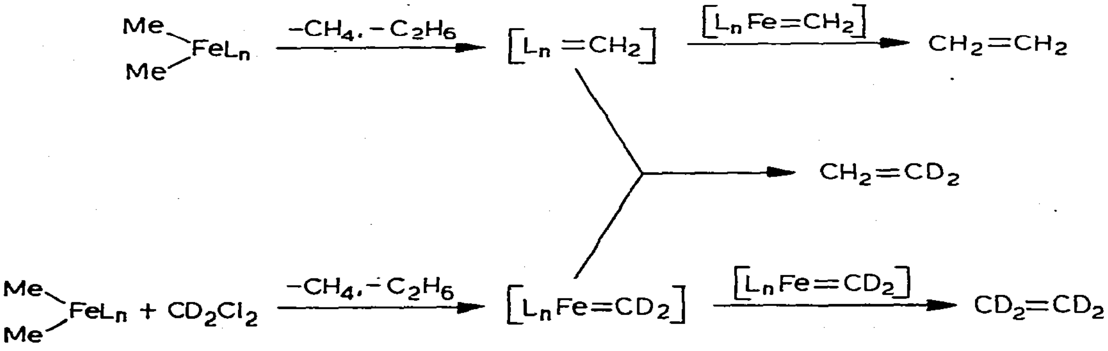
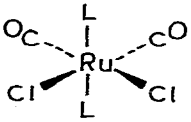
Scheme 31



Scheme 32



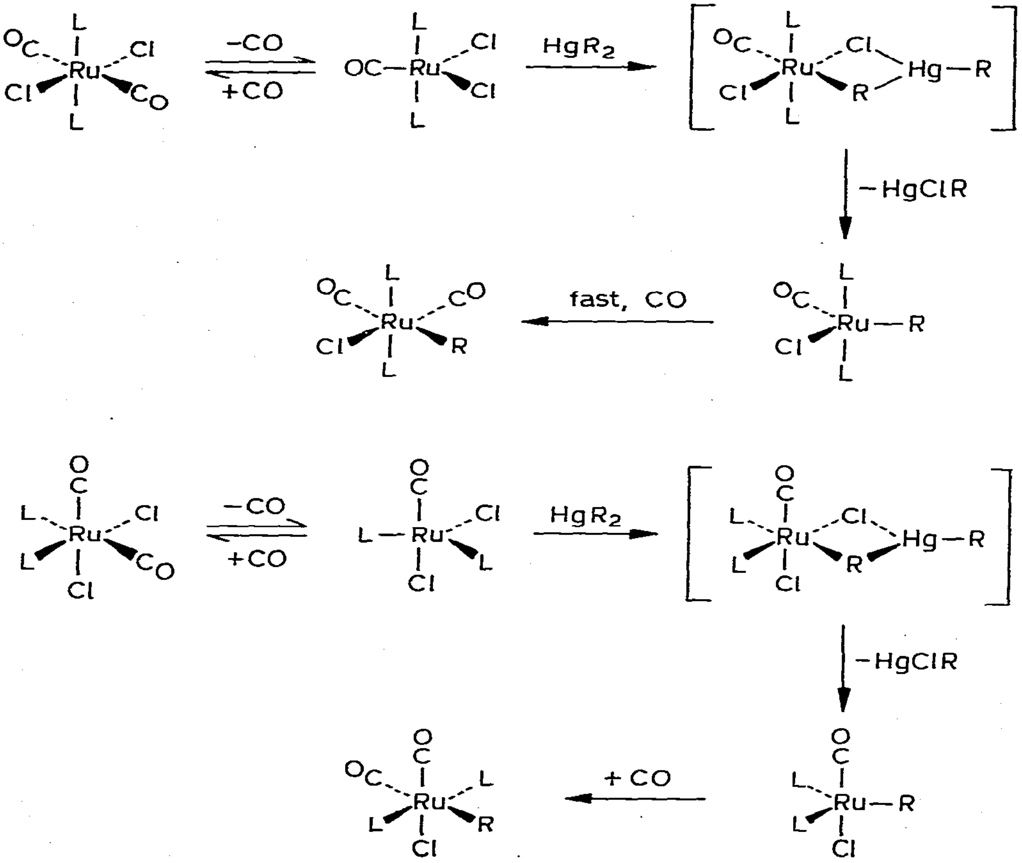
A series of mono-alkyl and -aryl complexes have been prepared (227) by treating various isomers of $Ru(CO)_2L_2Cl_2$ (L = PMe_2Ph or $PMePh_2$) with HgR_2 (R = Me, Et or Ph) or $SnMe_4$. The mechanisms of formation of alkyl species from the all-*trans* and all-*cis* isomers are shown in Scheme 33, and it was observed that [197] did not react



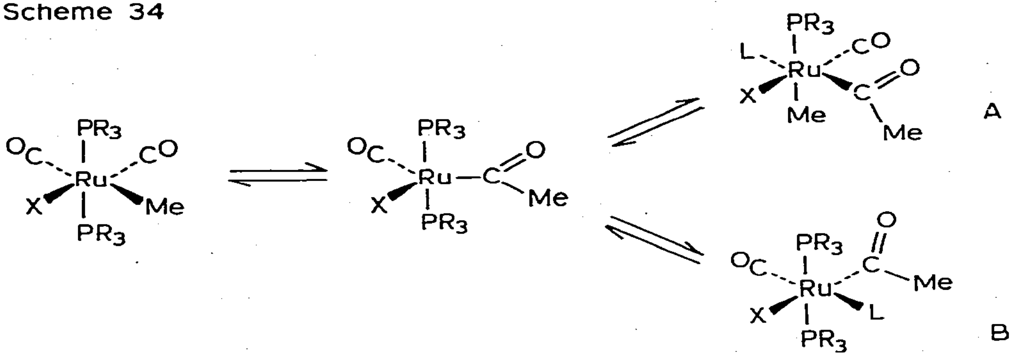
197

with HgR_2 or $SnMe_4$. In the reaction between $Ru(CO)(PMe_2Ph)_3Cl_2$ and HgR_2, giving $Ru(CO)(PMe_2Ph)_3ClR$, the transfer of alkyl or phenyl ligand between Hg and Ru was reversible. The species $Ru(CO)_2(PMe_2Ph)MeX$ (X = Cl, Br or I) reacted rapidly and reversibly with CO giving (228) $Ru(CO)_2(PMe_2Ph)_2(COMe)X$ according to Scheme 34. When X = Cl, mainly isomer A was obtained, with X = Br an equilibrium mixture of A and B was produced, and when X = I, isomer B only was isolated.

Scheme 33



Scheme 34



Methylation of $Na_2Os(CO)_4$ afforded (229) $Os(CO)_4Me_2$ and no $[Os(CO)_4Me]^-$, but treatment of $[Os(CO)_4H]^-$ with methylating agents (e.g. $MeSO_3F/CF_3CO_2H$) afforded a mixture of $Os(CO)_4H_2$, $Os(CO)_4HMe$ and $Os(CO)_4Me_2$ (1:2:1) according to the following reactions:

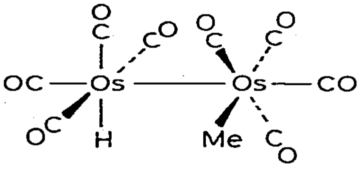
$$[Os(CO)_4H]^- + MeX \longrightarrow Os(CO)_4HMe + X^-$$

$$[Os(CO)_4H]^- + Os(CO)_4HMe \longrightarrow Os(CO)_4H_2 + [Os(CO)_4Me]^-$$

$$[Os(CO)_4Me]^- + MeX \longrightarrow Os(CO)_4Me_2 + X^-$$

The hydrido methyl complex slowly decomposed in the absence of heat and light yielding methane (but no CO); $Os_2(CO)_8HMe$, [198] and $Os_3(CO)_{12}Me_2$, [199]. The hydrido methyl dimer reacted with CCl_4 giving $ClOs(CO)_4Os(CO)_4Me$.

Treatment of $Fe(CO)_4(n\text{-}C_3F_7)I$ with $AgPF_6$ in acetonitrile gave (230) $[Fe(CO)_2(NCMe)_3(C_3F_7)][PF_6]$, [200] (a or b). Although there was no confirmatory evidence, the isomer a was preferred. It was noted that the two mutually equivalent MeCN groups were noticeably less labile than the unique acetonitrile ligand. Thus, ex-



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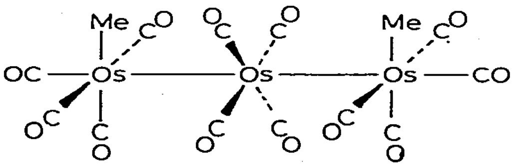

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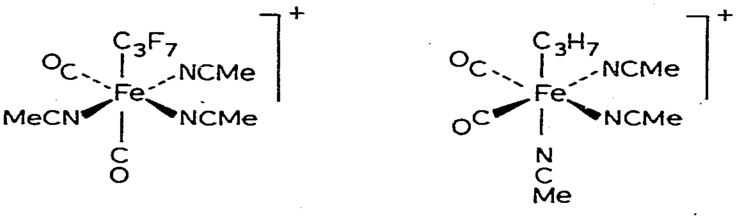
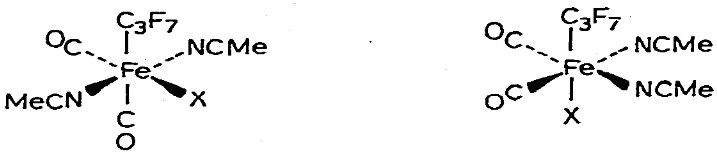


a

b

200

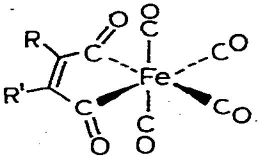
change with CD_3CN occurred exclusively with the unique nitrile group, and treatment with L (PPh_3, $AsPh_3$; $P(OR)_3$, R = Me, Et or Ph) gave [201] (a or b; a again preferred) With diphos and with KI, [200] afforded $[\{Fe(CO)_2(NCMe)_2(C_3F_7)\}_2(diphos)]^{2+}$ and $Fe(CO)_2(NCMe)_2(C_3F_7)I$ respectively. *Cis*- and *trans*-isomers of $Fe(CO)_4(CF{=}CFCF_3)I$ have been detected (231).



a

b

201



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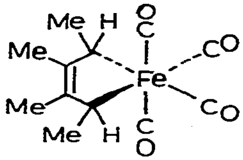

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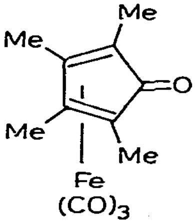

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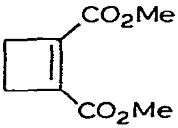

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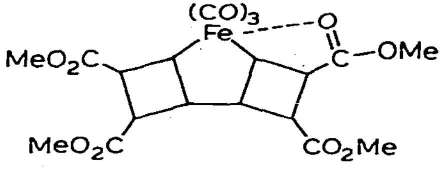

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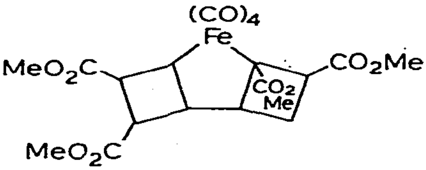

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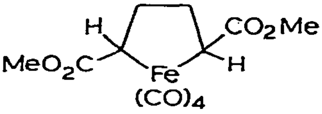


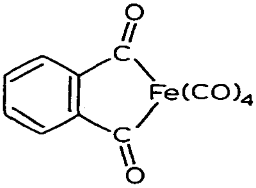
208

Metallocyclic species

Photolysis of $Fe(CO)_5$ and dimethylacetylene in THF (232) has given [202] (R = Me, R' = C≡CMe) whose structure has been confirmed crystallographically (233). In cyclohexane the same reaction afforded $Fe(CO)_4(Me_4C_4)$, thought to be either [203] or [204]. When heated together, $Fe(CO)_5$ and the acetylene gave the ferrocyclopentadiene species [204] (R, R', R" = Me, C≡CMe).

Reaction of the cyclobutene [205] with $Fe_2(CO)_9$ at room temperature afforded [206] whereas under u.v. light, [207] was produced (234). Photolysis of $Fe(CO)_5$ with $CH_2{=}CHCO_2Me$ gave $Fe(CO)_4(CH_2{=}CHCO_2Me)$ and [208]. Reaction of the bicyclopentane species [209] (X = o-C_6H_4 or CH_2CH_2) with $Fe(CO)_5$ under u.v. light proceeded (235) according to Scheme 35. Photolysis of o-diiodobenzene and cis-2,3-dibromobut-2-ene in the presence of iron carbonyls afforded (236) [202] (R = R' = Me) and [209].

The mechanisms of the photochemically initiated reactions of the diazaferrole species [210] with PPh_3, diphenylacetylene and 2,3-dimethylbutadiene have been investigated (237) and are summarised in Scheme 36. The species [211] decomposed giving [212] and [213]. Alkylmethacrylates, $CH_2{=}CMeCO_2R$ (R = Me, Et, Pr^i or Bu^n) reacted (238) with $Ru(PPh_3)_4H_2$ or $Ru(C_2H_4)(PPh_3)_3$ giving [214] whose structure was established crystallographically. When $CHD{=}CMeCO_2Et$ was used, [214] partially deuteriated at the hydride, β-C and α-methyl positions was isolated. When ethyl methacrylate reacted with $Ru[P(C_6D_5)_3]_4D_2$, [214] in which only the triphenylphosphine ligands were deuteriated, was formed. Pyrolysis of [214] afforded methacrylate esters, small amounts of their hydrogenated derivatives and benzene (presumably derived from PPh_3). Similar treatment of the partially deuteriated [214] gave ethyl methacrylate (R = Et) in which 70% of the vinylic and α-methyl protons were deuteriated. Further, the o-positions of the PPh_3 ligands became deuteriated revealing an H/D exchange between the methacrylate ligand and PPh_3 perhaps via species like [215]. Reaction of [214] with H_2 gave alkyl isobutyrate and $Ru(PPh_3)_3H_4$, and with HCl, $CH_2{=}CMeCO_2Et$ and hydrogen were formed. With methyl iodide, however, an oxid-



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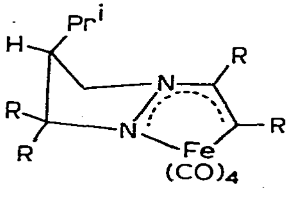

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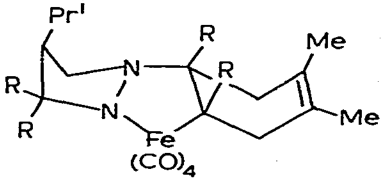

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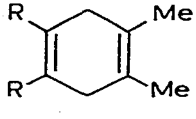

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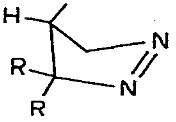

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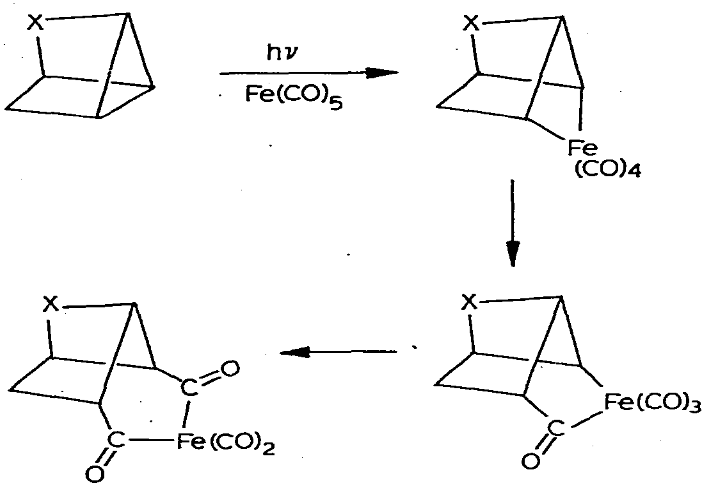
Scheme 35

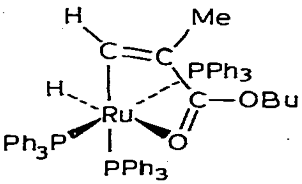


X = benzo, CH_2CH_2

ative addition followed by a series of reductive-eliminations occurred, as shown in Scheme 37. Reaction of $Ru(CO)(PPh_3)_3H_2$ with methyl propiolate (239) gave [216], possibly via H_2 elimination, giving $Ru(CO)(PPh_3)_3$, followed by oxidative addition and H migration, involving HC_2CO_2Me, viz. $[Ru(CO)(PPh_3)_3H(C_2CO_2Me)] \longrightarrow [Ru(CO)(PPh_3)_3(C{=}CHCO_2Me)]$.

Formyl, acetyl and related compounds.

Previously, salts of $[Fe(CO)_4CHO]^-$ had been obtained (240) by treatment of $Na_2Fe(CO)_4$ with acetic anhydride. However, this formyl salt may also be synthesised (241) in good yield by reducing $Fe(CO)_5$ with a salt of $[HB(OR)_3]^-$ (R = Me or Pr^i). Treatment of $[Fe(CO)_4CHO]^-$ with HCl in THF gave formaldehyde, and in the presence of of PPh_3, both $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$ were formed. It was implied that the $NaBH_4$-facilitated preparation of these phosphine complexes (242) could proceed via a formyl derivative. Reaction of $Fe(CO)_4[P(OPh)_3]$ with $KHB(OPr^i)_3$ gave trans-$[Fe(CO)_3\{P(OPh)_3\}(CHO)]$.



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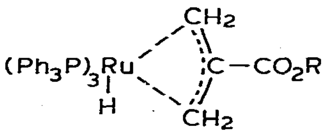

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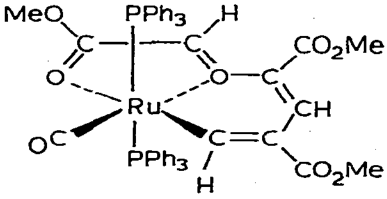

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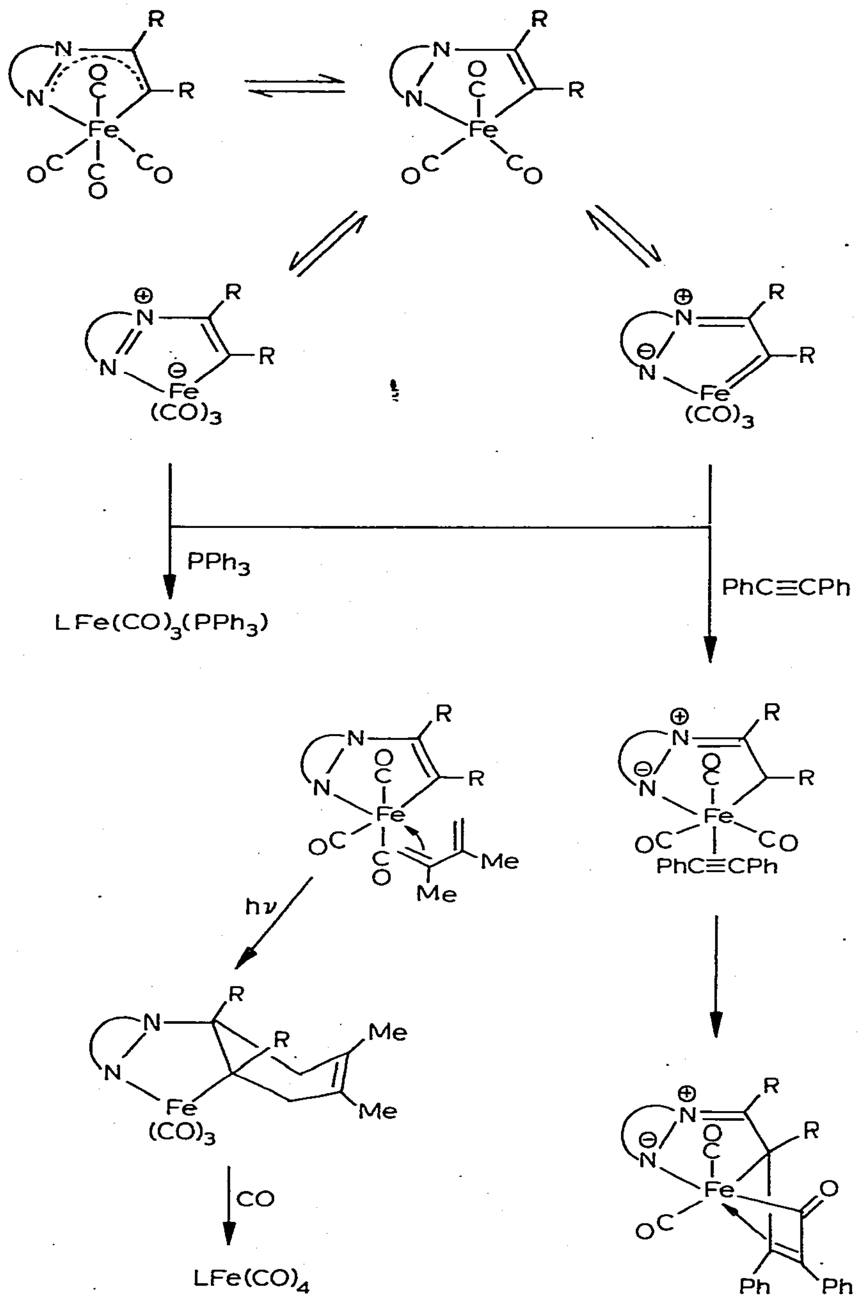
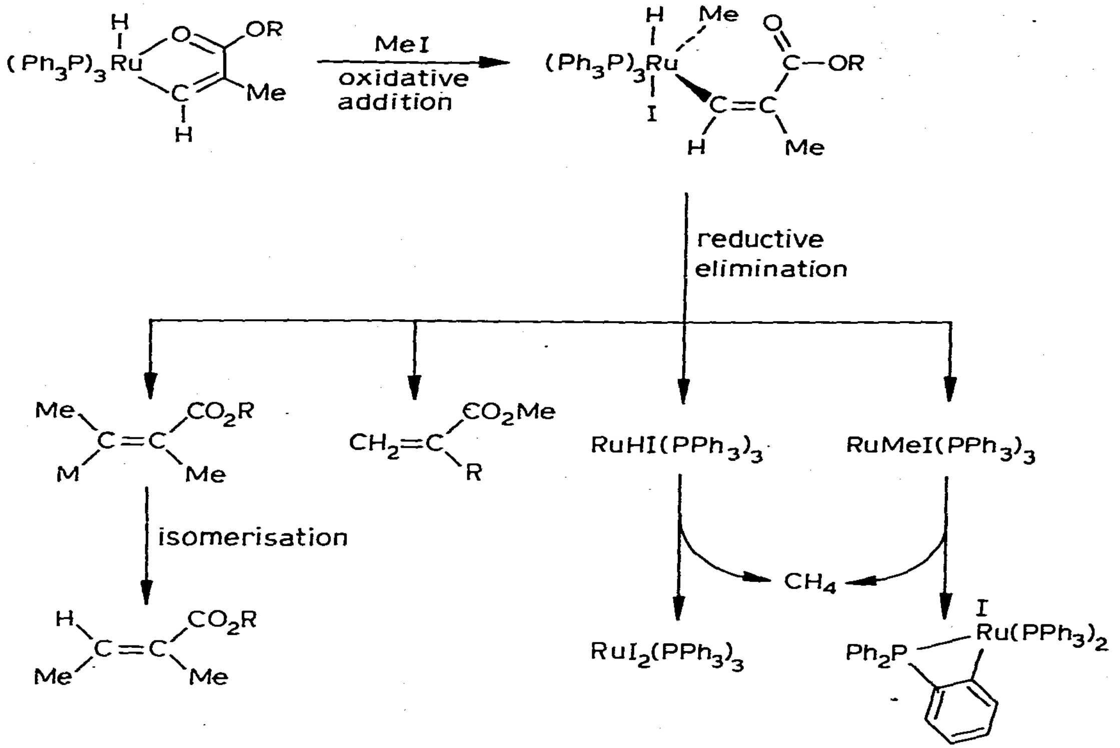
Scheme 36

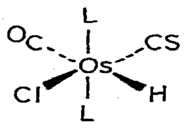


Scheme 37



Treatment of $Os(CS)(PPh_3)_3HCl$ with CO gave (243) $Os(CO)(CS)(PPh_3)_2HCl$, [217] and then the blue thioformyl complex [218]. The reactions of this compound with CF_3SO_3Me, followed by treatment with either $MeNH_2$ or OH^-, are given in Scheme 38. The formyl species [219] may be involved in the rapid reaction of $Os(CO)_3(PPh_3)_2$ with HCl which gave $Os(CO)_2(PPh_3)_2Cl_2$. It was previously suspected (244) that this reaction proceeded via $Os(CO)_2(PPh_3)_2HCl$, but this species is extremely inert towards HCl and so is unlikely to be involved.

Reaction of $Fe(CO)_3(PMe_3)_2$ with RI gave (245) $Fe(CO)_2(PMe_3)_2(COR)I$ (R = Me, Et, Pr^n or Bu^n). Acetyl derivatives are involved in the reactions (246) of $Na[Fe_2(CO)_8H]$, [220], with α,β-unsaturated compounds, as shown in Scheme 39. These reactions were regiospecific and it was observed that cleavage of the Fe-Fe bond in $Na[Fe_2(CO)_8(RCH_2CH\text{-}COR')]$ was faster than proton addition and reductive elimination giving RCH_2CH_2COR'. Treatment of $Fe(CO)_5$ with $(Me_2N)_3COR$ gave $[(Me_2N)_3C][Fe(CO)_4\{C(=O)OR\}]$ (247).



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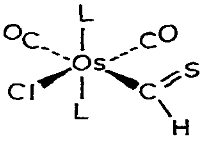

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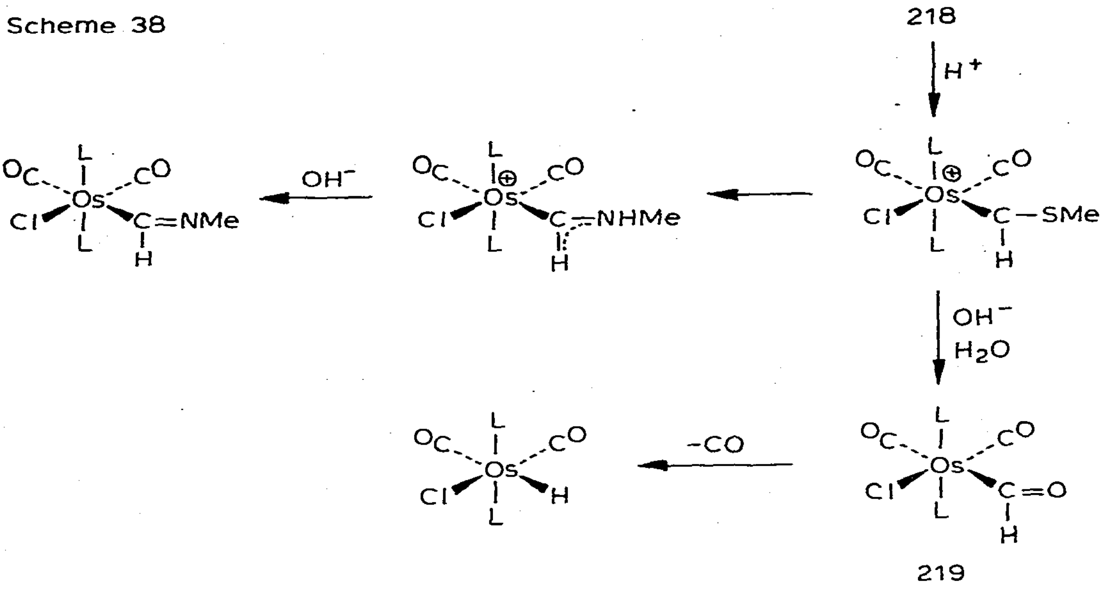
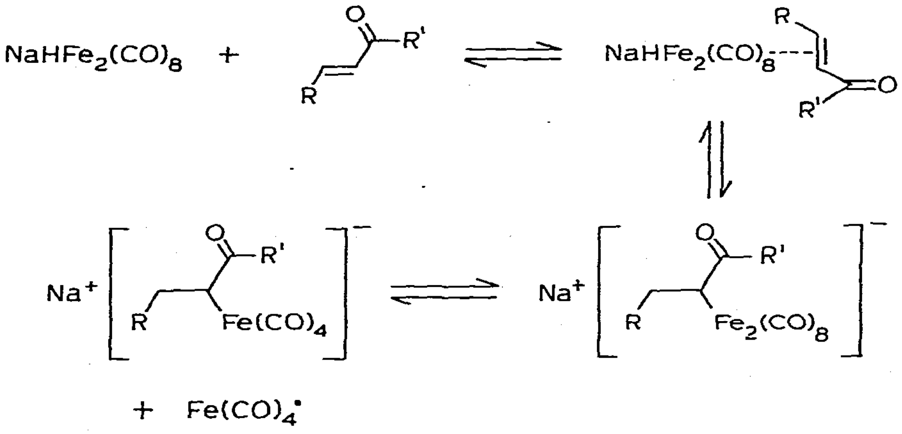
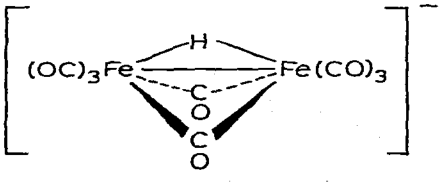
Scheme 38



Scheme 39





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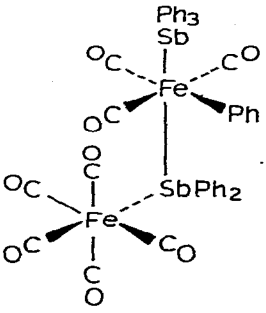


221

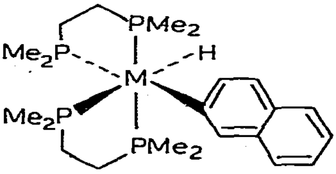
Aryl complexes and o-metallation

Triphenylstibine reacted (248) with $Fe_3(CO)_{12}$ under u.v. light giving [221] whose structure was established unequivocally by X-ray methods. Under identical conditions, however, PPh_3 and $AsPh_3$ gave only $Fe(CO)_4L$ and $Fe(CO)_3L_2$.

Reduction of $Fe(dmpe)_2Cl_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) with sodium naphthalenide afforded (249) the hydrido naphthyl species [222] (M = Fe), analogous to the known Ru (250) and Os(251) complexes. Treatment of this compound with other arenes (ArH) gave $Fe(dmpe)_2H(Ar)$ whose stability decreased in the order Ar = $o\text{-}C_6H_3(CF_3)_2 > C_6H_4CN > C_{10}H_7 > Ph > C_6H_4Me > C_6H_4NH_2$. The ruthenium complex behaved similarly but under more vigorous conditions. With MeCN, RC_2H and C_5H_6, [222](M = Fe) afforded trans-$[Fe(dmpe)_2H(CH_2CN)]$, trans-$[Fe(dmpe)_2H(C_2R)]$, and trans-$[Fe(dmpe)_2H(\eta^1\text{-}C_5H_5)]$, respectively. With Lewis bases (L = CO, RC_2R', olefins or PR_3), [222] (M = Fe or Ru) gave the zerovalent complexes $M(dmpe)_2L$. The olefin-containing compounds, e.g. $Fe(dmpe)_2(CH_2{=}CHR)$ were fluxional and the barrier to intramolecular site exchange increased in the order R = Me < H < $CH{=}CH_2$ < CO_2Me < CN, and the species with L = $CH_2{=}CHCN$ was rigid on the n.m.r. time scale. In the reactions of [222] (M = Fe) with phosphines, the species $Fe(dmpe)_2(PR_3)$ (R = F, OMe, Et; PR_3 = $P(OCH_2)_3CEt$) were readily isolated, but the reaction with PPr^i_3 did not go to completion, and with PPh_3 only $Fe(dmpe)_2H(C_6H_4PPh_2)$ could be obtained. The isolation of $Fe(dmpe)_3(PEt_3)$ contrasts with attempts to prepare $Fe(PMe_3)_5$ (252) where only $Fe(PMe_3)_3H(CH_2PMe_2)$ could be detected.

Treatment of $FeCl_2$ with mesityl Grignard reagents afforded (253) $Fe(C_6H_2Me_3)_2$.

By using the appropriate solvent, the extent of substitution of $Ru(CO)(PPh_3)_3HCl$ by $P(OPh)_3$, and o-metalation of the latter, could be controlled (254) (Scheme 40). Treatment of $Ru(PPh_3)_4H_2$ with $P(OPh)_3$ in boiling xylene afforded [223].



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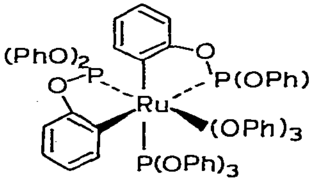
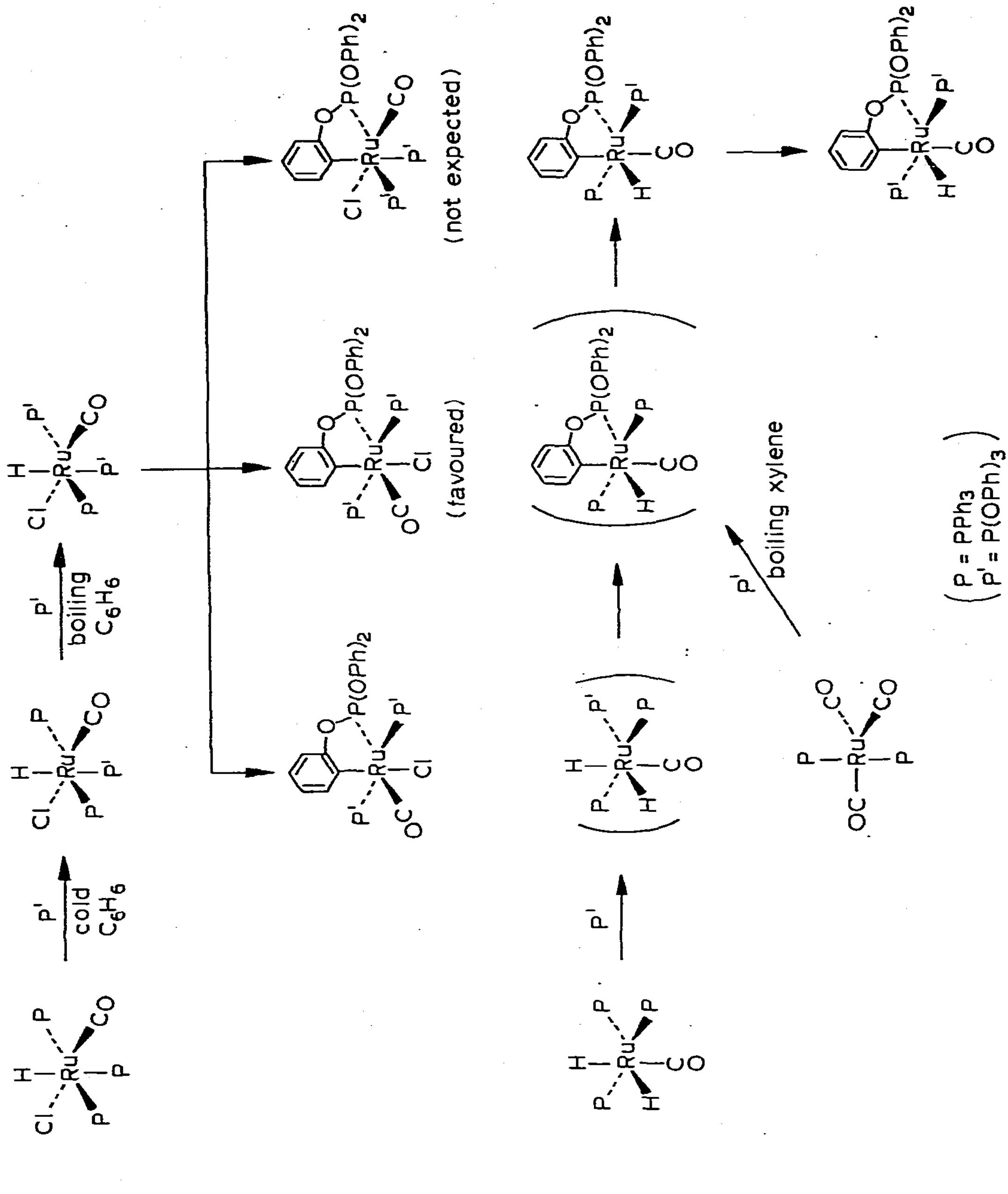


223

Silyl compounds

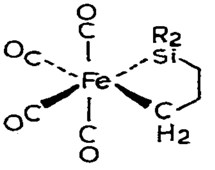
In the presence of $Fe(CO)_5$, trialkylsilanes, $SiHR_3$, reacted with olefins giving (255) alkanes, SiR_3R' and SiR_3R'' (R' = alkyl and R'' = alkenyl) in a ratio depending on temperature and relative initial concentrations of the reactants. It was suggested that an important intermediate in this reaction was $Fe(CO)_3(alkene)H(SiR_3)$. The silyl complexes $Ru(PRR'R'')_3H_3(SiR^1R^2R^3)$ (R, R', R'' = aryl, alkyl or aryl-alkyl; R^1, R^2, R^3 = H, halide, alkoxide, alkyl, aryl or aryl-alkyl) were obtained (256) from reactions between $Ru(PRR'R'')_4H_2$ with $SiHR^1R^2R^3$.

Scheme 40


P'
cold
C_6H_6
P'
boiling
C_6H_6
(favoured)
(not expected)
P'
P'
boiling xylene
P = PPh_3
P' = $P(OPh)_3$

Treatment of the strained heterocyclic organosilane, $\mathrm{Me_2\overline{SiCH_2CH_2CH_2}}$, with $Fe_2(CO)_9$ gave [224] while with $\mathrm{Me_2\overline{SiCH_2CH_2CHMe}}$ and [225], only [226] and [227] (R = Me or Ph), respectively, were obtained (257). With the two isomers of $\mathrm{RMeSiCH_2CH(Me)CH_2}$ (R = OMe or Bu^n), reaction was stereospecific, there being no significant change in the isomer ratio between reagents and products. It was concluded that the mechanism of the reaction involved $Fe(CO)_4$ and was probably an electrophilic C-Si cleavage process.

The bis(silyl) chelated complexes [228], [229] (R = Me or Ph) and [230] were obtained (258) by reaction of either $Fe_2(CO)_9$ or $Ru_3(CO)_{12}$ with 1,2-$\mathrm{(Me_2HSi)_2C_6H_4}$, 1,2,4,5-$\mathrm{(R_2HSi)_4C_6H_2}$ (R = Me or Ph), and 1,2,3,4,-$\mathrm{(Me_2HSi)_4C_6H_2}$, respectively.



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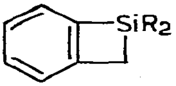

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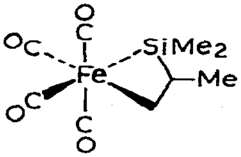

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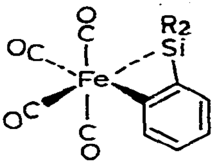

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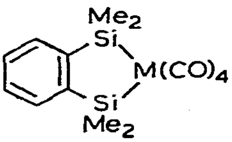

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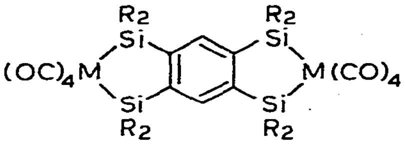

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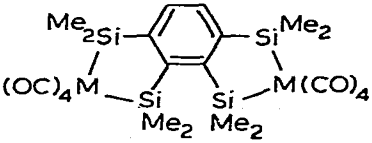
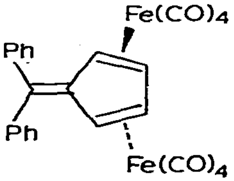


230

MONOALKENE COMPLEXES

Reaction of $\mathrm{Ph_2P(=O)CH=CH_2}$ with $Fe_3(CO)_{12}$ gave (259) $\mathrm{Fe(CO)_4[Ph_2P(=O)CH=CH_2]}$ in which the vinyl group was bound to the metal. On pyrolysis, this complex was converted into the polymeric species $\mathrm{[Fe(CO)_4\{CH_2CHP(=O)Ph_2\}_5]_n}$. The structure of [231] was determined crystallographically (260), and it was shown that the two $Fe(CO)_4$ groups are mutually trans to the olefinic bonds of the five-membered ring.



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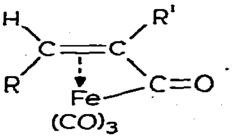

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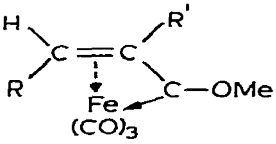

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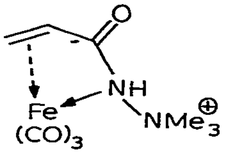
Treatment of $[Fe(CO)_4H]^-$ with RC_2R' ($R = R' = CO_2Me$; $R = H$, $R' = COMe$ or CO_2Me; $R = CO_2Me$, $R' = H$) gave (261) the η^3-vinylacyl derivative [232]. The species [232] ($R = H$, $R' = CO_2Me$) was also prepared by reaction of cis-$BrCH{=}CH(CO_2Me)$ with $[Fe(CO)_4]^{2-}$. Methylation of [232] gave [233] which could be converted by pyridine-N-oxide into $Fe(CO)_3(pyr)[CHR{=}CR'(CO_2Me)]$. Oxidation of this compound by Ce^{4+} in methanol afforded $RCH(OMe)CHR'(CO_2Me)$. Protonation of [232] by CF_3CO_2H gave the olefin complex $Fe(CO)_4(RCH{=}CHR')$.

Reaction of $RCH{=}CHCONMe_2$ with $Fe_2(CO)_9$ gave $Fe(CO)_4(RCH{=}CHCONMe_2)$ (R = H or Ph) which could also be formed, together with $Fe(CO)_3(RCH{=}CHCONMe_2)$, from $Fe_3(CO)_{12}$ (262). With $[CH_2{=}CHCONHNMe_3]^+$, $Fe_3(CO)_{12}$ afforded $[Fe(CO)_3(CH_2{=}CHCONHNMe_3)]^+$, [234]. The complexes $Fe(CO)_4(CH_2{=}CHCONHR)$ reacted (263) with $[Et_3O]^+$ giving [235] which, on further reaction with R'_2NH, afforded the metallocycle [236] ($R = R' = Me$; $R = H$, $R' = Me$; $R = H$, Me, $R' = (CH_2)_5$) whose structure was confirmed by X-ray methods.



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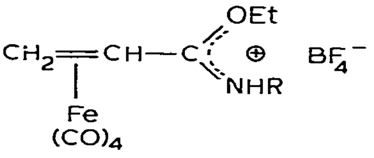

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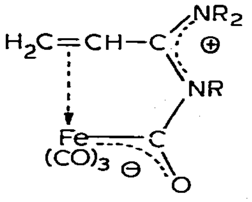

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Electrochemical reduction of $Ru(PPh_3)_3Cl$ in acetonitrile afforded (264) $Ru(\eta^2\text{-}NCMe)(PPh_3)_4.MeCN$ in which one acetonitrile molecule is π-bonded via the CN group to the metal, whereas the other is uncoordinated. The species did not react with CCl_4 giving $CHCl_3$, and using $P(2,6\text{-}C_6H_3D_2)_3$ and CD_3CN had no significant influence on the spectral properties of the complex. Thus the species is not a hydride and probably has a trigonal bipyramidal structure with the η^2-MeCN occupying an equatorial site. Treatment of $Ru(\eta^2\text{-}MeCN)(PPh_3)_4$ with CO gave $Ru(CO)(PPh_3)_4$ and $Ru(CO)_2(PPh_3)_3$ in steps, and with $PMePh_2$ a species of empirical formula $Ru(PMePh_2)_4$ was produced. This last did react with CCl_4 giving $CHCl_3$, indicating the presence of a Ru-H bond, and one $PMePh_2$ ligand may be o-metalated, either at the phenyl or methyl subsituent.

ALLYL COMPLEXES

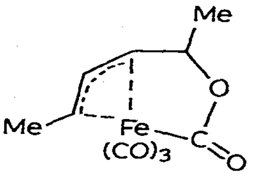
Reduction of $Fe(\eta^3\text{-}C_3H_5)(CO)_2(PPh_3)X$ with zinc dust gave (265) the paramagnetic $Fe(CO)_2(PPh_3)(C_3H_5)$, while with sodium amalgam, diamagnetic $[Fe(CO)_2(PPh_3)(C_3H_5)]^-$ was formed. These species, in solutions free of reducing agents, were effective debromination reagents for vicinal organic dibromides. While the radical species did notreact stereospecifically, the anionic species did, with anti elimination.

The structure of [237], obtained (266) by reaction of the monoepoxide of cis,trans hexa-2,4-diene and iron carbonyl, wasdetermined crystallographically (267). Treatment of $Fe_2(CO)_9$ with $RMe_2SiSi(CH{=}CH_2)Me_2$ (R = Me or $CH{=}CH_2$) afforded (268) the η^3-

1-silapropenyl derivative [238] which reacted with PPh_3 giving $Fe(CO)_3(PPh_3)_2$.

The mechanisms of photoinsertion of haloalkenes into the Fe-C bonds of diene iron tricarbonyl species, and the subsequent hydrolysis of the products on silica gel, have been investigated (269). The conclusions are summarised in Scheme 41.

The ^1H n.m.r. spectra of $Fe(\eta^4-C_4H_4)(CO)_3$ in FSO_3H at low temperature has been investigated (270) and it was concluded that the species present should be represented as [239] and not [240] as previously suggested (271). A similar ^1H and ^{13}C n.m.r. spectral study of $Fe(CO)_3(C_6H_8)$ in acid solution has also been reported (272). It was concluded, in confirmation of earlier reports (273), that perhaps the best representation of the product, $[Fe(CO)_3(C_6H_9)]^+$, is [241] where the hydride is bridging between Fe and C. The ^{13}C n.m.r. spectra of $[Fe(\eta^3-C_3H_4R)(CO)_4]^+$ (R = H or Me) were also reported and it was observed that $Fe(\eta^3-C_3H_5)(CO)_3(OCOCF_3)$ did not dissociate in solution giving $[Fe(\eta^3-C_3H_5)(CO)_3]^+$.



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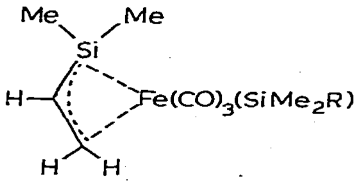

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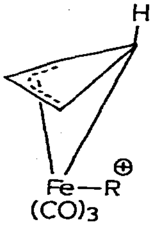

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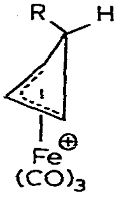

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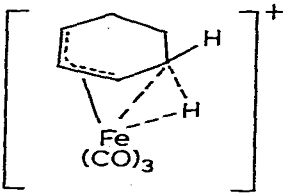

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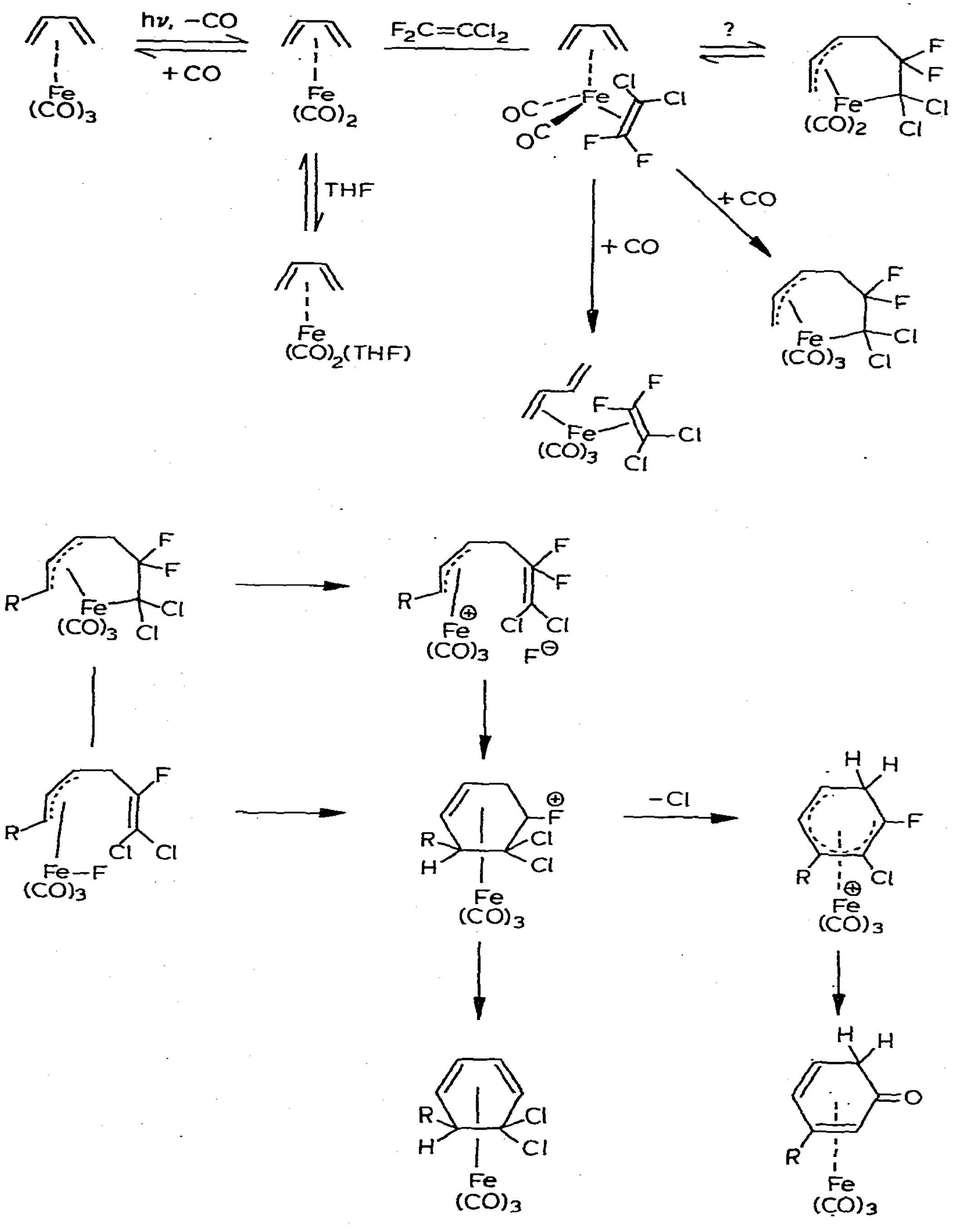
Low temperature photolysis (274) of a mixture of tricyclo$[3.2.2.0.0^{2,7}]$hept-3-ene with $Fe(CO)_5$ gave a series of complexes as shown in Scheme 42. The structure of [242] was established by X-ray techniques, and it was shown that the carbene ligand occupies an apical position at one trigonal bipyramidal atom while it is in the trigonal plane at the other Fe atom. The Fe-Fe distance is 2.63 Å, which is typical of such carbene-bridged species (275).

Treatment of tropone iron tricarbonyl with TCNE gave [243], in a cycloaddition reaction involving initial electrophilic addition to the un-coordinated double bond (276).

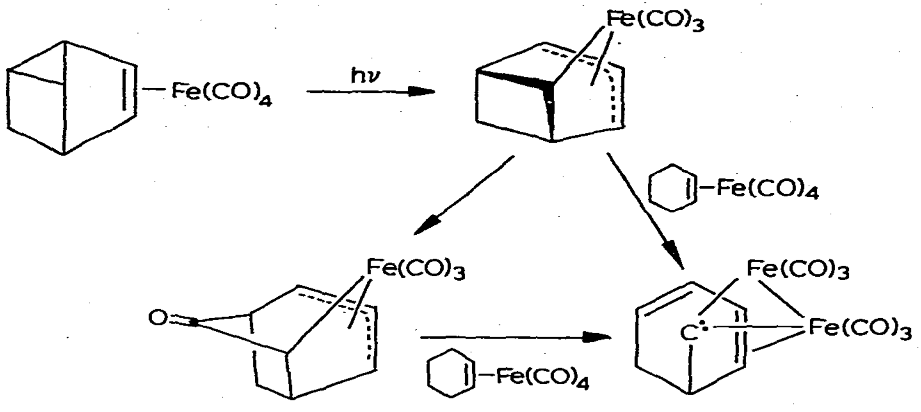
CYCLOBUTADIENE AND TRIMETHYLENEMETHANE COMPLEXES

^{13}C n.m.r. spectra studies have been made of $Fe(\eta^4-C_4H_4)(CO)_3$ (277) and $Fe(\eta^4-$

Scheme 41



Scheme 42



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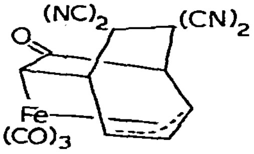

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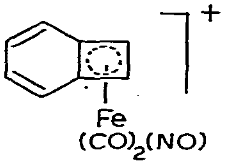

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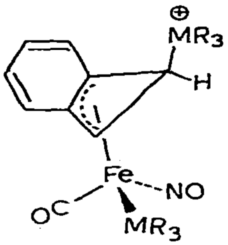

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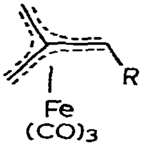

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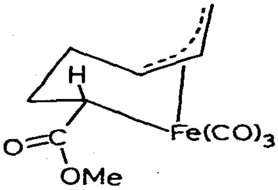
$C_4H_3CHROH)(CO)_3$ (R = H, Me or Ph)(278). The latter group was investigated in acid solution, and it was suggested that there was extensive donation of electron density from the metal via the C_4 unit to the exocyclic electron-deficient C atom, giving a highly stabilised carbonium ion (see also ref. 270).

Reaction of the benzocyclobutadiene complex $Fe(\eta^4-C_8H_6)(CO)_3$ with $NOPF_6$ or NO_2PF_6 gave (279) the nitrosyl cation [244]. Addition to this species of L(PR_3 or AsR_3, R = alkyl or aryl) afforded the metal-stabilised phosphonium salt [245].

From v.t. ^{13}C n.m.r. spectral studies, it was established (280) that [246] (R = H, COMe, CH(OH)Me, Et and CH(OAc)Me) was fluxional, undergoing an effective ligand rotation with $\Delta G^{\neq}$ = 17-18 kcal/mol.

Acyclic diene species

The enthalpies of thermal decomposition of a series of olefin complexes of iron, viz. $Fe(CO)_4(C_2H_4)$, $Fe(CO)_3(diene)$ and $Fe(CO)(diene)_2$ (diene = C_4H_6, diethylmuconate and methylsorbate) have been determined (281). For the Fe-ethylene bond, the bond enthalpy contribution was 23.1 kcal/mol, whereas an average bond enthalpy contribution for the diene-Fe interaction was ca. 44 kcal/mol. It was noted that $Fe(CO)_3$-$(C_4H_6)_2$ decomposed thermally or on melting to give dimers and trimers of butadiene, whereas $Fe(CO)_3(C_6H_8)$ under similar conditions gave $(C_6H_8)_2$. Measurements were also made of the enthalpies of sublimation or vaporisation of these complexes.



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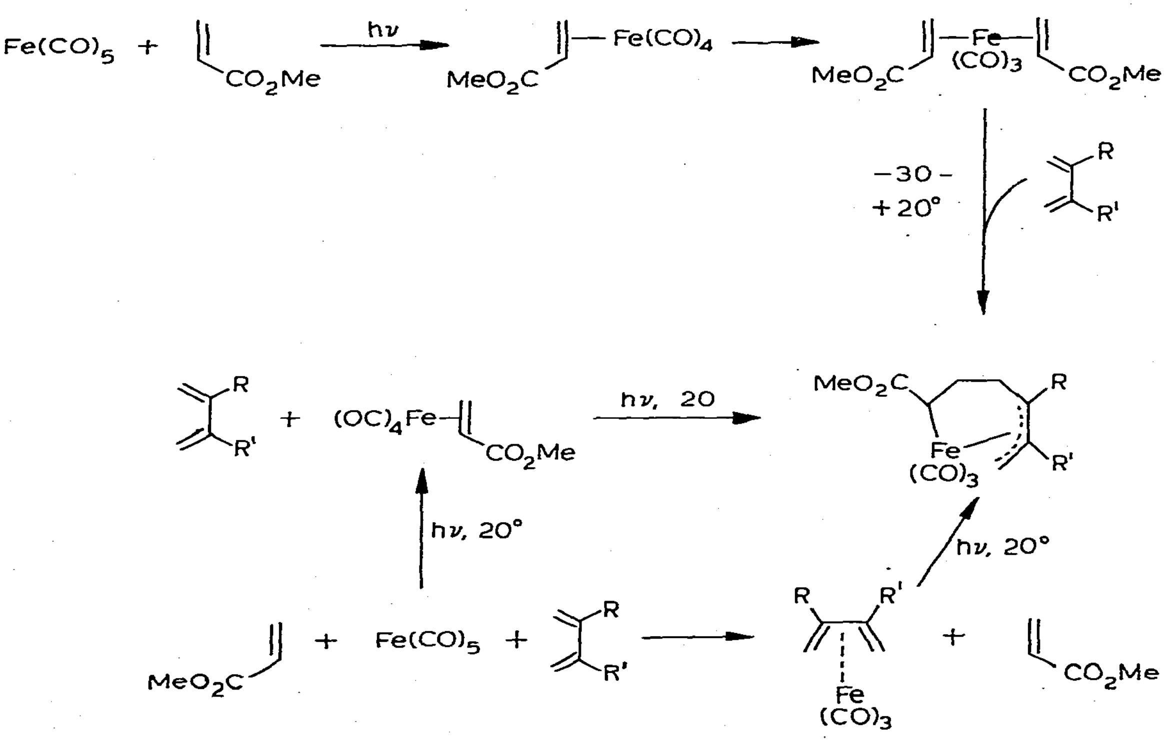
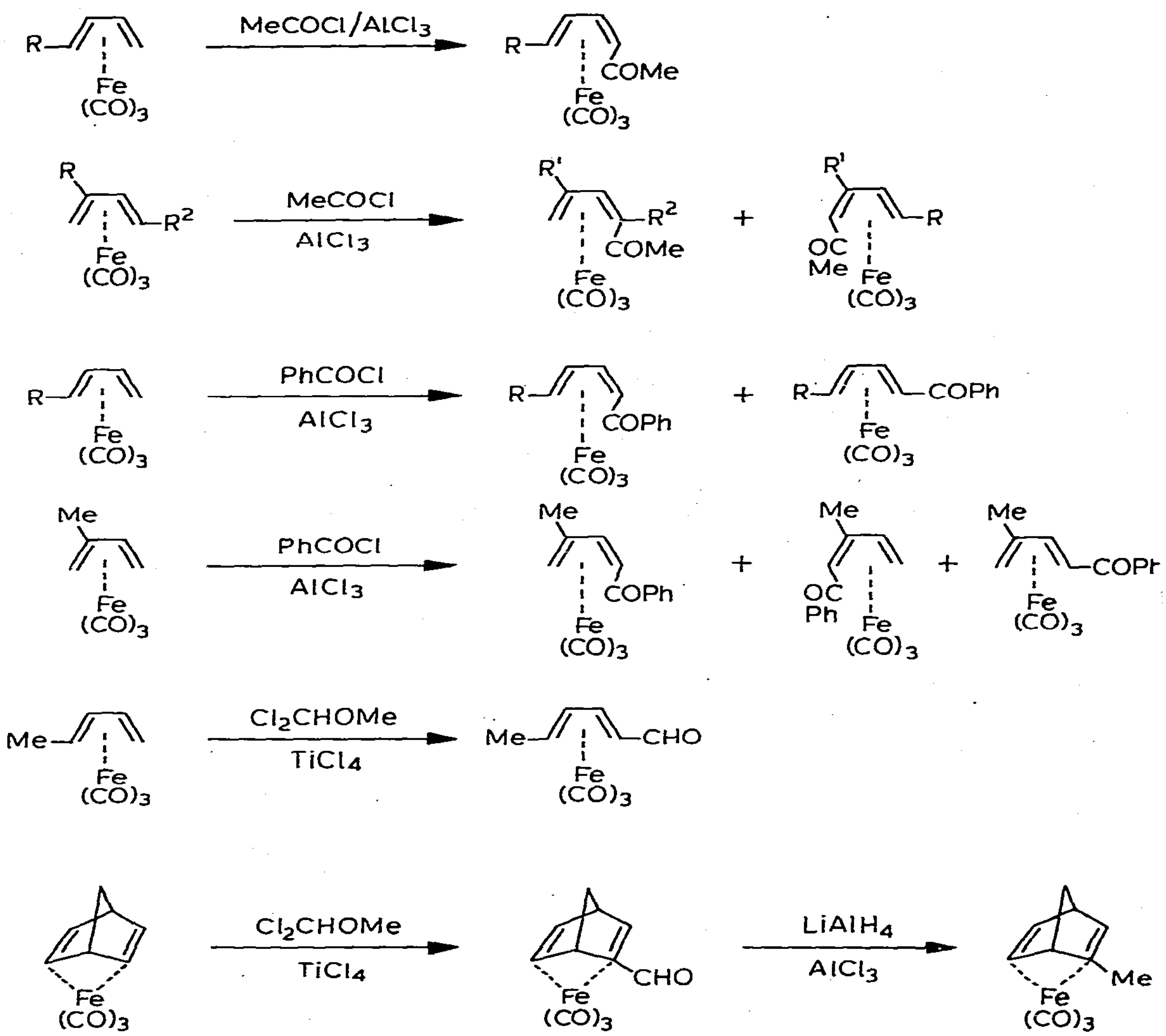
Scheme 43

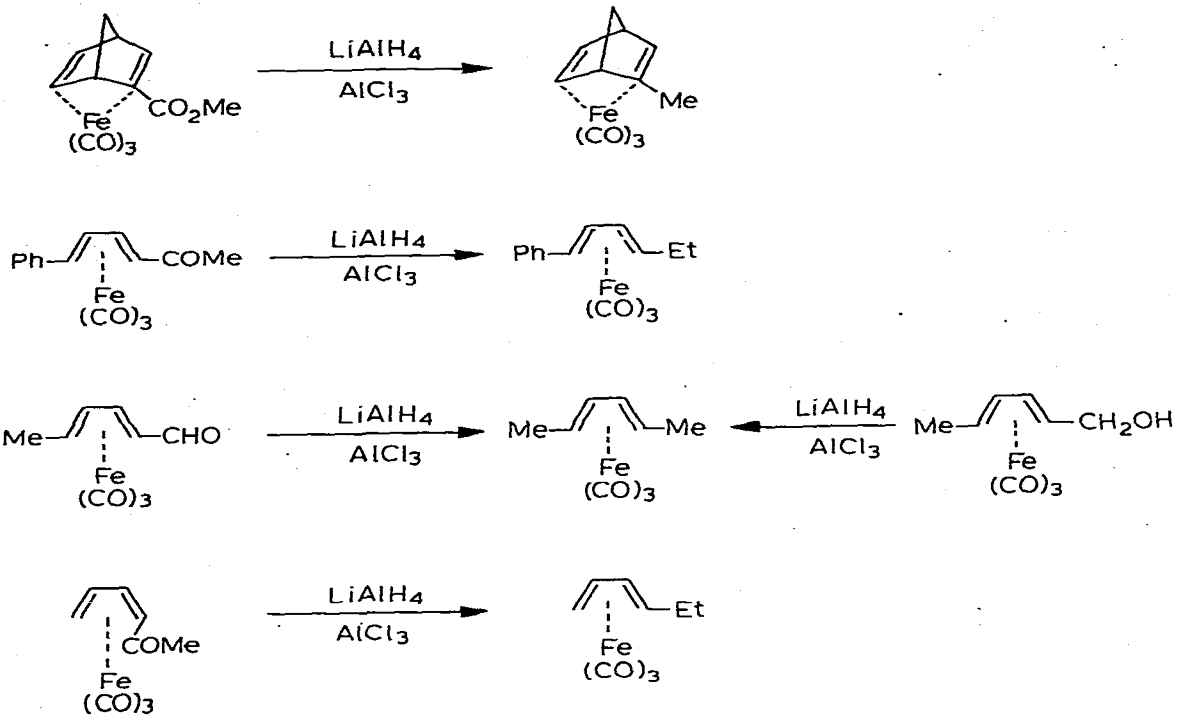


Photolysis of $Fe(CO)_5$ in the presence of a mixture of methyl acrylate and a 1,3-diene proceeded (282) according to Scheme 43, and the structure of [247] was established crystallographically. Acylation of $Fe(CO)_3$(diene) complexes using $RCOCl/AlCl_3$ in dichloromethane at 0° afforded (283) dienone complexes in high yields. Substitution occurred at unsubstituted terminal C atoms of the diene unit. On quenching the reaction mixture with cold aqueous ammonia, the *cis*-dienone isomers were obtained exclusively, and the *trans* forms could be subsequently produced by treatment of the *cis* isomers with methanolic NaOMe. Formylation of the diene complexes was achieved using $MeOCH_2Cl/AlCl_3$, and treatment of these and the dienone species, related dienol or dienoic ester complexes with $AlCl_3/LiAlH_4$ (4:1) effected complete removal of the oxygen function from the complex giving *trans*-$Fe(CO)_3$(diene) complexes in good yields. Some of these results are summarised in Scheme 44. Acylation and reaction of myrcene

Scheme 44



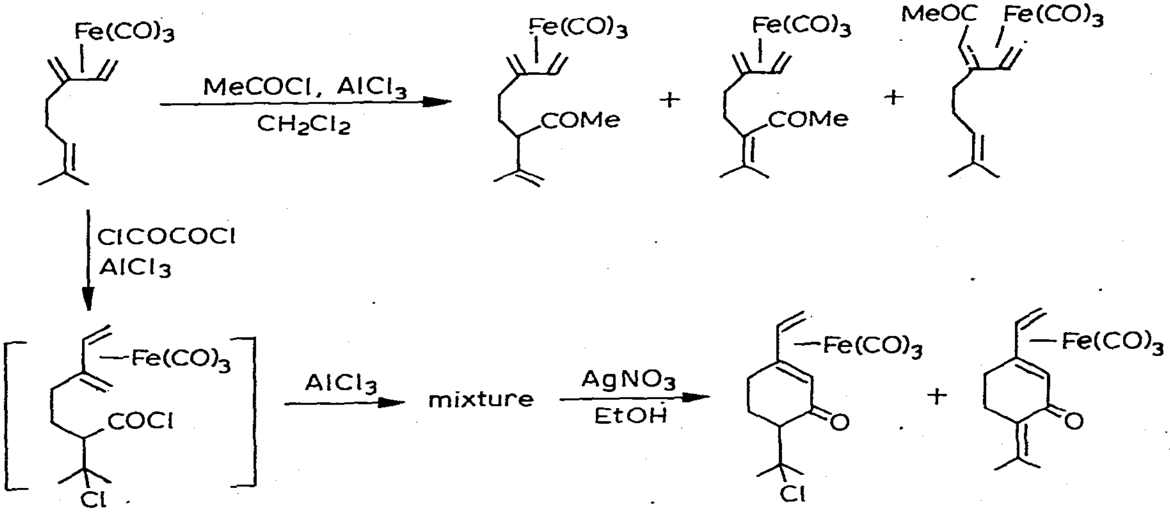
Scheme 44 contiuned



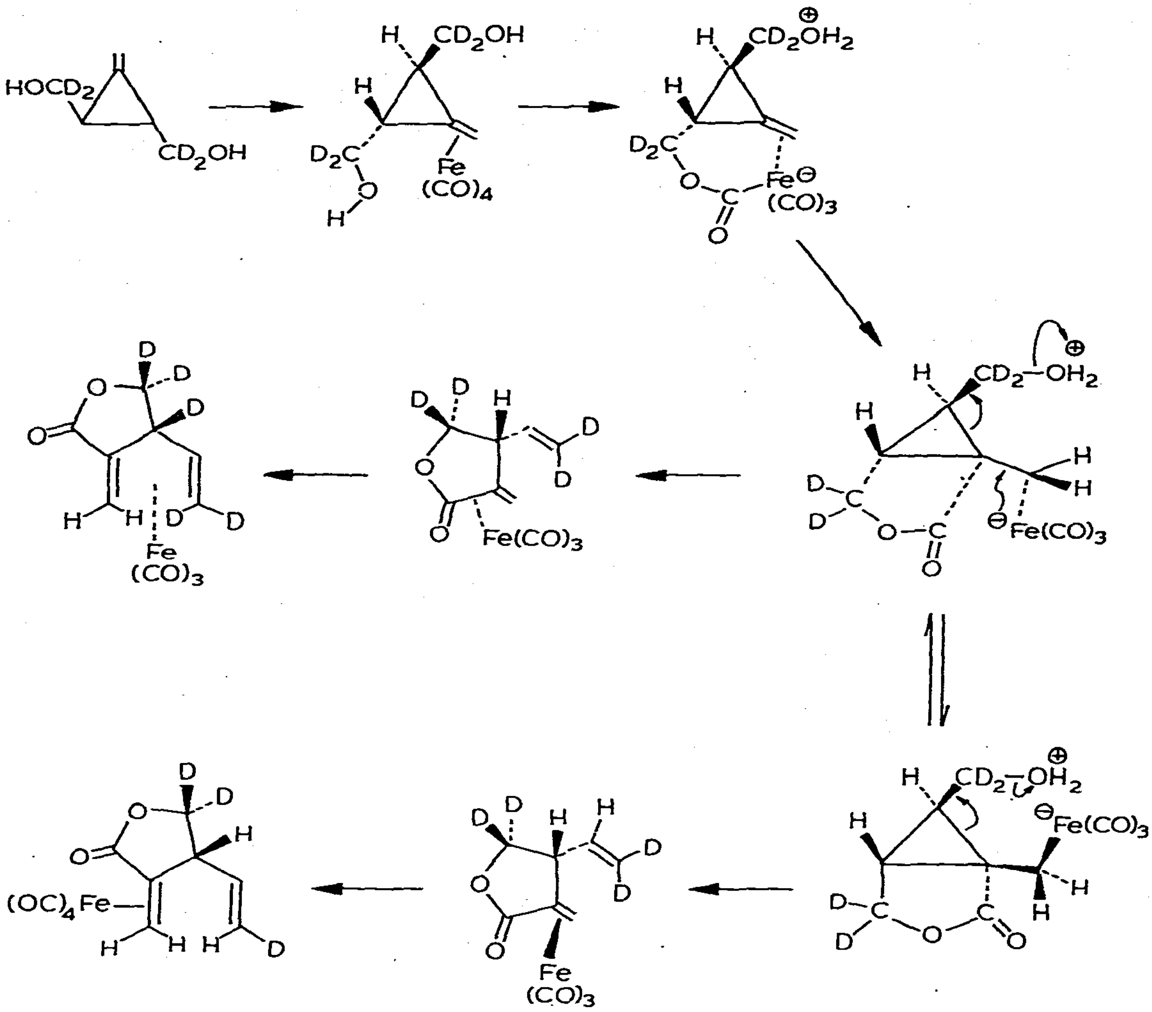
iron tricarbonyl with oxalyl chloride (284) is shown in Scheme 45.

The ring opening of 2,3-bis(hydroxymethyl)methylenecyclopropane by $Fe_2(CO)_9$ has been thoroughly investigated (285) and the proposed mechanism, supported by some crystallographic studies, is outlined in Scheme 46. The regiospecific thermal re-

Scheme 45



Scheme 46

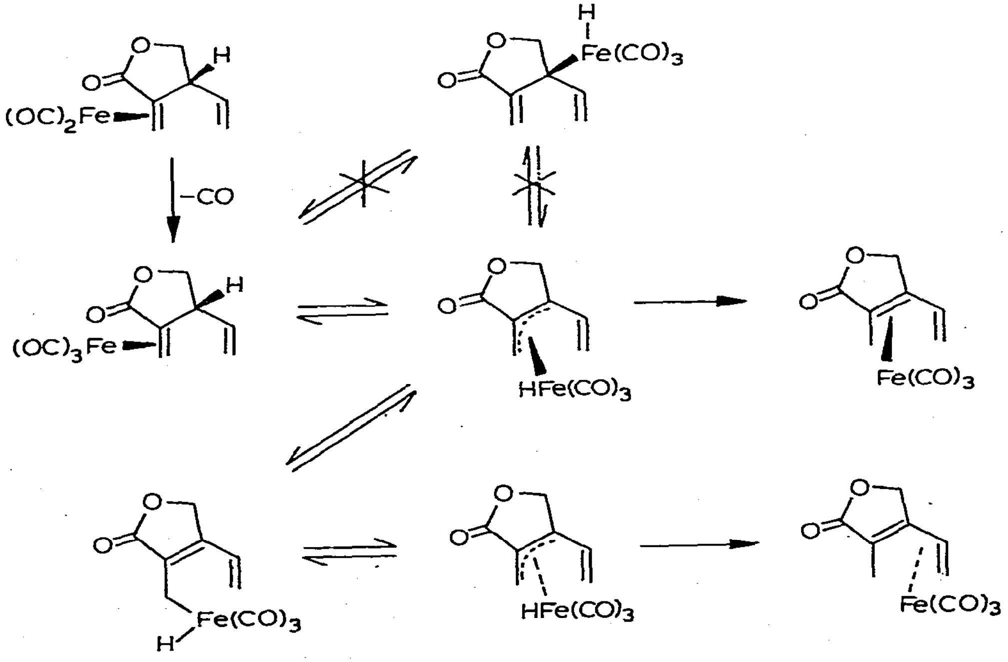


arrangements of the products obtained (285) from the above study have been extensively reported (286), and the important results are shown in Scheme 47. The data imply that where sufficient flexibility exists, direct insertion of a metal into an allylic C-H bond, giving a σ-allylic species, and the collapse of such a species via a direct hydrogen transfer from the metal to an olefin carbon atom, can proceed as a low energy olefin-isomerisation pathway without requiring the intermediacy of a π-allylic metal bond (Scheme 48). It was concluded that any metal-promoted sigmatropic 1,3-suprafacial hydrogen shift in these systems is certainly not of low enough energy to compete effectively with the σ-allyl metal hydride or π-allyl metal hydride mechanism for olefin isomerisation.

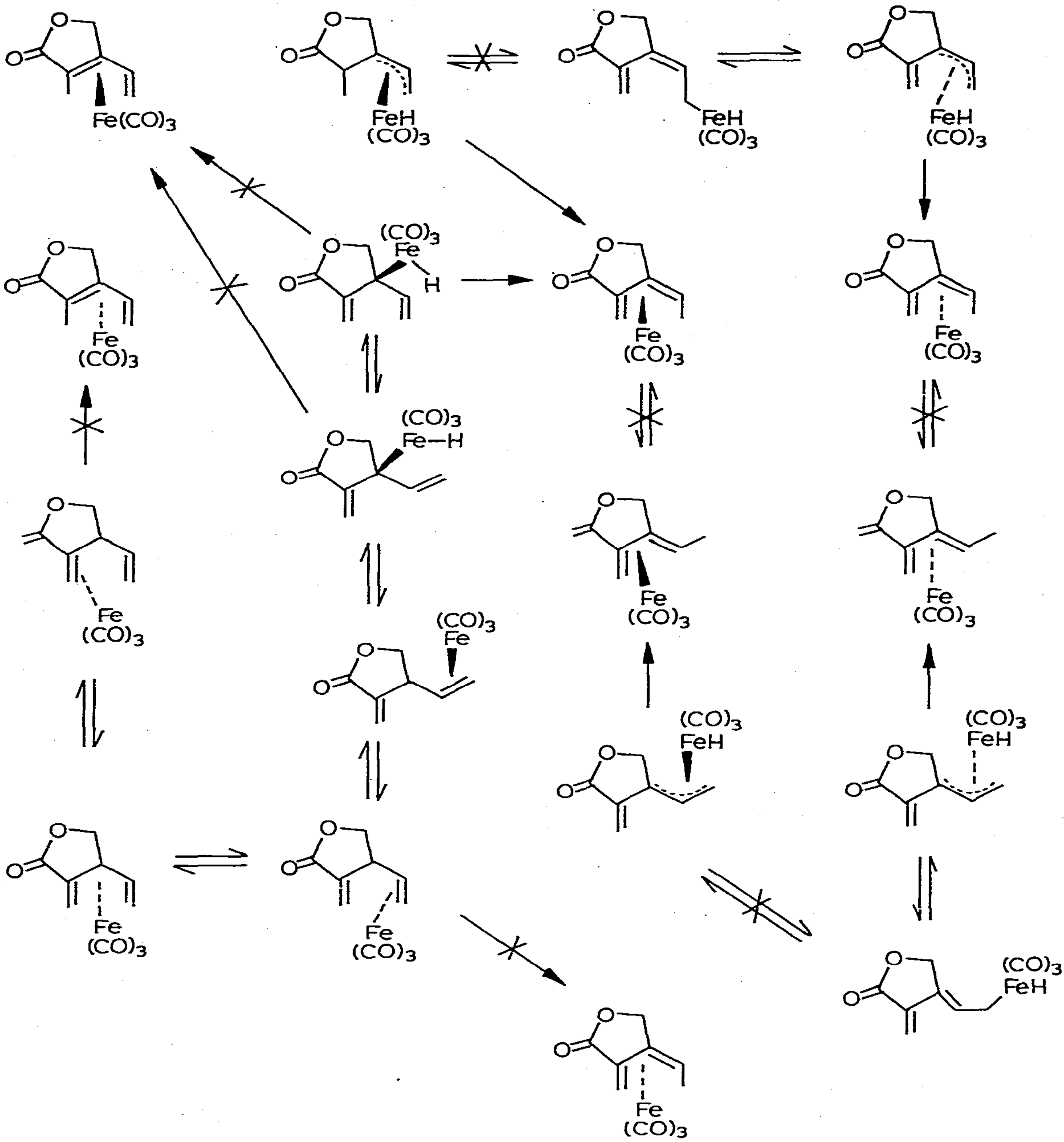
Reaction of $Fe_2(CO)_9$ with PhCH=CHCH=CHCH(OH)(Ph) afforded (287) the appropriate iron tricarbonyl complex which, on treatment with HBF_4, gave [248] whose behaviour with $NaBH_3CN$, $NaBD_3CN$ and $LiAlH(Omen)_3$ (Omen = mentholate), giving *inter alia* [249] and [250], is summarised in Scheme 49. A mixture of 1- and 2-phenylcyclohexa-1,3-diene reacted with $Fe(CO)_5$ giving the expected iron tricarbonyl compounds which, when treated with CF_3CO_2D, afforded [251] and [252], consistent with previous studies (288). Hydride abstraction by $[Ph_3C]^+$ from [251] gave [253] (i.e. only H^- was eliminated), whereas [252], under similar conditions, afforded a mixture of [254] and [255] (2:1). The absence of [255] as a product of the hydride abstraction from [251] is presumably a reflection of the steric requirements for such a reaction involving $[Ph_3C]^+$. The dienone [256] reacted with $Fe_2(CO)_9$ giving the anticipated complex whose subsequent reactions, affording [257] and [258], are shown in Scheme 50. The complex [259], obtained from the appropriate diene and $Fe_2(CO)_9$, reacted with CF_3CO_2H giving [260] which did not undergo hydride abstraction with $[Ph_3C]^+$, presumably also because of steric reasons. Thermolysis of [249], [250], [257], [258] and [260], afforded species in which deuterium underwent a 1,3-shift (Scheme 51), possibly via π-allyl iron hydride intermediates. Certain cyclic diene species, however, were found to undergo 1,5-shifts (Scheme 52). When the cyclic compounds contained an aromatic substituent, metal epimerisation was also observed (Scheme 53) , and epimerisation must be faster than hydride abstraction to give a π-allyl metal hydride. *Cis,trans*-isomerisation was also rationalised in terms of a π-allyl metal hydride mechanism, as with [249] in Scheme 54, in line with earlier suggestions (289).

Two polymorphic forms of the bis(tricarbonyliron) complex of deca-1,3,7,9-tetraene, [261], were identified crystallographically (290). The structure of the iron tricarbonyl complex of *trans*, *trans*-3,5-heptadien-2-ol was also determined by X-ray methods (291)

Scheme 47

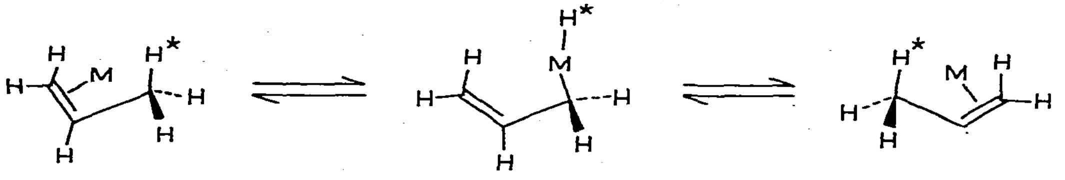


Scheme 47 contiuned

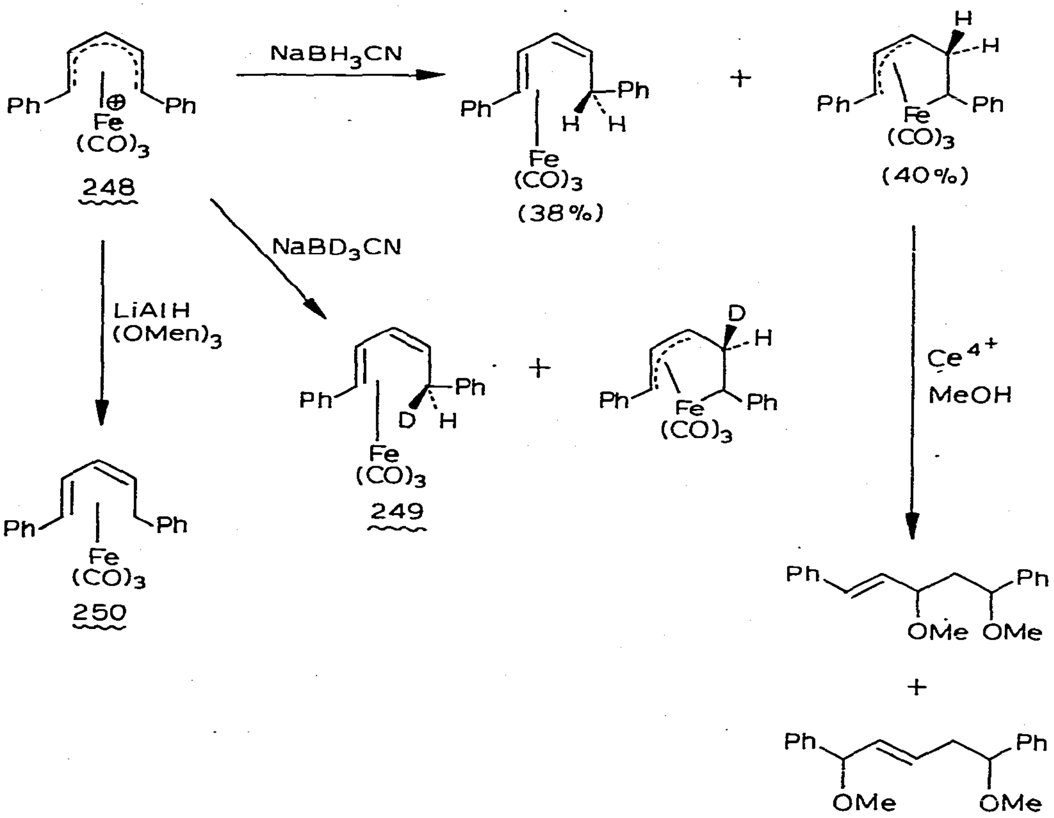


The protonation of myrcene iron tricarbonyl caused a cyclisation of the hydrocarbon ligand to occur (292) (Scheme 55). The synthesis of cyclic hydrocarbons via intramolecular coupling of bis(pentadienyl iron tricarbonyl) species has been achieved (293)(Scheme 56). The complex [262] (n = 3) was characterised crystallographically and it was shown that the two diëneFe(CO)$_3$ groups are disposed *trans* to each other

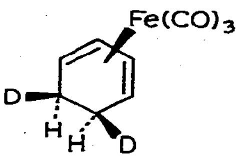
Scheme 48



Scheme 49



relative to the five-membered ring. Dimethylenecyclobutane (which contains 85% [263] and ca. 15% [264]) reacted (294) with $Fe_3(CO)_{12}$ giving [265] and $Fe(CO)_2C_{12}H_{16}$, [266]. The former product did not react with an excess of the cyclobutane giving [266], suggesting that [265] is not an intermediate in the formation of [266]. With $Fe_2(CO)_9$ at room temperature, dimethylenecyclobutene probably afforded [267] which, on warming, was converted into [268]. $Fe_3(CO)_{12}$ reacted with [269] giving the η^4-cyclobutadiene complex [270]. Treatment of $Fe(CO)_5$ with 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane giving [271] which rearranged (295) in the presence of $AgClO_4$ to give [272] and [273], both of which are fluxional.



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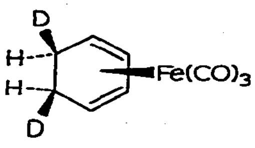

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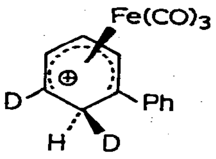

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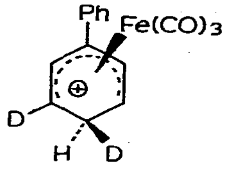

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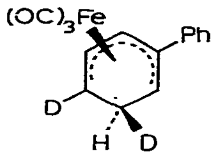

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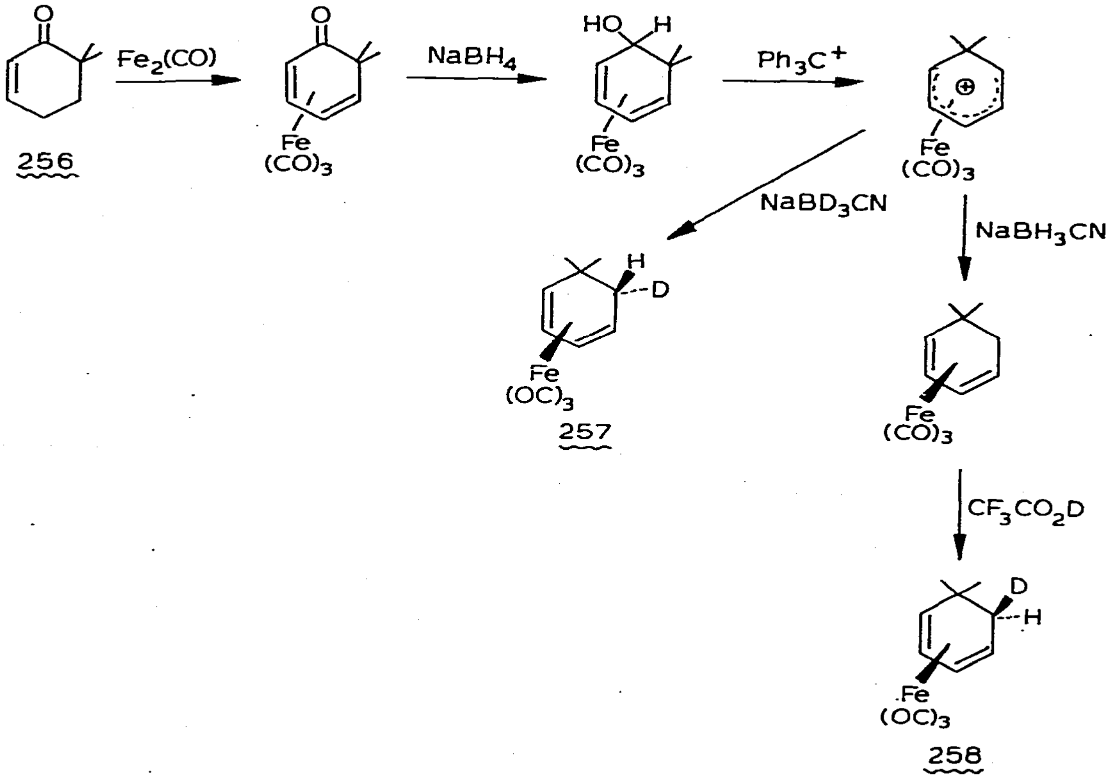
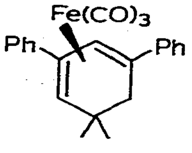
Scheme 50





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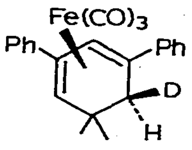

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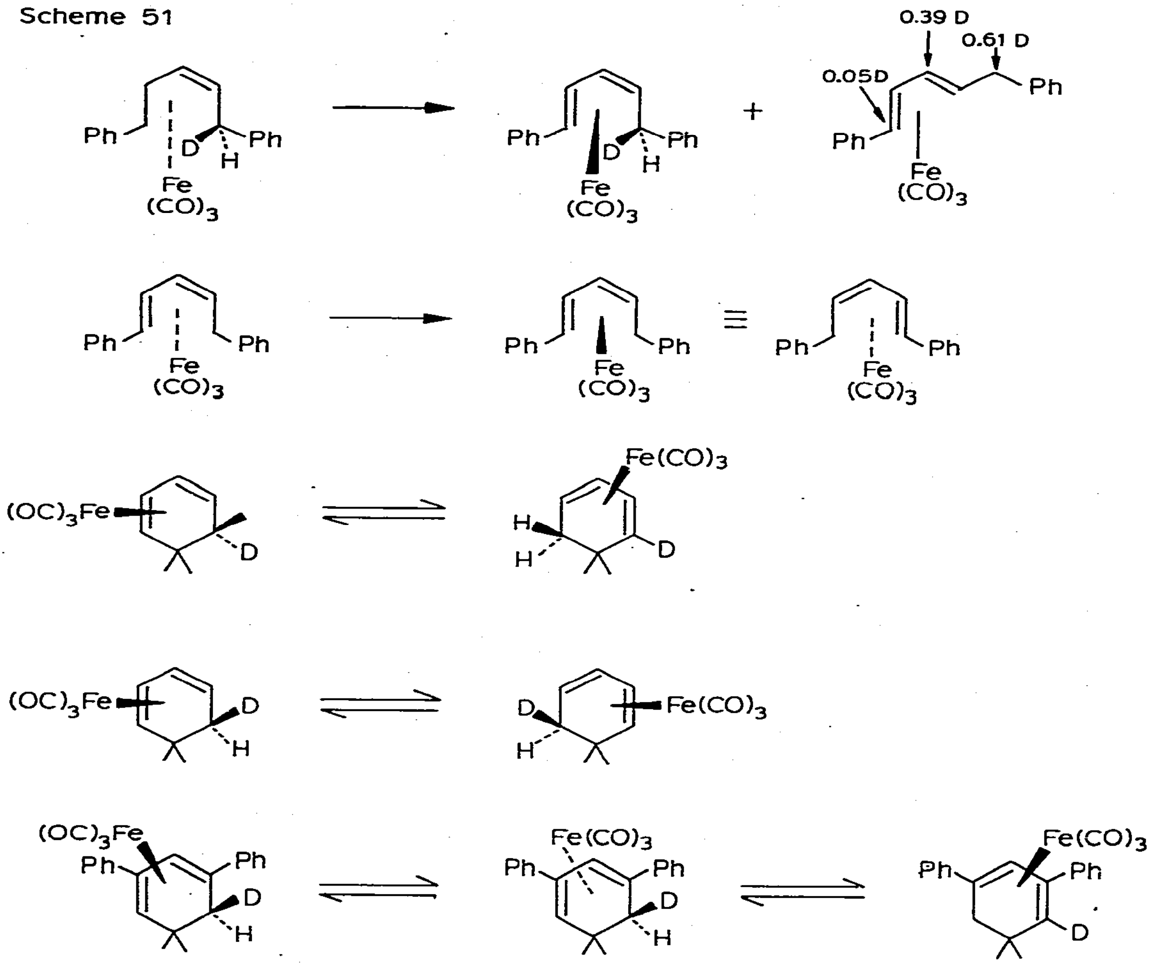
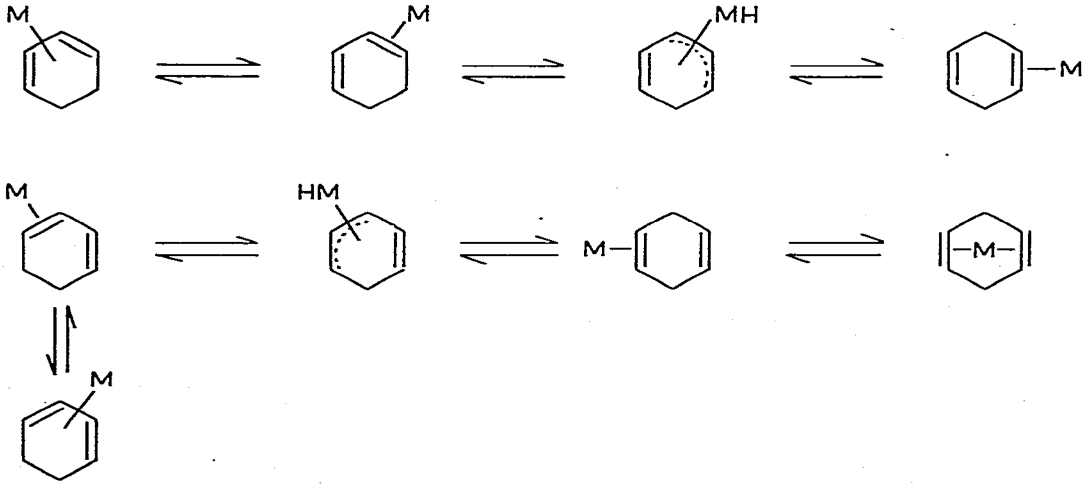
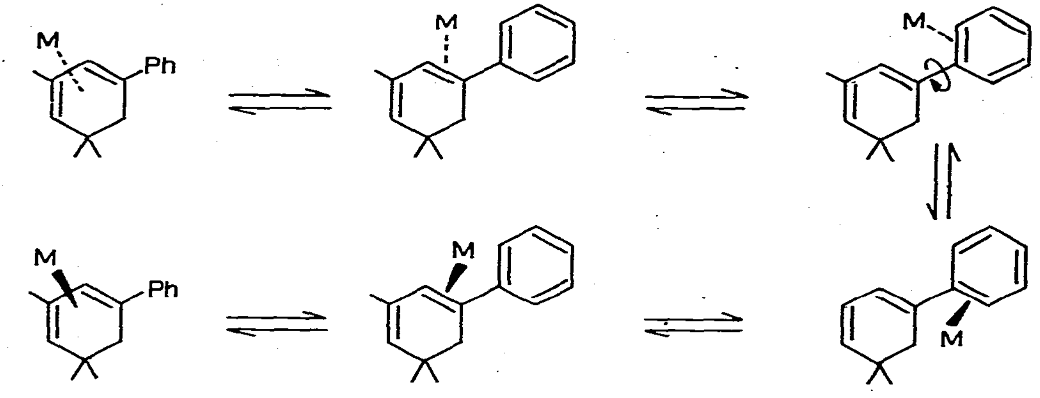
Scheme 51



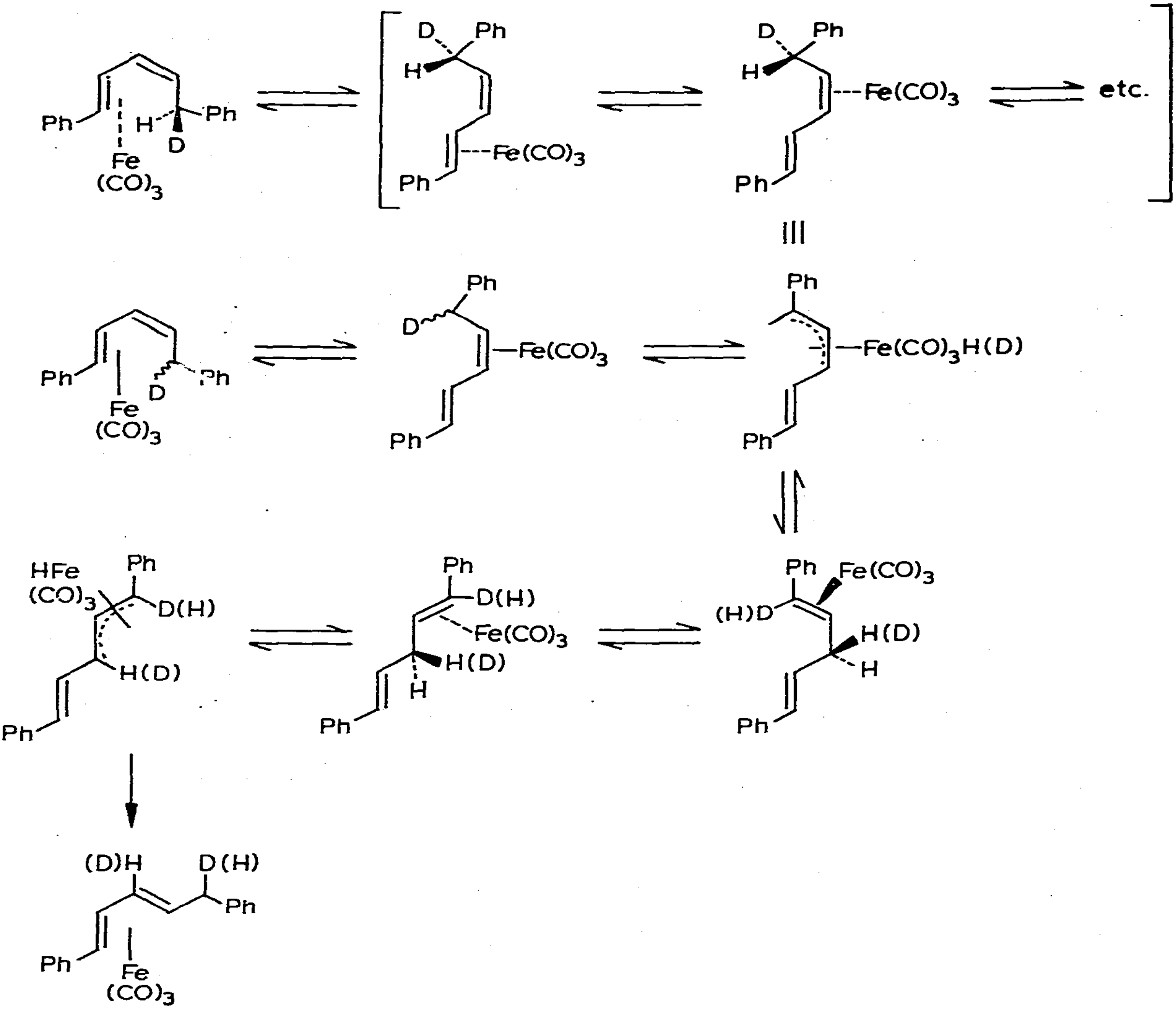
Scheme 52



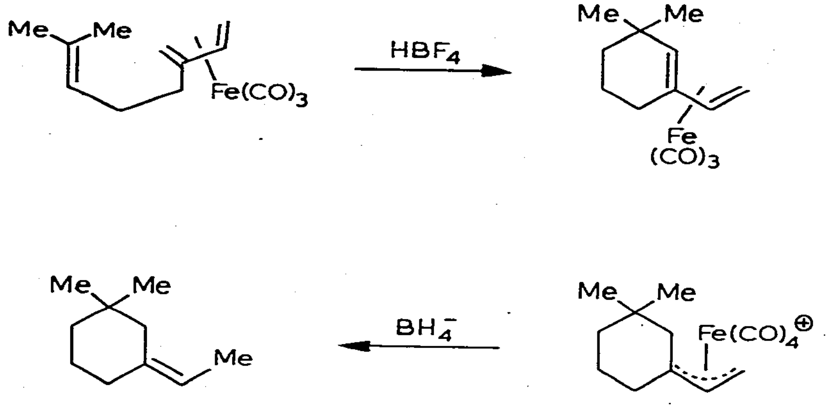
Scheme 53



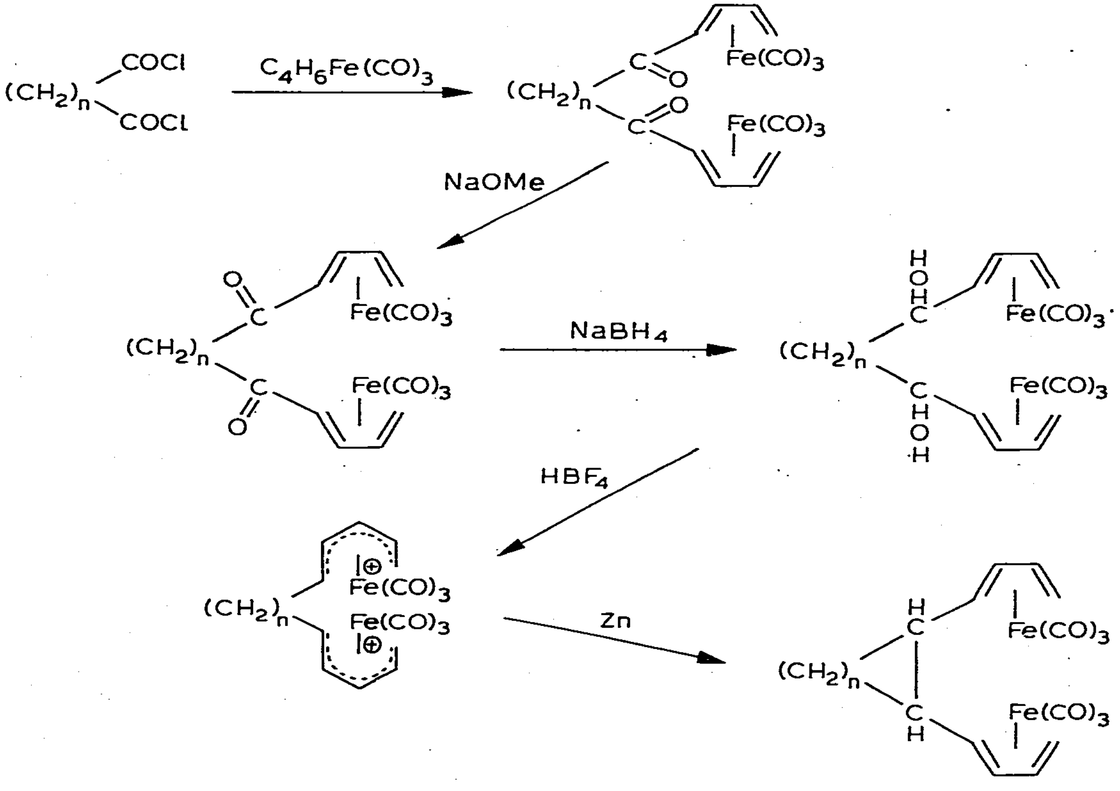
Scheme 54



Scheme 55



Scheme 56



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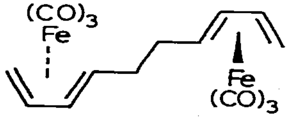

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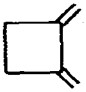

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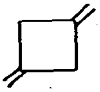

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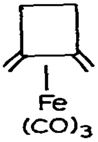

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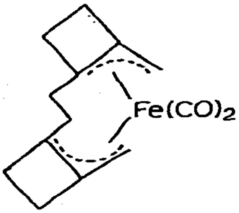

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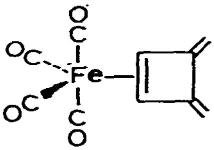

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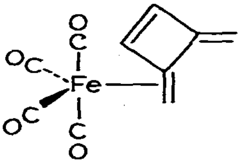

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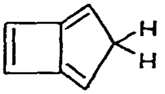

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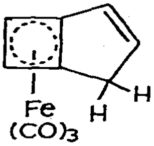

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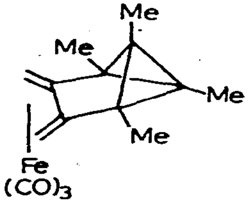

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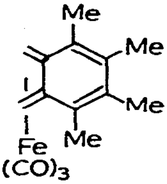

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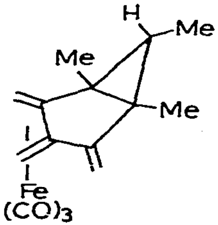

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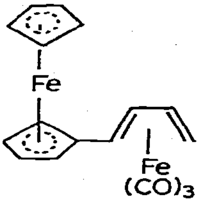

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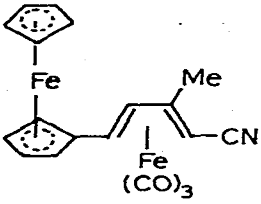

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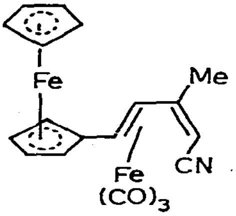

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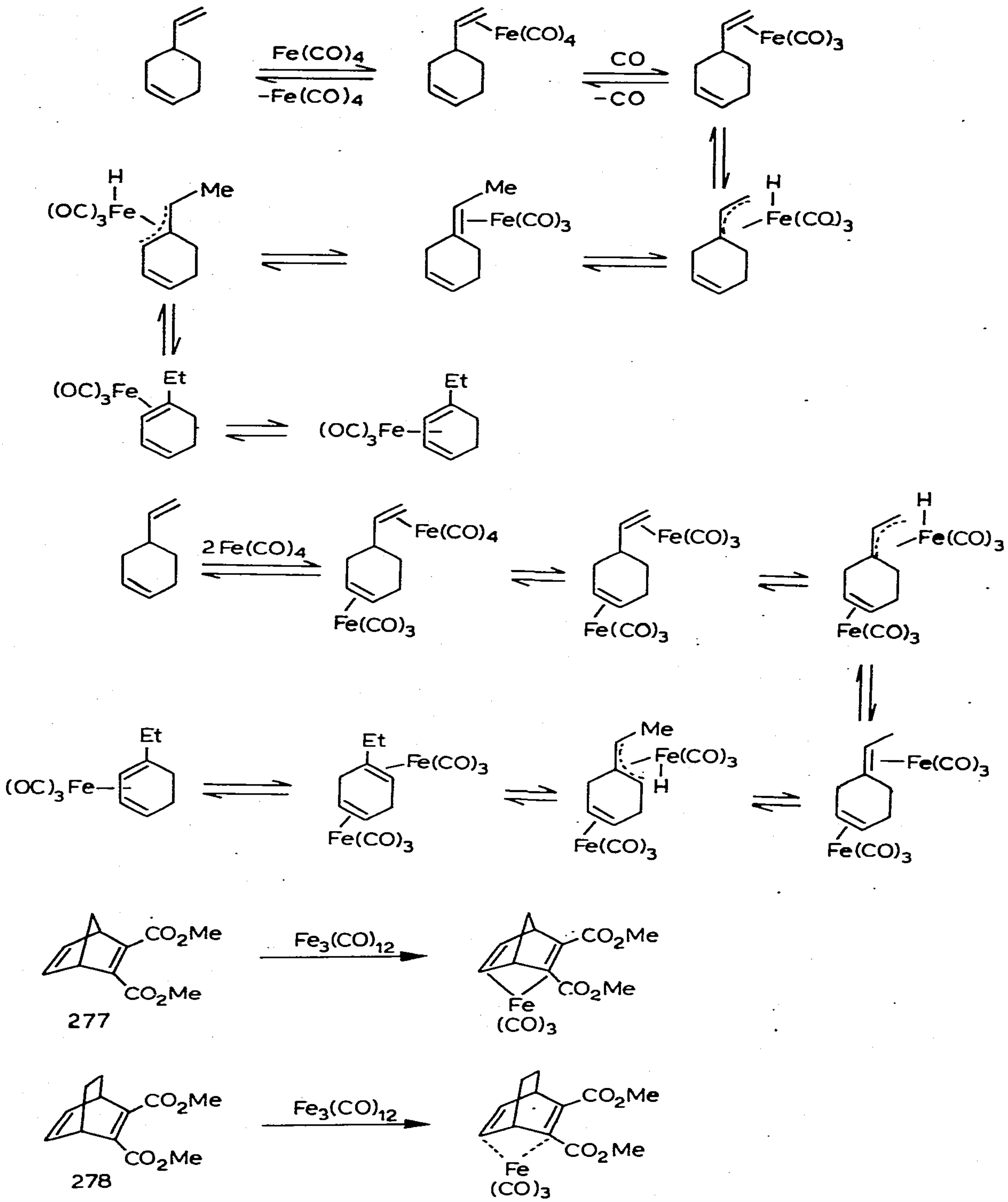
The ferrocenyl alcohol $(\eta^5-C_5H_5)Fe[\eta^5-C_5H_4CH{=}CHC(OH)Me]$ reacted (296) with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ in the presence of $CuSO_4$ giving the 1-ferrocenyl-substituted diene complex [274] and $(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4CH_2CH_2COMe)$, while $(\eta^5-C_5H_5)Fe[\eta^5-C_5H_4CH(Me)-(OH)CH{=}CH_2]$ gave the 2-ferrocenyl derivative. The electronic effect of the ferrocenyl substituent in [274] and its 2-substituted analog as been discussed (297). The species $(\eta^5-C_5H_5)Fe[\eta^5-C_5H_4CH{=}CHCMe(OH)CH_2CN]$ afforded [275] in the presence of $Fe_3(CO)_{12}$ and $CuSO_4$, but when the copper(II) salt was omitted, [276] was produced. Iron carbonyls reacted with 4-vinylcyclohexene giving a mixture of 1- and 2-ethylcyclohexa-1,3-diene iron tricarbonyls, according to Scheme 57. While the dienes [277] and [278] formed the expected diene iron tricarbonyl complexes without skeletal rearrangement, [279] gave [280] with $Fe_3(CO)_{12}$. Reaction of [281] (R = CHO or COMe) with $Fe_3(CO)_{12}$ afforded 1-R-cyclohexadiene iron tricarbonyl with loss of the NEt_2 group.

Scheme 57



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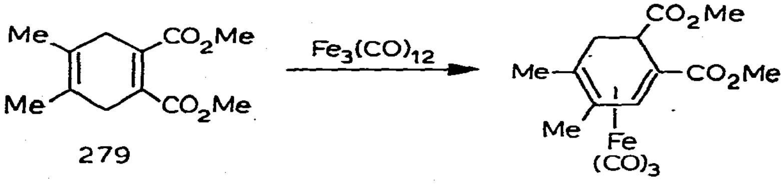
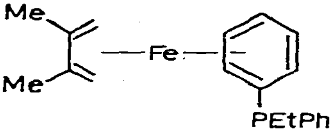
Scheme 57 continued



279 280

Photolysis of $Fe(PEtPh_2)_3(N_2)H_2$ in the presence of 2,3-dimethylbutadiene afforded (298) first [281] and then [282]. However, in the presence of the anhydride [283] (L), the iron phosphine dinitrogen complex gave $[FeL_2]_n$ which, on hydrolysis, afforded [284].

Treatment of $Fe(CO)_3$(diene) (diene = buta- or cyclohexa-diene; C_8H_8) with Na-$[N(SiMe_3)_3]$ gave (299) anionic cyanide complexes, $[Fe(CO)_2(CN)(diene)]^-$. Protonation or ethylation ($[Et_3O]^+$) of these afforded $Fe(CO)_2(CNR)$(diene) (R = H or Et).



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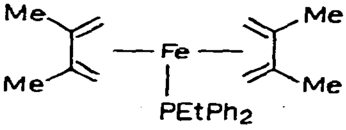

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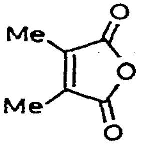

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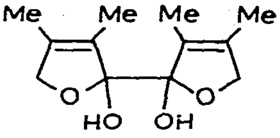
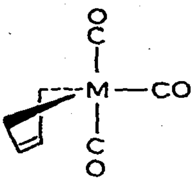


283

Cyclic diene and higher olefin species

The He(I) photoelectron spectra of a series of $M(CO)_3$(diene) complexes (M = Fe, diene = C_4H_6, C_6H_8, C_7H_{10}, C_8H_{12}; M = Ru, diene = C_6H_8 or C_7H_{10}), and of $Fe(CO)_3$-(C_7H_8) and $Fe(CO)_3(C_8H_8)$, have been measured (300). It was observed that the ionisation energies of the iron diene complexes showed a regular variation with ring size, in contrast to those of the parent cyclic dienes.

A study by v.t. ^{13}C n.m.r. spectroscopy of the intramolecular rearrangements of $M(CO)_3$(diene)(M = Fe or Ru; diene = C_4H_6, certain cyclopentadienones, C_6H_8, norbornadiene, cycloheptatriene and -trienone, cycloheptadienone, C_8H_{12} and C_8H_8) revealed (301) that there was a difference in the rate of CO scrambling between species containing conjugated and non-conjugated hydrocarbons. The higher activation barrier to CO scrambling in the conjugated species was attributed to the mixing in of "six-coordinated character", e.g. [285] into the ground state of a formally five-



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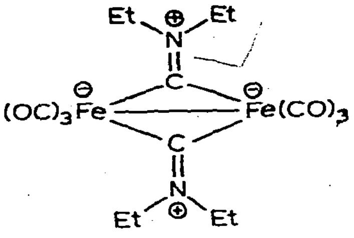

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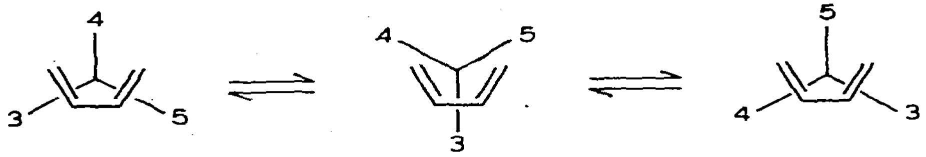
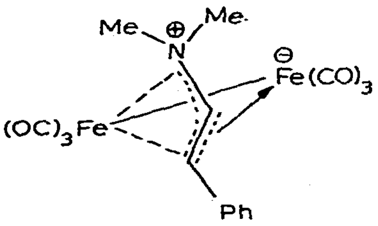
coordinate species. The favoured mechanism of CO site exchange is illustrated in Scheme 58.

Reaction of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with $Et_2NC_2NEt_2$ has given (302) the cyclopentadienone complex $Fe(CO)_3[C_5(NEt_2)_5CO]$ and $Fe_2(CO)_6[C_2(NEt_2)_2]$, [286]. With PhC_2NMe_2 and MeC_2NEt_2, $Fe(CO)_5$ afforded [287] and [288], respectively, whereas with HC_2NMe_2, the ferracyclopentadienyl species [289], or its symmetrical isomer, was produced. Reaction of $Fe_3(CO)_{12}$ with acetylene gave (303) the fulvene complex $Fe_2(CO)_6(C_5H_4CH_2)$ and a polymer formulated as $[FeOC_5H_4Fe(CO)_3]_n$.

It has been observed (304) that of the two isomers [290] (a and b), only a can isomerise to [291] by migration of the C(5)-endo H atom, presumably via a metal hydride mechanism. In this reaction, some 3-methoxy- as well as unsubstituted

Scheme 58





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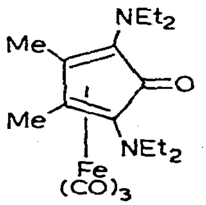

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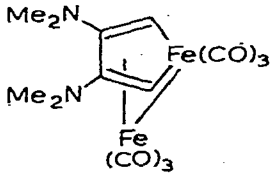

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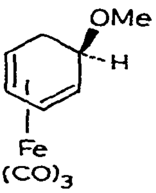
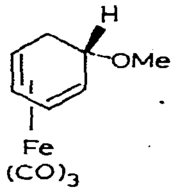


a



b

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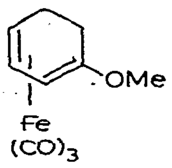

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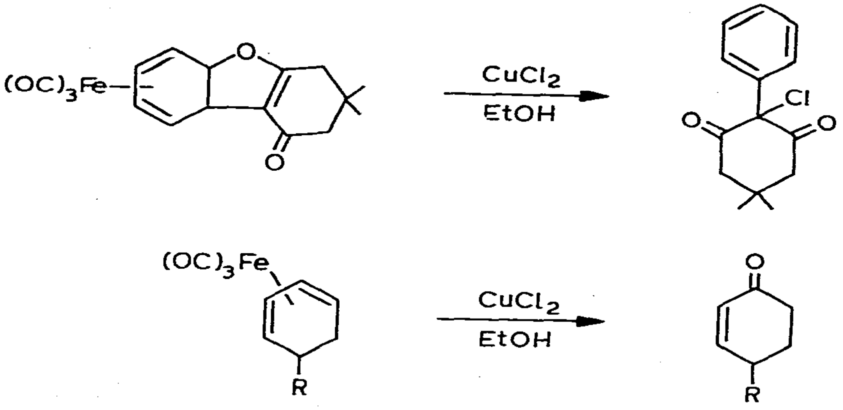
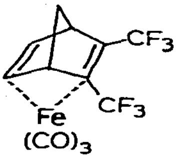
cyclohexa-1,3-diene iron tricarbonyl was produced. Ethanolic cupric chloride (305) proved a useful reagent for removing the $Fe(CO)_3$ group from diene metal complexes, as shown in Scheme 59.

Scheme 59



The substituted norbornadiene complex [292] was obtained (306) by direct reaction of the diene with $Fe_2(CO)_9$. Treatment of the complexes $[Ru(C_7H_8)Cl_2]_n$ and $[Ru(C_8H_{12})Cl_2]_n$ (C_7H_8 = norbornadiene; C_8H_{12} = cycloocta-1,5-diene) with a variety of amines, L (mono-, di- and tri-alkylamines, piperidine, anilines and pyridines) gave (307) the complexes Ru(diene)L_2Cl_2, [293] and [294], whose structures were established crystallographically.

Oxidation of $Fe(CO)_2L(C_xH_y)$ (C_xH_y = η^4-C_4Ph_4, norbornadiene, cycloheptatriene and C_8H_8; L = CO, PPh_3 or $P(OCH_2)_3CMe$) by Ag^+ or NO^+ afforded (308) stable paramagnetic cations, $[Fe(CO)_2L(C_xH_y)]^+$ which could also be detected voltammetrically. Some of these cations reacted with the solvent (usually dichloromethane) forming $[Fe(CO)_2L(C_xH_{y+1})]^+$, but on oxidation of $Fe(CO)_3(\eta^4$-$C_7H_8)$, $[Fe(CO)_3(\eta^5$-$C_7H_7)]^+$ was obtained.



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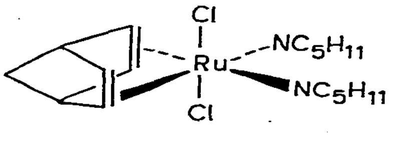

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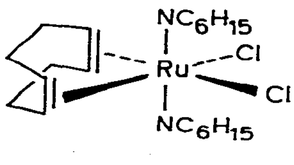

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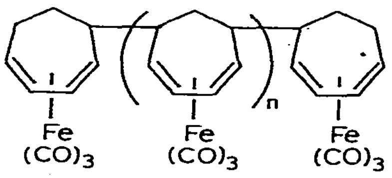

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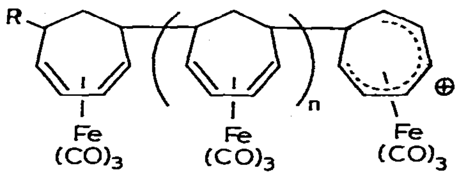

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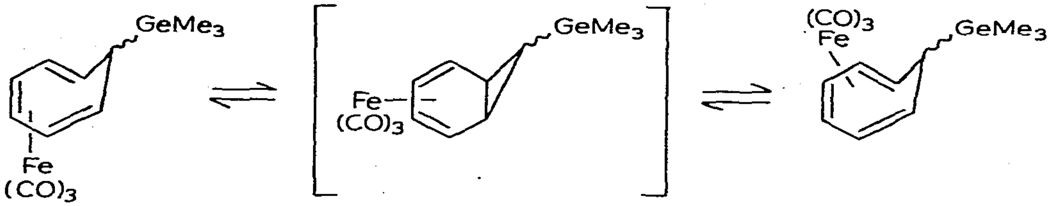
Polymerisation of $Fe(CO)_3(C_7H_7R)$ (R = H), giving [295], was effected (309) by $[C_7H_7][PF_6]$. However, treatment of the cycloheptatriene complex with $[Fe(CO)_3(\eta^5-C_7H_8R)]^+$ ($R = CH_2(Me)C_4H_4MeFe(CO)_3$) afforded [296].

Reaction of $[Fe(CO)_3(C_7H_7)]^-$ with $ClCO_2Me$ gave $Fe(CO)_3(7\text{-}MeO_2CC_7H_7)$ and possibly its 1-carbomethoxy analog (310), but with MMe_3Cl (M = Si or Ge) only $Fe(CO)_3(7\text{-}Me_3MC_7H_7)$ was produced (310, 311). The fluxional properties of these silyl and germyl complexes were investigated (311) and it was concluded that the $Fe(CO)_3$ group underwent an oscillatory movement equivalent to a 1,3-shift (or possibly successive 1,2-shifts) about the ring (see *Scheme 60*). Treatment of $[Fe(CO)_3(C_7H_7)]^-$ with $SnMe_3Cl$ gave a mixture of $Fe(CO)_3(Me_3SnC_7H_7)$ and $Fe(\eta^5-C_7H_7)(CO)_2SnMe_3$.

Scheme 60

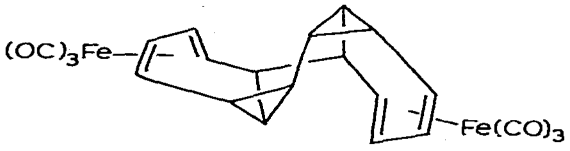


Treatment of $[Ru(C_8H_{12})Cl_2]_2$ with 1,1-dimethylhydrazine gave $[Ru(C_8H_{12})H(NH_2NMe_2)_3]^+$ (312). The hydrazine could be displaced by tertiary phosphines or phosphites ($P(OMe)_3$, $P(OCH_2)_3CMe$, $P(OMe)Ph_2$, PMe_2Ph or $PMePh_2$). Olefin exchange could be achieved when $[Ru(C_8H_{12})H(PMe_2Ph)_3]^+$ was allowed to react with buta- or hexa-1,3-diene, and the structure of $[Ru(C_4H_6)H(PMe_2Ph)_3][PF_6]$ was determined crystallographically. It has a *fac* arrangement of phosphine ligands in a distorted octahedral structure. The cyclooctadiene and hydrazine ligands can be displaced (313) from $[Ru(C_8H_{12})H(NH_2NMe_2)_3]^+$ by chelating diphosphines, L-L ($Ph_2P(CH_2)_nPPh_2$, n = 2, 3 or 4), giving $[Ru(L\text{-}L)_2H]^+$ which takes up hydrogen giving $[Ru(L\text{-}L)_2H_3]^+$. Hydrogen could be displaced from this trihydride by CO, affording $[Ru(CO)(L\text{-}L)_2H]^+$. It appears that $[Ru(diphos)_2(MeOH)H]^+$, obtained from $[Ru(C_8H_{12})H(NH_2NMe_2)_3]^+$ and diphos in methanol, reacted with PhC_2H giving $Ru(diphos)_2(C_2Ph)(CH{=}CHPh)$.

Reduction of $Fe(CO)_3(C_8H_8)$ to the 1,3,5-cyclooctatriene complex was achieved (314) either chemically, using potassium metal in THF, or electrochemically in the presence of $[Me_3NH]Br$; the latter method giving 100% yields. From a v.t. ^{13}C n.m.r. spectral investigation, it was confirmed (315) that $Ru(CO)_3(C_8H_8)$ underwent a series of 1,2-shifts. Activation parameters for the fluxional behaviour of this species and its iron analog were calculated and found to be in satisfactory agreement with data obtained from ^1H n.m.r. spectra. The mechanisms of site exchange in $Fe(CO)_3(C_8H_8)$ were shown definitely to be via 1,2-shifts. Pulsed ^1H n.m.r. spectral studies have been made (316) of $Fe(CO)_3(C_8H_8)$, $Fe_2(CO)_5(C_8H_8)$ and $Ru_3(CO)_4(C_8H_8)_2$ in the solid state. By comparison with solution data, it appeared that the lattice arrangement of these species does not lead to locked or instantaneous structures, and the data further suggested that lattice interactions are not even the major contributions to the energy barriers in the solid state. Interestingly, ring movement occurred in $Fe_2(CO)_5(C_8H_8)$ even below 77°K, revealing that limiting spectra could never be obtained in solution.

The olefin metathesis reaction has been applied (317) to $Fe(CO)_3(C_8H_8)$. Thus, when the complex was treated with $WCl_6/AlEtCl_2$ in ethanol, $Fe_2(CO)_6(C_{16}H_{16})$, [297], was produced, the structure of which was elucidated crystallographically. The hydrocarbon ligand skeleton contains five fused rings and has not been reported previously either as a hydrocarbon or as a metal complex (318), although other polycyclic isomers of $C_{16}H_{16}$ are known (319).

U.V. radiation of $Fe(CO)_5$ and 2,4,6-cycloocatrienone gave (320, 321) the trienone complex [298]. However, if the triene was allowed to react with $Fe(CO)_3(PhCH{=}CHCOMe)$ or its 3-penten-2-one analog, bicyclo[4.2.0]octa-2,4-dien-7-one could be trapped as an $Fe(CO)_3$ complex, [299]. Some reactions of this species are shown in Scheme 61, and the bicyclic ligand could be released intact by oxidation of [299] with Ce^{4+}.



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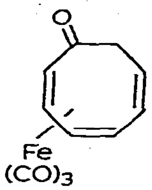

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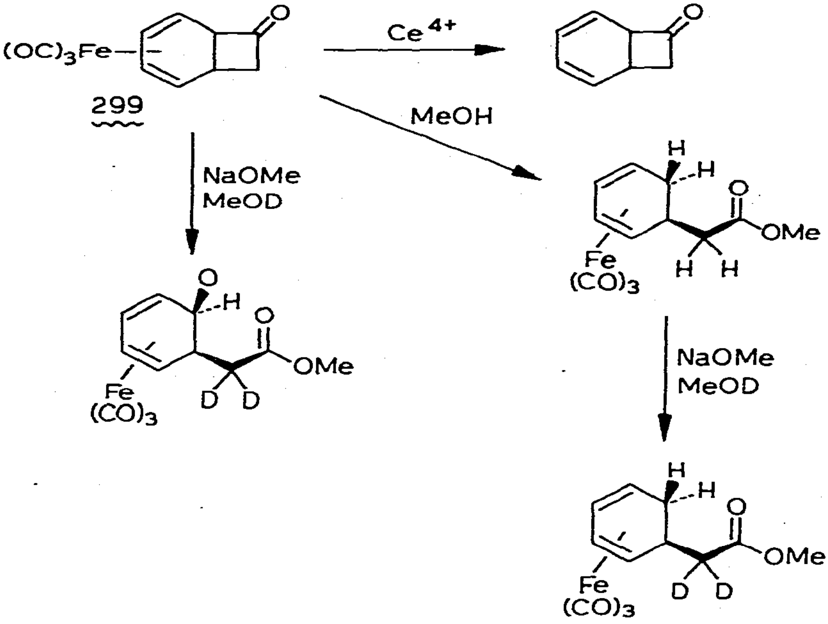
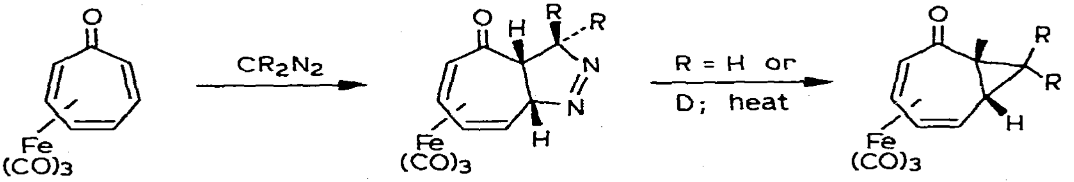
Scheme 61



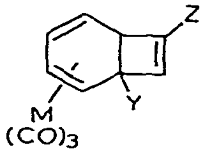
Methoxycyclooctatetraene reacted with $Fe_3(CO)_{12}$ giving (321) mainly the fluxional $Fe(CO)_3(C_8H_7OMe)$ and a small amount of $Fe_2(CO)_6(C_8H_7OMe)$. In attempts to expand a coordinated C_7 to a C_8 ring, tropone iron tricarbonyl was treated with diazomethane. However, this reaction afforded bicyclic derivatives, as illustrated in Scheme 62.

Scheme 62



Thermolysis of $M(CO)_3(1,3,5\text{-}R\,R'R''C_8H_5)$ (M = Fe or Ru, R, R', R'' = H, $SiMe_3$, $GeMe_3$, CPh_3 or Ph) in octane afforded (322) the bicyclo[4.2.0]octa-2,4,7-triene derivatives [300] (M = Fe or Ru; X, Z = H, $SiMe_3$, $GeMe_3$, CPh_3 or Ph), $M_2(CO)_5(C_8H_7QMe_3)$ (M = Fe or Ru; Q = Si; M = Ru, Q = Ge), $Ru_2(CO)_6(C_8H_7CPh_3)$ or $Ru_3(CO)_4(C_8H_7CPh_3)_2$. The structure of [300] (M = Fe, Y = $SiMe_3$, Z = CPh_3) was determined crystallographically. Reaction of $Ru(CO)_3(C_8H_8)$ with $[Ph_3C]^+$ gave $Ru(CO)_3(C_8H_7CPh_3)$ and [301]. Thermolysis of $Ru(CO)_3(C_8H_7SiMe_3)$ gave exclusively [302], and [300] was not observed. The $GeMe_3$ analog was obtained directly from $C_8H_7GeMe_3$ and $Ru_3(CO)_{12}$. However, on heating $Ru(CO)_3(C_8H_7CPh_3)$, both [300] (Y = H, Z = CPh_3) and $Ru_3(CO)_4(C_8H_7CPh_3)_2$ were produced.

Bicyclo[6.1.0]nona-2,4,6-triene reacted (323) with $Fe_2(CO)_9$ giving [303] which, on heating, isomerised to [304]. Treatment of a syn-dimethoxynorbornene derivative with $Fe(CO)_5$ afforded (324) [305].



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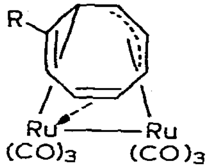

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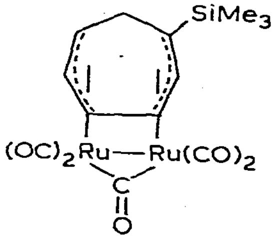

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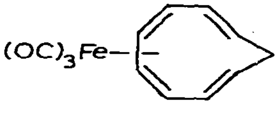

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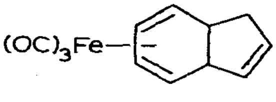

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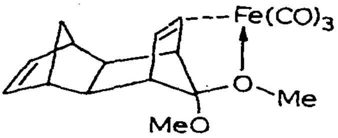

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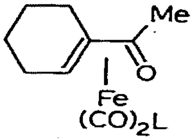
Heterodiene species

Thermolysis of $Fe(CO)_3L(PhCH{=}CHCOR)$ (L = $P(OMe)_3$ or $P(OPh)_3$; R = H, Me or Ph) gave (325) $Fe(CO)_2L(PhCH{=}CHCOR)$ in which the keto group of the hydrocarbon ligand is bonded to the metal. Reaction of $Fe_2(CO)_9$ with 1-acetylcyclohexene in the presence of $P(OMe)_3$ or $P(OPh)_3$ afforded [306]. A variety of heterodiene iron tricarbonyl complexes, $Fe(CO)_3(RCH{=}CHCOR')$ (R = Ph, R' = H, Me or Ph; R = ferrocenyl, R' = Ph; R = $Cr(\eta^6-C_6H_5)(CO)_3$, R' = $p-MeOC_6H_4$) reacted with PMe_2Ph, $P(OMe)_3$, $P(OPh)_3$ or $SbPh_3$ giving (326, 327) $Fe(CO)_3L(RCH{=}CHCOR')$ in which only the ethylenic bond is attached to the metal. However, [307] reacted with PMe_2Ph or $P(OMe)_3$ giving [308].



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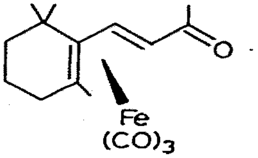

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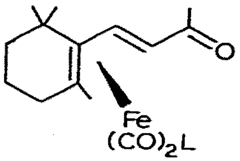

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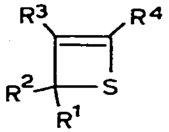
The thietes [309] ($R^1 = R^2 = R^3 = R^4$ = H; $R^1 = R^4$ = H, R^2 = Me, R^3 = Et or $R^2 = R^3 = (CH_2)_5$) reacted (328) with $Fe(CO)_5$ or $Fe_2(CO)_9$ giving [310] from which one CO group could be displaced by PPh_3 or $P(OEt)_3$. While [310] ($R^1 = R^2 = R^3 = R^4$ = H) appeared to be dimeric in solution, the structure of $Fe(CO)_2(PPh_3)(\eta^4-C_3H_4S)$ was determined crystallographically, and this species at least is monomeric. However, on heating or photolysis, [310] ($R^1 = R^2 = R^3 = R^4$ = H; $R^1 = R^4$ = H, R^2 = Me, R^3 = Et) gradually lost CO giving [311] whose structure was also established by X-ray methods. Oxidation of [310] by H_2O_2 in acetic acid afforded, for example, isomers of $[Fe(CO)_3(\eta^4-C_3H_2R^2R^3SO)$, in which the isomerism was defined by the exo- or endo-nature of the S=O bond, but oxidation using *m*-chloroperbenzoic acid gave [312]. Hydride abstraction from [310] [$R^1 = R^2 = R^3 = R^4$ = H) gave $[Fe(CO)_3(C_3H_3S)]^+$ which may be either [313] or [314].

The tetraphenyl-1-silycyclopentadiene complexes [315] underwent a variety of substitution reactions at silicon (329), as shown in Scheme 63. While the silacyclopentadiene C_4Ph_4SiHMe reacted with $Fe_3(CO)_{12}$ giving (330) [315] (R = Me, R' = H), with $Ru_3(CO)_{12}$ it afforded $Ru(CO)_4H(SiMeC_4Ph_4)$, which was not isolated, but dimerised giving [316]. However, $C_4Ph_4SiMe_2$ or $C_4Ph_4SiPhCl$ reacted with $Ru_3(CO)_{12}$ giving the ruthenium analogs of [315] (the structure of the dimethylsilyl derivative has already been reported (331)).

Treatment of $Fe_2(CO)_9$ with 2,5-dihydrothiophene-1-oxide afforded (332) [317] which, on heating, was converted into [318]. ESCA measurements of $Fe(CO)_3(C_4H_4S)$, [317], [318], $Fe(CO)_3(C_4H_4SO_2)$ and their 2,5-dimethyl substituted analogs have been made and discussed (333). The use of Me_3NO as a mild and general reagent for the removal of organic ligands from $Fe(CO)_3$ groups has been described (334). By using $Fe(CO)_3(C_4H_4SO_2)$, the mechanism of this decomplexing reaction has been probed (335) and of particular interest was the isolation of [319]. This may be formed prior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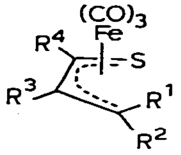
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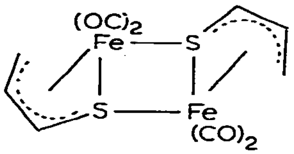
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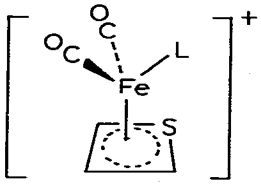
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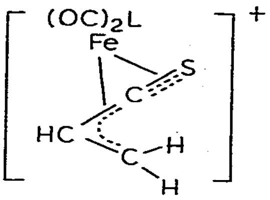
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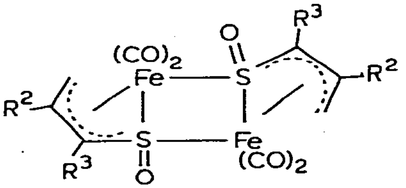
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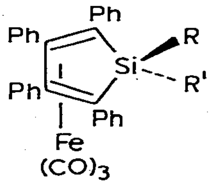
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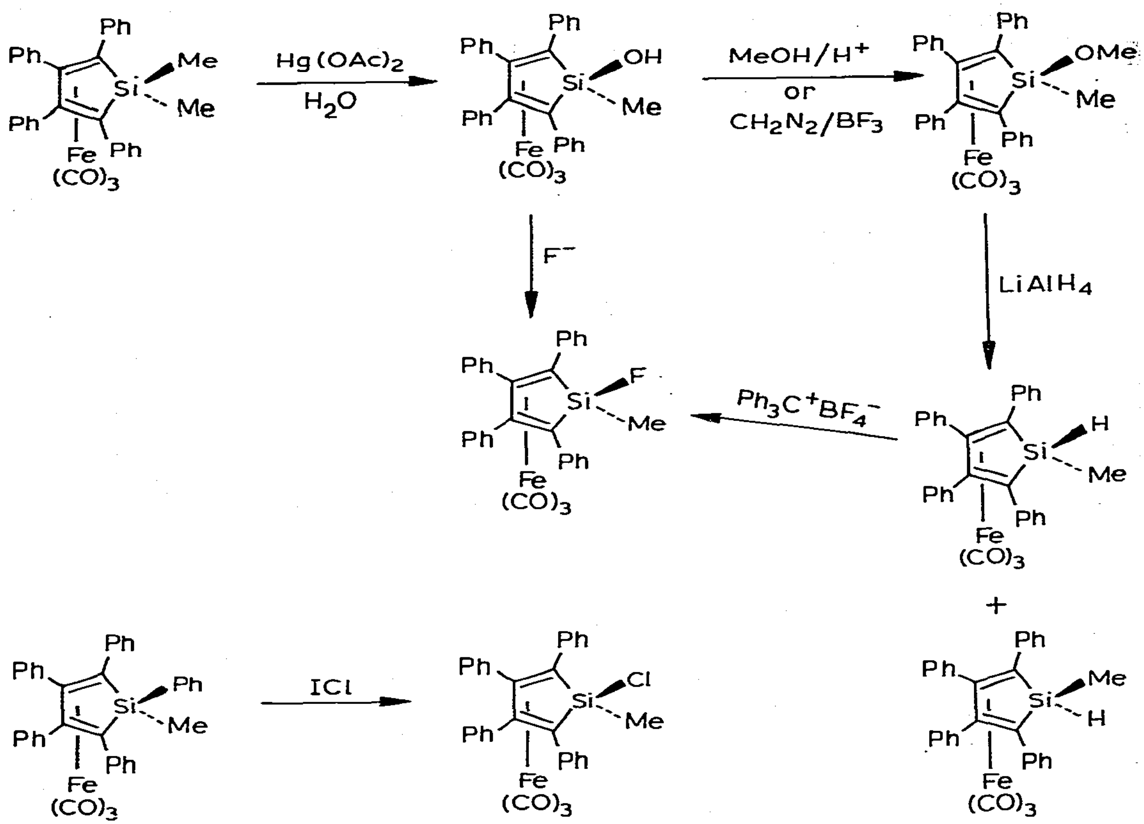
to loss of the thiophene dioxide according to Scheme 64.

Solvent and concentration dependent ^{1}H n.m.r. and i.r. spectral studies of the diazepine complexes [320] (R = H) revealed (336) that fluxional pathways in this species involve intermolecular proton transfer. The fluxional processes are strongly acid-catalysed and proceed through a fluxional η^4-imminium ion complex, [321] (R = H), which can be directly observed by n.m.r. spectroscopy. The crystal structure of a representative salt of this imminium complex has been determined (337). It was found that protonation of non-fluxional diazepine complexes, e.g. [320] (R = Me) or 1-acetyldiazepine iron tricarbonyl led to static η^4-imminium species, e.g. [321] (R = Me) or [322].

Scheme 63



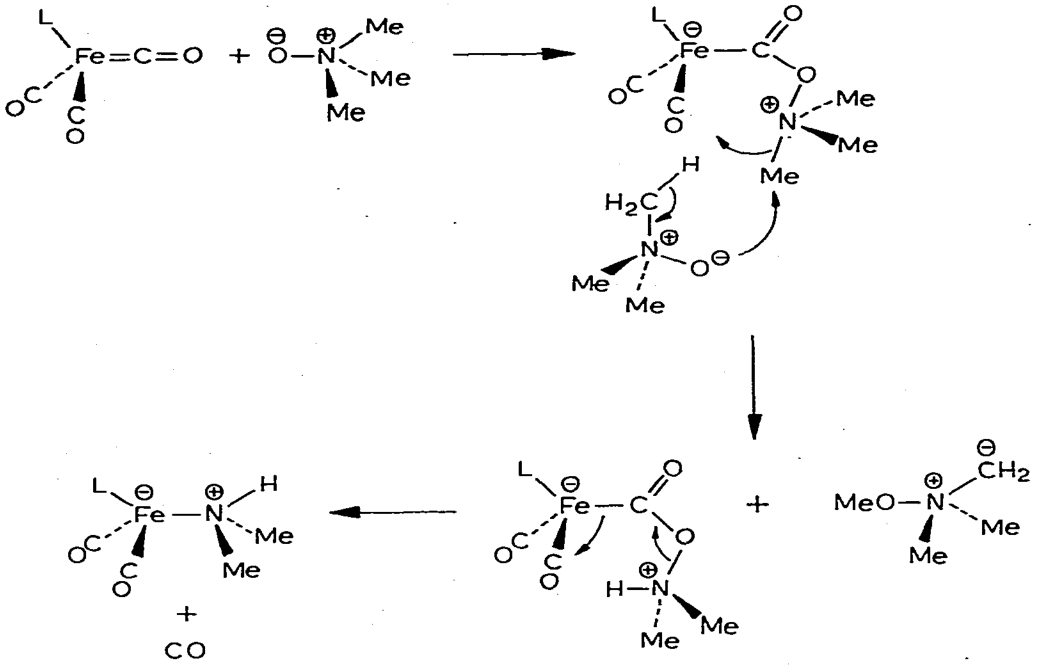
Bis-olefin complexes

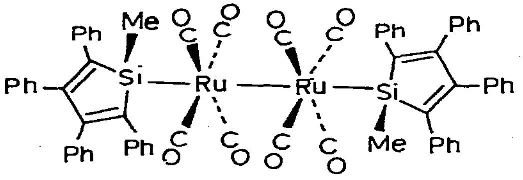
Reaction of iron atoms at -196° with butadiene, follwed by $P(OMe)_3$, afforded (338) $Fe(C_4H_6)_2[P(OMe)_3]$ and $Fe(C_4H_6)[P(OMe)_3]_3$. With 2,3-dimethylbutadiene, only $Fe(C_4H_4Me_2)[P(OMe)_3]_3$ could be obtained. Styrene and phenylacetylene reacted with Fe atoms giving polystyrene and triphenylbenzene, respectively. However, when a mixture of styrene, Fe atoms and CO was allowed to warm from -196° to -20°, the styrene complex [323], $Fe(CO)_4(CH_2{=}CHPh)$ and $Fe(CO)_5$ were formed. There was no evidence for C-H bond activation and no stable complexes could be produced in the absence of $P(OMe)_3$ or CO. Cycloocta-1,5-diene reacted with iron atoms giving (339) the known $Fe(C_8H_{12})_2$ (340) which reacted with CO and $P(OR)_3$ giving $Fe(CO)_5$ and the fluxional $Fe(C_8H_{12})[P(OR)_3]_3$ (R = Me, Et or Pr^i), respectively.

From v.t. ^{13}C n.m.r. spectral studies of $Ru(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_7H_8)$, [324], it was suggested (341) that the spectrum in the slow exchange limit was inconsistent with a series of 1,2-shifts but could be explained in terms of a "piano-stool" ($\eta^8\text{-}C_8H_8$) type of transition state, or a series of 1,3-shifts, the former being preferred.

The electric dipole moments of $Fe(C_4H_6)_2L$ (L = CO or $P(OMe)_3$), $Fe(CO)(C_4H_4Me_2)_2$, $Fe(CO)(C_6H_8)_2$, $Fe(CO)_3(C_4H_6)$, $Fe(CO)_3(C_8H_8)$ and $Fe(CO)_4[P(OMe)_3]$ have been measured (342) permitting an assessment of the magnitude of the Fe-C-O group moment (ca. 2 D).

Scheme 64





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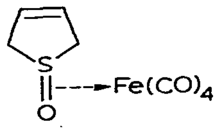

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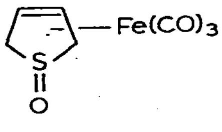

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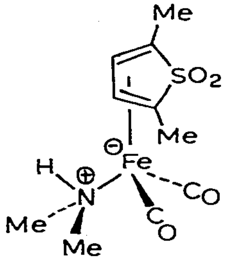
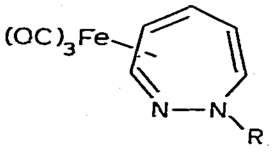


319

DIENYL COMPLEXES

^{13}C n.m.r. spectral data for the pentadienyl cations [325] and [326] (R^1, R^2, R^3 = H and/or Me) have been correlated (343) with charge density at the C atoms as calculated from extended Hückel m.o. theories. The "leakage" of the ψ-endo to the ψ-exo isomer during solvolysis of [327] (R = H, R' = dinitrobenzoate) (Scheme 65) did not proceed (344) via a syn,syn cis-diene $Fe(CO)_3$ cation, e.g. [328]. The most



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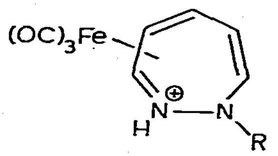

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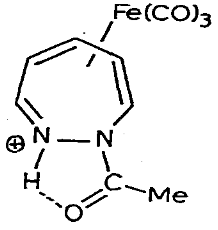

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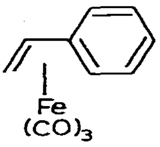

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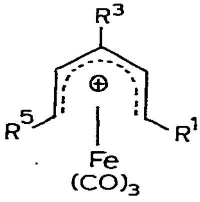

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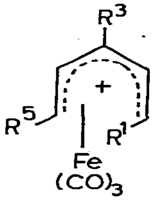

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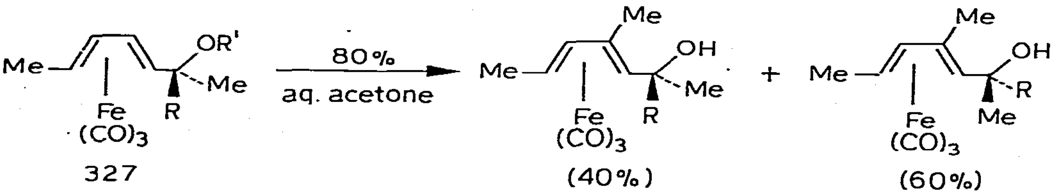
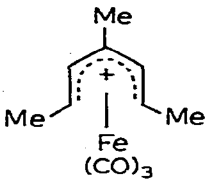
Scheme 65



probable mechanism for the production of both isomers involves non-stereospecific ionisation of the dinitrobenzoate ester giving [329]. Using [327] (R = D, R' = dinitrobenzoate), solvolysis with intervention of a species like [328] would give deuterium scrambling, e.g. [327] (R = D, R' = H), [330] and [331], which is not observed. However, [327] (R = D, R' = H), on treatment with alumina, gave a mixture of [327] (R = D, R' = H), [330] and [331], and solvolysis of [327] (R = D, R' = dinitrobenzoate) in unbuffered aqueous acetone afforded these three compounds also, the third being produced by dinitrobenzoic acid catalysed dehydration of [330], giving deuterium substituted [328] followed by hydrolysis.

The 1-methylpentadienyl iron tricarbonyl cation reacted (345) with NEt_3 giving [332] which, on heating, eliminated $[Et_3NH]^+$ giving the triene complex [333]. Similar adducts were obtained with PPh_3 and $AsPh_3$, the former giving a syn-anti complex analogous to [332], and also a syn-syn form.

The geometrical deformations of η^5-cyclohexadienyl and other iron complexes have been described (346) in terms of an electronic factor. It was suggested that in C_6H_7 species there is a secondary M...CH_2 interaction which is destabilising leading to substantial deformation of the methylene group out of the C_5 plane. This effect is also present in cyclopentadiene $Fe(CO)_3$ species, but is less or absent in cyclopentadienone and cyclobutenyl complexes. In fulvene iron carbonyl derivatives, there should be a bending of the methylene group towards the metal.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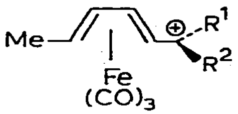
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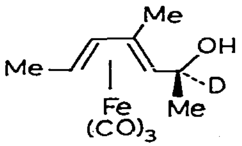
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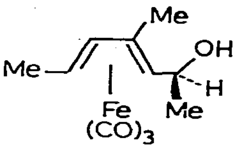
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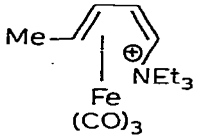
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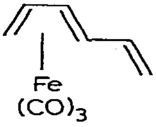
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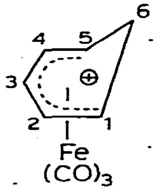
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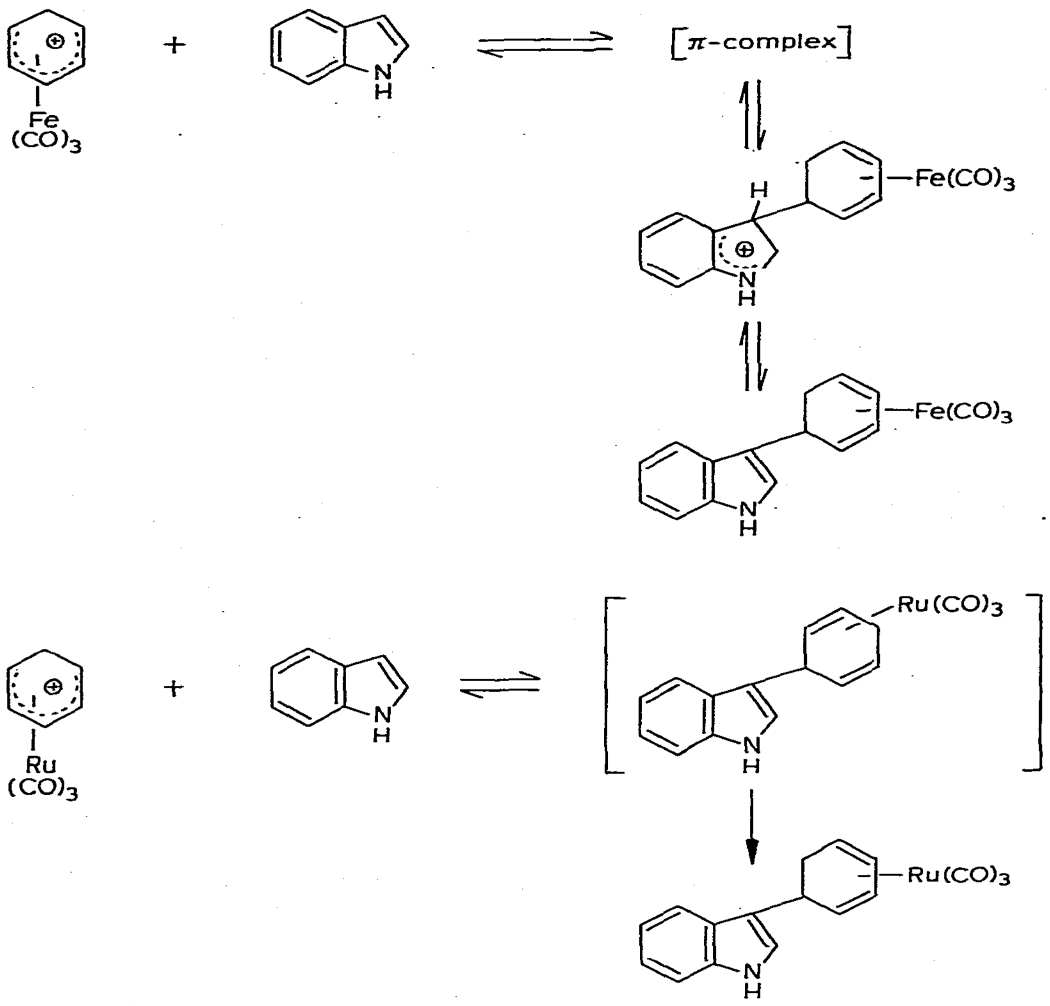
INDO calculations have been made on $[Fe(\eta^5-C_6H_7)(CO)_3]^+$ (347) and it was suggested that there may be a correlation between the bond index (of free valence) values at each dienyl C atom, and the site of nucleophilic addition. Coordination of $\{Fe(CO)_3\}$ by $C_6H_7^+$ was seen to increase, relative to free $C_6H_7^+$, the positive charge at C(2), [334], which arises mainly via π-electron interactions. The charge data predicted that site preference for nucleophilic addition to be C(2) > C(3) > C(1) which is contrary to the experimental observations (348) that C(1) is preferred. The bond index values, however, are consistent with the experimental facts, predicting the preference for addition to be C(1) > C(3) > C(2).

The reactions of cyclohexadienyl iron and ruthenium tricarbonyl cations with nucleophiles have been investigated. Thus, kinetic data obtained from the reactions of these cations with indole have been interpreted (349) (Scheme 66) in terms of a π-complex intermediate. With the Fe species, the formation of this intermediate is the rate determining step whereas with the Ru complex, the slow rearrangement of this intermediate to a Wieland-type σ-complex is the rate determining step. Addition of PBu^n_3 and $P(OBu^n)_3$ to $[Fe(\eta^5-C_6H_7)(CO)_3]^+$ gave (350) the phosphonium complex salts [335]. The kinetics of the addition of acetylacetone (acacH) to $[M(\eta^5-C_6H_7)(CO)_3]^+$ and related $\eta^5-C_6H_6OMe$ and $\eta^5-C_7H_9$ complexes have been studied (351) in various solvents and compared with previous data (352). It was shown that the reactions are not subject to solvent changes and it appears that the overall mechanism involved a rapid pre-equilibrium dissociation of acetylacetone to $[acac]^-$ which then added directly to the dienyl rings. Methylation of the cyclohexadienyl ring in $[Fe(\eta^5-2-RC_6H_6)(CO)_3]^+$ (R = H, Me or OMe), giving $Fe(CO)_3(2-R-5-MeC_6H_6)$, was achieved (353) stereospecifically and regioselectively using $LiCuMe_2$. Organo-cadmium complexes, CdR_2 (R = Ph, CH_2Ph, $CHMe_2$, $CH_2CH{=}CH_2$, $CH_2CH{=}CHMe$ or $CH{=}CHMe$) also reacted similarly (354) with $[Fe(\eta^5-2-RC_6H_6)(CO)_3]^+$.

Hydride abstraction by Ph_3C^+ from [336] afforded (355) the silacyclohexadienyl complex [337].

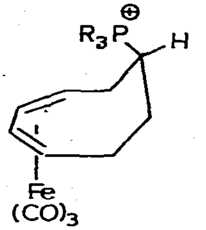
Scheme 66



Nucleophilic addition (N_3^-, OEt^-, PBu^n_3 or PEt_3) to the cycloheptadienyl iron tricarbonyl cation proceeded (356) via addition to the metal, follwed by transfer of the nucleophile to the ring.

Treatment of $[Fe(\eta^5-C_7H_7)(CO)_3]^+$ with $Fe(\eta^5-C_5H_5)(CO)_2(\eta^1-C_3H_5)$ and a related species [338] gave (357) [339] and [340] (a and b). The reactions of [339] are summarised in Scheme 67. Reaction of $[Fe(\eta^5-C_7H_7)(CO)_3]^+$ with the η^1-allene complex $Fe(\eta^5-C_5H_5(CO)_2CH_2C{=}C{=}CH_2$ or its propargyl analog afforded [341] (R = H or Me).

Deuteriation of tropone iron tricarbonyl, follwed by treatment of the product with base and then addition of HBF_4, gave (358) the tri-deuteriate species [342] (X = Y = Z = D). Nucleophilic addition to this species by hydride, and also OMe^-,



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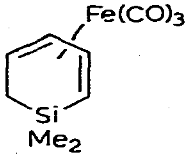

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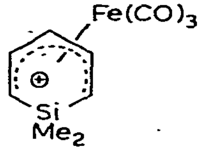

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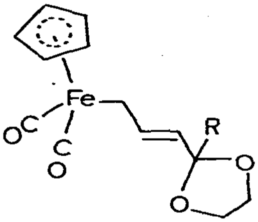

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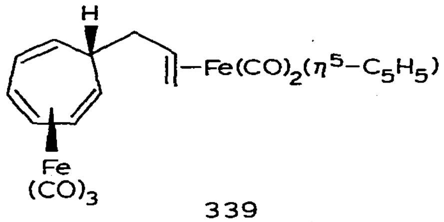

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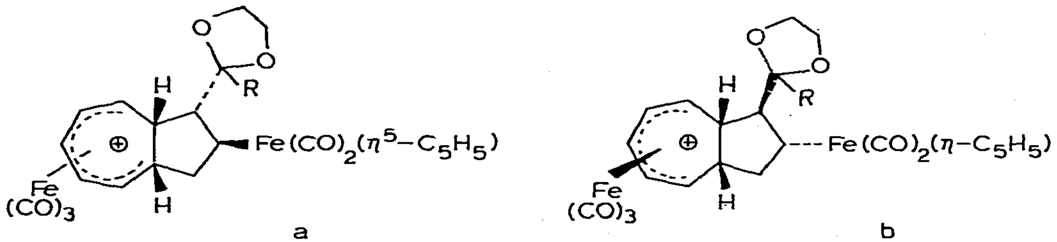

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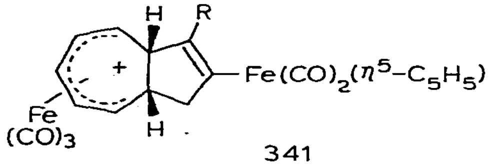

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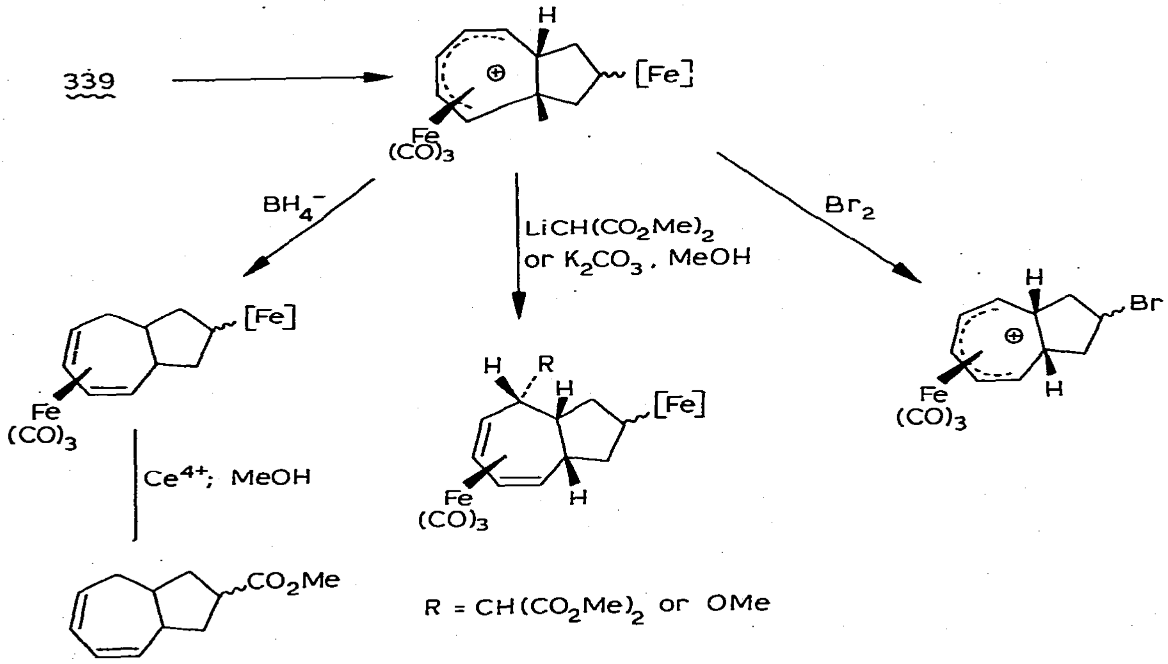
NHR$^-$ (R = Bu^t or Ph) and N$_3^-$, occurred at the 3-position, giving [343], while CN$^-$ attack gave [344]. The species [345] reacted with CN$^-$ affording [346] and [347].

Reaction of [Fe(CO)$_3$(C$_7$H$_7$)]$^-$ with Mn(CO)$_5$Br and [Re(CO)$_3$(THF)Br]$_2$ gave (359) FeM(CO)$_6$(C$_7$H$_7$) (M = Mn or Re), [348]. With [Rh(CO)$_2$Cl]$_2$, the cycloheptatrienyl anion afforded [349] whose structure was established crystallographically. The Rh-Fe distance, 2.76 Å, is somewhat longer than those in [Rh{Fe(PPh$_2$)(CO)$_2$(η^5-C$_5$H$_5$)}$_2$]$^+$ (2.67 and 2.66 Å)(360), RhFe$_3$(η^5-C$_5$H$_5$)(CO)$_9$ (2.57 and 2.62 Å) and Rh$_2$Fe$_2$(η^5-C$_5$H$_5$)$_2$-(CO)$_8$ (2.60 and 2.57 Å)(361, 362).

Reaction of cycloheptadiene with Os(CO)$_4$(MR$_3$)$_2$ or [Os(CO)$_4$(MR$_3$)]$_2$ (M = Si or Ge; R = Me or Et; or SiMe$_2$Ph) afforded (363) [350] (the major product) and [351]. With

Scheme 67

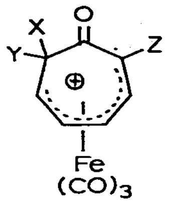
$[Fe] = Fe(\eta^5\text{-}C_5H_5)(CO)_2$



$Os(CO)_4H(SiEt_3)$, only [350] was formed, and neither this nor [351] could be obtained from $[Os(CO)_4Q]_2$ (Q = $SiPh_3$ or $SiMe_2Cl$). The species [351] is analogous to $Ru_2(C_7H_7)(CO)_5(MMe_3)$ (364). Both [350] and [351] are fluxional, there being in the former restricted rotation about the $Os\text{-}C_7H_9$ bond which permits the existence of conformational isomers which interconvert rapidly at ambient temperatures. Reaction of [350] with bromine or iodine gave $Os(\eta^5\text{-}C_5H_9)(CO)_2X$ (X = Br or I) and treatment of these species with $P(OMe)_3$ or $[Re(CO)_5]^-$ gave $[Os(\eta^5\text{-}C_7H_9)(CO)\{P(OMe)_3\}_2]I$ and $Os(\eta^5\text{-}C_7H_9)(CO)_2Re(CO)_5$.

Co-condensation of iron atoms with cycloheptatriene gave (365, 366) the fluxional η^5-cycloheptadienyl-η^5-cycloheptatrienyl species [352] whose structure was established crystallographically. The complexed rings are essentially planar and the open faces of the two η^5- rings are skew to each other; the structure being analogous to $Ru(\eta^5C_7H_7)(\eta^5C_7H_9)$ (367). A second product from this reaction, $Fe(C_{14}H_{18})$, was thought to be $Fe(\eta^5\text{-}C_7H_9)_2$. Co-condensation of iron atoms with C_8H_8 gave intractable polymers.

Protonation of $M(CO)_3(C_8H_8)$ (M = Fe or Ru) occurred (368) by two different routes (Scheme 68) and the species $Fe(\eta^3\text{-}C_8H_9)(CO)_3Cl$ was isolated.



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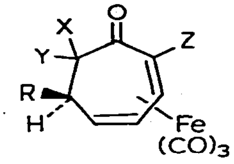

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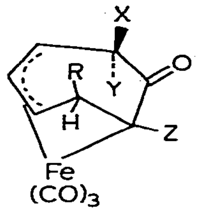

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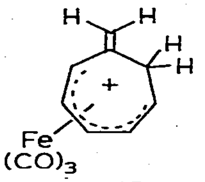

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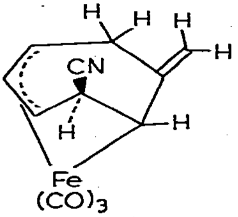

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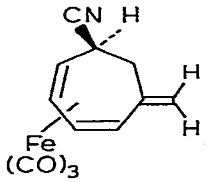

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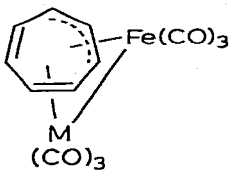

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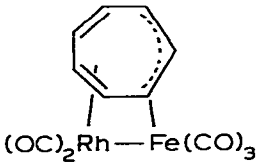

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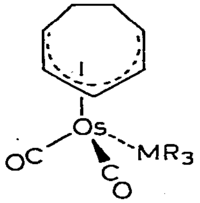

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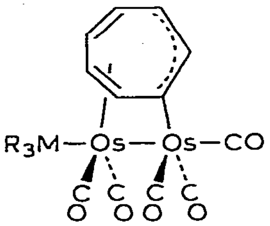

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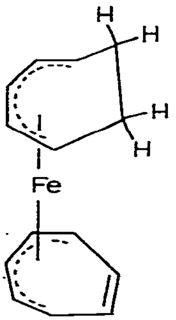


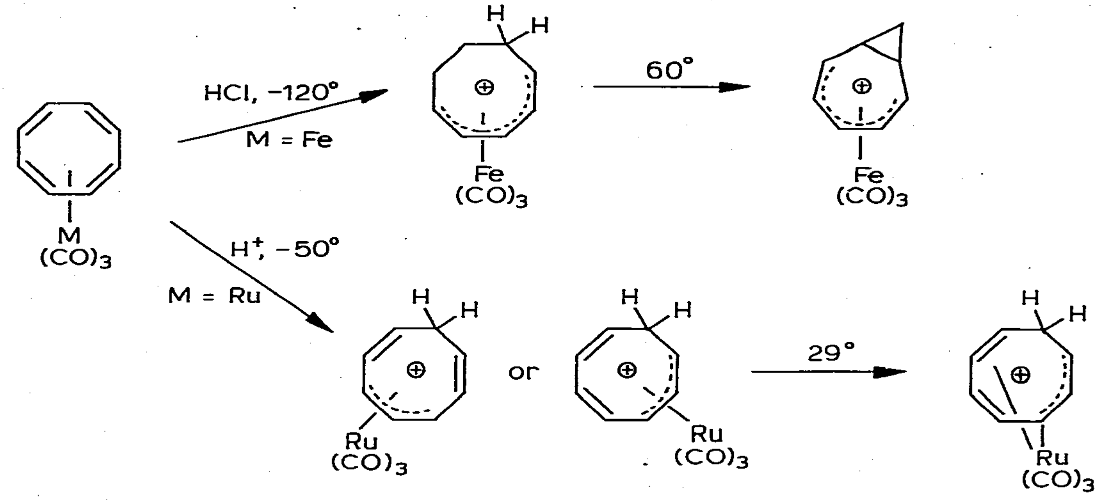
352

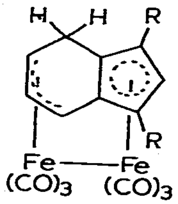
CYCLOPENTADIENYL COMPLEXES

Binuclear species

Iron pentacarbonyl reacted (369) with $[1,3\text{-}(Me_3Si)_2C_5H_3]^-$ giving $[Fe\{\eta^5\text{-}1,3\text{-}(Me_3Si)_2C_5H_3\}(CO)_2]_2$. Treatment of $Fe_2(CO)_9$ with 1-H-indenes afforded (370) the binuclear species [353], a 4-indenyl derivative (R = H or Me). A somewhat similar

Scheme 68





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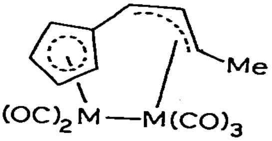

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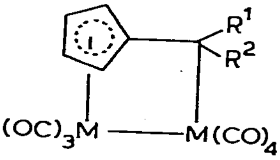

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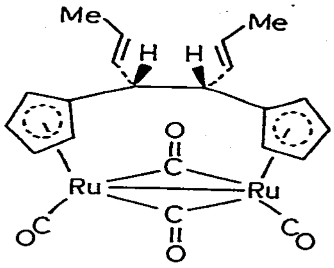

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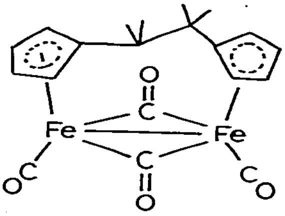

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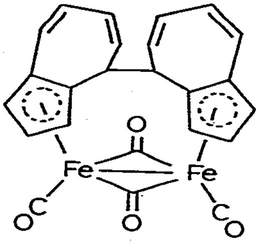

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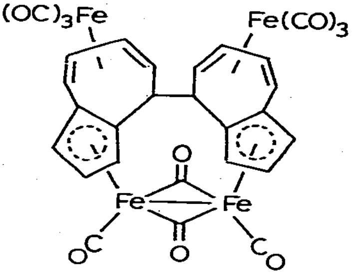

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species, [354], was obtained (371) from the reaction between $Fe_2(CO)_9$ or $Ru_3(CO)_{12}$ and 6(trans-prop-1-enyl)fulvene, other products being [355] (R^1. R^2 = H, Pr^i) and [346].

A detailed study of the v.t. ^1H and ^{13}C n.m.r. spectra of $[M(\eta^5\text{-dienyl})(CO)_2]_2$ (M = Fe or Ru; dienyl = C_5H_5, MeC_5H_4, indenyl, tetrahydroindenyl) has been reported (372). A major difference in spectral behaviour between the Fe and Ru complexes was detected in that in the latter both bridged and non-bridged isomers could be observed, and it was noted that bridge opening to non-bridge rotamers was a rate determining step for the interconversions of the ruthenium complexes. It was observed that the new data could not be fully satisfactorily interpreted in terms of the proposals of Cotton, Roberts and their coworkers (373) although the mechanisms proposed are essentially the same (Scheme 69). The activation energies of the CO interchange process are given in Table 3. The barriers to rotation of the non-bridged iron dimers seem to be markedly greater than those of their Ru analogs. It was suggested that metal-metal bonding in these complexes may be directional and hence at least part of the rotational barrier in the non-bridged species may be due to hindered internal rotations about the metal-metal bond. Spectral data for $FeNi(\eta^5\text{-}C_5H_5)_2(CO)_3$ were also reported, and only the trans isomer was detected in solution.

TABLE 3

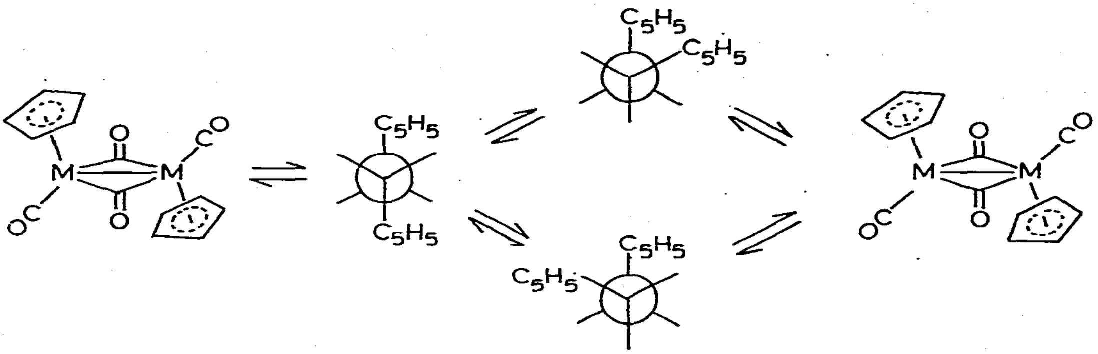
Activation energies for the structural interconversion of $[M(\eta^5\text{-dienyl})(CO)_2]_2$ and related species

M	η^5-dienyl	isomer	E_a[a]
Fe	C_5H_5	trans	7.1±0.8
		cis	11.2±0.3
	MeC_5H_4	trans	8.0±0.6
		cis	11.3±0.6
	C_9H_{11}[b]	trans	8.8±0.6
		cis	18.3±2.2
	C_9H_7[c]	trans	10.4±0.6
		cis	28.8±2.0
Ru	C_5H_5		7.8±0.4
	C_5H_4Me		10.0±0.3
	C_9H_{11}		14.9±0.5
	C_9H_7		14.0±0.5

M	η^5-dienyl	isomer	E_a[a]
$FeNi(\eta^5\text{-}C_5H_5)_2(CO)_3$			9.5±0.4
$[Cr(\eta^5\text{-}C_5H_5)(NO)_2]_2$			>21.5
$[Mn(\eta^5\text{-}C_5H_5)(CO)(NO)]_2$			>13.8±0.6

[a] activation energy in kcal/mol; [b] tetrahydroindenyl; [c] indenyl

Scheme 69

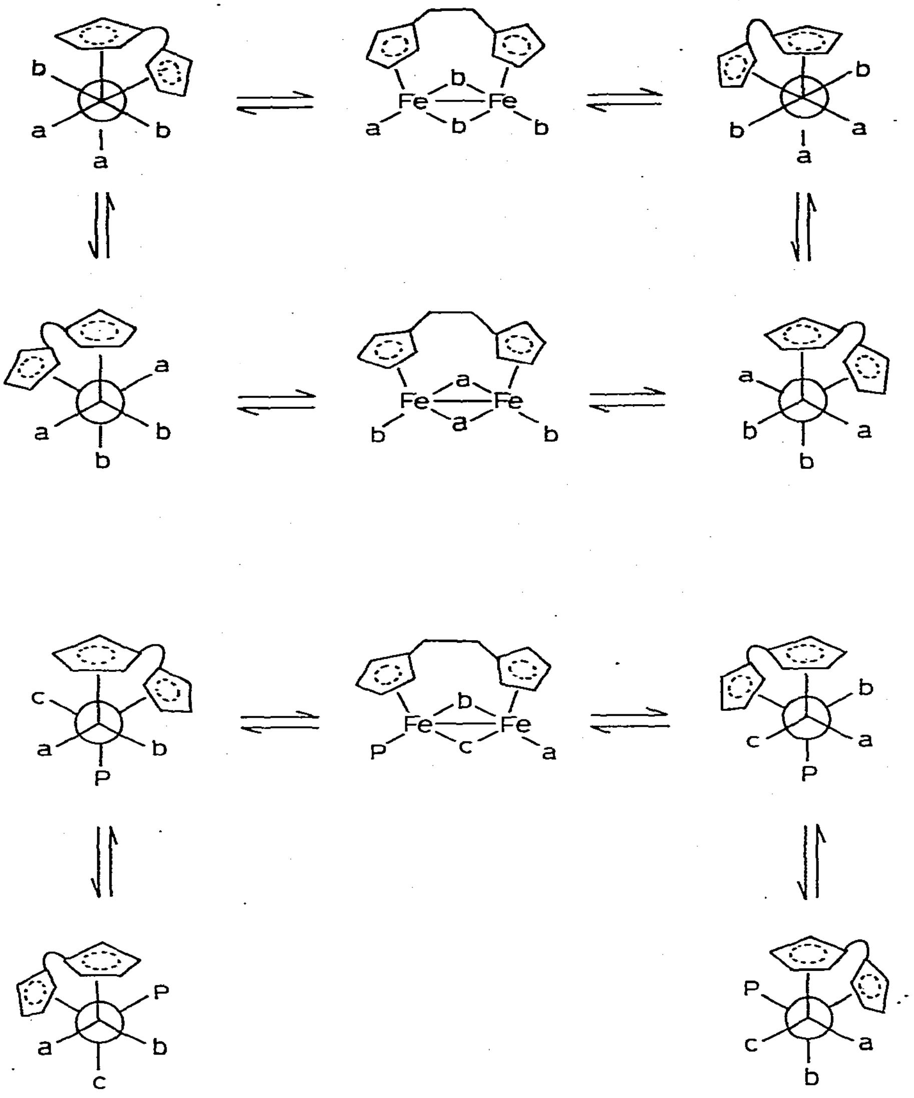


The dynamic properties of linked η^5-dienylring species [357] (L = CO or $P(OPh)_3$), obtained from L = CO by reaction with $P(OPh)_3$, [358], obtained from $Fe_3(CO)_{12}$ and azulene, and [359], prepared from [358] by reaction with $Fe_3(CO)_{12}$, have been described (374). The structure of [357] (L = $P(OPh)_3$) was determined crystallographically (Fe-Fe 2.50 Å). Bridge-terminal CO group exchange occurred in [357] (L = CO) as rapidly as in cis-$[Fe(\eta^5-C_5H_5)(CO)_2]_2$, more slowly in [358] and [359], and not at all in [357] (L = $P(OPh)_3$). These results are in accord with previously proposed mechanisms (375) which require that bridged species pass directly to staggered configurations of non-bridged intermediates and assume the necessity for internal rotation about the metal-metal bond in order that bridge-terminal group exchange can occur. The proposed mechanism of exchange for [357] (L = CO) and an explanation of the lack of CO exchange in [357] (L = $P(OPh)_3$) is summarised in Scheme 70. From a comparison of the i.r. spectra of [357] (L = $P(OPh)_3$) with that of $Fe_2(\eta^5-C_5H_5)_2(CO)_3[P(OPh)_3]$ indicated that the cis-isomer of the latter is predominant in solution in non-polar solvents, in contrast to $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ where the populations of cis and trans-isomers are almost equal at room temperature.

In an X-ray photoelectron spectral study of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$, separate O 1s peaks were detected (376) for the terminal and bridging CO oxygen atoms. A kinetic determination of Fe-Fe bond dissociation energies has been made (377) for the disproportionation of $Fe_2(\eta^5-C_5H_5)(\eta^5-C_5H_4Me)(CO)_4$ into $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ and $[Fe(\eta^5-C_5H_4Me)(CO)_2]_2$ in benzene. The reaction proceeded via radical species, viz. $Fe(\eta^5$-dienyl$)(CO)_2$, and $\Delta H^{\ddagger} = 26.9 \pm 2.7$ kcal/mol and $\Delta S^{\ddagger} = 2.0 \pm 3.2$ cal mol^{-1} deg^{-1}. The Mössbauer spectra of a series of binuclear iron complexes, e.g. $Fe_2(\eta^5-C_5H_5)_2(CO)_3L$ (L = CO, tertiary phosphine or phosphite), $[Fe(\eta^5-C_5H_5)(CO)]_2(Ph_2PRPPh_2)$ (R = CH_2, C_2H_4 or NEt), $Fe(\eta^5-C_5H_5)(CO)_2(\mu-PPh_2)Fe(CO)_2L_2$ (L = CO or PR_3), and $Fe(\eta^5-C_5H_5)(CO)(\mu-CO)(\mu-PPh_2)(CO)_2L$ (L = CO or PR_3) have been measured (378). Many of the compounds studied had non-equivalent iron environments, and various lines in the spectra were analysed.

Carbon monoxide could be displaced from $[Fe(\eta-C_5H_5)(CO)_2]_2$ by primary amines giving (379) the cis and trans-isomers of $Fe_2(\eta^5-C_5H_5)_2(CO)_3(NH_2R)$ (R = Et, Bu^n,

Scheme 70



C_6H_{11}, CH_2Ph; RNH_2 = piperidine, morpholine, bipyridyl or o-phen).

Reduction of $[Fe(\eta^5-C_5H_5)(CO)_2(CS)]^+$ by NaH afforded (380) cis and trans-$Fe(\eta^5-C_5H_5)(CO)(CS)]_2$. An X-ray crystallographic study of the cis form revealed bridging CS and a metal-metal bond (2.48 Å) significantly shorter than in cis-$Fe(\eta^5-C_5H_5)(CO)_2]_2$. The trans-isomer slowly converted into a cis/trans mixture in xylene.

Anionic and cationic species

Alkali metal reduction of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ in hexamethylphosphoramide gave (381), as expected, salts of $[Fe(\eta^5-C_5H_5)(CO)_2]^-$. Magnesium amalgam reacted (382) with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ in THF giving $[Mg(THF)_2][Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$. Solution spectral studies of $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ in ethereal solvents in the presence of dibenzo-18-crown-6 revealed (383) the presence of three distinct ion pairs, one of these involving a direct Na...Fe interaction, another a more normal Na...OC interaction, and the third a solvent-separated ion pair. Conductivity studies of $[Fe(\eta^5\text{-}C_5H_5)(CO)_3][BPh_4]$, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(PMe_2Ph)][BPh_4]$ and $[(Ph_3P)_2N][Fe(CO)_4H]$ revealed (384) that these species, too, formed ion-pairs.

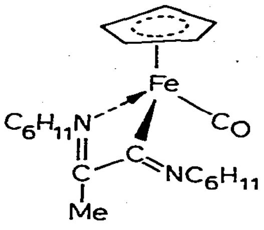
Treatment of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CS)]^+$ with Lewis bases L (PPh_3, $AsPh_3$, $SbPh_3$, $P(C_6H_{11})_3$; also $P(p\text{-}XC_6H_4)_3$, X = F or OMe) gave (385) $[Fe(\eta^5\text{-}C_5H_5)(CO)(CS)L]^+$. The loss of CO in this substitution suggested that the strength of the Fe-CS bond is greater than that of the Fe-CO bond. ^{13}C n.m.r. spectral studies indicated that the deshielding of the ^{13}CS resonance increased as the CS force constant decreased, and the shielding of the carbonyl resonances of $[Fe(\eta^5\text{-}C_5H_5)(CO)(CS)(PPh_3)]^+$ relative to $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)]^+$ was attributed to an increased π-acceptor ability of the CS ligand relative to CO. The thiocarbonyl cation reacted with RNH_2, N_3^- or N_2H_4, and OMe^-, affording $[Fe(\eta^5\text{-}C_5H_5)(CO)L(CNR)]^+$, $Fe(\eta^5\text{-}C_5H_5)(CO)(L)NCS$, and $Fe(\eta^5\text{-}C_5H_5)(CO)(L)C(=S)OMe$. Nucleophilic attack by $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$, and its C_5H_4Me and C_5Me_5 analogs, on CS_2 afforded (386) the adduct $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CS_2)]^-$, which, although it was not isolated, gave, on treatment with MeI, $Fe(\eta^5\text{-}C_5H_5)(CO)_2C(=S)SMe$. Reaction of the CS_2 adduct with $SnPh_3Cl$ and with $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ afforded $Fe(\eta^5\text{-}C_5H_5)(CO)_2C(=S)SSnPh_3$ and $Fe(\eta^5\text{-}C_5H_5)(CO)_2C(=S)SFe(CO)_2(\eta^5\text{-}C_5H_5)$, respectively.

Carbene complexes

Treatment of the iminoacyl complexes [360] with Bu^tNC gave (387) the carbene species [361] (R = H). The compound previously formulated (388) as [362] should now be described as [361] ($R = p\text{-}XC_6H_4$; X = H or Cl). Protonation of $Fe(\eta^5\text{-}C_5H_5)(CO)_2C(=NC_6H_{11})CH_2C_6H_4X$ (X = H or Cl) gave the carbene complex [363] whereas similar treatment of [362] affored the bis-carbene species [364].

Alkene derivatives

Oxidation of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ by Ph_3C^+ in the presence of an alkene gave (390) $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^2\text{-alkene})]^+$ (alkene = 1-heptene, 1- or 4-octene, cyclo-heptene or -octene). Treatment of such species (alkene = propene, isobutene, heptene, styrene, allylbenzene or cyclopentene) with $NaBH_3CN$ afforded (391) the corresponding alkyl derivatives in good yield. Thus, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2{=}CHR)]^+$ could be converted into a mixture of $Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2CH_2R$ and $Fe(\eta^5\text{-}C_5H_5)(CO)_2CHMeR$ (with alkene = propene, only the former was produced). While $NaBH_3CN$ reduction of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2{=}CMe_2)]^+$ gave exclusively $Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2CHMe_2$, $NaBH_4$ gave a 3:1 mixture of the t-butyl and i-butyl derivatives. Reduction of the acenaphthylene cation by $NaBD_3CN$ afforded [365]. Attempts to produce alkyl derivatives from $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(alkene)]^+$ where alkene = cyclo-heptene, -octene or norbornadiene were unsuccessful.



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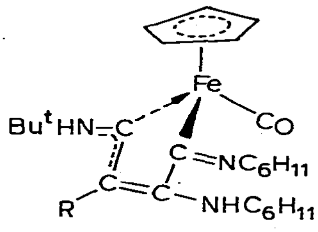

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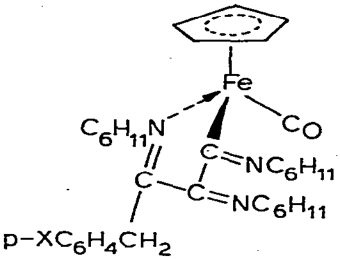

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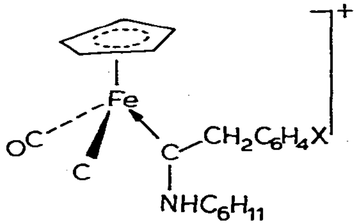

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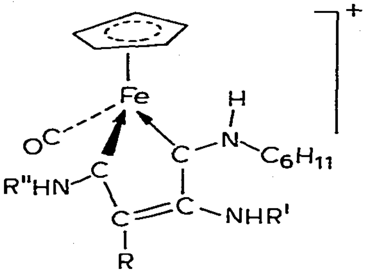

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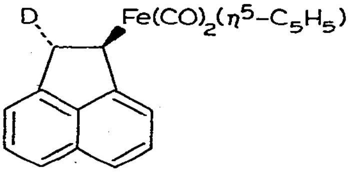

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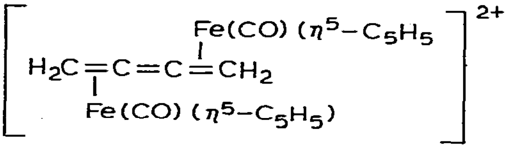


$$\left[\overset{\hphantom{Fe(CO)(\eta^5-C_5H_5)}\ \ Fe(CO)(\eta^5-C_5H_5}{H_2C{=}C{=}C{=}CH_2}\atop Fe(CO)(\eta^5-C_5H_5)\right]^{2+}$$

366

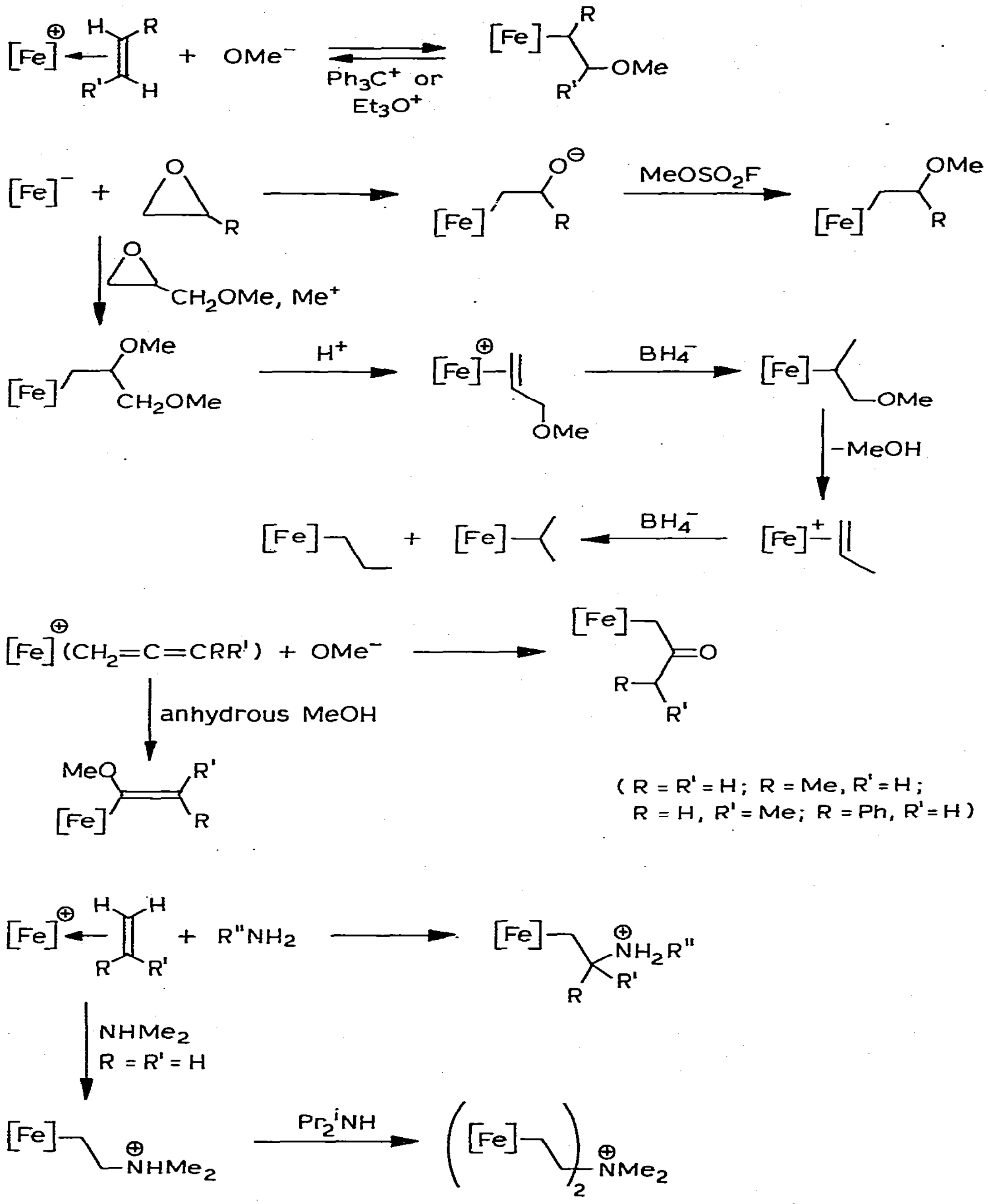
The addition of heteroatomic nucleophiles to $[Fe(\eta^5-C_5H_5)(CO)_2(CHR{=}CHR')]^+$ (R = R' = H or Me; R' = H, R = Me or Ph, CHO or CH_2OMe) occurred (392) with high regioselectivity giving a single, monosubstituted alkene adduct (Scheme 71).

Hydride abstraction by Ph_3C^+ from $Fe(\eta^5-C_5H_5)(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(\eta^5-C_5H_5)$ gave (393) the butatriene complex [366] whose reactions are summarised in Scheme 72. Reaction of 1,2-dichlorocyclobutene with $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ afforded (394) [367] and [368] whose behaviour with Ag^+ or Ph_3C^+ is shown in Scheme 73. Oxidation of [368] by Ag^+ in the presence of cyclopentadiene and [369] gave the cationic complexes [370] and [371], whereas oxidation in the absence of a diene produced the tricyclooctadiene complex [372]. These reactions with dienes strongly indicate the presence of the η^2-cyclobutadiene complex [373], and the production of the tricyclooctadiene cation via [373] is depicted in Scheme 74. It was observed that the formation of syn-tricyclooctadiene cannot be considered as prima facie evidence for the intermediacy of C_4H_4 in reactions involving transition metals.

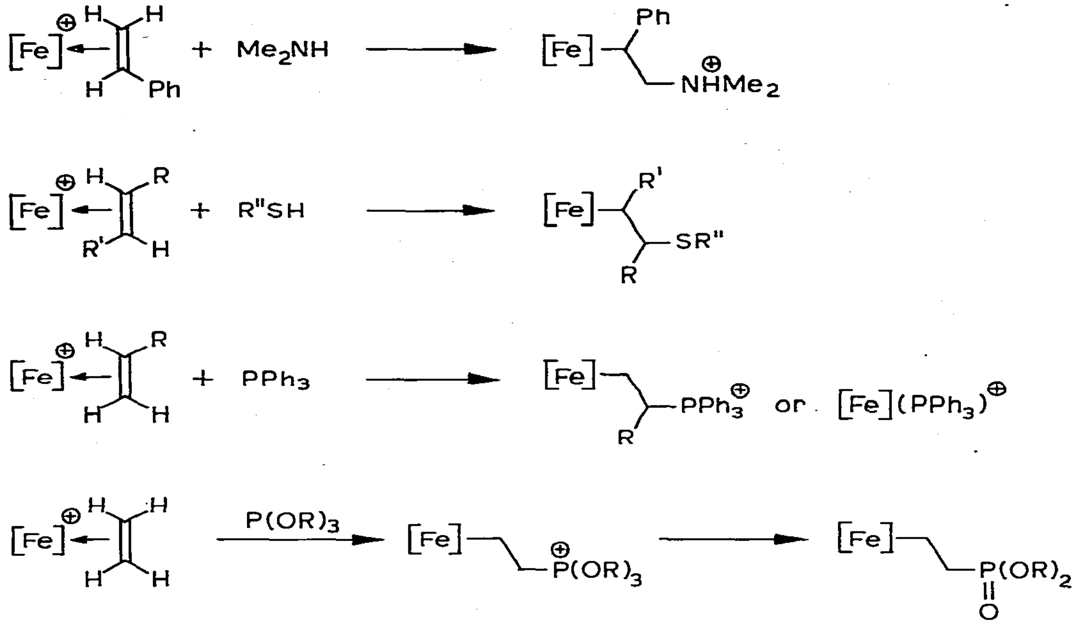
Benzocyclobutenylidene, [373], and naphtho[b]cyclobutenylidene, [374], iron tricarbonyl cations have been prepared (395) by routes outlined in Scheme 75. The reactions of [373] and [374] are also shown in this Scheme 75. The chemical behaviour of the η^2-benzocyclobutadiene complex [375] is summarised in Scheme 76.

Scheme 71

$Fe(\eta^5-C_5H_5)(CO)_2 \equiv [Fe]$

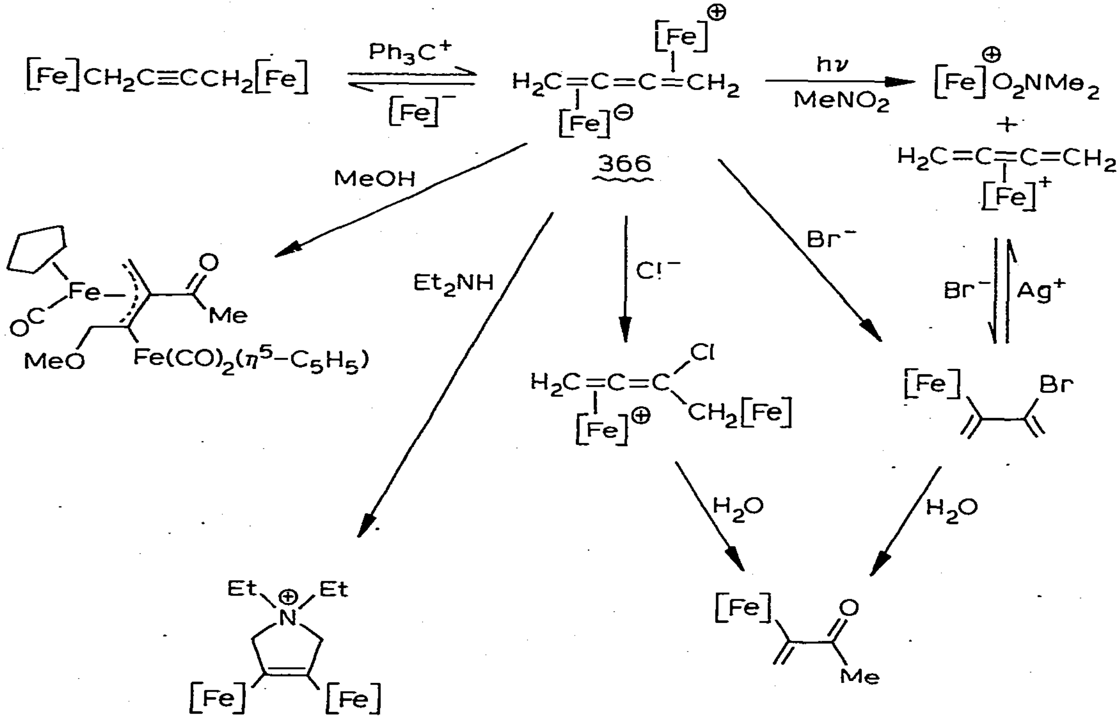


Scheme 71 continued



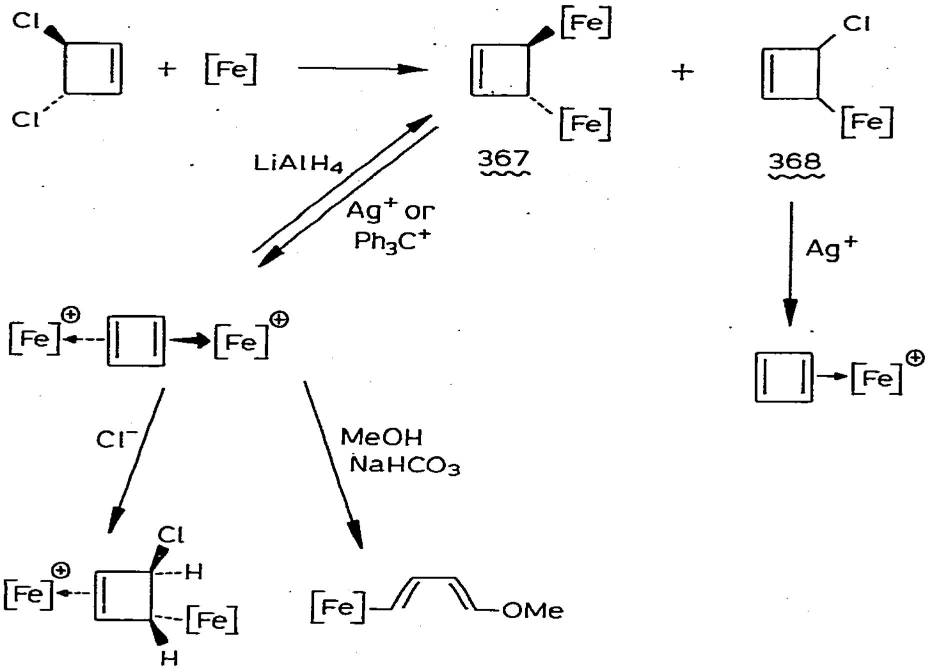
Scheme 72

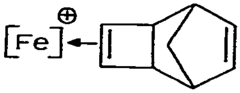
$Fe(\eta^5\text{-}C_5H_5)(CO)_2 \equiv [Fe]$



Scheme 73

$Fe(\eta^5\text{-}C_5H_5)(CO)_2 \equiv [Fe]$





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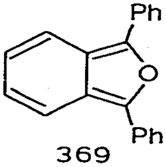

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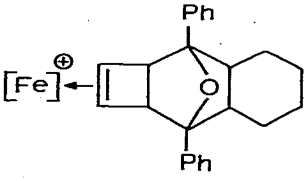

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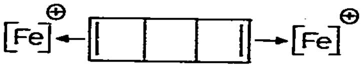
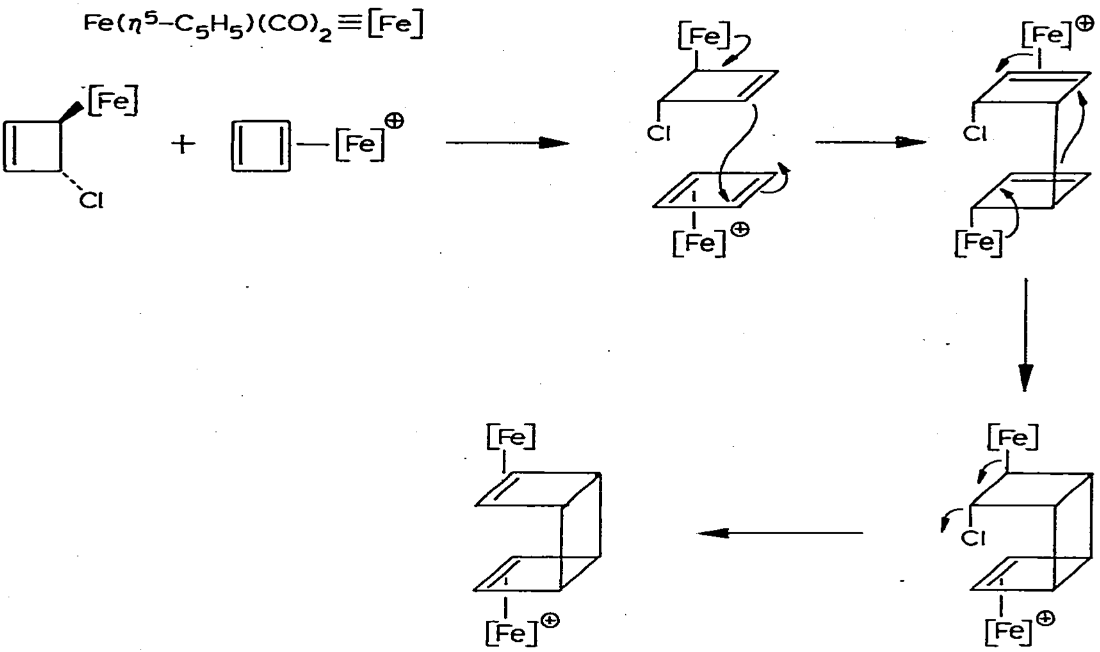


372

Scheme 74



Complexes containing M-C σ-bonds

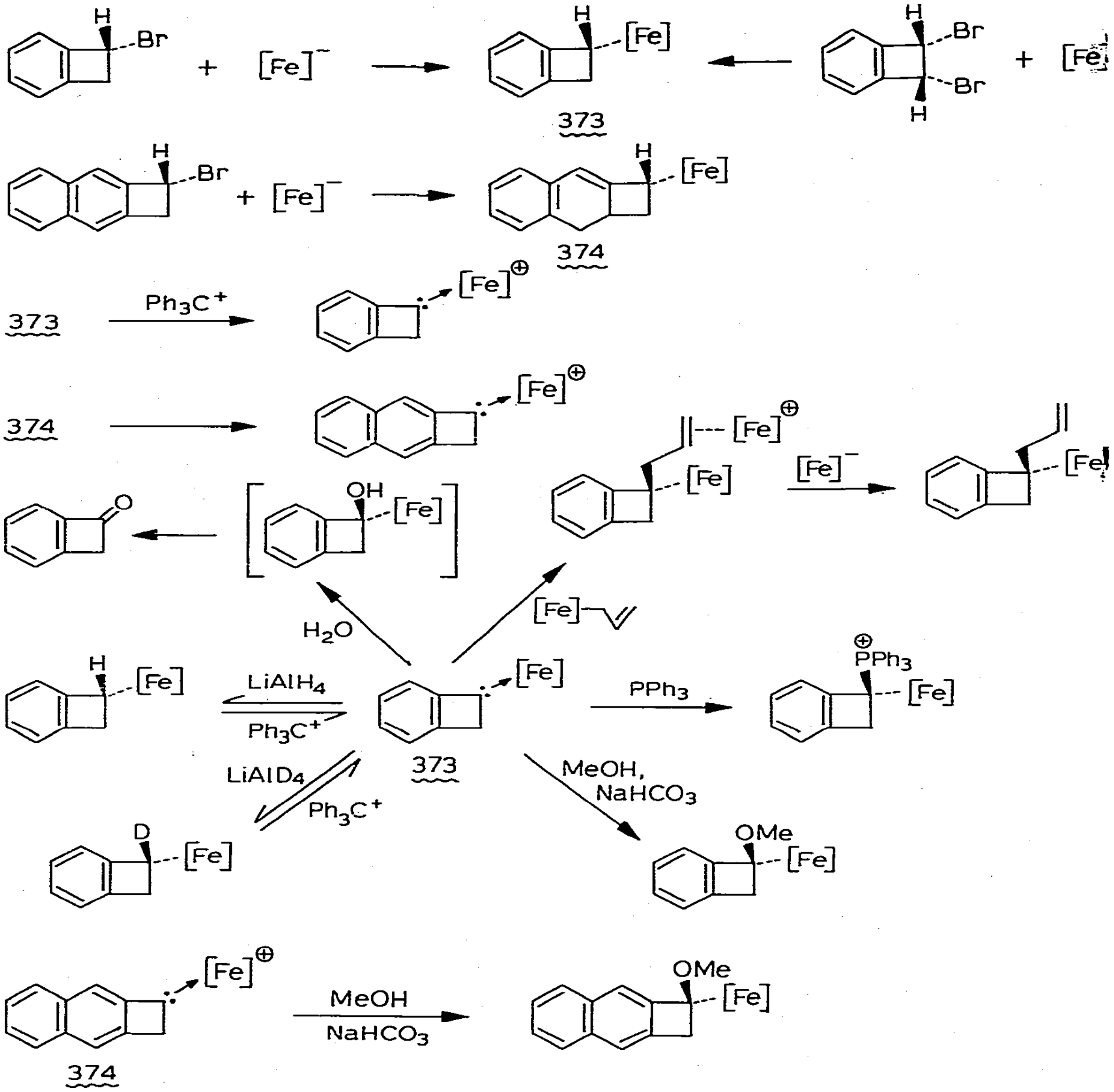
The ionisation energies for M-C σ-bonded species have been obtained from the photoelectron spectra (396) of $M(\eta^5\text{-}C_5H_5)(CO)_2Me$ (M = Fe or Ru) and $Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2CN$.

Reaction of 2-adamantyl halides (RX) with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ gave (397) $Fe(\eta^5\text{-}C_5H_5)(CO)_2R$, while a similar reaction with R'COCl (R' = 1-adamantyl) afforded $Fe(\eta^5\text{-}C_5H_5)(CO)_2COR'$. Decarbonylation of the latter to $Fe(\eta^5\text{-}C_5H_5)(CO)_2R'$ was achieved using $Rh(PPh_3)_3Cl$, but the PPh_3 released in this reaction reacted with the 1-adamantyl species giving $Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)COR'$. Treatment of $Fe(\eta\text{-}C_5H_5)(CO)_2\text{-}COBu^t$ with $Rh(PPh_3)_3Cl$ gave $Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)COBu^t$ in good yield, but the corresponding pivaloyl derivative could not be decarbonylated. Carbonylation of $Fe(\eta^5\text{-}C_5H_5)(CO)_2R$ (R = 2-adamantyl) with CO, and reaction with PPh_3, gave $Fe(\eta^5\text{-}C_5H_5)(CO)_2COR$ and $Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)COR$, respectively.

Reaction of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ with $SiMe_2RCH_2Cl$ afforded (398) $Fe(\eta^5\text{-}C_5H_5)(CO)_2\text{-}CH_2SiMe_2R$ (R = Me or Ph). Treatment of this with Lewis bases L (PPh_3, $PMePh_2$, or $PEtPh_2$) gave $Fe(\eta^5\text{-}C_5H_5)(CO)LCH_2SiMe_2R$ and $Fe(\eta^5\text{-}C_5H_5)(CO)(L)COCH_2SiMe_2R$, while with SO_2, $Fe(\eta^5\text{-}C_5H_5)(CO)_2SO_2CH_2SiMe_2R$. Treatment of $Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)COCH_2SiMe_3$ with traces of acid afforded $Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)COMe$. Direct synthesis of $Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)R$ (R = Bu^n, CH_2CHMe_2 or CHMeEt) was achieved (399) by action of the appropriate alkyl lithium reagent on the iron iodide complex. The structures of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2(CH_2)_n$ (n = 3 or 4) have been determined (400) crystallographically and it was found that the Fe atoms in each compound were joined by simple σ-bonded CH_2 groups, the C-C and Fe-C bond lengths being similar in each species.

Scheme 75

$Fe(\eta^5\text{-}C_5H_5)(CO)_2 \equiv [Fe]$

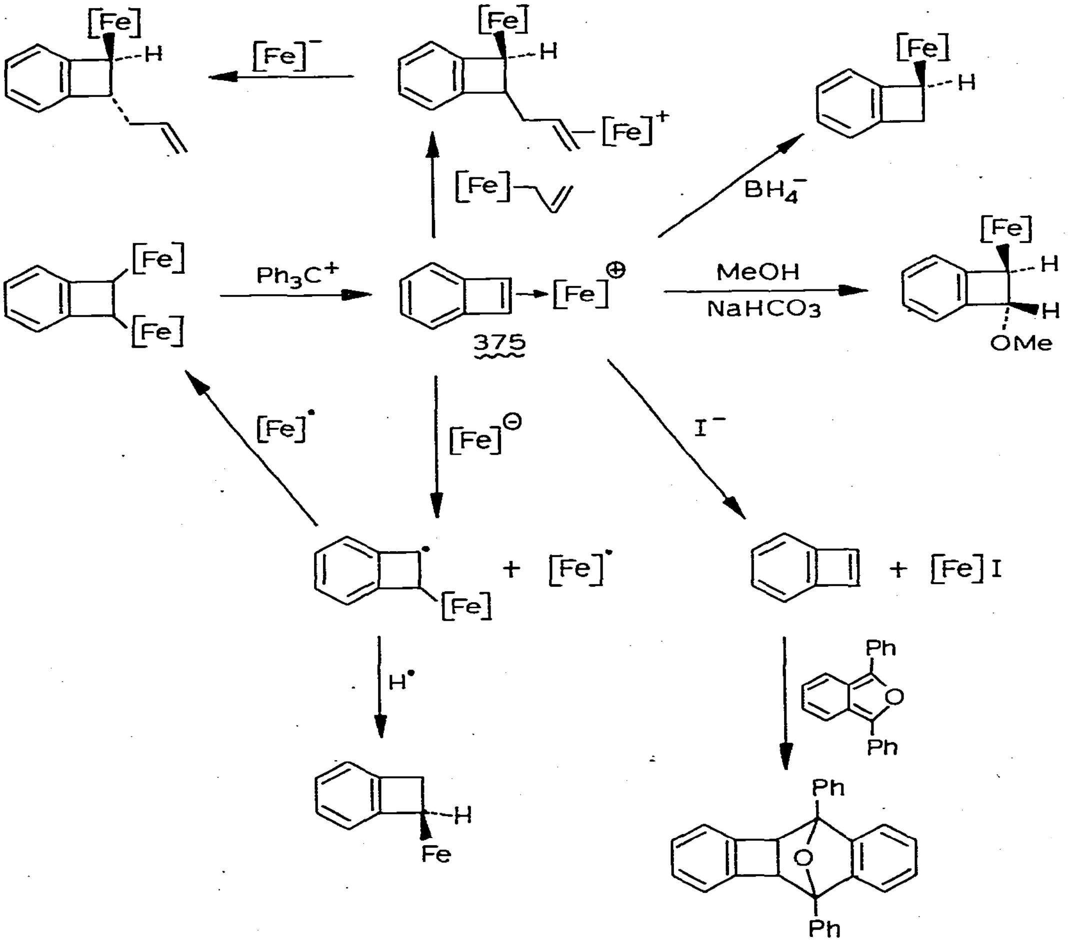


The thermal decomposition of $Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)R$ (R = Et, Bu^n, Bu^s, or Bu^i and 2-methylpropyl) into $Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)H$ and alkene has been investigated (401). The essentials of the mechanism are outlined in Scheme 77.

The reaction of threo $Fe(\eta^5\text{-}C_5H_5)(CO)_2CHDCHDPh$ with halogens has been studied (402) under a variety of conditions. The major product in most cases was threo-α,β-dideuteriophenethyl halide, although the methyl ether was obtained in methanol.

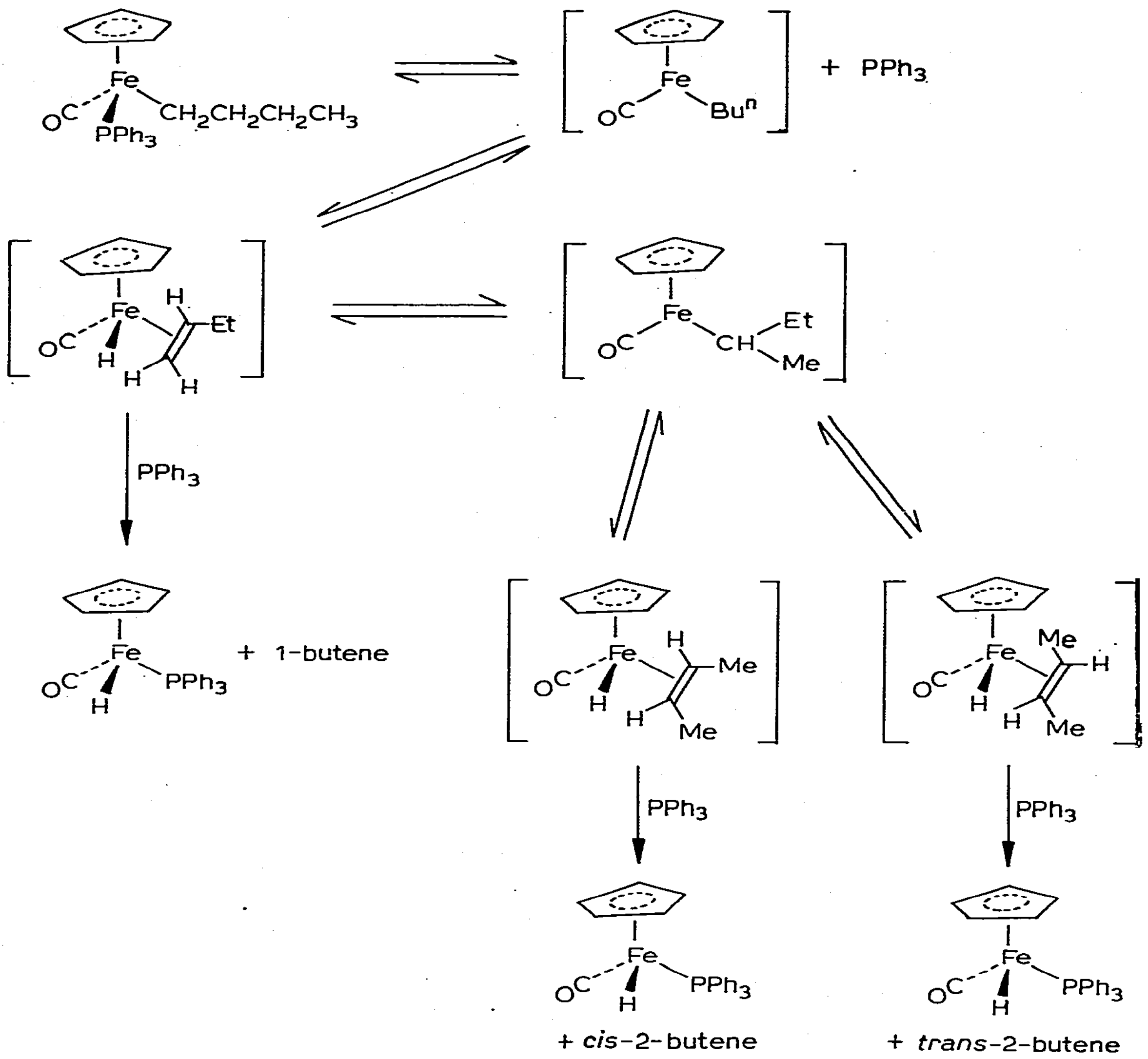
Scheme 76

$Fe(\eta^5\text{-}C_5H_5)(CO)_2 \equiv [Fe]$



Analogous cleavage reactions of samples labelled with ^{13}C at the α-C atom showed that, in most cases, the methylene C atoms became equivalent at some point along the reaction pathway. This was not easy to explain but one mechanism (Scheme 78) was preferred over an alternative (Scheme 79) involving a phenonium ion intermediate. The overall mechanism proposed (Scheme 80) involved initial oxidation of the metal to give a fluxional cation $[Fe(\eta^5\text{-}C_5H_5)(CO)_2X(CHDCHDPh)]^+$, followed by reductive elimination of *threo*-phenethyl halide. The cationic intermediate can also give *erythro*-phenethyl halide, not by nucleophilic attack on the intermediate by X^-, but more probably via non-chain radical processes. It was proposed that the halogen cleavage of transition metal alkyls containing non-bonding d electrons may generally proceed via initial oxidation of the metal, and the long-accepted S_E2 (cyclic) mechanism for cleavage of main-group metal alkyl compounds is a symmetry-forbidden process.

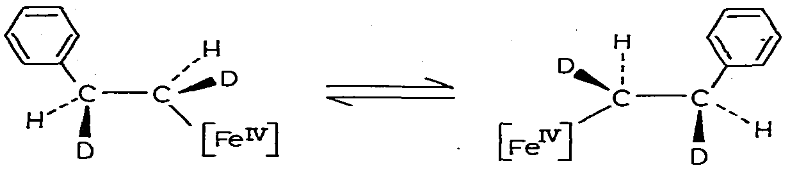
Scheme 77



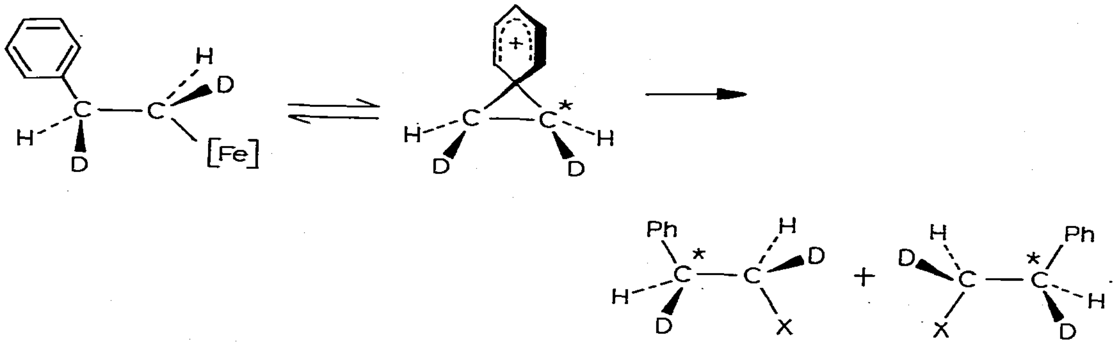
Spiro[4.4]nona-1,3-diene, [376], and spiro[2.4]hepta-2,6-diene, [377], reacted (403) with $Fe_2(CO)_9$ giving [378] and [379], respectively. While dimethylfulvene reacted (404) with $Ru_3(CO)_{12}$ giving [380], whose structure was established crystallographically, diethylfulvene afforded [381].

Treatment of 1,4-dihalo-2-butynes with $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ gave (405) $Fe(\eta^5-C_5H_5)(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(\eta^5-C_5H_5)$, $Fe(\eta^5-C_5H_5(CO)_2C(=CH_2)CH=CH_2$, and $Fe(\eta^5-C_5H_5)(CO)_2CH_2C{\equiv}CMe$. The last two could also be produced by treating $Fe(\eta^5-C_5H_5)(CO)_2H$ with butatriene in THF. Protonation of the bimetallic acetylene species afforded [382] which was transformed to $Fe(\eta^5-C_5H_5)(CO)_2C(=CH_2)CH=CH_2$ by treatment with

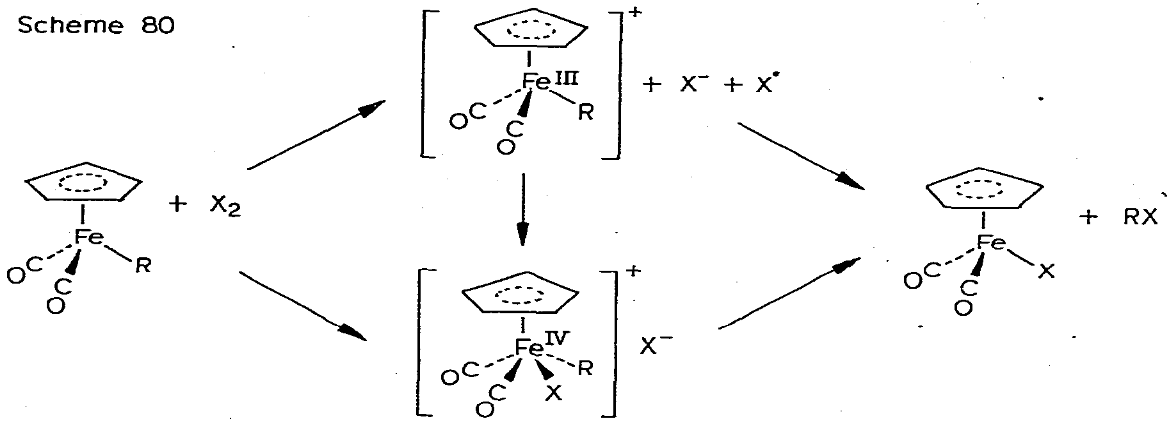
Scheme 78 $Fe(\eta^5\text{-}C_5H_5)(CO)_2 \equiv [Fe]$



Scheme 79



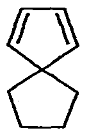
Scheme 80



$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$. Attack upon $XCH_2C_2CH_2X$ (X = Cl, Br or OSO_2Ph) by $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ gave the η^3-allyl complex [383], also obtained by reaction of $Fe(\eta^5\text{-}C_5H_5)(CO)_2C(=CH_2)CH=CH_2$ with $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ or NaOMe in methanol. When [383] was prepared in MeOD, the η^3-allyl group was monodeuteriated at the C(3) methyl group and at C(2). A mechanism for these reactions is given in Scheme 81.

Treatment of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ with $RO_2CCH=CHI$ (R = H, Me or Et) gave (406) *cis*- and *trans*-$Fe(\eta^5\text{-}C_5H_5)(CO)_2CH=CHCO_2R$.

A general synthetic route to $Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-allyl})$ has been worked out (407) and is shown in Scheme 82, together with some rearrangements of the alkene inter-



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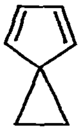

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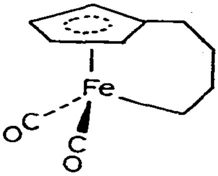

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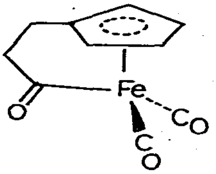

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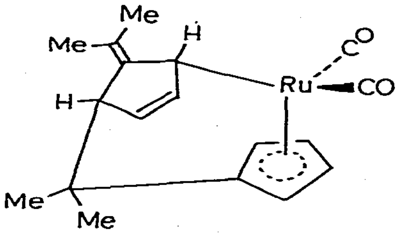

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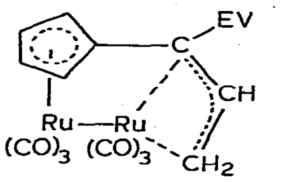

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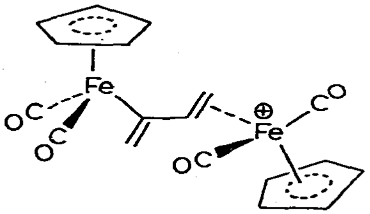

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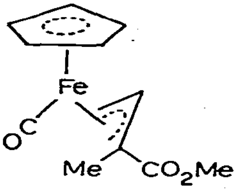
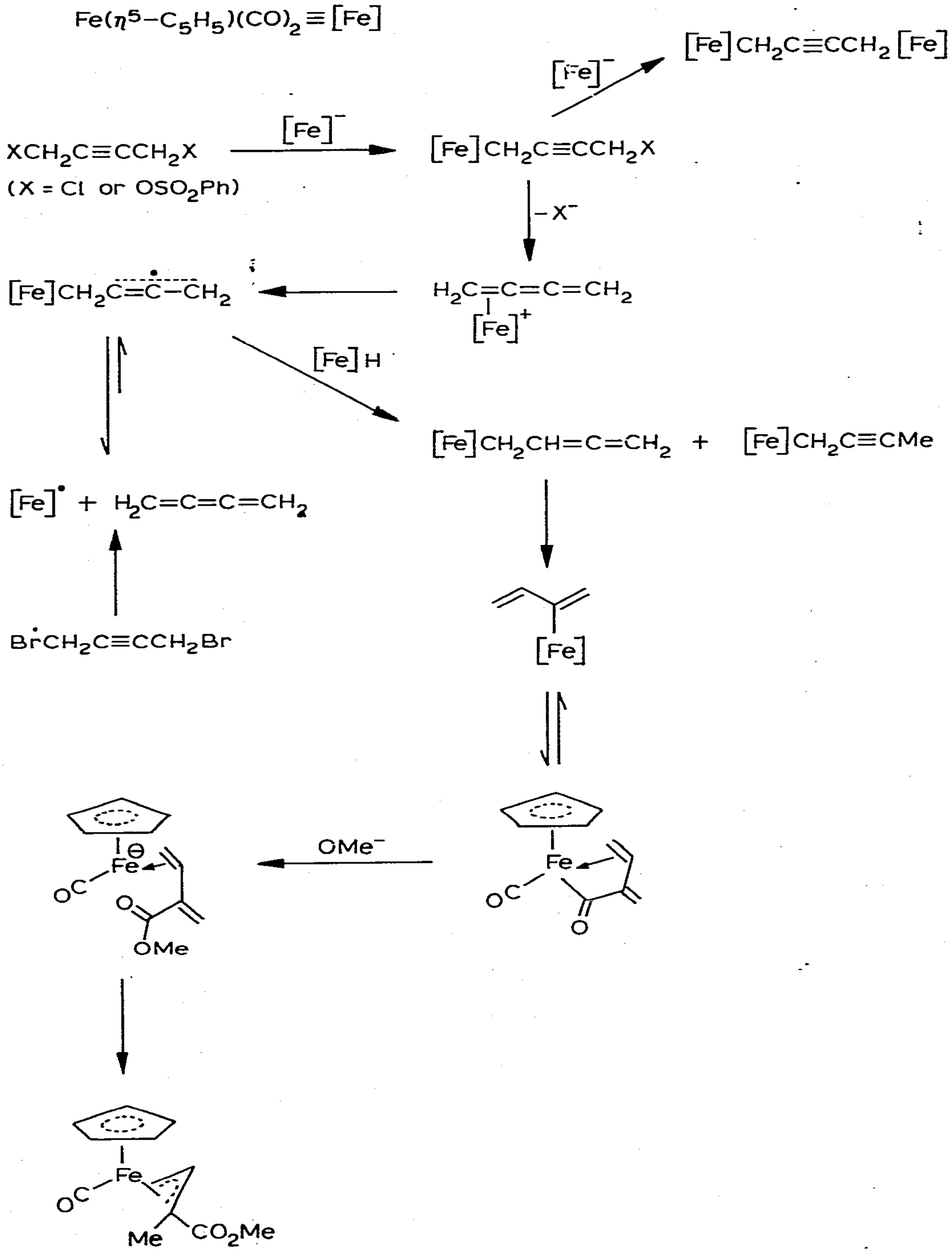


381

mediates crucial to the formation of the η^1-allylic species. Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ with the bis-epoxide [384] gave selectively [385], and deprotonation of the cyclopentene complex [386] gave $Fe(\eta^5-C_5H_5)(CO)_2(\eta^5-C_5H_5)$ and not [387]. The cycloheptene cation $[Fe(\eta^5-C_5H_5)(CO)_2(C_7H_{12})]^+$ could not be deprotonated since there were no accessible allylic protons trans to the Fe-η^2-olefin bond in either the boat or chair conformation of the olefin. Cycloaddition reactions of $Fe(\eta^5-C_5H_5)(CO)_2$-(η^1-allyl) with TCNE and certain isocyanates gave (407) [388], [389], [390] and [391] but with certain systems, as shown in Scheme 83, there could be a competitive 'insertion' reaction. Mercury(II) chloride reacted (408) with the η^1-allylic species $Fe(\eta^5-C_5H_5)(CO)_2CH_2CR{=}CR^1R^2$ (R, R^1 = H or Me, R^2 = Me or Ph) giving $Fe(\eta^5-C_5H_5)(CO)_2$-$[CH_2CR{=}CR^1R^2HgCl_2]$ which, on treatment with NH_4PF_6, was converted into [392]. Treatment of [392] with $HgCl_2$ afforded some $Fe(\eta^5-C_5H_5)(CO)_2HgCl$.

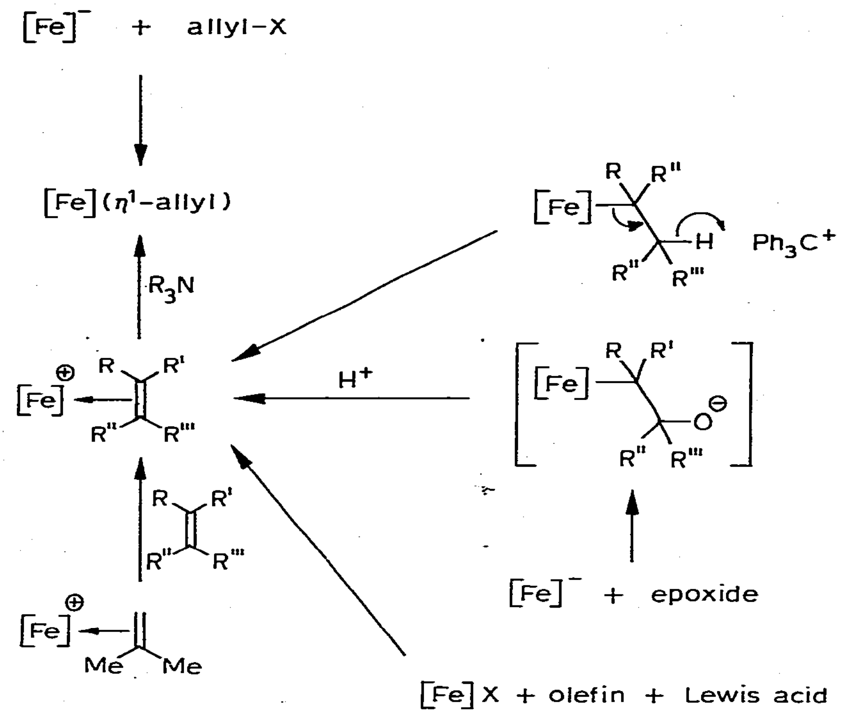
Thermolysis of the complexes [367] and [368] described earlier (394) afforded (409) $Fe(\eta^5-C_5H_5)(CO)_2CH{=}CHCH{=}CHFe(CO)_2(\eta^5-C_5H_5)$ and $Fe(\eta^5-C_5H_5)(CO)_2CH{=}CHCH{=}CHCl$. The former, on iodination, gave ICH=CHCH=CHI and $[\{Fe(\eta^5-C_5H_5)(CO)_2\}_2(C_4H_6)]^{2+}$, and this dication could also be produced by treatment of $Fe(\eta^5-C_5H_5)(CO)_2CH{=}CHCH{=}CH$-$Fe(CO)_2(\eta^5-C_5H_5)$ with HCl. Protonation of [367] by HBF_4 gave probably [393] which reacted with Et_3N giving [394]. Hydrolysis and dehydration of [368] on alumina gave eventually trans-$Fe(\eta^5-C_5H_5)(CO)_2CH_2CH{=}CHCHO$, according to Scheme 84.

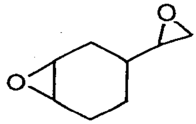
Scheme 81


Fe(η5–C5H5)(CO)2 ≡ [Fe]
XCH2C≡CCH2X
(X = Cl or OSO2Ph)
[Fe]⁻
[Fe]CH2C≡CCH2X
[Fe]⁻
[Fe]CH2C≡CCH2[Fe]
–X⁻
H2C=C=C=CH2
[Fe]⁺
[Fe]CH2C=C–CH2
[Fe]H
[Fe]CH2CH=C=CH2
+
[Fe]CH2C≡CMe
[Fe]• + H2C=C=C=CH2
Br•CH2C≡CCH2Br
[Fe]
Fe
OC
O
OMe⁻
Fe
OC
O
OMe
Fe
OC
Me
CO2Me

Scheme 82

$Fe(\eta^5-C_5H_5)(CO)_2 \equiv [Fe]$

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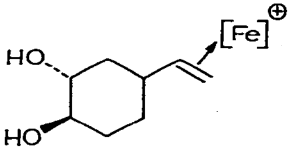

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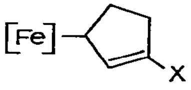

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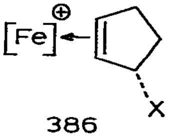

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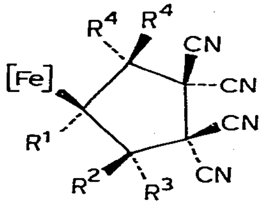

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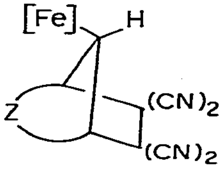

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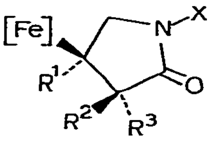

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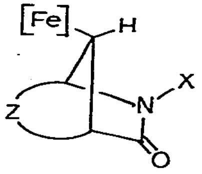
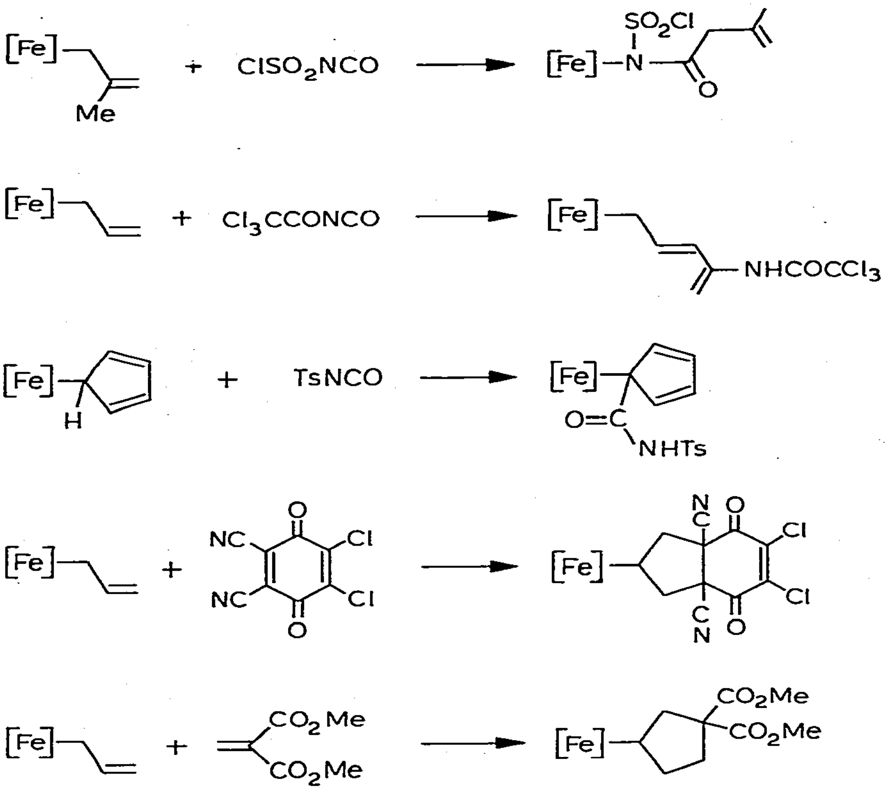


391

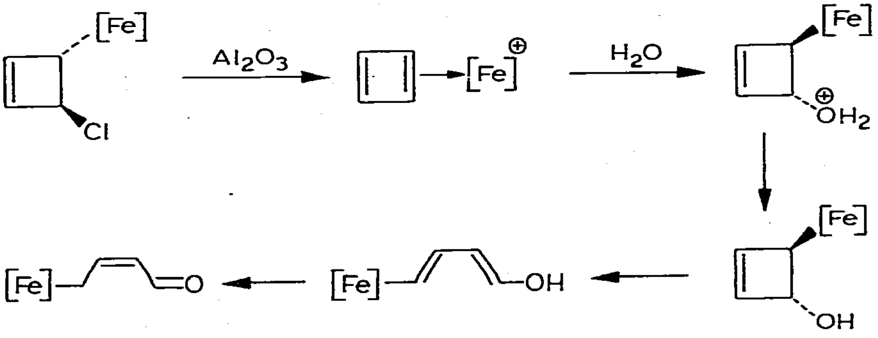
Scheme 83

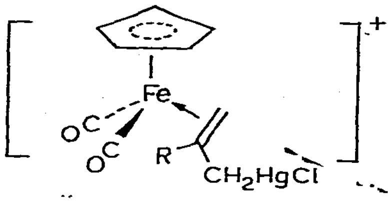
$Fe(\eta^5-C_5H_5)(CO)_2 \equiv [Fe]$



Scheme 84

$Fe(\eta^5-C_5H_5)(CO)_2 \equiv [Fe]$

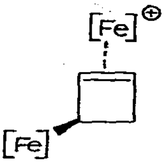




392

Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ with Ph_4As^+ or Ph_4P^+ gave (410) 35-45% yields of $Fe(\eta^5-C_5H_5)(CO)_2Ph$ and $[Fe(\eta^5-C_5H_5)(CO)_2]_2$. The ammonium salts $[PhMe_3N]^+$ and $[(PhCH_2)Me_3N]^+$ reacted slowly with the carboxylate anion affording $Fe(\eta^5-C_5H_5)(CO)_2Me$ and $Fe(\eta^5-C_5H_5)(CO)_2CH_2Ph$, respectively. The overall course of the reaction with $[Ph_3P]^{\dot{+}}$ was thought to involve initial formation of $Ph_4PFe(CO)_2(\eta^5-C_5H_5)$ which dissociated giving $[Ph_4P]^{\cdot}$ and $[Fe(\eta^5-C_5H_5)(CO)_2]^{\cdot}$. The former radical further dissociated giving Ph_3P and phenyl radicals which could either attack the iron species giving $Fe(\eta^5-C_5H_5)(CO)_2Ph$, or dimerise affording biphenyl. The iron radical could also dimerise to give $[Fe(\eta^5-C_5H_5)(CO)_2]_2$.

From ^{13}C n.m.r. spectral comparisons of $Fe(\eta^5-C_5H_5)(CO)_2Ph$, $Fe(\eta^5-C_5H_5)(CO)-[P(OPh)_3]Ph$ and [395] with [396] (M = Fe, L = CO and $P(OPh)_3$), it has been shown that it is possible to differentiate between metallated and non-metallated PhO groups within the same molecule. The species [395] was obtained by heating (411) $Fe(\eta^5-C_5H_5)(CO)(PPh_3)Ph$ with $PhO\overline{POCH_2CH_2O}$.



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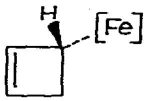

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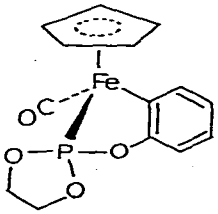

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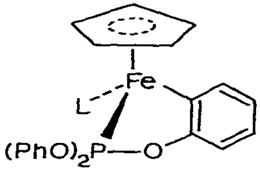
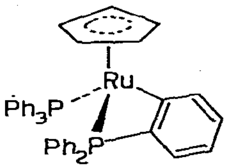


396

In refluxing decalin, $Ru(\eta^5-C_5H_5)(PPh_3)_2Me$ was converted (412) into [397] which further reacted with $CF_3C_2CF_3$ giving [398]. Triphenylphosphite reacted with $Ru(\eta^5-C_5H_5)(PPh_3)_2Cl$ giving $Ru(\eta^5-C_5H_5)[P(OPh)_3]_2Cl$ which, in refluxing decalin in the presence of dicyclohexylamine, afforded [396] (M = Ru, L = $P(OPh)_3$) which did not react with $CF_3C_2CF_3$. The azo compounds $p-RC_6H_4N=NC_6X_5$ (X = H or F) reacted with $Ru(\eta^5-C_5H_5)(PPh_3)_2Me$ giving [399], [400] (X = H, R = H, Me, OMe, CO_2Et or CF_3;

X = F, R = H, Me or CF_3) and [401] (X = F). Complexes similar to [399] and [400] were obtained with 3,5-$(MeO_2C)_2C_6H_3N{=}NC_6X_5$ (X = H or F). Treatment of Ru(η^5-C_5H_5)$(PPh_3)_2$Me with $[C_6F_5N{=}]_2$ gave [412]. These reactions confirmed the expected tendency for the low-valent electron-rich Ru species to engage in nucleophilic o-metallation reactions with fluorinated rings. The reactions may involve abstraction by the metal of fluorine and it was shown that Ru(η^5-C_5H_5)$(PPh_3)_2$Cl reacted with NH_4F in methanol in the presence of Ag_2CO_3 giving Ru(η^5-C_5H_5)$(PPh_3)_2$F.

Treatment of [Fe(η^5-C_5H_5)$(CO)_2$]$^-$ with RCOCl (R = 2-thienyl, 2-furyl, 5-methyl-2-furyl, 4,5-benzo-2-furyl) gave (413) Fe(η^5-C_5H_5)$(CO)_2$COR which reacted with PPh_3 giving Fe(η^5-C_5H_5)(CO)(PPh_3)(COR). Photolysis of Fe(η^5-C_5H_5)$(CO)_2$COR afforded Fe(η^5-C_5H_5)$(CO)_2$R which, under u.v. light, reacted with PPh_3 affording Fe(η^5-C_5H_5)(CO)(PPh_3)R. Reaction of Fe(η^5-C_5H_5)$(CO)_2$R (R = 2-thienyl or 4,5-benzo-2-furyl) with $HgCl_2$ gave (414) the mercurated species [403] and [404], and treatment of the former with $Na_2S_2O_3$ afforded [405].



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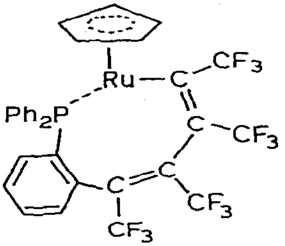

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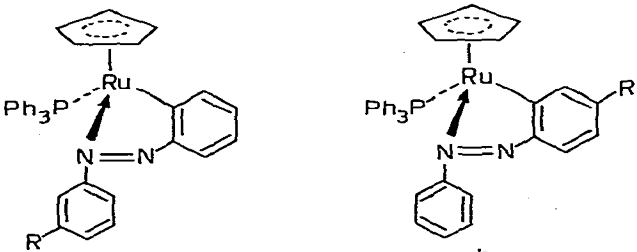
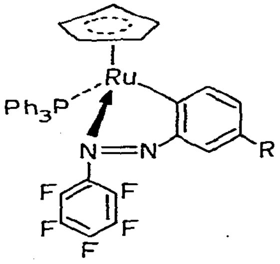


a

b

399



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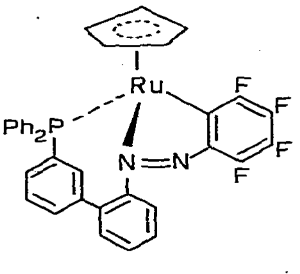

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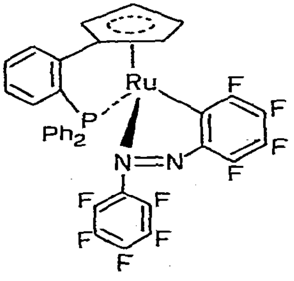

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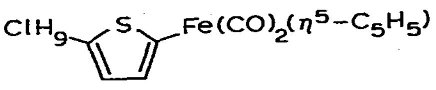

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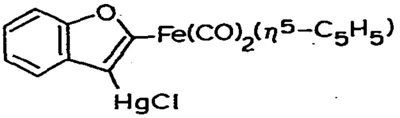

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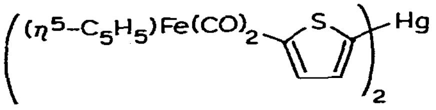

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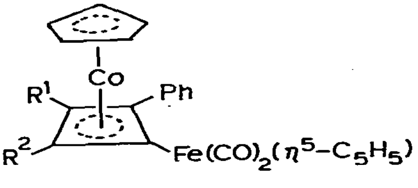


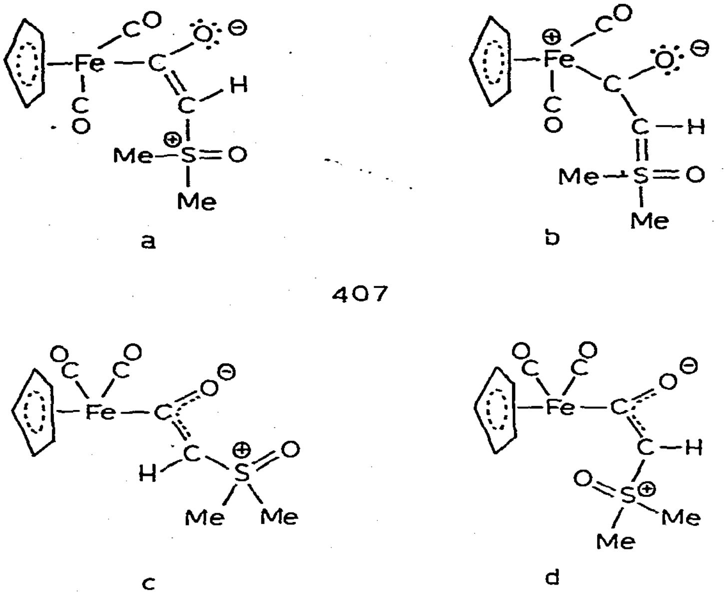
406

In hot diglyme, $Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2)_nPh$ (n = 0 or 1) reacted (415) with $Cr(CO)_6$ giving $Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2)_n[(\eta^6\text{-}C_6H_5)Cr(CO)_3]$. Reaction of $Co(\eta^5\text{-}C_5H_5)(PPh_3)\text{-}(R^1C_2R^2)$ ($R^1 = R^2$ = Ph or CO_2Me; R^1 = Ph, $R^2 = CO_2Me$) with $Fe(\eta^5\text{-}C_5H_5)(CO)L(C_2Ph)$ (L = CO or Ph) afforded (416) [406], from which the Fe atom could be cleaved by HCl only with difficulty, giving $Co(\eta^5\text{-}C_5H_5)(PPh_3)(\eta^4\text{-}C_4Ph_3H)$.

Treatment of $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COCH_2Cl)$ with $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ in THF afforded (417) $Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4COCH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ together with $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\text{-}COMe)$ and $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$. In dimethoxyethane, $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COCl)$ reacted with the carbonylate ion giving $Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4COFe(CO)_2(\eta^5\text{-}C_5H_5)]$. On photolysis or heating this species in trimethylpentane, modest yields of $Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ could be obtained. Reaction of $Fe(\eta^5\text{-}C_5H_5)\text{-}(\eta^5\text{-}C_5H_4CH_2Cl)$ with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ gave $Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4CH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)]$. Electrochemical studies of these species revealed that the electron transfer behaviour of the two Fe centres were independent of each other. Reaction of $Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4COCH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)\}]$ with $HgBr_2$ gave (418) $Fe(\eta^5\text{-}C_5H_5)(CO)_2Br$ and $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COCH_2HgBr)$, while with HX (X = Cl, HSO_4 or ClO_4), $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4C(OH)CH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)\}]X$ was formed.

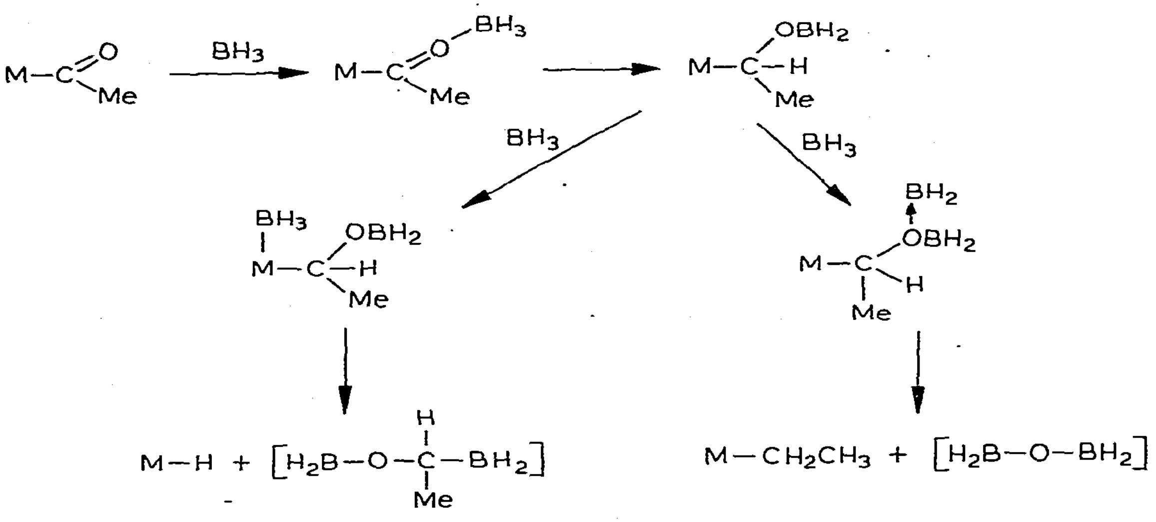
Treatment of $[Fe(\eta^5\text{-}C_5H_5)(CO)_3]^+$ with $Me_2S(=O)CH_2$ in THF afforded (419) $Fe(\eta^5\text{-}C_5H_5)\text{-}(CO)_2[C(O)CHS(O)Me_2]$, [407] (a, b, c or d); form (d) was apparently present in solution at room temperature.

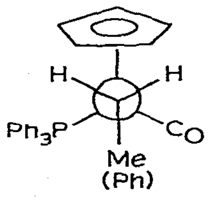
Reduction of $M(\eta^5\text{-}C_5H_5)(CO)LCOMe$ (M = Fe, L = PPh_3, $P(OPh)_3$, $P(C_6H_{11})_3$, PMe_2Ph or CO; M = Ru, L = PPh_3) to $M(\eta^5\text{-}C_5H_5)(CO)(L)Et$ was achieved (420) using BH_3.THF or B_2H_6 in benzene; $M(\eta^5\text{-}C_5H_5)(CO)(L)H$ being an occasional addition product. It was suggested that the rate of reduction increased with increasing electron density at the metal centre, and the proposed mechanism of reduction is shown in <u>Scheme 85</u>. It was noted that $Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Et$ probably has the conformation as shown in [408], and that related species containing PMe_2Ph, $P(OPh)_3$ or $P(CH_2Ph)_3$ have lower steric requirements permitting free rotation about the $Fe\text{-}CH_2\text{-}CH_3$ bonds.


a
b
c
d

407

Scheme 85





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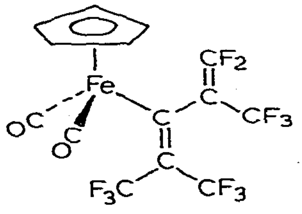

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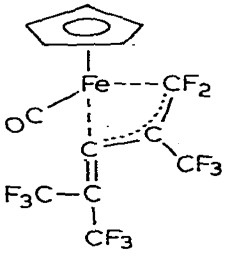
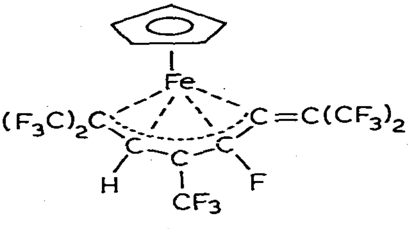


410

Fluoro-alkyl and -aryl compounds

Reaction of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ with $(CF_3)_2C{=}C{=}C(CF_3)_2$ has given, under a variety of conditions (421), the species $Fe(\eta^5\text{-}C_5H_5)(CO)_2[C\{C(CF_3){=}CF_2\}{=}C(CF_3)_2]$, [409], $Fe(\eta^5\text{-}C_5H_5)(CO)[\eta^3\text{-}CF_2C(CF_3)C{=}C(CF_3)_2]$, [410] and $Fe(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C(CF_3)CHC(CF_3)\text{-}CFC{=}C(CF_3)_2]$, [411]. The structures of $Fe(\eta^5\text{-}C_5H_5)(PPh_3)[\eta^3\text{-}CF_2C(CF_3)C{=}C(CF_3)_2]$, obtained by photolysis of [410] in the presence of PPh_3, and [411] were determined crystallographically.



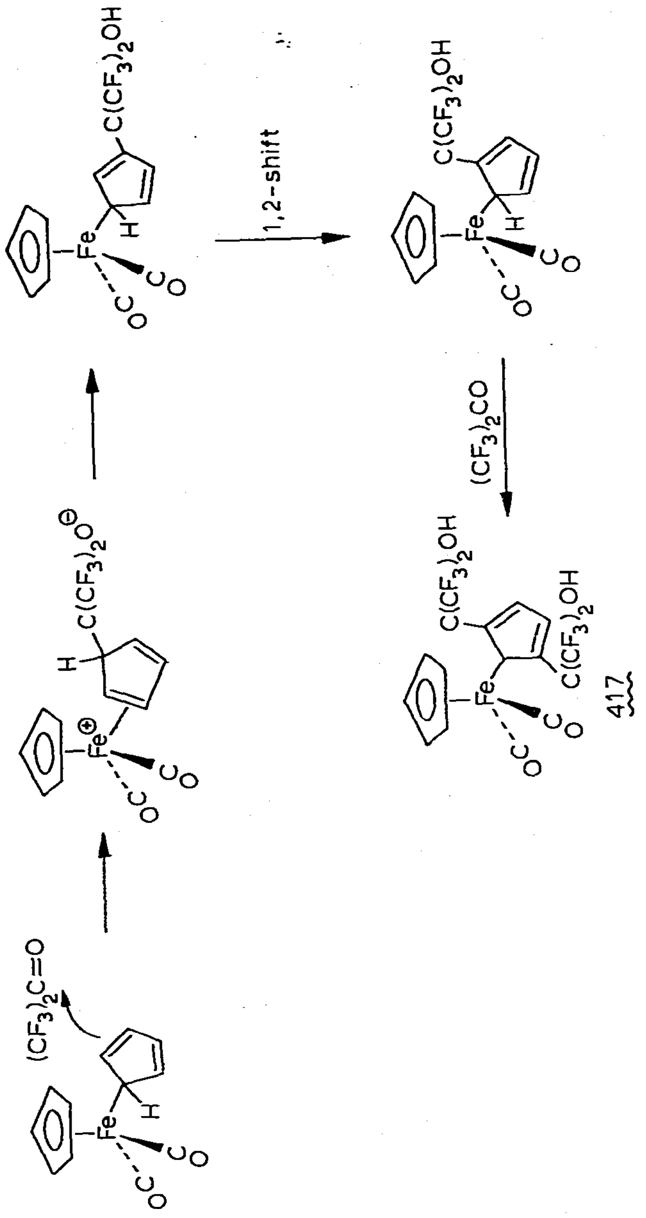
411

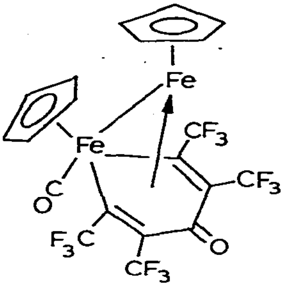
Irradiation of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ with $CF_3C_2CF_3$ gave [412] whose structure was confirmed by X-ray methods (422) (Fe-Fe 2.59 Å). Similar treatment of $[Ru(\eta^5\text{-}C_5H_5)(CO)_2]_2$ gave first *trans*-$Ru(\eta^5\text{-}C_5H_5)(CO)_2C(CF_3){=}CH(CF_3)$, also produced by heating $Ru(\eta^5\text{-}C_5H_5)(CO)_2H$ with $CF_3C_2CF_3$, and then $Ru(\eta^5\text{-}C_5H_5)(CO)C(CF_3){=}C(CF_3)C(CF_3){=}CHCF_3$. These latter reactions are closely related to the behaviour of $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2H$ with $CF_3C_2CF_3$ (423), but the apparent change in stereochemistry of the fluorocarbon ligand formed on replacement of PPh_3 by CO implied a change in mechanism of reaction. Treatment of $Fe(\eta^5\text{-}C_5H_5)(CO)_2Me$ with $CF_3C_2CF_3$ gave two conformers, [413] (a and b), which rapidly interconvert in solution. With hexafluorobut-2-yne, the η^1-allyl species $Fe(\eta^5\text{-}C_5H_5)(CO)_2(C_3H_5)$ afforded mainly [414] and on photolysis of $Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C_5H_5)$ with the acetylene, [415] and some ferrocene was produced. This latter reaction is an example of a (2 + 4)π addition (Diels-Alder) where the acetylene does not enter the coordination sphere of the metal in the early stages of the reaction. A product similar to [415] was obtained with $MeO_2CC_2CO_2Me$. While there was no reaction between $Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C_3H_5)$ and C_2F_4, $Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C_5H_5)$ afforded ferrocene and [416], whose structure was established crystallographically. Of note here is the cleavage of the $F_2C{=}CF_2$ bond. The η^1-cyclopentadienyl complex also reacted with $(CF_3)_2CO$ giving [417] by a mechanism illustrated in Scheme 86. The structure of $Ru(\eta^5\text{-}C_5H_5)(PPh_3)[C(CO_2Me){=}C(CO_2Me)C(CF_3){=}CH(CF_3)]$, [418], obtained by reaction of $Ru(\eta^5\text{-}C_5H_5)(PPh_3)[C(CF_3){=}CH(CF_3)]$ (423), has been confirmed (424) by X-ray techniques.

In the reaction between benzene, C_6F_5H and Cr atoms, $Cr(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6F_5H)$ was produced (425) which, on lithiation by $LiBu^t$, gave $Cr(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6F_5Li)$. Treatment of this species with $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ gave $Cr(\eta^6\text{-}C_6H_6)[\eta^6\text{-}C_6F_5Fe(CO)_2(\eta^5C_5H_5)]$.

The structure of the product obtained (426) by reaaction of $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2Me$ with decafluoroazobenzene has been identified crystallographically (427) as [419].

Scheme 86


(CF$_3$)$_2$C=O
Fe
H
CO
OC
Fe$^{\oplus}$
C(CF$_3$)$_2$O$^{\ominus}$
C(CF$_3$)$_2$OH
1,2-shift
(CF$_3$)$_2$CO
417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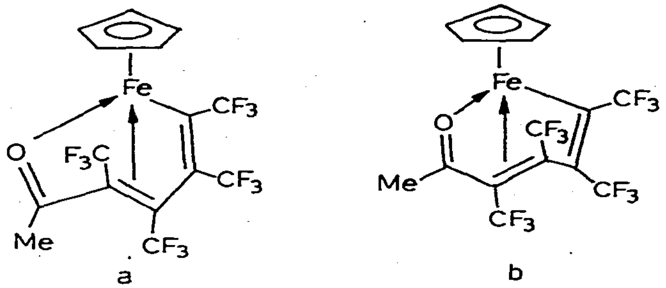
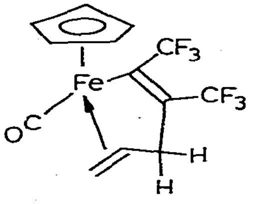

a

b

413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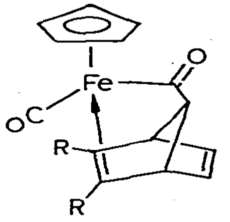
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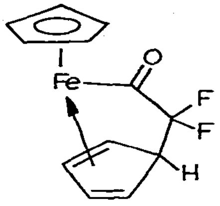
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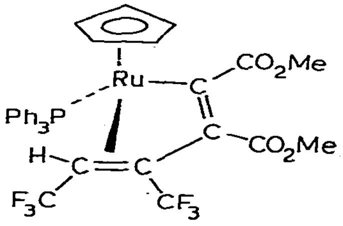
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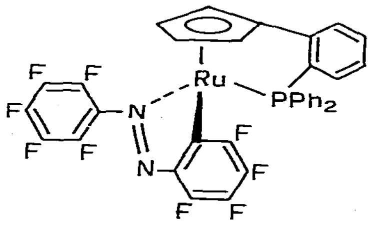
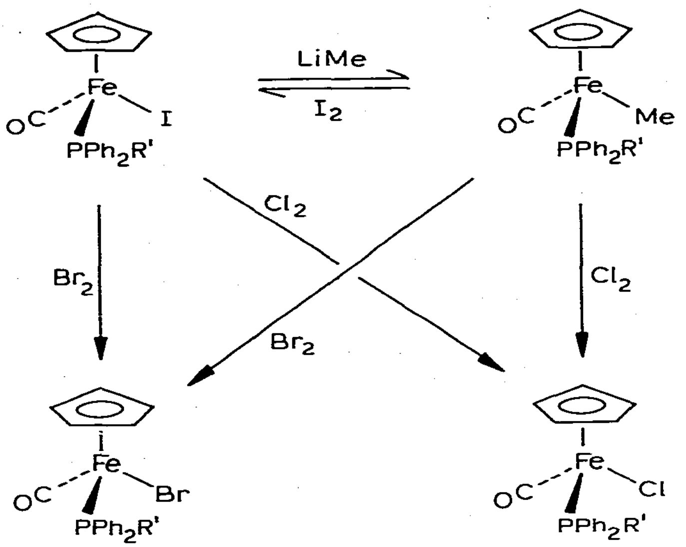

419

Optically-active and chiral complexes

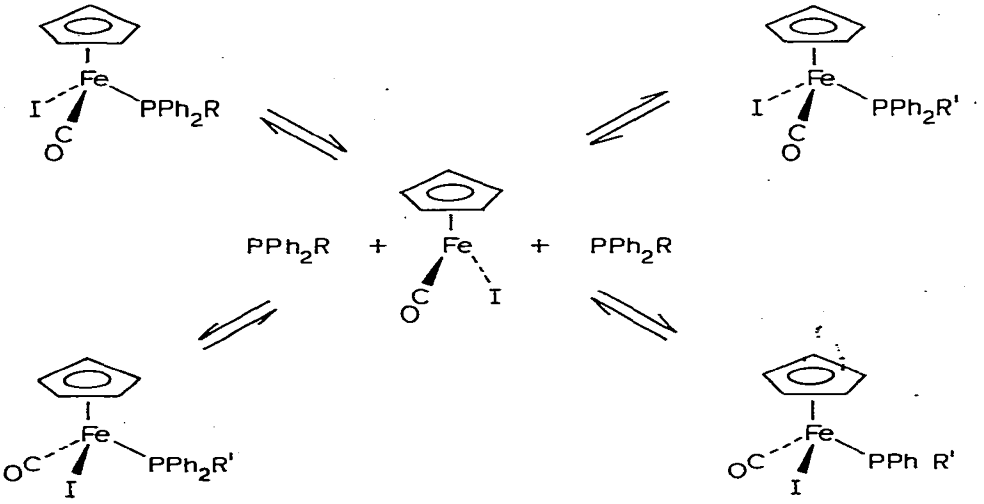
The reactions of the optically pure $Fe(\eta^5-C_5H_5)(CO)(PPh_2R)X$ (R = NMeCHMePh; X = I or Me) with Cl_2, Br_2 or I_2 and LiMe occurred (428) with retention of configuration (Scheme 87). The varying degrees of epimerisation of the unreacted starting materials and isolated products were interpreted in terms of pseudo-rotation of a coordinatively unsaturated intermediate formally five-coordinate at Fe (assuming the $\eta^5-C_5H_5$ ring to occupy three coordination positions). This intermediate was also invoked in explaining the rates of epimerisation of $Fe(\eta^5-C_5H_5)(CO)(PPh_2R)I$ as determined by polarimetry, and PPh_2R exchange measured by n.m.r. spectroscopy (429), which were the same (see Scheme 88). The absolute configuration of $Fe(\eta^5-C_5H_5)(CO)(PPh_3)[CO_2(2-Pr^i-5-MeC_6H_3)]$ has been determined crystallographically (430).

Treatment of $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ with $MenOCCH_2X$ or $MenCH_2X$ (Men = mentholate, [420]) gave $Fe(\eta^5-C_5H_5)(CO)_2R$ (R = CH_2COMen or CH_2Men, respectively) which, on photolysis with PPh_3, afforded (431) [421] (R = CH_2OMen or CH_2Men). The species [421]

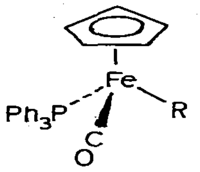
Scheme 87



Scheme 88



(R = CH$_2$OMe) was resolved by recrystallisation after column chromatography, while [421] (R = CH$_2$Men) was resolved by recrystallisation alone. From crystallographic studies, it is known that these species have the R-conformation. Reaction of [421] (R = CH$_2$Men) with HX (X = Cl, Br or I) afforded Fe(η^5-C$_5$H$_5$)(CO)(PPh$_3$)CH$_2$X with retention of configuration, and X could be metathesised by H$^-$, CN$^-$, OMe$^-$, R'$^-$ (R' = Me, Et, Pr^i, Ph or cyclopropyl) upon treatment of the halomethylene species with NaBH$_4$, KCN, KOMe in methanol, LiR' or MgR'X, respectively, again with retention of configuration. However, treatment of [421] (R = CH_2COMen) with HCl or H_2SO_4 in methanol gave racemic $Fe(\eta^5-C_5H_5)(CO)(PPh_3)CH_2CO_2R''$ (R" = H or Me). Reaction of $Fe(\eta^5-C_5H_5)(CO)(PPh_3)CH_2Br$, [421] (R = CH_2Br), with an excess of <u>trans</u>-PhCH=CHMe at 25° gave $Fe(\eta^5-C_5H_5)(CO)(PPh_3)Br$ and [422] as a 9% enantiomeric excess of the (+)-(1S)(2S) cyclopropane. Treatment of [421] (R = CH_2R', where R' = H, Me, Et, Pr^i or Ph) with SO_2 afforded $Fe(\eta^5-C_5H_5)(CO)(PPh_3)[S(=O)_2CH_2R']$, the extent of racemisation being dependent on temperature and on the nature of R'. Greater then 95% stereospecific insertion occurred in dichloromethane or dimethylformamide when R' = H. Treatment of [421] (R = CH_2Men or CH_2OMe) with SO_2 gave either $Fe(\eta^5-C_5H_5)(CO)(PPh_3)$-$[CH_2S(=O)_2R]$ or $Fe(\eta^5-C_5H_5)(CO)(PPh_2)[CH_2OS(=O)R]$ (R = men or OMe), the former being favoured on the basis of spectroscopic data. Reaction of [421] (R = CH_2R', R' = cyclopropyl) with SO_2 gave $Fe(\eta^5-C_5H_5)(CO)(PPh_3)[S(=O)_2CH_2CH_2CH=CH_2]$ with 40% net stereospecificity. The abnormal insetion of SO_2 into the C-O bond of [421] (R = CH_2Men or CH_2OMe), in comparison to the more usual formation of $Fe-S(=O)_2-R$ species, may be understood as a reflection of increased electron density at the metal centre which is provided by PPh_3. This increases the stability of the polar species $[Fe(\eta^5-C_5H_5)(CO)(PPh_3)=CH_2]^+[OR]^-$ which contributes to the ground state bonding. It proved impossible to obtain $Fe(\eta^5-C_5H_5)(CO)(PMe_2Ph)CH_2Men$, the only product which could be isolated being $Fe(\eta^5-C_5H_5)(CO)(PMe_2Ph)Me$. The large-scale synthesis of racemic [421] (R = CH_2R', R' = alkyl), that is compounds where CH_2R' contains β hydrogen atoms, is very conveniently achieved by the following route:



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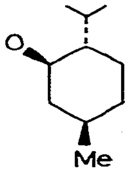

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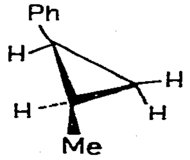


422

$$\begin{tikzcd}
{[Fe(\eta^5-C_5H_5)(CO)_2]_2} \arrow[r] & {Na[Fe(\eta^5-C_5H_5)(CO)_2]} \arrow[r] & {Fe(\eta^5-C_5H_5)(CO)_2CH_2OMe} \arrow[d, "{PPh_3,\ h\nu}"] \\
 & {Fe(\eta^5-C_5H_5)(CO)(PPh_3)CH_2Cl} \arrow[d, "R'MgX"] & {Fe(\eta^5-C_5H_5)(CO)(PPh_3)CH_2OMe} \arrow[l] \\
 & {Fe(\eta^5-C_5H_5)(CO)(PPh_3)CH_2R'} &
\end{tikzcd}$$

This pathway is superior to reaction of $Fe(\eta^5-C_5H_5)(CO)_2CH_2R'$ with PPh_3 (see ref. 401) or of $Fe(\eta^5-C_5H_5)(CO)(PPh_3)I$ with $MgCH_2R'X$.

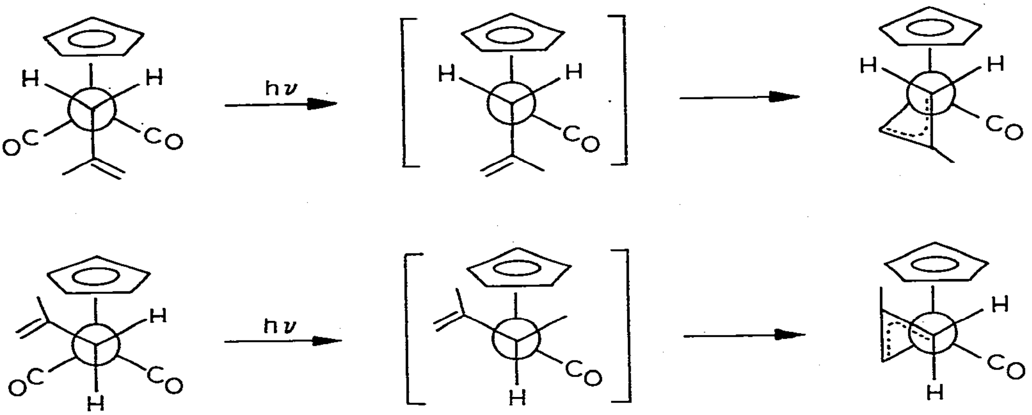
In the complexes $Fe(\eta^5-C_5H_5)(CO)(alkene)SnR_3$ and $Fe(\eta^5-C_9H_7)(CO)(alkene)SnR_3$ (R = Me or Ph, alkene = C_2H_4 or C_3H_6), the olefin rotates about the metal-alkene bond (432) with a barrier to rotation varying from 11 to 14 kcal/mol, permitting the observation of both averaged and non-averaged n.m.r. spectra. Evidence for restricted rotation about the Sn-C bonds in $SnPh_3$-containing derivatives was also obtained.

The chemical shift differences resulting from the substitution of C_5H_5 by C_9H_7 permitted the determination of the preferred orientations in the propene complexes. Decomposition of these complexes proceeded with loss of the alkene in a process whose rate was not altered by added PPh_3.

η^3-Allylic species

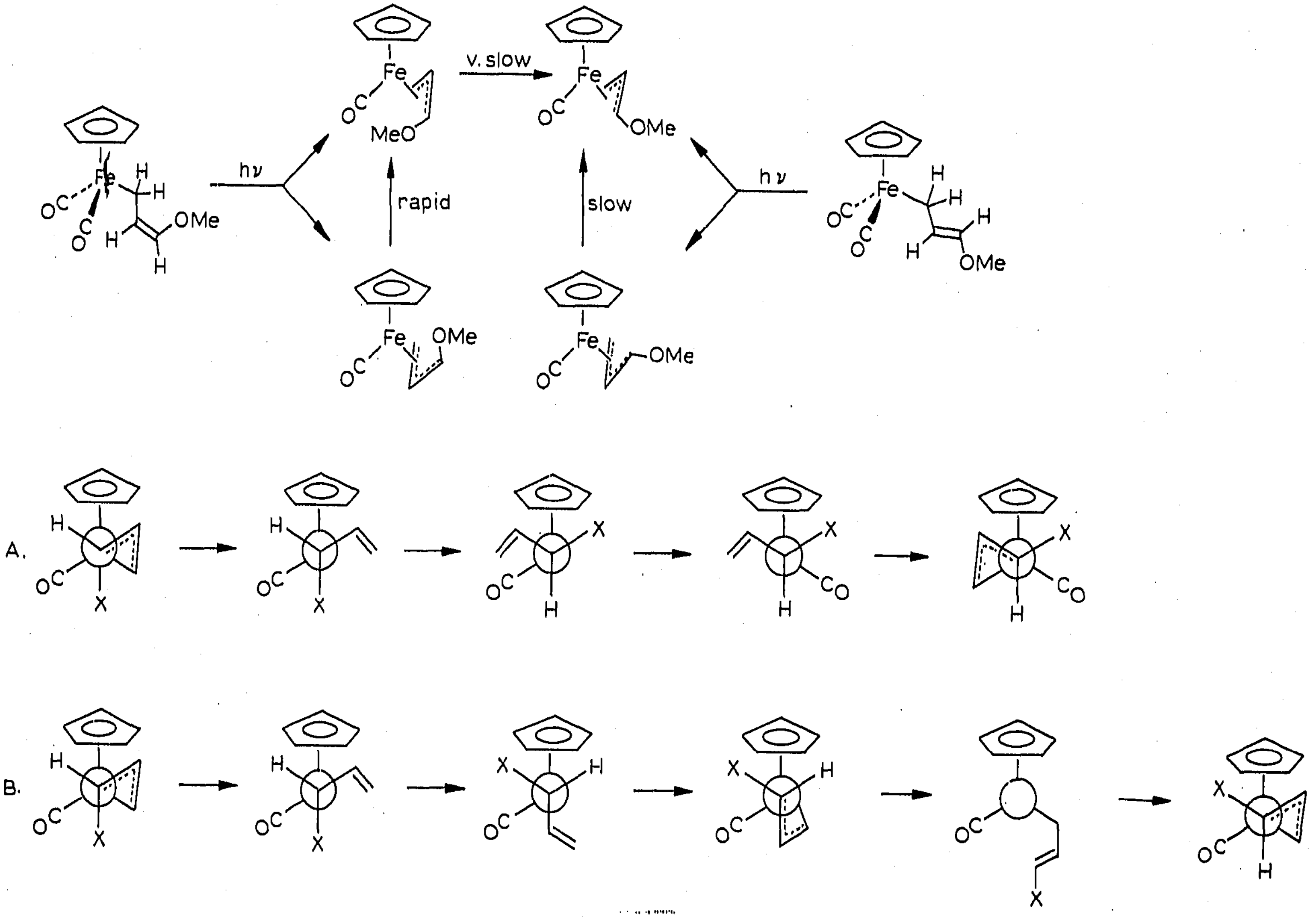
Photolysis of $Fe(\eta^5-C_5H_5)(CO)_2(\eta^1-C_3H_5)$ at 10° afforded (433) the endo- and exo-isomers of $Fe(\eta^5-C_5H_5)(CO)(\eta^3-C_3H_5)$, and on heating the endo-form, the exo-isomer was produced at a moderate rate. Similarly, $Fe(\eta^5-C_5H_5)(CO)_2(\eta^1-2-MeC_3H_4)$ could be converted to endo- and exo-allylic species. If the photochemical process involved CO dissociation (Scheme 89) followed by collapse of the coordinatively unsaturated intermediate, then the initial product ratio might be expected to reflect conformational preferences, provided that the collapse was rapid compared to rotations about the Fe-C and C-C bonds. Photolysis of cis- and trans-1-substituted η^1-allylic species gave a number of syn- and anti-η^3-allylic species as a mixture of endo- and exo-isomers. Approximate rates for the thermal interconversions of the different stereoisomers were determined and it was found that the anti-to-syn conversion occurred at a rate comparable to endo-to-exo isomerism. This implied a similar mechanism involving $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ transformations. Some mechanistic information is given in Scheme 90. The absence of anti $\rightleftharpoons$ syn exchange in the isomerism of endo to exo complexes is expected, since the reaction would be anticipated to proceed via a preferred 1-substituted allylic intermediate in which the configuration at the substituted C atom is left unchanged.

Scheme 89



Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ with $Me_3SiCH{=}CHCH_2Cl$ gave (434) $Fe(\eta^5-C_5H_5)(CO)_2-CH_2CH{=}CHSiMe_3$ which, on photolysis, was converted into $Fe(\eta^5-C_5H_5)(CO)(\eta^3-1-Me_3Si-C_3H_4)$. Treatment of $Fe(CO)_5$ with $2-Me_3SiC_3H_4I$ afforded $Fe(\eta^3-2-Me_3SiC_3H_4)(CO)_3I$.

Scheme 90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From i.r. and v.t. ^{1}H and ^{13}C n.m.r. spectral studies, it was established (435) that rotation about the C-C bonds in the μ-allylic species $[\{Fe(\eta^5-C_5H_5)(CO)_2\}_2(\mu-CH_2CHCH_2)]^+$ and $[\{Fe(\eta^5-C_5H_5)(CO)_2\}_2(\mu-CH_2CMeCH_2)]^+$ required about 12 kcal/mol.

Compounds containing Group IVA ligands other than C

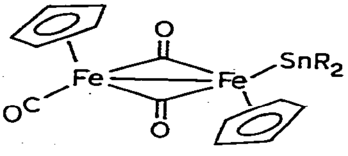
Treatment of $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ with $Me(CH_2)_{15}Cl$ gave (436) $Fe(\eta^5-C_5H_5)(CO)_2(CH_2)_{15}Me$ which underwent insertion with $GeCl_2$.dioxane affording $Fe(\eta^5-C_5H_5)(CO)_2GeCl_2(CH_2)_{15}Me$. Related species $Fe(\eta^5-C_5H_5)(CO)_2GeR_2(CH_2)_nMe$ ($R = Cl$ or OAc, $n = 6$; $R = OAc$, $n = 4$) were also obtained and, in relation to their surface active properties, the critical concentrations for micelle formation by these complexes were determined.

UV irradiation of $[Fe(\eta^5-C_5H_5)(CO)_2]_2SnMe_2$ gave (437) unreacted starting material, $[Fe(\eta^5-C_5H_5)(CO)_2]_2$, and the cis- and trans-isomers of the known $[Fe(\eta^5-C_5H_5)(CO)]_2(\mu-CO)(\mu-SnMe_2)$ (438). Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ with $SnMe_2Br_2$ gave $[Fe(\eta^5-C_5H_5)(CO)_2]_2SnMeBr$ and $Fe(\eta^5-C_5H_5)(CO)_2SnBrMe_2$. Treatment of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ with $Sn[CH(SiMe_3)_2]_2$ gave (439) $Fe_2(\eta^5-C_5H_5)_2(CO)_2\{Sn[CH(SiMe_3)_2]_2\}$, [423], whereas $Fe(\eta^5-C_5H_5)(CO)_2R$ ($R = Cl$ or Me) afforded $Fe(\eta^5-C_5H_5)(CO)_2Sn[CH(SiMe_3)_2]_2R$ whose Mössbauer spectrum has been measured. The tin(II) alkyl also reacted with $Fe_2(CO)_9$ giving [424]. Contrary to a recent report (440), $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ reacted (441) with SnX_2 ($X = Cl$, Br or I) in the absence of air and moisture, giving $[Fe(\eta^5-C_5H_5)(CO)_2]_2SnX_2$. Irradiation of $Fe(\eta^5-C_5H_5)(CO)_2SnX_3$ with $P(OPh)_3$ gave (442) $Fe(\eta^5-C_5H_5)[P(OPh)_3]_2SnX_3$ ($X = Cl$ or Br), and with AgF, these complexes were converted into $Fe(\eta^5-C_5H_5)[P(OPh)_3]_2SnF_3$. The kinetics of the iodination of $Fe(\eta^5-C_5H_5)(CO)_2MMe_3$ ($M = Si$, Ge, Sn or Pb) in carbon tetrachloride have been determined (443). The reactivity of the compounds increased in the order $Si < Ge < Sn < Pb$, as a consequence of vertical hyperconjugation and the increasing stability of the MMe_3^+ ion. The reactions were thought to be akin to aromatic substitution.

Compounds containing Group VA ligands

Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ with a series of 2-alkyl or -aryl imidazoles (HL) gave (444) only FeL_2. However, treatment of $Fe(\eta^5-C_5H_5)(CO)_2I$ with sodium benzotriazolide afforded (445) [425] and [426] which were readily protonated at an uncomplexed N atom. No isolable metal carbonyl derivatives could be obtained from the reaction between $Fe(\eta^5-C_5H_5)(CO)_2NPh_2$ and CO at 190 atm and 150° (446).

Treatment of $[Fe(\eta^5-C_5H_5)(CO)_2(NCMe)]^+$ with $Ph_2P(CH_2)_nPPh_2$ gave $[Fe(\eta^5-C_5H_5)(CO)_x\{Ph_2P(CH_2)_nPPh_2\}]^+$ ($x = 1$ or 2; $n = 1$ or 2) (447). Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ with $P(=E)R_2X$ ($E = S$ or Se; $R = Me$, OEt or Ph; $X = Cl$ or Br) gave (448) $Fe(\eta^5-C_5H_5)(CO)_2[PR_2(=E)]$ which appears, on spectral evidence, to contain Fe-P rather than Fe-E-P bonds. Carbon monoxide could be displaced from the phosphido species by PPh_3 or PMe_2Ph (L) giving $Fe(\eta^5-C_5H_5)(CO)L[PR_2(=E)]$, and reaction with MeI or $[Me_3O]^+$ afforded $[Fe(\eta^5-C_5H_5)(CO)_2\{PR_2(EMe)\}]^+$; similar ethylated species could be obtained from $Fe(\eta^5-C_5H_5)(CO)_2[PMe_2(=S)]$.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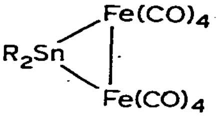
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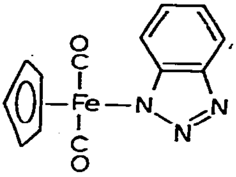
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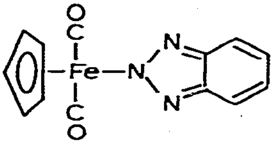
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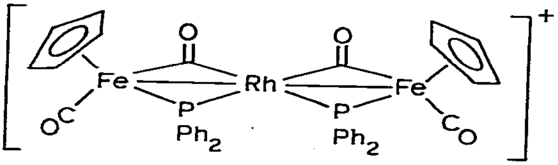
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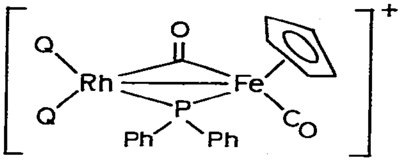
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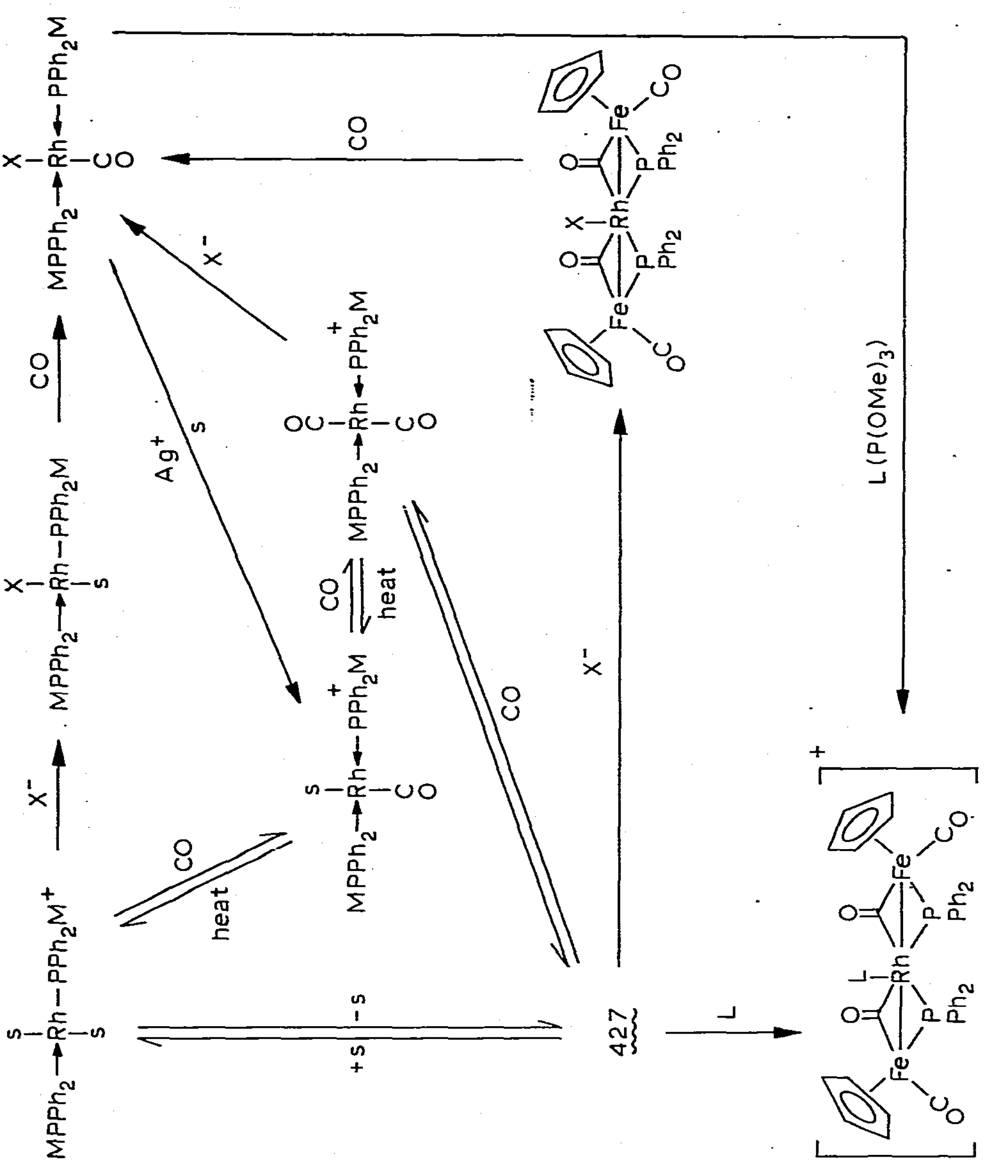
The species $Fe(\eta^5-C_5H_5)(CO)_2[P(CF_3)_2]$, L, functioned (449) as a ligand towards Ni, Co, Fe and Mn carbonyl derivatives. Thus, the species $Ni(CO)_3L$, $Co(CO)_2(NO)L$, $Co_2(CO)_6L_2$, $Fe(CO)_4L$, $Fe(CO)(NO)_2L$, $Mn(CO)_3(NO)L$ and trans-$Mn(CO)_4LH$ were obtained, and from i.r. spectral studies it was estimated that the donor/acceptor ability of L was intermediate between triarylphosphines and trialkylphosphites. In $Co(CO)_2(NO)L$ and $Mn(CO)_3(NO)L$, i.r. spectral data indicated the presence of rotational isomers due to rotation about the P-Co and P-Mn bonds.

In a similar vein, $Fe(\eta^5-C_5H_5)(CO)_2PPh_2$ and $Fe(\eta^5-C_5H_5)(CO)_2SR$ (R = Et, Bu^t or Ph) could act as ligands towards Rh carbonyl species (450). Thus, with $[Rh(CO)_2Cl]_2$ $Fe(\eta^5-C_5H_5)(CO)_2PPh_2$, L', afforded $Rh(CO)L'_2Cl$ which, on treatment with SbF_6^- in methanol, was converted into $[RhL'_2][SbF_6]$, [427], whose structure was established earlier by crystallography (451). The mechanism of formation and some reactions of [427] are summarised in Scheme 91. Reaction of $[Rh(C_8H_{12})(EtOH)_2]^+$ (C_8H_{12} = cyclo-otad-1,5-diene) with $Fe(\eta^5-C_5H_5)(CO)_2SR$ (R = Et or Bu^t; L") gave $[RhL"_2]^+$ which contains bridging CO and SR. However, with $Fe(\eta^5-C_5H_5)(CO)_2SPh$, Q, $[Rh(C_8H_{12})Q_2]^+$ was isolated which contained only terminal CO groups. Treatment of $[Rh(CO)_2Cl]_2$ with $Fe(\eta^5-C_5H_5)(CO)_2SR$ gave only $[Rh(CO)_2SR]_2$. Reaction of $[RhL_2(EtOH)_2]^+$ (L = $P(OPh)_3$; $L_2 = C_8H_{12}$) with an equimolar amount of $Fe(\eta^5-C_5H_5)(CO)_2PPh_2$ afforded [428].

The stibines $SbMe_2Br$ and $SbBr_3$ reacted with $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ giving (452) $Fe(\eta^5-C_5H_5)(CO)_2SbR_2$ (R = Me or Br) and $[Fe(\eta^5-C_5H_5)(CO)_2]_2SbBr$. The species

Scheme 91

M = Fe(η^5-C_5H_5)(CO)(μ-CO) ; s = solvent



$[Fe(\eta^5-C_5H_5)(CO)_2]SbR_2ML_n$ (R = Me or Br; M = Cr or W, L = CO, n = 5; ML_n = $Mn(CO)_2(\eta^5-C_5H_5)$) were obtained from the appropriate iron complex and "activated" metal carbonyl derivatives. The bis-iron complex $[Fe(\eta^5-C_5H_5)(CO)_2]_2SbBrML_n$ was similarly prepared. A number of these species exhibited conformational isomerism at room temperature with respect to the Sb-M bond. A mixture of $Na[Fe(\eta^5-C_5H_5)-(CO)_2]$ and SbX_3 (1:3; X = halide) afforded (453) $[Fe(\eta^5-C_5H_5)(CO)_2]_3Sb$ which reacted with $M(CO)_6$ (M = Cr or W) giving $[Fe(\eta^5-C_5H_5)(CO)_2]_3SbM(CO)_5$. This species was also obtained by treatment of $Fe(\eta^5-C_5H_5)(CO)_2SbF_2M(CO)_5$ with $[Fe(\eta^5-C_5H_5)(CO)_2]^-$. The structure of $[Fe(\eta^5-C_5H_5)(CO)_2Cl]_4[SbCl_3]_4$, [429], obtained (454) by reaction of $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ with $SbCl_3$, has been determined crystallographically (455).

Complexes containing sulphur ligands

Voltammetric studies of $Fe_2(\eta^5-C_5H_5)_2S_2(SEt)_2$, [430], revealed (456) that the complex underwent two one-electron oxidative processes, one reversible (at +0.21 V vs. SCE in CH_3CN) and one quasi-reversible (at +0.90 V). The species also underwent irreversible reduction. The monocationic species $[Fe_2(\eta^5-C_5H_5)_2S_2(SEt)_2]^+$ was prepared electrochemically, was paramagnetic (one unpaired electron per dimer) and has been characterised crystallographically (457). The important dimensions of the neutral species (458) are compared in Table 4 with those of the new cation.

TABLE 4

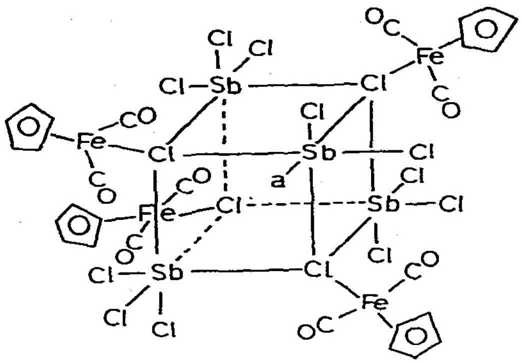
Structural data obtained from $[Fe_2(\eta^5-C_5H_5)_2S_2(SEt)_2]_2^z$, z = 0 or +1

Distance (Å)	z = 0	z = +1
Fe-Fe	3.307(1)	3.059(1)
Fe-S(sulfide)	2.129(2)	2.135(1)
Fe-S(mercaptide)	2.281(2)	2.500(1)
S-S	2.123(3)	1.787(1)

In both species the Fe-S-S-Fe bridge is planar and, upon oxidation, there is a contraction of the intermetallic distance as would be expected for the formation of a one-electron metal-metal bond. Further oxidation of the monocation in acetonitrile afforded $[Fe(\eta^5-C_5H_5)(NCMe)(SEt)]_2^{2+}$.

Halide and cyanide complexes

The He(I) photoelectron spectra of $Fe(\eta^5-C_5H_5)(CO)_2X$ (X = Cl, Br, I or Me) have been measured (459), and there has been a general discussion of the m.o. description of these complexes. Photolysis by visible light of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ in chlorinated solvents afforded (460) $Fe(\eta^5-C_5H_5)(CO)_2X$ (X = Cl or Br), and further irradiation of this species gave $Fe(\eta^5-C_5H_5)_2$ and FeX_2. The complexes $Fe(\eta^5-C_5H_5)-(CO)LI$ and $[Fe(\eta^5-C_5H_5)(CO)_2L]I$ (L = Ph_3As or Ph_3Sb) have been obtained (461) from $Fe(\eta^5-C_5H_5)(CO)_2I$. Reaction of $Fe(\eta^5-C_5H_5)(CO)(EPh_3)I$ (E = P, As or Sb) with bipy or o-phen (L-L) gave $[Fe(\eta^5-C_5H_5)(L-L)(EPh_3)]I$. The species $Fe(\eta^5-C_5H_5)(CO)LX$ (L = $P(OCH_2)_3R$, R = Me, Et or Pr^n; X = Cl, Br or I) have been described (462).



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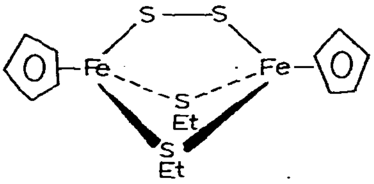

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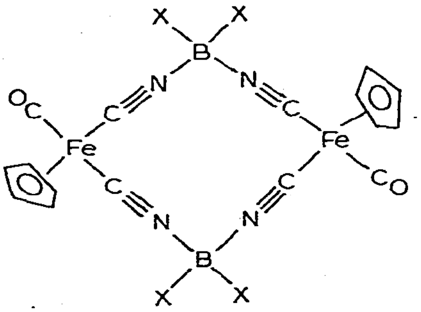

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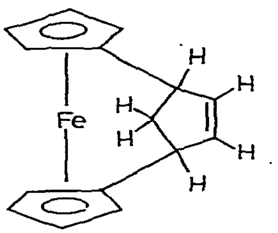

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Treatment of $K[Fe(\eta^5-C_5H_5)(CO)(CN)_2]$ with BX_3 (X = F or Br) and Ph_2BCl gave (463) $[Fe(\eta^5-C_5H_5)(CO)(CN)_2BR_2]_2$ (R = F, Br or Ph), [431]. With BPh_3, $K[Fe(\eta^5-C_5H_5)(CO)(CNBPh_3)_2]$ was formed, while $AlCl_3$ gave $[Fe(\eta^5-C_5H_5)(CO)(CN)_2(AlCl_2)]_2$.

Reaction of $Ni(PPh_3)(acac)Et$ with $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ in the presence of PPh_3 gave (464) ethylene, ethane and $Ni(PPh_3)_2(CO)_2$ as the only identifiable organometallic species. However, $Fe(\eta^5-C_5H_5)(CO)_2I$ reacted with the nickel complex in the presence of PPh_3 affording $[Fe(\eta^5-C_5H_5)(CO)_2(PPh_3)]I$.

ARENE AND RELATED COMPLEXES

There has been a detailed m.o. description(465) of the fragments $M(\eta^6-C_6H_6)$, $M(\eta^5-C_5H_5)$ and $M(CO)_3$, particularly in relation to the binding of these groups to other metals. It was concluded that in such a bonding situation, the $M(\eta^6-C_6H_6)$ and $M(\eta^5-C_5H_5)$ fragments had a stronger σ-interaction with another metal, but the $M(CO)_3$ group was more effective at π-bonding.

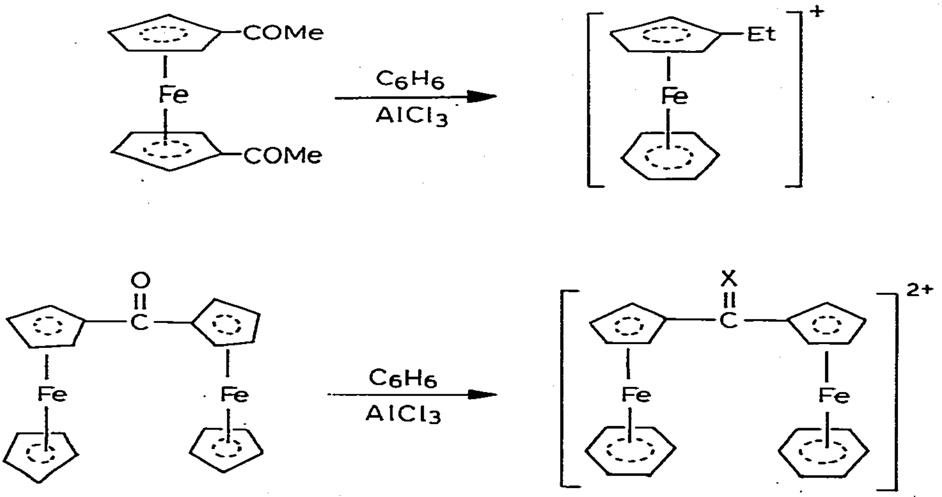
A detailed examination has been made (466, 467) of the exchange of cyclopentadienyl rings in ferrocene with aromatic rings. The ability to undergo exchange has been correlated with the extent and site of substitution on both the C_5 and C_6 rings. Thus, the ease of ligand substitution of cyclopentadiene groups from ferrocene by benzene and alkylbenzenes decreased in the order $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4-$

OMe) $\gg$ Fe(η^5-$C_5H_4R)_2$ (R = alkyl) > Fe(η^5-C_5H_5)(η^5-C_5H_4R) > Fe(η^5-$C_5H_5)_2$ $\gg$ Fe(η^5-$C_5H_4COMe)_2$, the product being $[Fe(\eta^5\text{-}C_5H_4R^1)(\eta^6\text{-}C_6H_3R^2R^3R^4)]^+$ (R^1 = H, COMe or alkyl; R^2, R^3, R^4 = H or alkyl). Under certain conditions, removal of both cyclopentadienyl rings could also occur, viz.

$$Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COMe) + C_6H_3Me_3 \xrightarrow{AlCl_3} [Fe(\eta^5\text{-}C_5H_4R)(\eta^6\text{-}C_6H_3Me_3)]^+ + [Fe(C_6H_3Me_3)_2]^{2+} \quad (R = H,\ COMe,\ Et)$$

From mechanistic studies (466), it appears that (a) ligand exchange, even when catalysed by $AlCl_3$, is not quantitative, (b) the cleaved cyclopentadiene ring can be protonated and act as an electrophile in a Friedel-Crafts alkylation of alkyl ferrocenes and arenes, as, for example, in the reaction of ferrocene with benzene, $AlCl_3$ and Al, which gave $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$ and [432], (c) the presence of $AlCl_3$ is not actually necessary for the ring cleavage of ferrocenes, and (d) alkyl substitution of the rings does not modify the nature of the ligand exchange process. However, in some exchange reactions, functional group modification occurred (467) as shown, for example, in Scheme 92.

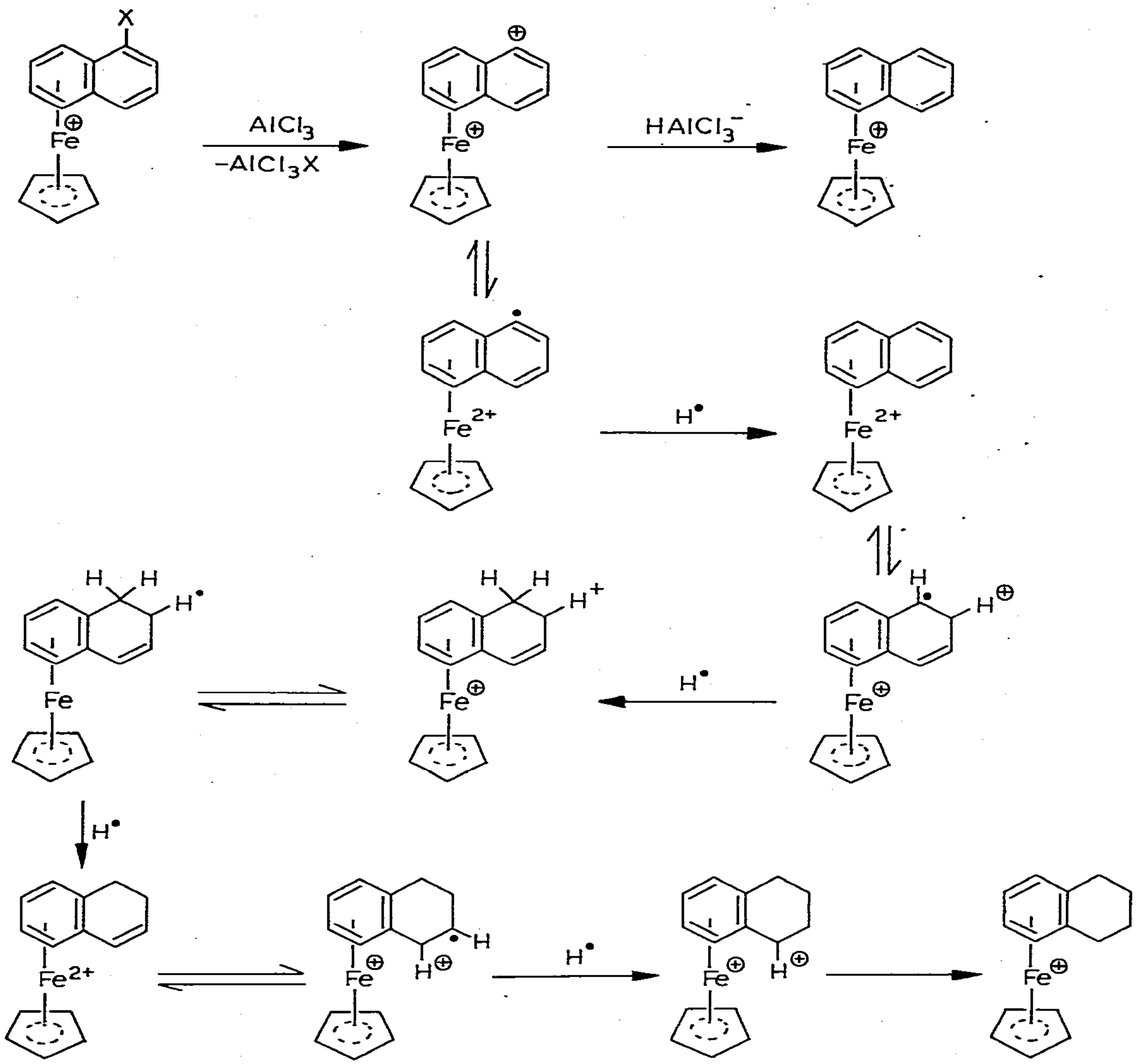
Scheme 92



X = O or Ph_2

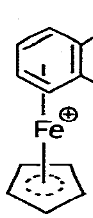
In the reaction between ferrocene, 1-halonaphthalene and Al/$AlCl_3$, the species [433] (X = F, Cl or Br) was produced (468). With 2-methylnaphthalene, the two possible isomers of $[Fe(\eta^5\text{-}C_5H_5)(2\text{-}MeC_{10}H_7)]^+$ were obtained. However, with 1-bromonaphthalene, a mixture of [433] (X = Br), $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)]^+$ and the tetralin complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_{12})]^+$ was formed. When this last reaction was carried out in the presence of iodine or DPPH, the tetralin species was not formed, and when $C_{10}D_8$ was used instead of $C_{10}H_8$, extensive H/D scrambling was observed. These results suggested that radical species might be key intermediates in these reactions (Scheme 93).

Scheme 93



Treatment of ferrocene with fluorene ($C_{13}H_{10}$) and Al/AlCl$_3$ gave (469) [Ge(η^5-C_5H_5)-(η^6-$C_{13}H_{10}$)]$^+$ which could be deprotonated by KOBu^t giving the Zwitterionic species [434] whose structure was confirmed by X-ray crystallography. Reaction of [434] with MeSO$_2$F gave stereospecifically the exo-9-methylfluorene iron complex, and si similar species were obtained using MeI and p-BrC$_6$H$_4$CH$_2$Br. Protonation of the complex also occurred but non-stereospecifically.

Addition of hydride ion to [Fe(η^5-C_5H_5)(η^6-$C_6H_5CO_2Me$)]$^+$ occurred (470) exclusively at the arene ring and mainly at the position ortho to the CO$_2$Me group. It seems that the product distribution in such reactions is controlled mainly by differences in the positive charge at the various arene C atoms as determined by the ring



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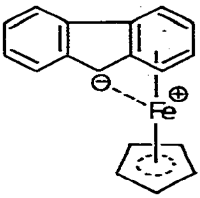

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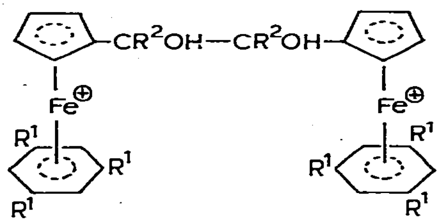

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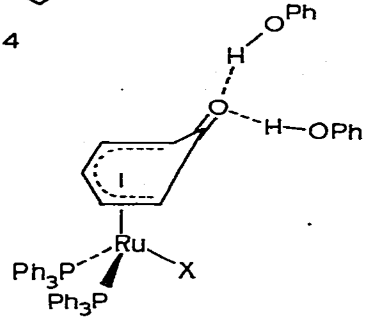


436

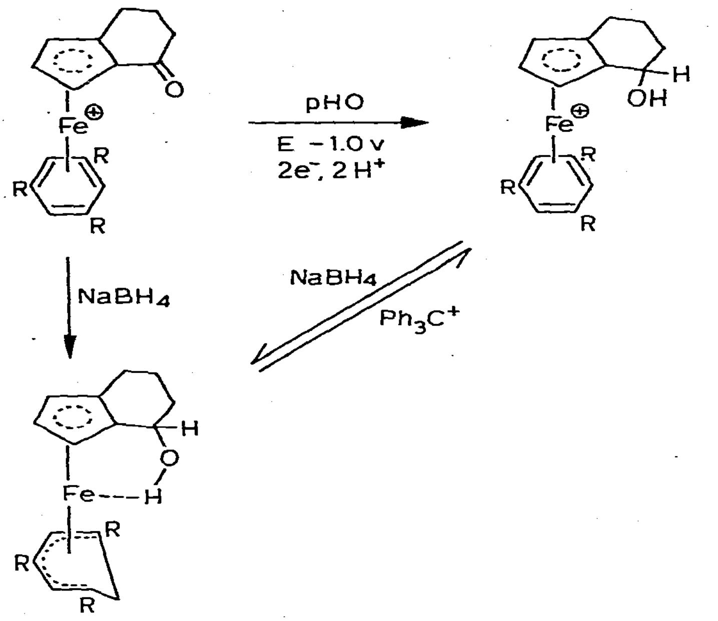
substituents. Borohydride reduction of $[Fe(\eta^5-C_5H_4COR)(\eta^6-C_6H_6)]^+$ (R = Me or Ph) and $LiAlH_4$ or LiMe reduction of $Fe(\eta^5-C_5H_5)(\eta^5-1-MeO_2CC_6H_6)$ gave (471) $Fe(\eta^5-C_5H_4CHROH)(\eta^5-C_6H_7)$ and $Fe(\eta^5-C_5H_5)(\eta^5-1-HOCR_2C_6H_6)$ (R = H or Me), respectively. Treatment of these alcohols with CF_3CO_2H gave $[Fe(\eta^5-C_5H_4Y)(\eta^6-C_6H_5X)]$ (X = H, Y = CH_2Me or CH_2Ph; X = Me, Y = H; X = $CHMe_2$, Y = H). The most likely mechanism involved acid-promoted dehydroxylation followed by intramolecular hydride transfer from the C_6H_7 ring to the formal C^+ centre of the resulting carbenium ion.

Regio- and stereo-specific reduction of acylcyclopentadienyl arene iron cations has been achieved (472) electrochemically. Thus, at pH = 0 in aqueous media, $[Fe(\eta^5-C_5H_4COR^2)(\eta^6-C_6H_3R^1_3)]^+$ underwent a two-electron reduction giving $[Fe(\eta^5-C_5H_4CHR^2OH)(\eta^6-C_6H_3R^1_3)]^+$ (R^1 = H, R^2 = Me or Ph; R^1 = R^2 = Me; R^1 = Me, R^2 = Ph), while at pH = 13 - 14, one-electron reduction (with uptake of a proton) afforded [435] (R^1 = R^2 = Me; R^1 = Me, R^2 = Ph) which could be reduced by BH_4^- to the corresponding neutral bis-η^5-cyclohexadienyl complexes. Other stereoselective reactions of a substituted cyclopentadienylarene iron cation are shown in Scheme 94. Electrochemical reduction of $[Fe(\eta^5-C_5H_5)(\eta^6-C_6H_5CO_2H)]^+$ at pH = 0 afforded $[Fe(\eta^5-C_5H_5)-(\eta^6-C_6H_5CH_2OH)]^+$.

Treatment of $[Ru(\eta^6-C_6H_6)Cl_2]_2$ with $NaPF_6$ in methanol, and with NaOH, afforded (473) $[Ru_2(\eta^6-C_6H_6)_2(\mu-Cl)_3][PF_6]$ and $[Ru_2(\eta^6-C_6H_6)_2(\mu-OH)_3]Cl.3H_2O$, respectively. With CsCl in aqueous HCl, the ruthenium arene complex was converted into $Cs[Ru(\eta^6-C_6H_6)Cl_3]$ which reacted with Lewis bases (L = tertiary phosphines) giving $Ru(\eta^6-C_6H_6)-LCl_2$ and not *fac*-RuL_3Cl_3.

In methanol, $Ru(PPh_3)_4H_2$ or $Ru(PPh_3)_3H(OAc)$ reacted (474) with HBF_4 giving $[Ru(\eta^6-C_6H_5PPh_2)(PPh_3)_2H][BF_4]$. In the presence of benzene or toluene, it was possible to prepare $[Ru(\eta^6-C_6H_5R)(PPh_3)_2H][BF_4]$ (R = H or Me) by this route.

Scheme 94



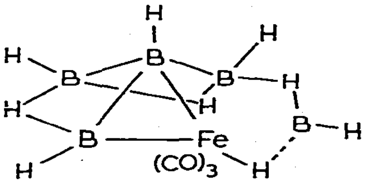
Reaction of $Ru(PPh_3)_4H_2$ with phenol gave $Ru(C_6H_5O)(PPh_3)_2H$ and $Ru(C_6H_5O)(PPh_3)_2H$.-2PhOH, probably [436], from which the uncomplexed phenol could be displaced by methanol.

Treatment of $[Ru(\eta^6\text{-arene})Cl_2]_2$ or $Ru(\eta^6\text{-arene})(pyr)Cl_2$ (arene = C_6H_6, 1,3,5-$Me_3C_6H_3$ or C_6Me_6) with $M_2C_8H_8$ (M = Li, Na or K) gave (475) the fluxional species $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_8)$. The structure of the hexamethylbenzene complex was established crystallographically and it was shown that the η^6-arene ring was planar while the geometry of the C_8H_8 ring was identical to that in $M(CO)_3(C_8H_8)$ (M = Fe or Ru), $Fe(CO)(C_4H_6)(C_8H_8)$ and $Fe(\eta^4\text{-}C_8H_8)(\eta^6\text{-}C_8H_8)$ (476).

Reaction of ferrocene with tetramethylthiophene in the presence of $Al/AlBr_3$ gave (477) $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4Me_4S)]^+$.

BORANE AND CARBORANE COMPOUNDS

Reaction of $Fe(CO)_5$ with B_5H_9 in a hot-cold reactor afforded (478) $Fe(CO)_3(B_4H_8)$, $Fe(CO)_3(B_5H_9)$ and a red, volatile liquid which, at 5°, gave an orange solid $Fe(CO)_5B_5H_3$. Treatment of $Fe(CO)_3(B_5H_9)$, [437], with KH gave $K[Fe(CO)_3(B_5H_8)]$, whose structure, [438], as the $[Bu^n_4N]^+$ salt, was determined crystallographically. It was suggested that [437] and [438] could be represented as valence bond structures analogous to B_6H_{10} and $[B_6H_9]^-$, respectively, where $Fe(CO)_3$ replaced a BH vertex and served as a two-electron donor to the polyhedral skeleton. From spectral studies of $Fe(CO)_5B_5H_3$, it was suggested that this species containing B-CO bonds, viz. [439].



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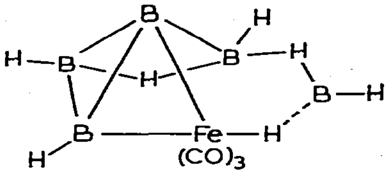

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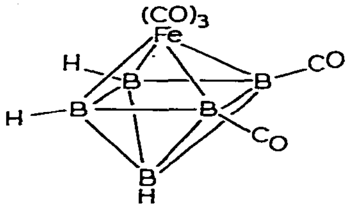

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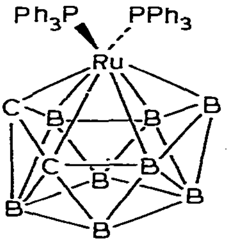
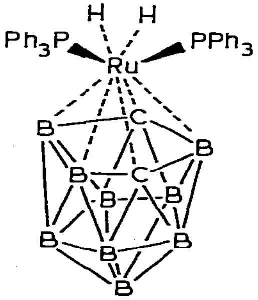
Treatment of $FeCl_2$ at low temperature with Na[$Me_2C_2B_4H_5$] gave (479) Fe(C,C'-$Me_2C_2B_4H_4)_2H_2$, [440], whose reactions are outlined in Scheme 95. It was suggested that the hydride ligands bound to Fe in [440] probably occupied bridging positions over triangular faces in the polyhedron. Reaction of Ru($PPh_3)_3$HCl with Na[$C_2B_7H_{12}$] gave (480) Ru($C_2B_7H_9$)($PPh_3)_2$, [441], which may be obtained by the reductive elimination of hydrogen from Ru($C_2B_7H_9$)($PPh_3)_2H_2$ (481). The species [441] did not undergo oxidative addition with H_2 and showed virtually no catalytic activity towards the hydrogenation of alkenes. With CO it gave Ru($C_2B_7H_9$)(CO$)_2$(PPh_3). Treatment of Ru($PPh_3)_3$HCl with 7,9-[$C_2B_9H_{12}]^-$ gave (481) 2,1,7-Ru($C_2B_9H_{11}$)($PPh_3)_2H_2$, [442], whose structure was established crystallographically. On heating [442] at 160°, hydrogen was lost and a dark blue species, probably 2,1,7-Ru($C_2B_9H_{11}$)($PPh_3)_2$ was formed. This reacted with hydrogen regenerating two species, one of which was [442]. Both [442] and its dehydrogenated product reacted with CO and HCl giving 2,1,7-Ru($C_2B_9H_{11}$)(CO)($PPh_3)_2$ and 2,1,7-Ru($C_2B_9H_{11}$)($PPh_3)_2Cl_2$, respectively. Treat-



H atoms omitted for simplicity

441



H atoms omitted for simplicity

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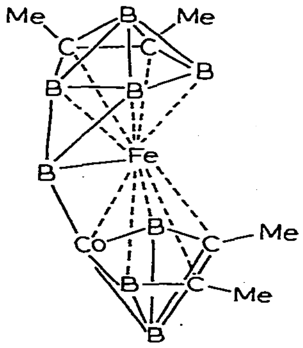

H atoms omitted for simplicity

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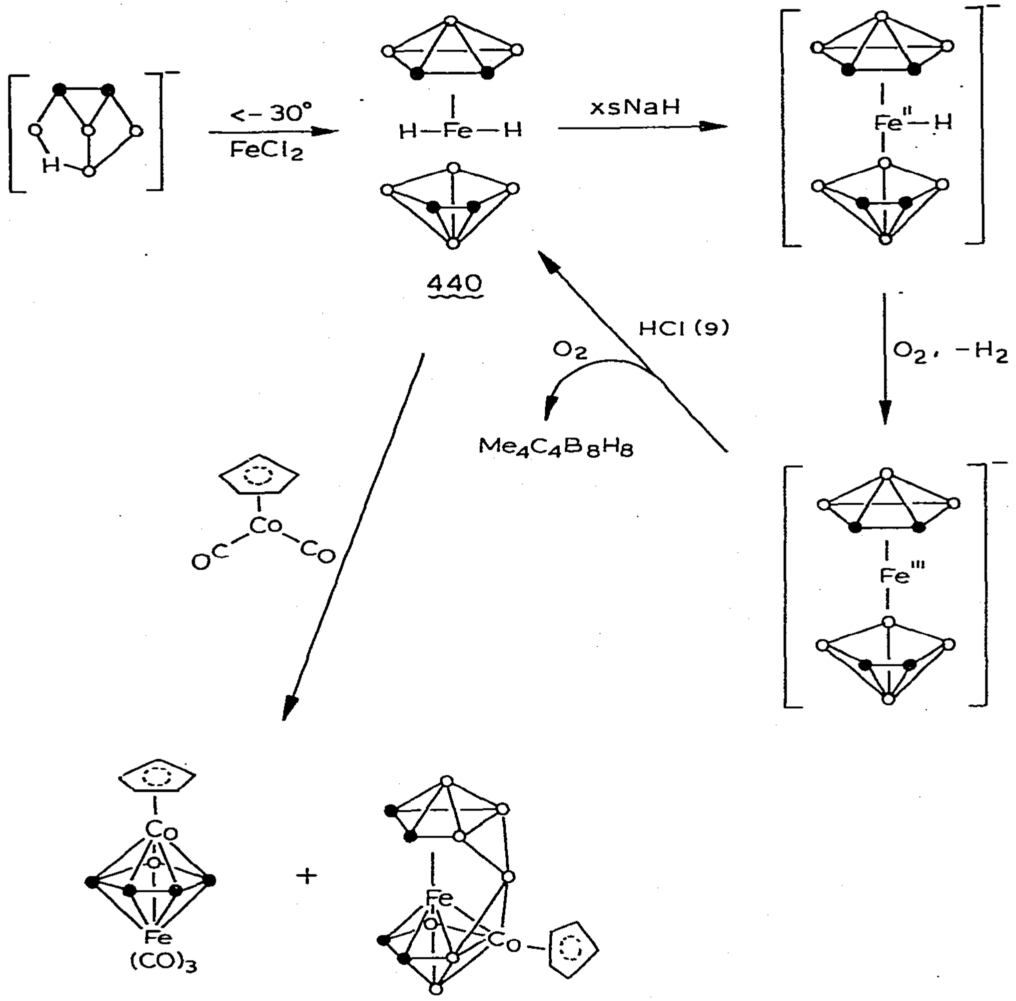
Scheme 95

o = CMe; ● = BH

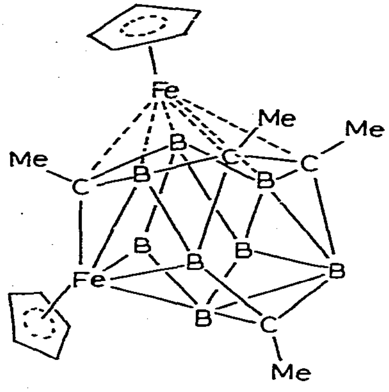


ment of $Ru(PPh_3)_3HCl$ with $7,8-[C_2B_9H_{12}]^-$ gave $3,1,2-Ru(C_2B_9H_{11})(PPh_3)_2H_2$ which, unlike [442], underwent irreversible loss of H_2 on heating, although it formed similar compounds with CO and HCl. Both [442] and its dehydrogenated derivative catalysed the hydrogenation of olefins.

From the reaction between $Fe(2,3-Me_2C_2B_4H_4)_2H_2$ and $Co(\eta^5-C_5H_5)(CO)_2$, $FeCo(\eta^5-C_5H_5)-(Me_4C_4B_8H_8)$, [443], has been obtained (482). The structure of this species has been determined by X-ray methods. There is a direct Co-Fe bond and the two pentagonal bipyramidal units are fused at the common Fe atom with an additional BH group capping a triangular face on both polyhydra simultaneously. The structure could be rationalised in terms of a shortage of two electrons in the cage framework relative to the normal requirements for this polyhedral cluster, and this caused one BH group to adopt a capping position.

Reaction of $FeCl_2$ with $NaC_{10}H_8$, NaC_5H_5 and $Me_4C_4B_8H_8$ gave (483) at least four isomers of $Fe_2(\eta^5\text{-}C_5H_5)_2Me_4C_4B_8H_8$, two of which, [444] and [445], have been characterised crystallographically. Neither complex has the closo structure predicted from electron counting rules, and instead contain a five- and a four-membered open face, resepctively.

Treatment of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ with 3,4-diethyl-2,5-dimethyl-1,2,5-thiadiborolene gave (484) the triple-decker sandwich molecule [446].



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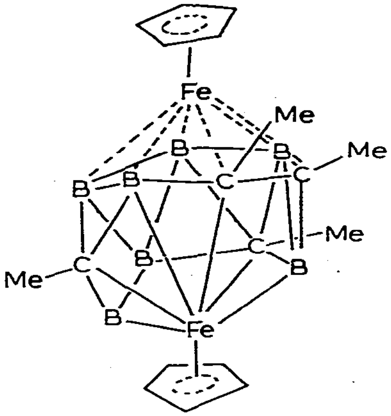

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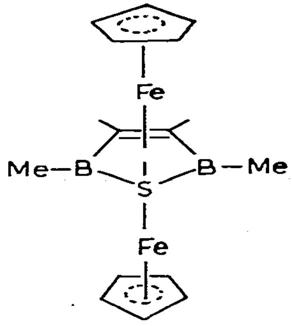


446

ORGANOMETALLIC SPECIES IN SYNTHESIS AND CATALYSIS

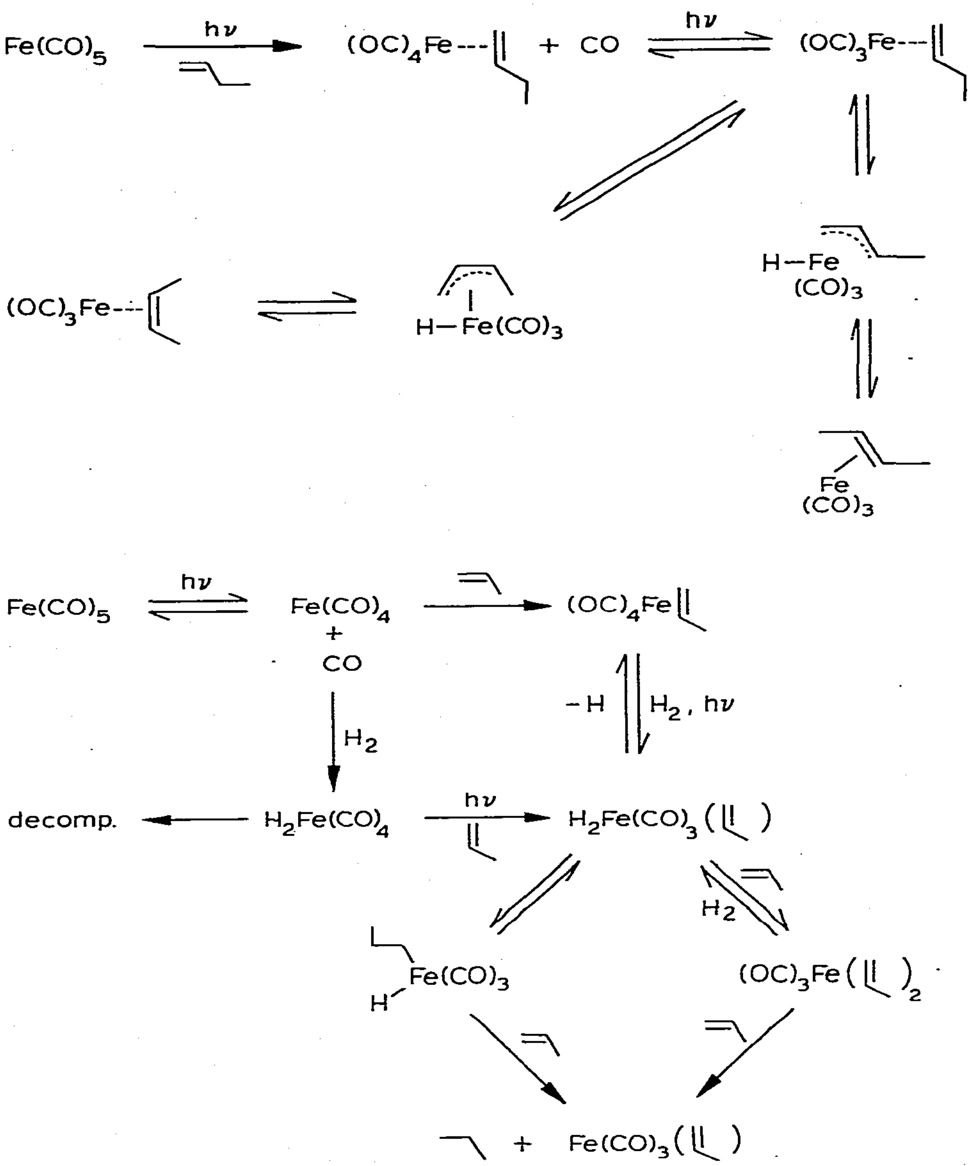
Hydrogenation and hydroformylation

A general mechanism for transition-metal catalysed hydrogenation of alkenes and alkynes has been proposed (485) which unifies various features of these reactions. It was suggested that hydrogenation on metal surfaces should be interpreted as hydrogen transfer between an adsorbed hydrocarbon and the adsorbed olefin and should not be regarded as addition of hydrogen directly to the olefin.

Hex-1-ene and acrylic ethyl ester have been rapidly hydrogenated (486) by $Ru(PPh_3)_3HCl$ generated in situ in methanol or ethanol/benzene mixtures. Reaction of ruthenium(II) acetate with an excess of $Ph_2PCH_2CH_2Si(OEt)_3$, L, gave (487) $RuL_2(OAc)_2$ which was de-ethoxylated on silica gel, giving support-bound $\{-O\overline{)_3}SiCH_2CH_2PPh_2\}_2Ru(OAc)_2$. This material subsequently hydrogenated hex-1-ene and cyclohexene under moderate pressures (15 atm), even after treatment with HBF_4. The silyl phosphine also reacted with $Ru(C_{10}H_{16})Cl_2$ giving RuL_3Cl_2 which was similarly attached to silica, and also acted as a hydrogenation catalyst.

The isomerisation and hydrogenation of terminal olefins was photocatalysed (488) by $Fe(CO)_5$. The observed quantum efficiency for the conversion of pent-1- to pent-2-ene approached 500, implying the generation of a thermally active catalyst, possibly an alkyl hydride intermediate (Scheme 96). Hydrogenation of olefin occurred under very mild conditions and at low temperature under D_2, it was established that

Scheme 96

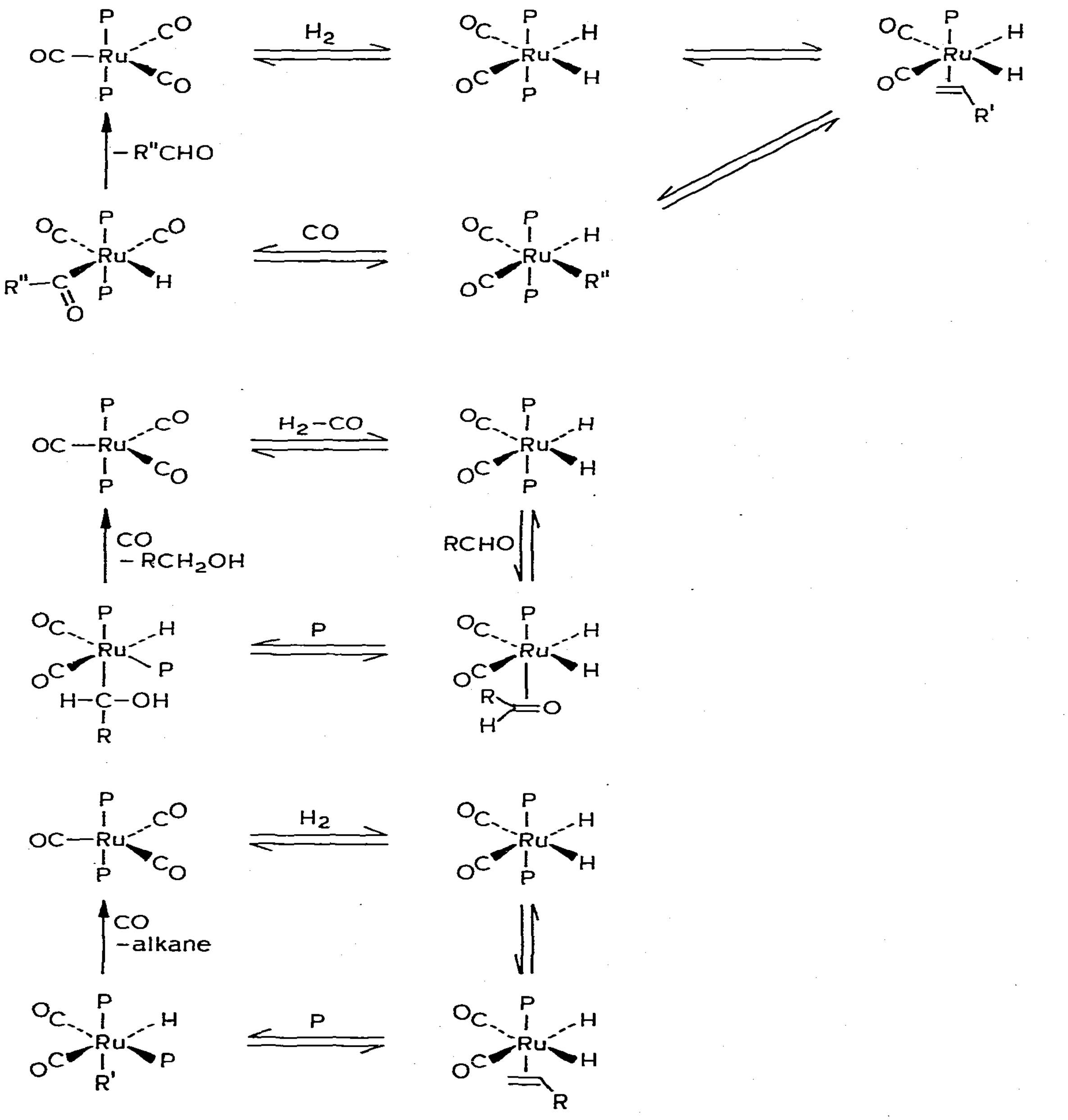


H/D exchange within the olefin occurred competitively with alkane formation. The mechanisms of hydrogenation is also shown in Scheme 96.

A variety of ruthenium complexes can homogeneously catalyse the hydroformylation of alkenes (489). Among the complexes investigated were $Ru(CO)_3(PPh_3)_2$, $Ru(CO)_2(PPh_3)_2H_2$, $Ru(NO)(PPh_3)_3H$, $Ru(PPh_3)_xH_y$ ($x = 3$, $y = 4$; $x = 4$, $y = 2$), $Ru(PPh_3)_2X_2$ ($X = OAc$, $OCOCF_3$, $OCOBu^t$), $Ru(CO)_2(PPh_3)_2(O_2C_6Cl_4)$ and $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2H$. The ruthenium complex recovered from the reaction was invariably $Ru(CO)_3(PPh_3)_2$, and a mechanism of reaction involving $Ru(CO)_2(PPh_3)_2H_2$ as the catalyst precursor has been suggested both for the production of aldehyde and of alkane (Scheme 97).

The evolution of hydrogen from mildly alkaline suspensions of $Fe(OH)_2$ may involve (490) elemental iron as an intermediate. This process is inhibited by acetylene, ethylene, CO and N_2, and it is claimed that N_2 may be reduced to ammonia and hydrazine. It is further suggested that acetylene can be further reduced to ethylene at one Fe atom, to ethane at two Fe atoms, and that methane formation occurs at small Fe clusters.

Scheme 97



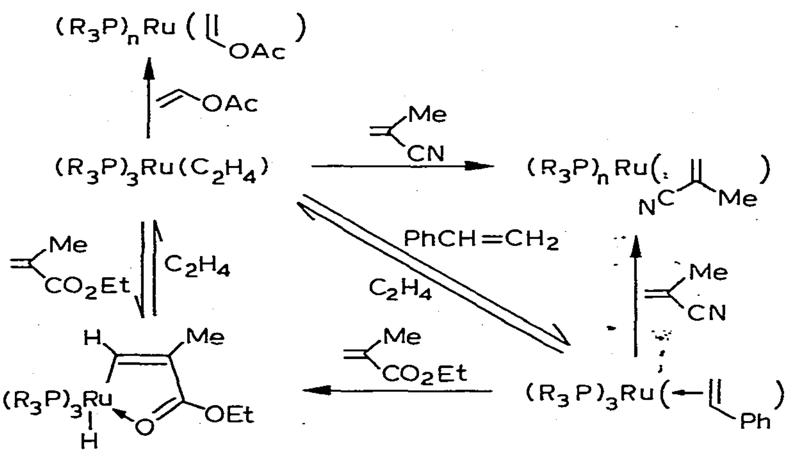
C-C bond formation

Radicals have been detected (491) by CIDNP in the Fe(II) catalysed halogen-metal exchange reaction between a Grignard reagent and an alkyl halide.

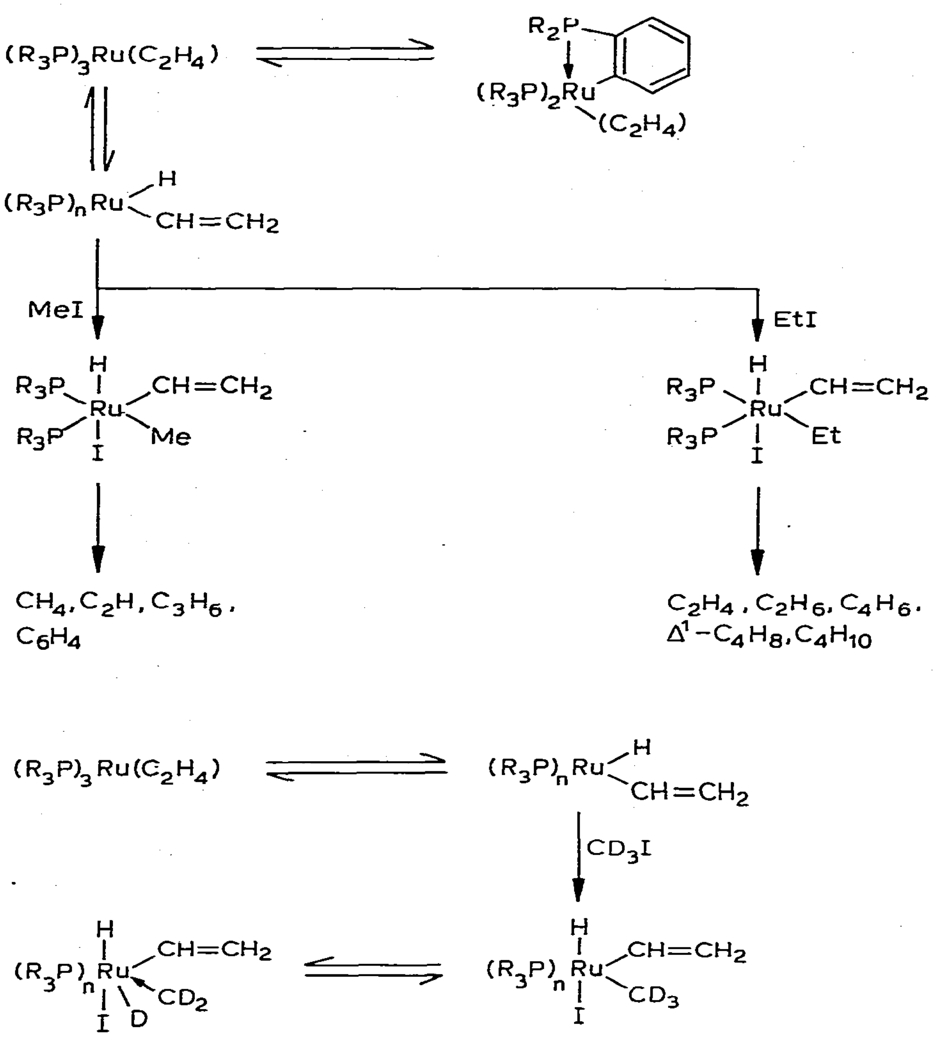
Dicyclopropylacetylene is cyclotrimerised (492) by $Fe_3(CO)_{12}$ to hexakis(cyclopropyl benzene; tetrakis(cyclopropyl)cyclopentadienone also being formed. Electrochemical reduction of $Fe(acac)_3$ in DMF at a nickel electrode in the presence of 1-bromobutane, PPh_3 and $[Et_4N]Br$ gave (493) modest yields of octane. Similarly, 3,4-dimethylhexane was produced from 2-bromobutane. Using an aluminium electrode, good yields of hexaderane, octene and octane were generated from 1-octyl bromide, and yields of these products were further increased by exclusion of PPh_3. Acrylonitrile was catalytically hydrodimerised (494) to 1,4-adiponitrile by $Ru(SbPh_3)_3Cl_2$ in the presence of N-methylpyrrolidine in 3-methylheptanone-2-acetone, or by $RuCl_3.nH_2O$ with N-methylmorpholine in methylcellosolve in the presence of $[Et_4N][SnCl_3]$.

Reaction of $Ru(PPh_3)_4H_2$ with alkenes gave (495) $Ru(PPh_3)_3(\eta^2\text{-alkene})$ (alkene = C_2H_4, C_3H_6, $PhCH=CH_2$ or C_4H_6) together with equimolar amounts of alkane. Exchange of the bound olefin could be effected by $CH_2=CHOAc$, $CH_2=CMe(CO_2Et)$ or $CH_2=C(CN)OMe$. These η^2-alkene complexes reacted with hydrogen giving alkane, and $Ru(PPh_3)_4H_2$ was identified as a smooth catalyst for the formation of alkane from these alkenes. However, $Ru(PPh_3)_3(C_2H_4)$ reacted with MeI giving propylene, traces of butadiene, methane, ethylene and traces of ethane and butanes. The formation of propylene suggested an oxidative addition of MeI to $Ru(PPh_3)_3(C_2H_4)$, and also cleavage of a C-H bond in the bound C_2H_4 giving a σ-vinyl species. When these reactions were carried out using CD_3I, mixtures of CD_4, CD_2H_2 and CD_3H were identified, suggesting the involvement of α-hydrogen abstraction from the Ru-methyl species. An explanation for these observations is summarised in Scheme 98.

Scheme 98



Scheme 98 continued

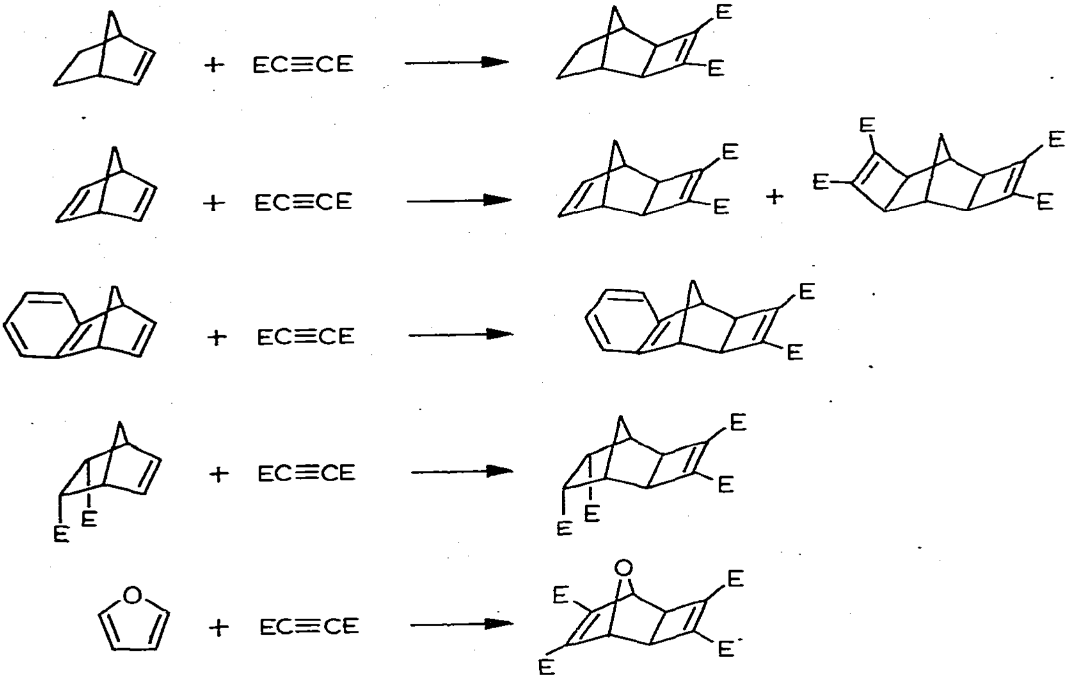


The species $Ru(PPh_3)_4H_2$ catalysed (496) the [2π + 2π] cross-addition of norbornene derivatives with $MeO_2CC_2CO_2Me$ (Scheme 99). It was thought that a zerovalent Ru olefin or acetylene complex was formed, with successive formation of a metallocyclopentene complex and reductive elimination of the product.

N-C bond formation

Alkyl- or aryl-amido Grignard reagents, RNHMgBr (R = Ph, p-MeC_6H_4, $Me(CH_2)_{11}$ or C_6H_{11}) reacted with nitro compounds $R'NO_2$ (R' = Ph, p-RC_6H_4 (R = Me, MeO or Cl), $Me(CH_2)_{11}$ or C_6H_{11}) giving N,N'-substituted ureas, RNHCONHR' (497). A likely intermediate was thought to be $[MgBr^+][Fe(CO)_4(CONHR)]^-$. Indeed, treatment of the species obtained from $Fe(CO)_5$ and PhNHBgBr with methyl iodide gave acetanilide.

Scheme 99



C-Cl bond activation

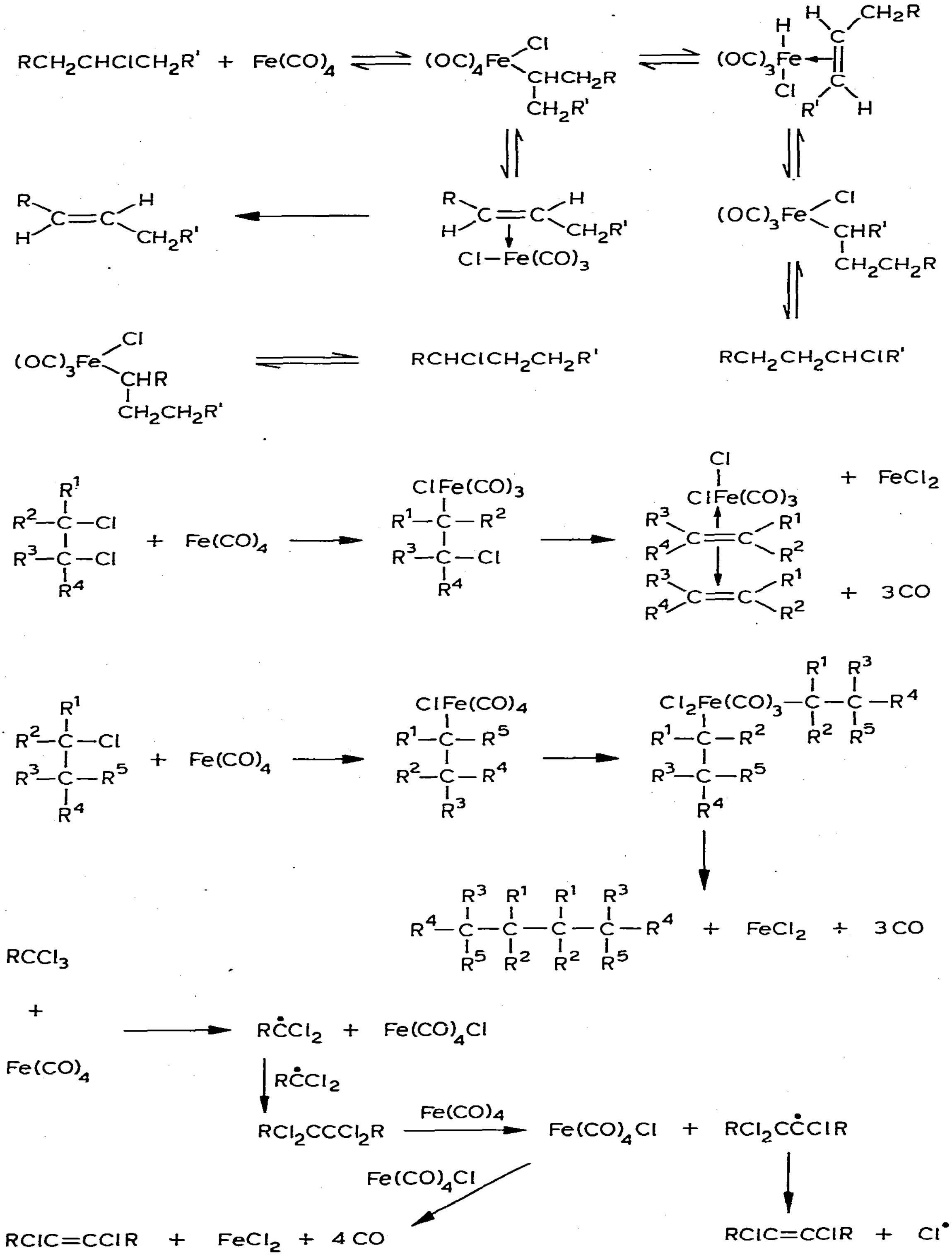
In the presence of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$, mixtures of chloroethanes and alkanes afforded (498) a variety of organic products. In general, the chloroethanes were converted into the corresponding chloroethylenes while the alkanes were transformed into the monochloroalkanes and alkenes. Isomerisation and dimerisation of the chloroalkanes also occurred, and the postulated mechanisms of these reactions are outlined in Scheme 100.

REVIEWS, DISSERTATION ABSTRACTS, AND ARTICLES IN INORGANIC SYNTHESES

Reviews. The following reviews have appeared which contain material of relevance to iron, ruthenium and osmium organometallic chemistry:

"Metal Carbonyls", by E.W.Abel and F.G.A.Stone, (499).
"Carbonyl Compounds", by B.H.Robinson, (500).
"Binary carbonyls of transition metals", by S.C.Tripathi, (501).
"Metal carbonyls: some new observations in an old field", by F.A.Cotton (502)
"Advances in platinum metal carbonyls and their substituted derivatives. 1. Ruthenium and Osmium", by S.C.Tripathi, S.C.Srivastava, R.P.Mani and A.K.Shrimal, (503).
"Carbon monoxide and metals: their influence on each other. Part 2. Reactivity of carbon monoxide: Part 3. Metal carbonyl complexes", by R.J.Haines (504, 505)

Scheme 100


RCH2CHClCH2R' + Fe(CO)4
(OC)4Fe(Cl)CH(CH2R')CH2R
(OC)3Fe(H)(Cl)
Cl–Fe(CO)3
(OC)3Fe(Cl)CHR'CH2CH2R
(OC)3Fe(Cl)CHRCH2CH2R'
RCHClCH2CH2R'
RCH2CH2CHClR'
+ Fe(CO)4
ClFe(CO)3
+ FeCl2
+ 3CO
ClFe(CO)4
Cl2Fe(CO)3
+ FeCl2 + 3CO
RCCl3
+
Fe(CO)4
RĊCl2 + Fe(CO)4Cl
RĊCl2
RCl2CCCl2R
Fe(CO)4
Fe(CO)4Cl + RCl2ĊCClR
Fe(CO)4Cl
RClC=CClR + FeCl2 + 4 CO
RClC=CClR + Cl•

"Substitution reactions of metal and organometal carbonyls with Group V and VI Donor ligands", by D.A.Edwards (506).

"High nuclearity metal carbonyl clusters", by P.Chini, G.Longoni and V.G.Albano (507).

"Carbido-carbonyl complexes with penta- and hexa-coordinated carbon", M.Nonoyama, (508).

"Structural and bonding patterns in cluster chemistry", by K.Wade (509).

"Nitrosyl, dinitrogen and dioxygen complexes", by J.E.Fergusson and G.A.Rodley (510).

"Mutual effects of ligands in Ru and Os nitrosyl complexes", N.M.Sinitsyn and A.A. Svetlov, (511).

"Organic-inorganic systems for the chemical modification of molecular nitrogen under mild conditions", by E.E.van Tamelen (512).

"Organic azides and isocyanates as sources of nitrene species in organometallic chemistry", by S.Cenini and G. La Monica (513).

"Complexation and activation of diazenes and diazo compounds by transition metals", by A.Albini and H.Kisch (514).

"Complexes containing metal-carbon σ bonds", by B.L.Booth (515).

"Polycyanovinyl transition metal derivatives", by R.B.King (516).

"Reactions of CO with transition metal-carbon bonds", by G.Henrici-Olivé and S.Olivé (517).

"On the way to carbene and carbyne complexes", by E.O.Fischer (518).

"Coordination chemistry of the allenes", by F.L.Bowden and R.Giles (519).

"Acetylene and allene complexes: their implication in homogeneous catalysis", by S.Otsuka and A.Nakamura (520).

"Allyl complexes of 2nd and 3rd row transition metals", by J.Powell (521).

"Coordination of unsaturated molecules to transition metals", by S.D.Ittel and J.A. Ibers (522).

"Reactions of simple unsaturated molecules with the polynuclear carbonyls of some Group VIII elements", by J.Lewis and B.F.G.Johnson (523).

"Hydrocarbon metal π-complexes", by B.L.Booth (524).

"π-Cyclopentadienyl complexes", by G.R.Knox and W.F.Watts (525).

"Pentamethylcyclopentadienyl metal complexes: an entry to metal carbonyl derivatives with metal-metal multiple bonds", by R.B.King (526).

"Metal complexes containing six-electron and seven-electron ligands", by T.A. Stephenson (527).

Hydrocarbon-metal π-complexes other than allyl, cyclopentadienyl and arene complexes", by R.D.W.Kemmitt (528).

"Ten years of metallocarboranes", by K.P.Callahan and M.F.Hawthorne (529).

"Organometallic complexes containing metal-metal bonds between transition metals and main group metals or metalloids", by A.T.T.Hsieh (530).

"Carboxylato complexes of the platinum group metals", by A.Dobson and S.D.Robinson, (531).

"Carbon dioxide fixation by transition metal complexes", by T.Ito and A.Yamamoto, (532).

"Reactions of transition metal atoms with organic substrates", by P.S.Skell and M.J.McGlinchey (533).

"Synthetic reactions of metal atoms at temperatures of 10 to 273^{o}K, by P.L.Timms, (534).

"Use of activated metals in organic and organometallic synthesis", by R.D.Rieke (535).

"The laser-evaporation of metals and its applications to organometallic synthesis", by E.Koerner von Gustorf, O.Wolfbeis and C.R.Eady (536).

"Reactions of metal atoms with fluorocarbons", by K.J.Klabunde (537).

"Iron", by J.R.Wasson and H.J.Stoklosa (538).

"Elements of the 1st transitional period. Part 1. Manganese and iron", by R.Davis (539).

The noble metals. Part 1. Ruthenium, osmium, rhodium and iridium", by L.A.P. Kane-Maguire (540).

"Transition metal chemistry", by J.R.Dilworth, G.J.Leigh and R.L.Richards (541).

"Applications of ^{13}C n.m.r. in inorganic chemistry", by M.H.Chisholm and S.Godleski, (542).

"Some applications of mass spectrometry in inorganic and organometallic chemistry", by J.M.Miller and G.L.Wilson (543).

Disssertation Abstracts

"Structural and chemical studies of transition metal carbonyl complexes", by H.B. Chin (544).

"The synthesis and characterisation of the thallium derivatives of various transition metal carbonyls", by T.W.Theyson (545).

"Decarbonylation of simple hydrides by ruthenium(II) phosphine complexes", by R.R.Hitch (546).

"Reactions of aromatic amines with ruthenium nitrosyl complexes", by W.L.Bowden (547).

"Nitrosyl transfer reactions and studies in pentacoordinate intramolecular rearrangement", C.B.Ungermann (548).

"Transition metal complexes of aryldiazo, aryldiazene and nitrosyl ligands", by B.L.Haymore (549).

Reaction of transition metal σ-bonded unsaturated hydrocarbon complexes with electrophilic olefins and acetylenes", by J.P.Williams (550).

"Dihaptocyclobutadienoid iron complexes", by A.Sanders (551).

"Substituted butadiene tricarbonyl iron complexes derived from 2-pyrones", by A.R.Banks (552).

"1. C-C bond formation between π-ligands coordinated to iron. 2. Thermolysis and photolysis of (cyclopentadiene)tricarbonyliron", by J.Shelly (553).

"New reactions of bis(arene)iron(II) salts", by G.G.Cash (554).

"Ligand-bridged ruthenium complexes", by E.C.Johnson (555).

"Synthesis, characterisation and reactions of binuclear iron(II) mercaptide complexes", by K.D.Karlin (556).

"Synthesis and structural characterisation of some sulphur-bridged cyclopentadienyl ruthenium complexes", by K.M.Wagner (557).

Articles in Inorganic Syntheses

The syntheses of $Ru_3(CO)_{12}$ (558), $M_3(CO)_{10}(NO)_2$ (M = Ru or Os) (559), $[Ru(CO)_3Cl_2]_2$ (560), $Fe(CO)_4(PF_2NEt_2)$ (561), $[Ru(NO)_2(PPh_3)_2Cl][BF_4]$ (562), ammine complexes of osmium nitrosyls (563), $Fe(NO)(S_2CNEt_2)_2$ (564) and reagents for the syntheses of η-diene complexes of $Fe(CO)_3$ and $Ru(CO)_3$, e.g. $Fe(CO)_3$(PhCH=CHCOMe) and $Ru(CO)_3(1,3\text{-}C_8H_{12})$, have been described in detail(565).

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