IRON, RUTHENIUM AND OSMIUM: SURVEY FOR THE YEAR 1977 *

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Iron, ruthenium and osmium; Annual Survey covering the year 1976 see J. Organometal. Chem., vol. 183 (1979) 281 - 453.

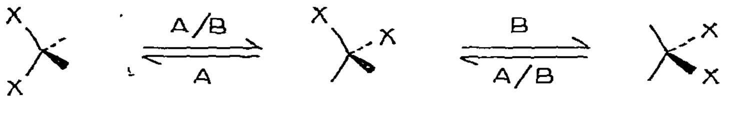
METAL CARBONYLS

Simple carbonyls, carbonylate anions, formyl and carbamoyl species

The data necessary for the estimation of the enthalpy of disruption of the Fe–CO bond in $Fe(CO)_5$ has been reexamined (1) in the light of high-energy factored force-field models for the stretching force constants of $Fe(CO)_5$, the results of SCF-MO Calculations of electron configuration and charge, and recent thermochemical experiments. It was shown that $\Delta H^{\ddagger}$ for the Fe–CO bond is effectively 365 ± 10 KJ/mol.

By a combination of uv and ir laser-induced photochemistry, it has been possible to identify (2) the intramolecular ligand exchange processes ocurring in $Fe(CO)_4$ (C_{2v} symmetry, structure similar to SF_4). This was achieved by uv photolysis of $Fe(CO)_5$ which was 40% ^{13}CO enriched in an argon matrix at 10°K. Irradiation of this species with a CW CO ir laser at a frequency corresponding to one particular isomer promoted selective intramolecular rearrangement of this isomer providing a non-statistical distribution of $^{13}C^{18}O$ in $Fe(^{12}C^{16}O)_{4-x}$-$(^{13}C^{18}O)_x$. Ligand site-exchange involves non-Berry pseudorotation (Scheme 1), and so differs from the thermal rearrangements in SF_4. The temperature dependence of the mcd spectrum of matrix-isolated $Fe(CO)_4$ shows (3) that the species is paramagnetic.

Scheme 1

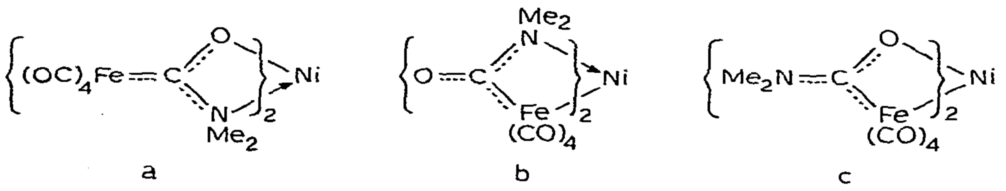


Reaction of $Fe(CO)_5$ with acetic acid/acetic anhydride mixtures under nitrogen in dimethylformamide afforded (4) $Fe(O_2CMe)_2$, but similar treatment with benzoic acid/anhydride mixture gave $[Fe_3(DMF)_3O(O_2CPh)_6][O_2CPh]$ DMF.

It is known (5) that $Na_2Fe(CO)_4$. 1·5 (dioxane) contains a highly distorted $[Fe(CO)_4]^{2-}$ anion. However, the carbonylate species in $[Na(crypt)]_2[Fe(CO)_4]$ (crypt = $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$) has an essentially undistorted tetrahedral geometry (6). The X-ray structural determination of $K_2Fe(CO)_4$ revealed that the carbonylate anion had an intermediate amount of distortion, and it was suggested (6) that this trend in distortion reflected the decreasing charge along the series Na^+, K^+ and $[Na(crypt)]^+$, reinforcing the belief that distortions of $[Fe(CO)_4]^{2-}$ are caused by the presence of highly charged species in close proximity. These studies are of considerable significance in relation to the dramatic effects of ion-pairing on alkyl migration reactions of $[Fe(CO)_4R]^-$ (R = alkyl or acyl) (7).

The extent of association between cation and anion in $Na[Fe(CO)_4H]$ and $[(Ph_2P)_2N][Fe(CO)_4H]$ has been determined (8) by conductivity measurements in THF. Extensive association was noted and it was observed that there is a strong interaction between Na^+ and an equatorial CO group in $[Fe(CO)_4H]^-$.

Neither $Fe(CO)_5$ nor $Fe(CO)_4(PPh_3)$ reacted with KH giving $K[Fe(CO)_4(CHO)]$ (9). However, the formyl anion could be produced by treating $Fe(CO)_5$ either $KBH(OMe)_3$ or $LiBHEt_3$. Reaction of $Fe(CO)_4(PPh_3)$ with $KBH(OMe)_3$ afforded only $K_2Fe(CO)_4$. The stability of $[Fe(CO)_4(CHO)]^-$ in THF depended on the cation present in solution, decreasing in the order $[(Ph_2P)_2N]^+ > K^+ > Na^+ > Li^+$. Reaction of the carbamoyl anion $[Fe(CO)_4\{C(:O)NMe_2\}]^-$ (as its $[C(NMe_2)_3]^+$ salt, with $NiBr_2$



a b c

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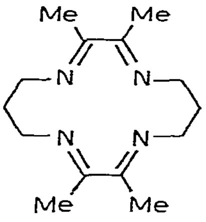
afforded (10) the mixed metal complex Ni[$\{Me_2N\ C(:O)\}$ $Fe(CO)_4]_2$ (three possible structures are shown, 1a, b and c).

Complexes with Group IV ligands

Thermal decomposition of $Fe(CO)_4(SiH_3)_2$ afforded (11) β-$FeSi_2$. The structure of cis-$Fe(CO)_4(SiMe_3)_2$ is best described (12) as a pseudo-bicapped tetrahedron in which form CO groups are arranged tetrahedrally around the metal, and the MeSi groups are the capping ligands. The fluxional behaviour of this species may involve cis ⇌ trans ⇌ cis isomerism. The ^{13}C VT nmr spectral studies of cis-$Fe(CO)_4(SnR_3)_2$ (R = Me, Et, Pr^n, Bu^n and Cl) established (13) that all complexes, except that containing $SnCl_3$, were stereochemically non-rigid. Their fluxionality, like that of the silyl complex mentioned above (12), could be explained in terms of cis ⇌ trans ⇌ cis interconversion. The structure of cis-$Fe(CO)_4(SnPh_3)_2$ was determined crystallographically, and it was found that the species deviated markedly from octahedral geometry.

Complexes with Group V Ligands

The substitution reactions of $Fe(DMGH)_2L_2$ ($DMGH_2$ = dimethylglyoxime) (L = pyr, CO, $PhCH_2NC$ or methylimidazole) proceeded (14) by a dissociative mechanism in non-aqueous solvents. Both CO and $PhCH_2NC$ were substantially more inert in the DMGH complex than in corresponding porphyrin and phthalocyanin systems.



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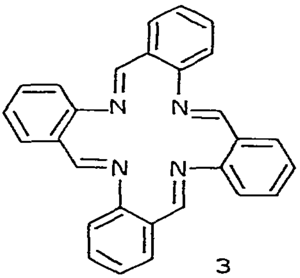

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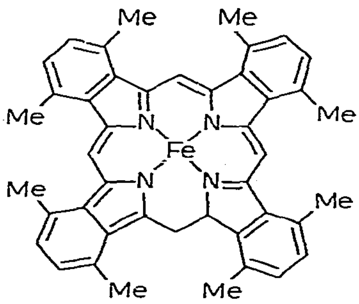

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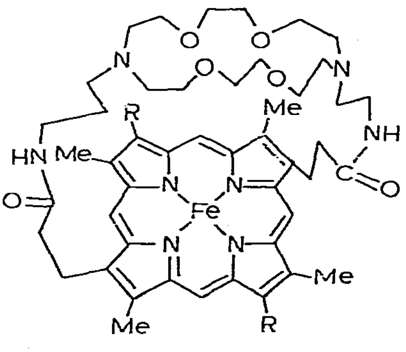

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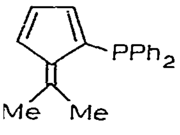
The selective labilisation of CO in trans-$Fe(TIM)(CO)(NCMe)]^{2+}$ (TIM = 2) has been achieved (15) photochemically, and is controlled by the solvent. Thus, in acetonitrile, CO is replaced by MeCN, whereas in acetone, the MeCN is removed. The kinetics and equilibria of CO and $PhCH_2NC$ binding to $[Fe(TAAB)][FeCl_4]$ (TAAB = 3) have been measured (16), and the data compared with those obtained from DMGH, porphyrin and phthalocyanin systems. Of all of the heme models studied, $[Fe(TAAB)]^{2+}$ is the poorest at binding axial π-acceptors. Octamethyltetrabenzoporphyrin iron (II) complexes (4) reversibly bound (17) CO in toluene. The equilibrium constants for the reaction

$$Fe(OMBP)L_2 + CO \rightleftharpoons Fe(OMBP)(CO)L + L,$$

where L = 1-methylimidazole, pyridine or piperidine, are intermediate to those found for comparable protoporphyrin and tetraphenylporphin complexes. The OMBP ligand exerts a substantial cis-influence in this system.

A crowned porphyrin complex of iron, 5, which picks up CO, has been prepared (18) and hemoglobin models having two conformationally linked heme groups have been isolated (19). This last system exhibited two distinct rates of CO binding.

The effects of phenyl-ring substituents on the rates of t-butyl-pyridine exchange in $Ru(STPP)(CO)(Bu^tpyr)$ (STPP = p-substituted tetraphenylporphin; substituent = CF_3, Cl, Me, Pr^i, OMe or NEt_2) were investigated (20) by VT NMR spectroscopy. The effects of these substituents on the rates of phenyl ring rotation were also examined (21).



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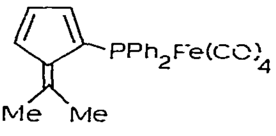

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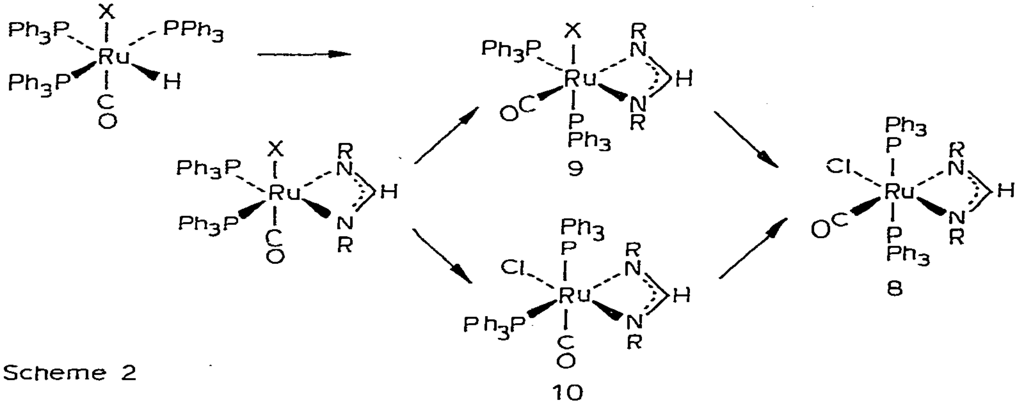
Treatment of $Fe(CO)_5$ with the cyclopentadienylphosphine sulfide, $Ph_2(C_5H_5)P{:}S$, afforded (22) the desulfurised complex $Fe(CO)_4\{P(C_5H_5)Ph_2\}$. Similar treatment of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ gave the ferrocene derivative $Fe(\eta^5\text{-}C_5H_4PPh_2)$. However, reaction of $Fe(CO)_5$ with 6 gave the appropriate phosphine complex 7. The complexes $Fe(CO)_4PFc_3$ and $Fe(CO)_3(PFc_3)_2$ PFc_3 = triferrocenylphosphine) could be obtained (23) photochemically or thermally by reaction of $Fe(CO)_5$ with PFc_3. However, treatment of $Fe(CO)_3(C_4H_6)$ with PFc_3 gave $Fe(CO)_2(PFc_3)_3$. Reaction of $Fe(CO)_5$ and $Fe(CO)_2(NO)_2$ with $AsHMe_2$ gave (24) $Fe(CO)_4(AsHMe_2)$ and $Fe(CO)(NO)_2(AsHMe_2)$ which, on aerial oxidation, dimerised giving $(OC)_4FeAsMe_2AsMe_2Fe(CO)_4$ and $(NO)_2(CO)FeAsMe_2\text{-}AsMe_2Fe(CO)(NO)_2$, respectively.

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

Photolysis of $Ru(CO)(PPh_3)_2HCl$ afforded (25) $Ru(PPh_3)_2HCl$, which is a potent hydrogenation catalyst. Under CO, $Ru(CO)(PPh_3)_2HCl$ may be irradiated giving $Ru(CO)_2(PPh_3)_2HCl$. Dehydrogenation of $Ru(CO)(PPh_3)_3H_2$ may be achieved by uv light, giving the transient $Ru(CO)(PPh_3)_3$ which may ultimately be converted to an o-metallated phosphine complex. If irradiation was effected under CO, $Ru(CO)_3(PPh_3)_2$ was produced. The species $Ru(CO)_2(PPh_3)_2HCl$ could be photoisomerised, but reverted to its initial geometry in the dark.

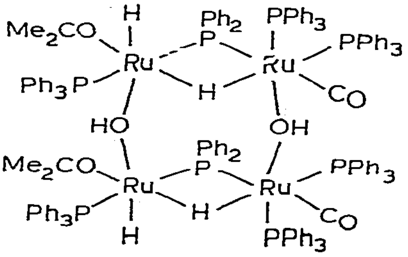
Reaction of $M(CO)(PPh_3)_3HX$ (M = Ru or Os; X = Cl, Br or $OCOCF_3$) with RN:C:NR (R = p-MeC_6H_4) gave (26) $M(CO)(PPh_3)_2X(RNCHNR)$, 8 (M = Ru) and 9 or 10 (M = Os). If the reaction was carried out under more vigorous conditions, then 8 (M = Os) was formed. It would appear that a system of isomerisations occurs (Scheme 2).



Scheme 2

Treatment of $M(CO)(PPh_3)_3H_2$ with RN:C:NR afforded $M(CO)(PPh_3)_2H(RNCHNR)$, 8 (X = H).

The interaction of $Ru(PPh_3)_3HCl$ with NaOH or KOH in THF, acetone or t-butyl alcohol led (27) first to $Ru(PPh_3)_2$ H(OH)(solvent) (solvent = THF or H_2O), second to $(PPh_3)_2H(solv)Ru(\mu\text{-}OH)_2Ru(solv)H(PPh_3)_2$ (solv = acetone, THF, H_2O or Bu^tOH) and finally to $Ru_4(CO)_2(PPh_3)_6H_4(OH)_2(PPh_2)(Me_2CO)_2$. The structure of this tetramer is not known with certainty but may be 11 or 12. Under slightly different conditions, KOH reacted with $Ru(PPh_3)_3HCl$ in refluxing acetone, giving $Ru(CO)(PPh_3)_3H_2$. Treatment of the ruthenium hydrido-chloride with NaOMe gave,



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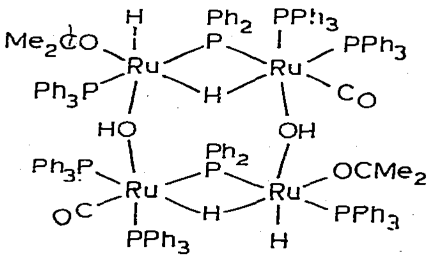

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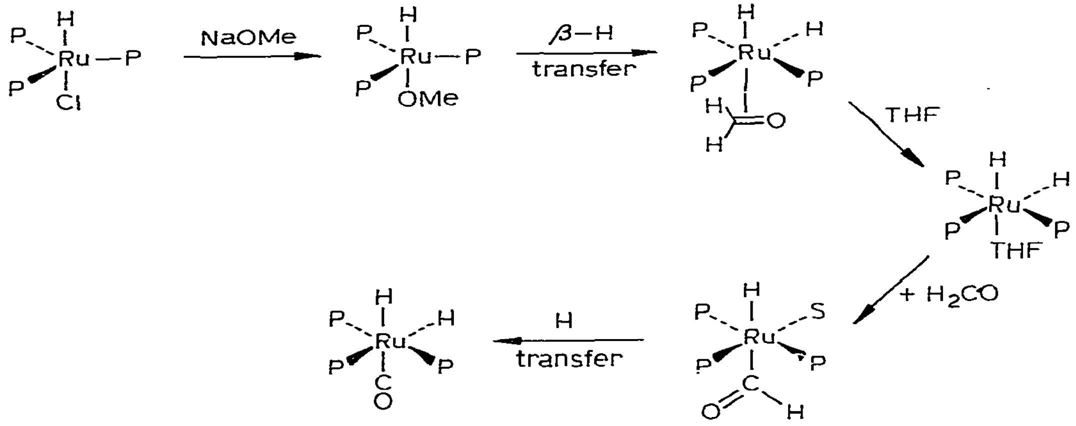
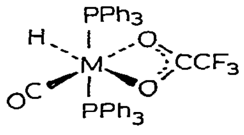
depending on conditions, either $Ru(CO)(PPh_3)_3H_2$, or two other compounds exhibiting $\nu(C{=}O)$. One of the latter two species may be $Ru(PPh_3)_3H(CHO)(solv)$ and the other is probably $Ru(PPh_3)_3H_2(OCH_2)$. It was noted that $Ru(PPh_3)_4H_2$ reacted with formaldehyde giving $Ru(CO)(PPh_3)_3H_2$. These reactions are similar to the alcohol dehydrogenation conditions described earlier (28) and are outlined in Scheme 3. It was observed that $Ru(PPh_3)_2(H_2O)H(OH)$ reacted with ROH (R = Me, Et or Bu^t) giving $Ru(CO)(PPh_3)_2(ROH)H_2$ and small amounts of $Ru(CO)_2(PPh_3)_2H_2$ and $Ru(CO)_3(PPh_3)_2$.

Scheme 3

(P = PPh_3; S = Solvent)



Treatment of $M(CO)(PPh_3)_2(OCOCF_3)_2$ (M = Ru or Os) with boiling ethanol or hydrogen afforded (29) $M(CO)(PPh_3)_2H(O_2CCF_3)$ 13. On treatment with CF_3CO_2H and with PPh_3, 13 regenerated the starting material and $M(CO)(PPh_3)_3H(OCOCF_3)$, 14,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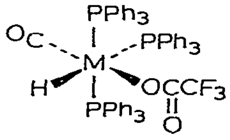
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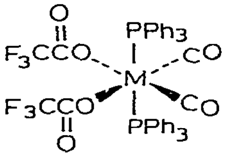
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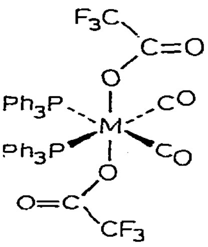
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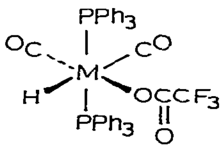
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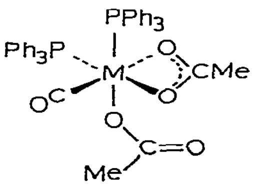
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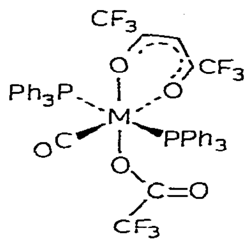

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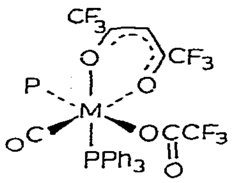

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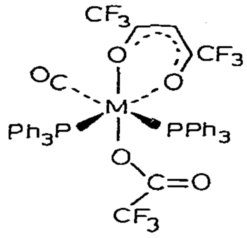

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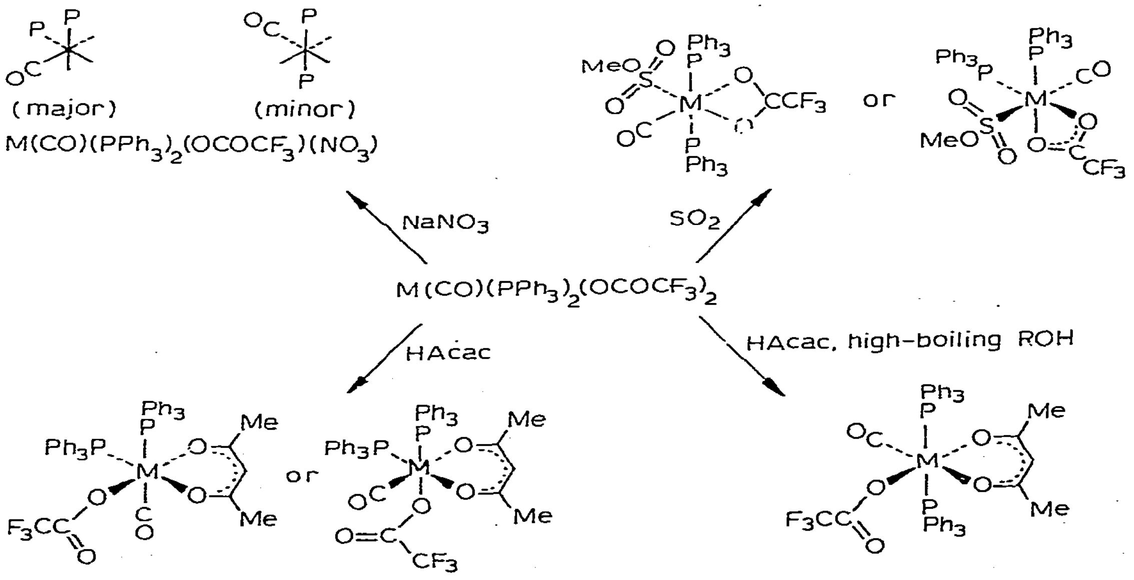
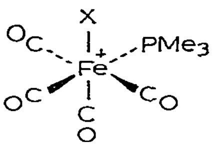
respectively; 14 was also produced directly by treatment of $M(CO)(PPh_3)_2(OCOCF_3)_2$ with PPh_3, although it seems probable that the reaction proceeds via 13. Under CO in boiling benzene, $M(CO)(PPh_3)_2(OCOCF_3)_2$ was converted into $M(CO)_2(PPh_3)_2(OCOCF_3)_2$, 15 or 16, while 13 gave either $M(CO)_2(PPh_3)_2H(OCOCF_3)$, 17, or possibly $M(CO)(PPh_3)_2H_3(OCOCF_3)$. Sodium acetate reacted with $M(CO)(PPh_3)_2(OCOCF_3)_2$ in boiling methanol to give $Ru(CO)(PPh_3)_2H(OCOMe)$ and fluxional $(MeOCO)_2M(CO)(PPh_3)_2$, 18. However, in ethanol, $M(CO)(PPh_3)_2H(OCOMe)$, probably analogous to 13, was formed, possibly via an ethoxide which underwent a β-elimination reaction. Further reactions of $M(CO)(PPh_3)_2(OCOCF_3)_2$, with $NaNO_3$ in boiling methanol, with SO_2 also in methanol, and with acetylacetone in ethanol, methoxyethanol or higher boiling alcohols, are summarised in Scheme 4. When $M(CO)(PPh_3)_2(OCOCF_3)_2$ was treated with KOH and acetylacetone, $M(CO)(PPh_3)_2H(acac)$, similar to 13, was formed. However, with $CF_3COCH_2COCF_3$, the species $M(CO)(PPh_3)_2(OCOCF_3)(CF_3COCHCOCF_3)$, 19 (M = Ru), and either 20 or 21, were produced.

Scheme 4

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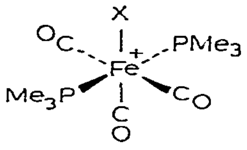
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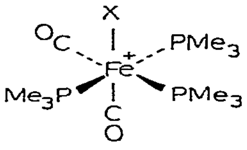
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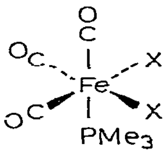
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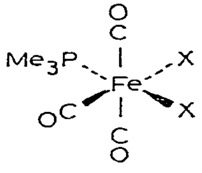
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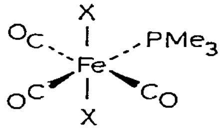
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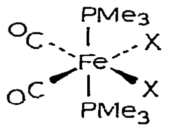
Treatment of $Fe(CO)_{5-n}(PMe_3)_n$ (n = 1, 2 or 3) with X_2 (X = Cl, Br or I) afforded (30) first $[Fe(CO)_{5-n}(PMe_3)_nX]^+$ and then $Fe(CO)_{4-n}(PMe_3)_nX_2$. This last species could also be prepared by addition of PMe_3 to $Fe(CO)_4X_2$. Reaction of $Fe(CO)_4X_2$ with X^- gave $[Fe(CO)_3X_3]^-$, which could be isolated as the salt of a bulky organic cation. The structures of some of these species are represented as 22 to 33; the structure of $[Fe(CO)_3X_3]^-$ is analogous to 25 (L = X). Reaction of $Fe(CO)_4I_2$ with PMe_3 afforded $[Fe(CO)_3(PMe_3)_2I][Fe(CO)_3I_3]$, while 26 isomerised in the dark to 25 which existed in a light-controlled equilibrium with 27. Treatment of trans-$Fe(CO)_3(PMe_3)_2$ with ICN gave $Fe(CO)_2(PMe_3)_2I(CN)$ which, on further iodination, afforded 30 and ultimately 28. Reaction of $Fe(CO)_4I_2$ with $Ph_2PCH_2CH_2PPh_2$ (diphos) gave $Fe(CO)_2(diphos)I_2$ (trans-I, cis-CO) and then, on exposure to light, the corresponding cis-iodo-trans-carbonyl isomer.

In DMF, $RuCl_3.nH_2O$ reacted (31) with $PhP(CH_2CH_2PPh_2)_2$ (triphos), $(Ph_2PCH_2CH_2PPhCH_2)_2$ (tetraphos-1) and $P(CH_2CH_2PPh_2)_3$ (tetraphos-2) giving $Ru(CO)(triphos)Cl_2$ and $[Ru(CO)_2Cl]_2L$ (L = tetraphos-1 and 2), respectively. Tin (II) and mercury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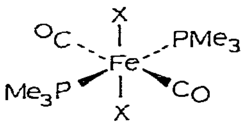
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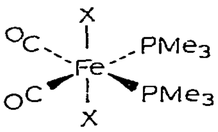
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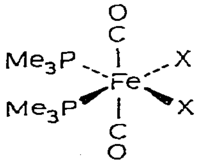
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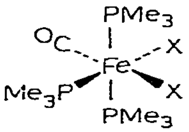
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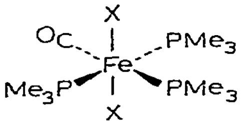
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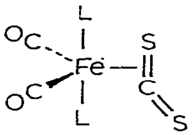
iodides reacted with $[Ru(CO)_3(PPh_3)_2I]I$ in a 1:1 molar ratio affording (32) $[Ru(CO)_3(PPh_3)I][MI_3]$ (M = Sn or Hg). With a 2:1 ratio, HgI_2 gave the $[HgI_4]^{2-}$ salt. Treatment of $Ru(CO)_3(PPh_3)_2$ with SnI_4 afforded $[Ru(CO)_3(PPh_3)_2I][SnI_3]$ while, in refluxing benzene, SnI_2 and cis-$Ru(CO)_2(PPh_3)_2I_2$ were obtained. Under CO at atmospheric pressure, $[Os(Ph_2PCH_2CH_2CH_2PPh_2)_2Cl]PF_6$ was converted (33) into $[Os(CO)(Ph_2PCH_2CH_2CH_2PPh_2)_2Cl]PF_6$.

Sulphur-containing compounds

Reaction of the heterodiene complex $Fe(CO)_3$(enone) with CS_2 in the presence of tertiary phosphine or phosphite ligands L(PPh_3, PBu_3^n, PMe_2Ph, PMe_2, $P(OMe)_3$ or $P(OEt)_3$) gave (34) $Fe(CO)_2L_2(\eta^2\text{-}CS_2)$, 34. When L = PPh_3, one phosphine ligand could be substituted by either PMe_3 or PMe_2Ph. The X-ray structural determination of 34 confirmed the equatorial position of the $\eta^2\text{-}CS_2$ group.



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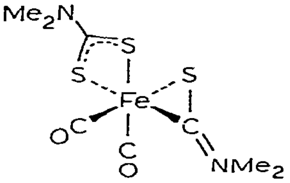

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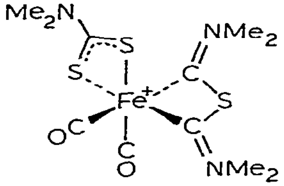

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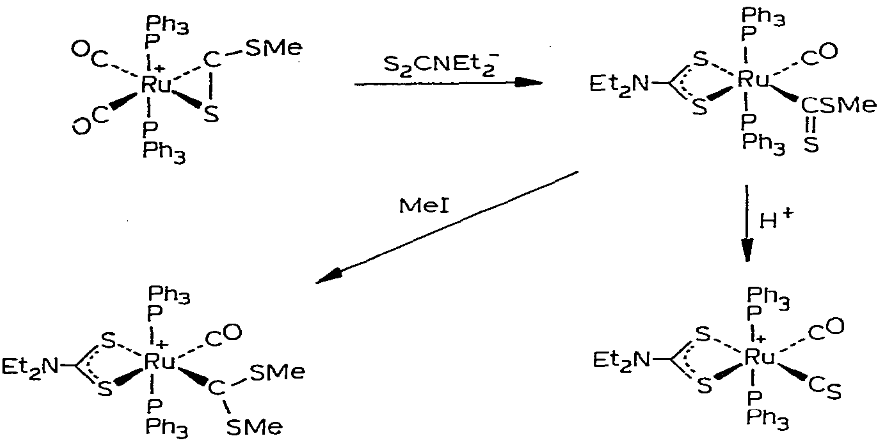
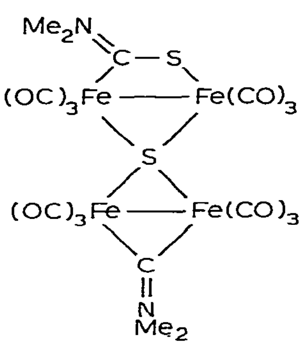
There was no reaction between $Fe(CO)_5$ and Me_2NCSCl even in refluxing THF, but under u.v. radiation, low yields of the previously known (35) cis-$Fe(CO)_2(S_2CNMe_2)_2$, were obtained (36). However, Me_2NCSCl reacted with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ giving 35 whose structure was established crystallographically. This species could also be obtained by reaction of $Fe_2(CO)_9$ with $[Me_2NC(:S)S]_2$, and is fluxional in solution. Treatment of $[Fe(CO)_4]^{2-}$ with Me_2NCSCl gave a mixture of 35 and the salt 36, which is also fluxional. Reaction of the thio-carbamoyl chloride with $[Fe_2(CO)_8]^{2-}$ afforded $Fe_4(CO)_{12}S(CSNMe_2)_2$, 37, which could be methylated by Me_3O^+ giving 38. There was no reaction of Me_2NCSCl with $[Fe_3(CO)_{11}H]^-$ and no isolable products could be obtained with $[Fe_2(CO)_8H]^-$ and $[Fe_3(CO)_{11}]^{2-}$. $Fe_2(CO)_9$ reacted with ClCSSEt giving 39.

The structure of the previously reported (37) $[Ru(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2Me)]^+$, 40, has been confirmed (38) by X-ray methods. Treatment of 40 with CN^- gave initially $Ru(CO)_2(PPh_3)_2(CN)(\eta^1\text{-}CS_2Me)$ and finally $Ru(CO)(PPh_3)(CN)(\eta^2\text{-}CS_2Me)$. Reactions of 40 with $[S_2CNEt_2]^-$ are summarised in Scheme 5, but treatment of $[Ru(CO)_2(PPh_3)_2\{\eta^2\text{-}CSN(p\text{-}C_6H_4Me)Me\}]^+$, with diethyldithiocarbamate afforded $Ru(CO)(PPh_3)(\eta^2\text{-}S_2CNEt_2)\{\eta^2\text{-}CSN(p\text{-}C_6H_4Me)$ [illegible] $\}$. Treatment of $Ru(CO)(PPh_3)_2I(CS_2Me)$ with primary amines RNH_2 (R = Me, Pr^n, Pr^i, Bu^s, $PhCH_2$) gave (39) the binuclear isonitrile complexes 41a or 41b (the latter is favoured). The possible mechanism of this reaction is outlined in Scheme 6.

Scheme 5

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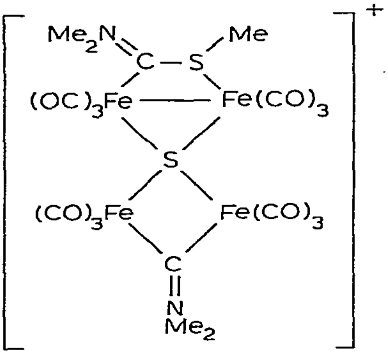
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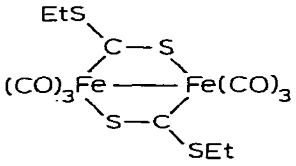
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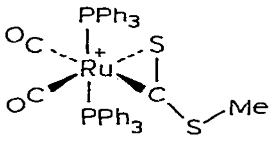
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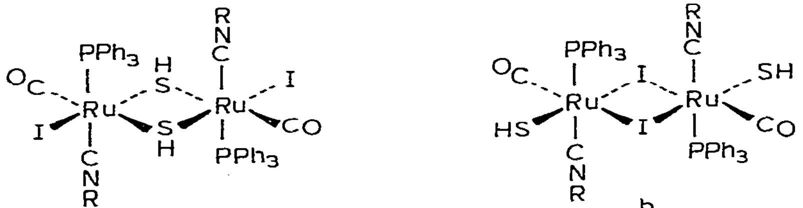
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b

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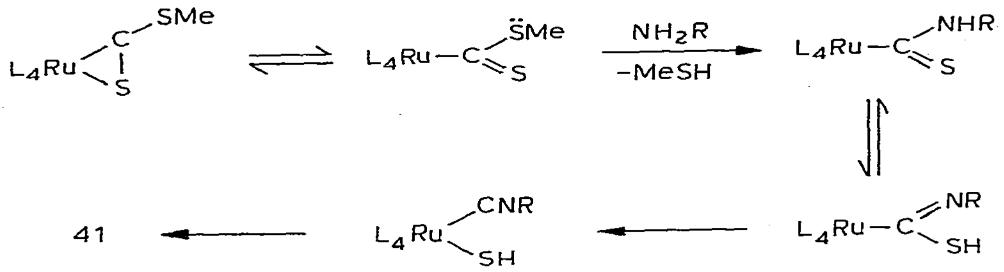
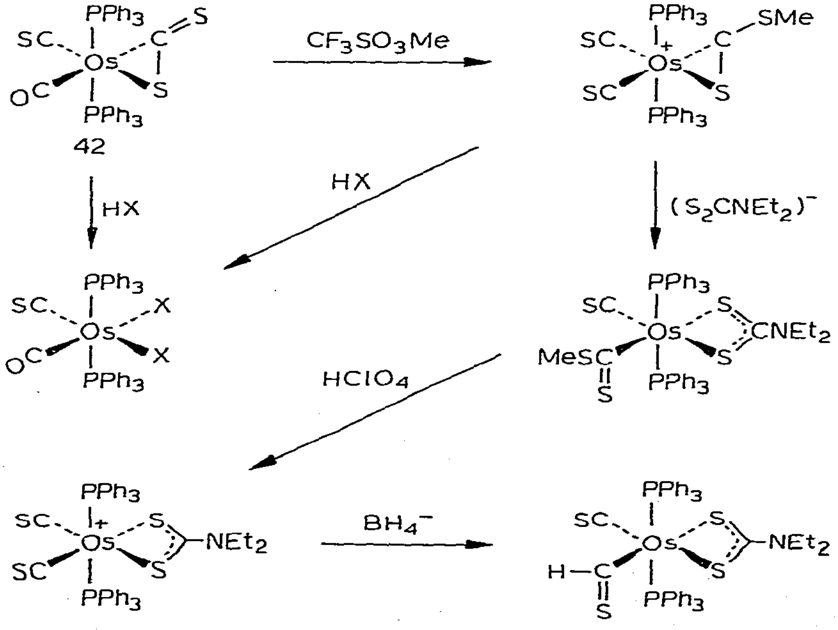
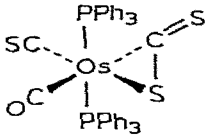
Scheme 6



In refluxing benzene, $Os(PPh_3)_3Cl_2$ reacted with CS_2 and an excess of PPh_3 to give (40) the thiocarbonyl derivative $Os(CS)(PPh_3)_3Cl_2$. This was converted into $Os(CS)(PPh_3)_3H_2$ and reaction of the dihydride with $HClO_4$ gave $Os(CS)(PPh_3)_3H(OClO_3)$. Under CO, this perchlorate afforded $[Os(CO)(CS)(PPh_3)_3H]^+$ which, on neutralisation by NaOH, gave $Os(CO)(CS)(PPh_3)_3$. Treatment of $Os(CS)(PPh_3)_3H(OClO_3)$ with Cl^- afforded $Os(CS)(PPh_3)_3HCl$, also obtainable by treatment of $Os(CS)(PPh_3)_3H_2$ with HCl. Isonitrile addition to the hydrido-chloride produced $Os(CS)(CNR)(PPh_3)_2HCl$ ($R = p\text{-}MeC_6H_4$). Ethylene and diphenylacetylene reacted with $Os(CO)(CS)(PPh_3)_3$ giving $Os(CO)(CS)(C_2H_4)(PPh_3)_2$ and $Os(CO)(CS)(Ph_2C_2)(PPh_3)_2$, respectively. Treatment of $Os(CO)(CS)(PPh_3)_3$ with CS_2 in benzene afforded (41) $Os(CO)(CS)(PPh_3)_2(\eta^2\text{-}CS_2)$, 42, some of whose reactions are shown in Scheme 7. It is thought that conversion of $[Os(CO)(CS)(PPh_3)_2(\eta^2\text{-}CS_2Me)]^+$ into $Os(CS)(PPh_3)_2(\eta^2\text{-}S_2CNEt_2)(\eta^1\text{-}CS_2Me)$ occurred via $Os(CO)(CS)(PPh_3)_2(\eta^1\text{-}S_2CNEt_2)(\eta^1\text{-}CS_2Me)$, which could be isolated.

Scheme 7





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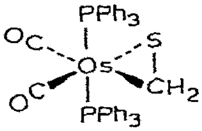

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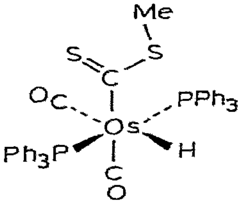

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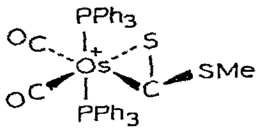

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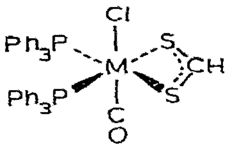

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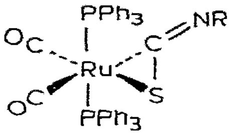

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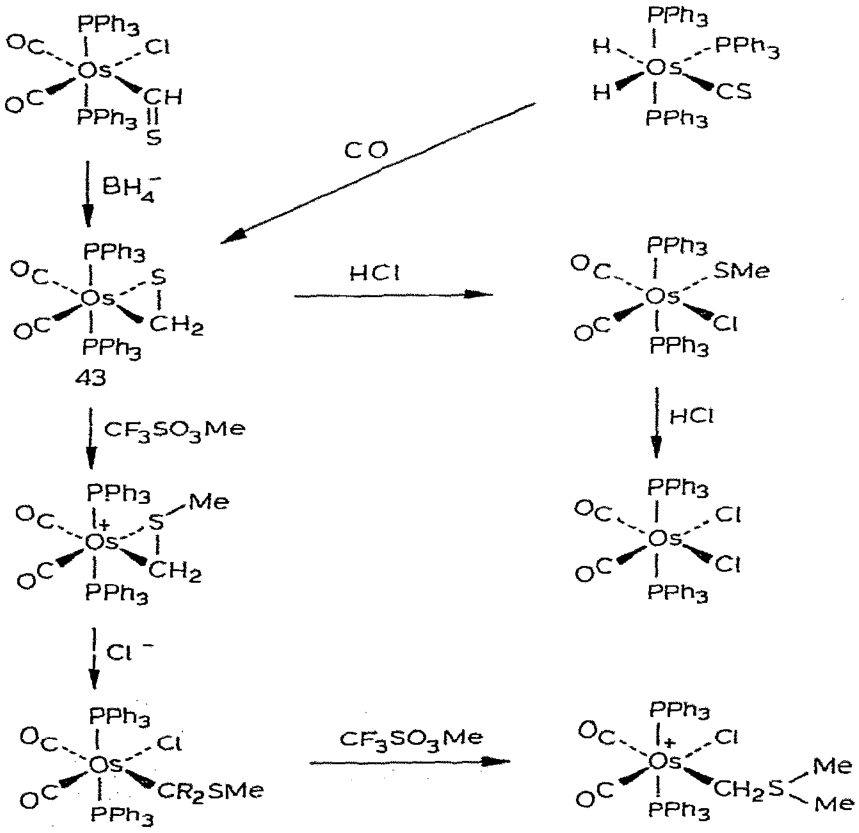
Treatment of $Os(CO)_2(PPh_3)_2Cl(CSH)$ with BH_4^-, or of $Os(CS)(PPh_3)_3H_2$ with CO under rigorous conditions, afforded (42) $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2S)$, <u>43</u>. Reactions of this compound are outlined in Scheme 8. The structure of the previously

Scheme 8

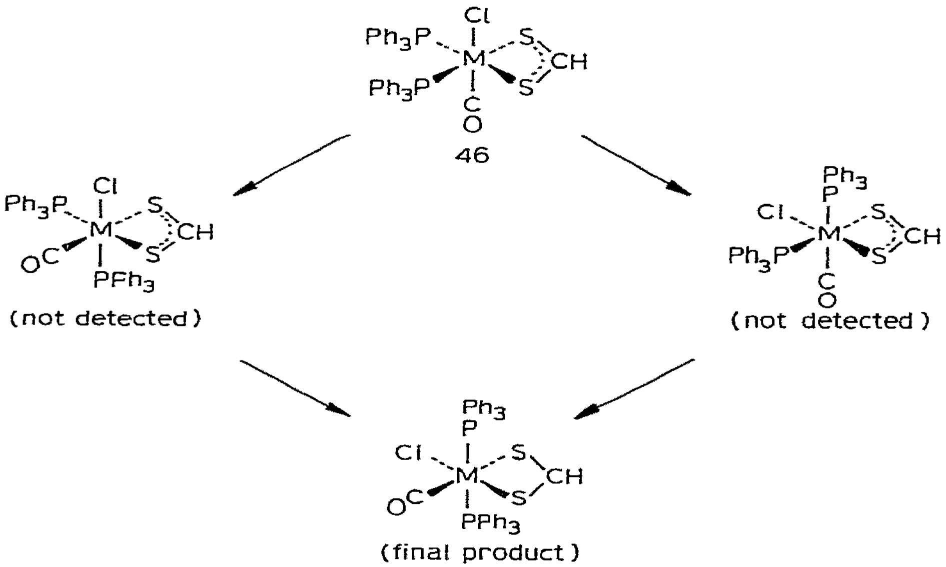


prepared (43) $Os(CO)_2(PPh_3)_2H(\eta^1\text{-}CS_2Me)$, 44, has been determined (44) crystallographically. The Os-H distance was 1·64(6)Å, and it was suggested that there was a π-interaction between the apical C atoms and the adjacent S atoms but not the metal.

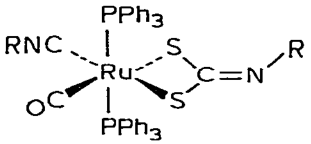
Sulphur reacted with $M(CO)_2(PPh_3)_3$ (M = Ru or Os) giving (45) $M(CO)_2(PPh_3)_2(S_2)$. Treatment of the osmium compound with $MeSO_3CF_3$ gave $[Os(CO)_2(PPh_3)_2(S_2Me)]$-$[SO_3CF_3]$, and an X-ray structural investigation of the cation, as ClO_4^- salt, established that the compound contains an $\eta^2\text{-}S_2Me$ group, 45. Here, the S–S distance (2·03Å) is close to that found in S_8 (2·04Å) whereas the S=S distance in gaseous S_2 is shorter (1·89Å). Treatment of 45 with I^- gave $Os(CO)_2(PPh_3)_2$-$I(\eta^1\text{-}S_2Me)$.

Insertion into the metal hydride bond occurred when $M(CO)(PPh_3)_3HCl$ (M = Ru or Os) was treated (46) with CS_2, giving the dithioformato complexes $M(CO)(PPh_3)_2$-$Cl(S_2CH)$, 46. These complexes readily isomerised, as shown in Scheme 9.

Scheme 9



Reaction of $Ru(CO)_2(PPh_3)_3$ with organic isothiocyanates afforded (47) either 47 or 48 (R = Me, Et or Ph), depending on the concentration of RNCS. However, insertion of isothiocyanate into the M-H bond of $M(CO)(PPh_3)_3HX$ (M = Ru or Os; X = Cl, Br or $OCOCF_3$) gave (49) $M(CO)(PPh_3)_2X(RNCHS)$, as a mixture of three isomers 49a, b and c, all of which were detected spectroscopically. With $M(CO)$-$(PPh_3)_3H_2$, PhNCS afforded $M(CO)(PPh_3)_2H(PhNCHS)$ which, under more vigorous conditions gave some $Ru(CO)(PPh_3)(PhNCHS)_2$ and other, unidentified S-containing products.



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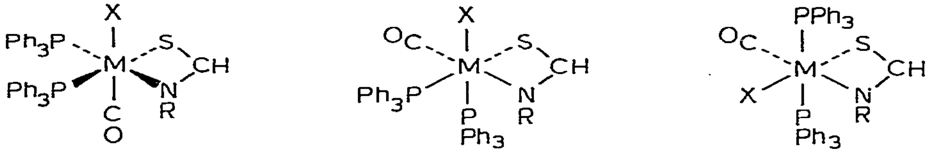

a b c

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An X-ray crystallographic examination of the previously reported (49) Ru(CO)(CSe)(PPh$_3$)$_2$Cl$_2$ established (50) that the carbonyl and selenocarbonyl groups were cis, the phosphine ligands trans and the trans-influence of the CSe group was relatively strong.

Hydrido and halo-carbonyl complexes

The molecular structure of Fe(CO)$_4$H$_2$ has been investigated (51) by gas-phase electron diffraction. The molecule has C_{2v} symmetry with a configuration between octahedral and tetrahedral geometries. The H atoms are mutually cis with an H-Fe-H ample of 100±10° and Fe-H = 1·56Å.

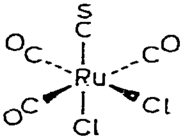
A VT ^{13}C nmr spectral study of cis-M(CO)$_4$X$_2$ (M = Fe, Ru and Os; X = H or I) and cis-Os(CO)$_4$Me$_2$ established (52) that only the iron hydride was fluxional. Ru(CO)$_4$H$_2$ was stereochemically rigid between -50 and -20°, and decomposed above this temperature.

Reaction of [Ru(CO)$_3$Cl$_2$]$_2$ with primiary amines gave (53) the carbamoyl complexes Ru(CO)$_2$(NH$_2$R)$_2$Cl(CONHR) (R = Bu^n, Bu^t, p-MeO and p-Me-C$_6$H$_4$). Treatment of the species where R = p-MeC$_6$H$_4$ with PPh$_3$ and HCl afforded Ru(CO)$_2$(PPh$_3$)$_2$Cl(CONHR) and [Ru(CO)$_3$(NH$_2$R)$_2$Cl]Cl. The products of reaction between Ru(PPh$_3$)$_3$Cl$_2$, RNH$_2$ (R = p-Me- and p-Me-C$_6$H$_4$) and CO could not be fully characterised, but may include Ru(CO)(PPh$_3$)(NH$_2$R)$_2$Cl$_2$. When the hydrazines N$_2$H$_4$ and PhNHNH$_2$ were substituted for RNH$_2$, [Ru(PPh$_3$)$_2$(NH$_2$NHR)$_n$Cl$_2$]$_m$ (R = Ph, n = 2, m = 1; R = H; n = 1, m = 2) was formed, and this reacted with CO giving Ru(CO)(PPh$_3$)$_2$(NH$_2$NHPh)Cl$_2$ and [Ru(CO)(PPh$_3$)(N$_2$H$_4$)Cl$_2$]$_2$, respectively.

Decarbonylation of halogen-exchange with, trans-[Os(CO)$_2$Br$_4$]$^-$ gave (54) [Os(CO)X$_5$]$^{2-}$ (X = Cl, Br or I).

In refluxing heptane, Ru$_3$(CO)$_{12}$ reacted with CSCl$_2$ giving (55) Ru(CO)$_3$(CS)Cl$_2$, probably 50. Treatment of this thiocarbonyl chloride with PPh$_3$ and C$_6$H$_{11}$NC gave

$Ru(CO)_2(CS)(PPh_3)Cl_2$, 51 and $[Ru(CO)_2(CS)(CNC_6H_{11})_2Cl]^+$, respectively. Reaction of 50 with $Ph_2ECH_2CH_2EPh_2$ (E = P or As) afforded a mixture, in each case, of at least two species, but only $[Ru(CO)_2(CS)(Ph_2AsCH_2CH_2AsPh_2)Cl]^+$ could be characterised. The isonitrile complexes $Ru(CO)_3(CNR)Cl_2$ and $Ru(CO)_2(CNR)(PPh_3)Cl_2$ were obtained by treating 50 and 51, respectively, with RNH_2 (R = C_6H_{11}, Ph, p-Me- or p-MeO-C_6H_4). In general, the reactivity of the thiocarbonyl complexes was markedly higher than that of their ordinary carbonyl analogs (56).



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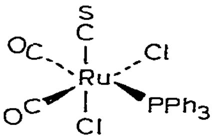

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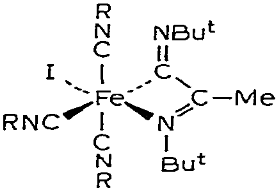

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Compounds containing Group IIB metals

The compound $(NH_3)_2CdFe(CO)_4$, which has been described previously (57), reacted with dry pyridine giving (58) $(pyr)_2CdFe(CO)_4$. On heating in the solid state, ammonia was driven off and $CdFe(CO)_4$ formed, which could be recrystallised from acetone/water; with THF, $(THF)_2CdFe(CO)_4$ was produced. An X-ray structural determination of $CdFe(CO)_4$ established that the molecule contained a nearly planar centrosymmetric 8-membered ring of alternating Cd and cis-$Fe(CO)_4$ units. The geometry deviated from D_{4h} square symmetry principally in that there was a slight distortion indicating weak coordination of two Cd atoms with O atoms of acetone of crystallisation. The Cd-Fe distance was 2·562(3)Å. The structure of $(bipy)CdFe(CO)_4$, obtained (58) by treatment of $CdFe(CO)_4$ with 2,2'-bipyridyl, revealed (59) that the molecule was trimeric, containing a nearly planar ring of cis-$Fe(CO)_4$ and Cd(bipy) units. The Fe atom coordination is significantly distorted from octahedral towards tetrahedral, in which the Cd atoms cap two faces. There was some evidence for a weak semi-bridging interaction between a carbonyl C atom and Cd. The bonding in this trimer appears to be more ionic than in $[CdFe(CO)_4]_4$, and there was some dissociation in benzene solution. A Raman and ir spectroscopic examination of $(en)CdFe(CO)_4$ (en = ethylenediamine) revealed (60) that the Fe atom had essentially octahedral coordination in a centrosymmetric structure.

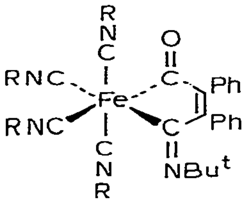
The reaction between $Fe(CO)_5$ and $HgCl_2$ proceeded (61) via two consecutive reactions:

(i) $Fe(CO)_5 + HgCl_2 \longrightarrow$ cis-$Fe(CO)_4(HgCl)_2 + COCl_2$;
(ii) cis-$Fe(CO)_4(HgCl)_2 + 2HgCl_2 \longrightarrow$ cis-$Fe(CO)_4(HgCl.HgCl_2)_2$.

ISOCYANIDE AND CARBENE COMPLEXES

Isocyanide Complexes

Reduction of $FeBr_2$ by sodium amalgam in the presence of Bu^tNC afforded (62) the fluxional $Fe(CNBu^t)_5$. The structure of this molecule was determined crystallographically and it was shown to deviate markedly from idealised trigonal bipyramidal geometry. There are two equatorial and one axial isonitrile ligands which are non-linear and it was suggested that this reflected substantial back-donation to the π (CNR) orbitals from the metal. Treatment of $Fe(CNBu^t)_5$ with PPh_3, or reduction of $FeBr_2$ in the presence of both isonitrile and phosphine gave $Fe(CNBu^t)_4(PPh_3)$. Reaction of $Fe(CNBu^t)_5$ with n-C_3F_7I gave trans-$Fe(CNBu^t)_4I\{CF(CF_3)_2\}$ and with MeI, 52 was probably formed; the latter may have been produced via initial formation of a Fe-CH_3 bond, followed by insertion of $CNBu^t$. With allyl chloride and diphenylcyclopropenone, $Fe(CNBu^t)_5$ afforded trans-$Fe(CNBu^t)_4Cl(\eta^1$-$C_3H_5)$ and 53, respectively.



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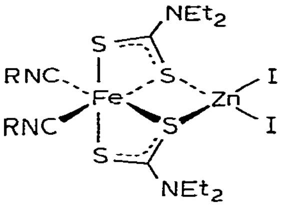

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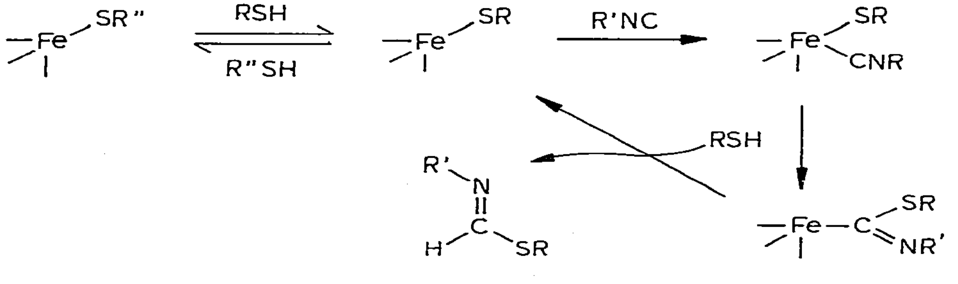
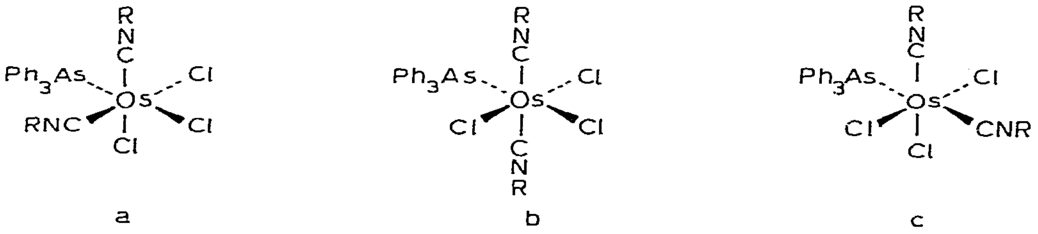
The Mössbauer spectra of $[Fe(CNR)_{5-n}\{PPh(OEt)_2\}_nX][ClO_4]$ (n = 3, 2NO; X = Br or I; R = Ph, O- or p-MeC_6H_4, p-NO_2- or p-MeO-C_6H_4, 2,6-$Me_2C_6H_3$) and Fe(p-$MeC_6H_4NC)_4X_2$ (X = Br or I) have been determined (63). The phthalocyaninate complexes $FePcL_2$ (L = 1-methylimidazole, piperidine or pyridine) reversibly bound $PhCH_2NC$ via a dissociative mechanism (64). Thermodynamically, $PhCH_2NC$ is bound to FePc in preference to CO by a factor of 10^3 and the complex is similarly more inert than the corresponding carbonyl. In the presence of EtSH, p-ClC_6H_4NC is catalytically converted by $[Fe_4S_4(SR)_4]^{2-,4-}$ in tetramethylurea into p-ClC_6H_4N:CH(SEt) (65). Other isocyanides behave similarly, and the proposed mechanism, investigated electrochemically, is shown in Scheme 10.

Scheme 10



Treatment of $[Fe(S_2CNEt_2)_3]^+$ with p-ClC_6H_4NC gave (66) $[Fe(CNC_6H_4Cl)_4(S_2CNEt_2)]^+$, which could be electrochemically oxidised at very positive potentials. In the absence of air and light, $Fe(S_2CNEt_2)_3$ reacted with RNC giving cis-$Fe(CNR)_2(S_2CNEt_2)_2$ (R = Pr^i, Bu^t, p-ClC_6H_4) and in refluxing acetone under CO, cis-$Fe(CO)_2(S_2CNEt_2)_2$ was formed. Treatment of $Fe(S_2CNEt_2)_2I$ with $TlPF_6$ in the presence of p-ClC_6H_4NC afforded $[Fe(CNC_6H_4Cl)_2(S_2CNEt_2)_2]^+$ and the existence of this monocation was further demonstrated by a voltammetric study of $Fe(CNC_6H_4Cl)_2(S_2CNEt_2)_2$ obtained by direct combination of $Fe(S_2CNEt_2)_2$ and the isocyanide. This neutral species reacted with ZnI_2, giving a 1:1 adduct, 54, whose structure was established crystallographically.

Reduction of trans-$Ru(CNBu^t)_4Cl_2$ by Na/Hg in the presence of Bu^tNC afforded (67) $Ru(CNBu^t)_5$, and if PPh_3 was included in the reaction mixture, $Ru(CNBu^t)_4(PPh_3)$ was produced. An X-ray structural examination of the phosphine complex, which is fluxional in solution, revealed that the PPh_3 group was equatorial and that the equatorial $CNBu^t$ ligands were significantly bent, presumably due to substantial back donation from the metal, as in $Fe(CNBu^t)_5$ (62). Reduction of trans-$Fe(CNPr^i)_4Cl_2$ in the presence of Pr^iNC afforded $Fe_2(CNPr^i)_9$, a preliminary X-ray diffraction study of which revealed it to be isostructural with $Fe_2(CO)_9$ (Ru-Ru distance 2·63Å).



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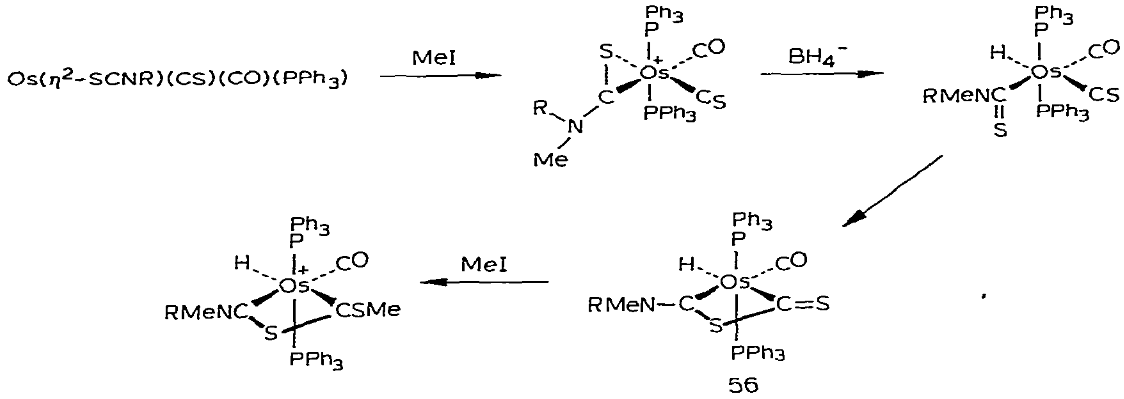
Three isomers of $Os(CNC_6H_4Me)_2(AsPh_3)Cl_3$, 55a, b and c, have been isolated and identified structurally (68) using spectroscopic methods. Treatment of $Os(CS)(PPh_3)_2Cl_2$ with CNR (R = p-MeC_6H_4) gave (69) $Os(CS)(CNR)(PPh_3)_2Cl_2$. With $AgClO_4$, this compound afforded $Os(CS)(CNR)(PPh_3)_2Cl(OClO_3)$ which was converted under CO into $[Os(CO)(CS)(CNR)(PPh_3)_2Cl][ClO_4]$. The reaction of this cation with SH^- was complicated and solvent dependent: in acetone $Os(CO)(CS)(PPh_3)_2(\eta^2\text{-SCNR})$ was formed whereas in a mixture of dichloromethane and ethanol, both this species and $Os(CO)(CNR)(PPh_3)_2(\eta^2\text{-CS}_2)$ (85% to 15%) were produced, indicating that SH^- could attack at both CNR and CS. The reactions of $Os(CO)(CS)(PPh_3)_2(\eta^2\text{-SCNR})$ are outlined in Scheme 11, and the structure of 56 was confirmed crystallographically. It was noted that the previously prepared (70) hydride $Os(CO)(CS)(PPh_3)_2H(\eta^1\text{-CS}_2Me)$ did not undergo a rearrangement to give a carbene complex similar to 56.

Scheme 11



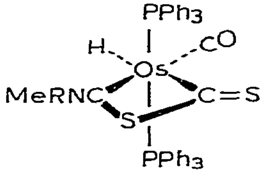
Carbene Complexes

Reaction of $Fe(CO)_5$ with the 'electron rich' olefin 57, Q_2, (R = Me), afforded (71) fluxional $Fe(CO)_4Q$ and $Fe(CO)_3(Q)_2$. The latter could be obtained from the former by further treatment with Q_2, or directly from $Fe(CO)_3(C_7H_8)$ and Q_2. Reaction of the tetracarbonyl carbene complex with PEt_3 or PPh_3 gave $Fe(CO)_3Q(PR_3)$, and iodination of $Fe(CO)_3Q_2$ provided cis-$Fe(CO)_2(Q)_2I_2$. Treatment of $Fe(CO)_2(NO)_2$ with Q_2 (R = Me) afforded $Fe(CO)Q(NO)_2$ and $Fe(Q)_2(NO)_2$, and with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, $Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3Q$ (R = Me or Et) was formed. Reaction of $Ru_3(CO)_{12}$ with Q_2 (R = Et) gave $Ru_3(CO)_{11}Q$.

Oxidation of $Fe(CO)_2QLL'$ (L = Q (R = Me) PPh_3 or PEt_3, L' = CO; L = PPh_3, L' = Q; L = L' = PPh_3, PEt_3, $P(OPh)_3$) and of $Fe_2(CO)_6(Q)_2(\mu_2\text{-}Ph_2PCH_2CH_2PPh_2)$, 58, obtained by reaction of $Fe(CO)_4Q$ (R = Me), with Ag^+ afforded (72) paramagnetic carbene complexes $[Fe(CO)_3QLL']^+$ and $[Fe_2(CO)_6(Q)_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)]^+$. Silver (I) oxidation of $Fe(CO)_3QL$ followed by treatment of the monocation with $(Q)_2$ or THF afforded $Fe(CO)_2(Q)_2L$ and $Fe(CO)_2Q(THF)_2$, respectively. These oxidised species were characterised by spectroscopic techniques and cyclic voltammetry, and it appears that the unpaired electron is substantially metal-centred. It seems that the carbene ligand contributes to the stability of the monocations by virtue of its strong Fe–C bond and its ability to delocalise the positive charge.

Treatment of Fe(TPP) (TPP = tetraphenylprophinate) with CCl_4 in the presence of an excess of a reducing agent afforded (73) the carbene complex $Fe(CCl_2)$-(TPP). On heating, this species released C_2Cl_4, and on treatment with pyridine, $Fe(CCl_2)(TPP)(pyr)$ and $Fe(TPP)(pyr)_2$ were isolated. Other polyhalogenated carbon-compounds behaved similarly.

The 'electron-rich' olefin $(Q)_2$, 57 (R = p-MeC_6H_4) reacted (74) with $Ru(PPh_3)_3$-Cl_2 giving 59 (L = L' = PPh_3). Treatment of this o-metalated species with $(Q)_2$ (R = Et), and PEt_3 gave 59 (L = PPh_3, L' = Q, R = Et) and 59 (L = L' = PEt_3), respectively. Carbon monoxide reacted with the latter and with 59 (L = L' =



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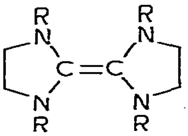

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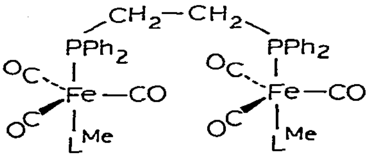

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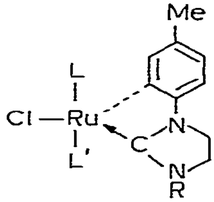

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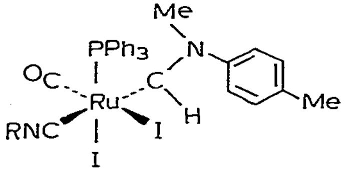

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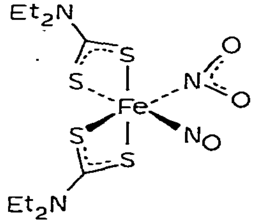


61

PPh_3) giving 1:1 adducts without displacement of the other ligands. An X-ray crystallographic examination of <u>59</u> ($L = L' = PEt_3$) confirmed that the species is essentially five-coordinate, but that a sixth position is occupied by an ortho-H atom on the tolyl ring which is not metalated. The Ru .... H contact distance is 2·2Å, and the Ru–C (carbene) distance (1·91Å) is consistent with a bond order of nearly two.

The structure of $Ru(CO)\{CHNMe(p\text{-}MeC_6H_4)\}\{CN(p\text{-}MeC_6H_4)\}(PPh_3)I$, <u>60</u>, obtained previously (75) by treatment of $Ru(CO)(CHNR)(PPh_3)(O_2CMe)$ with CNR ($R = p\text{-}MeC_6H_4$), MeI and I_2, has been determined crystallographically (76). In this species, the Ru–C (carbene) distance (2·05Å) is somewhat longer than that in most other Ru-carbene complexes.

NITROSYL AND DIAZENATO COMPLEXES

Mononitrosyl Compounds

ESCA studies have been made (77) of the nitrosyl, diazenato and diimine complexes $ML(PPh_3)_2X_3$ (M = Ru; L = NO or $p\text{-}YC_6H_4N_2$, Y = Me, Cl or NO_2; X = Cl; M = Os; L = NO or $p\text{-}YC_6H_4N_2$; X = Br), $[RuL(PPh_3)_2Cl]^+$ (L = NO or $p\text{-}MeC_6H_4N_2$), $Ru(NO)_2(PPh_3)_2$ and $Ru(CO)(HN_2C_6H_4OMe)(PPh_3)_2Cl_2$. There was a good correlation between the N 1s binding energies of the nitrosyl complexes and their diazenato analogs and this was seen as support for the view that these ligands have similar coordination characteristics.

The solution structures and reactivity of $M[Fe(CO)_3(NO)]$, $M = Na^+, K^+$ or $(Ph_3P)_2N^+$ have been investigated (78) by ir spectroscopy. There was evidence for ion-pairing involving cation...nitrosyl interaction, and the chemical reactivity of the anion was influenced by the cation. Thus, it was confirmed (79) that $[(Ph_3P)_2N][Fe(CO)_3(NO)]$ reacted with I_2 giving $[(Ph_3P)_2N][Fe(NO)_2I_2]$, while the 18-crown-6 ether coordinated K^+ salt reacted similarly but decomposed. Treatment of $K[Fe(CO)_3(NO)]$ with moderate amounts of iodine afforded $[Fe(NO)_2I]_2$, but with an excess of I_2, $K[Fe(NO)I_3]$ was formed. Reduction of $Na[Fe(CO)_3(NO)]$ with Na in liquid ammonia afforded (80) $Na_5[Fe(CO)_3(NO)]$. It was suggested that reduction was primarily associated with the ligands.

One-electron reduction of $[Fe(CN)_5(NO)]^{2-}$ in aqueous solution using CO_2^-, $e^-(aq)$, $^{\bullet}CH_2OH$, $Me_2COH^{\bullet}$ or $H^{\bullet}$ gave (81) $[Fe(CN)_5(NO)]^{3-}$ whose electronic spectrum was independent of pH in the range 1→ 8·5. The trianion underwent first order decay with loss of the trans-CN^- ligand, giving $[Fe(CN)_4(NO)]^{2-}$ which was sensitive to O_2, giving $[Fe(CN)_5(NO)]^{2-}$, $[Fe(CN)_4(NO)(OH)]^{2-}$ and polymeric species. When reduction of $[Fe(CN)_5(NO)]^{2-}$ was carried out using $^{\bullet}CH_2C(Me)_2OH$, the N-C bonded species $[Fe(CN)_5\{N(O)CH_2C(Me)_2OH\}]^{3-}$ was formed. The X-ray crystal structure determination of $[Ph_4As]_2[Fe(CN)_5(NO)]$ confirmed (82) that the nitroprusside ion has a somewhat distorted octahedral structure.

In a study of the rate of exchange of coordinated NO in $[MX_5(NO)]^{2-}$ in solution with gaseous NO, it was observed (83) that the reactivity of the M-NO bond decreased in the order $[Fe(CN)_5(NO)]^{2-} \gg [Ru(CN)_5(NO)]^{2-} > [Ru(NO)Cl_5]^{2-} > [Ru(NO)Br_5]^{2-}$.

The structures of two crystalline forms of Fe(NO)(TPP)(4-Mepyr) (TPP = tetraphenylporphinate) have been investigated (84) by X-ray methods. One form crystallised as a chloroform solvate while the other form was insolvate. Both species contained bent Fe-N-O groups: for the $CHCl_3$ solvate Fe-N(O) = 1·72Å, Fe-N-O = 138·5° and Fe-N(base) = 2·33Å while for the other species Fe-N(O) = 1·74Å, Fe-N-O = 143·7° and Fe-N(base) = 2·46Å. The structures of the o-phenylenebis(dimethylarsine) (diars) $\{Fe(NO)\}^7$ complexes $[Fe(NO)(diars)_2][ClO_4]_2$ and $[Fe(NO)(diars)_2(NCS)[BPh_4]$ (acetone solvate) have been determined (85). The former species has a tetragonal pyramidal structure with apical NO, and Fe-N-O bond angle of 173° and Fe-N(O) = 1·65Å. There was a weak interaction (2·66Å) between the metal and one oxygen atom of one ClO_4^- group. The latter species is essentially octahedral with a trans-ON-Fe-NCS arrangement where Fe-N(O) and Fe-N(CS) = 1·72 and 2·00Å, respectively, and the Fe-N-O bond angle is 159°. Irradiation of the charge transfer bands in $[Fe(NO)(diars)_2X][ClO_4]_2$ (X = Cl, Br or I) in methanol or acetone with or without H^+ and X^- afforded (86) $[Fe(diars)_2X_2]^+$. The reaction was regarded as a formal oxidation of Fe^{II} to Fe^{III} and a reduction of NO^+ to NO^-.

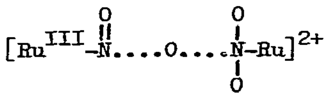
Treatment of $Fe(NO)(S_2CNR_2)_2$ (R = Me, Et or Ph) with Br_2 or I_2 afforded (87) $Fe(NO)(S_2CNR_2)X$. With NO_2, the cis-nitrosylnitrite, $Fe(NO)(S_2CNR_2)_2(NO_2)$, <u>61</u>, also obtainable by treatment of $Fe(NO)(S_2CNR_2)_2I$ with $AgNO_2$ or of trans-$[Fe(NO)(S_2CNR_2)(NCMe)]^+$ with NO_2^-, could be produced. The structure of <u>61</u> was established crystallographically and the Fe-N-O and (O)N-Fe-N(O_2) bond angles are 175° and 91°, respectively. VT nmr spectral studies of <u>61</u> revealed that it was fluxional undergoing a process which probably involved a bond rupture rather than a trigonal twist. The cation trans-$[Fe(NO)(S_2CNR_2)_2(NCMe)]^+$ was prepared by treating $Fe(S_2CNR_2)_2$ with $NOBF_4$ in acetonitrile, and reacted with NCS^- giving trans-$Fe(NO)(S_2CNR_2)_2(NCS)$. This species could also be prepared by reacting trans-$[Fe(NO)(S_2CNR_2)_2(NCMe)]^+$ with thiocyanogen, and the nitrosyl cation also reacted with CNMe, pyridine and Cl^- affording cis-$[Fe(NO)(S_2CNR_2)_2(CNMe)]^+$, trans-$[Fe(NO)(S_2CNR_2)_2(pyr)]^+$ and a mixture of cis-$Fe(NO)(S_2CNR_2)_2Cl$ and $Fe(NO)(S_2CNR_2)_2$, respectively. In the dark, $Fe(^{15}NO)(S_2CNR_2)_2I$ underwent complete isotopic exchange with ^{14}NO giving $Fe(^{14}NO)(S_2CNR_2)_2I$ and ^{15}NO. Similar exchange reactions occurred between $Fe(^{14}NO)(S_2CNR_2)_2$ and cis-$Fe(^{15}NO)(S_2CNR_2)_2I$, and between $Fe(^{15}NO)(S_2CNR_2)_2$ and trans-$[Fe(^{14}NO)(S_2CNR_2)_2(NCMe)]^+$. The kinetic data obtained from a study of these reactions were consistent with the dissocative process $Fe(NO)(S_2CNR_2)_2X \rightleftharpoons Fe(NO)(S_2CNR_2)_2 + X^{\bullet}$.

X-ray photo-electron spectral measurements have been made (88) of the S 2p binding energies in the complexes $Fe(NO)(S_2CNR_2)_2$ (R = Me or Et), $Fe(NO)(S_2CNEt_2)_2I$, $[Ph_4P][Fe(NO)\{S_2C_2(CN)_2\}_2]$, $[Fe(NO)_2(\mu\text{-}SEt)]_2$, $[Fe(CO)_3(\mu\text{-}SEt)]_2$ and $[NH_4][Fe_4S_3(NO)_7]$.

Treatment of $[Ph_4P]_2[Fe(WS_4)_2]$ with NO afforded (89) the paramagnetic species $[Fe(NO)(WS_4)_2]^{2-}$. The analogous Mo complex was also synthesised and it was suggested that the unpaired electron spins were delocalised over the two metals. Reaction of $[Fe\{SCH_2CH_2NMe(CH_2)_nNMeCH_2CH_2S\}]_2$ (n = 2 or 3) with NO^+ or NO_2^+ gave (90) the monomeric, paramagnetic nitrosyl complexes $Fe(NO)\{SCH_2CH_2NMe(CH_2)_nNMeCH_2CH_2S\}$ (n = 2 or 3). The X-ray structural examination of the species where n = 2 revealed that the molecule has a distorted square pyramidal structure in which the NO ligand occupies the apical position. There were two independent molecules in the unit cell, both exhibiting bent Fe-N-O groups (155 and (158°).

Reduction of $[Ru(NO)(H_2O)_5]^{3+}$ by $[Cr(H_2O)_6]^{2+}$ afforded (91) $[(H_2O)_5Ru\text{-}NH\text{-}Cr(H_2O)_5]^{5+}$. Similar treatment of $[Ru(NO)(NH_3)_5]^{3+}$ gave a mixture of $[Cr(H_2O)_6]^{3+}$, $[Ru(NH_3)_5(H_2O)]^{3+}$, $[Cr_2(OH)_2]^{4+}$, an uncharacterised Ru/Cr dimer and free ammonia. It was suggested that this reaction also proceeded via a -NH-bridged bimetallic species. This intermediate could be described as two valence resonance structures: $[L_5Ru^{II}\text{-}NH\text{-}Cr^{III}(H_2O)_5]^{5+}$ or $[L_5\text{-}Ru^{IV}\text{-}\overset{-}{N}H\text{-}Cr^{III}(H_2O)_5]^{5+}$.

Electrochemical oxidation of $Ru(bipy)_2(NO_2)Cl$ (bipy = 2,2'-bipyridyl) afforded (92) a mixture of $[Ru(bipy)_2(NO_3)Cl]^+$ and $[Ru(NO)(bipy)_2Cl]^{2+}$. This reaction was thought to proceed via a bimetallic intermediate

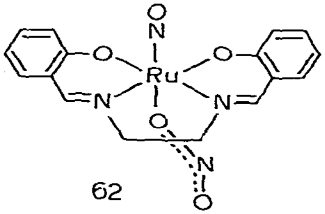


$[Ru^{III}\text{-}\overset{O}{\overset{\|}{N}}\cdots O\cdots\underset{O}{\overset{O}{N}}\text{-}Ru]^{2+}$

which dissociated into $[Ru^{II}(NO)]^+$ and $[Ru^{III}(NO_3)]^+$; oxidation of the nitrosyl would afford $[Ru^{II}(NO^+)]^{+2}$. Electrochemical studies of $[Ru(NO)(bipy)_2X]^{n+}$ (X = N_3, Cl or NO_2, n = 2; X = NH_3, pyr or MeCN, n = 3) revealed (93) that the nitrosyl underwent a reversible one-electron reduction and a further irreversible reduction in acetonitrile. The one-electron reduction product $[Ru(NC)(bipy)_2Cl]^I$ was isolated and it was established that reduction was largely associated with the NO group.

Reaction of the Schiff base complex $Ru(Sal_2en)(PPh_3)_2$ with NO gave (94) $[Ru(NO)(Sal_2en)]_2O$ and $Ru(NO)(Sal_2en)(NO)_2$ THF, 62. An X-ray crystallographic examination of the latter confirmed that it was six-coordinate with a trans-ON-Ru-ONO arrangement.

Treatment of $[Ru(NO)(bipy)_2Cl]^{2+}$ with acetylacetone afforded 63 (95), and $Na_2[Ru(NO)(NO_2)_4(OH)]$ reacted with barbituric acid in water giving (96) the violurate complex 64. A similar reaction was observed with 1,3-dimethylbarbituric acid, and treatment of 64 with $NaNO_2$ and HX afforded cis-$Ru(NO)(H_2va)_2X$ (H_2va = anion of violuric acid, X = Cl, Br or unidentate H_2va).



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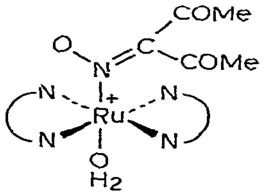

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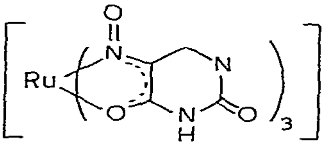

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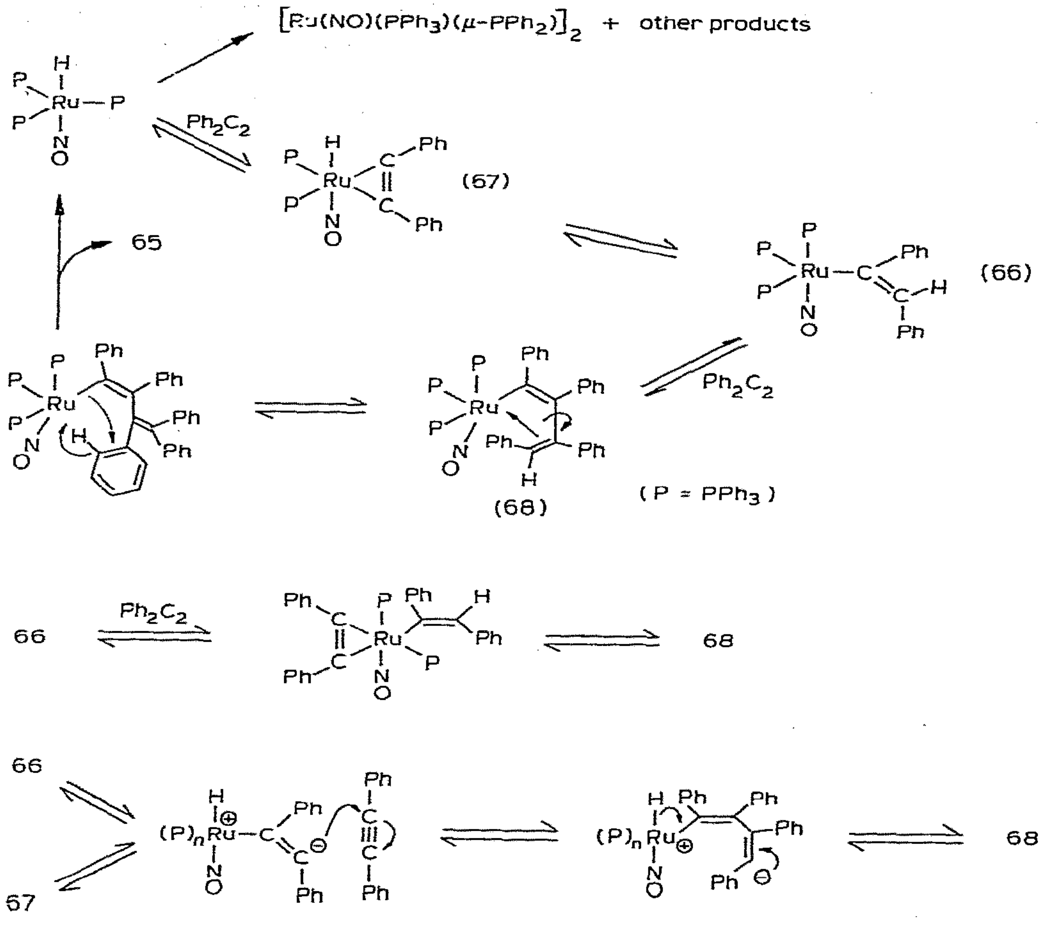
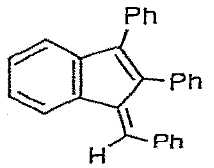
In concentrated ammonia solution containing $[NH_4]_2[Os(NO)X_5]$ (X = Cl, Br or I) and $Na_2[Ru(NO)(NO_2)_4(OH)]$ could be converted (97) into $Os(NO)(NH_3)_2X_3$, $[Os(NO)(NH_3)_3(H_2O)X]X_2$, $[Ru(NO)(NH_3)_3(H_2O)Cl]Cl_2$ and $[Ru(NO)(NH_3)_3Cl_2]Cl.H_2O$. Reaction of $[Os(NO)X_5]^{2-}$ with o-phenylenebis(dimethylarsine) afforded (98) trans-$[Os(NO)(diars)_2X]X_2$ (X = Cl, Br or I). When the nitrosyl cations were treated with OH^- and $N_2H_4.H_2O$, respectively, the species $Os(diars)_2Cl(NO_2)$ and $Os(diars)_2Cl(N_3)$ were formed. However, under special conditions, OH^- attack on $[Os(NO)(diars)_2Cl]Cl_2$ afforded $[Os(NO)(diars)_2(OH)]Cl_2$. With phenylhydrazine, the nitrosyl cation gave a mixture of trans-$[Os(N_2)(diars)_2Cl]Cl$ and $Os(diars)_2(ONNNHPh)Cl$, and the latter was oxidised by O_2 providing $[Os(N_2)(diars)_2Cl]Cl$, $Os(diars)_2Cl(NO_2)$ and $[Os(NO)(diars)_2Cl]Cl_2$. Attack on $[Os(NO)(diars)_2Cl]Cl_2$ by hydroxylamire afforded trans-$[Os(NO)(diars)_2(OH)]Cl_2$ and other unidentified products. It was noted that the nitrosyl cations exhibited ν(NO) close to 1865cm^{-1}, and it had previously been proposed (99) that all complexes with ν(NO) $>$ 1886cm^{-1} only would be susceptible to nucleophilic attack. However, these results indicated that this 'rule' should serve only as a guide to reactivity.

The structure of $[Ru(NO)\{Ph_2P(CH_2)_3PPh_2\}_2][BPh_4]$ has been determined crystallographically (100). The molecule is trigonal bipyramidal with two axial P atoms, the Ru-N-O group being equatorial and linear. $Ru(NO)(PPh_3)_3H$ reacted (101) with an excess of diphenylacetylene giving 65, as the only organic product, and a complicated mixture of Ru-containing compounds. The overall proposed mechanism is outlined in Scheme 12, and the possible modes of conversion of $Ru(NO)(PPh_3)_2(CPh{=}CHPh)$, 66, or $Ru(NO)(PPh_3)_3(\eta^2\text{-}PhC_2Ph)H$, 67 into $Ru(NO)(PPh_3)_2(CPh{=}CH\text{-}CPh\text{-}CHPh)$, 68 are also shown.

Scheme 12

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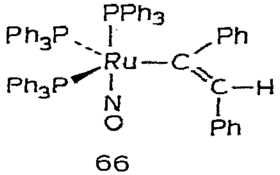
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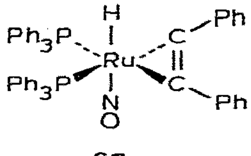
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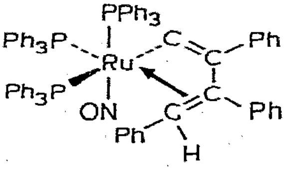
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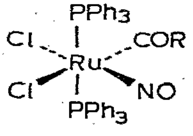
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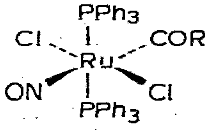
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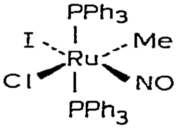
Oxidative addition of acylchlorides to $Ru(NO)(PPh_3)_2Cl$ afforded (102) 69 or 70 (R = Ph or Me) whereas with methyl iodide and benzyl chloride 71 and 72 were formed, respectively. With TCNE and fumaronitrile, 1:1 adducts, 73, were isolated, and a series of o-quinones afforded species of the type 74 which underwent one-electron reduction reactions.

Dinitrosyl Complexes

There was ir spectroscopic evidence for the formation of $Fe(CO)(NO)_2$, when $Fe(CO)_2(NO)_2$ underwent uv photolysis (103) in either argon or methane matrices at 20°K. In a nitrogen matrix both $Fe(CO)(N_2)(NO)_2$ and $Fe(N_2)_2(NO)_2$ were formed but under CO, $Fe(CO)_5$ was generated. The e.s.r. spectrum of $Fe(NO)_2(PR_3)Br$ has been measured and interpreted (104).

Reaction of $Ru(NO)(PPh_3)_2Cl$ with NO_2BF_4 afforded (105) a mixture of $[Ru(NO)_2(PPh_3)_2Cl][BF_4]$ and $[Ru(NO)(PPh_3)_2Cl(NO_2)][BF_4]$.

When $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ was photolysed with NO in either chloroform or CCl_4, $Fe(NO)_3Cl$ was produced (106). The trinitrosyl could also be generated from $[Fe(NO)_2Cl]_2$ and NO in non-coordinating solvents.



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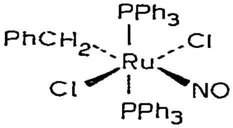

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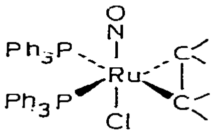

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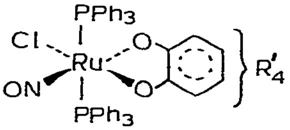

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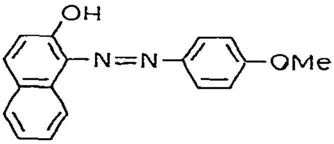

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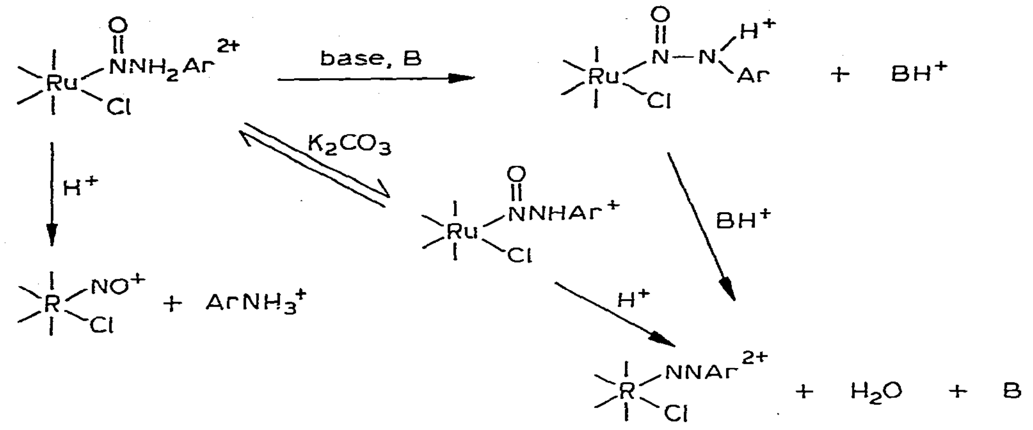
Diazenato Complexes

Treatment of $[Ru(bipy)_2(NO)Cl]^{2+}$ or $[Ru(bipy)_2(NO)(NCMe)]^{3+}$ with aromatic amines $NH_2C_6H_4Y$ (Y = H, Me, OMe) gave (107) the diazenato complexes $[Ru(bipy)_2N_2C_6H_4Y)Cl]^{2+}$ or $[Ru(bipy)_2(N_2C_6H_4Y)(NCMe)]^{3+}$. When the ^{15}NO labelled complex was used, $[Ru(bipy)_2(^{15}N^{14}NC_6H_4OMe)Cl]^{2+}$ was isolated. On the basis of this observation and kinetic measruements, a mechanism for this 'diazotisation' reaction was proposed (Scheme 13). On heating, $[Ru(bipy)_2(N_2C_6H_4Me)Cl]^{2+}$ in acetone, N_2 and toluene were liberated and with KI, p-MeC_6H_4I was formed. Treatment of $[Ru(bipy)_2(N_2C_6H_4OMe)Cl]^{2+}$ with β-naphthol afforded $Ru(bipy)_2(OH)Cl$ and 75. One-electron electrochemical reduction of $[Ru(bipy)_2(N_2C_6H_4Me)Cl]^{2+}$ in MeCN gave (107) (108) $[Ru(bipy)_2(NCMe)Cl]^+$, N_2 and toluene. When $Ru(bipy)_2Cl_2$ was used to reduce $[Ru(bipy)_2(N_2C_6H_4OMe)Cl]^{2+}$ $[Ru(bipy)_2(NCMe)Cl]^+$, was again

Scheme 13



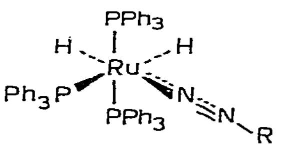
formed, together with $[Ru(bipy)_2Cl_2]^+$ and C_6H_5OMe. It proved impossible to prepare $[Ru(bipy)_2(N_2C_6H_4Y)Cl]^{2+}$ directly from $Ru(bipy)_2Cl_2$, since N_2, C_6H_5Y and $[Ru(bipy)_2Cl_2]^+$ were preferentially formed, and reaction of $[Ru(bipy)_2(NO)Cl]^{2+}$ with the ferrocenyl amine $Fe(\eta^5\text{-}C_5H_4NH_2)(\eta^5\text{-}C_5H_5)$ gave, instead of the anticipated 'diazenato' complex, $[Ru(bipy)_2(NO)Cl]^+$ and the appropriate ferricinium amine.

The structure of $Ru(N_2B_{10}H_8SMe_2)(PPh_3)_3H_2$, (76), (R = $B_{10}H_8SMe$) as its tris-benzene solvate, has been determined crystallographically (109). The Ru-N-NR bond angle is 176° and so this group must be regarded as being essentially linear.

CLUSTER COMPOUNDS

Binuclear Species (excluding $\eta^5\text{-}C_5H_5$ Compounds)

Reaction of trans-RCOCH=CHI with $Fe_2(CO)_9$ gave (110) $Fe(CO)_4$ (η^2-RCOCH=CHI) (R = Me or MeO) and small amounts of 77. Photolysis of the former compound with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ afforded 78. The structure of $[Fe(CO)_3(\mu_2\text{-}CNEt_2)]_2$, 79, obtained (111) by reacting $Fe(CO)_5$ with $Et_2NC{\equiv}CNEt_2$, has been determined crystallographically (112). The Fe-Fe distance is 2·48Å, the C=N distance 1·29Å, significantly shorter than a C-N single bond (1·46Å) and the coordination geometry at the Fe atom is distorted octahedral. The bridging diethylimmonio-carbene ligand is similar to that in $Ru_3(CO)_{10}H(C{=}NMe_2)$ (113).



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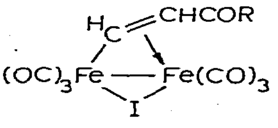

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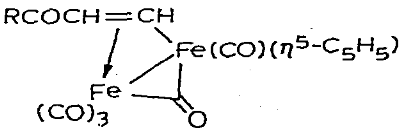

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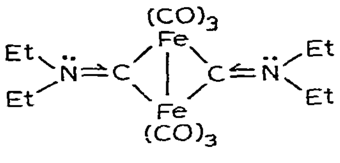
Photolysis of cyclopropyl acetylene in the presence of $Fe(CO)_5$ afforded (114) a black precipitate which, on oxidation, gave 80 and 81. On similar treatment of dicyclopropylacetylene, several compounds including 80–88, and an orange-red species $Fe_2(CO)_6(C_8H_{10})_2CO$. When dicyclopropylacetylene was photolysed with $Fe(CO)_5$ in excess, violet 89, red 90, 85 and other unidentified compounds were produced. Oxidation of 85 by Ce^{4+} afforded the appropriately substituted maleic anhydride. Photolysis of 89 in the presence of dicyclopropylacetylene



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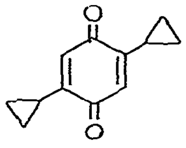

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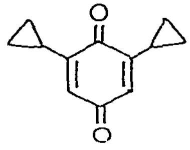

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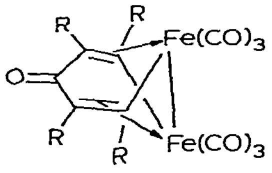

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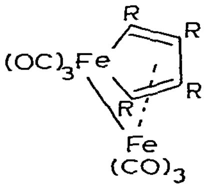

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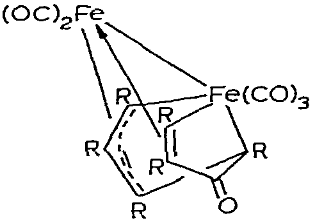

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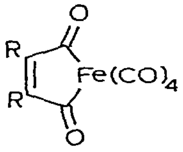

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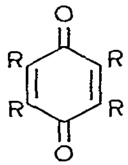

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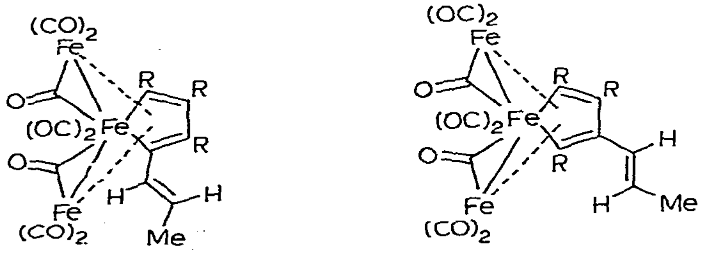

a

b

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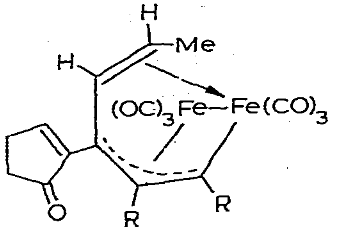

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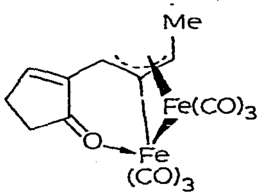

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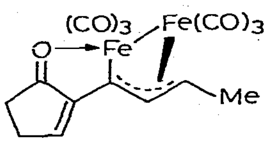

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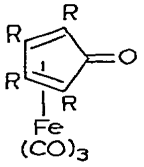

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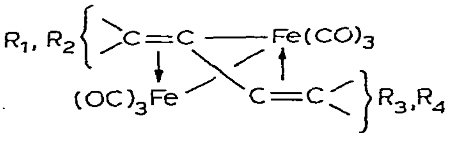

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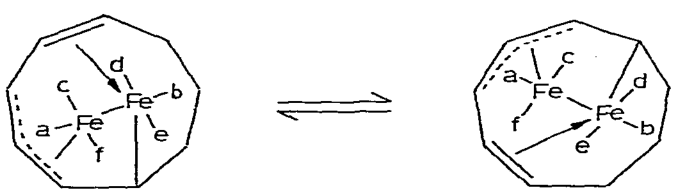
gave a mixture of 82, 83, and other unidentified species, and similar treatment of 82 gave 83. When 82 was refluxed in toluene, 91 was produced. The structure of 88 was confirmed by X-ray methods.

Treatment of $R^1R^2C(OH)C{\equiv}CC(OH)R^3R^4$ or $R^1R^2C(OH)C(I){=}C(I)C(OH)R^3R^4$ with $Fe_3(CO)_{12}$ afforded (115) the binuclear species 92 (R^1, R^2, R^3, R^4 = H, Me, Ph or R^1R^2C, R^3R^4C = cyclohexadienyl). However, reaction of $MeCH(OH)C{\equiv}CC(OH)HMe$ with $Fe_3(CO)_{12}$ occasionally gave $Fe_2(CO)_6(MeCOCH{=}C{=}CHMe)$. The influence of steric factors on the reactions of $Fe_2(CO)_6$(butatriene) derivatives with halogens has been investigated (116).

The fluxional behaviour of $Fe_2(CO)_6(C_9H_{10})$ has been investigated (117). From −140° to −110°, a 'twitch process' (Scheme 14) occurs, but above −110°, this is followed by localised scrambling of the CO groups first on the allyl-bound Fe atom and then on the other Fe atom. Thus, the dynamic properties of this molecule, $Fe_2(CO)_6(C_8H_{10})$ and $Fe_2(CO)_6(C_{10}H_{12})$ are entirely similar (118).

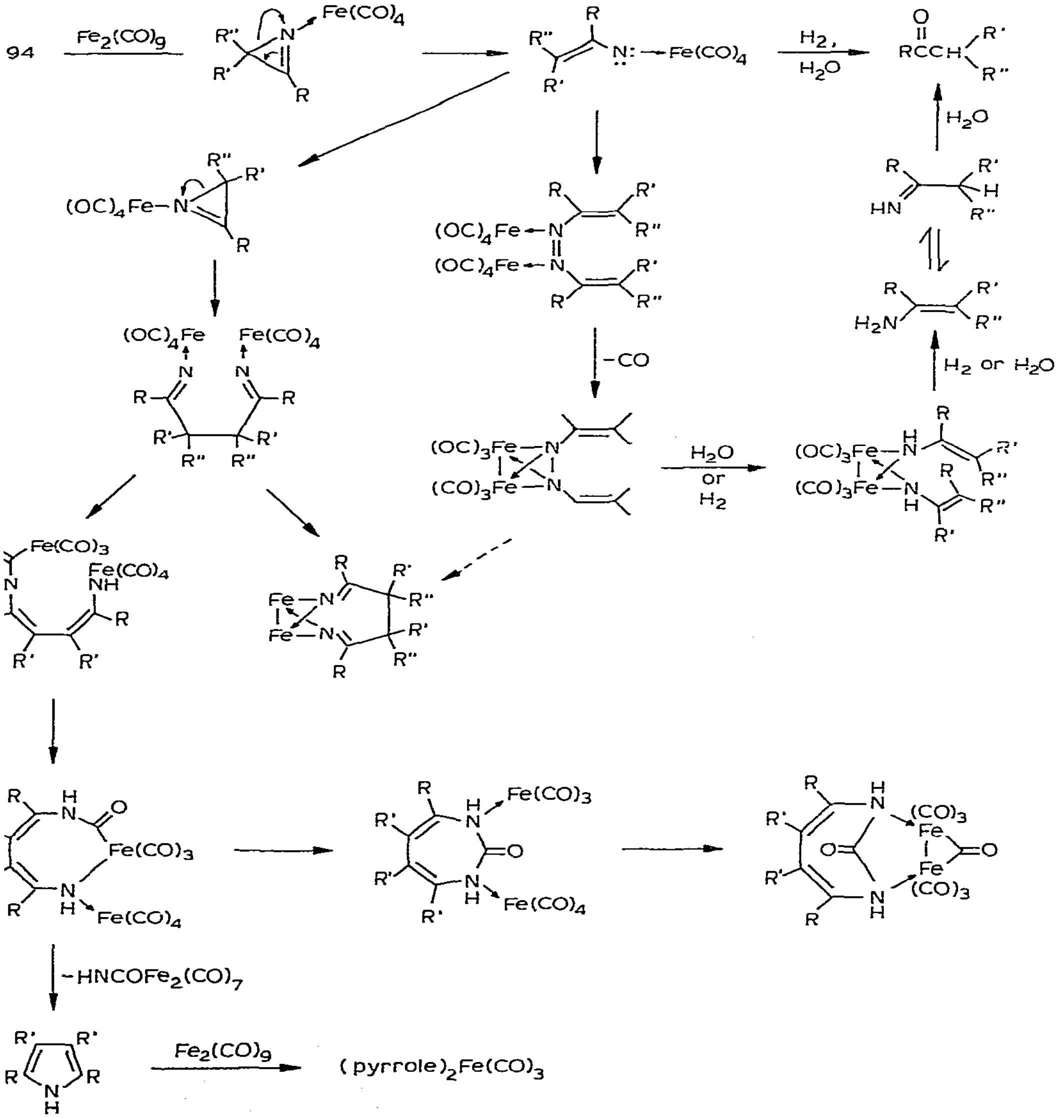
Scheme 14



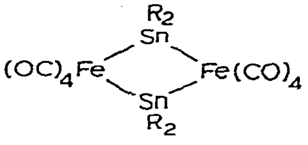
Treatment of $Fe(CO)_5$ with R_2SnO, $[R_2SnS]_3$ or $R_2Sn(OAc)_2$ gave (119) $[Fe(CO)_4(\mu_2\text{-}SnR_2)]_2$, 93, (R = Me, Et, Bu^n, octyl, Ph). Reaction of 93 (R = Bu^n) with PPh_3, $Ph_2PCH_2CH_2PPh_2$, $P(OPh)_3$ and $P(OMe)_3$ gave, respectively, $[Fe(CO)_3(PPh_3)(\mu_2\text{-}SnBu^n_2)]_2$, $[Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)(\mu_2\text{-}SnBu^n_2)]_2$, $Fe_2(CO)_7\{P(OPh)_3\}(\mu_2\text{-}SnBu^n_2)_2$, nd [Fe{P(OMe)$_3$}$_4$($\mu_2$-SnBu$^n{}_2$)]$_2$. These reactions revealed that 93 would undergo CO substitution when treated with PR$_3$, whereas reactions with N- or O-containing bases caused homolysis of the Fe$_2$(μ_2-SnR$_2$)$_2$ unit. Reaction of K$_2$Fe$_2$(CO)$_8$ ith PhSnCl$_3$ afforded (12) the Fe-Fe bonded species [Fe(CO)$_4$SnPh$_3$]$_2$, and with h$_2$SnCl$_2$, the analogous [Fe(CO)$_4$SnPh$_2$Cl]$_2$ was formed. Similar compounds conaining SnMe$_3$ and SnMe$_2$Cl were prepared.

Treatment of Fe$_2$(CO)$_9$ with the azirine 94 gave (121) a series of compounds as utlined in Scheme 15 (R, R', R" = H, Me, Et, Ph, p-MeC$_6$H$_4$, p-Bu^{t}C$_6$H$_4$). No vidence was obtained for the formation of 95.

cheme 15



The structure of 1,2-diazepin complex $Fe_2(CO)_7(C_4N_2H_4)$, 96, (122) has been determined crystallographically (123). A new mode of CO scrambling in this molecule was observed by VT ^{13}C nmr studies. The low temperature fluxional process involves exchange of the five essentially coplanar equatorial CO groups over both Fe atoms, and at higher temperatures, localised CO scrambling is super-imposed on this process.



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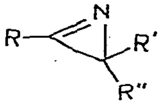

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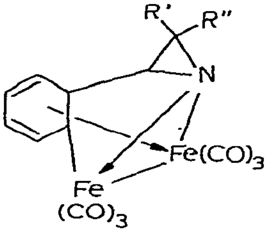

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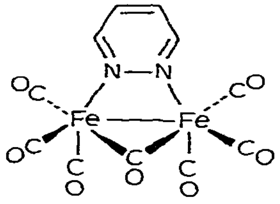

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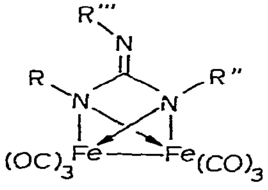

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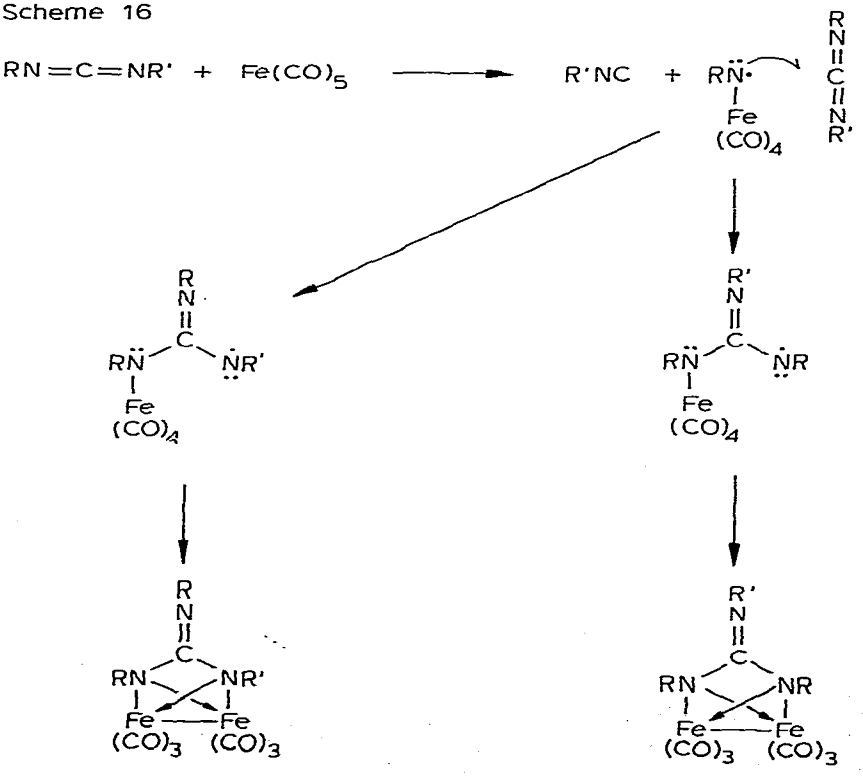
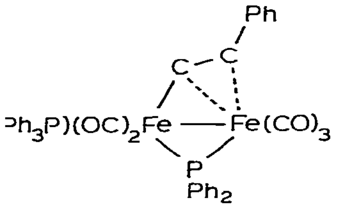
Scheme 16



Reaction of $Fe(CO)_5$ or $Fe_2(CO)_9$ with $MeN{=}C{=}NBu^t$ gave (124) two dehydroguanidino complexes 97 ($R = R' = Me$, $R'' = C_6H_{11}$) could be isolated. It is thought that the mechanism of formation of these products could occur as in Scheme 16.

Reaction of $Fe_2(CO)_9$ with $RC{\equiv}CPR'R''$ ($R, R', R'' = Ph, C_2Ph, Bu^t, Pr^i, C_6H_{11}$) afforded (125) $Fe_2(CO)_6(C_2R)(PR'R'')$ which, on treatment with PPh_3, was converted into $Fe_2(CO)_5(PPh_3)(C_2R)(PR'R'')$, 98 ($L = PPh_3$). The structure of 98 $L = PPh_3$; $R = R' = R'' = Ph$) has been confirmed by X-ray methods, and the Fe-Fe and C-CPh bonds are 2·65 and 1·23Å, respectively. The formation of 98 $L = CO$) may proceed via $Fe(CO)_4(R'R''PC_2R)$, which can be isolated from this reaction, and $Fe_2(CO)_8(R'R''PC_2R)$, 99. The photolysis of $Fe(CO)_4(Ph_2PC_2Bu^t)$ gave 98 ($L = Ph_2PC_2Bu^t$; $R = Bu^t$, $R' = R'' = Ph$). The structure of $Fe_2(CO)_6$-$Ph_2PC_2Ph)_2$, 100, prepared from $Fe_2(CO)_9$ and Ph_2PC_2Ph, has also been determined rystallographically (126); there is no Fe-Fe bond, but the C-CPh distance is ·26-1·27Å.



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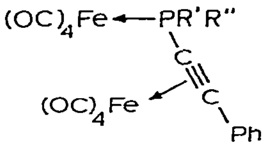

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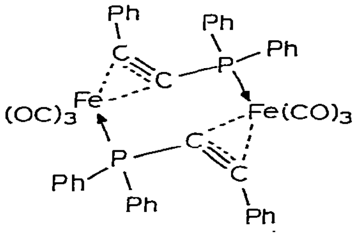

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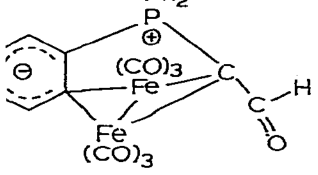

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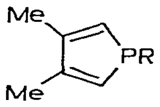

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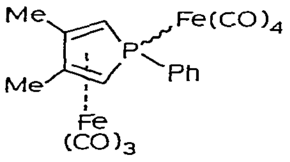

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Treatment of $Fe_3(CO)_{12}$ with $(Me_3Sn)_2C{=}PPh_3$ gave (127) a mixture of $Fe(CO)_4$-$Me_3)_2$ and $Fe_2(CO)_6\{C(CHO)PPh_2(C_6H_4)\}$, 101, whose structure was determined X-ray techniques (Fe-Fe 2·47Å). In this species, the P atom could be ought of, in valence bond terms, as being the centre for a phosphonium ion, ith the counter negative charge being delocalised over the O-metallated ring. ere was no evidence for a bridging hydrido ligand.

Extended Hückel MO Calculations have been made (128) on $[Fe(CO)_3(\mu_2\text{-}ER_2)]_2$ = N, P or As). The experimentally observed structural changes, with amatic increases in Fe-Fe distances in the species where E = P and R is H, or Ph, could be correlated with the HOMO in these species. The HOMO is bonding with respect to the two Fe atoms, but is Fe-P antibonding, and the balance between these two forces significantly controls the equilibrium geometry. If R = CF_3, the Fe-P repulsions are reduced in the HOMO, and a longer Fe-Fe distance results. It was stated that the importance of the Fe-P interactions could be clearly demonstrated and should be considered together with the Fe-Fe interaction when thinking of the structures of these and similar molecules. The M-M and M-E-M dihedral angles of these and related molecules are given in Table 1.

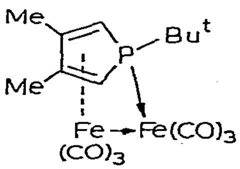
TABLE 1

M-M distances and M-E-M bond angles in binuclear complexes

Complex	M-M(Å)	M-E-M(°)
$Fe_2(CO)_6(\mu_2\text{-}NH_2)_2$	2·40	104
$Fe_2(CO)_6\{\mu_2\text{-}(NMe_2)_2CO\}$	2·39	92
$Fe_2(CO)_6\{\mu_2\text{-}(NPh_2)_2CO\}$	2·42	92
$Fe_2(CO)_6\{C_6H_4(\mu\text{-}NPh)(\mu\text{-}NH)\}$	2·37	95
$Fe_2(CO)_6(\mu_2\text{-}PMePh)_2$	2·62	101
$Fe_2(CO)_6\{\mu_2\text{-}P(CF_3)_2\}_2$	2·82	119
$Fe_2(CO)_6\{As_2(\mu\text{-}AsMe)_2Me_2\}$	2·66	125
$Co_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}PPh_2)_2$	2·56	105
$Ni_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}PPh_2)_2$	3·36	180

Reaction of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with the phosphine 102, (L, R = Ph) gave (129) $Fe(CO)_4L$ and 103 (R = Ph), and with 102 (L, R = Bu^t) and $Fe_3(CO)_{12}$, 104 (R = Bu^t) was formed. Treatment of $Fe_2(CO)_9$ with the sulfide, LS (R = Ph) also afforded a mixture of $Fe(CO)_4L$ and 103.

In the reaction between $Fe_2(CO)_9$ and $(EtO)_2POP(OEt)_2$, a series of compounds, including $\{Fe(CO)_4\}_2\{\mu_2\text{-}(EtO)_2POP(OEt)_2\}$, 105, 106 and 107, were obtained (130). Treatment of $Fe(\eta^5\text{-}C_5H_5)(CO)_2X$ (X = Cl or I) with the di-phosphite afforded a mixture of $\{Fe(\eta^5\text{-}C_5H_5)(CO)X\}_2\{\mu_2\text{-}(EtO)_2POP(OEt)_2\}$ and $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2\{\mu_2\text{-}(EtO)_2POP(OEt)_2\}]^{2+}$ (as BPh_4^- salt). Reaction of $Fe_3(CO)_{12}$



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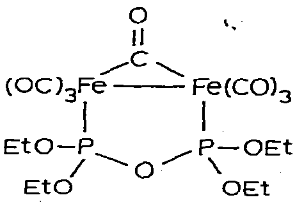

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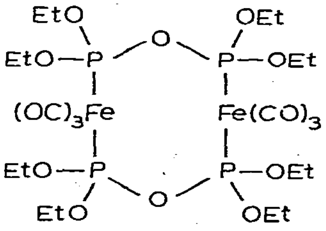

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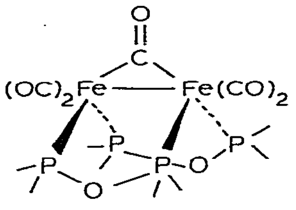

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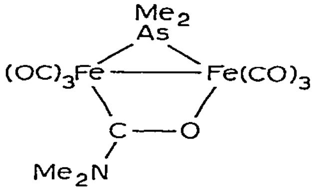

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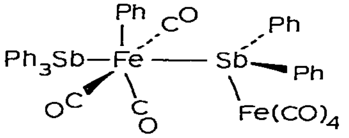

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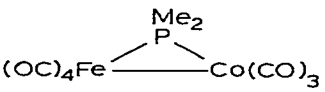
with $MeN(PF_2)_2$ afforded (131) $\{Fe(CO)_3\}_2\{\mu_2\text{-}NMe(PF_2)_2\}$, analogous to 106. In solution, this species lost CO, giving $Fe_2(CO)_5\{\mu_2\text{-}NMe(PF_2)_2\}_2$, similar to 107, whose structure was established crystallographically. The Fe–Fe distance is 2·66Å, and the geometry of each Fe atom could be described either as distorted octahedral or distorted trigonal bipyramidal depending on whether the Fe–Fe bond formally occupies a coordination site. Treatment of $Fe_2(CO)_9$ with $MeN(PF_2)_2$ gave a mixture of $(OC)_4FePF_2N(Me)PF_2Fe(CO)_4$ and $Fe_2(CO)_7\{\mu_2\text{-}NMe(PF_2)_2\}$, analogous to 104 and $Fe_2(CO)_7\{\mu_2\text{-}CH_2(PPh_2)_2\}$ (132).

Reaction of $Fe_2(CO)_9$ with Me_2AsNMe_2 in the presence of $NHMe_2$ afforded (132) the μ_2-carbamoyl complex 108. The structure of this complex was established by diffraction methods (Fe–Fe 2·64Å) and it was thought that 108 might be formed via $Fe(CO)_4AsMe_2NMe_2$. A Mossbauer spectral study has been made (134) of the species 109, and the nature of the Fe–Sb bonds have been discussed.

The structures of $FeCo(CO)_7(\mu\text{-}PMe_2)$, 110, and $Fe_2(CO)_6(\mu\text{-}AsMe_2)_2$, have been determined crystallographically and it was shown (135) that the Fe–Co bond in 110 (2·67Å) is only 0·04Å shorter than in the corresponding $AsMe_2$ complex. The metal-metal distance in the latter (2·74Å) is 0·12Å longer than in the corresponding μ_2-PMe_2 complex.

Treatment of $Fe(CO)_4AsMe_2Cl$ with $NaM(CO)_5$ (M = Mn or Re), $NaFe(CO)_3(NO)$ or $NaCo(CO)_4$ afforded the bimetallic species $Fe(CO)_4AsMe_2Q$ (Q = $M(CO)_5$, $Fe(CO)_3(NO)$ or $Co(CO)_4$). Upon photolysis or even spontaneously, these species lost CO giving the metal-metal bonded species $Fe(CO)_4AsMe_2Q'$, 111 (Q' = $M(CO)_4$, $Fe(CO)_2(NO)$ or $Co(CO)_3$). When tertiary phosphines or phosphites L (PPh_3, PMe_2NMe_2, PMe_3, $P(OMe)_3$) were added to 111, the metal-metal bond was reopened, giving $Fe(CO)_4AsMe_2Q''$ (Q'' = $M(CO)_4L$, $Fe(CO)_2(NO)L$ or $Co(CO)_3L$). When 111 (Q' = $Mn(CO)_4$ or



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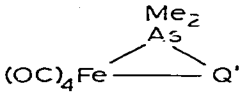

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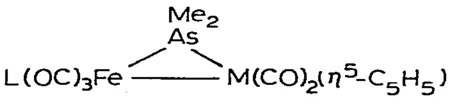


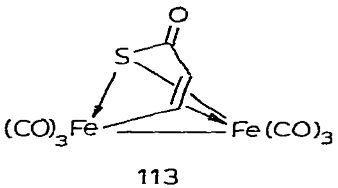
112

$Re(CO)_4$) was treated with PMe_3 or $PMe_2(NMe_2)$, (L), however, $Me_2AsFe(CO)_4M(CO)_4L$ could be isolated. When the metal-metal bonded species $Fe(CO)_4(\mu_2\text{-}AsMe_2)M(CO)_2\text{-}(\eta^5\text{-}C_5H_5)$, 112 (M = Mo or W; L = CO), was treated with L' (PPh_3, PMe_3, $PMe_2(NMe_2)$, $P(OMe)_3$), the species $Fe(CO)_4(\mu_2\text{-}AsMe_2)M(CO)_2L'(\eta^5\text{-}C_5H_5)$ (no Fe-M bond), 112 (L = L') and $Fe(CO)_3L'(\mu_2\text{-}AsMe_2)M(CO)_2L'(\eta^5\text{-}C_5H_5)$ (no Fe-M bond), were formed (137). Reaction of $Mo(\eta^5\text{-}C_5H_5)(CO)_2L'AsMe_2$ with $Fe_2(CO)_9$ gave $Fe(CO)_4(\mu\text{-}AsMe_2)\text{-}Mo(CO)_2L'(\eta^5\text{-}C_5H_5)$ (L' = PMe_3 or $PMe_2(NMe_2)$). When $Fe(CO)_4\{P(OMe)_3\}$ was treated with $AsMe_2NMe_2$, $Fe(CO)_3\{P(OMe)_3\}\{AsMe_2(NMe_2)\}$ was produced. On treatment of this with HCl, $Fe(CO)_3\{P(OMe)_3\}(AsMe_2Cl)$ was formed which reacted with $Na[Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ giving $Fe(CO)_3\{P(OMe)_3\}(\mu_2\text{-}AsMe_2)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ and finally 112 (M = Mo, L = $P(OMe)_3$).

The structure of syn-$[Fe(CO)_2(PMe_3)(\mu_2\text{-}SMe)]_2$ has been determined crystallographically (138) (Fe–Fe = 2·52Å). The compound was obtained by treatment of $[Fe(CO)_3(\mu_2\text{-}SMe)]_2$ with PMe_3 in boiling hexane. VT nmr studies have been made (139) of the conversion of the syn and anti isomers of $[Fe(CO)_3(\mu_2\text{-}SBu^t)]_2$ and $Fe_2(CO)_5L(\mu_2\text{-}SBu^t)_2$ (L = tertiary phosphine). The interconversion of the isomers of these species is ca. 10^3 times faster than that of other related alkyl and aryl derivatives. Mercury (II) chloride formed (140) 1:1 and 2:1 adducts with $[Fe(CO)_2L(\mu_2\text{-}SMe)]_2$ (L = PMe_3, PPh_3 or $P(OMe)_3$).

Treatment of $[Fe(CO)_3(\mu_2\text{-}SMe)]_2$ with $AsMe_2NMe_2$ gave (141) $Fe_2(CO)_5(AsMe_2NMe_2)\text{-}(\mu_2\text{-}SMe)_2$ which, on addition of HCl, could be converted into $Fe_2(CO)_5(AsMe_2Cl)\text{-}(\mu_2\text{-}SMe)_2$. Reaction of this last species with carbonylate anions afforded $Fe_2(CO)_5(AsMe_2Q)(\mu_2\text{-}SMe)_2$, where Q = $M(CO)_5$ (M = Mn or Re), $Co(CO)_4$ or $Fe(CO)_2\text{-}(\eta^5\text{-}C_5H_5)$. When $Fe_2(CO)_6(\mu_2\text{-}SMe)_2$ was treated with $M(\eta^5\text{-}C_5H_5)(CO)_3AsMe_2$, similar mixed metal compounds were produced. On thermolysis of these compounds a mixture of $Fe_2(CO)_6(SMe)_2$ and several unidentified products, which apparently did not contain Fe-M bonds, was generated. Photochemically induced insertion of alkynes into the metal-metal bond in $[Fe(CO)_3E]_2$ (E = SMe, SPh or PMe_2) afforded (142) $[Fe(CO)_3E]_2(C_2R_2)$ where R = CF_3 or CO_2Me. Comparable reactions had been reported earlier (143) and treatment of these 'insertion' products with PMe_3 gave $[Fe(CO)_2(PMe_3)E]_2(C_2R_2)$.

Reaction of thiomalic anhydride with $Fe(CO)_5$ gave (144), in low yield, the binuclear species 113 whose structure was determined by X-ray methods (Fe-Fe 2·53Å). Treatment of the binuclear Fe(II) complex $[Fe\{SCH_2CH_2N(Me)CH_2CH_2N(Me)\text{-}$



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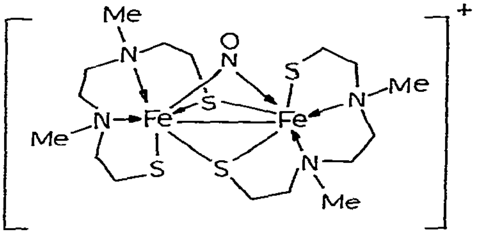

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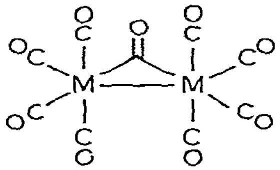

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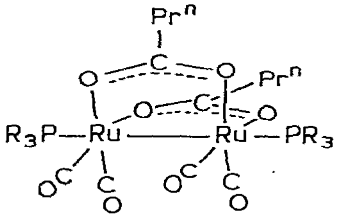

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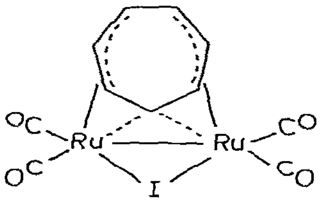

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$CH_2CH_2S\}]_2$ or its mononuclear dicarbonyl analogue with NO^+ afforded (145) the nitrosyl-bridged dimer 114. An X-ray examination of this compound revealed that the metal atoms had distorted octahedral geometries and were bridged by two S atoms and a symmetrically bridging NO group. The Fe-Fe distance, 2·47Å, is consistent with a single bond.

UV irradiation of $M(CO)_5$ (M = Ru or Os) in n-heptane at low temperature produced (146) $M_2(CO)_9$. The ruthenium species was very unstable in solution and in the solid state, rapidly decomposing into $Ru(CO)_5$ and $Ru_3(CO)_{12}$. The osmium compound decomposed less rapidly. Both species appear to have the structure 115, and the mass spectral decomposition of $Os_2(CO)_9$ revealed fragments consistent with $[Os_2C(CO)_m]^+$. Reaction of $Os_2(CO)_9$ with hydrogen afforded $Os_2(CO)_8H_2$ and this was produced, together with $Os(CO)_4(PPh_3)$ when the nonacarbonyl reacted with PPh_3 in the dark. $Os(CO)_5$ does not react with PPh_3 under these conditions. With PEt_3, $Os_2(CO)_9$ gave only $Os_2(CO)_8H_2$, even in deuteriated solvents, indicating that the source of hydride ligand must be the phosphine.

Treatment of $Ru_3(CO)_{12}$ with $PBu^t{}_3$ and butyric acid gave (147) 116 whose structure was determined crystallographically (Ru-Ru 2·73Å). The Ru-P bonds are rather longer than expected, probably because of steric effects.

Reaction of $Ru_3(CO)_6(C_7H_7Ph)(C_7H_9Ph)$ with iodine afforded (148) $Ru_2I(CO)_4$-(C_7H_6Ph), 117. From a crystallographic study it was clear that while the C_7 ring presents a concave face to the Ru-Ru bond (2·87Å), the structure is in every way different to that of $Ru_2(CO)_5(SiMe_3)(C_7H_6SiMe_3)$ (149). A vt nmr spectral study of the fluxional behaviour of $Ru_2(CO)_6(\eta^5\text{-}C_{10}H_{12})$ established (150) a pattern similar to that of other $M_2(CO)_6$(polyolefin) species (118). In general, the activation energies for the 'twitching' process and localised CO scrambling were higher than those for comparable processes in the iron analogues.

Trinuclear Species

It has been shown conclusively (151), by observation of ^{57}Fe-^{13}C coupling, that CO ligand scrambling on $Fe_3(CO)_{12}$ is intramolecular and that all CO groups have equal access to all three Fe atoms. VT ^{13}C nmr studies of $Fe(CO)_4L$ (L = amine) revealed that the activation energy for intramolecular CO group exchange was raised from ca. 2 kcal/mole in $Fe(CO)_5$ to ca. 5·0-5·5 kcal/mol in the tetracarbonyl species. The structure of the complex with L = pyridazine was determined crystallographically, and is similar to its pyridine and pyrazine analogues. Scrambling of the three CO groups in $Fe(CO)_3(C_9H_8O)$ (C_9H_8O = barbaralone) was observed to proceed in a concerted manner.

The redox behaviour of $Fe_3(CO)_{12-n}L_n$ ($n = 0 \rightarrow 3$) and $Fe(CO)_{5-n}L_n$ (n = 0 2) was investigated (152) using dc polarography at Hg electrodes and dc cyclic voltammetry at Pt in acetone and in dichloromethane. The tri-iron species underwent a chemically reversible one electron reduction, and the $E_{1/2}$ values for this process became increasingly negative with increasing phosphine substitution. Further electrochemical reduction of $Fe_3(CO)_{12-n}L_n$ afforded $[Fe_3(CO)_{12-n}L_n]^{2-}$ which rapidly decomposed. A one-electron oxidation step was detected in the voltammograms of $Fe_3(CO)_9\{P(OMe)_3\}_3$. Both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ underwent irreversible reductions which led to rapid decomposition. The mononuclear iron complexes underwent a chemically reversible one-electron oxidation and a well-defined two-electron reduction step at a Hg-electrode, but no evidence could be obtained for the radical anion $[Fe(CO)_5]^{\dot{-}}$.

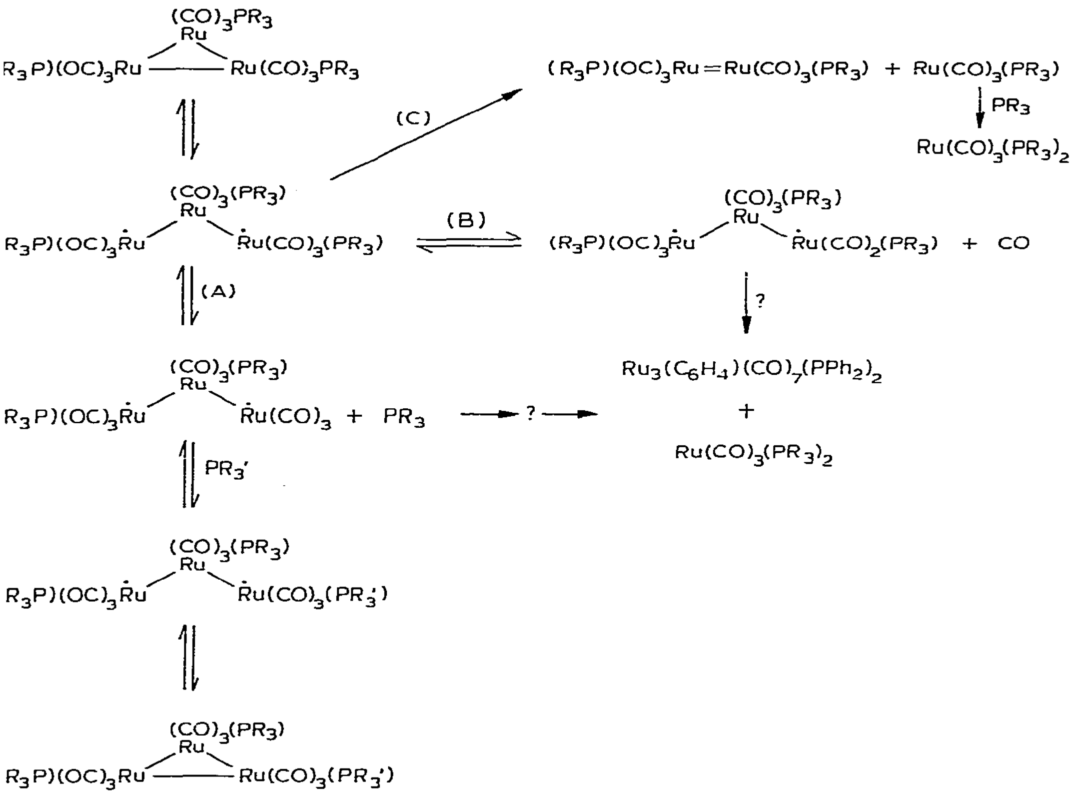
The structure of $Ru_3(CO)_{12}$ has been redetermined crystallographically (153). The Ru-Ru (2·85–2·86Å) and Ru–C distances so obtained were more accurate and reliable than those reported earlier (154).

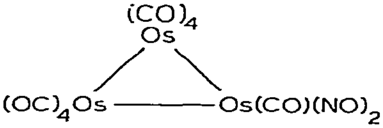
In refluxing heptane, $Os_3(CO)_{12}$ reacted with isonitriles giving (155) $Os_3(CO)_{12-n}(CNR)_n$ (R = Me, n = 1, 2; R = Bu^t or Ph, n = 1–4; R = p-MeC_6H_4, n = 1–3). Pyrolysis of these compounds in refluxing octane afforded $Os_6(CO)_{18-n}(CNR)_n$ (R = Me or Bu^t, n = 1–5).

The kinetics of substitution of $Fe_3(CO)_{12}$ by PPh_3 has been studied (156) at various temperatures and at different concentrations. The reactions are first order with respect to the carbonyl and an induction period was always observed. A kinetic study of the reaction of $[Ru(CO)_3(PPh_3)]_3$ with oxygen in the presence of PPh_3 in decalin revealed (157) that the carbonyl broke up into two species, $[Ru(CO)_3(PPh_3)]_2$ and the unstable high-spin tetrahedral $Ru(CO)_3(PPh_3)$. However, by adjusting the conditions, e.g. by including CO and perhaps another phosphine (PBu^n_3) in the reaction mixture, three distinct reaction pathways could be detected (158) (Scheme 17).

Reaction of $Ru_3(CO)_{12}$ with $Ph_2PCH_2PPh_2$ (dppm) gave (159) $Ru_3(CO)_{10}$(dppm), <u>118</u>. An examination of the VT ^{13}C nmr spectra of this compound revealed that it underwent two distinct intramolecular CO exchange processes: at low temperatures only the CO groups on the phosphine-bridged metal atoms exchanged (via a double CO bridge), whereas at higher temperatures, CO groups were exchanged between all metal atoms (via single CO bridges).

Treatment of $Os_3(CO)_{12}$ with NO in refluxing n-octane gave (160) $Os_3(CO)_9(NO)_2$ (<u>119</u>) & small amounts of the known (161) $Os_3(CO)_{10}(NO)_2$ (<u>120</u>). The latter could be obtained by treating the former with CO in boiling hexane, but under CO in cyclohexane at 25°, a species of empirical formula $Os_3(CO)_{10}(NO)_2$ was formed which exhibited no bands due to coordinated NO.. $Os_3(CO)_9(NO)_2$ reacted with cheme 17





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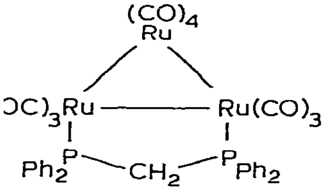

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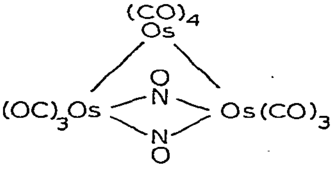

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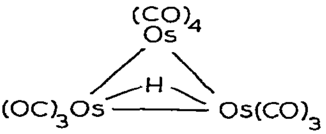

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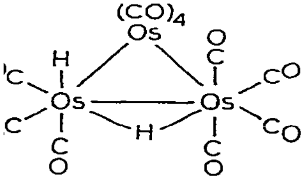

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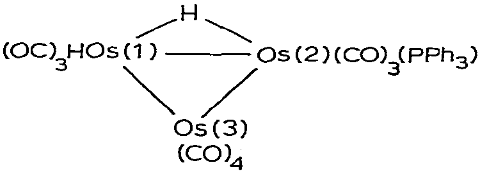
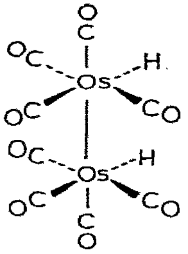


123

$(OMe)_3$ giving $Os_3(CO)_8\{P(OMe)_3\}(NO)_2$, which had terminal NO groups, and this reacted with CO giving $Os_3(CO)_9\{P(OMe)_3\}(NO)_2$ which did not contain bridging NO groups.

The molecular structures of $Os_3(CO)_{12}$ and $Os_3(CO)_{11}H_2$, 121, have been compared (162). The Os–Os bonds in the former are 2·88Å, whereas the bridged Os–Os distance in 121 is 2·99Å. The X-ray crystallographic examination of $Os_3(CO)_{10}$-$(\mu_2\text{-}H)_2$, 122, revealed (163) that the bridged metal-metal bond was 2·68Å, whereas the other two intermetal distances were 2·82Å. The shortness of the bridged bond suggested that the metal interaction could be described as a doubly protonated double bond. Treatment of 122 with PPh_3 afforded (164) the substituted dihydride $Os_3(CO)_{10}(PPh_3)H_2$, 123, whose structure was determined (165) crystallographically. The metal-metal distances are 3·02 (Os_1–Os_2), 2·87 (Os_2–Os_3) and 2·92 (Os_3–Os_1), respectively.

Carbonylation of OsO_4 in the presence of hydrogen gave (166) the hydrides $[Os(CO)_4]_nH_2$ (n = 1–4). Reduction of $Os_2(CO)_8X_2$ and $Os_3(CO)_{12}X_2$ (X = Cl or Br) with zinc in glacial acetic acid also afforded the hydrides where n = 2 or 3. Treatment of $Os_2(CO)_9$ with hydrogen probably produced $Os_2(CO)_8H_2$, 124, but this was



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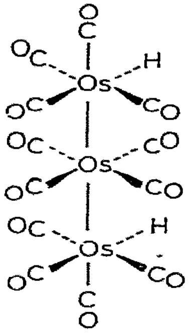

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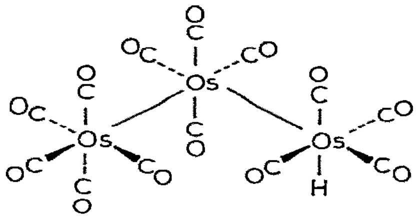

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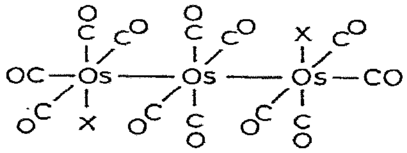

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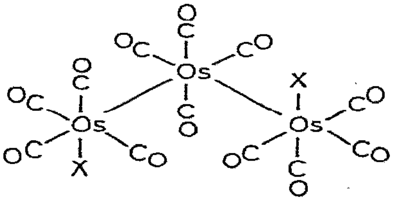

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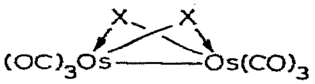
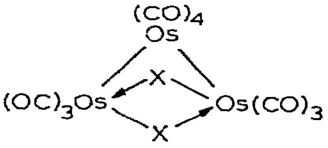


129

not confirmed. However, $Os_3(CO)_{12}$ reacted under pressure with H_2 giving mainly $Os_3(CO)_{10}H_2$, either 125 or 126, together with some $Os_2(CO)_8H_2$ and cis-$Os(CO)_4H_2$. The structure of $Os_3(CO)_{12}H_2$ can be either 125 or 126, although, in view of the known (167) structure of $Os_3(CO)_{12}I_2$, 127 (X = I), 125 is preferred. The halides $Os_3(CO)_{12}X_2$ (X = Cl or Br) were obtained (167) by treating the hydrides with CX_4. These trimetallic species can have a structure analogous to 127 (X = I), or be V-shaped, 128. When the bimetallic halides $Os_2(CO)_8X_2$ were heated in vacuo, $Os_2(CO)_6X_2$, 129 and $Os_3(CO)_{10}X_2$, 130 (X = Cl or Br) were formed. The former could also be obtained in refluxing n-heptane, as $Os_2(CO)_6I_2$ had been reported earlier (168). Direct chlorination of $[Os(CO)_4]_nH_2$ (n = 2 or 3) gave a mixture of $Os_2(CO)_8Cl_2$ and $Os_3(CO)_{10}Cl_2$, whereas bromination afforded $Os(CO)_4Br_2$, and iodination a mixture of $Os(CO)_4I_2$ and $Os_2(CO)_8I_2$. Whereas $Os(CO)_4H_2$ reacted with $SnCl_4$ giving cis-$Os(CO)_4H(SnCl_3)$, $Os_2(CO)_8H_2$ afforded $Os_2(CO)_8H(SnCl_3)$ which subsequently reacted with CX_4 giving $Os_2(CO)_8X(SnCl_3)$ (X = Cl or Br). Reaction of $Os_2(CO)_8H_2$ with PPh_3 gave $Os_2(CO)_6(PPh_3)_2H_2$ (131a, b or c), $Os_2(CO)_7(PPh_3)H_2$ (132a or b), $Os(CO)_3(PPh_3)H_2$ and $Os(CO)_4(PPh_3)$. However, treatment $Os_3(CO)_{12}H_2$ with PPh_3 gave a complicated mixture of products containing the group $\{Os(CO)_4PPh_3\}$. On heating in benzene, $Os(CO)_4H_2$ was converted exclusively into $Os_4(CO)_{12}H_4$, but while thermolysis of $Os_3(CO)_{12}H_2$ at 160° gave only $Os_3(CO)_{12}$, at 120° many products, including $Os(CO)_4H_2$, $Os_2(CO)_8H_2$, $Os_3(CO)_{12}H_2$, $Os_4(CO)_{10}H_2$, $Os_3(CO)_{12}$ and $Os_3(CO)_{10}H_2$, were identified. A similar mixture of compounds could be obtained by heating $Os_2(CO)_8H_2$. It would seem that these reactions could occur via the scission of Os_2 or Os_3 fragments into $Os(CO)_4H_2$ and $Os(CO)_4$, and that this latter group could insert into Os-H bonds. An alternative mechanism might involve homolytic cleavage of the Os-Os and Os-H bonds. In exploiting this type of reaction, $Os_3(CO)_{12}H_2$ was heated with $Re(CO)_5H$. The products included $Os(CO)_4H\{Re(CO)_5\}$ and $[Os(CO)_4]_nH_2$ (n = 1-4), and treatment of the former with CCl_4 gave $Os(CO)_4Cl\{Re(CO)_5\}$. Cis-$Os(CO)_4H_2$ reacted with C_2F_4 at 116° to give cis- and trans-$Os(CO)_4(C_2F_4H)_2$.



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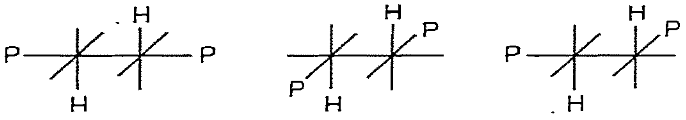


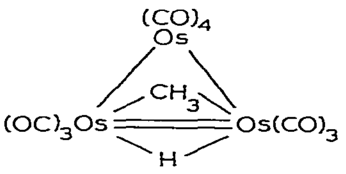
(a) (b) (c)

131

(a) (b)

132

When $Ru_3(CO)_{12}$ was treated with traces of water, such as might occur in hydrocarbon solvents, α-$Ru_4(CO)_{12}H_4$ and α-$Ru_4(CO)_{13}H_2$ were formed (169). It was stated that great care should be exercised in interpreting reactions involving apparent activation of hydrocarbons by $Ru_3(CO)_{12}$ since traces of water would inevitably lead to the formation of these hydrides which could be the activating species. Similar treatment of $Os_3(CO)_{12}$ at 230° led to the formation of $Os_3(CO)_{10}H(OH)$, $Os_4(CO)_{13}H_2$, $Os_4(CO)_{12}H_4$, $Os_5(CO)_{16}H_2$, $Os_5(CO)_{15}H_2$, $Os_6(CO)_{18}H_2$ and $Os_7C(CO)_{19}H_2$. $Os_5(CO)_{15}H_2$ is isoelectronic with $Os_5(CO)_{16}$ and may have a trigonal bipyramidal arrangement of metal atoms. $Os_5(CO)_{16}H_2$ is isoelectronic with $Os_5C(CO)_{15}$ and may either have a square-based pyramidal geometry or consist of a tetrahedron of metal atoms with one bridged edge. $Os_7C(CO)_{19}H_2$ may consist either of a pentagonal bipyramid of Os atoms with a body-centred C atom, or of a trigonal prism bridged on one square face, perhaps with a C atom in the centre of the prism.



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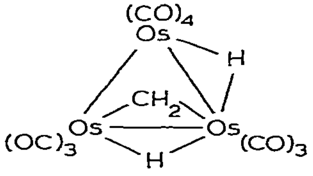

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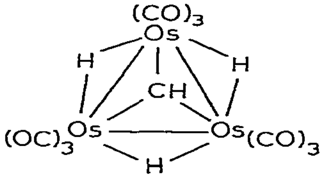
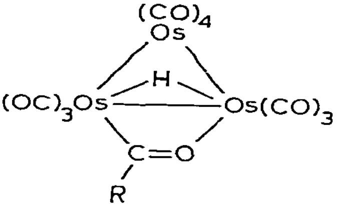


135

The structures of $Os_3(CO)_{10}H_2$, $Os_3(CO)_{10}H(SEt)$ and $Os_3(CO)_{10}(OMe)_2$ have been compared by X-ray crystallography (170). In these, the non-bridged metal-metal bond lengths are 2·81, 2·85 and 2·82Å, respectively. The distances between the bridged metal atoms were 2·67, 2·86 and 3·08Å, respectively, consistent, formally, with bond orders 2, 1 and 0.

When $Os_3(CO)_{10}H_2$ was methylated by one equivalent of diazomethane in ether, the $Os_3(CO)_{10}H(CH_3)$, 133, and $Os_3(CO)_{10}H_2(CH_2)$, 134, which readily interconverted, were formed (171). At low temperatures (−20°), this reaction afforded 133 only, but as the temperature was allowed to rise, 134 was also produced. In the reaction between a mixture of 133 and 134 with PMe_2Ph, only the former appeared to eliminate methane and form $Os_3(CO)_{10}(PMe_2Ph)_2$; there was no evidence for $Os_3(CO)_{10}(PMe_2Ph)H(CH_3)$. On heating 133 and 134 in xylene at 110°, $Os_3(CO)_9H_3(CH)$, 135, was produced.

When $Os_3(CO)_{12}$ was treated with RCHO, $Os_3(CO)_{10}H(COR)$, 136 (R = Pr^i, n-C_5H_{11}, n-C_6H_{13}, CH_2Ph, Ph), was formed (172), but with formaldehyde $Os_3(CO)_{10}H(OMe)$ was produced, perhaps via 136 (R = H) which could be readily decarbonylated to $Os_3(CO)_{10}H_2$, which also reacted with formaldehyde giving the hydrido-$\mu_2$methoxide. With acetaldehyde, however, $Os_3(CO)_{10}H_2$ afforded $Os_3(CO)_{10}H(OCOMe)$. In all of the μ-acyl species, ν(CO) never exceeded 1500cm^{-1}, and there was no nmr evidence for rapid exchange of the bridging RCO group between the two Os atoms. Carbonylation at 150° of 136 (R = Pr^i) afforded Pr^{i}CHO and $Os_3(CO)_{10}$. In an attempt to prepare 136 (R = Me) by treatment of $Os_3(CO)_{10}H_2$ with ketene, 137 (R = H) was obtained, and similar species where R = Me or Ph could be produced using the respective ketenes. On heating 137 (R = Me) in a sealed tube at 150°, 136 (R = Pr^i) was formed. There was no direct evidence for the thermal conversion of acyl into enolato ligands but 136 could afford decarbonylated products derived from 137, and vice versa. Thus, on heating 137 (R = H) in cyclohexane, traces of 136 (R = Me), $Os_3(CO)_9H_2(OCH{=}CH)$, 138 and 135 were formed. It was suggested that 138 was generated via H-atom transfer from the β-atom of the enolato ligand whereas 135 arose by decarbonylation of 136 (R = Me) to $Os_3(CO)_{10}H(Me)$ which, as was previously noted (171), can isomerise to $Os_3(CO)_{10}H_2(CH_2)$ and, ultimately, 135. Both 138 and 135 could also be obtained directly from 136 (R = Me), but 135 could not be obtained from 138 even on heating to 150°. Decarbonylation of 136 (R = n-C_5H_{11}, n-C_6H_{13} or Ph) afforded $Os_3(CO)_9H_2(OC_2HR')$ (R' = n-C_4H_9, n-C_5H_{11} or CH_2Ph), analogues of 138, but similar treatment of 136 (R = Ph) gave $Os_3(CO)_9H_2(C_6H_4)$. Decarbonylation of 137 (R = Ph) afforded $Os_3(CO)_9H(PhCC_6H_4)$, 139 which is similar to a known Ru complex (173).



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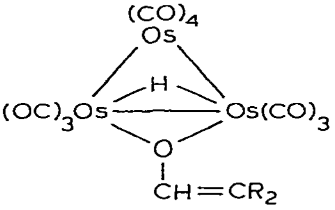

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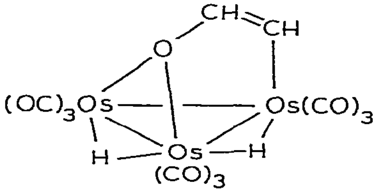

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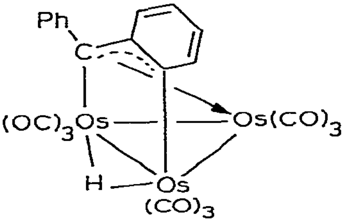

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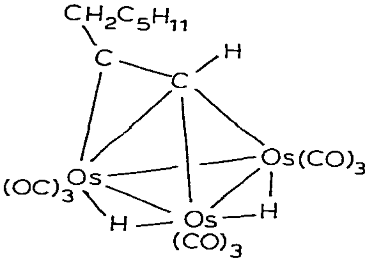

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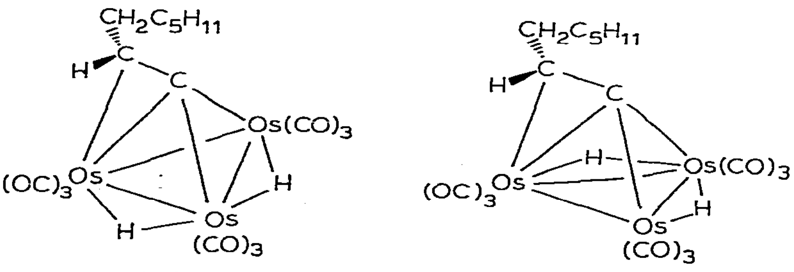


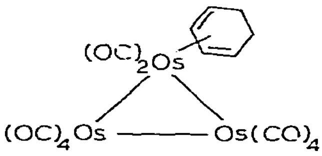
(a)

(b)

140

Reaction of $Os_3(CO)_{10}H_2$ with ethylene in cyclooctene under moderate pressures gave (174) the labile $Os_3(CO)_{10}(C_8H_{14})_2$ which, on heating in acetonitrile, could be converted into $Os_3(CO)_{10}(NCMe)_2$ which is also very reactive. On heating $Os_3(CO)_{10}(C_8H_{14})_2$ with an excess of the olefin, the known $Os_3(CO)_9H_2(C_8H_{12})$ was produced (175). On treatment of these labile species $Os_3(CO)_{10}L_2$ ($L = C_8H_{14}$ or MeCN) with tertiary phosphines or isonitriles L' (PPh_3, PPh_2Me, $PPhMe_2$, $P(OMe)_3$, CNMe or $CNCH_2Ph$), $Os_3(CO)_{10}L'_2$ was formed and, in some cases, two isomers of these compounds could be detected by nmr spectroscopy at low temperatures. By sequential adding of ligands, $Os_3(CO)_{10}\{P(OMe)_3\}\{P(p\text{-}MeC_6H_4)_3\}$ could be isolated. Reaction of $Os_3(CO)_{10}L_2$ with an excess of dienes (1,5-cyclooctadiene, norbornadiene or 1,5-hexadiene) afforded $Os_3(CO)_{10}$(diene) species which are only accessible by this route. With diphenylacetylene, $Os_3(CO)_{10}(C_2Ph_2)$ was produced, and other terminal acetylenes behaved similarly, giving species obtainable by other routes, but in this case in higher yields since the 'insertion' products $Os_3(CO)_{10}H$ (CH=CHR) were not formed. The cleavage of H–Y bonds can, however, be effected by $Os_3(CO)_{10}L_2$, so that with hydrogen under pressure $Os_3(CO)_{10}H_2$ was formed and α-olefins afforded $Os_3(CO)_{10}H(CH{=}CHR)$. By appropriate use of HY, the species $Os_3(CO)_{10}H(Y)$, Y = Cl, Br, OEt, NHPh, SPh and C_5H_4N, were isolated, and $Os_3(CO)_{10}L_2$ was also very useful in preparing ^{13}CO labelled species.

Reaction of $Os_3(CO)_{12}$ with $RR'C{=}CH_2$ (1-octene, propene, $PhMeC{=}CH_2$ or $MePr^iC{=}CH_2$) gave (176) the fluxional species $Os_3(CO)_9H_2(C_2RR')$. Two principal isomers of these species, 140 and 141, were detected, and 140 existed also in two isomeric forms, a and b. The formation of these species represented one of the first examples of competitive 1,1- and 1,2-elimination of hydrogen from olefins using $Os_3(CO)_{12}$.



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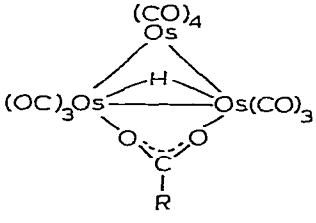

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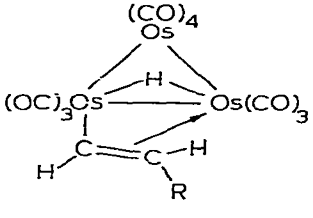

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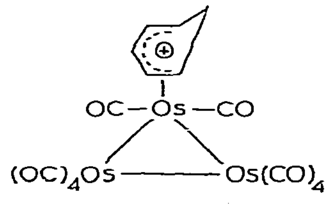

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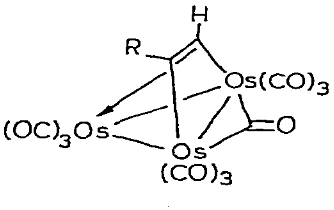

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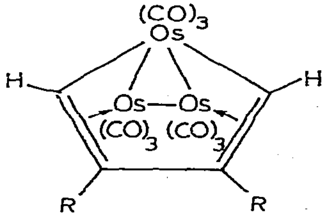
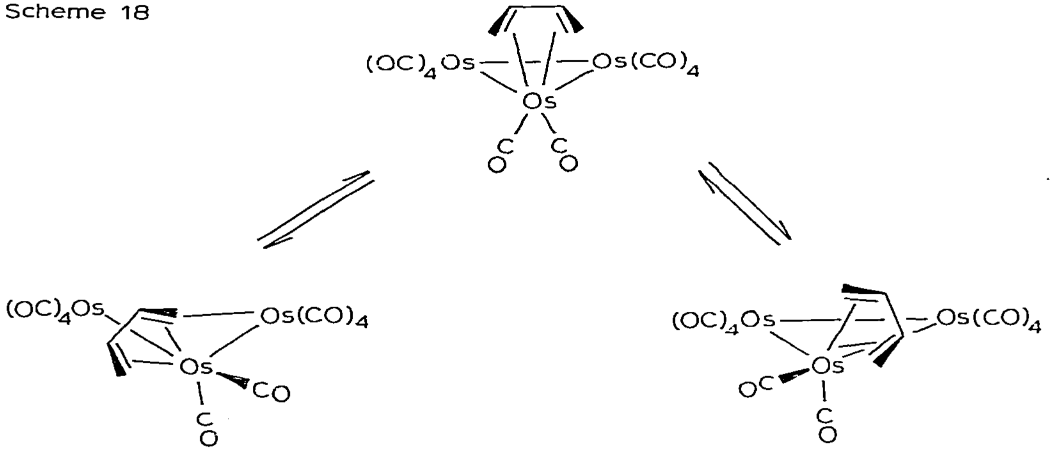


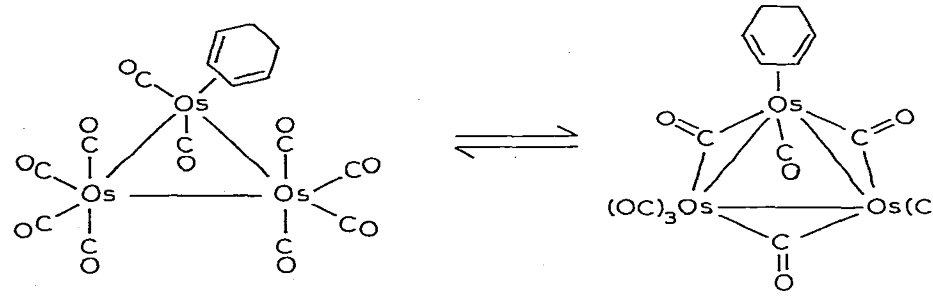
147

Treatment of $Os_3(CO)_{10}H_2$ with either 1,3- or 1,4-cyclohexadiene under moderate conditions afforded (177) the useful intermediate $Os_3(CO)_{10}(C_6H_8)$, 142. Like the species $Os_3(CO)_{10}L_2$ ($L = C_8H_{14}$ or NCMe) mentioned previously (174), 142 can function as the precursor of a wide variety of species $Os_3(CO)_{10}HY$ (Y = SR, R = H, Et or Pr^i; OR, R = H, Et, C_6H_{11} or Ph; Cl or Br; O_2CR, 143, R = H, Me, CF_3, Et, Ph, $p\text{-}ClC_6H_4$, $p\text{-}O_2NC_6H_4$ or CO_2Et) and $Os_3(CO)_{10}H(CH{:}CHR)$, 144 (R = H or Ph). With Ph_3C^+, the cyclohexadienyl cluster cation 145 could be obtained. With alkynes, 142 could be converted into 146, 147 and 148 (R = H or Ph). The cyclohexadiene complex is also stereochemically non-rigid, exhibiting (178) four distinct fluxional modes: (a) rocking of the diene above the Os_3 plane about one axial and two equatorial coordination sites on one Os atom (Scheme 18), (b) the scrambling of the C_6H_8 ligand around one Os atom generating a plane of symmetry orthogonal to that produced in process (a), (c) CO group exhange via exchange of equatorial groups as in Scheme 19, and (d) complete scrambling of all CO groups via a simple twist mechanism about individual metal atoms coupled with CO bridging. A VT ^{13}C nmr spectral study of $Os_3(CO)_{10}(C_7H_8)$ (C_7H_8 = norbornadiene) indicated (179) further that there could be restricted equilibration of the in-plane or equatorial CO groups, as indicated above in Scheme 19.

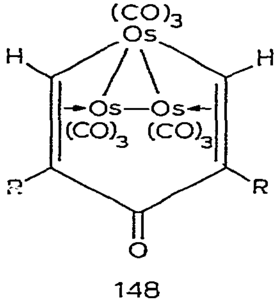
Scheme 18



Scheme 19



The reaction of $Fe_3(CO)_{12}$ with MeC_2H has afforded (180) many bi- and tri-nuclear carbonyl complexes, including $Fe_3(CO)_8(HC_2Me)_3$ (181) and $Fe_3(CO)_8(HC_2Me)_4$. This last compound, 149, has been reformulated as $Fe_3(CO)_8CEt\{C_5H_2Me_2(C_2H_3)\}$, on the basis of an X-ray crystallographic examination (182). The Fe_3C core is very similar to the Co_3C unit in $Co_3(CO)_9CY$ and the metal-metal bond lengths are 2·53 (1–2), 2·58 (1–3) and 2·52 (2–3), respectively. The molecule undergoes two fluxional processes, the first involving interchange of terminal CO groups perhaps via an intermediate having a bridging CO group between Fe(1) and Fe(3), and the second involving exchange of all CO groups. If these observations are correct, they represent one of the first examples of exchange of terminal before bridging CO groups.



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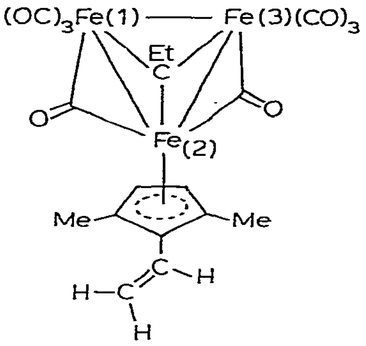

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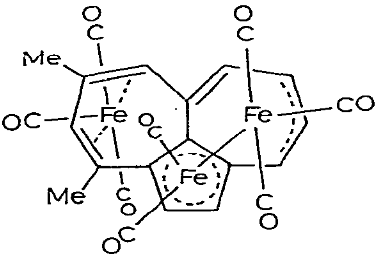
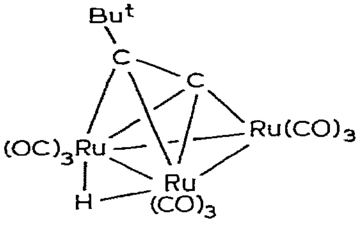


150

The reaction of 3,5-dimethylaceheptylene with $Fe_3(CO)_{12}$ afforded (183) the tri-iron complex 150. In this species, whose structure was established by X-ray methods, one $Fe(CO)_3$ group is attached to an η^3-allyl residue, another to an η^4-cis-dienoidal unit, and both $Fe(CO)_3$ groups are bonded to an $Fe(CO)_2$ group (Fe-Fe 2·79Å) which is itself bound to an η^5-C_5 ring.

A neutron diffraction analysis of the structure of $Ru_3(CO)_9H(C_2Bu^t)$, 151 established (184) the existence of a μ_2-H group, as had been previously suggested (185). The symmetrical bent Ru-H-Ru interaction was described as an open bond and not as a three-centre system.

The structure of $Os_3(CO)_{10}(C_2Ph_2)$, 152, obtained (186) directly from $Os_3(CO)_{12}$ and diphenylacetylene, has been determined (187) crystallographically. The metal-metal distances are 2·84 (1–2), 2·88 (1–3) and 2·71 (2–3), respectively and the trans-CO groups attached to the 'electron-rich' Os(1) atom appear to be semi-bridging with respect to Os(2) and Os(3). On the basis of ^{13}C nmr studies, it would seem that the related species $Os_3(CO)_{10}(C_2Et_2)$ (188) has the structure 153. Pyrolysis of 154 gave 155, whose geometry was determined crystallographically (189). The metal-metal bond distances in 155 are 2·82 (1–2), 2·89 (2–3) and 3·01 (1–3), respectively. The pyrolysis of two other isomers of $Os_3(CO)_9\{(EtC_2H)_2CO\}$ would also seem to involve hydrocarbon ring contraction.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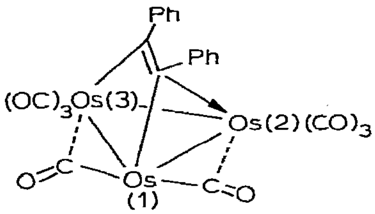
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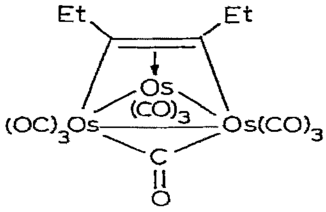
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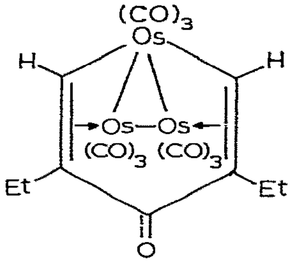
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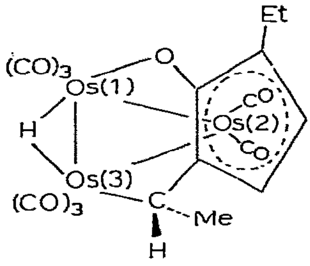
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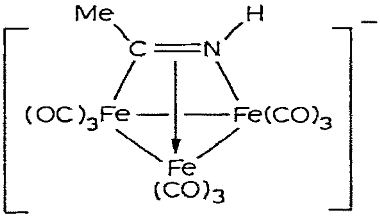
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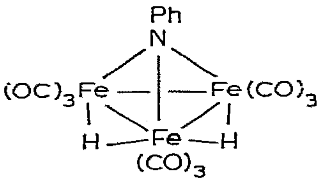
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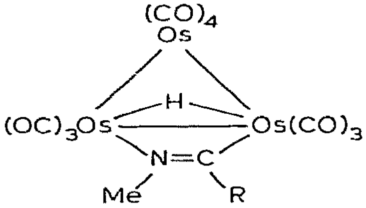
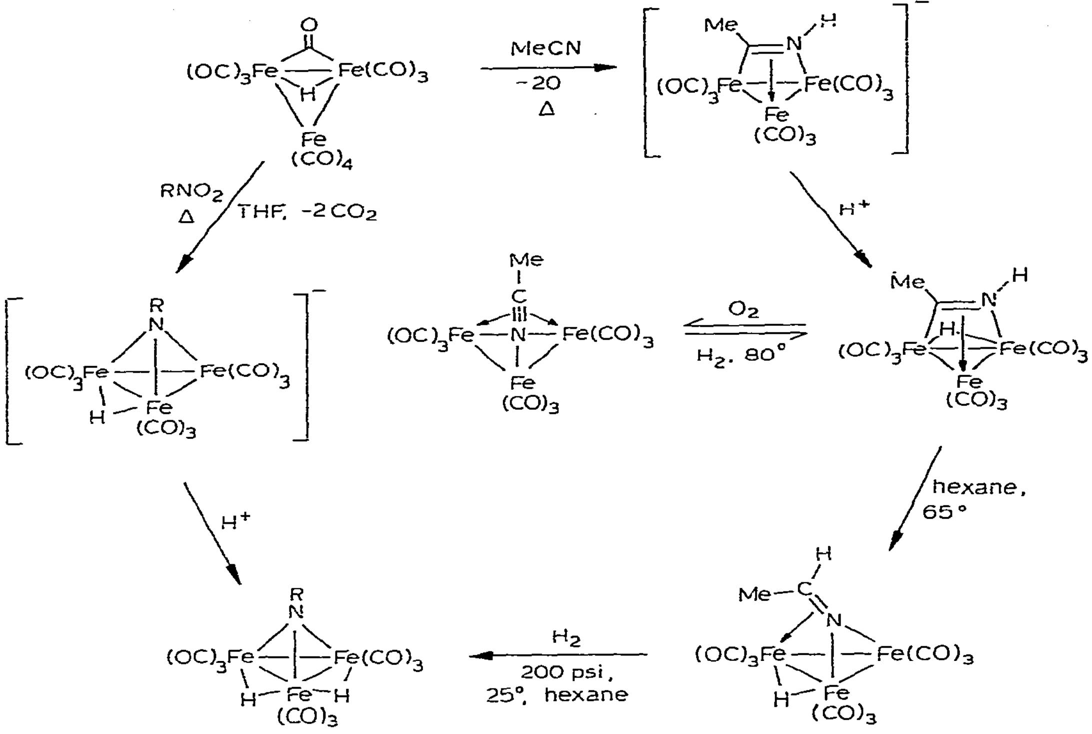

158

The reaction of $[Fe_2(CO)_8]^{2-}$ with $[W(CO)_5I]^-$ in acetonitrile adventitiously afforded (190) the tri-iron species $[Fe_3(CO)_9(NHCMe)]^-$, 156. The behaviour of this species with H^+, H_2 and air is summarised in Scheme 20. It was found that $[Fe_3(CO)_{11}H]^-$, the important precursor in these reactions, which is presumably formed in the reaction between $[Fe_2(CO)_8]^{2-}$ and the tungsten carbonylate, also reacted with $PhNO_2$, giving first $[Fe_3(CO)_9(\mu_2\text{-}H)(\mu_3\text{-}NPh)]^-$, which could be acidified affording $[Fe_3(CO)_9H_2(NPh)]$, 157. This last species readily decomposed releasing aniline. The general reaction between $[Fe_3(CO)_{11}H]^-$ and acetonitrile leading to the reduction of the C≡N bond would seem to indicate a competition between (a) Fe-H addition or nucleophilic attack by $[Fe_3(CO)_{11}H]^-$ on MeCN, followed by H^+ transfer from the metal to N, giving 156, and (b) nucleophilic cleavage by MeCN of $[Fe_3(CO)_{11}H]^-$ giving $[Fe(CO)_4H]^-$. It was thought that $[Fe(CO)_4H]^-$, $[Fe_2(CO)_8]^{2-}$ and $[Fe_2(CO)_8H]^-$ were not responsible for the formation of 156.

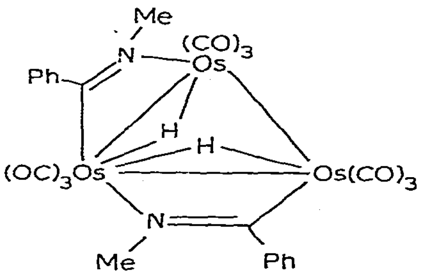
Reaction of $Os_3(CO)_{12}$ with PhCH:NMe gave (191) $Os_3(CO)_{10}H(PhC{=}NMe)$, 158 (R =

Scheme 20



(R = Et)

Ph), Os$_3$(CO)$_8$H$_2$ (PhC=NMe)$_2$, 159 and cis-Os(CO)$_2$(o-C$_6$H$_4$=NMe)$_2$, 160, a series of reactions which are reminiscent of the behaviour of pyridine with Os$_3$(CO)$_{12}$ (192). With PhCH$_2$NMe$_2$ under various conditions, Os$_3$(CO)$_{12}$ afforded 158 (R = Ph), Os$_3$(CO)$_{10}$H(C=NRR'), 161 (R = Me, R' = CH$_2$Ph), Os$_3$(CO)$_9$H(CH=NMe), 162, and 160, together with (PhCH$_2$)$_2$NMe. Trimethylamine reacted with Os$_3$(CO)$_{12}$ giving 161 (R = R' = Me), 162, Os$_3$(CO)$_{10}$H(CH=NMe), 158 (R = H) Os$_3$(CO)$_{10}$H(NH$_2$) and Os$_3$(CO)$_{10}$H(OH). The last two probably arose because of traces of ammonia and water as impurities in NMe$_3$.



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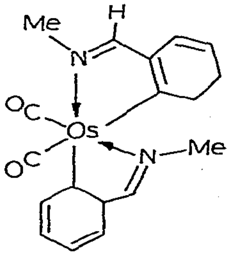

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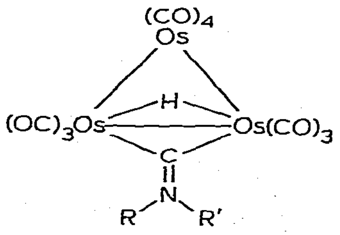

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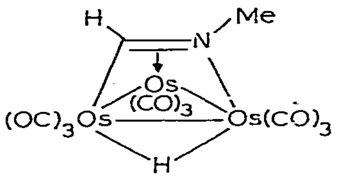

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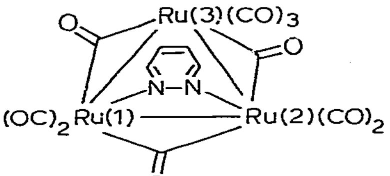
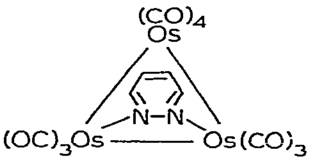


163

Treatment of $Ru_3(CO)_{12}$ with 1,2-diazine afforded $Ru_3(CO)_{10}(C_4H_4N_2)$, 163, whose structure was established crystallographically (193). The metal-metal bond lengths are 2·74 (1-2), and 2·86 (2-3; 1-3) respectively. The three CO bridges are slightly asymmetric and the molecule exhibits three modes of fluxionality which were detected by ^{13}C VT nmr spectroscopy. In the lowest temperature range, the molecule underwent equivalencing of the six equatorial CO groups, in the mid-temperature range it appeared that axial CO groups at Ru(1) and Ru(2) exchanged with the equatorial carbonyl ligands, and in the high temperature range, all CO groups scrambled over all sites. The exchange of equatorial CO groups is similar to that reported above in $Os_3(CO)_{10}(C_6H_8)$ (178) and $Os_3(CO)_{10}(C_7H_8)$ (179). Reaction of $Os_3(CO)_{12}$ with 1,2-diazine, in the presence of $Me_3NO(H_2O)_2$, likewise afforded $Os_3(CO)_{10}(C_4H_4N_2)$, 164, which contained only terminal CO groups (194). A ^{13}C VT nmr spectral study of this molecule revealed that it underwent two fluxional processes, the low energy- one involving probably the exchange of six equatorial and the two unique axial CO groups on the N-substituted Os atoms, and the high energy process requiring total CO-scrambling.



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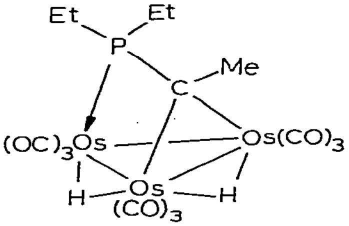

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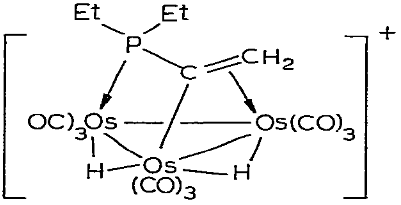

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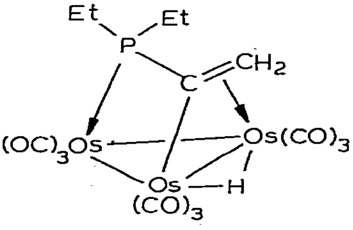

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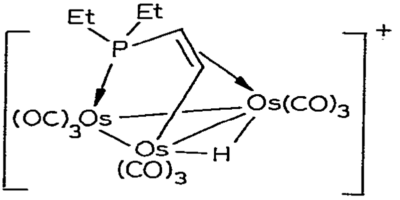

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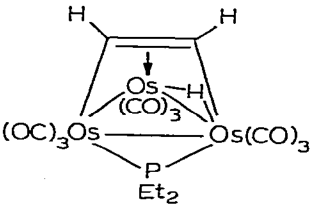

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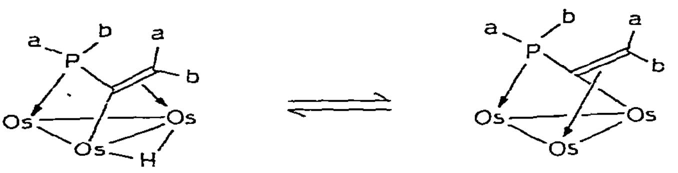
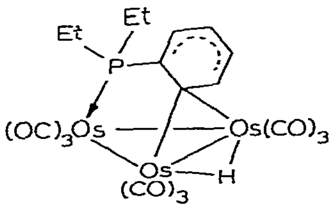
Scheme 21



Carbonyl group substitution occurred (195) when $Os_3(CO)_{12}$ was treated under mild conditions with PEt_3. The products were $Os_3(CO)_{12-x}(PEt_3)_x$ (x = 1-3). When $Os_3(CO)_{11}(PEt_3)$ was refluxed in nonane $Os_3(CO)_9H_2(MeCPEt_2)$, 165, was formed, and treatment of this with Ph_3C^+ gave 166. Deprotonation of the latter afforded $Os_3(CO)_9H(CH_2{=}CPEt_2)$, 167, which was fluxional, as shown in Scheme 21. Thermolysis of 167 gave $Os_3(CO)_9H(PEt_2)(C_2H_2)$, 168, possibly via 169. In refluxing nonane, $Os_3(CO)_{11}(PEt_2Ph)$ was thermolysed to $Os_3(CO)_9H(Et_2PC_6H_4)$, 170, $Os_3(CO)_9H(PEt_2)(C_6H_4)$, 171, analogous to 169, and $Os_3(CO)_9H(EtPCH{=}CH_2)$, 172. This work revealed that neither alkyl nor aryl phosphines can be used at temperatures above 100° to modify the steric and/or electronic properties of $Os_3(CO)_{12}$. The structure of the product obtained by reaction of $Os_3(CO)_{10}H(CH{=}CH_2)$ with PMe_2Ph, namely $Os_3(CO)_{10}H(CH_2CH_2PMe_2Ph)$, 173, was determined (196) by X-ray methods. The metal-metal bond distances were 2·80 (1-2) and 2·87Å (1-3, 2-3), respectively.

Treatment of $Na_2Fe(CO)_4$ with $PhAsCl_2$ gave $Fe_3(CO)_9(\mu_3\text{-}AsPh)_2$, 174, whose structure was established (197) by X-ray methods. The Fe(1)-Fe(2) and Fe(2)-Fe(3) bond distances (2·75-2·80Å) were commensurate with bond order 1, but Fe(2)-Fe(3) was 3·71Å and is a non-bonding distance. Reaction of $Na_2Fe(CO)_4$ with AsX_3



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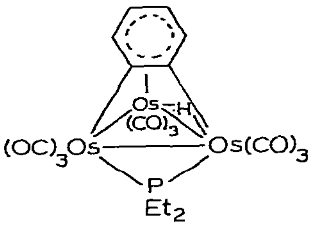

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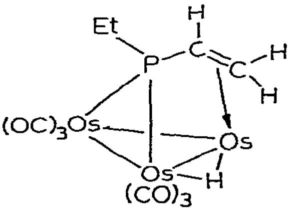

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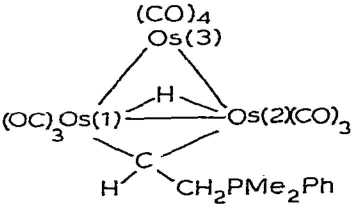

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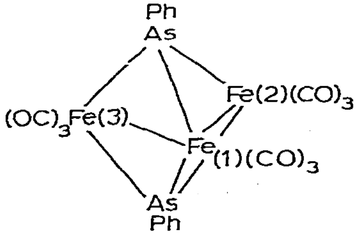

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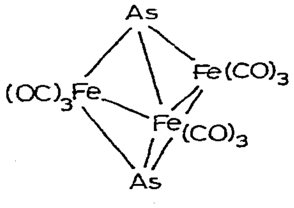

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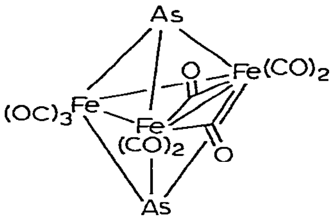

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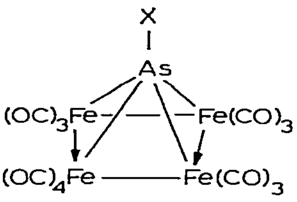

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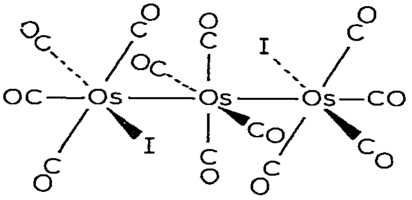


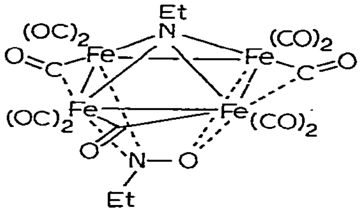
178

(X = Cl or Br) afforded (198) $Fe_3(CO)_9(\mu_3\text{-}As)_2$, which appears to exist in the equilibrium 175 $\rightleftharpoons$ 176, $Fe_4(CO)_{14}(\mu_4\text{-}AsX)$, 177, and $Fe_3(CO)_{12}$. The mass spectra, differential thermal analyses and thermograms of $Fe_2(CO)_6X_2$ and $Fe_3(CO)_9X'_2$ (X = S or Se; X' = S, Se or Te) have been obtained (199).

A ^{13}C nmr spectral study of intermolecular CO exchange with $Os_3(CO)_{10}X_2$ (X = Cl, Br, I, OEt) established (200) that stereospecific exchange of labelled CO occurred at the pseudo-equatorial sites on the X-bridged Os atoms. However, the labelled group could be distributed over the other sites on these two Os atoms by intramolecular exchange processes. The structure of $Os_3(CO)_{12}I_2$, 178, obtained by reaction of $Os_3(CO)_{12}$ with I_2 in the absence of light, was determined crystallographically (201). The I atoms occupy equatorial sites on a linear Os_3 chain (Os–Os 2·94Å) and are trans to each other. The equatorial CO groups on the terminal Os atoms are staggered with respect to, and lean towards, the central $Os(CO)_4$ group.

Polynuclear Species

The structure of $Fe_4(CO)_{11}(NEt)(ONEt)$, 179, obtained (202) from the reaction of $Fe_3(CO)_{12}$ with nitroethane, has been reported. The semi-bridged Fe–Fe distances are 2·48–2·49Å, while the other two metal-metal bond lengths are 2·53–2·55Å. The synthesis of $Fe_4(CO)_{14}AsX$ (X = halide) has been briefly reported (203).



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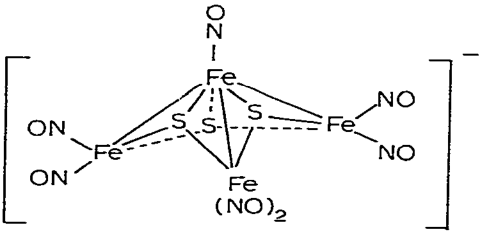

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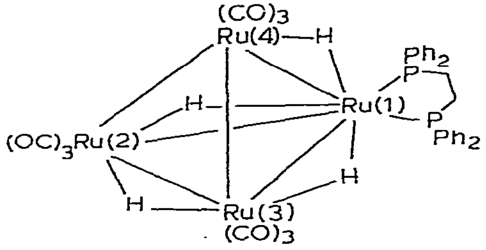
Sodium amalgam reduction of $Fe_4(NO)_4S_3$ has given (204) $[Fe_4(NO)_7(\mu_3\text{-}S)_3]^-$, 180, (Roussin's blacksalt) whose structure, as the $[AsPh_4]^+$ has been redetermined. The overall molecular geometry is identical to that of the previously reported (205) Cs^+ salt. (Fe(1)-(2) 2·71, (1)-(3) 2·71, and (1)-(4) 2·68Å, respectively.)

The nature of the isomerism reported in $Ru_4(CO)_{13}H_2$ and $Ru_4(CO)_{12}H_4$ has been reexamined (206). These hydrides could be obtained by reaction of $Ru_3(CO)_{12}$ with $NaBH_4$ or by carbonylation of methanolic or ethanolic solutions of $RuCl_3$ or $[Ru(\eta^6-C_6H_6)Cl_2]_2$. From a detailed spectral examination, no evidence for the so-called β-isomers could be obtained, so both hydrides exist only in the α-form. In the reaction between $Ru_3(CO)_{12}$ and $NaBH_4$, a number of products in addition to $Ru_4(CO)_{13}H_2$ and $Ru_4(CO)_{12}H_4$ were produced, and these included $Ru_3(CO)_9H_3(CMe)$, $Ru_3(CO)_9H_3(CH)$, $Ru_3(CO)_{10}H_2(CH_2)$, $Ru_3(CO)_{10}H_2(CHMe)$, $Ru_3(CO)_9H_2(C_2H_2)$ and $Ru_3(CO)_9H_2(C_2HMe)$. The hydrogenation of pentyne has been catalysed (207) by $Ru_4(CO)_{12}H_4$.

Reaction of $Ru_4(CO)_{12}H_4$ with $Ph_2PCH_2CH_2PPh_2$ (diphos) afforded (208) several products, including $Ru_4(CO)_{10}(diphos)H_4$ whose structure, 181, has been determined crystallographically. The intermetallic distances were Ru(1)-(2) and (1)-(3) 3·00, Ru(1)-(4) 2·95 and (2)-(3) 2·93Å. The non-hydride bridged distances, Ru(2)-(4) and (3)-(4) were 0·18Å shorter than the bridged bonds, being 2·79 and 2·80Å, respectively. The fluxional behaviour of this species has been investigated by VT nmr studies. The structure of $Ru_4(CO)_{12}(C_2Ph_2)$, 182, has been determined crystallographically (209). The metal-metal bonds varied from 2·71 to 2·85Å. VT nmr studies of this complex revealed that there was CO exchange on individual Ru atoms, but not between Ru atoms at temperatures lower than 373°K.



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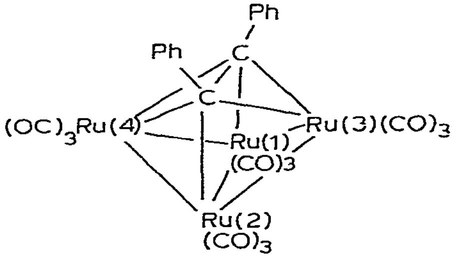

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The pyrolysis of mixtures of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ gave (210) a 1:2:2:1 mixture of $Ru_3(CO)_{12}$, $Ru_2Os(CO)_{12}$, $RuOs_2(CO)_{12}$ and $Os_3(CO)_{12}$, in contrast to only $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$ as had been reported earlier (211). However, reaction of $[Fe(CO)_4]^{2-}$ with $Ru_2Os(CO)_{12}$, followed by acidification of the carbonylate ion mixture so produced, gave $FeRu_2Os(CO)_{13}H_2$. Similar treatment of $RuOs_2(CO)_{12}$ afforded $FeRuOs_2(CO)_{13}H_2$. Reaction of other trimetal dodecacarbonyls with $[M(CO)_4]^{2-}$ (M = Fe, Ru or Os) are summarised in Table 2, and in some cases, adequate separation of these products proved impossible. The structures of $FeRu_2Os(CO)_{13}H_2$, 183a or b, $FeRuOs_2(CO)_{13}H_2$, 184, $FeRu_3(CO)_{13}H_2$, 185, and Fe_2Ru_2-

$(CO)_{13}H_2$, 186 were established by a combination of spectral methods. VT ^{13}C nmr spectral studies of $FeRu_3(CO)_{13}H_2$ and $FeRuOs_2(CO)_{13}H_2$ revealed (212) that these

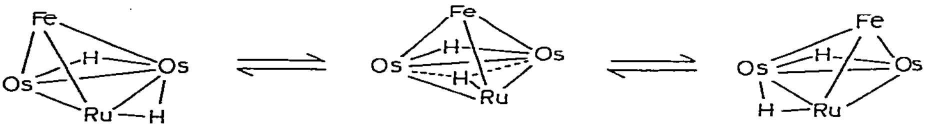
TABLE 2

Reaction of $[M(CO)_4]^{2-}$ with trimetal dodecacarbonyls

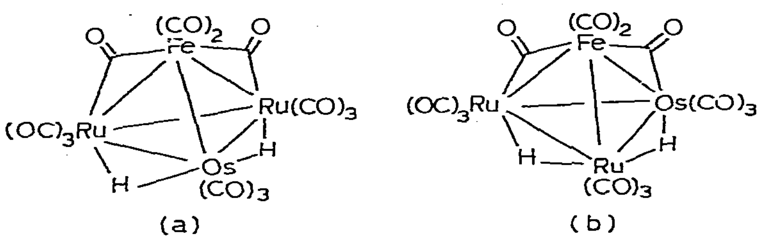
$M_3(CO)_{12}$	$M(CO)_4^{2-}$	Products
Fe_3	Ru	$Fe_2Ru_2(CO)_{13}H_2$, $FeRu_3(CO)_{13}H_2$*, $Fe_2Ru(CO)_{12}$*, $FeRu_2(CO)_{12}$, $Ru_4(CO)_{13}H_2$, $Ru_4(CO)_{12}H_4$, $Ru_3(CO)_{12}$
	Os	$Os_3(CO)_{12}$, $Fe_2Os(CO)_{12}$*, $Os_4(CO)_{13}H_3$, $Os_4(CO)_{12}H_4$
Fe_2Ru	Fe	$Fe_2Ru_2(CO)_{13}H_2$, $FeRu_3(CO)_{13}H_2$*, $Fe_2Ru(CO)_{12}$*, $FeRu_2(CO)_{12}$, $Ru_3(CO)_{12}$, $Ru_4(CO)_{12}H_4$
$FeRu_2$	Fe	$Fe_2Ru_2(CO)_{13}H_2$, $FeRu_3(CO)_{13}H_2$*, $Fe_2Ru(CO)_{13}H_2$*, $FeRu_2(CO)_{12}$, $Ru_3(CO)_{12}$, $Ru_4(CO)_{12}H_4$
Ru_3	Fe	$FeRu_3(CO)_{13}H_2$, $Ru_4(CO)_{13}H_2$*, $Ru_4(CO)_{12}H_2$
	Os	$RuOs_3(CO)_{13}H_2$, $Ru_2Os_2(CO)_{13}H_2$*, $Ru_3Os(CO)_{13}H_2$*, unidentified product
Ru_2Os	Fe	$FeRu_2Os(CO)_{13}H_2$, $Fe_2Os(CO)_{12}$*, $Ru_4(CO)_{12}H_4$, unidentified product
$RuOs_2$	Fe	$FeRuOs_2(CO)_{13}H_2$, $Fe_2Os(CO)_{12}$*, $Ru_4(CO)_{12}H_4$, unidentified product
Os_3	Fe	$FeOs_3(CO)_{13}H_2$, $Os_3(CO)_{10}H_2$*, $Fe_2Os(CO)_{12}$
	Ru	$Ru_4(CO)_{12}H_4$, $Ru_3Os(CO)_{13}H_2$, $Ru_2Os_2(CO)_{13}H_2$*, $RuOs_3(CO)_{13}H_2$, $Os_4(CO)_{12}H_4$*

species exhibited three fluxional modes: low temperature bridge-terminal CO-exchange localised at Fe, higher temperature CO exchange between Fe and two Ru atoms as the same plane in $FeRu_3(CO)_{12}H_2$ (185), and, at the highest temperature, general CO scrambling. There is evidence that the general CO scrambling is assisted by intermetallic rearrangement, as shown for 183 in Scheme 22.

Scheme 22



The structure of the previously reported (213) cluster $Os_3Re(CO)_{15}H$, 187, has been determined crystallographically (214). The four metal atoms form a planar triangulated rhombus, in which the Os-Re distances vary from 2·94 to 2·96Å.


(a) (b)

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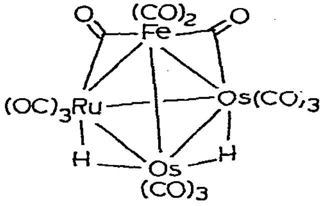
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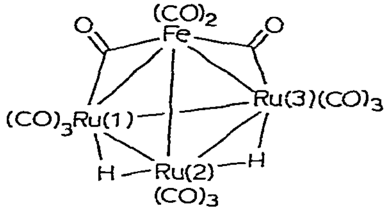
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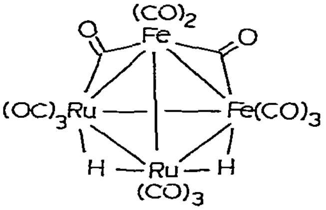
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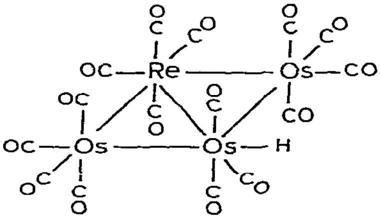
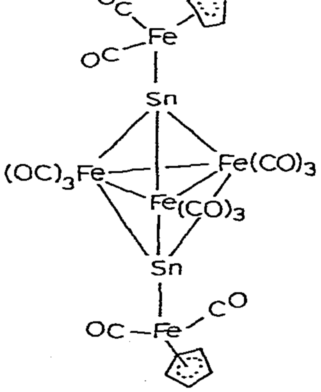

187

Declusterification of $FeCo_3(CO)_{12}H$ was achieved (215) photochemically, giving $Co_4(CO)_{12}$ and unidentified products. Similar treatment of $FeCo_3(CO)_{10}(PPh_3)_2$ afforded $Co_2(CO)_6(PPh_3)_2$. Thermal decomposition of $[Fe(CO)_4Sn(C_5H_5)_2]_2$ afforded (216) $\{Fe(\eta^5-C_5H_5)(CO)_2\}_2Sn_2Fe_3(CO)_9$, 188, whose structure was established by X-ray methods. The Fe-Fe distances are 2·79Å, and bromination of the cluster afforded $Fe(\eta^5-C_5H_5)(CO)_2Br$ and $SnBr_4$. Treatment of $Ni(PPh_3)_2X_2$ or $Ni(NO)(PPh_3)_2X$ (X = Cl, Br or I) with $Na[Fe(CO)_3(NO)]$ afforded (217) the mixed metal species $Ni(NO)(PPh_3)_2Fe(CO)_3(NO)$ which decomposed giving $Ni(CO)_2(PPh_3)_2$, FeO, N_2O and CO. Similar treatment of these metal salts with $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ gave only $Ni(CO)_2(PPh_3)_2$ and possibly some $[Fe(\eta^5-C_5H_5)(NO)]_2$. It was suggested that migration of ligands between metals might follow an intermolecular pathway for PPh_3,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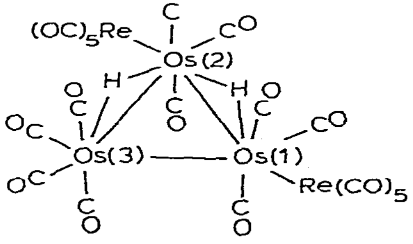
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but an intramolecular route in a bimetallic intermediate for CO and NO. Reaction of $Fe(CO)_2(pyr)_2(HgCl)_2$ with $Pt(PPh_3)_3$ afforded (218) at low temperature, $ClHgFe(pyr)_2(CO)_2HgPt(PPh_3)_2Cl$. As the temperature was raised, progressive formation of $ClHgFe(CO)_2(pyr)_2Pt(PPh_3)_2Cl$, $Cl(PPh_3)_2PtHgFe(CO)_2(pyr)_2Pt(PPh_3)_2Cl$ and, finally, $Fe(CO)_2(pyr)_2[Pt(PPh_3)_2Cl]_2$, was observed.

Treatment of $Os_3(CO)_{10}(C_8H_{14})_2$ with an excess of $Re(CO)_5H$ gave (219) a high yield of $Re_2Os_3(CO)_{20}H_2$, <u>189</u>. The structure of <u>189</u> was establihsed by X-ray techniques, and the Os–Os distances varied from 2.88 (non-bridged) to 3.08Å (H-bridged), while the Os–Re bond lengths were 2.95–2.98Å. Treatment of $Os_3(CO)_{12}$ with Me_3NO followed by addition of an excess of $Re(CO)_5H$ gave $ReOs_3(CO)_{16}H$, <u>190</u>, which further reacted with Me_3NO in acetonitrile giving $ReOs_3(CO)_{15}H$, also obtainable directly from $Os_3(CO)_{10}(NCME)_2$, Me_3NO and $Re(CO)_5H$. Reaction of $Re_2Os_3(CO)_{20}H_2$ with Me_3NO in acetonitrile provided, $Re_2Os_3(CO)_{19}H_2$.

Pyrolysis of $Os_3(CO)_{12}$ in a sealed tube afforded (220), inter alia, $Os_7(CO)_{21}$ whose structure was determined crystallographically (221). The metal framework can be described as a fairly regular capped octahedron with average Os–Os distances of 2.86Å; all CO groups are terminal. Extended Hückel MO calculations have been made on $Os_6(CO)_{18}$ and $Os_7(CO)_{21}$ (222).

METAL-CARBON σ-BONDED SPECIES

Metal Alkyls and Acyls

Thermolysis of a mixture of cis-$Os(CO)_4D(CH_3)$ and $Os(CO)_4H(CD_3)$ gave (223) substantial quantities of CD_4, indicating a binuclear reductive elimination pathway for the formation of methane. When $Os(CO)_4H(CH_3)$ was decomposed in the presence of CD_4, only CH_4 and CD_4 could be detected in the gaseous products. Rate studies of the reaction

$$2\ Os(CO)_4H(CH_3) \longrightarrow CH_4 + HOs(CO)_4Os(CO)_4(CH_3)$$

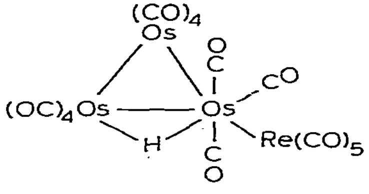
revealed that the rate of disappearance of $Os(CO)_4H(CH_3)$ was first order in that compound and that it appeared that dissociation of CO was not the rate-determining step (when the reaction was carried out in the presence of ^{13}CO, no incorporation of the labelled molecule was observed in the final organometallic product). Treatment of $Os(CO)_4H(CH_3)$ with PEt_3 gave $Os(CO)_4(PEt_3)$ and CH_4 but similar treatment of a mixture of $Os(CO)_4D(CH_3)$ and $Os(CO)_4H(CD_3)$ gave only CD_3H and CH_3D, and no CD_4, indicating that simple intramolecular reductive-elimination was facilitated by an incoming nucleophile. A possible mechanism seems to be:

$$Os(CO)_4H(CH_3) \longrightarrow A \qquad \text{(rate determining step)}$$
$$A + Os(CO)_4H(CH_3) \longrightarrow HOs(CO)_4Os(CO)_4CH_3 + CH_4 \qquad \text{(fast)}$$
$$A + PEt_3 \longrightarrow Os(CO)_4(PEt_3) + CH_4 \qquad \text{(fast)}$$

It would seem that A, which is not a CO-dissociation product, might be the five-coordinate and as yet undetected acyl product, $Os(CO)_3H(COCH_3)$.

When a mixture of cis-$Os(CO)_4(CH_3)_2$ and cis-$Os(CO)_4(CD_3)_2$ was thermally decomposed (224), the evolved methane consisted of CH_4, CH_3D, CH_2D_2, CHD_3 and CD_4. The presence of CH_2D_2 suggested that CH_4 or CD_4 was attacked during the decomposition process. When $Os(CO)_4(CD_3)_2$ was decomposed in the presence of one equivalent of CH_4, or $Os(CO)_4(CH_3)_2$ was similarly treated in the presence of CD_4, CHD_3 was detected, and these observations indicated that methyl radicals were involved in the decomposition pathway. A kinetic isotope effect was observed in rate studies of the decomposition of $Os(CO)_4(CD_3)_2$ in various solvents, and this confirmed the likely involvement of a radical process. When $Os(CO)_4(CH_3)_2$ was thermolysed in the presence of PPh_3, acetone was produced. These reactions contrast with the binuclear decomposition pathway observed for $Os(CO)_4H_2$ (225) and $Os(CO)_4H(CH_3)$ (223) and it has been suggested that binuclear elimination can only occur when hydride ligands are present or available.

By treatment of $Li_2[FePc].5\cdot5THF$ (Pc = phthalocyaninato) with alkyl or aryl halides, or addition of LiR to Fe(II) or Fe(III) phthalocyaninato complexes, the species $Li[FeR(Pc)]_xTHF$ (R = Me, CH=CHPh, CH_2Ph or Ph), $Li[Fe\{(CH_2)_4Br\}(Pc)].LiBr.8THF$, $Li_2[(Pc)Fe(CH_2)_4Fe(Pc)].10THF$, $Li[Fe(C_2Ph)(Pc)(pyr)].4THF$, and $Li_2[Fe(C_2Ph)_2(Pc)]7THF$, have been prepared (226).



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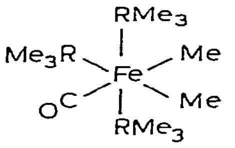

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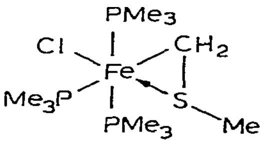


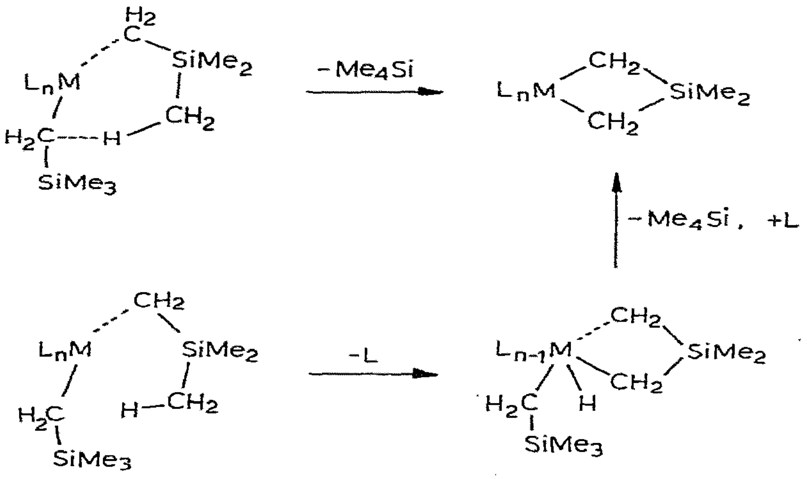
192

Addition of methyl bromide or iodide to an equilibrium mixture of $Fe(PMe_3)_4$ and $Fe(PMe_3)_3H(CH_2PMe_2)$ in solution gave $Fe(PMe_3)_4MeX$ (X = Br or I) (227). This species (X = Cl or Br), together with $Fe(PMe_3)_4Me_2$, could also be prepared by treatment of $Fe(PMe_3)_2X_2$ with LiMe and PMe_3, and reaction of the dimethyl with CO, $P(OMe)_3$ and HX afforded respectively $Fe(CO)(PMe_3)_3Me_2$, 191, cis-$Fe(CO)(PMe_3)_2\{P(OMe)_3\}Me_2$ and $[Fe(PMe_3)\ X_2]_n$ (X = Cl, Br, I, OH or OMe). When "$Fe(PMe_3)_4$" was treated with $MeSCH_2Cl$, or $Fe(PMe_3)_2Cl_2$ with $LiCH_2SMe$ and PMe_3, $Fe(PMe_3)_3Cl(CH_2SMe)$, 192, was formed.

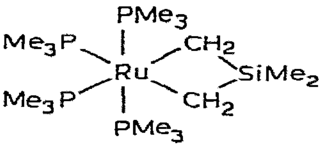
Cyclohexene inserted (228) into the Fe-H bond of $Fe(PEtPh_2)_3(N_2)H_2$ in solution giving $Fe(PEtPh_2)_2H(C_6H_{11})$(solvent), and reduction of $Fe(acac)_3$ with $Al(CH_2Ph)_3$ in ether in the presence of PPh_3 afforded (229) $Fe(PPh_3)_3(OEt_2)_2(CH_2Ph)$. The structure of $[Fe(acac)_2]_4$ has been determined crystallographically (230). The terminal Fe atoms of the tetrameric chain are coordinated by six acetylacetonato O atoms in a markedly distorted octahedral geometry. These FeO_6 groups are joined to the inner Fe atoms via three Fe–O–Fe bridges, but the inner metal atoms are coordinated by only five O atoms. The sixth coordination site is filled by C atoms of adjacent acac ligands, although the Fe–C interaction is rather weak and the bond is quite long (2·79Å).

Reaction of $Ru_2(OCOMe)_4Cl$ with MgR_2 (R = Me or CH_2SiMe_3) at 0° in the presence of PMe_3 gave (231) cis-$Ru(PMe_3)_4Me_2$ and $Ru(PMe_3)_4\{(CH_2)_2SiMe_2\}$, 193. The formation of the latter may occur by loss of a γ-hydrogen atom either by direct elimination of $SiMe_4$ or by intermediate hydride formation via oxidative addition to the metal followed by reductive elimination of $SiMe_4$ (Scheme 23). Also obtained in the same reaction, but in very low yield, was the μ_2-methylene complex $Ru_2(PMe_3)_6(\mu_2\text{-}CH_2)_3$, 194. This species could be produced (232) in higher yield by reaction of $[Ru_3O(OCOMe)(H_2O)_3][OCOMe]$ with $MgMe_2$ and PMe_3, and its structure has been confirmed crystallographically. The formation of the μ-CH_2 groups was thought to occur by transfer of H from a Ru–CH_3 group in an intermediate.

Scheme 23



By slow addition of iodine to $Fe(CO)_5$ in $(CF_3CO)_2O$, $Fe(CO)_4I(COCF_3)$ was produced (233). Treatment of $Na_2Fe(CO)_4$ with $CH_2{=}C{=}CHCH_2CH_2Br$ gave (234) the carbonylate ion $[Fe(CO)_4CH_2CH_2CH{=}C{=}CH_2]^-$ which rearranged via 195 to 196 and on treatment with acid released 2-methyl-cyclopent-2-ene. However, alkylation of $Na_2Fe(CO)_4$, using RX (R = Et, Pr^n, Bu^n, n-C_5H_{11} or n-C_6H_{13}, X = Br or I),



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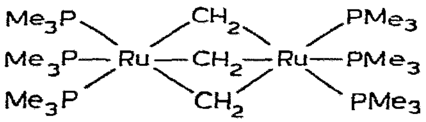

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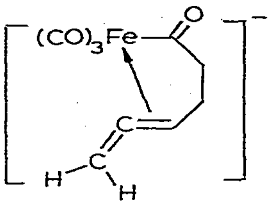

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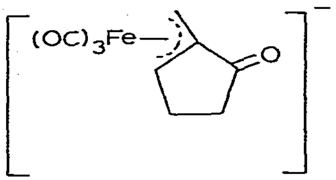

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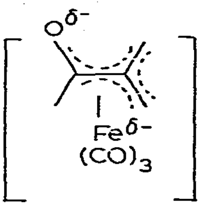

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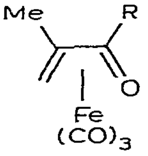

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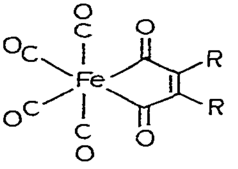


199

followed by treatment of $[Fe(CO)_4R]^-$ in situ with allene, gave 197 which, on acidification, afforded the stable 198. The hydrocarbon ligand could be released by treatment of 198 with Me_3NO.

The structures of 3-cyclopentene-2,5-dienetetracarbonyliron, 199 (R = H), and the related species 199 (R = cyclopropyl) have been determined crystallographically (235).

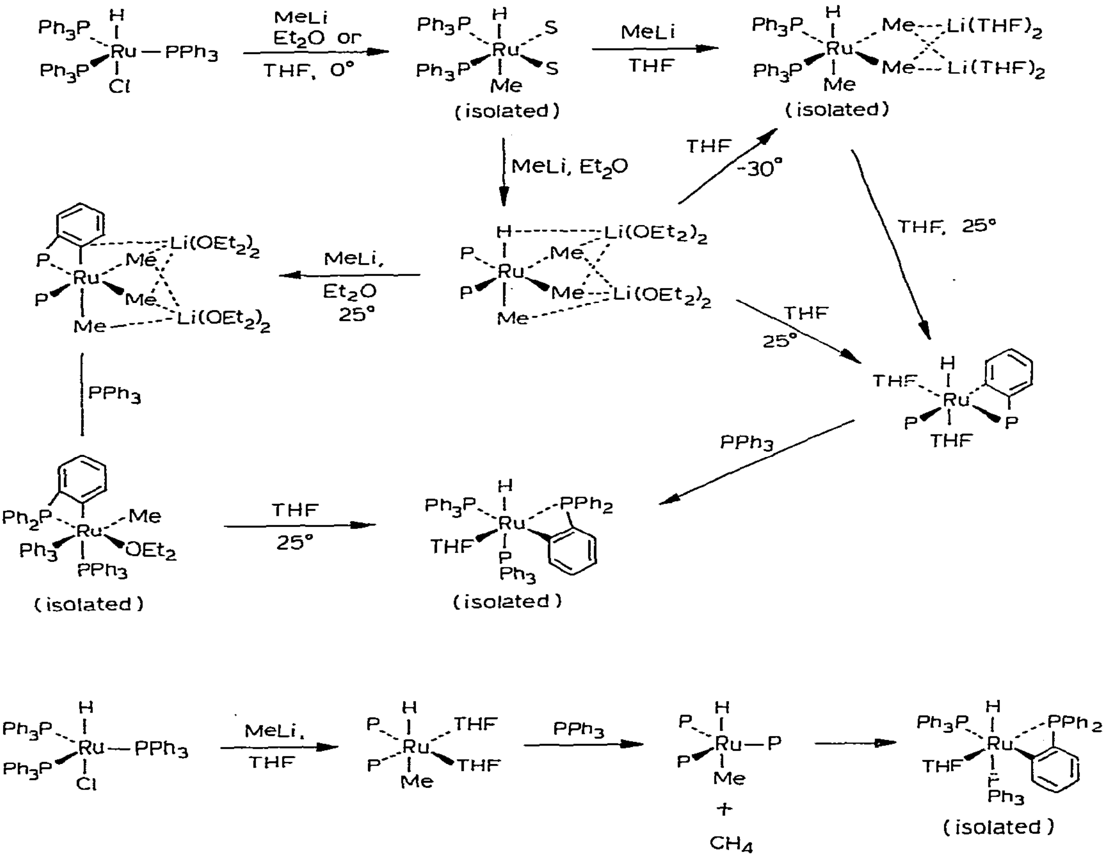
Aryl derivatives and o-metalated species

Treatment of $FeCl_2$ with an excess of lithium phenyl afforded $Li_2[FePh_4]$ (236). When $FeCl_3$ was reduced (237) by an excess of hydrogen in the presence of MgBrPh, between 3·5 and 4·2 moles of hydrogen were absorbed per mole of Fe. On extraction with THF, the species $FeH_4Mg_4X_4(THF)_8$ (X = Br and Cl) could be isolated which decomposed on heating yielding THF and/or hydrogen. On hydrolysis, only metallic iron, MgX_2 and H_2 could be detected in the products.

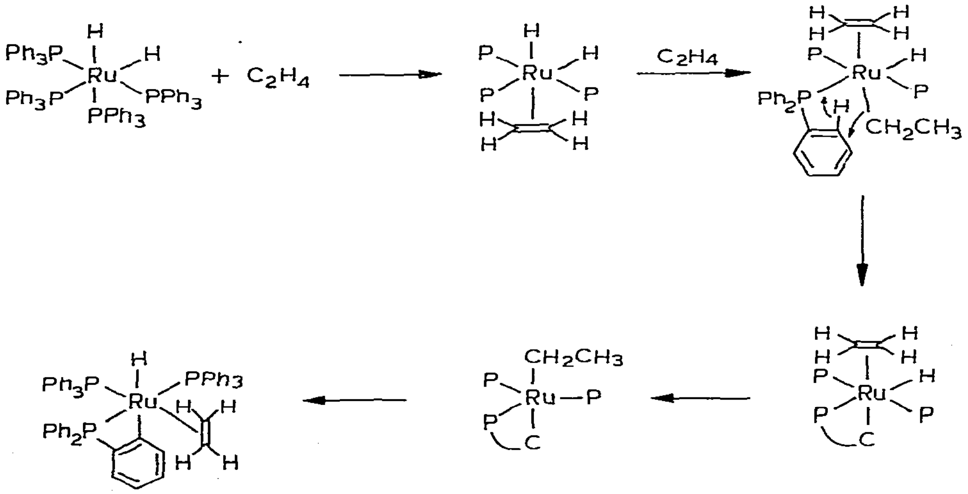
Reaction of $Ru(PPh_3)_3HCl$ with an excess of LiR (R = Me or CH_2SiMe_3) in ether or THF afforded (238) the air and moisture-sensitive $Ru(PPh_3)_2(C_6H_4PPh_2)H(S)$ (S = Et_2O or THF). Slow recrystallation of this product from THF gave $Ru(PPh_3)_3(THF)H_2$, but on treatment with water, $Ru(PPh_3)_2(H_2O)H(OH)$ was isolated. The formation of $Ru(PPh_3)_2(C_6H_4PPh_2)H(S)$, which contains o-metalated PPh_3, and could occur by two alternative routes, is shown in Scheme 24. Reaction of $Ru(PPh_3)_3HCl$ with $AlMe_3$ afforded some $Ru(PPh_3)_4H_2$, but with $ZnMe_2$ and $MgMe_2$, compounds containing Zn and Mg could be isolated. The species derived from dimethylzinc analysed perhaps as a 1:1 cocrystallising mixture of $Ru(PPh_3)_2(C_6H_4PPh_2)H(ZnMe_2)$ and $Ru(PPh_3)_2(C_6H_4PPh_2)H(ZnMeCl)$ or the dimer 200, and the magnesium-containing species could be analogous, viz. 201.

The reactions of $Ru(PPh_3)_4H_2$ with ethylene, which have been reported (239) as giving $Ru(PPh_3)_3(C_2H_4)$, have been reinvestigated (240). In fact, this reaction

Scheme 24

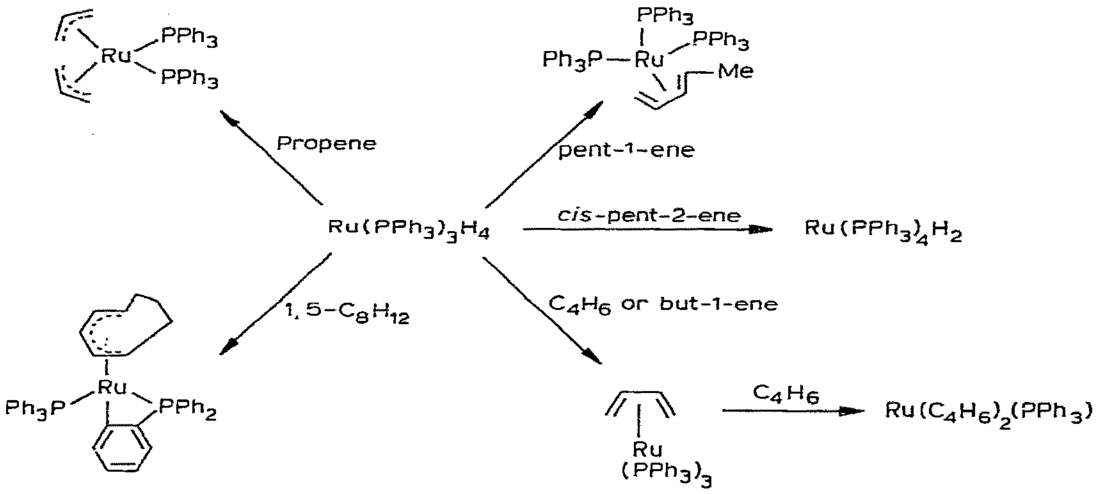


Scheme 25

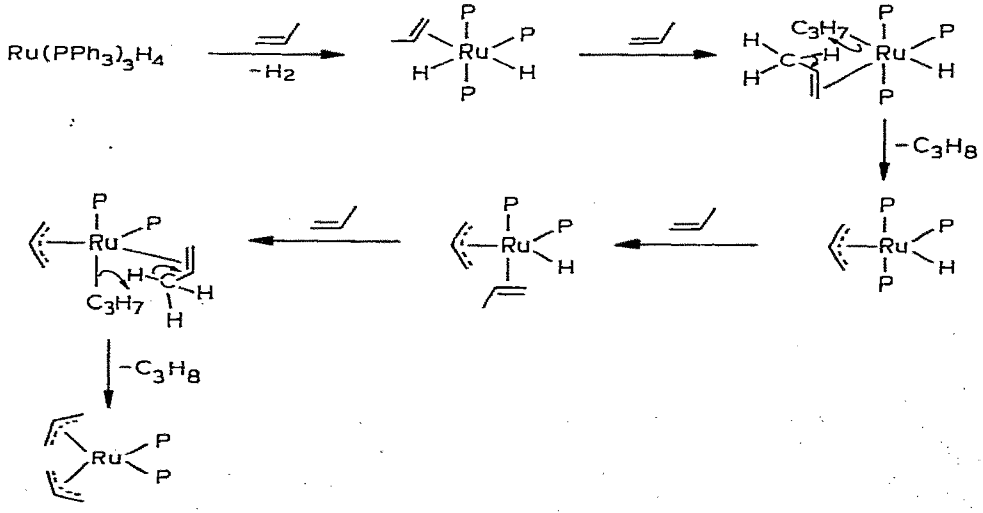


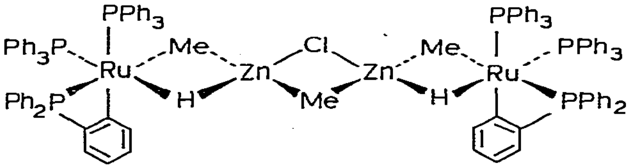
afforded $Ru(PPh_3)_2(C_2H_4)(C_6H_4PPh_2)H$, 202, a reaction which may occur according to Scheme 25 (the two isomers of 202 were detected). The species 202 could also be prepared by reacting $Ru(PPh_3)_2(C_6H_4PPh_2)(OEt_2)H$ or $Ru(PPh_3)_3H_4$ with ethylene. Other reactions of $Ru(PPh_3)_3H_4$ with certain olefins are summarised in Scheme 26; there was no detectable reaction with isobutylene or cyclohexene. It may be noted that the reactions with pentenes had previously been reported (241) to give $Ru(PPh_3)_3(C_5H_{10})$, but this must now be discounted. The reaction between $Ru(PPh_3)_3H_4$ and propene, which gave $Ru(\eta^3-C_3H_5)_2(PPh_3)_2$, may be envisaged as occurring as shown in Scheme 27. Reaction of $Ru(PPh_3)_4H_2$ with benzophenone afforded $Ru(PPh_3)_2\{C_6H_4C(:O)Ph\}H$, 203, but the dihydride hydrogenated enolis-

Scheme 26



Scheme 27





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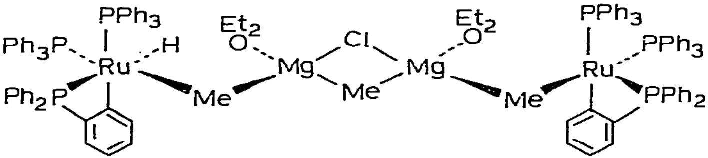

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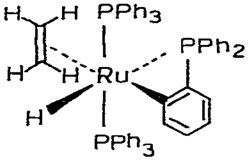

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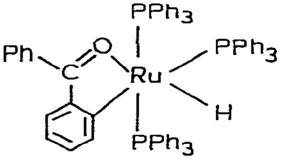

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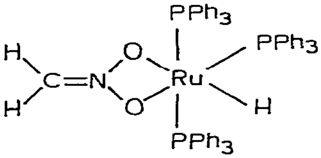

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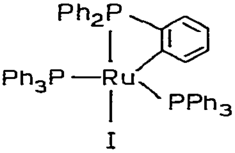
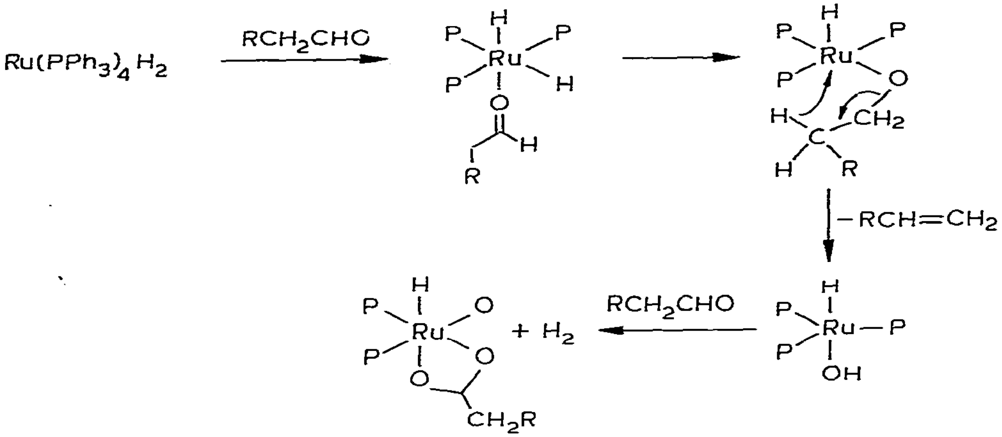


205

able ketones, producing the corresponding secondary alcohols, and also forming $Ru(CO)(PPh_3)_3H_2$. With hexaldehyde and propionaldehyde, however, the species $Ru(PPh_3)_3H(O_2CCH_2R)$ and some $Ru(CO)(PPh_3)_2H_2$ (see Scheme 28), in contrast to previous reports (242). $Ru(PPh_3)_2(C_6H_4PPh_2)(OEt_2)H$ reacted with water in THF giving $Ru(PPh_3)_2(OH_2)H(OH)$ and with methanol giving either $Ru(CO)(PPh_3)_3H_2$ or, if the reaction was carried out in ether, a mixture of this with $Ru(PPh_3)_4H_2$ and $Ru(CO)(PPh_3)_2(MeOH)H_2$. With an excess of phenol, $Ru(PPh_3)_2(C_6H_4PPh_2)(OEt_2)H_2$ gave $Ru(PPh_3)_2H(OPh)\cdot3PhOH$ and with nitromethane both the hydrido etherate and $Ru(PPh_3)_4H_2$ afforded $Ru(PPh_3)_3H(CH_2NO_2)$, probably 204. $Ru(PPh_3)_2(C_6H_4PPh_2)$-$(OEt_2)H$ reacted with CO giving $Ru(CO)_3(PPh_3)_2$, with N_2 giving $Ru(PPh_3)_2(C_6H_4PPh_2)$-$(N_2)H$ and with MeI giving, probably, $Ru(PPh_3)_2(C_6H_4PPh_2)I$, 205.

Reaction of $M(CO)(PPh_3)_3HCl$ (M = Ru or Os) with $Hg(C_6H_4Me)_2$ afforded (243) the square pyramidal complexes $M(CO)(PPh_3)_2Cl(C_6H_4Me)$ (apical tolyl group). With CO this was converted to $M(CO)_2(PPh_3)_2Cl(C_6H_4Me)$ and there was ir spectral

Scheme 28



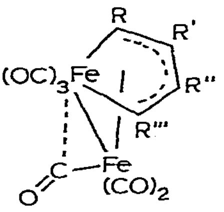
evidence in solution for the equilibrium

$$Ru(CO)_2(PPh_3)_2ClR \rightleftharpoons Ru(CO)(PPh_3)_2Cl\{C(:O)R\}$$

the acyl ligand possibly being dihapto .

Ferracyclopentadiene Complexes

From a cocondensation of iron atoms with thiophenes, followed by warming of the product under a CO atmosphere, the complexes 206 (R_1 = R^{111} = H or Me; R^{1} = R^{11} = H; R = H, R^{111} = Me; R^{1} = R^{11} = H) were obtained (244) from a ^{13}C VT nmr spectral study of these species which was established that while the CO groups attached to the ferracyclopentadienyl iron atom were stereochemically rigid, those on the η^4-bound $Fe(CO)_3$ group were fluxional. From the reaction between thiophenes and $Fe_3(CO)_{12}$, similar ferracyclopentadienyl complexes, 206 (R = Me; R^{1} = R^{11} = R^{111} = H; R = R^{11} = R^{111} = H, R^{1} = Me) could be obtained (245) together with $Fe_2(CO)_6(MeC_6H_3S)$, 207, the structure of which was determined crystallographically (Fe-Fe 2.55Å).



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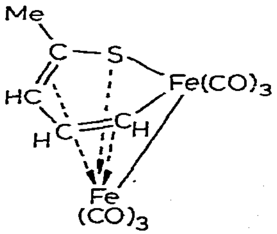

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MONOALKENE COMPLEXES

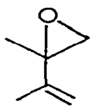
IR spectral studies have been made (246) of a series of olefin complexes Fe-$(CO)_4$(alkene) (alkene = C_2H_4, cis- and trans-$C_2H_2X_2$ (X = Cl or Br), 1,1-$C_2H_2Cl_2$, C_2HCl_3, C_2H_3X (X = Cl, Br, CN or CO_2H), maleic anhydride, fumaric acid, vinylene-carbonate, acenaphthylene, and divinylsulphone). It was concluded that the olefinic bond had a bond order between 1·25 and 1·5, depending on the nature of the substituents.

Reaction of $Fe_2(CO)_9$ with cinnamic acids gave $Fe(CO)_4(\eta^2\text{-}XC_6H_4CH = CHCO_2H)$ (X = 4-Me, -OMe, -Cl or H; 3-Cl, -OMe) (247). From spectroscopically measured pK_a values, it was established that the $Fe(CO)_4$ group was electron-releasing. Treatment of $Fe(CO)_4(\eta^2\text{-}CH_2 = CHR)$ (R = H or CO_2Me) with $Na[R^1C(CO_2R^{11})_2]$ afforded (248) $(R^{11}O_2C)_2CR^1CH_2CH_2R$ (R^1, R^{11} = H, Me or Et), perhaps via the carbonylate anion $[Fe(CO)_4\{CHRCH_2CR^1(CO_2R^{11})_2\}]^-$.

The reaction between $Fe(acac)_3$, $AlEt_3$ or $AlEt_2(OEt)$ and $Ph_2PCH_2CH_2PPh_2$ (diphos), which was earlier reported (249) to give $Fe(C_2H_4)(diphos)_2$ at 0°, has been further investigated (250). If the reaction was carried out at -78° and then allowed to warm to room temperature, $Fe(diphos)_2H_2$ was obtained, possibly via β-elimination from $Fe(diphos)_2Et_2$. With $AlEt_3$ in a deficiency at 0°, the paramagnetic $Fe(diphos)(acac)_2$ was produced. When $Fe(C_2H_4)(diphos)_2$ was treated with Hacac, both $Fe(diphos)(acac)_2$ and $Fe(diphos)_2H_2$ were isolated.

ALLYL COMPLEXES

Vibrational spectroscopic studies have been made (251) of $Fe(CO)_3(\eta^3\text{-}C_3H_5)X$ (X = Br, NO_3 or $\eta^3\text{-}C_3H_5Fe(CO)_3$). Photolysis of the epoxides 208, 209 and 210 with $Fe(CO)_5$ afforded (252) 211, the previously known (253) 212 and 213. Treament of these η^3-allyl species with Ce^{4+} effected the release of the organic ligands as 214, 215 and 216, respectively. Reaction of $Fe(CO)_3(\eta^3\text{-}C_3H_5)I$ with the sodium salt of benzotriazole gave (254) the N-allylbenzotriazole complex 217 whose structure was established crystallographically. The related isomer, 218, was obtained by reaction of $Fe_2(CO)_9$ with the 2-N-allylbenzotriazole.



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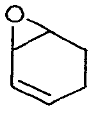

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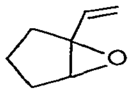

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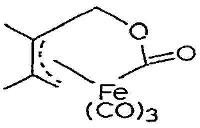

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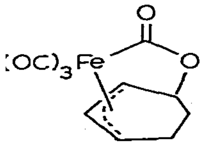

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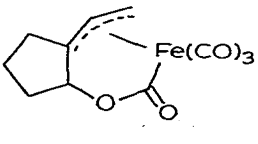

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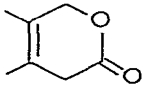

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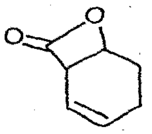

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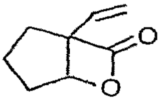

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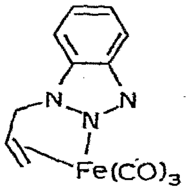

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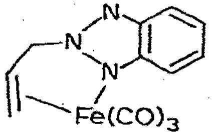

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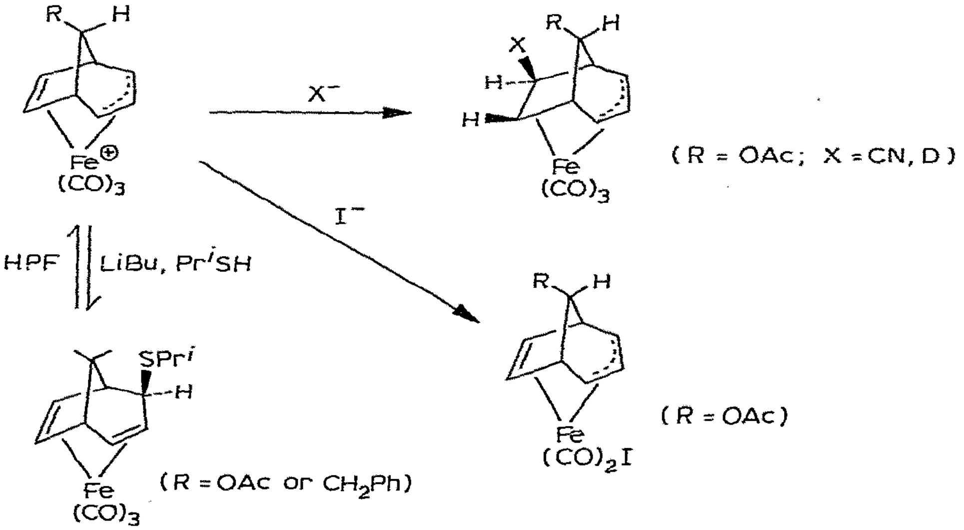
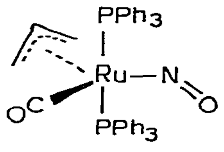
Treatment of $Ru(NO)(PPh_3)_2Cl$ with $Sn(C_3H_5)_4$ afforded (255) $Ru(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2$ whose X-ray structural examination revealed that the molecule had a distorted pseudo-tetrahedral geometry with a linear NO group. In chlorinated solvents, this allyl nitrosyl was converted into $Ru(NO)(PPh_3)_2Cl_3$ whereas under CO, the adduct $Ru(CO)(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2$, 219, thought to contain a bent Ru-N-O group, was formed. This species reacted further with CO giving $Ru(CO)_3(PPh_3)_2$.

Acylation of the cyclooctatetraene complex $Fe(CO)_3(\eta^4\text{-}C_8H_8)$ gave (256) the [3.2.1]-cyclooctadienylium ion, 220, and not 221 as expected (257). Addition of nucleophiles to 220 proceeded as outlined in Scheme 29.

Scheme 29



The cycloaddition of electronegatively-substituted unsaturated species to the N-methoxycarbonylazepine iron and ruthenium complexes 222 (M = Fe or Ru) has been extensively studied (258) and the results are summarised in Scheme 30. In almost all cases, η^3-allylic species were generated and it appeared that electrophilic attack occurred at the uncoordinated double bond leading to a 1,3- or 1,6-



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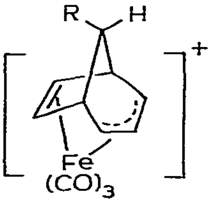

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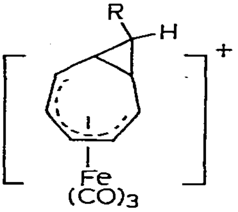

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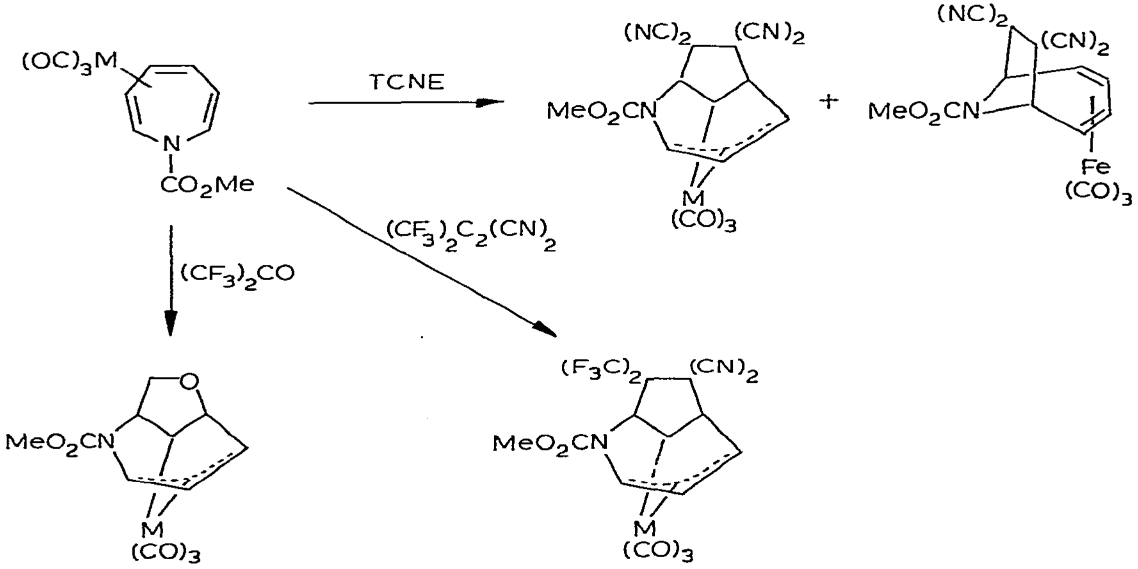
Scheme 30



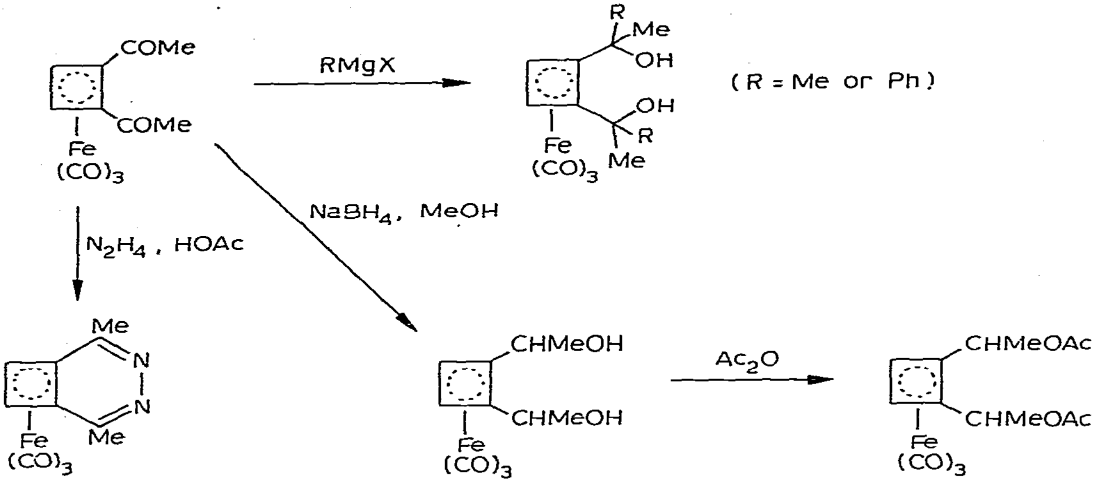
cyclo-addition product. The general accepted dipolar mechanism for these cycloadditions was critically assessed and alternative concerted reaction pathways presented.

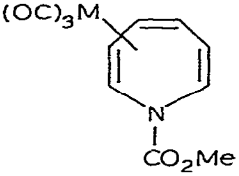
CYCLOBUTADIENE AND TRIMETHYLENEMETHANE COMPLEXES

Calculations have been made (259) of the ^{13}C nmr paramagnetic shielding terms in $Fe(\eta^4-C_4H_4)(CO)_3$. Acylation of $Fe(\eta^4-C_4H_4)(CO)_3$ afforded (260) the mono- and 1,2-disubstituted products $Fe(\eta^4-C_4H_3COMe)(CO)_3$ and $Fe\{\eta^4-C_4H_2(COMe)_2\}(CO)_3$. The reactions of the disubstituted products are illustrated in Scheme 31.

Nucleophilic addition of alkyl phosphines PRR'_2 ($R,R' = Me, Et, Pr^n, Bu^n$ or Ph, but not PPh_3) to $[Fe(\eta^4-C_4H_4)(CO)_2(NO)]^+$ gave (261) the cyclobutenyl cation 223. When this compound was heated, conversion to $[Fe(\eta^4-C_4H_4)(CO)(NO)(PRR'_2)]^+$ occurred, and this type of species was also obtained when $[Fe(\eta^4-C_4H_4)(CO)_2(NO)]^+$ was treated with EPh_3, E=P, As or Sb. It was considered that nucleophilic addition occurred directly to the cyclobutadiene ring without participation of

Scheme 31





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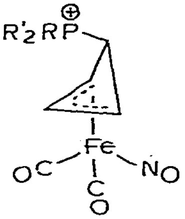

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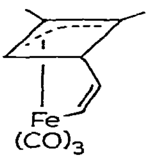

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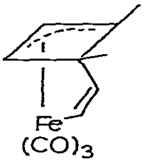


225

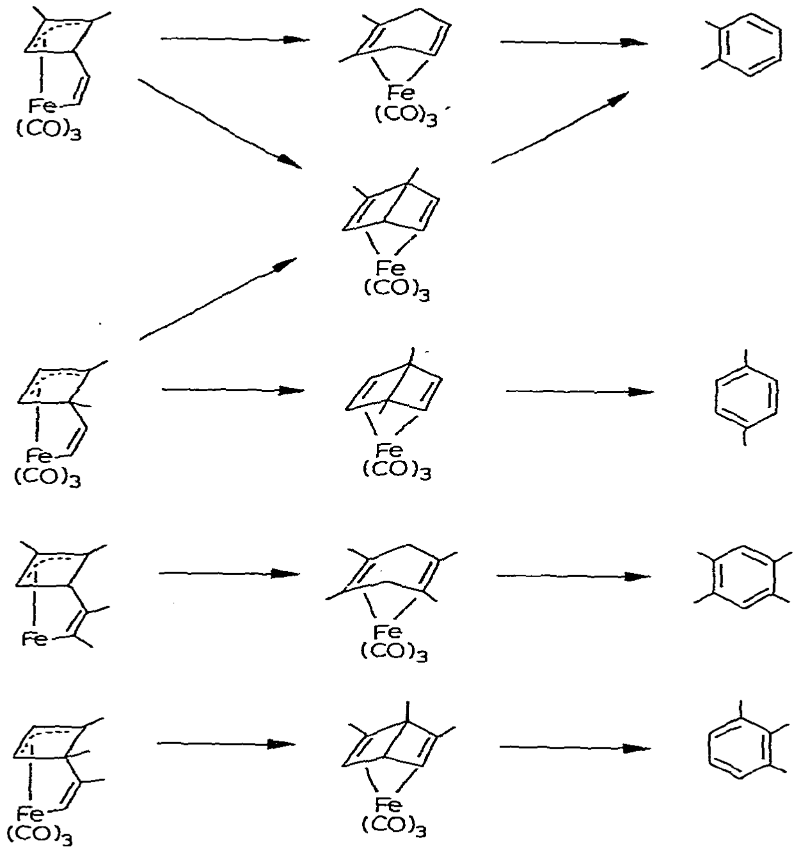
the metal, and a kinetic study (262) substantiated this view. The order of reactivity of phosphine addition to the ring was $[\mathrm{Fe}(\eta^4\text{-}C_4H_4)(CO)_2(NO)]^+ > [\mathrm{Fe}(\eta^5\text{-}C_6H_7)(CO)_3]^+ > [\mathrm{Cr}(\eta^7\text{-}C_7H_7)(CO)_3]^+ > [\mathrm{Mn}(\eta^6\text{-}C_6H_6)(CO)_3]^+$.

When the 1,2-dimethylcyclobutadiene complex $\mathrm{Fe}(\eta^4\text{-}C_4H_2Me_2)(CO)_3$ was photolysed in the presence of acetylene, propyne and but-2-yne, a series of methyl-substituted benzenes were obtained (263) in good yields. The general mechanism of reaction, seen as involving the intermediates 224 and 225, is outlined in Scheme 32.

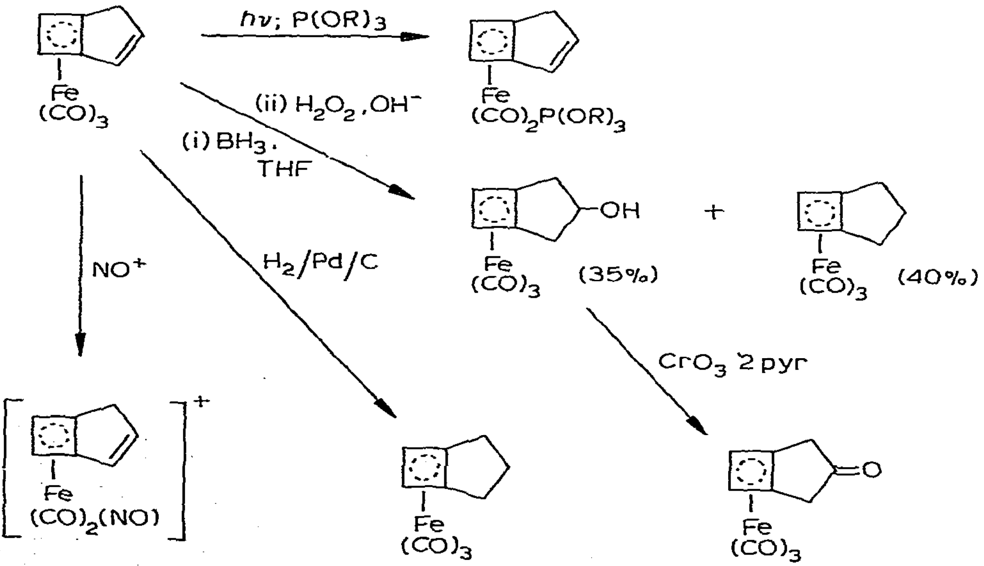
The formation of 226 in the reaction between $Fe_3(CO)_{12}$ and bicyclo[3.2.0]-hepta-1,4,6-triene has been already reported (264) and its yield has been increased (265) by using modified procedures. Some reactions of 226 are shown in Scheme 33. When 226 was treated with LiBu^n, the anionic species 227 was produced. The related $P(OMe)_3$ substituted species was also prepared and it was shown spectroscopically that some negative charge was localised on the metal atom. Reactions of 227 are summarised in Scheme 34.

The oxidation of 228 (R = H or Me) by Ce^{4+} occurred (266) according to Scheme 35 and when R = Me, the tricyclic product was obtained with a large optical rotation. This suggested that the cyclobutenyl intermediate is still under the

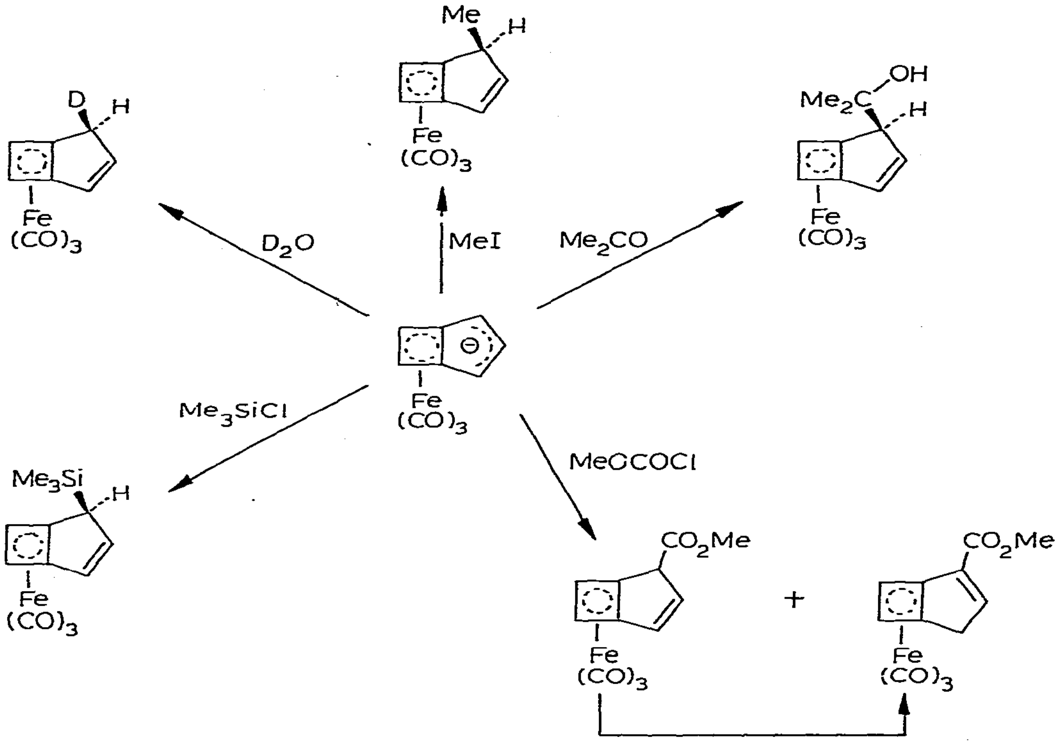
Scheme 32



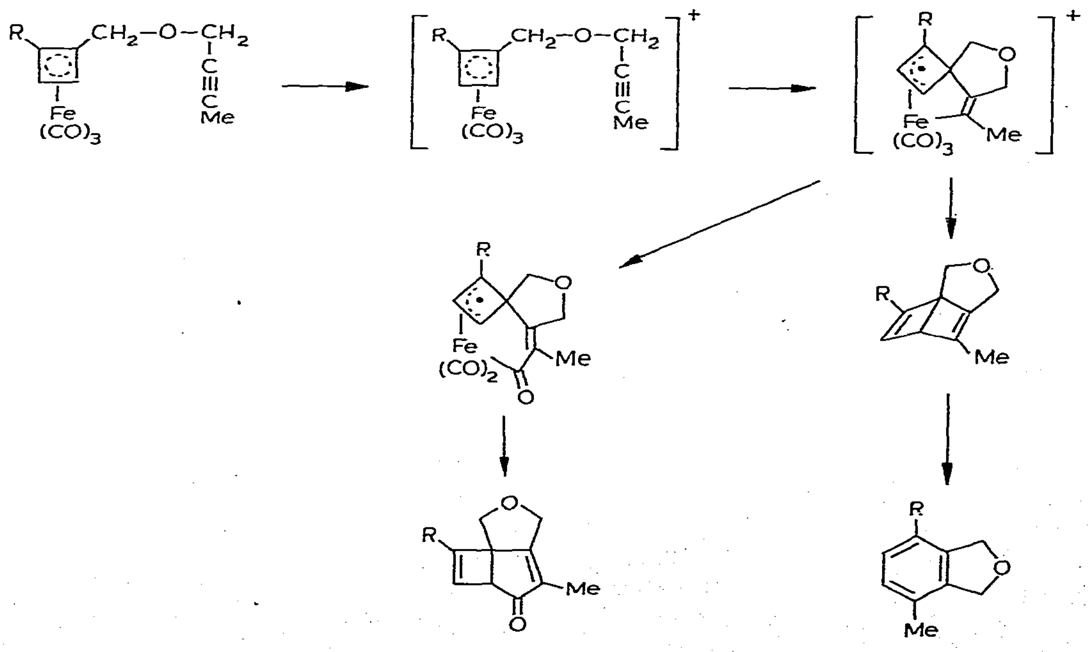
Scheme 33



Scheme 34



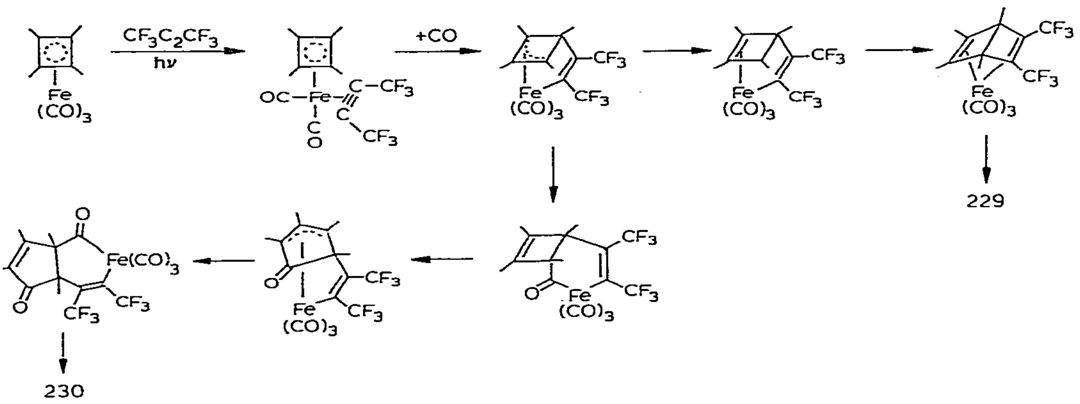
Scheme 35



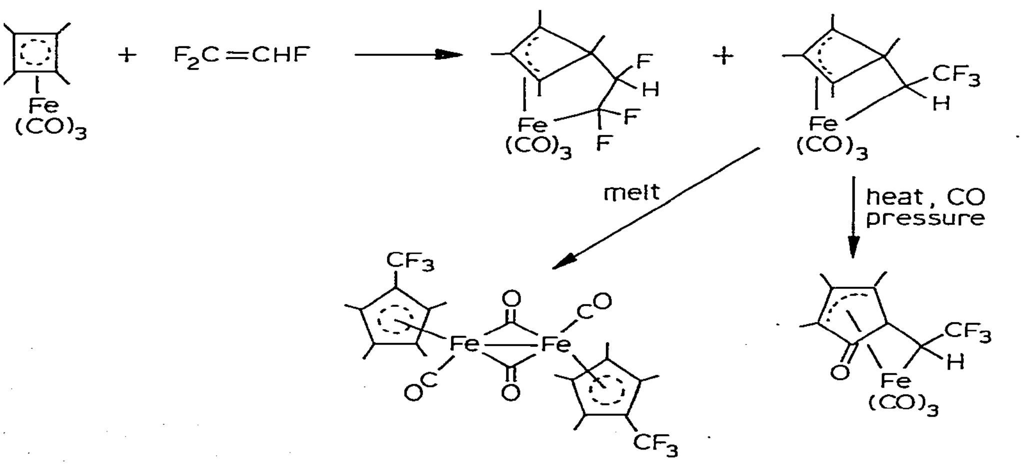
chiral influence of the metal, since in the absence of the metal no optically active products would be formed.

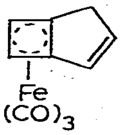
Photolysis of $Fe(\eta^4\text{-}C_4Me_4)(CO)_3$ in the presence of $CF_3C_2CF_3$ gave (267) two compounds, 229 and 230, by a mechanism outlined in Scheme 36. With CF_2CHF, different products were produced, as shown in Scheme 37. Treatment of the 1,2-dialdehyde $Fe\{\eta^4\text{-}C_4H_2(CHO)_2\}(CO)_3$ with $[(Ph_3PCH_2)_2CO]Cl_2$ and lithium ethoxide in DMF gave 231 which, on oxidation with Ce^{4+} in the presence of cyclopentadiene, afforded (268) (269) endo-1,4,4a,9b-tetrahydro-1,4-methanobenzo[3,4]cyclobuta-[1,2-d]tropone. Similar treatment with $[Ph_3P(CH_2)_3PPh_3]Br_2$ gave 232 and its isomer 233, and hydride abstraction using Ph_3C^+ afforded 234. The further exploitation (269) of the Wittig reaction using the bis-phosphonium salts 235 and 236 gave 237 and 238, respectively and these species underwent Diels-Alder

Scheme 36



Scheme 37





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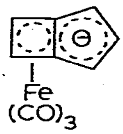

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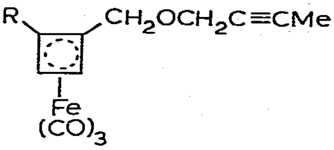

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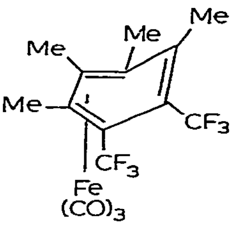

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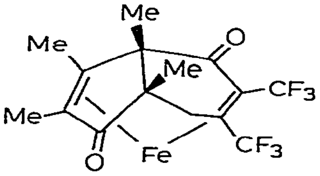

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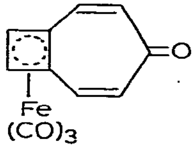

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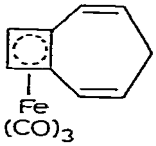

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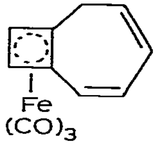

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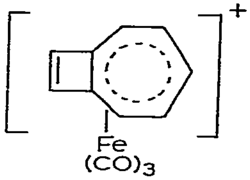

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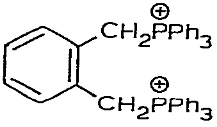

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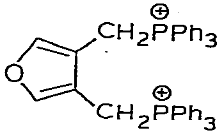

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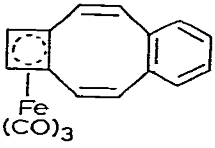

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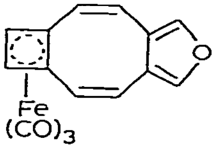

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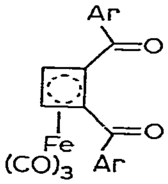

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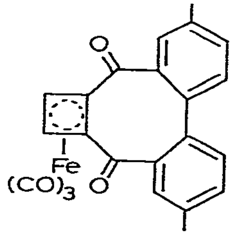

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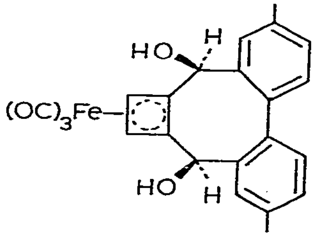

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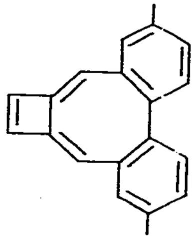


242

addition with N-phenylmaleimide. No cyclic derivatives could be obtained using $[Ph_3PCH_2CH = CHCH_2PPh_3]Br_2$.

Treatment of $Fe\{\eta^4\text{-}C_4H_2(COCl)_2\}(CO)_3$ with $(p\text{-}MeC_6H_4)_2$ and $AlCl_3$ in CS_2 gave (270) a mixture of 239 and 240, and reduction of the latter with $AlH(Bu^i)_2$ afforded 241. Treatment of 241 with HCl failed to provide 242 but when a similar sequence of reactions was carried out with 243, 244 was eventually obtained via two tetracyclic cyclobutadiene iron carbonyl intermediates. The structure of 240 was determined crystallographically (271) and it was noted that the 8-membered ring was flattened from a boat conformation while the 6-membered rings were twisted from coplanarity to an angle of 74°.

The ESCA spectra of the trimethylenemethane complex $Fe\{\eta^4\text{-}C(CH_2)_3\}(CO)_3$ were interpreted (272) in terms of greater donation from the iron to the $\{C(CH_2)_3\}$ ligand than to butadiene.

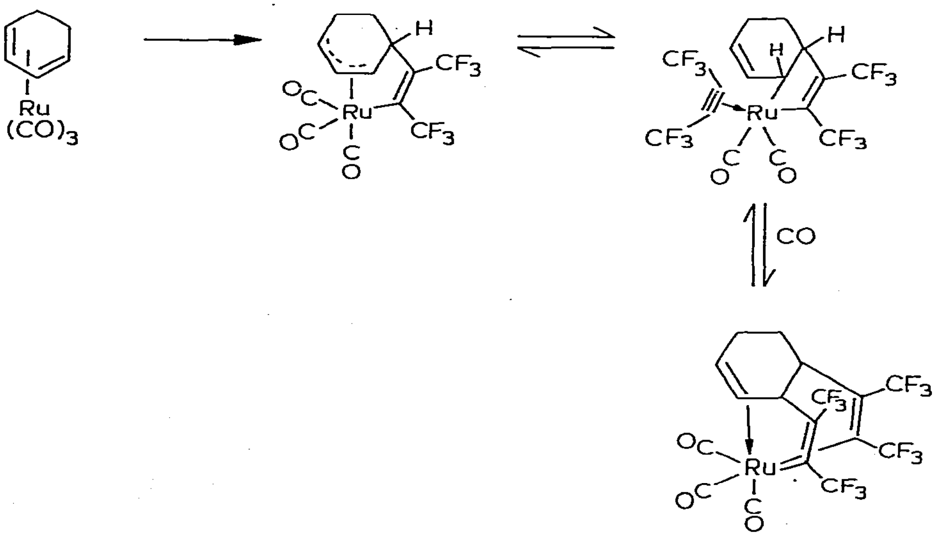
DIENE AND HIGHER OLEFIN COMPLEXES

Acyclic Diene Species

The structure of the proton skeleton in $Fe(\eta^4\text{-}C_4H_6)(CO)_3$, which is non-planar, was determined (273) by orientation in a nematic liquid crystal solvent. Cyclooctadiene was displaced (274) from $Ru(CO)_3(C_8H_{12})$ by butadiene in a sealed tube in benzene at 100°, giving $Ru(CO)_3(\eta^4\text{-}C_4H_6)$ whose ^1H and ^{13}C nmr spectra were recorded. The complexes $Fe(CO)_3(\eta^4CH_2{=}CHCH{=}CHOSiMe_2R)_3$ $Fe(CO)_3\{\eta^4\text{-}CH_2{=}CHCH{=}CHO)\}_2SiMe_2$ and $Fe(CO)_3\{\eta^4\text{-}PhCH{=}CHC(OSiMe_3){=}CH_2\}$, were obtained (275) by reacting $Fe_3(CO)_{12}$ with the appropriate siloxybutadienes.

Reaction of $Fe(CO)_3(\eta^4\text{-diene})$ (diene = 1,3-pentadiene, hexadiene, 2,3-dimethylbutadiene) with $NaN(SiMe_3)_2$ afforded (276) the cyano-complex $Na[Fe(CO)_2(diene)CN]$.

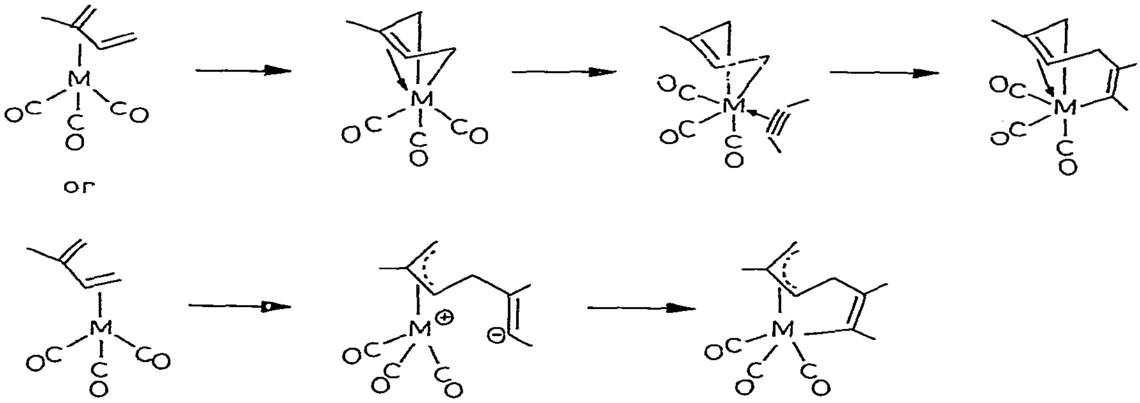
Scheme 38



Treatment of $Fe_2(CO)_9$ with tetrasubstituted butatrienes gave (277) three geometrical isomers of $Fe(CO)_4(\eta^2\text{-}R^1RC{=}CC{=}CRR^1)$ (R, R^1 = Ph, p-MeC_6H_4 or p-$MeOC_6H_4$).

Under uv light, $Fe(CO)_3(\eta^4\text{-}C_4H_4R_2)$ (R = H or Me) reacted (278) with $CF_3C_2CF_3$ and CF_3C_2H giving 245 and 246, respectively. The diphenyl o-styrylphosphine complex of iron tricarbonyl similarly underwent addition of $CF_3C_2CF_3$, producing 247. The cyclohexa-1,3-diene complex $Ru(CO)_3(\eta^4\text{-}C_6H_8)$ and its 2-methyl analogue also reacted with $CF_3C_2CF_3$, affording 248 (L = CO), perhaps via the route outlined in Scheme 38. Treatment of 248 (L = CO) with $P(OCH_2)_3CMe$ gave 248 (L = $P(OCH_2)_3CMe$), whose X-ray structure determination established the nature of 248. The necessity to use uv radiation to achieve these results was considered. Two reaction pathways, one involving photo-induced dissociation of one CO ligand, and the other conversion of the η^4-diene to an η^2-diene, were discounted. Two other possibilities, illustrated in Scheme 39, seemed to be more attractive.

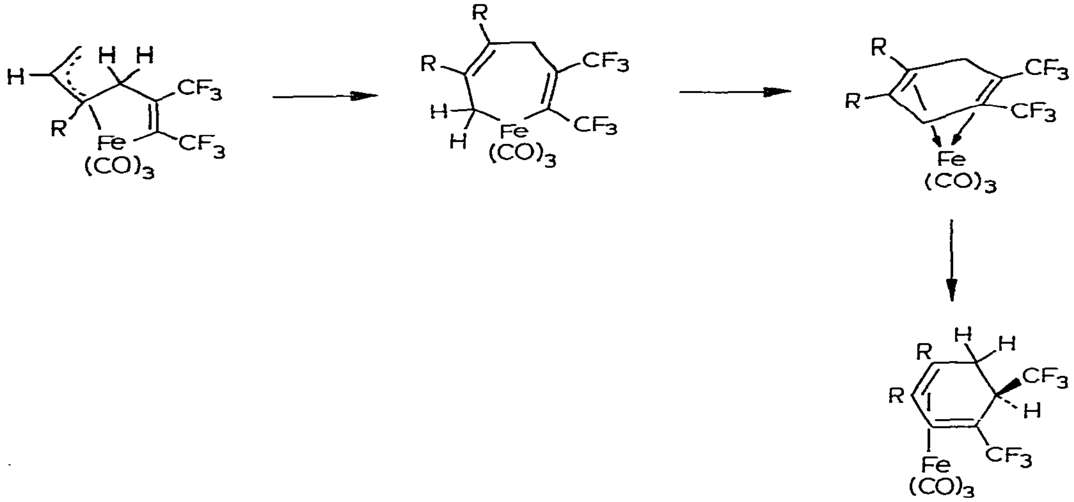
Scheme 39



Treatment of 245 (R = Me) with CO under pressure gave either 249 or 250, but when 245 was refluxed in certain solvents, a cyclohexadiene complex was produced, perhaps via the route shown in Scheme 40.

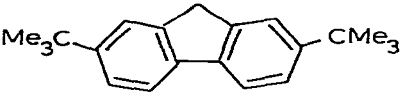
Treatment of $Fe_2(CO)_9$ with 1,3,5-hexatriene afforded (279) the η^4-triene complex 251. Reaction of this with diborane gave the alcohol $Fe(CO)_3(\eta^4\text{-}CH_2{=}CHCH{=}CHCH_2CH_2OH)$. There was no reaction between 251 and Simmons-Smith reagent (Zn/Cu/CH_2I_2), but osmium tetroxide afforded the cis-diol $Fe(CO)_3\{\eta^4\text{-}CH_2{=}CHCH{=}CH_2\text{-}CH(OH)CH_2OH\}$. Similar behaviour was observed with the methylated analogue of 251, $Fe(CO)_3(\eta^4\text{-}MeCH{=}CMeCH{=}CHCH{=}CMe_2)$, although the presence of the methyl groups considerably increased the nucleophilicity of the uncomplexed double bond. Treatment of 251 with $Hg(OCOMe)_2$ gave $Fe(CO)_3\{\eta^4\text{-}CH_2{=}CHCH{=}CHCH(OMe)CH_2\text{-}Hg(OCOMe)\}$ in low yield, and with HBF_4 in propionic anhydride, the cation 252 was produced. The latter was readily deprotonated on basic alumina, regenerat-

Scheme 40



ing 251 (280), but with Et_3N deportonation did not apparently occur, in contrast to an earlier report (281) and instead a quaternary ammonium salt was isolated. Reaction of 252 with $KOBu^t$ gave $Fe(CO)_3\{\eta^4\text{-}CH_2{=}CHCH{=}CHCH(OBu^t)Me\}$, and with 2,6-dimethylpyridine dimerisation with formation of a C–C bond occurred, giving 253.

The 2-pyrone complex of tricarbonyl iron reacted (282) with OR^- (R = H, Me or COMe) or LiR (R = Me, $CH = CH_2$, H, Ph, NEt_2) giving numerous 1,4-disubstituted butadiene iron tricarbonyl complexes in high yield. Thus, with OR^-, a blood red solution, perhaps containing 254, was obtained from which could be isolated 255 (R^1 = H, Me or COMe) on addition of acid, MeI or Me_2SO_4, or acetic anhydride



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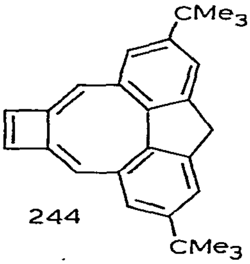

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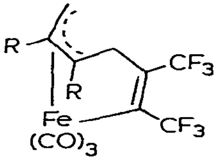

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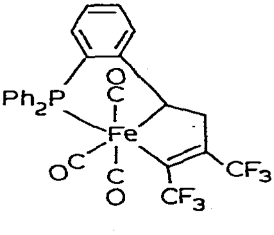

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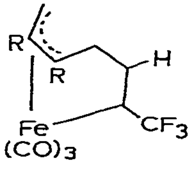

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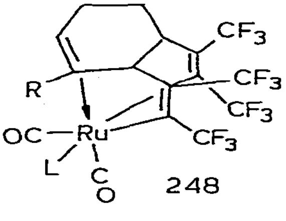

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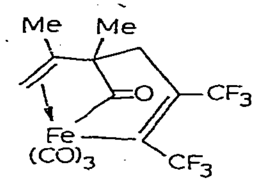

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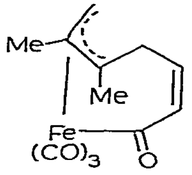

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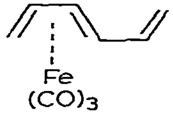

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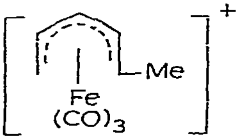

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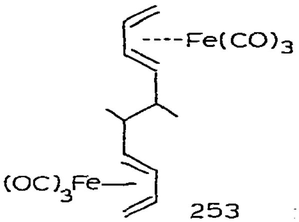

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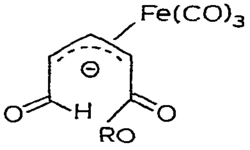

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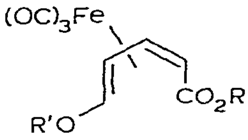

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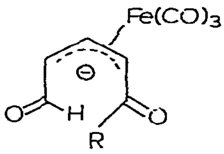

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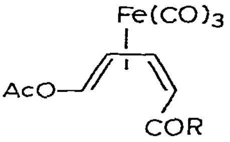
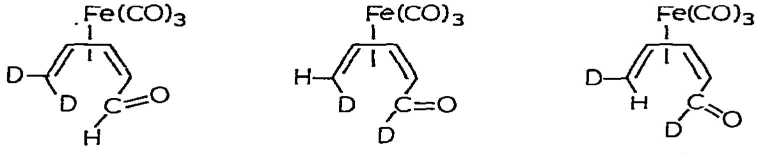


257

The Z, E isomer of 255 so obtained could be converted to the E, E form by heating in benzene. Attack on the 2-pyrone complex by LiR afforded the intermediate 256, similar to 255, which, in acetic anhydride, produced 257. Deuteriation of the 2-pyrone complex was achieved using LiAlD$_4$ followed by aqueous acid at low temperature, and three diene isomers, 258a, b and c were isolated in relative yields of 50%, 40% and 10%, respectively. If the deuterated reaction product was quenched using acetic anhydride rather than H$_3$O$^+$, then the two isomers 259a and b were obtained. Treatment of the normal proton-containing analogue of 259a with methoxide permitted the isolation of an air-sensitive solid, believed to contain either 260 or 261. Treatment of 2-pyrone iron tricarbonyl with OH$^-$, acetic anhydride, (COCl)$_2$ and finally LiAlH(OBu^t)$_3$ afforded Fe(CO)$_3$(η^4-MeOCOCH=CHCH=CHCH$_2$OH), and with LiAlH$_4$ followed by aqueous ammonium chloride, Fe(CO)$_3$(η^4-HOCH=CHCH=CHCH$_2$OH) was produced. On a silica gel column or in the presence of HCl, this last compound was converted into 262.

Separation of cis- and trans-dienone, and ψ-endo and -exo dienol iron tricarbonyl complexes has been achieved (283) by HPLC techniques on microparticulate silica using CH$_2$Cl$_2$ or CH$_2$Cl$_2$/MeCN mobile phases.

Treatment of Fe(CO)(η^4-EtO$_2$CCH=CHCH=CHCO$_2$Et)$_2$ with the "diazadienes" bipyridyl or 263 (DAD) afforded (284) the complexes Fe(CO)(DAD)(η^4-EtO$_2$CCH=CHCH=CHCO$_2$Et). These species could also be obtained by photolysis of Fe(CO)$_3$(η^4-EtO$_2$CCH=CHCH=


(a) (b) (c)

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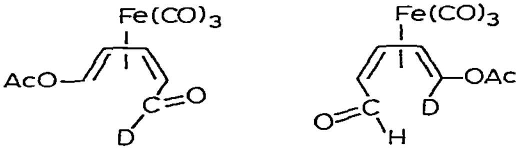
(a) (b)

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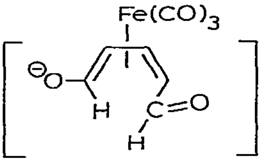
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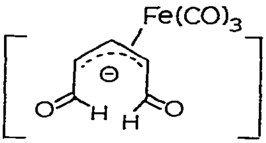
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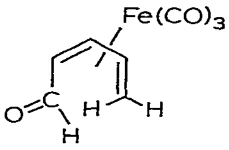
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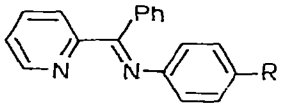
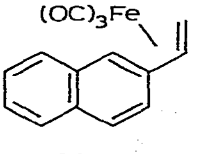

263

CHCO$_2$Et) in the presence of DAD, and the bipyridyl complex was characterised crystallographically. The geometry of this species approximates to a square pyramid with one bipyridyl N atom occupying the apical position.

Cyclic Diene Species

A simplified Hückel m.o. model has been developed (285) to account for the bond lengths in a wide range of η^4-olefin complexes. The calculations were able to reproduce the relative insensitivity of the C–C bond lengths of the coordinated butadienoidal fragment towards the number of phenyl rings in phenyl-substituted butadiene iron tricarbonyl complexes, and in 264 and 265, and also demonstrated the fixation of one double bond in the phenyl ring which is fused adjacent to the butadiene moiety. Calculations were also made with respect to $Fe(CO)(\eta^4-C_4H_6)(\eta^4-C_8H_8)$ and $Ru(\eta^6-C_6H_6)(\eta^4-C_6H_6)$. Within the Hückel approximation, metal η^3- and η^4-hydrocarbon complexes were shown (286) to have alternant bonding networks. The application of the pairing theorem to such systems threw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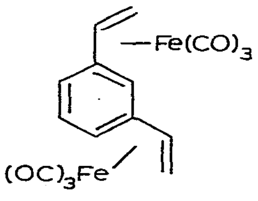
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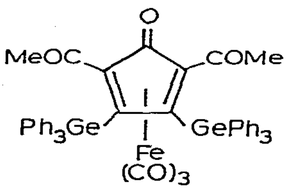
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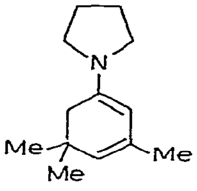
some light on the origins of the 18-electron rule in such species as Fe(η^4-C$_4$H$_4$)-(CO)$_3$, Fe(η^4-C$_6$H$_6$)(CO)$_3$, Fe(CO)$_3$(η^4-C$_8$H$_8$), Fe$_2$(CO)$_6$(C$_8$H$_8$), 265, and Fe(η^3-C$_3$H$_5$)-(CO)$_3$X.

The conformational preferences and rotational barriers in polyene M(CO)$_3$ systems have been calculated (287). The structures of the cyclopentadienone complexes Fe(CO)$_3$(η^4-C$_4$H$_4$CO) and Fe(CO)$_3$ $\{\eta^4$-C$_4$(COMe)$_2$(GePh$_3$)$_2$CO$\}$, 266, obtained by reaction of Fe$_2$(CO)$_9$ with Ph$_3$GeC$_2$COMe, have been determined crystallographically (288) (289). In both cases, the ketonic group tilted up out of the C$_4$-butadiene plane, as predicted theoretically.

Lanthanide shift reagents have been employed (290) to facilitate spectroscopic identification of 5-exo and 5-endo-methoxycyclohexadiene iron tricarbonyl isomers. On treatment of [Fe(CO)$_3$(η^5-C$_6$H$_7$)]$^+$ with methanol, 5-exo-Fe(CO)$_3$(η^4-C$_6$H$_7$OMe) is produced rapidly but on heating, isomerisation to the 5-endo form occurred, so that the equilibrium ratio was 3:2 exo:endo. On protonation of these methoxy-derivatives, the endo form reacted less rapidly than its exo isomer. Spectroscopic studies using Eu(fod)$_3$ indicated that the endo-isomer was more sterically hindered.



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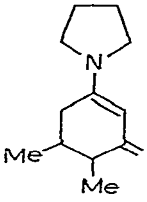

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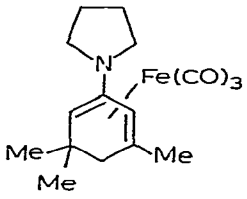

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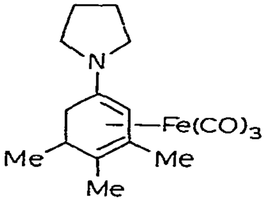
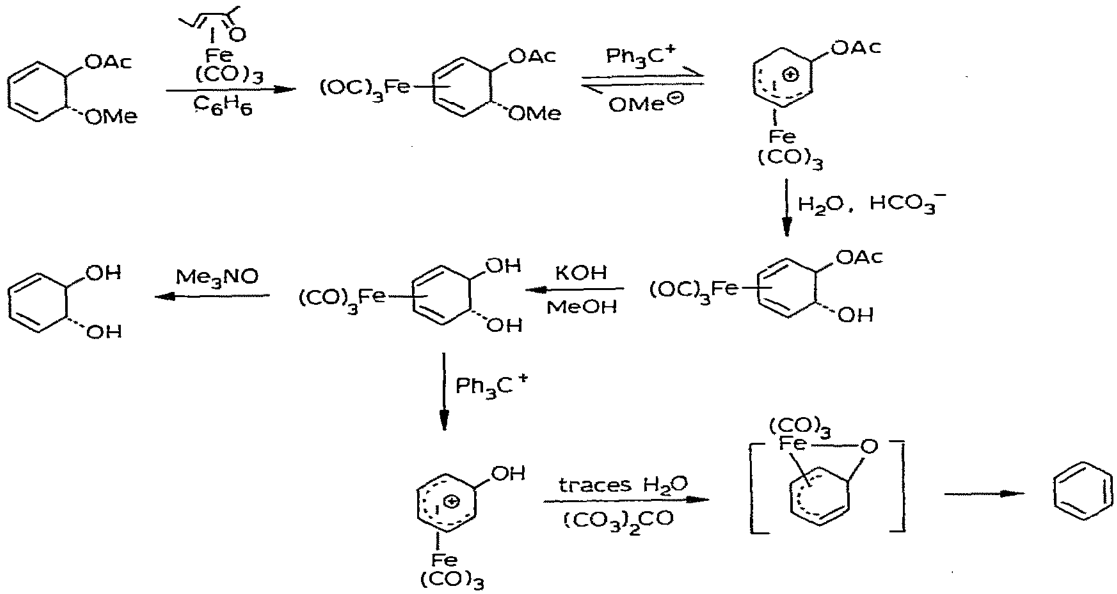


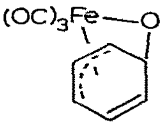
270

Reaction of a mixture of cyclic dienamines, 267 and 268 with Fe(CO)$_5$ afforded (291) the diene complexes 269 and 270, and the syntheses of a variety of substituted 1,3-cyclohexadiene iron tricarbonyls has been reported (292).

The syntheses of 6-endo-acetoxy and -hydroxy-cyclohexadienyl iron tricarbonyl cations via appropriate diene intermediates is summarised (293) in Scheme 41. Treatment of trans-dihydroxycyclohexadiene iron tricarbonyl with Me$_3$NO effected release of the hydrocarbon ligand, but hydrolysis of the hydroxycyclohexadienyl salt by traces of water in acetone afforded only benzene, perhaps via the intermediate 271. Addition of cyanide ion to 272 and 273, the latter being obtained from 274 via reaction with Fe(CO)$_5$ followed by treatment of the organometallic with Ph$_3$C$^+$, occurred (294) at the more electron-deficient terminus of the dienyl cation system, giving quaternary centres as in 275 and 276. Friedel-Crafts acetylation of Fe(CO)$_3$(η^4-C$_6$H$_8$) afforded (295) at 4:1 mixture of the 5-exo and -endo isomers of Fe(CO)$_3$(η^4-C$_6$H$_7$COMe). The exo-isomer was synthesised stereospecifically by addition of CN$^-$ to the cyclohexadienyl salt [Fe(CO)$_3$(η^5-C$_6$H$_7$)]$^+$, followed by treatment of the resulting 5-exo-cyanocyclohexadiene complex with MgMeI, and aqueous NH$_4$Cl.

Scheme 41





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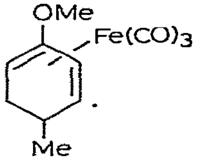

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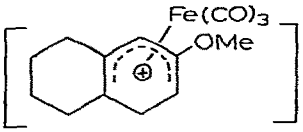

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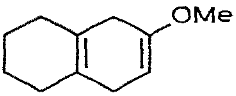

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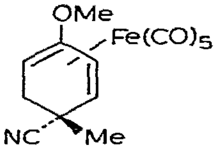

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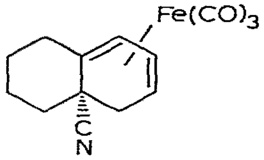

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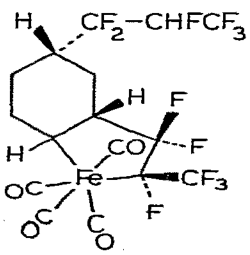

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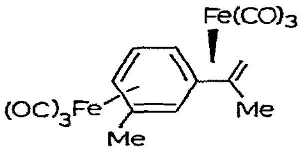

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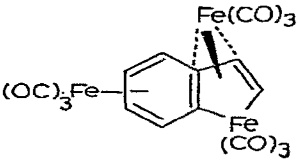

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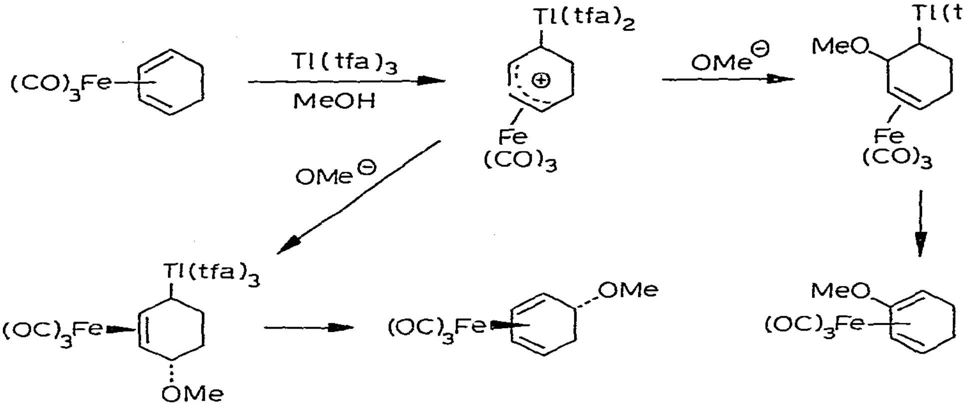
It has been reported (296) that oxidation of $Fe(CO)_3(\eta^4\text{-}C_6H_7CH_2COMe)$ by $Tl(OCOCF_3)_3$ in CCl_4 gave $C_6H_5COCOMe$. However, similar treatment of $Fe(CO)_3(\eta^4\text{-}C_6H_8)$ in methanol gave (297) 5-exo-methoxy and hydroxycyclohexadiene iron tricarbonyl as well as the 3-methoxy-substituted complex. The production of the hydroxy derivative could be suppressed by adding K_2CO_3 to the reaction mixture. The postulated mechanism of these reactions is depicted in Scheme 42.

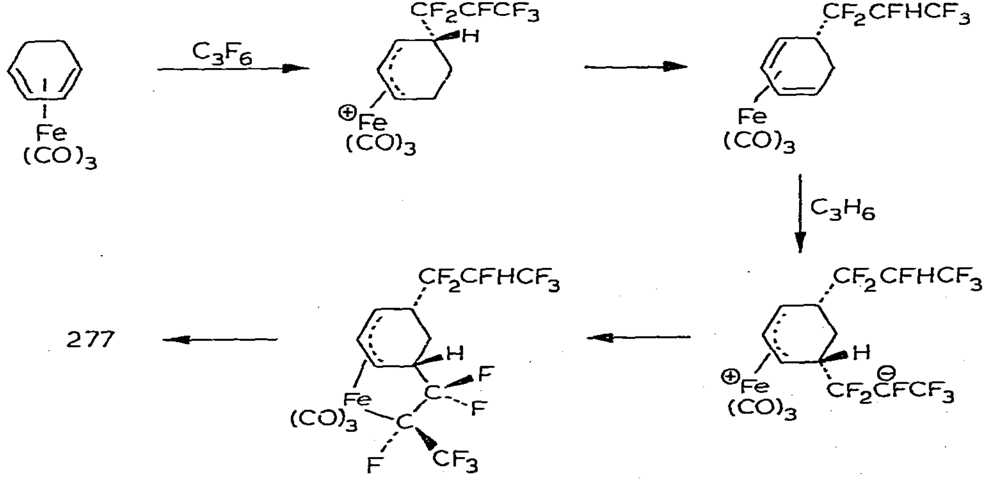
Scheme 42



The uv irradiation of mixtures of $Fe(CO)_3(\eta^4\text{-}C_6H_8)$ and $CF_3CF{=}CF_2$ has been reported (298) to give a mononuclear product containing two molecules of perfluoropropene. This has been confirmed (299) crystallographically, the mechanism of formation of the product, 277, being shown in Scheme 43.

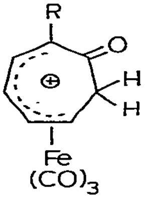
The structures of 278 and 279 have been determined (300) by X-ray methods. In the former the planes of the two isoprenoid $Fe(CO)_3$ group intersect at an

Scheme 43



angle of 34°. In the latter, the Fe-Fe bond is 2·51Å, and the ferrole moiety does not interact with the unique butadienoidal fragment.

It has been suggested (301) that $Fe(CO)_3(\eta^4\text{-}C_7H_8)$ undergoes a 1,3-shift process in its fluxional behaviour. However, by use of the Forsen-Hoffman spin saturation nmr method, it has been shown (302) that the fluxional process could occur either by a 1,2- or a 1,3-shift mechanism. Reaction of C_7H_7Ph with $Fe_2(CO)_9$ afforded (303) the 6-exo isomer of $Fe(CO)_3(\eta^4\text{-}C_7H_7Ph)$, whose structure was established by X-ray methods. At low temperatures, η^4-troponeirontricarbonyl could be protonated (304) at the O-atom, but at higher temperatures, 280 (R = H) was formed. The 7-methyltropone analogue behaved similarly, with eventual formation of 280 (R = Me). Proton addition to the cycloheptatriene complex $Fe(CO)_3(\eta^4\text{-}C_7H_8)$ has been shown to occur (305) exclusively exo to the $Fe(CO)_3$ group in CF_3CO_2H and H_2SO_4. On heating, the 7-exo-deuterio isomer of $Fe(CO)_3\text{-}(\eta^4\text{-}C_7H_7D)$ underwent H/D scrambling over C(1) to C (6).



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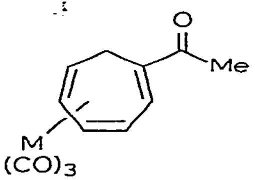

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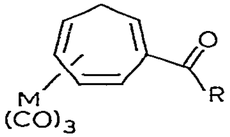

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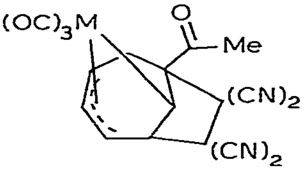

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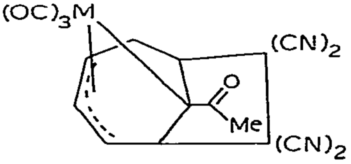

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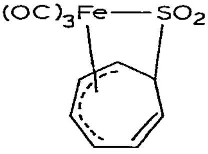

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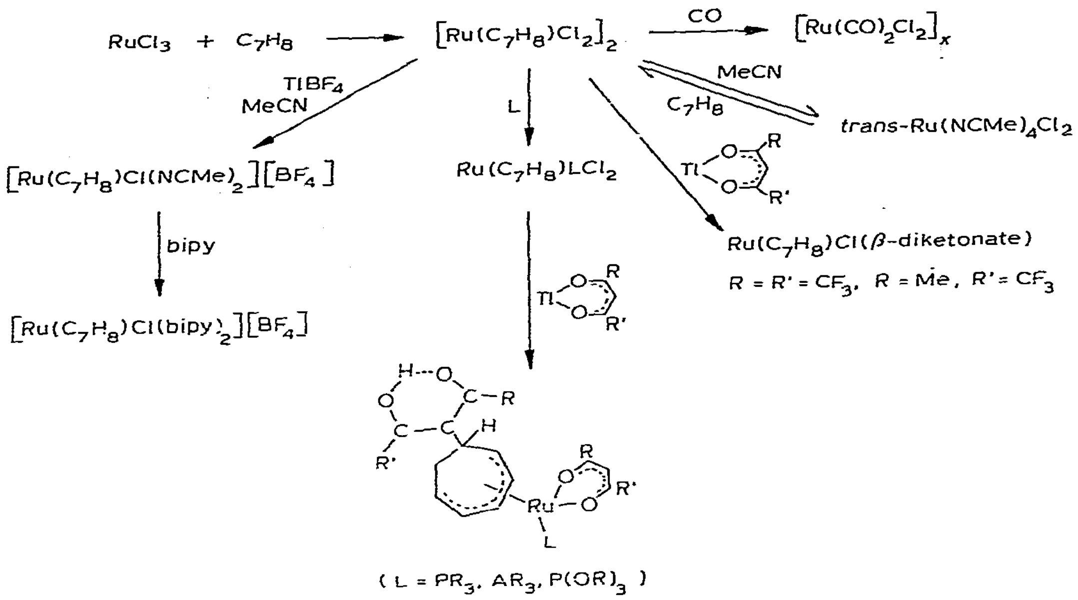
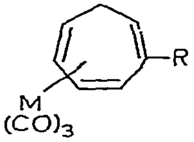
Treatment of the 1-acetyl species, 281, with NaOMe in methanol gave (306) its 2-acetyl isomer, 282. Reaction of these with TCNE afforded 283 and 284, respectively, indicating that the cyanoolefin underwent 1,3-cycloaddition to the uncoordinated side of the ring in both molecules. Reaction of $Fe(CO)_3(C_7H_8)$ with SO_2 gave 285, while protonation of the arylated cycloheptatriene complexes 286 and 287 (R = Ph or p-MeC_6H_4), obtained by treatment of troponeirontricarbonyl with MgRX followed by chromatography on silica gel, afforded the dienyl cations 288 and 289. Cycloaddition of TCNE to 290 gave (307) the bicyclic species 291 which, on oxidation with Ce^{4+}, afforded 292. Troponeirontricarbonyl and its cyclooctatrienone analogue 293 behaved similarly, giving 294 and 295, respectively, and on oxidation with Ce^{4+}, these released 296 and 297.

Scheme 44





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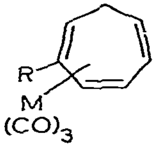

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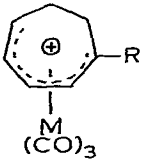

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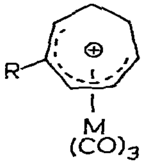

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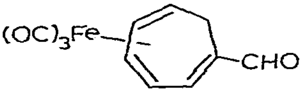

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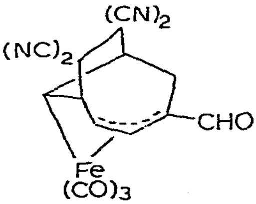

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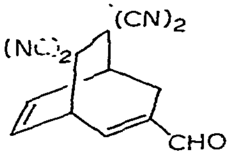

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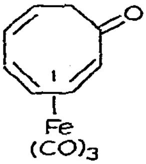

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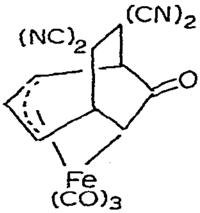

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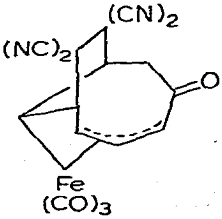

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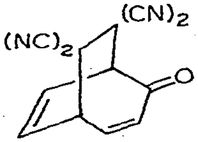

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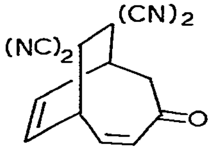

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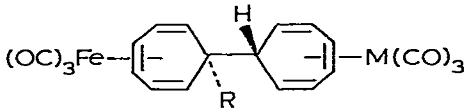

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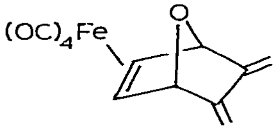
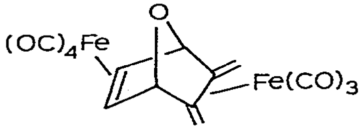


299

Cycloheptatriene reacted with $RuCl_3$ in aqueous ethanol giving (308) $[Ru(C_7H_8)Cl_2]_2$, some of whose reactions are outlined in Scheme 44. The 1,5-cyclooctadiene complex $[Ru(C_8H_{12})Cl_2]_n$ reacted with nitriles, RCN (R = Me or Ph) giving $Ru(C_8H_{12})(NCR)_2Cl_2$, $[Ru(C_8H_{12})(NCMe)_4]^{2+}$ and $Ru(NCMe)_6{}^{2+}$. Treatment of the first with 2,2'-bipyridyl afforded $Ru(C_8H_{12})(bipy)Cl_2$. The norbornadiene complex $[Ru(C_7H_8)(bipy)_2]^{2+}$ was obtained (309) by treating cis-$Ru(bipy)_2Cl_2$ with $AgClO_4$ in the presence of C_7H_8, and $Ru(C_7H_8)(bipy)Cl_2$ could be prepared by treatment of $[Ru(C_7H_8)Cl_2]_n$ with the stoichiometric amount of bipyridyl. In acetone, the species $[RuL(NH_3)_5][PF_6]_2$ (L = cyclohexene, norbornene, acetylene, 1-octyne, 1-hexyne or 3-hexyne) were obtained by direct addition of L to $[Ru(NH_3)_5(H_2O)][PF_6]_2$. It was noted that $E_{1/2}$ of the Ru^{II}/Ru^{III} couple for $[RuL(NH_3)_5]^{2+}$ indicated that Ru^{II} was significantly more stable when L = pyridine.

Reaction of the cycloheptatriene complex $Fe(CO)_3(\eta^4\text{-}C_7H_8)$ with allyl bromide in the presence of $M'(CO)_3(\eta^6\text{-}C_7H_8)$ (M' = Mo or W) afforded (310) the dimers 298 (M = Mo or W). Elimination of the $M(CO)_3$ fragment gave $Fe(CO)_3(\eta^4\text{-}C_7H_7C_7H_7)$ which reacted with $Fe(CO)_3(PhCH{=}CHCOMe)$ to give the exo-isomer of 298 (M = $Fe(CO)_3$). When $Fe(CO)_3(\eta^4\text{-}C_7H_8)$ was treated with allyl bromide alone, the endo form of 298 (M = $Fe(CO)_3$) was produced.

Under mild conditions, 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene reacted (311) with $Fe(CO)_5$ (hv) or $Fe_2(CO)_9$ giving 299 and 300. Under more drastic conditions, 301 and 302 were formed. The complex 303 was also prepared.



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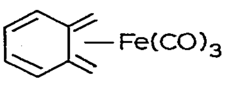

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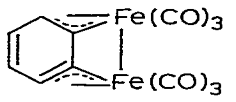

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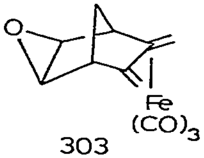
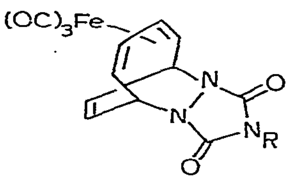


303

In THF, $Fe(CO)_5$ reacted with Me_3NO at -30° evolving (312) CO_2 and forming $Fe(CO)_4(NMe_3)$. This species reacted with cyclooctatetraene giving $Fe(CO)_3(\eta^4\text{-}C_8H_8)$, demonstrating that the trimethylamine complex is probably an intermediate in the formation of $Fe(CO)_3$(diene) complexes from $Fe(CO)_5$, diene and Me_3NO (313). The amine complex also acted as a catalyst for the addition of CCl_4 to olefins.

Treatment of $Fe(CO)_3(\eta^4\text{-}C_8H_8)$ with triazolinediones gave (314) the cycloaddition products 304 (R = Me or Ph), from which the barbarolone derivatives 305 were obtained on oxidation of 304 using Ce^{4+}.

Reaction of 5-bicyclo[2.2.1]heptene and -heptane and related octene and octane complexes afforded (315) exo- and endo-isomers of 306, 307, 308 and 309, respectively. Hydrogenation of the uncomplexed double bond in both exo- and endo forms of 306 and 308 gave the respective isomers of 307 and 309, but hydrogen addition in both isomers occurred from the exo-side of the molecules. Treatment of 5,6,7,8-tetramethylenebicyclo[2.2.2]-oct-2-ene afforded (316) a series of $Fe(CO)_3$ complexes 310, 311, and 312, and addition of $Mo(CO)_3(NCMe)_3$ to 310 gave 313.



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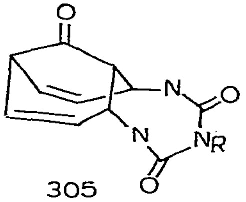

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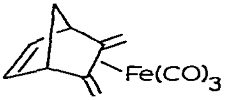

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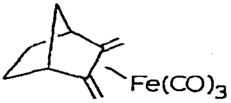

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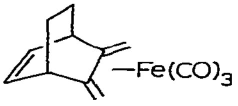

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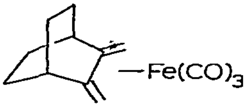

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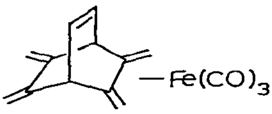

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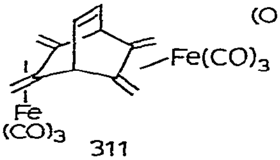

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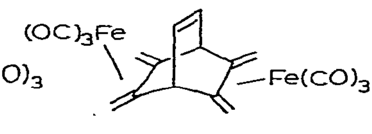

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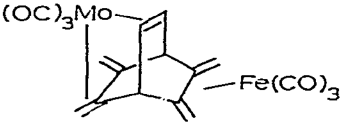


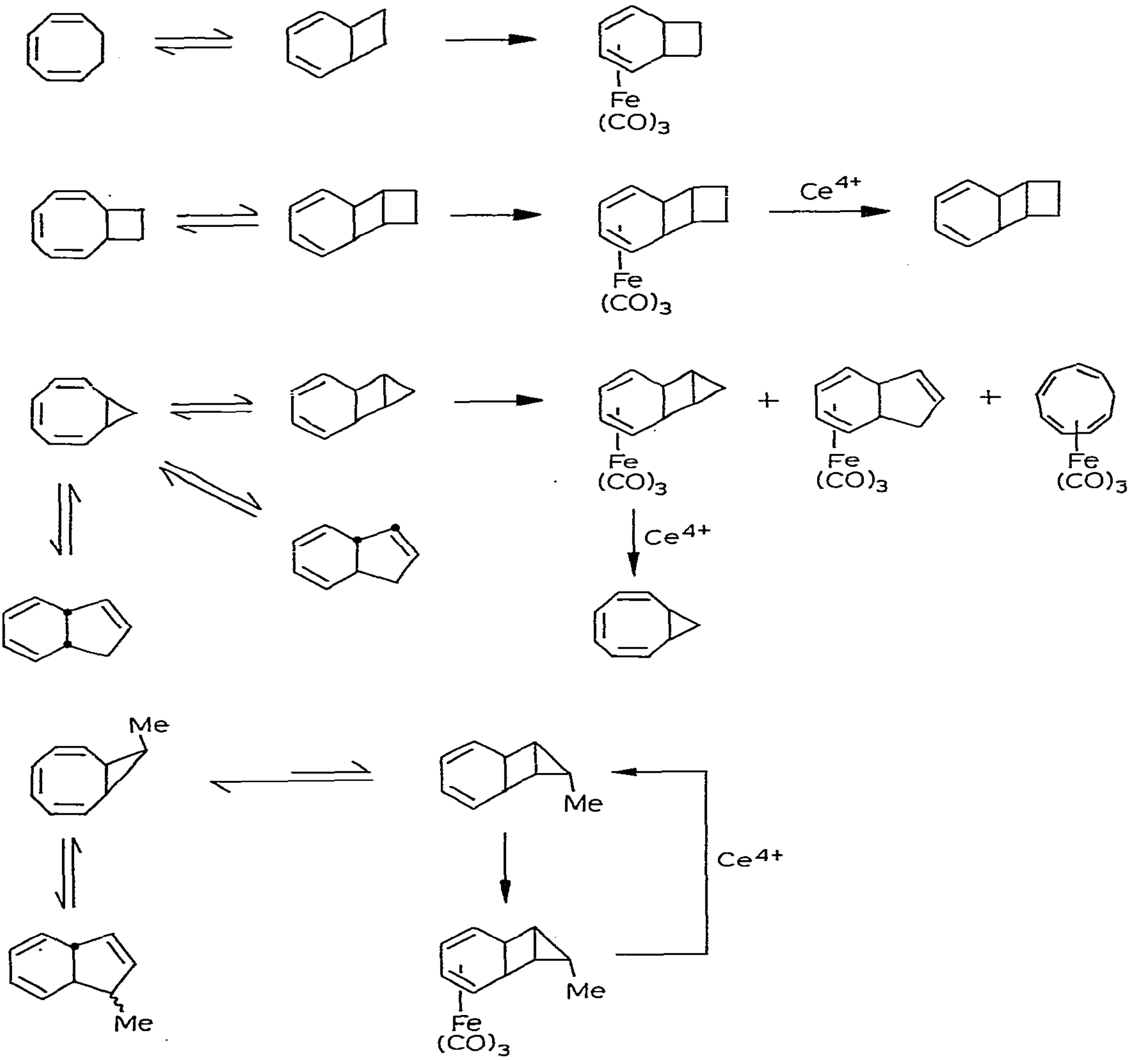
313

The reactions of benzylideneacetone irontricarbonyl with 1,3,5-cyclooctatriene and its derivatives (317) are summarised in Scheme 45. The hydrocarbon products were obtained by oxidation of $Fe(CO)_3$(diene) with Ce^{4+}. A kinetic study of the reaction between $Fe(CO)_3(\eta^4\text{-}PhCH{=}CHCOMe)$ and 1,3,5-cyclooctatriene established that the rate determining step for the reaction was ring closure to give 314.

Treatment of 9-anti-methoxy-cis-bicyclo[6.1.0]nonatriene with $Fe_2(CO)_9$ afforded (318) a mixture of two compounds, 315 and 316. The reactions of 316 are shown in Scheme 46, and reaction of 317 with Ph_3C^+ gave an unidentified cation which could be reduced to 318 using BH_4^-. Thermolysis of 315 gave 319.

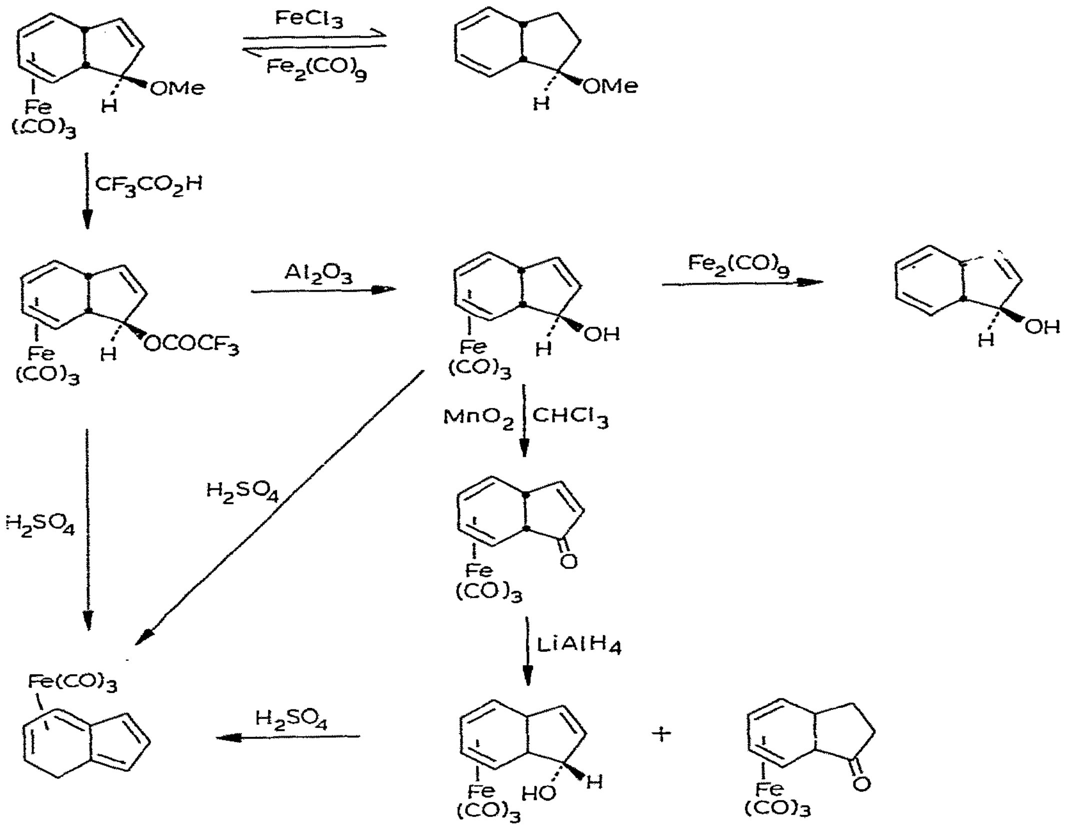
Addition of hydrazines to the norbornadiene and cycloocta-1,5-diene complexes $[Ru(diene)Cl_2]_n$ gave (319) $[Ru(diene)(N_2H_4)_4]^{2+}$, $[Ru(diene)(NH_2NHMe)_4]^{2+}$ or $[Ru(diene)(NH_2NRR')_3H]^+$ (R = R' = Me; R = R' = H), obtained as the BPh_4^- salts. On refluxing in acetone, $[Ru(C_8H_{12})(N_2H_4)_4][BPh_4]_2$ (C_8H_{12} = cyclooctadiene) was converted into $Ru(\eta^6\text{-}C_6H_5BPh_3)(C_8H_{11})$, 320, but in the presence of L (pyridine,

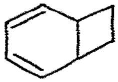
Scheme 45



4-methylpyridine, DMSO, MeCN), the species $[Ru(diene)L_4][BPh_4]_2$ and $[RuL_6]$-$[BPh_4]_2$, were obtained. Using phosphites, $[Ru(NH_2N{=}CMe_2)_2L_4]^{2+}$, L = $P(OMe)_3$, $P(OEt)_3$, $P(OCH_2)_3CR$ (R = Me or Et) and $PPh(OMe)_2$, was similarly prepared. Treatment of $[Ru(C_8H_{12})(NH_2NHMe)_4][PF_6]_2$ with $PPh(OMe)_2$ in acetone afforded $[Ru(NH_2NHMe)_2\{PPh(OMe)_2\}_4][PF_6]_2$. The hydride, $[Ru(C_8H_{12})(NH_2NMe_2)_3H]^+$, whose structure, 312, as the PF_6^- salt was determined crystallographically (320), reacted with pyridines or MeCN (L) giving $[Ru(C_8H_{12})L_3H]^+$ and with phosphines or phosphites (L'), $[RuL'_5H]^+$ (L' = $PPh(OMe)_2$, $P(OEt)_3$, $Ph(OEt)_2$, PMe_2Ph). With LiX (X = Cl or Br) in acetone, however, the binuclear species

Scheme 46





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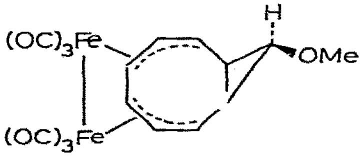

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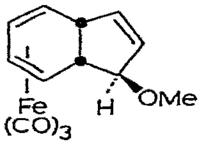

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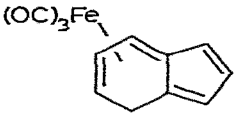

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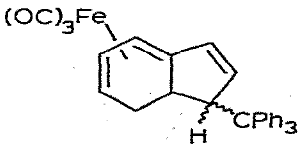

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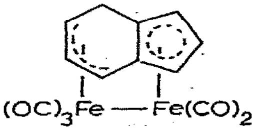
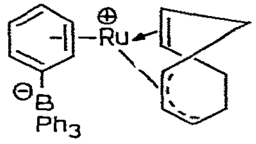


319

$[Ru(C_8H_{12})HX]_2NH_2NMe_2$, 322, was obtained. The structure of this triply-bridged complex was established (321) by X-ray methods and it was noted that the NMe_2 group of the hydrazine was attached to the less sterically hindered Ru atom (Ru-



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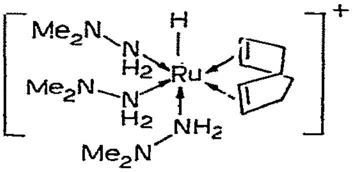

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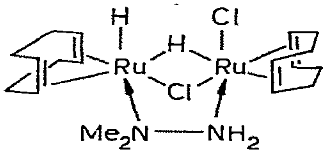

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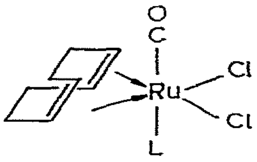

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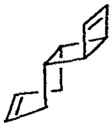

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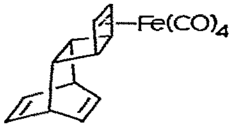

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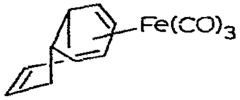

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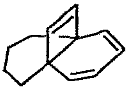

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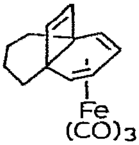

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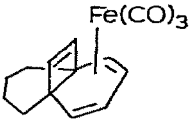

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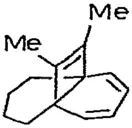

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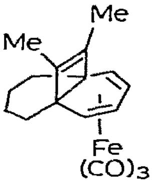
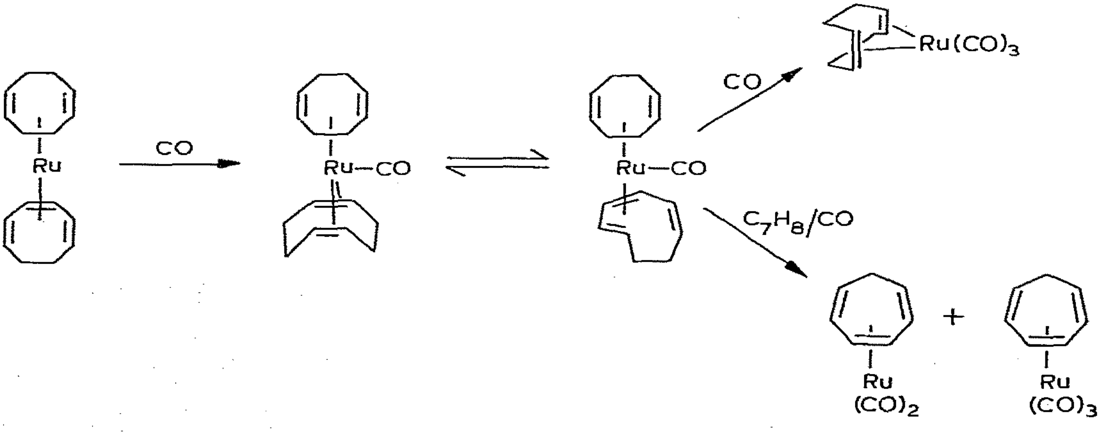


331

Ru distance 2·91Å). Treatment of 322 with Lewis bases gave $Ru(C_8H_{12})L_2HX$ (L = $PMePh_2$, $AsPh_3$, $SbPh_3$, pyridine), RuL_3HX (L = PPh_3), or $[RuL_5H]^+$ (L = $P(OMe)_3$ or $PPh(OMe)_2$). Reaction of $[Ru(C_8H_{12})L_3H]^+$ with HX in a refluxing mixture of acetone and methanol afforded (322) the triply-bridged salts $[Ru_2L_6(\mu_2\text{-}X)_3]^+$ (L = PMe_2Ph, $PMePh_2$, $PPh_2(OMe)$; X = OH, SH, SMe, I or F).

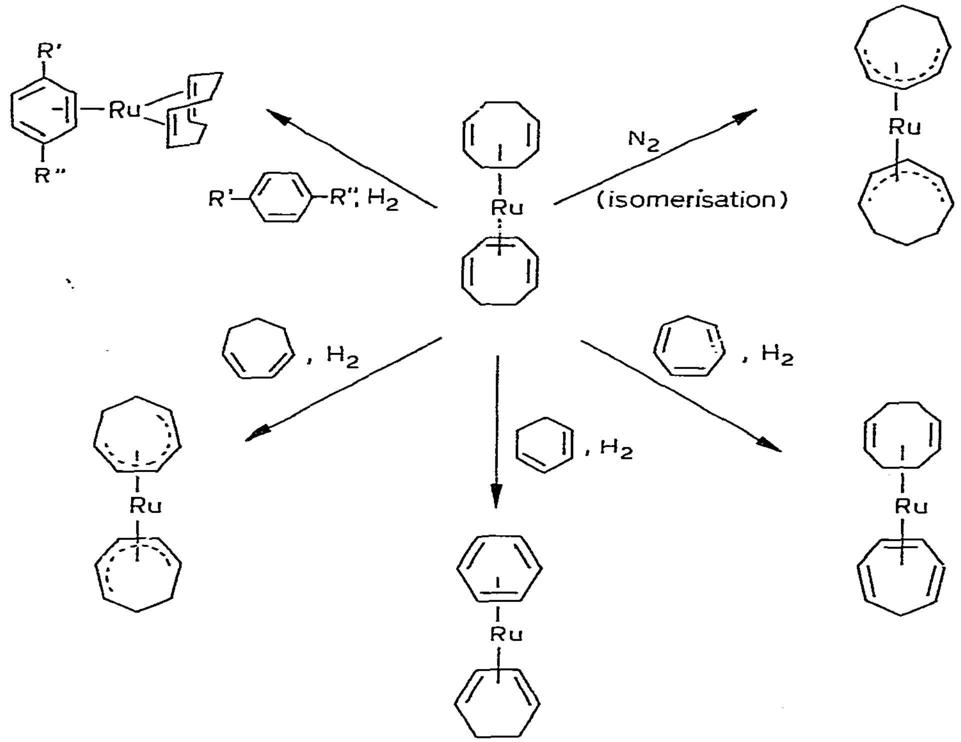
Nitriles reacted with $[Ru(CO)(C_8H_{12})Cl_2]_2$ giving (323) the mononuclear $Ru(CO)(C_8H_{12})(NCR)Cl_2$ (R = Me, cyclopropyl, CH_2=CH), and the structure of the species with R = Me, 323, was established by X-ray methods.

Scheme 47



Carbonylation of $Ru(\eta^6-C_8H_{10})(\eta^4-C_8H_{12})$ occurred (324) readily at room temperature and 1 atm. CO pressure. The course of this reaction is outlined in Scheme 47, and if the monocarbonylated product was treated with cycloheptatriene, both $Ru(CO)_2(\eta^6-C_7H_8)$ and $Ru(CO)_3(\eta^4-C_7H_8)$ were formed. Other reactions (325) of $Ru(\eta^6-C_8H_{10})(\eta^4-C_8H_{12})$ are shown in Scheme 48. In none of the reactions outlined here was cyclooctatriene detected in the mother liquors.

Scheme 48



Reaction of the tricyclic olefin 323 with $Fe_2(CO)_9$ gave (326) initially 325 which isomerised on heating to 326. The propellene 327 reacted with $Fe(CO)_3(\eta^4$-PhCH:CHCOMe) to give (327) a mixture of 328 and 329, both of which were stable to heat and inert to reagents which normally attack the cyclobutene double bond. The related triene 330 reacted with $Fe(CO)_3(\eta^4$-PhCH:CHCOMe) giving 331.

Heterodiene Complexes and Related Species

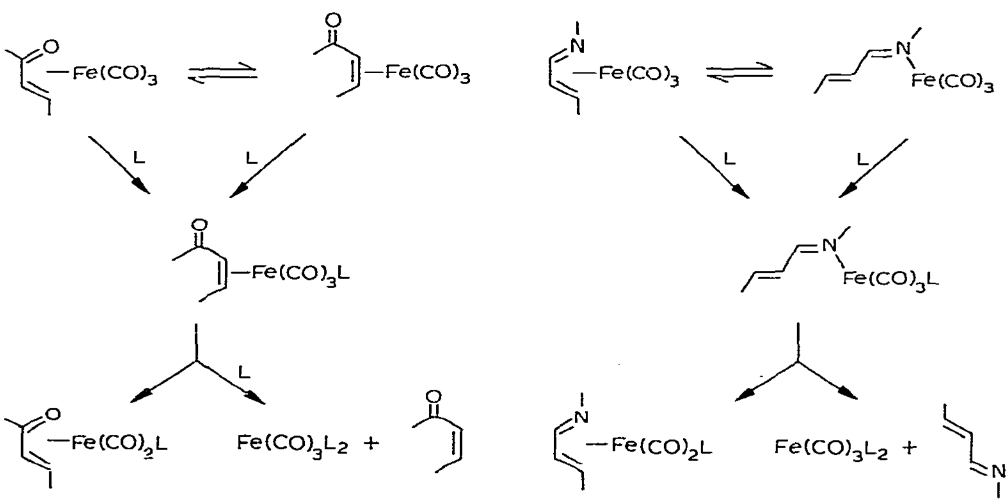
The conversion of $Fe(CO)_4\{\eta^2-N(C_6H_4X)=CHCH = CHPh\}$ into $Fe(CO)_3(\eta^4-PhCH=CHCH=NC_6H_4X)$ (X = 4-Br or -OMe, H) was studied (328) the presence of the Schiff base ligand and of CO. The reaction mechanism is in accord with the reaction pathways.

$$\begin{tikzcd}
Fe(CO)_4L \arrow[r, shift left] & L + Fe(CO)_4 \arrow[l, shift left] \arrow[r, "CO"] \arrow[d, shift right] & Fe(CO)_5 \\
 & CO + Fe(CO)_3 \arrow[u, shift right] \arrow[r, "L"] & Fe(CO)_3L
\end{tikzcd}$$

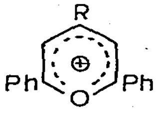
The reactions between this type of complex and the related aldehyde species $Fe(CO)_3(\eta^4{-}C_6H_4XCH{=}CHCHO)$ (X = 4-NMe_2, -OMe, -Me, -Cl; 3-OMe; H) with tertiary phosphines, arsines and stibines have been extensively studied (329). The overall reaction pathways are summarised in Scheme 49.

The structures of $Fe(CO)_3\{CH_2{=}CHC(NMe_2)(N(Me)C(O)\}$ and $[Fe(CO)_3\{CH_2{=}CHC(pip)N(Me)C(OEt)\}]BF_4$ (pip = piperidine) have been determined (330) crystallographically. The former contains a carbamoyl group and the latter a carbene moiety attached to the metal.

Scheme 49



Reaction of pyrylium iodides, 332, (R = Ph) with $Fe_2(CO)_9$ afforded (331) a mixture of 333 with traces of $Fe(CO)_3(\eta^4{-}PhC({:}O)CH{=}CPhCH_2COPh)$. The latter was also prepared by reaction of $PhCOCH{=}CPhCH_2COPh$ with $Fe_2(CO)_9$. Using 332 (R = H), 334 was obtained, and the proposed mechanisms of these reactions are summarised in Scheme 50.



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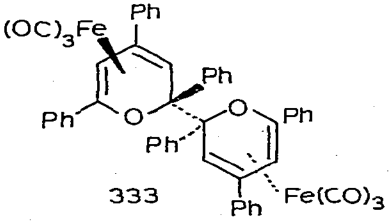

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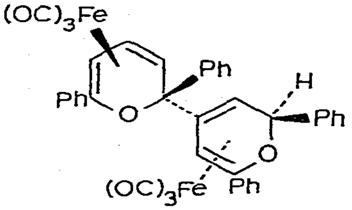

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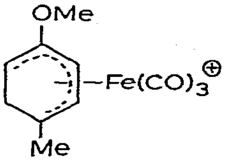

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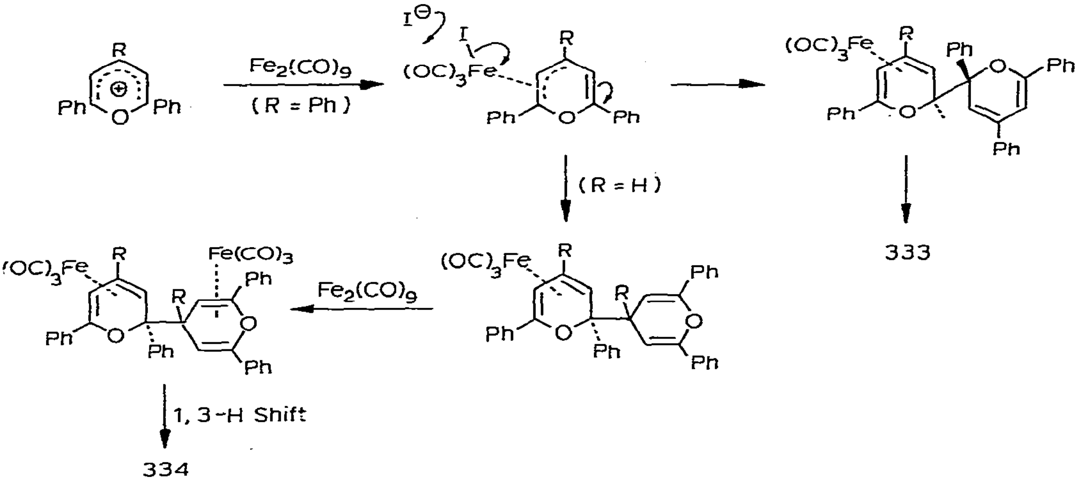
Scheme 50



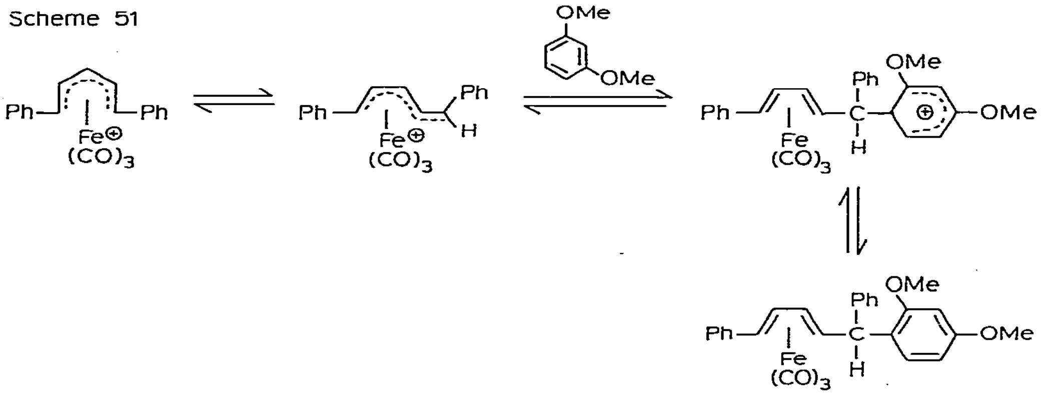
The structure of the dimethylthiophene-1,1-dioxide complex $Fe(CO)_3(\eta^4-C_4H_2Me_2-SO_2)$ was determined crystallographically (332). Because of steric effects, the S atom was pushed out of the diene plane by nearly 27°. Reaction of tetraphenyl-1-sila- and 1-germa-cyclopentadiene with $Fe(CO)_5$ under uv light gave (333) $Fe(CO)_3(\eta^4-C_4Ph_4ER_2)$ (E = Si, $R_{exo} = R_{endo}$ = Me or CH_2Ph; $R_{exo} = CH_2Cl$, R_{endo} = Me; R_{exo} = Me, R_{endo} = Cl and R_{exo} = Cl, R_{endo} = Me; E = Ge, $R_{exo} = R_{endo}$ = Me, Et, R_{exo} CH_2Cl, R''_{endo} = Me). Treatment of $Fe(CO)_3(\eta^4-C_4Ph_4GeMe_2)$ with $SnCl_4$ gave $Fe(CO)_3(\eta^4-C_4Ph_4GeClMe)$ (Cl exo), and using $LiAlH_4$ this was converted into $Fe(CO)_3(\eta^4-C_4Ph_4GeHMe)$ which had the same configuration at Ge.

DIENYL COMPLEXES

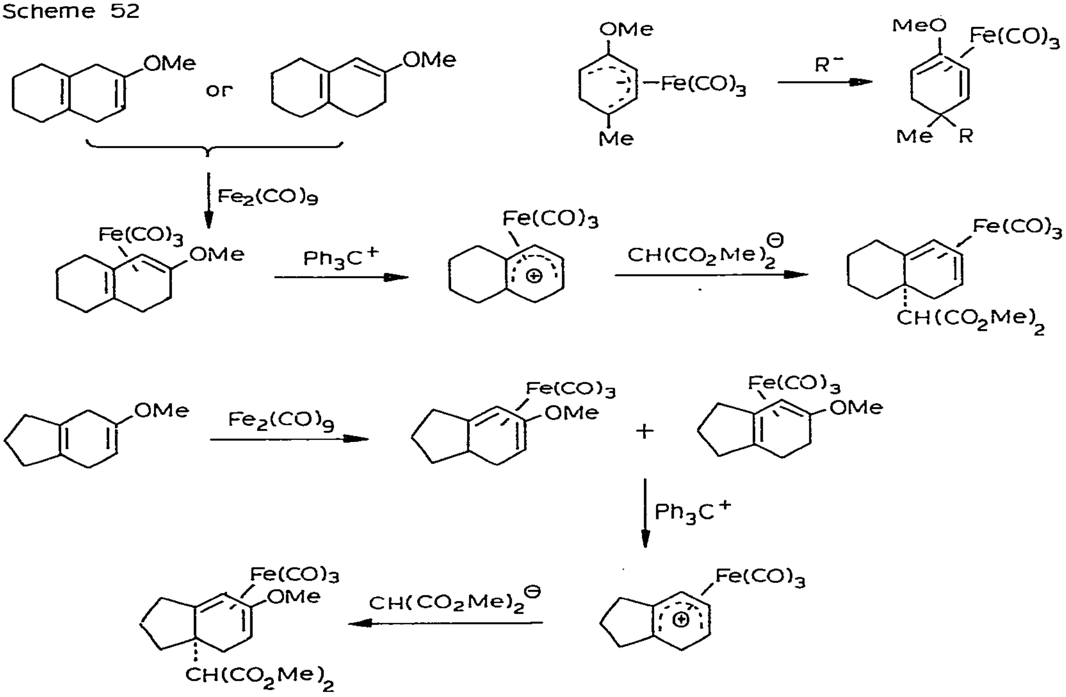
The kinetics of the electrophilic substitution of methoxybenzenes by some open-chain cationic pentadienyl iron tricarbonyl complexes have been investigated (334). The proposed reaction mechanism is outlined in Scheme 51.

The treatment of the cyclohexadienyl complex 335 with carbanions provided (335) a route to angular substitution in 5- and 6-membered ring systems (Scheme 52). Similarly, alkylation of cyclohexadienyl iron carbonyl cations

Scheme 51

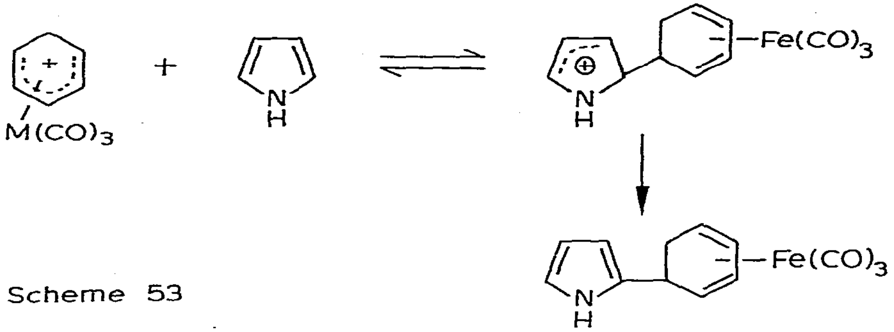


Scheme 52

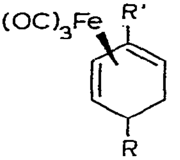


could be achieved (336) using mixed lithium alkylcuprates, LiCuR(SPh), or di-n-butylcadmium, giving species of the type 336 (R' = H, R = CH = CH$_2$, Me, SPh, Bu^t; R' = Me, R = CH=CH$_2$, SPh, Pr^i, Bu^n, Bu^t; R = OMe, R = Bu^n) and 337 (R' = Me, R = CH = CH$_2$, Pr^i, Bu^n, Bu^t).

A mechanistic study of the reaction between $[M(CO)_3(\eta^5\text{-}C_6H_7)]^+$ (M = Fe or Ru) with pyrroles and indoles has been interpreted (337) (Scheme 53) in terms of electrophilic attack of the dienyl cations on the heterocycles. The relative susceptibility of aromatic heterocycles towards attack by $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$ was established in both nitromethane and acetonitrile, and the order of reactivity was generally pyrrole $>$ indole $\gg$ furan $>$ thiophen.



Scheme 53



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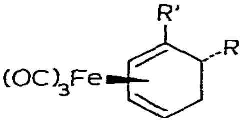

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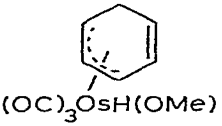

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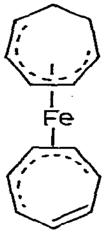

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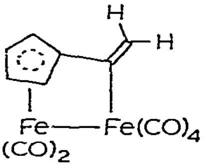

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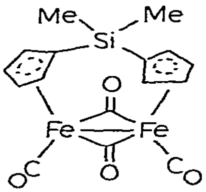

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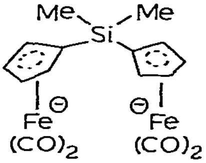


342

When $[Os(CO)_3(\eta^6-C_6H_7)]^+$ was treated (338) with methoxide ion, $Os(CO)_2(\eta^6-C_6H_7)(CO_2Me)$ was formed. On heating, this carboxymethyl complex rearranged specifically to give the exo isomer of $Os(CO)_3(\eta^4-C_6H_7OMe)$. However, the endo isomer was prepared (as the major product) by heating $[Os(CO)_3(\eta^6-C_6H_7)]^+$ in methanol, when 338 appears to have been formed (this was not isolated). This species then rearranged to endo-$Os(CO)_3(\eta^4-C_6H_7OMe)$.

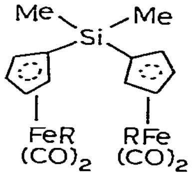
The fluxional behaviour of $Fe(\eta^5-C_7H_7)(\eta^5-C_7H_9)$, 339, apparently involves (339) a 1,2-shift process of the metal with respect to the C_7H_7 ring. Absolute assignments were made of the ^{13}C nmr spectrum, and the low temperature rocking modes of both rings was frozen out at -70°C.

CYCLOPENTADIENYL COMPLEXES

Binuclear Species

Appearance potentials have been obtained (340) from the EI mass spectrum of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$. Photolysis of the dimer at temperatures $\leqslant -30°$ in the presence of nitrosodurene (RNO) afforded (341) the "metallo-radical" species $Fe(\eta^5-C_5H_5)(CO)_2\{N(O)R\}$.

While reaction of fulvene with $Fe_2(CO)_9$ gave (342) $[Fe(\eta^5-C_5H_4Me)(CO)_2]_2$, fulveneallene afforded 340. Treatment of $Fe(CO)_5$ with $Me_2Si(C_5H_5)_2$ and with $2,4-B_5H_5C_2(SiMe_2\ C_5H_5)_2$ provided (343) the binuclear species $Me_2Si[(\eta^5-C_5H_4)Fe(CO)_2]_2$, 341, and the related $2,4-B_5H_5C_2[(\eta^5-C_5H_4SiMe_2)Fe(CO)_2]_2$, both of which contain an Fe-Fe bond. Both of these species could be reduced polarographically in two one-electron steps, the final products being dianions, e.g. 342. This contrasts with the behaviour of binuclear species where there is no connection between the η^5-rings, when reduction occurs in one two-electron step. These dianions could also be produced by reduction of the neutral precursors with sodium amalgam, and alkylation of these with RI (R = Me or Et) or with α,ω-dihalides, gave 343, 344, (n = 3, 4 or 5) and their $2,4-B_5H_5C_2$-containing counterparts, respectively. The structure of $[Fe(\eta^5-C_5H_5)(CO)(\mu-CNPh)]_2$ has been determined crystallographically (344) and it was observed that the Fe-Fe distance (2.53Å) was virtually the same as in cis- and trans-$[Fe(\eta^5-C_5H_5)(CO)_2]_2$, cis-$Fe_2(\eta^5-C_5H_5)_2(CO)_2(\mu-CO)(\mu-CNPh)$ and cis-$[Fe(\eta^5-C_5H_5)(CO)(\mu-CNMe)]_2$.



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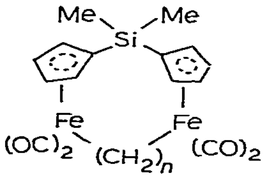

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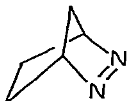

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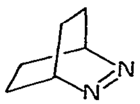

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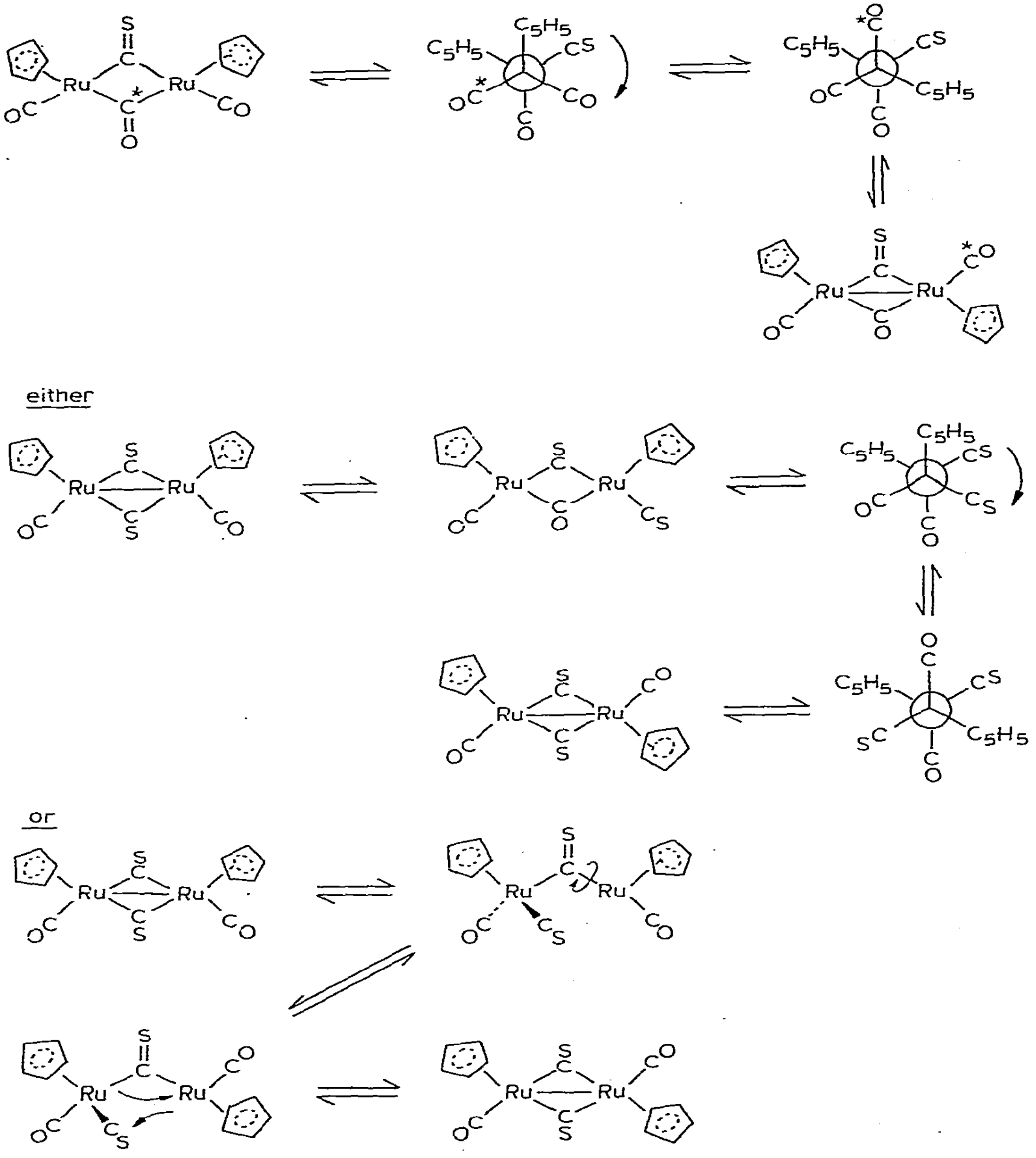
Treatment of $[Ru(\eta^5-C_5H_5)(CO)_2]^-$ with CS_2 gave (345) the C-bonded carbon disulfide adduct, $[Ru(\eta^5-C_5H_5)(CO)_2(CS_2)]^-$ which, on methylation, was converted into $Ru(\eta^5-C_5H_5)(CO)_2\{C(=S)SMe\}$. Acidification of the last by CF_3SO_3H gave $[Ru(\eta^5-C_5H_5)(CO)_2(CS)]^+$ which could be reduced by NaH giving $[Ru(\eta^5-C_5H_5)(CO)(CS)]_2$ and $Ru_2(\eta^5-C_5H_5)_2(CO)_3(CS)$. These species were obtained as their cis- and trans-isomers which were detected by nmr spectroscopy. Their fluxional behaviour (Scheme 54) was investigated by VT nmr spectral methods and it was established that the rate of cis/trans isomerisation decreased in the order $[Ru(\eta^5-C_5H_5)(CO)_2]_2 > Ru_2(C_5H_5)_2(CO)_3(CS) > [Ru(\eta^5-C_5H_5)(CO)CS)]_2$. Although the presence of CS does not substantially retard the isomerisation, it does appear that the thiocarbonyl group prefers to assume a bridging position. Reaction of $[Ru(\eta^5-C_5H_5)(CO)(CS)]_2$ with iodine gave a mixture of $Ru(\eta^5-C_5H_5)(CO)(CS)I$ and $Ru(\eta^5-C_5H_5)(CO)_2I$.

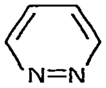
Treatment of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ with the cyclic cis-azo ligands 345, 346 and 347 (L) afforded (346) the bridged species $[Fe(\eta^5-C_5H_5)(CO)]_2L$, 348. Oxidation of these dimers by Ag^+ or I_2 gave $[Fe(\eta^5-C_5H_5)(CO)_2L]^+$, which could also be obtained from $[Fe(\eta^5-C_5H_5)(CO)_2(H_2O)]^+$ and L, and which contains monodentate L.

Scheme 54



Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ with P-phenyl phospholes, L (349), afforded (347), depending on temperature, either $Fe_2(\eta^5-C_5H_5)_2(CO)_3L$ or a mixture of this together with the phosphaferrocenes 350 and 351. However, with 1-phenylphosphole itself, only phosphaferrocenes could be isolated.

Irradiation of $[Fe(\eta^5-C_5H_5(CO)]_4$ at appropriate wavelengths in halocarbon



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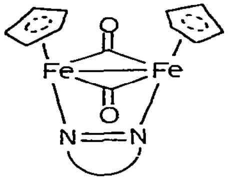

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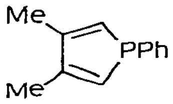

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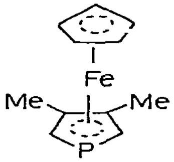

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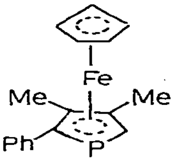

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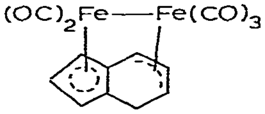

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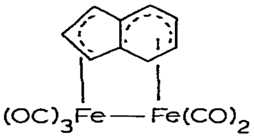

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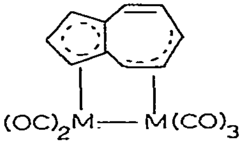

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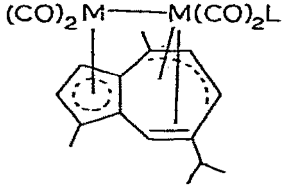
solvents gave (348) quantitative yields of $[Fe(\eta^5-C_5H_5)(CO)]_4{}^+$. This was the only photoreaction observed for any irradiation wavelength longer than 300nm, and in the absence of charge acceptor solvents, no photooxidation occurred.

Treatment of $Fe(\eta^5-C_5H_5)(CO)_2I$ with $AgBF_4$ gave (349) the bimetallic iodide-bridged species $[\{Fe(\eta^5-C_5H_5)(CO)_2\}_2I][BF_4]$. Reaction of $C_5H_5CH_2$-substituted polystyrene-divinylbenzene copolymers with $Fe(CO)_5$ or $Fe_2(CO)_9$ afforded (350) a material which appeared to be Ⓟ$-CH_2C_5H_5Fe(CO)_2H$ (Ⓟ = polystyrene backbone). This hydride was substantially more stable than its simple $\eta^5-C_5H_5$ analog.

The structure of the indenyl complex $Fe_2(CO)_5(C_9H_8)$, 352 has been determined crystallographically (351) (Fe-Fe 2·78Å). This species and its phosphine substituted analog $Fe_2(CO)_4(PEt_3)(C_9H_8)$ exhibited two fluxional processes - localised low-temperature scrambling of CO groups on the $Fe(CO)_3/(Fe(CO)_2PEt_3)$ moiety and, at higher temperatures, exchange of CO groups between the two metal sites. It was observed that in $Fe_2(CO)_4(PEt_3)(C_9H_8)$, only three of the four CO groups engaged in site exchange, one on the $Fe(CO)_2(PEt_3)$ unit remaining inert. It is possible that an intermediate for internuclear scrambling of CO is 353. The fluxional behaviour of the azulene complexes $M_2(CO)_5(C_{10}H_8)$, 354 (M = Fe or Ru) has also been investigated (352). The low temperature limiting of the Ru complex is consistent with the structure already established (353) for its Fe analog. Both species exhibit two fluxional modes: localised scrambling on the $M(CO)_3$ group and internuclear CO scrambling. Similar data have been accumulated (354) from a closely related series of guaiazulene complexes, 355 (M = Fe, L = CO or PEt_3; M = Ru, L = CO) and an isomer 356. The structures of three of these species, 355 (M = Fe, L = CO), 355 (M = Fe, L = PEt_3) and 356 were determined by X-ray methods and it was noted that the Fe-Fe distances (2·79, 2·80 and 2·81, respectively) did not vary significantly. A possible mechanism permitting internuclear CO exchange is outlined in Scheme 55.



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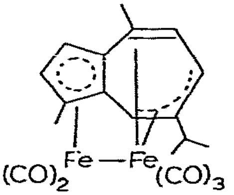

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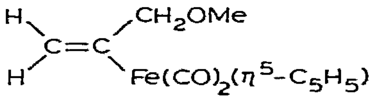

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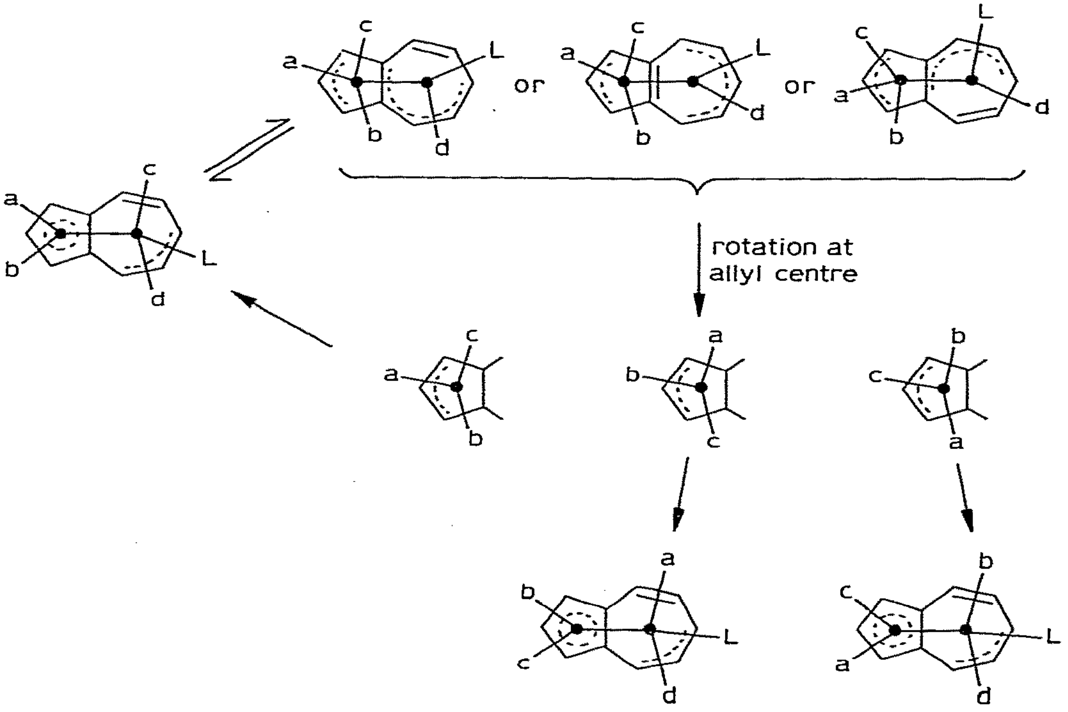
Scheme 55

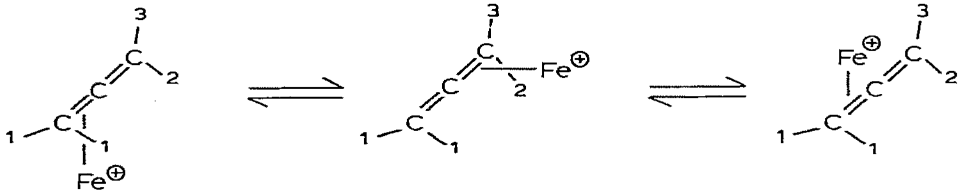


Cationic Species

A synthesis of $[Fe(\eta^5-C_5H_5)(CO)_2(THF)][BF_4]$, from $Fe(\eta^5-C_5H_5)(CO)_2I$, $AgBF_4$ and THF, has been described (356), and this cation has proved to be a very convenient precursor to $[Fe(\eta^5-C_5H_5)(CO)_2(olefin)]^+$. Thus treatment of the THF containing cation with alkene in the presence of gaseous BF_3 in dichloromethane afforded high yields of the desired olefin cations (olefin = $\eta^2-1,5-C_5H_{12}$, $\eta^2-1,4-C_6H_8$, $\eta^2-C_7H_{12}$, $\eta^2-C_6H_{10}$, C_2H_4). When cyclooctatetraene was used, $[Fe(\eta^5-C_5H_5)(\eta^6-C_8H_8)][BF_4]$ was produced in low yield, and if PPh_3 or aniline (L) were employed, the expected $[Fe(\eta^5-C_5H_5)(CO)_2L][BF_4]$ was formed. Reaction of $Fe(\eta^5-C_5H_5)(CO)_2I$ with $AgNO_3$ in THF afforded $Fe(\eta^5-C_5H_5)(CO)_2(NO_3)$, and treatment of $Fe(\eta^5-C_5H_5)(PPh_3)I$ with $AgBF_4$ in THF gave $[Fe(\eta^5-C_5H_5)(CO)(PPh_3)(THF)][BF_4]$.

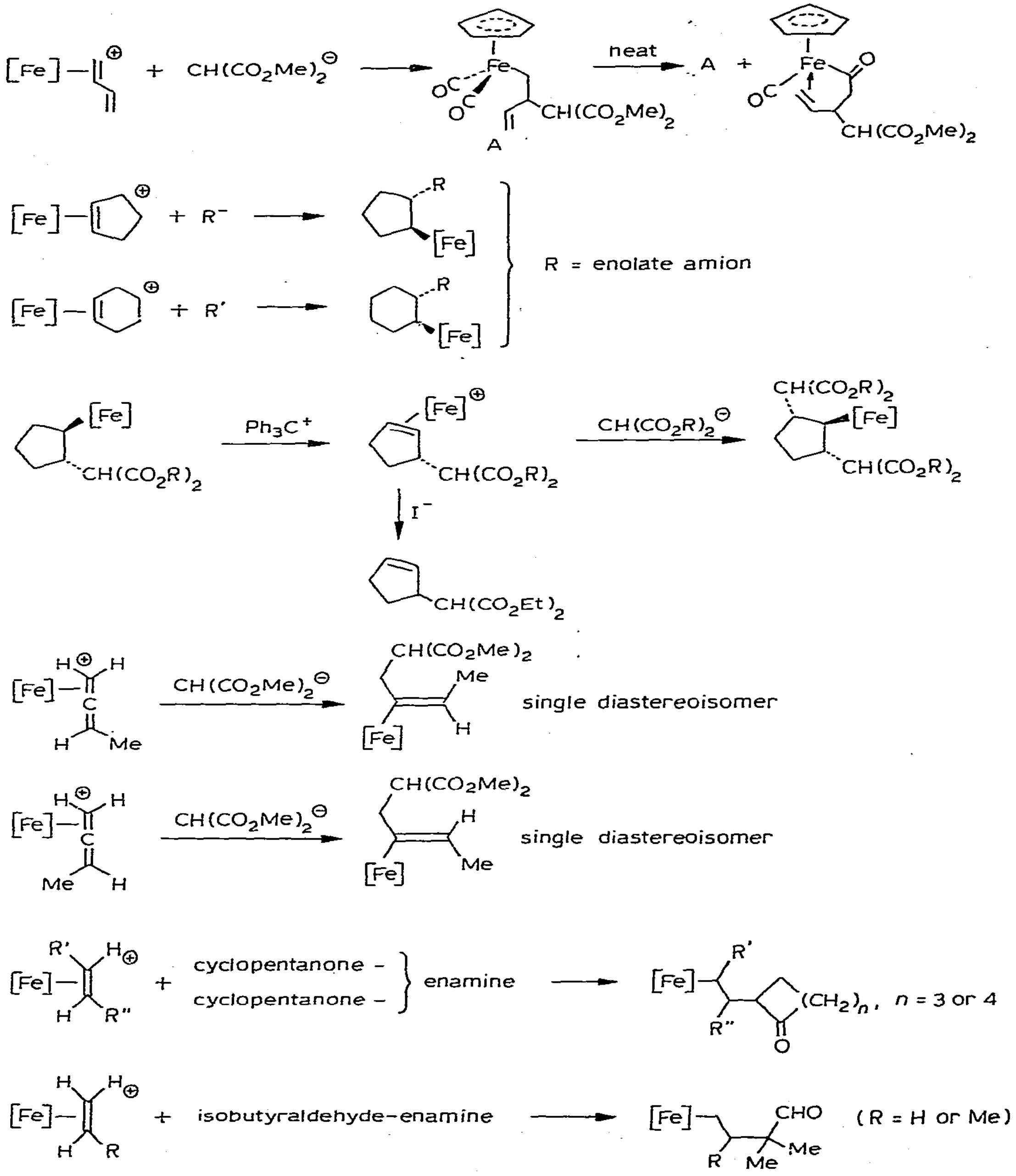
Reaction of the isobutylene complex $[Fe(\eta^5-C_5H_5)(CO)_2(CH_2{=}CMe_2)]^+$ with ferrocenylethylene gave (356) $[Fe(\eta^5-C_5H_5)(CO)_2(CH_2{=}CHC_5H_4FeC_5H_5)]^+$. Nucleophilic attack on this cation by PPh_3, I^-, CN^-, OH^-, H^-, or $O_2CCF_3^-$ (X^-) afforded only the ferrocenylethylene and $CpFe(CO)_2X$. The η^2-allene complexes $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CRR^1{=}C{=}CR^{11}R^{111})]^+$ (R,R^1,R^{11},R^{111} = H, Me) were prepared (357) by reaction of the above-mentioned isobutylene complex with the appropriate allene. For those allene complexes capable of existing in stereoisomeric forms, the syn isomer could be obtained stereospecifically by protonation of $Fe(\eta^5\text{-}C_5H_5)(CO)_2\text{-}CH_2C{\equiv}CR$. The energy barrier to rotation about the Fe-olefin bond was found to be controlled mainly by the syn-3-substituent. From a careful VT nmr study of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(Me_2C{=}C{=}CMe_2)]^+$, it was established that exchange of ligand coordination site occurred via the non-dissociative pathway illustrated in Scheme 56. Reaction of 4-methoxy-2-butyryl-1-benzenesulfonate with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ gave not $Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2CH{=}CHCH_2OMe$, but 357 which, on protonation by HBF_4 in ether, was converted into 358; there was no evidence for cationic cumulene or acetylene complexes.

Scheme 56



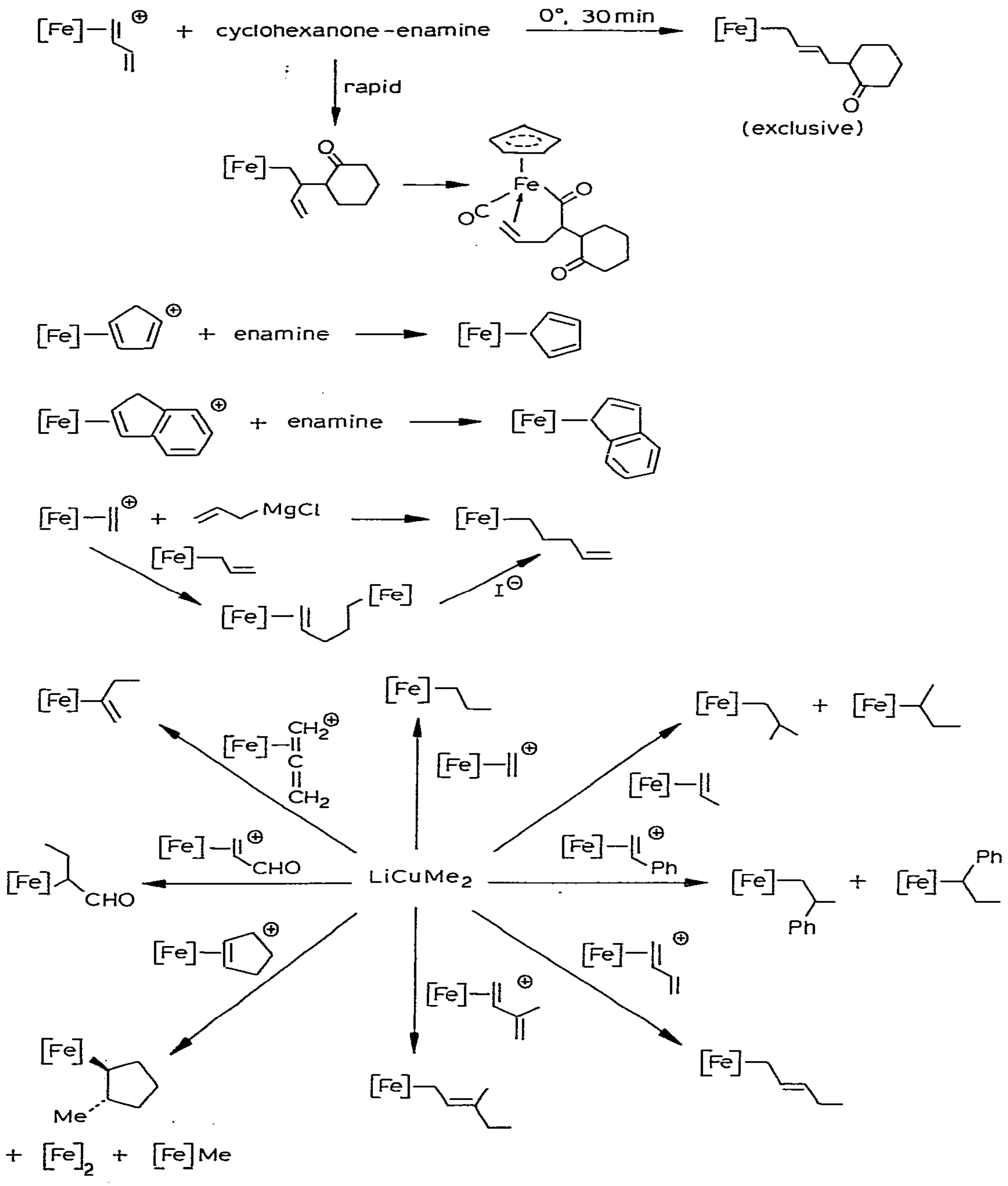
Carbon-carbon bond formation by the reaction of carbon-based nucleophiles on $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(olefin)]^+$ has been extensively investigated (358). The basic cation precursors contained $CH_2{=}CHR$ where R = H, Me, Ph, $CH{=}CH_2$, CH_2CH_2Ph, $CMe{=}CH_2$, and also were derived from cyclo-pentene and -hexene. The nucleophiles were based on enolate types (malonate, acetoacetate, cyanoacetate, nitromethane) or on enamines (from isobutyraldehyde, cyclopentanone or cyclohexanone). The addition of the nucleophile occurred mainly trans to the Fe-olefin bond, and it was noted that the regiospecificity of addition was low for the propylene complexes but high for their styrene analogues. The reactions are summarised in Scheme 57. Treatment of the η^2-cyclopentadiene and -indene complexes $[Fe(\eta^5\text{-}C_5H_5)(CO)_2L]^+$ ($L = C_5H_6$, C_9H_8) with isobutyraldehyde or cyclohexanone pyrrolidine enamine afforded the η^1-cyclopentadienyl and indenyl complexes, $Fe(\eta^5\text{-}C_5H_5)(CO)_2\text{-}(\eta^1\text{-}C_5H_5)$ and $Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C_9H_7)$, respectively. In general, reaction of the alkene cations with an excess of Grignard reagents or lithium alkyls led to olefin displacement and reduction of the organometallic fragment. However, the reactions of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)]^+$ with $Mg(C_3H_5)Cl$ gave, in low yield $Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_2)_3CH{=}CH_2$ (see Scheme 57). However, better results were obtained using $LiCuMe_2$ and these, too, are summarised in Scheme 57.

Scheme 57



Treatment of $[Ru(\eta^5-C_5H_5)(CO)_2(CS)]^+$ with NCO^- and N_3^- gave (345) $Ru(\eta^5-C_5H_5)(CO)_2CN$, and COS, and $Ru(\eta^5-C_5H_5)(CO)_2NCS$ and N_2, respectively. The latter reaction contrasted with the behaviour of $[Ru(\eta^5-C_5H_5)(CO)_3]^+$ which afforded $Ru(\eta^5-C_5H_5)(CO)_2SCN$ on treatment with NCS^-. The N-bonded thiocyanato complex was also

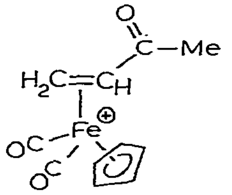
Scheme 57 continued:



obtained when $[Ru(\eta^5\text{-}C_5H_5)(CO)_2(CS)]^+$ was reacted with hydrazine. Reaction of the thiocarbonyl cation with methoxide ion afforded several products of which only $Ru(\eta^5\text{-}C_5H_5)(CO)(CS)\{C(=O)OMe\}$ and $[Ru(\eta^5\text{-}C_5H_5)(CO)(CS)]_2$ were identified. When the related iron thiocarbonyl cation was similarly treated, $[Fe(\eta^5\text{-}C_5H_5)$-

$(CO)_2]_2$, $Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CS)$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)(CS)]_2$ were produced. With iodide ion, $[Ru(\eta^5\text{-}C_5H_5)(CO)_2(CS)]^+$ was converted into $Ru(\eta^5\text{-}C_5H_5)(CO)_2I$ while, as mentioned earlier, NaH effects the formation of $[Ru(\eta^5\text{-}C_5H_5)(CO)(CS)]_2$ and $Ru_2(\eta^5\text{-}C_5H_5)_2(CO)_3(CS)$.

While $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ reacted (359) with NO in benzene giving $[Fe(\eta^5\text{-}C_5H_5)(CO)(NO)]_2$, 359 (the original was shown having a Fe-Fe bond but this seems unlikely), $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ afforded $Fe(\eta^5\text{-}C_5H_5)(CO)(NO)I$. Reaction of $Fe(\eta^5\text{-}C_5H_5)(CO)LI$ (L = Ph_3P, Ph_3As or Ph_3Sb) with NO gave $Fe(\eta^5\text{-}C_5H_5)(NO)LI$, while $[Fe(\eta^5\text{-}C_5H_5)(CO)_2L]I$ afforded the cationic species $[Fe(\eta^5\text{-}C_5H_5)(NO)_2L]I$ (the nature of the Fe-N-O bonds in this species is not known).



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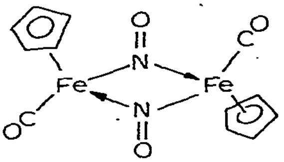

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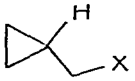


360

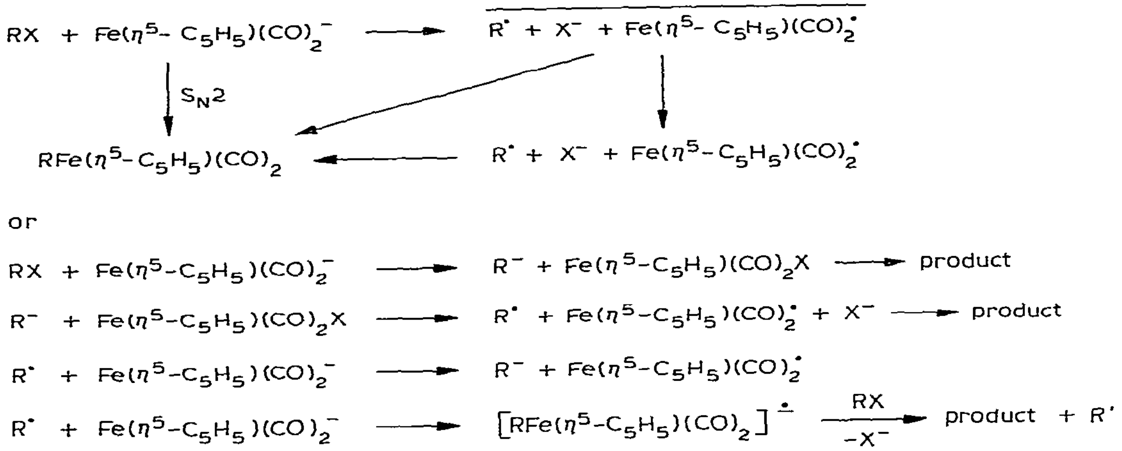
Reaction of $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ with $Ph_3P{=}CHR$ (R = H or Me) gave (360) the phosphonium species $[Fe(\eta^5\text{-}C_5H_5)Fe(CO)_2\{CHR(PPh_3)\}]I$, which was finally isolated as a BF_4^- salt. Similarly, Ph_3PCH_2 reacted (361) with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2L(THF)]^+$ giving $[Fe(\eta^5\text{-}C_5H_5)(CO)L(CH_2PPh_3)]^+$ (L = CO or PPh_3). Furthermore, $[Fe(\eta^5\text{-}C_5H_5)(CO)_4(PPh_3)(C_2H_4)]^+$ added Ph_3PCH_2 and $P(O)(OMe)_2^-$ giving, respectively $[Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(CH_2CH_2CH_2PPh_3)]^+$ and $Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)\{CH_2CH_2P(O)(OMe)_2\}$.

Complexes Containing M-C σ bonds

During the reaction between $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ and Pr^iI an esr signal due to the isopropyl radical was detected (362). Similar behaviour was detected during reactions involving other alkyl iodides, but not when bromides or chlorides were used. Treatment of $Na[Fe(\eta^5\text{-}C_5H_5(CO)_2]$ with 360 (X = Br or I) gave a mixture of 360 (X = $Fe(CO)_2(\eta^5\text{-}C_5H_5)$) and $Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2CH_2CH{=}CH_2$. An esr signal was detected in reactions involving X = I, and the ratios of 360 (X = $Fe(CO)_2(\eta^5\text{-}C_5H_5)$) to the butenyl complex were 97:3 for X = Br and 70:30 for X = I. In a series of reactions involving $LiSnMe_3$, similar results were observed, indicating that a substantial fraction of reactions of this type may occur via a radical pathway. These reactions may occur by a pathway involving initial one-electron transfer followed by non-geminate (and presumably also geminate) radical combination processes, or a radical chain process (Scheme 58).

An nmr study of the photolysis of $Fe(\eta^5\text{-}C_5H_5)(CO)_2Me$ in the presence of PPh_3, $AsPh_3$, SEt_2, pyridine, diarsine, etc., revealed (363) that dissociation of CO

Scheme 58



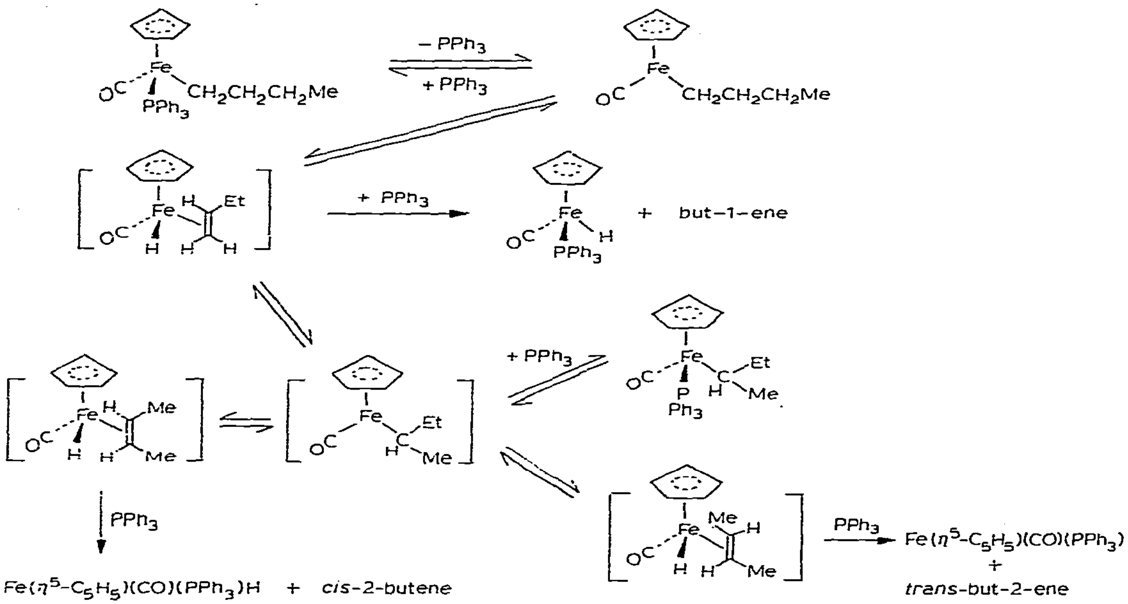
occurred as the first step, giving $[Fe(\eta^5-C_5H_5)(CO)Me]$ which combined with L to give $Fe(\eta^5-C_5H_5)(CO)LMe$. However, in liquid ammonia, $Fe(\eta^5-C_5H_5)(CO)_2Me$ was converted (364) into $Fe(\eta^5-C_5H_5)(CO)(NH_3)(COMe)$; the NH_3 was readily displaced by pyridine.

In reactions of $M[Fe(\eta^5-C_5H_5)(CO)_2]$ (M = Li or Na) with epoxides, in which alkyl species were formed, it was found (365) that the Li^+ salt was more reactive than the corresponding Na^+ salt. On heating $Fe(\eta^5-C_5H_5)(CO)(PPh_3)\{CHMeEt\}$ in xylene at 63°, isomerisation to $Fe(\eta^5-C_5H_5)(CO)(PPh_3)Bu^n$ occurred (366) together with formation of $Fe(\eta^5-C_5H_5)(CO)(PPh_3)H$ and butenes. When $Fe(\eta^5-C_5H_5)(CO)(PPh_3)CD_2CHMe_2$ was heated, deuterium scrambled throughout the σ-butyl moiety, and the 2-methylpropene which was collected also had exhibited distribution of D. It appears that the $[Fe(\eta^5-C_5H_5)(CO)(PPh_3)]$ fragment prefers to be attached to a primary rather than a secondary C atom, but that tertiary C-bound intermediates, e.g. $Fe(\eta^5-C_5H_5)(CO)(PPh_3C(CD_2H)Me_2$, are accessible. The proposed general reaction mechanism is shown in Scheme 59.

By reaction of racemic or resolved $Fe(\eta^5-C_5H_5)(CO)\{P(OPh)_3\}$ I with racemic $MgBr(CHPhSiMe_3)$, mixtures of the two diastereoisomers of $Fe(\eta^5-C_5H_5)(CO)(PPh_3)(CH_2PhSiMe_3)$ were obtained (367). Selective decomposition of the RR, SS diastereomer, predicted to be the more highly hindered, occurred above room temperature, however, leading to the pure RS, SR isomer. Sulfonylation reactions of both diastereomers were reversible and provided a route, via the diastereoisomeric sulfinate complexes, to epimerisation of these alkyl complexes. Kinetic and thermodynamic studies in mixtures of SO_2 and $CDCl_3$ revealed that although (RS, SR)-$Fe(\eta^5-C_5H_5)(CO)(PPh_3)(CHPhSiMe_3)$ is the thermodynamically more stable diastereomer, (RR,SS)-$Fe(\eta^5-C_5H_5)(CO)(PPh_3)(CHPhSiMe_3)$ could be formed in disproportionate amounts by the interaction of the (RS,SR)-form with SO_2.

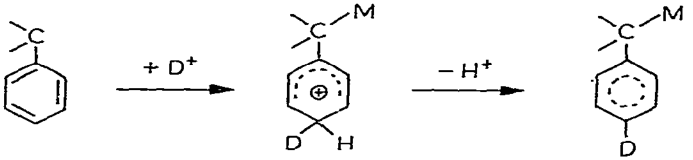
Reaction of $o-ClCH_2C_6H_4CN$ with $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ afforded (368) $Fe(\eta^5-C_5H_5)$-

Scheme 59



$(CO)_2CH_2C_6H_4CN$, in which the CN group did not coordinate to the metal. It was observed (369) that optically pure $Fe(\eta^5-C_5H_5)(CO)_2CHMePh$ (370) underwent aromatic H/D exchange in CH_3CO_2D/– or CF_3CO_2D/CH_2Cl_2 mixtures. This process occurred without racemisation, indicating that Fe–C bond rupture did not occur (Scheme 60).

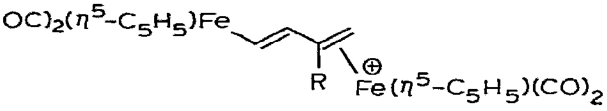
Scheme 60



Treatment of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ with $LiBHEt_3$ afforded (371), in good yield, $[Fe(\eta^5-C_5H_5)(CO)_2]^-$, from which $Fe(\eta^5-C_5H_5)(CO)_2R$, R = COPh, COCH=CHPh and $SnPh_3$, were prepared in good yield by addition to the anion of the appropriate chloride. Reaction of $[(OC)_5MnMn(CO)_4CHO]^-$, obtained from $Mn_2(CO)_{10}$ and $LiBHR_3$, with $Fe(CO)_5$ gave $[Fe(CO)_4CHO]^-$ and $Mn_2(CO)_{10}$.

Addition of carbonium ions derived from $MeOSO_2F$ or $[CH(OMe)_2]^+$ to $Fe(\eta^5-C_5H_5)-(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(\eta^5-C_5H_5)$ afforded (372) the bimetallic cation <u>361</u> (R = Me, Et or $CH(OMe)_2$). The η^2-bound $Fe(\eta^5-C_5H_5)(CO)_2$ fragment could be removed from 361 by its treatment with I^-. The species 361 (R = H) could be obtained by careful protonation of $Fe(\eta^5-C_5H_5)(CO)_2CH=CHCH=CHFe(CO)_2(\eta^5-C_5H_5)$, and spectroscopic studies of 361 suggested that the carbenoid form 362 played an important role in the bonding description, and hence the chemistry, of these compounds.

Treatment of $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ with isobutyryl or diphenylacetyl chloride gave (373) the acyl species $Fe(\eta^5-C_5H_5)(CO)_2COCHR_2$ (R = Me or Ph). Methylation of these using LiMe afforded, after hydrolysis, 363 (Q = $CHMe_2$ or $CHPh_2$). Reaction of $Fe(\eta^5-C_5H_5)(CO)_2COMe$ with LiMe, followed by HCl, gave 363 (Q = Me), but if methylation was followed by addition of $AlCl_3$, the Al(III) complex 364 was produced. If a similar reaction was carried out using 363 (Q = $CHMe_2$ or $CHPh_2$), a variety of isomers of the Al chelates could be isolated. Treatment of $Ni(PPh_3)(acac)Et$ with either $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ or $Fe(CO)_5$ in the presence of PPh_3 afforded (374) a mixture of $Ni(CO)_2(PPh_3)_2$, $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$.



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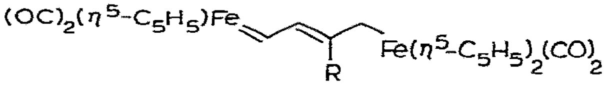

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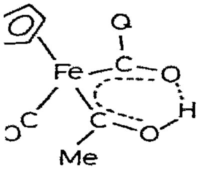

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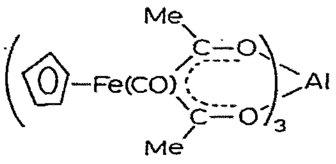

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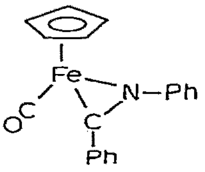

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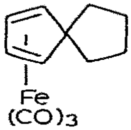


366

Reaction of $Na[Fe(\eta^5-C_5H_5)(CO)_2]$ with PhC(Cl) = NPh gave (375) the η^1-iminoacyl omplex, $Fe(\eta^5-C_5H_5)(CO)_2(PhCNPh)$ which, on photolysis, eliminated CO giving 5.

Photolysis of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ in the presence of benzaldehyde afforded 76), as the only organometallic product, $Fe(\eta^5-C_5H_5)(CO)_2Ph$. In acetonitrile, $_2(\eta^5-C_5H_5)_2(CO)_3(NCMe)$ was produced. There was thought to be two possible chanisms for this reaction:-

$$\begin{array}{lcl}
[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2 & \xrightarrow{h\nu} & 2[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet} \\
[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet} + PhCHO & \longrightarrow & Fe(\eta^5\text{-}C_5H_5)(CO)_2H + PhCO^{\bullet} \\
[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet} + PhCO^{\bullet} & \longrightarrow & Fe(\eta^5\text{-}C_5H_5)(CO)_2COPh \\
Fe(\eta^5\text{-}C_5H_5)(CO)_2COPh & \xrightarrow{h\nu} & Fe(\eta^5\text{-}C_5H_5)(CO)_2Ph + CO \\
2\ Fe(\eta^5\text{-}C_5H_5)(CO)_2H & \longrightarrow & [Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2 + H_2
\end{array}$$

or, as the more favoured process -

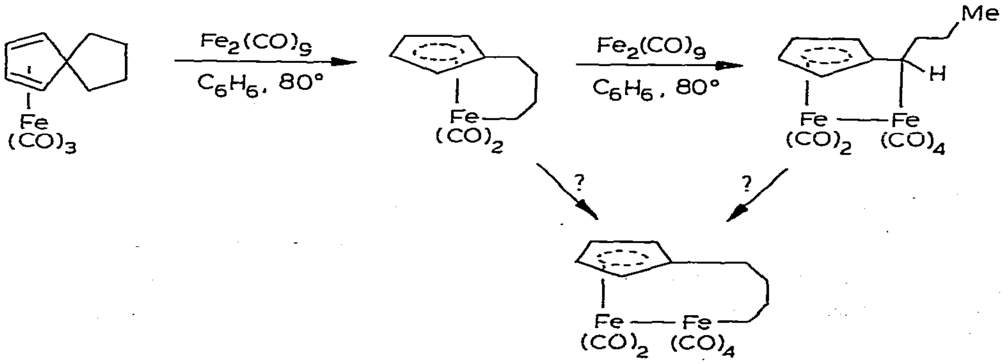
$$\begin{array}{lcl}
[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^{\bullet} + PhCHO & \longrightarrow & [Fe(\eta^5\text{-}C_5H_5)(CO)(PhCHO)]^{\bullet} + CO \\
[Fe(\eta^5\text{-}C_5H_5)(CO)(PhCHO)]^{\bullet} & \longrightarrow & [Fe(\eta^5\text{-}C_5H_5)(CO)H(COPh)]^{\bullet} \\
[Fe(\eta^5\text{-}C_5H_5)(CO)H(COPh)]^{\bullet} & \longrightarrow & Fe(\eta^5\text{-}C_5H_5)(CO)(COPh) + \tfrac{1}{2}H_2 \\
Fe(\eta^5\text{-}C_5H_5)(CO)(COPh) & \longrightarrow & Fe(\eta^5\text{-}C_5H_5(CO)_2Ph
\end{array}$$

Reaction of $Fe(\eta^5\text{-}C_5H_5)(CO)_2Br$ with CuR in THF gave (377) the aryl complexes $Fe(\eta^5\text{-}C_5H_5)(CO)_2R$ (R = m- or p-FC_6H_4, Ph). From the corresponding copper carboranes, o-, and m-$HCB_{10}H_{10}CFe(CO)_2(\eta^5\text{-}C_5H_5)$ and o- and m-$Fe(\eta^5\text{-}C_5H_5)(CO)_2\text{-}CB_{10}H_{10}CFe(CO)_2(\eta^5\text{-}C_5H_5)$ were also produced. It has been suggested (378) that halogenation of the o-carboranylmethyl complex $MeCB_{10}H_{10}CCH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ gave $MeCB_{10}H_{10}CCH_2COFeX_2(CO)(\eta^5\text{-}C_5H_5)$ (X = Cl, Br or I) which, on hydrolysis, was converted into $MeCB_{10}H_{10}CCH_2CO_2H$.

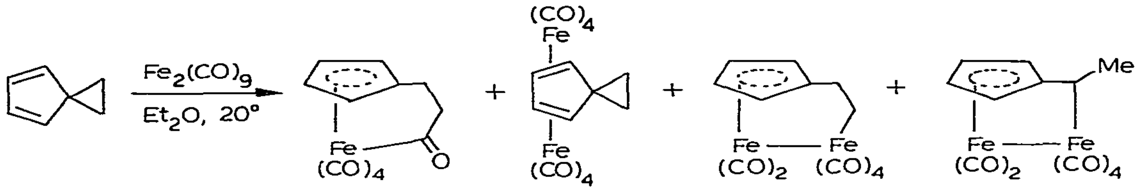
Cleavage of C-C single bonds within $Fe(CO)_3$ complexes of 1,1-dialkyl-substituted cyclopentadienes is promoted (379) by $Fe_2(CO)_9$. Thus $C_5H_4RR^1$ is converted at 20° in THF into $Fe(CO)_3(\eta^4\text{-}C_5H_4RR^1)$ and at 80° in benzene, the endo-alkyl group is intramolecularly transferred from the diene to the metal, giving $Fe(\eta^5\text{-}C_5H_4R)\text{-}(CO)_2R^1$ ($R = R^1$ = Me or Et, R = Me, R^1 = Et, R = Et, R^1 = Me). In a similar process, the spiro-diene complex <u>366</u> rearranged (380) as shown in Scheme 61, and other related reactions are illustrated in Scheme 62.

The structure of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2C_3H_5]^+$, <u>367</u>, obtained (381) previously by treating $\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2C_3H_6$ with Ph_3C^+, has been determined crystallo-

Scheme 61

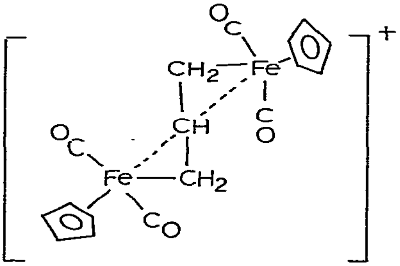


Scheme 62



graphically (382). The positive charge is best represented as being localised on the β-C atom. While Fe-C(α) is 2·12-2·13Å, Fe...C(β) is 2·72 or 2·59Å, perhaps representing a weak interaction.

Reaction of $Fe(\eta^5-C_5H_5)(CO)_2(\eta^1-C_5H_5)$ with $P(OMe)_3$ occurred (383) via an Arbuzov-like rearrangement, giving $Fe(\eta^5-C_5H_5)(CO)\{P(OMe)_3\}P(=O)(OMe)_2$. With $PMePh_2$, only $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ could be recovered, but $Fe(\eta^5-C_5H_5)(CO)\{P(OPh)_3\}(\eta^1-C_5H_5)$ was obtained using triphenylphosphite. The behaviour of the VT nmr spectrum of the $P(OPh)_3$-containing complex in solution was very similar to that of $Fe(\eta^5-C_5H_5)(CO)_2(\eta^1-C_5H_5)$.



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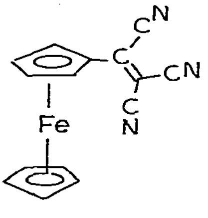

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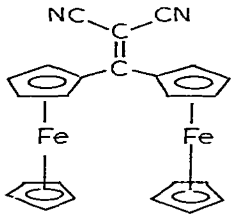

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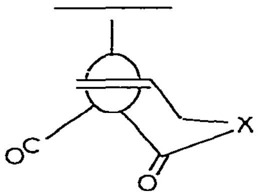

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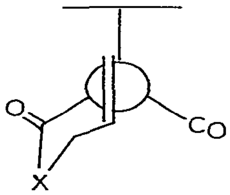

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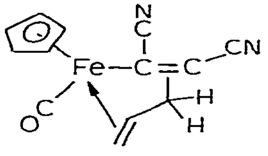
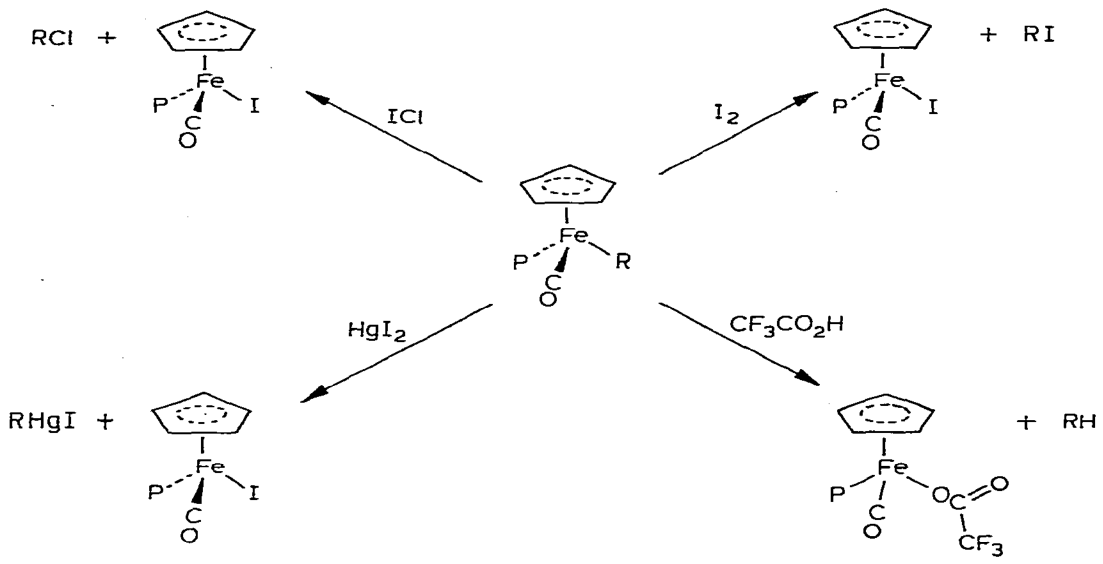


372

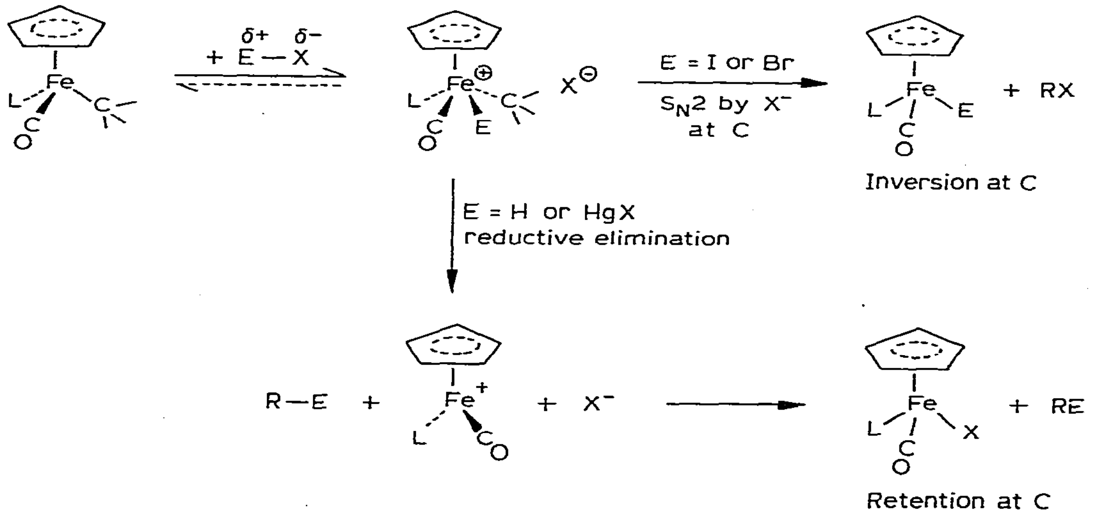
Treatment of TlC_5H_5 with TCNE afforded $Tl[C_5H_5(CN)C=C(CN)_2]$ which reacted (384) with $Fe(\eta^5-C_5H_5)(CO)_2I$ giving 368. If 368 was then treated with TlC_5H_5 followed by $Fe(\eta^5-C_5H_5)(CO)_2I$, the binuclear 369 was produced.

Electrophilic cleavage of the Fe-C bond in $Fe(\eta^5-C_5H_5)(CO)(PPh_3)R$ (R = Me, Et, CH_2CO_2 menthyl and CH_2O menthyl) by I_2, ICl and $HgCl_2$ has been investigated (385)

Scheme 63



Scheme 64



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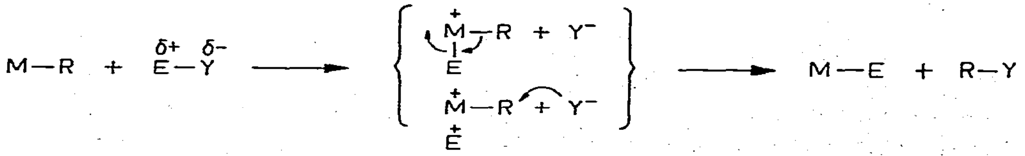
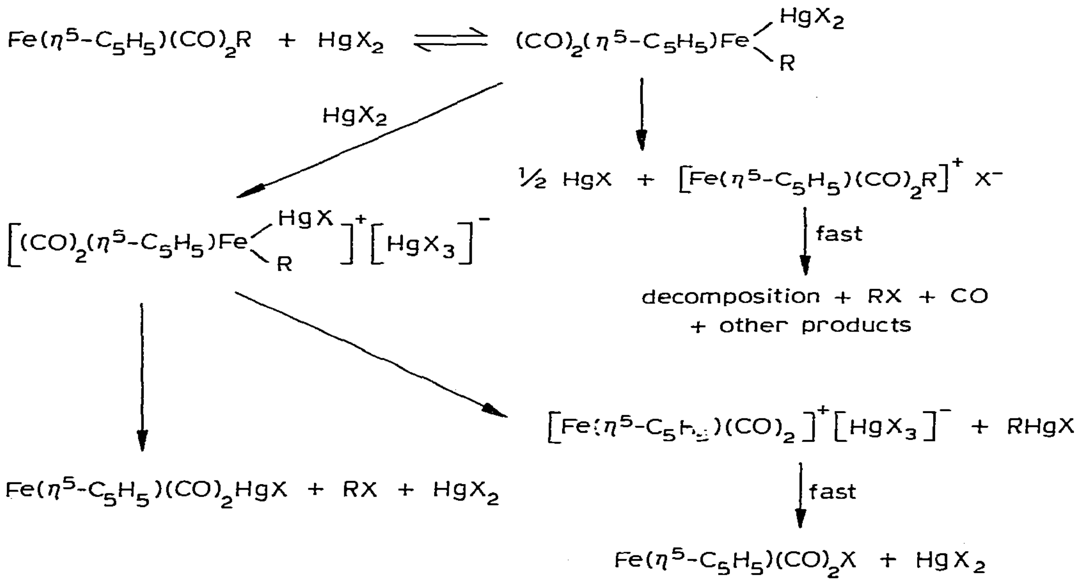


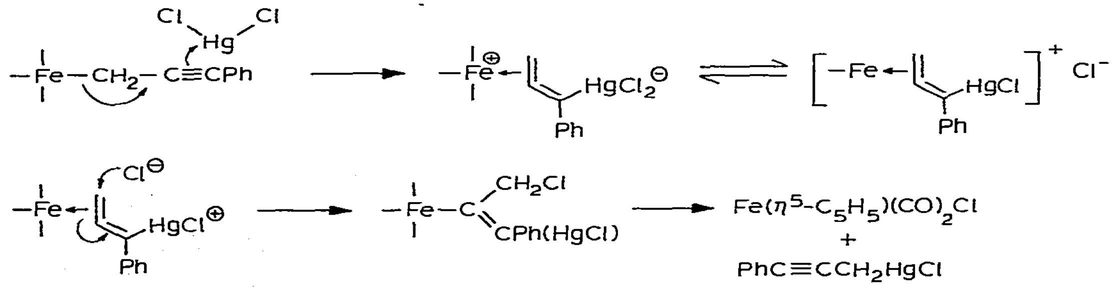
using the resolved chiral complexes. It has been observed (Scheme 63) that the reaction proceeded with net retention of configuration at iron, although the stereospecificity was not high and was insensitive to the nature of the R-group. The formation of $Fe(\eta^5-C_5H_5)(CO)(PPh_3)I$ from cleavage via ICl indicated that the initial electrophilic attack occurred at the metal. The favoured mechanism is illustrated in Scheme 64.

In either THF or isopropanol, three distinct pathways for the elimination of alkyl or aryl groups from $Fe(\eta^5-C_5H_5)(CO)_2R$ using Hg(II) halides have been observed (386). These lead to the formation of (i) $Fe(\eta^5-C_5H_5)(CO)_2X$ and HgRX, (ii) $Fe(\eta^5-C_5H_5)(CO)_2HgX$ + RX, and (iii) Hg_2X_2 plus various substances derived from the decomposition of oxidised $Fe(\eta^5-C_5H_5)(CO)_2R$. The overall proposed reaction pathways are shown in Scheme 65. In a parallel series of studies involving 2-alkenyl and 2-alkynyl complexes, it was found (387) that 1:1 adducts were formed initially (Scheme 66) but that these broke up giving organomercurial products and $Fe(\eta^5-C_5H_5)(CO)_2X$.

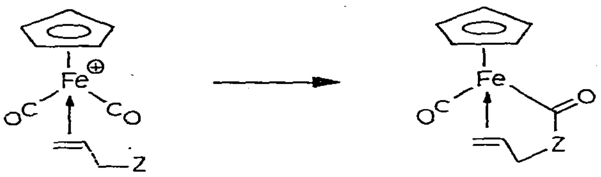
Scheme 65



Scheme 66



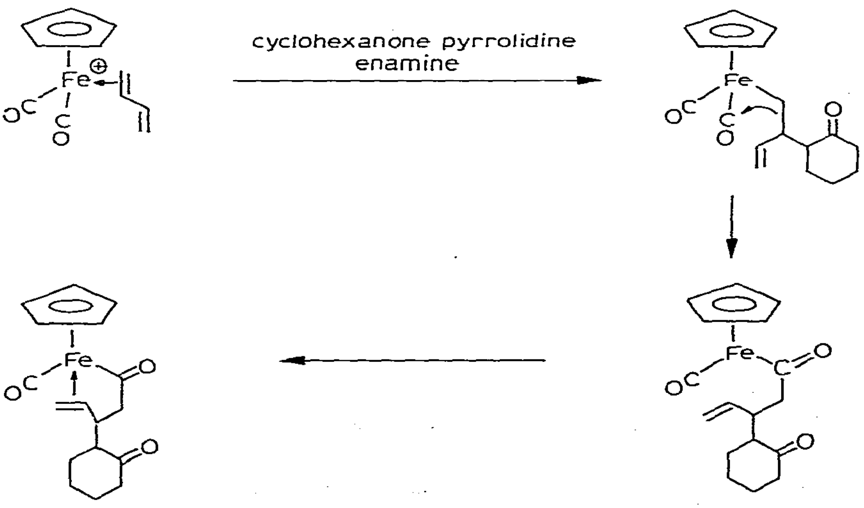
Scheme 67



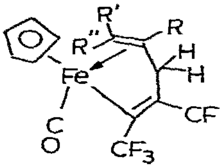
Three types of intramolecular cyclisation reactions of the type in Scheme 67, where there is one or more chiral centres, have been shown to proceed with high diastereospecificity (388). In each transformation, a new chiral centre in addition to those already present at the olefin, is created at the metal by chelation. In many, if not all, cases, a single diastereomer was produced. A study of suitable models showed that the closure of Z to one of the two diastereotopic CO groups constrained the olefin ligand to a plane either roughly parallel to or perpendicular to that of the cyclopentadienyl ring. Hence a structure was produced with a minimal or a maximal interference between these two interacting groups (e.g. <u>370</u> or <u>371</u>). Perhaps the most striking example of this type of situation occurred in the reaction between $[Fe(\eta^5-C_5H_5)(CO)_2(\eta^2-C_4H_6)]^+$ and cyclohexanone pyrrolidone enamine (Scheme 68) when only three of the possible eight diastereomeric pairs were formed and of those, one was produced in only relatively minor amounts.

Treatment of the η^1-allyl species $Fe(\eta^5-C_5H_5)(CO)_2CH_2CR{=}CR^1R^{11}$ ($R = R^1 = R^{11} =$ H; $R = R^1 =$ H, $R^{11} =$ Me; $R =$ H, $R^1 = R^{11} =$ Me) with dicyanoacetylene afforded

Scheme 68



(389) the insertion product Fe(η^5-C_5H_5)$(CO)_2C(CN)$=$C(CN)CR^1R^{11}C(R)$=CH_2 which, on photolysis, rearranged to 372. However, direct reaction of the η^1-allyl species with $CF_3C{\equiv}CCF_3$ afforded 373, Fe(η^5-C_5H_5)$(CO)_2C(CF_3)$=$C(CF_3)H$, and 374 (R = CF_3); there was no reaction between 373 and PPh_3. The propargyl complex Fe(η^5-C_5H_5)-$(CO)_2CH_2C{\equiv}CPh$ reacted with $NCC{\equiv}CCN$ and $CF_3C{\equiv}CCF_3$ giving 1:2 adducts, neither of which could be characterised. However, with Fe(η^5-C_5H_5)$(CO)_2CH_2C{\equiv}CMe$, hexafluorobut-2-yne afforded an adduct which, after chromatography, was identified, as Fe(η^5-C_5H_5)$(CO)_2C(CH_2OH)$=$CHMe$. Fumaronitrile and $(NC)(CF_3)C$=$C(CF_3)CN$ reacted with Fe(η^5-C_5H_5)$(CO)_2$(η^1-C_5H_5) giving 375 (R = H, R^1 = CN; R = CN, R^1 = CF_3). Similarly, bis-cyano and -trifluoromethylacetylene afforded 374 (R = CN or CF_3), but the species with R = CF_3 isomerised on storage giving 376. Irradiation of this latter species provided a route to 377.



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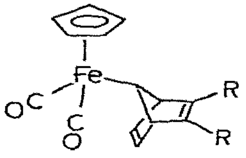

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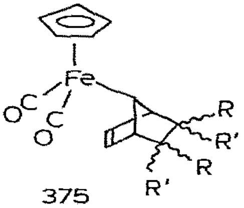

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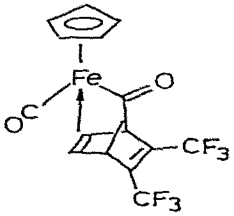

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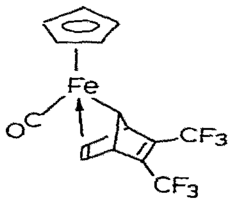
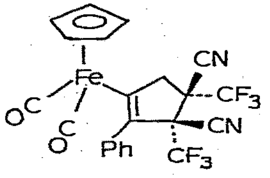


377

The stereochemistry of cycloaddition of $NC(CF_3)C$=$C(CF_3)CN$ to Fe(η^5-C_5H_5)$(CO)_2$-$CH_2C{\equiv}CPh$, was investigated (390). Both the trans and cis-isomers of the olefin afforded two products, 378a and b, 378b being the main product. With trans-NC-$(CF_3)C$=$C(CF_3)CN$, the allenyl complexes Fe(η^5-C_5H_5)$(CO)_2CH$=C=CHR gave 1:1 adducts, and when R = H, two isomers were obtained, one of which was a mixture of the two diastereomers of 379. With η^1-allyl complexes, Fe(η^5-C_5H_5)$(CO)_2CH_2CR$=$CR^1{}_2$, no reliable or readily interpretable stereochemical data could be obtained but four isomers are possible, 380a, b, c and d, and some were detected. The results obtained ruled out the possibility of a converted mechanism for the reactions involving the propargyl complexes, and a two-step process, involving the intermediate 381, obtained from {Fe-$CH_2C{\equiv}CR$} and {E=N}, was thought to be realistic.



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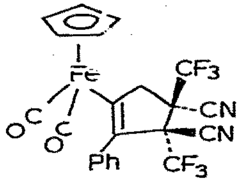

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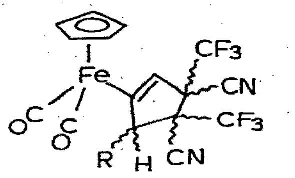

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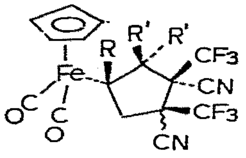

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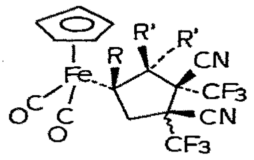

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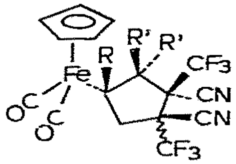

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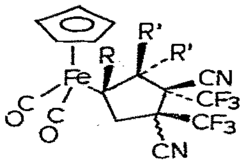
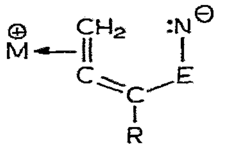


380 d



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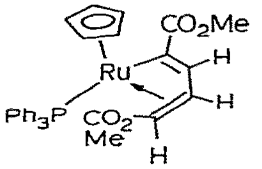

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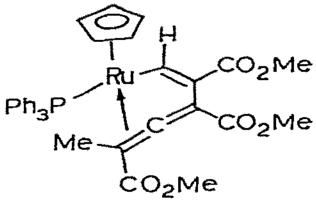

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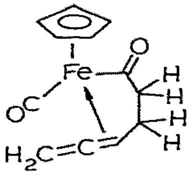

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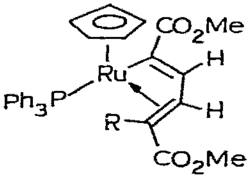

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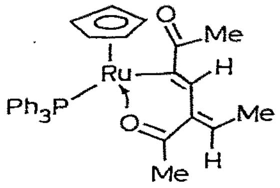

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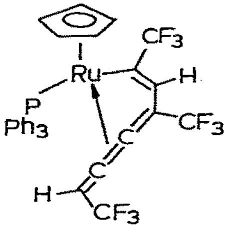

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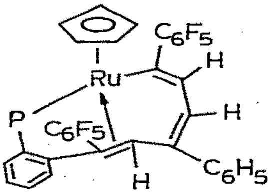

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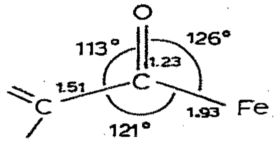
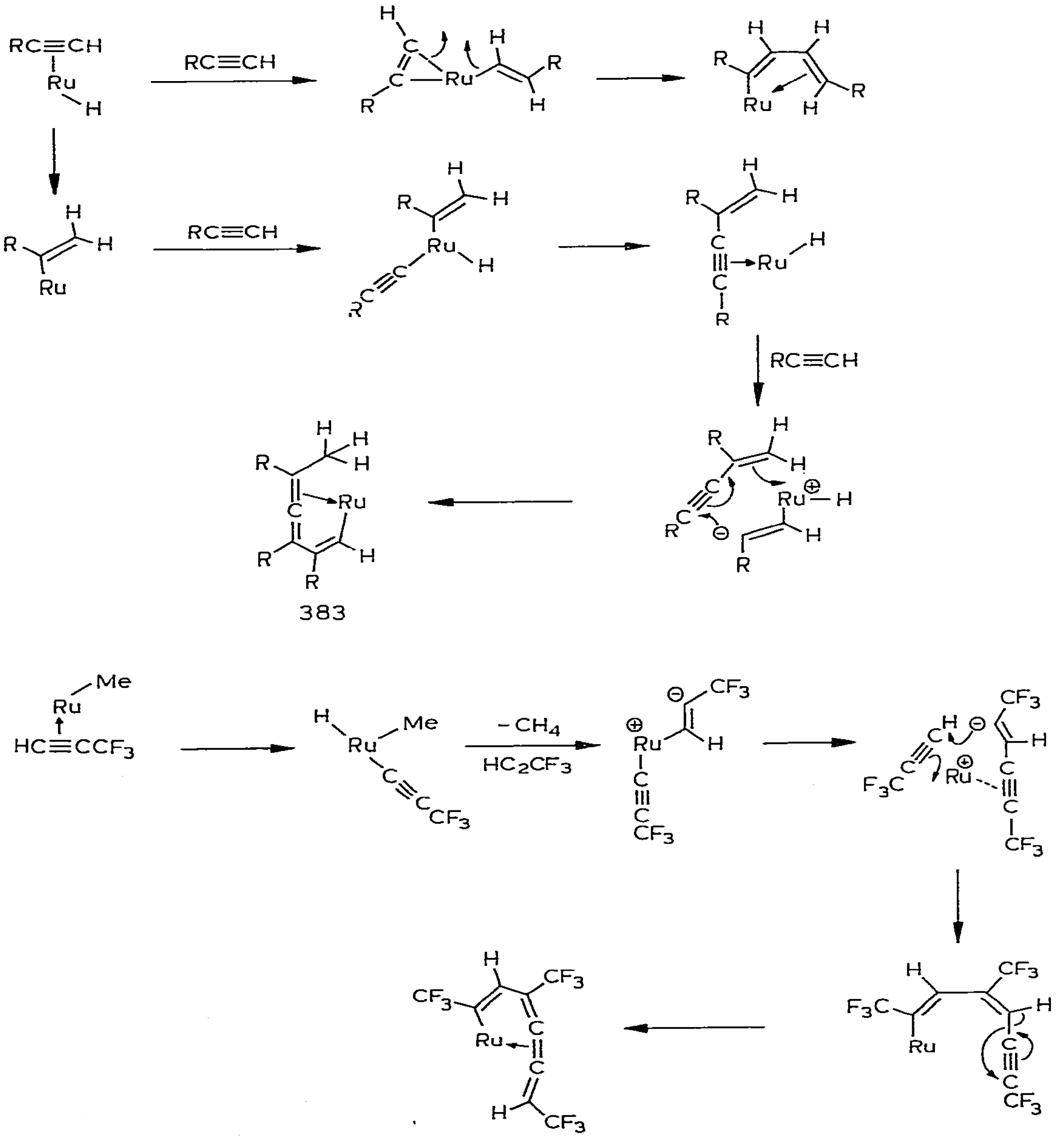


389

Treatment of Ru(η^5-C_5H_5)(PPh_3)$_2$H with HC≡CCO$_2$Me gave (391) three products: Ru(η^5-C_5H_5)(PPh_3)$_2$C≡CCO$_2$Me, 382 and 383. The last may be analogous to the previously reported (392) complex 384. Reaction of Ru(η^5-C_5H_5)(PPh_3)$_2$R (R = Me or CH$_2$Ph) with HC≡CCO$_2$Me gave only 385, (R = Me or CH$_2$Ph), but Ru(η^5-C_5H_5)-

$(PPh_3)_2Me$ was converted by HC≡CCOMe into 386, and by $HC{\equiv}CCF_3$ into 387 whose structure was confirmed crystallographically. Treatment of $Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2H$ with $HC{\equiv}CC_6F_5$ afforded 1,2,4-$C_6H_3(C_6F_5)_3$ and 388. A partial mechanism for the formation of some of these products is shown in Scheme 69.

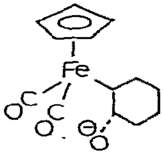
Scheme 69



Carbene Complexes

Reaction of $Fe(\eta^5-C_5H_5)(diphos)MgBr$ (diphos = $Ph_2PCH_2CH_2PPh_2$) with PhCOCl, or photolysis of $Fe(\eta^5-C_5H_5)(CO)_2COPh$ with diphos afforded (393) $Fe(\eta^5-C_5H_5)$-(diphos)(COPh). This species exhibited a particularly low value of $\nu(CO)$ ($1510cm^{-1}$) and an X-ray structural determination revealed that the benzoyl group was significantly distorted (389). Treatment of this benzoyl complex with HBF_4 gave the carbene cation $[Fe(\eta^5-C_5H_5)(diphos)\{C(OH)Ph\}]^+$, and with $[Me_3O][BF_4]$, $[Fe(\eta^5-C_5H_5)(diphos)\{C(OMe)Ph\}][BF_4]$ was produced. Reduction of the latter with $NaBH_4$ afforded $Fe(\eta^5-C_5H_5)(diphos)CH(OMe)Ph$, but treatment of this with HBF_4 did not give $[Fe(\eta^5-C_5H_5)(diphos)CHPh]^+$.

Cyclohexene oxide reacted (394) with $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ giving 390 and 391 in equilibrium (which favoured the latter). With $[Me_3O][BF_4]$, a mixture of 392 and 393 (1:1) was produced. Similar reactions occurred with cis- and trans-butene epoxides, but on treatment with trimethyl oxonium tetrafluoroborate, no carbene species were produced. With Ph_3C^+, 391 was converted into 394 and deprotonation of this, giving 395, was effected by NEt_3. Addition of HBF_4 in ether under CO to 391 afforded 396 which could also be deprotonated by NEt_3 producing 397. Reaction of $[Fe(\eta^5-C_5H_5)(CO)_2(H_2C{=}C{=}CH_2)]^+$ with water gave 398 which, on treatment with $LiBu^t$ at -20° and then $[Me_3O][BF_4]$ was converted into a mixture of 399 and 400. Chromatography of the latter on alumina gave 401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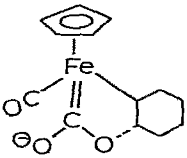
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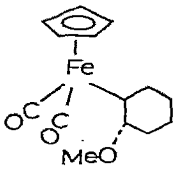
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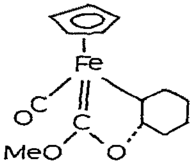
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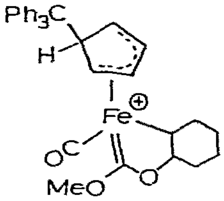
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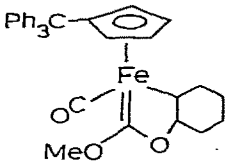
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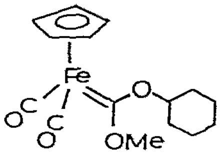
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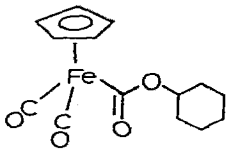
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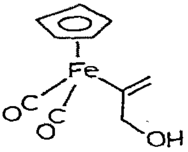
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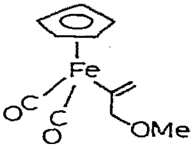
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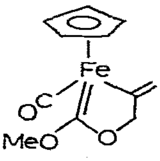
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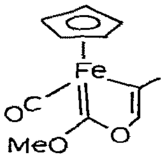
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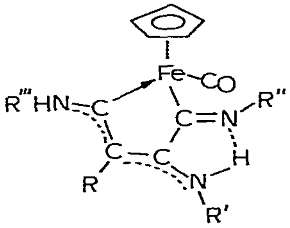

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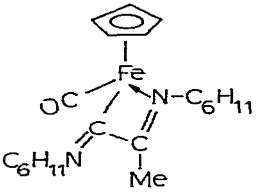

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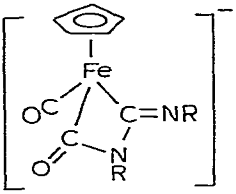

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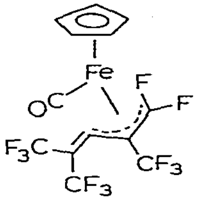


405

which did not appear to undergo Diels-Alder addition with maleic anhydride.

Treatment of $Fe(\eta^5-C_5H_5)(CO)_2CH_2OMe$ with HSO_3F/SO_2ClF at −100° in CD_2Cl_2 gave (395) a red solution whose nmr spectrum revealed the presence of $[Fe(\eta^5-C_5H_5)(CO)_2(C_2H_4)]^+$ and $[Fe(\eta^5-C_5H_5)(CO)_2]_2$. If $[Fe(\eta^5-C_5H_5)(CO)_2CH_2]^+$ had been formed, it must have disproportionated quite rapidly, even at −80°. However, treatment of $Fe(\eta^5-C_5H_5)(CO)_2CHPh(OMe)$ with CF_3CO_2H, HSO_3F or triflic acid gave $[Fe(\eta^5-C_5H_5)(CO)_2CHPh]^+$ and the related $[Fe(\eta^5-C_5H_5)(CO)(PPh_3)CHPh]^+$ was similarly prepared from $Fe(\eta^5-C_5H_5)(CO)(PPh_3)CHPh(OMe)$. Addition of methanol to these cationic carbene complexes caused regeneration of the appropriate alkyls.

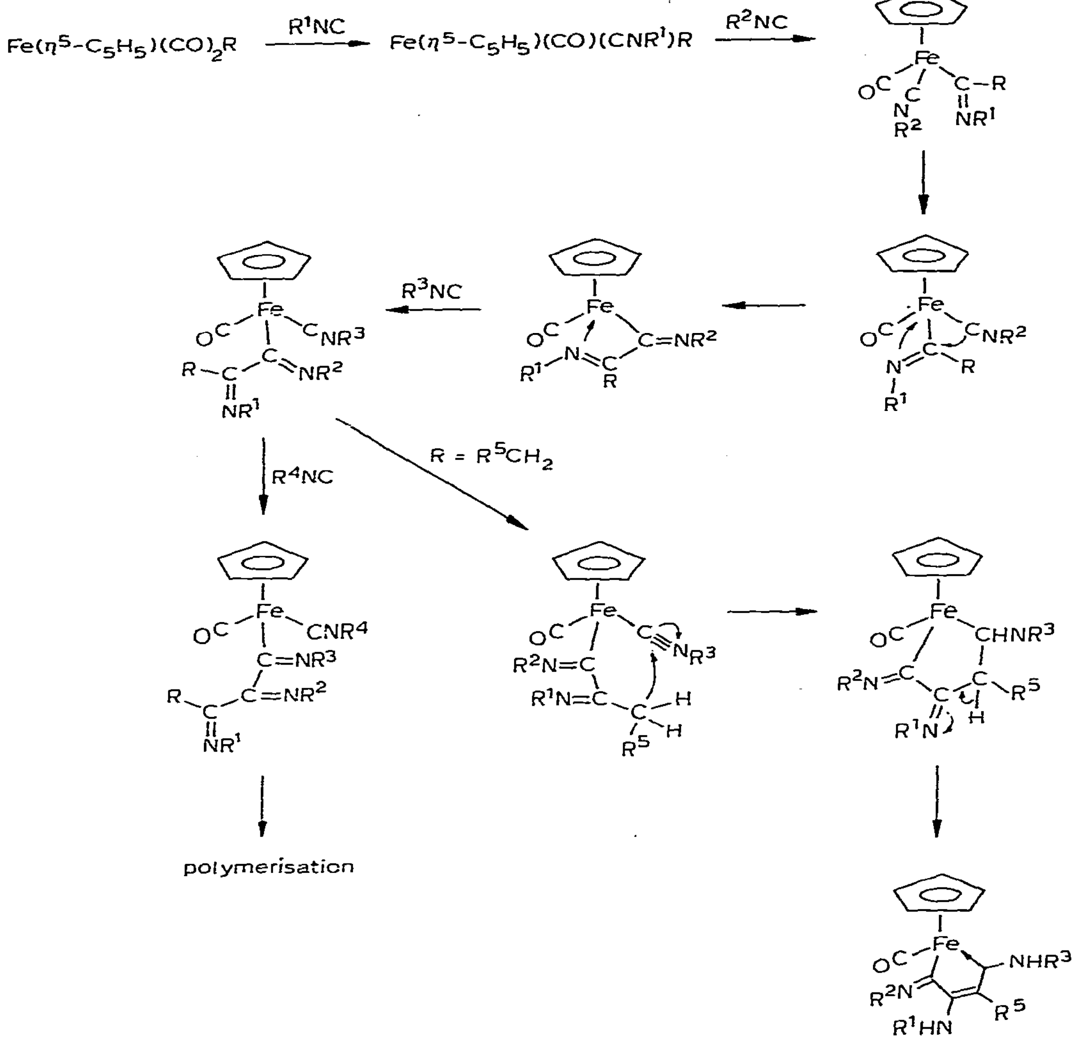
Addition of $C_6H_{11}NC$ to $Fe(\eta^5-C_5H_5)(CO)(CNC_6H_{11})CH_2R$ (R = Ph or p-ClC_6H_4) in THF or refluxing benzene afforded (396) the insertion product 402 ($R^1 = R^{11} = R^{111} = C_6H_{11}$). Whereas $Fe(\eta^5-C_5H_5)(CO)(PPh_3)Me$ similarly reacted with $C_6H_{11}NC$ giving 402 (R = H; $R^1 = R^{11} = R^{111} = C_6H_{11}$), $Fe(\eta^5-C_5H_5)(CO)_2Me$ gave only $Fe(\eta^5-C_5H_5)(CO)(CNC_6H_{11})COMe$. Cyclohexylisonitrile reacted with $Fe(\eta^5-C_5H_5)(CO)(CNBu^t)R$ (R = Me or CH_2Ph) or $Fe(\eta^5-C_5H_5)(CO)(CNCH_2Ph)CH_2Ph$ giving adducts similar to 402. Reaction of 403 with Bu^tNC $Fe(\eta^5-C_5H_5)(CO)(CNBu^t)\{C(=NC_6H_{11})-CMe=NC_6H_{11}\}$ which rearranged to 402 (R = H, $R^1 = R^{11} = C_6H_{11}$, $R^{111} = Bu^t$). However, $Fe(\eta^5-C_5H_5)(CNBu^t)Me$ underwent a simple insertion reaction with Bu^tNC, affording $Fe(\eta^5-C_5H_5)(CO)(CNBu^t)\{C(=NBu^t)Me\}$. Treatment of $Fe(\eta^5-C_5H_5)(CO)-(ONR)C_6H_4X$-p (X = H or Cl) with $C_6H_{11}NC$ gave $Fe(\eta^5-C_5H_5)(CO)(CNC_6H_{11})C(=NC_6H_{11})-CR=NR^1$ (R = Ph, $R^1 = Bu^t$; R = p-ClC_6H_4, $R^1 = C_6H_{11}$). The latter species with R = p-ClC_6H_4, $R^1 = C_6H_{11}$ acted as a polymerisation catalyst for $C_6H_{11}NC$ in toluene at 120°. The mechanism of formation of some of these species is outlined in Scheme 70.

Addition of carbodiimides RN=C=NR (R = Ph or C_6H_{11}) to $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ afforded (397) $[Fe(\eta^5-C_5H_5)(CO)_2\{C(NR)_2\}]^-$, actually 404. Protonation of this gave $[Fe(\eta^5-C_5H_5)(CO)_2\{C(NHR)_2\}]Cl$, but with $COCl_2$, $[Fe(\eta^5-C_5H_5)(CO)(CNR)_2]Cl$ (R = Ph) was isolated.

Fluorocarbon Complexes

Reaction of $Fe(CO)_4(C_3F_7)I$ with $C_4R_4C=N_2$ (R = H, Cl or Br) gave (398) with loss of N_2, $Fe(\eta^5-C_5R_4I)(CO)_2C_3F_7$. Treatment of $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ with $EtO_2C-(CF_3)C=CF_2$ in THF at low temperature gave (399) a mixture of cis- and trans-$Fe(\eta^5-C_5H_5)(CO)_2CF=C(CF_3)CO_2Et$.

Scheme 70



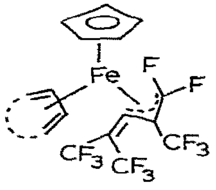
Lithiation of Cr(η^6-C_6F_5H)(η^6-C_6H_6) gave (400) Cr(η^6-C_6F_5Li)(η^6-C_6H_6) which, on treatment with Fe(η^5-C_5H_5)$(CO)_2I$, was converted into Cr{η^6-C_6F_5[Fe(η^5-C_5H_5)$(CO)_2$]} (η^6-C_6H_6).

Photolysis (uv) (401) of Fe(η^5-C_5H_5)$(CO)_2${$C(=CCF_3)_2C(CF_3)=CF_2$} gave 405 (L = CO) which subsequently reacted with PPh_3, $P(OPh)_3$ or benzothiazole (L) giving 405 (L as stated). Photolysis in the presence of butadiene or 1,3-cyclohexadiene in pentene or bezene gave 406.

Complexes Containing Group IV and Other Metals

In the X-ray crystallographic examination of Fe(η^5-C_5H_5)(CO)H$(SiF_2Me)_2$, 407, the H atom was located (402). Chiral and non-chiral complexes of the type Fe-

$(\eta^5\text{-}C_5H_5)(CO)L(SiRR^1R^{11})$ have been prepared (403). Thus, treatment of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ with S(−)- and R(+)-SiClPh(1-$C_{10}H_7$)Me afforded R(+)- and S(−)-408 respectively. Treatment of R(+)-408 with PPh_3 gave R(−)- and R(+)-409 with retention of configuration, as did S(−)-408. Similar results were obtained with $P(C_6H_{11})_3$ and $P(OEt)_3$, and the $SiRR^1R^{11}$ fragment could be $SiPh_3$, $SiPh_2Me$, $SiPhMe_2$, or $SiPh_2(CH{=}CH_2)$. When the environments at Fe and Si were asymmetric, it was possible to isolate diastereoisomers. The Fe-Si bond was particularly stable and could be cleaved with retention of configuration by some nucleophiles (e.g. H_2O or H^-). Electrophilic cleavage, e.g. by halogens, was more complex leading to both retention and inversion depending on the nature of the reagent and substrate.



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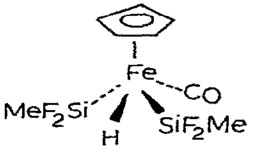

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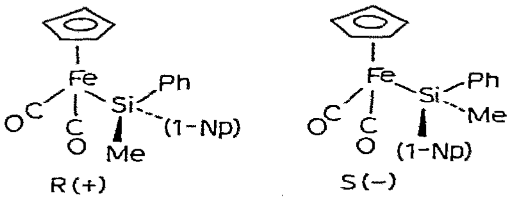

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UV irradiation of $Fe(\eta^5\text{-}C_5H_5)(CO)_2SiRR^1R^{11}$ (R = Me, R^1 = Ph, R^{11} = 1-$C_{10}H_7$) in the presence of $P(OPh)_3$ gave (404), initially, $Fe(\eta^5\text{-}C_5H_5)(CO)\{P(OPh)_3\}(SiRR^1R^{11})$. This then rearranged first to 410 and then, in the presence of $P(OPh)_3$, to 411. If the reaction was carried out with $P(OEt)_3$, only $Fe(\eta^5\text{-}C_5H_5)(CO)\{P(OEt)_3\}$-$(SiRR^1R^{11})$ was produced.

The kinetics of reaction of $Fe(\eta^5\text{-}C_5H_5)(CO)_2MR_3$ (M = Si or Ge, R = Me; M = Sn, R = Me, Bu^n or C_6H_{11}) with HgX_2 were interpreted (405, 406) in terms of the formation of a 1:1 adduct between reagent and substrate. In most cases, formation of $Fe(\eta^5\text{-}C_5H_5)(CO)_2X$ and R_3MX occurred, but with $Fe(\eta^5\text{-}C_5H_5)(CO)_2SnPh_3$, Sn–C bond cleavage was observed (406), the product being $Fe(\eta^5\text{-}C_5H_5)(CO)_2SnBrPh_2$.

Irradiation of $Mo(\eta^5\text{-}C_5H_5)(CO)_3Fe(\eta^5\text{-}C_5H_5)(CO)_2$ in the presence of CCl_4 or i-$C_5H_{11}I$ (RX) gave rise to (407) $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, Mo-$(\eta^5\text{-}C_5H_5)(CO)_3X$ and $Fe(\eta^5\text{-}C_5H_5)(CO)_2X$. The reaction involved the generation of radical species such as $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^\bullet$, and cleavage of other heterobimetallic species occurred similarly. Treatment of either $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ with $Na[W(\eta^5\text{-}C_5H_5)(CO)_3]$ or of $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ with $W(\eta^5\text{-}C_5H_5)(CO)_3I$ afforded (408) $Fe(\eta^5\text{-}C_5H_5)(CO)_2W(\eta^5\text{-}C_5H_5)(CO)_3$.

Reaction of $M(CO)_4\{(AsMe_2Cl\}_2$ (M = Cr, Mo or W) with $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ gave (409) $M(CO)_4\{AsMe_2Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2$. These complexes could also be prepared by addition of $Fe(\eta^5\text{-}C_5H_5)(CO)_2AsMe_2$ to $M(CO)_4(C_7H_8)$ (C_7H_8 = norbornadiene). The iron dimethylarsine compound also reacted with $Fe(CO)_2(NO)_2$, $Co(CO)_3$-(NO), $Mn(\eta^5\text{-}C_5H_5)(CO)_3$, $Fe(CO)_5$ and $Ni(CO)_4M(CO)_nL$ giving (410) $Fe(\eta^5\text{-}C_5H_5)(CO)_2$-

$AsMe_2M(CO)_{n-1}L$. Treatment of $Fe(CO)_5$ or $Fe(CO)_2(NO)_2$ with $M(\eta^5\text{-}C_5H_5)(CO)_3AsMe_2$ (M = Mo or W) gave $M(\eta^5\text{-}C_5H_5)(CO)_3AsMe_2Q$, where Q = $Fe(CO)_4$ or $Fe(CO)(NO)_2$. These complexes could be photolysed giving a variety of products which are summarised in Table 3. Reaction of $Fe(\eta^5\text{-}C_5H_5)(CO)_2AsMe_2$ with $Co(\eta^5\text{-}C_5H_5)(CO)_2$ afforded (411) the trimetallic species <u>413</u>.

TABLE 3

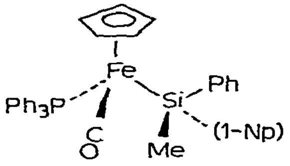
Photolysis products of heterobimetallic species bridged by $AsMe_2$

Complex	Product
$M(\eta^5\text{-}C_5H_5)(CO)_3AsMe_2\text{-}Fe(CO)_4$	<u>412</u>
$\text{-}Fe(CO)(NO)_2$	Starting material, $M(\eta^5\text{-}C_5H_5)(CO)_2(NO)$, unknown
$Fe(\eta^5\text{-}C_5H_5)(CO)_2AsMe\text{-}Fe(CO)_4$	Starting material, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, $[Fe(CO)_3AsMe_2]_2$
$\text{-}Fe(CO)(NO)_2$	no reaction
$\text{-}Cr(CO)_5$	$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, $Cr(CO)_6$, unknown
$\text{-}Mo(CO)_5$	$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, $Mo(CO)_6$, $[Mo(CO)_4\text{-}AsMe_2$, unknown
$\text{-}W(CO)_5$	$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, $W(CO)_6$, $[W(CO)_4\text{-}AsMe_2]_2$, unknown
$\text{-}Mn(CO)_2(\eta^5\text{-}C_5H_5)$	$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$, $Mn(\eta^5\text{-}C_5H_5)(CO)_3$, $[Fe(\eta^5\text{-}C_5H_5)(CO)AsMe_2]_2$

The Fe-C σ-bond in $Fe(\eta^5\text{-}C_5H_5)(CO)_2\{(\eta^5\text{-}C_5H_4)Mn(CO)_3\}$ was cleaved (412) by $HgBr_2$, I_2 or CF_3CO_2H, and when iodine was used, the products included $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ and $Mn(\eta^5\text{-}C_5H_4I)(CO)_3$. The metallated cyclopentadienyl species was converted on photolysis in the presence of PPh_3 into $Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)\{(\eta^5\text{-}C_5H_4)Mn(CO)_3\}$. Oxidation of $Fe(\eta^5\text{-}C_5H_5)(CO)_2\{(\eta^5\text{-}C_5H_4)Mn(CO)_3\}$ with $[MeCO]\text{-}[BF_4]$ in acetonitrile gave $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(NCMe)][BF_4]$ and $[Mn(\eta^5\text{-}C_5H_4)(CO)_3]_2$. Reaction of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ with $Mn(\eta^5\text{-}C_5H_4CH_2Cl)(CO)_3$ gave (413) $Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2(\eta^5\text{-}C_5H_4)Mn(CO)_3$. Treatment of $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ with $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_2CH_2O_3SC_6H_4Me)$ gave <u>414</u>, which could be oxidised (414) to the corresponding substituted ferricinium ion.

Reaction of $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$ with PAr_2H (Ar = Ph or p-MeC_6H_4) in the presence of KPF_6 gave (415) the salt $[Fe(\eta^5\text{-}C_5H_5)(CO)_2PAr_2H][PF_6]$. Deprotonation of this cation by 1,8-bis(dimethylamino)naphthalene in acetone afforded $Fe(\eta^5\text{-}C_5H_5)(CO)_2PAr_2$. Treatment of this with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2PAr_2H]^+$ provided $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2PAr_2]^+$, but with $[Rh(CO)_2Cl]_2$, the mixed metal species $\{Fe(\eta^5\text{-}C_5H_5)(CO)_2PAr_2\}_2Rh(CO)Cl$ was produced. When this last species was treated with

Ag$^+$ (as BF_4^- or PF_6^-), 415 (M = Rh, M^1 = Fe) was isolated. Related iridium complexes containing Fe(η^5-C_5H_5)(CO)$_2${P(p-MeC$_6$H$_4$)$_2$} and its Ru analogue, were also prepared (416) using Ir(CO)$_2$(p-toluidine)Cl. NMR spectral studies of these complexes revealed that they underwent racemisation by flexing the M-Rh-M skeleton. The barriers to racemisation were ca. 13 (Fe_2Rh), 17·5 (Fe_2Ir) and 17·8 kcal/mol (Ru_2Ir), respectively. It seemed probable that the mechanism of



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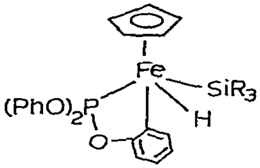

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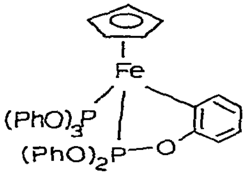

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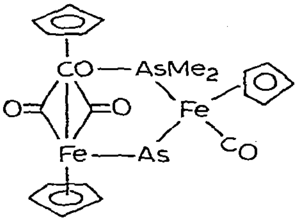

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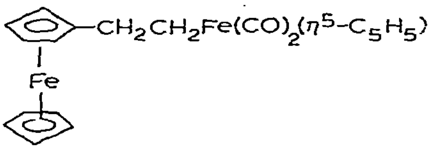

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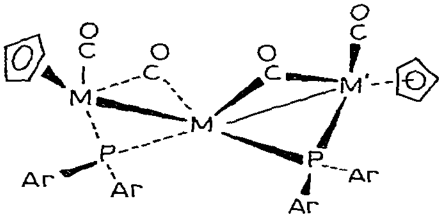

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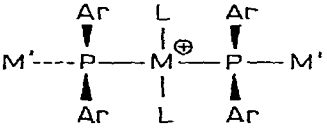

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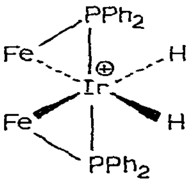

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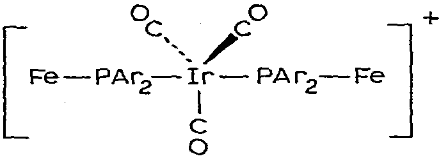

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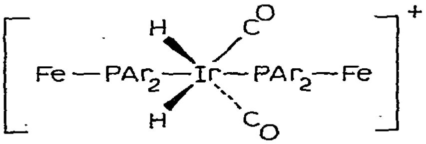

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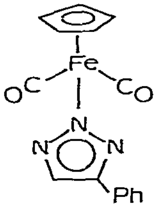
racemisation might involve an open structure, as in 416. The iridium complex 415 ($M = Ir$, $M^1 = Fe$) reacted reversibly with hydrogen in solution forming a burgundy-red species which may be 417; the species 415 ($M = Ir$, $M^1 = Ru$) behaved similarly but there was no apparent reaction between hydrogen and 415 ($M = Rh$, $M^1 = Fe$). With CO, 415 ($M = Ir$, $M^1 = Fe$) afforded a 1:1 adduct 418 which further absorbed hydrogen, with loss of CO, giving 419. Hydrogen could be displaced from the latter by CO, thereby reforming 418.

Complexes Containing Group VA Ligands

Under mild conditions in benzene, $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ reacted (417) with amines (L) giving $Fe(\eta^5\text{-}C_5H_5)L_2I$ ($L = C_6H_{11}NH_2$, $PhCH_2NH_2$, Bu^nNH_2, piperidine or morpholine). Under more vigorous conditions, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2L]I$ was isolated.

The sodium salts of certain triazoles and imidazoles, NaL, reacted (418) with $Fe(\eta^5\text{-}C_5H_5)(CO)_2X$ (X = halide) giving $Fe(\eta^5\text{-}C_5H_5)(CO)_2L$. Protonation of this by HY afforded $[Fe(\eta^5\text{-}C_5H_5)(CO)_2\{LH\}]Y$ in which the stabilisation of the cations was ensured by hydrogen bonds between either the cation and Y, or the cation and molecules of the solvent in the outer coordination sphere. The structure of the benzimidazole complex $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(C_7H_6N_2)][BPh_4]$ was determined crystallographically, and it was found that thermal decomposition of this salt gave $Fe(\eta^5\text{-}C_5H_5)(CO)_2(C_7H_5N_2BPh_3)$. Treatment of $Fe(\eta^5\text{-}C_5H_5)(CO)_2X$ with the sodium salt of triazole, benzotriazole or 4-phenyl-1,2,3-triazole (NaL) gave (419) $Fe(\eta^5\text{-}C_5H_5)(CO)_2L$ as two isomers, e.g. 420a and b. These compounds underwent isomeric rearrangement when heating in neutral or acidic media. Protonation of 420a or b with sulphuric acid gave 421.



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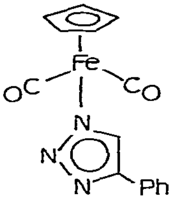

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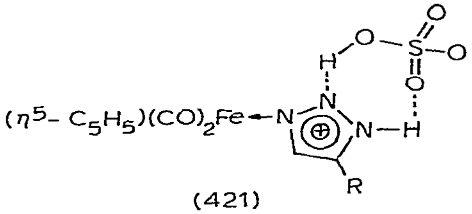


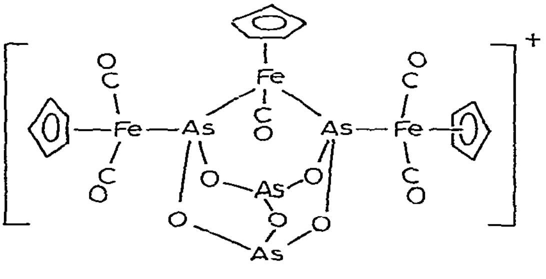
(421)

Reaction of $Fe(\eta^5\text{-}C_5H_5)(CO)_2I$ with Ph_3E (E = P, As or Sb) gave (420) $Fe(\eta^5\text{-}C_5H_5)(CO)(EPh_3)I$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(EPh_3)]I$. With $Ph_2As(CH_2)_2AsPh_3$ and trimethylolpropane phosphite, similar compounds were obtained. With $MeN(PF_2)_2$, (L), $Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$ was converted (421) into either $Fe(\eta^5\text{-}C_5H_5)(CO)LCl$ or $Fe(\eta^5\text{-}C_5H_5)L_2Cl$, depending upon conditions. Both species contained monodentate P-bound $MeN(PF_2)_2$. The complexes $Fe(\eta^5\text{-}C_5H_5)(CO)L'X$ and $[Fe(\eta^5\text{-}C_5H_5(CO)_2L^1]\text{-}[BF_4]$ (X = I or CN; L = neomenthyldiphenylphosphine) showed (422) intense circular dichroism spectra in the region >300mμ which is generally associated with metal-metal electronic transitions. In refluxing ethanol, $RuCl_3$, PPh_3 and

C_5H_6 reacted together (423) to give $Ru(\eta^5-C_5H_5)(PPh_3)_2Cl$. Related complexes containing Os and $P(p-MeC_6H_4)_3$ were produced in the same way.

Reaction of $Fe(\eta^5-C_5H_5)(CO)_2Cl$ with $Ph_2PCH_2CH_2PPh_2$(diphos) gave (424) $[Fe(\eta^5-C_5H_5)(CO)(diphos)]Cl$. Photolysis of this complex ultimately led to the formation of $Fe(\eta^5-C_5H_5)(diphos)Cl$. However, under N_2, photolysis gave $[\{Fe(\eta^5-C_5H_5)-(diphos)\}_2(\mu_2-N_2)]^+$, but attempts to reduce the nitrogen using HX, Zn/HCl, dithionite or borohydride gave only $Fe(\eta^5-C_5H_5)(diphos)H$. Photolysis of $[Fe(\eta^5-C_5H_5)(CO)Br]_2(\mu_2$-diphos) with hydrazine, or reaction with hydrazine in the dark, did not lead (425) to doubly bridged species containing N_2 or hydrazine. However, either reduction occurred, or $Fe(\eta^5-C_5H_5)(diphos)Br$ was produced.

Treatment of $Fe(\eta^5-C_5H_5)\{P(OPh)_3\}_2I$ with $Me_2PCH_2CH_2PMe_2$(dmpe) gave (426) $Fe(\eta^5-C_5H_5)(dmpe)I$, and with (−)-DIOP, $Fe(\eta^5-C_5H_5)(DIOP)I$ was produced. Reaction of $[Fe(\eta^5-C_5H_5)(dmpe)\{P(OPh)_3\}]I$ (or BF_4) with KI in acetone under uv light also afforded $Fe(\eta^5-C_5H_5)(dmpe)I$. With CO in the presence of $TlBF_4$, $Fe(\eta^5-C_5H_5)-(diphos)I$ was converted into $[Fe(\eta^5-C_5H_5)(CO)(diphos)]BF_4$. However, when this reaction was attempted using alkenes in place of CO, a crystalline species thought to be $\{[Fe(\eta^5-C_5H_5)(diphos)][BF_4]\}$ was produced. When this compound was treated with CO and with KI in acetone, $[Fe(\eta^5-C_5H_5)(CO)(diphos)][BF_4]$ and $Fe(\eta^5-C_5H_5)(diphos)I$, respectively, were produced. Reduction of $\{[Fe(\eta^5-C_5H_5)-(diphos)][BF_4]\}$ using $NaBH_4$ afforded $Fe(\eta^5-C_5H_5)(diphos)H$. The failure to obtain an ethylene complex was attributed to the greater steric requirements of the diphos ligand when compared to CO in $[Fe(\eta^5-C_5H_5)(CO)_2]^+$. However, treatment of $Fe(\eta^5-C_5H_5)(dmpe)I$ with Tl^+ in the presence of diethylmaleate or methylacrylate (alkene) afforded $[Fe(\eta^5-C_5H_5)(dmpe)(alkene)]^+$, but no analogues were obtained with heptene, cyclopentene or cyclohexene.



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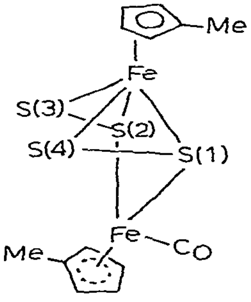

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Treatment of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ with AsF_3 in m-xylene in pyrex glass afforded (427) $[Fe_3(\eta^5-C_5H_5)_3(CO)_5As_4O_5][BF_4]$, 422, as a result of hydrolysis and abstraction of boron from the glass. The geometry of the molecule, determined crystallographically, may be regarded as being derived from the cubic (T_d) As_4O_6 molecule by replacement of one of its six edged-bridged O atoms with an $[Fe(\eta^5-C_5H_5)(CO)]^+$ bridge.

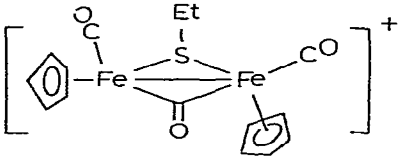
Complexes Containing Sulphur Ligands

Cyclic voltammograms of $Fe_4(\eta^5-C_5H_5)_4S_4$ revealed (428) four electrochemically reversible waves corresponding to the formation of $[Fe_4(\eta^5-C_5H_5)_4S_4]^Z$, Z = 1, +1, +2 and +3. The monocation was prepared (429) by oxidation of the precursor using Ag^+, iodine or bromine, and the structure of a representative salt was determined crystallographically. One-electron oxidation distorts the Fe_4S_4 core in the neutral molecule from D_{2d}-42m geometry containing two electron-pair bonding and four non-bonding Fe-Fe distances of 2·64 and 3·36Å, respectively, into an orthorhombic D_{2d}-222 geometry having three pairs of Fe-Fe distances of 2·65, 3·19 and 3·32Å. This preferential shortening of two of the four long Fe-Fe distances in the monocation relative to the neutral species was attributed to the removal of an electron from an antibonding Fe_4-cluster orbital. The dication was generated (428) by controlled potential electrolysis in acetonitrile, and was isolated as the PF_6^- salt. The structure of $[Fe_4(\eta^5-C_5H_5)_4S_4]^{2+}$ was established by X-ray methods and was found to differ markedly from that of the neutral and monocationic species. The structure is analogous to that of the known (430) dithiolene species $[Fe_4\{S_2C_2(CF_3)_2\}_4S_4]^{2-}$ in that the Fe_4S_4 core possesses tetragonal D_{2d} geometry with four Fe-Fe distances of 2·83 and two of 3·25Å (the molecule has S_4-4 site symmetry). It was predicted, on the basis of structural correlations and a simple m.o. treatment, that in $[Fe_4(\eta^5-C_5H_5)_4S_4]^{3+}$ there should be a further shortening of the Fe-Fe distance with maintenance of D_{2d} point group symmetry while in the monoanion, an orthorhombic D_2 geometry would be expected.

Photolysis of $[Fe(\eta^5-C_5H_4R)(CO)_2]_2$ (R = H or Me) with sulphur afforded (431) a mixture of species, of which 423 was characterised by X-ray techniques. The Fe-Fe distance (3·40Å) is non-bonding while the S(2)-S(3) and S(1)-S(4) distances are 2·01 and 1·98Å, respectively. The four S atoms are coplanar and the S(1)-S(2) and 3(3)-S(4) separations 2·95 and 3·18Å, respectively; a normal S-S single bond is 2·06Å.

Reaction of thiobenzophenones with $[Fe(\eta^5-C_5H_5)(CO)_2]^-$ afforded (432) diarylfulvenes, $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ and $[Fe_n(CO)_mSH]_y$. The structure of $[Fe_2(\eta^5-C_5H_5)_2(CO)_2(\mu_2-SEt)]^+$, 424, was determined crystallographically (433). The Fe-Fe distance, 2·58Å, is equivalent to a two-electron metal-metal bond, and solution ir and nmr data indicated that the cation retained its cis geometry in solution. Treatment of $Fe(\eta^5-C_5H_5)(CO)_2COR$ (R = Me or Ph) with P_4S_{10} or B_2S_3 gave (434) a mixture of $Fe(\eta^5-C_5H_5)(CO)_2S(C{=}S)R$ and $Fe(\eta^5-C_5H_5)(CO)(S_2CR)$. The thiocarbamato complex $Fe(\eta^5-C_5H_5)(CO)_2(OSCNC_4H_8)$ was prepared (435) and is considered to contain an S-bonding pyrrolidonethiocarbamate ligand. Reaction of $Li[PhC({=}S)NMe]$ with $Fe(\eta^5-C_5H_5)(CO)_2Cl$ afforded (436) a mixture of 425 and 426. Mossbauer, ir and, where appropriate, ^1H nmr spectral studies have been made (437) of the dithiocarbamato species $Fe(\eta^5-C_5H_5)(CO)(S_2CNR_2)$ and $Fe(CO)_2(S_2CNR_2)_2$.

In sulphur dioxide solution, $K[Fe(\eta^5-C_5H_5)(CO)_2]$ formed (438) $K[Fe(\eta^5-C_5H_5)$-



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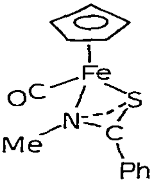

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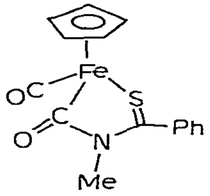


426

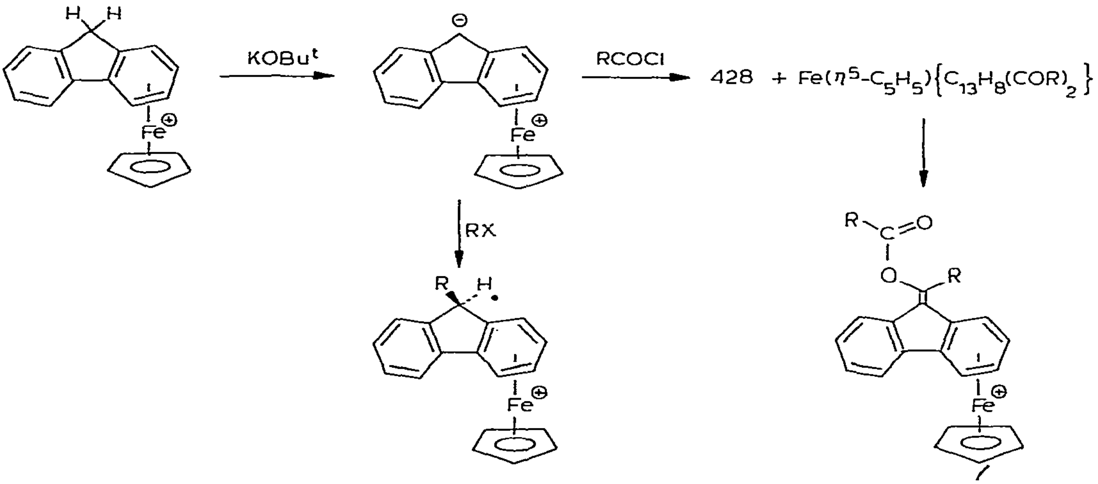
$(CO)_2(SO_2)]$ as a hemi-sulphur dioxide salt. Treatment of this with MeI or MeOSO$_2$F gave $Fe(\eta^5-C_5H_5)(CO)_2S(=O)_2Me$ (9%), $Fe(\eta^5-C_5H_5)(CO)_2S(=O)OMe$ (20%), $[Fe(\eta^5-C_5H_5)(CO)_2(SO_2)]_2$ (3%) and, when appropriate, $Fe(\eta^5-C_5H_5)(CO)_2I$ (33%).

ARENE AND RELATED COMPLEXES

Iron Cyclopentadienyl arene and bis-arene complexes

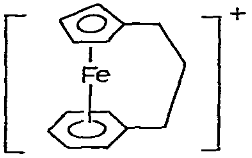
Gas-phase formation of ionic mixed sandwich complexes of iron was achieved (439) via ion-molecule reactions using ferrocene and various aromatics. In heptane, $Fe\{\eta^5-C_5H_4(CH_2)_3Ph\}_2$ reacted with $AlCl_3$ and aluminium giving the cation 427 whose structure was established crystallographically (440). Reaction of ferrocene with fluorene in the presence of $AlCl_3$ and Al afforded (441) the cationic species 428 which was isolated as the PF_6^- salt. Reactions of 428 are illustrated in Scheme 71. Other new arene complexes were similarly prepared (442) from ferrocene, Ph_2NH, carbazole, benzimidazole and Ph_3CH. Treatment of the fluorene complex 428 with $NaH(SiMe_3)_2$ was thought to give 429 which may be another representation of the species produced by treatment of 428 with KOBu^t (441). Deprotonation of $Fe(\eta^5-C_5H_5)(\eta^6-C_6H_5NHPh)$ using $NaN(SiMe_3)_2$ afforded 430, and similar treatment of the carbazole and trityl cations gave 431 and 432, respectively.

Scheme 71



(R = Me or p-BrC$_6$H$_4$CH$_2$)

(R = Me or Ph)



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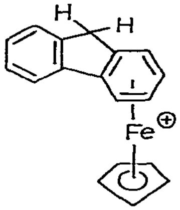

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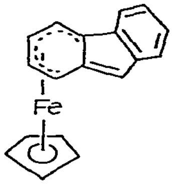

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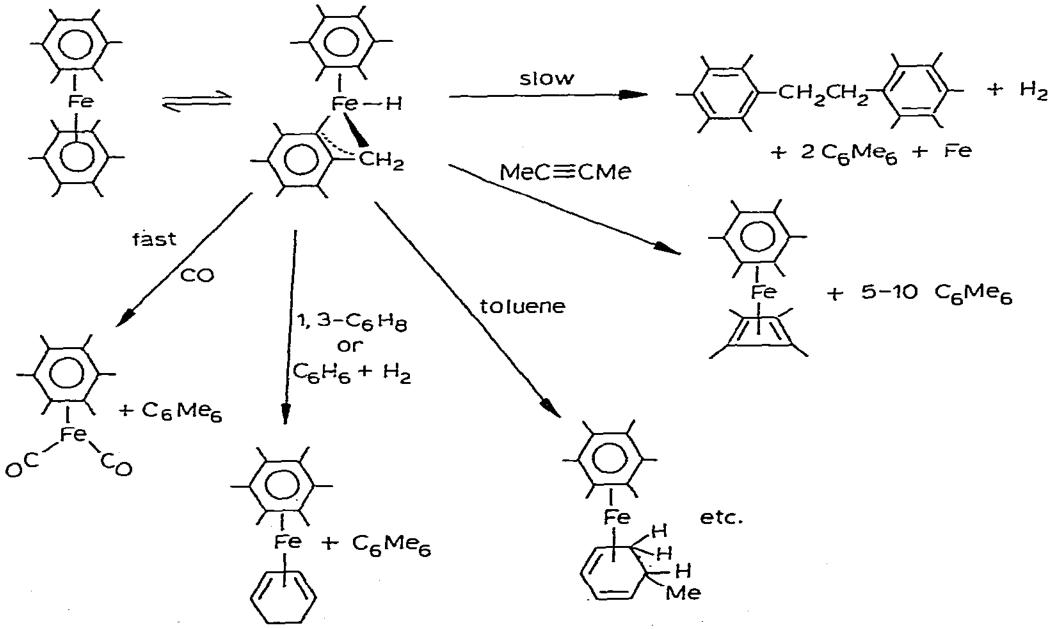
Reduction of $[Fe(\eta^5-C_5H_4R)(\eta^6-C_6H_{6-n}Me_n)]^+$ in aqueous media afforded (443) initially $Fe(\eta^5-C_5H_4R)(\eta^6-C_6H_{6-n}Me_n)$. This paramagnetic species was stable when $n = 6$, but otherwise decomposed giving, when R = H, cyclopentadiene, benzene and iron, or dimerised, affording 433. The radical species $Fe(\eta^5-C_5H_5)(\eta^6-C_6H_6)$ also reacted with organohalogen derivatives RX giving (444) the cyclohexadienyl species $Fe(\eta^5-C_5H_5)(\eta^5-C_6H_6R)$ and $[Fe(\eta^5-C_5H_5)(\eta^6-C_6H_6)]X$.

Thermal decomposition of $Fe(C_6Me_6)_2$ in the presence of CO gave (445) $Fe(CO)_2$-$(\eta^6-C_6Me_6)$. Reaction of $Fe(C_6Me_6)_2$ with either $1,3-C_6H_8$ or benzene afforded $Fe(\eta^6-C_6Me_6)(\eta^4-C_6H_8)$, and the yield of this product from benzene was much enhanced in the presence of hydrogen. Kinetic and isotope distribution studies using D_2 indicated that the primary step in these reactions was not direct loss of a hexamethylbenzene ring, but rather an insertion of the metal into one of the ligand methyl C-H bonds (Scheme 72).

Scheme 72

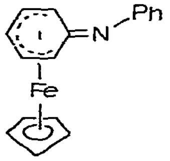


Ruthenium Complexes

Treatment of $[Ru(\eta^6\text{-arene})Cl_2]_2$ (arene = C_6H_6 or p-$MeC_6H_4Pr^i$) with hydrazines gave (446) $[Ru(\eta^6\text{-arene})L_3]^{2+}$ (L = N_2H_4 or NH_2NMe_2), while with ethylenediamine (en), $[Ru(\eta^6\text{-arene})(en)Cl]^+$ was formed. Reaction of $[Ru(\eta^6\text{-arene})(N_2H_4)_3]^{2+}$ with pyridine afforded $[Ru(\eta^6\text{-arene})(pyr)_3]^{2+}$ but with PMe_2Ph, only $[Ru(PMe_2Ph)_6]^{2+}$ was produced.

Treatment of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ with an excess of o-phenanthroline or bipyridyl (N-N) afforded (447) the monocations $[Ru(\eta^6\text{-}C_6H_6)(N\text{-}N)Cl]^+$. Addition to these of PMe_2Ph or $PMePh_2$(L) gave $[Ru(\eta^6\text{-}C_6H_6)(N\text{-}N)_5L]^{2+}$ which underwent nucleophilic attack by H^-, CN^- or OH^- (Y^-) giving the cyclohexadienyl complex $[Ru(\eta^5\text{-}C_6H_6Y)(N\text{-}N)L]^+$. Reduction of $[Ru(\eta^6\text{-}C_6H_3Me_3)(phen)(PMe_2Ph)]^{2+}$ by BH_4^- gave $[Ru(\eta^6\text{-}C_6H_4Me_3)(phen)(PMe_2Ph)]^+$. Treatment of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ with TlC_5H_5 gave $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]Cl$ which reacted with BH_4^- giving small amounts of $Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_7)$ and with NaOMe providing $Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6H_6OMe)$. With NaOH or NaCN, ring displacement occurred. When $[(\eta^6\text{-}C_6H_6)Ru(\mu_2\text{-}OH)_3Ru(\eta^6\text{-}C_6H_6)]^+$ was treated with BH_4^-, as yet uncharacterised 1,3-cyclohexadiene species were produced.

The chiral complex <u>434</u> was readily obtained (448) by reacting $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ with $[NH_2CHRCO_2]^-$ (R = H or Me) in methanol. The Cl atom could be displaced by water giving $[Ru(\eta^6\text{-}C_6H_6)(H_2O)(NH_2CHRCO_2)]^+$ and ^1H and ^{13}C nmr spectral studies



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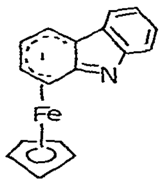

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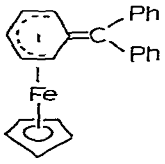

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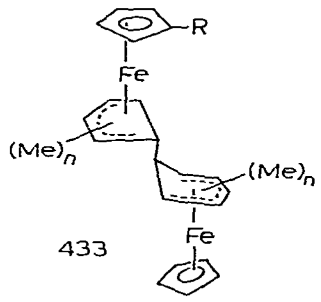

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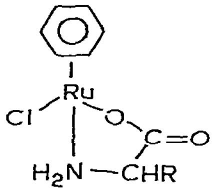

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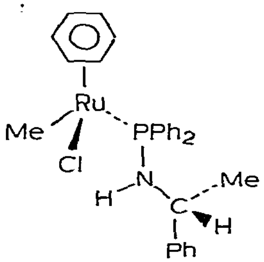

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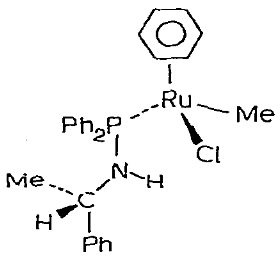

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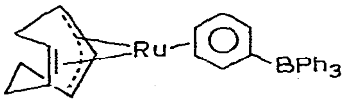
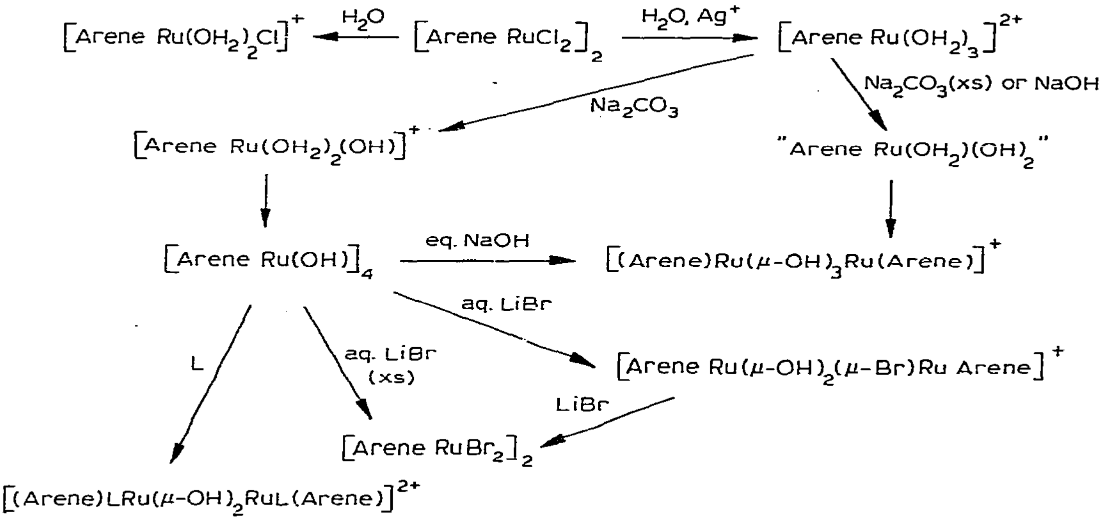


436

permitted identification of the diastereoisomers when R = Me, indicating that epimerisation of these complexes is a relatively slow process.

Treatment of $[Ru(\eta^6-C_6H_6)Cl_2]_2$ with $HgMe_2$ in acetonitrile in the presence of $PPh_2NHCHMePh$ gave 435a and b which were separated chromatographically (449). Reaction of the dimeric benzene complex with aqueous Na_2CO_3 or Na_2SO_4 afforded (450) the tetrameric species $[Ru(\eta^6-C_6H_6)(OH)]_4^{4+}$. The general chemistry of this species and of $[Ru(\eta^6-C_6H_6)Cl_2]_2$ in aqueous media is summarised in Scheme 73.

Scheme 73



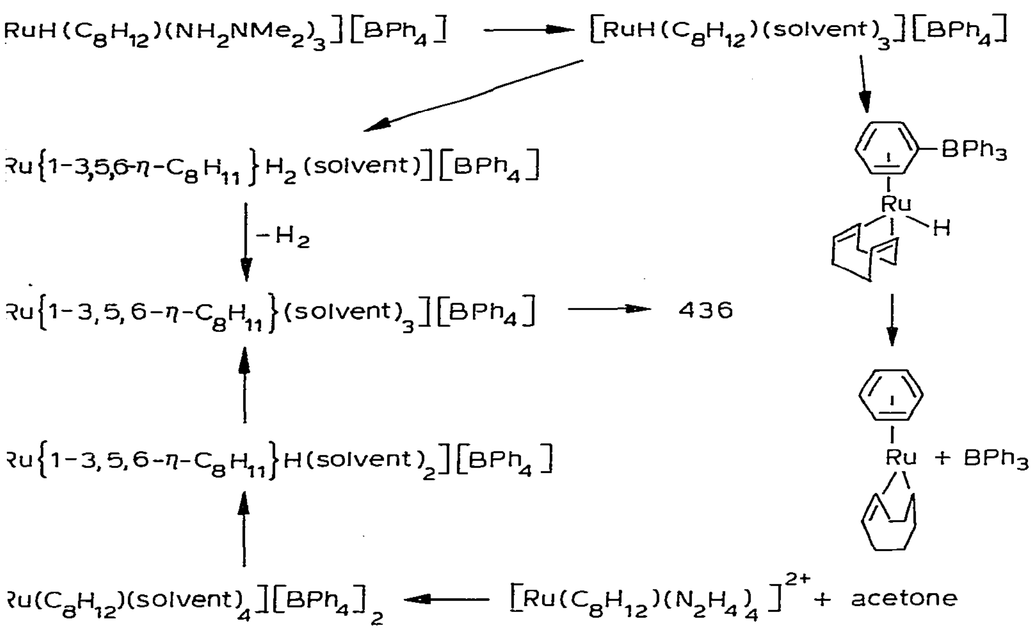
(L = pyridine, etc.)

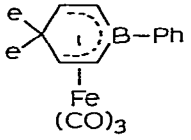
Tetracyanoethylene and $NaBPh_4$ reacted (451) with $Ru(\eta^6-C_6H_6)(S_2PPh_2)Cl$ giving $Ru(\eta^6-C_6H_6)(S_2PPh_2)(NCBPh_3)$. In refluxing acetone $[Ru(C_8H_{12})(N_2H_4)_3][BPh_4]_2$ or $[Ru(C_8H_{12})H(NH_2NMe_2)_3]BPh_4$ were converted (452) into $Ru(\eta^6-C_6H_5BPh_3)(C_8H_{11})$, 436. If this reaction was carried out in benzene, a mixture of 436 and $Ru(\eta^6-C_6H_6)(\eta^4-C_8H_{12})$ was produced. Treatment of 436 with HBF_4 or HPF_6 in acetonitrile afforded $Ru(\eta^6-C_6H_5BF_3)(C_8H_{11})$ whose structure was confirmed crystallographically. The mechanism of formation of 436 is illustrated in Scheme 74.

Heteroaromatic Complexes

Thermolysis of the boracyclohexadiene complex 437 gave (453) the borabenzene derivatives 438 (R = H, 54%; R = Me, 14%). Treatment of $[Fe(\eta^5-C_5H_5)(CO)_2]_2$ with 439 (R = H or Me) in xylene afforded (454) the phosphaferrocene 440 (R = H) whose structure was confirmed by X-ray techniques. The phospholyl ligand is not strictly planar in that the P atom lies 0·041Å out of the C_4 plane away from the Fe atom. Reaction of 440 (R = H) with $MeCOCl/AlCl_3$ gave 440 (R = COMe).

cheme 74





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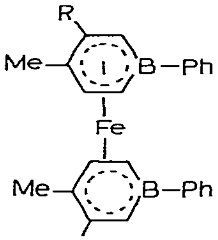

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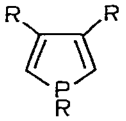

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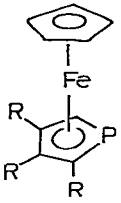

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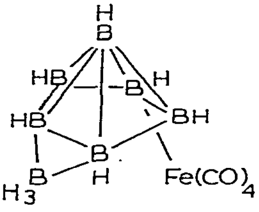
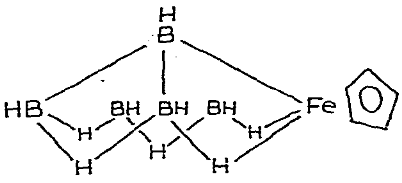


441

RANE AND CARBORANE COMPLEXES

Reaction of $B_{10}H_{12}X$ (X = Se or Fe) with $FeCl_2$ in the presence of KOH afforded 55) the selena- and tellura-borane complex anions $[Fe(B_{10}H_{10}X)_2]^{2-}$, isolated the Me_4N^+ salt. Treatment of $Fe_2(CO)_9$ with B_6H_{10} has been reported (456) $(CO)_4(B_6H_{10})$ which eliminated hydrogen on treatment with KH, producing $[Fe(CO)_4$- $_6H_9)]^-$. Reaction of the $Bu^n{}_4N^+$ salt of this anion with B_2H_6 provided $[Bu^n{}_4N]$- $e(CO)_4(B_7H_{12})]$, 441, whose structure has been determined crystallographically 57). The molecule may be described as a pentagonal bipyramidal B_6H_9 unit into ich a BH_3 and $Fe(CO)_4$ fragment has been inserted into non-adjacent basal B-B nd sites to form apparent three-centre bonds.

Treatment of $FeCl_2$ with NaC_5H_5 and NaB_5H_8 (458) 2-(η^5-C_5H_5)FeB_5H_{10}, 442, ich rearranged thermally at 175° to give 443. Photolysis, in either ether or



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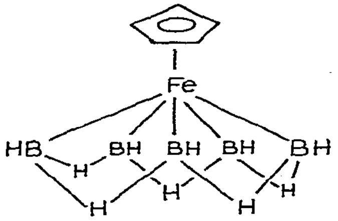

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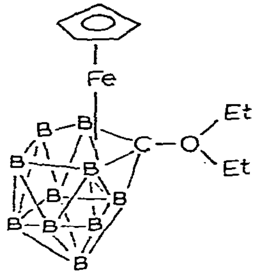

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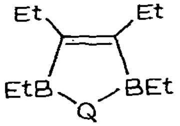

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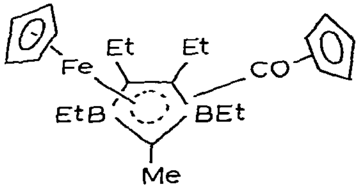

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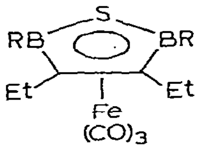

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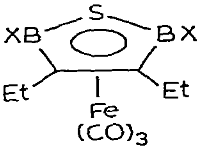
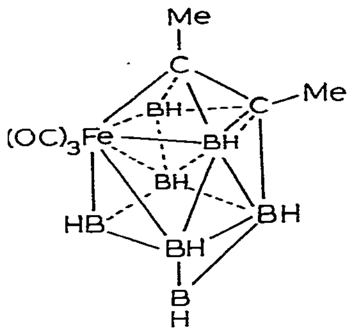


448

THF, of 6-[Fe(η^5-C_5H_5)(CO)$_2$]$B_{10}H_{13}$, led (459) to the formation of the icosahedral metallocarborane Fe(η^5-C_5H_5)(η^5-$B_{10}H_{10}$CL) (L = ether or THF), 444. This reaction is believed to proceed via insertion of one of the carbonyl groups into the boron cage framework.

Treatment of the diborolene 445 (Q = CHMe; R = Et) with Co(η^5-C_5H_5)(CO)$_2$ and [Fe(η^5-C_5H_5)(CO)$_2$]$_2$ in ($EtOCH_2CH_2$)$_2$O gave (460) the η-diborolenyl complex 446. Reaction of the thiadiborolene 445 (Q = S; R = Cl, Br, I, Me, NMe$_2$, OEt, SMe) with $Fe_2(CO)_9$ afforded (461) the half-sandwich species 447, and treatment of 447 (R = I) with NHMe$_2$, Et$_2$CO, Me$_2$S$_2$ or LiBH$_4$ gave 447 (R = NMe$_2$, OEt, SMe or H). With AsF$_3$ in ether, 447 (R = I) was converted into 448.

Carbonylation of Fe($Me_2C_2B_4H_4$)$_2$H$_2$ gave (462) 2,1,4-Fe(CO)$_3$($Me_2C_2B_7H_7$), 449 which is an analogue of closo-$C_2B_8H_{10}$. Reaction of Fe($Me_2C_2B_4H_4$)$_2$H$_2$ with sodium hydride afforded Na[Fe($Me_2C_2B_4H_4$)$_2$H] which, on addition of GeI$_2$, PbBr$_2$ and SnCl$_2$, gave Fe($Me_2C_2B_4H_4$)$_2$Ge, 450 (M = Ge), $Me_4C_4B_8H_8$ and Fe($Me_2C_2B_4H_4$)$_2$Sn, 450 (M = Sn), respectively. Treatment of Fe($Me_2C_2B_4H_4$)$_2$H$_2$ with CoCl$_2$, KOH and C_5H_6 in ethanol afforded seven products including the known (463) Fe(η^5-C_5H_5)-



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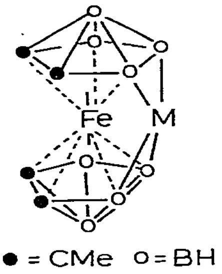

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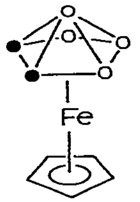

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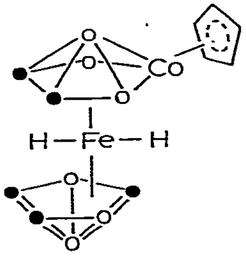

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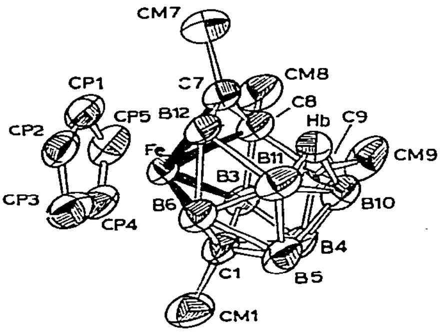

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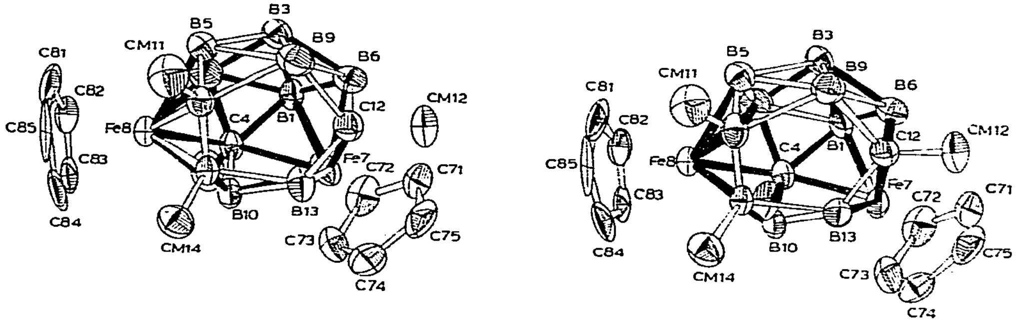
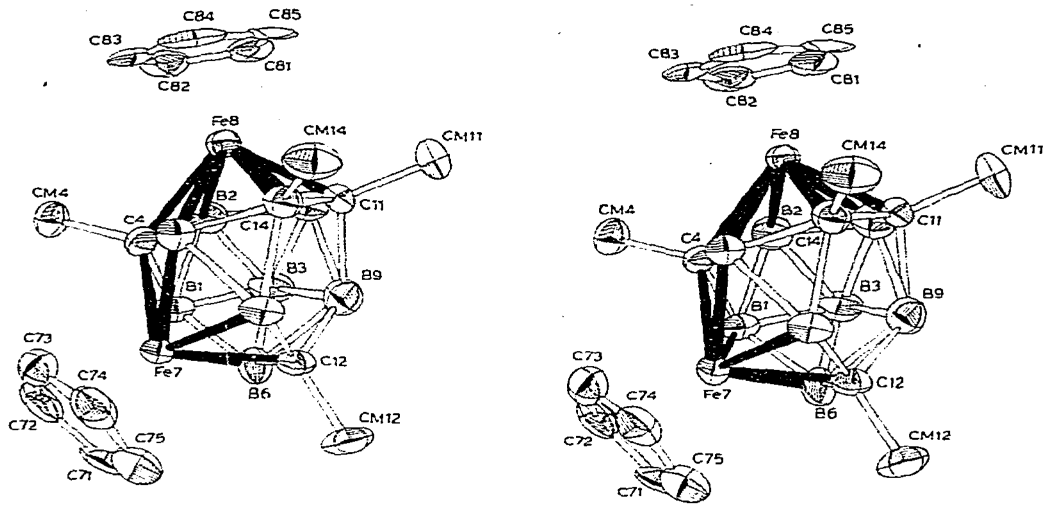
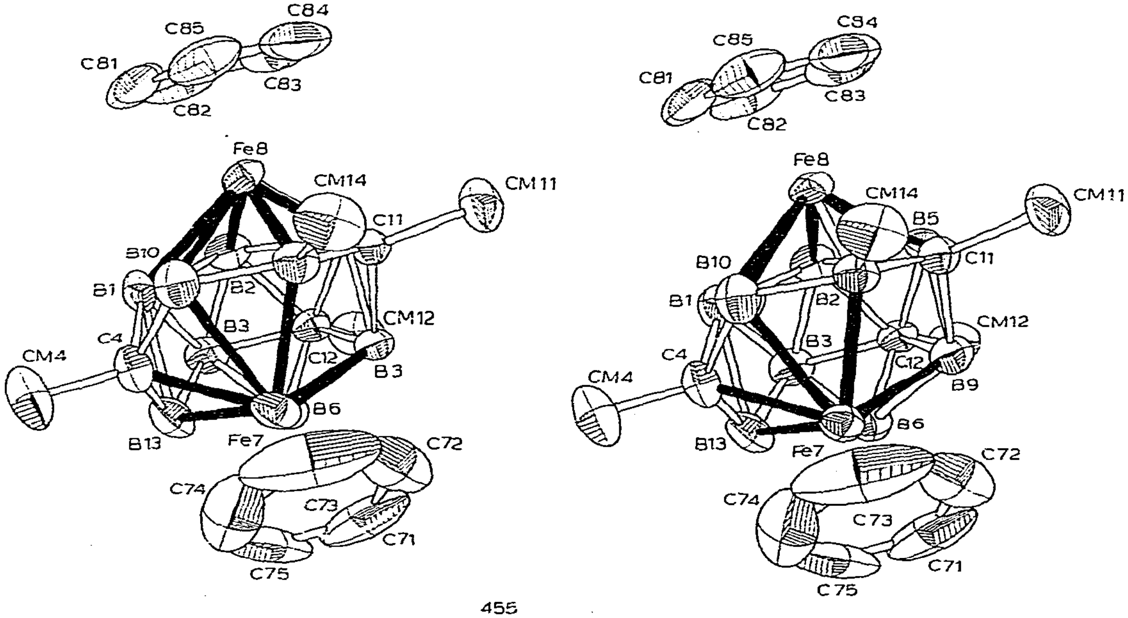


454

$(Me_2C_2B_4H_4)$ and a derivative, $Fe(\eta^5-C_5H_5)(B-\sigma-EtO-Me_2C_2B_4H_3)$, $Fe(\eta^5-C_5H_5)Co(\eta^5-C_5H_5)Me_2C_2B_3H_3$, 451, and $Co(\eta^5-C_5H_5)[Me_2C_2B_3H_3]FeH_2(Me_2C_2B_4H_4)$, 452.

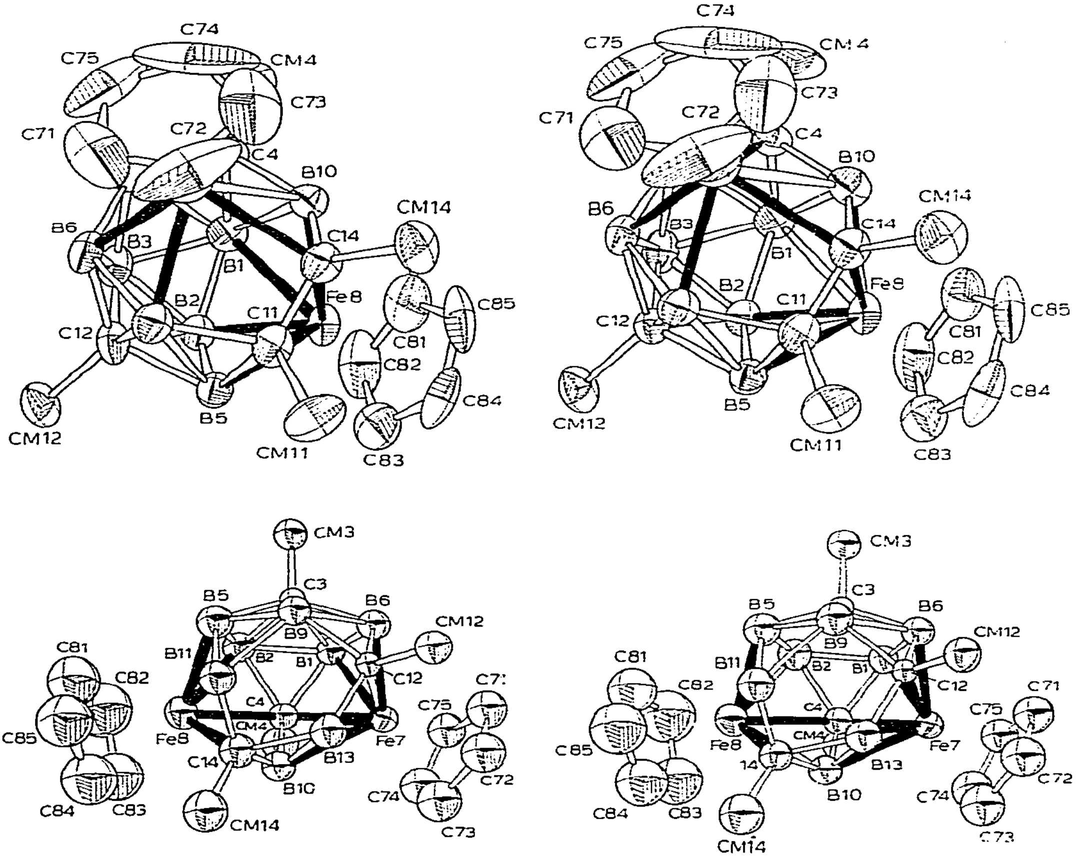
Reduction of $Me_4C_4B_8H_8$ with Na in THF or with $NaC_{10}H_8$ gave (464) $[Me_4C_4B_8H_8]^{2-}$ which reacted with $FeCl_2$ and NaC_5H_5 affording four isomers of the (4-vertex carborane complex $Fe_2(\eta^5-C_5H_5)_2(Me_4C_4B_8H_8)$, and one isomer of the nido-12-vertex species $Fe(\eta^5-C_5H_5)(Me_4C_4B_7H_8)$, 453. The thermal rearrangement of the





455

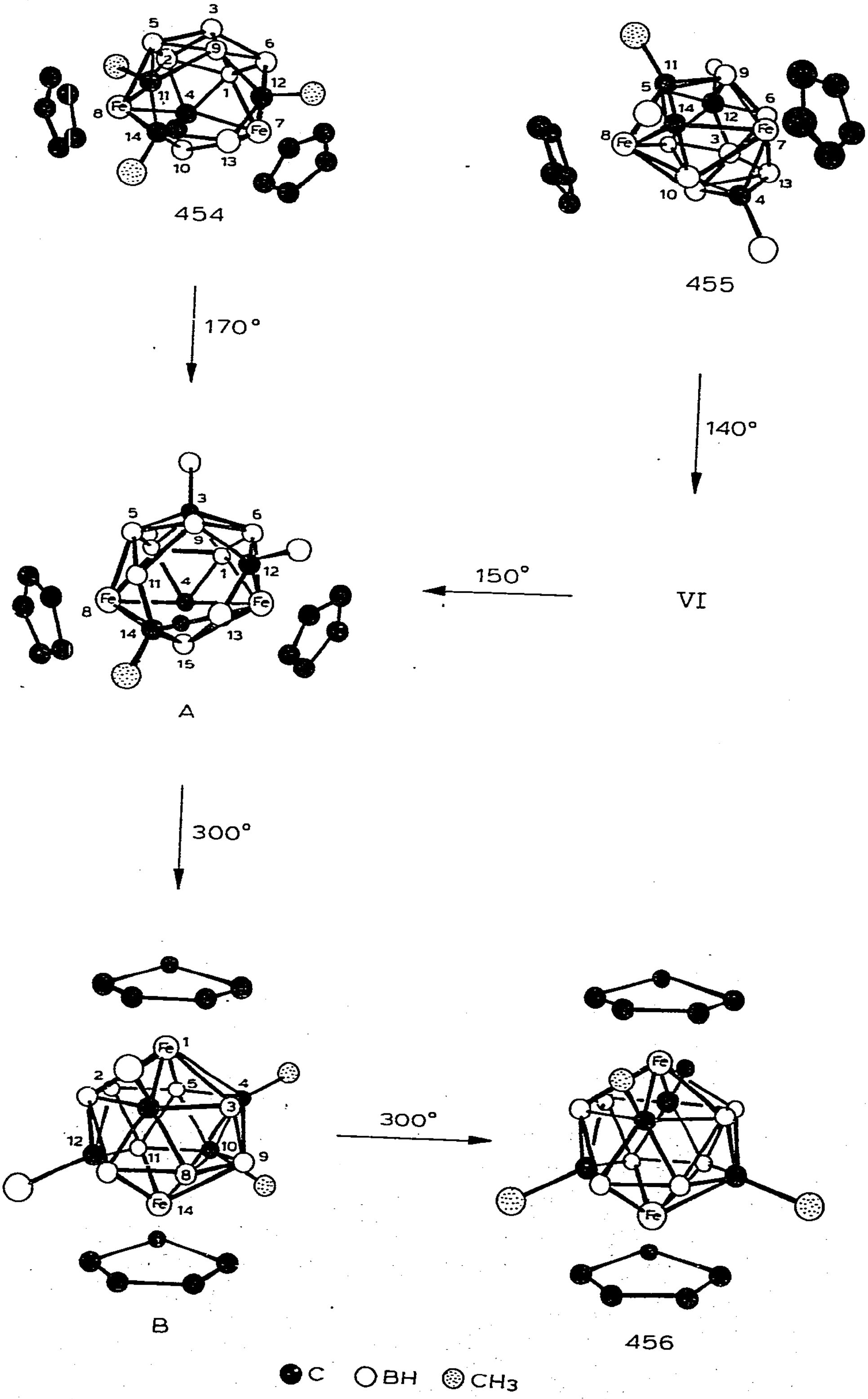
various isomers of $Fe_2(\eta^5\text{-}C_5H_5)_2(Me_4C_4B_8H_8)$ have been investigated (465). In the reaction between $FeCl_2$, NaC_5H_5 and $[Me_4C_4B_8H_8]^{2-}$ at 25°, two isomers, 454 and 455 can be isolated. The structures of these two compounds, determined crystallographically, are noticeably different, having a nido arrangement with a five- and a four-sided open face, respectively. These results are in violation of the conventional skeletal electron-count theory for polyhedral compounds, which predicts closo geometry. Both 454 and 455 rearranged at 170° to a common isomer, A, which has a structure similar to that of 454 but with a BH and



456

CMe group interchanged. In 454, 455 and A, the distribution of framework C atoms is unusual, with C atoms residing in both low- and high-coordinate polyhedral vertices. A rearranged at 300° to B and 456 whose structure was also determined crystallographically. This species has a closo arrangement consisting of a bicapped hexagonal antiprism, with the metal atoms in the capping positions. When B was continually heated at 300°, only 456 and decomposition fragments were produced. In the conversion of A to B, two non-adjacent cage C atoms evidently migrate to adjacent vertices indicating that a drive to achieve cage closure takes precedence over the normal tendency for framework C atoms to separate from each other in thermal rearrangements. The species 454, 455 and A constitute a new class of polyhedra; cages for which closo geometry is favoured but which are effectively frozen into nido configurations for steric reasons. The general pattern of these thermal rearrangements is shown in Scheme 75.

Scheme 75

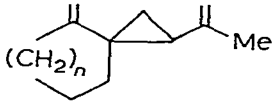


SYNTHETIC AND CATALYTIC REACTIONS INVOLVING ORGANO-IRON RUTHENIUM AND OSMIUM COMPOUNDS

Synthesis of Organic Compounds

Cyclohexylamine reacted (466) with $Fe(CO)_5$ under CO pressure giving $C_6H_{11}NHCHO$ and $Fe(CO)_4(NH_2C_6H_{11})$. The reaction apparently occurred via the equilibrium formation of a carbamoyl complex in which a proton was transferred from the amino group to the metal, giving a metallohydride derivative. In a second equilibrium step, this broke down to give the formamidine and $Fe(CO)_4$ which promptly accepted cyclohexylamine as a ligand.

Photolysis of 457 in the presence of $Fe(CO)_5$ afforded (467) a presumed intermediate 458 which eliminated $Fe(CO)_3$ giving 459 and 460, although the uncharacterised organoiron complexes $Fe(CO)_3C_{n+10}H_{2n+14}$ and $Fe_2(CO)_6C_{n+10}H_{2n+14}$ were also obtained. When norbornadiene was photolysed in the presence of $Fe(CO)_5$ and acetylenes, the cyclopentanone 461 and a variety of other products, e.g. 462 ($R = R^1 = CO_2Me$ or Ph; $R = H$, $R^1 = CO_2Et$), 463 ($R'' = Me$ or Et), and 464 ($R = R^1 = Ph$), were formed (468). Reaction under these conditions with phenylacetylene afforded 465 and 464 ($R = Ph$, $R^1 = H$). Photolysis of norbornene



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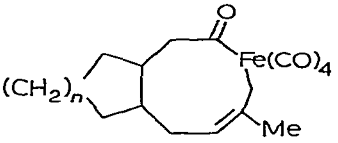

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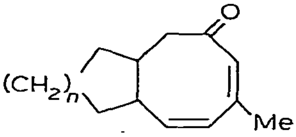

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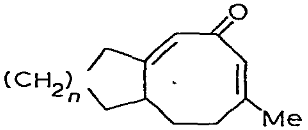

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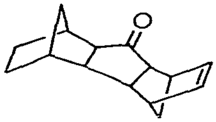

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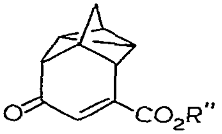

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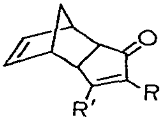

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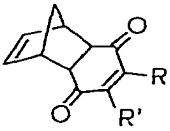

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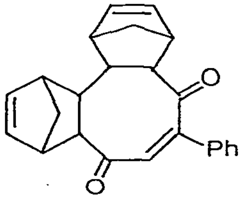

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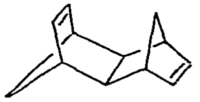

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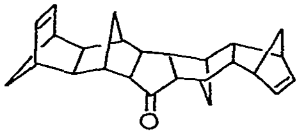

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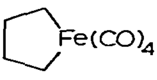

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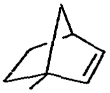

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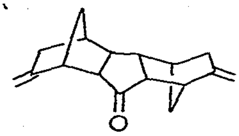

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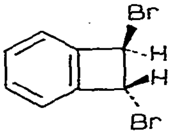
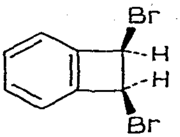
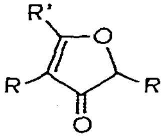


472 a



472 b



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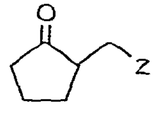

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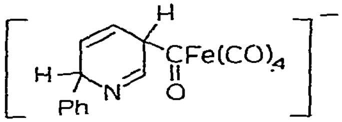


475

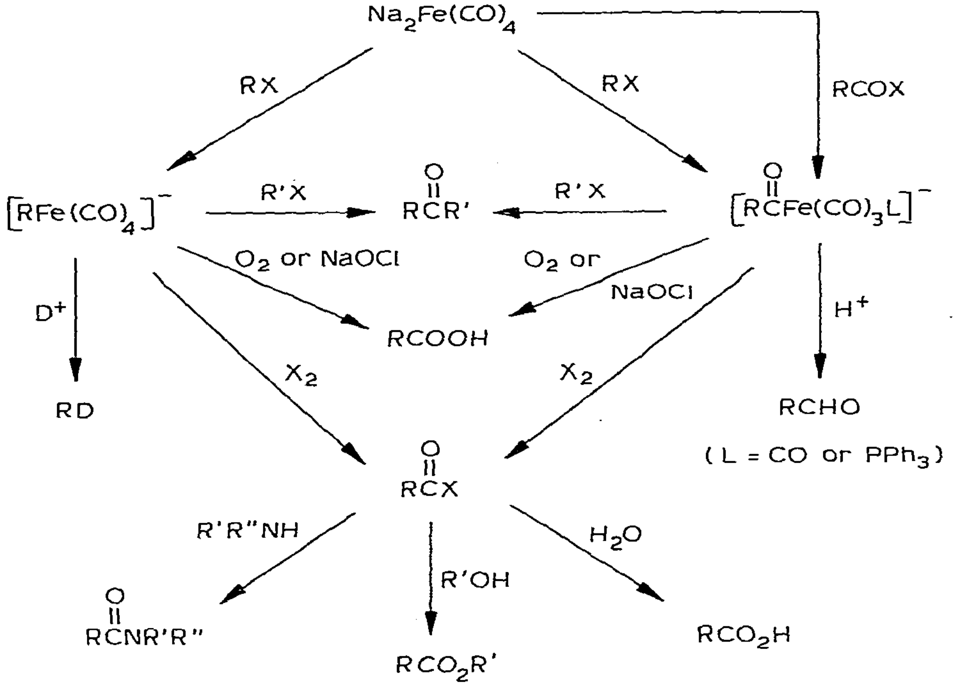
with $Fe(CO)_5$ and $RC{\equiv}CR^1$ gave norbornane analogues of 462 ($R = R^1 = CO_2Me$) and 464 ($R = Ph$, $R^1 = H$). When 466 was photolysed or heated in the presence of $Fe(CO)_5$, 467 was produced exclusively (469). It was thought that this reaction proceeded via a metallocyclic pathway, but it was noted that 1-methylnorbornene reacted with $Fe(CO)_5$ giving only 468 and no cyclopentanone product, furthermore, while 469 provided only a very small amount of the expected cyclopentanone, 470 formed 471 in good yield when heated with $Fe(CO)_5$.

Reaction of α,α,α',α'-tetrabromo-o-xylene with $Fe(CO)_5$ led easily (470) to the synthesis of the trans-1,2-dibromobenzocyclobutenes, 472a and b. Also, some α,α'-dibromo-o-xylene and polymer was produced and, depending on solvent occasionally o-$C_6H_4(CH_2Ph)_2$ was formed. Reaction of p-$C_6H_4(CHBr_2)_2$ with $Fe(CO)_5$ in benzene gave p-$C_6H_4(CH_2Ph)_2$ in low yield. Reaction of BrCHRCOCHRBr (R = Me, Et, Pr^i or Bu^t) with R^1CONMe_2 (R^1 = H, Me or Ph) in the presence of $Fe_2(CO)_9$ afforded (471) the 3(2H)-furanones 473. Via this route, 4-methyl muscarine iodide (473, R = Me, $R^1 = CH_2NMe_3{}^+I^-$) was prepared in six steps.

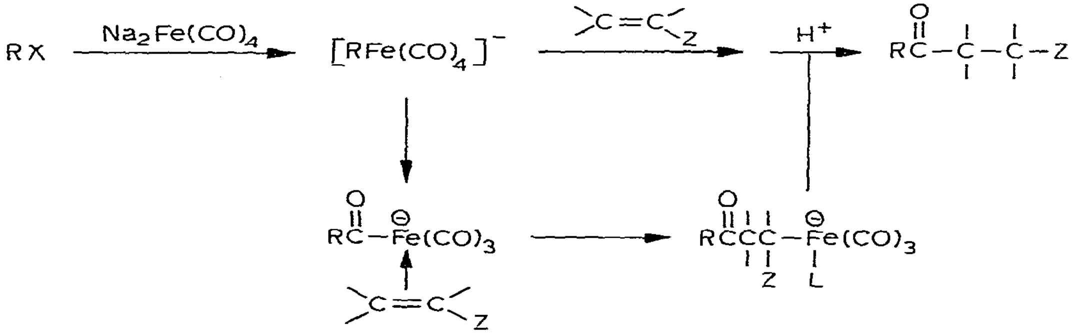
A detailed kinetic and mechanistic study has been made (472) of the oxidative addition reactions of alkyl halides and tosylates to $Na_2Fe(CO)_4$ in both THF and N-methylpyrrolidone. The mechanism involves a two-electron S_N2 reaction, with no detectable competing one-electron atom abstraction and/or radical chain processes. Evidence was also presented to underline the importance of ion-pairing in these oxidative addition reactions. Thus, in N-methylpyrrolidone, $Na_2Fe(CO)_4$ dissociates predominantly to the solvent-separated supernucleophilic ion pair $[Na^+{:}S{:}Fe(CO)_4{}^{2-}]$, the kinetically dominant species, with no kinetic contribution from 'free' $[Fe(CO)_4]^{2-}$. In THF, however, $Na_2Fe(CO)_4$ is much less dissociated, with the tight ion paired species $[NaFe(CO)_4]^-$ being the kinetically dominant species. The synthetic conversions effected by $Na_2Fe(CO)_4$ were renewed (Scheme 76).

Reaction of $[RFe(CO)_4]^-$ (R = Et, Bu^n, or n-C_6H_{13}) with the 'Michael acceptors'

Scheme 76

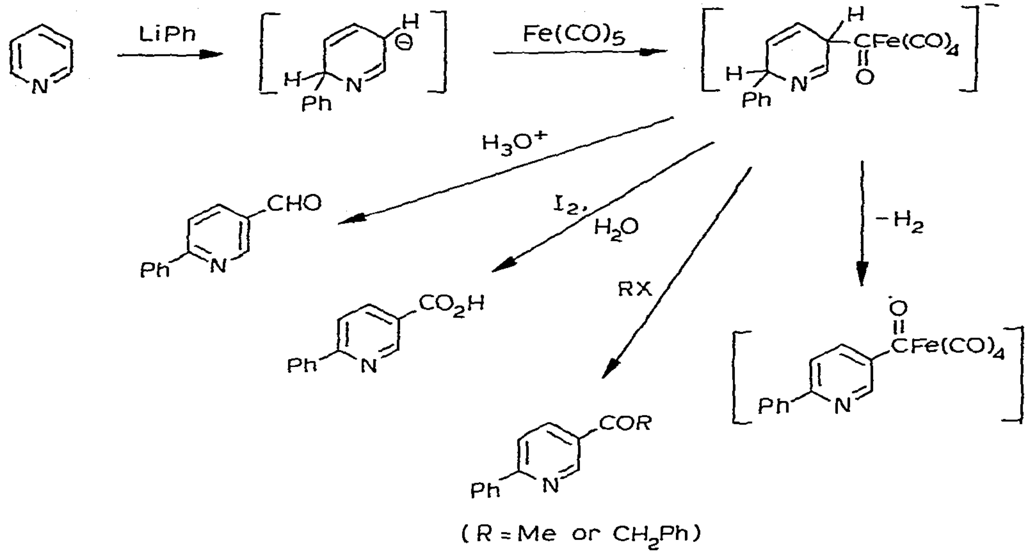


Scheme 77



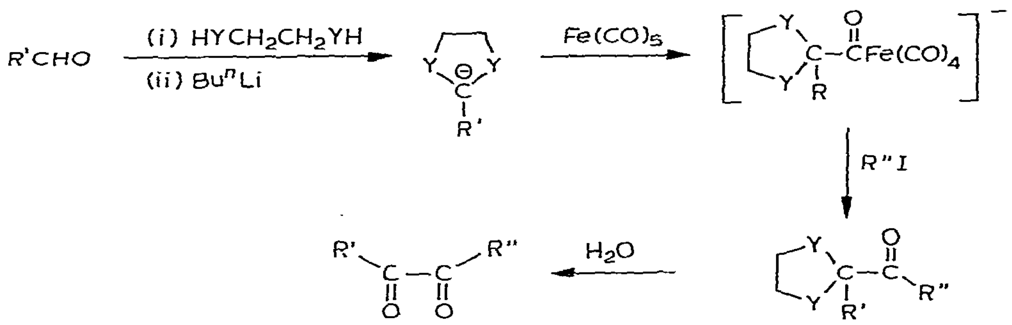
$RCH{=}CR^1Z(R, R^1 = H$ or Me; $Z = CO_2Et$ or CN) led (473) to hydroacylated products via insertion reactions into the Fe-R bond, as shown in Scheme 77. However, using $I(CH_2)_3CH{=}CHZ$ ($Z = CO_2Et$ or CN), the cyclopentanone 474 was produced via the intermediate $[Fe(CO)_4(CH_2)_3CH{=}CHZ]^-$. Treatment of pyridine with lithium phenyl afforded an adduct which, on addition of $Fe(CO)_5$, gave (474) the acyl anion 475; reactions of this species are summarised in Scheme 78. Reaction of 3-lithiopyridine with $Fe(CO)_5$, followed by hydrolysis, led to the formation of pyridine-3-aldehyde. A new synthesis of α-diketones from aldehydes and alkyl

Schema 78



(R = Me or CH_2Ph)

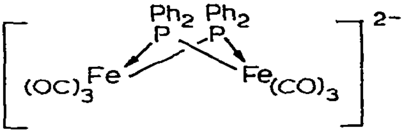
Scheme 79



iodides, using $Fe(CO)_5$ as shown in Scheme 79, has been devised (475).

Reaction of $Na_2Fe(CO)_4$ with $Fe(CO)_5$ gave $Na_2Fe_2(CO)_8$ which, on treatment with PPh_2Cl, was converted (476) into $Fe_2(CO)_6(\mu_2\text{-}PPh_2)_2$. Reduction of this μ_2-phosphide by Na in THF afforded $Na_2[Fe_2(CO)_6(PPh_2)_2]$, 476 which reacted with alkyl halides giving 477. This last species could also be obtained by treatment of $Fe_2(CO)_6(PPh_2)_2$ with LiR. Preliminary X-ray crystallographic results obtained from $LiFe_2(CO)_5(\mu_2\text{-}PPh_2)_2(COPh).3THF$ indicated that the Fe-Fe distance was 2·67Å. Protonation of 477 led to the isolation of aldehydes.

Treatment of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(H_2C{=}CHMe)]^+$ with benzylamine afforded (477) the adduct $[Fe(\eta^5\text{-}C_5H_5)(CO)_2CH_2CHMeNH_2CH_2Ph]^+$. Oxidation of this with chlorine, followed by addition of NEt_3, provided the β-lactam 478. Similar compounds were obtained using $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(alkene)]^+$, where alkene = cis-



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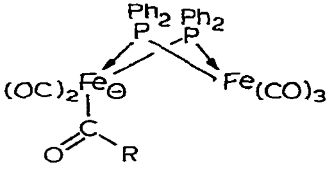
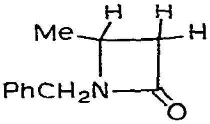


477



478

and trans-but-2-ene. The results were in accord with the stereochemical sequence involving trans addition to the olefin complex followed by carboxamidation with retention of configuration at the Fe-C bond.

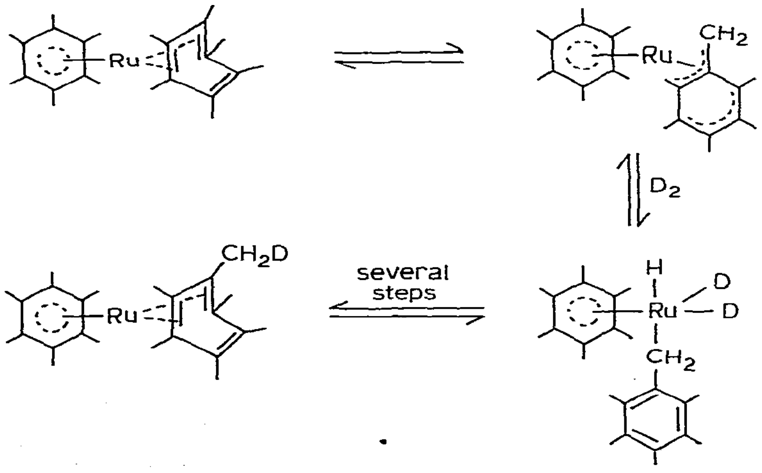
Mono- and di-substituted alkynes reacted (478) with $FeCl_3$ giving polymers, $RCH{=}CClR$ or $RCCl{=}CH_2$ and $FeCl_2$.

Hydrogenation and Dehydrogenation

The kinetics of the hydrogenation of hex-1-ene at 20° under H_2 (1 atm), catalysed by $Ru(PPh_3)_3H(BH_4)$, indicated (479) that the reaction proceeded via dissociation of the catalyst, formation of an alkyl complex and their oxidative addition of hydrogen in the rate determining step. The kinetics of hydrogenation of acrylamide to propionamide catalysed by $[Ru(PPh_3)_2HCl]_2$ suggested (480) that the mechanism included competitive oxidative addition reactions of hydrogen and propionamide (via C-H bond cleavage).

The cluster complex $Ru_6(CO)_{14}C(\eta^6\text{-}C_6H_5Me)$ did not undergo arene ligand exchange, but it reacted (481) with hydrogen (150°, 2-3 atm) giving methylcyclohexane and ruthenium metal quantitatively (there was no recoverable toluene). However, with the analogous benzene complex, only traces of cyclohexane could be obtained, and this was only produced by the Ru metal formed after decomposition. Even in the presence of CO, this reaction was not suppressed. However, the previously described (482) arene complex $Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$

Scheme 80



proved to be a long-lived catalyst for the hydrogenation of aromatics from the reaction system, no hexamethylbenzene could be recovered, and it was noticed in general that hydrogenation rates decreased with an increase in the alkyl substitution of the substrate. Thus, C_6Me_6 could not be hydrogenated. Very extensive H/D exchange was observed when $Ru(C_6Me_6)_2$ was maintained under D_2, and a possible mechanism for this is outlined in Scheme 80.

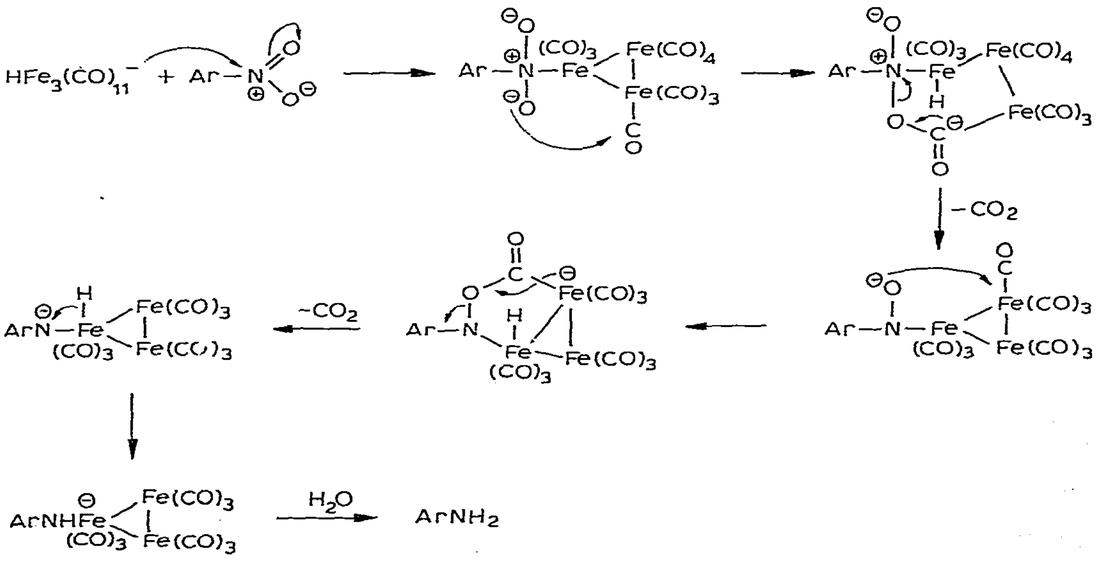
Selective homogeneous hydrogenation of cis, trans, trans-cyclododecatriene to trans-cyclododecene, of 1,5-cyclooctadiene to cyclooctene, and of ethyl-2-acetyl-4,9-decadienoate to the corresponding 4-decenoate, was achieved (483) at room temperature using $Ru(PPh_3)_3Cl_2$. Catalytic hydrogenation of citraconic and mesaconic acids, giving (-)-(S)-methylsuccinic acids and a mixture of - lactones was achieved (484) using $Ru_4(CO)_8[(-)\text{-DIOP}]_2H_4$. The ratio of the products was dependent on the nature of the substrate and the reaction temperature. An exceptionally high regioselectivity was obtained in the hydrogenation of the more sterically hindered mesaconic acid. $Ru_6(CO)_{18}[(-)\text{-DIOP}]$ could also be used as a catalyst in these reactions.

Scheme 81

$$PhCH_2NEt_3^+Cl^- + OH^- \longrightarrow PhCH_2NEt_3^+\,OH^-\ \text{(aqueous)}$$

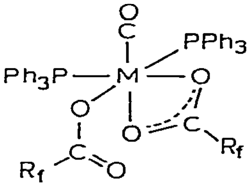
$$\left.\begin{aligned} PhCH_2NEt_3^+\,OH^- + Fe_3(CO)_{11} \longrightarrow\ & [PhCH_2NEt_3^+]_2[Fe_3(CO)_{11}^{2-}]\ + \\ & +\ [PhCH_2NEt_3^+]_2[CO_3^{2-}] + 2\,H_2O \end{aligned}\right\}\ \text{(organic)}$$

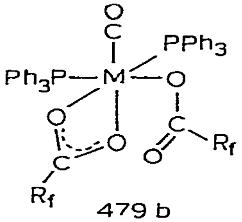
$$Fe_3(CO)_{11}^{2-} + H_2O \longrightarrow [HFe_3(CO)_{11}]^- + OH^-\ \text{(aqueous)}$$

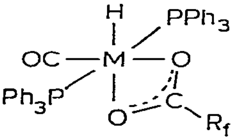


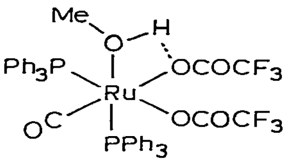
By using the phase-transfer catalytic system $Fe_3(CO)_{12}$/aqueous NaOH/benzene/ $[PhCH_2NEt_3]Cl$, hydrogenation of nitroarenes to the corresponding anilines was effected (455). It appeared that $[Fe_3(CO)_{11}H]^-$ may be the catalyst intermediate, and the mechanism of the process is outlined in Scheme 81.

The importance of the molecular asymmetry induced by olefins, e.g. benzalactone or trans-stilbene, in the enhancement of the enantioselective dehydrogenation of racemic alcohols, RR^1CHOH, catalysed by RuL_3Cl_2(L = (+)-neomenthyldiphenylphosphine), has been investigated (486). The use of $Ru(PPh_3)_3Cl_2$ as a catalyst for the dehydrogenation of 9,10-dihydroanthracene, 1,4-dihydronaphthalene and dibenzyl has been evaluated (487) and the thermal decomposition of $Fe(\eta^5-C_5H_5)-(CO)_2GeEt_3$ gave (488) a stable heterogeneous catalyst for the dehydrogenation of isopropanol and EtMeCHOH.


479 a


479 b


480

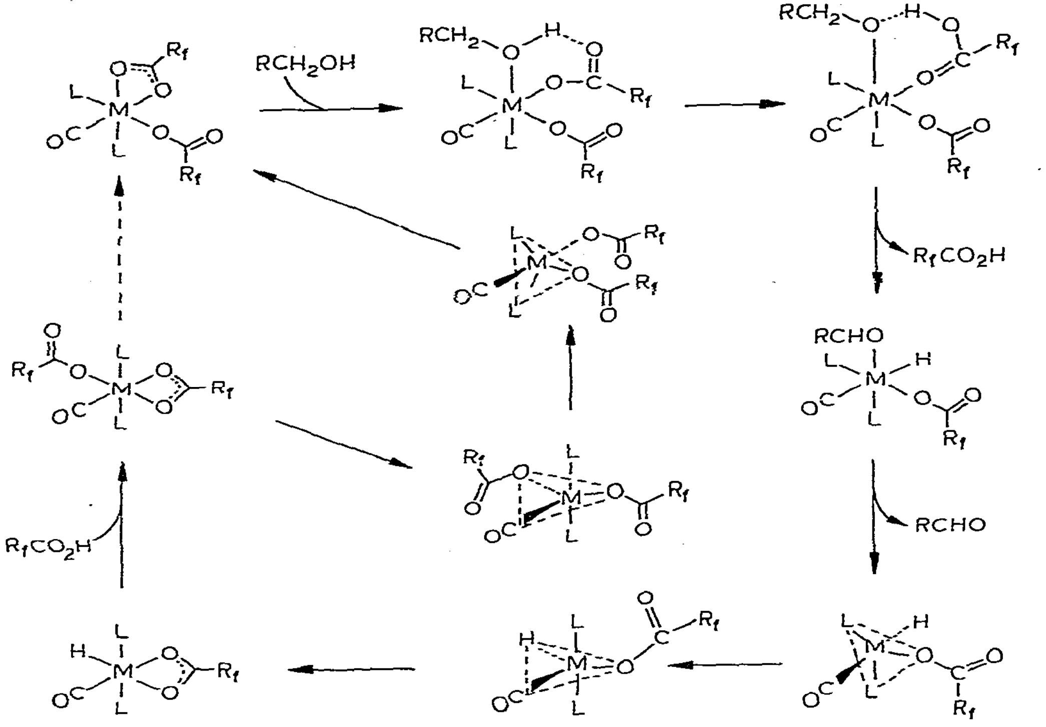

481

The complexes $M(CO)(PPh_3)_2(OCOR_f)_2$, 479a and b (M = Ru or Os; $R_f = CF_3$, C_2F_5 or C_6F_5), which are in dynamic equilibrium, functioned (489) as catalysts for the dehydrogenation of primary and secondary alcohols to aldehydes and ketones, respectively. The catalytic activity is promoted by small amounts of R_fCO_2H, but inhibited by large concentrations of the acid and by an accumulation of the aldehydes or ketones. In the presence of R_fCO_2H, $M(CO)(PPh_3)_2H-(OCOR_f)$, 480, also acted as a catalyst, which was not surprising in view of the conversion of the hydride 480 by acid into 479. The detailed mechanism of the dehydrogenation process is shown in Scheme 82, and the structure of a methanol solvate, 481, was established by X-ray crystallography.

Water-Gas Shift Reaction, Methanation of CO and Related Reactions

Treatment of $Fe(CO)_5$ with OH^- led (490) to the formation, at pH 12, of $[Fe(CO)_4-H]^-$ with elimination of CO_2. As the pH was decreased by heating and on addition of water, $Fe(CO)_4H_2$ was formed, although traces of $[Fe_3(CO)_{11}H]^-$ could also be

Scheme 82



detected. If ethylene and CO were added to this system at 100° at moderate pressures, propanol was produced, even at pH ca. 8, and if acetaldehyde was added at the beginning, ethanol was formed before the propanol. It was observed that basic solutions of $[Fe(CO)_4H]^-$ under CO evolved H_2 when the pH was lowered to 10·7, and this was consistent with the presence of $Fe(CO)_4H_2$. Indeed, 1,5-cyclooctadiene could be isomerised to its 1,3-isomer by using $K[Fe(CO)_4H]$ in aqueous solutions at pH 10.7, and it is known (491) that $Fe(CO)_4H_2$ is a catalyst for this process. It was noted that it was easier to form $Fe(CO)_4H_2$ from $Fe(CO)_5$, water and base than directly from $Fe(CO)_5$ and H_2, and so, if the system was operated in the absence of alkene, catalysis of the water-gas shift reaction could be achieved:

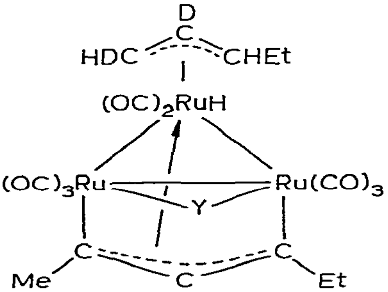
$$
\begin{array}{lcl}
Fe(CO)_5 + OH^- & \longrightarrow & [Fe(CO)_4H]^- + CO_2 \\
{[Fe(CO)_4H]^-} + H_2O & \longrightarrow & Fe(CO)_4H_2 + OH^- \\
Fe(CO)_4H_2 & \longrightarrow & Fe(CO)_4 + H_2 \\
Fe(CO)_4 + CO & \longrightarrow & Fe(CO)_5 \\
\hline
CO + H_2O & \longrightarrow & CO_2 + H_2
\end{array}
$$

The hydroformylation of alkenes using H_2O and CO could be more effectively achieved using $M_4(CO)_{12}H_4$ (M = Ru or Os) or $Os_3(CO)_{10}H_2$. Catalysis of the water-gas shift reaction was also effected (492) by $Ru_3(CO)_{12}$, aqueous KOH and CO (1 atm) at 100°. This system also catalysed the decomposition of formic acid to H_2 and CO_2.

Surface carbonyl species have been implicated in the catalytic formation of hydrocarbons from CO and hydrogen over Ru/Al_2O_3 surfaces (493). It has been reported (494) that hydrocarbons of C_1–C_7 content containing paraffinic and olefinic components have been prepared by reaction of CO and hydrogen (1:1 ratio) at 260° and varying pressures using 2% Ru supported on TiO_2. When compared to Ru on other supports, e.g. Al_2O_3 or carbon, Ru/TiO_2 exhibited higher selectivity towards olefin formation and suppressed the formation of CH_4 and high molecular weight hydrocarbons. The interactions of hydrocarbons with Fe surfaces has been examined theoretically (495). The interactions of H and C atoms, produced by catalystic C–C, C–H and H–H bond rupture, leads to the weakening of Fe–Fe bonds. It was suggested that on the metal surfaces, ethylene and acetylene effectively dissociated into CH_2 and CH fragments. These, in turn, dehydrogenated with a low activation energy.

Isomerisation, Oligomerisation and Polymerisation

The catalytic isomerisation of pent-1-ene to its cis- and trans-2-isomers has been achieved (496) using $Ru_4(CO)_{13}H_2$ at 70° and $Ru_3(CO)_9H(C_6H_9)$ at 55° and 70° in toluene. The data obtained from the reaction with $Ru_4(CO)_{13}H_2$ and $[1,2\text{-}D_2]$-pent-1-ene suggested the involvement of a metal hydride addition-elimination reaction. In the reaction of this deuterated pentene with $Ru_3(CO)_9H(C_6H_9)$, 482 was isolated as an intermediate.

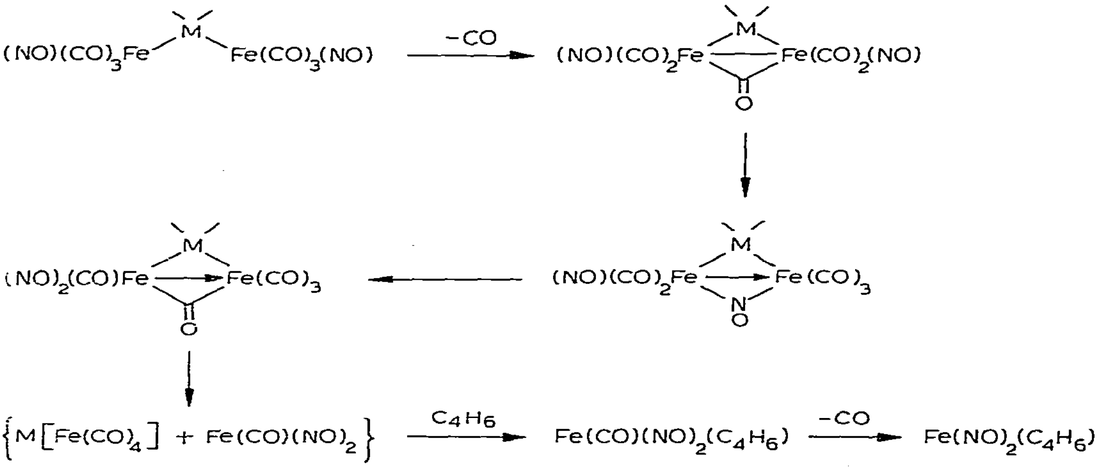


482

Treatment of $FeCl_2$ with $RN{=}C(R^1)C(R^1){=}NR$, (L), (R^1 = H, R = Pr^i, Bu^t, C_6H_{11}, $CHPr^i{}_2$; R^1 = H or Me, R = o-MeC_6H_4, $C_6H_3Me_2$, $C_6H_3Me_2$, C_6H_{11}, Ph) gave (497) the adduct FeL_2Cl_2 which was reduced by Na on the presence of L to give the paramagnetic Fe(0) complex FeL_2. This complex reacted with CO giving, initially and reversibly, $Fe(CO)L_2$, and finally, $Fe(CO)_3L$. In the presence of $AlEt_2(OEt)$ or $AlEt_3$, FeL_2 exhibited high catalytic activity towards the dimerisation of dienes such as C_4H_6, 1,5-C_8H_{12} and isoprene.

Selective dimerisation of butadiene could be catalysed (488) by $Na[Fe(CO)_3(NO)]$ alone with low efficiency, but a moderate increase in activity could be achieved by adding $ZnCl_2$, $CdCl_2$, $HgCl_2$ or $Hg(CN)_2$. However, when mixtures of $[Fe(CO)_3(NO)]^-$ with $FeCl_3$, $FeBr_2$, FeI_2, $[Fe(NO)_2X]_2$ or $Na[Co(CO)_4]$ or of $[Fe(NO)_2Cl]_2$ plus $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$ or $Na[Co(CO)_4]$, were employed, the yields of dimerised butadiene were excellent. The reactions of $Na[Fe(CO)_3(NO)]$ with MX_2 are envisaged in Scheme 83. Reduction of $[Fe(NO)_2Cl]_2$ with Cu or Zn powder afforded (499) a catalyst precursor capable of cyclodimerising norbornadiene, isoprene, phenylacetylene and, of cause, butadiere. If this reduction was carried out in the presence of PPh_3 or $Ph_2PCH_2CH_2PPh_2$, then $Fe(NO)_2(PPh_3)_2$ or $Fe(NO)_2$(diphos) were formed. Both $[Fe(NO)_2L_n]X$ (L = RCN where R = Me or $CH_2{=}CH$, or PPh_3; Y = BF_4, PF_6, BPh_4 or ClO_4), or the species produced (500) when $[Fe(NO)_2Cl]_n$ was treated with AgX in the presence of olefin, acted as catalysts for the polymerisation of acrylonitrile and styrene, and the selective dimerisation of norbornadiene.

Scheme 83

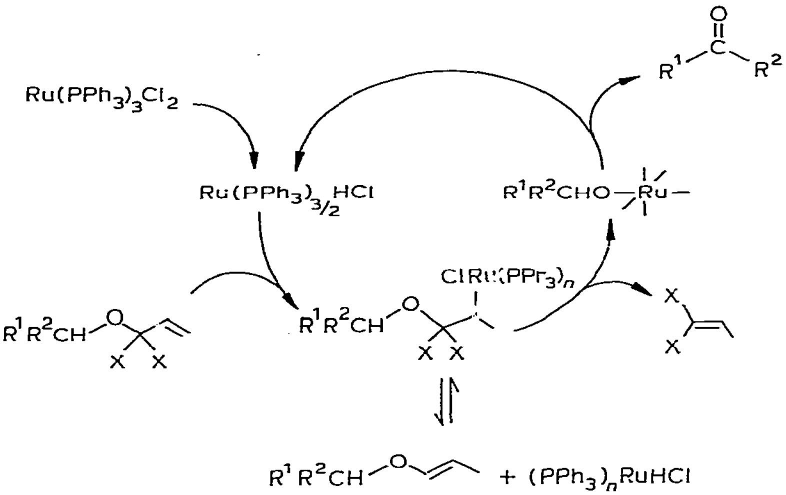


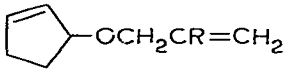
Other Reactions

Catalysis of the redox fragmentation of allyl ethers has been observed (501) using $Ru(PPh_3)_3Cl_2$. Thus, α,α-dimethylallylbenzylether was converted into benzaldehyde and 2-methyl-2-butene. Also, the conversion of the cyclopentenylether 483 into 484 and 485, and of $CH_2{=}C(Me)CH_2OCH_2CH{=}CH_2$ into $CH_2{=}C(Me)CH_2CHMe\text{-}CHO$, was effected by this catalyst. It would appear that cleavage of the allyl C–O bond is the rate determining step, thereby leading to the formation of a Ru(II) alkoxide. The proposed mechanism is shown in Scheme 84.

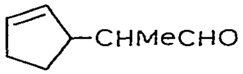
Complexes formed between polyethyleneimine or poly(vinylpyrrolidone) and

Scheme 84

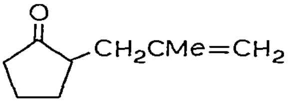




483



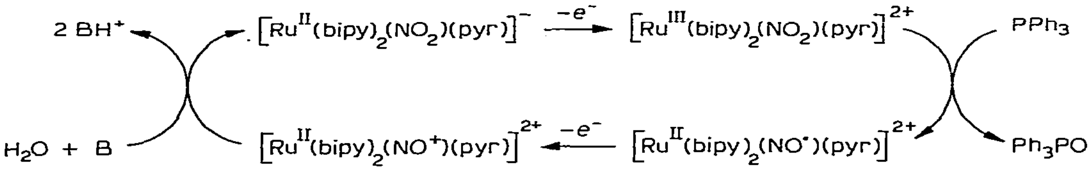
484



485

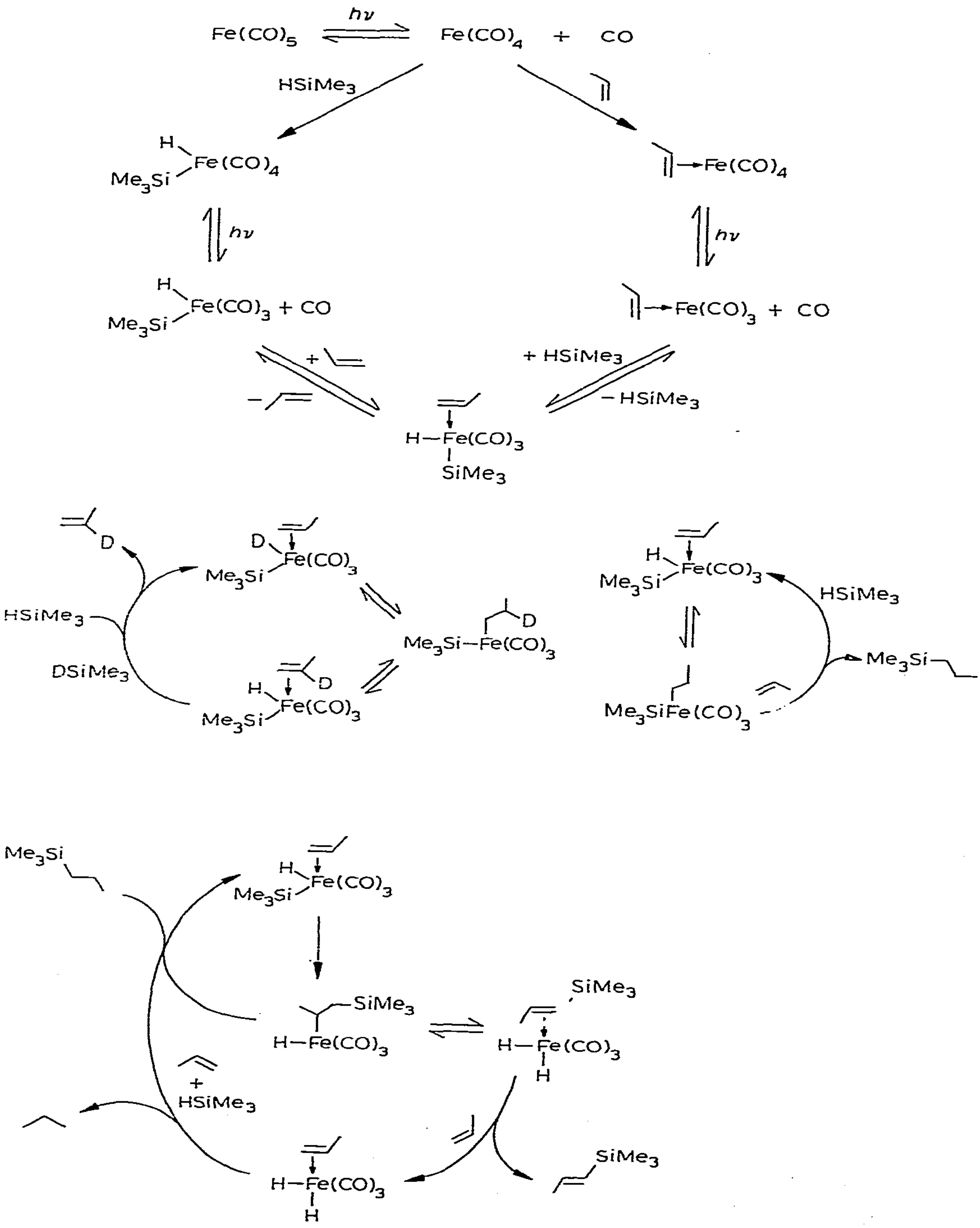
Fe(CO)$_5$ were water soluble and effected (502) the catalytic decomposition of isopropybenzenehydroperoxide to dimethylphenylcarbinol. The complex [Ru(NO)-(bipy)$_2$(pyr)]$^{3+}$ catalysed (503) the oxidation of Ph$_3$P to Ph$_3$PO, as shown in Scheme 85.

Scheme 85



The uv irradiation of Fe(CO)$_5$ in the presence of R$_3$SiH (R = Me or Et) and alkene achieved the catalytic production (504) of a mixture of alkanes, alkyl and alkenyl trialkylsilanes. The photogenerated species was thought to be Fe(CO)$_3$(alkene)H(SiR$_3$) and the overall mechanism is outlined in Scheme 86.

Scheme 86


Fe(CO)$_5$
hν
Fe(CO)$_4$ + CO
HSiMe$_3$
Me$_3$Si Fe(CO)$_4$
Fe(CO)$_4$
hν
Fe(CO)$_3$ + CO
Fe(CO)$_3$ + CO
+ HSiMe$_3$
− HSiMe$_3$
H—Fe(CO)$_3$
SiMe$_3$
D
HSiMe$_3$
DSiMe$_3$
Me$_3$Si Fe(CO)$_3$
Me$_3$Si—Fe(CO)$_3$
Me$_3$SiFe(CO)$_3$
Me$_3$Si
SiMe$_3$
H—Fe(CO)$_3$
H
+
HSiMe$_3$

DISSERTATION ABSTRACTS AND REVIEWS

Dissertation Abstracts

The following titles have appeared:

'Some aspects of organo-iron chemistry' (505);

'Structural studies of metalation products; synthetic, spectroscopic and structural studies of hydrido-mixed metal carbonyl clusters' (506);

'Synthesis, structure and bonding of new types of iron nitrosyl clusters containing tri-, tetra- and penta-coordinated S and/or N atoms' (507);

'Protonation and oxidation reactions of indenyl-iron complexes, I. Structure and reactivity of hexahapto complexes of iron and manganese with fluorenyl anion, II' (508); and

'1. Selective trapping of dienes by benzilideneacetone iron tricarbonyl.
2. Attempted synthesis of the Z,Z,Z,Z-cyclononatetraenyliron tricarbonyl cationic and anionic complexes' (509).

Reviews

The general chemistry of iron (510) and more specific details relating to the syntheses of mononuclear organoiron compounds have been reported (511). The coordination and organometallic chemistry of iron, ruthenium and osmium has been reviewed (512, 513, 514, 515). Aspects of the organometallic chemistry or iron, ruthenium and osmium, with reference to synthesis and reactivity (516), and to metallo-carbenes, -carbynes, ylides, clusters, and metallocarboranes (517), have been discussed. Syntheses of organometallic complexes using metal atoms, and of organic syntheses achieved via transition metal vapours have been reported (518, 519).

Insertion reactions of carbon monoxide have been reviewed (520), and types of thio- and seleno-carbonyl complexes discussed (521, 522). Dinitrogen and hydrido complexes (particularly of ruthenium) have also been described (523, 524).

The reactivity of the NO group in transition metal nitrosyl complexes has been discussed (525). The preparation of π-alkenyl and σ-organometallic compounds has been reported, and a study made of some of their properties (526). Orthometalation reactions and olefin complexes have also been reviewed (527, 528). There have been discussions of cyclobutadiene complexes (529) and of the interaction of iron carbonyls with macrocyclic alkadiynes (530).

Sandwich compounds, and in particular η^6-arene-η^5-cyclopentadienyl iron cations have been reviewed (531, 532). A survey has been made (533) of triple-layered complexes containing B-heterocyclic ligands.

Summaries of the organic reactions of selected π-complexes (534) and of transition metal derivatives in organic syntheses (535, 536) have been published. Reports of homogeneous hydrogenation catalysts in organic synthesis (537) and of transition metal cluster complexes as catalysts particularly with respect to the relationship between homo- and hetero-geneous systems (538) have been compiled.

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