IRON, RUTHENIUM AND OSMIUM

Annual Survey Covering the Year 1975*

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* Iron, ruthenium and osmium, Annual Survey covering the year 1974 see J. Organometal. Chem., Vol. 119(1976) p.261-405. Reprints not available.

METAL CARBONYLS

Simple carbonyls and carbonylate anions

It has been shown[1] that $Fe(CO)_5$ undergoes cathodic reduction in tetrahydrofuran to give $[Fe_2(CO)_8]^{2-}$. From X-ray photoelectron spectroscopic studies[2] of $Fe(CO)_5$ in the gas phase, the binding energies of the C(1s), O(1s) and $Fe(2p_{3/2})$ orbitals have been obtained, and bond enthalpy contributions of coordinated organic ligands and related groups in olefin iron carbonyls have been calculated. A simplified form of quasi-equilibrium theory has been applied[3] to the mass spectrum of $Fe(CO)_5$.

Ion cyclotron resonance spectroscopic studies have been made[4] of $Fe(CO)_5$. In mixtures of $Fe(CO)_5$ with other species (see Table 1), substitution reactions were observed in which CO was replaced by a variety of other σ- and π-bonding ligands. The basicity of $Fe(CO)_5$ in the gas phase was determined by examining

Table 1. ICR Studies of Ion-Molecule Reactions of $Fe(CO)_5$[a]

MeCl: $[Fe(MeCl)(CO)_{n-1}]^+$ (n=1-4)
$[Fe(MeCl)_2(CO)_{n-2}]^+$ (n=3,4)

HCN: $[Fe(HCN)_x(CO)_{n-x}]^+$ (x=1,n=1-5)
(x=2,n=2-4)
(x=3,n=3,4)
$[HFe(CO)_n]^+$ (n=4,5)

AcacH:[c] $[Fe(AcacH)(CO)_{n-2}]^+$ (n=2-5)
$[Fe(AcacH)(CO)_{n-1}]^+$ (n=1,2)
$[Fe(AcacH)_2]^+$

C_2D_4: $[Fe(C_2D_4)_x(CO)_{n-x}]^+$ (x=1,n=1-4)
(x=2,n=2-4)

Anions: $Fe(CO)_5 + F^- \rightarrow [FeF(CO)_3]^-$
$Fe(CO)_5 + OEt^- \rightarrow [Fe(OEt)(CO)_3]^-$

Benzene: $[Fe(CO)_5]^+$, $[Fe(C_6H_6)(CO)_2]^+$,
$[Fe(C_6H_6)_2]^+$

H_2O: $[Fe(H_2O)(CO)_{n-1}]^+$ (n=1-4)
$[Fe(H_2O)_2(CO)_{n-2}]^+$ (n=2-4)
$[Fe(H_2O)_3(CO)_{n-3}]^+$ (n=4)
$[HFe(CO)_n]^+$ (n=4,5)[b]

HCl: $[HFe(CO)_n]^+$ (n=4,5)
(No other products)

Me_2O, NH_3: $[FeL_x(CO)_{n-x}]^+$ (x=1,n=1-5)
(x=2,n=2-5)
(x=3,n=4)
$[HFe(CO)_5]^+$

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[a] order of relative rates of substitution in the primary ions is $[Fe(CO)_3]^+ > [Fe(CO)_2]^+ > [Fe(CO)]^+ > [Fe(CO)_4]^+ > [Fe(CO)_5]^+$;

[b] H^+ is derived from H_3O^+;

[c] AcacH = $CH_3COCH_2COCH_3$.

proton transfer reactions in mixtures with species of known proton affinity. Thus $Fe(CO)_5$ appears to be only slightly less basic than NH_3. From a sequence of positive ion-molecule reactions in $Fe(CO)_5$, evidence was obtained for the species $[Fe(CO)_n]^+$ ($n = 0 \rightarrow 5$), $[Fe_2(CO)_n]^+$ ($n = 4 \rightarrow 8$), $[Fe_3(CO)_n]^+$ ($n = 7 \rightarrow 11$) and $[Fe_4(CO)_n]^+$ (n = 10, 11 or 12). The only negative ion-molecule reaction which was observed was

$$[Fe(CO)_3]^- + Fe(CO)_5 \rightarrow [Fe_2(CO)_6]^- + 2CO ,$$

in agreement with other reports.[5]

Ozone rapidly oxidises[6] $Fe(CO)_5$ giving one mole of CO_2 per mole of complex at low pressure; the remaining CO is recovered quantitatively and the iron is converted to oxide. The catalysis of oxidation of CO by O_3 in the presence of metal carbonyls has been discussed. Treatment of $Fe(CO)_5$ with poly(4-pyridylethylene) (L) at room temperature gave[7] FeL_3, from which $[FeL_2]_n$ and $[FeL]_m$ could be obtained. With poly-1-vinyl-2-pyrrolidinone (L'), $[FeL']_n$ was similarly prepared.[8]

Monomeric species containing Group V donor atoms

Photolysis of $Fe(CO)_5$, or direct reaction of $Fe_2(CO)_9$, with RN=CR'CR'=NR (R'=H, R=Bu^t, $Me_3CCH_2CMe_2$, Me_2CH, C_6H_{11}, p-$MeOC_6H_4$, 2,6-$Me_2C_6H_3$, p-$Me_2NC_6H_4$; R'=Me, R=Ph or o-MeC_6H_4) gave[9] $Fe(CO)_3$(RNCR'CR'NR), 1. Photolysis of $Fe(CO)_5$ in a glassy matrix consisting of 2-methyltetrahydrofuran (L) and isopentane afforded[10] $Fe(CO)_4L$ and $Fe(CO)_3L_2$. The former species contains axial L whereas the latter is a mixture of bis-axial and axial-equatorial isomers. There was some evidence for prephotolytic L...$Fe(CO)_5$ interaction and the formation of mixtures of $Fe(CO)_3L_2$ could explain the complexity of the i.r. spectra of mixtures of $Fe_2(CO)_9$ and amines in THF. It was also noted that photolysis of $Fe(CO)_5$ in hydrocarbon/NEt_3 mixtures gave $Fe(CO)_4NEt_3$.

Treatment of $Fe(CO)_5$ with tertiary phosphines or phosphites (L; PPh_3, $P(p\text{-}MeC_6H_4)_3$, $P(CH_2CH_2CN)_3$, $P(OEt_3)$, $P(OMe)_3$, $P(OPh)_3$, $AsPh_3$ or $SbPh_3$) in the presence of $LiAlH_4$ or $NaBH_4$ in refluxing THF gave[11] high yields of $Fe(CO)_4L$. The mechanism of this reaction is thought to be as follows:

$$Fe(CO)_5 + H^- \rightleftharpoons [HCOFe(CO)_4]^- ; \rightleftharpoons [HFe(CO)_4]^- + CO$$

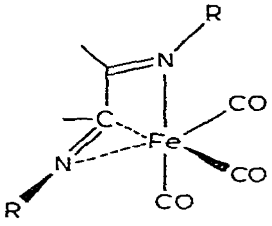
$$[HFe(CO)_4]^- + L \rightleftharpoons [HCOFe(CO)_3L]^- \rightleftharpoons H^- + Fe(CO)_4L \quad .$$

The vibrational spectrum of *trans*-$Fe(CO)_3\{P(OMe)_3\}_2$ has been discussed,[12] and photolysis of $Fe(CO)_5$ with $PBu^t_{3-x}(MMe_3)_x$ (M = Si, Ge or Sn; x = 0-3) afforded[13] $Fe(CO)_4\{PBu^t_{3-x}(MMe_3)_x\}$ (axial phosphine). Reaction of the ferrocenyl ligand L, 2, with iron carbonyls provided $Fe(CO)_4L$. In diglyme, $Fe(CO)_5$ reacted[15] with P_4O_6 giving $Fe(CO)_4P_4O_6$, 3, together with *trans*-$Fe(CO)_3(P_4O_6)_2$ and P_4O_7. Reaction of P_4O_6 with $Fe_2(CO)_9$ under CO, or with $Fe_3(CO)_{12}$, gave $[Fe(CO)_4]_n(P_4O_6)$ (n = 1-4). From a multi-nuclear n.m.r. spectral investigation[16] of $Fe(CO)_3(Me_2PCF_2CH_2PMe_2)$, $Fe(CO)_3(Ph_2PCH_2CH_2CH_2PPh_2)$ and $Fe(CO)_3(diars)$ (diars = o-phenylenebis-dimethylarsine), it has been established that these complexes are fluxional down to −70°C. The diars complex, which has nearly ideal trigonal bipyramidal geometry,[17] is fluxional at −140°C.

Infrared spectral studies have shown[18] that $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$ form adducts with $AlCl_3$. Reaction of $Fe_2(CO)_9$ with $MeSb\{M(CO)_3(\eta\text{-}C_5H_5)\}_2$ (M = Cr, Mo or W) gave[19] $Fe(CO)_4\ MeSb\{M(CO)_3(\eta\text{-}C_5H_5)\}_2$.

Reduction of $Ru(PPh_3)_3Cl_2$ with sodium amalgam or sodium alkoxides under CO gave[20] $Ru(CO)_3(PPh_3)_2$; under CO/H_2 mixtures afforded $Ru(CO)(PPh_3)_2H_2$ while under NO $Ru(NO)_2(PPh_3)_2$ was formed. The complexes $Ru(CO)_4L$ (L = PPh_3, $PMePh_2$ or PBu^n_3) can be prepared[21] conveniently by photolysing $Ru_3(CO)_{12}$ in the presence of an excess of L, or by high pressure carbonylation of *trans*-$Ru(CO)_3L_2$. Unlike the corresponding iron complex, $Ru(CO)_4(PPh_3)$ in the solid state forms $Ru_3(CO)_9(PPh_3)_3$ when heated, while in solution the tetracarbonyl reacts with an excess of L giving *trans*-$Ru(CO)_3L_2$. The mechanism of this latter reaction is probably dissociative, i.e.

$$Ru(CO)_4L \rightleftharpoons [Ru(CO)_3L] + CO;\ + L \rightarrow Ru(CO)_3L_2$$



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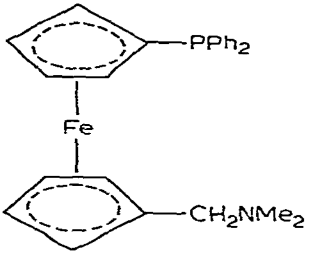

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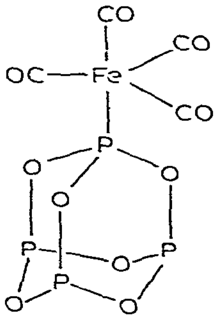

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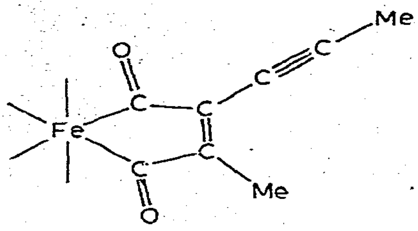
Alkyl, Acyl and Carbene complexes

The structure of $[(Ph_3P)_2N][Fe(CO)_4C_3H_7]$[22] has been determined;[23] the n-propyl group is axial and the Fe–C bond is 2.20Å while the Fe-C(O) distances are 1.75Å. Treatment of $[Fe(CO)_4R]^-$ and $[Fe(CO)_3(NO)]^-$ with $TlNO_3$ gave[24] stable Tl(I) derivatives, viz. $TlFe(CO)_4R$ (R = CH_2CN, COPh, CN, or $SnPh_3$) and $TlFe(CO)_3(NO)$, respectively. The substituted species $TlFe(CO)_3\{P(OC_6H_4Cl)_3\}$-$SnPh_3$, and $TlFe(CO)_2L(NO)$ (L = PPh_3, $P(OC_6H_4Cl)_3$) were also prepared. These species contain a weak Tl–Fe bond which is not extensively dissociated.

Metal-carbon bond strengths for a variety of alkyl and acetyl iron carbonyl complexes have been inferred[25] from an ion cyclotron resonance spectral study of the reaction of $Fe(CO)_5$ with methyl, isopropyl, allyl, t-butyl and



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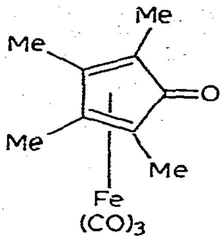

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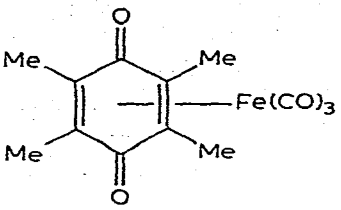

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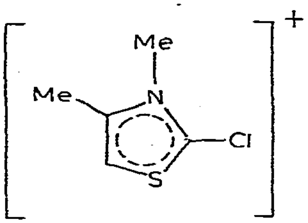
acetylchloride. Limits on several metal ion olefin bond strengths have been inferred from HX elimination reactions. Reaction of $C_3H_7^+$ with $Fe(CO)_5$ gave three products, $[Fe(CO)_5H]^+$ (predominantly), $[Fe(CO)_4C_3H_7]^+$ and $[Fe(CO)_3(C_3H_5)]^+$, while $C_3H_5^+$ gave $[Fe(CO)_5H]^+$ (dominant), $[Fe(CO)_3C_3H_5]^+$ and $[Fe(CO)_2(C_3H_5)]^+$.

Reaction of $Fe(CO)_5$ with $C(NMe_2)_4$ or $CH(NMe_2)_3$ gave[26] salts of $[Fe(CO)_4(CONMe_2)]^-$. UV irradiation of $Fe(CO)_5$ with MeC≡CC≡CMe in THF afforded **4**, whose structure has been determined crystallographically.[27] When the



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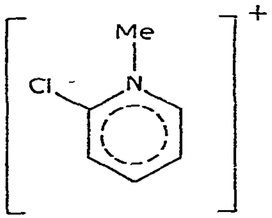

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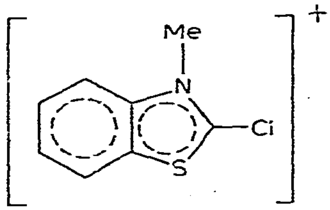

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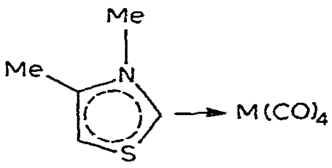

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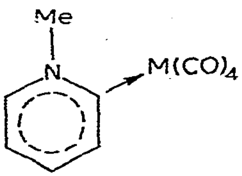

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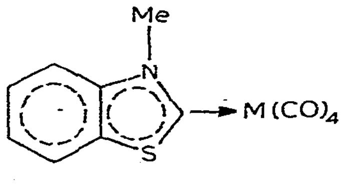

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photolysis is carried out in cyclohexane, the cyclopentadienone complex 5 is probably formed, while irradiation of $Fe(CO)_5$ with MeC≡CMe gave 6.[28]

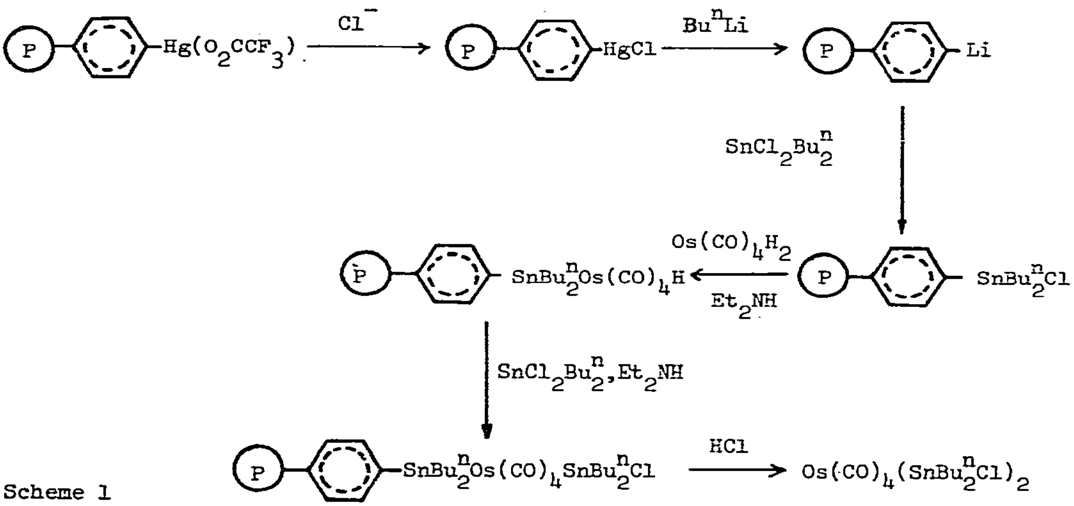
The carbene complex $Fe(CO)_4(CHNMe_2)$ could be prepared[29] from $Na_2Fe(CO)_4$ using either $[Me_2N{=}CH_2]I$ or $[Me_2NCHSMe]Br$; the latter also afforded low yields of $[Fe(CO)_3SMe]_2$. Treatment of $Fe_2(CO)_9$ with $[Me_2NC(Cl){=}NMe_2]Cl$ gave[30] $Fe(CO)_4\{C(NMe_2)_2\}$.

The salts 7, 8 and 9 reacted with $Na_2M(CO)_4$ (M = Fe or Os) giving[31] the carbene complexes 10, 11 and 12. It was suggested that the carbene ligand occupied an equatorial position in these species. Treatment of 10 with PPh_3 afforded $M(CO)_3(PPh_3)L$ (L = carbene ligand), and protonation of 10 or 12 (M = Os) afforded $[Os(CO)_4LH]^+$ (L = carbene ligand); deprotonation could be achieved using Et_3N. The methyl cations $[Os(CO)_4LMe]^+$ were prepared by reacting 10 and 12 with $[Me_3O][BF_4]$.

Complexes with Group IV ligands

Complete vibrational spectrum assignments and valence force field calculations have been made[32] of $[Fe(CO)_4SiCl_3]^-$ and $Fe(CO)_4H(SiCl_3)$. Treatment of $[Et_4N][HFe_3(CO)_{11}]$ with $LiGePh_3$ gave[33] $[Et_4N][Fe(CO)_4GePh_3]$, and the already known Si and Sn analogs could be prepared similarly. Protonation of the germyl complex afforded the air-sensitive and unstable cis-$Fe(CO)_4$-$H(GePh_3)$.

The ^{119}Sn n.m.r. double resonance spectra of $Fe(CO)_4(SnMe_3)_2$ and $[Fe(CO)_4(SnMe_2)]_2$ have been determined,[34] and the data have been interpreted in terms of a large paramagnetic contribution to the chemical shift arising from small average excitation energies associated with $d_\pi - d_\pi$ bonding. An unusual solid-phase synthesis of $Os(CO)_4(SnClBu^n_2)_2$ has been developed,[35] and is shown in Scheme 1.



Scheme 1

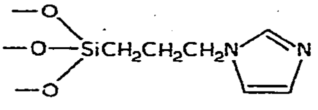
This synthetic scheme can be further extended by two steps to give $Bu_2^nSn[Os(CO)_4SnBu_2^nCl]_2$.

Metal complexes of macrocyclic nitrogen ligands

In dichloromethane at low temperature, Fe(TPP)L_2 (TPP = mesotetraphenylporphyrinate, L = pyridine, piperidine or 1-methylimidazole) reacts[36] with CO by a dissociative process:

$$Fe(TPP)L_2 \rightleftharpoons Fe(TPP)L + L; \quad Fe(TPP)L + CO \rightleftharpoons Fe(CO)(TPP)L$$

It was suggested that this system might serve as a satisfactory model for natural CO-carrying systems. Indeed Fe(TPP)L(O_2) reacts in a 1st order process readily with CO to give the thermodynamically more stable Fe(CO)(TPP)L. Imidazole attached to silica gel, 13, has been used[37] to bind Fe(TPP), and the polymer-bound complex readily formed an adduct with CO. The effect of extraplanar ligands on the redox properties and site of oxidation of Fe, Ru and Os porphyrin complexes has been investigated;[38] some potential data are given in Table 2. The electrochemical properties of Os(OEP)(CO)(pyr) are similar to those of Ru(OEP)(CO)(THF),[39] and consist of a chemically and voltammetrically reversible oxidation to a monocation, followed by an irreversible oxidation to a dication. These electron transfer reactions are remarkable in that they



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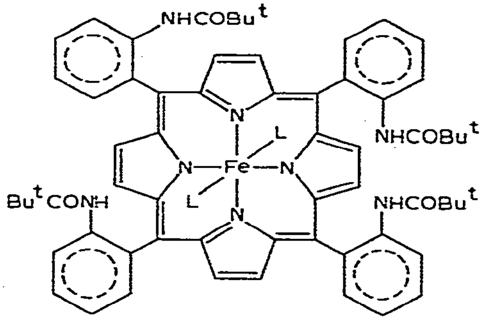

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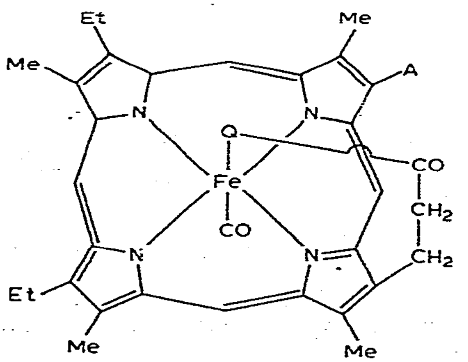


(15a) A = H;

Q = —$NHCH_2CH_2CH_2N$ 

(15b) A = $CH_2CH_2CO_2Me$;

Q as in (a)

(15c) A = $CH_2CH_2CONHCH_2CH_2CH_2N$ 

Q as in (a)

are associated with two distinct "oxidation sites": the first process corresponds to the oxidation of the metal, and the second to the removal of an electron from the porphyrin ligand. The species $\mathrm{Fe(etio.1)(CO)(Im)}$, generated by exhaustive controlled potential reduction of CO-saturated solutions containing $\mathrm{Fe(etio.1)Cl}$ and an excess of imidazole, was oxidised (irreversibly) at a potential nearly 0.6 V more positive (vs. SCE) than the corresponding $\mathrm{Fe(etio.1)(Im)_2}$. This reflects the π-acceptor property of CO and its relative ability to stabilise Fe(II).

Reaction of $\mathrm{Ru_3(CO)_{12}}$ with octaethylporphyrin ($\mathrm{H_2OEP}$) gave, in THF or ethanol-benzene mixtures, $\mathrm{Ru(OEP)(CO)(L)}$ (L = THF or EtOH). Similar tetraarylporphyrin complexes (containing as ligand substituents $\mathrm{C_6H_5}$, p-$\mathrm{CF_3C_6H_4}$ and p-$\mathrm{Pr^iC_6H_4}$) were also isolated, and contained L = THF, EtOH or 4-t-butylpyridine. Treatment of these complexes with CO gave *trans*-$\mathrm{Ru(CO)_2(OEP)}$ etc. but these lost CO on standing or on grinding. Treatment of the dicarbonyl with 4-t-butylpyridine (L) gave $\mathrm{Ru(OEP)(CO)L}$ and it was observed that the strength of binding of the second CO group increased as a function of porphyrin substituent, in the order $\mathrm{CF_3C_6H_4} < \mathrm{Pr^iC_6H_4} < \mathrm{Ph} \ll \mathrm{Et}$. These data were consistent with observations made of Fe(porphyrin)(CO)(piperidine).[41] Treatment of $\mathrm{[Ru(OEP)]_2}$ with CO and suitable ligands (L = pyridine, DMSO) gave[42] $\mathrm{Ru(OEP)(CO)L}$, also obtained from $\mathrm{Ru(OEP)(pyr)_2}$ and CO. The dimeric species was produced by heating the bis-pyridine adduct at 220°C.

Iron(II) porphyrin complexes, which may act as models for the active site of myoglobin and oxymyoglobin, have been synthesised[43] and characterised by a variety of spectroscopic techniques. The "picket fence" porphyrin, 14, has great steric bulk and creates a non-protic cavity on one side of the

Table 2 Redox Properties of Some Porphyrin Complexes of Fe, Ru and Os

Couple[a]	$E_{\frac{1}{2}}$(V)[b]
$\mathrm{[Ru^{III}(etio.1)(CO)(THF)]^+/[Ru^{II}(etio.1)(CO)(THF)]}$	>0.64
$\mathrm{[Ru^{II}(etio.1^+)(CO)(THF)]^+/[Ru^{II}(etio.1)(CO)(THF)]}$	0.64
$\mathrm{[Ru^{II}(OEP^+)(CO)(THF)]^+/[Ru^{II}(OEP)(CO)(THF)]}$	0.61
$\mathrm{[Os^{III}(OEP)(pyr)_2]^+/[Os^{II}(OEP)(pyr)_2]}$	0.48
$\mathrm{[Fe(etio.1)(CO)(Im)]^+/[Fe(etio.1)(CO)(Im)]}$	0.32[c]
$\mathrm{[Ru^{III}(OEP)(pyr)_2]^+/[Ru^{II}(OEP)(pyr)_2]}$	0.08
$\mathrm{[Fe^{III}(etio.1)(Im)_2]^+/[Fe^{II}(etio.1)(Im)_2]}$	-0.52

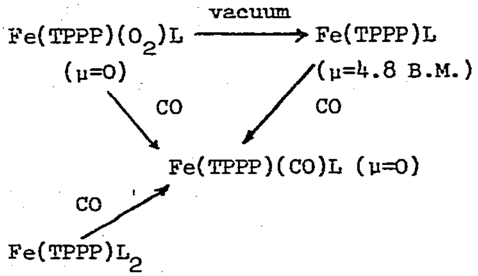
[a] etio.1= etioporphyrinate 1; OEP = octaethylporphyrinate; Im = imidazole;

[b] volts vs. saturated NaCl calomel electrode;

[c] Ep (cyclic voltammetry) only.

molecule. The complex, as its oxygen and/or methylimidazole or THF adduct, reacts with CO giving diamagnetic CO adducts (Scheme 2). The CO stretching frequencies of these complexes are similar to those of CO adducts of haemoglobin,[44] and preliminary X-ray structural data indicate that the Fe-C-O bond is linear, in disagreement with previous suggestions that the bond angle is significantly less than 180°. Other models for the active site of myoglobin,

Scheme 2



TPPP = *meso*-tetra(α,α,α,α-O-pivalamidophenyl)porphyrinate
L = THF or 1-alkylimidazole (alkyl = Me or Bu^n).

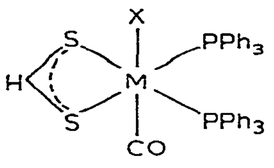
e.g. 15, have been investigated. At low pH values, the bases in 15a,b and c, readily displace CO but 15d binds CO more strongly than 15e, whereas the differences between binding energies in 15b and 15c are very small. Mixtures of FeP, CO and NaSMe (P = "picket-fence" porphyrin or proto-porphyrin IX diethylester) afford[46] an adduct which has a Soret band at 449 nm very similar to that in cytochrome P450. This model system suggests that there is an axial SMe group.

Dithioformate Complexes, Fixation of CO_2 by Phosphine Complexes, Dithiocarbamate and Dithiolene Compounds

The complexes $M(CO)(PPh_3)_3HX$ (M = Ru, Os; X = Cl, Br), $M(CO)(PPh_3)_2$-$H(OCOCF_3)$ (M = Ru or Os), $Ru(PPh_3)_4H_2$ and $Os(PPh_3)_3H_4$ react[47] with CS_2 in boiling benzene to give $M(CO)(PPh_3)_2X(S_2CH)$ (two isomers, 16a and 16b), $M(CO)(PPh_3)_2(OCOCF_3)(S_2CH)$ (structures similar to 16), and $M(PPh_3)_2(S_2CH)_2$, 17; 16a could be converted on heating to 16b. Treatment of $Ru(PPh_3)_4H_2$, $Ru(PPh_3)_3(N_2)H_2$ and $Ru(PPh_3)_3H_4$ with CO_2 gave[48] $Ru(PPh_3)_3H(O_2CH)$. Treatment of this formate with CO, CS_2, MeI or H_2SO_4 resulted in elimination of CO_2. However, $Fe(diphos)_2H_2$ or $Ru(PPh_3)_4H_2$ reacted[49] with CO_2 and H_2 in the presence of ethanol and Et_3N to give low yields of ethylformate.

Treatment of $M(PPh_3)_3H(OCOMe)$ or $Ru(PPh_3)_4H_2$ with NaS_2CNR_2 or NaS_2COR afforded[50] the six-coordinate complexes analogous to 17.[55] However, similar reactions involving $M(CO)(PPh_3)_2Cl(OCOMe)$ gave $M(CO)(PPh_3)(S_2CNR_2)_2$, 18

(M = Ru or Os), also produced by treating $Ru(CO)(PPh_3)_2HX$ (X = H or Cl) with $\{Me_2NCS_2\}_2$. $Os(CO)(PPh_3)_2Cl(OCOCF_3)$ also reacted with NaS_2CNEt_2 giving $Os(CO)(PPh_3)_2Cl(S_2CNEt_2)$, 19 (X = Cl). Reaction of $M(CO)(PPh_3)_3HCl$ with NaS_2CNR_2 or NaS_2COR gave $M(CO)(PPh_3)_2H(S_2CQ)$ (Q = OR or NR_2), analogous to 19 (X = H).



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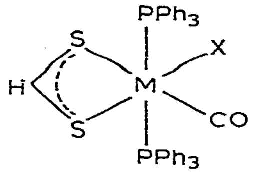

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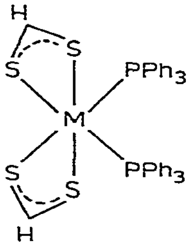

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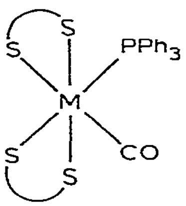

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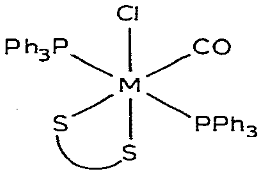

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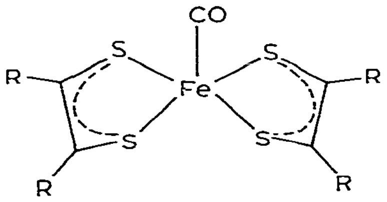


(20)

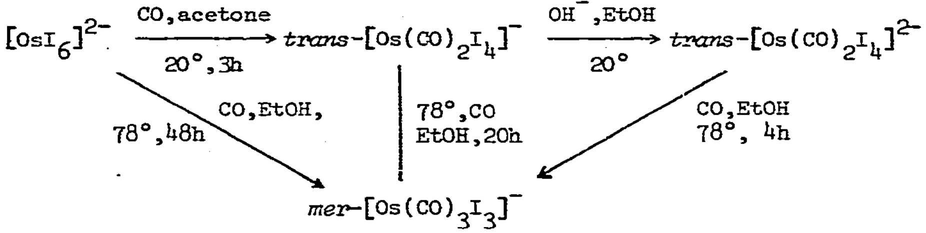
Evaporation of dichloromethane solutions of $[Fe\{S_2C_2(CF_3)_2\}_2]_2$ under CO gave[57] blue $Fe(CO)\{S_2C_2(CF_3)_2\}_2$, 20. This complex readily loses CO on heating or treatment with N_2H_4 and is structurally similar to $Fe(AsPh_3)\{S_2C_2(CF_3)_2\}_2$.[52] Its treatment with PR_3 gave $Fe(PR_3)_2\{S_2C_2(CF_3)_2\}_2$. It was also noted that $[(\eta\text{-}C_5H_5)Fe(CO)]_4$ reacted with $(CF_3)_2C_2S_2$ giving $(\eta\text{-}C_5H_5)Fe\{S_2C_2(CF_3)_2\}$, which has been reported earlier.[53] This complex could be reduced polarographically to a monoanion.

Hydrides and Halide Complexes

Assignments of the Raman spectra of $M(CO)_4H_2$ (M = Fe, Ru or Os) have been made,[54] and are consistent with a *cis* geometry. Photoelectron spectral measurements have been made of *cis*-$Fe(CO)_4X_2$ (X = Br or I), and some assignments were attempted. Brief mention has been made[56] of the electrochemical oxidation of $Fe(CO)_4Br_2$. An irreversible electron transfer occurred at a potential more positive than the oxidation of $Mn(CO)_5Br$.

Carbonylation by CO at normal pressure of $[OsX_6]^{2-}$ afforded[57] *trans*-$[Os(CO)_2X_4]^-$ (X = Br or I), which was reduced by ethanolic alkali to *trans*-$[Os(CO)_2X_4]^{2-}$. The reactions of $[OsI_6]^{2-}$ with CO are shown in Scheme 3. *trans*-$[Os(CO)_2Br_4]^-$ reacted with HBr giving $[Os(CO)Br_5]^{2-}$ and the former could be regenerated from the latter under CO:

Scheme 3



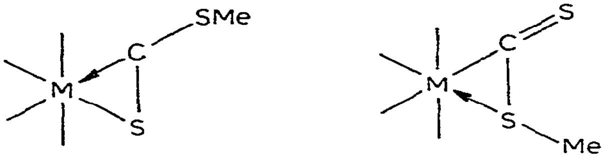
Trans-$[Os(CO)_2X_4]^-$ could be isomerised to the *cis*-isomer on heating. The *cis*-dianions, $[Os(CO)_2X_4]^{2-}$ (X = Cl, Br, or I) were also prepared[58] by heating $[OsX_6]^{2-}$ with various unsaturated alcohols.

Metal(II) phosphine complexes

Carbon disulphide reacted[59] with $Ru(CO)_2(PPh_3)_3$ giving the known $Ru(CO)(PPh_3)_2(CS_2)$,[60] and the related osmium complex was obtained from $Os(CO)_2(C_2H_4)(PPh_3)_2$. Treatment of these CS_2 adducts with MeCl or MeI afforded $[M(CO)_2(PPh_3)_2(CS_2Me)]^+$ with possible structures shown in figure 1. Reaction of $[Ru(CO)_2(PPh_3)_2(CS_2Me)]^+$ with X^- (halide) gave $Ru(CO)(PPh_3)_2X(CS_2Me)$, but the Os complex was inert. Treatment of $[M(CO)(PPh_3)_2(CS_2Me)]^+$ with aqueous HCl in ethanol gave $M(CO)(CS)(PPh_3)_2Cl_2$ and MeSH, and $Os(CO)_2(PPh_3)_2(CS_2)$ reacted with HCl to give the same dichloride and H_2S. Treatment of $Ru(CO)_2(PPh_3)_2$ with CSe_2 afforded[61] $Ru(CO)_2(PPh_3)_2(CSe_2)$ which reacted in the same way as its CS_2 analogue. Thus, $Ru(CO)(PPh_3)_2X(CSe_2Me)$ (X = Cl or Br) and $Ru(CO)(CSe)(PPh_3)_2X_2$ (X = Cl or Br) were prepared. Chromatography of impure $Ru(CO)(CSe)(PPh_3)_2I_2$ on alumina afforded $Ru(CO)(CSe)(PPh_3)_2I(OH)$. The structure of $Ru(CO)(CSe)(PPh_3)_2Cl_2$, 21, was determined crystallographically. The Ru-Cl distances (2.43Å *trans* to CO and 2.48Å *trans* to CSe) are both long in relation to those in comparable complexes (2.29-2.39Å) and it is clear that CSe (C-Se 1.67Å) has a relatively strong *trans*-influence.

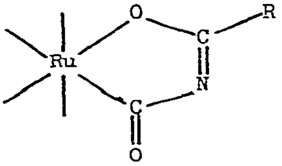
Reaction of $Ru(CO)_3(PPh_3)_2$ with RN_3 (p = p-$MeC_6H_4SO_2$, p-MeC_6H_4CO, PhCO or 2-carbonylfuran) gave[62] $Ru(CO)_2(PPh_3)_2(RNCO)$ (all R except 2-carbonylfuran),

Figure 1



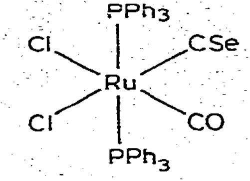
ureas, $Ru(CO)_2(PPh_3)_2(RNCONR)$ ($R = p\text{-}MeC_6H_4SO_2$), and amides. Under certain conditions the bis-amido complex $Ru(CO)_2(PPh_3)_2(NHCOR)_2$ (R = 2-furyl) could be obtained. The complex $Ru(CO)_2(PPh_3)_2(RNCONR)$ ($R = p\text{-}MeC_6H_4SO_2$) could also be prepared via oxidative addition of $(RNH)_2CO$ or RNCO to $Ru(CO)_3(PPh_3)_2$. The complexes containing coordinated RNCO ($R = p\text{-}MeC_6H_4CO$ or PhCO) probably contain the chelate ring shown in figure 2. Their treatment with HBF_4 afforded

Figure 2



$[Ru(CO)_2(PPh_3)_2(CONHR)][BF_4]$ which, on addition of LiCl, gave $[Ru(CO)(PPh_3)_2(CONHR)Cl]_n$. However, reaction of the species with $R = p\text{-}MeC_6H_4SO_2$ with mineral acids gave only p-toluenesulfonamide, while HCl reacted to give $Ru(CO)_2(PPh_3)_2Cl_2$. The isocyanate complexes reacted only slowly with ethanol (but faster under CO) causing displacement of the organonitrogen ligand and formation of $Ru(CO)_3(PPh_3)_2$. Protonation of $Ru(CO)_2(PPh_3)_2(NHR)_2$ (R = 2-carbonylfuran) with HBF_4 gave $[Ru(CO)_2(PPh_3)_2(NH_2R)_2][BF_4]_2$.

Trifluoroacetic acid reacts with $Ru(CO)(PPh_3)_3HCl$ giving[63] $Ru(CO)(PPh_3)_2Cl(\eta^2\text{-}O_2COF_3)$, 22. Molecular weight determinations of this compound suggest that it exists in an equilibrium with the dimer 23. Similar treatment of $Os(CO)(PPh_3)_3HCl$ gave $Os(CO)(PPh_3)_3Cl(\eta^1\text{-}OCOR)$ ($R = CF_3$ or C_2F_5), probably of structure 24a, although 24b and 24c are also possibilities. Reaction of $Os(CO)(PPh_3)_3H_2$ with RCO_2H afforded $Os(CO)(PPh_3)_3H(\eta^1\text{-}OCOR)$ ($R = CF_3$ or C_2F_5), 25 while $M(CO)(PPh_3)_3H_2$, under different conditions, afforded $M(CO)(PPh_3)_2(OCOR)_2$ ($R = CF_3$, C_2F_5 or C_6F_5). These bis-carboxylates contain one mono- and one bi-dentate carboxylato ligand. It was observed that the tendencies of the carboxylate ligand to be displaced by alcohol was controlled more by the nature of the *trans* group than by the basicity of PPh_3. Thus, monodentate carboxylate was susceptible to alcoholysis when *trans* to good σ-donors, but inert to solvolysis when *trans* to poor σ-donors, e.g. CO or RCO_2^-. These solvolysis studies have helped to establish a *fac* geometry of the $M(CO)(PPh_3)_2$ group in these bis-carboxylates, and variable temperature ^{19}F n.m.r. spectral



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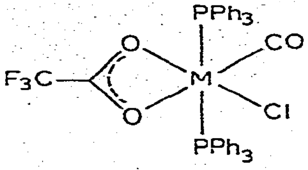

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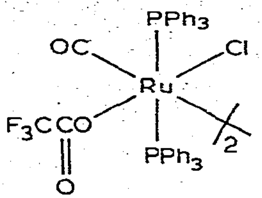

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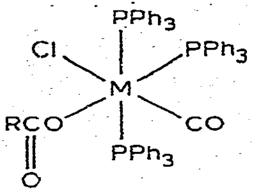

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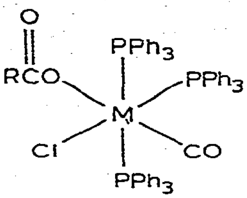

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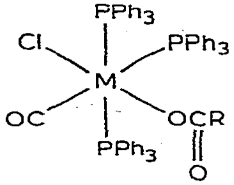


(24c)

studies reveal that there is rapid interchange of mono- and bi-dentate carboxylate ligands. Treatment of $Os(CO)_2(PPh_3)_2H_2$ with RCO_2H gave $Os(CO)_2(PPh_3)_2H(OCOR)$ ($R = CF_3$ or C_2F_5), <u>26</u>, which, on further treatment with acid, afforded $Os(CO)_2(PPh_3)_2(OCOR)_2$, probably <u>27</u>. These dicarboxylates could be similarly directly prepared, together with their Ru analogue, under more vigorous conditions from $Os(CO)_2(PPh_3)_2H_2$ or $Ru(CO)_3(PPh_3)_2$. It was noted that conversion of $Os(CO)_2(PPh_3)H_2$to $Os(CO)_2(PPh_3)_2H(OCOR)$ and then to $Os(CO)_2(PPh_3)_2$-$(OCOR)_2$ involved a *cis* → *trans-cis* rearrangement of the carbonyl ligands. It was suggested that these rearrangements probably involved stereochemically non-rigid seven-coordinate osmium(IV) intermediates, perhaps formed by protonation of the Os(II) precursors in the presence of RCO_2H (see Scheme <u>4</u>).

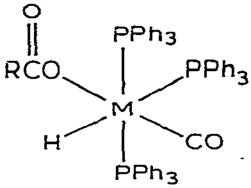
<u>Scheme 4</u>

$$\begin{tikzcd}
Os(CO)_2(PPh_3)_2H_2 \arrow[r, "RCO_2H"] & {[Os(CO)_2(PPh_3)_2H_3][OCOR]} \arrow[r, "-H_2"] & Os(CO)_2(PPh_3)_2H(OCOR) \arrow[d, "RCO_2H"] \\
& Os(CO)_2(PPh_3)_2(OCOR)_2 & {[Os(CO)_2(PPh_3)_2H_2(OCOR)][OCOR]} \arrow[l, "-H_2"']
\end{tikzcd}$$

Finally, it was found that $Ru(PPh_3)_4H_2$ and $Os(PPh_3)_3H_4$ reacted with CF_3CO_2H in boiling alcohol giving $M(PPh_3)_3H(OCOCF_3)_3$ <u>28</u>, while $C_2F_5CO_2H$ afforded with $Os(PPh_3)_3H_4$, in boiling 2-methoxyethanol, $Os(CO)(PPh_3)_3H(OCOC_2F_5)$.

Treatment of $Ru(CO)_3(PPh_3)_2$ with tetrachloro- or tetrabromo-o-quinone gave[64] $Ru(CO)_2(PPh_3)_2(O_2C_6X_4)$, <u>29</u>. These species could be oxidised voltammetrically to mono- and di-cations, and spectroscopic data was obtained from $[Ru(CO)_2(PPh_3)_2(O_2C_6X_4)]^+$.

A series of ruthenium(II) carbonyl phosphine complexes containing phenyl and anisyl arsonic acids viz. $Ru(CO)_2L_2(O_3AsAr)$ ($L = PPh_3$, $AsPh_3$, $P(p\text{-}MeC_6H_4)_3$, $As(p\text{-}MeC_6H_4)_3$; $Ar = C_6H_5$ or $p\text{-}MeOC_6H_4$) and $Ru(CO)_2L_2\{O_5As_2Ar_2\}$, have been reported.[65] They are alleged to contain seven- and eight-coordinate Ru(II), i.e. 30 and 31.



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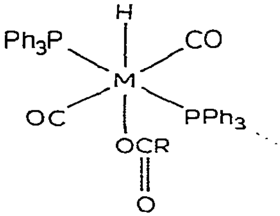

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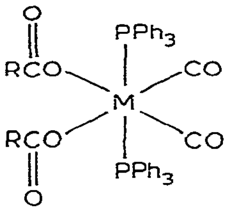

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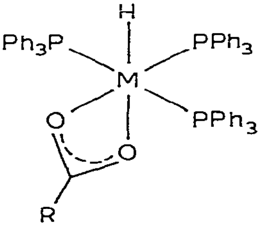

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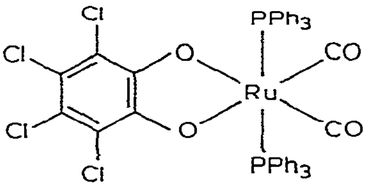

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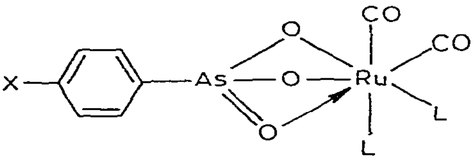

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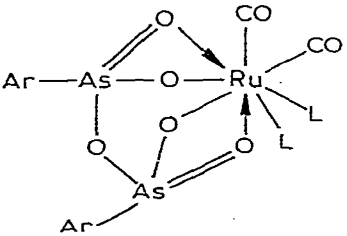

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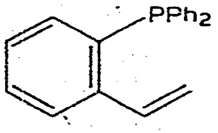

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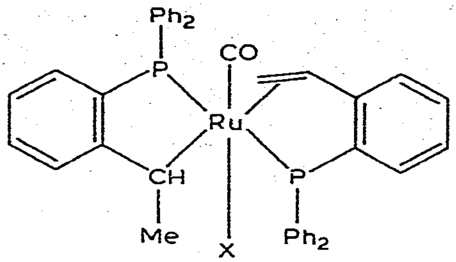
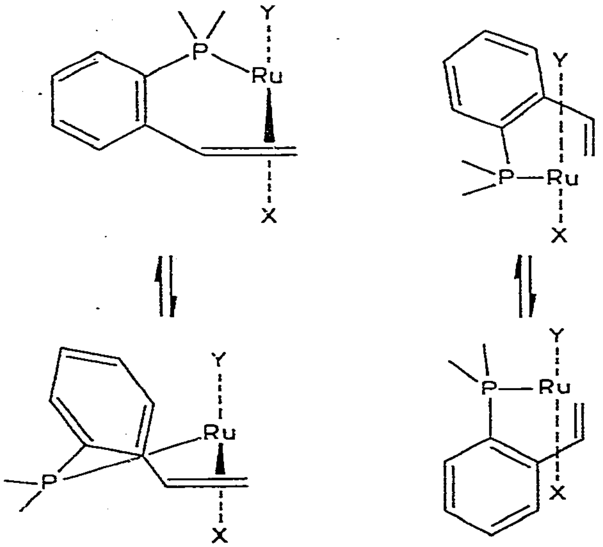


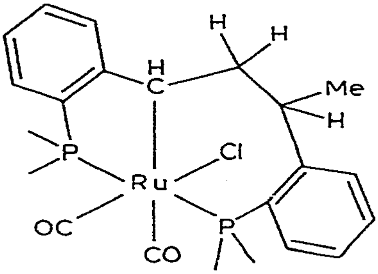
(33)

By boiling the o-styryldiphenylphosphine (SP, <u>32</u>) complex Ru(CO)$_2$(SP)$_2$Cl$_2$ in 2-methoxyethane the C-metalated complex <u>33</u> (Q = Cl) was obtained.[66] Treatment of this with Ag$^+$ under CO gave [Ru(CO)$_2$(o-MeCHC$_6$H$_4$PPh$_2$)(SP)]$^+$, <u>33</u> (Q = CO). Each of these compounds exists in solution in an equilibrium involving two isomers, and the mechanism of interconversion may be explained in terms of an intramolecular reorientation of the coordinated vinyl group in the two possible sets of isomers as shown in figure 3. This mechanism would involve cleavage of the metal olefin bond, thereby allowing bonding to either "face" of the olefin.

<u>Figure 3</u>



Two other complexes were isolated from the same reaction which gave <u>33</u>. The first, <u>34</u>, could also be obtained by refluxing <u>33</u> (Q = Cl) under CO in 2-methoxyethanol, or by heating Ru(CO)$_3${o-MeCHC$_6$H$_4$PPh$_2$}Cl, obtained by treating Ru(CO)$_3$SP with HCl, with an excess of SP in the same solvent. Carbonylation of



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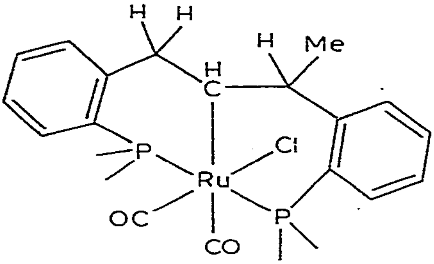

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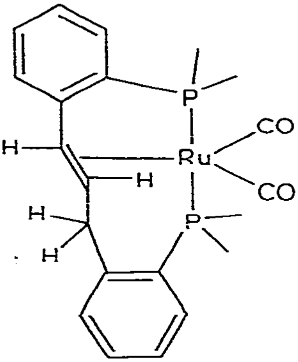

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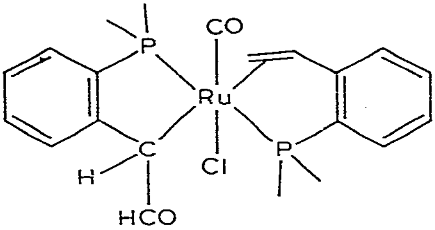

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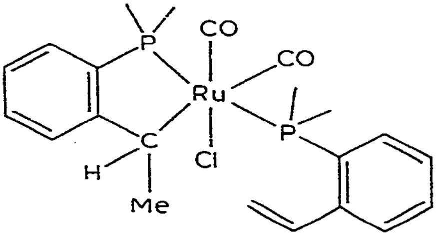

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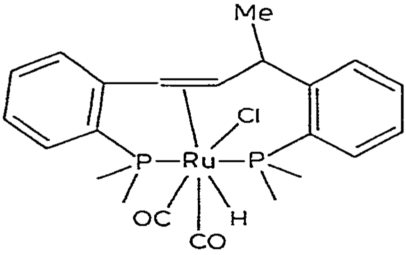
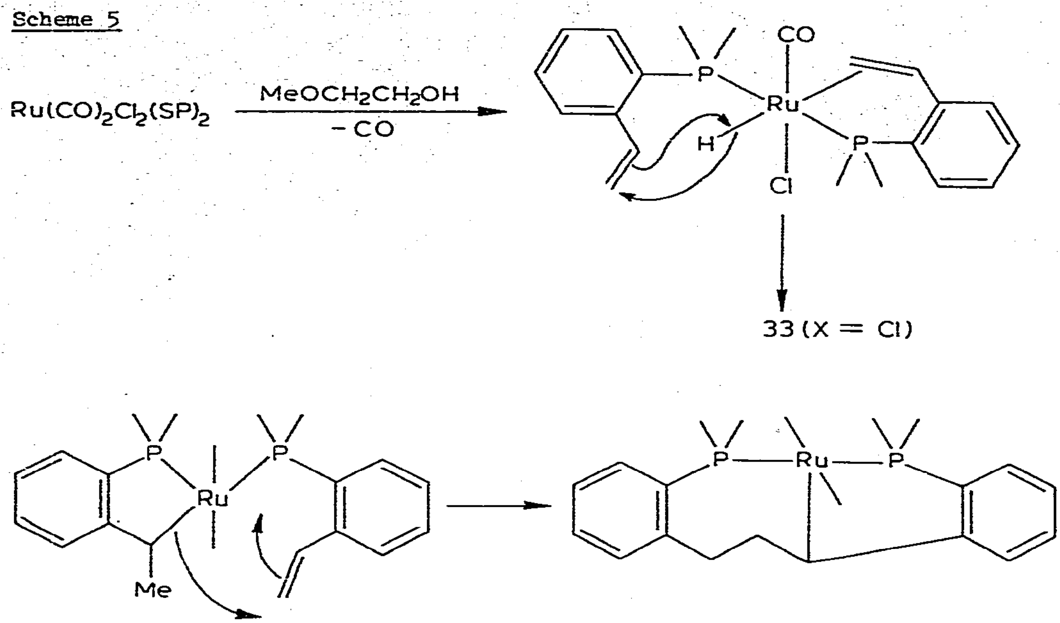


(39)

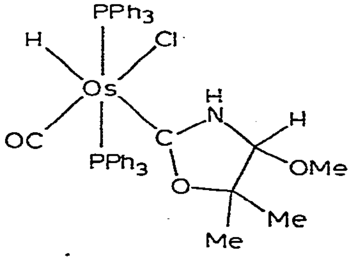
33 also afforded an isomer of 34, namely 35 which was prepared independently via 1,3-bis{o-(diphenylphosphino)phenyl}-trans-1-butene, Q. Q reacted with $Ru_3(CO)_{12}$ to give 36, and treatment of this with HCl gave 35. The second additional compound isolated from the original reaction which afforded 33 was identified crystallographically as 37. A plausible reaction route which results in the conversion of $Ru(CO)_2(SP)_2Cl_2$ into 33 (Q = Cl) and 34 is outlined in Scheme 5.

Scheme 5



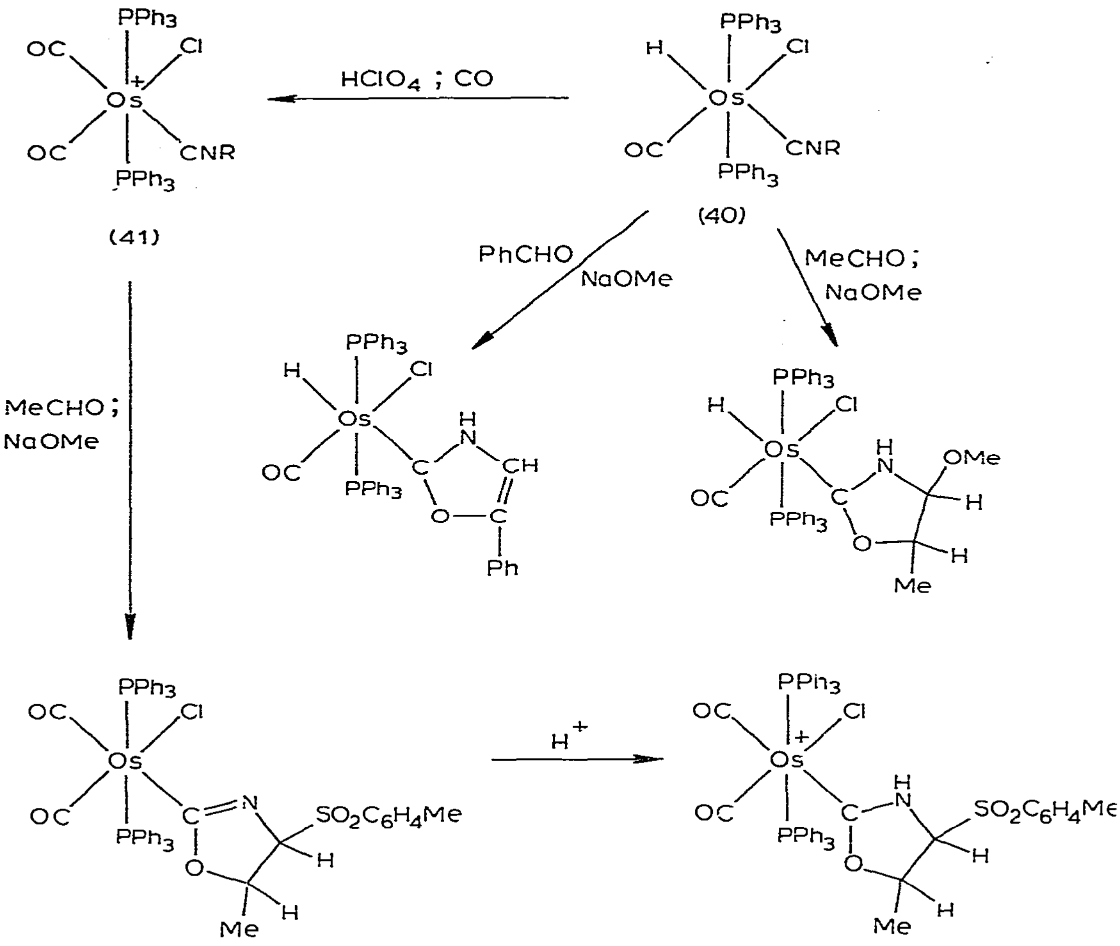
There was no convincing method of explaining the formation of 35 or why 2-methoxyethane is necessary for its production. It was expected that the formation of 33 and 35 might proceed via a common intermediate, e.g. 38, and the isomerisation of 35 to 34 might occur via 39. The origin of 37 is unknown but arises possibly via a π-bonded formyl or acyl complex. When 33 is heated at 100° in 2-methoxyethanol in a sealed tube, 34 and $Ru(CO)_2(o\text{-}Ph_2PC_6H_4Et)_2Cl_2$ was formed, the latter by hydrogenation of the vinyl groups in SP.

Treatment of $Os(CO)(PPh_3)_3HCl$ with $p\text{-}MeC_6H_4SO_2CH_2NC$ (Q) afforded[67] $Os(CO)(PPh_3)_2(Q)HCl$, 40. Reaction of this with $HClO_4$ and CO gave $[Os(CO)_2(PPh_3)_2QCl]^+$, 41. In the presence of acetaldehyde or benzaldehyde and sodium methoxide, 40 and 41 afforded a series of carbene complexes isolated as in Scheme 6. Treatment of 40 with acetone gave 42 in a relatively slow reaction.

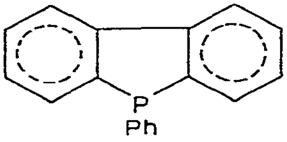


(42)

Scheme 6



Dipole moment studies, X-ray photoelectron spectroscopy and electrochemical measurements have been used[68] to evaluate the electronic charge distribution in certain complexes, including *mer-cis*-$Ru(CO)(PEt_2Ph)_3Cl_2$, *cis-trans-cis*-$Os(CO)_2(PEt_2Ph)_2Cl_2$ and *mer-trans*-$Ru(NO)(PEt_3)_2Cl_3$. The data are consistent with PR_3 and Cl^- being good electron donors, and CO and NO being powerfully electron withdrawing. Ruthenium(II) carbonyl chloride complexes containing the phospholes 43 and 44, have been described.[69]



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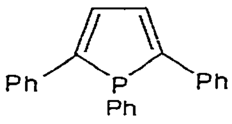


(44)

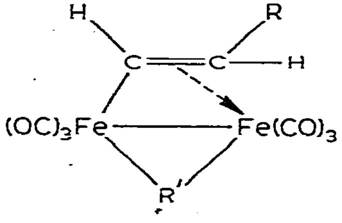
Bimetallic Species

In dry deoxygenated THF, $Fe(CO)_5$ reacts with KC_8 giving[70] $K_2Fe_2(CO)_8$ together with CO and carbon. A fresh study of the Fe-Fe bond vibrations in $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ has been made by laser Raman spectroscopy.[71]

Photolysis of $Fe(CO)_4L$ (L = *cis*- or *trans*-CHBr=CHBr, *cis*-CHB=CHF and *cis*- or *trans*-CHCl=CHCl) resulted[72] in the elimination of L and CO. The species $Fe(CO)_3L$ underwent intramolecular insertion of Fe into a C-halogen bond followed by CO addition and reaction with $Fe(CO)_4$ giving 45 (R,R' = Br,Br; F,Br; Cl,Cl). *Trans*-1,2-dihalogenoethylenes also reacted[73] with $Fe_2(CO)_9$ giving 45. Alcoholysis of 45 (R,R' = Br,Br) afforded CH_2=CH(CO_2R) R = Me or Et), $Fe(CO)_4\{\eta^2\text{-}CH_2=CH(CO_2R)\}$, $Fe_3(CO)_{10}(C_2H_2)$, which may have the structure 46a or 46b. and 45 (R = CO_2Me, R' = Br). In concentrated acetic acid 45 (R,R' = Br,Br) gave 47 and 48 (R=OH) and 48 (R=OH) was also produced on thermolysis of 45 (R,R' = Br,Br). Exchange of the bridging bromide in 45 (R,R' = Br,Br) with iodide afforded (reversibly) 45 (R = Br, R' = I).

Reaction of $Fe_3(CO)_{12}$ with 1,4,7,10-tetraphenyl-1,2,3,7,8,9-cyclododecahexaene has afforded[74] $Fe_2(CO)_6$ and $Fe_2(CO)_8$ complexes. The structure of $Fe_2(CO)_6C_4Ph_4$, 48 (R=Ph), the product of a reaction between $Fe(C_7H_8)(CO)_3$ and PhC≡CPh, has been determined crystallographically;[75] the Fe-Fe distance is 2.15Å. Treatment of the ferrole complex 48 (R=OH) with $CF_3C≡CCF_3$ afforded[76] 48 (R=OC(CF_3):CHCF

The ^{13}C n.m.r. spectrum of $Fe_2(CO)_7(C_2Ph_2)_2$, 49, at -40° in solution[77]



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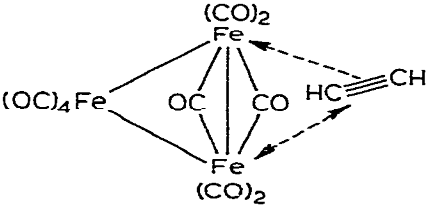

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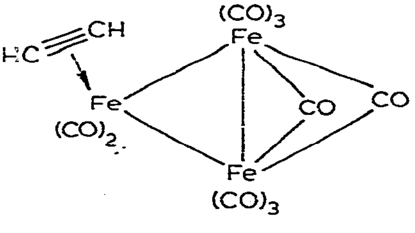

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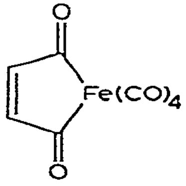

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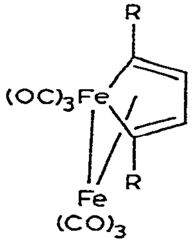

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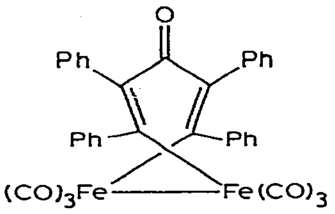
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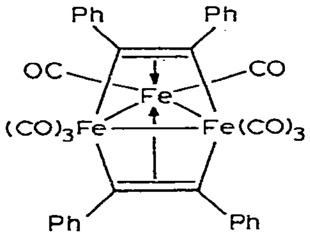
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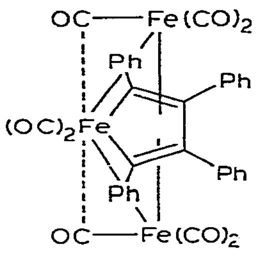
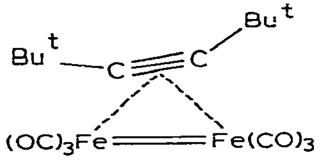

(51)

is consistent with its known structure,[78] but although the three CO group resonances coalesced and the dienone fragment exhibited fluxionality as the temperature rose to +41°, the mechanisms of these processes could not be unravelled. The ^{13}C n.m.r. spectral study of the violet isomer of $Fe_3(CO)_8$–$(C_2Ph_2)_2$, 50[79] has established that the complex is stereochemically rigid, but over the range −62° to +96°, the green isomer, 51,[79] underwent scrambling of terminal and bridging CO groups. In this process, the bridging CO groups appear to be preferentially moving towards those Fe atoms with which they have shortest Fe–C distances, as indicated in the structure of 51.

From the reaction between $Fe_2(CO)_9$ and a commercial sample of $Bu^tC{\equiv}CBu^t$, two complexes have been isolated and studied crystallographically. The first, 52, has a short Fe-Fe bond (2.32Å), regarded as being consistent with bond order 2, and a long C-C distance (1.32Å). This compound is reported as being identical to a species suggested to be $Fe_2(CO)_7(C_2Bu^t_2)$.[81] Other compounds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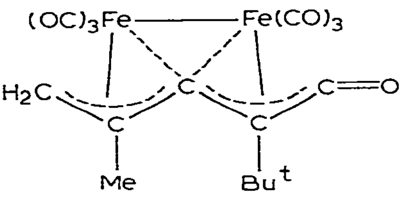
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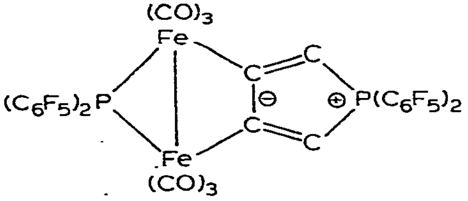
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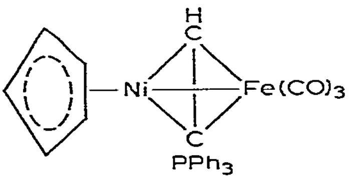
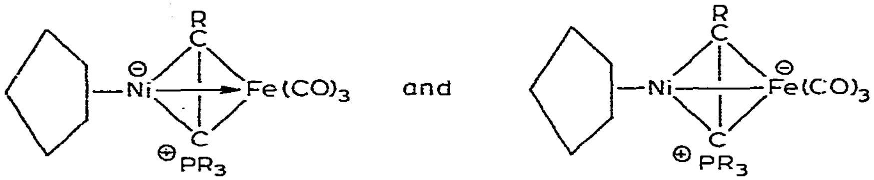

(55)

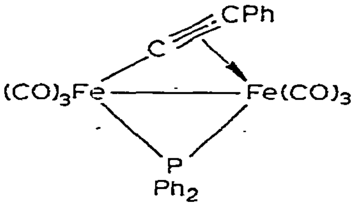
regarded formally as containing Fe=Fe bonds are $Fe_2(CO)_4(Bu^tC_2Bu^t)_2$ (2.22Å),[82] $Fe_2\{SCH_2CMe_2C_2CMe_2CH_2\}_2(CO)_4$ (2.23Å)[83] and $[Fe(\eta-C_5H_5)(NO)]_2$ (2.33Å).[84] The other product, 53, clearly arises from the reaction of an impurity in the acetylene, perhaps $CH_2=C(Me)C\equiv CBu^t$, and has an Fe-Fe bond length of 2.74Å. Reaction of $Fe_2(CO)_9$ with $(C_6F_5)_2PC\equiv CPh$ afforded[85] 54 which is envisaged as containing a phosphoriadiene ring. Crystallographic studies revealed that each Fe atom has a pseudo-octahedral geometry (Fe-Fe 2.70Å). The product obtained[86] from the reaction of $Fe_2(CO)_9$ with $Ni(\eta-C_5H_5)(PPh_3)C\equiv CH$ has been identified[87] crystallographically as 55 (Ni-Fe 2.42A). The acetylene bridge is regarded as being similar to that in $Ni_2(\eta-C_5H_5)_2(PhC_2Ph)$ and $Co_2(CO)_6(PhC_2Ph)$. The structure of 55 is regarded as an intermediate of the two shown in figure 4.

Figure 4



Reaction of $Ni(\eta-C_5H_5)_2$ or $Co_2(CO)_8$, $Fe_2(CO)_9$ and $[Ph_3PC\equiv CPh]Br$ gave $Ni(\eta-C_5H_5)Fe(CO)_3(Ph_3C_2Ph)$, and $CoFe(CO)_6(Ph_3PC_2Ph)$, respectively. Treatment of 56 with $P(OR)_3$ (R = Me, Et, Bu^n) afforded[88] 57 which contains, formally, a two-carbon, three-electron donor, hydrocarbyl ligand (the C-C distance, 1.34Å, in the phosphonium betaine indicates considerable multiplicity). The structure of this complex bears a formal resemblance to $Fe_2(CO)_6[C\{C_6H_3(OMe)_2\}]OEt$[89] and $Fe_2(CO)_6\{CPh(O)\}_2$.[90]

From ^{13}C n.m.r. spectral studies it has been shown[91] that η^6-cyclooctatriene complex[92] $Fe_2(CO)_6(C_8H_{10})$, 58, exhibits three fluxional processes: two at low temperature and one at higher temperature. The low temperature spectrum is consistent with the molecular structure of 58 in the solid state[93] and as the temperature rises, a "twitching" process occurs (Figure 5). The two enantiomorphous forms of the structure interconvert by a minimal movement of the $Fe_2(CO)_6$



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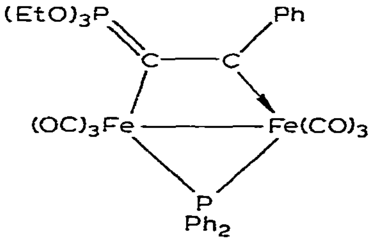

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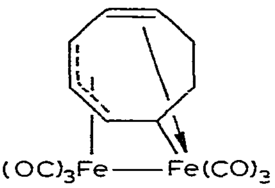
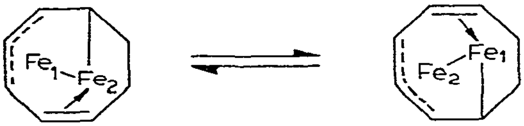


(58)

Figure 5

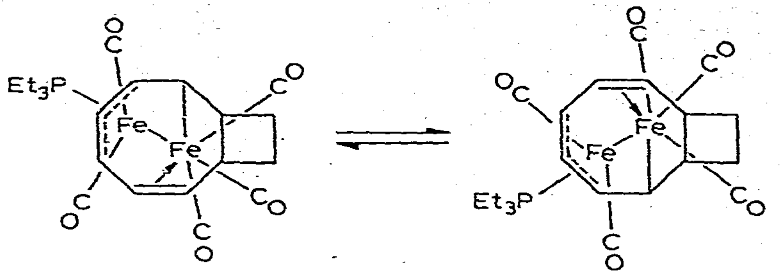
group relative to C_8H_{10} without interchanging the ends of that group. Furthermore, in the second low temperature process, three CO groups on one of the Fe atoms are simultaneously scrambled among themselves. At higher temperature the other group of three CO groups undergoes site exchange, but at no time is there interchange of CO groups between the two Fe atoms. The observations rule out a "gliding" mechanism (Figure 6).

Figure 6



The fluxional properties of $Fe_2(CO)_6(C_{10}H_{12})$, 59 $Fe_2(CO)_5(PEt_3)(C_{10}H_{12})$, and $Fe_2(CO)_6(C_9H_{10})$ 60 can be explained similarly,[94,95] the low temperature scrambling of the CO groups apparently occurring at the Fe atom bound to the allylic group. It may be seen that the structure of $Fe_2(CO)_5(PEt_3)(C_{10}H_{12})$ is qualitatively the same as 59, and it may be noted that the Fe-Fe distances in $Fe_2(CO)_6(C_8H_{10})$, 58,[93] $Fe_2(CO)_{60}(C_9H_{10})$,[95] $Fe_2(CO)_6(C_{10}H_{12})$ and $Fe_2(CO)_5(PEt_3)(C_{10}H_{12})$ are 2.76, 2.77, 2.79 and 2.80A, respectively.

In the reaction between $Ru_4(CO)_{12}H_4$ and cyclooctatetraene, the species $Ru_2(CO)_5(C_{16}H_{16})$, 61, is produced.[96] The structure of this complex (Ru-Ru 2.89A) is very similar to that of $Ru_2(CO)_6(C_8H_8)$[97] and 58. The complex is fluxional (Figure 7), and this appears to be one of the first examples of a 1,3-shift rearrangement in cyclic polyolefin complexes. Under 10 atm of CO, 61 gives $Ru_2(CO)_6(C_{16}H_{16})$, whose i.r. spectrum is nearly identical to that of $Ru_2(CO)_6(C_8H_{10})$;[98] a possible structure is 62. Treatment of $Ru_3(CO)_{12}$ or



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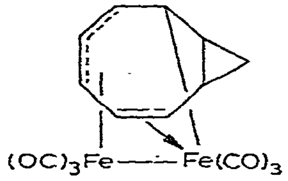

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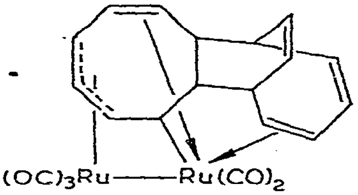
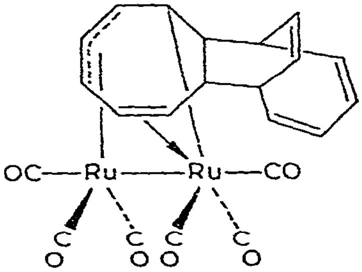


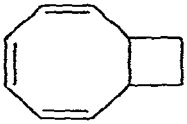
(61)

$Ru_4(CO)_{12}H_4$ with an authentic sample of the cyclooctatetraene dimer did not afford 61. Reaction of $Ru_3(CO)_{12}$ with 63 gave[99] 64, in which the three rings have *exo* configurations, and which probably has an iron analogue,[100] and the fluxional 65. In boiling toluene 65 rearranged to 64.



(62)

Treatment of bis-5,8-trimethylsilyl-1,3,6-cyclooctatriene with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ afforded[101] 66 and 67, neither of which was fluxional. The structure of the previously reported[102] $Ru_2(CO)_5(C_7H_6SiMe_3)(SiMe_3)$, 68, has been determined;[103] the Ru-Ru distance being 2.94A and the interplanar angle between diene and allyl fragments being 57°. The Ru-Ru-CO chain is almost linear while the $SiMe_3$ group is bent away from the hydrocarbon ligand giving a Ru-Ru-Si angle of 173°. The bonding of the $C_7H_6SiMe_3$ ligand is said to veer slightly away from idealised η^3-allyl/η^4-diene bonding to the more symmetrical situation found in $Ru_3(CO)_6(C_7H_7)(C_7H_9)$.[104]



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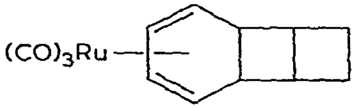

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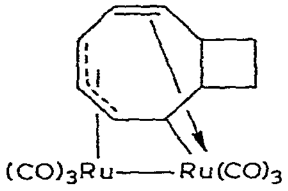

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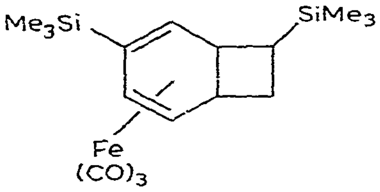

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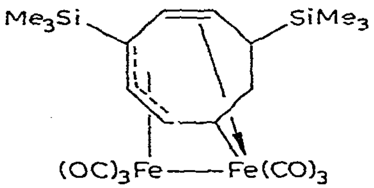

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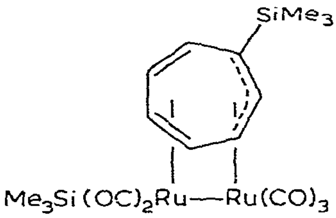
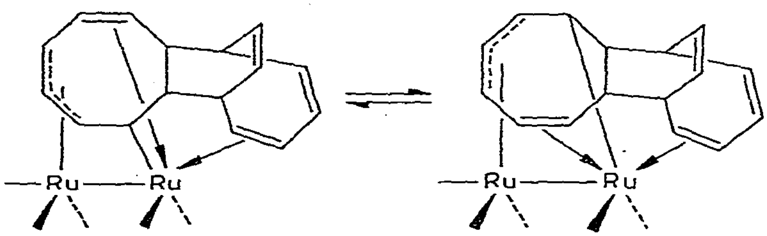


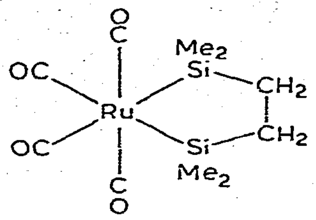
(68)

Reaction of 69 with cyclooctatetraene afforded[105] 70 as the major, and 71 as the minor, products. By heating 70 with Ru(CO)$_4$(SiMe$_3$)$_2$, 71 could be produced in good yield, but on heating 71, 72 was formed; a similar ring opening does not occur with 70. In 70, the Ru–Ru distance is 2.94Å whereas in 72 it is 2.91Å. In the latter, the two diene fragments are independent of each other, the 4 C atoms which comprise them being coplanar.

Details of the synthesis of 73 (L = CO) have been reported[106] and reaction with PPh$_3$, Ph$_3$As and Ph$_3$Sb, giving 73 (L = Lewis base), described.

Figure 7





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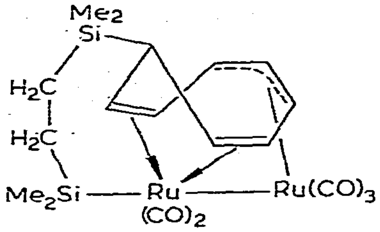

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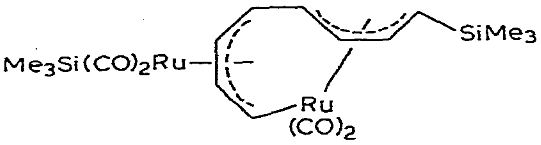

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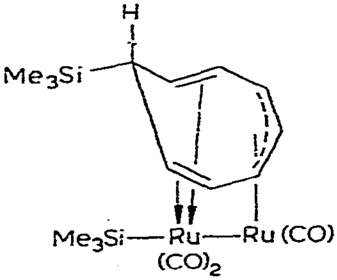
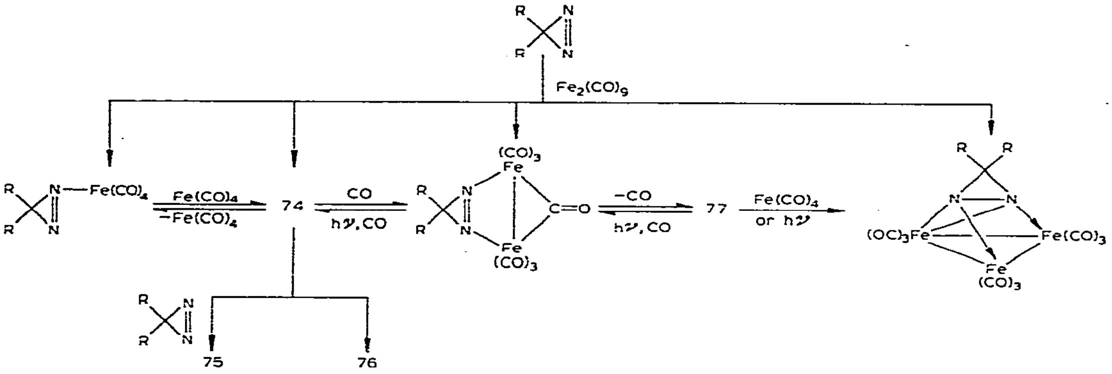


(71)

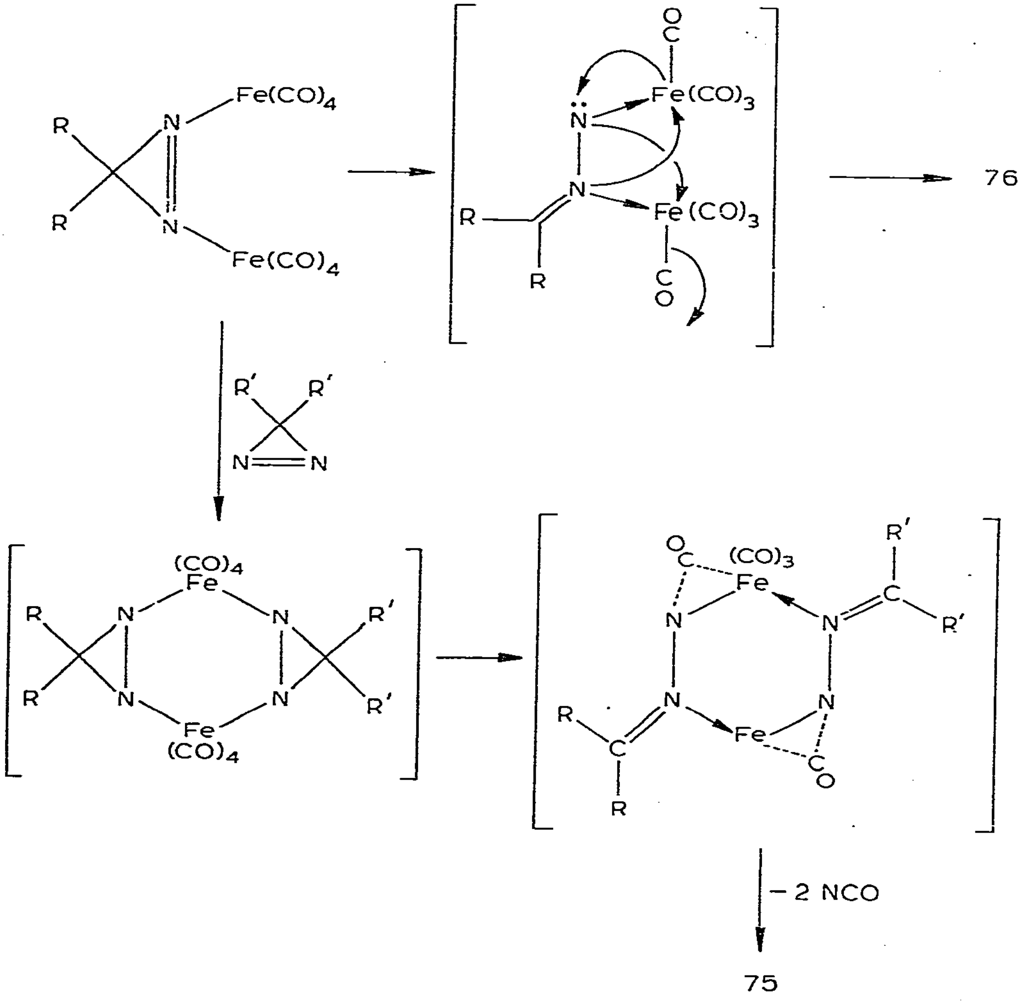
The reactions of diazirines with iron carbonyls have received considerable attention.[107] These are outlined in Scheme 7 (the ligands investigated were diazirine itself, 3,3-dimethyl-diazirine and 3,3-pentamethylene diazirine). The proposed mechanism of formation of 75 and 76 from 74 is outlined in Scheme 8. Treatment of 76 with methanol afforded a mixture of 78 and 79. The stepwise cycloaddition of acetylenes to compounds of type 77 (see Scheme 7) has been investigated.[108] Thus 80 (R = CO_2Me, R' = Ph or i-Pr) reacted with R"C≡CR" (R" = Ph) giving 81, 82 and 83. The structure of 81 was confirmed crystallographically,[109] and it was found that the N-N bond distance was consistent with unit bond order. It was suggested that the compound obtained[110] by reaction of μ-1,2-(3,6-diphenylpyridazine)hexacarbonyldi-iron has a similar structure.

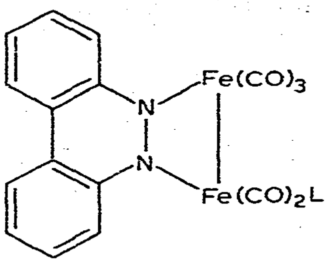
Other products obtained in the reaction with diphenylacetylene included Fe(η^4-C_4Ph_4)$(CO)_3$, and the tetraphenylferrole complex, 46. With acetylene itself (R" = H) only 82 (R' = H) was obtained, and other species with R" = CO_2Me

Scheme 7



Scheme 8





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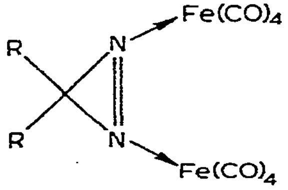

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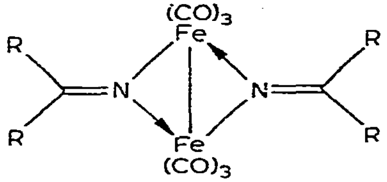

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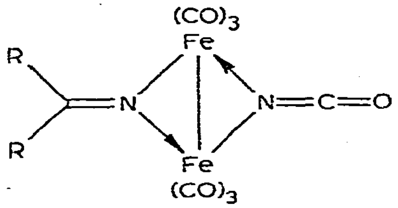

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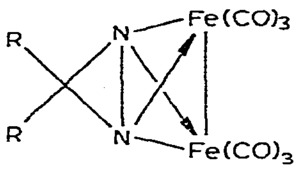

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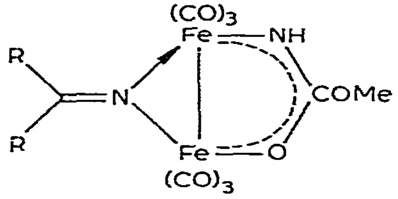

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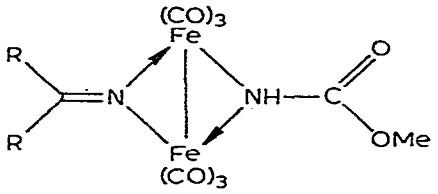
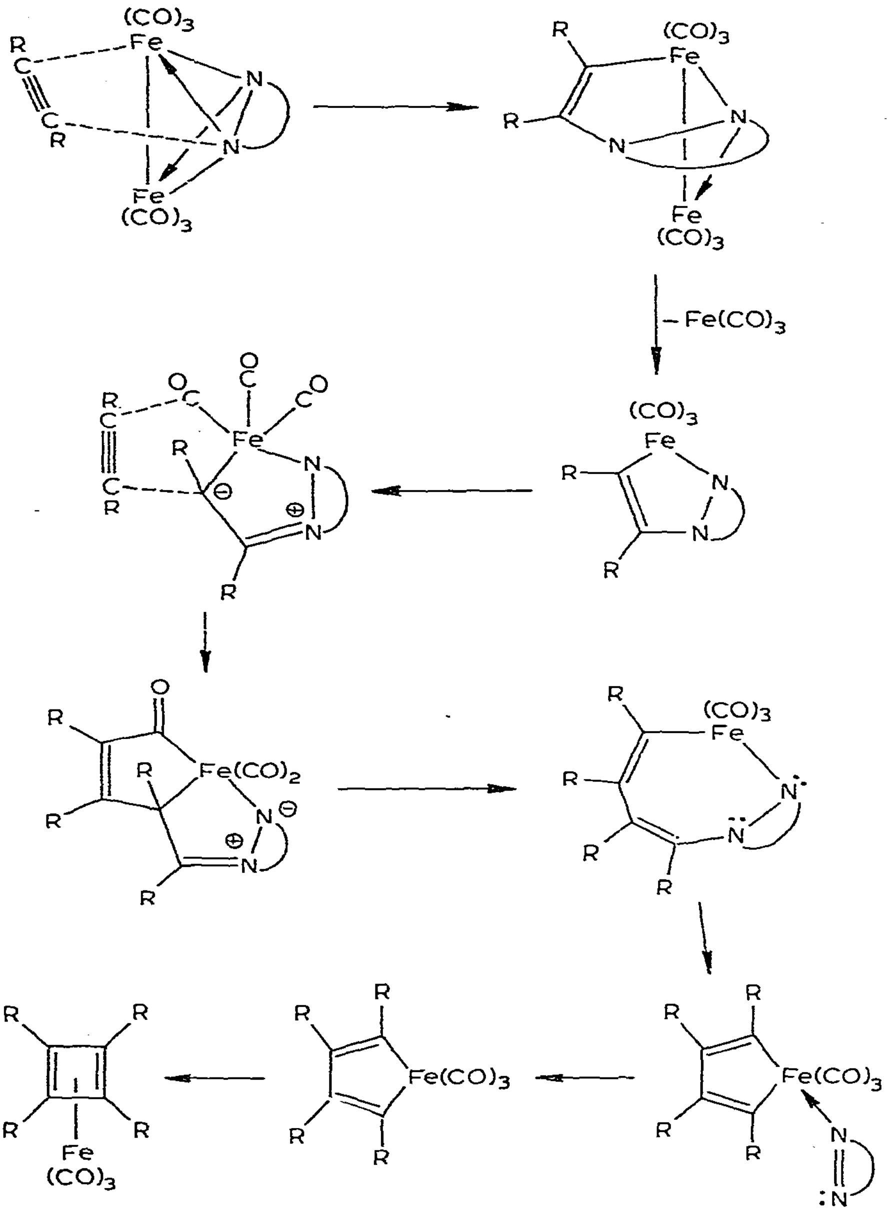


(79)

were also prepared. Irradiation of 80 with PhC≡CPh afforded 83, which was produced alternatively by heating 82 with the acetylene. A similar series of products were obtained with 84 but only the analogue of 81 could be prepared from 85. The proposed overall mechanism is depicted in Scheme 9.

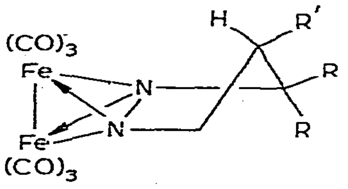
Treatment of the bridged complexes 86 (M = Mn, n = 4; M = Co, n = 3) with the phosphines PR_2R' (R = NMe_2, OMe, Me or Ph; R' = NMe_2, OMe or Ph) afforded[111] non-bridged species $(OC)_4Fe(\mu\text{-}AsMe_2)M(CO)_{n-1}(PR_2R')$.

Scheme 9



The dynamic n.m.r. spectral properties of the species $Fe_2(CO)_6(\mu ER_n)_2$ (ER_n = PMe_2, AsMePh, $AsMe_2$, SMe or SEt) have been studied.[112] The species containing bridging SR groups showed no evidence of axial-equatorial exchange of the R group prior to the beginning of thermal decomposition. However, the other compounds exhibited three essentially independent fluxional processes: (i) CO scrambling on individual metal atoms, (ii) axial-equatorial site interchange of the R groups in a concerted manner such that it occurred in both ER_2 groups simultaneously, and (iii) axial-equatorial R group interchange so that isomers of an ERR'-bridged species were interconverted. It was suggested that the low activation energy for process (i) was not inconsistent with the observations made of many other $M(CO)_3$ systems, that process (ii) might occur without bridge opening, and that the relatively high activation energy for process (iii) is consistent with the necessity for configurational inversion at P or As in a bridge-open intermediate.

Reaction of $Fe_2(CO)_9$ with the appropriate hexadentate tertiary phosphine afforded[113] the bimetallic complex 87. Treatment of $Fe(CO)_5$ with $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3 or 4) gave[114] $[Fe(CO)_4]_2\{Ph_2P(CH_2)_nPPh_2\}$, but when n = 1, the species $Fe(CO)_4(Ph_2PCH_2PPh_2)$, $Fe(CO)_3(Ph_2PCH_2PPh_2)$ and $Fe_2(CO)_7(Ph_2PCH_2PPh_2)$ were also formed; the last could have the structures 88 or 89 and could also be prepared from $Fe_2(CO)_9$. A superior route for the form-



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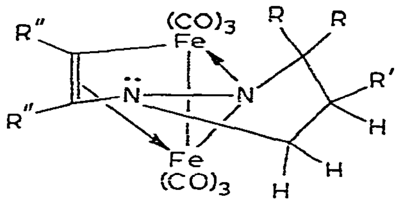

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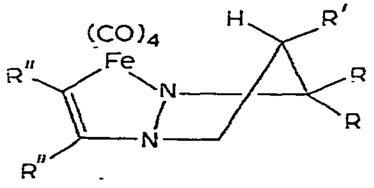

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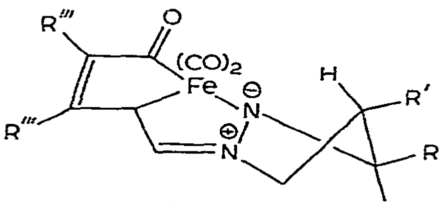

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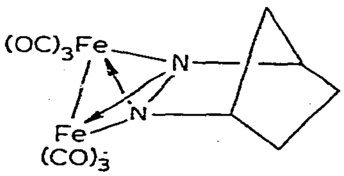

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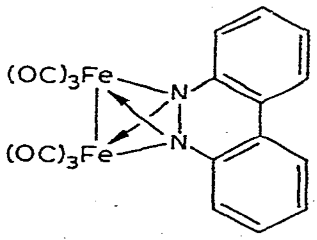

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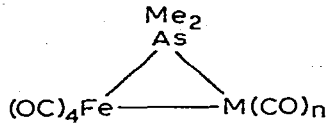

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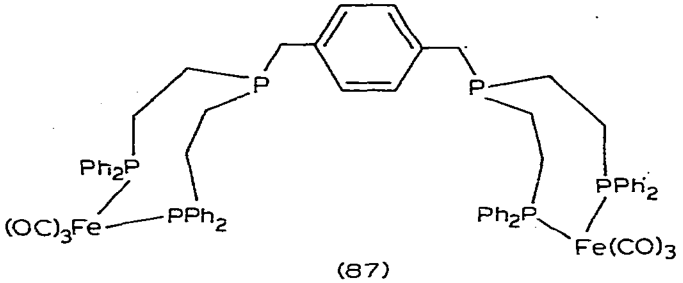

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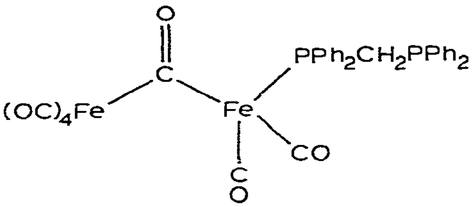

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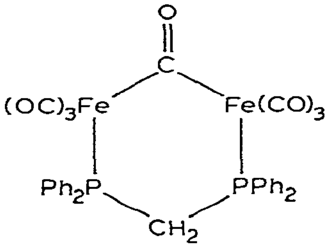

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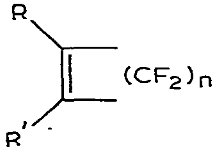

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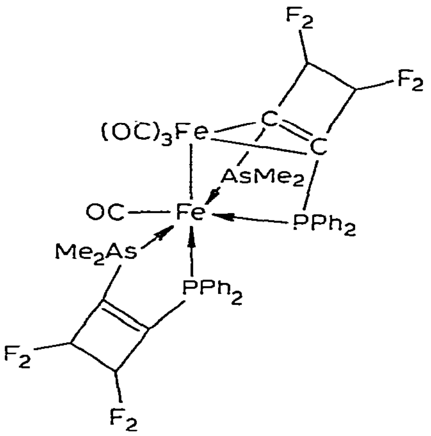
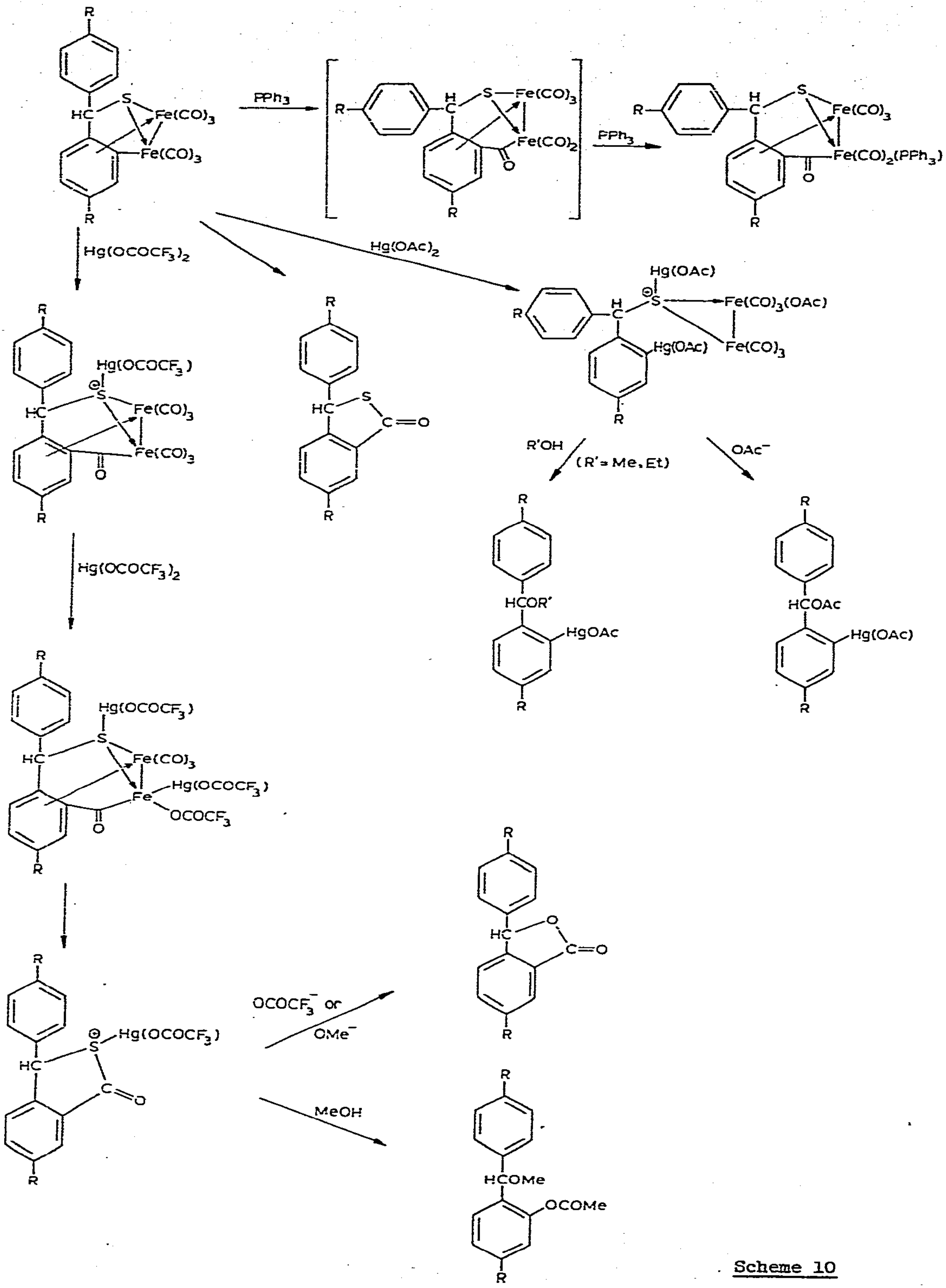


(91)

ation of $Fe_2(CO)_6(L-L')$ (L-L' = 90) has been described[115] and those compounds with 90, n = 3 or 4, R = R' = $AsMe_2$ are new. These complexes react with monodentate ligands (L" = Ph_3P, Ph_3As, Ph_3Sb, $(PhO)_3P$, $Ph_2AsCH_2CH_2AsPh_2$) giving $Fe_2(CO)_5L''(L-L')$, $Fe_2(CO)_4L''_2(L-L')$ and $Fe_2(CO)_3L''_3(L-L')$. The compound $Fe_2(CO)_4(L-L')_2$ (L-L' = 90; n = 2, R = $AsMe_2$, R' = PPh_2) may have the structure 91.

Reactions between $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ and thiols, disulphides and RSR have been systematically investigated[116] and it was reported that


PPh3
PPh3
Fe(CO)3
Fe(CO)2
Fe(CO)2(PPh3)
Hg(OCOCF3)2
Hg(OAc)2
Hg(OAc)
Fe(CO)3(OAc)
R'OH
(R' = Me, Et)
OAc−
HCOR'
HgOAc
HCOAc
Hg(OAc)
Hg(OCOCF3)
Hg(OCOCF3)2
OCOCF3
OCOCF3− or OMe−
MeOH
HCOMe
OCOMe
R

Scheme 10

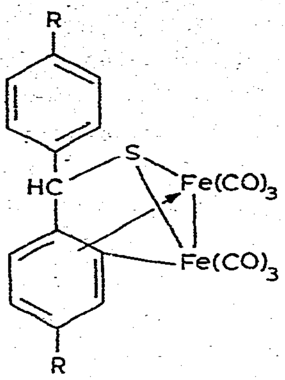
reactivity towards formation of $Fe_2(CO)_6(\mu\text{-}SR)_2$ increased in the order $Fe_1 < Fe_2 < Fe_3$ and $R_2S < RSSR < [RSH]$. Treatment of $[Et_3NH][Fe_3(CO)_{11}H]$ on the gave $Fe_2(CO)_6(\mu\text{-}SPh)_2$. Reaction of $Fe_2(CO)_6(\mu\text{-}SPh)$ with RSH (R = dodecyl) in boiling methanol afforded[117] *syn*- and *anti*-$Fe_2(CO)_6(\mu\text{-}SR)_2$ in equilibrium with $Fe_2(CO)_6(\mu\text{-}SPh)_2$. High resolution i.r. spectral studies have been made of $Fe_2(CO)_6X_2$ (X = Br, I, S, Se, SC_6F_5, SMe, $PH(C_6H_{11})$, PMePh, PHMe, PMe_2) and the effects of the bridging ligands in the CO stretching frequencies evaluated. New non-parameterised m.o. calculations have been made[119] of the metal-metal interactions in the species $Fe_2(CO)_6(\mu\text{-}X)_2$ (X_2 = $(SMe)_2$, $(NH)_2$, S-S, MeN=NMe, $(PR_2)_2$). These have revealed that variation of X does not markedly affect the nature of the Fe-Fe interactions. The orbital character of the highest occupied molecular orbital in each species corresponds closely to the "bent" Fe-Fe bond, while the lowest unoccupied molecular orbital is its antibonding counterpart. The calculations also indicated that in the species $[Fe_2(CO)_6(\mu\text{-}PR_2)_2]^z$, z = -1 and -2, the metal-metal interaction corresponds to a "one-electron" and a "no-electron" Fe-Fe bond.

A detailed kinetic and mechanistic study has been made[120] of the reaction between $Fe_2(CO)_6(\mu\text{-}SPh)_2$ and PPh_3. Under CO, the two step substitution reaction does not go to completion. The unsubstituted complex undergoes direct attack by PPh_3 either on the predominant *anti* form or on the very reactive *syn* form which is produced in the rate determining *anti-syn* isomerisation. The monosubstituted species $Fe_2(CO)_5(PPh_3)(\mu\text{-}SPh)_2$ reacts with CO via an S_N2 mechanism, but a CO dissociative process is involved in its reaction with the bulkier PPh_3 ligand. The species $[Fe(CO)_2(PPh_3)(\mu\text{-}SPh)]_2$ is unable to undergo S_N2 displacement even by CO. These results are in good agreement with others obtained earlier.[121]

Diaryl sulfines ($Ar_2C{=}S{=}O$) reacted[122] with $Fe_2(CO)_9$ giving Ar_2CS and/or 92 (Ar = p-Me- or p-$MeOC_6H_4$). A detailed report has been made[123] of the reactions of 92 (Scheme 10)

Reaction of 92 with TCNE or with light afforded 93, but with a combination of both, 93 and $Fe(CO)_4(TCNE)$ were formed. Treatment of 92 with OH^-, OMe^-, N_3^-, NCS^- or CNBr also afforded 93 (R = OMe or Me) in good yield, whereas $KOBu^t$ gave also some $[(p\text{-}RC_6H_4)_2CH]_2$ (R = OMe). Attack by nucleophiles on 92 is thought to occur via the intermediate 94. With O-alkyl thioesters, $Fe_2(CO)_9$ afforded[124] 95 and 96, a possible mechanism being outlined in Scheme 11.

For all the ring-substituted O-methylthioesters, the major product was 96, suggesting that coordination of O to iron is more readily achieved than o-metalation leading eventually to 95. The increase in proportion of 95 with an increase in the effective size of R' in the O-alkylthiobenzoates is probably a consequence of steric hindrance to coordination of oxygen at Fe, the steric effect arising from repulsion of R" by $Fe(CO)_n$ groups. Further information about ring steric effects was obtained in the reaction between $Fe_2(CO)_9$ and 97



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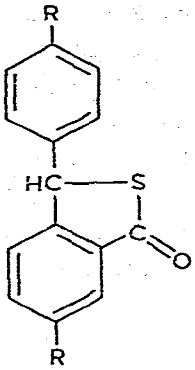

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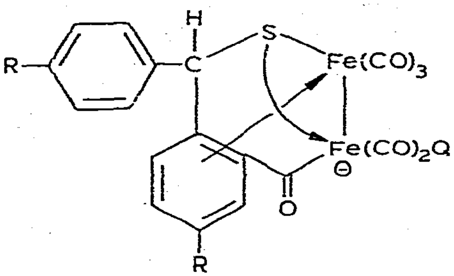

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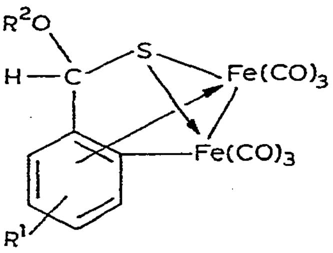

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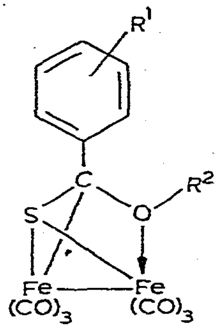
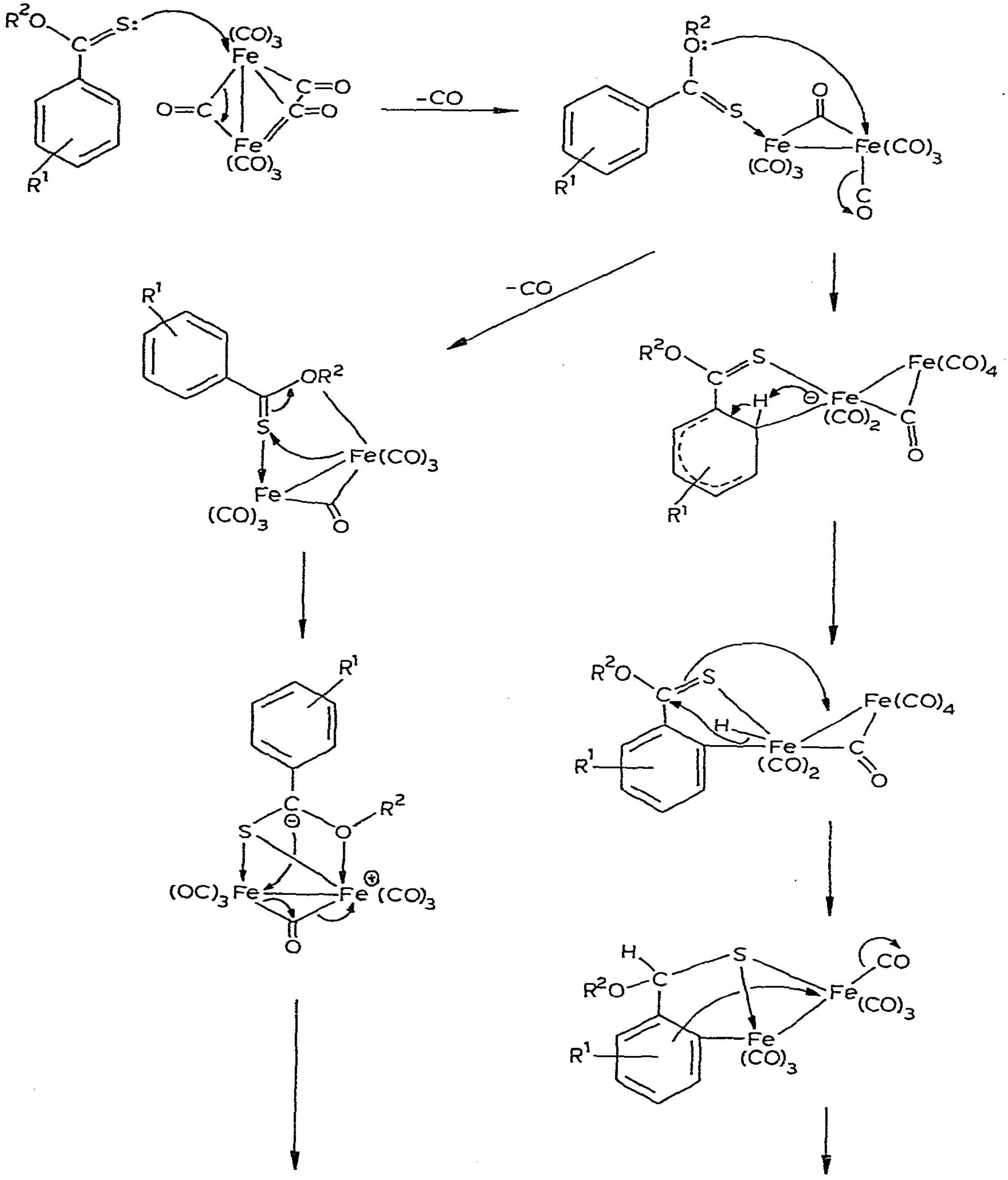


(96)

which afforded 98 and some $Fe_3(CO)_9S_2$, but no O-S bonded species presumably because the species 99 is too sterically strained. Oxidation of 98 by ceric ion gave 100.

Addition of methyliodide to $Fe_2(CO)_{6-n}(PMe_3)_n(\mu\text{-}SMe)_2$ (n = 2 or 3) afforded[126] $Fe(CO)_2(PMe_3)_2I_2$, $Fe(CO)_3(PMe_3)I_2$ and $Fe(CO)_2(PMe_3)_2MeI$. When n = 4, the species 101 was also obtained. Treatment of $Fe_2(CO)_6(\mu\text{-}SR)_2$ (R = Me, Et, Ph) or $Fe_2(CO)_6(\mu\text{-SePh})_2$ with $(CF_3)_2C_2S_2$ afforded[127] the salt $[Fe_2(CO)_6(\mu\text{-XR})_3]$-$[Fe\{S_2C_2(CF_3)_2\}_2]$, species originally formulated[128] as $[Fe(CO)\{S_2C_2(CF_3)_2\}(\mu\text{-XR})]_4$ but shown crystallographically to contain[129] a binuclear triply-bridged monocation and a binuclear monoanion. A possible reaction mechanism is



Scheme 11 96 95

$$4(CF_3)_2C_2S_2 + Fe_2(CO)_6(XR)_2 \rightarrow [Fe\{S_2C_2(CF_3)_2\}_2]_2 + RX\text{-}XR + 6CO$$

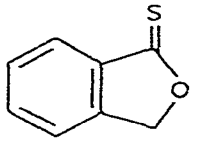
$$[Fe\{S_2C_2(CF_3)_2\}_2]_2^- + Fe_2(CO)_6(XR)_2 \rightarrow [Fe\{S_2C_2(CF\ )_3\}_2\ _2]_2^- + [Fe_2(CO)_6(XR)_2]^+$$

$$2[Fe_2(CO)_6(XR)_2]^+ + RXXR \rightarrow 2[Fe_2(CO)_6(XR)_3]^+$$

Parts of this mechanism were confirmed by the observation that $Fe_2(CO)_6(XR)_2$ (X = S, R = Me or Ph) reacted with the powerful oxidant $[Fe\{S_2C_2(CF_3)_2\}_2]_2$, and it was found that $Fe_2(CO)_6(\mu\text{-}SPh)_2$ reacted with $NOPF_6$ in the presence of PhSSPh giving $[Fe_2(CO)_6(\mu\text{-}SPh)_3][PF_6]$ together with small amounts of $Fe_2(NO)_4(\mu\text{-}SPh)_2$.

Reaction of $Fe_2(CO)_9$ with $MeB(SMe)_2$ afforded[130] $Fe_2(CO)_6(\mu\text{-}SMe\ )_2$, via an intermediate containing boron, possibly $Fe(CO)_3\{(MeS)_2BMe\}$. With 2-dimethyl-1,3,-2-dithiaborolane, μ-S,S'- ethylenedithiolato(hexacarbonyl)diiron was obtained, whereas the borthiin 102 afforded 103.

Species previously formulated[131] as $Ru(CO)(S_2CNR_2)_2$ are thought to be binuclear, and the structure of a representative member of this group of molecules, $Ru_2(CO)_2(S_2CNEt_2)_4$, 104, has been determined[132] crystallographically. The distance between the metal atoms is 3.65Å, indicating the absence of a Ru-Ru bond.



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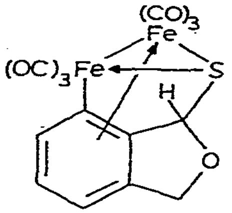

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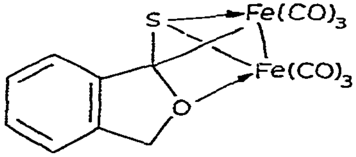

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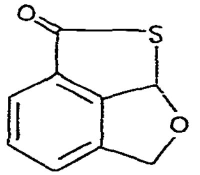

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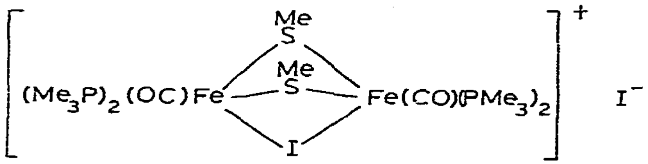

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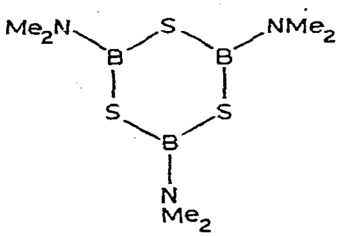

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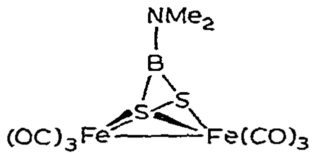

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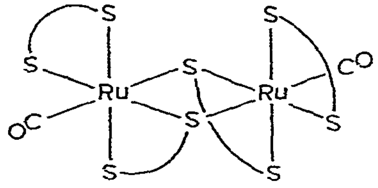

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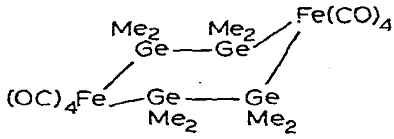

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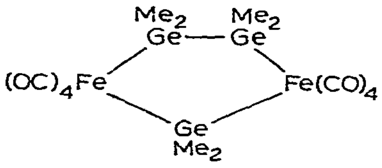

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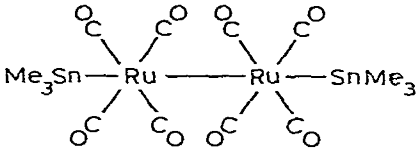
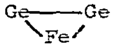


(107)

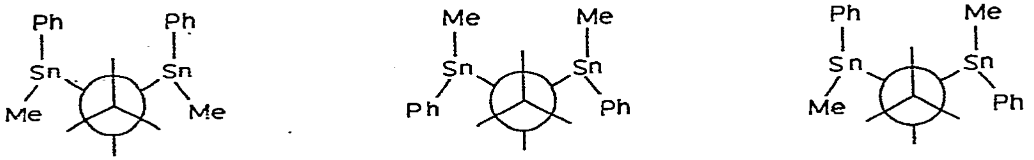
Reaction of $Na_2Fe(CO)_4$ with $ClGe(Me)_2Ge(Me)_2Cl$ afforded[133] a mixture of 105 and 106, but no species containing a Ge=Ge bond or  $\underset{\diagdown Fe \diagup}{Ge—Ge}$ group. Small amounts of the known[134] $Fe_2(CO)_6(\mu\text{-}CreMe_2)_3$ were also detected. The compound 105 is isoelectronic with $Cr_2(CO)_8(AsMe_2)_4$,[135] and is fluxional (figure 8). Photolysis of 105 or 106 gave $Fe_2(CO)_6(\mu\text{-}GeMe_2)_3$ in a reaction which involves Ge=Ge bond rupture; 106 cannot be formed from 105.

Tin(II) halides (Cl or Br) and β-diketonates (RCOCHCOR'; R=R'=Me, CF_3 or

Figure 8

Ph; R=Me, R'=Ph or CF_3) reacted[136] with $Fe_2(CO)_9$ giving $\{Fe(CO)_4SnX_2\}_n$. The halides and acetylacetylacetonate are dimeric (n=2) but some dissociation occurs when the R,R' groups are bulky. In pyridine $Fe(CO)_4SnX_2(pyr)$ is formed, and varying degrees of dissociation occurred in less nucleophilic solvents such as THF and MeCN. Small amounts of $Fe_2(CO)_8\{Sn(PhCOCHMe)_2\}$, 107, were detected, and ^{57}Fe Mössbauer spectral data were collected. Reaction of $Na_2Fe(CO)_4$ with $SnMePhCl_2$ afforded $Fe_2(CO)_8(\mu\text{-}SnMePh)_2$ which, on irradiation, afforded[137] $Fe_2(CO)_6\{\mu\text{-}CO)(\mu\text{-}SnMePh)_2$. This complex can exist as three geometric isomers (figure 9) and n.m.r. spectral data are consistent with an equilibrium mixture of

Figure 9

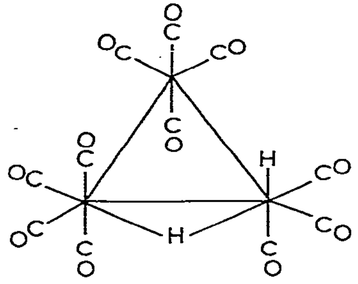


of c with either a or b, probably a. The compound is fluxional undergoing, at low temperatures, a deformation process which may be facilitiated by, or occurs in concert with, rapid bridge-terminal exchange of CO. At higher temperatures, the CO exchange process is best explained in terms of cleavage of the Sn-Fe bonds to give stannylene intermediates. Treatment of $Fe_2(CO)_9$ with $Sn(C_5H_5)_2$ gave[138] $Fe_2(CO)_8\{\mu\text{-}Sn(C_5H_5)_2\}_2$ in which the Fe atom has distorted octahedral geometry. The structure of $Ru_2(CO)_8(SnMe_3)_2$ has been determined[139] and the Sn-Ru-Ru-Sn system is almost linear, the CO groups adopting an eclipsed configuration and leaning slightly towards the outer $SnMe_3$ groups. The Ru-Ru distance, 2.94Å, is rather larger than the usual single bond length, and the Ru-Sn distance (2.69Å) is rather shorter than usual.

Trimetallic and other metal atom cluster compounds

Treatment of $Fe_3(CO)_{12}$ with RNC gave[140] $Fe(CO)_4(CNR)$ and $Fe_3(CO)_{12-n}(CNR)_n$ (R = Me or Bu^t, n = 1-3). The complex $Fe_3(CO)_{10}(CNBu^t)_2$ existed as isomers but there was no evidence for bridging isocyanide in the series of compounds. ^1H n.m.r. spectral studies indicated that the complexes were fluxional. Conformation transformations in the series $M_3(CO)_{12}$ (M = Fe or Ru) and $Fe_2(CO)_9$ have been discussed.[141]

Reaction of $Os_3(CO)_{10}H_2$ with L (CO, CNMe, PMe_2Ph, $AsMe_2Ph$, PPh_3 or PhCN) afforded[142] $Os_3(CO)_{10}LH_2$ which could be decarbonylated to give $Os_3(CO)_9LH_2$ (L = CO or PR_2R'); addition of CO or PhCN was readily reversible. The structure of $Os_3(CO)_{11}H_2$, 108, was determined crystallographically, the intermetallic distances being Os_1-Os_2 2.99, Os_2-Os_3 2.86, and Os_1-Os_3 2.91Å, respectively. The bridging hydride was located by implication from bond length data. It is



(108)

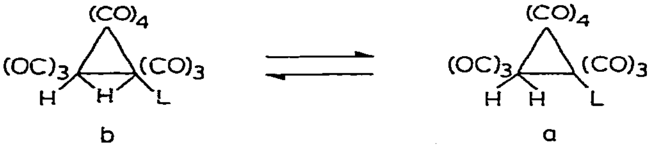
clear from ^{1}H n.m.r. spectral data that exchange of bridging and terminal hydride ligands occur via a non-bridged intermediate (figure 10). A possible mechanism whereby $Os_3(CO)_{12}$ may be converted to $Os_3(CO)_{10}H_2$ is outlined in the equation below:

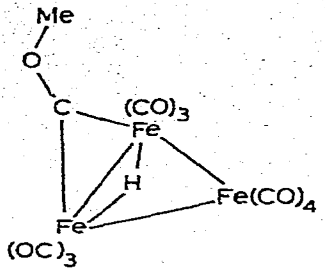
$$Os_3(CO)_{12} \xrightarrow{-CO} Os_3(CO)_{11} \xrightarrow{H_2} Os_3(CO)_{11}H_2 \rightarrow Os_3(CO)_{11}H_2 \rightarrow Os_3(CO)_{10}(\mu_2\text{-}H)_2$$

Alkylation of the N,N'-dimethyltriethylenediamine salt of $[Fe_3(CO)_{11}]^{2-}$ by $MeSO_3F$ afforded the corresponding salt of $[Fe_3(CO)_{10}(COMe)]^-$ which, on treatment with HCl, gave $Fe_3(CO)_{10}H(COMe)$, 109, whose structure was determined crystallographically.[143] Reaction of $Ru_3(CO)_{12}$ with $Me_2NCH_2SnMe_3$ gave[144] $Ru(CO)_4(SnMe_2)_2$ and $Ru_3(CO)_{10}H(CNMe_2)$, 110. The structure of the latter has been determined and the unit cell contains two independent molecules; the metal-metal distances were Ru_1-Ru_2 2.80 (both molecules), Ru_1-Ru_3 2.83 (both) and Ru_2-Ru_3 2.83 and 2.82Å. It was noted that the species formulated[145] as $Fe_3(CO)_{11}H(NMe_2)$ has recently been characterised[146] as $Fe_3(CO)_{11}H(C{:}NMe_2)$.

The X-ray crystallographic determination[147] of the structure of $Ru_3(CO)_9H_3(CMe)$, 111 (Ru-Ru 2.84Å) has been used in a reinterpretation of the nematic phase ^{1}H n.m.r. spectrum[148] of this compound. From the new data, the Ru-H distance and Ru-H-Ru bridge bond angle was calculated to be 1.81Å (1.72Å from X-ray data) and 103° (112(7)° from X-ray data) respectively. It was suggested that the data obtained from n.m.r. measurements were probably more accurate than the crystallographic results.

Figure 10





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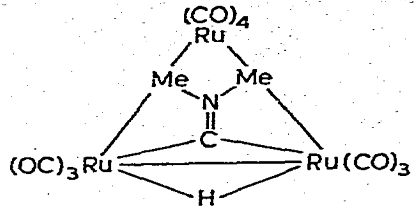

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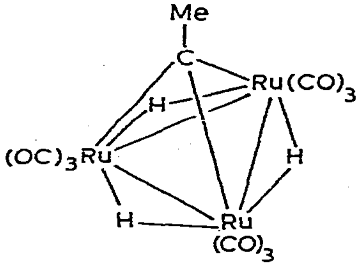


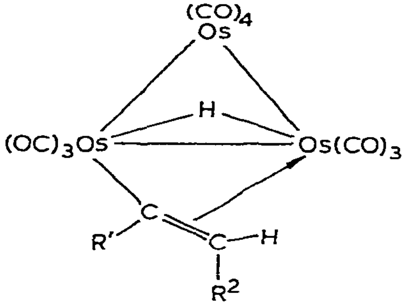
(111)

The reactions of $Os_3(CO)_{10}H_2$ with acetylenes have been investigated[149] extensively. Thus, in general terms, the dihydride reacted with RC≡CR giving $Os_3(CO)_{10}H(RC_2HR)$, 112, (R = R' = H, Me or Ph; R = H, R' = Me, Et, Bu^t or Ph) together with $Os_3(CO)_{10}(RC_2R)$, which may have the structure 113 or 114 (R = R' = H, Me or Ph; R = H, R' = Me), $Os_3(CO)_{10}(RC_2R')_2$ (structure unknown), $Os_3(CO)_9(RC_2R')$, 115 (R = R' = Ph; R = H, R' = Me), $Os_3(CO)_9H(C_2R')$, 116 (R = H, R' = Me, Bu^t, Ph), $Os_3(CO)_9(RC_2R')$, 117 (R = R' = Ph), $Os_3(CO)_8H(RC_2R')(RC_2H)$, 118 (R = R' = Ph), $Os_2(CO)_6H_2(RC_2R')_2$, 119 (R = H, R' = Me), $Os_2(CO)_6(RC_2R')_2$, 120 (R = H, R' = Ph), $Os_3(CO)_9\{(RC_2R')_2CO\}$, 121 R = R' = H, alkyl, Ph, CO_2Me) and $Os_3(CO)_{10}H(C_2R')$, 122 (R' = Ph). When 112 (R = R' = H) was heated in octane, 123 was formed, and this can also be prepared directly from $Os_3(CO)_{12}$ and ethylene. When 112 (R = R' = Me, Ph; R = H, R' = Me) was treated similarly, or with hydrogen, 124 was formed. Treatment of 124 (R = R' = Ph) with $P(OMe)_3$ or PPh_3 (L) gave $Os_3(CO)_9L(C_2Ph_2)$ which reacted further with PPh_3 in the presence of PhC≡CPh affording $Os_3(CO)_8(PPh_3)(C_4Ph_4)$, a derivative related to 117. When 113 or 114 (R = R' = Me) was heated in refluxing heptane $Os_3(CO)_9H(C_4H_5)$, for which two structures, 125 and 126, have been suggested (the former is preferred). On heating in toluene at 156°, this compound isomerised to 127 which is analogous to a compound obtained[150] from $Ru_3(CO)_{12}$ and butadiene.

Dynamic n.m.r. studies have been made[151] of $Os_3(CO)_9H_2(C{:}CH_2)$, 123 (R = R' = H). This was achieved by random deuterium distribution achieved as follows:

$$Os_3(CO)_9H_2(C{:}CH_2) \xrightarrow{CF_3CO_2D} [Os_3(CO)_9H_2D(C{:}CH_2)]^+ \xrightarrow{D_2O} Os_3(CO)_9HD(C{:}CH_2) + Os_3(CO)_9H_2(C{:}CH_2)$$

The deuterium was equally distributed over the two possible sites, and no exchange was observed between hydridic H/D and the CH_2 protons up to 40°, although at 100°, some scrambling did occur. Furthermore, $Os_3(CO)_{12}$ reacted with $CH_2{:}C(Me)CH_2CHMe_2$ giving $Os_3(CO)_9H_2\{C{:}C(Me)CH_2CHMe_2\}$ which exists as two



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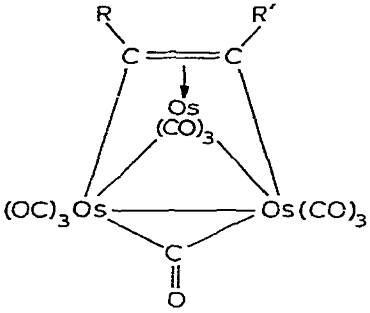

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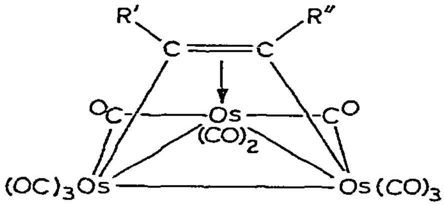

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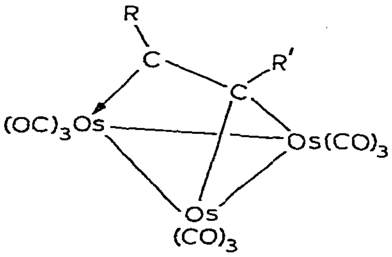

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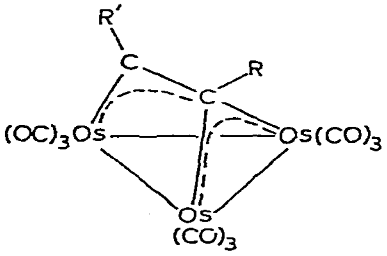

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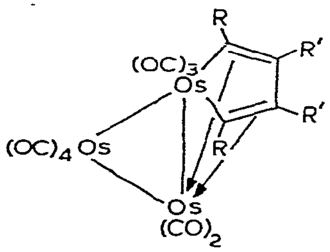

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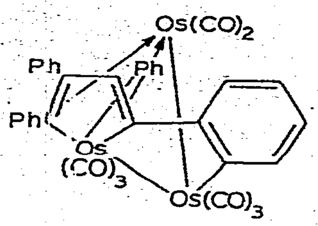

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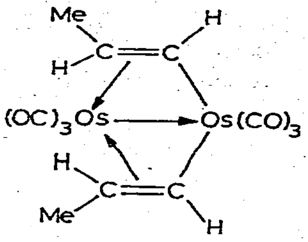

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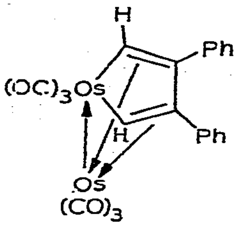

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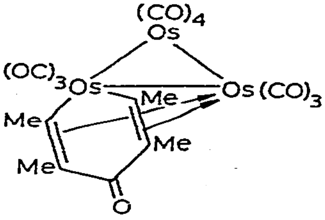

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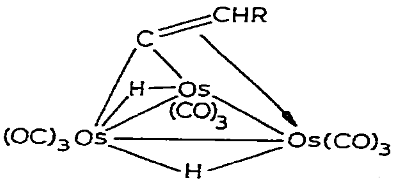

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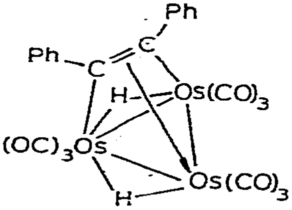

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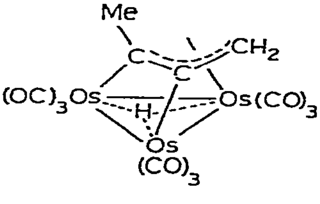

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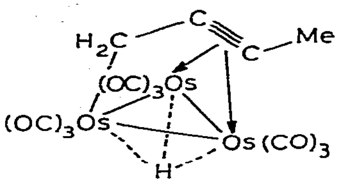

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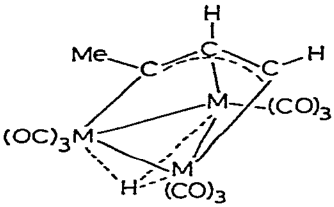

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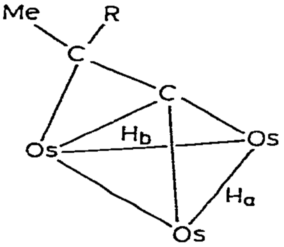

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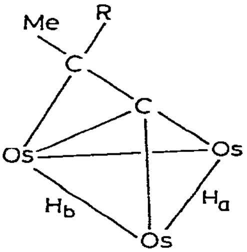
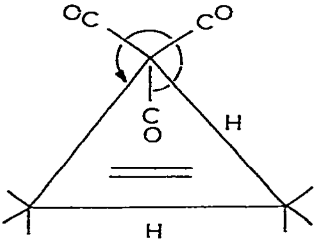


(129)

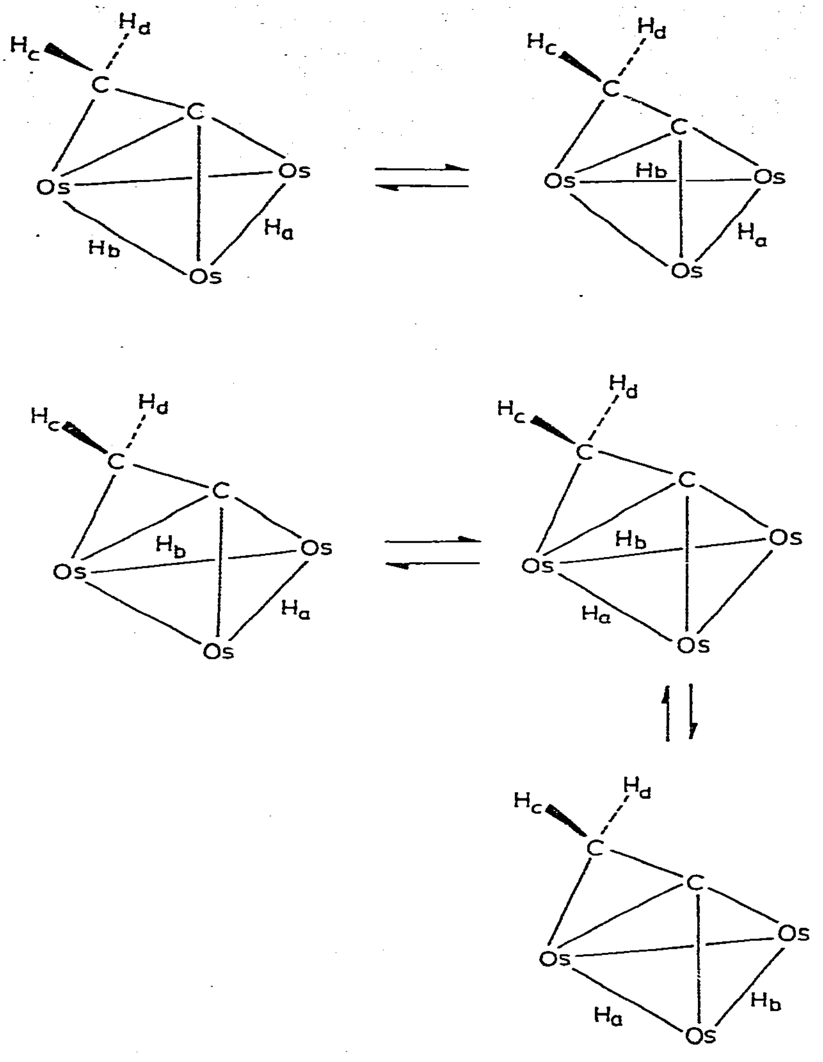
isomers 128 and 129. Studies of this compound established that, under conditions of hydridic H interchange, the Os-C(Me)CH_2CHMe_2 bond remained intact. A satisfactory explanation of the fluxional properties of $Os_3(CO)_9H_2(C{:}CH_2)$ is illustrated in Scheme 12.

These studies verify earlier predictions[152] that hydrogen exchange occurs directly by hydride migration from one edge of the metal triangle to the other. For the complexes $Ru_3(CO)_9H_2(C_8H_{12})$, $Os_3(CO)_7(AsMe_2)_2(C_6H_4)$[153] and $Os_3(CO)_9H_2(MeC_2Me)$ (113 or 114 (R = R' = Me)), another mechanism, involving olefin rotation is necessary to explain their fluxional processes. It was observed that these three complexes underwent localised CO scrambling and it was suggested that a mechanism as in figure 11 could account for this.

Figure 11

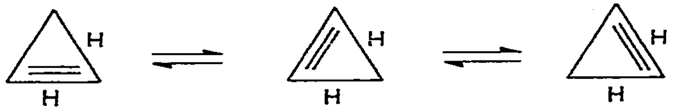


Scheme 12



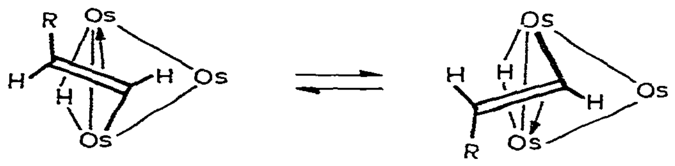
However it was suggested that an alternative process could involve olefin rotation (figure 12) and this could account for the observation, in the fast exchange limit, of only one ^{13}C carbonyl resonance and interchange of the hydride sites. However in these systems, as in $Os_3(CO)_9H_2(C{:}CRR')$, a number of exchange mechanisms can operate independently.

Figure 12

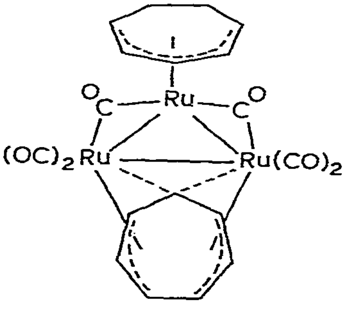


Reaction of $Os_3(CO)_{10}H_2$ with an excess of ethylene afforded[154] ethane and $Os_3(CO)_{10}H(CHCH_2)$ (112, R = R' = H) which rearranges in refluxing octane to $Os_3(CO)_9H_2(C{:}CH_2)$ (123, R = R' = H) and $Os_3(CO)_{12}$. The vinyl complex is fluxional (figure 13).

Figure 13



In refluxing heptane, $Ru_3(CO)_{12}$ reacted with cycloheptatriene giving[155] $Ru_3(CO)_6(C_7H_7)(C_7H_9)$, 130, the structure of which has been confirmed crystallographically,[156] $Ru_2(CO)_6(C_7H_8)$, 131, $Ru(CO)_3(C_7H_8)$ and $Ru(CO)_3(C_7H_{10})$. The cycloheptatriene complex $Ru(CO)_3(C_7H_8)$ could be prepared either by photolysis of $Ru_3(CO)_{12}$ in the presence of the triene, or by displacement[157] of cycloocta-1,5-diene from $Ru(CO)_3(C_8H_{12})$; $Ru(CO)_3(C_7H_{10})$ could be obtained by the last process. When 130 was refluxed in the presence of C_7H_8, $Ru(CO)_3(C_7H_8)$ was formed but on heating the latter on its own, 130 was regenerated, while with addition C_7H_8, $Ru(CO)_2(C_7H_8)$ was formed. These results suggest that 130 is not formed directly from $Ru_3(CO)_{12}$ with retention of the Ru_3 triangle, but is produced via $Ru(CO)_3(C_7H_8)$ which is the source of all the other products. It was also observed that when $Ru_3(CO)_{12}$ and C_7H_8 reacted in dichloromethane, $Ru_2(CO)_4(C_7H_7)Cl$, 132 (X = Cl; R = H) was produced. Analogues of this compound were prepared by reacting 130 with CCl_4, CBr_4 or I_2, a byproduct being $Ru(CO)_2(\eta^5\text{-}C_7H_9)X$. Treatment of $Ru_3(CO)_{12}$ with substituted cycloheptatrienes C_7H_7R (R = Me or Ph) afforded analogues of 130, $Ru_3(CO)_6(C_7H_6R)(C_7H_8R)$ and $Ru(CO)_3(C_7H_7R)$; the former reacted with iodine giving $Ru(CO)_2(C_7H_8R)I$ and



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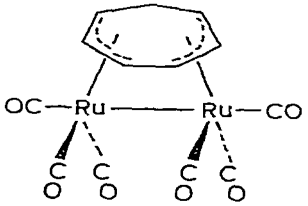
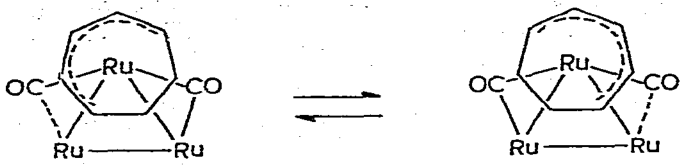


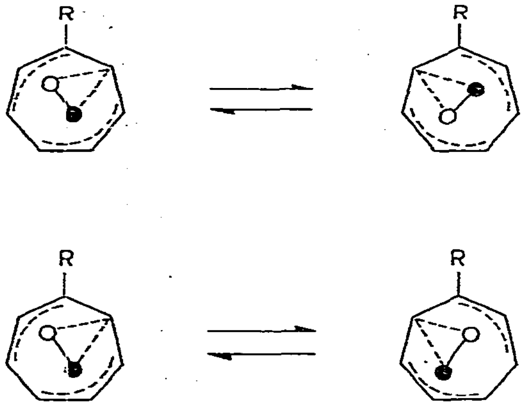
(131)

Figure 14

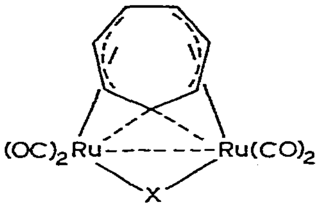


$Ru_2(CO)_4(C_7H_6R)I$, 132 (X = I, R = Ph). Even at -100°, 130 is fluxional[158] (figure 14). For 132 (R = Me or Ph), likewise non-rigid at -100°, two pathways whereby the $Ru_2(CO)_4X$ fragment can oscillate about the ring have been proposed (figure 15).

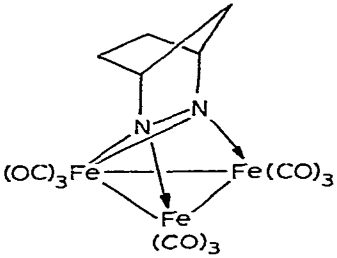
Figure 15



Reaction of $Fe_3(CO)_{12}$ with nitroethane in boiling benzene afforded[159] iron oxides together with $Fe_3(CO)_9(\mu_3\text{-NH})(\mu_3\text{-NEt})$, $Fe_3(CO)_9(\mu_3\text{-NEt})$, $Fe_3(CO)_3(\mu_3\text{-NEt})(\mu_3\text{-CO})$, $Fe_2(CO)_6(\mu\text{-EtNNEt})$ and $Fe_2(CO)_6(\mu\text{-EtNCONEt})$. Treatment of iron carbonyls with 2,3-diazanorbornene gave[160] $Fe(CO)_4(C_5H_8N_2)$, $Fe_2(CO)_6$-$(C_5H_8N_2)$ (see Schemes 7 and 8, ref. 107) and $Fe_3(CO)_9(C_5H_8N_2)$, 133. With the fluorinated azobenzenes, $C_6F_5N_2(1,2,3,4\text{-}XC_6H)$ (X = H or F), $Ru_3(CO)_{12}$ afforded[161] 134. Pyridine reacted with $Os_3(CO)_{12}$ giving[162] a series of complexes $Os_3(CO)_{10}H(NC_5H_4)$ (135, either, a or b), $Os_3(CO)_9(pyr)H(NC_5H_4)$ (also as two isomers), $Os_3(CO)_8H_2(NC_5H_4)_2$ (no fluxional) and $Os_2(CO)_6(NC_5H_4)_2$ (136, isomers a or b). The reaction pathway is outlined in Scheme 13; 4-methylpyridine behaved similarly. Isoquinoline also reacted with $Os_3(CO)_{12}$ giving a mixture of 137 and 138 (16 and 14% respectively), while quinoline afforded 138 and 139.



(132)



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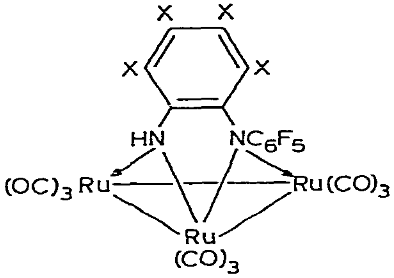
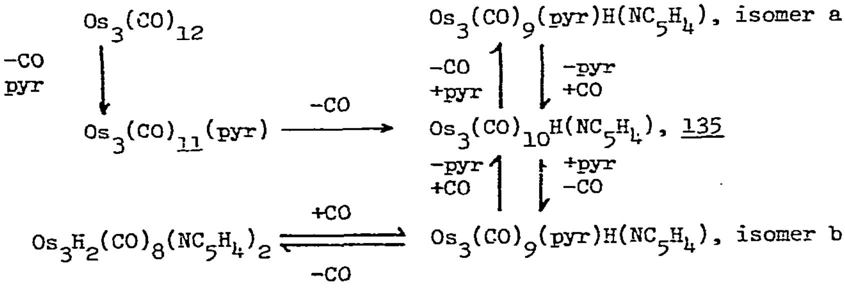
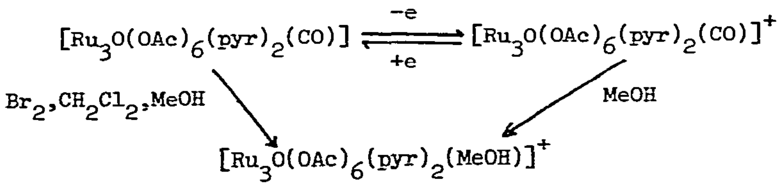


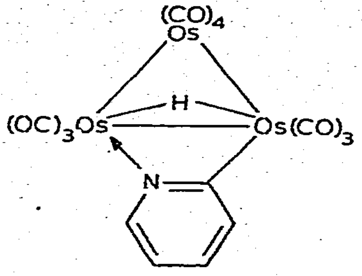
(134)

Scheme 13

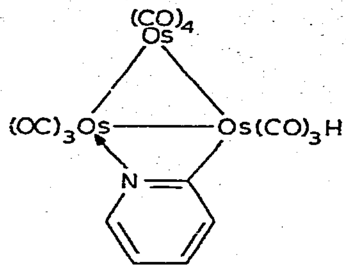


It has been found that the triruthenium oxy clusters can be oxidised as outlined below:

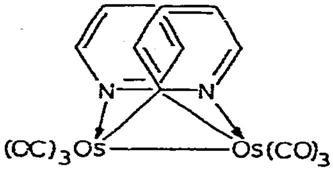




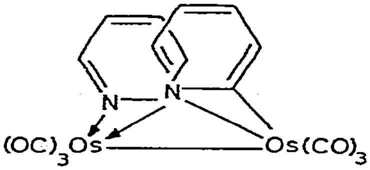
(135 a)



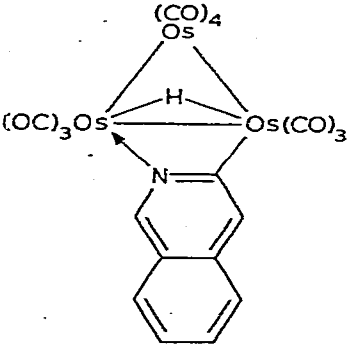
(135 b)



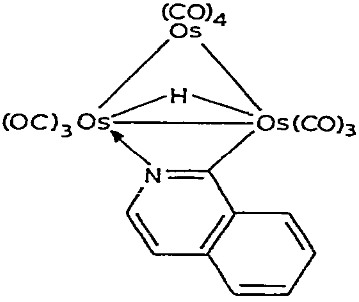
(136 a)



(136 b)



(137 a)



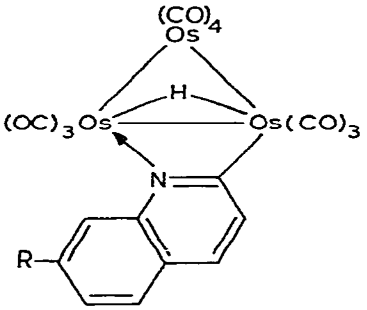
(137 b)

I.R. and mass spectral data obtained from[164] $Fe_3(CO)_6L_3S_2$ (L = pyr or $C_5H_{10}N$), $Fe_3(CO)_7L_2S_2$ (L = NEt_3, PPh_3; L_2 = bipy or o-phen) and $Fe_3(CO)_8LS_2$ (L = NCMe or PPh_3) indicates that there is strong bonding within the Fe_2S_2 group. The position of substitution in the precursor $Fe_3(CO)_9S_2$ was difficult to establish, although only one Fe atom appeared to be involved. Reaction of $Fe(CO)_5$ with $[FC(:O)S]_2$ gave[165] $Fe_3(CO)_9S_2$.

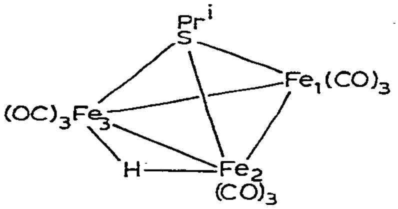
Mössbauer spectral and X-ray crystallographic studies have been made of

$Fe_3(CO)_9H(SR)$ (R = Pr^i or Bu^t), 137. The mercapto group is 1.5Å above the Fe_3 plane, while the Fe_1-Fe_2, Fe_2-Fe_3 and Fe_1-Fe_3 bond lengths are 2.65, 2.68 and 2.64Å, respectively. It was noted that arguments involving lengthening of metal-metal bonds as evidence for the presence of bridging hydride cannot be applied to cases where another bridging group imposes stereochemical constraints.

From a mixture of $RuCl_3$ and MeS_2CNEt_2 in methanol under CO which had been alllowed to stand for a week, the complex $Ru_3(CO)_3Cl_2(S_2CNEt_2)_4$ was obtained.[167] The structure of this compound, 138, was established crystallo-



(137c)



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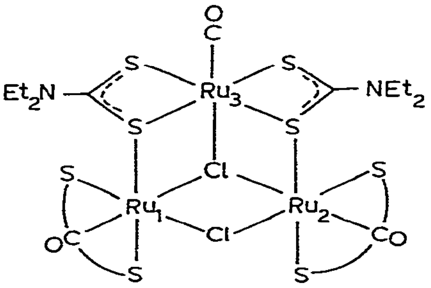

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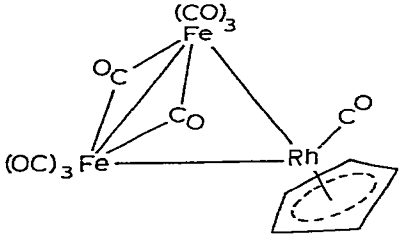

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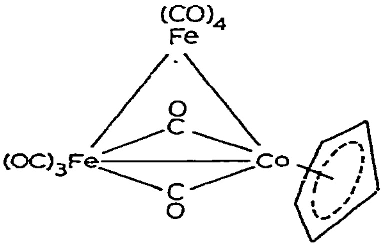

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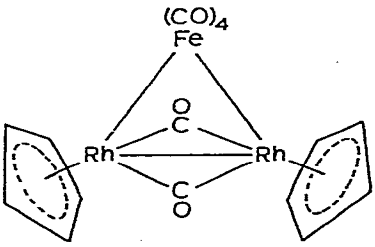

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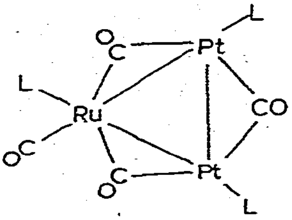
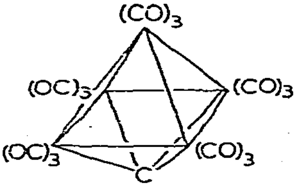


(142)

graphically; Ru_1-Ru_2 3.74, Ru_3-Ru_1, 3.70 and Ru_3-Ru_2 3.67Å, respectively.

From ^{13}C n.m.r. spectral studies it has been established[168] that $Fe_2M(\eta-C_5H_5)(CO)_9$ (M = Rh, 139; M = Co, 140) were fluxional, and limiting low temperature spectra could not be obtained. However, a spectrum consistent with the structure of $FeRh_2(\eta-C_5H_5)_2(CO)_6$, 141, was observed, and the mechanism of CO site exchange was found to be similar to that in $Fe_3(CO)_{12}$. The structure of the previously reported[169] $RuPt_2(CO)_5(PPh_2Me)_3$, 142, has been determined crystallographically.[170] The phosphine ligands attached to Pt are coplanar with the $RuPt(CO)_3$ cluster while the ligands attached to Ru are bound axially. The equatorial CO groups do not bridge the Ru-Pt bonds symmetrically, perhaps for steric reasons. The Ru-Pt bond distances are unequal (2.71 and 2.73Å), the longer bond lying opposite to the larger Pt-Ru-CO angle (Pt-Pt = 2.65Å).

When $Ru_3(CO)_{12}$ was heated at *ca.* 150° in a sealed tube, $Ru_6(CO)_{17}C$ was formed,[171] establishing that the carbide atom is derived from CO; at 180°, the carbonyl decomposes to Ru metal. On heating $Ru_3(CO)_{12}$ in benzene, very small amounts of $Ru_6(CO)_{14}(C_6H_6)C$ were formed. The implications of this work are that the carbide atoms in $Fe_5(CO)_{15}C$, $[Fe_5(CO)_{14}C]^{2-}$ and $[Fe_6(CO)_{16}C]^{2-}$ might also be derived from CO. Attempts to prepare $Fe_6(CO)_{17}C$ and $Fe_5(CO)_{15}C$ by the pyrolysis of $Fe_3(CO)_{12}$ failed. The results of pyrolysis of $Os_3(CO)_{12}$ at various temperatures are summarised in Table 3. It may be noted that the size of the metal atom cluster tends to increase with temperature, culminating in the formation of Os metal. The structures of these complexes have been predicted in terms of the "18-electron rule" and Wade's theory,[172] and the results are



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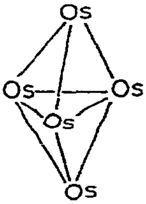

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Table 3 Pyrolysis products obtained from $Os_3(CO)_{12}$, as a function of temperature

Product	Colour	Temperatures and Yields		
		210°	250°	260°
$Os_6(CO)_{18}$	dark brown	80%	60%	–
$Os_5(CO)_{16}$	pink-red	7%	–	–
$Os_7(CO)_{21}$	orange	10%	20%	yield increased
$Os_8(CO)_{23}$	orange	2%	5%	yield increased
$Os_8(CO)_{21}C$	yellow	–	8%	–
$Os_5(CO)_{15}C$	purple	–	5%	–
Os metal		–	–	main product

included in Table 4. The structure of $Os_5(CO)_{15}C$, and its ruthenium analogue, is probably similar to $Fe_5(CO)_{15}C$, 143,[173] while in $Os_5(CO)_{16}$, 144, there may be a variable formal oxidation state for some metal atoms, as in $Os_6(CO)_{18}$, 145. For the last, the "18-electron rule" predicts an octahedral arrangement of metal atoms, which has been shown to be incorrect.[174] However, it may be noted that $Ru_6(CO)_{18}H_2$ (86 valence electrons) has an octahedral Ru_6 arrangement.[175] For $Os_7(CO)_{21}$, the "18-electron rule" predicts an edge-bridged octahedron, but the

Table 4 Structural predictions for osmium carbonyl clusters

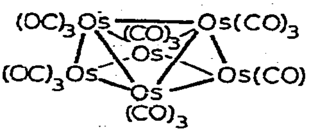
Compound	No. of Valence Electrons	No. of Os-Os bonds for cluster to obey 18-electron rule	No. of skeletal electron pairs	(a)	(b)
$Os_5(CO)_{15}C$, 143	74	$\frac{1}{2}(50-34)=8$	7(n+2)	sq. based prism	sq. based prism
$Os_5(CO)_{16}$, 144	72	$\frac{1}{2}(50-32)=9$	6(n+1)	tbp[c]	tbp[c]
$Os_6(CO)_{18}$, 145	84	$\frac{1}{2}(60-36)=12$	6(n)	reg. octa.	
$Os_7(CO)_{21}$, 146	98	$\frac{1}{2}(70-42)=14$	7(n)	edge bridged octa	monocapped octa
$Os_8(CO)_{23}$ 147 $Os_8(CO)_{21}$ 148	110	$\frac{1}{2}(80-46)=17$	7(n-1)	edge and face-bridged octa. or bicapped tp[d]	

[a] If 18-electron rule is obeyed by *each* metal atom and bridging carbonyls may be involved;

[b] According to Wade's rules (ref. 172);

[c] tbp = trigonal bipyramid;

[d] tp = trigonal prism.



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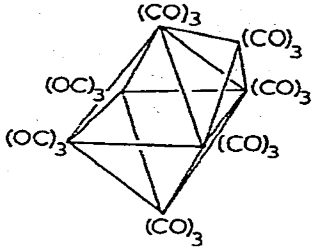

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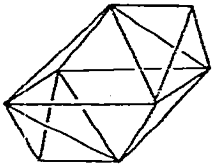
isoelectronic $[Rh_7(CO)_{16}]^{3-}$ has been found[176] to contain a monocapped octahedral Rh_7 cluster; preliminary X-ray crystallographic studies appear to confirm this situation in $Os_7(CO)_{21}$. For $Os_8(CO)_{23}$, two alternatives, 147 and 148, have been proposed, and $Os_8(CO)_{21}C$ could have either structure with the carbon atom in the centre of either cluster. ^{13}C n.m.r. spectral studies have shown[177] that $Os_6(CO)_{18}$, while maintaining its bicapped tetrahedral structure in solution up to 100°, undergoes three fluxional processes corresponding to localised CO scrambling. These are a low temperature localised site exchange about Os(3) and Os(3'), a mid-temperature localised site exchange about Os(3), Os(3'), Os(2) and Os(2') and, at 100°, complete localised CO scrambling about each metal atom. It



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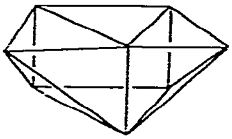
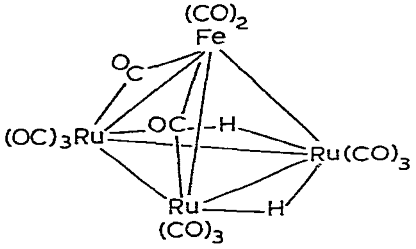


(148)

was observed that CO migration does not occur in this molecule although it has been observed in $Os_3(CO)_{12}$[178] and this is thought to be due to the relative intermetallic distances in the molecule (CO bridges do not commonly occur in osmium carbonyl complexes). It was noted that ^{13}CO enriched $Os_6(CO)_{18}$ could not be prepared by ^{13}CO exchange with the complex, but was produced by pyrolysis of enriched $Os_3(CO)_{12}$. Reduction of $Os_6(CO)_{18}$ with zinc dust afforded $[Os_6(CO)_{18}]^{2-}$ which, on the basis of ^{13}C n.m.r. spectral data, appears to have an octahedral Os_6 cluster as predicted by Wade's theory.

Hydrogenation, at atmospheric pressure and 120°, of $M_3(CO)_{12}$ (M = Ru and Os) in hydrocarbon solvents afforded[179] good yields of pure $M_4(CO)_{12}H_4$. Reaction of $Os_3(CO)_{10}H_2$ with more hydrogen gave $Os_4(CO)_{12}H_4$, and $Ru_4(CO)_{12}D_4$ was prepared using D_2; extensive H/D was observed between $Os_4(CO)_{12}D_4$ and hydrocarbon solvent. Treatment of $Ru_4(CO)_{13}H_2$ with D_2 gave $Ru_4(CO)_{12}H_2D_2$ and $FeRu_3(CO)_{12}H_4$ was obtained similarly from $FeRu_3(CO)_{13}H_2$ but reaction of

$FeRu_2(CO)_{12}$ with H_2 failed to provide a mixed metal carbonyl hydride cluster. The thermal decomposition of a variety of Ru_4 carbonyl hydride clusters, viz. α-$Ru_4(CO)_{12}H_4$, $Ru_4(CO)_{10}L_2H_4$ (L = PPh_3), $Ru_4(CO)_9L_3H_4$ (L = PPh_3 or PBu^n_3), and $Ru_4(CO)_8L_4H_4$ (L = PPh_3 or PBu^n_3) has been investigated.[180] The data suggest release of CO and phenyl or butyl groups leading to the formation of phosphorus-containing metallic residues.



(149)

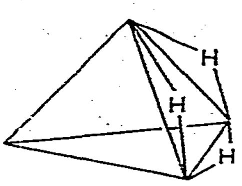
^{13}C n.m.r. spectral studies of $FeRu_3(CO)_{13}H_2$, 149, have revealed[181] that there are three fluxional activities associated with the CO groups. These are (i) a bridge opening process at Fe, the CO moving to Fe, and localised CO scrambling, (ii) localised CO scrambling at the three Ru atoms, and (iii) a general CO exchange between all metal atoms.

Treatment of $Ru_4(CO)_{12}H_4$ with alcoholic KOH gave[182] $[Ru_4(CO)_{12}H_3]^-$ (isolated as the Ph_4As^+ salt). Raman spectra indicated the presence of bridging hydride ligands while n.m.r. spectral data revealed the presence of two isomers with several possible structures, e.g. 150 a, b or c or 151 a or b.

Reaction of $Fe_5(CO)_{15}C$ with phosphines or phosphites (L = PPh_3, PMe_2Ph, $P(OPr^n)_3$ or $P(OPh)_3$) gave $Fe_5(CO)_{15-n}L_n$ (n = 1-3). While the carbide was unaffected by strong acid it reacted with PhC≡CPh and MeC≡CPh with fragmentation of the cluster giving $Fe_2(CO)_6(RC_2R')_2$ and $Fe_3(CO)_9(RC_2R)$. Reduction of the carbide cluster with NaOH, $NaBH_4$ or Na/Hg afforded $[Fe_5(CO)_{14}C]^{2-}$ and it was observed that the i.r. spectrum of this salt is at variance with that previously reported for $[Fe_5(CO)_{14}C]^{2-}$ obtained[184] from reaction of $Fe(CO)_5$ with $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^-$. This latter product has been reformulated as $[Fe_6(CO)_{16}C]^{2-}$.

Acetylenes (RC_2R'; R = Ph, R' = Me, Et or Ph; R = R' = CH_2OMe) reacted[185] with $Ru_2(CO)_{12}$ giving $Ru_4(CO)_{12}(RC_2R')$, 152, which could be protonated to give $[Ru_4(CO)_{12}H(RC_2R')]^+$ (edge bound H^+). Further treatment of 152 with PhC_2R'' (R'' = Me or Et) gave 153 (tentative proposal), and it was noted that 152 (R = R' = Ph), in refluxing heptane under hydrogen, gave $Ru_4(CO)_{12}H_4$ and *trans*-stilbene.

Reaction of $Fe_3(CO)_{12}$ with 2-mercaptopyridine gave 154 (Fe(1)-Fe(2)



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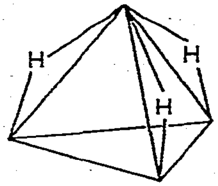

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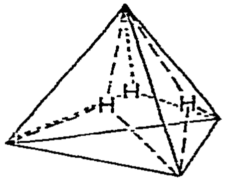

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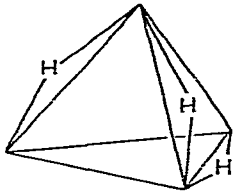

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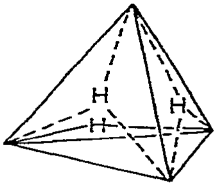
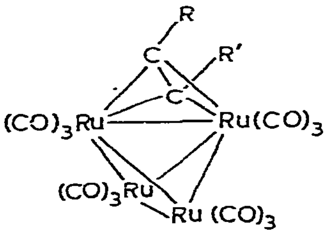


(151 b)

2.60Å, Fe(3)-Fe(4) 2.53Å); the S atom has tetrahedral geometry. Treatment of $Fe_2(CO)_6S_2$ with PhSSPh, PhSH and NaOMe in methanol gave $[Fe_4S_4(SPh)_4]^{2-}$, (basic structure 155) while using $[p\text{-}Me_3NC_6H_4S]_2[PF_6]_2$, $[Fe_4S_4(SC_6H_4NMe_3)_4][PF_6]_2$ was found. A similar reaction using 2,2'-bis(benzo[d]thiazoline)4,4'-dinitrophenyl disulfide gave 156 as a dianion.

Treatment of $FeCo_3(CO)_{12}H$ with $P(OMe)_3$ gave $FeCo_3(CO)_{12-n}\{P(OMe)_3\}_n$



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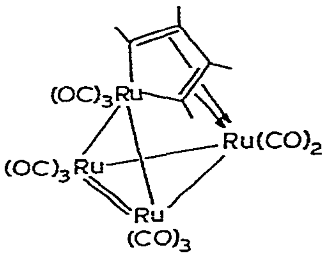

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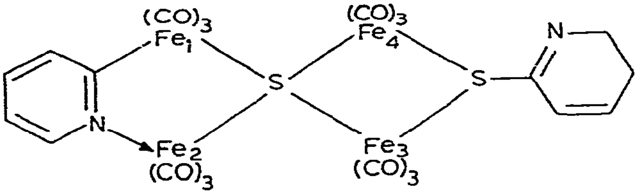

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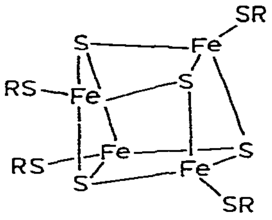

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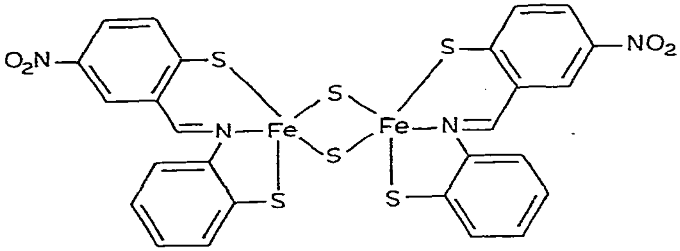
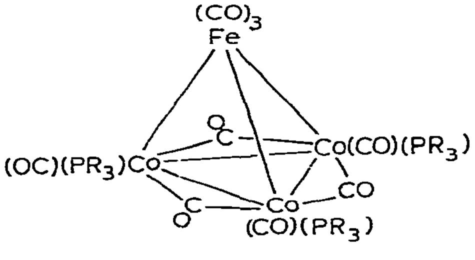


(156)

(n = 1-4), and the structure of the complex where n = 3, <u>157</u>, has been determined[188] crystallographically. The hydride ligand lies on the three-fold axis and is 0.75Å out of the Co_3 plane; Fe-Co = 2.56Å and Co-Co = 2.49Å. Similar phosphine complexes $FeCo(CO)_{12-n}L_n$ (L = PPh_3, $PMePh_2$, PEt_3, $P(OPh)_3$, $P(OPr^n)_3$, and L_2 = $Ph_2PCH_2CH_2PPh_2$, n = 1-3) have been reported,[189] and Mössbauer spectral data have revealed that substitution takes place preferentially at cobalt, each Co atom being successively substituted to give $FeCo_3(CO)_9L_3H$. The complex $FeCo_3(CO)_8(Ph_2PCH_2CH_2PPh_2)H$ exists as a mixture of isomers, one of which has substitution at the Fe atom.



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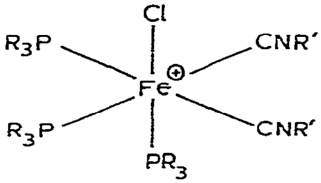
METAL ISOCYANIDES

Treatment of $FeCl_2$ with $PPh(OEt)_2$ and RNC (R = C_6H_5, p-RC_6H_4 (R = Me, OMe, NO_2), o-MeC_6H_4 and 2,6-$Me_2C_6H_3$) gave[190] $[Fe(CNR)_2\{PPh(OEt)_2\}_3Cl]^+$, <u>158</u> while with

PPh_3 and p-MeC_6H_4NC, $[Fe(CNR)_3(PPh_3)_2Cl]^+$, 159 (two possible isomers; a favoured on i.r. spectral basis), was formed. With $C_6H_{11}NC$ and $PPh(OEt)_2$, $FeCl_2$ afforded $[Fe(CNC_6H_{11})_3\{PPh(OEt)_2\}_3]^{2+}$, 160. Mössbauer and i.r. spectral data were compiled for these compounds. The isocyanide adducts of ferrous phthalocyanin, FeLL'Pc, (L = L' = $C_6H_{11}NC$, Bu^nNC; L = $C_6H_{11}NC$, L' = N-methylimidazole) have been reported.[191]

Reaction of the Fe(IV) complex, $[Fe(S_2CNEt_2)_3]^+$, with CNR (R = Pr^i, Bu^t or p-ClC_6H_4) gave $[Fe(CNR)_4(S_2CNEt_2)]^+$, which could be electrochemically oxidised to a dication. Treatment of $Fe(S_2CNEt_2)_3$ with CNR afforded the stereochemically rigid *cis*-$Fe(CNR)_2(S_2CNEt_2)_2$, which could be voltammetrically oxidised to a monocation.



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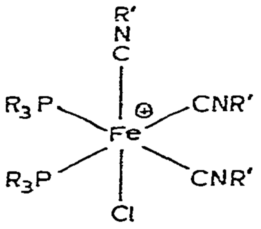

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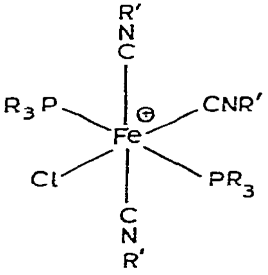

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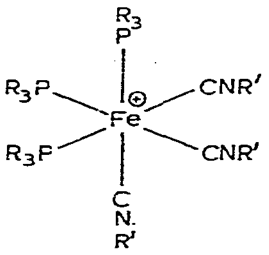

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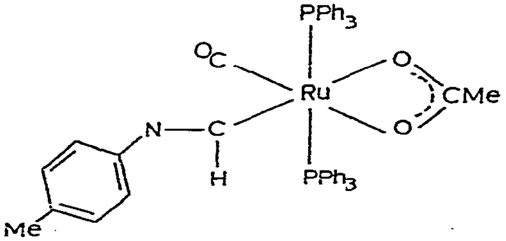


(161)

Carbene species derived from isocyanide complexes. The structure of the complex $Ru(CO)(p\text{-}MeC_6H_4NCH)(PPh_3)_2OAc$, 161, obtained[193] by treatment of $Ru(CO)\{CN\text{-}(p\text{-}MeC_6H_4)\}(PPh_3)_2(O_2)$ with ethanol, has been determined[194] crystallographically. The Ru-C (carbene) distance, 1.96Å, is only a little shorter than that estimated for a Ru-C(sp^2) bond (2.00Å). Thus, the Ru-C (carbene) bond order is close to unity, and the C-N distance (1.24Å) is shorter than that expected for bond order 2. The Ru-C-N bond angle is 135°.

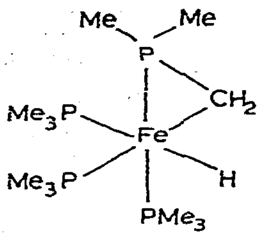
From Mössbauer spectral data, it has been estimated[195] that in $[Fe(CNMe)_5(carbene)]^{2+}$, and $[Fe(CNMe)_4(carbene)_2]^{2+}$, (carbene = $RNH\ddot{C}N(R')\ddot{C}NHR'$ and $RNH\ddot{C}NHNH\ddot{C}NHR'$), the carbene ligands are very good σ-donors and relatively poor π-acceptors. They are better σ-donors and poorer π-acceptors than CNMe.

PHOSPHINE AND PHOSPHITE COMPLEXES

Photoelectron spectroscopic studies of $M(PF_3)_5$ (M = Fe or Ru) have shown[196] that PF_3 is a stronger electron-withdrawing ligand than CO. The phosphite complexes $Fe\{P(OR)_3\}_5$ (R = Me, Et or Pr^n), prepared[197] by reduction of $FeBr_2$ by Na/Hg in the presence of $P(OR)_3$ in THF, are fluxional, undergoing Berry rotations, as expected. ^{31}P n.m.r. spectral studies showed that the barrier of rotation increased with increasing length of the substituent R, indicating that steric crowding in the transition state is important.

Reduction of $Fe(PMe_3)_2Cl_2$ with Na/Hg or Mg in the presence of PMe_3 afforded[198] 162 which appears to be in equilibrium with $Fe(PMe_3)_4$. This complex reacted with hydrogen giving $Fe(PMe_3)_4H_2$, and with PF_3 affording the fluxional $Fe(PF_3)_2(PMe_3)_3$, in which the PF_3 ligands are equatorial. There is also some evidence for the equilibrium $Fe(PMe_3)_4 + PMe_3 \rightleftharpoons Fe(PMe_3)_5$. Reduction of $Fe(PMe_3)_2Cl_2$ in the presence of butadiene gave $Fe(PMe_3)(\eta^4\text{-}C_4H_6)_2$, while reduction in the presence of acetonitrile afforded first $[Fe(PMe_3)_3(NCMe)_3]^{2+}\text{-}[FeCl_4]^{2-}$, and then 163. Reduction of $Fe(PMe_3)_2Cl_2$ in the presence of $MeC{\equiv}CMe$ gave 164 together with hexamethylbenzene, and $Fe(PMe_3)_4$ catalysed the trimerisation of $MeC{\equiv}CMe$ as well as the oligomerisation to tetra-, penta- and hexa-mers.

Triple chloro-bridged binuclear complexes of ruthenium containing PF_3 and/or CO have been prepared[199] as outlined in Scheme 14. The complex 165 (L = PF_3) can also be prepared from a mixture of $Ru(PPh_3)_3Cl_2$ and *cis*-$Ru(PF_3)_2(PPh_3)_2Cl_2$. Treatment of $(Ph_3P)_2(CO)Ru(\mu_2\text{-}Cl)_3Ru(PPh_3)_2Cl$ with PF_3 gave $(Ph_3P)_2(CO)Ru(\mu_2\text{-}Cl)_3Ru(PF_3)(PPh_3)Cl$, while, under certain conditions, PF_3 reacted with $Ru(PPh_3)_3Cl_2$ giving $(Ph_3P)_2(F_3P)Ru(\mu_2\text{-}Cl)_3Ru(PPh_3)_2Cl$. The complex $(Ph_3P)_2(F_3P)Ru(\mu_2\text{-}Cl)_3Ru(PF_3)(PPh_3)Cl$ exists as three isomers (166, a 74%, b 16% and c 10%).



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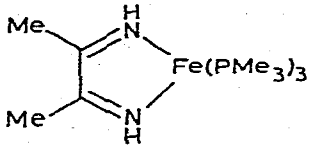

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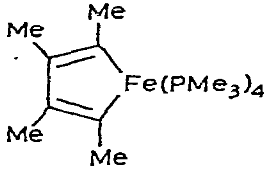

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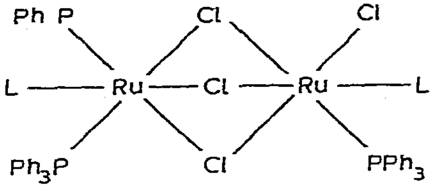

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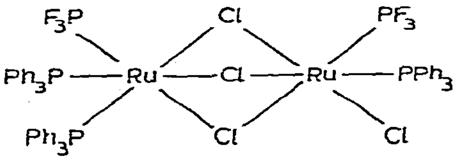

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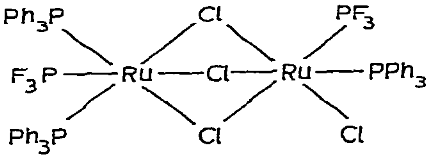

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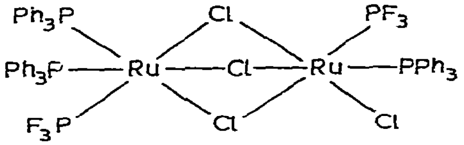

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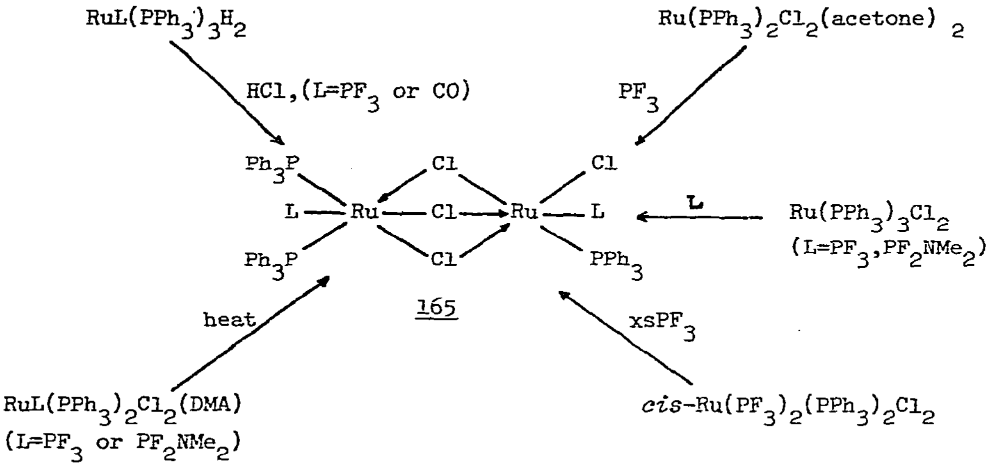
METAL NITROSYL AND ARYLDIAZO COMPLEXES

Mononitrosyl Compounds. ESCA studies of nitrosyl complexes provide[200] a complementary method to i.r. spectroscopy for attempting to distinguish between bent and linear M-N-O groups. Among the iron and ruthenium complexes studies were $Na_2[Fe(NO)(CN)_5].2H_2O$, $Fe(NO)(S_2CNMe_2)_2$, $Ru(NO)(S_2CNMe_2)_3$, $Ru(NO)(PPh_3)_3H$, $Ru(NO)(PPh_3)_2Cl_3$ and $[Ru(NO)_2(PPh_3)_2Cl]BF_4$. The relative shifts of the binding

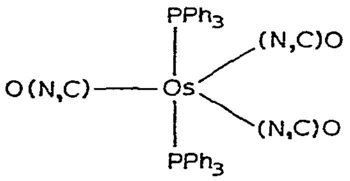
Scheme 14



energies of the O 1s and N 1s electrons fell in the range 132 ± 1 eV for linear M-N-O and 128 ± 2 eV for bent M-N-P. These assignments are a reversal of previous assignments[201] of N 1s binding energies in nitrosyl complexes. Evaluation of the N 1s binding energies illustrates that the "NO^-" in a bent nitrosyl complex actually may have less electron density associated with the N atom than "NO^+" in a linear nitrosyl system.

Treatment of $Na[Fe(CO)_4H]$ with $AgNO_3$ in aqueous methanol gave[202] $[Fe(CO)_4HAg]AgNO_3$, and a similar reaction with $Na[Fe(CO)_2(NO)\{P(OPh)_3\}]$ afforded $[\{Fe(CO)_2(NO)[P(OPh)_3]\}Ag]_n$. This latter compound reacted with o-phenanthroline giving $[\{Fe(CO)_2(NO)[P(OPh)_3]\}Ag(o\text{-}phen)]_n$.

The structure of the known[203] $[Os(CO)_2(NO)(PPh_3)_2][ClO_4]$, 167, has been determined crystallographically;[204] it was not possible to differentiate the CO and NO groups because of statistical disordering.. Treatment of $Os(CO)(PPh_3)_3HCl$ with $p\text{-}MeC_6H_4SO_2N(NO)Me$ gave[205] $Os(CO)(NO)(PPh_3)_2Cl$, which, on reaction with $AgPF_6$ in acetone, afforded $[Os(CO)(NO)(PPh_3)_2(acetone)][PF_6]$. This is a useful intermediate giving, with ethylene, $[Os(CO)(NO)(PPh_3)_2(C_2H_4)]$, 168. From ^{13}C n.m.r. studies, it has been established unequivocally that the olefin undergoes



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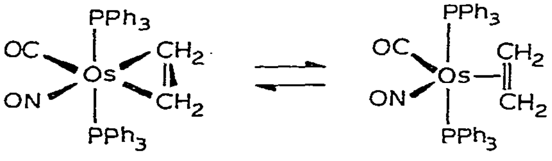

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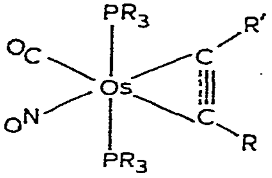
rotation about the $Os\text{---}\overset{C}{\underset{C}{\|}}$ bond and not about the C-C bond ($\Delta G^{\neq}$ 9.5 ± 0.2 kcal/mol). Treatment of $[Os(CO)(NO)L_2(acetone)][PF_6]$ ($L = P(C_6H_{11})_3$ or PPh_3) with acetylenes afforded[206] $[Os(CO)(NO)L_2(RC_2R')][PF_6]$, 169 (R = R' = H, Ph or CO_2Me; R = H, R' = Ph). These species, like their ethylene analogue, 168 are fluxional, undergoing rotation about the $Os\text{---}\overset{C}{\underset{C}{|||}}$ bond ($\Delta G^{\neq}$ ranges from 11.5 - 14.4 kcal/mol).



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Treatment of $Na_2[Fe(NO)(CN)_5].2H_2O$ with α,α'-bipyridyl gave[207] *cis*- and *trans*-$Fe(NO)(bipy)(CN)_3$. The products of the one-electron reduction of $[Fe(NO)(CN)_5]^{2-}$ to $[Fe(NH_2OH)(CN)_5]^{3-}$ have been characterised[208] spectroscopically. These include $[Fe(NO)(CN)_5]^{3-}$ (unpaired electron on NO), $[Fe(NHO)(CN)_5]^{4-}$ and $[Fe(NO)(CN)_5]^{4-}$. These reduction processes resemble the stepwise reversible reduction of nitrobenzene to phenylhydroxylamine in alkali. A reversible reaction occurs between mercaptide ion and nitroprusside, viz.

$$[Fe(NO)(CN)_5]^{2-} + RS^- \rightleftharpoons [Fe\{N(O)SR\}(CN)_5]^{3-}$$

The adduct decomposes irreversibly to give $[Fe(NO)(CN)_5]^{3-}$ and is thought to contain the group $Fe\text{---}\overset{+}{N}\genfrac{}{}{0pt}{}{\lessdot O}{\diagdown SR}$.

In 0.1 M NaOH over 7 days, $[Ru(NO)(NH_3)_5]^{3+}$ afforded $[Ru(NH_3)_5(N_2)]^{2+}$ (25%), *cis*-(11%) and *trans*-$[Ru(NO)(NH_3)_4(OH)]^{2+}$ (8%). The mechanism of this reaction may be as follows:

$$[Ru(NO)(NH_3)_5]^{3+} + OH^- \rightleftharpoons [Ru(NO)(NH_3)_4(NH_2)]^{2+}$$

$$\begin{array}{r}
[Ru(NO)(NH_3)_5]^{3+} + [Ru(NO)(NH_3)_4(NH_2)]^{2+} \rightarrow [(NH_3)_5Ru\{N(:O)NH_2\}Ru(NO)(NH_3)_4]^{5+} \\
\Big\downarrow {\scriptstyle OH^-} \quad\quad \\
[Ru(NH_3)_5(N_2)]^{2+} + [Ru(NO)(NH_3)_4(OH)]^{2+}
\end{array}$$

At high pH values in air $[Ru(NH_3)_6]X_3$ (X = Cl or Br) was oxidised[210] to $[Ru(NO)(NH_3)_5]^{3+}$. In the presence of $^{15}NH_3$, the only nitrosylated product was $[Ru(^{14}NO)(NH_3)_5]^{3+}$, indicating that only coordinated ammonia is oxidised; there is no $^{14}NH_3/^{15}NH_3$ exchange between $[Ru(^{14}NH_3)_6]^{3+}$ and $^{15}NH_3$. Reaction of

$[Ru(NO)(NH_3)_5]^{3+}$ with an excess of $[Ru(NH_3)_6]^{3+}$ in the presence of OH^- gave *trans*-$[Ru(NO)(NH_3)_4(OH)]^{2+}$ in a process which is markedly pH-dependent. Radiolysis of $[Ru(NO)(NH_3)_5]^{3+}$ in aqueous t-butanol gave[211] $[Ru\{N(:O)\text{-}CH_2CMe_2(OH)\}(NH_3)_5]^{2+}$, a complex of an alkynitroso ligand. The alkylation is viewed as occurring via $^{\cdot}CH_2CMe_2(OH)$ generated by attack of hydroxyl radicals on t-butanol. The complex can be regarded as either $Ru^{II}\text{-}N(:O)R$ or $Ru^{III}\text{-}N(:O^{\cdot})R$.

The complexes $[Ru(NO)(bipy)_2X]^{z+}$ ($z = 2$, $X = N_3$, Cl, NO_2; $z = 3$, $X = NH_3$, pyridine or MeCN) underwent[212] a voltammetrically reversible one-electron reduction followed by an irreversible one-electron process. Chemical reduction of the nitrosyl gave $[Ru(NO)(bipy)_2Cl]^+$ or $[Ru(NO)(bipy)_2(NCMe)]^{2+}$, and it seems clear that the first electron transfer process is associated mainly with the NO ligand. Photolysis of $[Ru(NO)(bipy)_2Cl]^{2+}$ in acetonitrile gave $[Ru(bipy)_2(NCMe)Cl]^{2+}$. It was suggested that the redox properties of these ruthenium complexes could be regarded as consistent with the NO being present as a modified nitrosonium ion.

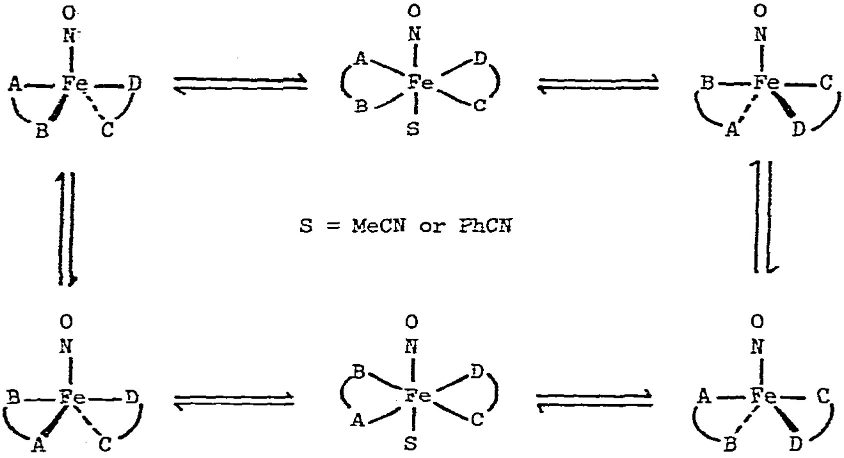
Protonation of $Na_2[Ru(NO)(NO_2)_4(OH)]$ gave[213] $Ru(NO)(NO_2)_2(OH)(H_2O)_2$ which reacted with 1,3-dimethylbarbituric acid (HL) affording $Ru(NL)L(NO_2)(OH)(H_2O)$ and *trans*-$Ru(NO)L_2(OH)$. Attack by OH^- on the latter gave $[Ru_2(NO_2)(OH)]^{2-}$ which produced, on addition of more barbituric acid, $RuL_3(OH)$. Attack on this hydroxide by NO_2^- and acid gave $[Ru(NO)L_3]2H_2O$, and further NaOH led to the formation of $Na_2[RuL_3(NO_2)]$.

Treatment of $Fe(CO)_5$ with iodine and α,γ-dimethyl-α,γ-dihydrooctaethyl porphyrin (H_2L) gave[214] LFe-O-FeL which afforded, with NO, Fe(NO)L. By reductive nitrosylation (NO/KOH/pyridine) of Fe(TPP)Cl (TPP^{2-} = tetraphenylporphyrinate) Fe(NO)(TPP) was formed.[215] From X-ray crystallographic studies it was established that the Fe-N-O bond angle was bent (149°), and that the Fe atom was displaced from the coplanar porphyrinato N atoms by 0.21Å. A series of other porphyrin and heme complexes have been nitosylated[216] using NO or HNO_2, and it was found that nitrosylheme complexes could nitrosylate secondary amines (e.g. $Ph_2NH \rightarrow Ph_2NNO$). Resonance Raman spectral studies have been made[217] of the NO adduct of haemoglobin.

Treatment of $M(NO)_2(PPh_3)_2$ (M = Ru or Os) with RCO_2H ($R = CF_3$ or C_2F_5) afforded[218] $Ru(NO)(PPh_3)_2(OCOR)_3$ and either $Os(NO)(PPh_3)_2H(OCOR)_2$ or $[Os(NO)_2(PPh_3)_2(OCOR)][OCOR]$, depending on solvent. Prolonged treatment of $Os(NO)(PPh_3)_2H(OCOR)_2$ with RCO_2H did not give the tri-carboxylate. It was suggested that the mechanism of formation of these complexes involved protonation of NO.

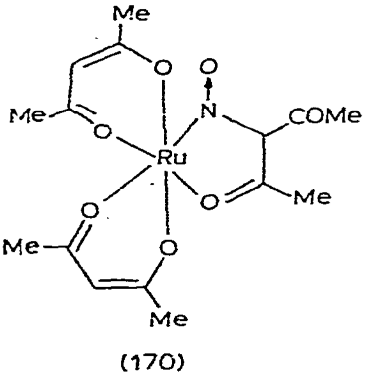
Reaction of $Fe(diars)_2Cl_2$ (diars = o-phenylenebis(dimethylarsine) with $NaBPh_4$ under CO gave[219] $[Fe(CO)(diars)_2Cl][BPh_4]$, while with NO, $[Fe(NO)(diars)_2Cl][BPh_4]$ was formed. The nitrosyl could also be obtained by acidolysis of $Fe(diars)_2Cl(NO_2)$. Zinc reduction of $[Fe(H_2O)_6][ClO_4]_2$ in the presence of diars and NO gave the blue $[Fe(NO)(diars)_2][ClO_4]_2$ which could be further reduced by Jones reduction affording $[Fe(NO)(diars)_2][ClO_4]$. Salts of the latter could also be prepared by a Jones reduction of the product of nitrosylation of $Fe(diars)_2Cl_2$ or $[Fe(NO)(diars)Cl]Cl_2$. The monocation, $[Fe(NO)(diars)_2]^+$ is diamagnetic, is thought to have trigonal bipyramidal geometry and is fluxional (figure 16).

Figure 16



S = MeCN or PhCN

Reaction of $Ru(NO)^{3+}$ salts with acetylacetone gave[220] $Ru(acac)_2(hia)$, 170 (Hhia = (3-hydroxyimino)acetylacetone), $Ru(NO)(acac)_2Cl$, and $[Ru(NO)(acac)_2]_4$, the last of which is said to contain bridging NO. Treatment of $Ba[Ru(LH_2)_3]_2$ with $NaNO_2$ gave[221] $Ru(NO)(LH_2)_3$ or $Ru(NO)(LH_2)_2X$ (LH_3 = 171). When the pH of a solution containing $[NH_4]_2[Os(NO)Cl_5]$ was adjusted[222] to 12 by KOH, followed by treatment with HCl, $Os(NO)(OH)_3.2H_2O$ was formed.



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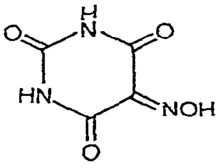

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An LCAO molecular orbital study has been made[223] of the mutual effect of ligands in $[Ru(NO)X_5]^z$ complexes. It was noted that the NO group stabilises the *trans*-Ru-X bond (X = H_2O, NH_3, Cl or CN). Addition of HX and QX (Q = NH_4, K, Rb, Cs, $(C_7H_{17})_3NH$; X = Cl, Br or I) to $Na_2[Os(NO)(NO_2)_4(OH)]$ led to the formation[224] of $Q_2[Os(NO)X_5]$.

Dinitrosyl Complexes. Reaction of $[Fe(CO)_4]^{2-}$ with NOCl gave[225] $Fe(CO)_2(NO)_2$ which afforded, with an excess of nitrosyl chloride, $Fe(NO)_3Cl$, also obtainable directly from $Fe(CO)_5$ and NOCl. Treatment of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ with NOCl in THF gave only $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, while this dimer and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnPh_3$ reacted with NOCl giving $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SnCl_nPh_{3-n}$ (n = 0-3), respectively. With $[Et_4N][SnCl_3]$, $Fe(NO)_2L_2$ (L = CO or PF_3) gave[226] $[Et_4N]_2[Fe(NO)_2(SnCl_3)_2]$, and it was observed that $SnCl_3^-$ has π-acceptor properties similar to PCl_3. Reaction of $Hg[Fe(CO)_3(NO)]_2$ with $(\eta^5\text{-}C_5H_5)_2M(ER)_2$ (M = Ti, ER = SMe, SEt, SeMe, SePh, TePh; M = Nb, ER = SPh, SePh, TePh) afforded[227] the diamagnetic $(\eta^5\text{-}C_5H_5)_2M(\mu_2\text{-}ER)Fe(NO)L$ (M = Ti, L = NO; M = Nb, L = CO).

The structure of the previously reported[228] $[Os(NO)_2(PPh_3)_2(OH)][PF_6]$, 172, has been determined crystallographically. The apical Os-N-O bond angle is 133.6° while the equatorial angle is 177.6°. The structure is comparable with that of $[Ru(NO)_2(PPh_3)_2Cl]^+$ (apical Ru-N-O 138°).[230] The structure of $Os(NO)_2(PPh_3)_2.\frac{1}{2}C_6H_6$ has been established crystallographically.[231] The molecule has pseudo tetrahedral geometry and although this configuration was rationalised in terms of $Os(-II)(d^{10})/NO^+$ system, ESCA studies revealed that the NO groups have

Table 5 Structural data obtained from complexes of the type $M(NO)_2LL'$

Complex	M-N (Å)	M-P (Å)	N-O (Å)	MNO (°)	NMN (°)	LML' (°)
$Fe(NO)_2(CO)(PPh_3)$[a]	1.69-1.73	2.26	1.15	177-179	113-117	104
$Fe(NO)_2(diphos)$[b,c]	1.66,1.65	2.24,2.25	1.18,1.18	178.8	125	87
$Fe(NO)_2(PPh_3)_2$[d]	1.65	2.27	1.19	178.2	124	112
$Ru(NO)_2(PPh_3)_2$[e]	1.76,1.78	2.34,2.35	1.19,1.19	178,171	139	104
$Os(NO)_2(PPh_3)_2$	1.78,1.77	2.32,2.34	1.20,1.21	179,174	139	104

[a] Disorder CO and NO ligands; V. G. Albano, A. Araneo, P. L. Bellon, G. Ciani, and M. Manassero, J. Organometal. Chem., 67 (1974) 413;

[b] diphos = $Ph_2P\overline{C{=}C(PPh_2)CF_2CF_2C}F_2$;

[c] W. Harrison, and J. Trotter, J. Chem. Soc. A, (1971) 1542;

[d] Reference as in (a);

[e] A. P. Gaughan, B. J. Corden, R. Eisenbere, and J. A. Ibers, Inorg. Chem., 13 (1974) 786.

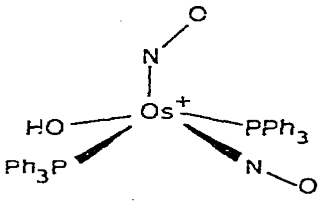
a large amount of negative charge. The structure of the compound may be compared with that of other similar complexes (Table 5). A number of general rules concerning coordination geometries of transition metal nitrosyls, especially 5-coordinate species, were proposed. These are as follows:

(i) without the assistance of special ligands, first row transition metals do not usually have enough reducing power by themselves to cause M-N-O bond angle bending; second row metals often do, and third row metals usually do. Thus $Fe(CO)(NO)(PPh_3)_2Cl$ has trigonal bipyramidal (TBP) geometry[232] (linear Fe-N-O) whereas the related Ru and Os complexes should be square pyramidal (SP) (bent M-N-O). However, $Ru(CO)(NO)(PPh_3)_2I$ may be an exception[233] to this rule since ν(NO) is very dependent on X (halide) and so also may be the geometry of the complex;

(ii) the number and size of bulky ligands plays an important role in structure determination: they usually occupy the least hindered positions and hence when one such large ligand is present it usually occupies a non-axial position. Two bulky ligands prefer to be *trans* to each other (axial in TBP and non-axial in SP) while with three, SP geometry is not known, all occupying equatorial positions in TBP. Thus $Os(CO)(NO)(PPh_3)_2Cl$ has *trans*- non-axial PPh_3 ligands in SP geometry;

(iii) strong π-acceptor ligands such as CO and NO, and also σ-donors with large *trans*- influence (H and bent NO) prefer not to be *trans* to each other (isocyanide complexes may be similar in behaviour to phosphine complexes). Although hydride ligand normally prefers to be *trans* to PR_3 in preference to NO, the steric bulk of three phosphine ligands may overcome this. Thus $Ru(NO)(PPh_3)_3H$[235] and $[Os(CO)(NO)(PPh_3)_3]^+$[236] have equatorial PPh_3 in TBP geometry, $[Os(CO)_2(NO)(PPh_3)_2]^+$[236] and $[Os(NO)_2(PPh_3)_2H]^+$ have trigonal bypyramidal structures, but $[Os(NO)_2(PPh_3)_2Cl]^+$[238] is like $[Os(NO)_2(PPh_3)_2(OH)]^+$, 172, in having SP geometry (one bent NO group);

(iv) bidentate ligands such as $Me_2NCH_2CH_2NMe_2$, o-phenanthroline, α,α'-bipyridyl, o-phenylenebis(dimethylarsine) and $Ph_2PCH_2CH_2PPh_2$ usually favour TBP structures with equatorial NO when two such ligands are present. Because of their small bite angles they prefer to span axial-equatorial sites rather than two equatorial sites. Also, because of unfavourably close ligand-ligand contacts, if two ligands are to occupy four coordination positions in one plane, TBP geometry is favoured over SP. This rule may not apply to xanthates, dithio-



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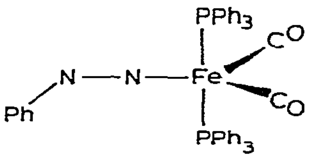


(173)

carbamates or $MeSCH_2CH_2S$ which is sterically less bulky. Thus $[Ru(NO)(Ph_2PCH_2CH_2PPh_2)_2]^+$ has a TBP structure;[239]

(v) special multidentate ligands promote one geometry over another. For example, $HC(CH_2PPh_2)_3$ stabilises a trigonal bipyramid while tetraphenylporphyrinate stabilises square pyramidal or axial-equatorial-axial TBP geometry;

(vi) ligands which deactivate the metal by removing electron density from it, thereby decreasing its reducing power, favour TBP geometry. An excessive number of CO or olefinic ligands, without the presence of strong σ-donors, will deactivate the metal. Replacing Cl by OCOR (R = perfluro-alkyl or -aryl) could shift the electronic balance and also effectively deactivate the metal;

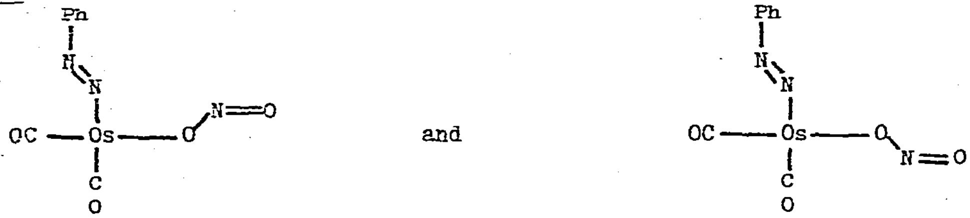
(vii) the "16-18 electron rule" is almost an infallible guide for all common coordination numbers. Occasionally "17 and 18-electron" complexes are formed by 4- and 5-coordinate species. If the integrity of NO is maintained (i.e. it is not converted to a hyponitrite ion), all "20-electron" systems must contain bent NO. Six-coordinate "17- and 18-electron" complexes contain linear NO groups; e.g. $Os(NO)(PPh_3)_2Cl_3$.[240] Six-coordinate species having "19-electron" configurations probably have a "partially" bent NO group with M-N-O distinctly larger than 120°, e.g. as in $[Fe(NO)(diars)_2Cl]^+$.[241] All "16-electron" systems contain a linear M-N-O group, e.g. $Ru(NO)(PPh_3)_2Cl$.[242]

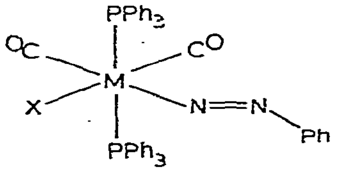
Thionitrosyl, Nitrous Oxide and Nitrogen Complexes. Treatment of $OsL_2(NO)X_3$ (L = PMe_2Ph, $AsPh_3$; L_2 = bipy; X = Cl or Br) with S_2Cl_2 in dichloromethane afforded[243] $Os(NS)L_2X_2Cl$. Under pressure, $[Ru(NH_3)_5(OH_2)]^{2+}$ reacted[244] with N_2O giving salts of $[Ru(N_2O)(NH_3)_5]^{2+}$. Under argon, $[Os(N_2)_2(NH_3)_4]^{2+}$ reacted[245] with N-heterocyclic bases (L, pyrazine, N-methylpyrazinium salts, isonicotinamide or isonicotinic acid) giving $[Os(N_2)L(NH_3)_4]^{2+}$.

Aryldiazo Complexes. The structure of the previously reported[246] $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$, 173 has been determined crystallographically.[247] The short Fe-N (1.70Å) and N-N (1.20Å) distances indicate multiple bonding. Structural and spectroscopic data suggest that PhN_2 is a good π-acceptor but poor σ-donor, although in neither aspects is it as effective as NO.

Reaction of $M(CO)_3(PPh_3)_2$ (M = Ru, Os) with $[PhN_2][PF_6]$ afforded[248] $[M(CO)_2(N_2Ph)(PPh_3)_2][PF_6]$ which is analogous to $[Fe(CO)_2(N_2Ph)(PPh_3)_2]^+$. 173.[247] Treatment of $[Os(CO)_2(N_2Ph)(PPh_3)_2]^+$ with BH_4^- gave $Os(CO)_2(PPh_3)_2H_2$ while its ruthenium analogue, in the presence of additional PPh_3, provided $Ru(CO)(PPh_3)_3H_2$. Nucleophilic attack by X^- (F, Cl, Br, I, NCO, N_3, NO_2, HCO_2 or $MeCO_2$) afforded $Os(CO)_2(N_2Ph)(PPh_3)_2X$ which could be protonated by HPF_6 giving $[Os(CO)_2(NHNPh)(PPh_3)_2X][PF_6]$. Treatment with CN^-, NCS^-, SPh^- or OH^- resulted in decomposition but with thiocyanate, a low yield of $Os(CO)_2(PPh_3)_2(NCS)_2$ was isolated. Similar treatment of $[Ru(CO)_2(N_2Ph)(PPh_3)_2]^+$ afforded $Ru(CO)_2(N_2Ph)(PPh_3)_2X$ (X = Cl, Br, I or NCO) and the structure of $M(CO)_2(N_2Ph)(PPh_3)_2X$ is thought to be 174. The formato, acetato and nitrito complexes contain monodentate X and $Os(CO)_2(N_2Ph)(PPh_3)_2(NO_2)$ exists as two isomers (figure 17). With iodide or nitrite ion, $[Ru(CO)_2(N_2Ph)(PPh_3)_2]^+$ afforded a mixture of $Ru(CO)_2(N_2Ph)(PPh_3)_2X$ and $Ru(CO)(N_2Ph)(PPh_3)_2X$, the former being more stable at low temperature. The latter would not accept CO to regenerate the latter but, in benzene, gave $Ru(CO)_2(PPh_3)_2X_2$. Reaction of $Ru(CO)(PPh_3)_3H_2$ with $[PhN_2][PF_6]$ afforded $[Ru(CO)(NHNPh)(PPh_3)_3H][PF_6]$ which gave with CO $[Ru(CO)_2(NHNPh)(PPh_3)_2H][PF_6]$; the osmium analogue of the latter was obtained by reaction of $Os(CO)_2(PPh_3)_2H_2$ with $[PhN_2][PF_6]$. Neutralisation of these last complexes gave $M(CO)_2(N_2Ph)(PPh_3)_2H$, 175. The ruthenium hydride changed from green to brown and then decarbonylated giving $Ru(CO)(N_2Ph)(PPh_3)_2H$, which contains linear Ru-N-NPh, 176; $Os(CO)(N_2Ph)(PPh_3)_2H$ was produced by u.v. irradiation of the corresponding dicarbonyl. These complexes could be produced alternatively in the following sequence of reactions:

Figure 17





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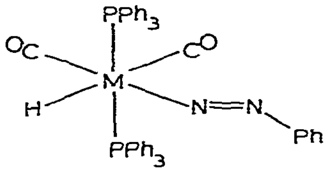
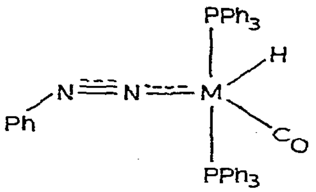


(175)

$$M(CO)(PPh_3)_3H_2 + PhN_2^+ \rightarrow M(CO)(NHNPh)(PPh_3)_3H^+; + NaOH \rightarrow M(CO)(N_2Ph)PPh_3)_2H$$

Treatment of $Os(CO)(N_2Ph)(PPh_3)_2Cl$ with an excess of HCl gave $Os(CO)(NHNPh)(PPh_3)_2Cl_2$, also produced by reaction of $Os(CO)(NHNPh)(PPh_3)_2HCl$ with an excess of HCl. This last hydrido chloride may be formed by stoichiometric reaction of $Os(CO)(N_2Ph)(PPh_3)_2H$ with HCl. In the presence of LiCl, $Os(PPh_3)_3Cl_2$ reacted with PhN_2^+ giving $Os(N_2Ph)(PPh_3)_2Cl_2$ which does not react with H^+ and has a structure similar to $Ru\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2Cl_3$.[249]

The structure of $Os(CO)(N_2Ph)(PPh_3)_2H.CH_2Cl_2$, 176 (M = Os), has been confirmed[250] crystallographically. The Os-N distance (1.87A) is unusually long,



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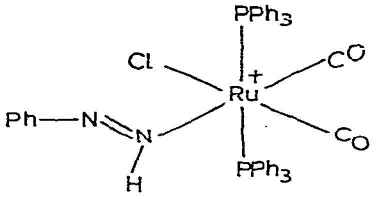

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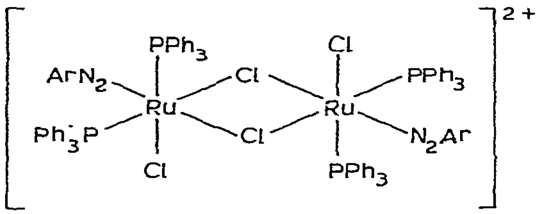

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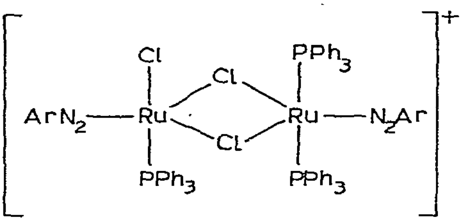
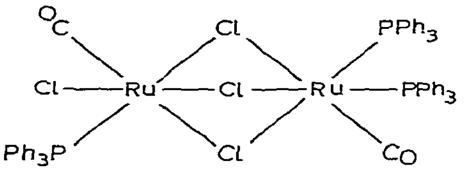


(179)



(180)

significantly more so than comparable distances in related Ru and Os nitrosyl and aryldiazo complexes; only $[Os(CO)_2(NO)(PPh_3)_2][ClO_4]$ has[251] a comparably long Os-N bond length (1.89Å). The Os-N-N bond angle is 171°. The structure of $[Ru(CO)_2(NHNPh)(PPh_3)_2H][ClO_4].CH_2Cl_2$, 177, has also been determined crystallographically.[252] The Ru-N distance is 2.09Å and the *cis*-diazene group behaves as a normal σ-donor ligand. There is a short non-bonded contact between the diazene N-H and the *ortho*-H of the phenyl group causing rotation of the phenyl group about the N-C bond.

Treatment of $Ru(PPh_3)_3HCl$ with ArN_2X (Ar = *p*-MeC_6H_4, *o*-, *m*- or *p*-$MeOC_6H_4$; X = BF_4 or PF_6) gave[253] $[Ru(N_2Ar)_2(PPh_3)_2Cl]X$ which is believed to be similar to $[Ru(NO)_2(PPh_3)_2Y]^+$ in having a bent and a linear aryldiazo group. With $Ru(PPh_3)_3Cl_2$, $[Ru(N_2Ar)(PPh_3)_2Cl_2]_n[X]_n$ and $[Ru_2\{N_2(p\text{-}MeOC_6H_4)\}_2(PPh_3)_3Cl_3][PF_6]$ were formed; the former may be monomeric and five-coordinate, or dimeric, 178 while the latter may have the structure, 179. Chlorination of $[Ru\{N_2(p\text{-}MeC_6H_4)\}_2$-

$(PPh_3)_2Cl][BF_4]$ afforded $Ru\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2Cl_3$ and $[p\text{-}MeC_6H_4N_2]Cl$. In acetonitrile, $Ru(CO)(PPh_3)_3HCl$ reacted with $[ArN_2][PF_6]$ (Ar = o, m or p-$MeOC_6H_4$) giving $[Ru(NHNAr)(NCMe)(PPh_3)_2Cl][PF_6]$ and with isonitriles giving $Ru(CO)(CNR)$-$(PPh_3)_2HCl$ (R = Pr^i, Bu^t or p-ClC_6H_4). In methanol, $Ru(CO)_2(PPh_3)_2HCl$ reacted with gaseous HCl giving $Ru(CO_2)(PPh_3)_2Cl_2$ and $Ru(CO)_2(PPh_3)_2$, <u>180</u>, while nitrous acid gave $Ru(NO)(PPh_3)_2Cl_3$. The structures of $Ru(NO)(PPh_3)_2Cl_3$ and $Ru\{N_2(p\text{-}MeC_6H_4)\}(PPh_3)_2Cl_3.CH_2Cl_2$ have been compared[254] crystallographically. Both are pseudooctahedral species, the $Ru\text{-}\hat{N}\text{-}Q$ (Q = O or $N(p\text{-}MeC_6H_4)$) being essentially linear. In the nitrosyl the Ru-N(O) distance is 1.74Å while the comparable length in the aryldiazo complex is 1.78Å.

Extensive isotopic labelling studies (^{15}N and D) have been made[255] of the N-N vibration in aryldiazo and diazene complexes. There is a resonance interaction of ν_{NN} with weak phenyl vibrational modes. From relative intensities of respective bands, unperturbed values of ν_{NN} have been estimated, and correlations made with the bonding mode of the ArN_2 group.

MONO-OLEFIN COMPLEXES

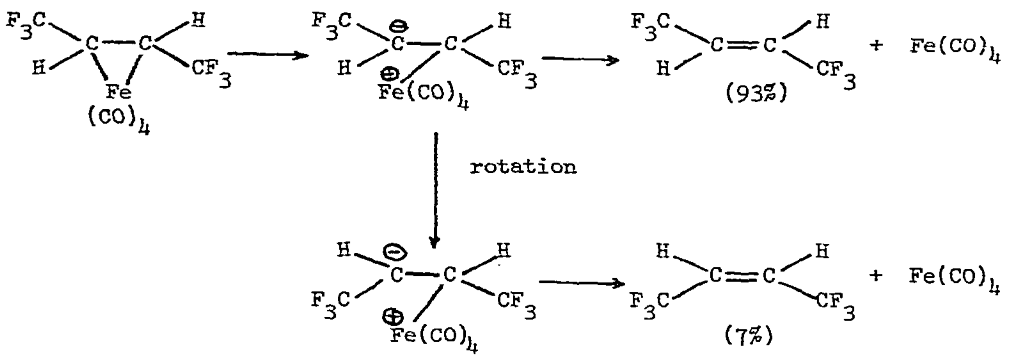
A study has been made[256] of vibrational force constants in $Fe(CO)_4(C_2H_4)$, and comparison has been made with other π-ethylene complexes. The $Fe\text{-}C_2H_4$ bond is weaker than that in the $Pt\text{-}C_2H_4$ system. From electric dipole moment measurements of a series of π-olefin complexes $Fe(CO)_4L$ (L = *trans* PhCH=CHCOR (R = Me or Ph), *trans*-PhCH=CHCHO, CH_2:CHO and CH_2:CHCN), it was found[257] that the ligand plane is never parallel to the axis of the trigonal pyramid formed by $Fe(CO)_4L$. In the carbonyl-containing ligands, the CO group was always displaced from the C=C-C plane. It was noted that the structure of $Fe(CO)_4$-(CH_2:CHCN) in solution was similar to that in the solid state.[258] The ketonic ligands have the same conformation in the $Fe(CO)_4$ complexes as they do as free ligands, but the aldehydes, present only as the *S-trans*-conformers in the free state, form both isomers when bound to $Fe(CO)_4$.

The kinetics of the transformation of $Fe(CO)_2$(PhCH:CHCOR) into Fe(CO) -(η^2-PhCH:CHCOR) are first order[259] with respect to the tetracarbonyl species. The results cannot be interpreted in terms of intramolecular chelation, and a possible mechanism is outlined below:

$$\begin{tikzcd}
Fe(CO)_4(\text{olefin}) \arrow[r, leftrightharpoons] & \text{olefin} + Fe(CO)_4 \arrow[r, "CO"] \arrow[d, shift left] & Fe(CO)_5 \\
 & CO + Fe(CO)_3 \arrow[r, "\text{olefin}"] \arrow[u, shift left] & Fe(CO)_3(\text{olefin}
\end{tikzcd}$$

Halogenated olefins (CH_2:CHF, CH_2:CF_2, CHF:CF_2, CHBr:CF_2, CHCl:CF_2, CF_3CF:$CFCF_3$, CF_3CH:$CHCF_3$, $(CF_3)_2$ C:C$(CF_3)_2$, CCl_2:CCl_2) reacted[260] with $Fe_2(CO)_9$ giving $Fe(CO)_4$(olefin). Thermal decomposition of these complexes gives rise to the original olefin and $Fe(CO)_5$, although traces of isomerised olefin may be detected, e.g. $Fe(CO)_4$(*trans*-$CF_3CH{:}CHCF_3$) → *cis*-$CF_3CH{:}CHCF_3$. This effect may arise via an intermediate Zwitterion in which rotation about the original double bond is possible (Scheme 15).

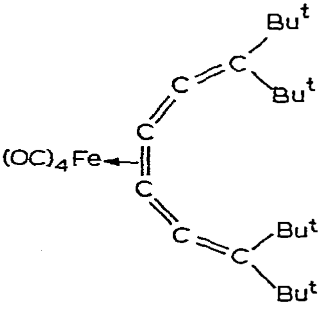
Scheme 15



Reaction of $Fe_2(CO)_9$ with $CF_2{:}CFI$ afforded $Fe(CO)_4(CF{:}CF_2)I$ and $[Fe(CO)_4(C_2F_3I)]_2$.

Treatment of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with $Bu^t_4C_6$ (a hexa-pentaene) gave[261] 181 and 182, while $Fe_3(CO)_{12}$ reacted with $(Me_2C(Cl)C{\equiv}C)_2$ in the presence of zinc dust giving a complex $Fe_2(CO)_6(C_{10}H_{12})$ not wholly identical with 182. Reaction of $Fe_2(CO)_9$ with an excess of acenaphthene gave 183, the structure determination of which is regarded[262] as being highly accurate.

Treatment of the methylenecyclopropane esters, 184 (R = Me or Et) with $Fe_2(CO)_9$ afforded a mixture of 185 and 186. The much slower rate of formation of the ethyl esters compared to their methyl homologues was attributed to steric rather than electronic factors. Treatment of 185 with $CuBr_2$ afforded the original cyclopropane together with 187, whereas 186 produced only the free



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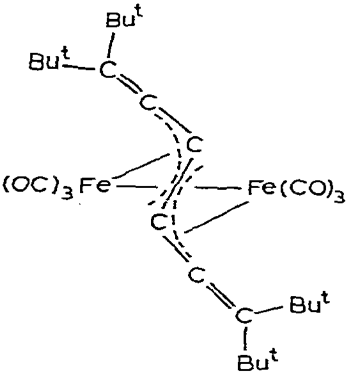
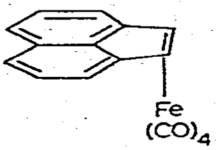


(182)



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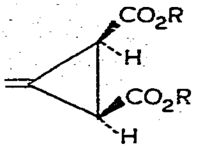

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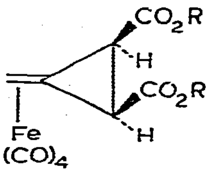

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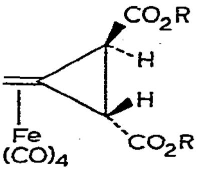

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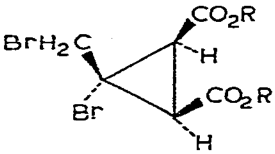
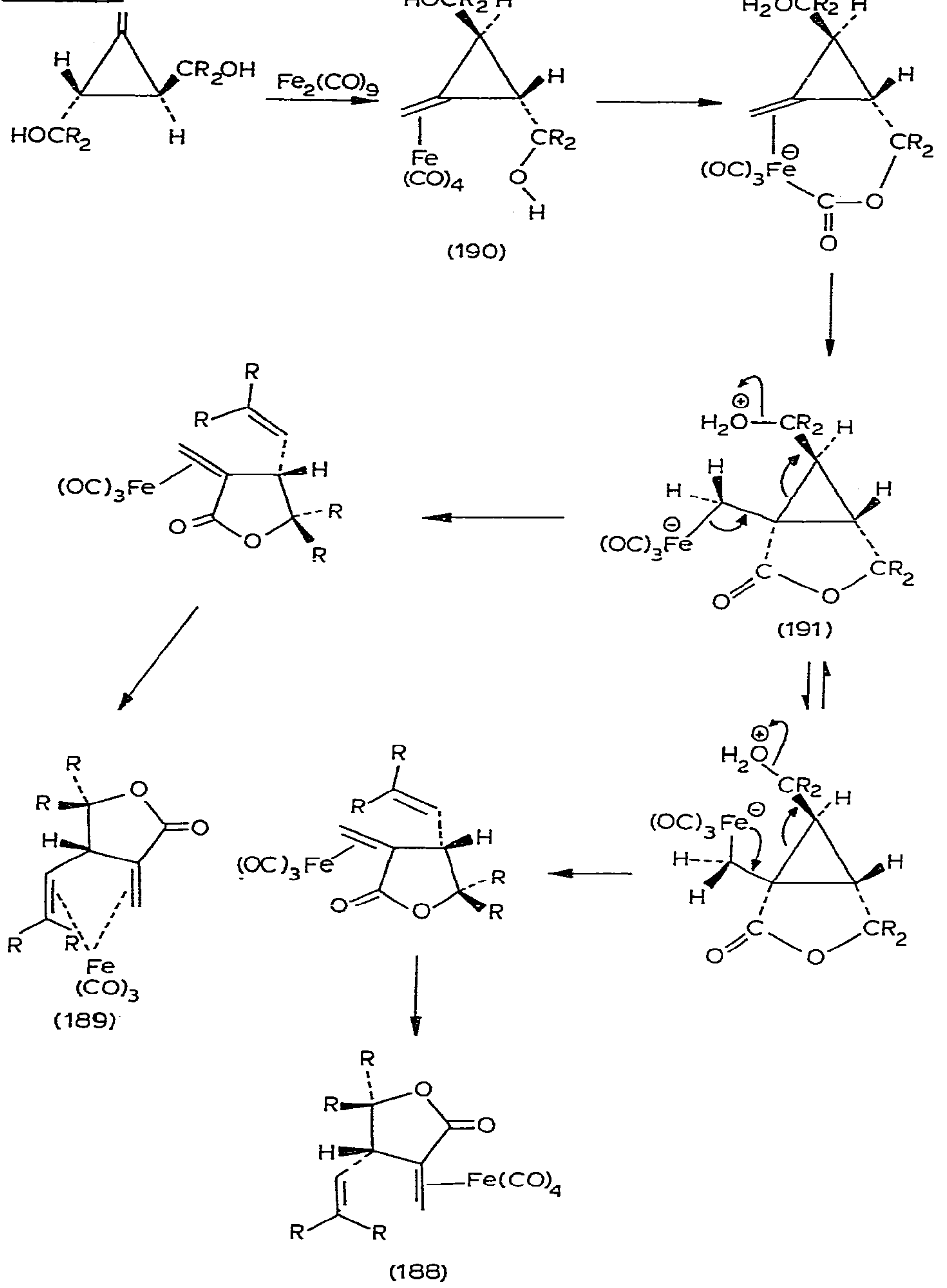


(187)

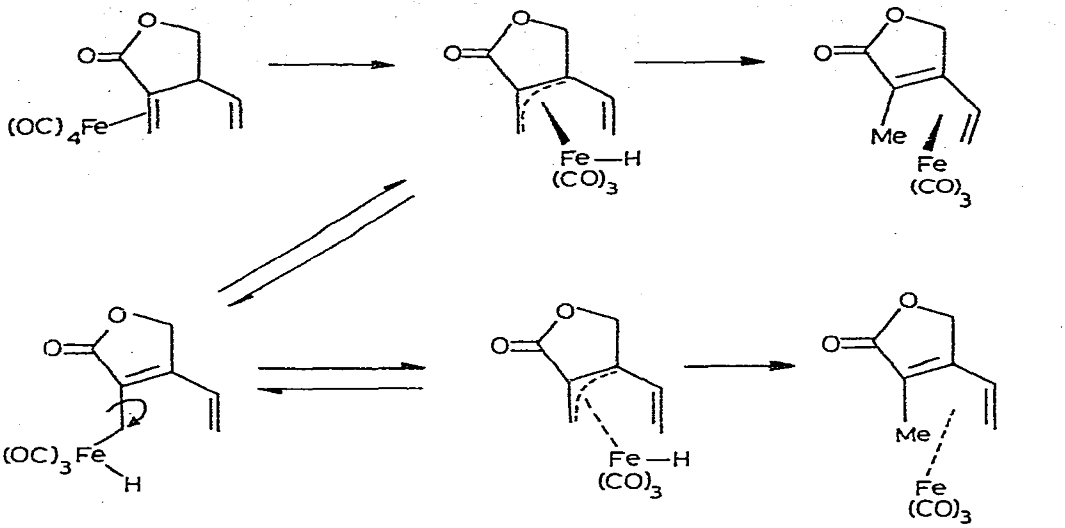
cyclopropane. Conversion of 185 to 186 was effected using NaOEt in ethanol, in a process which parallels the same reaction with the free cyclopropane. Resolved (+)-Feist's acid could be methylated by CH_2N_2 giving (+)-184 (R = Me), which could be successively treated with $Fe_2(CO)_9$, NaOEt/EtOH and $CuBr_2$ giving (−)-184 (R = Me). These data contradict previous findings which suggested that the cyclopropane ring would be broken during the formation of iron carbonyl complexes. However, the ring-opening reactions of methylenecyclopropanes by $Fe_2(CO)_9$ have received study[265] (Scheme 16). A single crystal X-ray study has been made of 188, and 189 is detected as a minor reaction product whose yield is improved if the reaction is carried out under CO (its structure has been preliminarily confirmed crystallographically). By using deuterated methylenecyclopropane precursor (R = D), 188 (R = D) and 189 (R = D) were produced exclusively with no H/D scrambling. A plausible intermediate in Scheme 16 is 190, molecular models of which show that the *endo*-CR_2OH group is ideally placed for intramolecular attack on coordinated CO giving 191. This mechanism accounts for the formation of 188 and 189 from either *cis*- or *trans*-bis(hydroxymethylenecyclopropane), since the stereochemistry of one of the ring C atoms must be lost

Scheme 16

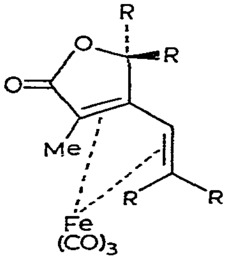


in the ring opening process. It may be noted that the stereochemistry of the other C atoms must be retained. When 188 was refluxed in ether, rearrangement to 192 occurred,[266] in a process which occurred with regiospecificity but extensive racemisation (Scheme 17).

Scheme 17



Similar treatment of 189 gave a mixture of 193 and 194 without H/D scrambling. The ratio and optical activity of 193 and 194 were identical if 189 rearranged in refluxing hexane, and 193 and 194 were not interconverted, nor did they show any loss of optical activity after prolonged refluxing in hexane. The proposed mechanism of rearrangement is shown in Scheme 18. The only intermediate which can give rise to 193 and 194 is 195, formation of which must arise via a direct



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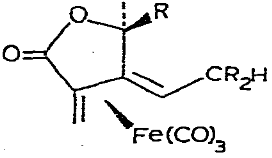
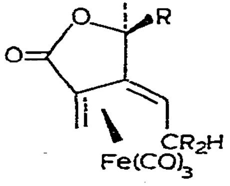
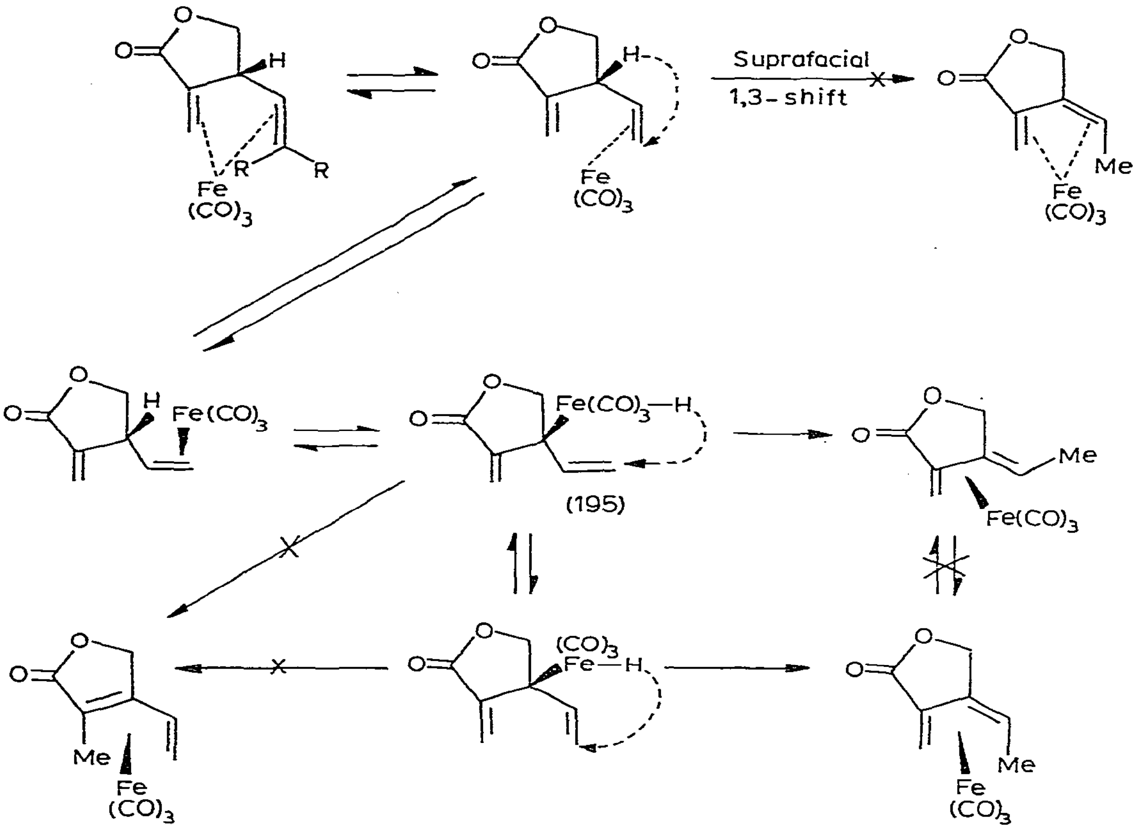


(193)



(194)

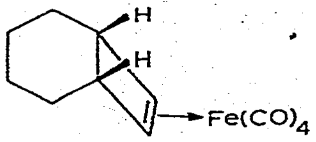
Scheme 18



insertion of the metal into a C-H bond. Formation of the products must occur via a direct hydrogen transfer from the metal to the terminal C atom of the vinyl group. It was conclusively demonstrated that a metal-promoted suprafacial 1,3-hydrogen shift, giving 194 (R = H) of opposite configuration to 193 (R = H) (which was not observed), cannot effectively compete with the allyl-metal-hydride mechanism as a low energy isomerisation process in this system.

Bicyclo[4,2,0]oct-7-ene is catalytically rearranged[267] by $Fe_2(CO)_9$ to a mixture of hydrocarbons probably via 196 as an intermediate. Iron pentacarbonyl induced[268] stereospecific CO insertion into the cyclobutane rings of α and β-pirene (Scheme 19). Smooth cleavage of the C-O bond in alkenyl carboxylates to afford ruthenium carboxylato complexes which released alkene under ambient conditions was achieved[269] using $Ru(PPh_3)_4H_2$ (Scheme 20).

These reactions proceeded with the formation of a small amount of ethane or propane, and could also be achieved with $Ru(PPh_2R)_4H_2$ (R = H or Me) but not with $Ru(PPh_3)_4HCl$. Ethyl-, amyl - and phenyl-acetates did not react and while $Fe(PPh_2Et)_3(N_2)H_2$ afforded, with $MeCO_2CH{=}CH_2$, N_2, ethylene and ethane; $Fe(diphos)_2H_2$ was inert.



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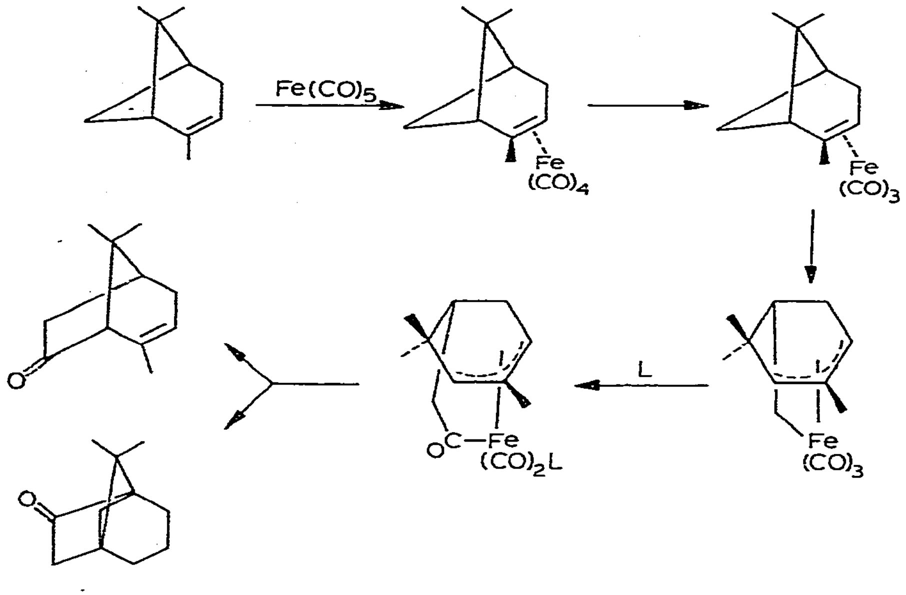
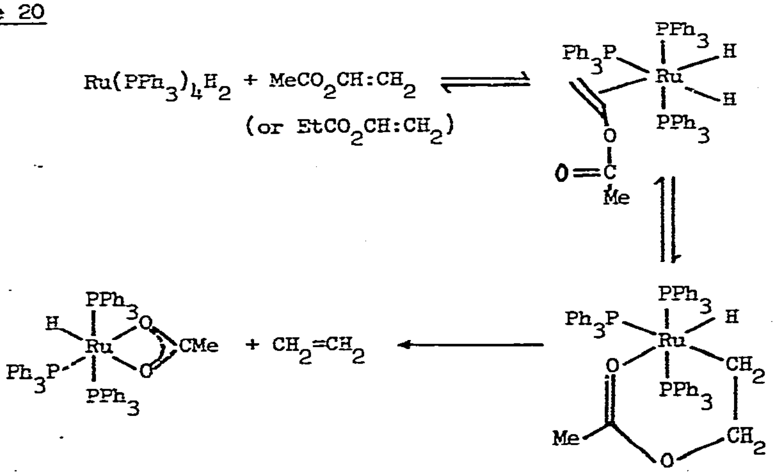
Scheme 19



Scheme 20



ALLYL COMPLEXES

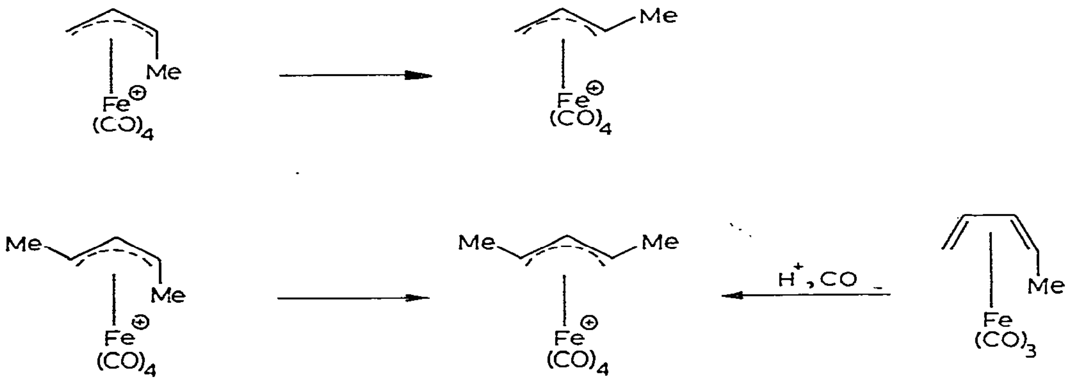
Mono-allylic species. Mössbauer spectral studies have been made[270] of $[Fe(CO)_4(\eta^3-C_3H_5)]^+$, $[Fe(CO)_3(\eta^3-C_3H_5)]^+$, $Fe(CO)_3(\eta^3-C_3H_5)Cl$ and related π-allyl complexes, and the isomer shifts and quadrupole splittings discussed in terms of electronic configuration and geometry. The ^{13}C n.m.r. spectra of $Fe(CO)_3$-$(\eta^3-C_3H_5)X$ (X = halide, ONO, OCOMe or $OCOCF_3$) and $Fe(CO)_3(\eta^3-C_3H_4R)X$ (R = 1-Me or 1-Ph, X = Cl, Br or $OCOCF_3$; R = 2-Me or 2-Br, X = halide, ONO_2 or $OCOCF_3$) have been measured[271] and the influence of X and R on chemical shifts of allyl and carbonyl C atoms discussed. It was noted that the influence of increasing polarity of the Fe-X bond had a significant effect on δ(C). ESR studies have been made[272] of the system

$$[Fe(CO)_2L(\eta^3-C_3H_5)]_2 \rightleftharpoons 2[Fe(CO)_2L(\eta^3-C_3H_5)]$$

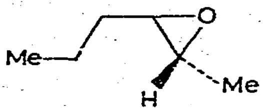
where L = CO, tertiary phosphine or $P(OMe)_3$. The neutral allyl species forms an adduct with olefins (1- or 2-hexene, 2-butyne) giving $Fe(CO)_2L$(olefin)-$(\eta^1C_3H_5)$, and the system isomerises 1-hexene to *trans*-2-hexenes, initiates vinyl polymerisation and polymerisation of allene to the solid $\{C(:CH_2)-CH_2\}_x$

The species $[Fe(CO)_4(\eta^3\text{-allyl})]^+$ having *anti*-1 substituents are isomerised to the corresponding *syn*-isomers on heating in CF_3CO_2H or SO_2 (Scheme 21). However, 197 reacts with HCl via a series of intermediates as shown.

Scheme 21



Epoxidation of (E,E)-2,4-, (Z,Z)-2,4-, and (Z,E)-2,4-hexadienes afforded[274] 198, 199 and a mixture of 200 and 201, respectively. Reaction of these with $Fe(CO)_5$ under light in benzene gave 202, 203 and a mixture of 204 and 205, respectively; the structure of 204 was confirmed crystallographically. It was observed that in the conversion of 198 to 202, retention of configuration occurred at C(2) relative to C(3); this is tantamount to rotation about C(2)-C(3). Conversion of 199 to 203 occurred with overall retention of configuration.



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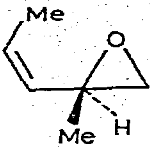
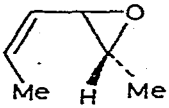


(199)

(200)



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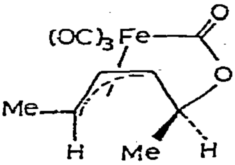

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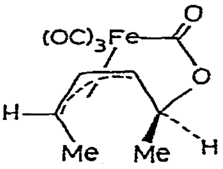

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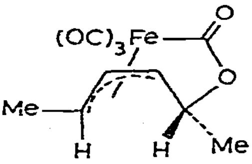

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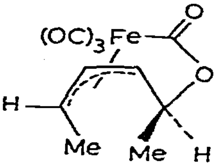

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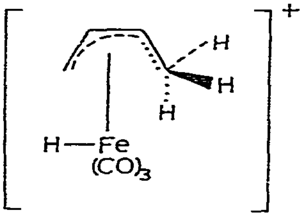
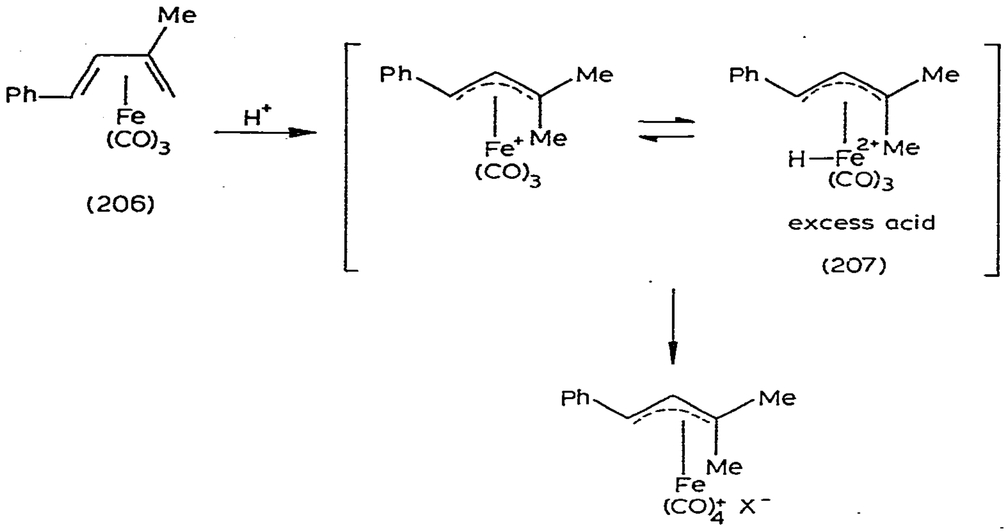


(208)

Further studies have been made of the nature of the intermediates produced by protonation of diene iron tricarbonyl complexes. Thus, protonation of 206 occurred[275] according to Scheme 22, the n.m.r. spectra being consistent with the equilibrium shown, and that of 207 being similar to that reported earlier.[276] However, treatment of $Fe(CO)_3(\eta^3-C_3H_5)I$ with $AgOCOCF_3$ afforded $Fe(CO)_3(\eta^3-C_3H_5)-(OCOCF_3)$ which, in HBF_4, produced $[Fe(CO)_3(\eta^3-C_3H_5)]BF_4$; this, in turn, decomposing to $[Fe(CO)_4(\eta^3-C_3H_5)]^+$. Spectral studies of a similar reaction undertaken with 206 are consistent with the processes outlined in Scheme 23. This Scheme is preferable to the description[276] of protonated diene complexes as, for example, 208. Treatment of $[Fe(CO)_4(\eta^3-1-MeC_3H_4)]^+$ with CdR_2 (R = Ph, $PhCH_2$ or C_6H_4) afforded[277] mixtures of unstable alkylated butene complexes of $Fe(CO)_4$.

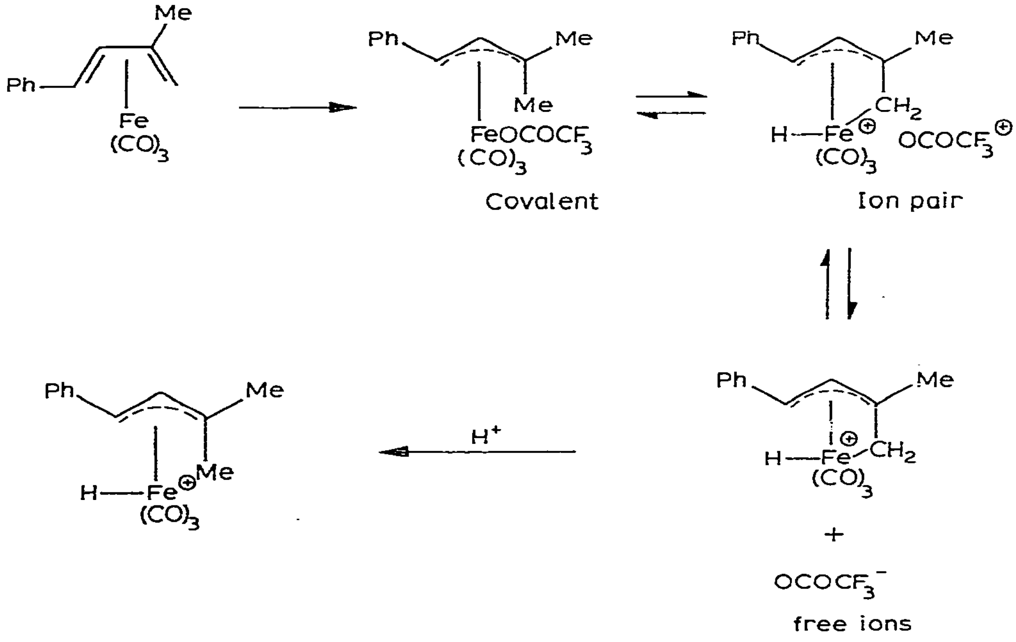
Scheme 22



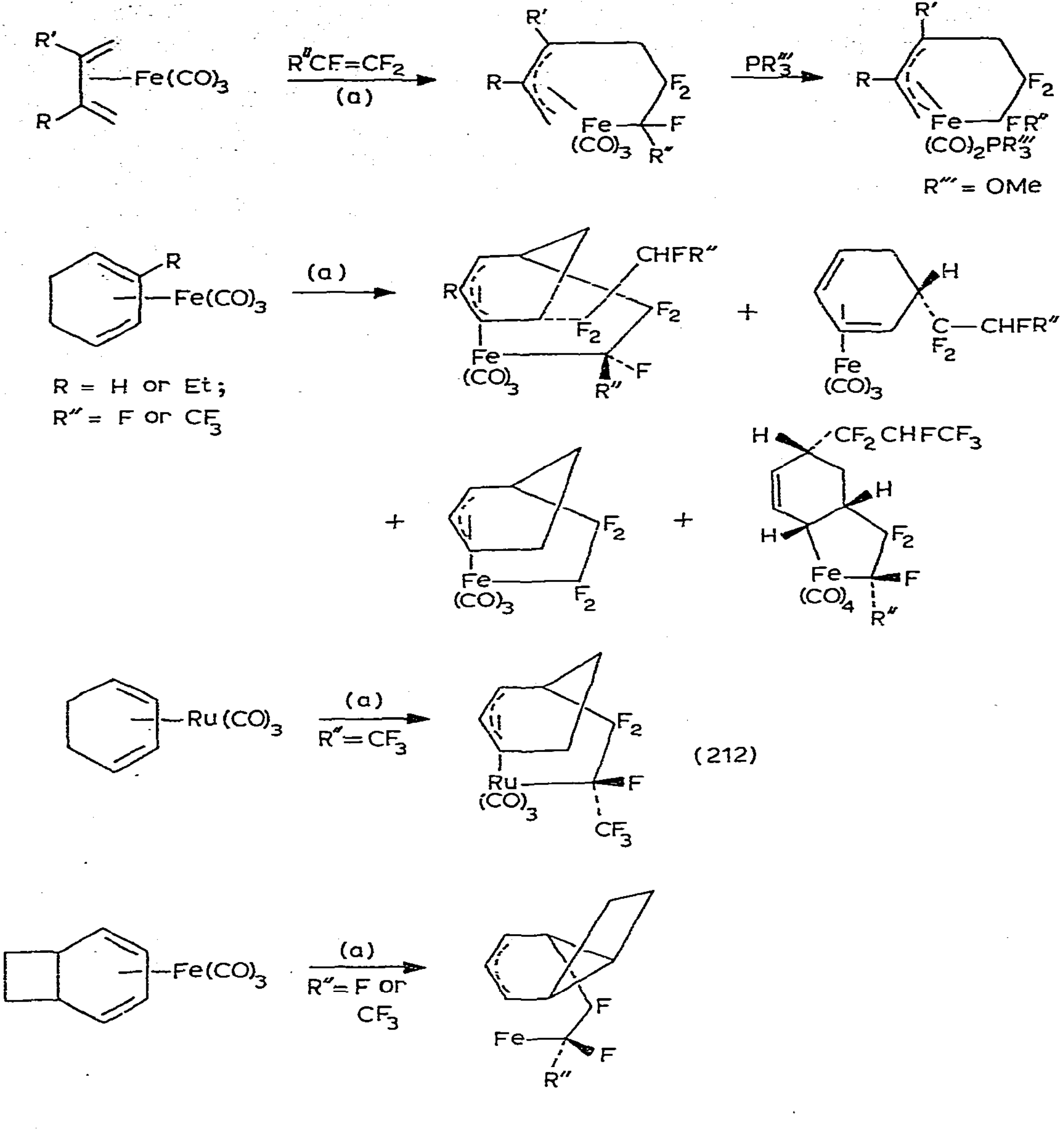
On chromatography, cis-$RCH_2CH=CHMe$ and some $RCH(Me)CH:CH_2$ could be recovered. Treatment of $Na[Fe(CO)_3(\eta^3\text{-}C_3H_5)]$ with benzyl chloride gave[278] a mixture of $Fe(CO)_4(CH_2:CHCH_2CH_2Ph)$ and $Fe(CO)_3(\eta^4\text{-}MeCH:CHCOPh)$ in the ratio 10:1.

Substituted butadiene iron tricarbonyl complexes react[279] with the fluoroolefins, $CF_2:CFR$ ($R = F$, CF_3, Cl or H) giving a variety of complexes as

Scheme 23

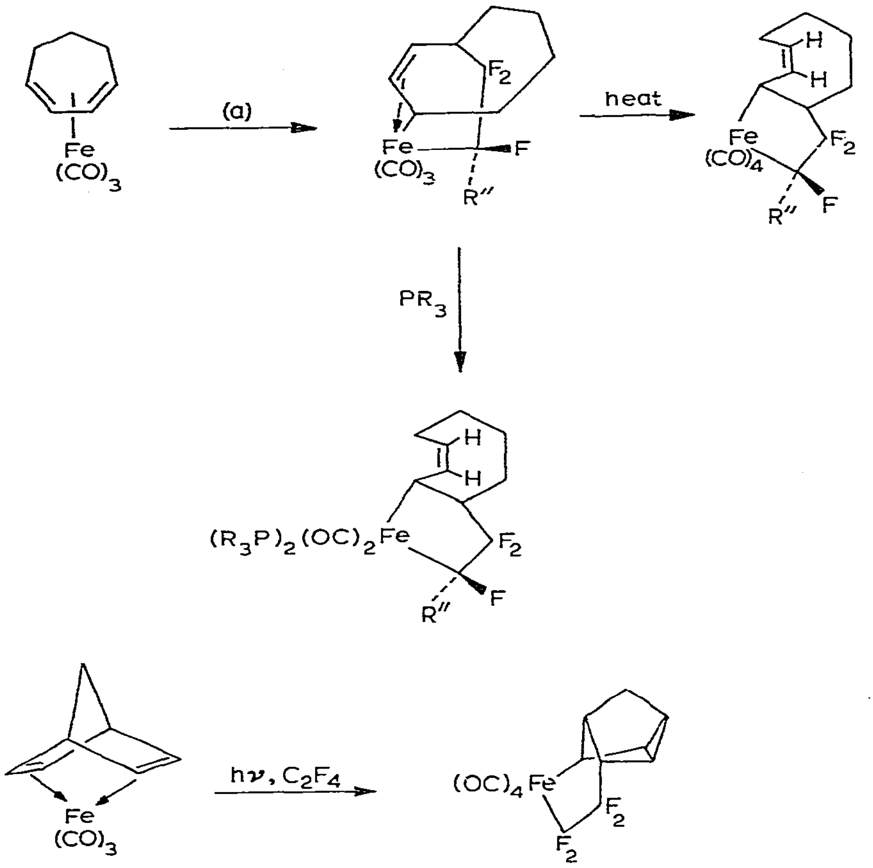


Scheme 24



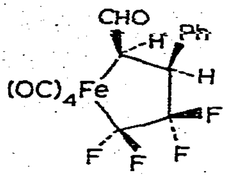
shown in Scheme 24. Some reactions of these compounds with $P(OMe)_3$ are also included in the Scheme. Reaction of $Fe(CO)_n$(*trans*-cinnamaldehyde) (n = 3 or 4) with C_2F_4 afforded the ferracyclopentanes 209 and 210. Treatment of $Fe(CO)_3$-($Ph_2PC_6H_4CH{:}CH_2$) with $CF_2{:}CFR$ (R = F, Cl, H or CF_3) gave 211. The mechanism of addition of fluorocarbon is thought to involve zwitterionic intermediates (Scheme 25) and addition of radical inhibitors had no effect on the reactions. Treatment of $Ru(CO)_3(C_6H_8)$ with $CF_2{:}CFCF_3$ afforded 212 only. With $(CF_3)_2CO$,

Scheme 24 (continued)



methyl- and dimethylbutadiene iron tricarbonyl complexes produced[280] 213 and 214; the latter, on heating in boiling hexane, afforded 215 and 216.

The addition of acrylonitrile to Ru(CO)$_3$(η^3-C$_3$H$_5$)Cl gave[281] [Ru(CO)$_2$-(η^1-C$_3$H$_5$)(η^2-CH$_2$:CHCN)Cl]$_n$ which, in the solid state, contained bridging Cl. Treatment of this with PPh$_3$ gave Ru(CO)$_2$(η^1-C$_3$H$_5$)(η^2-CH$_2$:CHCN)(PPh$_3$)Cl. With acetylenes, RC⋮CR' (R = R' = H or Ph; R = Ph, R' = H), [Ru(CO)$_2${OCC(R):C(R')-C$_3$H$_5$}Cl]$_2$ was formed by insertion into the η^1-allyl Ru bond. Treatment of this with HCl afforded α,β-unsaturated aldehydes. When R = R' = H, reaction with CO in methanol gave n-hexanoate while butadiene afforded 217. With EtO$_2$CC⋮CCO$_2$Et, 218 was produced, while HC⋮CCO$_2$Et gave either Ru(CO)$_2${OCCH:C(CO$_2$Et)C$_3$H$_5$}Cl or Ru(CO)$_2${OC(CO$_2$Et):CHC$_3$H$_5$}Cl. Hydrogen reacted with Ru(CO)$_3$(η^3-C$_3$H$_5$)Cl at 1-15 atm. giving, initially, Ru(CO)$_3$(C$_3$H$_6$)HCl which rearranged to Ru(CO)$_3$(CH$_2$CH$_2$Me)Cl These two species underwent CO insertion giving [Ru(CO)$_2$(OCCH$_2$CH$_2$Me)Cl]$_n$ and



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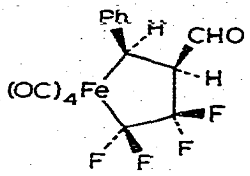

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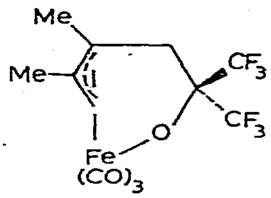

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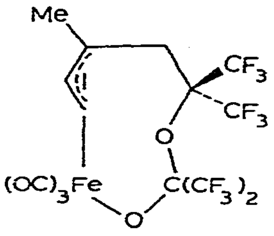

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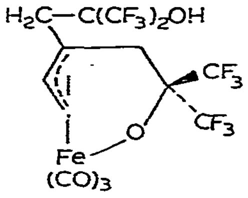

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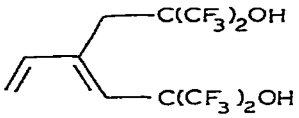

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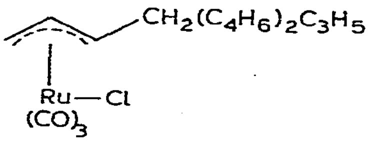

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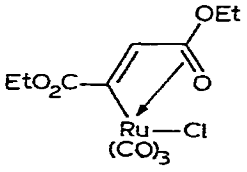

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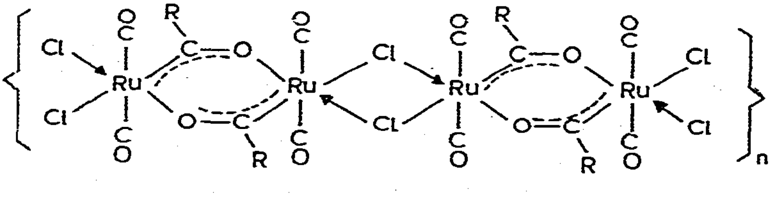
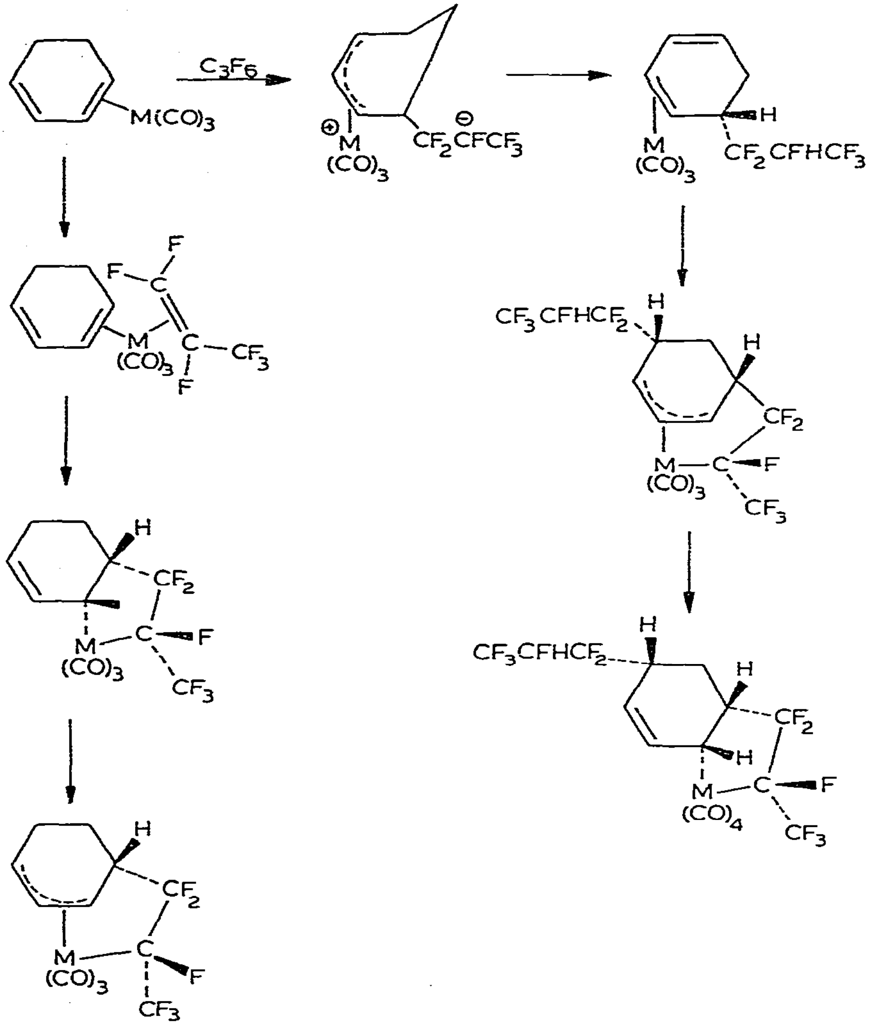


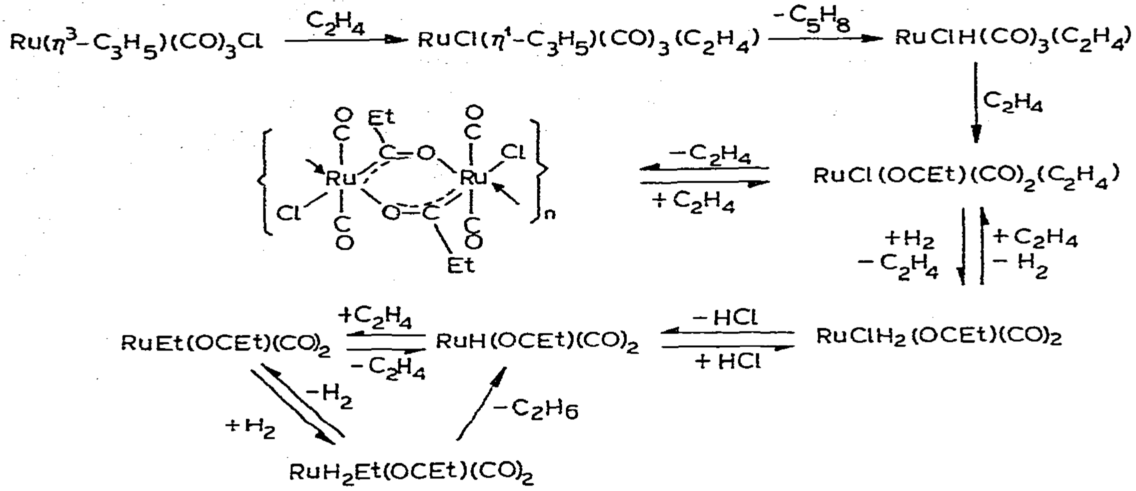
(219)

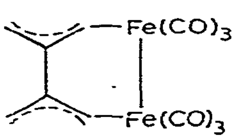
Scheme 25



$[Ru(CO)_2(COCHMe_2)Cl]_n$, which are mixtures of isomeric polymeric complexes, possibly 219. With PPh_3, 219 gave isomers of $Ru(CO)(PPh_3)_2(OCC_3H_7)Cl$. At atmospheric pressure, $Ru(CO)_3(\eta^3\text{-}C_3H_5)Cl$ reacted with hydrogen giving a dark red solid, possibly $[Ru(CO)_3Cl]_2$ containing a Ru-Ru bond, possibly analogous to $[Ru(CO)_2(PPh_3)Cl]_2$.[282] The system $Ru(CO)_3(\eta^3\text{-}C_3H_5)Cl/H_2$ is an effective catalyst for the homogeneous hydrogenation of terminal, internal and cyclic alkenes and carbonyl compounds. It was noted that very fast isomerisation occurred during the hydrogenation process and the catalytic system is different from those involving $Ru(PPh_3)_3HCl$ and $Ru(PPh_3)_3H(O_2CR)$.[283] The overall reaction with ethylene and hydrogen is illustrated in Scheme 26. The rate determining step in this system appears to be the alkene coordination by Ru.

Scheme 26





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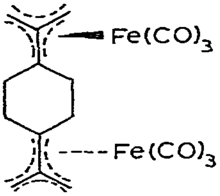

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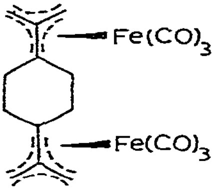

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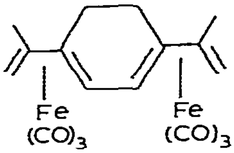

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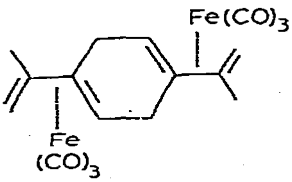

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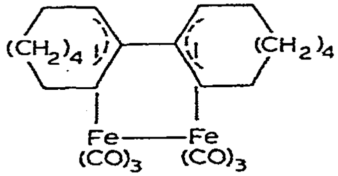
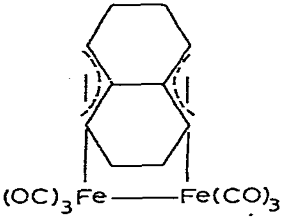


(225)

Figure 18

Reaction of $Fe_2(CO)_9$ with 2,3-bis(bromomethyl)-1,3-butadiene afforded[284] a mixture of 220, 221 and 222. Treatment of 221 with concentrated H_2SO_4 gave 223 and 224, and from the latter, 1,4-diisopropenylbenzene and 1,4-diisopropenyl-1,4-cyclohexadiene were released on addition of ceric ion. 1,2-Cyclononadiene reacted[285] with $Fe_2(CO)_9$ giving 225, the structure of which was confirmed crystallographically (Fe-Fe 2.97Å). The hydrocarbon ligand is bound asymmetrically and the fluxional properties of the molecule were interpreted as in figure 18. Reaction of 1,2,6,7-cyclododecatetraene and 1,2,9,10-cyclohexadecatetraene with $Fe_3(CO)_{12}$ in boiling hexane afforded[286] 226 and 227, respectively. Treatment of the former with Ce^{4+} gave 1,2,3,4-tetrahydronaphthalene. The structures of $Ru(PF_3)_2(C_{10}H_{16})Cl_2$, 228 and $Ru(PF_3)_2(PPh_3)_2Cl_2$ have been determined[287] crystallographically. The former is based on a trigonal bipyramidal geometry and the Ru-PF_3 bond is 2.24Å. In the latter, which has *cis*-Cl and *cis*-PF_3 ligands, with *trans*-PPh_3, the Ru-PF_3 distances are 2.16-2.18Å.

Photolysis of 9-oxabicyclo[6.1.0]nona-2,4,6-triene in the presence of $Fe(CO)_5$ afforded[288] 229, which subsequently rearranged as shown in Scheme 27; treatment with Me_3NO subsequently led to the isolation of 9-oxabicyclo[4.2.1]-nona-2,4,7-triene as shown.



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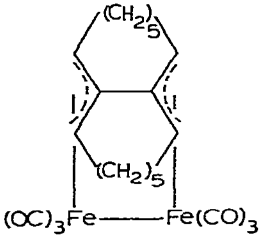

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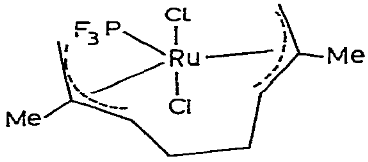

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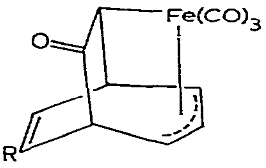

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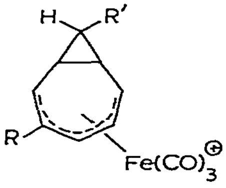
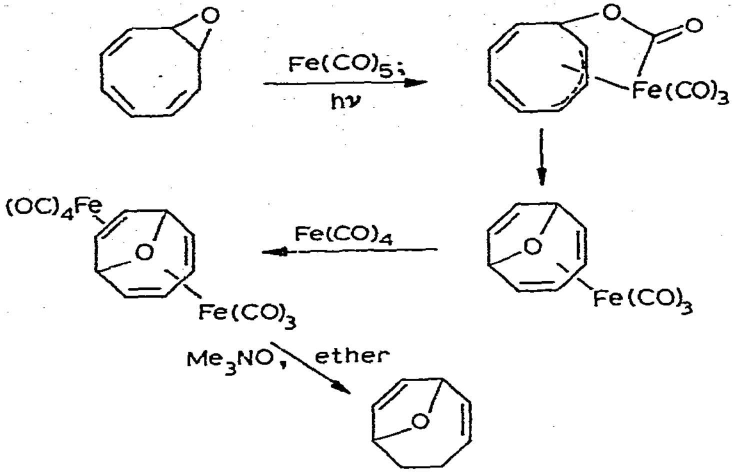


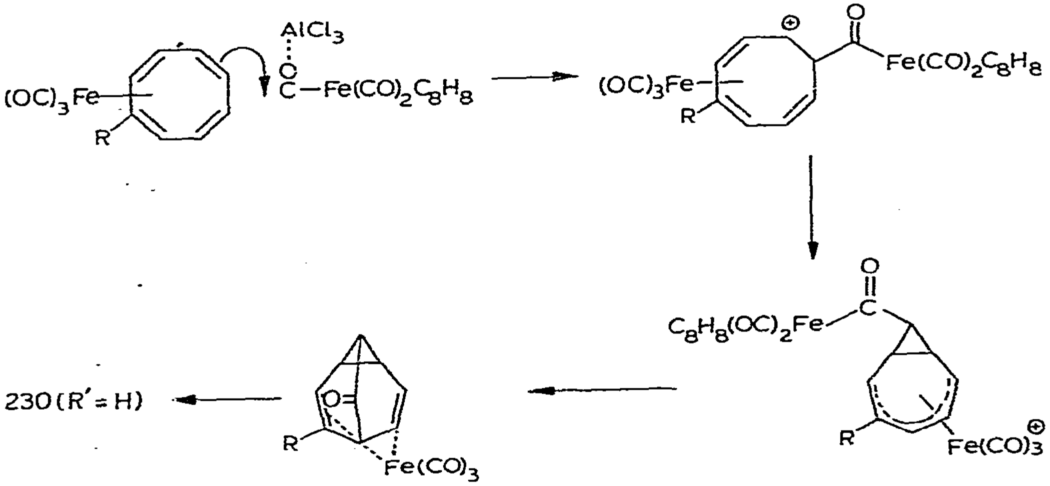
(231)

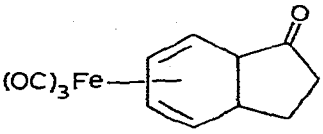
Scheme 27



Reaction of $Fe(CO)_3(C_8H_8)$ with $AlCl_3$ in benzene afforded[289] 230 (R = H) which has been prepared previously[290] from barbaralone and $Fe_2(CO)_9$. Similar treatment of $Fe(CO)_3(C_8H_7Me)$ gave 230 (R = Me). In acetic acid, $BF_3.OEt_2$ reacted with $Fe(CO)_3(C_8H_8)$ giving initially $Fe(CO)_3(C_8H_7OH)$ which, on protonation with HPF_6, gave 231 (R = R' = H). The mechanism for the formation of 230, which is derived from the isolation of 231, is shown in Scheme 28. Carbonylation of 230 (R = H) afforded barbaralone. Treatment of $Fe(CO)_3(C_8H_{10})$ (C_8H_{10} = cycloocta-1,3,5-triene) with $AlCl_3$ afforded 232 while the related norbornadiene complex gave a mixture of 233 and 234. The latter was also produced from quadricyclene and $Fe_2(CO)_9$. The reactions of $Fe(CO)_3(C_8H_{11}R)$ with $AlCl_3$ are summarised in Scheme 29; it was observed that cyclo-hexa-1,3-diene, -heptatriene, and -1,5-octadiene tricarbonyl iron complexes did not react with $AlCl_3$.

Scheme 28





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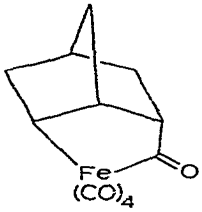

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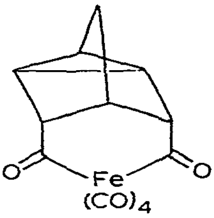

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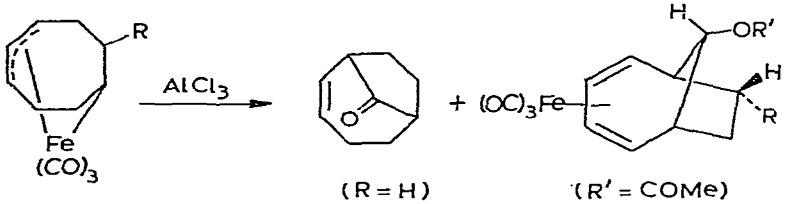
Scheme 29

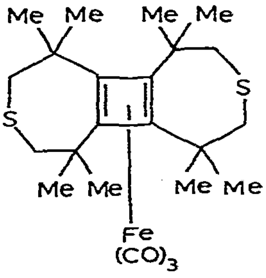


(R = H) (R′ = COMe)

CYCLOBUTADIENE AND TRIMETHYLENEMETHANE COMPLEXES

The electronic structure of the group $Fe(\eta^4\text{-}C_4H_4)$ and its reactivity has been compared[291] with those of the isoelectronic $Ni(\eta^2\text{-}C_2H_4)$, $Co(\eta^3\text{-}C_3H_5)$, $Mn(\eta^5\text{-}C_5H_5)$ and $Cr(\eta^6\text{-}C_6H_6)$ groups. The mass spectra of benzocyclobutadiene complexes $Fe(CO)_3(\eta^4\text{-}C_8H_6)$ and $Fe(CO)_2L(\eta^4\text{-}C_8H_6)$ ($L = PPh_3$, $AsPh_3$ or $SbPh_3$) have been measured.[292] Structural studies of 235 have revealed[293] that the Fe atom is displaced from its central position above the four-membered ring due to interactions of the CO groups and the four-membered ring atoms and between the CO and methyl groups.

Treatment of $Fe(CO)_3(\eta^4\text{-}C_4H_3CHO)$ with Ph_3PCRR' afforded[294] the vinyl complexes $Fe(CO)_3(\eta^4\text{-}C_4H_3CH{:}CRR')$ ($R = R' = H$, Me; $R = H$, R' = Ph, Me or CO_2Et). Reaction of $Fe(CO)_3(\eta^4\text{-}C_4H_4)$ with sulphuric acid in acetic anhydride gave[295] $Fe(CO)_3(C_4H_3SO_3H)$, and related ethyl-substituted derivatives were prepared



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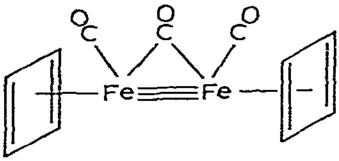
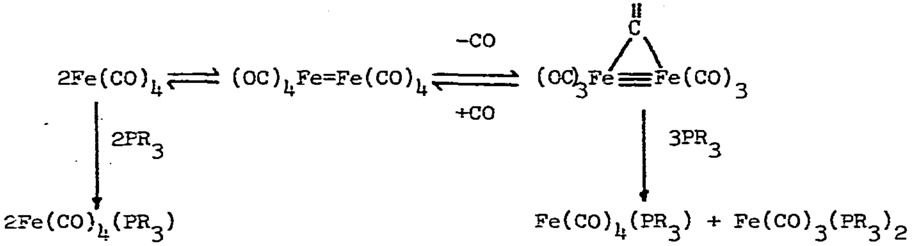


(236)

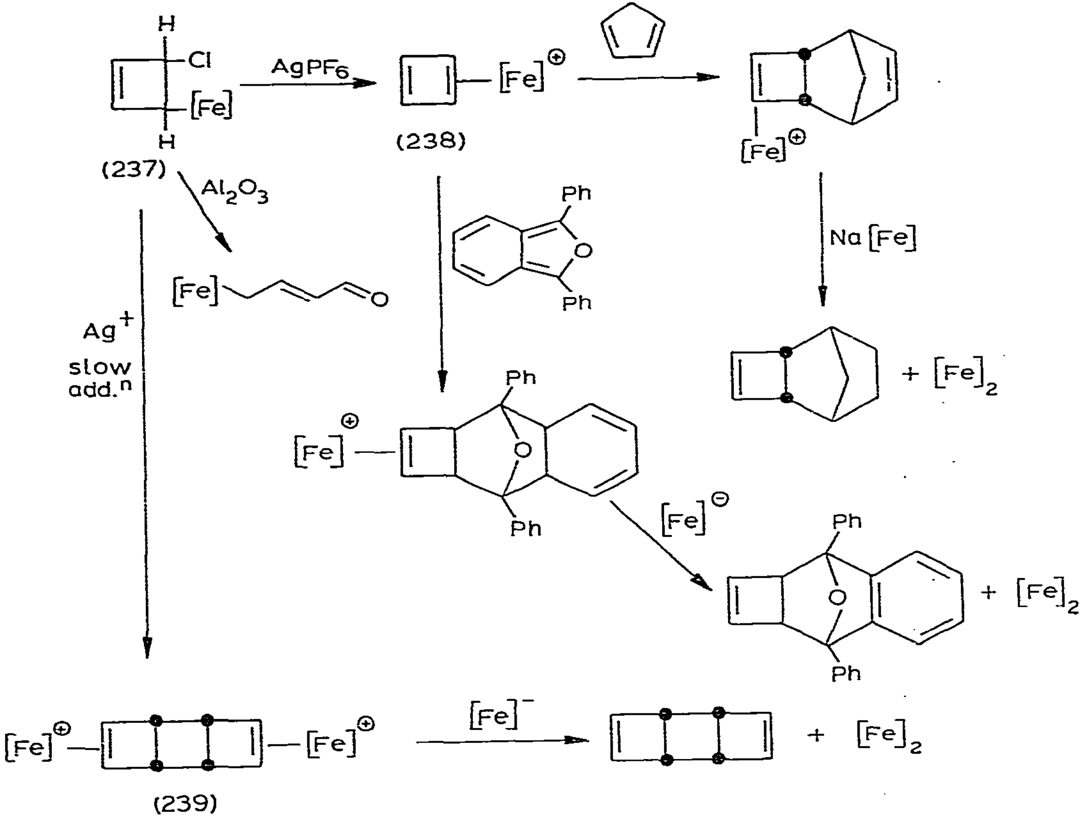
similarly. Treatment of $Fe(CO)_3(\eta^4-C_4H_3SO_3H)$ with PCl_5 gave,[296] as expected, $Fe(CO)_3(\eta^4-C_4H_3SO_2Cl)$, which, on addition of RR'NH, afforded $Fe(CO)_3(\eta^4-C_4H_3NRR')$ ($R = Bu^n$, $PhCH_2$, C_3H_5, $R' = H$, Me or Et).

Photolysis of $Fe(CO)_3(\eta^4-C_4H_4)$ in the presence of $P(OMe)_3$ gave[297] $Fe(CO)_2\{P(OMe)_3\}(\eta^4-C_4H_4)$. However, in THF under nitrogen at low temperatures and at appropriate wavelengths, the binuclear $Fe_2(CO)_3(\eta^4-C_4H_4)_2$, <u>236</u>, was produced (an assumed intermediate is $Fe(CO)_2(N_2)(C_4H_4)$). Under CO, the dimer reverted to $Fe(CO)_3(\eta^4-C_4H_4)$ while, with $P(OMe)_3$, a mixture of $Fe(CO)\{P(OMe)_3\}_2(\eta^4-C_4H_4)$ and $Fe(CO)\{P(OMe)_3\}_2(\eta^4-C_4H_4)$ was formed. By carefully controlling the conditions of photolysis of $Fe(CO)_3(\eta^4-C_4H_4)$ in THF in the absence of N_2, an intermediate, $Fe(CO)_2(N_2)(\eta^4-C_4H_4)$, could be detected, but on removal of the solvent, <u>236</u> was generated apparently via the species $(\eta^4-C_4H_4)(CO)_2Fe{=}Fe(CO)_2(\eta^4-C_4H_4)$. These observations prompted the suggestion that PR_3 reacts with photolytically generated $Fe(CO)_4$ as follows:



Treatment of *cis*-1,2-dichlorobutene with $Na[Fe(CO)_2(\eta^5-C_5H_5)]$ *afforded*[298] the 2-chlorocyclobutenyl complex <u>237</u>, whose reactions, particularly with Ag^+, are summarised in Scheme <u>30</u>. Of particular interest is the intermediate cyclobutadiene complex <u>238</u>. It was noted that <u>237</u> readily hydrolysed over alumina to give $Fe(CO)_2(\eta^5-C_5H_5)(CH_2CH{:}CHCHO)$. The adducts formed between <u>238</u> and other 1,3-dienes are cited as strong evidence for the existence of a η^2-cyclobutadiene complex. The alternative mechanism, involving generation of free C_4H_4, would require dissociation of <u>238</u> followed by the formation of the Diels-Alder adduct. This process is probably unlikely since displacement of olefins from $[Fe(CO)_2(\eta^2\text{-olefin})(\eta^5-C_5H_5)]^+$ requires that the rate determining dissociative step has an activation energy of 16–25 kcal/mol. Cyclobutene ligands are relatively non-labile, and the binuclear species <u>239</u>, although dicationic, failed to react with iodide ion. Cyclobutadiene is expected to be a better donor ligand than cyclobutenes, and so <u>238</u> should be even more stable than <u>239</u> and its cyclobutene analogues. If dissociation occurred, the resultant cation $[Fe(CO)_2(\eta^5-C_5H_5)]^+$ should react very rapidly with cyclobutadiene, giving an olefinic adduct, but this was not observed. Further, treatment of <u>237</u> with Ag^+ in the presence of dimethylfumarate failed to give the expected Diels-Alder adduct if dissociated C_4H_4 has been present. Thermolysis of <u>240</u> afforded <u>238</u>, which was trapped by

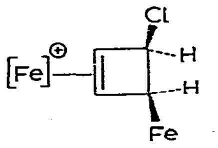
Scheme 30



$[Fe] = Fe(\eta5\text{-}C_5H_5)(CO)_2$

adduct formation as shown in Scheme 30. The formation of 239 can be accounted for by a sequence of metal-assisted cycloadditions as shown in figure 19. These results support the view that transient C_4H_4 complexes generated[299] by oxidative degradation of $Fe(CO)_3(\eta^4\text{-}C_4H_4)$ are *not* involved in the formation of cyclobutadiene dienophile adducts. However, the possibility that $\eta^2\text{-}C_4H_4$ species are involved cannot be discounted.

Treatment of two moles of $Fe(CO)_3(\eta^4\text{-}C_4H_4)$ with one mole of dieneophilic acetylenes, RCOC≡CCOR (R = Ph or Me) gave[300] the tetracyclic product 241.



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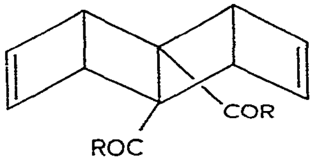
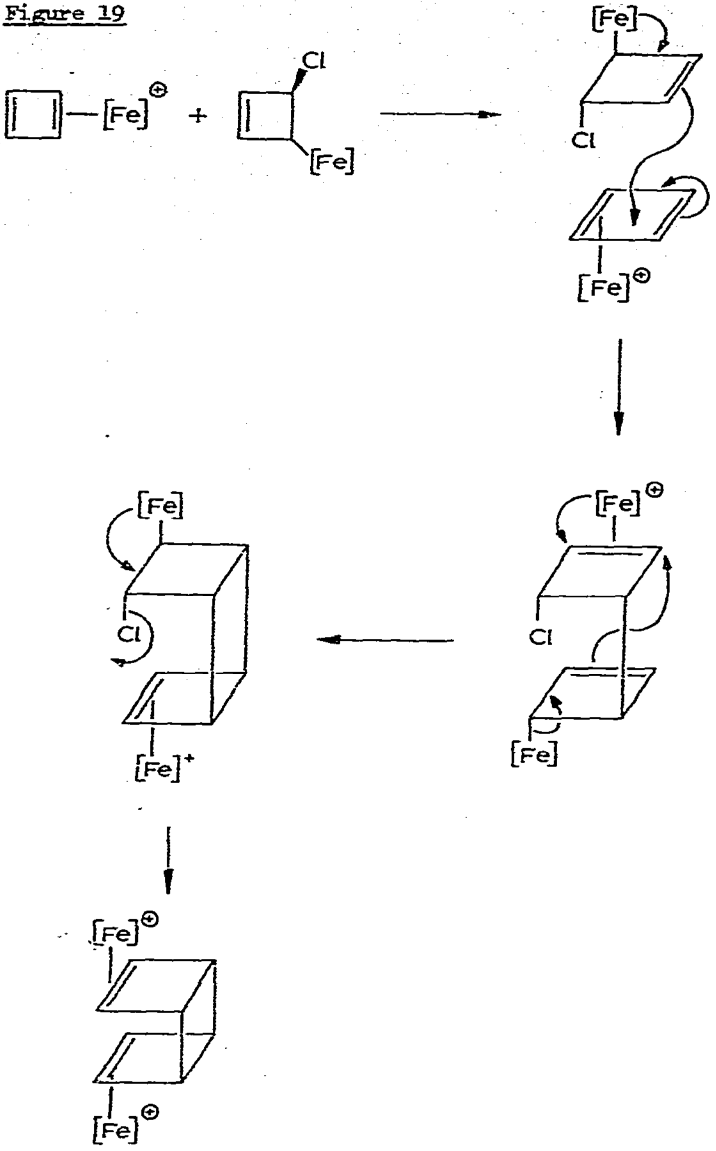


(241)

Figure 19



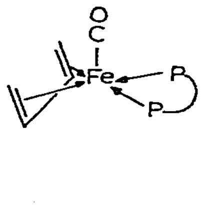
From a valence force field calculation based on i.r. spectral studies, the vibrational force constants of the trimethylenemethane complex, $Fe(CO)_3\{C(CH_2)_3\}$, were obtained.[301]

DIENE METAL COMPLEXES

Acyclic Mono-diene Compounds

A new method of synthesis of diene iron tricarbonyl complexes has been developed.[302] This involves treatment of $Fe(CO)_5$ with the hydrocarbon in the presence of Me_3NO, when $Fe(CO)_3$(diene), Me_3N, CO and CO_2 are produced. It is assumed that Me_3NO facilitates the rapid generation of $Fe(CO)_4$, and the utility of the reactions lies in that it occurs at or below 0°, depending on solvent, and requires gentle refluxing to effect completion. This contrasts with the relatively high temperatures required to effect combination of $Fe(CO)_5$ directly with dienes, or room temperature reaction of the insoluble $Fe_2(CO)_9$ with hydrocarbons. It may be noted that this reaction is formally the reverse of that involving the cleavage of diene from $Fe(CO)_3$(diene) by Me_3NO in aprotic solvents.[303]

Molecular orbital calculations have been made[304] of the bonding capability of $Fe(CO)_3$ with respect to conjugated dienes. Reaction of $Fe(CO)_5$ under UV light or of $Fe_2(CO)_9$ thermally, with $C_4H_{6-n}Me_n$ afforded[305] $Fe(CO)_3(C_4H_{6-n}Me_n)$, and CO substitution by PF_3, giving $Fe(CO)_{3-x}(PF_3)_x(C_4H_{6-n}Me_n)$ was achieved photochemically. The CO stretching force constants were altered in an additive way depending on the number and positions of the methyl groups on the butadiene group. The PF_3 ring seems to prefer the apical position in the square-based pyramidal species $Fe(CO)_2(PF_3)(C_4H_{6-n}Me_n)$. Variable temperature n.m.r. studies of $Fe(CO)_{3-x}(PF_3)_x(C_4H_{6-n}Me_n)$ have confirmed[306] the apical site preference of PF_3, and when x=2 the second PF_3 group prefers a basal position *trans* to the butadiene substituent in $Fe(CO)(PF_3)_2(C_4H_5Me)$. The nature of the fluxional processes in these compounds is shown in fig. 20. Treatment of $Fe(CO)(C_4H_6)_2$ with $Ph_2PCH_2CH_2PPh_2$ (diphos) afforded[307] $Fe(CO)(diphos)(C_4H_6)$, as a 4:1 mixture of isomers. One of these isomers was identified spectroscopically as 242 while the other may be 243a or 243b. These compounds are fluxional, interconverting according to the scheme $\underline{243a} \overset{\underline{242}}{\rightleftharpoons} \underline{243b}$.



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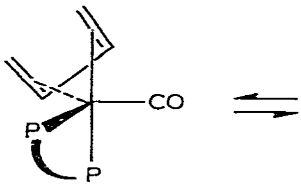
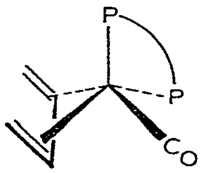
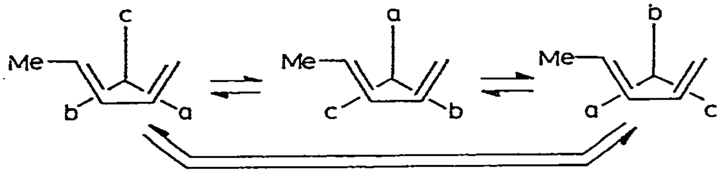


(243a)

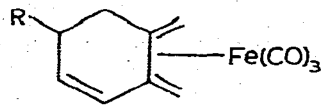


(243b)

Figure 20



Reaction of o-$C_6H_4(CH_2Br)_2$ with $Na_2Fe(CO)_4$ gave[308] 244 (R = H) which, on acetylation, afforded 244 (R = COMe). Addition of $AlCl_3$ afforded 5-acetyl-2-indanone. Treatment of 245 with $AlCl_3$ gave 246 which reacted with CO producing 247. Action of $AlCl_3$ on $Fe(CO)_3(C_4H_6)$ afforded low yields of a mixture of 2- and 3- cyclopentanone, but the major product was unreacted starting material.



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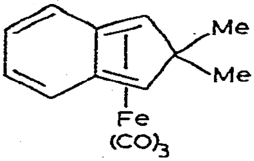

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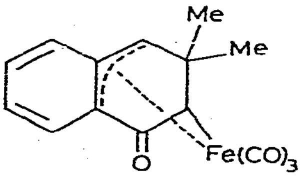

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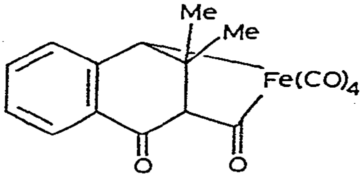
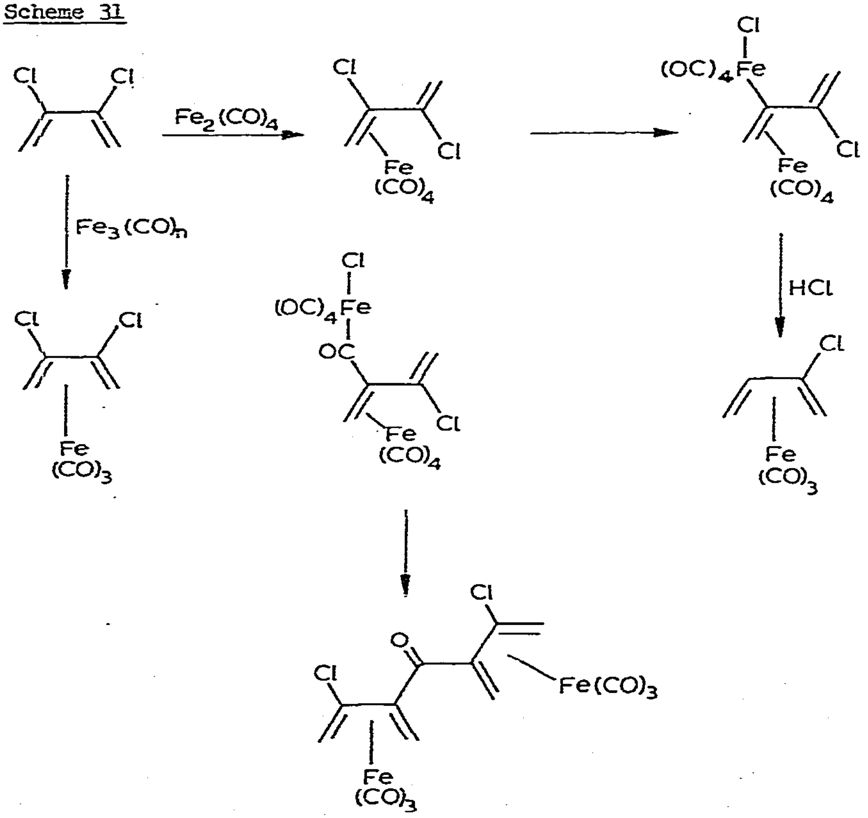
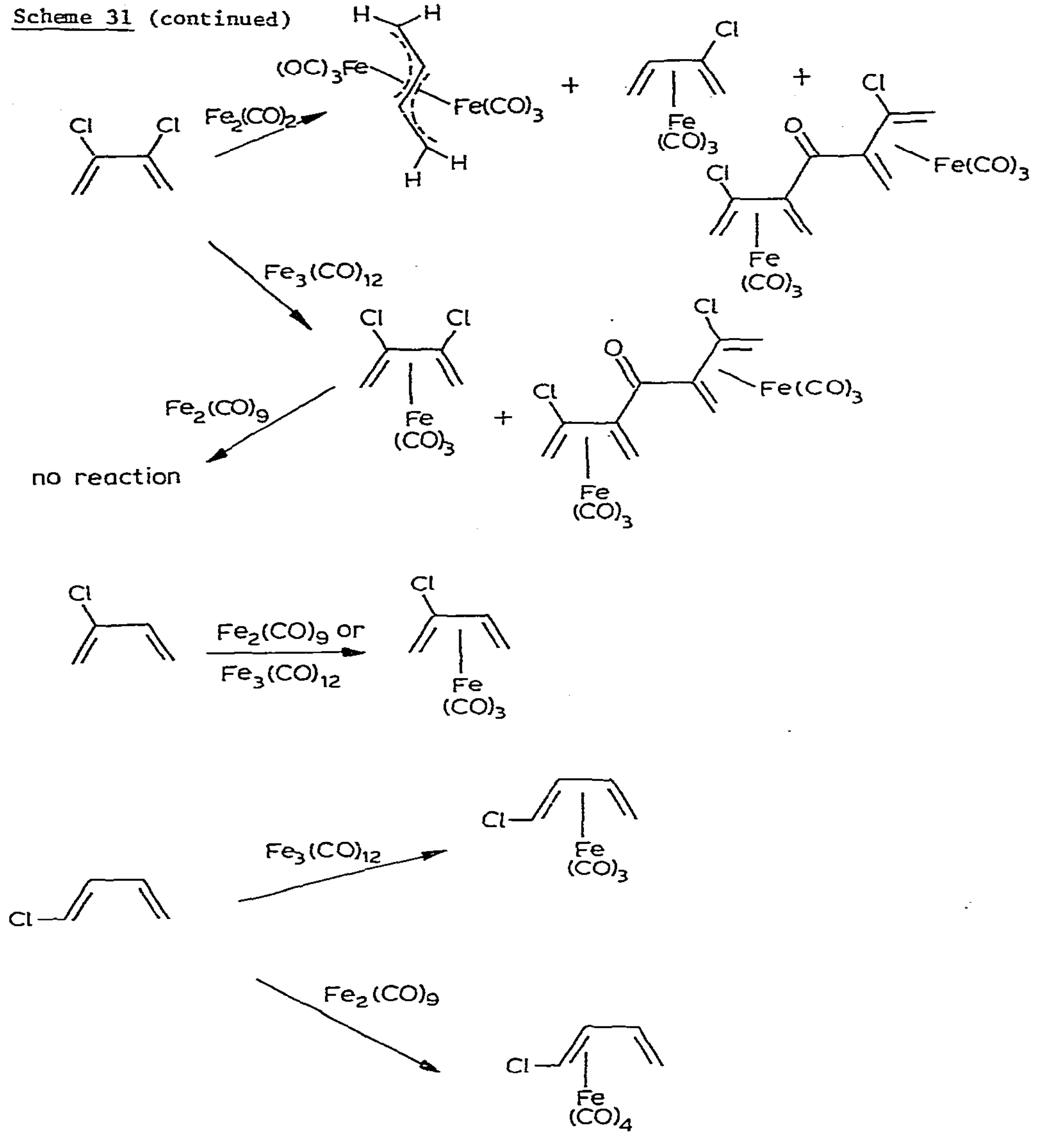


(247)

Scheme 31



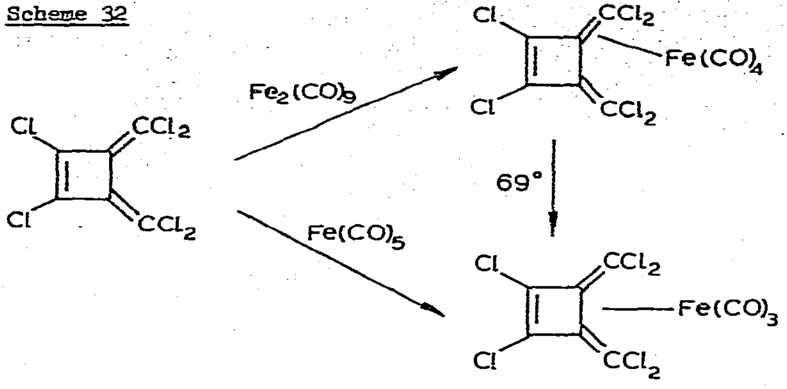
Scheme 31 (continued)



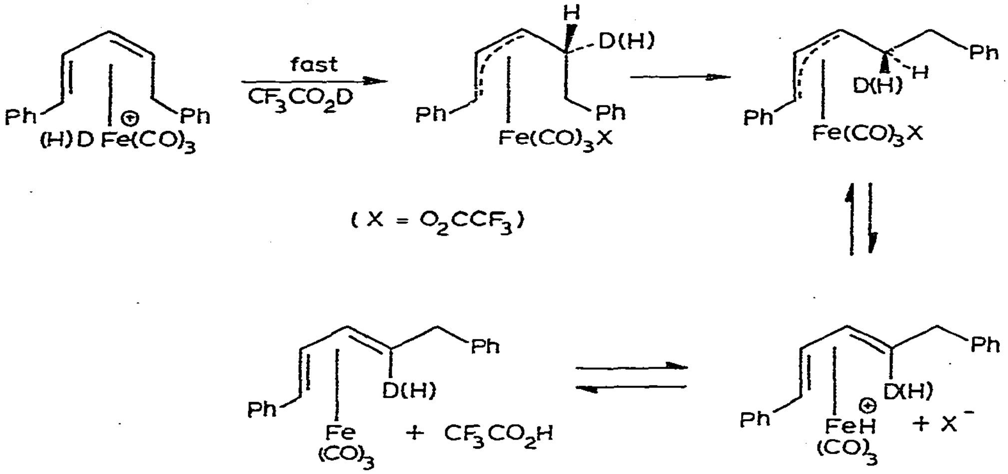
Reaction of 2,3-dichlorobutadiene with iron carbonyls afforded[309] a variety of products as depicted in Scheme 31. The results suggested that the chlorine substituent on a carbon atom of a coordinated double bond of a η^2-diene, or on the terminal C atom of an η^4-diene, may be activated towards insertion of an Fe carbonyl group. A chlorine substituent at a central carbon atom of an η^4-diene appears to be unreactive in this respect. Reaction of perchloro(3,4-dimethylenecyclobutene) with $Fe(CO)_5$ and $Fe_2(CO)_9$ occurred[310] according to Scheme 32.

The acid-catalysed *cis-trans* isomerisation of certain diene iron tricarbonyl complexes occurred[311] with an unusually large deuterium isotope effect. A

Scheme 32



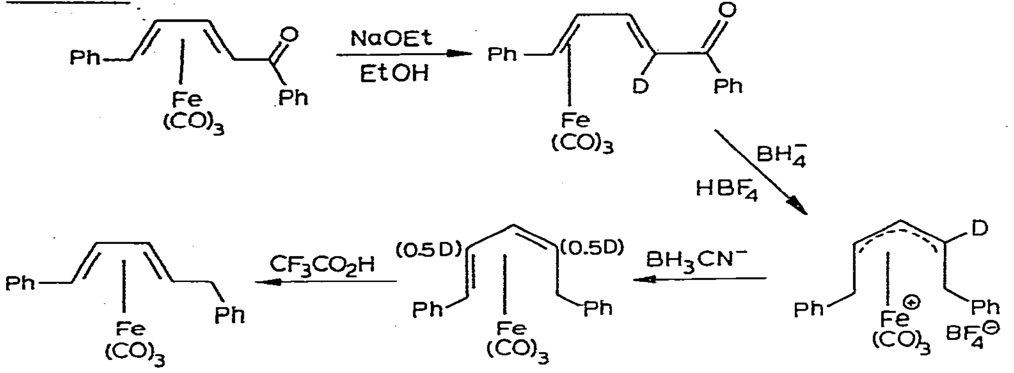
Scheme 33



reasonable mechanism for a particular compound is shown in Scheme 33. It was noted that no dideuterated species were formed, even though relatively long reaction periods were involved. The stereospecificity of this process was confirmed by the reactions outlined in Scheme 34. These results, coupled with the slow rate of exchange of *trans*-Fe(CO)$_3$(PhCH:CHCH:CHCH$_2$Ph), indicated that there was essentially stereospecific protonation/deprotonation of these diene complexes, and that in Scheme 33, reaction (b) is faster than reaction (a).

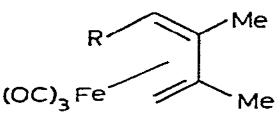
Friedel-Crafts acylation (MeCOCl or PhCOCl) of 248 (R = H) gave[312] *anti*-247 (R = Me or Ph) which, on treatment (R = Me) with LiAlH$_4$/AlCl$_3$, afforded a 1:1 mixture of the *syn* and *anti*-forms of 250. Similar treatment of 251 gave 252, while acylation of Fe(CO)$_3$(1,3-C$_6$H$_8$) afforded 253 which was reduced by LiAlH$_4$ to 254.

Scheme 34



(51.3 ± 1.5 % d_1)

The photochemical reactions of $Fe(CO)_3(C_4H_4R_2)$ (R = H or Me) with $CF_3C{\equiv}CCF_3$, and the thermal conversions of the products,[313] are shown in Scheme 35. It may be noted that a regiospecific 1,3-hydrogen shift occurs in the thermal processes. The overall reaction involves a stepwise Diels-Alder addition of the butyne to a coordinated 1,3-diene, which is a thermally "allowed" concerted process in the absence of a transition metal. It is possible that the reaction of but-2-yne with butadiene catalysed[314] by $Fe(C_8H_8)_2$, which gave 1,2-dimethylcyclohexadiene, occurs via a similar pathway.



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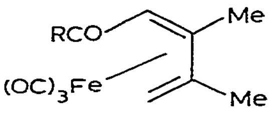

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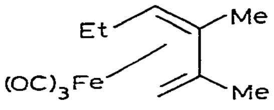

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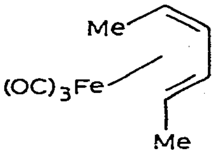

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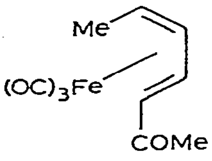

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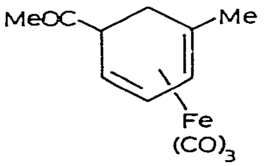

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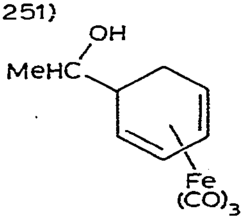
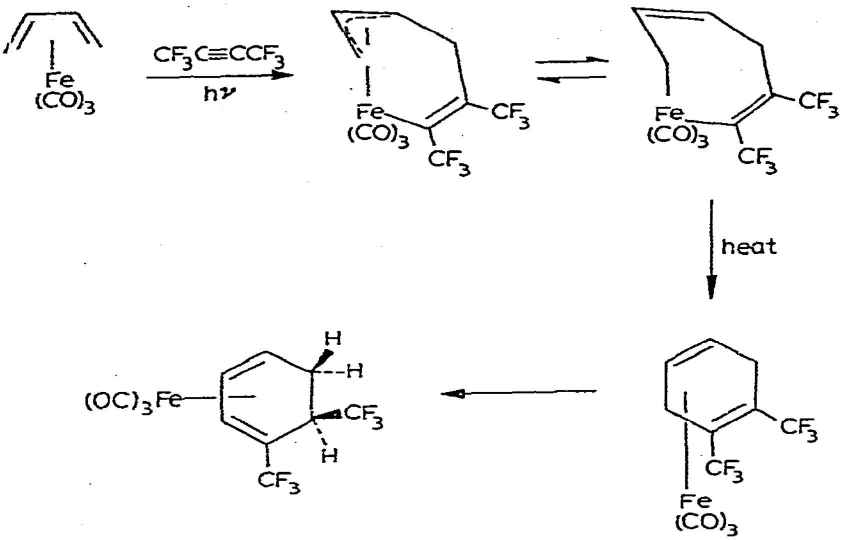


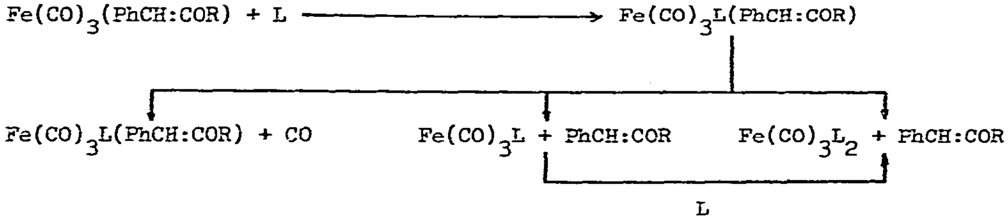
(254)

Scheme 35



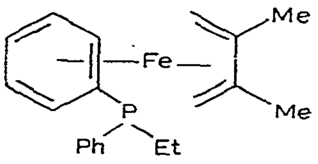
Attempts to probe the nature of the bonding in η^4-heterodiene iron tricarbonyl complexes have been made[315] via electric dipole moment studies. Among the compounds studied were $Fe(CO)_3$(*trans*-PhCH:COR) (R = H, Me or Ph), $Fe(CO)_3$(*trans*,*trans*-PhCH:CH:CHPh) and $Fe(CO)_3(CH_2:CHCHO)$. Vectorial analysis of the moments indicated that in all of the complexes the hydrocarbon ligands bond via π-electrons of the C=C and C=O bonds, and there is no involvement of the oxygen lone pair electrons. Metal-to-metal back-bonding is stronger in the heterodiene species than that in the butadiene complex. Kinetic studies have been made[316] of the reactions of $Fe(CO)_3$(PhCH:COR) (R = H, Me or Ph) with L (PPh_3, $AsPh_3$ and $SbPh_3$), and the results are summarised in Scheme 36.

Scheme 36



It appears that in the first, associative, step the C=O group is displaced by L.

Acyclic Bis-diene Complexes. Reduction of $FeCl_3$ in the presence of CO and dienes (butadiene, isoprene, 1,3-pentadiene) afforded[317] $Fe(CO)(diene)_2$, which is an effective catalyst for the polymerisation of butadiene. Treatment of



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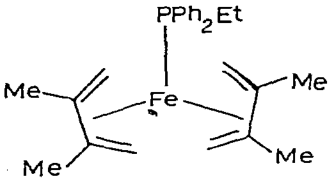

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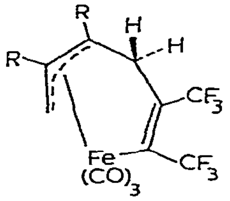

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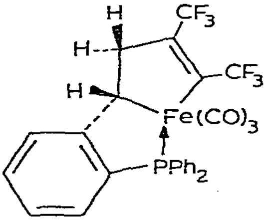
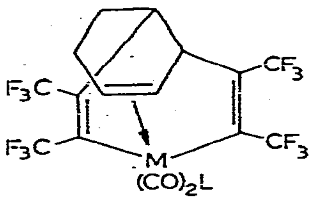


(258)

$Fe(C_8H_8)_2$ with butadiene and CO, or reduction of $FeCl_3$ in the presence of C_8H_8, C_4H_6 and CO, gave[318] $Fe(CO)(\eta^4-C_4H_6)(\eta^4-C_8H_8)$, an effective catalyst for the dimerisation of C_4H_6 to 4-vinylcyclohexene and cycloocta-1,5-diene. Photolysis of the arene complex 255 in the presence of 2,3-dimethylbutadiene afforded[319] the bis-diene complex 256. By electrolytic reduction of FeQ_3 (HQ = β-diketones, aromatic o-hydroxy- and o-amino-aldehydes or carboxylic acids, Schiff base ligands or polyamines) in polar organic solvents in the presence of unsaturated hydrocarbons, catalytically active organo-iron complexes could be prepared.[320] From $Fe(acac)_3$, PPh_3 and C_4H_6, by electrolysis in methanol containing LiCl at -10°, the species $Fe(PPh_3)(\eta^4-C_4H_6)_2$ was produced.

Cyclic Polyolefin Complexes. Dichloroacetylene reacted with $Fe_2(CO)_9$ giving[321] the tetrachlorocyclopentadienone complex $Fe(CO)_3(C_4Cl_4CO)$. UV irradiation of $Fe(CO)_3$(diene) (diene = isoprene, *cis* or *trans*-pentadiene) with $CF_3C_2CF_3$ gave[322] the known cyclopentadienone complex $Fe(CO)_3\{C_4(CF_3)_4CO\}$.[323] However, when diene = C_4H_6 or 2,3-dimethylbutadiene, the species 257, analogous to those fluoroolefin adducts described earlier (ref. 279, Scheme 24, 25; page were formed. The o-styryldiphenylphosphine complex $Fe(CO)_3(Ph_2PC_6H_4CH{:}CH_2)$ similarly gave 258. However, $M(CO)_3(C_6H_8)$ (M = Fe or Ru) reacted with hexafluorobutyne to give 259 (L = CO; R = H), and there was no evidence for intermediates similar to 257 or 258; further treatment of 259 with $P(OCH_2)_3CMe$ gave 259 (R = H; L = $P(OCH_2)_3CMe$). The structure of the 259 (M = Ru; R = H; L = phosphite) has been determined crystallographically, and it was established that the cyclohexene ring remains nearly planar. Treatment of $Ru(CO)_3(\eta^4-2-MeC_6H_7)$ with $CF_3C_2CF_3$ gave 259 (M = Rh; R = Me; L = CO), indicating that the acetylene



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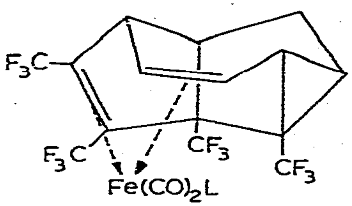


(260)

prefers to attack at the unsubstituted double bond. Treatment of $Fe(CO)_3(\eta^4-C_7H_8)$ (C_7H_8 = cycloheptatriene) with $CF_3C_2CF_3$ gave 260 (L = CO) which subsequently reacted with $P(OCH_2)_3CMe$ giving 260 (L = phosphite). The structure of this compound was also determined crystallographically and it was shown that addition of acetylene had taken place at the *endo* face of the original C_7 ring generating two new five-membered rings and one three-membered ring. The iron coordination geometry is approximately trigonal bipyramidal.

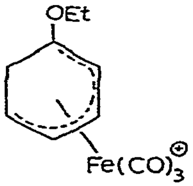
By refluxing 4-vinylcyclohexene with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, a 3:1 mixture of 1- and 2-ethylcyclohexadiene complexes of iron tricarbonyl were obtained.[324] Isomerisation of the 1-ethyl to the 2-ethyl species was achieved in concentrated H_2SO_4. The ^1H and ^{13}C n.m.r. spectra of $Fe(CO)_3(\eta^4-1-MeOC_6H_7)$ have been reinvestigated[325] and a determination of $^1J_{CH}$ and the energy barrier for basal-apical CO ligand exchange has been made. There was a discussion of the stability and lability of this complex in terms of electronic perturbations.

Treatment of $Fe(CO)_3(\eta^4-C_6H_8)$ with $MeCOCl/AlCl_3$ in chlorinated hydrocarbons gave[326] a mixture of $Fe(CO)_3(\eta^4-MeCOC_6H_7)$ and $[Fe(CO)_3(\eta^5-C_6H_7)]^+$. Similar reactions with $Fe(CO)_3(\eta^4-1-MeC_4H_5)$ and $Fe(CO)_3(\eta^4-2,3-Me_2C_4H_4)$ gave $Fe(CO)_3(\eta^4-1-Me-4-MeCOC_4H_4)$, $[Fe(CO)_3(\eta^5-C_4H_7)]^+$ and $Fe(CO)_3(\eta^4-\mathit{anti}-1-MeCO-2,3-Me_2C_4H_3)$, respectively.

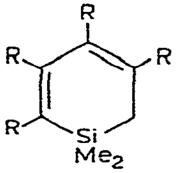
Reaction of $Fe(CO)_3(\eta^4$-cyclohexadienone) with $p-RC_6H_4NH_2$ (R = H, NO_2, OMe) afforded[327] $p-RC_6H_4NHPh$, and $1,4-(PhNH)_2C_6H_4$. However, treatment of the cyclohexadienone complex with $[Et_3O][BF_4]$ gave 261 which subsequently reacted with $C_6H_{11}NH_2$ and Et_2NH giving N-phenylcyclohexylamine and phenyldiethylamine, respectively.

Treatment of the silacyclohexadiene 262 (R = Ph) with $Fe(CO)_5$ caused[328] isomerisation to 263, while 262 (R = H) afforded 264. Treatment of 265 (R = Me or Et) or its 2,5-isomer with $Fe_2(CO)_9$ afforded[329] 266, and from this 265 could be liberated unchanged using Me_3NO.

The structure of tricyclo[6.4.0.0.^{2,7}]dodeca-3,5-dienetricarbonyl iron,[330] 267, has been determined crystallographically.[331] Under the influence of the fused cyclohexadiene ring, the C_4 ring would tend to be planar while the cyclohexane ring would tend to have a chair conformation. The actual result is a



(261)



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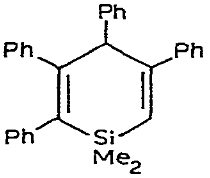

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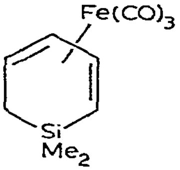

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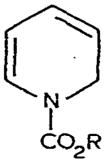

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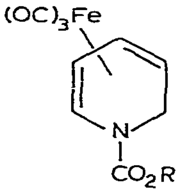

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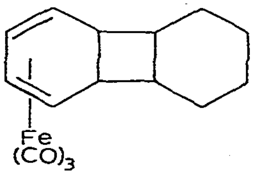

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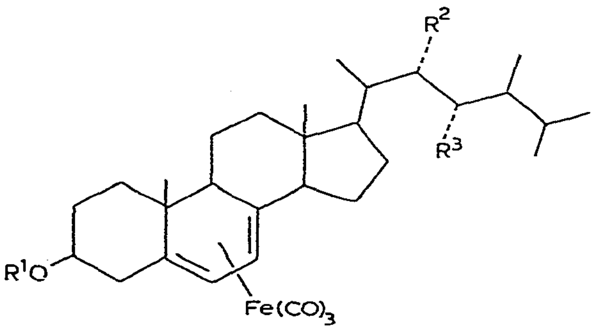
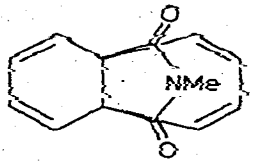


(268)

compromise, the C_4 ring being folded by 15° along its diagonal axis, and the cyclohexane ring having a conformation intermediate between planarity and a chair. Treatment of $Fe(CO)_3(\eta^4\text{-PhCH:CHCOMe})$ with acetylergosterol gave[332] 268 (R^1 = MeCO, R^2, R^3 = H). Treatment of this with B_2H_6, followed by $NaOH/H_2O_2$, gave 268 (R^1 = MeCO, R^2 = H, R^3 = OH), 268 (R^1 = MeCO, R^2 = OH, R^3 = OH), 268 (R^1 = H, R^2 = OH, R^3 = H), and 268 (R^1 = H, R^2 = H, R^3 = OH). Treatment of 269



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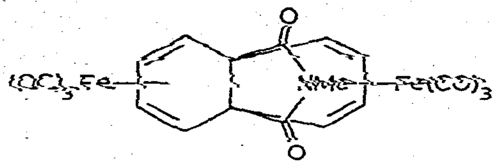

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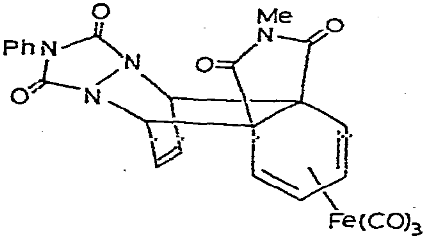

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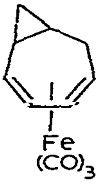

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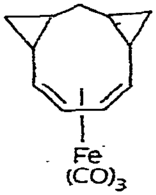

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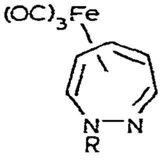

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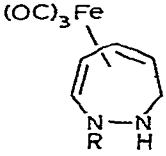

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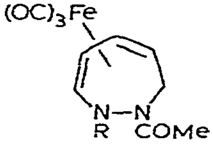


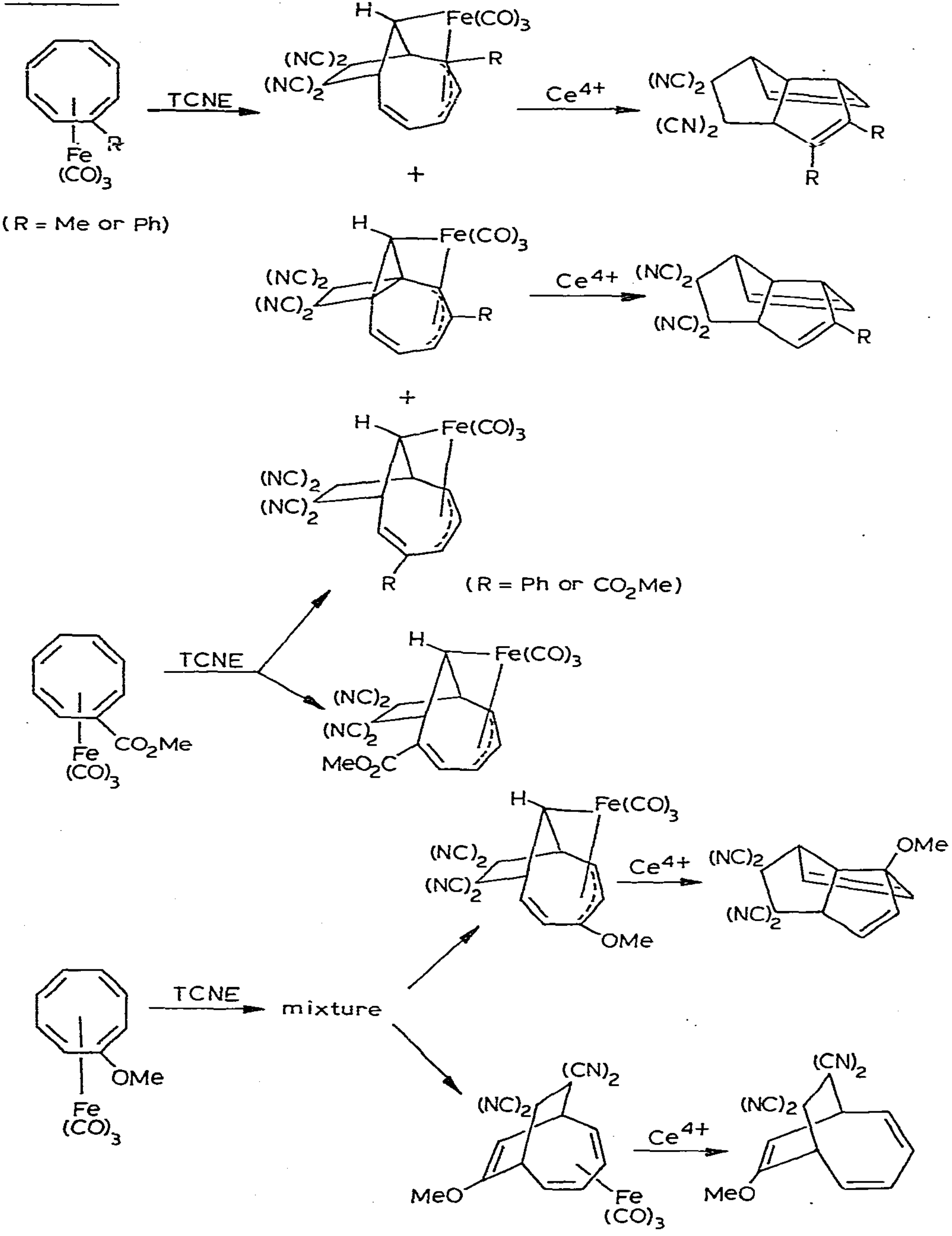
(276)

with $Fe(CO)_5$ or $Fe_2(CO)_9$ afforded[333], as *exo,exo* and *exo,endo* products, 270 which, on addition of Ce^{4+}, gave 271.

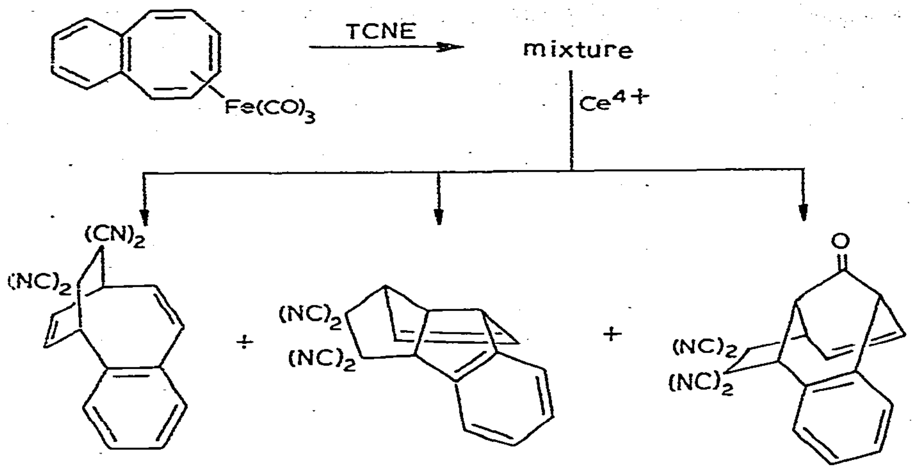
A vibrational spectral analysis has been made[334] of the norbornadiene complex $Fe(CO)_3(C_7H_8)$. Treatment of the cycloheptatriene isomer with CH_2I_2 gave[335] 272 and none of the species bi(cyclohepta-2,4,6-trienyl)hexacarbonyl-diiron reported elsewhere.[336] Similar treatment of $Fe(CO)_3(C_8H_8)$ afforded 273. Addition of allyl halides to the anion $[Fe(CO)_3(C_7H_7)]^-$ gave[337] the C–C bound dimer $[Fe(CO)_3(\eta^4-C_7H_7)]_2$ which has the *endo* configuration; alkyl halides afforded $Fe(CO)_3(\eta^4-C_7H_8)$. A suggested intermediate was the species $Fe(CO)_3(\eta^3-C_7H_7)-(\eta^1-C_3H_5)$. Treatment of $[M(CO)_3(\eta^7-C_7H_7)]^+$ with $[Fe(CO)_3(\eta^4-C_7H_7)]_2$ likewise afforded C–C bonded dimers, viz. $[M(CO)_3(\eta^6-C_7H_7)]_2$ with *exo*-configuration.

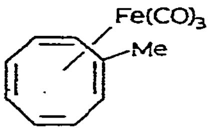
Reduction of the diazepine complexes 274 (R = COMe or CO_2Et) with borohydride ion gave[338] 275 which was further acylated in acetic anhydride giving 276. The three compounds so formed could also be obtained independently from the parent hydrocarbon and $Fe_2(CO)_9$.

Scheme 37



Scheme 37 (continued)





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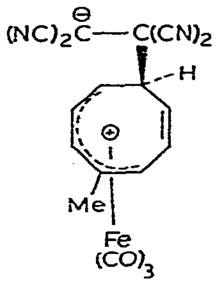

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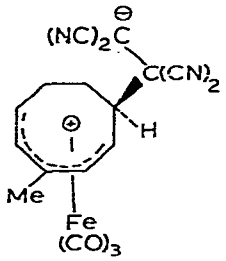
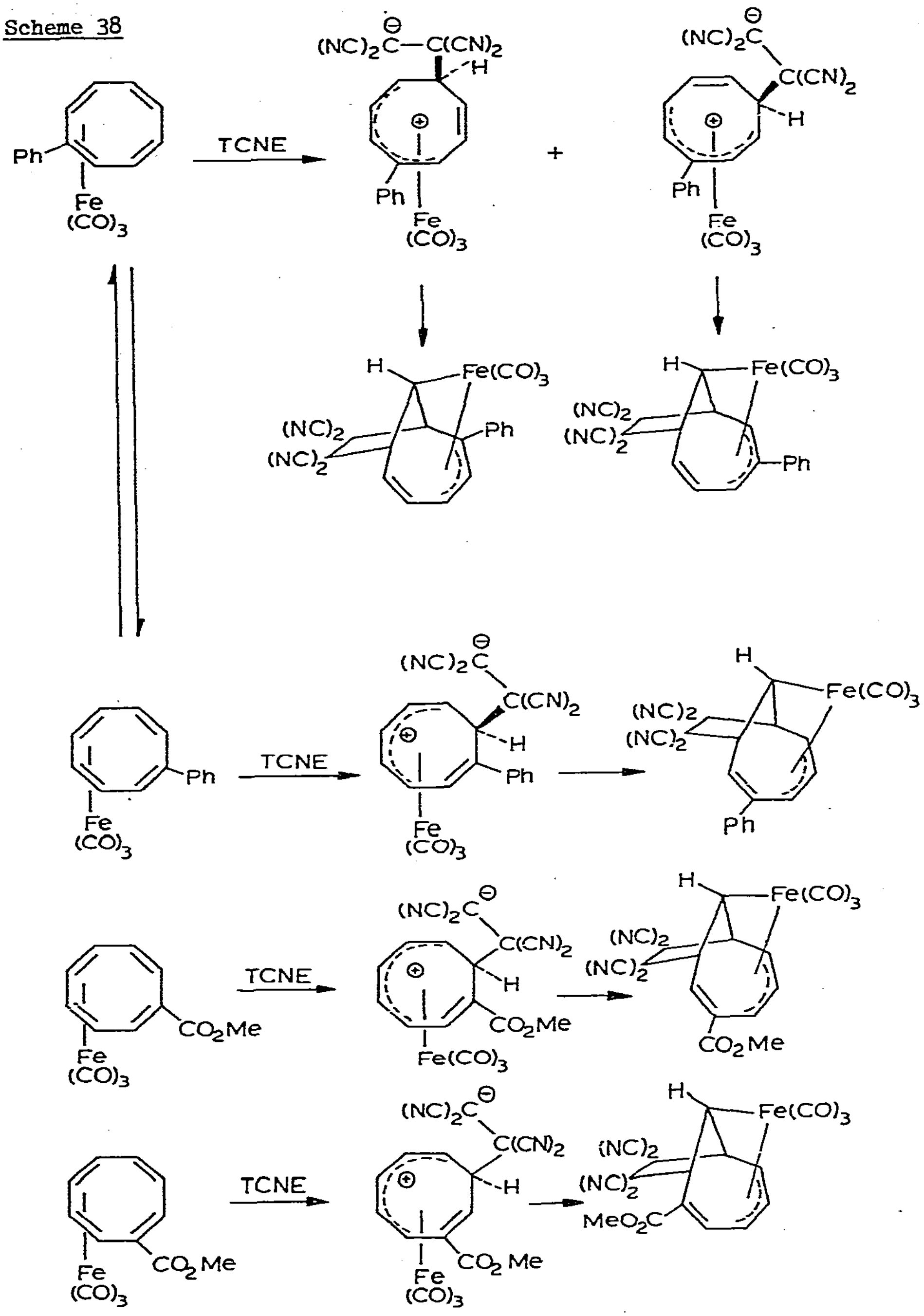


(279)

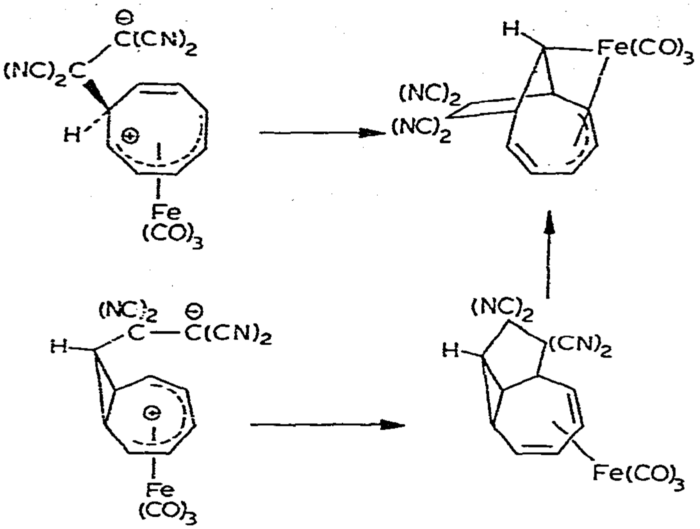
Reaction of cyclooctatetraene complexes of tricarbonyl iron with tetracyanoethylene afforded[339] several products, their ratio depending on solvent. These reactions are summarised in Scheme 37. Although the reaction appears to be general, the site of initial attack by the electrophile is markedly influenced by electronic factors. Thus $Fe(CO)_3(\eta^4-C_8H_7Me)$ afforded two complexes from attack at the γ (71%) and δ (21.5%) ring C atoms (positions relative to the substituent). For $Fe(CO)_3(\eta^4-C_8H_7Ph)$, however, α (39%) attack was found to be competitive with γ (16%) and δ (23%) addition. For $Fe(CO)_3(\eta^4-C_8H_7CO_2Me)$, the electrophile is directed to α (23%) and β (64%) sites preferentially. The inference drawn from the reaction with $Fe(CO)_3(\eta^4-C_8H_7OMe)$ is that binding to the γ-C atom is kinetically preferred, while in the benzocyclooctatetraene complex, the C atom adjacent to the site of benzo-fusion is attacked exclusively, as it is in protonation. It appears that the tautomer of $Fe(CO)_3(C_8H_7Me)$. 277 is kinetically the most reactive under the conditions applied, the zwitterions 278 and 279 being formed. Regioselectivity considerations suggest that 279 is

Scheme 38



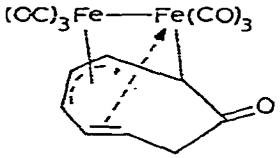
formed at a rate three times greater than that of 278 which will give the relative proportions of the products. The relative proportions of the products obtained from $Fe(CO)_3(C_8H_7R)$ (R = Ph, CO_2Me or OMe) can be similarly explained (Scheme 38). The formation of the Fe-C bond could either occur directly, or via

Scheme 39

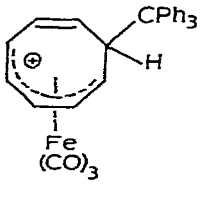


three-membered ring intermediate, as shown in Scheme 39. However, the greatest electron deficiency appears to be at the γ-C atom, suggesting that the zwitterion collapses directly to give the bicyclic product. Oxidation of the adducts with Ce^{4+} afforded dihydrotetracyanotriquinacenes, as indicated in Scheme 37. In the reactions to give $Fe(CO)_3(\eta^4\text{-}C_8H_7R)$ from $Fe_2(CO)_9$ and the appropriate cyclooctatetraenes, the species with R = OMe also afforded the tropone complex $Fe(CO)_3\{\eta^4\text{-}C_7H_8(CO)\}$ and 280, which is structurally analogous to $Fe_2(CO)_6(C_8H_{10})$, 58.[93]

Reaction of $Fe(CO)_3(C_8H_8)$ with Ph_3C^+ gave[340] the cation 281 which, on deprotonation with base, produced the fluxional $Fe(CO)_3(C_8H_7CPh_3)$. Protonation of this trityl derivative gave, reversibly, 282, while thermolysis at 160° *in*



(280)



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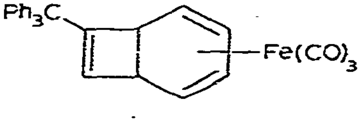
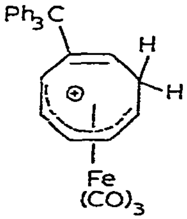


(283)

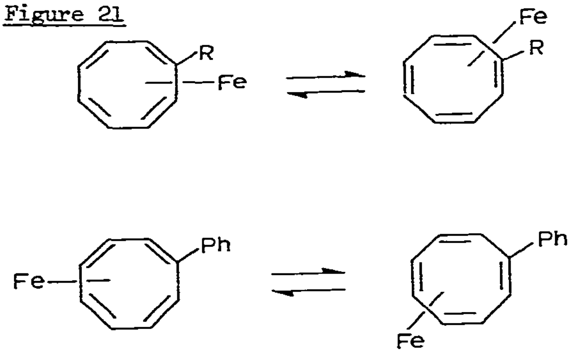


(282)

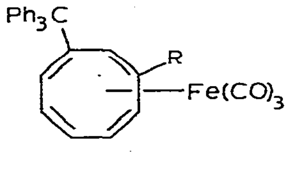
vacuo afforded the stereochemically non-rigid 283. Oxidation of the last with Ce^{4+} afforded tritylcyclooctatetraene, $C_8H_7CPh_3$. These results confirm previous observations.[341]

Treatment of $Fe_2(CO)_9$ with C_8H_7R (R = $SiMe_3$, $GeMe_3$, $SnMe_3$, $SiMe_2(CH_2CH{:}CH_2)$ and $Fe(CO)_2(\eta^5\text{-}C_5H_5)$) afforded[342] $Fe(CO)_3(C_8H_7R)$ and $Fe_2(CO)_6(C_8H_7R)$ (R = $SiMe_3$ or $SnMe_3$). It may be noted that the species $Fe(CO)_2(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_8H_7)$ was obtained by reaction of $Fe(CO)_2(\eta^5\text{-}C_5H_5)Cl$ with LiC_8H_7. Addition of trityl tetrafluoroborate to $Fe(CO)_3(C_8H_7R)$ (R = $SiMe_3$ or $GeMe_3$) gave a salt which, on hydrolysis, afforded 284 (the structure of the species R = $SiMe_3$ has been confirmed crystallographically[343]). Reaction of $Fe(CO)_3(C_8H_7Ph)$ with Ph_3C^+, followed by hydrolysis, gave $Fe(CO)_3\{C_8H_6Ph(CPh_3)\}$. The fluxional properties of the species $Fe(CO)_3(C_8H_7R)$ and $Fe(CO)_3(C_8H_7Ph)$ are different (fig. 21). Protonation of $Fe(CO)_3(C_8H_7Me)$ at low temperatures afforded two monocyclic isomers which showed that electrophilic attack occurred at an internal C atom of the uncomplexed diene, in contrast to reactions of Ph_3C^+ where attack occurs at the outer C atom of the free diene (see also ref. 340).

Figure 21

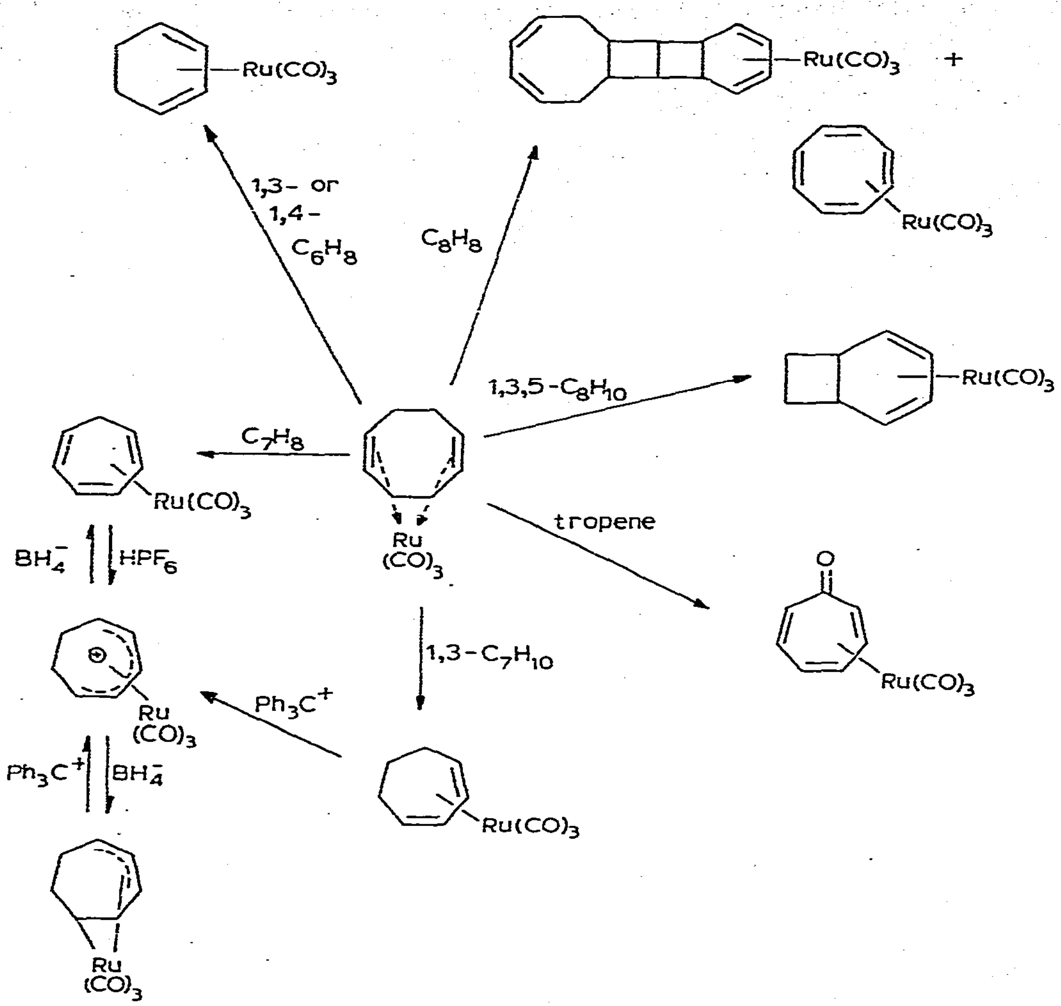


Reaction of $Ru_3(CO)_{12}$ with 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene gave[344] 285, the structure of which was determined crystallographically. Some substitution reactions[345] of $Ru(CO)_3(\eta^4\text{-}1,5\text{-}C_8H_{12})$ are outlined in Scheme 40. Reaction of cyclooctatetraene with $Ru_4(CO)_{12}H_4$ in refluxing heptane gave[346] ruthenium carbonyl complexes of C_8H_8 and of cyclooctatrienes, $Ru_2(CO)_5(C_{16}H_{16})$ 61[96], $C_{16}H_{16}$ and its ruthenium tri-carbonyl complex 286. The dimer of C_8H_8 is very unusual and has not been detected previously. The dimer, and 286, may be formed via $Ru(CO)_3(C_8H_8)$, and indeed in a reaction between C_8H_8 and $Ru(CO)_3(C_8H_8)$, 286 was produced. The uncoordinated 1,3-diene unit in $Ru(CO)_3(C_8H_8)$ is very



(284)

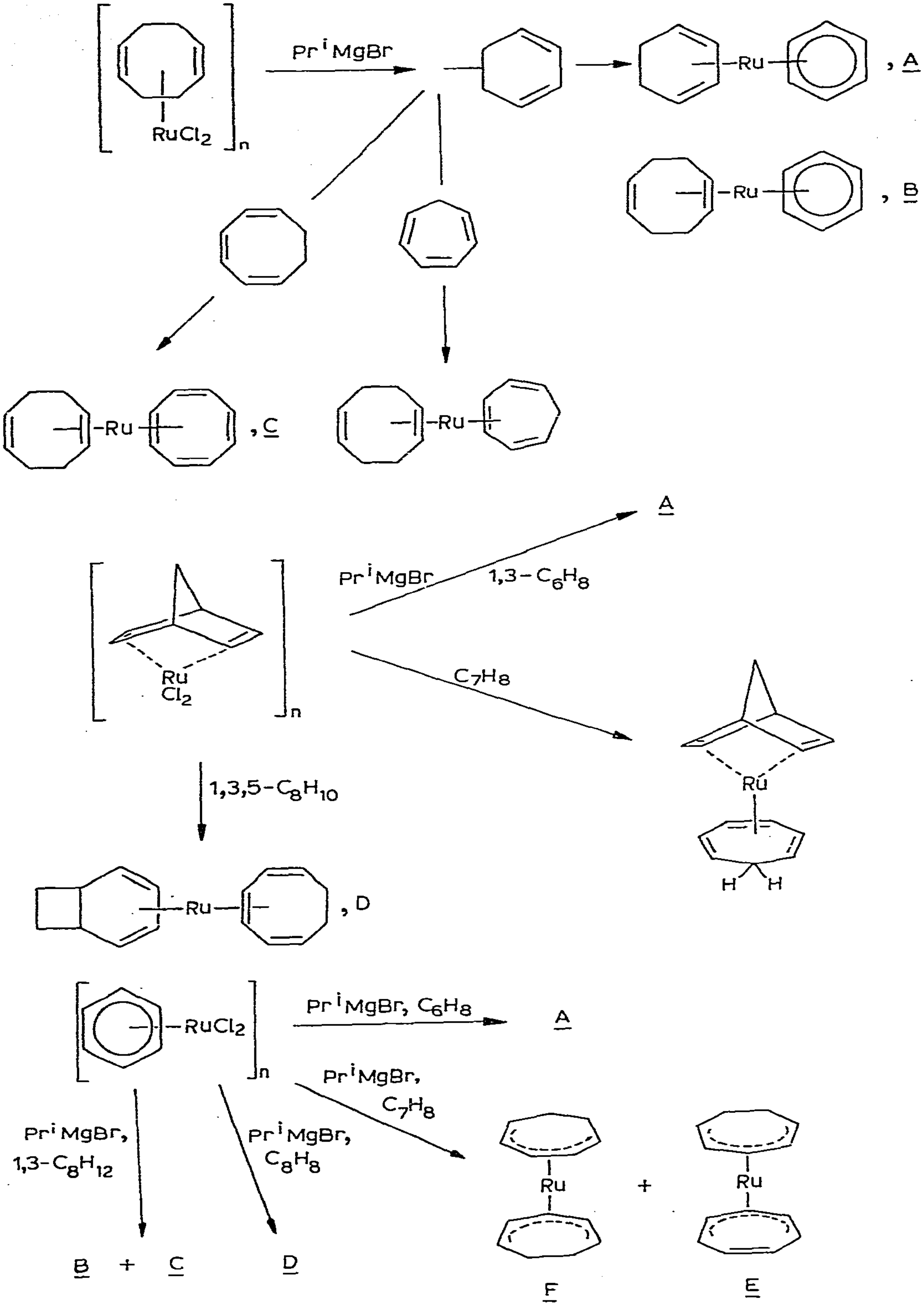
Scheme 40



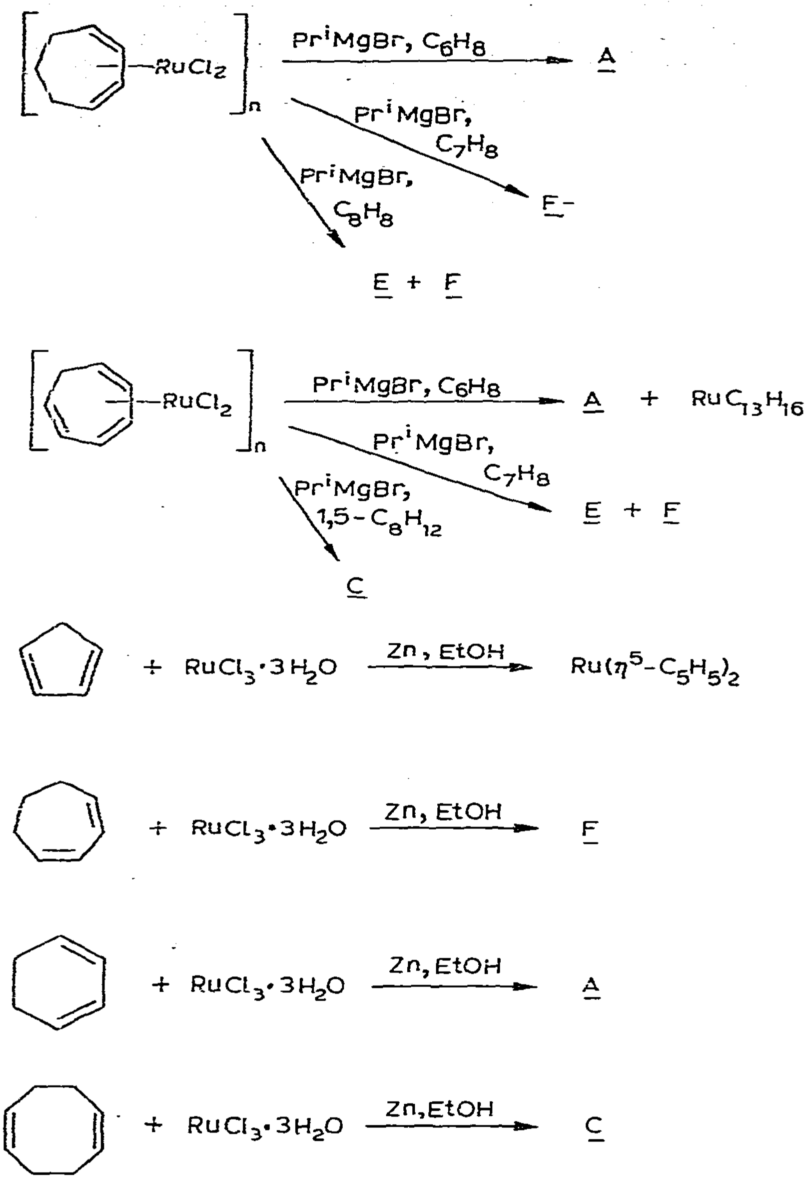
nearly planar[347] and so, unlike free C_8H_8, can undergo $(4+2)\pi$ cyclo-addition reactions. Whether Diels-Alder addition of C_8H_8 to Ru(CO)$_3$(C_8H_8) occurs directly at the coordinate olefin, or via preliminary coordination to the metal cannot be directly determined. However, in either event, Ru(CO)$_3$($C_{16}H_{16}$) would not be produced directly, and subsequent steps would be necessary. Reaction of Fe(CO)$_3$(C_8H_8) with C_8H_8 yielded[348] complexes of cyclooctatetraene dimers, but not analogous to 286; the Fe analogue of this particular dimer can only be obtained by treatment of Fe$_2$(CO)$_9$ with the parent hydrocarbon.

Norbornadiene and cycloocta-1,5-diene complexes of ruthenium containing aminoacid groups have been reported.[349] Treatment of [Ru(diene)Cl$_2$]$_n$ (diene = norbornadiene or cycloocta-1,5-diene) with NaS$_2$PMe$_2$ gave[350] Ru(diene)(S$_2$PMe$_2$)$_2$. The diene was readily replaced by various chelating di-phosphines and -arsines

Scheme 41

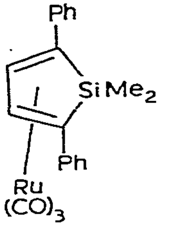

RuCl2
n
Pr i MgBr
Ru
, A
Ru
, B
Ru
, C
Ru
A
Pr i MgBr
1,3-C6H8
Ru
Cl2
n
C7H8
Ru
H
H
1,3,5-C8H10
Ru
, D
RuCl2
n
Pr i MgBr, C6H8
A
Pr i MgBr,
C7H8
Pr i MgBr,
1,3-C8H12
Pr i MgBr,
C8H8
Ru
+
Ru
B + C
D
F
E

Scheme 41 (continued)



(L–L) giving *cis*-Ru(L–L)(S_2PMe_2)$_2$. Reaction of anhydrous $RuCl_3$ or $[Ru(CO)_2Cl_2]_n$ with cycloocta-1,4-diene afforded[351] complexes of the 1,5-isomer, viz. $[Ru(C_8H_{12})Cl_2]_n$ and $[Ru(CO)(C_8H_{12})Cl_2]_2$, respectively. Treatment of $RuCl_3$ with 2,3-dicyanobicyclo[2.2.2]octa-2,5,7-triene and its 1,4,5,6,7,8-hexamethyl derivative gave[352] the octahedral polymeric species $[Ru(olefin)Cl_2]_2$, in which Ru atoms are bound to all three double bonds, but each metal atom is attached to only two double bonds.

Reduction of $[RuLCl_2]_n$ (L = benzene, 1,3-cycloheptadiene or 1,3,5-cycloheptatriene) or $RuCl_3$ with $MgPr^iBr$ or zinc dust in ethanol in the presence of certain cyclic oligoolefins gave[353] RuL(olefin) as outlined in Scheme 41. The ^{13}C n.m.r. spectral studies of $Ru(\eta^5-C_7H_9)_2$ revealed that it was fluxional.



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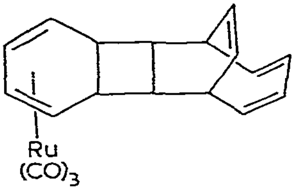


(286)

DIENYL COMPLEXES

Mass spectral studies of $Fe(\eta^5-C_5H_5)(\eta^5$-*exo*-$RC_6H_6)$ have shown[354] that the main fragmentation routes involve stereoselective migration of the *endo* hydrogen atom of the cyclohexadienyl ring to the metal. Field desorption mass spectra have been obtained[355] of $[Fe(CO)_3(\eta^5-L)]^+$ (L = C_6H_7, C_7H_9, $C_{10}H_{11}$, 2-$MeOC_6H_7$) and $[Fe(\eta^5-C_5H_5)(\eta^6-L')]^+$ (L' = benzene, toluene, mesitylene). In all cases, molecular or quasi-molecular ions for the cations were present, usually as the base peaks in the spectra. Fragment ions corresponding to metal-ligand cleavages were also observed in most cases.

NMR, particularly ^{31}P, spectral studies have been made[356] of the series $M(CO)_xL_{3-x}$(diene) and $[M(CO)_xL_{3-x}(\eta^5\text{-dienyl})]^+$, where M = Fe or Ru, L = $P(OCH_2)_3$-CEt, diene = C_6H_8 or C_7H_{10}, x = 0, 1 or 2 and dienyl = C_5H_5, C_6H_7, C_7H_9, x = 1 or 2. The fluxional properties of the diene and dienyl species were interpreted as shown in figure 22. For the cycloheptadiene complexes another form of fluxionality, associated with the ring (figure 23) was observed.
Rates for site exchange of the phosphite ligand in both diene and dienyl cases were generally faster for the iron complexes, and the cycloheptadiene ring inversion process was faster than phosphite site exchange.

By refluxing $[Fe(CO)_3(\eta^5-C_6H_7)]^+$ in methanol, three products, 287, 288 and $Fe(CO)_3(C_6H_8)$, were formed,[357] depending on conditions. Thus after 20 min, the products were mainly 287 and a trace of 288. After 90 min., the relative amount of 287 had decreased and 288 and $Fe(CO)_3(C_6H_8)$ were present. After 23 days, the ratio 286:287 was 65:35 in methanol and no further changes were detected. It was noted that cleavage of the methoxyl group from 288, giving

Figure 22

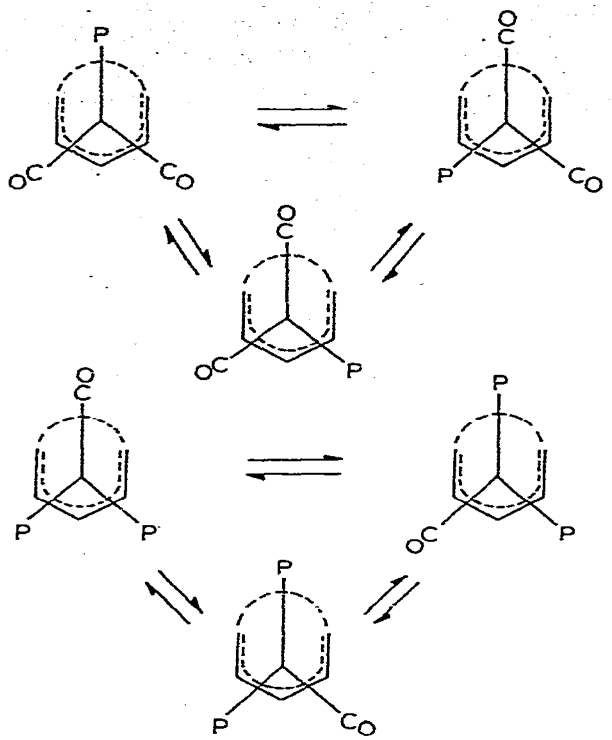
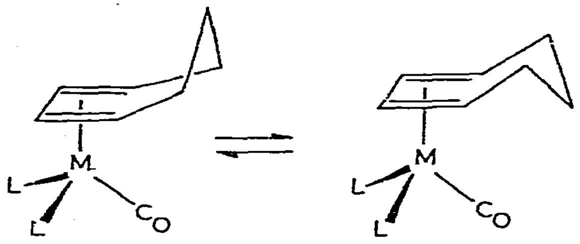
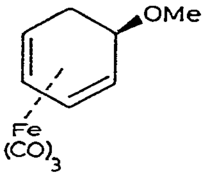


Figure 23



$[Fe(CO_3(\eta^5\text{-}C_6H_7)]^+$, occurred in HBF_4/propionic anhydride mixtures, and that 287 was converted to 288 when stirred at 20° in methanol containing a small amount of HBF_4. In a similar way, the endo derivatives $Fe(CO)_3(\eta^4\text{-}C_7H_9R)$ (R = OEt or $CH(CN)_2$) were prepared from $[Fe(CO)_3(\eta^5\text{-}C_7H_{10})]^+$. However, it has not so far been proved possible to make *endo* derivatives of bicyclo[5.1.0]octadienyl complexes. It was found that methoxyl group transfer from the CO group in $Ru(CO)_2(\eta^5\text{-}C_6H_7)(CO_2Me)$ gave specifically *endo*-$Ru(CO)_3(\eta^4\text{-}C_6H_7OMe)$.

Treatment of $[Fe(CO)_3(\eta^5\text{-}C_6H_6R)]^+$ (R = H, Me or OMe) with R'MgX, $Cd(C_3H_5)_2$ or ZnR'_2 gave[358] the diene complexes $Fe(CO)_3(C_6H_6RR')$, 289. Reaction of $[Fe(CO)_3(\eta^5-C_6H_7)]^+$ with Me_3MAr (M = Si or Sn, Ar = Ph, p-$MeOC_6H_4$, p-$Me_2NC_6H_4$, 2-furyl or 2-thienyl) gave[359] $Fe(CO)_3(\eta^4-C_6H_7Ar)$, 289 (R = H, R' = Ar). Preliminary kinetic data have been obtained and indicated that the order of reactivity is Ph < p-$MeOC_6H_4$ < p-$Me_2NC_6H_4$, that reactions of 2-thienyl and 2-furyl silyl compounds were considerably faster than those reported earlier,[360] and that the aryl tin compounds are more readily attacked than their silyl analogues. Preliminary studies showed that $[Fe(CO)_3(\eta^5-C_5H_7)]^+$ also behaved as an electrophile. Treatment of $[Fe(CO)_3(\eta^5-C_6H_7)]^+$ with $P(OMe)_3$ in methanol gave[361] 289 (R = H, R' = $P(:O)(OMe)_2$), and with hypophosphorous acid and $NaHSO_3$, the corresponding species with R' = $PH(:O)(OH)$ and SO_3H were produced. Reaction of



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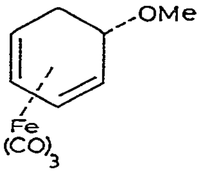

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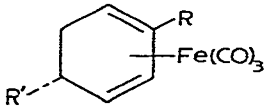

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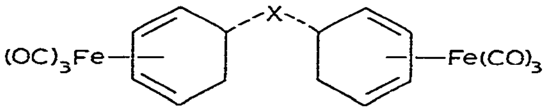

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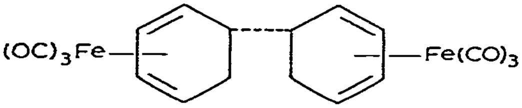

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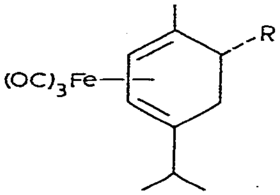

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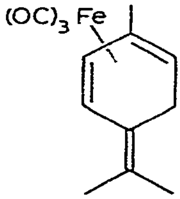


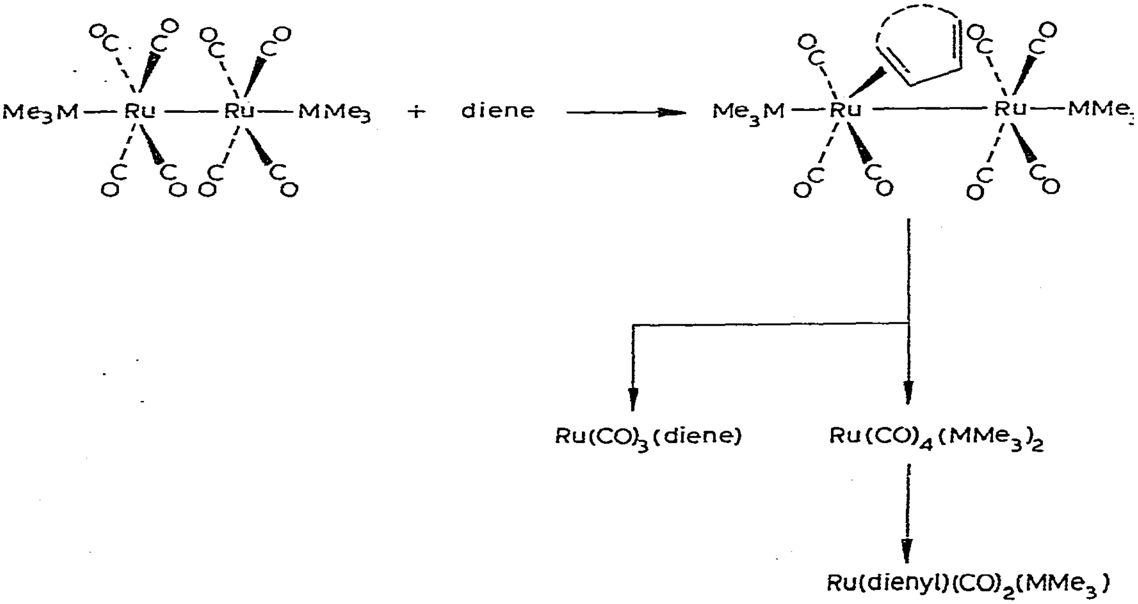
(293)

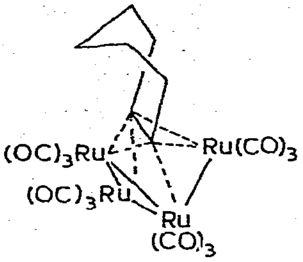
the dienyl cation with $NaHCO_3$ or Na_2S afforded the dimers 290 (X = O or S). While treatment of the dienyl cation with BH_4^- afforded $Fe(CO)_3(\eta^4-C_6H_8)$, reduction with Zn/Cu couple in THF or diisopropylamine in acetonitrile gave the C-C bound dimer 291. The dienyl iron tricarbonyl cation derived from (−)-α-phellandrene reacted similarly with $P(OMe)_3$ and $NaHSO_3$, giving 292 (R = $P(:O)(OMe)_2$ or SO_3H), but treatment with weak bases, e.g. $NaHCO_3$, $Na_2S_2O_4$, amines or enamines, gave only 291. Addition of $[Et_3NH][MCl_3]$ (M = Si, Ge or Sn) to $[Fe(CO)_3(\eta^5-C_6H_7)]^+$ gave[362] 289 (R' = MCl_3) in good yield.

Oxidation of $Fe(\eta^5-C_5H_5)(\eta^5-C_6H_6R)$ (R = Et, CH_2Ph or C_5H_5) by $[Ph_3C][BF_4]$ or N-bromosuccinimide proceeded[363] either by *exo*-R group abstraction or *endo*-H atom abstraction. Mixtures of $[Fe(\eta^5-C_5H_5)(\eta^6-C_6H_6)]^+$ and $[Fe(\eta^5-C_5H_5)(\eta^6-C_6H_5R)]^+$ were formed in the reactions, and the tendency for R group abstractions increased along the series R = C_5H_5 < Et < CH_2Ph. When heated, $Fe(\eta^5-C_5H_5)(\eta^5-C_6H_7)$ afforded ferrocene.

Reaction of $Ru(CO)_4(MMe_3)_2$ (M = Si or Ge) with C_5H_6, C_6H_8 or C_7H_{10} afforded[364] $Ru(CO)_2(\eta^5\text{-dienyl})MMe_3$. Yields of the cyclohexadienyl complex were low, the main product being the known $Ru(CO)_3(\eta^4-C_6H_8)$.[365] The mechanism of this reaction is thought to involve formation of $Ru(CO)_2(\eta^4\text{-diene})(MMe_3)_2$ which undergoes an intramolecular abstraction by Me_3M of an H atom from the ring. Similar reactions involving $[Ru(CO)_4MMe_3]_2$ also afforded $Ru(CO)_2(\eta^5\text{-dienyl})(MMe_3)$ together with $Ru(CO)$ $(\eta^4\text{-diene})$, by a reaction perhaps as outlined in Scheme 42. Evidence to support this has been obtained from spectral studies of

Scheme 42





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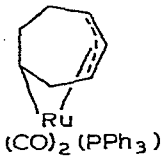
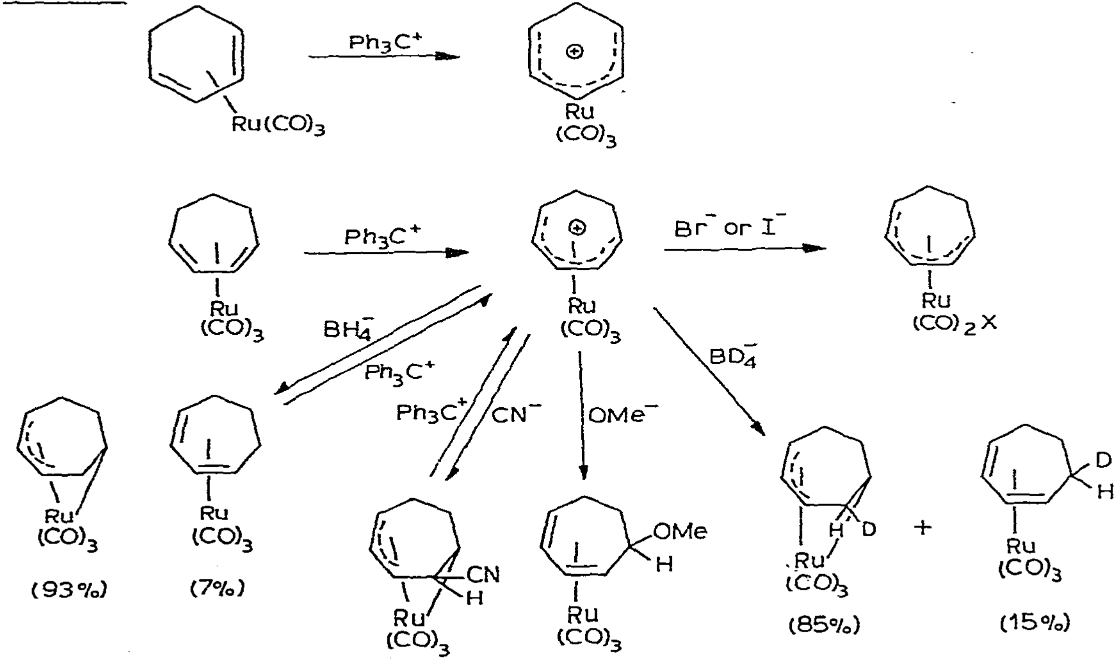


(295)

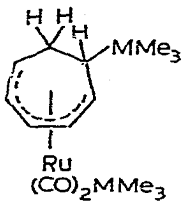
reactions involving $[Ru(CO)_4SiMe_3]_2$. Treatment of $Ru(CO)_4(MMe_3)_2$ or $[Ru(CO)_4GeMe_3]_2$ with indene gave low yields of $Ru(CO)_2(\eta^5\text{-}C_9H_7)(MMe_3)$. Reaction of $Ru_3(CO)_{12}$ with C_6H_8 or C_7H_{10} gave $Ru(CO)_3$(diene) complexes, but with C_7H_{10}, $Ru_3(CO)_3(\eta^5\text{-}C_7H_9)(\eta^7\text{-}C_7H_7)$ 130,[155] and $Ru_4(CO)_{12}(C_7H_{10})$, 294 were also formed. The species $Ru_3(CO)_6(\eta^5\text{-}C_7H_9)(\eta^7\text{-}C_7H_7)$, together with $Ru_2(CO)_4(\eta^7\text{-}C_7H_7)(C_7H_{12})$ was also obtained by reacting $Ru_3(CO)_{12}$ with cycloheptene. Comparison of 294 may be made with $Ru_4(CO)_{11}(C_8H_{10})$, whose structure is known.[366] Hydride abstraction from $Ru(CO)_3(C_6H_8)$ and $Ru(CO)_3(C_7H_{10})$ using Ph_3C^+ afforded the expected dienyl cations, and some reactions of $[Ru(CO)_3(C_7H_9)]^+$ are shown in Scheme 43. It is presumed that nucleophilic attack occurs at an *exo* position, as established[367] in $Ru(CO)_3\{1,2,3,6\text{-}\eta^4\text{-}C_8H_{11}(5\text{-}CN)\}$. Treatment of $Ru(CO)_3(\eta^4\text{-}C_7H_{10})$ with PPh_3 gave $Ru(CO)_2(PPh_3)(C_7H_{10})$ whereas iodide abstraction from $Ru(CO)_2(\eta^5\text{-}C_7H_9)I$ using Ag^+ in the presence of PPh_3 gave $[Ru(CO)_2(PPh_3)\text{-}$

Scheme 43



$(\eta^5\text{-}C_7H_9)]^+$ which, on reduction with BH_4^- afforded 295.

Reaction of $Ru(CO)_4(MMe_3)_2$ (M = Si or Ge) with C_7H_8 gave[368] $Ru(CO)_3$-$(\eta^5\text{-}C_7H_8MMe_3)(MMe_3)$, 296, while $Ru(CO)_4(SiMe_3)_2$ afforded with $C_7H_7C_6F_5$, 297, whose structure has been confirmed crystallographically.[367] An equimolar mixture of $Ru(CO)_4(SiMe_3)_2$, $Ru(CO)_4(GeMe_3)_2$ and C_7H_8 was heated and examined, using ^{13}C n.m.r. spectroscopy, for "cross-over" products. The major species identified was 296 (M = Si or Ge), and minor amounts of $Ru(CO)_2(C_7H_9)(MMe_3)$ (M = Si or Ge) together with very low amounts of $Ru(CO)_2\{1\text{-}5\text{-}\eta^5\text{-}C_7H_8(6\text{-}SiMe_3)\}$-$(GeMe_3)$ were detected. This very low yield and the absence of other "cross-over" products suggested that MMe_3 migration occurs substantially by intramolecular pathways. Iodination of 296 (M = Ge) gave 298 (M = Ge). In the reaction of $[Ru(CO)_4MMe_3]_2$ (M = Si or Ge) with C_7H_8, lower yields of 296 are obtained together with 299 and 300 (M = Si or Ge). The last is probably analogous to 68.[102,103] Treatment of $[Ru(CO)_4SiMe_3]_2$ with C_7H_7R (R = Me, Ph or



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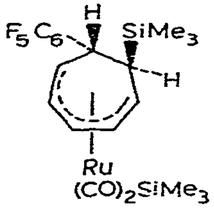

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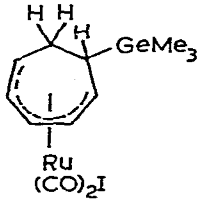

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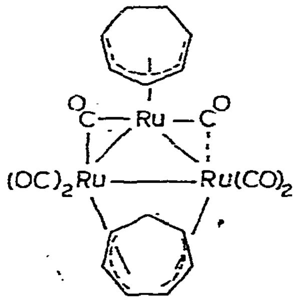

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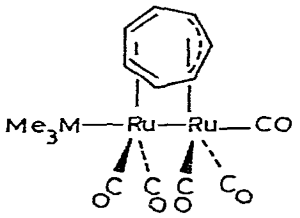

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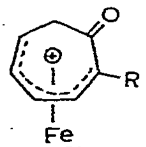

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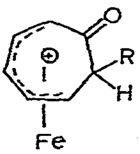
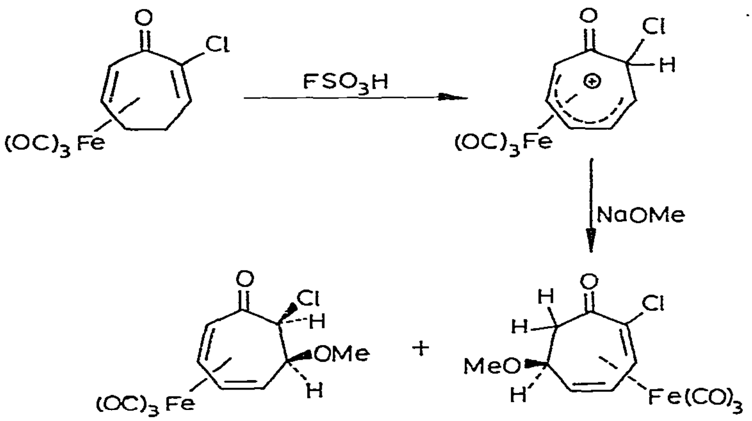


(302)

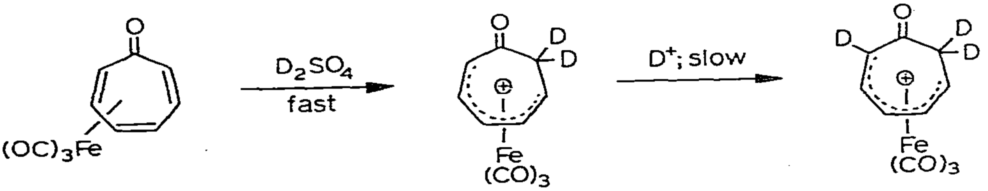
C_6F_5) gave $Ru_2(CO)_5(C_7H_6R)(SiMe_3)$, like 68 with the $SiMe_3$ group on the ring replaced by R, while C_7H_7R (R = CN or OBu^t) afforded $Ru_2(CO)_5(C_7H_7)(SiMe_3)$.

Reaction of tropone derivatives $2\text{-}RC_7H_5O$ (R = Me, Cl or Ph) with $Fe_2(CO)_9$ afforded[370] $Fe(CO)_3(2\text{-}RC_7H_5O)$. Protonation of this in concentrated H_2SO_4 gave 301, probably via the intermediate 302. Substantial backing for this pathway was obtained by studying the reactions of $Fe(CO)_3(2\text{-}ClC_7H_5O)$ in FSO_3H, followed by treatment with OMe^-, Scheme 44. Isolation of both methoxylated diene complexes indicates that a relatively high proportion of 302 must be formed and supports the view that the initial protonation occurs at an uncoordinated double bond in the starting material. This is then followed by a rapid 1,2-shift of the $Fe(CO)_3$ group and the overall reaction scheme seems to disprove recent suggestions[371] that the formation of 301 occurs via preferential attack of H^+ at a terminal C atom of the diene $Fe(CO)_3$ group in $Fe(CO)_3(C_7H_5O)$. It was observed that the rate of isomerisation of 302 to 301 was higher than that of the parent tropone species, Scheme 45.

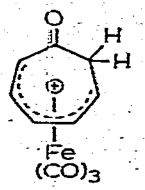
Scheme 44



Scheme 45



From a study of the attack by OMe^- on $[Fe(CO)_3(2\text{-}ClC_7H_6O)]^+$ it would appear that *exo* addition occurs and it was deduced that in FSO_3H at -78°, stereoselective protonation occurs from the *endo* rather than the *exo* side of the uncoordinated double bond. When $[Fe(CO)_3(2\text{-}RC_7H_6O)]^+$, 301, was quenched with Na_2CO_3/MeOH, the species 304 was formed in high yields. Protonation of $Fe(CO)_2(PPh_3)(C_7H_5O)$



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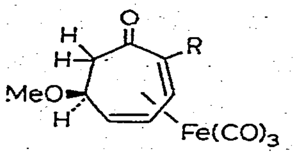

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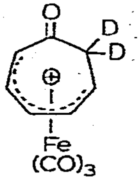

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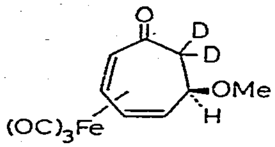


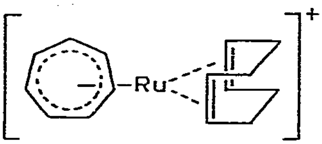
(306)

in D_2SO_4 gave 305 which, unlike $Fe(CO)_3(C_7H_5O)$, underwent no further D^+ uptake, possibly due to steric hindrance associated with PPh_3. Addition of NaOMe to 305 gave 306.

Treatment of $Fe(CO)_3(C_8H_{12})$ (C_8H_{12} = 1,3 or 1,5-cyclooctadiene) with Ph_3C^+ gave[372] 307 and 308 whose reactions with nucleophiles are summarised in Scheme 46. Addition of Ph_3C^+ to $Ru(C_7H_8)(C_8H_{12})$ afforded[373] $[Ru(\eta^7\text{-}C_7H_7)(C_8H_{12})]^+$ 309; and treatment of this with certain nucleophiles (R^- = Me or CN) gave 310. Protonation of 311 afforded 312, also produced by hydride abstraction from $Ru(\eta^5\text{-}C_7H_9)_2$. Treatment of 312 with 1,8-bis(dimethylamino)naphthalene afforded the adduct 313 (mode of attachment of the napththalene unspecified). Borohydride reduction of 311 caused regeneration of $Ru(\eta^5\text{-}C_7H_9)_2$, while CN^- attack gave $Ru(\eta^5\text{-}C_7H_9)(\eta^5\text{-}C_7H_8CN)$; treatment of the last with more Ph_3C^+ followed by CN^- ultimately produced $Ru(\eta^5\text{-}C_7H_8CN)_2$. Reaction of 311 with other nucleophiles (R = Me^-, OMe^-, NMe_2^-, NEt_2^-, $CH(CO_2Et)_2^-$) gave $Ru(\eta^5\text{-}C_7H_9)(\eta^5\text{-}C_7H_8R)$ in which the substituent occupies an *exo* position.

CYCLOPENTADIENYL COMPOUNDS

Binuclear carbonyl complexes. Thermal decomposition of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ above 165° gave[374] $Fe_4(CO)_4(\eta^5\text{-}C_5H_5)_4$ which, above 210°, afforded ferrocene. The reactions of various iron and ruthenium carbonyl compounds with AlR_3 (R = allyl) have been discussed.[375] The species $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2(AlR_3)_n$ (n = 1 or 2), $[Ru(CO)_2(\eta^5\text{-}C_5H_5)]_2(AlR_3)$ and $[Fe(CO)(\eta^5\text{-}C_5H_5)(AlR_3)]_4$ have been described and in all, the Al atom is bound to bridging CO groups. Treatment of $[Fe_3(CO)_{11}H]^-$ with $MeOSO_2F$ gave $Fe_3(CO)_{11}(COMe)H$, 109 (see ref. 143) and the effect of ion pairing on the reactivity of $M[Fe(CO)_4R]$ (R = allyl), particularly alkyl migrations, e.g. $M[Fe(CO)_4R] + L \rightarrow M[Fe(CO)_3L(COR)]$, was reviewed. It was



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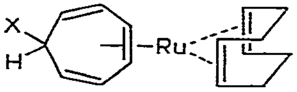

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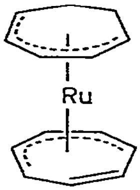

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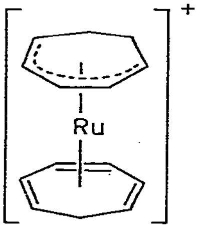

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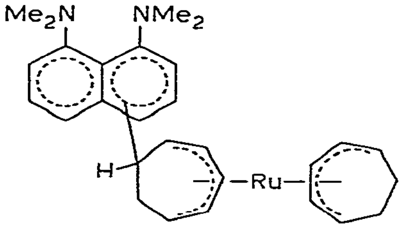


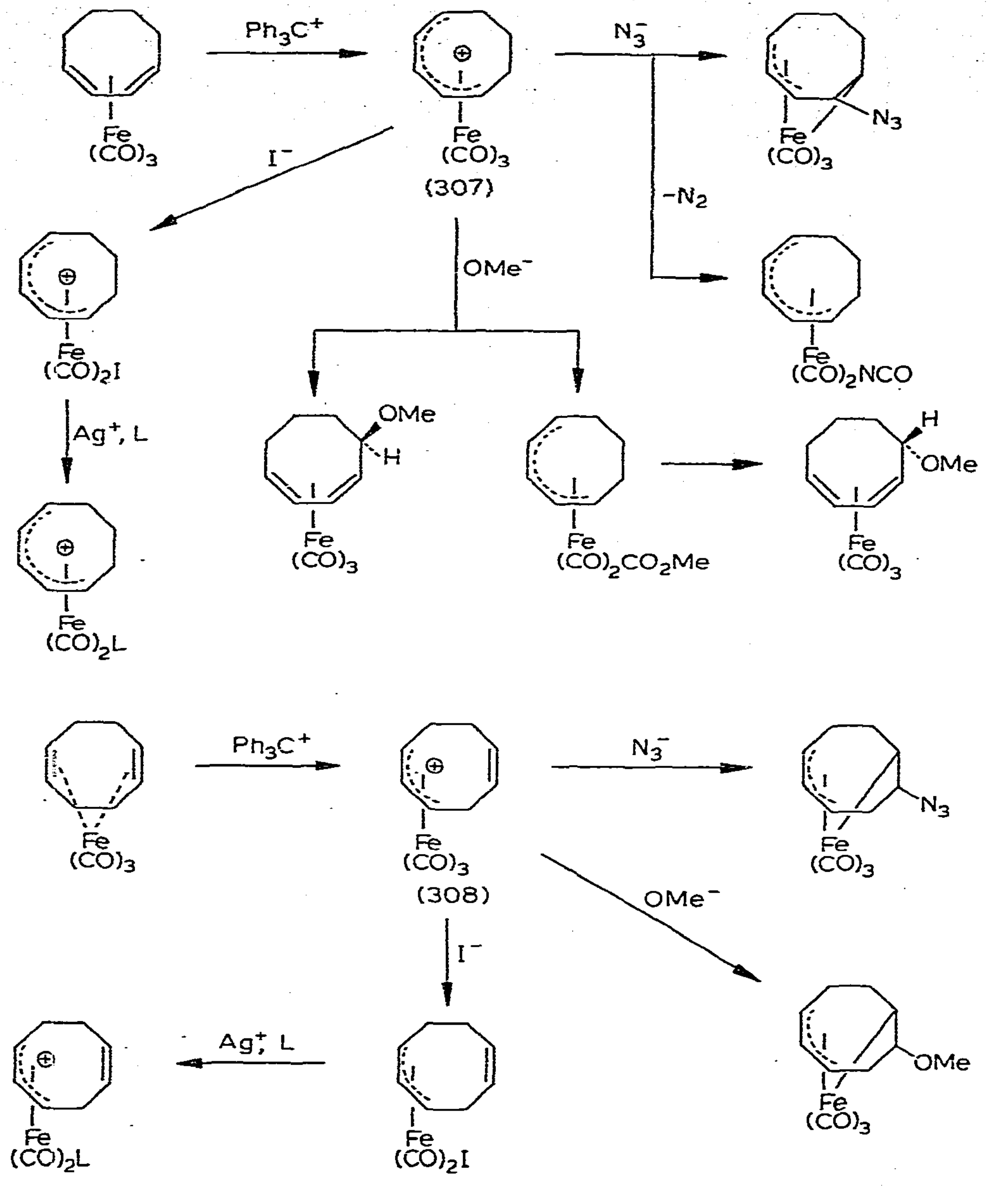
(313)

noted that the reactivity is enhanced by ion-pairing and decreases in the order $Li^+ > Na^+ >> (Ph_3P)_2N^+$.

The stereochemistry of compounds of the type $Fe(CO)_2(\eta^5\text{-}C_5H_5)Y$ (Y is a univalent group which can form bridges to Fe atoms) approximates closely to a regular octahedron.[376] In assuming that this goemetry is present in a wide range of structures and indicates a certain rigidity in this arrangement, it was shown that the tautomeric interconversions of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ must involve simultaneous making or breaking of two CO bridge systems. This mechanism has been suggested previously[377] but a geometrical explanation of this kind has not been advanced before.

The reactions of $Fe_2(CO)_9$ with pentafulvenes $C_6H_4R_2$ (R = Me, Et or Ph)[378] are summarised in Scheme 47. The structures of 314 and 315, which are related to 316, have been determined crystallographically, and that of 315 (Fe-Fe 2.77Å) may be compared with that of 317 (Fe-Fe 2.74Å).[379] Similar reactions with $Ru_3(CO)_{12}$[380] are outlined in Scheme 48, and the structure of 318 (Ru-Ru 2.85Å)

Scheme 46



is similar to that of 315. The structure of 319, prepared[381] from 320 and $Fe_2(CO)_9$, has been determined[382] crystallographically. The Fe–σ-acyl distance (1.96Å) is significantly shorter (ca. 0.14Å) than accepted Fe-C(sp^3) distances in other $Fe(CO)_2(\eta^5-C_5H_5)R$ compounds, and is comparable with the Fe-C(acyl) distance (1.97Å) in $Fe(CO)_2\{HB(pyz)_3\}(COMe)$.[383] This short distance is consistent with the representation of the bonds as in fig. 24

Scheme 47

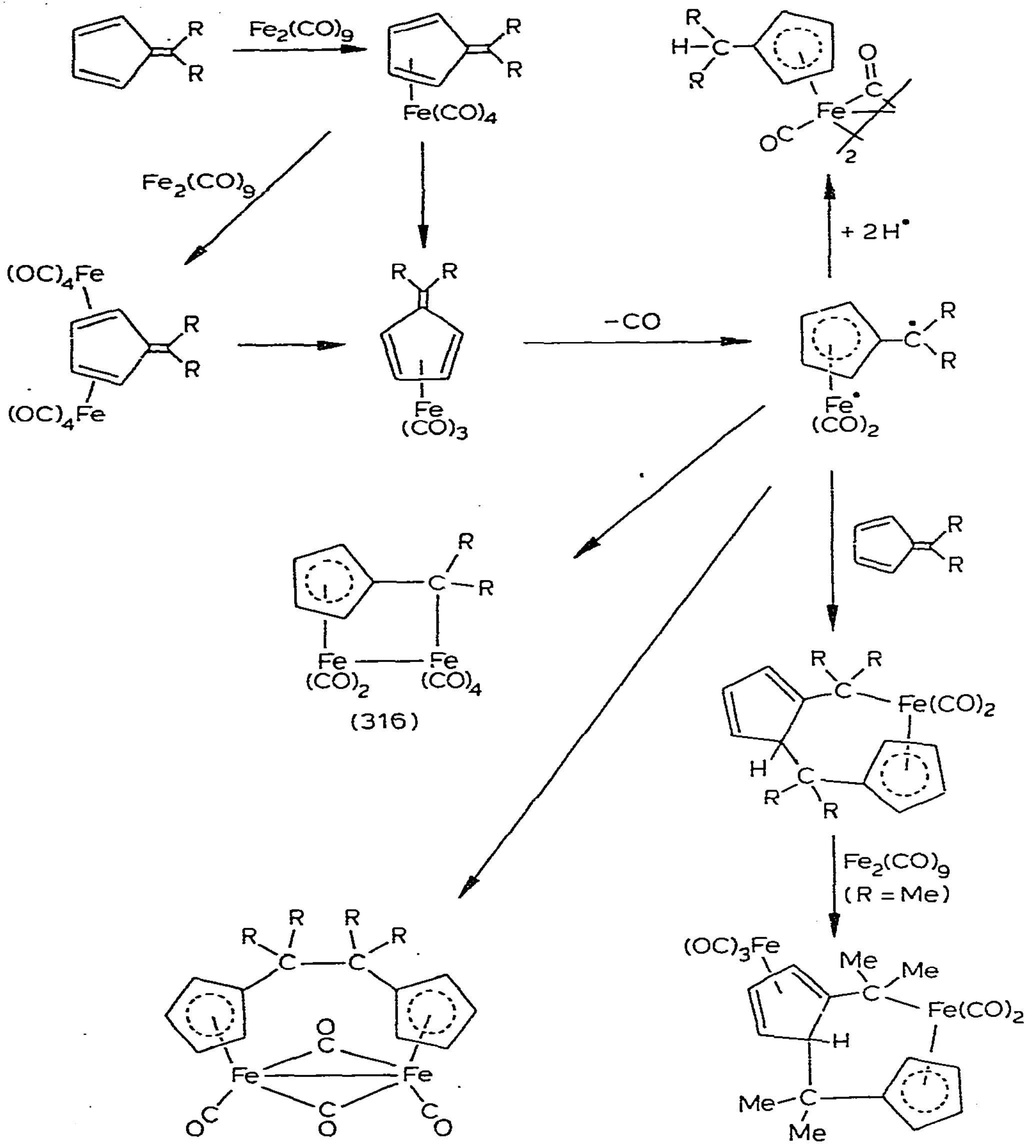
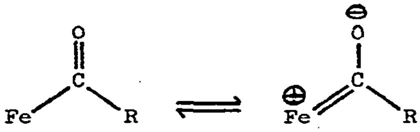
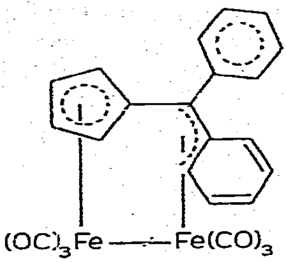


Figure 24





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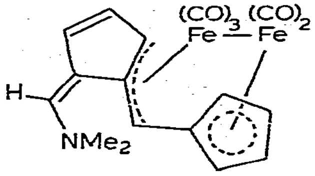
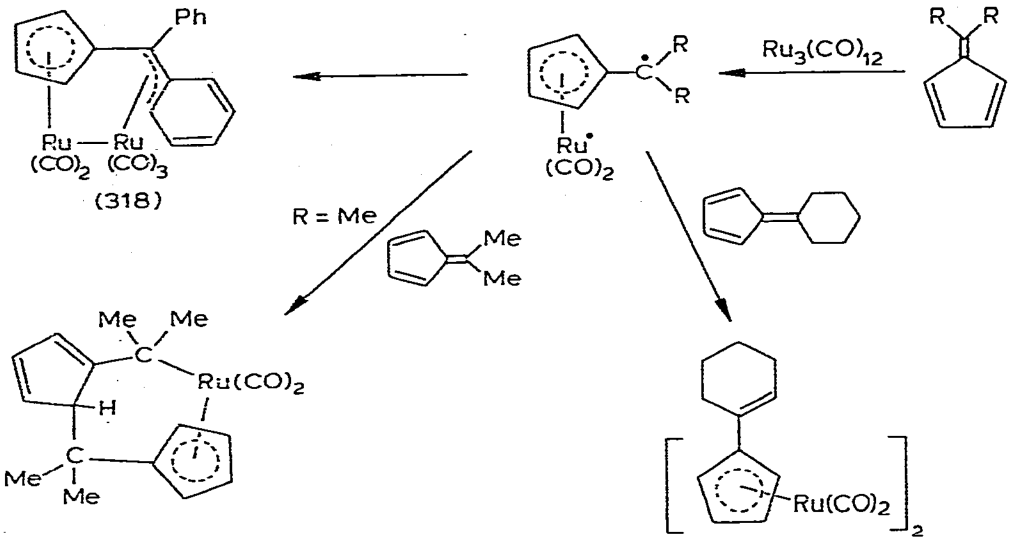


(317)

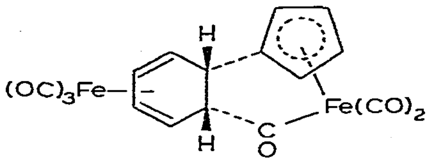
Scheme 48



It has been observed[394] that in the acenaphthalene complex 321 there is localised scrambling of the CO ligands in the Fe(CO)$_3$ group, that there is no exchange in the Fe(CO)$_2$ group, and that there is no CO ligand exchange between the two iron atoms. The Fe-Fe distance (2.77Å) is quite long, and this may be a factor in the lack of inter-metal CO exchange. Within the Fe(CO)$_3$ group, there may be a pairwise permutation, $abb' \rightleftharpoons bab'$ and $abb' \rightleftharpoons b'ba$ (see fig. 25). A similar situation obtains on the cycloheptatriene complex Fe$_2$(CO)$_6$(C$_7$H$_8$), where the Fe-Fe distance is even longer (2.87Å) than that in 321.

The structures of FeCo(CO)$_6$(η^5-C$_5$H$_5$), 322 and FeCo(CO)$_4$(C$_7$H$_8$)(η^5-C$_5$H$_5$) 323 (C$_7$H$_8$ = norbornadiene) have been determined crystallographically.[385,386] In the former the Fe-Co distance and the Fe(μ-CO)$_2$Co bond angle is 2.55Å and 144°, while in the latter they are 2.52Å and 161°, respectively.

Reduction of [Fe(CO)$_2$(η^5-C$_5$H$_5$)]$_2$ with Na/K$_{2.8}$ alloy afforded[387] [Fe(CO)$_2$-(η^5-C$_5$H$_5$)]$^-$ which reacted with [Bu$^n_4$N][ClO$_4$] and SnPh$_3$Cl giving [Bu$^n_4$N][Fe(CO)$_2$-



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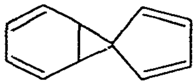

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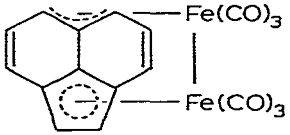

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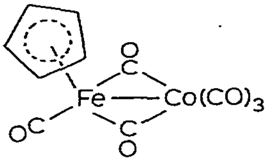

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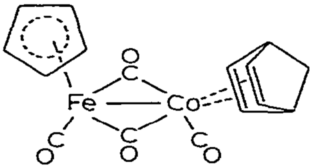
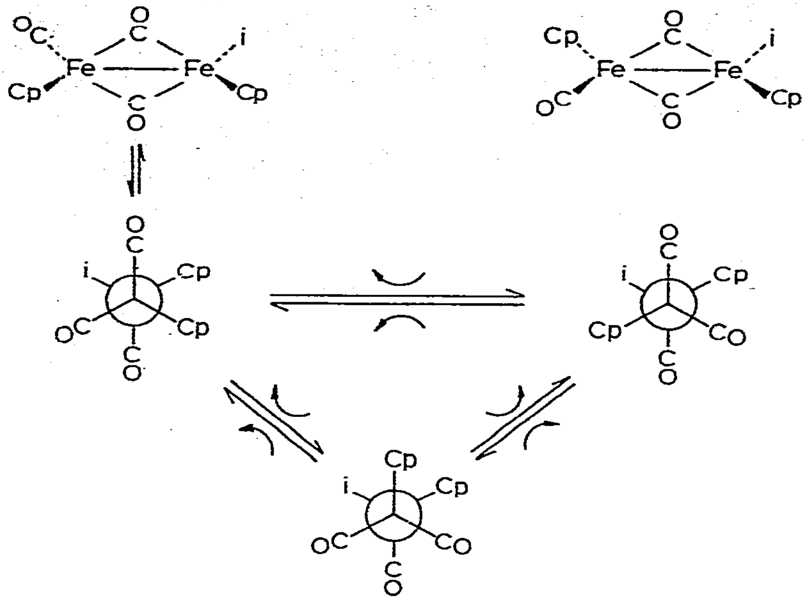


(323)

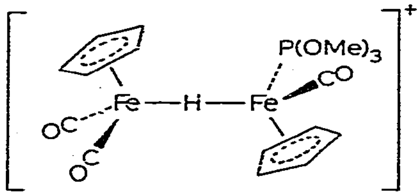
$(\eta^5\text{-}C_5H_5)]$ (as crystals) and $Fe(CO)_2(\eta^5\text{-}C_5H_5)SnPh_3$, respectively.

The crystal structure of $Fe_2(CO)_3(CNCH_2CHMe_2)(\eta^5\text{-}C_5H_5)_2$ has been determined;[388] The Fe-Fe distance is $2.52\,\text{Å}$, the rings are mutually *cis*, the isocyanide ligand is terminal and the $Fe(\mu\text{-}CO)_2Fe$ group non-planar. Reaction of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ with MeNC afforded[389] $Fe_2(CO)_{4-n}(CNMe)_n(\eta^5\text{-}C_5H_5)_2$ ($n = 1$, 2 or 3), for which mass spectra were obtained; no evidence could be found for $[Fe(CNMe)_2(\eta^5\text{-}C_5H_5)]_2$. Variable temperature ^{13}C *n.m.r.* spectral studies[390] of $Fe_2(CO)_3(CNR)(\eta^5\text{-}C_5H_5)_2$ have revealed that while the species with $R = Bu^t$ has terminal isonitrile and is fluxional (Scheme 49), the species containing CNPh has bridging isonitrile and is stereochemically rigid. Reaction of $Fe_2(CO)_{4-n}(CNR)_n(\eta^5\text{-}C_5H_5)_2$ ($n = 1$ or 2) with HX afforded[391] the species $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNHR)(\eta^5\text{-}C_5H_5)_2]^+$ and $[Fe_2(CO)_2(\mu\text{-}CNHR)_2(\eta^5\text{-}C_5H_5)_2]^+$ when R = Me, Et or CH_2Ph, but not Bu^t. Similar reactions with R'X (X = Br or I) gave $[Fe_2(CO)_2(\mu\text{-}CO)(CNRR')(\eta^5\text{-}C_5H_5)_2]^+$ and $[Fe_2(CO)(CNR)(\mu\text{-}CO)(\mu\text{-}CNRR')(\eta^5\text{-}C_5H_5)_2]^+$ (R,R' = Me, Et, CH_2Ph or n-alkyl but not Bu^t). It was noted that $[Fe(CO)(CNMe)(\eta^5\text{-}C_5H_5)]_2$ was more readily alkylated than $Fe_2(CO)_3(CNMe)(\eta^5\text{-}C_5H_5)_2$.

Scheme 49



Hydrido Species. The thermolysis and photolysis of $Fe(CO)_3(C_5H_6)$, giving $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$, has been extensively studied.392 The thermolytic process was explained by the mechanism outlined in Scheme 50. The pathway (i) is consistent with, and based on, previous work with PPh_3 (Scheme 51). The photolytic process was investigated using the 5-*exo*-deuteriated species $Fe(CO)_3(C_5H_5D)$, obtained by treatment of $[Fe(CO)_3(\eta^5\text{-}C_5H_5)]^+$ with $[BD_3(CN)]^-$. The mechanism is depicted in Scheme 52.



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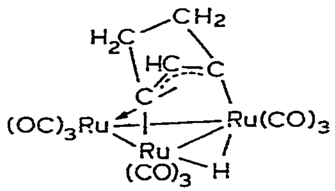

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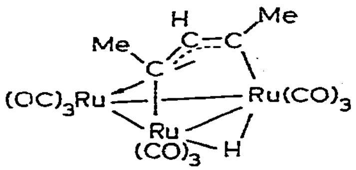

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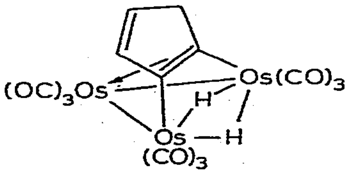
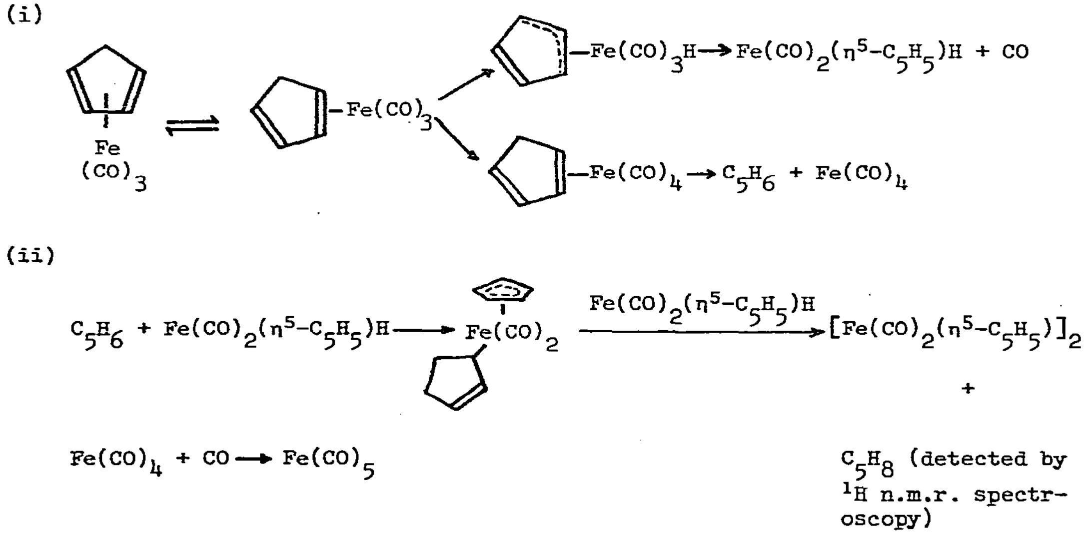


(327)

Protonation of $Fe_2(CO)_3\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)_2$ in acetic acid/sulphuric acid (98%) mixtures gave[393] $[\{Fe_2(CO)_3\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)_2\}_2H]^+$, 324, which was isolated as the BPh_4^- salt. The pK_b values for $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ and its mono-phosphite analogue were 7.5 ± 0.3 and 5.9 ± 0.3, respectively.

Treatment of $Ru_3(CO)_{12}$ or $Ru_4(CO)_{12}H_4$ with cyclopentadiene, in the absence of oxygen, afforded[394] $Ru(CO)_2(\eta^5\text{-}C_5H_5)H$ which, in the presence of air, readily oxidised in high yield to $[Ru(CO)_2(\eta^5\text{-}C_5H_5)]_2$. Treatment of the hydride with PPh_3 in boiling chloroform gave first $Ru(CO)(PPh_3)(\eta^5\text{-}C_5H_5)H$ and then its chloro-derivative $Ru(CO)(PPh_3)(\eta^5\text{-}C_5H_5)Cl$. Treatment of the phosphine hydride with CO under high pressure in the presence of $Et_2O.BF_3$ gave $[Ru(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)]\text{-}[BF_4]$. When $Ru_4(CO)_{12}D_4$ reacted with cyclopentadiene in the presence of PPh_3, only the hydride $Ru(CO)(PPh_3)(\eta^5\text{-}C_5H_5)H$ was formed; careful spectroscopic studies revealed that $Ru(CO)_3(C_5H_6)$ is an intermediate in these reactions and is the source of the hydride ligand. When $Ru_3(CO)_{12}$ was heated with cyclopentadiene in hexane, $Ru(CO)_3(C_5H_6)$ and $Ru_3(CO)_9(\eta^3\text{-}C_5H_5)H$, 325 were formed. The former reacted with Ph_3C^+ and PPh_3 giving, respectively $[Ru(CO)_3(\eta^5\text{-}C_5H_5)]^+$ and $Ru(CO)_3(PPh_3)_2$. The latter is analogous to $Ru_3(CO)_9(\eta^3\text{-}C_{12}H_{15})H$ and $Ru_3(CO)_9\text{-}(\eta^3\text{-}C_5H_7)H$.[395] Treatment of $Ru_3(CO)_{12}$ with penta-1,3-diene gave 326. While $Os_3(CO)_{12}$ reacted with cyclopentadiene giving $Os(CO)_3(C_5H_6)$ and traces of $Os(CO)_2(\eta^5\text{-}C_5H_5)H$, there was no reaction at all with $Os_4(CO)_{12}H_4$. However, $Os_3(CO)_{10}H_2$ or $Os(CO)_4H_2$ reacted with C_5H_6 giving $Os(CO)_3(C_5H_6)$ and the cyclopentadienyl hydride in modest yields. The diene tricarbonyl was thermally unstable, regenerating $Os_3(CO)_{12}$ and giving dicyclopentadiene; after a 20-day

Scheme 50



Scheme 50 (continued)

(iii)

$$Fe(CO)_3(C_5H_6) + Fe(CO)_4 \longrightarrow Fe(CO)_2(\eta^5\text{-}C_5H_5)H + Fe(CO)_5$$

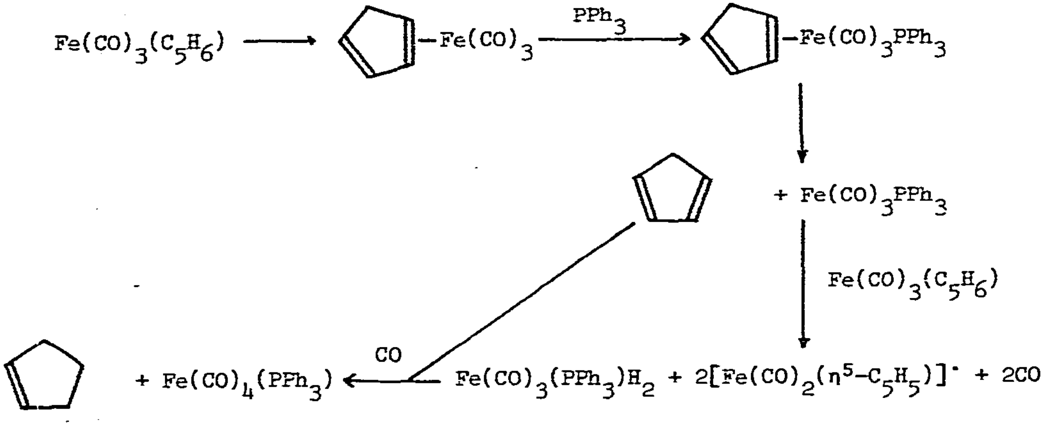
$$2[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^{\cdot} \rightleftharpoons [Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$$

(iv)

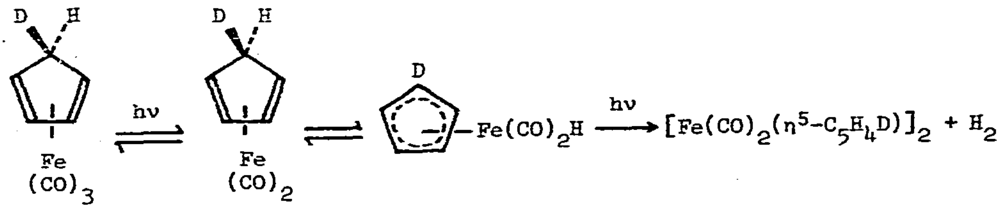
$$Fe'(CO)_3(C_5H_6) + [Fe''(CO)_2(\eta^5\text{-}C_5H_5)]^{\cdot} \longrightarrow [Fe'(CO)_2(\eta^5\text{-}C_5H_5)]^{\cdot} +$$

$$Fe''(CO)_2(\eta^5\text{-}C_5H_5)H + CO$$

Scheme 51



Scheme 52



reflux, some $Os(CO)_2(\eta^5-C_5H_5)H$ was found. The reaction with $Os_3(CO)_{10}H_2$ also afforded $Os_3(CO)_{12}$, $Os_4(CO)_{12}H_2$ and $Os_3(CO)_9(\eta^2-C_5H_4)H_2$, 327, (low yield) which is analogous to $Os_3(CO)_9(\eta^2-C_8H_{12})H_2$.[396]

Isocyanide and Carbene Species. Reaction of $[Fe(CO)_3(\eta^5-C_5H_5)]^+$ with NH_2Me gave $Fe(CO)_2(\eta^5-C_5H_5)(CONHMe)$ which, on treatment with $COCl_2/NEt_3$, afforded[397] $[Fe(CO)_2(CNMe)(\eta^5-C_5H_5)]Cl$. The carbene complex $[Fe(CO)\{CMe(OMe)\}(PPh_3)-(\eta^5-C_5H_5)][PF_6]$ was obtained[398] by alkylation of the appropriate acyl complex with $MeOSO_2F$ followed by metathetical anion exchange with PF_6^-.

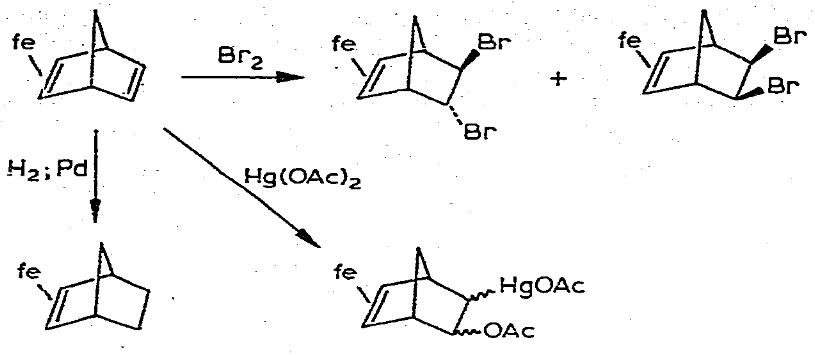
Olefin, allene and related Complexes. The barriers to rotation about the olefin-metal bond of olefins in $[Fe(CO)_2(olefin)(\eta^5-C_5H_5)]^+$, $[Fe(CO)_2(olefin)(\eta^5-C_9H_7)]^+$ and $[Ru(CO)_2(olefin)(\eta^5-C_5H_5)]^+$ (olefin = C_2H_4, C_3H_6, $1-C_4H_8$, $i-C_4H_8$, *cis*- and *trans*-$2-C_4H_8$) were found[399] to be *ca.* 8 kcal/mol. There was no observable dissociation about the C=C bond. The thermodynamically preferred orientations of the olefins in these complexes were determined using chemical shift differences resulting from substitution of an indenyl group for a C_5H_5 ligand. The preferred metal-C_2H_4 orientation is parallel to the C_5H_5-ring plane whereas methyl group substitution on the alkene induces a deviation from this preferred 'orientation', the dihedral angle in the C_3H_6 complex being estimated to be *ca.* 10°. The indenyl complexes, which are new, were obtained by hydride abstraction from $Fe(CO)_2-(\eta^5-C_9H_7)Et$ or by protonation of $Fe(CO)_2(\eta^5-C_9H_7)R$ (R = $CH_2CH:CH_2$ or $CH_2CMe:CH_2$).

Treatment of $[Fe(CO)_2(C_2H_4)(\eta^5-C_5H_5)]^+$ with a series of nucleophiles Q (pyridine, Me_3N, or PPh_3) afforded[400] $[Fe(CO)_2(\eta^5-C_5H_5)(CH_2CH_2Q)]^+$. With NH_3, the binuclear species $[\{Fe(CO)_2(\eta^5-C_5H_5)CH_2CH_2\}_2NH_2]^+$ was formed. Reaction of the ethylene cation with NaCN in water resulted in alkene displacement, but with $[Et_4N][CN]$ in acetonitrile, $Fe(CO)_2(\eta^5-C_5H_5)(CH_2CH_2CN)$ was produced in modest yield. Similar treatment of $[Fe\{P(OPh)_3\}_2(C_2H_4)(\eta^5-C_5H_5)]^+$ gave good yields of $Fe\{P(OPh)_3\}_2(\eta^5-C_5H_5)(CH_2CH_2CN)$. Reaction of $[Fe(CO)_2(C_2H_4)(\eta^5-C_5H_5)]^+$ with $[Mo(CO)_3(\eta^5-C_5H_5)CH_2CH_2O]^-$ afforded $(\eta^5-C_5H_5)(CO)_2FeCH_2CH_2OCH_2CH_2Mo(CO)_3-(\eta^5-C_5H_5)$.

One double bond in norbornadiene can be protected[401] by its coordination to $[Fe(CO)_2(\eta^5-C_5H_5)]^+$, thereby rendering it unreactive towards reagents which normally attack it (Scheme 53). Hydrogenation of related complexes $[Fe(CO)_2-(\eta^2-diene)(\eta^5-C_5H_5)]^+$ and a alkene-alkyne derivative using palladised charcoal is shown in Scheme 54, and an example of electrophilic aromatic substution is normally much shlower than electrophilic addition to C=C bonds) is outlined in Scheme 55.

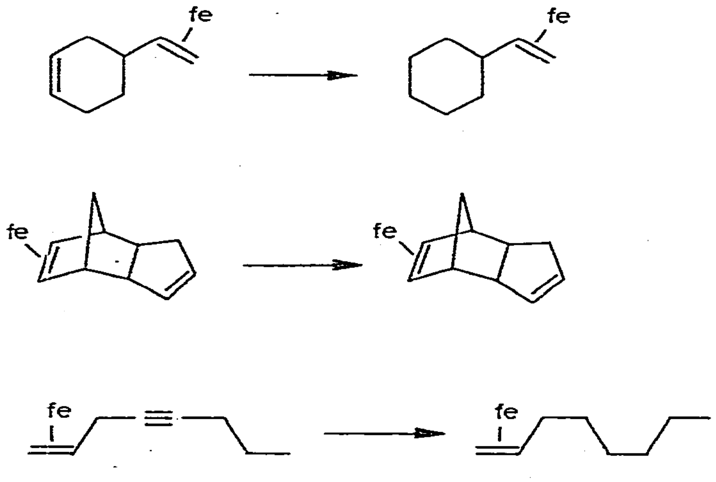
Methylvinylketone epoxide reacted[402] with $[Fe(CO)_2(\eta^5-C_5H_5)]^-$ giving 328 which, on treatment with the Li^+ salt of the enolate of cyclohexanone, or the corresponding silyl ether, or cyclohexanone enamine, afforded 329. By refluxing this compound in dichloromethane in the presence of basic alumina, the iron-

Scheme 53



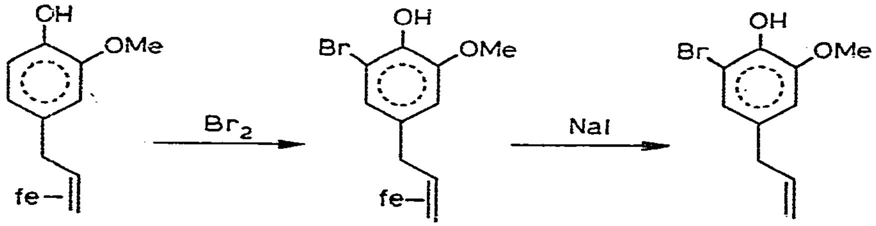
fe$\equiv$CpFe(CO)$_2^+$

Scheme 54



fe$\equiv$CpFe(CO)$_2^+$

Scheme 55



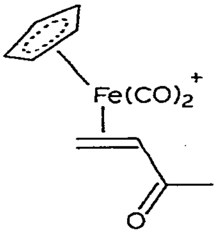
fe$\equiv$CpFe(CO)$_2^+$

carbonyl fragment was removed and 330 released. Other cyclic ketones, as their enol derivatives or enamines, behaved similarly.

Exchange of the olefin in $[Fe(CO)_2(CH_2CMe_2)(\eta^5-C_5H_5)]^+$ was effected[403] using acenapththalene, giving 331. Treatment of this salt with NaOMe, PPh_3 and NaI caused displacement of acenapththalene, and formation of $[Fe(CO)_2-(\eta^5-C_5H_5)]_2$, $[Fe(CO)_2(PPh_3)(\eta^5-C_5H_5)]^+$ and $Fe(CO)_2(\eta^5-C_5H_5)I$, respectively. However, treatment of 331 with $NaSBu^t$ or isobutyraldehyde pyrrolidine enamine afforded 332 (nucleophile = Q), and the preferred *anti* attack of Q can be understood in terms of approach by the nucleophile to the least sterically hindered face of the coordinated olefin. Cleavage of the Fe–C bond in 332, with the release of the appropriate hydrocarbon, was achieved using Br_2, Cu^{2+} in alcohols and $HgCl_2$.

General syntheses of monosubstituted η^2-olefin and mono-substituted η^1-allyl complexes of $Fe(CO)_2(\eta^5-C_5H_5)$ have been described[404] and these are related to other known routes.[405] These are outlined in Scheme 56, which deals with sulphonylation, alkylation, acylation, carboxylation, bromination and brominolysis. The general reactions[406] are shown first and specific reaction pathways related to these for each group of reactions.

A series of olefin exchange reactions were accomplished using $[Fe(CO)_2-(CH_2{:}CMe_2)(\eta^5-C_5H_5)]^+$ initially to give $[Fe(CO)_2(CH_2{:}CHCH_2E)(\eta^5-C_5H_5)]^+$ (E = OMe, OH, Ph or Ph_3P^+) in 1,2-dichloroethylene. The isobutylene could also be exchanged for cycloalkenes, cyclohexa-1,3- and 1,4-dienes, cycloocta-1,5-diene and norbornadiene. Many of these reactions have been described earlier.[407] In attempts to make an olefin complex with $CH_2{:}CHCH_2CN$, the species $[Fe(CO)_2-$



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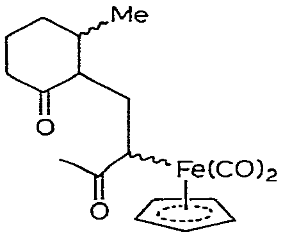

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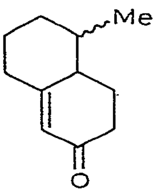

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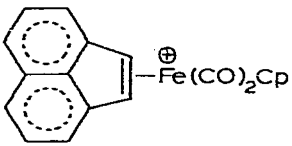

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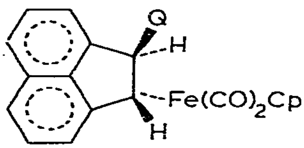

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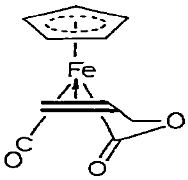
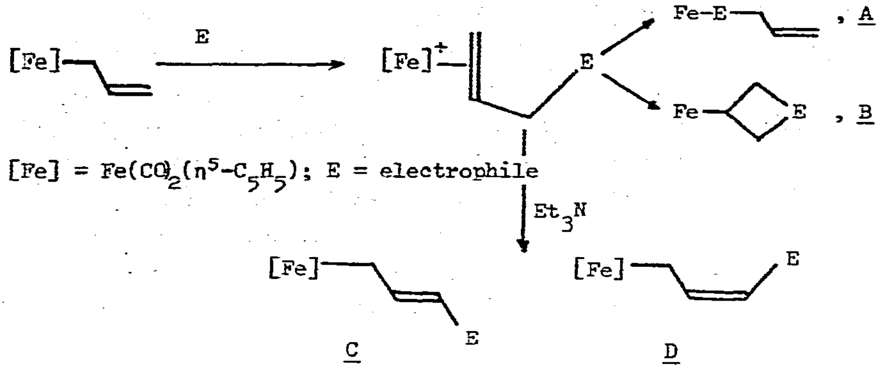


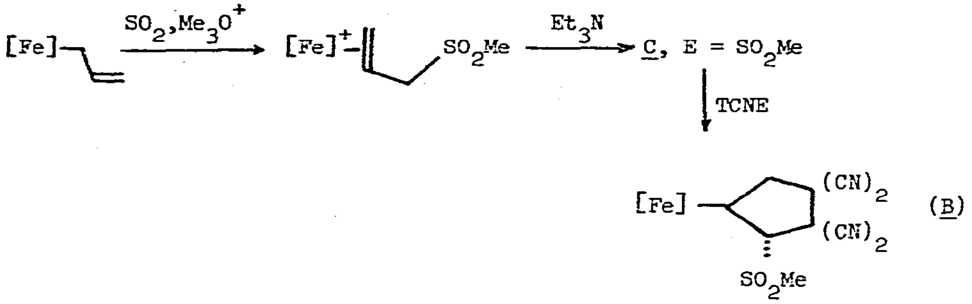
(333)

Scheme 56

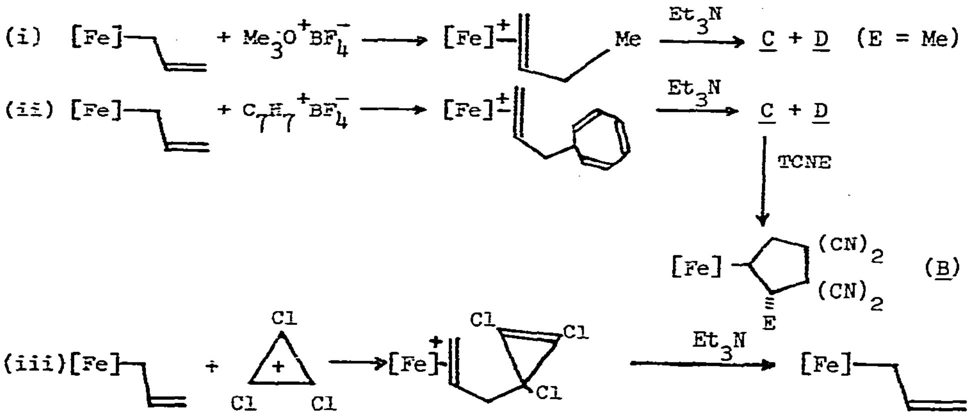


[Fe] = Fe(CO)$_2$(η^5-C$_5$H$_5$); E = electrophile

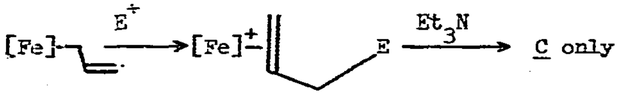
Sulphonylation. (pathway A), intermediate trapped by Me$_3$O$^+$BF$_4^-$



Alkylation



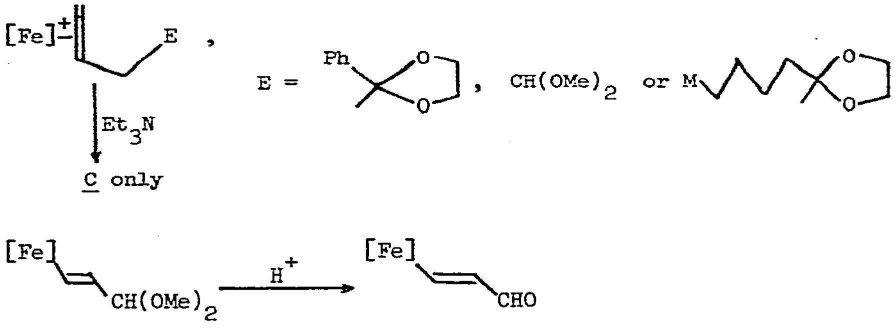
Acylation (RCOCl + AgSbF$_6$)



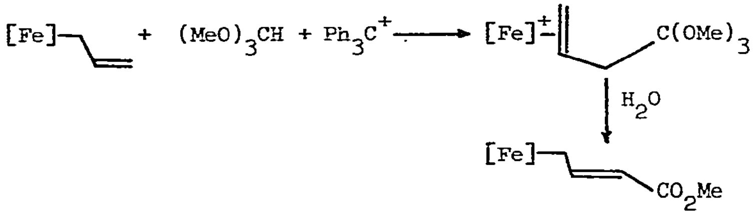
E$^+$ = PhCO or MeCO

Scheme 56 (continued)

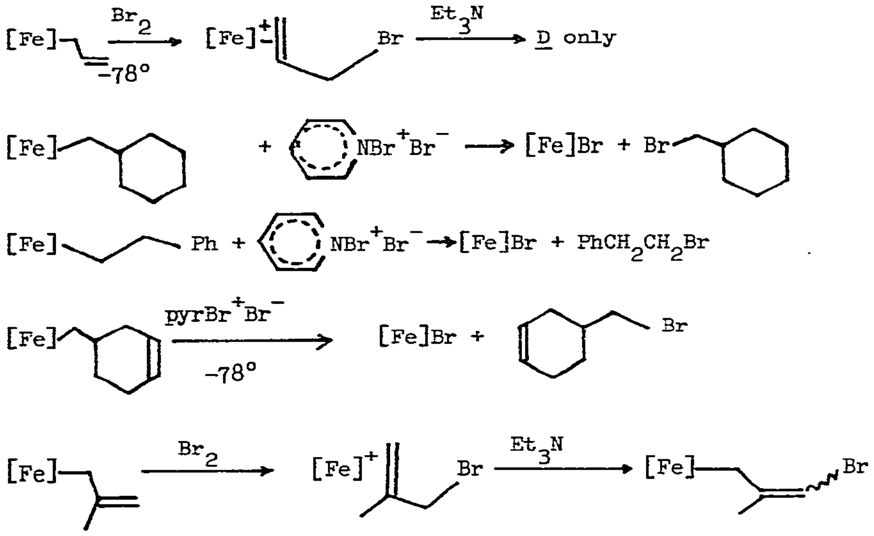
Dialkoxycarbenium ions can be generated via orthoformates or 1,3-dioxolones in the presence of Ph_3C^+, giving



Carboxylation

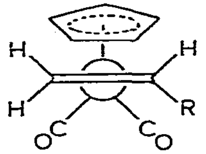


Bromination, Brominolysis



$(\eta^1\text{-NCCH}_2\text{CH:CH}_2)(\eta^5\text{-C}_5\text{H}_5)]^+$ was obtained. Deprotonation of $[\text{Fe(CO)}_2(\eta^2\text{-CH}_2\text{:-CHCH}_2\text{OMe})(\eta^5\text{-C}_5\text{H}_5)]^+$ occurred by pathway D (Scheme 56) only, and the product was unaffected by 3% aqueous HCl. From ^{1}H and ^{13}C n.m.r. spectral studies, it was deduced that the preferred conformation of the olefin cations is as shown in figure 25. The stereochemistry of the η^1-allyl complexes derived by deprotonation of the olefin cations could be accounted for in terms of preferred base abstraction of an allylic proton *trans* to the Fe-olefin bond. However, deprotonation of

Figure 25



$[\text{Fe(CO)}_2(\eta^2\text{:CH}_2\text{CHCH}_2\text{OH})(\eta^5\text{-C}_5\text{H}_5)]^+$ afforded a cyclised product 333 in a conformationally determined stereospecific intramolecular reaction. Deuteration of $\text{Fe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2\text{CH:CHPh})$ occurred non-stereospecifically.

Reactions of coordinated propargyl and allene complexes of $\text{Fe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$ have been reviewed.[408] Thus, protonation of $\text{Fe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)\text{CH}_2\text{C}\equiv\text{CR}$ (R = Me, Ph or $\text{Fe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$) with HBF_4/acetic anhydride afforded $[\text{Fe(CO)}_2(\eta^2\text{-CH}_2\text{=C=CHR})(\eta^5\text{-C}_5\text{H}_5)][\text{BF}_4]$. These cations react with nucleophiles (Q) in the following ways:

(a) with BH_4^-, NHEt_2 or PPh_3, addition occurs at C(1) of the allene, giving 334;

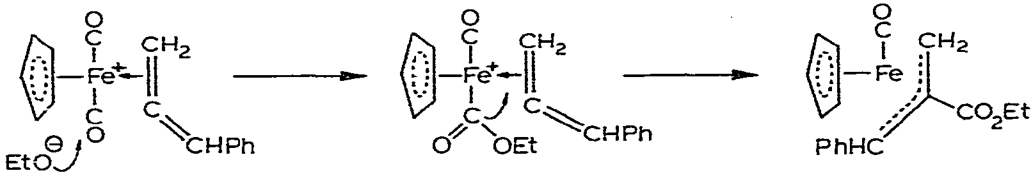
(b) with OMe^-, addition occurs at C(2) giving 335 and ultimately 336;

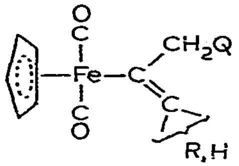
(c) with OEt^-, addition occurs at a CO group, giving the reaction as shown in Scheme 57;

(d) with NEt_3, deprotonation can occur causing regeneration of the parent propargyl complex; and

(e) with LiMe, non-selective reactions give a mixture of products.

Scheme 57





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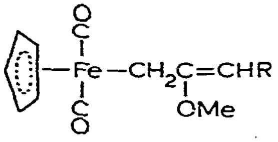

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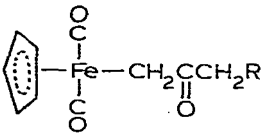
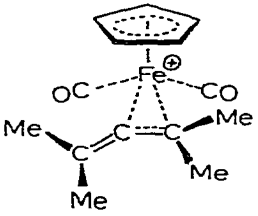


(336)

Of these, the most common is (a) and together with the initial protonation of the propargyl complex, stimulates the two-step (3 + 2) cycloaddition reactions between electrophiles and the $FeCH_2C{\equiv}CR$ group. The structure of $[Fe(CO)_2(\eta^2\text{-}Me_2C{:}C{:}CMe_2)(\eta^5\text{-}C_5H_5)]^+$, 337, has been determined[409] crystallographically. The C(3)-C(4)-C(5) angle (146°) is one of the smallest angles observed for allene species other than d^{10} metal complexes, and there is considerable asymmetry in the Fe-C distances (Fe-C(3) 2124Å, Fe-C(4) 2.06Å; C(3)-C(4) 1.37Å and C(4)-C(5) 1.34Å).

Reaction of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ with 1-methyl-2,3-bis(t-butyl) cyclopropenium ion gave[410] $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ and $(C_3Bu^t_2Me)_2$ quantitatively. However, with 1,2,3-tris(t-butyl)cyclopropenium ion, only a small amount of the carbonyl dimer was produced, the main product being 338. It was thought that this species was formed by prior electrophilic attack by $[C_3Bu^t_3]^+$ on a coordinated CO group, fig. 26, which then underwent ring expansion to give the oxocyclobutenyl ligand. Reaction of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ with $(CF_3)_2C{:}C{:}C(CF_3)_2$ gave[411] 339.



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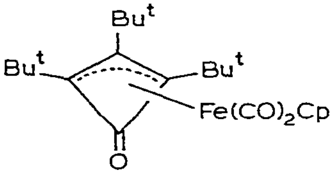
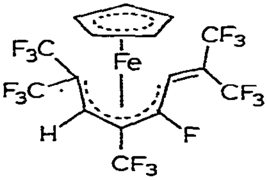


(338)

Species containing M-C σ-Bonds. The species $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$ is regarded[412] as one of the most nucleophilic of the carbonylate anions, and reacts with $Mo(CO)_3(\eta^5\text{-}C_5H_5)(CH_2CH_2CH_2Br)$[413] and $Mn(CO)_5SnPh_3$[414] causing displacement of the



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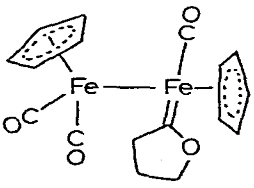
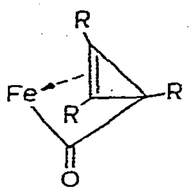


(340)

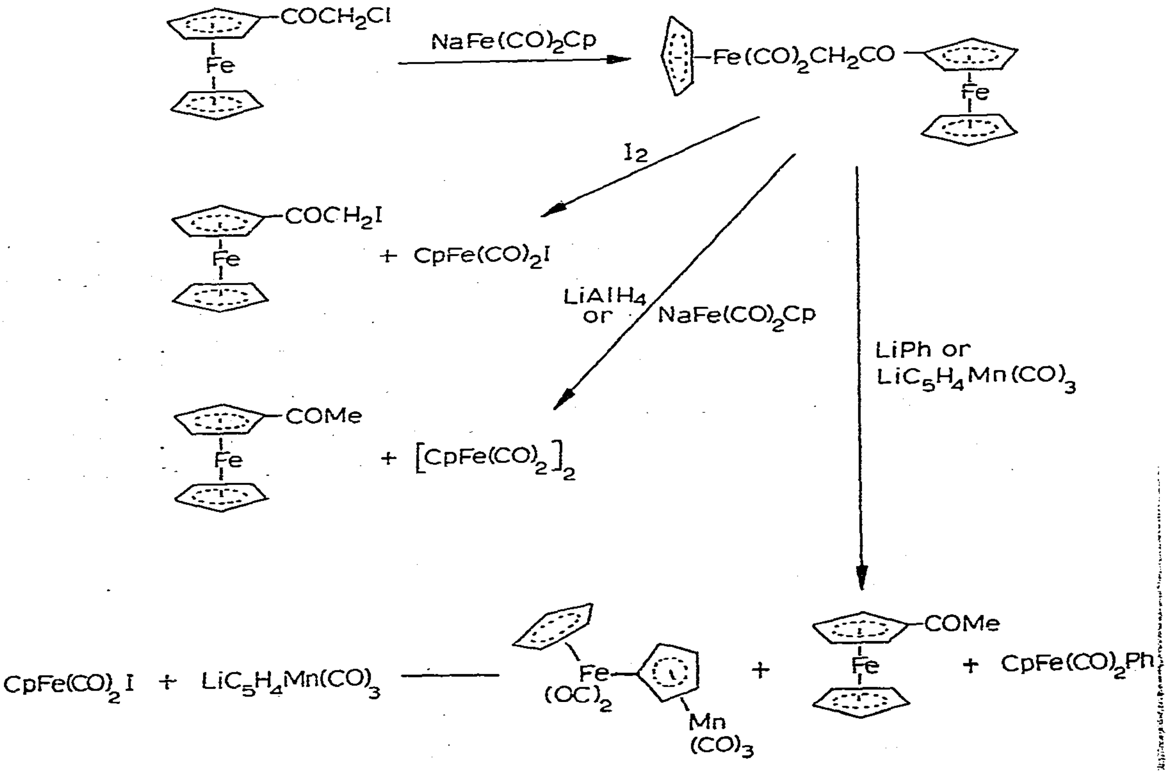
Figure 26



Mo and Mn atoms, giving $(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2CH_2CH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ (A) and $Fe(CO)_2(\eta^5\text{-}C_5H_5)(SnPh_3)$, respectively. However, $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$ reacted with $Fe(CO)_2(\eta^5\text{-}C_5H_5)(CH_2CH_2CH_2Br)$ giving only (A) and not 340 as was found in the comparable reactions[416] involving $Mn(CO)_5CH_2CH_2CH_2Br$ and $[Mn(CO)_5]^-$.

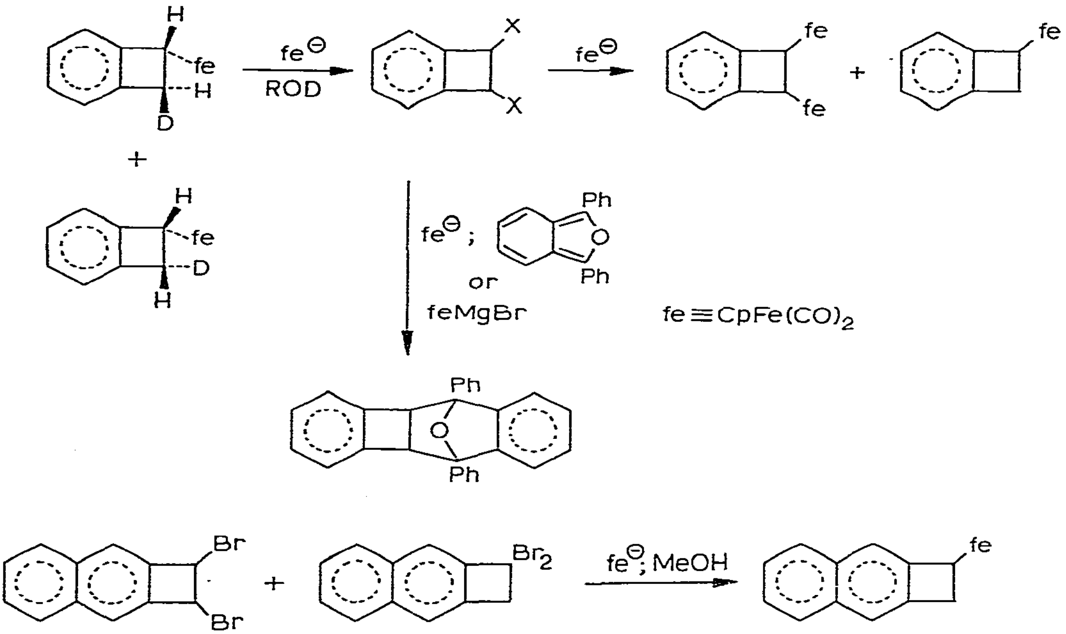
Reaction of the ferrocenyl compound $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COCH_2Cl)$ with $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ afforded[417] $Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4COCH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)\}$, some of whose reactions are summarised in Scheme 58. Treatment of $Fe(CO)_2(\eta^5\text{-}C_5H_5)I$ with $Mn(CO)_3(\eta^5\text{-}C_5H_4Li)$ gave the mixed metal species $Mn(CO)_3\{\eta^5\text{-}C_5H_4Fe(CO)_2(\eta^5\text{-}C_5H_5)\}$.

Scheme 58



Trans-1,2-dibromo, *cis*- or *trans*-1,2-diiodo-benzocyclobutene reacted[418] with Na[Fe(CO)$_2$(η^5-C$_5$H$_5$)] according to Scheme 59; small amounts of oligomeric species, *viz.* (C$_8$H$_6$)$_n$[Fe(CO)$_2$(η^5-C$_5$H$_5$)]$_2$, were also produced. There was no reaction between the dihalobenzocyclobutenes and MgBr[Fe(CO)$_2$(η^5-C$_5$H$_5$)]. From a mixture of dibromonaphthocyclobutenes, only a monosubstituted iron complex was obtained (Scheme 59), suggesting that in these reactions benzocyclobutene, 341, is formed in the initial steps. A possible mechanism for the reactions is outlined in Scheme 60. The involvements of carbanionic species such as 342, a cyclobutene intermediate 343, Fe(CO)$_2$(η^5-C$_5$H$_5$)H, or the stepwise reduction of the dihalobenzocyclobutene to a monohalo intermediate were discounted. The failure of MgBr[Fe(CO)$_2$(η^5-C$_5$H$_5$)] to react with dihalobenzocyclobutenes may be due to the fact that the rate of formation of the requisite organometallic radicals may be slower than the rate of dimerisation of benzocyclobutadiene.

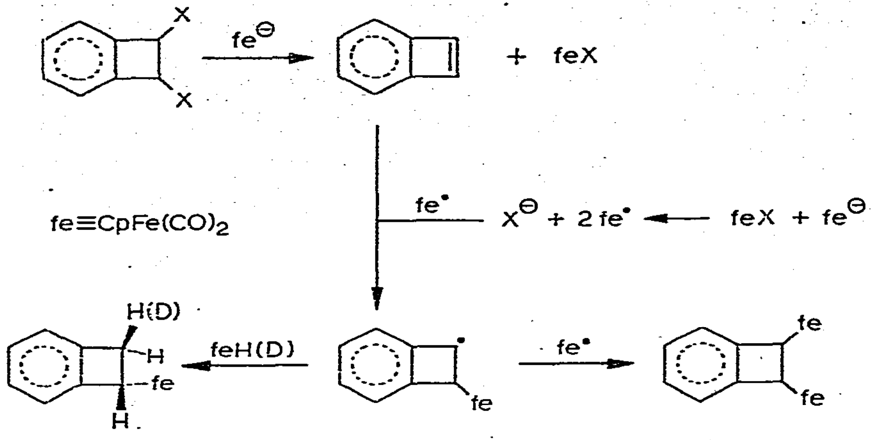
Scheme 59



Reaction of Me$_2$C:C(NMe$_2$)Cl with Na[Fe(CO)$_2$(η^5-C$_5$H$_5$)] afforded[419] Fe(CO)$_2$-(η^5-C$_5$H$_5$){C(NMe$_2$):CMe$_2$}, 344, which, on vacuum distillation may have given 345.

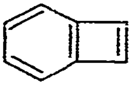
Copper(I) acetylides [CuC$_2$R]$_n$ reacted with Ru(PPh$_3$)$_2$(η^5-C$_5$H$_5$)Cl giving[420] the binuclear species 346 (R = Ph) or monomers, Ru(PPh$_3$)$_2$(η^5-C$_5$H$_5$)(C$_2$R)(CuCl) (R = Ph, p-MeC$_6$H$_4$ or Me); the structures of some of these have been confirmed.[421] Treatment of Ru(PPh$_3$)$_2$(η^5-C$_5$H$_5$)(C$_2$Ph)(CuCl) with MeC(CH$_2$PPh$_2$)$_3$ (L) gave CuLCl and Ru(PPh$_3$)$_2$(η^5-C$_5$H$_5$)(C$_2$Ph). Other compounds prepared included Ru(η^5-C$_5$H$_5$)-

Scheme 60



$(C_2R)_2\{Cu(PPh_3)\}$ (R = p-MeC$_6$H$_4$ or p-C$_6$H$_4$), 347 which, it was suggested, may contain the group $Cu^+\ldots Ru^-$. Treatment of $Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)Cl$ with $CuC_2C_6F_5$ gave $Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)(C_2C_6F_5)$ and 348. Reaction of $Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)(C_2Ph)$ with $Fe_2(CO)_9$ afforded 349.

Treatment of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ with $CF_3C{\equiv}CCF_3$ afforded[422] the bimetallic complex 350 whose structure was confirmed crystallographically (Fe-Fe 2.59Å). In this species the ferracyclohexa-2,5-dienone ring system has a boat conformation. A similar reaction involving $[Ru(CO)_2(\eta^5\text{-}C_5H_5)]_2$ gave initially *trans*-$Ru(CO)_2(\eta^5\text{-}C_5H_5)\{C(CF_3){:}CH(CF_3)\}$, also obtained by reaction of $Ru(CO)_2(\eta^5\text{-}C_5H_5)H$ with hexafluorobut-2-yne. The *trans*-geometry of this product may be contrasted with that of the cis-insertion product obtained[423] from $Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)H$ and $CF_3C{\equiv}CCF_3$. Further reaction of $Ru(CO)_2(\eta^5\text{-}C_5H_5)\{C(CF_3){:}CH(CF_3)\}$ with the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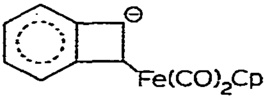

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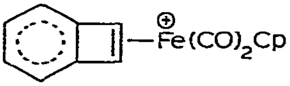

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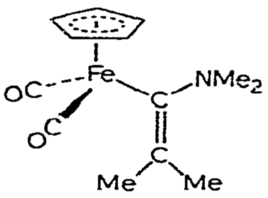

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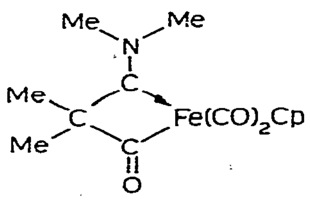

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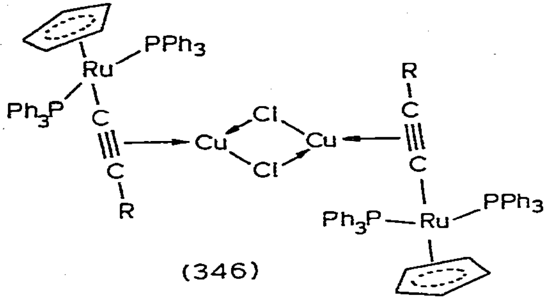

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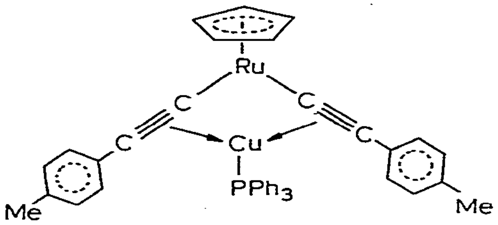

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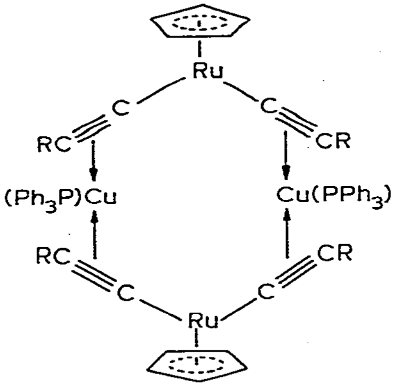

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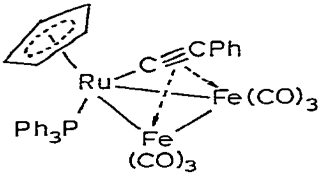

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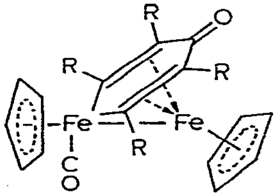

R = CF3

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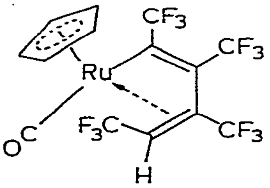

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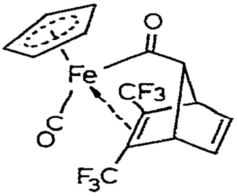

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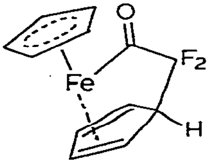
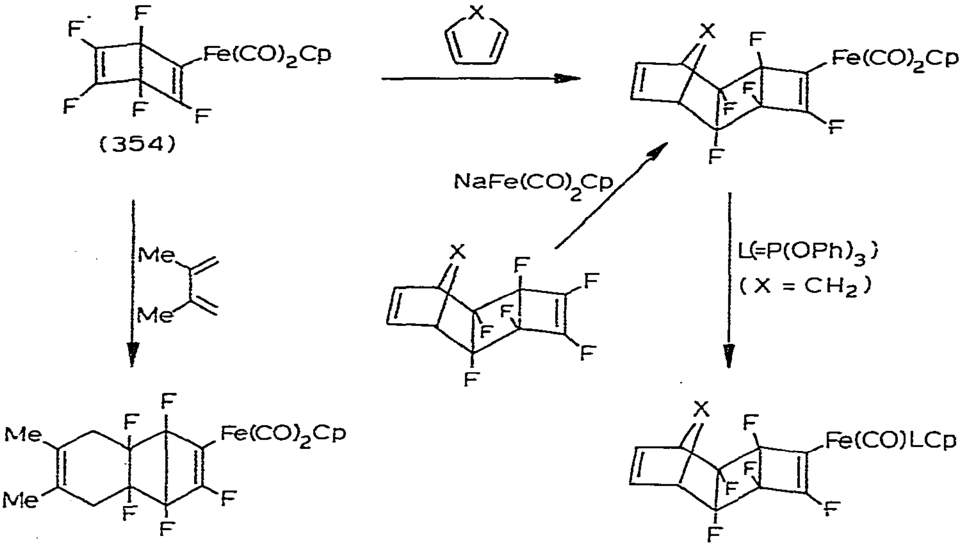


(353)

acetylene afforded 351. Diels-Alder addition occurred when $Fe(CO)_2(\eta^5-C_5H_5)-(\eta^1-C_5H_5)$ was treated with $CF_3C{\equiv}CCF_3$ giving, 352 but with C_2F_4, 353 was formed, the structure of which was confirmed crystallographically.

Treatment of hexafluorobicyclo[2.2.0]hexa-2,5-diene with $Na[Fe(CO)_2(\eta^5-C_5H_5)]$ gave[424] 354, which reacted with dienes according to Scheme 61;[425] one compound could be obtained independently as shown.

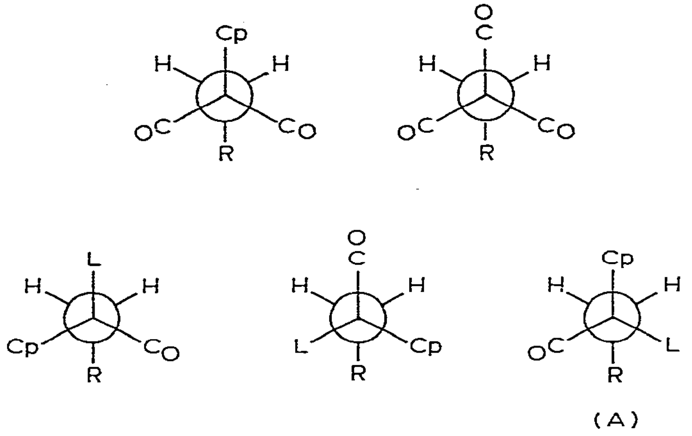
Scheme 61



Geometrical and Optical Isomerisation at M-C Bonds. A series of complexes $Fe(CO)_2(\eta^5-C_5H_5)(CH_2R)$ and $Fe(CO)L(\eta^5-C_5H_5)(CH_2R)$ (R = Ph, $SiMe_3$ or 1-naphthyl; L = $P(OMe)_3$, PMe_2Ph, $PMePh_2$ or PPh_3) has been synthesised.[426] IR spectral studies indicated that there is rotational isomerism about the Fe-C bond, while ^1H n.m.r. spectral data indicated that interconversion between various rotamers in both systems is rapid in the n.m.r. time scale. Variable temperature n.m.r. spectral studies of the monocarbonyl species suggested that steric considerations determine the rotamer preferences. The most stable rotamer, figure 27(A), is that in which the bulky η^5-cyclopentadienyl group is gauche to both the methylenic protons. The relative proportion of the other rotamers (fig. 27) for the ligands L, which were relatively small, was higher than might have been expected.

Reaction of racemic $Fe(CO)L(\eta^5-C_5H_5)I$ (L = PPh_3 or $P(OPh)_3$) with racemic $MgBr\{CHPh(SiMe_3)\}$ afforded[427] $Fe(CO)L(\eta^5-C_5H_5)\{CHPh(SiMe_3)\}$. ^1H n.m.r. spectral data indicated that this was formed as a single diastereoisomer or that the two possible diastereomers had coincident spectra. Treatment of this alkyl (L = $P(OPh)_3$) with SO_2 did not afford a stable sulphinate but caused

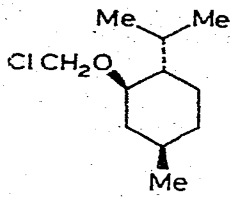
Figure 27



epimerisation giving the starting material (RS-SR) and its diastereomer (RR-SS).

Treatment of the optically pure menthyl compound 355 with Na[Fe(CO)$_2$-(η^5-C_5H_5)] gave[428] Fe(CO)$_2$(η^5-C_5H_5){CH_2O[(-)-menthyl]} which reacted further with PPh_3 under uv light affording (±)-Fe(CO)(PPh)(η^5-C_5H_5){CH_2O[(-)-menthyl]}, *X*. Reaction of (+)-*X* with HCl in ether gave (+)-Fe(CO)(PPh_3)(η^5-C_5H_5)(CH_2Cl) while the other optical isomer, (-)-*X* reacted similarly. The corresponding bromo- and iodo-methyl complexes were obtained similarly, and reacted, when optically pure, with MgXR or LiR giving Fe(CO)(PPh_3)(η^5-C_5H_5)(CH_2R) with retention of configuration. Borohydride reduction of Fe(CO)(PPh_3)(η^5-C_5H_5)-(CH_2Cl) gave Fe(CO)(PPh_3)(η^5-C_5H_5)Me, also with retention of configuration. Insertion of SO_2 into the Fe-C bond of Fe(CO)(PPh_3)(η^5-C_5H_5)(CH_2R) with OMe^-, CN^- or LiC_3H_5 (cyclopropyl) afforded Fe(CO)(PPh_3)(η^5-C_5H_5)CH_2Q (Q = OMe, CN or C_3H_5) and treatment of X or Fe(CO)(PPh_3)(η^5-C_5H_5)(CH_2OMe) with SO_2 gave Fe(CO)-(PPh_3)(η^5-C_5H_5){CH_2SO_3[(-)-menthyl]} and Fe(CO)(PPh_3)(η^5-C_5H_5)CH_2SO_3Me in contrast to results obtained[427] with Fe(CO)$_2$(η^5-C_5H_5)(CH_2OMe).

Cleavage of, and Insertion into, M-C Bonds. Reaction of Fe(CO)$_2$(η^5-C_5H_5)-CD_2CH_2Ph with bromine or iodine (X_2) gave[430] the corresponding β-phenethylhalide as a 1:1 mixture of $PhCH_2CD_2X$ and $PhCD_2CH_2X$. With an excess of bromine in the presence of $PhCH_2CD_2Br$, the same products were obtained without rearrangement of the added bromide. These results suggested the presence of the intermediate 356 (L = CO; E = Br or I), and the neutral fragment Fe(CO)L(η^5-C_5H_5)E could function as a stable leaving group resulting in the formation of the phenonium ion, 357. This cation could then undergo attack by X^- at either methylene group. It may further be observed that the double inversion at carbon resulting from this mechanism could explain the overall retention of configuration in the cleavage by halogens[431] of the Fe-C bond in Fe(CO)$_2$(η^5-C_5H_5)(CHDCHDPh). Cleavage of the Fe-C bond by H^+ or HgX^+ appears to occur faster than the process leading to 357



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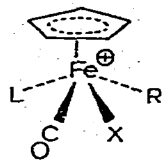

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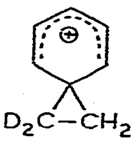

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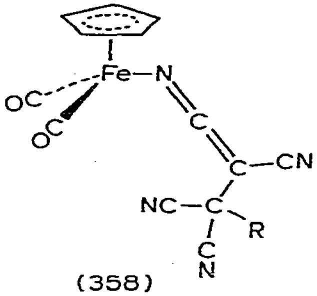


(358)

and hence HBr and HgBr$_2$ gave isomerically pure CHD$_2$CH$_2$Ph and HgBr(CD$_2$CH$_2$Ph).

Three pathways for the cleavage of the Fe–C bond in $Fe(CO)_2(\eta^5\text{-}C_5H_5)R$ by $HgCl_2$ have been identified:[432]

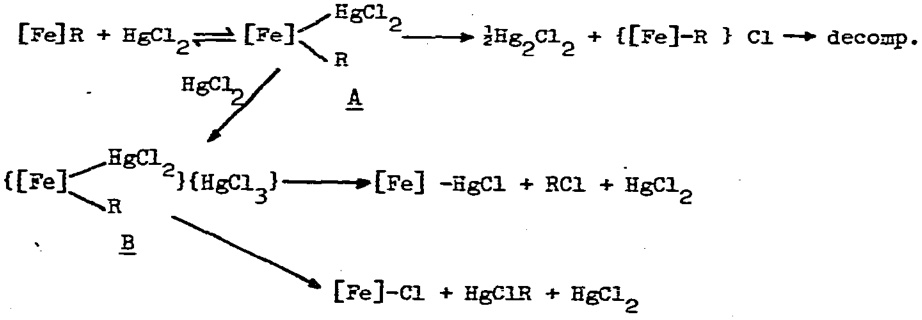
(i) $Fe(CO)_2(\eta^5\text{-}C_5H_5)R + HgCl_2 \text{ (an excess)} \rightarrow Fe(CO)_2(\eta^5\text{-}C_5H_5)Cl + HgClR$

(ii) $Fe(CO)_2(\eta^5\text{-}C_5H_5)R + HgCl_2 \rightarrow Fe(CO)_2(\eta^5\text{-}C_5H_5)HgCl + RCl$

(iii) $Fe(CO)_2(\eta^5\text{-}C_5H_5)R + HgCl_2 \rightarrow \text{Fe containing material} + \tfrac{1}{2}Hg_2Cl_2 + \text{organic products} + CO$

The kinetics of these reactions have been interpreted in terms of the mechanism shown in Scheme 62.

Scheme 62



$$[Fe]R + HgCl_2 \rightleftharpoons \underset{\underline{A}}{[Fe]{<}^{HgCl_2}_{R}} \longrightarrow \tfrac{1}{2}Hg_2Cl_2 + \{[Fe]\text{-}R\}\,Cl \longrightarrow \text{decomp.}$$

$$\underline{A} \xrightarrow{HgCl_2} \underset{\underline{B}}{\{[Fe]{<}^{HgCl_2}_{R}\}\{HgCl_3\}} \longrightarrow [Fe]\text{-}HgCl + RCl + HgCl_2$$

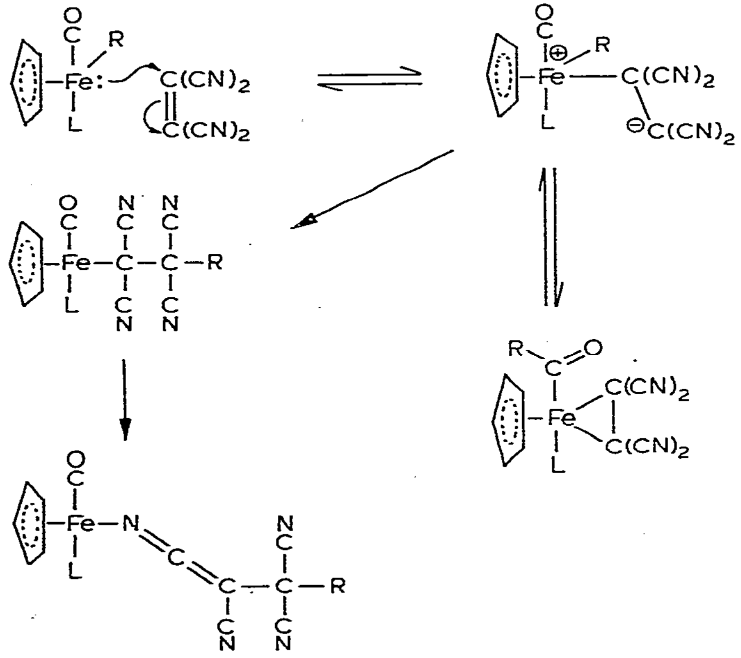
$$\underline{B} \longrightarrow [Fe]\text{-}Cl + HgClR + HgCl_2$$

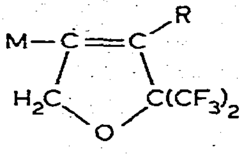
$[Fe] = Fe(CO)_2(\eta^5\text{-}C_5H_5)$

The nature of these reactions is determined by R. Thus, primary alkyl and aryl groups seem to promote reductive elimination of HgClR from B and entry of Cl^- would appear to account for the final products; bulky secondary and tertiary alkyl groups may be dissociated from B as carbonium ions, with assistance from solvent or Cl^-. This mechanism differs markedly from those of an S_E2 (retention or inversion) type considered[433] for Hg(II) cleavage reactions but is entirely consistent with studies involving $Fe(CO)(PPh_3)(\eta^5\text{-1-Me-3-PhC}_5H_3)Me$.

In a slow reaction, TCNE inserted[434] into the Fe–C bond of $Fe(CO)_2(\eta^5\text{-}C_5H_5)R$ (R = Me, Et, Br^n, CH_2Ph or CHMePh) giving $Fe(CO)_2(\eta^5\text{-}C_5H_5)\{C(CN)_2C(CN)_2R\}$ and $Fe(CO)_2(\eta^5\text{-}C_5H_5)\{N{:}C{:}C(CN)C(CN)_2R\}$, 358. These species do not interconvert in solution, and the order of reactivity towards insertion, viz. R = $PhCH_2$ > PhMeCH > Me, Et, Br^n >> Ph. Treatment of $Fe(CO)L(\eta^5\text{-}C_5H_5)(CH_2Ph)$ (L = PPh_3, $P(OPh)_3$ or PBu^n_3) with TCNE afforded complexes analogous to 358, but with the corresponding alkyl species (Me, Et or Br^n), the acyls $Fe(TCNE)L(\eta^5\text{-}C_5H_5)(COR)$ were obtained. On storage, these species, reverted to $Fe(CO)L(\eta^5\text{-}C_5H_5)R$ and/or $Fe(CO)L(\eta^5\text{-}C_5H_5)\{N{:}C{:}C(CN)C(CN)\}R$. A possible overall mechanism for the formation of these products is shown in Scheme 63. For the species $Fe(CO)L(\eta^5\text{-}C_5H_5)R$, the rate of insertion when R was held constant was L = PBu^n_3 > PPh_3 > $P(OPh)_3$, reflecting the increasing basicity of R and L. Using the optically active $Fe(CO)_2(\eta^5\text{-}C_5H_5)(CHMePh)$, both 358 and insertion products were formed but it proved very difficult to measure specific rotations. The

Scheme 63





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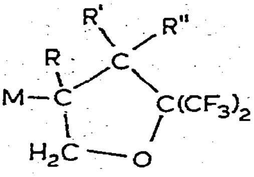
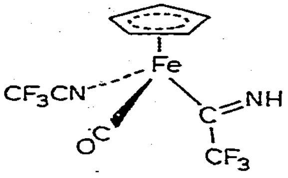
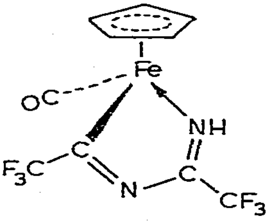


(360)



(361)

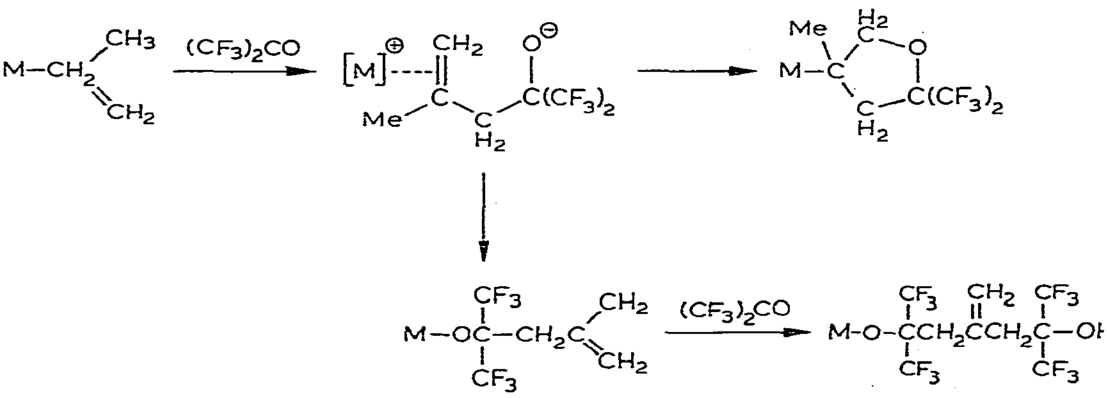


(362)

data were not inconsistent with a radical pathway in formation of the products.

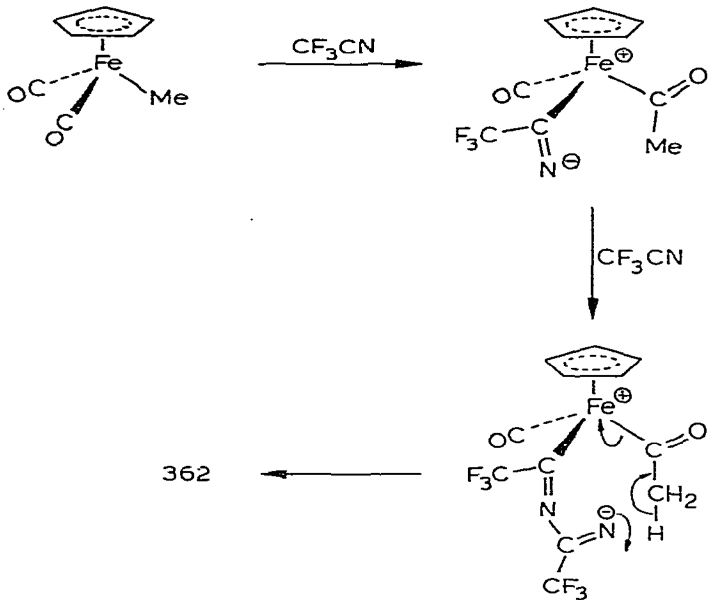
Treatment of 2-alkenyl and 2-alkynyl complexes of $\mathrm{Fe(CO)_2(\eta^5\text{-}C_5H_5)}$ with hexafluoroacetone afforded[438] complexes of the type 359 (R = Me or Ph) and 360 (R = H, R' = R" = Me; R = R' = H, R" = H, Me or Ph). It was noted that, as with $\mathrm{ClSO_2NCO}$, $\mathrm{Fe(CO)_2(\eta^5\text{-}C_5H_5)\{CH_2C(Me){:}CH_2\}}$ reacted with $\mathrm{(CF_3)_2CO}$ giving, in addition to the cyclic species 360, an insertion product, $\mathrm{Fe(CO)_2(\eta^5\text{-}C_5H_5)}$ - $\mathrm{\{OC(CF_3)_2CH_2C({:}CH_2)CH_2C(CF_3)_2OH\}}$. This may be attributed to a greater lability of the Fe olefin bond in a dipolar intermediate (Scheme 64) which favours dissociation and therefore apparent insertion. The possibility that enantiomeric pairs of molecules could be formed as a result of these reactions was discussed in the light of i.r. spectral data obtained from the products.

Scheme 64



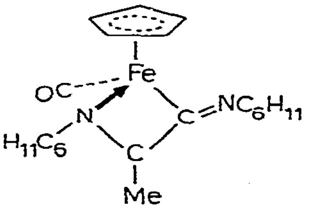
The product of the reaction of $Fe(CO)_2(\eta^5-C_5H_5)Me$, originally described[436] as 361, has been obtained[437] in improved yield in the presence of galvinoxyl, and has been reformulated as 362. A possible mode of formation is outlined in Scheme 65.

Scheme 65

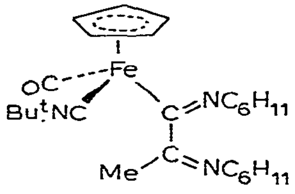


Photolysis of $Fe(CO)(CNC_6H_{11})(\eta^5-C_5H_5)(COMe)$ afforded[438] 363 which reacted further with Bu^tNC giving 364; 363 was also formed by reaction of $Fe(CO)_2$-$(\eta^5-C_5H_5)Me$ with $C_6H_{11}NC$ under or light. However, treatment of $Fe(CO)(CNBu^t)$-$(\eta^5-C_5H_5)Me$ with $C_6H_{11}NC$ gave only 365. A possible mechanism for these reactions is given in Scheme 66.

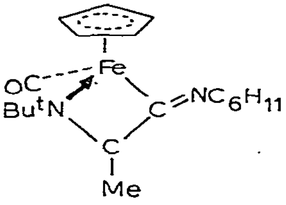
As mentioned earlier (ref. 427) the diastereoisomer [RSSR]$Fe(CO)\{P(OPh)_3\}$-$(\eta^5-C_5H_5)\{CHPh(SiMe_3)\}$ was epimerised[439] when treated with SO_2, giving, not the expected sulphinates which could not be isolated, but a mixture (40:60) of the starting material and the other diastereoisomer (RR-SS). It seems possible that



(363)

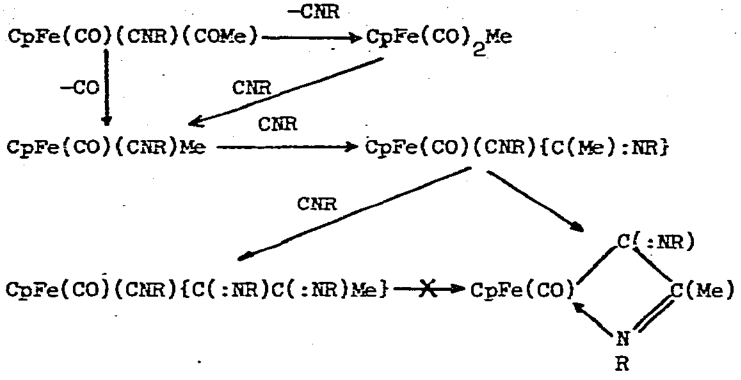


(364)



(365)

Scheme 66



the mechanism may involve the initial formation of the (RR-SS) sulphinate, viz. $Fe(CO)\{P(OPh)_3\}(\eta^5-C_5H_5)\{SO_2CHPh(SiMe_3)\}$, and this may epimerise giving a mixture of the (RR-SS) form and the (RS-SR) form. In turn, the latter could lose SO_2 giving the (RR-SS) alkyl. The pathway to the thermodynamically less stable (RR-SS) alkyl must involve the sequence

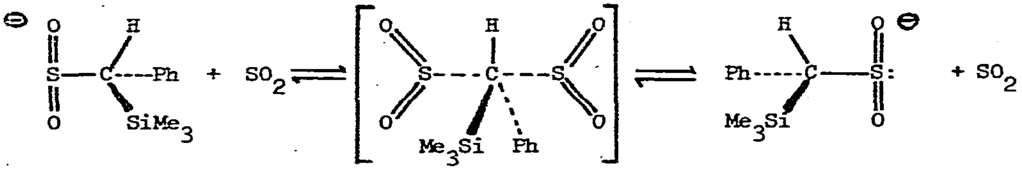
$$\text{(RSSR)-[Fe]R} + SO_2 \rightleftharpoons \text{(RRSS)-[Fe]}SO_2R \rightleftharpoons \text{(RSSR)-[Fe]}SO_2R \rightleftharpoons \text{(RRSS)-[Fe]R}$$

and is favoured over the pathway

$$\text{(RSSR)-[Fe]R} \rightleftharpoons \text{(RRSS)-[Fe]}SO_2R\ .$$

The rate of formation of (RSSR)-[Fe]R becomes competitive when sufficient heat is supplied to overcome the activation barrier for the above reaction, while retention of SO_2 in the reaction solution allows the system to equilibrate to the thermodynamically favoured product. Conversely, cooling the reaction mixture makes the conversion to the (RRSS)-alkyl more viable while rapid removal of SO_2 from a solution containing mainly this diastereomer would prevent its equilibration to the (RSSR)-form. It seems possible that the intermediate sulphinates may dissociate in polar solvents, giving $[Fe(CO)L(solvent)(\eta^5-C_5H_5)]^+$ and $[SO_2CHPh(SiMe_3)]^-$, and the latter would be susceptible to electrophilic attack by SO_2, resulting in Walden inversion (Scheme 67).

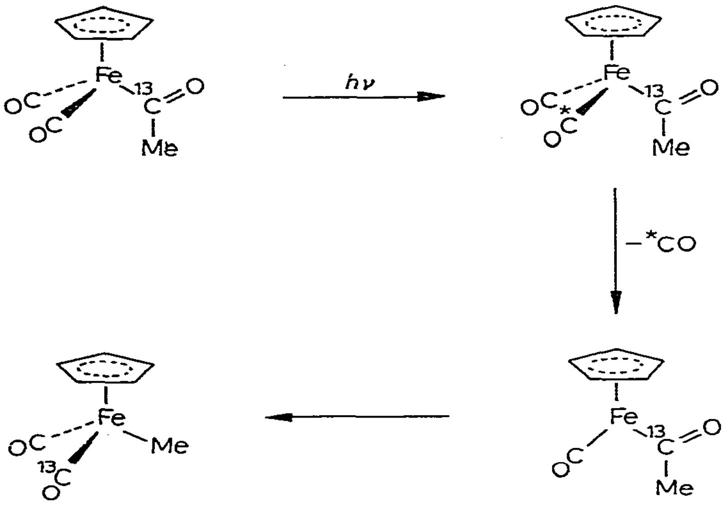
Scheme 67



It has been found that $Na[Fe(CO)_2(\eta^5-C_5H_5)]$ reacted with a large excess of SO_2 in THF at low temperatures giving[440] $(\eta^5-C_5H_5)(CO)_2FeS(:O)_2S(:O)_2Fe(CO)_2(\eta^5-C_5H_5)$. It seems likely that this species was obtained via $(\eta^5-C_5H_5)(CO)_2FeS(:O)_2Fe(CO)_2(\eta^5-C_5H_5)$, and selective removal of one SO_2 group was achieved from the 'double insertion' product under uv light, although decomposition and the formation of $[Fe(CO)_2(\eta^5-C_5H_5)]_2$ also occurred. Treatment of $[Fe(CO)_2(\eta^5-C_5H_5)(SO_2)]_2$ with MeI afforded $Fe(CO)_2(\eta^5-C_5H_5)(SO_2Me)$ and $Fe(CO)_2(\eta^5-C_5H_5)I$, as was found also with $[Fe(CO)_2(\eta^5-C_5H_5)_2](SO_2)$.

Carbonylation and Decarbonylation Reactions. UV irradiation of $Fe(CO)_2(\eta^5-C_5H_5)Me$ in the presence of $AsPh_3$ or $SbPh_3$ in acetonitrile gave[441] $Fe(CO)L(\eta^5-C_5H_5)(COMe)$. Photochemical or mass spectrometric decarbonylation of $Fe(CO)_2(\eta^5-C_5H_5)(COMe)$ occurs[442] with the loss of a terminal CO group, (Scheme 68).

Scheme 68



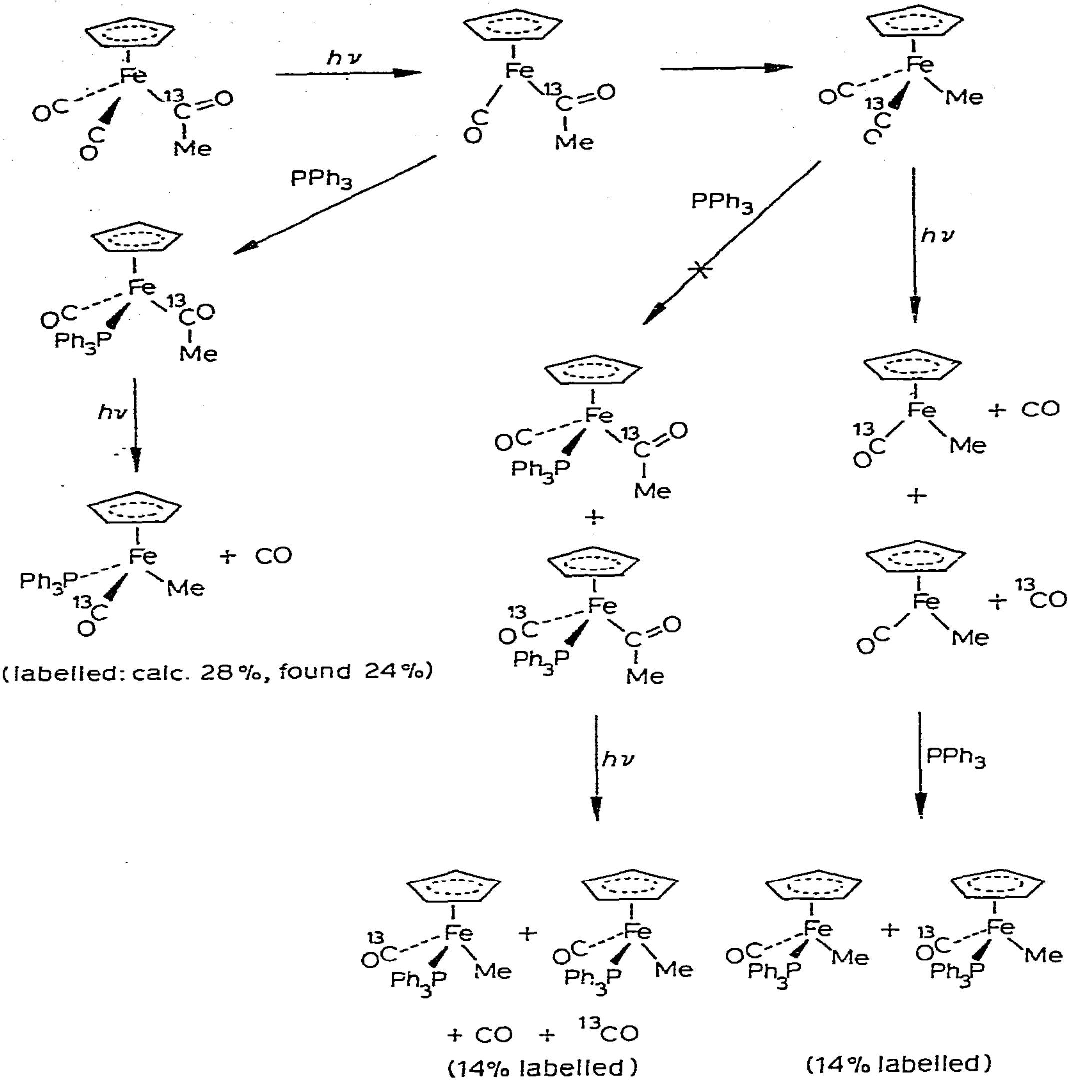
The intermediate, $Fe(CO)(\eta^5-C_5H_5)(COMe)$ can react with PPh_3 faster than the methyl group can migrate (Scheme 69).

Treatment of $Fe(CO)_2(\eta^5-C_5H_5)(COR)$ (R = cyclopropyl) with $Rh(PPh_3)_3Cl$ afforded[443] $Fe(CO)(PPh_3)(\eta^5-C_5H_5)(COR)$ and $Rh(CO)(PPh_3)_2Cl$.

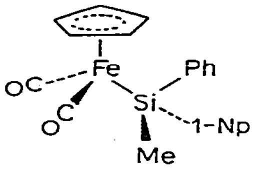
Compounds Containing Group IV Elements other than Carbon

Treatment of (−)-SiMePh(1-naphthyl)Cl with $[Fe(CO)_2(\eta^5-C_5H_5)]^-$ resulted[444] in inversion at silicon and the formation of (+)-366. Chlorination of this afforded (+)-SiMePh(1-naphthyl)Cl which, on reduction with $LiAlH_4$ underwent inversion group (−)-SiHMePh(1-naphthyl). However, UV irradiation of (+)-366

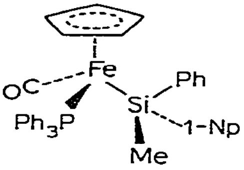
Scheme 69



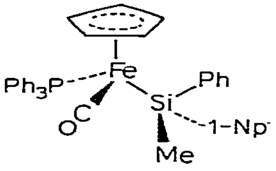
in the presence of PPh$_3$ gave the diastereomers (+)- and (−)-367. Chlorination of 367 proceeded with cleavage of the Fe-C bond but with retention of configuration at silicon (reduction with LiAlH$_4$ to the corresponding silane again occurred with inversion), whereas chlorination in the presence of PPh$_3$ resulted in inversion at the Si atom (giving, from (+)- and (−)-367, (−)-SiMePh(1-naphthyl)Cl and its (+)-diastereomer, respectively). It was noted that the Fe-Si bond 366 was not cleaved by Cl$_2$/PPh$_3$. Reaction of Na[Fe(CO)$_2$(η^5-C$_5$H$_5$)] with SiMe$_2$R(CH$_2$Cl) (R = H, Me or Ph) afforded[445] Fe(CO)$_2$(η^5-C$_5$H$_5$)(CH$_2$SiMe$_2$R). It was found that the chemical character of the Fe-C σ bond was relatively unaffected by



(366)



(367a)

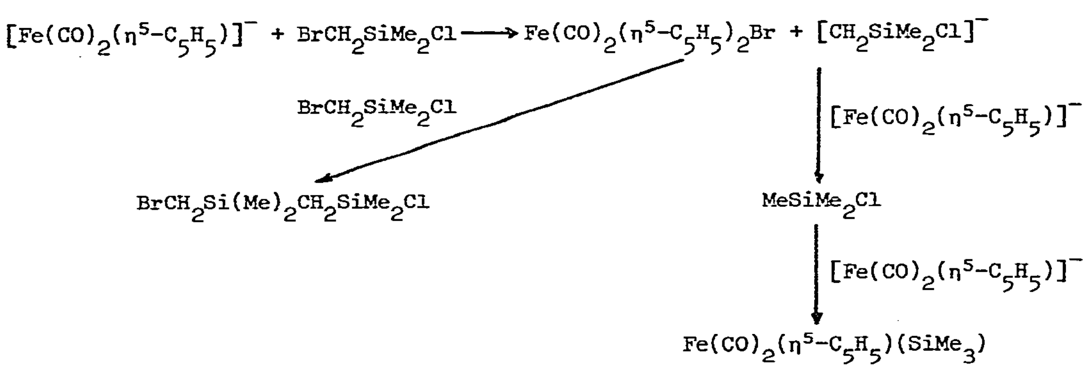


(367b)

the silyl substituent. Thus treatment with tertiary phosphines (L = PPh_3, $PMePh_2$; $PEtPh_2$; R = Me) gave $Fe(CO)L(\eta^5-C_5H_5)(COCH_2SiMe_2R)$ which, in the presence of traces of HCl (when L = PPh_3; R = Me), produced $Fe(CO)(PPh_3)(\eta^5-C_5H_5)(COMe)$ and $SiMe_3Cl$. Photolysis of $Fe(CO)_2(\eta^5-C_5H_5)(CH_2SiMe_2R)$ in the presence of tertiary phosphines gave $Fe(CO)L(\eta^5-C_5H_5)(CH_2SiMe_2R)$ (R = Me or Ph) while with SO_2 $Fe(CO)_2(\eta^5-C_5H_5)(SO_2CH_2SiMe_2R)$ was produced. Thermal decomposition or treatment with L, of $Fe(CO)_2(\eta^5-C_5H_5)(CH_2SiMe_2H)$, afforded $Fe(CO)_2(\eta^5-C_5H_5)(SiMe_3)$ and $Fe(CO)L(\eta^5-C_5H_5)(SiMe_2)$, respectively.

Reaction of $Na[Fe(CO)_2(\eta^5-C_5H_5)]$ with $SiMe_n(CH_2Cl)Cl_{3-n}$, $SiMe_2(CH_2Cl)Br$ or $SiMe_2(CH_2Br)Br$ afforded[446] $Fe(CO)_2(\eta^5-C_5H_5)$ $SiMe_n(CH_2Cl)Cl_{2-n}$ (n = 0, 1 or 2) and $Fe(CO)_2(\eta^5-C_5H_5)\{SiMe_2(CH_2Br)\}$. With $SiMe_3(CH_2Br)$, $Fe(CO)_2(\eta^5-C_5H_5)(CH_2SiMe_3)$ was produced. On heating, $Fe(CO)_2(\eta^5-C_5H_5)\{SiMe_n(CH_2Cl)Cl_{2-n}\}$ (n = 1 or 2) rearranged to $Fe(CO)_2(\eta^5-C_5H_5)\{CH_2SiMe_nCl_{2-n}\}$, while $Fe(CO)_2(\eta^5-C_5H_5)\{Si(CH_2Cl)Cl_2\}$ was catalytically rearranged by $AlCl_3$ to $Fe(CO)_2(\eta^5-C_5H_5)(CH_2SiCl_3)$. Treatment of $SiMe_2(CH_2Br)Cl$ with $Na[Fe(CO)_2(\eta^5-C_5H_5)]$ gave either $BrCH_2Si(Me)_2CH_2SiMe_2Cl$ or $Fe(CO)_2(\eta^5-C_5H_5)(SiMe_3)$, depending upon conditions, and a possible mechanism is shown in Scheme <u>70</u>.

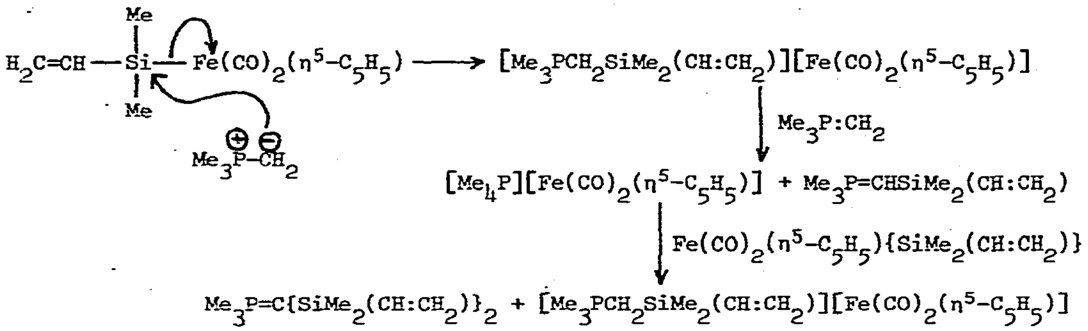
Scheme 70



Reaction of $SiR_2(CH:CH_2)Cl$ with $[Fe(CO)_2(\eta^5-C_5H_5)]^-$ afforded[447] $Fe(CO)_2(\eta^5-C_5H_5)\{SiR_2(CH:CH_2)\}$ (R = Me or Cl). These compounds, on treatment with HX reacted according to three pathways: (a) formation of $Fe(CO)_2(\eta^5-C_5H_5)H$ and

$SiR_2(CH{:}CH_2)X$; (b) formation of $Fe(CO)_2(\eta^5\text{-}C_5H_5)X$ and $SiR_2(CH{:}CH_2)H$; or (c) formation of $Fe(CO)_2(\eta^5\text{-}C_5H_5)\{SiR_2CH_2CH_2X\}$. Treatment of $Fe(CO)_2(\eta^5\text{-}C_5H_5)\text{-}\{SiCl_2(CH{:}CH_2)\}$ with $AgBF_4$ afforded first $Fe(CO)_2(\eta^5\text{-}C_5H_5)\{SiF_2(CH{:}CH_2)\}$ and then $Fe(CO)_2(\eta^5\text{-}C_5H_5)(SiF_2)$. The reactions of $Fe(CO)_2(\eta^5\text{-}C_5H_5)$ $\{SiMe_2(CH{:}CH_2)\}$ with phosphorus ylides are summarised in Scheme 71.

Scheme 71



Reaction of $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ with $SiMe_2(CH{:}CH_2)(CH_2Cl)$, $SiMe_2(OMe)\text{-}(CH_2Cl)$, $ClCH_2Si(Me)_2OSiMe_2CH_2Cl$, $ClCH_2Si(Me)_2NHSiMe_2CH_2Cl$, $O(SiMe_2O)_3SiMeCH_2Cl$ and $SiMe_2(NEt_2)(CH_2Cl)$ resulted[448] in cleavage of a C-Cl bond and formation of the appropriate monometallic or bimetallic alkyl derivative. Reaction with $SiHMe_2(CH_2I)$ gave $Fe(CO)_2(\eta^5\text{-}C_5H_5)\{CH_2SiMe_2H\}$ which decomposed thermally to $Fe(CO)_2(\eta^5\text{-}C_5H_5)(SiMe_3)$, but reacted with MeOH, Ph_3CCl and $[Ph_3C][BF_4]$ giving respectively, $Fe(CO)_2(\eta^5\text{-}C_5H_5)\{CH_2SiMe_2(OMe)\}$, $Fe(CO)_2(\eta^5\text{-}C_5H_5)(CH_2SiMe_2Cl)$ and $Fe(CO)_2(\eta^5\text{-}C_5H_5)(SiMe_2F)$. Reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2FeSiMe_2]_2O$ with BCl_3 afforded an unstable 1:1 adduct ($>O \rightarrow BCl_3$). Treatment of $(\eta^5\text{-}C_5H_5)(CO)_2\text{-}FeSi(Me)_2CH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ with HCl gave $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ and $SiMe_3Cl$ while $Fe(CO)_2(\eta^5\text{-}C_5H_5)(CH_2SiMe_2R)$ reacted with PPh_3 giving the acyl $Fe(CO)(PPh_3)\text{-}(\eta^5\text{-}C_5H_5)(COCH_2SiMe_2R)$. The following reactions of bimetallic species were also observed:

$$(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Si(Me)_2Fe(CO)_2(\eta^5\text{-}C_5H_5) + PPh_3 \longrightarrow$$

$$(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeCOCH_2Si(Me)_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$$

$$[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2SiMe_2]_2NH + PPh_3 \longrightarrow (\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeCOCH_2SiMe_2NH\text{-}$$

$$SiMe_2CH_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$$

$$+$$

$$[(\eta^5\text{-}C_5H_5)(CO)_2FeCOCH_2SiMe_2]_2NH$$

(also with -O- bridged species)

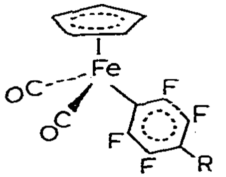
Treatment of $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)\{COCH_2SiMe_2(OMe)\}$ with water afforded $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)(COMe)$ and $SiMe_2(OMe)OH$.

Displacement of NaF occurred when $SiMe_3(C_6F_5)$ was treated[449] with $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$, the product being 368 ($R = SiMe_3$); similar products were obtained containing $R = SiPh_2(C_6F_5)$ and $SiMe_2(CH_2)_3SiMe_2$. Treatment of $SiPh_2(C_6F_5)_2$ or $(C_6F_5SiMe_2)_2O$ with $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$ afforded $(\eta^5\text{-}C_5H_5)(CO)_2FeQFe(CO)_2(\eta^5\text{-}C_5H_5)$, $Q = SiPh_2$ or $(Me_2Si)_2O$.

With HX (X = I or Br), $Fe(CO)_2(\eta^5\text{-}C_5H_5)(SiR_3)$ ($R = OMe$ or NHC_6H_{11}) gave[450] $Fe(CO)_2(\eta^5\text{-}C_5H_5)(SiX_3)$; $Fe(CO)_2(\eta^5\text{-}C_5H_5)\{Si(OMe)Br_2\}$ was also isolated. Exchange of Cl was achieved in metathetical reactions between $Fe(CO)_2(\eta^5\text{-}C_5H_5)$- and NaX ($X = N_3$, OCN or SCN), while with $LiAlH_4$, the trichlorosilyl complex afforded $Fe(CO)_2(\eta^5\text{-}C_5H_5)(SiH_3)$.

In a reaction between $Na[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$, MX_2 (M = Ge, Sn or Pb; X = halide) and RX (R = long chain alkyl group, C_7-C_{16}), the species $Fe(CO)_2(\eta^5\text{-}C_5H_5)(MRX_2)$ were formed.[451] Mass spectrometric studies of $Fe(CO)_2(\eta^5\text{-}C_5H_5)(GeCl_2R)$ (R = Cl, Me, Et, Pr^n or CH_2Ph) revealed[452] that, in the probe, rearrangement could occur, the C_5H_5 ring migrating to Ge or the Cl atoms migrating to Fe.

Reaction of $Ru(CO)_4(MMe_3)_2$ (M = Si or Ge) with azulene gave[453] 369 ($R = MMe_3$) which, when M = Ge, on treatment with iodine afforded 369 (R = I). With guaiazulene, $Ru(CO)_4(GeMe_3)_2$ produced 370 and/or 371, but 4,6,8-trimethylazulene did not give analogous products, presumably because a methyl group blocks C(6) thereby preventing migration of the $GeMe_3$ group. From this last reaction $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ and traces of $Ru(CO)_2(C_{10}H_6Me_3)$-



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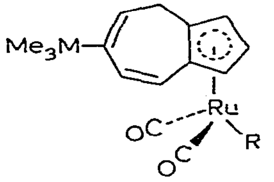

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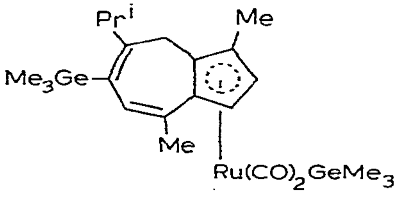

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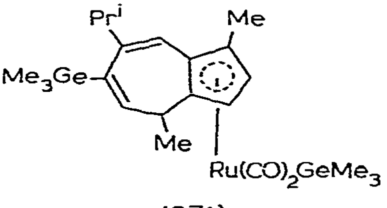

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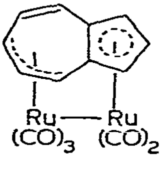

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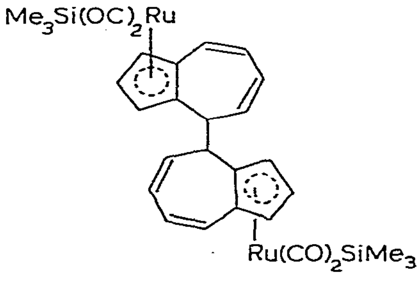
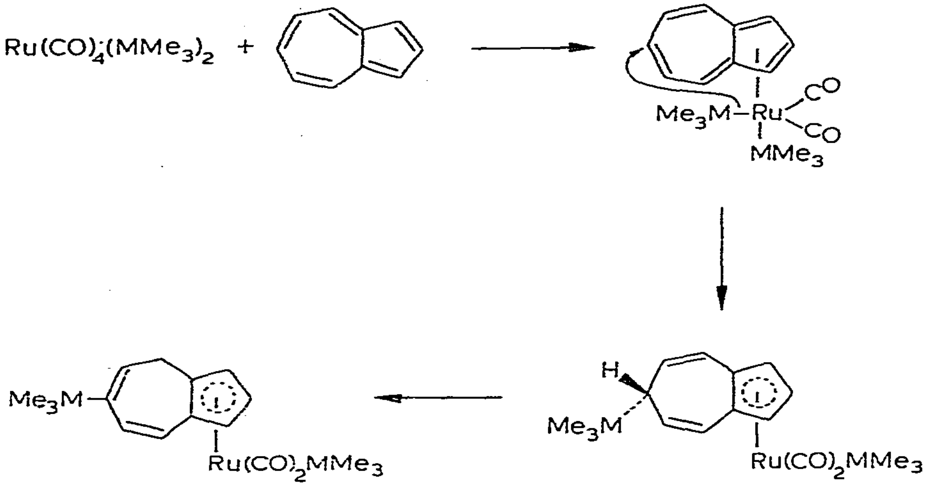


($GeMe_3$) were obtained. Reaction of $[Ru(CO)_4SiMe_3]_2$ with azulene gave 369 (E = $SiMe_3$) together with 372, and $[Ru(CO)_2(C_{10}H_8)(SiMe_3)]_2$, 373. Coupling of two azulene groups in the presence of iron carbonyls has already been observed[454] and the structure of 373 is believed to be essentially similar to that of $[Mn(CO)_3(C_{10}H_8)]_2$.[455] From the reaction between $Ru_3(CO)_{12}$ and guaiazulene, three products were obtained: $Ru_2(CO)_5\{C_{10}H_5(1,4\text{-}Me_2)(7\text{-}Pr^i)\}$, $Ru_3(CO)_7\text{-}\{C_{10}H_5(1,4\text{-}Me_2)(7\text{-}Pr^i)\}$ (thought to be similar to $Ru_3(CO)_7(C_{10}H_8)$,[456] and $Ru_4(CO)_9\{C_{10}H_5(1,4\text{-}Me_2)(7\text{-}Pr^i)\}$ (believed to be similar to $Ru_4(CO)_9\{C_{10}H_5\text{-}(4,6,8\text{-}Me_3)\}$[457]). The reaction sequence is outlined in Scheme 72, and may occur

Scheme 72

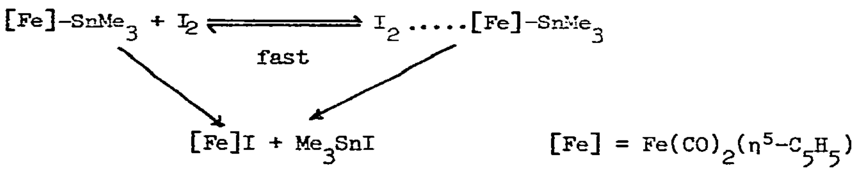


because of the driving force of azulene to form a cyclopentadienyl ring. The exclusive migration of the MMe_3 group to C(6) is perhaps due to steric factors, while the suprafacial 1,3-hydrogen shift can be attributed to increased stability of the conjugated as opposed to the non-conjugated diene system.

The rate of the (electrophilic) iodination of $Fe(CO)_2(\eta^5\text{-}C_5H_5)SnMe_3$ in carbon tetrachloride was faster than[458] that the comparable Mn, Mo and W compounds, and a mechanism is outlined in Scheme 73. Treatment of $[Fe(CO)_2\text{-}(\eta^5\text{-}C_5H_5)]_2SnCl_2$ with Li and PPh_3 gave[459] $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2SnCl$, while with $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2SnPh_2$, $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2SnPhCl$ was formed. Reaction of $Fe(CO)_2(\eta^5\text{-}C_5H_5)SnCl_3$ with $AgBF_4$ provided[460] $Fe(CO)_2(\eta^5\text{-}C_5H_5)SnF_3$.

Complexes Containing Group V Ligands. Voltammetric studies have shown[461] that $FeL_2(\eta^5\text{-}C_5H_5)X$ (L = CNR, PR_3 or P(OR) ; X = halide, H, Me or SnX_3) and $Fe(diphos)(\eta^5\text{-}C_5H_5)X$ (diphos = $Ph_2PCH_2CH_2PPh_2$; X = halide, Me, $SnMe_3$ or $SnCl_3$) are readily oxidised (except when X = $SnCl_3$) in a one-electron process. The

Scheme 73

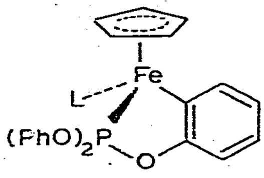


$E_{\frac{1}{2}}$-value for the process is strongly influenced by L or diphos and X, oxidation becoming more facile as the capacity of the ligand to remove charge from the system decreases. Treatment of Fe(diphos)(η^5-C_5H_5)X (X = Cl, Br, I, Me, $SnMe_3$) with $AgPF_6$ gave [Fe(diphos)(η^5-C_5H_5)X][PF_6]. Similarly, treatment of Fe{$P(OPh)_3$}$_2$-(η^5-C_5H_5)I with $NOPF_6$, a good and relatively mild one-electron oxidising agent, gave [Fe{$P(OPh)_3$}$_2$(η^5-C_5H_5) I][PF_6], but the identical reaction with Fe(CO) - {$P(OPh)_3$}(η^5-C_5H_5)I afforded [Fe(NO){$P(OPh)_3$}(η^5-C_5H_5)I][PF_6]. However, reaction of Fe(CO)(CNPh)(η^5-C_5H_5)I with $NOPF_6$ gave [Fe(CO)$(CNPh)_2$(η^5-C_5H_5)]-[PF_6] while Fe$(CNPh)_2$(η^5-C_5H_5)I afforded [Fe$(CNPh)_3$(η^5-C_5H_5)][PF_6].

The structures of $Fe(CO)_2$(η^5-C_5H_5){$P(CF_3)_2$} and $Fe(CO)_2$(η^5-C_5H_5){P(:O)-$(CF_3)_2$} have been determined crystallographically.[462] In the former, the Fe-P distance is 2.27Å while in the latter it is 2.19Å, the covalent radius of the phosphorus atom being essentially the same in both cases. These Fe-P bond lengths were interpreted in terms of increased Fe→P d_π-d_π bonding in the P(:O)$(CF_3)_2$ compound.

The species obtained[463] by photolysis of $Fe(CO)_2$(η^5-C_5H_5)R or Fe(CO)-{$P(OPh)_3$}(η^5-C_5H_5)R (R = Me or Ph) in the presence of $P(OPh)_3$ and described as [Fe{$P(OPh)_3$}$_2$(η^5-C_5H_5)]$_2$, has been reformulated[464] as 374 (L = $P(OPh_3)$ on the basis of mass and ^{31}P n.m.r. spectral measurements. UV irradiation of Fe(CO)-{$P(OPh)_3$}(η^5-C_5H_5)Ph was found to give 372 (L = CO). The ^{31}P n.m.r. spectrum of Fe(CO)($Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$)($\eta^5$-$C_5H_5$)(COMe) indicated[465] that it consisted of two isomers 375 and 376. Treatment of $Fe(CO)_2$(η^5-C_5H_5)I with $PhP(CH_2CH_2PMe_2)_2$ gave[466] [Fe{$PhP(CH_2CH_2PMe_2)_2$}(η^5-C_5H_5)]I, while [$Fe(CO)_2$(η^5-C_5H_5)]$_2$ reacted with $Me_2PCH_2CH_2PPh_2$ giving $Fe_2(CO)_2$($Me_2PCH_2CH_2PPh_2$)(η^5-C_5H_5)$_2$ which contained bridging but no terminal CO groups. Reaction of $Fe(CO)_2$(η^5-C_5H_5)Cl with diphos-($Ph_2PCH_2CH_2PPh_2$) afforded[467] [Fe(CO)(diphos)(η^5-C_5H_5)]Cl and conversion of this to the PF_6^- salt followed by UV irradiation under N_2 led to the formation of [{Fe(diphos)(η^5-C_5H_5)}(N_2)][PF_6], 377. In acetone, this dissociated to give [Fe(diphos)(acetone)(η^5-C_5H_5)][PF_6]which reacted with hydrazine or ammonia (L) to give [Fe(diphos)L(η^5-C_5H_5)]PF_6 (isolated as THF solvates).

Treatment of $Fe(CO)_2$(η^5-C_5H_5)I with L (PPh_3, $PMePh_2$, PMe_2Ph or PMe_3) and then with $AgBF_4$ and NaCN afforded[468] Fe(CO)L(η^5-C_5H_5)(CN). From n.m.r. spectral studies assisted by the shift reagent $Eu(fod)_3$, it was established that some of these complexes existed in preferred conformations. Thus, when L = $PMePh_2$, the



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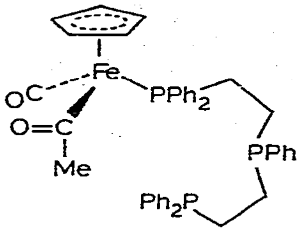

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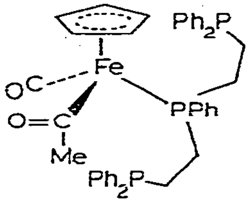

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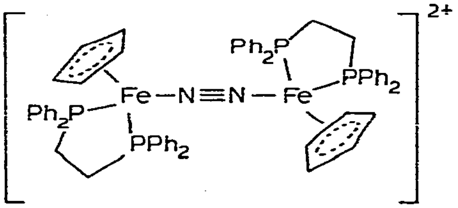
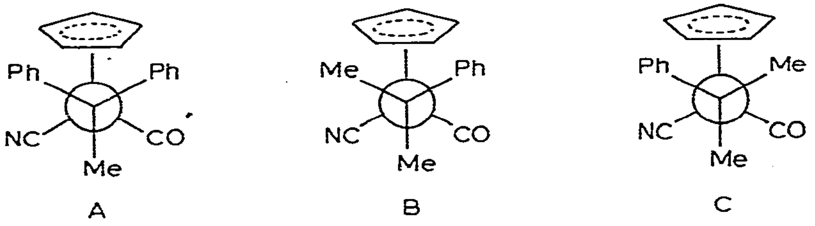


(377)

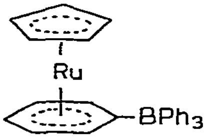
phenyl groups appear to adopt a conformation (figure 28A) in which they are orientated adjacent to the C_5H_5 ring, and when L = PMe_2Ph, similar conformations are preferred (figure 28A or C). The maximum barriers to rotation about the Fe-P and P-C bonds were estimated to be 8.0 and 7.6 kcal/mol, respectively. A method of assigning resonances of diastereotopic nuclei to particular nuclei was presented.

Figure 28



An excess of KCN reacted with $[Fe(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)]I$ giving[469] $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)(CN)$ which, on treatment with $[Et_3O][PF_6]$, afforded $[Fe(CO)(CNEt)(PPh_3)(\eta^5\text{-}C_5H_5)][PF_6]$. This species was shown clearly to contain an isonitrile ligand by comparison with $[Fe(CO)(NCMe)(PPh_3)(\eta^5\text{-}C_5H_5)][BF_4]$, and was found not to undergo reactions with nucleophiles to give additional products. While $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)I$ reacted with an excess of KCN giving $K[Fe(PPh_3)(\eta^5\text{-}C_5H_5)(CN)_2]$, the products obtained from $Fe(CO)_2(\eta^5\text{-}C_5H_5)I$ were solvent dependent: with KCN in ethanol, $Fe(CO)_2(\eta^5\text{-}C_5H_5)(CN)$ was produced whereas when water was present, $K[Fe(CO)(\eta^5-C_5H_5)(CN)_2]$ was formed. Reaction of $Fe(CO)(PPh_3)(\eta^5-C_5H_5)I$ with $LiCH_2CN$ or of $[Fe(CO)(C_2H_4)(PPh_3)(\eta^5-C_5H_5)]^+$ with KCN gave $Fe(CO)(PPh_3)(\eta^5-C_5H_5)\{(CH_2)_nCN\}$ (n = 1 or 2). The ^1H and ^{13}C n.m.r. spectra of these complexes, some of which have chiral metal centres, were measured in the presence of optically active shift reagents, and resolution of the enantioptic protons of the C_5H_5 ring in $Fe(CO)(PPh_3)(\eta^5-C_5H_5)(CN')$ and $Fe(CO)(PPh_3)(\eta^5-C_5H_5)(CH_2CN)$ was observed.

While $Ru(CO)_2(\eta^5-C_5H_5)Cl$ showed no tendency to dissociate in alcohols, $Ru(PPh_3)_2(\eta^5-C_5H_5)Cl$ revealed[470] considerable ionic behaviour. Thus, the latter very readily forms $[Ru(PPh_3)_2(\eta^5-C_5H_5)L]^z$, where z = +1 or 0 when L is a neutral or anionic ligand, L being CO, N_2, BPh_4^-, $BPh_3(CN)^-$ or $BH_3(CN)^-$. From methanol in the presence of BPh_4^-, the species $[Ru(PPh_3)_2(MeOH)(\eta^5-C_5H_5)][BPh_4]$ could be isolated, but under CO in ethanol, $[Ru(CO)(PPh_3)_2(\eta^5-C_5H_5)][BPh_4]$ was formed. Only under high pressure could the related $[Ru(CO)_3(\eta^5-C_5H_5)]^+$ be obtained, and when $Ru(PPh_3)_2(\eta^5-C_5H_5)Cl$ was treated with CO under pressure in benzene the known[471] $Ru(CO)(PPh_3)(\eta^5-C_5H_5)Cl$ was formed. The complexes $RuL_2(\eta^5-C_5H_5)(NCBX_3)$ (L = CO or PPh_3, X = H or Ph) rearranged readily forming $RuL_2(\eta^5-C_5H_5)(CN)$ or $RuL_2(\eta^5-C_5H_5)(CNBX_3)$. When $Ru(CO)_2(\eta^5-C_5H_5)Cl$ was refluxed with $NaBPh_4$ in methanol, $[Ru(CO)_2(MeOH)(\eta^5-C_5H_5)][BPh_4]$ was formed, which decomposed to $Ru(CO)_2(\eta^5-C_5H_5)Ph$. However on refluxing $[Ru(CO)_2(acetone)(\eta^5-C_5H_5)][BPh_4]$ in acetone, only $[Ru(CO)_2(\eta^5-C_5H_5)]_2$ was produced. A similar reaction involving $Ru(PPh_3)_2(\eta^5-C_5H_5)Cl$, $NaBPh_4$ and alcohols gave the η^6-arene complex, 378 (analogues containing $\eta^5-C_5H_4Me$ were also prepared). No reaction was observed when $Ru(PPh_3)_2(\eta^5-C_5H_5)Cl$ was heated in alcohol in the presence of benzene,



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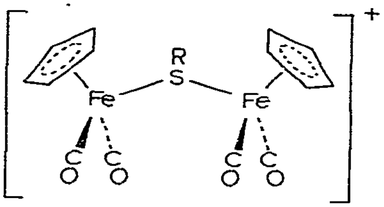

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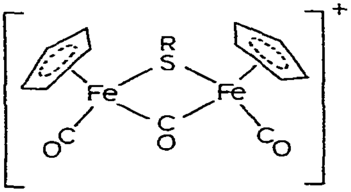

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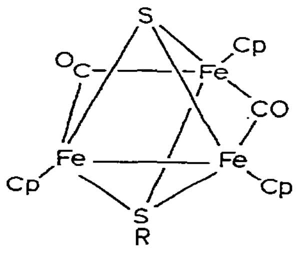


(381)

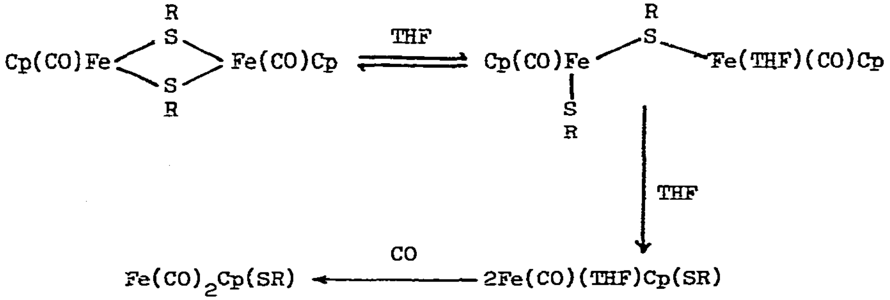
mesitylene, hexamethyl- or hexafluoro-benzene. Treatment of $Ru(CO)_2(\eta^5-C_5H_5)Cl$ with $BPh_3(CN)^-$ in refluxing ethanol afforded $Ru(CO)_2(\eta^5-C_5H_5)CN$, whereas the corresponding cations $[Ru(CO)_2(solvent)(\eta^5-C_5H_5)]^+$ (solvent = MeOH or acetone) gave $Ru(CO)_2(\eta^5-C_5H_5)(NCBPh_3)$. With $BPh_3(CN)^-$, $[Ru(PPh_3)_2(acetone)(\eta^5-C_5H_5)]^+$ gave $Ru(PPh_3)_2(\eta^5-C_5H_5)(CNBPh_3)$ (via the intermediate $Ru(PPh_3)_2(\eta^5-C_5H_5)(NCBPh_3)$), also obtainable from $Ru(PPh_3)_2(\eta^5-C_5H_5)CN$ and BPh_3. Treatment of $[Fe(CO)_2(acetone)(\eta^5-C_5H_5)]^+$ with $BPh_3(CN)^-$ provided $Fe(CO)_2(\eta^5-C_5H_5)(NCBPh_3)$ which did not isomerise to the isonitrile. Reaction of $[Ru(PPh_3)_2(acetone)(\eta^5-C_5H_5)]^+$ with $BH_3(CN)^-$ gave an inseparable mixture of $Ru(PPh_3)_2(\eta^5-C_5H_5)CN$ and $Ru(PPh_3)_2(\eta^5-C_5H_5)(CNBH_3)$, while $[Ru(CO)_2(acetone)(\eta^5-C_5H_5)]^+$ afforded a brown solid containing $[Ru(CO)_2(\eta^5-C_5H_5)]_2$.

The complexes $M(CO)_3(\eta^5-C_5H_5)SbMe_2$ (M = Mo or W) reacted with $Fe_2(CO)_9$ giving[472] $M(CO)_3(\eta^5-C_5H_5)Sb(Me)_2Fe(CO)_4$.

Compounds Containing Sulphur. Reaction of $Fe(CO)_2(\eta^5-C_5H_5)(SR)$ (R = Et or Bu^t) with $[Fe(CO)_2(acetone)(\eta^5-C_5H_5)]^+$ afforded[473] $[\{Fe(CO)_2(\eta^5-C_5H_5)\}_2(SR)]^+$, 379. Photolysis of this afforded $[Fe_2(CO)_3(\eta^5-C_5H_5)_2(SR)]^+$, probably 380, which, when R = Et, could be reduced using sodium amalgam to the unstable green $Fe_2(CO)_3(\eta^5-C_5H_5)_2(SEt)$ (μ ca. 1.5 B.M.) and red $[Fe_2(CO)_3(\eta^5-C_5H_5)(SEt)]^-$. On heating or photolysing 379 (R = Et, $Fe(CO)_2(\eta^5-C_5H_5)H$ was formed.

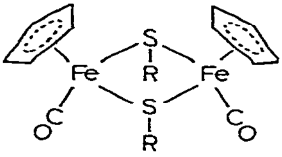
In THF, it was observed[474] that the unstable isomer of $[Fe(CO)(\eta^5-C_5H_5)\{S(p-MeC_6H_4)\}]_2$ reacted with CO at room temperature to give a 1:1 mixture of the stable and unstable isomer, together with a small amount of $Fe(CO)_2(\eta^5-C_5H_5)\{S(p-MeC_6H_4)\}$. The stable isomer behaved similarly, giving a 3:1 mixture of stable and unstable forms as well as the dicarbonyl monomer. When this latter mixture was refluxed in THF, under CO, 60% of the dicarbonyl was obtained. The mechanism of these reactions can be depicted in Scheme 74. Reaction of $[Fe(CO)_2(\eta^5 C_5H_5)]_2$ with R_2S_2 (R = Me, Et, Pr^i, Bu^n, Bu^t, CH_2Ph or Ph) gave[475] $Fe_3(CO)_2(\eta^5-C_5H_5)_3S(SR)$, 381 and $[Fe(CO)(\eta^5-C_5H_5)(SR)]_2$. The latter species could be isolated as two isomers when R = Me, Et, Pr^i or Bu^n, probably 382 and

Scheme 74



383, but as only one isomer when R = Bu^t or CH_2Ph; three isomers were observed when R = Ph,one certainly 384 and the others 385a, b or c. The trinuclear species 381 was observed voltammetrically to undergo two one-electron oxidation steps, and its treatment with iodine afforded $[Fe_3(CO)_2(\eta^5-C_5H_5)_3S(SR)]I$. This was unstable, however, and readily decomposed into $[Fe(CO)(\eta^5-C_5H_5)(SR)]_2^+$.

Reaction of $Fe(CO)_2(\eta^5-C_5H_5)(SR)$ (R = CF_3 or C_6F_5) with hexafluorobut-2-yne afforded[476] 386 which could be photolytically decarbonylated to 387. Photolysis of 387 (R = C_6F_5) with more $CF_3C{\equiv}CCF_3$ gave 388. Treatment of $[Fe(CO)_3(SR)]_2$ (R = CF_3 or C_6F_5) with $CF_3C{\equiv}CCF_3$ at moderate temperatures afforded 389 (L = CO), and the structure of the species where R = CF_3 has been confirmed by X-ray crystallography.[477] With PPh_3, 389 (L = CO) underwent displacement of one CO group, giving 389 (L = PPh_3). At higher temperatures, $[Fe(CO)_3(SR)]_2$ reacted with the butyne giving the cyclopentadieneone complex 390.



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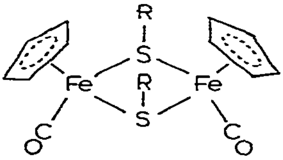

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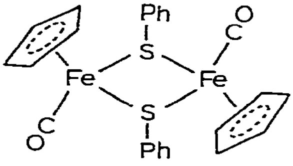

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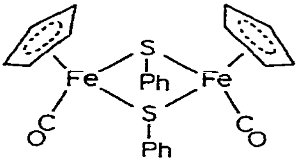

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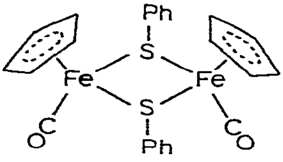

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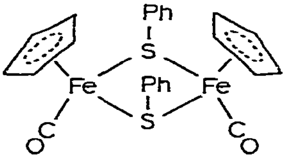

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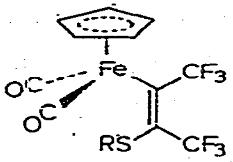

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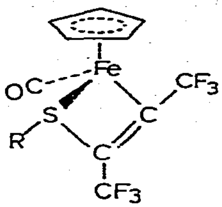

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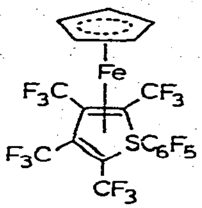

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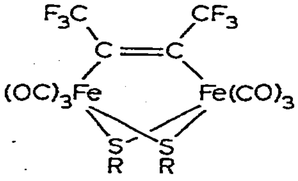

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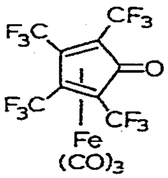


(390)

Upon irradiation at 366 nm in THF at 30°C, $Fe(CO)_2(\eta^5-C_5H_5)(SCN)$ and $Fe(CO)_2(\eta^5-C_5H_5)(NCS)$ are interconverted.[478] Using $Eu(fod)_3$ as a shift reagent, these isomers can be readily differentiated[479] by observing the substantial shifts of the cyclopentadienyl protons in $Fe(CO)_2(\eta^5-C_5H_5)(SCN)$.

Halide Compounds. Valence band photoelectron spectra have been obtained[480] for $Fe(CO)_2(\eta^5-C_5H_5)X$ (X = Cl, Br, I or Me) and $[Fe(CO)(\eta^5-C_5H_5)]_4$. The data have been compared with those obtained from $Fe(\eta^5-C_5H_5)_2$ and $Fe(CO)_4$ and interpreted in terms of molecular orbital theory.

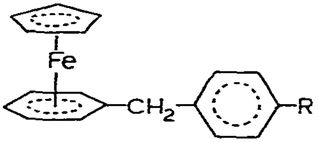
Compounds Containing Group II metals. Reaction of $[Bu^n_4N][AuBr_2]$ with $[Fe(CO)_2(\eta^5-C_5H_5)]^-$ gave[481] $[\{Fe(CO)_2(\eta^5-C_5H_5)\}Au]^-$, containing a linear Fe-Au-Fe bond system. Comparison of i.r. spectral data obtained from this compound with that obtained from $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$ established that the Fe-Au bond was weaker than the Fe-Hg interaction.

Treatment of $[Fe(CO)_2(\eta^5-C_5H_5)]_2$ with magnesium amalgam in THF, or of $Fe(CO)_2(\eta^5-C_5H_5)I$ with Mg powder in the same solvent, afforded[482] $[Fe(CO)_2(\eta^5-C_5H_5)]_2Mg(THF)_2$. Reaction of the dicarbonyl dimer with magnesium amalgam in benzene/pyridine mixtures gave the comparable $[Fe(CO)_2(\eta^5-C_5H_5)]_2Mg(pyr)_2$. These compounds were air-sensitive, readily forming MgO and reverting to the dicarbonyl dimer. Conductivity data indicated that they were not ionised in THF, molecular weight studies established that they were not associated in benzene, and i.r. spectral data revealed the absence, in THF or benzene, of the ion $[Fe(CO)_2(\eta^5-C_5H_5)]^-$. In THF, there may be an equilibrium $[Fe(CO)_2(\eta^5-C_5H_5)]_2Mg(THF)_2 + 2THF \rightleftharpoons [Fe(CO)_2(\eta^5-C_5H_5)]_2Mg(THF)_4$. On treatment with $Hg(CN)_2$, the $Mg(THF)_2$ adduct, very rapidly in THF or more slowly in benzene, afforded $[Fe(CO)_2(\eta^5-C_5H_5)]_2Hg$ implying that the enhanced nucleophilicity of the iron compound in polar solvents is due to a changeover from an Fe-Mg bonded system to a solvated ion-pair containing the group Mg–O≡C–Fe.

ARENE METAL COMPLEXES

η^5-Cyclopentadienyl Iron Compounds. Treatment of $[Fe(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)][BF_4]$ with LiEt at various temperatures gave[483] different products: at 25° in ether $Fe(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)$ was formed, at 0° in the same solvent $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-exo-}EtC_6H_6)$ was produced, while at 20° in THF, ferrocene was obtained. Reaction of the η^6-benzene cation with NaC_5H_5 in THF/ether mixtures at 0° afforded $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-exo-}C_5H_5C_6H_6)$, while $PhCH_2MgCl$ under the same conditions provided $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-exo-}PhCH_2C_6H_6)$. Treatment of 391 (R = H) with MeCOCl or PhCOCl and $AlCl_3$ in nitromethane gave[484] 391 (R = Me or Ph).

Protonation of the bis-indenyl complex $Fe(\eta^5\text{-}C_9H_7)_2$ with HCl or CF_3CO_2H afforded[485] 392. By judicious deuterium labelling it was confirmed that 392 is formed by stereospecific addition of H^+ to the indenyl C_5 ring and it was



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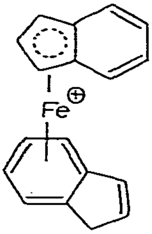

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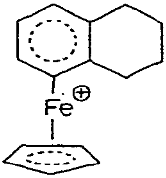

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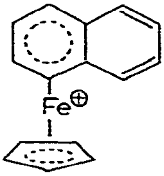

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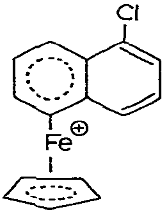

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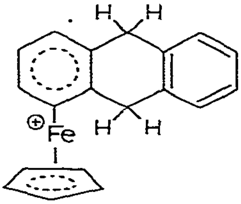

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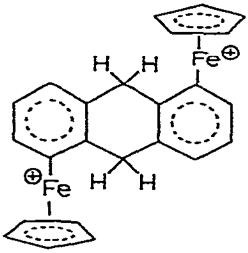

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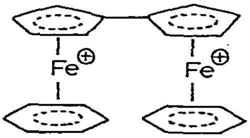


(398)

suggested that the most likely site for protonation is *endo*. This may occur via an intermediate where the proton is attached to the metal. Protonation of $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)$ similarly gave $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_9H_8)]^+$ and reaction of this with $LiBu^n$ afforded the starting material, probably by loss of an *exo*-proton.

Naphthalene reacted with $Fe(\eta^5\text{-}C_5H_5)_2$, Al and $AlCl_3$ giving[486] 393 and 394, also obtained from α-chloronaphthalene at 190°; at lower temperatures the chlorocarbon afforded 395. Anthracene, under similar conditions, gave 396 and 397.

The electronic structures of a series of η^6-arene-η^5-cyclopentadienyl iron cations has been probed[487] by a combination of polarographic/voltammetric, electronic and Mössbauer spectral techniques. The compounds investigated include $[Fe(\eta^6\text{-arene})(\eta^5\text{-}C_5H_5)]^+$ (arene = C_6H_6, C_6Me_6, C_6H_5Cl, diphenyl and naphthalene), $[Fe_2(\eta^6,\eta^6\text{-diphenyl})(\eta^5\text{-}C_5H_5)_2]^{2+}$, 398, 399, 400, $[Fe(\eta^6\text{-}C_6Me_6)_2]^{2+}$ and $[Fe(\text{phenylmesitylene})_2]^{2+}$ The electronic and Mössbauer spectra of the bimetallic dications were found to be generally similar to those of the corresponding mononuclear cations, and to have d-d electronic transitions analogous to those of ferrocene. Polarographic studies indicated that the differences between the two classes lay in that many of the dications exhibited two iron-based reduction waves in addition to reduction processes associated with the arene molecule. No oxidation waves for the compounds were detected within the limits of the experiments (up to +2.20 V vs. SCE). The two metal-based reduction waves for the dications have been assigned to the processes

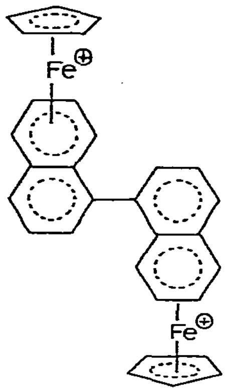
$$Fe^{II}Fe^{II} \xrightarrow{+e^-} Fe^{II}Fe^{I} \xrightarrow{+e^-} Fe^{I}Fe^{I} \quad .$$

In some species, e.g. $[Fe_2(\eta^6,\eta^6\text{-diphenyl})(\eta^5\text{-}C_5H_5)]^{2+}$, reduction of both metal centres occurred at the same potential. Asymmetric substitution of polyaromatic molecules led to a large separation between the two Fe-based reduction waves. For the system $[Fe_2(\eta^6,\eta^6\text{-arene})(\eta^5\text{-}C_5H_5)]^{2+}$ the following generalisations were made:

(a) for systems with large Fe-Fe separations and weak ring-propagated interaction owing to little conjugation between rings (as in dephenyl, trans-stilbene or p-terphenyl), only a single two-electron reduction wave associated with the process $Fe^{II} \rightarrow Fe^{I}$ was observed;

(b) for systems having fused aromatic rings (anthracene or chrysene), even with long Fe-Fe distances, two reduction waves, with potential separations of *ca*. 0.15 V, were observed;

(c) even though the Fe-Fe distance might be small, as in 398 and although the resonance ring interaction might be large, appreciable separation between reduction waves (*ca*. 0.40 v) could be observed.



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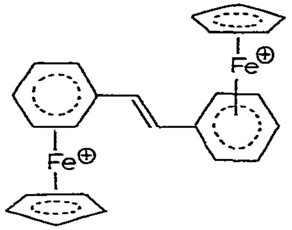

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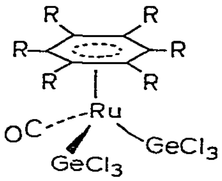

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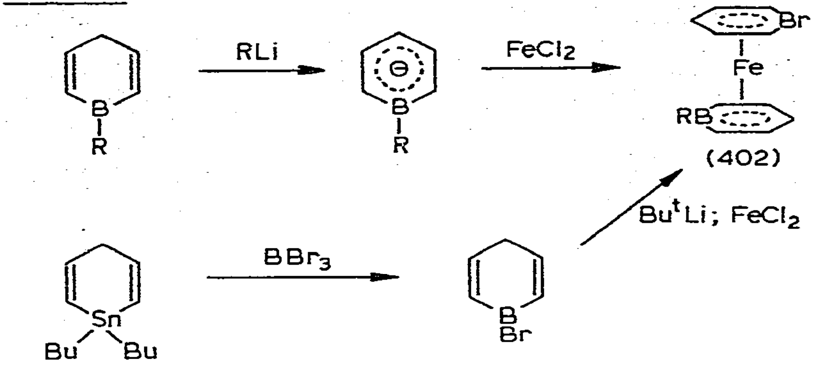
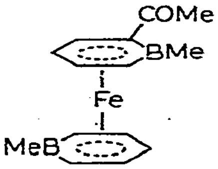
Ruthenium Arene Complexes. *Trans*-$Ru(CO)_4(GeCl_3)_2$ reacted with arenes at 150° or higher giving[468] $Ru(CO)(\eta^6\text{-arene})(GeCl_3)_2$, 401, (arene = benzene, toluene, *o*-, *m*- or *p*-xylene, mesitylene). The formation of 401 may proceed via the *cis*-isomer as suggested by a study of the reactions of benzene with *trans*-$Ru(CO)_4(SiCl_3)_2$ which gives $Ru(CO)(\eta^6\text{-}C_6H_6)(SiCl_3)_2$. The benzene in $Ru(CO)(\eta^6\text{-}C_6H_6)(GeCl_3)_2$ may be displaced by CO, giving back *trans*-$Ru(CO)_4(GeCl_3)_2$, and by mesitylene, providing $Ru(CO)(\eta^6\text{-}C_6H_3Me_3)(GeCl_3)_2$. The 'piano-stool' like structure of 401 (arene = C_6H_6) was confirmed[489] by X-ray crystallography (Ru-Cre = 2.41A). Treatment of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ with $K[B(C_3H_3N_2)_4]$ (tetrakis-(pyrazolyl)borate) afforded[490] $[Ru(\eta^6\text{-}C_6H_6)\{B(C_3H_3N_2)_4\}]^+$ (isolated as the PF_6^- salt) in which the pyrazolylborate ligand was tridentate.

Complexes Containing Heterocyclic Ligands. The bis(1-substituted borabenzene) iron complexes 402 (R = Me, Bu^t, Ph, Br) were prepared[491] as shown in Scheme 75; the compounds so formed are similar to those described[492] earlier. Mössbauer spectral data indicate that the η^6-1-phenylborabenzene ring withdraws somewhat more electron density from the iron atom than the η^5-cyclopentadienyl ring in ferrocene. Friedel-Crafts acylation ($MeCOCl/AlCl_3/CH_2Cl_2$) of 402 (R = Me) afforded 403, and the four protons α to the BR group exchange with CF_3CO_2D at 25° (no further exchange occurs after 24 hr). In competition experiments ferrocene reacts with CF_3CO_2D more rapidly than 402 (R = Me) which undergoes H/D exchange at approximately the same rate as mesitylene.

Reaction of $FeCl_2$ with tetramethylthiophene in the presence of $AlCl_3$ and PF_6^- afforded[493] $[Fe(\eta^5\text{-}C_4Me_4S)][PF_6]_2$, 404. This species could be voltammetrically reduced in two steps, the first of which was a reversible one electron process and the second of which was irreversible and led to decomposition. The half-wave reduction potentials for 404 were virtually the same as those for $[Fe(\eta^6\text{-}C_6H_3Me_3)_2]^{2+}$, viz. -0.27 and -1.17 V compared with -0.28 and -1.16 V (vs SCE in 50% aqueous acetone using KCl as supporting electrolyte); the corresponding potentials for $[Fe(\eta^6\text{-}C_6Me_6)_2]^{2+}$ were more negative, *i.e.* -0.48 and -1.46 V.

Scheme 75





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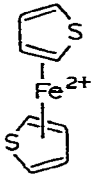


(404)

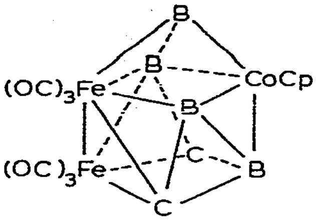
METAL ATOMS INCORPORATED IN BORON CAGES

Reaction of 1,2,3-(η^5-C_5H_5)$CoMe_2C_2B_4H_4$ with $Fe(CO)_4$ afforded[494] {$(OC)_3Fe$}$_2$-(η^5-C_5H_5)$CoMe_2C_2B_4H_4$, 405, which is a 9-vertex polyhedral cage. Thermal decomposition of $FeH_2(Me_2C_2B_4H_4)_2$ gave[495] $Me_4C_4B_8H_8$ as a single, air-stable isomer.

Treatment of 4,5-$C_2B_7H_9$ with sodium in THF, followed by NaC_5H_5 and $FeCl_2$ afforded[496] $Fe(\eta^5$-$C_5H_5)(C_2B_6H_8)$, two isomers of which are the known, paramagnetic $Fe_2(\eta^5$-$C_5H_5)_2(C_2B_6H_8)$ (μ = 3.05 BM at 300 K), and the known[497] $Fe(\eta^5$ $C_5H_5)$-$(C_2B_8H_{10})$. The species $Fe_2(\eta^5$-$C_5H_5)_2(C_2B_6H_8)$ underwent, voltammetrically, one-electron reduction and one-electron oxidation processes, both of which were reversible. On standing at room temperature, $Fe_2(\eta^5$-$C_5H_5)_2(C_2B_6H_8)$ became diagmagnetic, and the structure of this new species, 406, was determined crystallographically. The 10-vertex species is derived from a bicapped square antiprism.

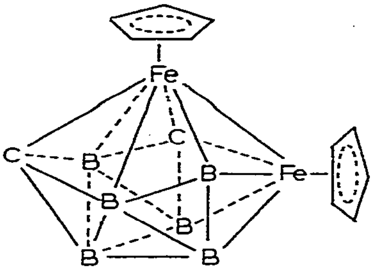
Reaction of $[Ru(CO)_3Cl_2]_2$ with $[7,8$-$B_9C_2H_{11}]^{2-}$ gave[498] $Ru(CO)_3(B_9C_2H_{11})$, 407 isolated as a benzene solvate. Similar treatment of $Ru(CO)_2(PPh_3)_2Cl_2$ afforded $Ru(CO)(PPh_3)_2(B_9C_2H_{11})$.

Treatment of $Fe(C_2Me_2B_{10}H_{10})_2$ (which contains a *nido* carborane ligand) with $CuCl_2$ in THF gave[499] in 30 min. *o*- (95%) and *m*- (5%) $C_2Me_2B_{10}H_{10}$ with a *closo* configuration. The amount of the *m*-isomer increased after 100 hr reaction time.



H atoms omitted

(405)



H atoms omitted

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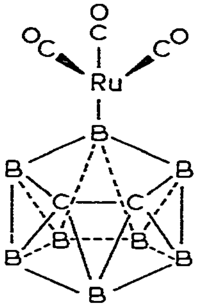

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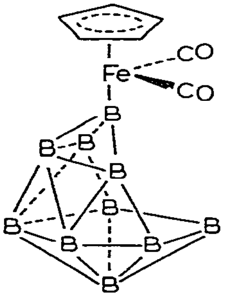

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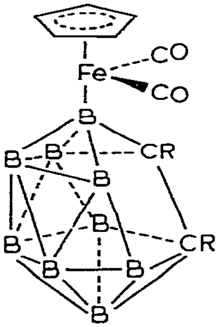


(409)

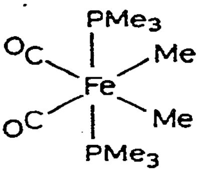
When treated with $B_{10}H_{13}^-$, $[Fe(CO)_2(cyclohexene)(\eta^5-C_5H_5)][PF_6]$ afforded[500] $Fe(CO)_2(\eta^5-C_5H_5)(B_{10}H_{13})$, 408. Reaction of this with bromine gave $Fe(CO)_2-(\eta^5-C_5H_4\{B_{10}H_{13}\})Br$, while Et_3N caused formation of $[Fe(CO)_2(\eta^5-C_5H_5)]_2$ and $[Et_3NH]_2[B_{10}H_{10}]$ (∿ 10% yield). Addition of $[Me_3NH][7,8-B_9H_{10}C_2R_2]$ (R = H or Me) to $[Fe(CO)_2(cyclohexene)(\eta^5-C_5H_5)]^+$ afforded $Fe(CO)_2(\eta^5-C_5H_5)(7,8-B_9H_{10}C_2R_2)$, 409, also produced (R = H) by reaction of K $[Fe(CO)_2(\eta^5-C_5H_5)(7,8-B_9C_2H_{11})]$ with HCl. Treatment of 409 (R = H) with Me_3N gave $[Me_3NH][Fe(CO)_2(\eta^5-C_5H_5)(7,8-B_9C_2H_{11})]$ which, in the presence of acetonitrile, afforded $[Fe(CO)_2(NCMe)-$

$(\eta^5\text{-}C_5H_5)][7,8\text{-}B_9C_2H_{12}]$. This salt was prepared alternatively by interaction of $[Fe(CO)_2(NCMe)(\eta^5\text{-}C_5H_5)][PF_6]$ and $[Me_3NH][7,8\text{-}B_9C_2H_{12}]$. With PPh_3 or CNC_6H_{11} (L), $[Me_3NH][Fe(CO)_2(\eta^5\text{-}C_5H_5)(7,8\text{-}B_9C_2H_{11})]$ afforded $[Fe(CO)_2L(\eta^5\text{-}C_5H_5)]\text{-}[B_9C_2H_{11}]$.

COMPOUNDS CONTAINING METAL-CARBON SIGMA BONDS

Treatment of $Fe(CO)_2(PMe_3)_2I_2$ with LiMe gave[501] $Fe(CO)_2(PMe_3)_2MeI$. Reduction of this with sodium in THF afforded $Na[Fe(CO)_2(PMe_3)_2Me]$ which, on addition of methyl iodide, provided $Fe(CO)_2(PMe_3)_2Me_2$, 410, and $Fe(CO)(PMe_3)HI$, 411. These last two compounds were also prepared by treatment of $Fe(CO)_2\text{-}(PMe_3)_2MeI$ with LiMe.

The structure of the product obtained from the reaction of 1,2-cyclobutadiene iron tricarbonyl and dimethylmaleate, 412 has been determined[502] by X-ray crystallography. The iron atom has a distorted octahedral geometry.



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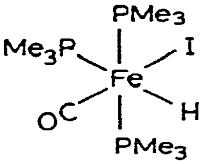

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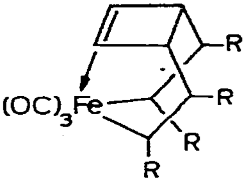

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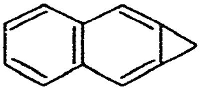

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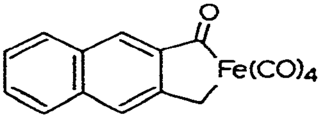

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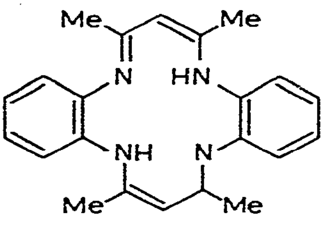

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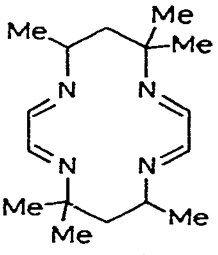

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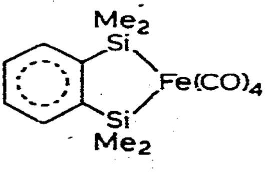

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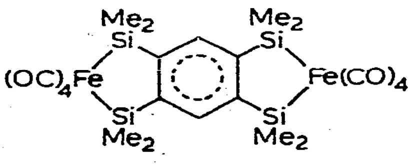

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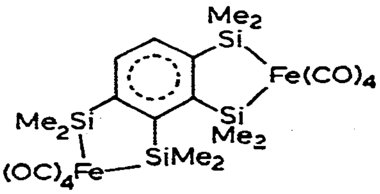


(419)

In a reaction between naphtho[b]cyclopropene, 413, and $Fe_2(CO)_9$, the species 414 was formed.[503] This compound is formally regarded as arising from the addition of an Fe-C bond of $Fe(CO)_5$ across one edge of the three-membered ring.

Treatment of $Fe\{o\text{-}C_6H_4(NH_2)_2\}_2(NCS)_2$ with $C_{22}H_{24}N_4$, 415, in the presence of Et_3N and acetonitrile afforded[504] the paramagnetic $Fe(C_{22}H_{22}N_4)$ (μ = 3.69 BM). With CO in toluene, this compound gave $Fe(CO)(C_{22}H_{22}N_4)$ and addition of pyridine to this carbonyl provided $Fe(CO)(pyr)(C_{22}H_{22}N_4)$. Reaction of $Fe(C_{22}H_{22}N_4)$ with RX (R = Me, Et or $PhCH_2$) gave $Fe(C_{22}H_{22}N_4)X$ and $Fe(C_{22}H_{22}N_4)R$, which is similar to compounds previously reported.[505] It was proposed that the reaction of $Fe(C_{22}H_{22}N_4)$ with RX proceeded in a two-step process, giving X^- abstraction with release of $R^{\bullet}$.

Lithium methyl or phenyl reacted[506] with $[Fe\{(tetraene)N_4\}Cl]^+$ ($\{(tetraene)N_4\}$ = 416) giving initially $Fe\{(tetraene)N_4\}Cl$ and then $Fe\{(tetraene)N_4\}R$ (μ = 2.1 B.M.). These compounds are sensitive to UV light and they were also electrochemically oxidised in two one-electron steps, formally corresponding to the generation of Fe(II) and Fe(III).

Treatment of $Fe(acac)_3$ with $AlEt_3$ or $AlEt_2(OEt)$ in the presence of PPh_3 afforded[507] $Fe(PPh_3)_3(acac)Et$; the corresponding reaction with $AlMe_3$ gave $Fe(PPh_3)_3Me_2$. Related compounds containing PPr^n_3 were also prepared.

Lamellar compounds of graphite containing iron were obtained[508] using $FeCl_x$ (x = 2 or 3), aromatic anion radicals, Na/NH_3 or $LiAlH_4$. There appeared to be two types of Fe atoms within the layers: a magnetically ordered form (ferromagnetic and superparamagnetic iron) and another paramagnetic form. It was suggested that the iron atoms were weakly complexed by the graphite layers.

Reaction of $Fe_2(CO)_9$ with 1,2-bis(dimethylsilyl)benzene gave[509] 417. The analogous species 418 and 419 were prepared similarly.

SYNTHETIC AND CATALYTIC REACTIONS

Synthetic Processes. Technical reactions of CO with unsaturated hydrocarbons in the presence of metal carbonyls as catalysts have been selectively discussed.[510] Thus, in the presence of $Ru_3(CO)_{12}$, acetylene and CO/H_2 or CO/H_2O (in appropriate ratios) combine to give hydroquinone. Using $Fe(CO)_4$, p-quinone is produced. Ethylene, CO and H_2O react, in the presence of $Fe(CO)_5$ and an organic base, to give propanol, and propene is similarly converted by $[R_3NH][Fe_3(CO)_{11}H]$ into butanol and Me_2CHCH_2OH.

A retro-Diels-Alder reaction occurred when $K[FeL_2(H_2O)]$ (H_2L = bicyclo-2.2.1 hept-5-en-*endo*-2,3-cis-dicarboxylic acid) was heated.[511] Sequential loss of two molecules of cyclopentadiene occurred and the final metal-containing species was $K[FeQ_2]$ (H_2Q = maleic acid).

The formation of ethyl ketones via sequential insertion reactions of alkyl tetracarbonylferrate ion has been studied.[512] The overall reaction is

$$\begin{tikzcd}
{[Fe(CO)_4]^{2-} + RX} \arrow[r] & {[Fe(CO)_4R]^-} \arrow[r, "C_2H_4"] & {[Fe(CO)_3(C_2H_4)(COR)]^-} \arrow[d, "C_2H_4"] \\
 & RCOCH_2CH_3 & {[Fe(CO)_3(C_2H_4)(CH_2CH_2COR)]^-} \arrow[l, "H^+"']
\end{tikzcd}$$

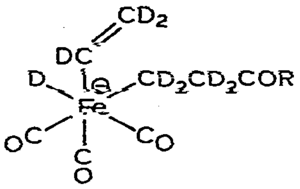
In the reaction involving CH_3CO_2D, no deuterium is incorporated in the ethyl ketone and hence $H^+(D^+)$ is not derived from an added source. However, reaction of $Na_2Fe(CO)_4$ with $C_9H_{19}Br$ in the presence of C_2D_4 and HOAc gave 3-dodecanone with greater than 92% deuteration (d_3) at C(1). The reaction appears to involve base-catalysed removal of exchangeable α-methylene D atoms in $[Fe(CO)_3(C_2D_4)(CD_2CD_2COR)]^-$, or to involve H/D exchange with another molecule of C_2D_4. A feasible process could involve oxidative addition of coordinated C_2D_4 in $Fe(CO)_3(C_2D_4)(CD_2CD_2COR)$, giving 420 which would then undergo reductive elimination of the appropriate ketone. Treatment of $Na_2Fe(CO)_4$ with n-nonyl bromide and $CD_2{=}CH_2$ gave, after removal of exchangeable deuterium, 3-dodecanone with deuteration at C(1) (12% d_0, 48% d_1, 38% d_2 and 1% d_3). In the absence of a large secondary isotope effect, comparable amounts of $[Fe(CO)_3(C_2H_2D_2)(CH_2CD_2COR)]^-$ and $[Fe(CO)_3(C_2H_2D_2)(CD_2CH_2COR)]^-$ should be formed. The overall data are consistent with intermediates such as 421 and 422, and the net uptake of two moles of ethylene without evolution of CO appears to favour 421. This process does not appear to be useful for higher alkenes. Thus, propene reacted with $Na_2Fe(CO)_4$ and n-pentyl bromide giving hexanal (70%) and 4-nonanone (10-15%) whereas hexene produced hexanal (94%). Acylation of β-oxoalkyltetracarbonylferrate species affords[513] a new route to enol esters, viz.

$$[Fe(CO)_4(CH_2COR)]^- + R'COX \longrightarrow RC(OCOR'){:}CH_2$$

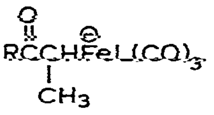
Here R = Me or Ph and R' = alkyl or aryl; it was noted that $RCOCH_2COR'$ was not formed.

Rearrangement of $CH_2{:}C(Me)CH_2OH$ to Me_2CHCHO was achieved[514] using $RuCl_3 \cdot 3H_2O$. Hetereocumulenes reacted[515] with phenylbromoacetylenes in the presence of THF giving 423 and $(PhC{\equiv}C-)_2$ according to the mechanism outlined in Scheme 76.

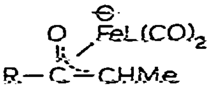
A similar reaction involving PhN:C:O afforded two hydantoin derivatives, 424 and 425, according to the mechanism proposed in Scheme 77. With $Ph_2C{:}C{:}O$, 426 was formed. Conversion of amide oximes RX(X):NOH into amidines RC(X):NH (X = NHPh, R = Ph; 2,4,6-$C_6H_2Me_3$; p-$C_6H_4NO_2$; R = Ph, X = p-ClC_6H_4NH, NMePh or NMe_2) was effected[516] using $Fe(CO)_5$.



(420)

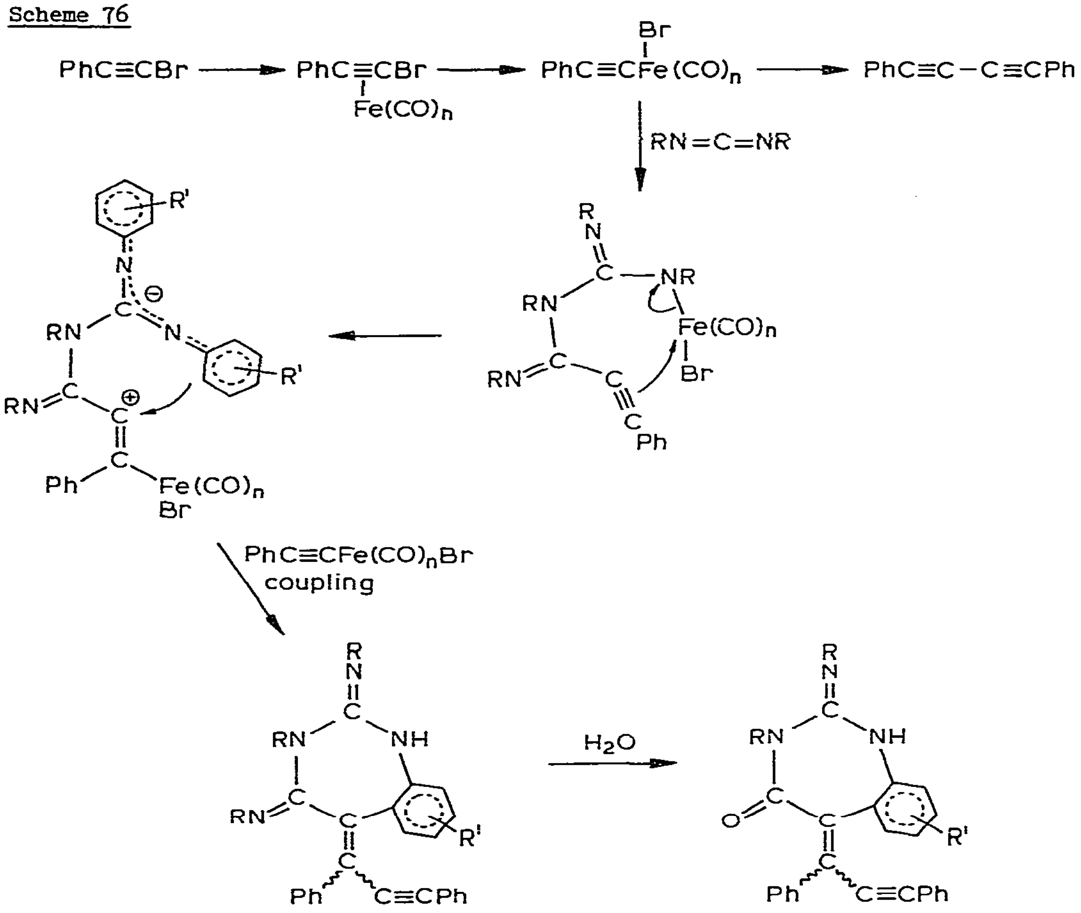


(421)



(422)

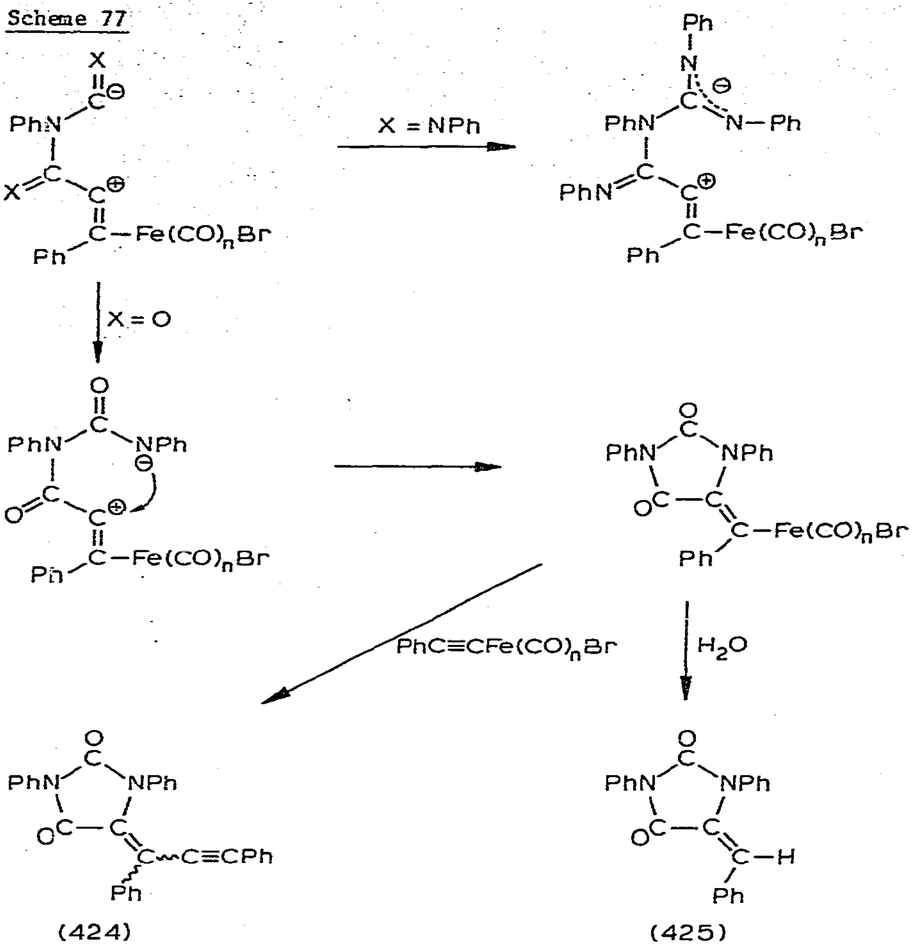
Scheme 76



(423)

Hydrogenation and Dehydrogenation. A series of styrene-divinylbenzene resins were converted into a poly(diphenylphosphine) species and complexed[517] via phosphine exchange by $Ru(CO)_2(PPh_3)_2Cl_2$. This polymer-supported catalyst system selectively hydrogenated 4-vinyl-cyclohexene to ethylcyclohexene, cycloocta-1,5-diene to (Z)-cyclooctene and *trans,trans,trans*-cyclododecatriene to (E)-cyclododecaene. The reactions were carried out in the presence of a large excess of PPh_3 and could not be achieved by an excess of polymer-bound PPh_2 groups alone.

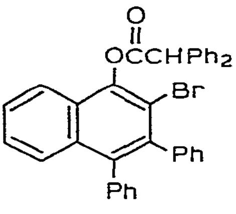
Scheme 77



The polymeric catalyst was a slower hydrogenating reagent than the comparable homogeneous species, in accordance with the diffusion retardation of the rate using the polymer-bound catalyst.

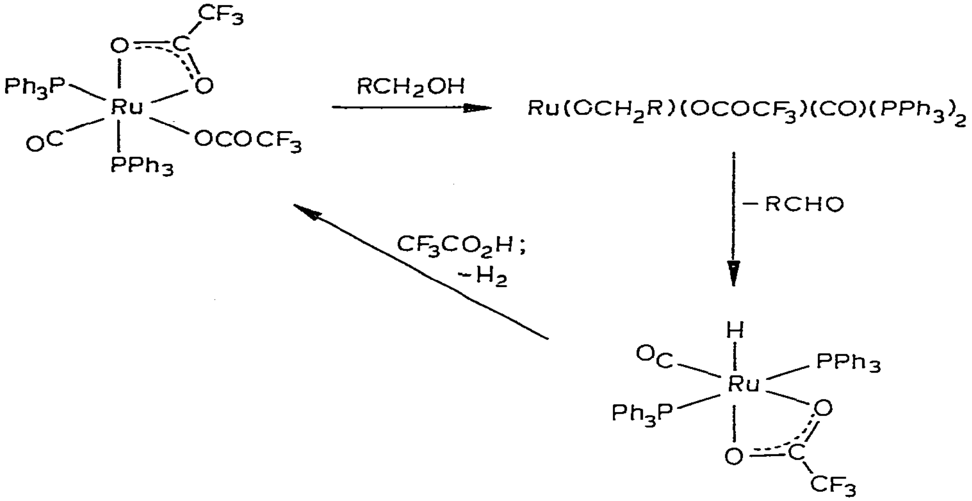
In methanol and p-toluenesulphonic acid, the rate of hydrogenation of mono- and di-alkenes by $Ru(PPh_3)_3(OAc)_2$ was highly dependent on acidity.[518] A rapid and highly selective reduction of cyclic dienes to the corresponding mono-enes occurred, and this was attributed principally to the superior coordinating abilities of dienes in comparison to mono-alkenes.

The species $Ru(CO)(PPh_3)_2(OCOCF_3)_2$ is an effective homogeneous catalyst for the dehydrogenation[519] by primary and secondary alcohols to aldehydes and ketones (Scheme 78). The catalytic reactions can be performed in neat boiling alcohol and, up to a certain concentration, CF_3CO_2H acts as a promoter; beyond this concentration inhibition occurs. The alcohols successfully dehydrogenated included RCH_2OH (R = Me, Et, Pr^n, Bu^n, C_5H_{11}, Ph), Me_2CHOH and cyclohexanol;



(426)

Scheme 78



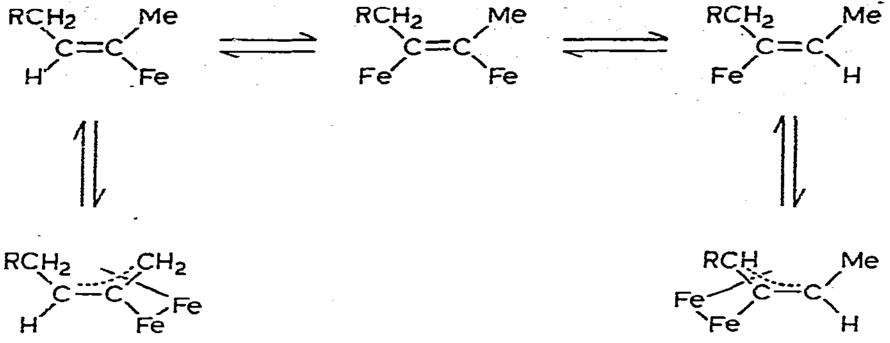
methanol and tertiary alcohols were inert but allyl alcohol was converted to acrolein while propargyl alcohol decomposed and deactivated the catalyst.

Isomerisation and H/D Exchange. Characteristic maxima have been observed in the deuterium distribution patterns of the isomers obtained[520] from various β-olefins and iron films in the presence of $CD_3CD:CD_2$. The results were interpreted by assuming interconversions between vinyl and allene surface complexes (Scheme 79).

The intermediates proposed also permit H/D exchange. On iron films H/D exchange of but-1-ene proceeds[521] via a dissociative adsorption involving the vinylic group: the most reactive H atom towards exchange is that bound to the ethyl-substituted C atom.

Oligomerisation and Polymerisation. The reaction of iodoalkanes with ethylene to produce higher molecular weight 1-iodoalkanes is promoted[522] by $Ru(CO)_3(PPh_3)_2$. With the exception of benzylbromide, organic chlorides and bromides did not react, the species $Ru(CO)_3L_2$ (L = PR_3, R = Bu^n, C_6H_{11}, p-MeC_6H_4; $Ph_2PCH_2CH_2PPh_2$; pyr; Ph_3As), $Ru(CO)_4(PPh_3)$ and $Ru(NCMe)_2(PPh_3)_4$ were effective

Scheme 79



catalysts, but Ru(acac)$_3$, RuCl$_3$.3H$_2$O, Ru(CO)$_2$(PPh$_3$)$_2$Cl$_2$ or Ru(CO)$_2$(PPh$_3$)$_2$I$_2$ were inactive. Ethyliodide and ethylene were converted by Ru(CO)$_2$(PPh$_3$)$_2$ to C_4H_9I (25%), $C_6H_{14}I$ (33%), $C_8H_{17}I$ (20%), $C_{10}H_{24}I$ (14%) and $C_{12}H_{25}I$ (8%) while Ru(CO)$_3${P(p-MeC$_6$H$_4$)$_3$}$_2$ gave C_4H_9I (25%), $C_6H_{13}I$ (30%), $C_8H_{17}I$ (20%), $C_{10}H_{21}I$ (11%), $C_{12}H_{25}I$ (4%), $C_{14}H_{29}I$ (2%) and $C_{16}H_{33}I$ (2%). In the reaction, Ru(CO)$_3$(PPh$_3$)$_2$ was converted to Ru(CO)$_2$(PPh$_3$)$_2$I$_2$ and, using EtI, the intermediate Ru(CO)$_2$(PPh$_3$)$_2$(Et)I may be formed in the absence of ethylene (when C_2H_4 was present higher alkyl complexes may have been present). The overall mechanism, shown below, involves a radical chain process:

$$RuL_5 + RI \longrightarrow RI....RuL_5 \longrightarrow RI....RuL_4 + L$$

$$RI....RuL_4 \longrightarrow R\cdot + RuL_4I$$

$$RI....RuL_5 \longrightarrow R^{\cdot} + RuL_4I + CO$$

$$R^{\cdot} + nCH_2{:}CH_2 \longrightarrow R(CH_2CH_2)_n^{\cdot}$$

$$R(CH_2CH_2)_n^{\cdot} + RI \longrightarrow R(CH_2CH_2)_nI + R^{\cdot}$$

$$RI....RuL_4 + RI \longrightarrow RuL_4I_2 + R^{\cdot}$$

$$2R^{\cdot} \longrightarrow R\text{-}R + RH + R(\text{-}H) \qquad \text{(possible chain termination)}$$

Support for the species Ru(CO)$_2$(PPh$_3$)$_2$RI as precursors for the formation of radicals came from comparison of the reactivity of Ru(CO)(PMe$_2$Ph)$_3$HI and Ru(CO)$_2$(PPh$_3$)$_2$HI which, under ethylene when ruthenium-ethyl complexes can be formed, behaved catalytically in the same way as Ru(CO)$_2$(PPh$_3$)$_2$.

Catalytic oligomerisation of butadiene has been achieved[523] by catalysts derived from metal atoms. The technique involved cocondensation of Fe vapour, with or without aluminium, and other carbon compounds at 77°K followed by warming, and the results are summarised in Table 6.

Table 6 Oligomerisation of butadiene by Fe atoms

Catalyst System and Reagents	Conversion of C_4H_6 (%)	Conditions	Products
Fe + $AlEt_2Cl$ benzene or toluene	100	20°C/1 hr.	immediately after warming 20% $C_4H_6 \rightarrow$ linear and cyclic dimers and trimers; otherwise polybutadiene (100%)
Fe + $AlEt_3$ benzene or toluene	100	20°C/1 hr.	immediately after warming linear trimers and dimers (10%) otherwise polybutadiene (100%)
Fe + Al + EtCl, benzene	90	20°C/6 hr.	immediately after warming, ttt-cyclododecatriene (10%) ctt-cyclododecatriene (15%) butenylbenzene (75%); otherwise polybutadiene (100%)
Fe + Al, C_6Cl_6	15	warming to room temp.	c,t,t-cyclododecatriene (25%) linear trimers (65%), butenyl benzenes (10%)
Fe + Al, benzene	20	warming to room temp.	c,t,t-cyclododecatriene (18%), dodecatriene (60%), cyclooctadiene (22%)
	40	55°C/4 hr.	c,t,t-cyclododecatriene (30%), dodecatriene (63%), cyclooctadiene (7%)
Fe + PPh_3, toluene or benzene	37	50°C/5 hr.	linear dimers (100%)
Fe + $P(OPh)_3$, toluene or benzene	0		
Fe + P_4, benzene or toluene	10	50°C/4 hr.	t,t,t-cyclododecatriene (100%)
Fe/benzene	90	50°C/2 hr.	c,t,t-cyclododecatriene (30%), linear trimers (63%) cyclooctadiene (7%)
'FeO', benzene	0		

Cyclooligomerisation of butadiene followed by selective hydrogenation was achieved[524] using polymer supported catalysts containing from $Ni(CO)_2$ and $Ru(CO)_2Cl_2$ derived by phosphine exchange of polymeric resins containing PPh_2 groups with $Ni(CO)_2(PPh_3)_2$ and $Ru(CO)_2(PPh_3)_2Cl_2$).

REVIEWS AND DISSERTATION ABSTRACTS

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

"The Chemistry of Metal Carbonyls: The Lifework of Walter Hieber" by H. Behrens.[525]

"Transition Metal Carbonyls", by R. A. Sokolik.[526]

"Transition Metal Carbonyl, Organometallic and Related Complexes", by R. J. Cross.[527, 528]

"The Reactivity Patterns of Metal Carbonyl Anions and their Derivatives", by J. E. Ellis.[529]

"$Na_2Fe(CO)_4$: a Transition Metal Analogue of a Grignard Reagent", by J. P. Collman.[530]

"S Atoms as Ligands in Iron Carbonyls and Related Clusters", by H. Vahrenkamp.[531]

"Isocyanide Complexes of Transition Metals", by L. P. Yur'eva.[532]

"Synthetic Methods in Transition Metal Nitrosyl Chemistry", by K. G. Caulton.[533]

"Coordination Chemistry of NO", by R. Eisenberg and C. D. Meyer.[534]

"Coordination Chemistry of Aryldiazonium Cations. Aryldiazenato (arylazo) Complexes of Transition Metals and the Aryldiazenato-Nitrosyl Analogy", by D. Sutton.[535]

"Transition Metal Chemistry of Azo Compounds", by M. I. Bruce and B. L. Goodall.[536]

"π-Complexes of Mono-olefins", by M. I. Rybinskaya.[537]

"Cyclobutadiene Complexes of Metals", by L. V. Rybin.[538]

"Polyolefin Carbonyl Derivatives of Iron, Ruthenium and Osmium", by G. Deganello and others.[539]

"Acetylene-π-Complexes of Transition Metals", by L. P. Yur'eva.[540]

"Mono-π-cyclopentadienyl Compounds of Transition Metals", by T. V. Nikitina.[541]

"Arene Transition Metal Chemistry", by W. E. Silverthorn.[542]

"Alkyl Derivatives of Metals and Related Compounds", by I. I. Kritskaya.[543]

"Organometallic Chemistry: A Historical Perspective", by J. S. Thayer.[544]

Perspectives in Organometallic Chemistry, the 100th volume of the Journal of Organometallic Chemistry, including the following articles:

(a) "Reactions of Dinitrogen in its Mononuclear Complexes", by J. Chatt;[545]

(b) "Fluxionality in Organometallics and Metal Carbonyls", by F. A. Cotton;[546]

(c) "Perspectives in Metallocarborane Chemistry", by M. F. Hawthorne;[547]

(d) "Perspectives in the Syntheses of Novel Organometallic Compounds using Metal Carbonyl Anions", by R. B. King[548]

(e) "The Coordination Chemistry of Bivalent Group IV Donors: Nucleophilic Carbene and Dialkylstannylene Complexes", by M. F. Lappert[549]

(f) "The Role of Cyclobutadiene Iron Tricarbonyl in the 'Cyclobutadiene' Problem", by R. Pettit[550]

(g) "Synthetic Applications of d^{10} Metal Complexes", by F. G. A. Stone.[551]

(h) "The Iron Sandwich. A recollection of the first four months", by G. Wilkinson.[552]

"Organometallic Chemistry. I. Transition Elements", by J. D. Jones and others.[553]

"Organometallic Complexes containing Bonds between Transition Metals and Group IIIB Metals", by A. T. T. Hsieh.[554]

"Oxidation - Reduction of Metal-Metal Bonds", by T. J. Meyer.[555]

Organo Iron Compounds in Gmelin Handbook of Inorganic Chemistry.[556]

"$RuCl_3$ and its Applications", by W. P. Griffith.[557]

"Oxidative Addition Reactions and their Industrial Implications", by G. Dolcetti and others.[558]

"The Chemistry of Fe, Co and Ni", "The Chemistry of Ru, Rh, Pd, Os, Ir and Pt" and "Compounds of Transition Elements Involving Metal-Metal Bonds", by D. Nicholls,[559] S. E. Livingstone,[560] and D. L. Kepert and K. Vrieze,[561] respectively.

"Metal Vapours as Reagents", by K. J. Klabunde and T. O. Murdock.[562]

"Synthesis Reactions with Metal Atoms from 10 to 273°K", by P. L. Timms.[563]

"The Flipping of CO Ligand Groups in Metal Carbonyl Compounds and its Frequency in $Fe(CO)_5$", by R. K. Sheline and K. Mahnke.[564]

"Reactions of Transition Metal Atoms with Organic Substrates", by P. S. Skell and M. J. McGlinchey.[565]

"The Laser-Evaporation of Metals and its Applications to Organometallic Syntheses", by E. A. Koerner von Gustorf and others.[566]

"Photochemistry in Matrices and its Relevance to Atom Syntheses", by J. J. Turner.[567]

Dissertation Abstracts

"Structural Studies of Organometallic Compounds of Iron", by K. -K. Lin.[568]

"Organometallic Chemistry of Iron", by A. J. Schultz.[569]

"Disodium Tetracarbonylferrate", by R. G. Komoto.[570]

"Reaction of $Fe(CO)_5$ with NaOMe", by J. L. McClean.[571]

"Complexes of NO. Synthesis, Structure, and Reactivity", by J. Reed.[572]

"Structural Studies of Bonding of NO in Transition Metal Complexes", by D. G. Van Dervier.[573]

"Reactivity of Ruthenium Nitrosyls", by R. P. Cheney.[574]

"Interaction of Transition Metals with Olefins", by R. S. Case.[575]

"Studies of Fe(0) Cyclooctatetraene Complexes", by M. T. Mocella.[576]

"Cycloaddition Reactions involving $Fe(CO)_3$ Complexes", by T. J. Devon.[577]

"Synthesis and Chemistry of $Fe(CO)_3$ Complexes of Push-Pull and Highly Hindered Cyclobutadienes", by G. Berens.[578]

"Synthesis and Spectroscopic Studies of Group VB Derivatives of Cyclopentadienyl Iron Dicarbonyl Dimer, and Related Tin Insertion Reactions", by T. N. Decoraro.[579]

"Alkyl Anion $Fe(CO)_3$ Chemistry", by R. L. Parton.[580]

"Borabenzene Anions and Their Iron(II) Complexes", by P. Shu.[581]

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