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METAL CARBONYLS

Simple Carbonyls and Carbonyl Hydride Anions

Under 2000 atm. and at 225⁰, Fe₂O₃ reacted with CO giving Fe(CO)₅ in good yield (1). The thiocarbonyl Fe(CO)₄(CS) was obtained by treatment of Na₂Fe(CO)₄ with CSCl₂ (?). Matrix-isolated Fe(CO)₄ has been studied using i.r. laser and broad-band near i.r. techniques (3). Laser irradiation in an N₂ matrix at 20⁰K caused isomerisation of Fe(¹²C¹⁶O)_{4-x}(¹³C¹⁸O)_x with little production of Fe(CO)₄(N₂). The axial and equatorial CO groups in Fe(CO)₅ have been distinguished by ESCA using both the C and O atom binding energies (4). An interpretation of the microwave dielectric relaxation of Fe(CO)₅ has been made in terms of the fluxional nature of the molecule (5).

Fe(CO)₅ reacted with S₂O₆F₂ giving FeO(SO₃F) and Fe(CO)₄(SO₃F)₂, the latter decomposing at 100⁰ to give Fe(SO₃)₂ (6). The Fe(III) intercalation compound FeCl₃C_{7.1} reacted with Fe(CO)₅ at 150⁰ under 150 atm. CO giving the Fe(II) interstitial compound FeCl_{1.96}C_{4.7} (7).

A detailed analysis of the CO vibrational modes in $[N(PPh_3)_2][Fe(CO)_4H]$ suggested (8) that the $[Fe(CO)_4H]^-$ ion exists in THF as a pseudo-trigonal-bipyramid, as in the solid state, with H in the apical position. Considerable deviation of the $OC_{ax}-Fe-CO_{eq}$ angle from 90° was observed in both the solid state and in solution (8). ^{13}C -labelled CO incorporation into $[N(PPh_3)_2]-[Fe(CO)_4H]$ was catalysed by Na^+ ion-pair interactions (8).

Carbonyl Complexes containing Lewis Bases.

N-donor atom ligands. Irradiation of $Fe(CO)_5$ in the presence of 1-allyl-pyrazoles(L) afforded $Fe(CO)_3L$ which reacted with PPh_3 affording trans- $Fe(CO)_3(PPh_3)_2$ (9).

P- and As-donor atom ligands. $Fe(CO)_4(PPh_2Cl)$ reacted with $Ph_3P:CH_2$ giving $Fe(CO)_4(PPh_2CH:PPh_3)$ (10). Phase-transfer catalysed ^{18}O labelling of $Fe(CO)_4(PPh_3)$ was achieved using a mixture of $Na^{18}OH$ in $H_2^{18}O$ and $[Bu_4^nN]I$ in dry benzene (11).

The He(I) photoelectron spectra of $Fe(CO)_x(PF_3)_{5-x}$ ($x = 0 \rightarrow 5$) (12), $Fe(CO)_4L$ ($L = PMe_3, PPh_3, AsPh_3, C_5H_5N$; L in axial position) (13), and $Fe(CO)_4L'$ ($L' = CH_2 = CHCN, CH_2 = CHCO$; L' in equatorial plane) (13) have been measured. The spectra were assigned by comparison with one another and with those available from $Fe(CO)_5$ and $Fe(CO)_4(C_2H_4)$ (13). CNDO calculations carried out for $Fe(CO)_4(C_5H_5N)$ and $Fe(CO)_4(CH_2=CHCN)$ were only of limited assistance in making the assignments (13).

Reaction of $Fe(CO)_5$ or $Fe_2(CO)_9$ with the cationic five-membered phosphorus-containing heterocycle $[PN(Me)CH_2CH_2N(Me)][PF_6]$ afforded $[Fe(CO)_4\{PN(Me)CH_2CH_2N(Me)\}][PF_6]$ (14). This compound could also be prepared by treating $Fe(CO)_4\{FPN(Me)CH_2CH_2N(Me)\}$ with PF_5 . The structure of the cationic complex was determined crystallographically, and revealed that the P-ligand was axial. Addition of PF_5 to $Fe(CO)_4\{P(NMe)_2\}$ similarly afforded $[Fe(CO)_4\{P(NMe)_2\}][PF_6]$ (14). Reaction of $FPN(Me)CH_2CH_2N(Me)$ with $[Fe(CO)_4]^{2-}$ gave what is thought to be volatile $\{(Me)NCH_2CH_2N(Me)P-PN(Me)CH_2CH_2N(Me)\}Fe(CO)_4$ where the Fe atom is bound to one P atom of the bi-heterocycle (15). It was also reported that $FPN(Me)CH_2CH_2N(Me)$ reacted with $[Fe(CO)_2(n-C_5H_5)]^-$ giving the salt $[(Me)NCH_2CH_2N(Me)P][Fe(CO)_2(n-C_5H_5)]$ (15). Treatment of $Fe(CO)_5$ with 1,2-bis(difluorophosphino)cyclohexane(L-L) afforded $Fe(CO)_3(L-L)$, in which an axial and an equatorial site was occupied by a PF_2 group, and $Fe(CO)(L-L)_2$ (16). Reaction of $Na_2Fe(CO)_4 \cdot 1.5$ dioxane with $AsPhCl_2$ gave, as one of the products, $Fe(CO)_4(n^2-PhAs_2Ph)$ (17). The X-ray structure determination showed that the complex was analogous to $Fe(CO)_4(n^2-olefin)$, with $Fe-As = 2.51 \text{ \AA}$ and $As-As = 2.37 \text{ \AA}$ (17).

S-donor atom ligands. Diphenylcyclopropenethione reacted with $Fe_2(CO)_9$ giving $Fe(CO)_4(C_3Ph_2S)$, in which the S atom was attached to the metal (18). The 2-X-1,3-dithiane ($X = H, Me, SiMe_3, GeMe_3, SnMe_3, PbMe_3$) complexes $Fe(CO)_4L$

have been studied by ^1H and ^{13}C n.m.r. spectroscopy and the energy barrier to ring inversion of the dithiane determined (19). Rapid site averaging of the carbonyl groups was detected as low as -80°C .

Carbon Disulphide Complexes. Reaction of $\text{Fe}(\text{CO})_3(\text{benzylideneacetone})$ with CS_2 and L (L = PPh_3 or $\text{P}(\text{OR})_3$, R = Me, Et or Ph) gave $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{L}'_2$ (20). Treatment of the species where L = PPh_3 with further Lewis base L' (L' = PMe_3 , PMe_2Ph , PMePh_2 , PBu_3^n) afforded $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{L}'(\text{PPh}_3)$ or $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{L}'_2$ (20). Trimethylphosphite displaced PPh_3 from $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PMe}_3)(\text{PPh}_3)$ giving $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PMe}_3)\{\text{P}(\text{OMe})_3\}$, whereas PMe_2Ph reacted with $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2$ giving $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})\{\text{P}(\text{OMe})_3\}(\text{PMe}_2\text{Ph})_2$. An X-ray crystallographic determination of $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PMe}_3)_2$ established the overall trigonal bipyramidal nature of the species, where the $\eta^2\text{-CS}_2$ group occupied an equatorial site and the phosphine ligands were axial.

Treatment of $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{LL}'$ with the acetylene RC_2R (R = CO_2Me) afforded the carbene species $\text{Fe}(\text{CO})_2\text{LL}'(\overline{\text{CSCR:CRS}})$, A, and/or the metallocycle $\text{Fe}\{\text{C}(\text{:S})\text{SCR:CR}\}(\text{CO})_2\text{LL}'$, B (21). When L = L' = PMe_3 , there was a rapid conversion of A into B, but when L = L' = PMe_2Ph or L = $\text{P}(\text{OMe})_3$, L' = PMe_3 , an equilibrium mixture of A and B was established. It appeared that more basic phosphorus-containing ligands tended to stabilise the carbene form A. Addition of $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PMe}_2\text{Ph})_2$ to A (L = L' = PMe_3) gave $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2(\text{PMe}_3)_2$ and A (L = L' = PMe_2Ph), revealing that there was a reversible system, $\text{A} \rightleftharpoons \text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{LL}' \rightleftharpoons \text{B}$, in operation.

Complexes of Group 4 Ligands

Si-containing species. $\text{Fe}_2(\text{CO})_9$ reacted with $\text{HSiMe}_2\text{SiMe}_2\text{R}$ (R = H or Me) (22). Treatment of the complex where R = Me with PhC_2Ph at 20° afforded a mixture of Z- $\text{Me}_3\text{SiCPh:CPhSiMe}_3$, E- and Z- $\text{Me}_3\text{SiCPh:CHPh}$, E,E- $\text{PhCh:CPhSiMe}_2\text{CPh:CHPh}$, $\text{Fe}(\text{CO})_3(\text{C}_2\text{Ph}_2)_2$ and $\text{Fe}_2(\text{CO})_7(\text{C}_2\text{Ph}_2)_2$. Reaction with PPh_3 and with PhCH:CHCH:CHPh gave $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ and $\text{Fe}(\text{CO})_3(\text{PhCH:CHCH:CHPh})$, respectively.

Treatment of $\text{Fe}_2(\text{CO})_9$ with the 1,2-silacyclobutenes $\text{Me}_2\text{SiCr:CR'SiMe}_2$ gave the metallocycle $\text{Fe}(\text{CO})_4\text{SiMe}_2\text{CRCR'SiMe}_2$ (R = R' = Ph; R = Ph, R' = SiMe_3) (23). Further reaction of the metallocycle with PhC_2Ph at 300° afforded the disilacyclohexadiene $\text{Me}_2\text{SiCPhCPhSiMe}_2\text{CR:CR}'$.

Ge-containing species. Methylbromogermane reacted with $\text{Na}_2\text{Fe}(\text{CO})_4$ giving *cis*- $\text{Fe}(\text{CO})_4(\text{GeMeH}_2)_2$ which rearranged in the dark into $[\text{Fe}(\text{CO})_4(\text{GeMeH})]_2$ and GeMeH_3 (24). Exposure of the *cis*-isomer to light apparently gave some $\text{Fe}_2(\text{CO})_7(\text{GeMeH})_2$. Reaction of $\text{Na}_2\text{Fe}(\text{CO})_4$ with GeMe_3Cl gave $\text{Fe}(\text{CO})_4(\text{GeMe}_3)_2$, mainly as the *cis*-isomer, which rearranged *in vacuo* to give $\text{Fe}(\text{CO})_5$, $\text{Fe}_3(\text{CO})_{12}$ and $(\text{Me}_3\text{Ge})_2\text{O}$ (25). The species $\text{Fe}(\text{CO})_4(\text{GeMe}_2\text{H})_2$ is unstable with respect to condensation to $[\text{Fe}(\text{CO})_4(\text{GeMe}_2)]_2$ with loss of GeMe_2H_2 (26). In light, or very slowly in the dark, this dimer lost CO, probably forming $\text{Fe}_2(\text{CO})_9(\text{GeMe}_2)_2$. Attempts to make $\text{Fe}(\text{CO})_4(\text{GeMe}_2\text{H})_2$ by a stoichiometric reaction of $\text{Na}_2\text{Fe}(\text{CO})_4$ with GeMe_2HBr

afforded $\text{Fe}(\text{CO})_4(\text{GeH}_3)_2$ or $\text{Fe}(\text{CO})_4(\text{GeMeH}_4)_2$, but the desired compound could be obtained in low yield in the dark by using a deficiency of the bromogermane (26).

$\text{Fe}(\text{CO})_4(\text{GeMeH}_2)_2$ reacted slowly with SiCl_4 giving (27) $\text{Fe}(\text{CO})_4(\text{GeMeClH})(\text{GeMeH}_2)$, A, $\text{Fe}(\text{CO})_4(\text{GeMeClH})_2$, B, and $\text{Fe}(\text{CO})_4(\text{GeMeCl}_2)(\text{GeMeClH})$, C. With CCl_4 , A, B, C and $\text{Fe}(\text{CO})_4(\text{GeMeCl}_2)_2$, D, were formed, and with HgCl_2 , A \rightarrow D and GeMeClH_2 were isolated. With HCl , A and H_2 were produced initially, and A was subsequently converted into $\text{Fe}(\text{CO})_4(\text{GeMeClH})\text{H}$ and GeMeClH_2 . Treatment of $\text{Fe}(\text{CO})_4(\text{GeMeH}_2)_2$ with SnCl_4 gave only A and B, while reactions with SiBr_4 and HBr were similar to their chloro-analogues, but faster. From spectral studies it was established that A, B, C and D contained trans-germyl residues over a period of time some of the compounds produced rearranged to $(\text{OC})_4(\text{Fe}(\mu\text{-GeMeR})(\mu\text{-GeMeR}')\text{Fe}(\text{CO})_4$ ($\text{R} = \text{R}'$, H, Cl; $\text{R} = \text{H}$, R' ; $\text{R}' = \text{Cl}$).

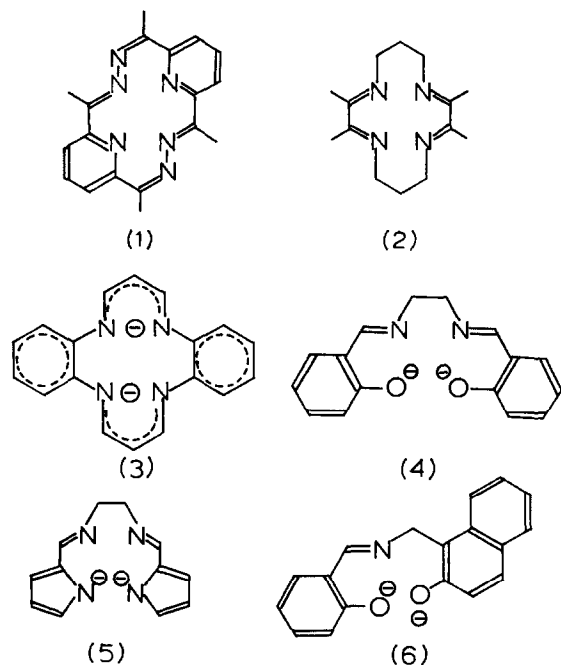
Sn-containing species. Photolysis of $[\text{Fe}(\text{CO})_4\text{SnCl}_3]^-$ in acetonitrile afforded some $[\text{Fe}(\text{SnCl}_3)_5]^{5-}$ (28). It had been reported that when the red solution formed by treating $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in ethanol with CO was treated with SnCl_2 and PPh_3 , lemon-yellow crystals of $\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})_2(\text{PPh}_3)_2(\text{OCMe}_2)_2$, A were formed (29). However, X-ray crystallographic studies established that this species was $\text{RuCl}(\text{SnCl}_3)(\text{CO})(\text{PPh}_3)_2(\text{OCMe}_2)$, as an acetone solvate (30). On warming solutions of this compound in benzene it was then converted into A, which readily lost SnCl_2 giving $(\text{PPh}_3)(\text{OC})\text{ClRu}(\mu\text{-Cl})_3\text{Ru}(\text{CO})(\text{PPh}_3)_2$ (30).

Divalent Halo-Complexes. $\text{cis}-[\text{Os}(\text{CO})_2\text{X}_4]^{2-}$ in liquid ammonia in the supercritical range at 170° afforded cis- $[\text{Os}(\text{CO})_2(\text{NH}_3)_4]\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (31). At room temperature, $[\text{Os}(\text{CO})_3\text{X}_3]^-$ reacted with liquid ammonia giving fac- $[\text{Os}(\text{CO})_3(\text{NH}_3)_3]\text{X}_2$. Under similar conditions, cis- $[\text{Os}(\text{CO})_2\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) formed apparently sequentially $[\text{Os}(\text{CO})_2(\text{NH}_3)_3\text{X}]^-$ (mer-X), $\text{Os}(\text{CO})_2(\text{NH}_3)_2\text{X}_2$ (cis-X and CO), $[\text{Os}(\text{CO})_2(\text{NH}_3)_3\text{X}]^+$ (fac-NH}_3), $[\text{Os}(\text{CO})_2(\text{NH}_3)_4]^{2+}$ (cis-CO), $[\text{Os}(\text{CO})_2(\text{NH}_3)_3\text{X}]^+$ (mer-NH}_3), $\text{Os}(\text{CO})_2(\text{NH}_3)_2\text{X}_2$ (cis-X and CO) and $[\text{Os}(\text{CO})_2(\text{NH}_3)_3\text{X}]^-$ (fac-X) (32). All isomers were separated by thin layer chromatography. The structures of $\text{Os}(\text{CO})_2(\text{NH}_3)_2\text{Cl}_2$ (cis-CO and NH}_3; cis-CO and Cl) and $[\text{Os}(\text{CO})_2(\text{NH}_3)_3\text{Cl}]\text{Cl}$ (fac-NH}_3) were determined by a combination of i.r., Raman and electronic spectroscopy (33).

Complexes of N-containing Polydentate and Macrocyclic Ligands.

A comparison has been made of the photochemical labilisation of CO in the Fe(II) complexes $\text{Fe}(\text{CO})(\text{C}_{18}\text{H}_{18}\text{N}_6)\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) and $\text{Fe}(\text{CO})(\text{TIM})\text{Cl}$ ($\text{C}_{18}\text{H}_{18}\text{N}_6 = \underline{1}$, $\text{TIM} = \underline{2}$) (34). Reaction of the dibenzo-tetra-aza[14]annulene ligand 3 (L^{2-} , $\text{C}_{22}\text{H}_{22}\text{N}_4^{2-}$) with $\text{Ru}_2(\text{OCOMe})_4\text{Cl}$ afforded $(\text{RuL})_2\text{Cl} \cdot \text{EtOH}$ which on addition of BF_4^- , afforded the mixed-valence species $[\text{Ru}(\text{II/III})\text{L}]_2[\text{BF}_4]_2$, A (35). Reduction of A with BH_4^- followed by addition of CO gave $\text{Ru}(\text{CO})\text{L}$, while treatment of A with CO in CH_3CN gave $\text{Ru}(\text{CO})\text{L}$ and $[\text{RuL}(\text{NCMe})_2]^+$. In ethanol in the presence of Cl^- , A was converted into $\text{Ru}(\text{CO})\text{L}$ and $\text{Ru}_2(\text{CO})_2(\text{L-L})\text{Cl}_2$ in which the heterocyclic ligand was coupled at the γ position of one of the pentane-2,4-di-iminato ligands (35).

Treatment of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ with $\text{Na}_2[\text{sal}_2\text{en}]$ ($\text{sal}_2\text{en}^{2-} = \underline{4}$) afforded $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$ which reacted with CO giving $[\text{Ru}(\text{CO})(\text{sal}_2\text{en})]_2$ (36). Treatment of $\text{Ru}(\text{pyr}_2\text{en})(\text{PPh}_3)_2$ ($\text{pyr}_2\text{en}^{2-} = \underline{5}$) with CO afforded $\text{Ru}(\text{CO})(\text{pyr}_2\text{en})(\text{PPh}_3)$, whereas addition of CO to a mixture of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ and $\text{Na}_2[\text{salnap}]$ ($\text{salnap}^{2-} = \underline{6}$) gave $\text{Ru}(\text{CO})(\text{salnap})(\text{PPh}_3)_2$ (36). Treatment of $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ or $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ with $\text{Na}_2[\text{sal}_2\text{en}]$ in THF afforded a red solution and the previously known yellow $[\text{Ru}(\text{CO})(\text{sal}_2\text{en})]_2$ (37). Chromatography of the red solution afforded *cis*- $\text{Ru}(\text{CO})_2(\text{sal}_2\text{en})$ (36). It was also reported that $[\text{Ru}(\text{C}_7\text{H}_8)\text{Cl}_2]_n$ ($\text{C}_7\text{H}_8 =$ norbornadiene) reacted with $\text{Na}_2[\text{sal}_2\text{en}]$ in THF group $\text{Ru}(\text{C}_7\text{H}_8)(\text{sal}_2\text{en})$, thought to be similar to *cis*- $\text{Ru}(\text{CO})_2(\text{sal}_2\text{en})$ (36).



The mono- and bis-carbonyl complexes $\text{Fe}(\text{CO})_x(\text{TPP})$ ($\text{TPP} =$ tetraphenylphorphyrinate(2-)) were both diamagnetic, as shown by n.m.r. spectral studies (38). The equilibrium constants for the formation of both carbonyls were determined and the rate of exchange of CO between $\text{Fe}(\text{TPP})$ and $\text{Fe}(\text{CO})(\text{TPP})$ measured.

Reaction of $\text{Fe}(\text{TPP})$ with CSCl_2 in the presence of Fe powder in a mixture of $(\text{MeS})_2\text{CS}$ and DMF gave the thio-carbonyl $\text{Fe}(\text{CS})(\text{TPP})$ (39). Recrystallisation of this species from ethanol afforded $\text{Fe}(\text{CS})(\text{TPP})(\text{EtOH})$ and it also reacted with pyridine and N-methylimidazole, (L), giving $\text{Fe}(\text{CS})(\text{TPP})\text{L}$. In an excess of pyridine (pyr), $\text{Fe}(\text{CS})(\text{TPP})(\text{pyr})$ was converted to $\text{Fe}(\text{TPP})(\text{pyr})_2$. The Fe-CS bond was stronger than the Fe-CO bond in the analogous $\text{Fe}(\text{CO})(\text{TPP})\text{L}$. Related

octaethylporphyrin, deuteroporphyrin dimethylester and protoporphyrin IX complexes were also reported (39).

Reaction of $\text{Ru}_3(\text{CO})_{12}$ with octaethylporphyrin (OEPH_2) in the presence of pyridine in benzene gave $\text{Ru}(\text{CO})(\text{OEP})(\text{pyr})$ (40). Treatment of this with NO in methanol/dichloromethane mixtures, and with pyridine, afforded $\text{Ru}(\text{NO})(\text{OEP})(\text{OMe})$ and $\text{Ru}(\text{OEP})(\text{pyr})_2$, respectively. Optical and emission spectra of these complexes were obtained and compared with related Fe and Os complexes. Photolysis of $\text{Ru}(\text{CO})(\text{OEP})(\text{EtOH})$ in acetonitrile gave $\text{Ru}(\text{OEP})(\text{NCMe})_2$, and the related TPP^{2-} complex behaved similarly (41). Treatment of this bis-acetonitrile adduct with CO in MeCN gave $\text{Ru}(\text{CO})(\text{OEP})(\text{NCMe})$ which was also formed from $\text{Ru}(\text{O}_2)(\text{OEP})(\text{NCMe})$ and CO.

Model compounds for the R- and T-state haemoglobins have been prepared, such that an imidazolate residue is covalently bound to a side-chain of mesohaem in such a way that the N-heterocycle is attached to the Fe atom without strain (42). CO binding kinetics of these models were shown to be like those of R-state haemoglobin.

Resonance coherent anti-Stokes Raman scattering spectral studies of carbonylated haemoglobin have shown that the Fe atom moves out of the haem plane to its location in deoxyhaemoglobin within 6 nanoseconds following photolytic dissociation of the Fe-CO bond (43). Resonance Raman spectral studies have been made of the photolabile CO adduct of cytochrome-P450 (44).

M(II) Complexes Containing Phosphine Ligands. Addition of hydrogen to $\text{M}(\text{CO})_2(\text{PPh}_3)_3$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) gave the cis-species $\text{M}(\text{CO})_2(\text{PPh}_3)_2\text{H}_2$ (45). Reaction of the ruthenium dihydride with CO or CO_2 (under pressure) and with O_2 afforded $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ and $\text{Ru}(\text{O}_2)(\text{CO})_2(\text{PPh}_3)_2$, respectively; the latter reacted with H_2 causing regeneration of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\text{H}_2$. Both $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\text{H}_2$ reacted with $\text{CH}_2=\text{CHCN}$ giving $\text{Ru}(\text{CH}_2=\text{CHCN})(\text{CO})_2(\text{PPh}_3)_2$. Cis- $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\text{H}_2$ was studied as a catalyst for the hydrogenation and isomerisation of a series of mono-alkenes and dienes, and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ isomerised hex-1-ene at room temperature in the absence of air (45).

The structure of $\text{Os}(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2(\text{SO}_2)\text{HCl}$ was determined by X-ray methods (46). The compound was six-coordinate with trans phosphines and contained a coplanar OsSO_2 group ($\text{Os-S} = 2.24 \text{ \AA}$). It was presumed that the H atom was trans to the SO_2 group. The complex reversibly lost SO_2 , giving $\text{Os}(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2\text{HCl}$, and reacted with O_2 in solution forming $\text{Os}(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2\text{Cl}(\text{SO}_4)$.

$\text{Ru}(\text{PR}_3)_3\text{Cl}_2$, A ($\text{PR}_3 = \text{P}(\text{p-MeC}_6\text{H}_4)_3, \text{PEtPh}_2$) added CO in DMF giving $\text{Ru}(\text{CO})(\text{PR}_3)_2(\text{DMF})\text{Cl}_2$, B (trans Cl and PR_3) (47). In refluxing CS_2 A was converted into $\text{Ru}_2(\text{CS})_2(\text{PR}_3)_4\text{Cl}_4$ and $\text{Ru}_2(\text{CS})(\text{PR}_3)_4\text{Cl}_4$ ($\text{R} = \text{p-MeC}_6\text{H}_4$), the last containing the $\text{Ru}(\mu\text{-Cl})_3\text{Ru}$ group. Reaction of A with B ($\text{R} = \text{p-MeC}_6\text{H}_4$) gave $\text{Ru}_2(\text{CO})(\text{PR}_3)_4\text{Cl}_4$, also containing the $\text{Ru}(\mu\text{-Cl})_3\text{Ru}$ moiety. Treatment of B with $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ gave $\text{Ru}_2(\text{CO})(\text{PPh}_3)_2(\text{PR}_3)_2\text{Cl}_4$ ($\text{R} = \text{p-MeC}_6\text{H}_4$). In carbon disulphide, $\text{Ru}(\text{PEtPh}_2)_3\text{Cl}_2$ was converted into $\text{Ru}_2(\text{CS})_2(\text{PEtPh}_2)_3\text{Cl}_4$ and

$[\text{Ru}(\text{PEtPh}_2)_2\{\text{S}_2\text{PEtPh}_2\}\text{Cl}_2]\text{CS}_2$ this latter containing the Zwitterionic ligand $\{\text{S}_2\text{C}^-\text{PEtPh}_2\}$, and having trans PR_3 groups. When this latter compound was dissolved in methanol containing $[\text{BPh}_4]^-$, it formed $[\text{Ru}(\text{PEtPh}_2)_2\{\text{S}_2\text{CPEtPh}_2\}\text{Cl}(\text{MeOH})][\text{BPh}_4]$ in which the PR_3 ligands were mutually cis.

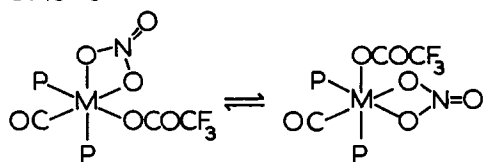
OsO_4 reacted with PPh_3 and HCl in refluxing ethanol to give $\text{Os}(\text{CO})_2(\text{PPh}_3)_2\text{Cl}_2$ (48). Arylation of $\text{Os}(\text{CS})(\text{PPh}_3)_3\text{HCl}$ with $\text{Hg}(\text{p-MeC}_6\text{H}_4)_2$ (HgAr_2) afforded (49) $\text{Os}(\text{CS})(\text{PPh}_3)_2\text{ArCl}$, A. Reaction of A with CO gave $\text{Os}(\text{CO})(\text{CS})(\text{PPh}_3)_2\text{ArCl}$ which, on heating, rearranged to $\text{Os}(\text{n}^2\text{-SCAr})(\text{CO})(\text{PPh}_3)_2\text{Cl}$. The analogous isonitrile $\text{Os}(\text{n}^2\text{-SCAr})(\text{CNR})(\text{PPh}_3)_2\text{Cl}$ ($\text{R} = \text{p-MeC}_6\text{H}_4$) was obtained from A by reaction with RNC . Exchange of Cl in A by trifluoroacetate afforded $\text{Os}(\text{CS})(\text{PPh}_3)_2\text{Ar}(\text{n}^2\text{-O}_2\text{CCF}_3)$ which picked up CO giving $\text{Os}(\text{CO})(\text{CS})(\text{PPh}_3)_2\text{Ar}(\text{OCOCF}_3)$ (carboxylate monodentate). Thermolysis of this last species afforded $\text{Os}(\text{n}^2\text{-SCAr})(\text{CO})(\text{PPh}_3)_2(\text{OCOCF}_3)$ whose structure was confirmed by X-ray methods. Treatment of $\text{Os}(\text{n}^2\text{-SCAr})(\text{CO})(\text{PPh}_3)_2\text{Cl}$ with NaS_2CNET gave $\text{Os}(\text{n}^2\text{-SCAr})(\text{CO})(\text{PPh}_3)_2(\text{n}^2\text{-S}_2\text{CNET}_2)$, and, in a slow reaction $\text{Os}(\text{n}^2\text{-SCAr})(\text{CNR})(\text{PPh}_3)_2\text{Cl}$ was methylated using $\text{MeOSO}_2\text{CF}_3$ giving $[\text{Os}\{\text{C}(\text{SMe})\text{Ar}\}\{\text{CNR}\}(\text{PPh}_3)_2\text{Cl}]^+$ and, after addition of Cl^- , $\text{Os}\{\text{C}(\text{SMe})\text{Ar}\}\{\text{CNR}\}(\text{PPh}_3)_2\text{Cl}_2$.

In 16M HNO_3 , $\text{M}(\text{CO})(\text{PPh}_3)_3\text{H}_2$ was converted into $\text{M}(\text{CO})(\text{PPh}_3)_2(\text{NO}_3)_2$ (50). This species contained mono- and bi-dentate NO_3 groups which interconverted their bonding modes (the 3 O-atoms were in a fac configuration). The Ru complex catalytically dehydrogenated alcohols to aldehydes, presumably via a β -elimination mechanism. Treatment of the bis-nitrates with ROH afforded $\text{M}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{NO}_3)$ (trans PPh_3 , H trans to O of bidentate NO_3). Nitric acid reacted with $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ and $\text{Os}(\text{CO})_2(\text{PPh}_3)_2\text{H}_2$ giving $\text{M}(\text{CO})_2(\text{PPh}_3)_2(\text{NO}_3)_2$ which contained monodentate nitrate (either trans- PPh_3 , cis- PPh_3 and CO). With CO , $\text{M}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{NO}_3)$ formed $\text{M}(\text{CO})_2(\text{PPh}_3)_2\text{H}(\text{NO}_3)$ (probably trans- PPh_3 , cis- CO) in which there may be a "hydrogen-bonded" interaction between an uncoordinated O atom of the nitrate and the hydride. Prolonged treatment of $\text{Ru}(\text{CO})(\text{PPh}_3)_3\text{H}_2$, $\text{Ru}(\text{PPh}_3)_2\text{H}(\text{O}_2\text{CMe})$ and $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{NO}_3)_2$ with HNO_3 gave $\text{Ru}(\text{NO})(\text{PPh}_3)(\text{OPPh}_3)(\text{ONO}_2)_3$ (trans ONO_2 , PPh_3 trans to OPPh_3).

Dilute HNO_3 reacted with $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{NO}_3)$ giving $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{NO}_3)$ which, in RCH_2OH , afforded $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{RCH}_2\text{OH})(\text{NO}_3)_2$ whose existence was established by analytical and spectral methods (51). This species lost HNO_3 forming the transient alkoxide $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{OCH}_2\text{R})(\text{NO}_3)$ which then eliminated aldehydes, reforming $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{NO}_3)$. This series of reactions is analogous to that involving the dehydrogenation of alcohols by $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{O}_2\text{CR})$ ($\text{R} = \text{perfluoroalkyl}$) (52). $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{NO}_3)_2$ was carbonylated by CO in boiling benzene or ethanol giving $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{NO}_3)_2$ which was similar to the compound obtained from $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ and HNO_3 in boiling ethanol. $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{NO}_3)$ reacted with CO giving first $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\text{H}(\text{NO}_3)$ and then $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, and PMePh_2 displaced PPh_3 from $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{NO}_3)_2$ affording $\text{Ru}(\text{CO})(\text{PMePh}_2)_3(\text{ONO}_2)_2$ (mer- PMePh_2). In cold benzene, trifluoroacetic acid reacted with $\text{Ru}(\text{CO})(\text{PPh}_3)_2$ -

$(\text{NO}_3)_2$ giving $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{O}_2\text{NO})(\text{OCOCF}_3)$, but in boiling toluene a mixture of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(\text{OCOCF}_3)_2$ and $\text{Ru}(\text{NO})(\text{PPh}_3)_2(\text{OCOCF}_3)$ was formed. There was no reaction of the bis-nitrate with acetic acid but NaOCOMe in cold methanol caused formation of $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{OCOMe})_2$; in boiling methanol, $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{OCOMe})$ was formed. $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{O}_2\text{NO})(\text{OCOCF}_3)$ apparently exists in a dynamic equilibrium as shown in Scheme 1, and reacted with RCH_2OH giving $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{NO}_3)$. In $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{OCOMe})_2$, one acetate ligand was monodentate and the other bidentate, there probably being a dynamic interchange between the bonding modes of the two ligands. $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{NO}_3)_2$ reacted with SO_2 in boiling methanol to give $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{O}_2\text{NO})\{\text{S}(\text{:O})_2\text{OMe}\}$. In the presence of NET_3 , the bis-nitrate reacted with acetylacetone (Hacac) giving $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{ONO}_2)(\text{acac})$ (trans- PPh_3 , bidentate acac^-) which, on recrystallisation from methanol, was converted into $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{acac})$ (trans- PPh_3). The bis-nitrate also reacted with $\text{NaS}_2\text{CNMe}_2$ in cold methanol to give $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{S}_2\text{CNMe}_2)\{\text{SC}(\text{:S})\text{NMe}_2\}$, but in boiling methanol $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{S}_2\text{CNMe}_2)_2$ (CO and PPh_3 mutually cis) was formed. Treatment of $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{NO}_3)$ with CS_2 gave $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{ONO}_2)(\text{S}_2\text{CH})$, and with $\text{NaS}_2\text{CNMe}_2$, $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{S}_2\text{CNMe}_2)_2$ (trans- PPh_3) was produced. In boiling methanol, $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{NO}_3)_2$ reacted with MeCOSH giving one isomer of $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{SOCMe})\{\text{SC}(\text{:O})\text{Me}\}$ (trans- PPh_3 , trans-S atoms) in which the two monothioacetate ligands interchanged their bonding modes. In cold methanol, a second isomer was formed which most probably contained cis- PPh_3 and cis-S atoms, the monothioacetate again interchanging dynamically their bonding modes.

Scheme 1



Both $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{NO}_3)_2$ and $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{H}(\text{NO}_3)$ reacted with PhC_2H in boiling ethanol or benzene giving $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{O}_2\text{NO})(\text{C}_2\text{Ph})$ (trans- PPh_3), whereas with PhC_2Ph , $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{O}_2\text{NO})\{\text{C}(\text{Ph})\text{:CHPh}\}$ was formed (either trans- PPh_3 , or cis- PPh_3 and CO trans to $\text{C}(\text{Ph})\text{:CHPh}$).

Depending on the reaction conditions, $[\text{Os}(\text{CO})(\text{solv})\text{X}_4]^-$ ($\text{solv} = \text{H}_2\text{O}$, MeOH or Me_2CO ; $\text{X} = \text{Cl}$, Br or I) reacted (53) with o-phenylenebis(dimethylarsine) (diars; $\text{C}_6\text{H}_4(\text{AsMe}_2)_2$) giving $[\text{Os}(\text{CO})(\text{diars})\text{X}_4]^-$, $\text{Os}(\text{CO})(\text{diars})_2\text{X}_2$ ($\text{X} = \text{Br}$ or I) or $[\text{Os}(\text{CO})(\text{diars})_2\text{X}]^+$. The first was isolated as $[\text{Bu}_4\text{N}]^+$ salts, was paramagnetic ($\mu = 2.01$ B.M.) and contained a monodentate diars trans to CO.

The second compound contained one mono- and one bi-dentate diars ligands, a mer arrangement of the three As atoms, and trans X groups (an X-ray structural determination of the species with X = Br confirmed this). The third cationic species was isolated in two forms, both of which contained two bidentate diars ligands. The isomer obtained on mild heating has mutually cis CO and X groups, and on strongly heating this, the species with trans CO and X groups was produced.

In 2-methoxyethanol, $\text{Ru}(\text{CO})(\text{PPh}_3)_3\text{HCl}$ reacted with β -diketones giving $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{Cl}\{\text{OC}(\text{CX}_2)\text{CHC}(\text{CX}_3)\text{O}\}$ (trans- PPh_3 ; X = Y = H, F, Ph; X = F, Y = H {two isomers depending on position of CO and Cl}) (54,55). Reaction of $\text{M}(\text{CO})(\text{PPh}_3)_3\text{H}_2$, $\text{M}(\text{CO})(\text{PPh}_3)_3\text{HCl}$ in the presence of NEt_3 (M = Ru, Os) or $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ with β -diketones affording $\text{M}(\text{CO})(\text{PPh}_3)_2\text{H}\{\text{OC}(\text{CX}_2)\text{CHC}(\text{CX}_3)\text{O}\}$ (X, Y as above).

M(II) Complexes containing Sulphur Ligands. Reaction of $\text{RuL}_2(\text{SOCPh})_2$ with CO afforded $\text{Ru}(\text{CO})_2\text{L}_2\{\text{SC}(\text{:O})\text{Ph}\}_2$ (L = PPh_3 and PMe_2Ph) (56). Both the phosphine and CO groups in the complex with L = PPh_3 are respectively trans, whereas in that with L = PMe_2Ph they are cis. Reaction of all-trans- $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\text{Cl}_2$ with $[\text{NH}_4][\text{SOCPh}]$ also gave $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\{\text{SC}(\text{:O})\text{Ph}\}_2$ (structure as above) (56).

Treatment of $\text{Na}_2\text{M}(\text{CO})_4$ (M = Fe or Ru) with CS_2 and MeI gave $\text{M}(\text{CO})_2(\text{S}_2\text{CMe})_2$ in low yields (57). Similar treatment of $\text{Na}[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ gave $\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)\text{Me}$ and small amounts of $\text{Fe}(\text{CO})(\eta\text{-C}_5\text{H}_5)(\text{S}_2\text{CMe})$ (57).

Reduction of $[\text{Ru}_2(\text{S}_2\text{CNET}_2)_5]^{1+}$ with BH_4^- followed by uv irradiation, in the presence of CO, of the $\text{Ru}_2(\text{S}_2\text{CNET}_2)_5$ so formed, gave cis- $\text{Ru}(\text{CO})_2(\text{S}_2\text{CNET}_2)_2$ and $[\text{Ru}(\text{CO})(\text{S}_2\text{CNET}_2)_2]_2$ (58). This reaction did not occur in the absence of uv light.

The structure of $\text{Fe}(\text{CO})_2(\text{CSNMe}_2)(\text{S}_2\text{CNMe}_2)$ has been determined by X-ray methods (59). The complex is six-coordinate, with cis-CO groups, and an η^2 - SCNMe_2 ligand: Fe-S 2.39 Å, Fe-C 1.88 Å (short), C-S 1.65 Å. The dithio-carbamate ligand was bidentate: Fe-S 2.33 Å, C-S 1.70-1.77 Å.

Reaction of Fe^{2+} in ethanolic alkali with CO and benzene-1,2-dithiol afforded (60) the labile cis- $[\text{Fe}(\text{CO})_2(\text{S}_2\text{C}_6\text{H}_4)_2]^{2-}$ which was not isolated but lost CO on heating or on oxidation by air. When the dithiol was replaced by $\text{p-C}_6\text{H}_4(\text{SMe})(\text{SH})$, cis- $\text{Fe}(\text{CO})_2\{\text{S}(\text{MeS})\text{C}_6\text{H}_4\}_2$ could be isolated, the CO groups again being labile and reversibly bound to the $\{\text{FeS}_4\}$ core.

Osmium(III) Carbonyl Halides. Stepwise hydrolysis of $[\text{Os}(\text{CO})\text{X}_5]^{2-}$ (X = Cl, Br, I) gave $[\text{Os}(\text{CO})(\text{H}_2\text{O})\text{X}_4]^-$, $\text{Os}(\text{CO})(\text{H}_2\text{O})\text{X}_3$ and $[\text{Os}(\text{CO})(\text{H}_2\text{O}_3\text{X}_2)]^+$ (61). The species $[\text{Os}(\text{CO})(\text{H}_2\text{O})\text{X}_{4-n}\text{Y}_n]^-$ (X = Y = Cl, Br or I; n = 1-3) could be made by halide substitution reactions involving appropriate aqua species.

Complexes containing Group 2B and Other Metals. The complexes $\text{Fe}(\text{CO})_4\{\text{ZnL}\}$, where L = dien and trien, and $\text{Fe}(\text{CO})_4\text{Zn}(\text{NH}_3)_3$ have been shown (62), by IR and Raman spectroscopy, to be monomeric, the Fe atom having trigonal bipyramidal geometry. Those complexes where L = $\text{NH}_2(\text{CH}_2)_3\text{NH}_2$, or $\text{NH}_2\text{CH}_2\text{CH}_2\text{NRR}'$ (R = H,

$R' = \text{Me}$; $R = R' = \text{Me}$) were polymeric and contained six-coordinate iron.

Reaction of $\text{Fe}(\text{CO})_4\text{Cd}(\text{NH}_3)_2$ with tren (tren = 2,2',2''-triamino-triethylamine) gave $\text{Fe}(\text{CO})_4\text{Cd}(\text{tren})$ (63). This, $\text{Fe}(\text{CO})_4\text{Cd}(\text{terpy})$ (terpy = 2,2':6,2''-terpyridyl), and the related zinc complexes $\text{Fe}(\text{CO})_4\text{Zn}(\text{pyr})_3$ and $\text{Fe}(\text{CO})_4\text{Zn}(\text{NH}_3)(\text{bipy})$, were thought to be monomeric whereas $\text{Fe}(\text{CO})_4\text{Zn}(\text{?},2'\text{-bipy})$, $\text{Fe}(\text{CO})_4\text{Cd}(4,4'\text{-bipy})$ and $\text{Fe}(\text{CO})_4\text{Cd}(4\text{-PhC}_5\text{H}_4\text{N})$ were believed to be oligomeric. The species $\text{Fe}(\text{CO})_4\text{Cd}(\text{pyr})_2$ was trimeric in the solid state, and $[\text{Fe}(\text{CO})_4\text{Cd}]_4$ and $\text{AgCo}(\text{CO})_4$ were isomorphous; $\text{PbFe}(\text{CO})_4$ was also associated in the solid state (63).

Formyl, Thioformyl and Related Complexes. Reaction of $\text{Fe}(\text{CO})_5$ with $\text{Li}[(\text{OC})_5\text{ReRe}(\text{CO})_4\text{CHO}]$ afforded $[\text{Fe}(\text{CO})_4(\text{CHO})]^-$ (64). In THF $[\text{Et}_4\text{N}][\text{trans-Fe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}\text{CHO}]$ decomposed giving $[\text{Et}_4\text{N}][\text{Fe}(\text{CO})_4\text{H}]$ and releasing $\text{P}(\text{OPh})_3$ (65). With trifluoroacetic acid, this formyl afforded methanol but no formaldehyde, in a reaction pathway perhaps either involving formaldehyde which reacted further with $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}(\text{CHO})]^+$ and acid to give MeOH, or involved, as intermediates, $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}\{\text{:CH}(\text{OH})\}]$ and $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}\text{CH}_2\text{OH}]^+$. Reaction of $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OAr})_3\}\text{CHO}]^-$ (Ar = 3,5-dimethylphenyl) with $n\text{-C}_7\text{H}_{15}\text{I}$ gave $\text{Fe}(\text{CO})_4\{\text{P}(\text{OAr})_3\}$, and $n\text{-C}_7\text{H}_{16}$ but very little $n\text{-C}_7\text{H}_{15}\text{CHO}$. However, treatment of $[\text{Et}_4\text{N}][\text{Fe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}\text{CHO}]$ with $\text{Re}_2(\text{CO})_{10}$ afforded $\text{cis-}[\text{Re}_2(\text{CO})_9\text{CHO}]^-$, and in a comparison of transformylation reactions between various metal formyl complexes and metal carbonyls it was established that the order of stability of the formyl iron complexes was $[\text{PPN}][\text{Fe}(\text{CO})_4\text{CHO}] > [\text{Et}_4\text{N}][\text{Fe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}\text{CHO}]$.

$\text{Os}(\text{CS})(\text{PPh}_3)_3\text{Cl}_2$ reacted with ethanolic alkali giving first $\text{Os}(\text{CS})(\text{PPh}_3)_3\text{HCl}$ (mer-PPh₃, H cis to two trans-PPh₃) and then $\text{Os}(\text{CS})(\text{PPh}_3)_3\text{H}_2$ (mer-PPh₃, cis-H) (66). The latter could also be obtained by direct reaction of $\text{Os}(\text{CS})(\text{PPh}_3)_3\text{Cl}_2$ with OH^- in 2-methoxyethanol. Treatment of $\text{Os}(\text{CS})(\text{PPh}_3)_3\text{HCl}$ with CO afforded $\text{Os}(\text{CO})(\text{CS})(\text{PPh}_3)_2\text{HCl}$ as an intermediate, which reacted further with CO giving $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{CHS})(\text{Cl})$ (trans-PPh₃, cis-CO; the bromide was prepared similarly). Using RNC (R = p-MeC₆H₄) instead of CO, $\text{Os}(\text{CS})(\text{PPh}_3)_2\text{HCl}$ was converted into $\text{Os}(\text{CS})(\text{CNR})(\text{PPh}_3)_2\text{HCl}$ (trans-PPh₃, CS and CNR trans) which, on heating, afforded the isomer with trans-PPh₃ and CS and CNR mutually cis. This last reacted with CO giving $\text{Os}(\text{CO})(\text{CNR})(\text{PPh}_3)_2(\text{CHS})\text{Cl}$. Under 4 atm CO pressure at 140°C, $\text{Os}(\text{CS})(\text{PPh}_3)_3\text{H}_2$ gave a carbonyl complex containing S, perhaps in bridging CHS group although this could not be characterised, and $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CH}_2\text{S})$, A, which could also be obtained by BH_4^- reduction of $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{CHS})\text{Cl}$. A was protonated by HCl to give $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{SMe})\text{Cl}$ (trans-PPh₃, cis-CO) and reacted further with HCl with loss of MeSH, affording $\text{Os}(\text{CO})_2(\text{PPh}_3)_2\text{Cl}_2$. Methylation of A at the S atom was achieved using $\text{CF}_3\text{SO}_3\text{Me}$, giving $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CH}_2\text{SMe})]^+$ and on addition of Cl^- , $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{CH}_2\text{SMe})\text{Cl}$ was produced. Further methylation of this with $\text{CF}_3\text{SO}_3\text{Me}$ afforded $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{CH}_2\text{SMe}_2)\text{Cl}]^+$ (trans-PPh₃, cis-CO). Reaction of $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{CHS})\text{Cl}$ with $\text{CF}_3\text{SO}_3\text{Me}$ gave $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{CHSMe}(\text{Cl}))]^+$, B (trans-PPh₃, cis-CO) and hydrolysis of this afforded $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{CHO})\text{Cl}$ (same

geometry as B). This was decarbonylated giving $\text{Os}(\text{CO})_2(\text{PPh}_3)_2\text{HCl}$, and reacted with HCl to give $\text{Os}(\text{CO})_2(\text{PPh}_3)_2\text{Cl}_2$. B also reacted with NH_2Me giving $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2\{\text{CH}(\text{NHMe})\}\text{Cl}]^+$ which could be reversibly deprotonated by base affording $\text{Os}(\text{CO})_2(\text{PPh}_3)_2\{\text{CH}(\text{:NMe})\}\text{Cl}$ (trans- PPh_3 , cis- CO). The isonitrile complex $\text{Os}(\text{CO})(\text{CNR})(\text{PPh}_3)_2(\text{CHS})\text{Cl}$ could also be methylated, using $\text{CF}_3\text{SO}_2\text{Me}$, to give $[\text{Os}(\text{CO})(\text{CNR})(\text{PPh}_3)_2(\text{CHSMe})\text{Cl}]^+$. Treatment of this with OH^- afforded $\text{Os}(\text{CO})(\text{CNR})(\text{PPh}_3)_2(\text{CHO})\text{Cl}$, and further methylation converted this formyl species into $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{CHOMe})\text{Cl}]^+$.

ISONITRILE COMPLEXES

UV irradiation of $\text{Fe}(\text{CNET})_5$ in ether afforded $\text{Fe}_2(\text{CNET}_2)_9$ which is structurally similar to $\text{Fe}_2(\text{CO})_9$ in having three bridging CNET groups, and two sets of three terminal isonitrile ligands ($\text{Fe}-\text{Fe} = 2.46 \text{ \AA}$) (67). Variable temperature ^1H and ^{13}C n.m.r. spectral studies established that the terminal and bridging CNET groups underwent intramolecular site exchange and that, at -50° , inversion at the N atoms of the bridging CNET groups was rapid (67). Reaction of $\text{Fe}(\text{CNBu}^t)_5$ with PhC_2Ph in THF at room temperature afforded $\text{Fe}(\text{CNBu}^t)_3\{\text{Bu}^t\text{NC}=\text{C}(\text{Ph})\text{C}(\text{Ph}=\text{CNBu}^t)\}$ whose overall structure (X-rays) is similar to that of $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_6)$. There was apparently minimal back-bonding from the metal to the CNBu^t ligands, and the isonitrile ligands underwent intramolecular site-exchange (n.m.r. studies) (67).

$\text{Ru}(\text{CNBu}^t)_5$ reacted with nido-2,3- Me_2 -2,3- $\text{C}_2\text{B}_4\text{H}_6$ giving $[\text{Ru}(\text{CNBu}^t)_5\text{H}][\text{nido-2,3-}\text{Me}_2\text{-2,3-}\text{C}_2\text{B}_4\text{H}_5]$ (68). The geometry of the cation was established from poor quality X-ray data, and was shown to have idealised C_{4v} symmetry.

A mixture of FeX_2 , PR_3 and RNC ($\text{R} = \text{p-MeC}_6\text{H}_4$) in ethanol containing LiClO_4 afforded (69) the salt $[\text{Fe}(\text{RNC})_n(\text{PR}_3)_{5-n}\text{X}][\text{ClO}_4]$ where $n = 4$, $\text{PR}_3 = \text{PPh}_2\text{OEt}$ and $\text{X} = \text{Br}$ or I , $n = 3$, $\text{PR}_3 = \text{PPh}_2\text{OEt}$ and $\text{X} = \text{Cl}$ or $\text{PR}_3 = \text{PPhEt}_2$, PPh_2Me or PPh_2Et and $\text{X} = \text{Br}$ or I , and $n = 2$, $\text{PR}_3 = \text{PPhMe}_2$ and $\text{X} = \text{I}$. The species with $n = 4$ has PR_3 and X mutually trans, that with $n = 3$ has mer- CNR and trans- PR_3 , and that with $n = 2$ has trans- PR_3 and cis- CNR . There was a tentative correlation between the steric hindrance of PR_3 , the influence of the π -acidity of PR_3 and CNR and the composition and structures of the compounds. IR, ^1H n.m.r. and Mössbauer spectral studies were made of these complexes.

The photochemical behaviour of PhCH_2NC complexes of haem models has been studied (70). The general system studied was $\text{Fe}\{\text{N}_4\}\text{L}_2 + \text{X}$, giving $\text{Fe}\{\text{N}_4\}\text{LX} + \text{L}$, where $\{\text{N}_4\}$ was dimethylglyoximate, phthalocyaninate or TIM (2), and $\text{L} = \text{N}$ -methylimidazole or NCMe , L being PhCH_2NC or CO . Reaction of $\text{Ru}(\text{PPh}_3)_2(\text{pyr})\text{Cl}_3$ with RNC afforded $\text{Ru}(\text{CNR})(\text{PPh}_3)_2\text{Cl}_3$ where $\text{R} = \text{C}_3\text{H}_5$, Bu^t , C_6H_{11} , CH_2Ph , $\text{p-MeC}_6\text{H}_4$ or $\text{p-MeNC}_6\text{H}_4$ (71).

Treatment of $\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{RCl}$ with RNC ($\text{R} = \text{p-tolyl}$) gave $\text{Ru}(\text{CO})(\text{ONR})(\text{PPh}_3)_2\text{RCl}$ (trans- PPh_3 , CO and CNR cis) (92). On heating, this species gave an isomeric species in which the R and CNR group became mutually cis, the CO group

being either trans to R or CNR, and this existed in an equilibrium with the η^2 -iminoacyl species $\text{Ru}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-RCNR})\text{Cl}$. This last was isolated and its structure was established by X-rays. It reacted with HCl giving $\text{Ru}(\text{CO})\{\text{CR}(\text{NHR})\}(\text{PPh}_3)_2\text{Cl}_2$.

The ^{13}C n.m.r. spectra of $\text{Os}(\text{CNR})_2(\text{PR}'_3)_2\text{Cl}_2$ ($\text{R} = \text{Me}, \text{Ph}, \text{p-C}_6\text{H}_4\text{NO}_2$ and $\text{p-C}_6\text{H}_4\text{OMe}$; $\text{PR}'_3 = \text{PETe}_3, \text{PETe}_2\text{Ph}, \text{PBu}_2\text{Ph}$), $\text{Os}(\text{CNMe})(\text{PETe}_3)_3\text{Cl}_2$, $[\text{Os}(\text{CNMe})_2(\text{PETe}_3)_3\text{Cl}]^+$ and $\text{Ru}(\text{CNPh})_2(\text{PMe}_2\text{Ph})_2\text{Cl}_2$ (various isomers) have been recorded, and $^2\text{J}(\text{P-M-CNR})$ obtained in some cases (73).

CARBENE COMPLEXES

$\text{Fe}(\text{CO})_5$ reacted with $\text{Ph}_3\text{P=CHR}$ in benzene giving (74) the salt $[\text{Ph}_3\text{PCH}_2\text{R}][\text{Fe}(\text{CO})_4\{\text{C}(\text{O})\text{CR:PPh}_3\}]$. Methylation using dimethyl sulphate gave $\text{Fe}(\text{CO})_4\{\text{C}(\text{O})\text{Me}\}(\text{CR:PPh}_3)$ ($\text{R} = \text{H}$ or Me). Reaction of 2,2-dichloro-1,3-benzodioxol with $\text{Fe}_2(\text{CO})_9$ afforded the benzodioxol-2-ylidene complex $\text{Fe}(\text{CO})_4\text{L}$ ($\text{L} = \text{C}_6\text{H}_4\text{OC}_2\text{O}$) (75).

Acetylenes, $\text{RC}_2\text{R}'$, reacted with $\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2(\eta^2\text{-CS}_2)$, A (trans- $\text{P}(\text{OMe})_3$, cis- CO), at room temperature giving (21,76) the carbene complexes $\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2\{\text{C}(\text{C}(\text{R}')\text{S})\}$, B, ($\text{R} = \text{R}' = \text{CO}_2\text{Me}$; $\text{R}, \text{R}' = \text{H}, \text{CO}_2\text{Et}$; p- ClC_6H_4 , CHO ; p- $\text{O}_2\text{NC}_6\text{H}_4$, COMe ; Ph , CHO). On standing in air in solution, B was converted into the dithiolene complexes $\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}\{\text{S}_2\text{C}_2\text{RR}'\}$, C, with concomitant formation of the dithiofulvalenes $\text{RR}'\text{C}_2\text{S}_2\text{C}=\text{CS}_2\text{C}_2\text{RR}'$ ($\text{R} = \text{R}' = \text{CO}_2\text{Me}$; $\text{R}, \text{R}' = \text{H}, \text{CO}_2\text{Et}$; p- ClC_6H_4 , CHO) in modest yields. The unstable dithiolene $\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_2\}\{\text{S}_2\text{C}_2\text{H}(\text{CO}_2\text{Et})\}$ could also be obtained. The dithiolene complexes C could also be obtained more readily by reaction of A with $\text{RC}_2\text{R}'$ ($\text{R}, \text{R}' = \text{p-O}_2\text{NC}_6\text{H}_4$, COMe or Ph , CHO) followed by chromatography in air. Carbene complexes analogous to B, but containing PMe_3 or PMe_2Ph were also prepared and there was some discussion of the mechanism of formation of these species.

The structure of the di-carbene complex $[\text{Fe}(\text{CO})_2\{\text{C}(\text{NMe}_2)_2\text{S}\}\{\text{S}_2\text{CNMe}_2\}]^-[PF_6]^{1/2}\text{C}_2\text{H}_4\text{Cl}_2$, whose preparation had been described earlier (77), has been determined crystallographically (78). The species has cis- CO groups and contains the four-membered $\text{FeC}(\text{NMe}_2)\text{SC}(\text{NMe}_2)$ chelate ring.

The 'electron-rich' olefins $\{\text{C}(\text{NR})\text{CH}_2\text{CH}_2\text{NR}\}_2$, L_2^{R} ($\text{R} = \text{Me}, \text{Et}$ or CH_2Ph) reacted with $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ giving trans- $\text{RuL}_4^{\text{R}}\text{Cl}_2$ (79). The species containing L^{Me} and L^{Et} can lose one carbene ligand, the Et derivative most readily, giving $\text{RuL}_3^{\text{R}}\text{Cl}_2$ the structure of which is thought to be trigonal bipyramidal with axial X. $\text{Ru}(\text{L}^{\text{CH}_2\text{Ph}})_4\text{Cl}_2$ does not undergo this dissociation. The structure of trans- $\text{Ru}(\text{L}^{\text{Et}})_4\text{Cl}_2$ has been determined crystallographically, the 4 carbene ligands adopting a "propellor" arrangement in the equatorial plane. Treatment of $\text{Ru}(\text{L}^{\text{Me}})_4\text{Cl}_2$ with CO gave trans- $[\text{Ru}(\text{CO})(\text{L}^{\text{Me}})_4\text{Cl}]^+$, and when this reaction was carried out in pyridine, trans- $[\text{Ru}(\text{CO})(\text{L}^{\text{Me}})_2(\text{pyr})_2\text{Cl}]\text{Cl}$ was produced. The methyl-carbene derivative reacted with $\text{P}(\text{OMe})_3$ and with PF_3 giving $[\text{Ru}(\text{L}^{\text{Me}})_2\text{P}(\text{OMe})_3]\text{Cl}^-\text{Cl}$ and trans- $[\text{Ru}(\text{L}^{\text{Me}})_4(\text{PF}_3)\text{Cl}]^+$ isolated as Cl^- and BF_4^- salts),

respectively. Chloride could be exchanged for iodide by reacting $\text{Ru}(\text{L}^{\text{Me}})_4\text{Cl}_2$ with NaI in acetone, the product being $\text{Ru}(\text{L}^{\text{Me}})_3\text{I}_2$. Treatment of $\text{Ru}(\text{L}^{\text{Et}})_4\text{Cl}_2$ with CO in methylcyclohexane or toluene at 100° gave initially trans- $\text{Ru}(\text{CO})(\text{L}^{\text{Et}})_3\text{Cl}_2$ and this could be converted to the cis-isomer in dichloromethane at room temperature. There was severe steric crowding in $[\text{Ru}(\text{L}^{\text{Me}})_4(\text{PF}_3)\text{Cl}]\text{Cl}$ and $\text{RuL}_n^{\text{R}}\text{Cl}_2$ ($\text{R} = \text{Et}, \text{CH}_2\text{Ph}; n = 3,4$), leading to restricted rotation of the carbene ligand about the Ru-C bond. Reaction of $\text{Os}(\text{PBU}_2^{\text{n}}\text{Ph})_3\text{Cl}_3$ with $(\text{L}^{\text{Me}})_2$ gave trans- $\text{Os}(\text{L}^{\text{Me}})_4\text{Cl}_2$ (79).

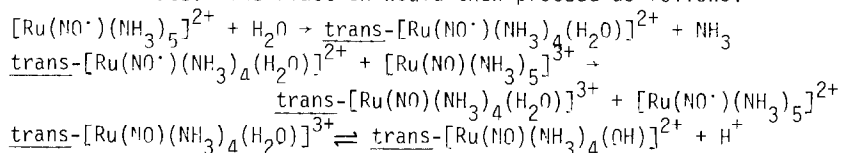
Treatment of $\text{Fe}(\text{TPP})$ (TPP = meso-tetraphenylporphyrin) with 2,2-bis-(*p*-chlorophenyl)-1,1,1-trichloroethane in methanol/dichloromethane mixtures in the presence of Fe powder gave (80) the vinylidene carbene complex $\text{Fe}\{\text{C}=\text{C}(\text{C}_6\text{H}_4\text{Cl})_2\}(\text{TPP})$ which could accept a further ligand molecule (methanol, N-methylimidazole, pyridine) giving six-coordinate species; an excess of pyridine caused displacement of the carbene ligand. Similar complexes were obtained with tolyl and *p*-chlorophenyl porphyrin, octaethylporphyrin and protoporphyrin IX.

Addition of acetamidine to $[\text{Fe}(\text{CNMe})_6]^{2+}$ afforded the complex $[\text{Fe}\{\text{C}(\text{NHMe})\text{NHC}(\text{Me})=\text{NC}(\text{NHMe})\}(\text{CNMe})_4]^{2+}$ whose structure (PF_6^- salt) confirmed the existence and nature of the six-membered chelate ring (81); the Fe-C distances occurred in the range 1.94-1.95 Å.

NITROSYL COMPLEXES

Simple Nitrosyl Complexes. Treatment of $\text{Fe}(\text{CO})_2(\text{NO})_2$ with NOPF_6 in dichloromethane afforded $[\text{Fe}_2(\text{NO})_6][\text{PF}_6]_2$ (82). This species may also be obtained by reaction either of $\text{Fe}(\text{NO})_3\text{Cl}$ with AgPF_6 in dichloromethane or of Fe powder with NOPF_6 in nitromethane. The species is formulated as having three terminal NO groups per Fe atom and a metal-metal triple bond. The complexes $[\text{Fe}(\text{NO})_3(\text{PR}_3)]-[\text{PF}_6]$ ($\text{R} = \text{Me}$ or Ph) have also been prepared (82).

Complexes containing Group 5 Donor Ligands. Reaction of one equivalent of $[\text{Ru}(\text{NO})(\text{NH}_3)_5]^{3+}$ with 0.02-0.1 equivalents of an electron via the reducing radicals produced via radiation chemical techniques in neutral aqueous solution, gave trans- $[\text{Ru}(\text{NO})(\text{NH}_3)_4(\text{OH})]^{2+}$ and NH_3 virtually quantitatively (83). It appeared that the initially produced one-electron reduced species $[\text{Ru}(\text{NO}\cdot)(\text{NH}_3)_5]^{2+}$ underwent trans- NH_3 detachment on aquation, so forming a catalyst, $[\text{Ru}(\text{NO}\cdot)(\text{NH}_3)_4(\text{H}_2\text{O})]^{2+}$ which could effectively reduce the remaining unreacted substrate. The reaction would then proceed as follows:



The complex $\text{Fe}(\text{NO})\text{L}$ ($\text{L} =$ protoporphyrin IX dimethyl ester) was characterised by i.r. and e.s.r. spectroscopy and it was shown that the e.s.r. parameters were

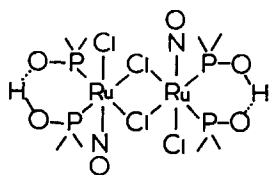
characteristic of rhombic symmetry (84).

$\text{Ru}(\text{NO})(\text{PPh}_3)_3$ was prepared in good yield by reaction of $\text{Ru}(\text{NO})\text{Cl}_3$, formed from RuCl_3 , NO and NO_2 at 100° in water, with PPh_3 and KOH in 78% ethanol under nitrogen (85). The structure of $\text{Ru}(\text{NO})(\text{PPh}_3)_2(\eta^2\text{-SO}_2)\text{Cl}\cdot 2\text{CH}_2\text{Cl}_2$, obtained by reaction of $\text{Ru}(\text{NO})(\text{PPh}_3)_2\text{Cl}$ with SO_2 (86), has been determined by X-ray methods (87). The complex has trigonal bipyramidal geometry with axial PPh_3 , a linear Ru-N-O group (Ru-N 1.74 Å), and contains the three-membered RuOS=O chelate ring (Ru-O 2.14 Å, Ru-S 1.34 Å, S-O 1.50 Å, S=O 1.46 Å); the OSO bond angle is 114° .

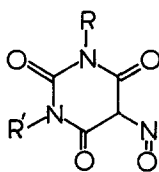
When $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}(\text{NO})\text{Me}$ and an excess of $\text{P}(\text{O}Ph)_3$ was refluxed in dry ethanol $\text{Ru}(\text{NO})\{\text{P}(\text{O}Ph)_3\}_2\text{Cl}_3$ may have been formed as an intermediate, but the species isolated was bimetallic, 7, and contained the ligand $[(\text{EtO})_2\text{PO-H}\dots\text{OP}(\text{OEt})_2]^-$ (88). The structure of the complex was confirmed crystallographically. If the reaction was carried out using Bu^tOH , only $\text{Ru}(\text{NO})\{\text{P}(\text{O}Ph)_3\}_2\text{Cl}_3$ was obtained.

Careful i.r. spectral studies have been made of trans- $[\text{Fe}(\text{NO})(\text{diars})_2\text{X}]\text{-}[\text{ClO}_4]_n$ (diars = *o*-phenylenebis(dimethylarsine), *o*- $\text{C}_6\text{H}_4(\text{AsMe}_2)_2$; $n = 2$, $\text{X} = \text{NCS}$; $n = 1$, $\text{X} = \text{Br}$) and of cis- $\text{Fe}(\text{NO})(\text{S}_2\text{CNMe}_2)_2\text{I}$ and $\text{Fe}(\text{NO})(\text{S}_2\text{CNMe}_2)_2$ (89).

Treatment of $\text{Ru}(\text{NO})(\text{H}_2\text{O})\text{Cl}_3$ with glycine (HL) in aqueous solution gave $[\text{Ru}(\text{NO})\text{L}(\text{OH})_3]^-$ (90), and when $\text{Ru}(\text{salen})(\text{PPh}_3)_2$ (salen = 4) was treated with NO in THF $[\text{Ru}(\text{NO})(\text{salen})]_2\text{O}$ and $\text{Ru}(\text{NO})(\text{salen})(\text{NO}_2)\cdot\text{THF}$ were formed (91). The last contained a trans arrangement of the NO and O -bonded NO_2 groups.



(7)



(8)

Complexes containing Group 6 Donor Ligands. Reaction of the tris(violurato) $\text{Ru}(\text{II})$ complex $[\text{Ru}(\text{H}_2\text{Vi})_3]^-$ ($\text{H}_2\text{Vi} = \underline{8}$, $\text{R} = \text{R}' = \text{H}$) with acidic nitrite afforded (92) the nitrosyl complex cis- $\text{Ru}(\text{NO})(\text{H}_2\text{Vi})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{OH}, \text{NO}_2$ or monodentate H_2Vi). The mechanism of nitrosylation may involve incorporation of NO^+ into the complex via breaking of a chelate ring. Solvolysis of the known cis- $\text{Ru}(\text{NO})(\eta^2\text{-H}_2\text{Vi})_2(\eta^2\text{-H}_2\text{Vi})$ indicated that the 'dangling' violurato ligand can be acid-solvolysed (92).

The species $\text{Fe}(\text{NO})\text{L}_2$, where $\text{HL} =$ monothiodibenzoylmethane or *N*-(morpholiniothiocarbonyl)betaine, have been reported (93). The complex containing monothiodibenzoylmethane was dimeric via *S*-atom bridges, and so each metal atom is six-coordinate. ESCA studies suggested that the species contain Fe^{3+} and NO^- . RT Mössbauer, i.r. and e.s.r. spectral studies have been made of

$\text{Fe}(\text{NO})(\text{S}_2\text{CNRR}')_2$ where $\text{R}, \text{R}' =$ piperidiny1, pyrrolidiny1, morpholiny1, and combinations of Me, Et, OMe, OEt, CH_2Ph , Ph and 3- ClC_6H_4 (94). The NO stretching frequency exhibited a nearly linear dependence on the "corrected" aqueous pK_a value of $[\text{NH}_2\text{RR}']^+$. It was suggested that the unpaired electron occupied the d_{z^2} orbital.

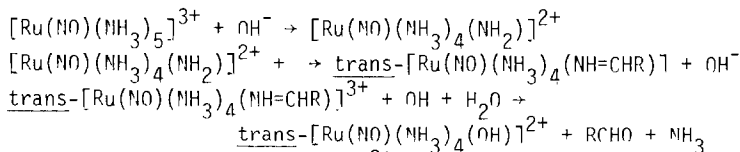
Carbene and Allyl Complexes. The 'electron-rich' olefin $(\overline{\text{CNRCH}_2\text{CH}_2\text{NR}})_2, \text{L}_2^{\text{R}}$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}$) reacted with $\text{Ru}(\text{NO})(\text{PPh}_3)_2\text{Cl}$ giving $[\text{Ru}(\text{NO})(\text{L}^{\text{Me}})_4]\text{Cl}$ and $\text{Ru}(\text{NO})(\text{L}^{\text{CH}_2\text{Ph}})_2\text{Cl}$ (95). Carbonylation of the former carbene gave trans- $[\text{Ru}(\text{CO})(\text{L}^{\text{Me}})_4]\text{Cl}$, and its oxidation by AgX afforded trans- $[\text{Ru}(\text{NO})(\text{L}^{\text{Me}})_4\text{Cl}]\text{X}_2$ ($\text{X} = \text{BF}_4$ or ClO_4). At 25° , $\text{Ru}(\text{NO})(\text{L}^{\text{CH}_2\text{Ph}})_2\text{Cl}$ absorbed CO, giving a 1:1 adduct which was thought to have a square pyramidal geometry with an apical, bent NO group and trans-basal carbenes. $\text{Ru}(\text{NO})(\text{L}^{\text{CH}_2\text{Ph}})_2\text{Cl}$ also reacted with MeI, PhCH_2Cl , Br_2 and I_2 giving, respectively, $\text{Ru}(\text{NO})(\text{L}^{\text{CH}_2\text{Ph}})_2\text{MeCl}$ (trans- L^{R} , NO trans to Cl), $\text{Ru}(\text{NO})(\text{L}^{\text{CH}_2\text{Ph}})_2\text{Cl}_3$ (trans- L^{R} , mer-Cl), and $\text{Ru}(\text{NO})(\text{L}^{\text{CH}_2\text{Ph}})_2\text{X}_2\text{Cl}$ (cis- L^{R} , fac- X_2Cl with X mutually cis; X = Br or I). The olefin $(\text{L}^{\text{Et}})_2$ reacted with $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$ in refluxing toluene to give $\text{Ru}(\text{NO})_2(\text{L}^{\text{Et}})(\text{PPh}_3)$.

$\text{Os}(\text{NO})(\text{PPh}_3)_2\text{Cl}_3$ was reduced to $\text{Os}(\text{NO})(\text{PPh}_3)_2\text{Cl}$ by treating the trichloride with $(\text{L}^{\text{Me}})_2$ in xylene at 140° (95). Further treatment of this reaction mixture with an excess of $(\text{L}^{\text{Me}})_2$ afforded $[\text{Os}(\text{NO})(\text{L}^{\text{Me}})_2]\text{Cl}$ which was converted to the BF_4^- salt by exchange with AgBF_4 . Reaction of $\text{Os}(\text{NO})(\text{PPh}_3)_2\text{Cl}_3$ with $(\text{L}^{\text{CH}_2\text{Ph}})_2$ gave $[\text{Os}(\text{NO})(\text{L}^{\text{CH}_2\text{Ph}})_3\text{Cl}_2]\text{Cl}$.

The π -allyl complex $\text{Ru}(\text{NO})(\eta^3\text{-C}_3\text{H}_5)(\text{PPh}_3)_2$ was prepared by reaction of $\text{Ru}(\text{NO})(\text{PPh}_3)_2\text{Cl}$ with $\text{Sn}(\text{C}_3\text{H}_5)_4$ (96). The complex has a pseudo-tetrahedral geometry (X-rays) assuming the $\eta^3\text{-C}_3\text{H}_5$ group to occupy one vertex, with a linear Ru-N-O group (174°).

Reactions of Coordinated NO. $[\text{Ru}(\text{NO})(\text{NH}_3)_5]^{3+}$ reacted with two equivalents of NH_2R ($\text{R} = \text{Me}, \text{Et}$) giving $[\text{Ru}(\text{N}_2)(\text{NH}_3)_5]^{2+}$, ROH and NH_2R^+ (97). It was thought that this reaction proceeded via a diazonium ion, RN_2^+ , possibly coordinated to the metal. A similar reaction with $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in the presence of OH^- afforded $[\{\text{Ru}(\text{NH}_3)_5\}_2\text{N}_2]^{4+}$ and an unidentified oxidation product (97).

Conversion of $[\text{Ru}(\text{NO})(\text{NH}_3)_5]^{3+}$ into trans- $[\text{Ru}(\text{NO})(\text{NH}_3)_4(\text{OH})]^{2+}$ using NaOH is catalysed by RCHO (98). From spectral studies it was suggested that the mechanism was as follows:



Treatment of $[\text{Ru}(\text{NO})(\text{bipy})_2\text{Cl}]^{2+}$ with acetylacetone gave (96), under mild conditions, $[\text{Ru}(\text{N}(\text{O})\text{C}(\text{COMe})_2)_2(\text{bipy})_2\text{Cl}]^+$, which could be isolated. Under more vigorous conditions $\text{MeCOCH}(\text{NO})\text{COMe}$ was obtained.

The nitroprusside ion, $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]$ reacted with N_2H_4 , NH_2OH and NH_3 in the presence of NaOH giving $\text{Na}_3[\text{FeL}(\text{CN})_5]$ ($\text{L} = \text{N}_2, \text{N}_2\text{O}, \text{N}_2\text{H}_4, \text{NH}_3$ or H_2O) and $\text{Na}_4[\text{Fe}(\text{CN})_5\text{X}]$ ($\text{X} = \text{N}_3$ or NO_2) (100).

METAL ATOM CLUSTERS

A new method has been outlined for assigning energies to the metal-metal and metal-ligand bonds of metal carbonyl clusters using lengths (d) and strengths (E) of bonds in metals as a basis (101). It was assumed that $E(\text{M-M})$ was proportional to $[d(\text{M-M})]^{-k}$, and the method revealed that the metal-metal bonds were generally weaker, and the metal-ligand bonds generally stronger than the values derived from previous treatments. It was also shown that the strength of bonding of CO to a particular metal increased with cluster nuclearity.

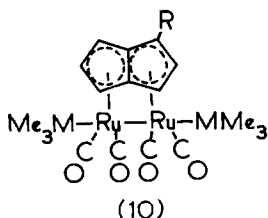
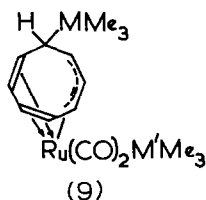
Species containing Two Transition Metals

Homobimetallic Compounds. A systematic m.o. study has been made of the electronic structure of complexes containing the $\text{Fe}_2(\text{CO})_6$ fragment bonded to acetylenes, C_4R_4 groups (as in ferroles), C_6R_6 (flyover bridges), dienes, azulenes, C_8H_8 , pentalenes, tetramethyleneethane, cycloheptatrienyl, hexatrienes, etc. (102).

The structure of $[\text{PPN}][\text{Fe}_2(\text{CO})_8\text{H}]$, obtained by reaction of $\text{Fe}_2(\text{CO})_9$ with KOH and $[\text{PPN}]\text{Cl}$, has been determined crystallographically (103). The complex contains two symmetrical $\mu\text{-CO}$ and are symmetrical $\mu\text{-H}$ ligands, and has a metal-metal bond (2.52 Å).

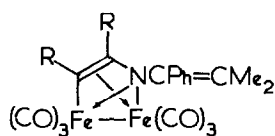
$\text{Fe}_2(\text{CO})_9$ reacted with the germyl silicyclobutane $\text{Ph}_3\text{GeSi}(\text{Me})\overline{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$ affording a polymer which was not characterised (104). However, $\text{Fe}(\text{CO})_5$ or $\text{Ru}_3(\text{CO})_{12}$ reacted with $\text{Me}_2\text{E}(\text{H})\text{XE}(\text{H})\text{Me}_2$ ($\text{E} = \text{Si}$ or Ge , $\text{X} = \text{O}$; $\text{E} = \text{Si}$, $\text{X} = \text{CH}_2$) giving $\text{M}_2(\text{CO})_8(\text{Me}_2\text{EXE})_2$ (105). Each metal is formally six-coordinate (including the M-M bond) and is bridged by the $[\text{Me}_2\text{E-X-EMe}_2]^{2-}$ ligand.

$\text{Cis-Ru}(\text{CO})_4(\text{MMe}_3)(\text{M}'\text{Me}_3)$ ($\text{M} = \text{M}' = \text{Si}$ or Ge , $\text{M} = \text{Si}$, $\text{M}' = \text{Ge}$) reacted with cyclooctatetraene in refluxing hexane giving (106) the fluxional $\text{Ru}(\text{Ct})_2(\eta^3, \eta^2\text{-C}_8\text{H}_8\text{MMe}_3)(\text{M}'\text{Me}_3)$, 9, ($\text{R} = \text{H}$; $\text{M} = \text{M}' = \text{Si}$, Ge ; $\text{M} = \text{Si}$, $\text{M}' = \text{Ge}$) whose structure was established crystallographically ($\text{M} = \text{M}' = \text{Si}$). However, the same reaction in heptane afforded the pentalene species $\text{Ru}_2(\text{CO})_4(\text{C}_8\text{H}_6)(\text{MMe}_3)_2$ ($\text{M} = \text{Si}$ or Ge), 10 ($\text{R} = \text{H}$). In both reaction solvents, there was competing ring closure, since the 1,2-trimethylene cyclopentadienyl species

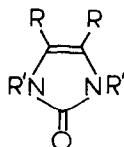


$\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_3\text{CP}_2\text{CH}_2\text{CH}_2)(\text{MMe}_3)$ ($\text{M} = \text{Si}$ or Ge) was formed in both cases. In hexane, $\text{cis-Ru}(\text{CO})_4(\text{SiMe}_3)_2$ reacted with $\text{C}_8\text{H}_7\text{R}$ ($\text{R} = \text{Me}$, Ph or SiMe_3) giving 9 ($\text{M} = \text{M}' = \text{Si}$). In the reaction of $\text{cis-Ru}(\text{CO})_4(\text{GeMe}_3)_2$ in the C_8H_8 , the bridging cyclooctatetraenyl species $\text{Ru}_2(\text{CO})_4(\text{C}_8\text{H}_8)(\text{GeMe}_3)_2$ was formed in addition to 9 ($\text{M} = \text{M}' = \text{Ge}$). In octane, $\text{Ru}(\text{CO})_4(\text{MMe}_3)_2$ reacted with $\text{C}_8\text{H}_7\text{R}$ ($\text{R} = \text{Me}$, Ph or SiMe_3) giving 10, and it was suggested that species of the type 9 are formed on the way to those of type 10. Thus, on heating 9 ($\text{R} = \text{H}$, $\text{M} = \text{M}' = \text{Si}$) in octane, a modest yield of 10 ($\text{R} = \text{H}$, $\text{M} = \text{Si}$) was formed, together with traces of $\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_3\text{CP}_2\text{CH}_2\text{CH}_2)(\text{SiMe}_3)$. Furthermore, on refluxing ($\text{R} = \text{Me}$ or SiMe_3 ; $\text{M} = \text{M}' = \text{Si}$) in octane, 10 ($\text{R} = \text{Me}$ or SiMe_3 ; $\text{M} = \text{Si}$) was formed. A possible mechanism for this reaction was discussed. The structure of 10 ($\text{R} = \text{H}$, $\text{M} = \text{Ge}$) was determined crystallographically and it was shown that the two C atoms common to both rings were bonded to both Ru atoms in the form of a transverse bridge (107). The remaining three atoms of each ring are each bonded as individual η^3 -allyl interannular limits (Ru-Ru distance 3.06 Å).

$\text{Fe}_2(\text{CO})_9$ reacted with 2,2-dimethyl-3-phenyl-2H-azirine giving $\text{Fe}_2(\text{CO})_6\{\text{RNC}(\text{:O})\text{NR}\}$, A ($\text{R} = \text{Me}_2\text{C}=\text{CPh}$) (108). Treatment of this species with Me_3NO released the urea as $(\text{Me}_2\text{C}=\text{CPhNH})_2\text{CO}$. UV irradiation of $\text{PhC}(\text{=CH}_2)\text{N}_3$ with $\text{Fe}(\text{CO})_5$, and mild heating of $\text{H}_2\text{C}=\text{CHNCO}$ with $\text{Fe}_2(\text{CO})_9$ afforded complexes similar to A ($\text{R} = \text{CH}_2=\text{CPh}$ and $\text{CH}_2=\text{CH}$). Reaction of the azirine mentioned above with both $\text{Fe}_2(\text{CO})_9$ and $\text{R}'\text{C}_2\text{R}'$ ($\text{R}' = \text{Ph}$ or CO_2Me) gave 11. A variable temperature ^{13}C n.m.r. spectral study of this complex showed that below -50° the CO ligands of only one of the $\text{Fe}(\text{CO})_3$ groups underwent intramolecular site exchange while above -50° , scrambling between both metal atoms occurred. When $\text{Fe}(\text{CO})_5$ was irradiated, or $\text{Fe}_2(\text{CO})_9$ in benzene treated, with the 1,4-diazadiene $\text{R}'\text{N}=\text{CRCR}=\text{NR}'$, $\text{Fe}_2(\text{CO})_6(\text{R}'\text{NCRNR}'')$ was formed (109) together with some of the heterocycle 12 ($\text{R} = \text{H}$, $\text{R}' = \text{Bu}^t$, C_6H_{11} ; $\text{R} = \text{Me}$, $\text{R}' = \text{p-MeOC}_6\text{H}_4$). The structure of the di-iron complex where $\text{R} = \text{H}$, $\text{R}' = \text{C}_6\text{H}_{11}$ was determined by X-ray methods.



(11)



(12)

$\text{Fe}_2(\text{CO})_9$ reacted with $(\text{MeO})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OMe})_2$ (L-L) giving $(\text{OC})_4\text{Fe-L-L-Fe}(\text{CO})_4$ (110), and with $\text{Bu}^t\text{C}_2\text{PPh}_2$ affording $\text{Fe}(\text{CO})_4(\eta^2\text{-Bu}^t\text{C}_2\text{PPh}_2\text{Fe}(\text{CO})_4)$ (111). When 2-chloro-1,3,2-dioxaphosphorinane reacted with $\text{Fe}_3(\text{CO})_{12}$ in benzene, the species $[\text{Fe}(\text{CO})_3(\eta^2\text{-POCH}_2\text{CMe}_2\text{CH}_2\text{N})]_2$ was formed (112). From VT n.m.r. spectral studies it was established that the heterocyclic organophosphorus ring was fluxional down to temperatures less than -75°C , and that the Fe_2P_2 ring was fluxional at

higher temperatures. An X-ray crystallographic study of the complex established (113) that the molecule had a "butterfly" geometry typical of the general class $[\text{Fe}(\text{CO})_3(\mu_2\text{-X})]_2$ (Fe-Fe 2.68 Å). There was no indication of steric interactions between the phosphorinane rings which might distort the molecule sufficiently so as to lower the barrier to Fe_2P_2 ring inversion.

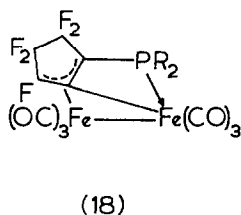
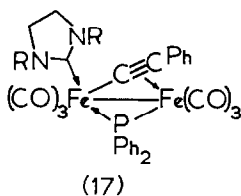
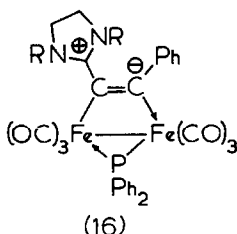
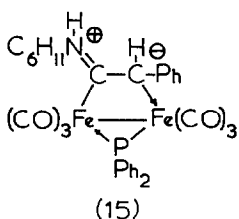
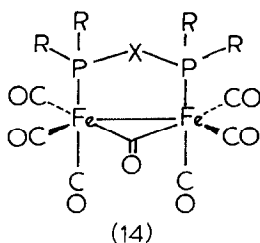
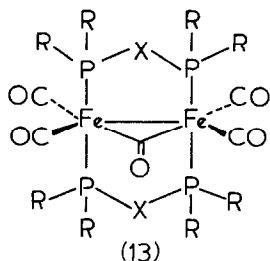
When $\text{Fe}(\text{CO})_5$ was heated with the cyclic diphosphine $\overline{\text{P}(\text{Ph})\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{CH}_2}$, the species $\text{Fe}_2(\text{CO})_6\{\mu_2\text{-PPh}(\text{CH}_2)_3\text{PPh}\}$, A, and $(\text{OC})_3\text{Fe}\{\overline{\text{P}(\text{Ph})\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{CH}_2}\}\text{Fe}(\text{CO})_3$ were formed (114). Photolysis of A with PPhMeR (R = Me or CH_2Ph) gave $\text{Fe}_2(\text{CO})_5(\text{PPhMeR})\{\mu_2\text{-PPh}(\text{CH}_2)_3\}$, and of $[\text{Fe}(\text{CO})_3(\mu_2\text{-AsMe}_2)]_2$ with the same ligand a mixture of $\text{Fe}_2(\text{CO})_5(\text{PPhMeR})(\mu_2\text{-AsMe}_2)_2$ and $(\text{OC})_3\text{Fe}(\mu_2\text{-AsMe}_2)_2\text{Fe}(\text{CO})(\text{PPhMeR})_2$. A VT ^{13}C n.m.r. spectral study of these species revealed no averaging of the diastereotopic CO ligand sites, which indicated that (a) there was no intramolecular metal-metal CO ligand interchange, (b) there were two processes which averaged the CO ligand on a given metal terminus, (c) neither of these processes was a formal Berry pseudo-rotation, at least on the $\text{Fe}(\text{CO})_2\text{PPhMeR}$ terminus, and (d) that averaging of the bridging ligand alkyl groups was more likely to arise via a non-dissociative molecular deformation rather than by a bridge-opening process.

UV irradiation of a 1:1 mixture of $\text{Fe}(\text{CO})_5$ and $\text{NMe}(\text{PF}_2)_2$ in THF gave $\text{Fe}_2(\text{CO})_5(\text{F}_2\text{PNMePF}_2)_2$, 13 (X = N, Me, R = F) (115). Using excess of $\text{NMe}(\text{PF}_2)_2$, the monomeric $\text{Fe}(\text{CO})(\text{F}_2\text{PNMePF}_2)_2$ was produced. $\text{Fe}_3(\text{CO})_{12}$ reacted with the fluorophosphine group giving 13 (X = NMe, R = F) and $\{\text{Fe}(\text{CO})_3\}_2(\text{F}_2\text{PNMePF}_2)_2$ in which two of the di-phosphine ligands bridge the trigonal bipyramidal $\text{Fe}(\text{CO})_3$ groups, the P atoms occupying apical sites; there was no Fe-Fe bond. With $\text{Fe}_2(\text{CO})_9$, $(\text{OC})_4\text{FeF}_2\text{PNMePF}_2\text{Fe}(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_7(\text{F}_2\text{PNMePF}_2)_2$, 14 (X = NMe, R = F) were formed, the latter containing an Fe-Fe bond, one bridging CO group and one bridging di-phosphine ligand. When $\text{Fe}_3(\text{CO})_{12}$ was photolysed with $\text{NMe}(\text{PF}_2)_2$ in ether, a complex of empirical $\text{Fe}_2(\text{CO})\{\text{MeN}(\text{PF}_2)_2\}_4$ was formed, the CO being replaced by $\text{P}(\text{OMe})_3$ or PPh_3 on irradiation in the presence of the phosphorus ligand (116). An X-ray crystallographic examination of this complex revealed that one of the di-phosphine ligands had been ruptured, so that the species contained two different Fe atoms, bridged by three $\text{F}_2\text{PNMePF}_2$ ligands and a PF_2 group, and one atom carried the CO group and the other a $[\text{PF}_2(=\text{NMe})]^-$ ligand. The Fe-Fe distance was 2.73 Å.

The structure of $\text{Fe}_2(\text{CO})_5\{(\text{EtO})_2\text{POP}(\text{OEt})_2\}_2$, 13 (X = O, R = OEt) and $\text{Fe}_2(\text{CO})_7\{(\text{EtO})_2\text{POP}(\text{OEt})_2\}$, 14 (X = O, R = OEt) have been determined crystallographically (117). In the former, the Fe-Fe distance is 2.67 Å, and from VT ^{13}C n.m.r. spectral studies it was established that the four coplanar groups underwent intramolecular site exchange via opening and closing of pairs of CO bridges. In the latter complex there were two fluxional processes, one the same as that in 13 (X = O, R = OEt) involving the exchange of only the four coplanar CO groups; and the second involving local intramolecular exchange on each Fe

atom. These two processes combined to effect complete site exchange of all the CO groups.

Nucleophilic attack by $\text{NH}_2\text{C}_6\text{H}_{11}$ on $\text{Fe}_2(\text{CO})_6(\mu_2\text{-PPh}_2)(\mu_2\text{-C}_2\text{Ph})$ afforded (118) the zwitterionic species $\text{Fe}_2(\text{CO})_6(\mu_2\text{-PPh}_2)\{\mu_2\text{-C}(\text{H}^+\text{NHC}_6\text{H}_{11})\text{Ph}\}$ and $\text{Fe}_2(\text{CO})_6(\mu_2\text{-PPh}_2)\{\mu\text{-C}(\text{NHC}_6\text{H}_{11})\text{CHPh}\}$, 15. The structures of these complexes were established crystallographically, and there was some discussion of the mechanism whereby these complexes were formed. Addition of $\text{PH}(\text{C}_6\text{H}_{11})_2$ to $\text{Fe}(\text{CO})_6(\mu_2\text{-PPh}_2)(\mu_2\text{-C}_2\text{Ph})$ gave $\text{Fe}_2(\text{CO})_6(\mu_2\text{-PPh}_2)\{\mu_2\text{-C}(\text{C}(\text{PH}(\text{C}_6\text{H}_{11})_2)\text{Ph})\}$, whose structure was established by X-ray methods (119). The bridging C atom is trigonal, and the $\text{C}=\text{C}(\text{PR}_3)\text{C}(\text{phenyl})$ system is virtually planar. Thus the unusual attack by a neutral nucleophile ($\text{NH}_2\text{C}_6\text{H}_{11}$ or $\text{PH}(\text{C}_6\text{H}_{11})_2$) at a C atom in a neutral complex ($\text{Fe}_2(\text{CO})_6(\mu_2\text{-PPh}_2)(\mu_2\text{-C}_2\text{Ph})$) appears to be general.

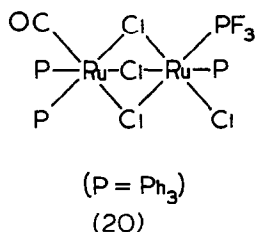
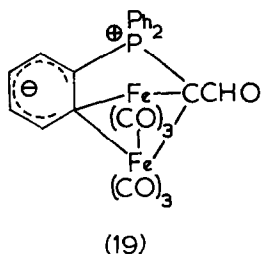


Addition of the 'electron rich' olefin $(\overline{\text{CN}(\text{R})\text{CH}_2\text{CH}_2\text{NR}})_2$ $\text{R} = \text{Bu}^t$ or Ph) to $\text{Fe}_2(\text{CO})_6(\mu_2\text{-PPh}_2)(\mu_2\text{-C}_2\text{Ph})$ gave 16 ($\text{R} = \text{Bu}^t$ or Ph) and 17 ($\text{R} = \text{Bu}^t$) (120). The structure of 16 ($\text{R} = \text{Me}$) was confirmed crystallographically.

Reaction of $\text{Fe}(\text{CO})_5$ with $\text{R}_2\text{PC}(\text{CFCF}_2\text{CF}_2\text{CF}_2)$ gave $\text{Fe}_2(\text{CO})_6[\text{R}_2\text{PCCFCF}_2\text{CF}_2]$ 18, and the structure of the complex where $\text{R} = \text{C}_6\text{H}_{11}$ was determined by X-ray methods (121). Treatment of $\text{Fe}_3(\text{CO})_{12}$ with $(\text{Me}_3\text{Sn})_2\text{C}=\text{PPh}_2$ afforded

$\text{Fe}_2(\text{CO})_6\{\text{C}(\text{CHO})\text{PPh}_2(\text{C}_6\text{H}_4)\}$, 19, whose structure was also confirmed crystallographically (122).

Reaction of $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$ or $\text{Fe}_3(\text{CO})_{12}$ with S_8 afforded (123) a mixture of $\text{Fe}_2(\text{CO})_6\text{S}_2$, $\text{Fe}_3(\text{CO})_9\text{S}_2$, FeS and CO . With H_2S , $\text{Fe}_3(\text{CO})_{12}$ gave $\text{Fe}_2(\text{CO})_6\text{S}_2$ which subsequently reacted with more $\text{Fe}_3(\text{CO})_{12}$ giving $\text{Fe}_3(\text{CO})_9\text{S}_2$. A series of complexes $[\text{Fe}(\text{CO})_3(\mu_2\text{-SR})]_2$ where R is a long-chain alkyl group have also been prepared, and their reactions with oxidising and reducing agents studied (123, 124). On heating $[\text{Fe}(\text{CO})_3(\mu_2\text{-SR})]_2$ under nitrogen, RSR was formed, whereas when heated in air, the complex decomposed giving RSSR (124). Heating $\text{Fe}_3(\text{CO})_{12}$ with a 1:1 mixture of RSH and $\text{R}'\text{SH}$ afforded $[\text{Fe}(\text{CO})_3(\mu_2\text{-SR})]_2$, $[\text{Fe}(\text{CO})_3(\mu_2\text{-SR}')]_2$ and $[\text{Fe}(\text{CO})_3(\mu_2\text{-SR})(\mu_2\text{-SR}')]$. On heating a 1:1 mixture of $[\text{Fe}(\text{CO})_3(\text{SR})]_2$ and $[\text{Fe}(\text{CO})_3(\text{SR}')]_2$ in air, mixtures of RSSR , RSSR' and $\text{R}'\text{SSR}'$ were isolated (124).



When $\text{Ru}_3(\text{CO})_{12}$ was heated with PBU_3^t in methanol, or when $\text{Ru}(\text{CO})_3(\text{PBU}_3^t)_2$ was refluxed in methanol, $[\text{Ru}(\text{CO})_2(\text{PBU}_3^t)(\mu_2\text{-OME})]_2$ was formed (125).

Reaction of $\text{Ru}(\text{CO})(\text{PPh}_3)_3\text{H}_2$ with HCl afforded (126) two isomers of $(\text{Ph}_3\text{P})_2(\text{OC})\text{Ru}(\mu_2\text{-Cl})_3\text{Ru}(\text{CO})(\text{PPh}_3)\text{Cl}$, which reacted with PF_3 giving $(\text{Ph}_3\text{P})(\text{OC})\text{Ru}(\mu_2\text{-Cl})_3\text{Ru}(\text{PPh}_3)(\text{PF}_3)\text{Cl}$, also as two isomers. The structure of the major isomer of the PF_3 complexes, 20, was determined by X-ray methods.

Heterobimetallic Species. Reaction of $\text{K}_2\text{Fe}_2(\text{CO})_8$ with SnClPh_3 and SnCl_2Ph_2 gave $[\text{Fe}(\text{CO})_4\text{SnPh}_3]_2$ and $[\text{Fe}(\text{CO})_4\text{SnClPh}_2]_2$, both with Fe-Fe bonds, respectively (127). Similar complexes containing SnMe_3 and SnClMe_2 were prepared.

$\text{Fe}(\text{CO})_5$ reacted with $\text{Nb}(\eta\text{-C}_5\text{H}_5)_2\text{H}_3$ giving $(\eta\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-H})\text{Fe}(\text{CO})_4$ (128). The structure of this species was determined by X-ray methods, and it was shown to contain a Nb-Fe bond (3.32 Å); the Nb-H-Fe bond angle was 141° . During the formation of this complex, a ^1H n.m.r. spectral study of the reaction mixture established the existence of transient formyl species.

$\text{K}_2\text{Fe}(\text{CO})_4$ reacted with $\text{M}(\text{CO})_4(\text{AsMe}_2\text{Cl})_2$ giving $(\text{OC})_3\text{Fe}(\mu_2\text{-AsMe}_2)_2\text{M}(\text{CO})_4$ (M = Cr, Mo or W) (129). Treatment of $\text{Fe}(\text{CO})_2\text{L}_2(\eta^2\text{-CS}_2)$ (L = $\text{P}(\text{OMe})_3$, PMe_3 or PMe_2Ph) with $\text{M}(\text{CO})_6$ and $\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{THF})$ afforded $\text{Fe}(\text{CO})_2\text{L}_2(\eta^2\text{-SC=Q})$ where Q = $\text{M}(\text{CO})_5$ or $\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2$ (130).

Treatment of PPh_2Cl with $\text{LiCo}_3(\text{CO})_{10}$ or $\text{Co}_2(\text{CO})_8$ gave an intermediate $\text{Co}(\text{CO})_4(\text{PPh}_2)$ which could be trapped using $\text{Fe}_2(\text{CO})_9$. This afforded $(\text{OC})_3\text{Co}(\mu_2\text{-PPh}_2)\text{Fe}(\text{CO})_4$, which contained a Co-Fe bond (131). Oxidative addition of $\text{Fe}(\text{CO})_2(\text{pyr})_2(\text{HgCl})_2$ to $\text{Pt}(\text{PPh}_3)_2$ afforded $(\text{ClHg})(\text{pyr})_2(\text{OC})_2\text{FeHgPt}(\text{PPh}_3)_2\text{Cl}$ (132). At room temperature this complex eliminated $\text{Hg}(\text{O})$ giving $(\text{ClHg})(\text{pyr})_2(\text{OC})_2\text{FePt}(\text{PPh}_3)_2\text{Cl}$ which further reacted with $\text{Pt}(\text{PPh}_3)_3$ giving $(\text{pyr})_2(\text{OC})_2\text{Fe}\{\text{HgPt}(\text{PPh}_3)_2\text{Cl}\}\{\text{Pt}(\text{PPh}_3)_2\text{Cl}\}$ and then, at -30° , $(\text{pyr})_2(\text{OC})_2\text{Fe}\{\text{Pt}(\text{PPh}_3)_2\text{Cl}\}_2$.

Species containing Three Transition Metals

Homotrimetallic Compounds. Extended Hückel m.o. calculations have been made (133) on $\text{Ru}_3(\text{CO})_{12}$ and assignments made of the compound's electronic spectrum measured at various temperatures. Calculations were also made on $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Os}$), $\text{Ru}_3(\text{CO})_9(\text{PEtPh}_2)_3$, $\text{Fe}_n\text{Ru}_{3-n}(\text{CO})_{12}$ ($n = 0 \rightarrow 3$) and $[\text{Mn}(\text{Fe}_2)(\text{CO})_{12}]^-$. The single crystal polarised electronic spectrum of $\text{Fe}_3(\text{CO})_{12}$ was measured, and an m.o. scheme constructed for $\text{M}_2\text{Fe}(\text{CO})_{14}$ ($\text{M} = \text{Mn}, \text{Re}$).

Negative-ion mass spectral studies have been made of $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$), $\text{MM}'_2(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{M}' = \text{Ru}; \text{M} = \text{Ru}, \text{M}' = \text{Os}; \text{M} = \text{Os}, \text{M}' = \text{Ru}$), $\text{M}_3(\text{CO})_{11}(\text{PEt}_2\text{Ph})$ ($\text{M} = \text{Ru}, \text{Os}$) and $\text{Fe}_3(\text{CO})_9\text{X}_2$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$) (134).

A review paper has appeared concerning synthetic methods of activation of osmium carbonyl clusters (135). In this connection, reaction of $\text{Os}_3(\text{CO})_{12}$ with Me_3NO has been particularly effective (135,136). Thus, in the presence of the amine oxide and C_2H_4 , CH_3CN or pyridine, the species $\text{Os}_3(\text{CO})_{11}\text{L}$ ($\text{L} = \text{C}_2\text{H}_4, \text{CH}_3\text{CN}$ or pyr) have been obtained. The species $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ is a useful intermediate, reacting with Lewis bases L ($\text{CO}, \text{PPh}_3, p\text{-MeC}_6\text{H}_4\text{SO}_2\text{NC}, \text{C}_2\text{H}_4$ or pyr) giving $\text{Os}_3(\text{CO})_{11}\text{L}$, and with H_2 and HX affording $\text{Os}_3(\text{CO})_{11}$ and $\text{Os}_3(\text{CO})_{10}\text{HX}$ ($\text{X} = \text{Cl}, \text{Br}$ or I). The bis-acetonitrile species $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ may be obtained either from $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ or via reaction of $\text{Os}_3(\text{CO})_{10}\text{H}_2$ with cyclooctene, which gave initially $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2$, the olefin then being displaced by MeCN . Treatment of the bis-acetonitrile adduct with Lewis bases L gave $\text{Os}_3(\text{CO})_{10}(\text{NCMe})\text{L}$ and $\text{Os}_3(\text{CO})_{10}\text{L}_2$.

NMR spectral data obtained from $\text{Fe}_3(\text{CO})_{12}$, principally via ^{57}Fe - ^{13}C coupling, established (137) that CO scrambling in the complex is intramolecular. A survey was also made of site exchange by CO group in various other $\text{Fe}(\text{CO})_3$ systems (137). A kinetic study of the substitution and fragmentation reactions of $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_3)$ and $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ has been made in decalin (138). At most temperatures (25 - 75°C), the complexes underwent substitution reactions with PPh_3 , but only the bis-phosphine species underwent simple substitution with CO. The retarding effect of CO in reactions with PPh_3 is quantitatively consistent with a simple CO-dissociation mechanism, but the considerable labilisation, compared with $\text{Ru}_3(\text{CO})_{12}$, caused by the presence of PPh_3 suggests a more complex mechanism is operating. Between 130 and 170°C , both complexes underwent fragmentation to

give monomeric species at rates independent of CO and PPh_3 . Activation enthalpies for the fragmentation of $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_3)_n$ ($n = 1 \rightarrow 3$) increased dramatically as n increased, with an almost compensating increase in ΔS^\ddagger . These trends were rationalised in terms of steric effects operating on proposed intermediates such as $\text{Ru}_2(\text{CO})_{8-n}(\text{PPh}_3)_n$ ($n = 0 \rightarrow 2$).

Reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{MeSi}(\text{PBU}_2)_3$ afforded $\text{Ru}_3(\text{CO})_9\{(\text{PBU}_2)_3\text{SiMe}\}$, in which each Ru atom was attached to one PBU_2 group, and the Ru-Ru bonds were each bridged asymmetrically by one CO group (established by X-rays) (139). In spite of the CO bridges and the capping-ligand, the Ru-Ru bond distances (2.92 Å) were significantly longer than those formed in non-bridged Ru_3 clusters (2.80-2.87 Å). The P-Si-P angle was notably smaller than tetrahedral, and it was said that all the distortions were due to imperfect "tailoring" of the capping ligand which introduced considerable strain into the complex.

The silylated phosphine, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OEt})_3$ reacted (140) with $\text{Os}_3(\text{CO})_{12}$ in toluene giving $\text{Os}_3(\text{CO})_{11}\{\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3\}$. Treatment of this with silica gel (SIL) afforded the anchored complex $\text{Os}_3(\text{CO})_{11}\{\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiSIL}\}$, which could also be obtained by pretreating the silica gel with the phosphine and then adding $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$. $\text{Os}_3(\text{CO})_{12}$ also reacted with $\text{CH}_2=\text{CHSi}(\text{OEt})_3$ giving, initially, $\text{Os}_3(\text{CO})_9\text{H}(\text{C}_2\text{Si}(\text{OEt})_3)$ which, on treatment with silica gel, was converted to the silica-bound species $\text{Os}_3(\text{CO})_9\text{H}(\text{C}_2\text{SiSIL})$. Treatment of $\text{Os}_3(\text{CO})_{10}\text{H}_2$ with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiSIL}$ gave $\text{Os}_3(\text{CO})_{10}\text{H}_2\{\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiSIL}\}$ which, on refluxing in hexane, was converted to $\text{Os}_3(\text{CO})_9\text{H}_2\{\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiSIL}\}$.

A semi-empirical method for predicting the location of H atoms in metal carbonyl hydride clusters, using X-ray structural information, has been described (141). The method was satisfactorily tested with $\text{Os}_3(\text{CO})_{10}\text{H}_2$, $\text{Os}_3(\text{CO})_9(\text{H})_2\text{S}$, $\text{Os}_3(\text{CO})_{10}\text{H}(\text{C}_2\text{H}_3)$, $\text{Ru}_3(\text{CO})_9\text{H}(\text{C}_2\text{Bu}^t)$ and $\text{FeCo}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_3\text{H}$. Qualitative agreement was found between the predicted and known positions in $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_3\text{H}_2$, and in $\text{Os}_6(\text{CO})_{18}\text{H}_2$, it was predicted that the two H atoms would each bridge two metal atoms on opposite edges of the capped tetragonal bipyramidal structure. It was also predicted that in $\text{Os}_4(\text{CO})_{11}\text{H}(\text{C}_6\text{H}_9)$, two H atoms would bridge two Os-Os bonds and the other might occupy an Os_4 face of the molecule.

Protonation of $[\text{PPN}][\text{Fe}_3(\text{CO})_{11}\text{H}]$ in deuteriodichloromethane at -90° by fluorosulphuric acid afforded $\text{Fe}_3(\text{CO})_{11}\text{H}_2$ (142). The structure of this species was suggested, on the basis of ^1H and ^{13}C n.m.r. studies, to be analogous to $\text{Fe}_3(\text{CO})_{12}$, in having one edge of the metal triangle bridged by H and by a $\text{C}=\text{OH}$ group.

An X-ray and neutron-diffraction study of $\text{Os}_3(\text{CO})_{10}\text{H}_2$ established (143) that Os-H-Os bridges were symmetrical, that Os-H = 1.85 Å and the Os-H-Os angle was 93° . The metal-metal distance in the bridged bond was 2.68 Å whereas the other distances were 2.98 Å. A similar structural study was made of $\text{Os}_3(\text{CO})_{10}\text{H}(\text{C}_2\text{H}_3)$ where the Os-H distance averaged 1.84 Å (it was slightly

asymmetrical), and the Os-H-Os angle was 101° . The bridged Os-Os distance was 2.92 \AA while the unbridged bond lengths averaged 2.96 \AA .

VT ^{13}C n.m.r. spectral studies of $\text{Os}_3(\text{CO})_{10}\text{HX}$ ($\text{X} = \text{SEt}, \text{SPh}, \text{NBu}^n\text{H}, \text{OH}, \text{Cl}, \text{Br}, \text{I}, \text{CO}_2\text{Me}, \text{CO}_2\text{CF}_3$) have given (144), in some instances, conclusive proof of CO ligand exchange processes involving polytopal rearrangements in an $\text{Os}(\text{CO})_4$ group.

Treatment of $\text{Os}_3(\text{CO})_{12}$ with KOH in methanol afforded (145) $[\text{Os}_3(\text{CO})_{11}\text{H}]^-$, whose structure, determined by low T ^{13}C n.m.r. spectroscopy, was similar to that of $[\text{Fe}_3(\text{CO})_{11}\text{H}]^-$ (146); i.e. in having two $\text{Os}(\text{CO})_3$ groups bridged by H and CO. Treatment of this anion, as the PPN^+ salt, with H_3PO_4 , HCl(gas) and I_2 gave $\text{Os}_3(\text{CO})_{11}\text{H}(\text{OH})$, $\text{Os}_3(\text{CO})_{11}\text{H}_2$ (which decarbonylated readily to $\text{Os}_3(\text{CO})_{10}\text{H}_2$ and $\text{Os}_3(\text{CO})_{10}\text{HI}$). The anion also reacted with $\text{Os}_6(\text{CO})_{18}$ giving $\text{H}(\text{OC})_{10}\text{Os}_3(\mu_3\text{-CO}_2)\text{Os}_6(\text{CO})_{17}$, which has a known structure (147) where an Os_3 unit is linked to an Os_6 cluster by a bridging CO_2 group; the C atom being attached to one metal atom of the Os_6 cluster while the two O atoms are each bonded to a metal in the Os_3 triangle. From ^{13}C n.m.r. studies it was established that the CO_2 group arose from $\text{Os}_6(\text{CO})_{18}$. Treatment of this Os_9 species with HCl gave $\text{Os}_6(\text{CO})_{18}$ and $\text{Os}_3(\text{CO})_{10}\text{HCl}$, and with H_2SO_4 , $\text{Os}_6(\text{CO})_{18}$ and $\text{Os}_3(\text{CO})_{10}\text{H}(\text{OH})$ was formed.

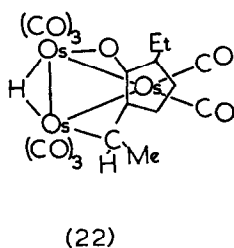
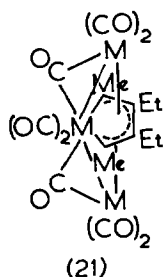
Methylation of $[\text{Os}_3(\text{CO})_{11}\text{H}]^-$ by MeOSO_2F afforded $\text{Os}_3(\text{CO})_{10}\text{H}(\text{COMe})$ and some $\text{Os}_3(\text{CO})_{10}\text{H}(\text{O}_2\text{CMe})$ (148). The ethyl analogue was obtained using $[\text{Et}_3\text{O}][\text{BF}_4]$, and reaction of $\text{Os}_3(\text{CO})_{10}\text{H}(\text{COMe})$ with CNBu^t afforded $\text{Os}_3(\text{CO})_9(\text{CNBu}^r)\text{H}(\text{COMe})$. The structure of these species was thought to involve a $(\text{OC})_3\text{Os-Os}(\text{CO})_3$ unit bridged by H and by $>\text{COR}$, thereby making the species different to previously described acyl derivatives (149). A VT ^{13}C n.m.r. spectral study of these compounds and of $\text{Fe}_3(\text{CO})_{10}\text{H}(\text{COMe})$ showed that there was no intramolecular CO exchange between the metal centres, but there was localised scrambling on the $\text{M}(\text{CO})_3$ and $\text{M}(\text{CO})_4$ groups; the alkyl groups also underwent 'flipping'.

Reaction of $\text{Os}_3(\text{CO})_{10}\text{D}_2$ with CH_2N_2 afforded a series of mixed hydrido/deuterio alkyl species " $\text{Os}_3(\text{CO})_{10}\text{CD}_2\text{H}_2$ " (150,151). From ^1H n.m.r. studies it was established (150) that in solution a mixture of species containing Os-CH_3 , $\text{Os-CH}_2\text{D}$ and OsCHD_2 groups was present indicating the possibility of an interaction of the type $\text{Os} \begin{array}{c} \text{CH}_2 \\ \text{---} \text{H} \\ \text{---} \end{array} \text{Os}$. It was further shown (151) that there was a preference for H over D in the hydride bridging site. A neutron diffraction study of the solid obtained from this reaction established that the molecule could be formulated as $\text{Os}_3(\text{CO})_{10}(\mu_2\text{-H})_2(\mu_2\text{-CH}_2)$, in which the Os-Os bond was bridged both by hydrogen and by the methylene group (Os-Os 2.83 \AA , Os-C 2.15 \AA , HCH angle 106°).

The species $\text{Os}_3(\text{CO})_{10}\text{H}(\mu_2\text{-COR})$ and $\text{Os}_3(\text{CO})_{10}\text{H}(\mu_2\text{-OCH=CR}_2)$ ($\text{R} = \text{H}, \text{Me}$ or Ph) could be decarbonylated thermally (152) giving unstable intermediates $\text{Os}_3(\text{CO})_{10}\text{H}(\text{R})$ which then underwent either α -elimination or o-metallation giving species containing μ_3 -liganded species, e.g. CH , C_6H_4 or PhCC_6H_4 . $\text{Ru}_3(\text{CO})_{12}$

reacted with RC_2H ($R = Bu^n$ or Pr^n) giving $Ru_3(CO)_9(\mu_2-H)(C_2R)$, in which it was suggested (153) that the acetylide residue was bonded to a $Ru(CO)_3$ opposite the $(CO)_3Ru-H-Ru(CO)_3$ group. However, when RC_2CH_2R' ($R = Et, R' = Me; R = Me, R' = Me, Et$) was used, $Ru_3(CO)_{10}(\mu_2-H)(CR=C=CHR')$ was thought to be formed where alkene residue was bonded to a Ru atom of the $(CO)_3RuHRu(CO)_3$ system. On heating, this species isomerised to the $\mu_3-\eta^3$ -allyl species $Ru_3(CO)_9(RCCHCR')$. Treatment of the last compound where $R = R' = Me$ with PhC_2Ph or MeC_2Et gave $Ru_3(CO)_8\{MeCC(Et)C(Ph)CPh\}$ or a mixture of $Ru_3(CO)_8\{MeCC(Et)CRCR'\}$ ($R = Me, R' = Et$ or $R = Et, R' = Me$), 21 ($M = Ru$). Thermolysis of $MeOs(CO)_4Os(CO)_4Os(CO)_4Me$ at 90° in solution gave $Os_3(CO)_{12}$ and methane, apparently by attack of methyl radicals on the solvent (154). With one equivalent of HBr , the dimethyl species was converted into $MeOs(CO)_4Os(CO)_4Os(CO)_4Br$, but with an excess of HBr , both methyl groups were eliminated, with formation of $BrOs(CO)_4Os(CO)_4Os(CO)_4Br$. Iodination gave a mixture of cis- $Os(CO)_4(Me)I$ and $MeOs(CO)_4Os(CO)_4I$, while ICl afforded as cis- $Os(CO)_4(Me)X$ ($X = Cl$ or I) and $Os_2(CO)_8(Me)X$ ($X = Cl; X = I$ major product). With Br_2 , cis- $Os(CO)_4XBr$ and $Os_2(CO)_8XBr$ ($X = Me$ or Br) were obtained. Treatment of $HOs(CO)_4Os(CO)_4Me$ with PPh_3 afforded $HOs(CO)_3(PPh_3)Os(CO)_4Me$ as two isomers. It appeared that $Os_2(CO)_8H(Me)$ underwent substitution much more rapidly than either cis- $Os(CO)_4H_2$ or cis- $Os(CO)_4H(Me)$.

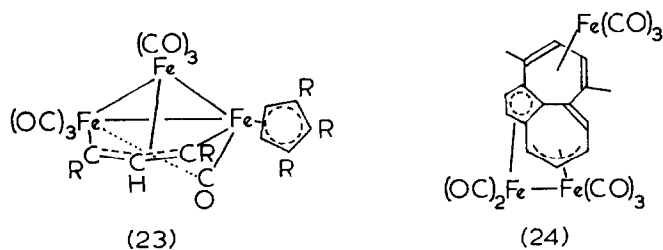
Reaction of $Ru_3(CO)_{12}$ with HC_2CH_2Me caused (155) hydrogen-transfer, alkyne oligomerisation and formation of $Ru_3(CO)_9H(C_2CMe_3)$ as the main product. Treatment of $Os_3(CO)_{10}(NCMe)_2$ with triethylamine afforded (156) both $Os_3(CO)_{10}H_2$ and $Os_3(CO)_{10}H(CHCHNET_2)$. From an X-ray structural determination of the latter it was established that one $Os-Os$ bond was bridged by H and by the group $CHCH=NEt_2$.



On heating $Os_3(CO)_8\{(EtC_2H)_2(CO)\}$, which was obtained in the reaction between $Os_3(CO)_{10}H_2$ and HC_2Et and contains an osmacyclohexadienone ring, the species $Os_3(CO)_8(\mu_2-H)\{C(O-)(CHMe)CHCHCtEt\}$ 22, was obtained (157). The structure of this compound was established by X-ray methods. The $Os(CO)_2$ group which is π -bonded to the tri-substituted cyclopentadienyl ring formally has an excess of bonding electrons, while the other two metal atoms have a deficiency. However, the cluster as a whole conforms to the normal 48-electron configuration, and is diamagnetic. Reaction of $Os_3(CO)_{10}H_2$ with $CF_3C_2CF_3$ afforded

$\text{Os}_3(\text{CO})_{10}\text{H}(\text{CF}_3\text{CCHCF}_3)$, in which a CCF_3 group bridges the $(\text{OC})_3\text{OsH}(\text{CO})_3$ group and is bonded to the CHCF_3 residue which, in turn, is σ -bonded to the other metal atom (158). An X-ray crystallographic examination revealed that the metal-metal distance in the $\text{Os}_2(\text{CO})_6(\mu\text{-H})(\mu\text{-CRCF}_3)$ unit was 2.78 \AA while in the other two bonds it was 2.91 \AA .

Reaction of $\text{Fe}_3(\text{CO})_{12}$ with HC_2R ($\text{R} = \text{Et}$ or Pr^n) afforded (159) various complexes including $\text{Fe}_3(\text{CO})_7(\text{HC}_2\text{R})_4$, $\text{Fe}_3(\text{CO})_8(\text{HC}_2\text{R})_3$ and $\text{Fe}_3(\text{CO})_8(\text{HC}_2\text{R})_4$. The structure of the first, 23 ($\text{R} = \text{Et}$), was determined crystallographically. There is at least one asymmetrically bridging CO group, and an $\eta^3\text{-EtCHCH}$ allylic ligand which is also σ -bonded to other two metals.

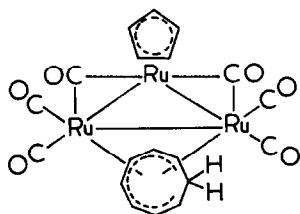


The structures of the previously reported (160) isomers $\text{Os}_3(\text{CO})_{10}(\text{S-cis-C}_4\text{H}_6)$ and $\text{Os}_3(\text{CO})_{10}(\text{S-trans-C}_4\text{H}_6)$ have been determined by X-ray methods (161). The S-cis-isomer has the diene bonded to a single metal atom of the cluster in axial and equatorial positions, whereas the S-trans-isomer has approximate C_2 symmetry, with the diene ligand bridging one Os-Os bond utilising equatorial sites at the adjacent metal centres.

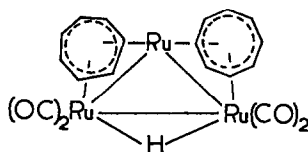
The structure of the aceheptylene complex, $\text{Fe}_3(\text{CO})_8(\text{C}_{14}\text{H}_8\text{Me}_2)$ (24), has been established crystallographically (162). The molecule contains an $\text{Fe}_2(\text{CO})_5$ unit bonded to one face of the ligand, and $\text{Fe}(\text{CO})_3$ group attached to the other face of the non-alternant aromatic ring. The crystals contained an ordered racemic mixture of two enantiomeric forms. The bonding of the $\text{Fe}_2(\text{CO})_5$ fragment is analogous to the metal ligand bonding in $\text{Fe}_2(\text{CO})_5$ (azulene) systems (163) and related to that in $\text{Fe}_2(\text{CO})_5$ (acenaphthylene) (164).

Reaction of $\text{Ru}_3(\text{CO})_{12}$ or $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ with a mixture of C_5H_6 and C_8H_8 in refluxing heptane gave $\text{Ru}_3(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)(\eta^7\text{-C}_8\text{H}_9)$, 25 as the major product (165) together with a small amount of $\text{Ru}_3(\text{CO})_6(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{CH}_2\text{CH}_2)(\eta^7\text{-C}_8\text{H}_9)$ in which the cyclopentadienyl ring in 25 is replaced by the trihydropentalenyl ring analogous to that in $\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{CH}_2\text{CH}_2)\text{MMe}_3$ (166). This latter species may also be obtained, again as a minor product, in the reaction between $\text{Ru}_3(\text{CO})_{12}$ and cyclooctatetraene alone (166). Both species were stereochemically non-rigid. Reaction of $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ with C_5H_6 and cycloheptatriene afforded a mixture of $[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]_2$, $\text{Ru}(\text{CO})_3(\text{C}_7\text{H}_{10})$ and a small amount of $\text{Ru}_3(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)(\eta^7\text{-C}_7\text{H}_7)$ in which the C_8H_9 ring is replaced by a cycloheptadienyl ring, which

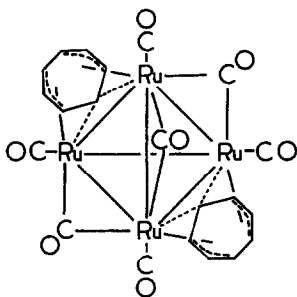
is bonded similarly to that in $\text{Ru}_3(\text{CO})_6(\eta^5\text{-C}_7\text{H}_9)(\eta^7\text{-C}_7\text{H}_7)$ (167). $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ reacted with a mixture of C_7H_8 and C_8H_8 giving about 12 products, many in very low yield. All except four were also formed in the reaction between $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ and C_8H_8 alone (168). Among the products identified were $\text{Ru}_3(\text{CO})_6(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{CH}_2\text{CH}_2)(\eta^7\text{-C}_7\text{H}_7)$, analogous to 25 with a trihydropentalene and cycloheptadienyl ring instead of C_5H_5 and C_8H_9 , the fluxional $\text{Ru}_3(\text{CO})_4\text{H}(\eta^7\text{-C}_7\text{H}_7)(\eta^8\text{-C}_8\text{H}_8)$ (four possible forms of which 26 is the best representation), and $\text{Ru}_4(\text{CO})_7(\eta^7\text{-C}_7\text{H}_7)_2$, 27. Cycloheptatriene reacted with $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ also giving 27, and this tetranuclear species reacted with I_2 giving the known (169) bimetallic $\text{Ru}_2(\text{CO})_4(\eta^7\text{-C}_7\text{H}_7)\text{I}$, 28. While most of the other clusters were destroyed on iodination, 26 was smoothly converted to $\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_3\text{CH}_2\text{CH}_2\text{CH}_2)\text{I}$ and the fluxional $\text{Ru}_2(\text{CO})_4(\eta^7\text{-C}_8\text{H}_9)\text{I}$, which is analogous to 28.



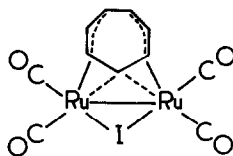
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(26)



(27)

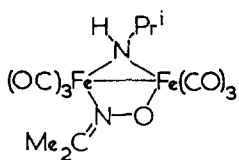


(28)

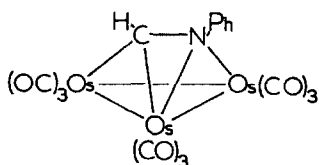
Reaction of $\text{Fe}_3(\text{CO})_{12}$ with EtNO_2 gave $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CO})(\mu_3\text{-NEt})$ in low yield and several other products including $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NEt})_2$, $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NH})(\mu_3\text{-NEt})$, $\text{Fe}_2(\text{CO})_6(\mu_2\text{-NEt})_2$, $\text{Fe}_2(\text{CO})_6\{\mu_2\text{-ON(=CHMe)}\}(\mu_2\text{-NHET})$, $\text{Fe}_2(\text{CO})_6(\mu_2\text{-O=NHET})(\mu_2\text{-N=CHMe})$ and $\text{Fe}_2(\text{CO})_6(\mu_2\text{-NHET})(\mu_2\text{-N=CHMe})$, this last species being the major product (170). Me_2CHNO_2 reacted similarly with $\text{Fe}_3(\text{CO})_{12}$ giving mainly $\text{Fe}_2(\text{CO})_6(\mu_2\text{-ON=CMe}_2)(\mu_2\text{-NHPr}^1)$, and also $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NPr}^1)_2$, $\text{Fe}_2(\text{CO})_6(\mu_2\text{-ON=CMe}_2)(\mu_2\text{-N=CMe}_2)$ (also obtained (171) from $\text{Na}_2\text{Fe}(\text{CO})_4$ and 2-bromo-2-nitropropane), $\text{Fe}_2(\text{CO})_6(\mu_2\text{-NHPr}^1)(\mu_2\text{-N=CMe}_2)$ and $\text{Fe}_2(\text{CO})_6(\mu_2\text{-N=CMe}_2)_2$. The structure of $\text{Fe}_2(\text{CO})_6(\mu_2\text{-ON=CMe}_2)-$

(μ_2 -NHPⁱ), 29, was established crystallographically (Fe-Fe 2.47 Å) and n.m.r. spectral studies showed that there were substantial torsional barriers about the Fe-N and N-O bonds, and localised intramolecular CO ligand exchange at the Fe(CO)₃ groups.

Os₃(CO)₁₂ reacted with benzylamine at 125° to give (172) two complexes, mainly Os₃(CO)₁₀{ μ_2 -OCNH(CH₂Ph)} and some Os₃(CO)₁₀H- $\{\mu_2$ -NH(CH₂Ph)\}, the former being decarbonylated to give the latter. Os₃(CO)₁₀(C₈H₁₄)₂ gave the same products at 60-70°, although the latter predominated. The first species may have a structure containing the bridging system either (OC)₂Os(μ -H)(μ -OCR)Os(CO)₃, where R = NH(CH₂Ph), or (OC)₃Os(μ -H){ μ -C(:O)NHR'}Os(CO)₃ (R' = CH₂Ph). Benzylalcohol also reacted with Os₃(CO)₁₂, giving only Os₃(CO)₁₀(μ_2 -H)(μ_2 -OCH₂Ph). Thermolysis of the μ -benzyloxy species at 146° afforded benzene, benzaldehyde, Os₃(CO)₁₂ and Os₄(CO)₁₂H₄. Related products were obtained from *p*-MeC₆H₄CH₂OH, but PhMeCHOH gave only PhCOMe. It was suggested that these reactions proceeded via the μ -benzyloxy species, via metalation of the benzene ring, giving ultimately Os₃(CO)₉(μ_2 -H)₂(μ_3 -C₆H₄) and its analogues, which decomposed to the appropriate benzenes.



(29)



(30)

The structure of Os₃(CO)₁₀(μ_2 -H)(μ_2 -MeN=CPh), which was obtained by reacting Os₃(CO)₁₂ with N-methylbenzaldiamine (173), has been determined crystallographically (174). The N=C bond length was 1.28 Å and it was believed that the H atom also bridged the same metals as the benzaldimine fragment. Reaction of Os₃(CO)₁₀H₂ with PhNC gave initially Os₃(CO)₁₀H₂(CNPh) which contained terminal and bridging H atoms (175), and a terminal isonitrile ligand. On refluxing in di-n-butylether, Os₃(CO)₉H(CHNPh), 30, was formed, whose structure was determined by X-ray techniques. The C-N bond distance (1.42 Å) is very long and although the H atom attached to the unique C atom was detected, the hydridic H atom was not. Reaction of Ru₃(CO)₁₂ with the diazine C₆H₁₁N₂ in toluene gave Ru₃(CO)₁₂(μ_2 -NCO)(μ_2 -N=C₆H₁₀) (X-ray structure determined) (176).

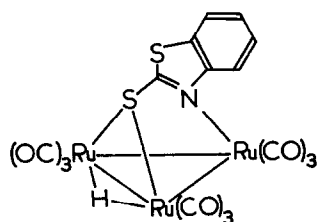
Phenol reacted with Os₃(CO)₁₂ giving, in a reaction dependent on temperature, Os₃(CO)₁₀(μ_2 -H)(μ_2 -OPh), Os₃(CO)₁₀(μ_2 -OPh)₂ and Os₃(CO)₉(μ_2 -H)₂(OC₆H₄), in which the aromatic ring is metalated by an Os(CO)₃ fragment *ortho* to the O atom (179).

Fe₃(CO)₁₂ reacted with H₂S as a gas at 50-55° giving Fe₂(CO)₆S₂ which combined further with Fe₃(CO)₁₂ giving Fe₃(CO)₉S₂ (178). Treatment of [Os₃(CO)₉(μ_2 -H)(μ_3 -S)]⁻ with R₃O⁺ gave Os(CO)₉(μ_2 -H)(μ_3 -SR) (R = Me or Et) which

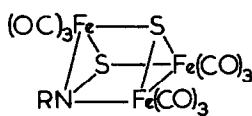
reacted further with L giving $\text{Os}_3(\text{CO})_9\text{L}(\mu_2\text{-H})(\mu_2\text{-SR})$ (L = CO, PPh_3 , MeCN, C_2H_4) (179). $\text{Os}_3(\text{CO})_9(\text{C}_2\text{H}_4)(\mu\text{-H})(\mu\text{-SMe})$ could also be obtained from $\text{Os}_3(\text{CO})_{10}\text{H}(\text{SMe})$ and Me_3NO in the presence of C_2H_4 , and reacted with ethylene at 125° giving $\text{Os}_3(\text{CO})_9(\mu_2\text{-H})(\mu_2\text{-CH=CH}_2)(\mu_3\text{-S})$. This last species was also obtained by treatment of $\text{Os}_3(\text{CO})_9\text{H}(\text{SH})$ with Me_3NO and C_2H_4 , which afforded $\text{Os}_3(\text{CO})_8\text{H}_2(\text{C}_2\text{H}_4)\text{S}$, and further reaction of this with acetylene. The structure of $\text{Os}_3(\text{CO})_{10}(\mu_2\text{-H})(\mu_2\text{-SMe})$ was determined crystallographically. Treatment of $\text{Ru}_3(\text{CO})_{12}$ with mercaptoethanoic acid and with 2-mercaptobenzothiazole gave (180) $\text{Ru}_3(\text{CO})_{10}(\mu_2\text{-H})(\mu_2\text{-SCH}_2\text{CO}_2\text{H})$ and $\text{Ru}_3(\text{CO})_9(\mu_2\text{-H})(\mu_3\text{-SC}_7\text{H}_4\text{NS})$, 31. The structure of both species were confirmed by X-ray methods.

When $\text{Fe}_2(\text{CO})_9$ reacted with RNSNR (R = Bu^t or $\text{p-MeC}_6\text{H}_4$) in benzene or hexane at RT, $\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})_2$, $\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})(\mu_3\text{-NR})$, $\text{Fe}_3(\text{CO})_9(\mu_3\text{-S})(\mu_3\text{-SNR})$, 32, and $\text{Fe}_2(\text{CO})_6(\mu_2\text{-SNR})$ were formed (181). The structure of 32 (R = Bu^t) was established by X-ray techniques, and $\text{Fe}_2(\text{CO})_9(\mu_2\text{-SNR})$ was carbonylated to give $\text{Fe}_2(\text{CO})_6\{\mu\text{-RNC}(\text{:O})\text{S}\}$, 33, (structure with R = $\text{p-MeC}_6\text{H}_4$ determined crystallographically). Thermolysis of this last compound gave RNR (R = p-toly1).

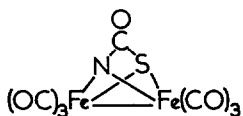
Reduction of $[\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_6(\text{pyr})_3][\text{PF}_6]$ with hydrazine afforded (182) $\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_6(\text{pyr})_3$ which absorbed CO in refluxing giving $\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_6(\text{CO})(\text{pyr})_2$, as a monobenzene solvate. This species exhibited redox behaviour, evidence being obtained voltammetrically (Pt, MeCN) for mono- and di-cationic and for mono-anionic species. The related $[\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_4(\text{DMF})_n][\text{OCOMe}]$ (DMF = dimethylformamide) reacted with H_2 (183) giving a dimeric Ru(I) species which, on treatment with Lewis bases, afforded $\text{Ru}_2(\text{CO})_4\text{L}_2(\text{O}_2\text{CMe})_2$ (L = PPh_3 , PPh_2Et , SbPh_3 , pyr). This species further reacted with hydrogen giving $[\text{Ru}(\text{CO})_3\text{H}]_n$.



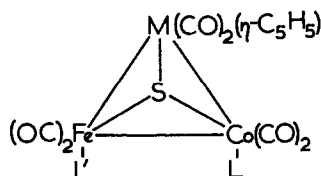
(31)



(32)



(33)



(34)

Heterotrimetallic Compounds. Reaction of $\text{Fe}_2(\text{CO})_9$ with $\text{Cr}(\text{CO})_5\text{PPhCl}_2$ afforded $\text{Fe}_2(\text{CO})_8[\text{PPh}_2\text{Cr}(\text{CO})_5]$ which, on photolysis (184), was converted into the tetrahedral cluster $\text{Fe}_2(\text{CO})_6\text{Cr}(\text{CO})_5(\mu_3\text{-PPh})$. Treatment of $[\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2\text{I}_2]$ with $\text{Na}_2\text{Fe}(\text{CO})_4$ gave the triangular cluster $\text{FeMo}_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_2$, in which the doubly-bonded $(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{Mo}=\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ unit was bridged by an $\text{Fe}(\text{CO})_4$ moiety (185). Thermolysis of this species gave $[\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$ and $\text{Fe}_3(\text{CO})_{12}$. Reaction of $\text{Fe}_2(\text{CO})_6[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2](\mu_3\text{-PPh})$ with PPh_3 caused (186) reversible opening of the cluster by addition to an $\text{Fe}(\text{CO})_3$ fragment and cleavage of a Mn-Fe bond.

$\text{Fe}_2(\text{CO})_9$ reacted with $\{\text{Co}(\text{CO})_4\}_2\text{PPh}$ giving $\text{FeCo}_2(\text{CO})_9(\mu_3\text{-PPh})$, a tetrahedral cluster (187). VT ^{13}C n.m.r. spectral studies have been used to investigate the dynamic behaviour of $\text{FeCo}_2(\text{CO})_9\text{S}$ (188). It was established that, on mono- and di-substitution, one and two Co atoms were involved, but on trisubstitution both Co atoms and the Fe atom were involved. Localised scrambling at each $\text{M}(\text{CO})_2\text{L}$ group did not occur prior to internuclear exchange. The kinetics and mechanism of CO replacement by L (AsPh_3 , $\text{P}(\text{OPh})_3$, PEt_2Ph), PBu_3^\dagger) in $\text{FeCo}_2(\text{CO})_9\text{S}$ were determined (189).

New clusters were obtained by conversion of $\text{FeCo}_2(\text{CO})_8\text{AsMe}_2\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ (As bonded to one Co) into $\text{FeCoM}(\text{CO})_8(\eta\text{-C}_5\text{H}_5)$, 34 ($\text{M} = \text{Cr, Mo, W}$; $\text{L} = \text{L}' = \text{CO}$) (190). Reaction of these species with PMe_2Ph gave $\text{FeCoM}(\text{CO})_6\text{LL}'(\eta\text{-C}_5\text{H}_5)$, 34 ($\text{L} = \text{CO}$, $\text{L}' = \text{PMe}_2\text{Ph}$; $\text{L} = \text{L}' = \text{PMe}_2\text{Ph}$) (190). Similar substitution occurred when $\text{FeCo}_2(\text{CO})_9\text{S}$ was treated with PMe_2Ph , replacement of CO groups only at the Co atoms occurring. $\text{Fe}_2(\text{CO})_9$ reacted with a mixture of $[\text{Ni}(\text{CO})(\eta\text{-C}_5\text{H}_5)]_2$ and PhC_2Ph giving $\text{Fe}(\text{CO})_3[\text{Ni}(\eta\text{-C}_5\text{H}_5)]_2(\text{PhC}_2\text{Ph})$ and other products (191). $\text{Fe}_2(\text{CO})_6(\text{Bu}^t\text{C}_2\text{Bu}^t)$ reacted stoichiometrically with H_2 in the presence of free acetylene with conversion of the bound acetylene to a mixture of cis and trans-alkenes and traces of alkanes (191).

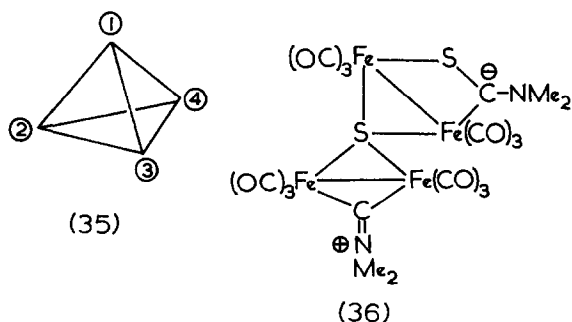
Complexes containing Four Metal Atoms

Homo-tetrametallic Species. The structures of $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ and $\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2\text{H}_4$, which contain a tetrahedral metal core, 35, have been examined crystallographically (192). Both compounds were slightly distorted because of the presence of Ru-H-Ru bridges. The H atoms were not located but in the former, there were four long (av. 2.95 Å; 35: 1-3, 1-4, 2-3, 2-4) and two short Ru-Ru bonds (av. 2.79 Å; 35: 1-2, 3-4). A similar situation obtained in the latter (av. distances 2.97 and 2.77 Å, respectively), the PPh_3 groups being bonded to atoms (1) and (2). The H atoms in $\text{Ru}_4(\text{CO})_{10}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{H}_4$ were located by X-ray techniques (193), bridging the bonds 1-3, 1-4, 2-3 and 3-4 in 35, the chelating phosphine being attached to Ru(3). The long Ru-Ru distances averaged 2.97 and the short 2.79 Å. A VT ^{13}C n.m.r. spectral study of $\text{Ru}(\text{CO})_{13}\text{H}_2$ at -72° revealed (194) that the bridging and five terminal CO ligands were involved in

intramolecular site-exchange and that CO scrambling was associated with one face of the tetrahedron.

Treatment of $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ with KOH in methanol, followed by addition of [PPN]I, afforded (195) two isomers of the PPN^+ salt of $[\text{Ru}_4(\text{CO})_{12}\text{H}_3]^-$. These were characterised by X-ray crystallography, using the lengths of the metal-metal bonds to identify the position of the hydride bridges. In one isomer, the H-atoms were located on the edges 1-3, 1-4 and 2-4, (bond lengths 2.92, short distances 2.80 Å) and in the other on edges 1-2, 1-4 and 2-4 (bond lengths 2.94 Å and 2.79 Å) in 35. Reaction of $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ with one equivalent of KH also afforded $[\text{Ru}_4(\text{CO})_{12}\text{H}_3]^-$, but with two equivalents of KH, $[\text{Ru}_4(\text{CO})_{12}\text{H}_2]^{2-}$ was obtained (196). This species was thought to contain three CO bridges (35; 2-3 2-4 and 3-4) and hydrogen atoms bridging edges 1-2 and 1-4.

Reaction of $\text{Os}_3(\text{CO})_{12}$ with NaBH_4 in THF afforded (197) a mixture of $[\text{Os}_3(\text{CO})_{11}\text{H}]^-$, $[\text{Os}_4(\text{CO})_{12}\text{H}_3]^-$ and $[\text{Os}_4(\text{CO})_{12}\text{H}_2]^{2-}$. The structure of the last was determined crystallographically, and although the H-atoms were not determined directly, their location was thought to be on the long bonds (35, 1-2 and 3-4, av. distance 2.94 Å); the short Os-Os distances averaged 2.79 Å.



In refluxing n-heptane, $\text{Fe}_3(\text{CO})_{12}$ reacted with an excess of alkyne $\text{RC}_2\text{R}'$ affording (198), in low yield, $\text{Fe}_4(\text{CO})_{11}(\text{RC}_2\text{R}')_2$ ($\text{R} = \text{R}' = \text{Me}$; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$, Et , Pr^i). The structure of this species was determined crystallographically. The four metal atoms were arranged in a tetrahedrally distorted square and each of the two alkyne ligands was σ -bonded to two Fe atoms on opposite vertices of the cluster and π -bonded to the other two. Of the 11 CO ligands, 8 were terminal, one formed a symmetrical bridge and two formed very asymmetric bridges. The substituted cluster had an Fe_4C_4 core in which the metal and C atoms occupied the vertices of a triangulated dodecahedron.

$\text{Fe}_2(\text{CO})_9$ reacted with AsH_2Me giving the cubane structure $[\text{Fe}(\text{CO})_3(\mu_3\text{-AsMe})]_4$ (199). While $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ ($\text{R} = \text{alkyl, aryl}$) does not apparently react with CO (200), $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$ afforded a 1:1 adduct which exhibited an e.s.r. signal. Treatment of $[\text{Et}_4\text{N}][\text{Fe}_2(\text{CO})_8]$ with ClCSNMe_2 gave $\text{Fe}_4(\text{CO})_{12}\text{S}(\text{CSNMe}_2)(\text{CNMe}_2)$ whose structure, 36, was determined crystallographically (201).

Hetero-tetrametallic Species. Reaction of $\text{FeCo}_3(\text{CO})_{12}\text{H}$ with $\text{P}(\text{OMe})_3$ afforded (202) the series $\text{FeCo}_3(\text{CO})_{12-x}\{\text{P}(\text{OMe})_3\}_x$ ($x = 1 \rightarrow 4$). The structure of the tris-phosphite species ($x = 3$) was determined at -139°C by X-ray techniques and it was established that the cluster formed a tetrahedron in which each Co atom carried a $\text{P}(\text{OMe})_3$ ligand. The position of the hydride ligand, bridging the Co_3 face, was determined both by X-ray and by neutron diffraction studies (203).

$\text{Cr}(\text{CO})_5(\text{THF})$ reacted with $\text{FeCo}_2(\text{CO})_9\text{S}$ giving $\text{FeCo}_2(\text{CO})_9\text{Cr}(\text{CO})_5$, in which the Cr atom was attached to the sulfur atom of the $\{\text{SFeCo}_2\}$ unit (structure confirmed by X-rays) (204). Insertion of $\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\text{H}$ into $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ gave two tetrahedral clusters, $\text{Os}_3\text{W}(\text{CO})_{12}(\eta\text{-C}_5\text{H}_5)(\mu_2\text{-H})$, A, and $\text{Os}_3\text{W}(\text{CO})_{11}(\eta\text{-C}_5\text{H}_5)(\mu_2\text{-H})_3$, B. The structures of both products were investigated crystallographically (205). In A, a $\text{W}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ group formed an apex of the tetrahedron, with one of the CO ligands forming an asymmetric bridge with an adjacent $\text{Os}(\text{CO})_3$ group; the "opposite" Os-Os bond being bridged by the H atom. In B, a $\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ group was incorporated into the tetrahedron, and the three edges of a Os_2W triangle were bridged by hydrogen. A could be converted to B by reaction with hydrogen in refluxing toluene, and related species containing Mo, and also $\text{Ru}_3\text{W}(\text{CO})_{12}(\eta\text{-C}_5\text{H}_5)(\mu_2\text{-H})$ were reported.

In refluxing heptane, $\text{Os}_3(\text{CO})_{10}\text{H}_2$ reacted with $\text{Co}_4(\text{CO})_{12}$ giving $\text{Os}_3\text{Co}(\text{CO})_{12}\text{H}_3$ (206) which had a tetrahedral geometry (X-rays) in which each Os-Os bond was bridged by hydrogen. Treatment of $\text{Os}_3(\text{CO})_{10}\text{H}_2$ with $\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)$ ($\text{R} = \text{Ph}$ or C_6H_{11}) gave (207) the fluxional $\text{Os}_3\text{Pt}(\text{CO})_{10}(\text{PR}_3)(\mu_2\text{-H})_2$. An X-ray structural determination of this tetrahedral cluster revealed that the molecule contained a $\text{Pt}(\text{CO})(\text{PR}_3)$ group, and that a Pt-Os and the "opposite" Os-Os bond were bridged by hydrogen. The cluster had a 58-electron configuration and, being therefore formally unsaturated, reacted with L ($\text{L} = \text{CO}, \text{PPh}_3, \text{AsPh}_3, \text{RC}_2\text{R}$) giving $\text{Os}_3\text{Pt}(\text{CO})_{10}(\text{PR}_3)\text{LH}_2$. Reaction of $\text{Os}_3(\text{CO})_{10}\text{H}_2$ with $\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$, $\text{Au}(\text{PPh}_3)\text{Me}$, and $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$ ($\text{acac} = \text{acetylacetonate}$) gave $\text{Os}_3\text{Ni}(\text{CO})_{10}(\text{PPh}_3)_2\text{H}_2$, $\text{Os}_3\text{Au}(\text{CO})_{10}(\text{PPh}_3)\text{H}$ and $\text{Os}_3\{\text{Rh}(\text{acac})\}(\text{CO})_{10}\text{H}_2$ (207). $\text{Os}(\text{CO})_4\text{H}_2$ reacted with $\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)$ ($\text{R} = \text{Me}, \text{C}_6\text{H}_{11}, \text{Ph}$) giving $\text{Os}_2\text{Pt}(\text{CO})_8(\text{PR}_3)_2\text{H}_2$ which had a "butterfly" structure as shown in 37 (207).

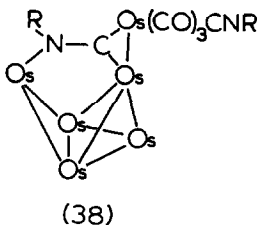
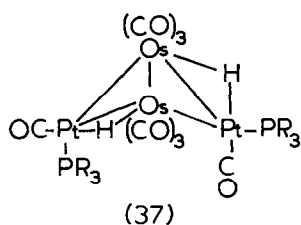
Complexes containing Five and Six Metal Atoms

Pyrolysis of $\text{Os}_3(\text{CO})_{11}\{\text{P}(\text{OMe})_3\}$ at 210° , followed by tlc of the product afforded $\text{Os}_5(\text{CO})_{15}(\mu_4\text{-POMe})$, whose structure was determined by X-ray techniques (208). The $\mu_4\text{-P}(\text{OMe})$ group capped a square face of a square pyramid of $\text{Os}(\text{CO})_3$ groups, and acted as a 4-electron donor. The species is electronically equivalent to $\text{Fe}_5(\text{CO})_{15}\text{C}$.

The structures of $\text{Os}_3\text{Re}_2(\text{CO})_{20}(\mu\text{-H})_2$ has also been elucidated crystallographically (209). The molecule consists of a triangle of Os atoms, two edges of which are bridged by H atoms. The two $\text{Os}(\text{CO})_3$ units, which are connected by

a metal-metal bond and one of the μ -H atoms, each carry an $\text{Re}(\text{CO})_5$ group.

$\text{Os}_6(\text{CO})_{18}$ reacted with $p\text{-MeC}_6\text{H}_4\text{NC}$ giving $\text{Os}_6(\text{CO})_{18}(\text{CNR})_2$ whose structure, determined by X-ray methods (210), is shown in 38. Thermolysis of $\text{Os}_3(\text{CO})_{11}(\text{CNBu}^t)$ afforded $\text{Os}_6(\text{CO})_{16}(\text{CNBu}^t)_2$ in which the basic structure of $\text{Os}_6(\text{CO})_{18}$ is retained, two CO ligands on different metal atoms being replaced by isonitriles, with some slight lengthening of the metal-metal bonds associated with each of the substituted metal atoms.



In *n*-decane at 165° , $\text{Os}_6(\text{CO})_{18}$ reacted with ethylene giving $\text{Os}_6(\text{CO})_{16}(\text{CMe})_2$ (211). The metal atoms in this species defined a monocapped square-based pyramid similar to that in $\text{Os}_6(\text{CO})_{18}\text{H}_2$ (212). One CMe group capped the Os_4 square plane while the other capped an adjacent Os_3 triangular face involving the metal atom which caps the square pyramid. It was suggested that the CMe group should be regarded as an ethylidene moiety functioning as a 3-electron donor. The cluster overall is an '86-electron' system. $\text{Os}_6(\text{CO})_{16}(\text{MeC}_2\text{Me})\text{C}$, also obtained from the reaction of $\text{Os}_6(\text{CO})_{18}$ with C_2H_4 , has also been investigated crystallographically (211). The metal atoms constituted an edge-bridged square-based pyramid, in which the bridging metal atom lies on the opposite side of the square basal plane to the apical Os atom. The acetylene moiety is η^2 -bonded to the bridging Os atom and σ -bonded to the other two Os atoms, while the carbon atom is located below the centre of the Os_4 basal plane. This cluster is an '88-electron' system and so requires the formal breakage of an Os-Os bond; this was not detected.

COMPLEXES CONTAINING M-C σ -BONDS

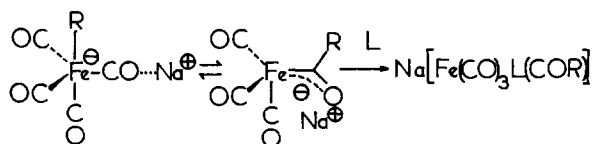
Alkyl Species. The ^{13}C relaxation times and mechanisms in cis- $\text{Os}(\text{CO})_4\text{Me}_2$ and $\text{Fe}(\text{CO})_2(n\text{-C}_5\text{H}_5)\text{Me}$ have been determined and barriers to M- CH_3 rotation calculated (213).

A kinetic and mechanistic investigation has been made (214) of the alkyl migration reactions of $[\text{Fe}(\text{CO})_4\text{R}]^-$. Particular attention was paid to the catalysis of these rearrangements by Lewis acid ion pairings, and the study included an analysis of several types of ion pairs derived from $\text{Na}[\text{Fe}(\text{CO})_4\text{R}]$ and $\text{Na}[\text{Fe}(\text{CO})_4\text{COR}]$ in THF. IR and ^{13}C n.m.r. data were interpreted in terms of acyl group in $[\text{Fe}(\text{CO})_4\text{COR}]^-$ being the cation bindings site. The cations

investigated were $[\text{PPN}]^+$, Na^+ and Li^+ , and the overall mechanism was thought to be that depicted in Scheme 2.

Reduction of $\text{Fe}\{\text{P}(\text{OMe})_3\}_3\text{Cl}_2$ with Na/Hg in the presence of an excess of $\text{P}(\text{OMe})_3$ gave $\text{Fe}\{\text{P}(\text{OMe})_3\}_5$ which could be alkylated by RI ($\text{R} = \text{Me}$ or Et) giving (215) the six-coordinate $[\text{Fe}\{\text{P}(\text{OMe})_3\}_5\text{R}]^+$, isolated as a $[\text{PF}_6]^-$ salt. The ethyl derivative was unstable, undergoing β -elimination to give $[\text{Fe}\{\text{P}(\text{OMe})_3\}_5\text{H}]^+$, also obtained by direct protonation of $\text{Fe}\{\text{P}(\text{OMe})_3\}_5$ by acid. Treatment of $\text{Fe}\{\text{P}(\text{OMe})_3\}_5$ with benzyl iodide afforded dibenzyl and $\text{Fe}\{\text{P}(\text{OMe})_3\}_2\text{I}_2$, whereas with allyl iodides small amounts of $[\text{Fe}\{\text{P}(\text{OMe})_3\}_4(\eta^3\text{-allyl})]^+$ and hexa-1,5-dienes were formed (other allyl halides did not give the $\eta^3\text{-allyl}$ species).

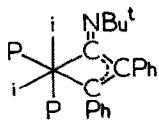
Scheme 2



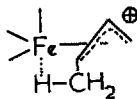
Reaction of $\text{Fe}\{\text{P}(\text{OMe})_3\}_5$ with CO in polar solvents caused formation of $\text{Fe}(\text{CO})\{\text{P}(\text{OMe})_3\}_4$ and $\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_3$. Reduction of $\text{Fe}\{\text{P}(\text{OMe})_3\}_3\text{X}_2$ by Na/Hg in the presence of acetylenes, $\text{RC}_2\text{R}'$ afforded $\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^2\text{-RC}_2\text{R}')$. The structure of the species where $\text{R} = \text{R}' = \text{Ph}$ was determined crystallographically, revealing that the molecule had a distorted square pyramidal structure, with one apical $\text{P}(\text{OMe})_3$ group, the $\eta^2\text{-PhC=CPh}$ group occupying two basal positions. Reaction of $\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\text{PhC}_2\text{Ph})$ with CO gave the trigonal bipyramidal $\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2(\text{PhC}_2\text{Ph})$, in which the phosphite ligands occupied apical sites, and the acetylene one of the equatorial positions. With Bu^tNC , $\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\text{PhC}_2\text{Ph})$ underwent insertion at an Fe-C bond, giving $\text{Fe}(\text{CNBu}^t)_2\{\text{P}(\text{OMe})_3\}_2\{\text{CPhCPhC}(\text{:NBu}^t)\}$, 39, ($i = \text{CNBu}_2^t$; $\text{P} = \text{P}(\text{OMe})_3$). On treatment of $\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\text{PhC}_2\text{Ph})$ with hydrogen in pentane solution, the acetylene was hydrogenated, a mixture of $\text{Fe}\{\text{P}(\text{OMe})_3\}_3\text{H}_4$, $\text{Fe}\{\text{P}(\text{OMe})_3\}_4\text{H}_2$ (minor component, and $[\text{Fe}\{\text{P}(\text{OMe})_3\}_2\text{H}]_n$ being formed, and when this reaction was carried out in benzene, some $\text{Fe}\{\text{P}(\text{OMe})_3\}_2(\eta^6\text{-C}_6\text{H}_6)$ was also produced. Traces of PhC_2Ph inhibited hydrogenation, but some hydrogen addition occurred in the presence of hex-3-yne. Hydrogenation and isomerisation of hex-1-ene was catalysed by $\text{Fe}\{\text{P}(\text{OMe})_3\}_2(\text{PhC}_2\text{Ph})$ and hydrogen.

Reduction of $\text{Fe}(\text{PMe}_3)_2\text{Cl}_2$ by Na/Hg in the presence of PMe_3 gave $\text{Fe}(\text{PMe}_3)_3(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ which, in the presence of PMe_3 was converted (reversibly) to $\text{Fe}(\text{PMe}_3)_5$ (215). Treatment of the $\eta^2\text{-CH}_2\text{PMe}_2$ species with PF_3 gave $\text{Fe}(\text{PF}_3)_2(\text{PMe}_3)_3$. Sodium amalgam reduction of $\text{Fe}(\text{PMe}_3)_2\text{Cl}_2$ in the presence of buta-1,3-diene and PMe_3 gave $\text{Fe}(\text{PMe}_3)_3(\eta^4\text{-C}_4\text{H}_6)$ which could be protonated affording $[\text{Fe}(\text{PMe}_3)_3(\text{C}_4\text{H}_6)\text{H}]^+$, probably best represented as 40. In acetonitrile

$\text{Fe}(\text{PMe}_3)_2\text{Cl}_2$ rearranged to $[\text{Fe}(\text{PMe}_3)_3(\text{NCMe})_2][\text{FeCl}_4]$ which, on reduction with Na/Hg in the presence of PMe_3 , afforded the di-imine complex $\text{Fe}(\text{PMe}_3)_3\{\text{HN:CMeCMe:NH}\}$. Sodium amalgam reduction of $\text{Fe}(\text{PMe}_3)_2\text{Cl}_2$ in the presence of but-2-yne gave the six-coordinate metallacyclic species $\text{Fe}(\text{PMe}_3)_4(\text{CMe:CMeCMe:CMe})$.



(39)



(40)

The 2-naphthyl complex cis- $\text{Fe}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) reacted (216) with acetylene and with HCN giving trans- $\text{Fe}(\text{dmpe})_2\text{H}(\text{Q})$ ($\text{Q} = \text{C}_2\text{H}$ or CN). In general $\text{Fe}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ reacted with any species containing activated sp^3 -hybridised C-H bonds, giving species of the type trans- $\text{Fe}(\text{dmpe})_2\text{H}(\text{CHXY})$ ($\text{X} = \text{H}, \text{Y} = \text{CN}; \text{X} = \text{CN}, \text{Y} = \text{CN}, \text{CH}_2\text{CN}, \text{CO}_2\text{Me}$). With propionitrile, cis- and trans- $\text{Fe}(\text{dmpe})_2\text{H}\{\text{CH}(\text{CN})\text{Me}\}$ was formed, which decomposed giving $\text{Fe}(\text{dmpe})_2\text{H}(\text{CN})$ and ethylene; $\text{Fe}(\text{dmpe})_2\text{H}\{\text{CH}(\text{CN})\text{CH}_2\text{CN}\}$ similarly decomposing to give $\text{CH}_2=\text{CHCN}$. Reaction with CD_3COCD_3 afforded trans- $\text{Fe}(\text{dmpe})_2\text{D}(\text{CD}_2\text{COCD}_3)$ and $\text{DFe}(\text{dmpe})_2\text{CD}_2\text{COCD}_2\text{Fe}(\text{dmpe})_2\text{D}$, which contained a bridging doubly deprotonated acetone dianion. With MeCOEt , a mixture of products was formed, including trans- $\text{Fe}(\text{dmpe})_2\text{H}(\text{CHCOMe})$, whereas with $(\text{PhCH}_2)_2\text{CO}$, trans- $\text{Fe}(\text{dmpe})_2\text{H}(\text{CH}_2\text{COCH}_2\text{Ph})$ was isolated. Cyclopentadiene reacted with the 2-naphthyl precursor affording trans- $\text{Fe}(\text{dmpe})_2\text{H}(\eta^1\text{-C}_5\text{H}_5)$, and methyl and ethylacetate gave trans- $\text{Fe}(\text{dmpe})_2\text{H}(\text{CH}_2\text{CO}_2\text{R})$ ($\text{R} = \text{Me}$ or Et); methyl acetate also afforded trans- $\text{Fe}(\text{dmpe})_2\text{Me}(\text{CO}_2\text{Me})$. Reaction of the 2-naphthyl hydride with $\text{MeP}(\text{O})(\text{OMe})_2$ gave trans- $\text{Fe}(\text{dmpe})_2\text{Me}\{\text{OP}(\text{O})\text{Me}(\text{OMe})\}$ and with *p*- MeOC_6H_4 , trans- $\text{Fe}(\text{dmpe})_2\text{Me}(\text{OPh})$ was formed. $\text{Fe}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ reacted with MeI , and with an excess of PhCl , $\text{CH}_2=\text{CHCl}$ or HCl giving $\text{Fe}(\text{dmpe})_2\text{MeI}$ and trans- $\text{Fe}(\text{dmpe})_2\text{Cl}_2$, respectively. In general $\text{Ru}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ reacted similarly although less readily, but the Os analogue was unreactive. $\text{Ru}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ reacted with CHCl_3 giving some trans- $\text{Ru}(\text{dmpe})_2\text{Cl}_2$, but mainly cis- $\text{Ru}(\text{dmpe})_2\text{Cl}(\text{C}_{10}\text{H}_7)$. Carbonylation of trans- $\text{Fe}(\text{dmpe})_2\text{H}(\text{CH}_2\text{CN})$ afforded $\text{Fe}(\text{CO})(\text{dmpe})_2$ and acetonitrile, but no aldehydes or other unsaturated products. This revealed that reductive elimination from trans- $\text{Fe}(\text{dmpe})_2\text{H}(\text{CRR}'\text{R}'')$ is much slower than naphthalene-elimination from cis- $\text{Fe}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$, as might be expected. Treatment of $\text{Fe}(\text{dmpe})_2\text{H}(\text{CH}_2\text{CN})$ with CO_2 gave trans- $\text{Fe}(\text{dmpe})_2\text{H}(\text{O}_2\text{CCH}_2\text{CN})$ which released cyanoacetate on addition of acid (as BF_3MeOH). A kinetic study of the reaction of acetonitrile with $\text{Fe}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ revealed $\text{Fe}(\text{dmpe})_2$ as a possible intermediate.

Treatment of cis- $\text{Fe}(\text{CO})_4(\text{C}_3\text{F}_7)\text{I}$ with $\text{Ag}(\text{NCMe})\text{C}_6\text{F}_5$ gave (217) the mixed fluoro-alkyl/-aryl species $\text{Fe}(\text{CO})_3(\text{NCMe})(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)$. Under CO pressure at 60°

this could be smoothly converted into $\text{Fe}(\text{CO})_4(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)$ (trans-alkyl/aryl), but in acetonitrile, $\text{Fe}(\text{CO})_2(\text{NCMe})_2(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)$ (cis-CO, cis-NCMe) was formed. The complexes $\text{Fe}(\text{CO})_3\text{L}(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)$ (L = PPh_3 , PMe_2Ph or $\text{P}(\text{OR})_3$, R = Me, Et or Ph) were also prepared using $\text{Ag}(\text{NCMe})\text{C}_6\text{F}_5$ in the presence of L, and $\text{Fe}(\text{CO})_2(\text{NCMe})_2(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)$ reacted with L affording $\text{Fe}(\text{CO})_2\text{L}_2(\text{C}_3\text{F}_7)(\text{C}_6\text{F}_5)$. $\text{Fe}_2(\text{CO})_9$ reacted with the silacyclobutane $\text{RHSiCH}_2\text{CH}_2\text{CH}_2$ giving $\text{Fe}(\text{CO})_4\text{SiHRCH}_2\text{CH}_2\text{CH}_2$, $\text{Fe}(\text{CO})_4\text{H}\{\text{Si}(\text{R})\text{CH}_2\text{CH}_2\text{CH}_2\}$, and some $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ (218).

Aryl Species. Treatment of FeX_2 (X = Cl or Br) with an excess of LiPh (219) or $2,6\text{-(MeO)}_2\text{C}_6\text{H}_3\text{Li}$ (220) gave $\text{Li}_2\text{Fe}(\text{Ar})_4$ (Ar = Ph or $2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$). Reaction of the latter complex with HgBr_2 and with iodine afforded $2,5\text{-(MeO)}_2\text{C}_6\text{H}_3\text{HgBr}$ and $[2,6\text{-(MeO)}_2\text{C}_6\text{H}_3]_2$, respectively (220).

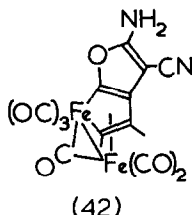
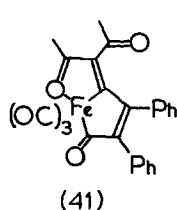
Reaction of Fe vapour with cyclooctadiene (COD) gave $\text{Fe}(\text{COD})_2$ which was not isolated, but which reacted with an excess of $\text{P}(\text{OPh})_3$ giving the bis-o-metallated species cis- $\text{Fe}\{\text{P}(\text{OPh})_3\}_2\{\text{P}(\text{OPh})_2\text{OC}_6\text{H}_4\}_2$ (221). Reaction of this with L (CO or $\text{P}(\text{OMe})_3$), H_2 and HCN afforded cis- $\text{FeL}\{\text{P}(\text{OPh})_3\}\{\text{P}(\text{OPh})_2\text{OC}_6\text{H}_4\}_2$, cis- $\text{Fe}\{\text{P}(\text{OPh})_3\}_4\text{H}_2$ and $\text{Fe}\{\text{P}(\text{OPh})_3\}_3\{\text{P}(\text{OPh})_2\text{OC}_6\text{H}_4\}(\text{CN})$ (mer-phosphite), respectively. Reaction of $\text{Fe}(\text{COD})_2$ with $\text{P}(\text{OCH}_2)_3\text{CEt}$ and with $\text{P}(\text{OMe})_3$ gave $\text{Fe}\{\text{P}(\text{OCH}_2)_3\text{CEt}\}_5$ and $\text{Fe}\{\text{P}(\text{OMe})_3\}_3(1,3\text{-C}_8\text{H}_{12})$, respectively. Reduction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ by Zn/Hg in the presence of $\text{P}(\text{OPh})_3$ afforded, initially, $\text{Ru}\{\text{P}(\text{OPh})_3\}_4\text{Cl}_2$, and further reduction using Na/Hg gave cis- $\text{Ru}\{\text{P}(\text{OPh})_2\text{OC}_6\text{H}_4\}$ whose reactions with CO and with $\text{P}(\text{OMe})_3$ were like those of its Fe analogue. Similar reduction of $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ gave both cis- $\text{Os}\{\text{P}(\text{OPh})_3\}_2\{\text{P}(\text{OPh})_2\text{OC}_6\text{H}_4\}_2$, which also behaves like its Fe analogue, and $\text{Os}\{\text{P}(\text{OPh})_3\}_3\{\text{P}(\text{OPh})_2\text{OC}_6\text{H}_4\}\text{H}$ (mer-phosphite).

Two-electron reduction of $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ in acetonitrile was thought (222) to proceed via $\text{Ru}(\text{PPh}_3)_2(\text{NCMe})\text{Cl}_2$ to $\text{Ru}(\text{PPh}_3)_2(\text{NCMe})$ and then $\text{Ru}(\text{PPh}_3)_3(\text{NCMe})$, finally yielding the o-metallated species $\text{Ru}(\text{PPh}_3)_2(\text{PPh}_2\text{C}_6\text{H}_4)(\text{NCMe})\text{H}$ (cis- PPh_3 , P atoms mer, H trans to o- C_6H_4). During the reaction a transient red species ($t_{1/2}$ ca. 1 min) was observed which was paramagnetic ($S = 1$). It was assumed that this was a Ru(0) species.

The reduction of $\text{Fe}(\text{dmpe})_2\text{Cl}_2$ (dmpe = $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) with sodium naphthalenide gave both $\text{Fe}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ and $\text{Fe}_2(\text{dmpe})_5$ (223). The latter was thought to contain 5-coordinate Fe atoms bridged by a dmpe ligand, and to arise via the decomposition of $\text{Fe}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$, giving $\text{Fe}(\text{dmpe})_2$ which reacted with dmpe giving $\text{Fe}(\text{dmpe})_3$. This tris-ligand species then reacted further with $\text{Fe}(\text{dmpe})_2$ giving the bis-iron species. A ^1H and ^{31}P n.m.r. spectral study of $\text{M}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ (M = Fe, Ru, Os) revealed that cis \rightleftharpoons trans interconversion in solution was facile for Fe but much slower (several hours) for the other metals, the cis form generally being more stable (at equilibrium, Fe 40%, Ru 94%, Os 75%). Reaction of $\text{M}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ with H_2 gave naphthalene and cis- $\text{M}(\text{dmpe})_2\text{H}_2$ (M = Fe, Ru), while with CO, $\text{M}(\text{CO})(\text{dmpe})_2$ was formed. With other tertiary phosphines and phosphites, $\text{M}(\text{dmpe})_2\text{L}$ could be obtained. Reaction of $\text{Ru}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ with

$P(OMe)_3$ gave both $Ru(dmpe)_2\{P(OMe)_3\}$ and trans- $Ru(dmpe)_2H\{CH_2P(:O)(OMe)_2\}$. $M(dmpe)_2H(C_{10}H_7)$ ($M = Fe, Ru$) reacted with ethylene giving $M(dmpe)_2(C_2H_4)$, and related Fe complexes containing other alkenes, fumaronitrile and azobenzene were also isolated. Treatment of $Fe(dmpe)_2H(C_{10}H_7)$ with TCNE may provide $[Fe(dmpe)_2H(C_{10}H_7)]^+[TCNE]^-$, but with butadiene and cyclohexa-1,3-diene, $Fe(dmpe)_2(\eta^2-C_4H_6)$ and $Fe(dmpe)_2(\eta^4-C_6H_8)$, in which one bis-phosphine ligand was monodentate, were formed. When $Fe(dmpe)_2H(C_{10}H_7)$ was treated with anthracene, $Fe(dmpe)_2(C_{14}H_{10})$ was formed, in which the anthracene was η^4 -bonded (cis-1,3-dienoidal) via an external C_6 ring, and again one of the bis-phosphine ligands was monodentate.

Metallacyclic Species. Photolysis of $Fe(CO)_5$ with 1,2-diphenyl-4,4-diacetyl-triafulvene gave 41 (224), whereas $Fe_3(CO)_{12}$ reacted with 1,2-dimethyl-4,4-dicyanotriafulvene giving 42 (225). The structures of both species were established crystallographically.



MONO-ALKENE COMPLEXES

Trans-cyclo-octene, -nonene and -decene reacted (226) with $Fe_2(CO)_9$ giving stable complexes of the type $Fe(CO)_4(\text{olefin})$ in which the trans-configuration was maintained. Similar tetracarbonyl iron complexes were obtained with trans, cis-cycloocta-1,5- and -1,3-dienes and with trans, trans, cis-2,8,12-trans-bicyclo[8,4,0]tetradecatriene. Bicyclo[4,3,1]deca-7,9-diene reacted only at the strained bridge-head double bond. The olefins all occupied an equatorial position in the trigonal-bipyramidal molecule. A detailed vibrational spectroscopic examination of $Fe(CO)_4(C_2H_4)$ and $Fe(CO)_4(C_2D_4)$ has been made (227).

Reaction of $[Fe(CO)_4H]^-$ with $MeO_2CC_2CO_2Me$ gave (228) the acyl $[Fe(CO)_3COCHR]^-$, isolated as a PPN^+ salt, an X-ray crystallographic study of which revealed that the double bond of the $COCHR$ fragment was bonded to metal. Similar complexes containing $R = H, R' = CHO, COMe$ or CO_2Me were also prepared.

Treatment of $Fe(acac)_3$ ($acac = \text{acetylacetonate}$) with $Ph_2PCH_2CH_2PPh_2$ ($dppe$) and $AlEt_3$ in ether gave the fluxional species $Fe(C_2H_4)(dppe)_2$, and the closely related $Fe(C_2H_4)(dppm)_2$ ($dppm = Ph_2PCH_2PPh_2$) was obtained similarly (229). On heating $Fe(C_2H_4)(dppe)_2$, the o-metallated species $Fe(dppe)\{C_6H_4P(Ph)C_2H_4PPh_2\}H$ was formed (hydride and o-metallated C_6H_4 ring mutually cis). When $AlPr_3$ or $AlBu_3^t$ was used instead of $AlEt_3$, only cis- $Fe(dppe)_2H_2$, as yellow and red isomers,

was obtained. Reaction of $\text{Fe}(\text{C}_2\text{H}_4)(\text{dppe})_2$ or $\text{Fe}(\text{dppe})_2\text{H}_2$ with CO gave, over 3 days, $\text{Fe}(\text{CO})(\text{dppe})_2$ and $\text{Fe}(\text{CO})_3(\text{dppe})$, but $\text{Fe}(\text{dppe})_2\text{HCl}$ did not react with CO. $\text{Fe}(\text{C}_2\text{H}_4)(\text{dppm})_2$ behaved similarly and gave $\text{Fe}(\text{CO})_4(\text{dppm})$ (dppm monodentate) as an additional product. Reaction of $\text{Fe}(\text{C}_2\text{H}_4)(\text{dppe})_2$ or $\text{Fe}(\text{dppe})_2\text{H}_2$ with PF_3 gave products similar to CO, but $\text{Fe}(\text{dppe})\{\text{C}_6\text{H}_4\text{P}(\text{Ph})\text{C}_2\text{H}_4\text{PPh}_2\}\text{H}$ afforded only $\text{Fe}(\text{dppe})_2(\text{PF}_3)$. Compounds similar to this last mentioned species were obtained with $\text{P}(\text{OR})_3$ (R = Me, Et, Pr^n), $\text{P}(\text{OMe})_2\text{Ph}$ and $\text{P}(\text{OCH}_2)_3\text{CEt}$, and $\text{Fe}(\text{dppm})\{\text{P}(\text{OMe})_3\}_3$ was also isolated. No reaction was observed between $\text{Fe}(\text{C}_2\text{H}_4)(\text{dppe})_2$ and phosphine or phosphite ligands having 'core angles' greater than 116° , in contrast to species like $\text{Fe}(\text{dmpe})_2(\text{PR}_3)$ (dmpe = $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$) where PR_3 can have core angles up to 141° (230). $\text{Fe}(\text{C}_2\text{H}_4)(\text{dppe})$, $\text{Fe}(\text{dppe})\{\text{C}_6\text{H}_4\text{P}(\text{Ph})\text{C}_2\text{H}_4\text{PPh}_2\}\text{H}$ and, more slowly, $\text{Fe}(\text{dppe})_2\text{H}_2$ react with HC_2R giving trans- $\text{Fe}(\text{dppe})_2\text{H}(\text{C}_2\text{R})$ (R = Bu^t , Ph, CF_3 , CO_2Et , COMe). $\text{Fe}(\text{C}_2\text{H}_4)(\text{dppe})_2$ reacted stoichiometrically with HCN giving trans- $\text{Fe}(\text{dppe})_2\text{H}(\text{CN})$, but with an excess of the acid, $\text{Fe}(\text{dppe})_2(\text{CN})_2$ was formed. In contrast to related complexes containing dmpe (216) there was no reaction between any of the dppe compounds and acetonitrile or acetone. However, with β -diketonates (dik^-), $\text{Fe}(\text{C}_2\text{H}_4)(\text{dppe})_2$, $\text{Fe}(\text{dppe})\{\text{C}_6\text{H}_4\text{P}(\text{Ph})\text{C}_2\text{H}_4\text{PPh}_2\}$, and even $\text{Fe}(\text{dppe})_2\text{H}_2$, afforded $\text{Fe}(\text{dppe})_2\text{HCl}$ and $\text{Fe}(\text{dppe})(\text{dik})_2$. Reaction of $\text{Fe}(\text{C}_2\text{H}_4)(\text{dppe})_2$ with cyclopentadiene gave $\text{Fe}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)\text{H}$ (cf. $\text{Fe}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$ which reacted with C_5H_6 giving $\text{Fe}(\text{dmpe})_2\text{H}(\eta^1\text{-C}_5\text{H}_5)$ (216). The ethylene complex reacted with TCNE at low temperature giving yellow $[\text{Fe}(\text{C}_2\text{H}_4)(\text{dppe})_2]^+[\text{TCNE}]^-$ or dark green $[\text{Fe}(\text{TCNE})(\text{dppe})_2]^+[\text{TCNE}]^-$, depending on reaction conditions, and finally $\text{Fe}(\text{dppe})_2\{\text{NCC}(\text{CN})=\text{C}(\text{CN})_2\}$.

An X-ray crystallographic examination of $\text{Ru}(\text{CO})(\eta^2\text{-C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2\text{Cl}_2$ revealed (231) that the molecule was formally six-coordinate overall, with cis-Cl and trans-phosphine ligands, the ethylene (C-C distance 1.38 Å) being essentially parallel to the P-Ru-P bonds. N.M.R. studies showed that there was rotation about the Ru-(C_2H_4) bond, even at -40°C .

Reaction of $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ or $\text{Ru}(\text{PPh}_3)_3\text{H}_4$ with styrene gave (232) $\text{Ru}(\text{CH}_2=\text{CHPh})_2(\text{PPh}_3)_2$ and not $\text{Ru}(\text{CH}_2=\text{CHPh})(\text{PPh}_3)_3$ as reported earlier (233). The structure of this coordinatively unsaturated species was shown (X-ray studies) to be that of a highly distorted tetrahedron. No evidence for the presence of Ru-H bonds could be found, but the species formed $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ in the presence of PPh_3 in a wide range of solvents including saturated hydrocarbons. The source of the H atom was thought to be PPh_3 and not the hydrocarbons present in solution (233,234). When $\text{Ru}(\text{CH}_2=\text{CHPh})_2(\text{PPh}_3)_2$ was warmed in C_6F_6 , or hexane containing PPh_3 , a mixture of species was produced, some which may have contained PPh_2^- , and including $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ (233). In styrene solution there appeared to be an equilibrium (234):



$\text{Ru}(\text{CH}_2=\text{CHPh})_2(\text{PPh}_3)_2$ reacted with water in THF giving $\text{Ru}(\text{PPh}_3)_2(\text{THF})\text{H}(\text{OH})$.

Reaction with ethylene afforded $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{CH}_2=\text{CHPh})(\text{PPh}_3)_2$, with propene cis-

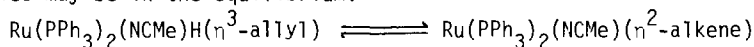
$\text{Ru}(\text{PPh}_3)_2(\eta^3\text{-C}_3\text{H}_5)_2$, and with but-1-ene or buta-1,3-diene, in the presence of PPh_3 , $\text{Ru}(\eta^4\text{-C}_4\text{H}_6)(\eta^2\text{-CH}_2=\text{CHPh})(\text{PPh}_3)_2$, as two isomers. In the absence of added PPh_3 , but-1-ene or C_4H_6 reacted with $\text{Ru}(\text{CH}_2=\text{CHPh})_2(\text{PPh}_3)_2$ giving $\text{Ru}(\eta^4\text{-C}_4\text{H}_6)_2(\text{PPh}_3)$. With hex-1-ene, $\text{Ru}(\eta^2\text{-CH}_2=\text{CHPh})(\text{PPh}_3)_2(\eta^3\text{-CH}_2\text{CHCHC}_3\text{H}_7)\text{H}$ was produced whereas *cis*- and *trans*-hex-2-ene afforded η^4 -hexadiene complexes $\text{Ru}(\eta^2\text{-CH}_2=\text{CHPh})(\eta^4\text{-C}_6\text{H}_{10})(\text{PPh}_3)_2$. In neat C_5H_6 , $\text{Ru}(\text{CH}_2=\text{CHPh})_2(\text{PPh}_3)_2$ formed $\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)\text{H}$, and with CO, in the presence of styrene and PPh_3 , $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ was produced.

ALLYL COMPLEXES

The structure of $[\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)]_2$ has been determined crystallographically (235). The coordination sphere about each Fe atom was best described as pseudo-octahedral, counting the metal-metal bond and a "bidentate" allyl group. The Fe-Fe bond was surprisingly long (3.14 Å) and this was deemed consistent with the low enthalpy value for dissociation of the dimer in solution. In solution, the compound slowly decomposed giving propene, $\text{Fe}(\text{CO})_5$, $\text{Fe}_3(\text{CO})_{12}$ and three di-iron ferracyclopentadiene complexes. Hydrogenation of $[\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)]_2$ proceeded rapidly giving propene, a small amount of propane, $\text{Fe}(\text{CO})_4(\eta^2\text{-C}_3\text{H}_6)$, $\text{Fe}_3(\text{CO})_{12}$ and a ferracyclopentadiene complex analogous to 21. The allyl dimer could affect isomerisation of olefins, and reacted with buta-1,3-diene giving $(\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_6))$.

The ^{13}C n.m.r. spectra of nine allyl cations, $[\text{Fe}(\text{CO})_4(\eta^3\text{-allyl})]^+$, and seven acyclic diene species, $\text{Fe}(\text{CO})_3(\eta^4\text{-diene})$, have been measured (236), and the effects of alkyl substitutions on $\delta(\text{C})$ of the ligand skeleton were described. There was a high barrier to intramolecular CO ligand exchange. The metal-allyl stretching modes have been identified in the vibrational spectra of $\text{Fe}(\text{CO})_2(\eta^3\text{-allyl})_2$, $\text{Fe}(\text{CO})_3(\eta^3\text{-allyl})$ and $\text{Fe}(\text{CO})_3(\eta^3\text{-allyl})\text{X}$ (237).

Treatment of $\text{Fe}(\text{CO})_4\text{H}(\text{SiCl}_3)$ with isoprene and with butadiene gave (238) $\text{Fe}(\text{CO})_3(\eta^3\text{-allyl})\text{SiCl}_3$ (allyl = 1-MeC₃H₄ or 1,1-Me₂C₃H₃), whereas with 1,3-dimethylbuta-1,3-diene, $\text{Fe}(\text{CO})_4(\eta^1\text{-C}_6\text{H}_{11})(\text{SiCl}_3)$ or $[\text{Fe}(\text{CO})_4\text{SiCl}_3]_2$ and C_6H_{12} were formed. Propene reacted under pressure in an oxidative addition reaction with $\text{Ru}(\text{PPh}_3)_4(\text{NCMe})_2$ giving $\text{Ru}(\text{PPh}_3)_2(\text{NCMe})\text{H}(\eta^3\text{-C}_3\text{H}_5)$ (239); $\text{Ru}(\text{PPh}_3)_2(\text{NCMe})\text{H}(\eta^3\text{-C}_4\text{H}_7)$ was obtained similarly from isobutenes. These allyl species may be in the equilibrium:



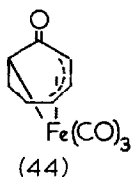
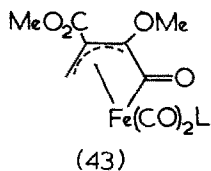
Reaction of the allyl complexes with PMePh_2 afforded, for example, $\text{Ru}(\text{PMePh}_2)_3\text{H}(\eta^3\text{-C}_3\text{H}_5)$.

Addition of RCOCl (R = Ph; p-XC₆H₄; X = Cl or NO₂; 2-phenyl-o-carboran-1-yl) or RSO_2Cl (R = Me, CH₂Ph or p-MeC₆H₄) to $\text{Na}[\text{Fe}(\text{CO})_3(\eta^3\text{-CH}_2\text{CHCHR}')]$ (R' = H or Me) afforded η^2 -alkene or η^4 -heterodiene species in which acyl or sulphonyl group was attached to a terminal C atom of the allyl ligand (24). Thus $[\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)]^-$ was converted by PhCOCl with $\text{Fe}(\text{CO})_4(\eta^2\text{-CH}_2=\text{CHCH}_2\text{COPh})$ and

$\text{Fe}(\text{CO})_3\{\eta^4\text{-MeCH=CHC(Ph)=O}\}$. Reaction of $\text{Fe}(\text{CO})_3\{\eta^3\text{-CH}_2\text{=C}(\text{CO}_2\text{Me})\text{-C(OMe)}\}$, and η^3 -vinyl-carbene complex (241), with CO or PPh_3 , gave (242) the η^4 -vinylketene complex $\text{Fe}(\text{CO})_2\text{L}\{\text{C}(\text{CO})\text{C(OMe)=C}(\text{CO}_2\text{Me)=CH}_2\}$, 43 ($\text{R} = \text{H}$, $\text{R}' = \text{CO}_2\text{Me}$, $\text{R}'' = \text{Me}$) the structure of the species with $\text{L} = \text{PPh}_3$ being established crystallographically. Acetylenes, $\text{RC}_2\text{R}'$, reacted with $[\text{PPN}][\text{Fe}(\text{CO})_4\text{H}]$ giving $\text{Fe}(\text{CO})_3\{\eta^3\text{-CHR=CR=C=O}\}$ ($\text{R} = \text{H}$, $\text{R}' = \text{CO}_2\text{Me}$, COMe , CHO ; $\text{R} = \text{CO}_2\text{Me}$, $\text{R}' = \text{H}$, CO_2Me) (243). The species with $\text{R} = \text{CO}_2\text{Me}$, $\text{R}' = \text{H}$ was also obtained by reaction of cis- $\text{CH}(\text{CO}_2\text{Me})=\text{CHBr}$ and $\text{Na}_2\text{Fe}(\text{CO})_4$. A crystal structure determination of the species where $\text{R} = \text{R}' = \text{CO}_2\text{Me}$ established the η^3 -nature of the $\text{CHR}\text{CR}'\text{CO}$ group. Acidification of these species afforded $\text{Fe}(\text{CO})_4\{\eta^2\text{-CHR=CHR}'\}$ quantitatively, whereas alkylation using $\text{R}''\text{OSn}_2\text{F}$ or $[\text{R}''_3\text{O}][\text{BF}_4]$ gave the vinyl carbenes $\text{Fe}(\text{CO})_3\{\eta^3\text{-CHR=CR}'\text{-COR}''\}$ ($\text{R} = \text{H}$, CO_2Me , $\text{R}' = \text{CO}_2\text{Me}$; $\text{R}'' = \text{Me}$ or Et). Oxidation of the vinyl carbene complexes by pyridine-N-oxide gave, $\text{Fe}(\text{CO})_3(\text{pyr})\{\eta^2\text{-CHR=C}(\text{CO}_2\text{Me})\}_2$. Reaction of substituted cyclopropenes with $\text{Fe}_2(\text{CO})_9$ in a 1:1 molar ratio gave (244) species analogous to 43 ($\text{L} = \text{CO}$) with OR'' replaced by Me or Ph , and R , $\text{R}' = \text{H}$, Me or Ph . The structure of $\text{Fe}(\text{CO})_3\{\eta^4\text{-C(:O)CPhCPhCHPh}\}$ was determined by X-ray methods.

Treatment of $\text{Fe}(\text{CO})_4\{\eta^2\text{-PhCH=CHCOPh}\}$ with BF_3 afforded (245) the intermediate $\text{Fe}(\text{CO})_4\{\eta^2\text{-PhCH=CHCOPh}^+\text{BF}_3^-\}$ which was converted by primary amines, NH_2R , to the η^3 -allyl- σ -carbamoyl species $\text{Fe}(\text{CO})_3\{\text{C(:O)NRCPh-CH-CHPh}\}$; the structure of the species with $\text{R} = \text{C}_6\text{H}_{11}$ being determined crystallographically.

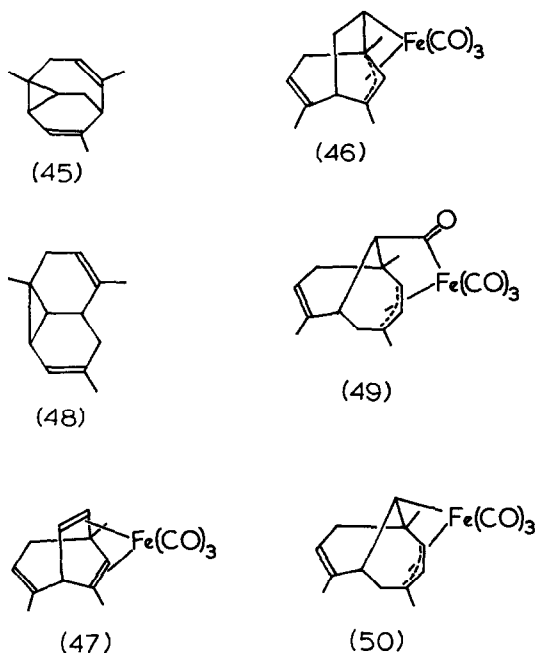
Under CO, $\text{Fe}(\text{CO})_3(\text{C}_6\text{H}_8)$ reacted with AlX_3 ($\text{X} = \text{Cl}$ or Br) giving 44 (246). On heating, this species rearranged to cyclohepta-1,3-dien-7-one iron tricarbonyl, whereas under CO pressure (100 atm) and with heating, bicyclo-[3,2,1]oct-2-ene-4,7-dione was formed.



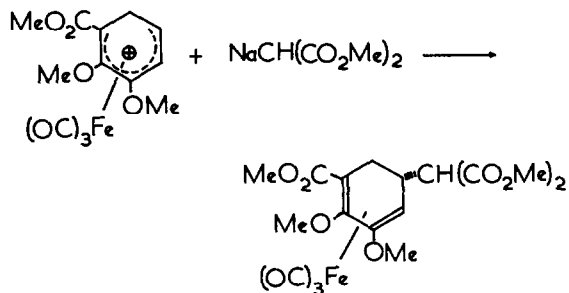
Protonation of the 1,3-cyclooctadiene complex $\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^4\text{-C}_8\text{H}_{12})$ gave (247) the η^3 -cyclooctenyl complex $[\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^3\text{-C}_8\text{H}_{13})]^+$. This species was fluxional on the n.m.r. timescale, and there was ^1H n.m.r. spectral evidence for interaction between the metal and an H atom endo to it with respect to the C_8H_{13} ring. This interaction was confirmed by a neutron-diffraction study of the cation (248). Treatment of the allyl cation with CO or Bu^tNC gave $[\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^3\text{-C}_8\text{H}_{13})]^+$, but there was no reaction with $\text{P}(\text{OMe})_3$. Similar cyclohexenyl and cycloheptenyl analogues were prepared. Reduction of $\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^3\text{-C}_8\text{H}_{13})[\text{BF}_4]$ by sodium amalgam afforded (249) the neutral, paramagnetic η^3 -cyclooctenyl complex. This was shown to be fluxional on the e.s.r. timescale. Reaction of $\text{Fe}\{\text{P}(\text{OMe})_3\}_5$ with allyl bromide gave

$[\text{Fe}\{\text{P}(\text{OMe})_3\}_4(\eta^3\text{-C}_3\text{H}_5)]^+$ which was also reduced by sodium amalgam to give the paramagnetic $\text{Fe}\{\text{P}(\text{OMe})_3\}_3(\eta^3\text{-C}_3\text{H}_5)$. E.S.R. spectral studies also revealed that $\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)$ and $\text{Fe}(\text{CO})_2(\text{PPh}_3)(\eta^3\text{-C}_3\text{H}_5)$ were fluxional, consistent with earlier observations (250).

UV irradiation of 45 with $\text{Fe}(\text{CO})_5$ gave 46 and 47, the hydrocarbon being liberated from the $\text{Fe}(\text{CO})_3$ residue by treatment with silica (251). Similarly, 48 was converted to 49, which was decarbonylated to give 50. Reactions of other tricyclic-vinylcyclopropanes containing epox-residues with $\text{Fe}_2(\text{CO})_9$ led to the opening of the epoxide ring, as shown in Scheme 3.

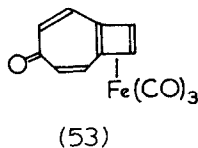
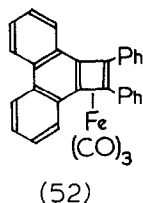
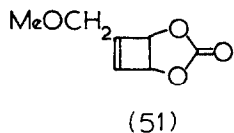


Scheme 3



CYCLOBUTADIENE COMPLEXES

The carbonate 51 reacted with $\text{Na}_2\text{Fe}(\text{CO})_4$ giving $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_3\text{CH}_2\text{OMe})$ (252). $\text{Fe}(\text{CO})_5$ caused cyclisation of 2,2'-bis(phenylacetylene)-1,1'-diphenyl giving the cyclobutadiene complex 52 (253). Treatment of $\text{Fe}(\text{CO})_3\{1,2\text{-C}_4\text{H}_2(\text{CHO})_2\}$ with $[(\text{Ph}_3\text{PCH}_2)_2\text{CO}]\text{Cl}_2$ afforded (254) tropone species to which the $\text{C}_4\text{H}_4\text{Fe}(\text{CO})_3$ group was annellated, e.g. 53. Oxidation of 53 by Ce^{4+} gave bicyclo[5.2.0]nona-1(7)-2,5,8-tetraen-4-one.



Photolysis (UV) of $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_4)$ and $\text{Fe}(\text{CO})_3\{\eta^4\text{-C}(\text{CH}_2)_3\}$ in frozen Ar or CH_4 matrices gave $\text{Fe}(\text{CO})_2(\text{ligand})$, and in frozen N_2 matrices, $\text{Fe}(\text{CO})_2(\text{N}_2)$ - (ligand) was identified (255). Nucleophilic substitution has been correlated with the frontier electron density parameters, the partial valence-inactive population, in $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_4)$, and also in $[\text{Fe}(\text{CO})_3(\eta^5\text{-dienyl})]^+$ (dienyl = C_5H_5 , C_6H_7 , C_7H_9) (256). In both series, nucleophilic substitution was shown to occur probably via initial attack at the Fe atom.

Sulphonation of $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_3\text{R})$ (R = H or Et) gave the 2-sulphonated species $\text{Fe}(\text{CO})_3\{\eta^4\text{-C}_4\text{H}_2\text{R}(\text{SO}_3\text{H})\}$ (257). Conversion of this to the sulphonyl chloride, followed by reduction gave $\text{Fe}(\text{CO})_3\{\eta^4\text{-C}_4\text{H}_2\text{R}(\text{SH})\}$ whereas reaction of the chlorosulphonate with primary and secondary amines afforded $\text{Fe}(\text{CO})_3\{\eta^4\text{-C}_4\text{H}_2\text{R}(\text{SO}_2\text{NR}'\text{R}'')\}$ (R = H, R' = R'' = H, Me, Et; R' = H, R'' = C_3H_5 , Bu^n , CH_2Ph ; NRR' = piperidyl, morpholinyl; R = Et, R' = R'' = Me).

The kinetics of nucleophilic addition of tertiary phosphines to $[\text{Fe}(\text{CO})_2(\text{NO})(\eta^4\text{-C}_4\text{H}_4)]^+$ indicated that PR_3 (R = Ph; $\text{p-XC}_6\text{H}_4$; X = Cl or Me) rapidly added to the cyclobutadiene ring giving a metal-coordinated phosphonium salt (258). The studies supported a mechanism consisting of a direct bimolecular attack on the ring, and it was established that the reactivity of rings towards nucleophilic addition of PR_3 was $[\text{Fe}(\text{CO})_2(\text{NO})(\eta^4\text{-C}_4\text{H}_4)]^+ > [\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]^+ > [\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_6\text{OMe})]^+$.

DIENE AND HIGHER OLEFIN COMPLEXES

Non-cyclic Diene and Related Species. The structure of 1,2,3,4- η^4 -(1-phenyl-1-benzyloxy)-1,3-butadiene tricarbonyliron was determined by X-ray methods (259). Photolysis of $\text{Fe}(\text{CO})_5$ in the presence of cis-1-methylbuta-1,3-diene (syn-isomer) gave $\text{Fe}(\text{CO})_4(\eta^4\text{-C}_4\text{H}_5\text{Me})$ and syn- $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_5\text{Me})$ but there was no evidence for the anti-isomer (260). Similar treatment of cis-1,1-dimethylbuta-1,3-diene afforded $\text{Fe}(\text{CO})_4(\eta^2\text{-C}_4\text{H}_4\text{Me}_2)$ (major product), $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_4\text{Me}_2)$ and $\text{Fe}(\text{CO})_3(\eta^4\text{-diene})$ (diene = syn or anti 1,3-dimethylbuta-1,3-diene). Thermolysis of $\text{Fe}(\text{CO})_4(\eta^2\text{-C}_4\text{H}_4\text{Me}_2)$ also gave the above-mentioned complexes.

Reaction of the trans-diene $\text{Fe}(\eta^5\text{-C}_5\text{H}_9)(\eta^5\text{-C}_5\text{H}_4\text{CH=CHCMe=CHCN})$ with $\text{Fe}_3(\text{CO})_{12}$ gave various isomers of the bimetallic species $\text{Fe}(\text{CO})_3(\eta^4\text{-diene})$ (261).

Treatment of the complex with KOH in ethanol led to removal of the $\text{Fe}(\text{CO})_3$ unit, and the CN group was largely unreactive possibly because of the bulk of the $\text{Fe}(\text{CO})_3$ moiety. However, treatment of the 1-cyano-2,4-cyclohexadiene complex $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{CN})$ with HCl in methanol at -5° to -10°C gave

$[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{C}(\text{NH}_2)\text{OMe})]^{+\text{Cl}^-}$, whereas NaOMe in methanol afforded

$\{\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7)\}_2\text{C}(\text{NH}_2)(\text{OMe})$, which contained the two cyclohexadienyl rings

bridged by a CRR' group. Reaction of the 1-aldehydocyclohexa-1,3-diene complex

$\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{CHO})$ with NaNH_2 in liquid ammonia gave $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{CH=CHCN})$ and protonation of this in methanol afforded $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{CH=CHC}(\text{:NH}_2)\text{OMe})]^{+\text{}}$.

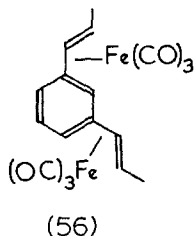
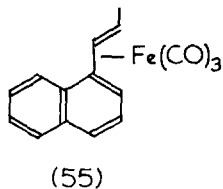
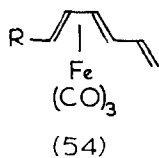
Addition of hydroxylamine to the aldehyde-complex gave $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{CH=NOH})$ and treatment of this with POCl_3 in chloroform caused formation of $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{CN})$.

Acylation of $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_5\text{R})$ ($\text{R} = \text{HMe}$) gave (262) syn and anti- $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_5\text{R}(\text{COMe}))$ (acylation occurred at the 4-position). Borohydride reduction afforded only the anti-alcohol $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_5(\text{CHMeOH}))$, and protonation subsequently produced the anti, anti-pentadienyl species $[\text{Fe}(\text{CO})_3(1\text{-R},5\text{-MeC}_5\text{H}_5)]^{+\text{}}$, A. Neutralisation of A with NEt_3 followed by heating the adduct in vacuo afforded the triene complex $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{R})$, 54. Addition of aniline or NHPH_2 to A occurred at the substituted end of the dienyl cation giving a cationic diene-amine adduct with syn-geometry, whereas PPh_3 or AsPh_3 added at the unsubstituted end giving quaternary phosphonium- or arsonium adducts having anti geometry.

Reaction of $\text{Fe}(\text{CO})_3(\eta^4\text{-diene})$ (diene = penta-1,3-, hexa-1,3 or 2,3-dimethylbuta-diene) with $\text{NaN}(\text{SiMe}_3)_2$ afforded $\text{Na}[\text{Fe}(\text{CO})_2(\eta^4\text{-diene})\text{CN}]$ (263).

Treatment of 3,3-dimethylcyclopropene with $\text{Fe}_2(\text{CO})_9$ gave $\text{Fe}(\text{CO})_2(\eta^4\text{-Me}_2\text{C:CHCH:C:O})$, whose structure was determined crystallographically (264). The bond lengths in the diene ligand were as follows: $\text{Me}_2\text{C}=\text{CH}$ 1.42 Å, $\text{CH}-\text{CH}$ 1.41 Å, $\text{CH}=\text{C}$ 1.44 Å, $\text{C}=\text{O}$ 1.19 Å; the angle in the CH:C:O group was 136.5° .

Reaction of 1-allylnaphthalene with $\text{Fe}_3(\text{CO})_{12}$ afforded 55 and of 1,3-diallylbenzene under the same conditions 56 (265).



Heterodiene Complexes. A kinetic study has been made of the exchange of the heterodiene in $\text{Fe}(\text{CO})_3(\eta^4\text{-enone})$ with cycloheptatriene, giving $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_7\text{H}_8)$ (266). It was shown that the reaction proceeded via competing associative and dissociative pathways.

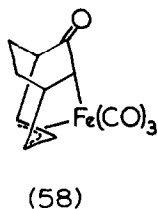
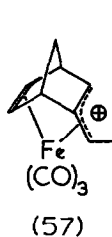
Treatment of $\text{Fe}(\text{CO})_4(\text{PPh}_3)$ with benzylidenacetone (bda) afforded $\text{Fe}(\text{CO})_2(\text{PPh}_3)(\text{bda})$, and other phosphine complexes could be made (267). Photolysis of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ with bda also gave $\text{Fe}(\text{CO})_2(\text{PPh}_3)(\text{bda})$. Triphenylphosphite reacted with $\text{Fe}(\text{CO})_3(\eta^4\text{-bda})$ giving $\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\text{bda})$. The species $\text{Fe}(\text{CO})_2\text{L}(\text{bda})$ was particularly useful as a means of preparing $\text{Fe}(\text{CO})_2\text{L}(\text{diene})$ complexes via exchange reactions. Thus it reacted with cyclohexa- and cycloheptadienes giving $\text{Fe}(\text{CO})_2\text{L}(\eta^4\text{-C}_6\text{H}_8)$ and $\text{Fe}(\text{CO})_2\text{L}(\eta^4\text{-C}_7\text{H}_{10})$ ($\text{L} = \text{PPh}_3, \text{P}(\text{OPh})_3$). Treatment of the latter with Ph_3C^+ gave $[\text{Fe}(\text{CO})_2\text{L}(\eta^5\text{-C}_7\text{H}_9)]^+$ which, on addition of NaOMe or morpholine, gave the 1-substituted-2,4-cyclic diene complexes $\text{Fe}(\text{CO})_2\text{L}(\eta^4\text{-C}_7\text{H}_9\text{R})$ ($\text{L} = \text{PPh}_3, \text{R} = \text{OMe}; \text{L} = \text{P}(\text{OPh})_3, \text{R} = \text{OMe, morpholine}$).

The electrochemical reduction of $\text{Fe}(\text{CO})_3(\text{bda})$ proceeded in two steps, giving, reversibly, a stable paramagnetic monoanion, and a dianion (268). The monoanion decomposed eventually releasing bda and giving $[\text{Fe}(\text{CO})_3(\text{solvent})]^-$, and reacted with $\text{MeCH}:\text{CHCH}_2\text{Br}$ giving first $[\text{Fe}(\text{CO})_3(\eta^3\text{-C}_4\text{H}_7)]^-$ and finally $\text{Fe}(\text{CO})_2(\eta^3\text{-C}_4\text{H}_7)_2$. The species $[\text{Fe}(\text{CO})_3(\text{solvent})]^-$ reacted with the tropylium cation giving the ditropylium species $\text{Fe}(\text{CO})_3(\text{C}_7\text{H}_7\text{C}_7\text{H}_7)$ and $\text{Fe}_3(\text{CO})_{12}$.

Complexes of Cyclic Non-Conjugated Dienes. The 2-aldehyde derivatives of norbornadiene reacted with $\text{Fe}_3(\text{CO})_{12}$ giving $\text{Fe}(\text{CO})_3(\text{C}_7\text{H}_7\text{CHO})$ which, on treatment (269) with MgMeI and acid, was converted into $\text{Fe}(\text{CO})_3(\text{C}_7\text{H}_7\text{CH}(\text{OH})\text{Me})$. Acidification of this alcohol afforded the cation $[\text{Fe}(\text{CO})_3(\text{C}_7\text{H}_7\text{CHMe})]^+$, probably 57.

Treatment of $[\text{Ru}(\text{diene})\text{Cl}]_2$ (diene = cycloocta-1,5-diene, norbornadiene) with $\text{NH}_2\text{C}_6\text{H}_{11}$, NHMe_2 or piperidine (L) gave $\text{Ru}(\text{diene})\text{L}_2\text{HCl}$, and the structure of $\text{Ru}(\text{C}_8\text{H}_{12})(\text{NHC}_5\text{H}_{10})_2\text{HCl}$ was determined crystallographically (270). The molecule was six-coordinate with the piperidine mutually cis and trans to the

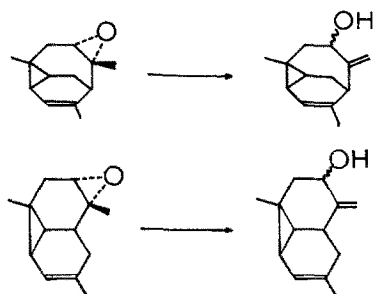
chelating di-olefin. Treatment of $\text{Ru}(\text{C}_8\text{H}_{12})\text{L}_2\text{HCl}$ with pyridine provided $\text{Ru}(\text{C}_8\text{H}_{12})(\text{pyr})_2\text{HCl}$. Addition of Lewis bases L (PMe_2Ph , $\text{P}(\text{OMe})_3$, $\text{P}(\text{OCH}_2)_3\text{CMe}$, $\text{P}(\text{OMe})\text{Ph}_2\text{PMe}_3$) and/or diene (buta- or hexa-1,3-diene) to $[\text{Ru}(\text{C}_8\text{H}_{12})(\text{NH}_2\text{NMe}_2)_3\text{H}][\text{PF}_6]$ afforded $[\text{Ru}(\text{diene})\text{L}_3\text{H}][\text{PF}_6]$ (271). The structure of $[\text{Ru}(\text{C}_4\text{H}_6)(\text{PMe}_2\text{Ph})_3\text{H}][\text{PF}_6] \cdot 0.5 \text{CH}_2\text{Cl}_2$, determined by X-ray methods, showed the phosphine ligands to be *fac* and the diene to be η^4 -bonded. An X-ray crystallographic examination of $[\text{Ru}(\text{C}_8\text{H}_{12})(\text{NH}_2\text{NMe}_2)\text{H}][\text{PF}_6]$ showed (272) that it had a similar geometry to its phosphine analogue (271), and that the hydrazine was bonded via the NH_2 -group. Treatment of $[\text{Ru}(\text{C}_8\text{H}_{12})(\text{NH}_2\text{NMe}_2)_3\text{H}]^+$ with LiX ($\text{X} = \text{Cl}$ or Br) afforded (273) the triply-bridged bimetallic species $(\text{C}_8\text{H}_{11})\text{Ru}(\mu\text{-H})(\mu\text{-X})(\mu\text{-NH}_2\text{NMe}_2)\text{Ru}(\text{C}_8\text{H}_{12})$, whose structure was confirmed crystallographically (274). There was apparently a metal-metal bond of length 2.91 Å. Reaction of the mother liquor obtained from crystallisation of this bimetallic with CO and PPh_3 afforded $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}(\text{PPh}_3)_2\text{HX}$, respectively. Reaction of the bimetallic with some Lewis bases L, e.g. PMePh_2 , SbPh_3 , AsPh_3 , pyridines, led to the formation of $\text{Ru}(\text{C}_8\text{H}_{12})\text{L}_2\text{HX}$, whereas with PPh_3 , $\text{P}(\text{OMe})\text{Ph}_2$, 4-MeC₅H₄N and NMe, $\text{Ru}(\text{PPh}_3)_3\text{HCl}$, $[\text{Ru}\{\text{P}(\text{OMe})\text{Ph}_2\}_5\text{H}][\text{PF}_6]$, $[\text{Ru}(\text{C}_8\text{H}_{12})\text{L}_3\text{H}]^+$ ($\text{L} = \text{NMe}$, 4-MeC₅H₄N) and $\text{Ru}(4\text{-MeC}_5\text{H}_4\text{N})_4\text{Cl}_2$ were isolated.



Complexes of Cyclic Conjugated Dienes and Related Olefins. The structure of the 2,5-dimethyl-3,4-dipropynylcyclopentadienone complex $\text{Fe}(\text{CO})_3\{\eta^4\text{-C}_5\text{Me}_2(\text{C}_2\text{Me})_2\text{O}\}$, obtained (275) by reaction of $\text{Fe}(\text{CO})_5$ with 2,4-hexadiyne, has been determined crystallographically (276). The similar 2,5-bis-(acetyl)-3,4-bis(triphenylgermyl)cyclopentadienone complex $\text{Fe}(\text{CO})_3\{\eta^4\text{-C}_5(\text{COMe})_2(\text{GePh}_3)_2\text{O}\}$ was prepared (277) by treatment of $\text{Ph}_3\text{GeC}_2\text{COMe}$ with $\text{Fe}_2(\text{CO})_9$.

Aluminium halides formed, reversibly, 1:1 adducts with $\text{Fe}(\text{CO})_3(\eta^4\text{-diene})$ (diene = C_6H_8 , C_7H_8 , C_8H_8) and involved Fe-AlX_3 bonding (278). However, on rearrangement, $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_8)$ gave 58 which also reversibly formed adducts with AlX_3 involving both the keto group and the metal. $\text{Fe}(\text{CO})_3$ derivatives of dihydroanionic esters have been prepared from the appropriate organic compound and $\text{Fe}(\text{CO})_5$ (279), and underwent H^+ abstraction using Ph_3C^+ to giving cyclohexadienyl iron tricarbonyl cations. Treatment of these with carboanions afforded new diene complexes, as shown in Scheme 4. $\text{Fe}(\text{CO})_5$ reacted with 1-methoxycyclohexa-1,3-diene giving two isomers of $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{OMe})$ (280).

Scheme 4



Treatment of these with Ph_3C^+ afforded the appropriate cyclohexadienyl salts, $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_6\text{OMe})]^+$ which, hydrolysed to give the iron tricarbonyl derivative of cyclohexa-2,4-dien-4-one.

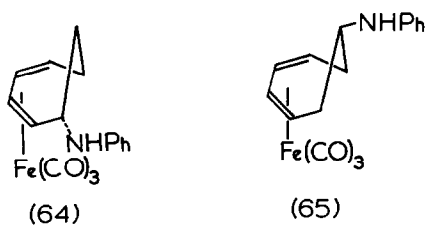
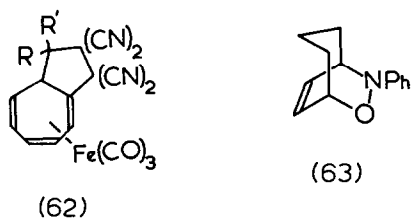
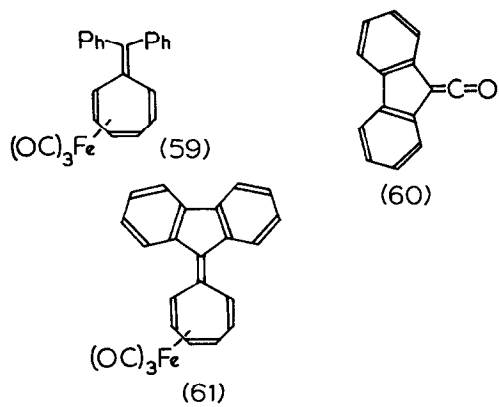
An X-ray structural examination of $\text{Fe}(\text{CO})_2(\text{CNEt})(\eta^4\text{-C}_6\text{H}_8)$ revealed (281) that the molecule had an overall square pyramidal structure with the diolefin, isonitrile and one CO ligand occupying the basal positions. The species was fluxional, and reacted with Ph_3C^+ giving $[\text{Fe}(\text{CO})_2(\text{CNEt})(\eta^5\text{-C}_6\text{H}_7)]^+$.

$\text{Fe}_3(\text{CO})_{12}$ reacted with 1-silacyclohexa-2,4-dienes, $\text{C}_5\text{H}_6\text{SiR}_2$ ($\text{R} = \text{Ph}, \text{Me}, \text{Cl}$) to give $\text{Fe}(\text{CO})_3(\eta^4\text{-diene})$ which could be photolysed in the presence of PPh_3 affording $\text{Fe}(\text{CO})_2(\text{PPh}_3)(\text{C}_5\text{H}_6\text{SiR}_2)$ (282). An X-ray crystallographic examination of $\text{Fe}(\text{CO})_3(\text{C}_5\text{H}_6\text{SiPh}_2)$ established that the ring when η^4 -bonded via the C atoms, and that the SiPh_2 group did not interact with the metal. Reaction of $\text{Fe}_3(\text{CO})_{12}$ with 1,1-dimethyl-1-sila-2-oxacyclohexa-3,5-diene similarly provided the species $\text{Fe}(\text{CO})_3(\eta^4\text{-diene})$ (283).

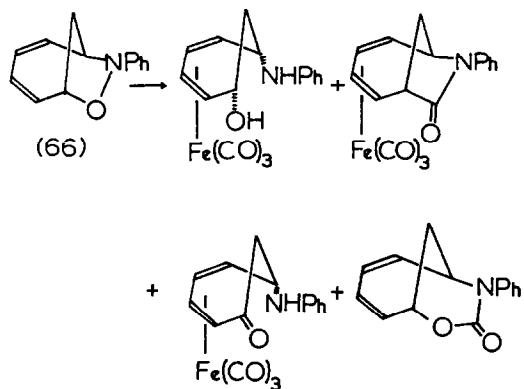
Detection and measurement of the rate of 1,3-shifts in $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_7\text{H}_8)$ and in the 1,1-disubstituted analogue $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_7\text{H}_6\text{Ph}(\text{CO}_2\text{Me}))$ has been made (284) via ^1H n.m.r. spectral studies using spin-saturation techniques (285).

Irradiation of the tropone complex $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_7\text{H}_6\text{O})$ by left- or right-hand circularly polarised light caused preferential destruction of one of the two enantiomers (286). Treatment of $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_7\text{H}_6\text{O})$ with diphenylketene afforded the diphenylheptafulvene complex 59 ($\text{R} = \text{R}' = \text{Ph}$), whereas with 60, the sesquifulvalene complex 61 was formed (287). Cycloaddition of TCNE to 59 ($\text{R} = \text{Me}, \text{R}' = \text{H}; \text{R} = \text{Ph}, \text{R}' = \text{H}, \text{Me}$) gave 62, in a reaction analogous to the known [8 + 2] cycloaddition reactions of 7-methylene-cycloheptatriene (288).

Reaction of the bicyclic 1,2-oxazirine 63 with $\text{Fe}_2(\text{CO})_9$ afforded 1-anilino-4-hydroxy-cyclohept-2-ene, and two isomers of anilino-substituted cycloheptadiene iron tricarbonyl, 64 and 65 (289). The diene could be released from 64 by its treatment with Me_3NO , and this reacted with $\text{Fe}_2(\text{CO})_9$ regenerating not only 64 and 65 but giving also the isomer of 64 in which the NPh substituent was *exo* to the $\text{Fe}(\text{CO})_3$ group. This last isomer was also obtained by reaction of the cycloheptadienyl salt $[\text{Fe}(\text{CO})_3(\text{C}_7\text{H}_9)]^+$ with aniline. Treatment of the oxazirine 66 with $\text{Fe}_2(\text{CO})_9$ is summarised in Scheme 5, and addition of aniline

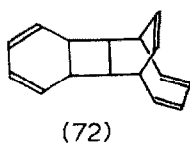
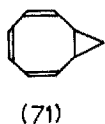
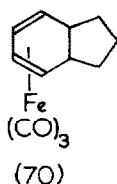
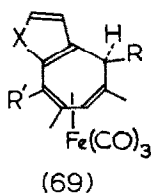
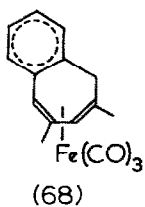
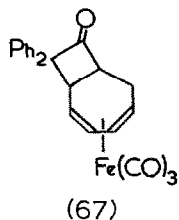


Scheme 5



to the cyclic dienyketone complex, $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_7\text{O})]^+$ afforded the *exo*-isomer of the ketone shown in Scheme 5. The mechanism of these reactions was discussed. Cycloaddition of diphenylketone to the cycloheptatriene complex $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_7\text{H}_8)$ afforded 67 (290). Iron tricarbonyl-induced vinylcyclopropane-cyclopentene rearrangements, especially in 4,5-homotropylidene species have been extensively investigated (291) using a combination of crystallographic and n.m.r. spectroscopic techniques. Successive cleavage of two bonds in cyclopropane rings within diene species occurred within the ligand sphere of an $\text{Fe}(\text{CO})_6$ unit.

The species 68 and 69 ($X = \text{O}$ or S ; $R = R' = \text{H}$; $R = \text{H}$, $R' = \text{Me}$; $R' = \text{Me}$, $R = \text{H}$) were obtained by reaction of the appropriately annelated tropylidenes with $\text{Fe}(\text{CO})_5$ (292). The structures of 69 ($X = \text{O}$ and S ; $R = R' = \text{H}$) were determined by X-ray methods.

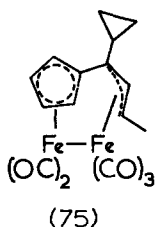
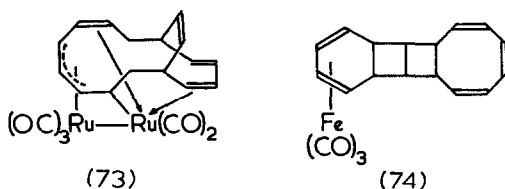


Under mild conditions cycloocta-1,3,5- and 1,3,6-trienes reacted (293) with $\text{Fe}_2(\text{CO})_9$ giving $\text{Fe}_2(\text{CO})_7(1,3,6\text{-C}_8\text{H}_{10})$, $\text{Fe}_2(\text{CO})_8(1,3,5\text{-C}_8\text{H}_{10})$ and $\text{Fe}_2(\text{CO})_7(1,3,5\text{-C}_8\text{H}_{10})$. The first contained $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$ groups, the latter attached to the *cis*-3,5-diene group, the second two $\text{Fe}(\text{CO})_4$ groups, and the third, like the first, $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$ units. At 65° , all three isomerised to the metal-metal bonded species $\text{Fe}_2(\text{CO})_6(1,3,5\text{-C}_8\text{H}_{10})$. At room temperature, 1,4,6-cyclononatriene reacted with $\text{Fe}_2(\text{CO})_9$ giving $\text{Fe}(\text{CO})_4(\eta^2\text{-C}_9\text{H}_{12})$, the metal being attached to the isolated double bond. At 70° this species converted to $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_9\text{H}_{12})$, in which the olefin had isomerised to 1,3,5-

C_9H_{12} , a species also obtained directly, together with the cyclopentadienyl complex $[Fe(CO)_2(\eta^5-C_5H_3CH_2CH_2CH_2CH_2)]_2$ when cyclononatriene was refluxed with $Fe_2(CO)_9$ in benzene. On heating $Fe(CO)_3(\eta^4-C_9H_{12})$, the cyclohexadiene complex 70 was formed. Reaction of the bicyclic triene 71, C_9H_{10} , with $Fe_2(CO)_9$ at room temperature gave $Fe(CO)_3(C_9H_{10})$, $Fe_2(CO)_6(C_9H_{10})$ and the iron tricarbonyl derivative of cyclonona-1,3,5,7-tetraene.

From a VT ^{13}C n.m.r. spectral study of $Fe(\eta^6-C_8H_8)(\eta^4-C_8H_8)$, it was shown (294) that site exchange between the η^4 - and η^6 -rings occurred via a mechanism where the transition states retained differentiation between the four different types of CH groups in the $\eta^6-C_8H_8$ ring. No evidence was found for any shifts within the $\eta^6-C_8H_8$ ring. Treatment of $Fe(C_8H_8)_2$ with $R_2PCH_2CH_2PR_2$ ($R = Ph$ or Me), $PhP(CH_2CH_2CH_2PPh_2)_2$ (triphos) or $P(OMe)_3$ gave (295) $Fe(C_8H_8)(Ph_2PCH_2CH_2PPh_2)(N_2)$, $Fe_2(C_8H_8)_2(Me_2PCH_2CH_2PMe_2)$, $Fe(C_8H_8)(triphos)$ and $Fe(C_8H_8)\{P(OMe)_3\}_3$. Nitrogen could be displaced from the first by CO or formic esters, giving the analogous monocarbonyl.

Formal Diels-Alder dimerisation of cyclooctatetraene, giving 72 ($C_{16}H_{16}$), occurred (296) in the reaction between C_8H_8 and $Ru_4(CO)_{12}H_4$. $Ru(CO)_3(C_{16}H_{16})$ and $Ru_2(CO)_5(C_{16}H_{16})$ and $Ru_2(CO)_5(C_{16}H_{16})$, 73, were also produced in this reaction, the $Ru(CO)_3$ unit in the former being attached to the cyclohexadiene ring in 72. The latter complex, 73, was fluxional, and reacted with CO giving $Ru_2(CO)_6(C_{16}H_{16})$ in which the coordinated double bond of the cyclic triene ring was displaced. It was noted that the complexes obtained from cyclooctatetraene and triruthenium carbonyls included $Ru(CO)_3(C_8H_8)$, $Ru_2(CO)_6(C_8H_8)$, $Ru_2(CO)_5(C_8H_8)$, $Ru_3(CO)_4(C_8H_8)_2$, $Ru_3(CO)_8(C_8H_8)$ and $Ru_3(CO)_6(C_8H_8)_2$ and it was suggested that the earlier reported (297) *trans*- $Ru_2(CO)_6C_8H_8$ is, in fact, the same as $Ru(CO)_3(C_{16}H_{18})$ reported above. In the formation of 72 and the complexes derived from it, $Ru(CO)_3(\eta^4-C_8H_8)$ was thought to be an intermediate. Indeed, thermal reaction of the last species with C_8H_8 gave both $Ru(CO)_3(C_{16}H_{16})$ and 73,



although uv irradiation afforded only $\text{Ru}_4(\text{CO})_5(\text{C}_8\text{H}_8)$ and $\text{Ru}_3(\text{CO})_4(\text{C}_8\text{H}_8)_2$. Reaction of either $\text{Ru}_3(\text{CO})_{12}$ or $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ with 72 gave $\text{Ru}(\text{CO})_3(\text{C}_{16}\text{H}_{16})$ in low yield, and also $\text{Ru}_3(\text{CO})_9(\text{C}_{16}\text{H}_{14})\text{H}_2$ which may be related to the known $\text{Ru}_3(\text{CO})_9(\text{C}_8\text{H}_{12})\text{H}_2$ (298), which is thought to contain 72 bridging a trimeric $\{\text{Ru}(\text{CO})_3\}_3(\mu_2\text{-H})_2$ unit. It was also noted that $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_8)$ reacted on refluxing with C_8H_8 to give a different complexed cyclooctatetraene dimer, 74.

CYCLOPENTADIENYL COMPLEXES

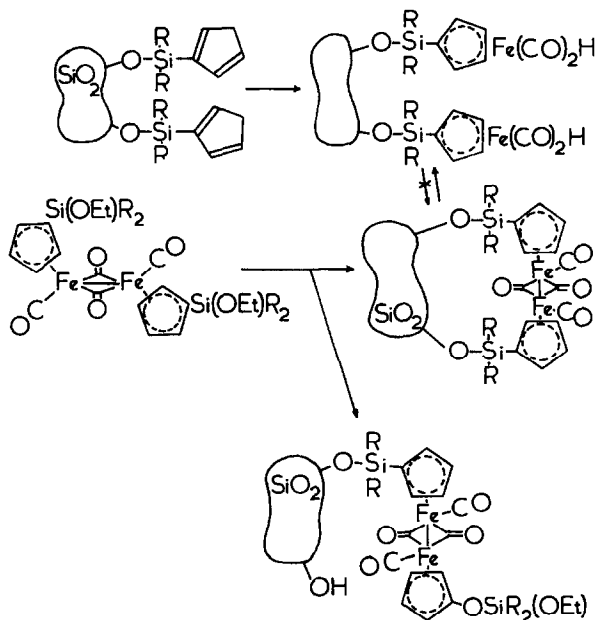
Throughout this section the cyclopentadienyl ring is assumed to be η^5 -bonded.

Neutral Binuclear Species. From X-ray and neutron diffraction studies, electron deformation density maps have been compiled for $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ (299). There appears to be no electron density in the region of the formal Fe-Fe bond!

Treatment of silica gel with $\text{Si}(\text{OEt})\text{Me}_2(\text{C}_5\text{H}_5)$ and $\text{Si}(\text{OEt})_3(\text{C}_5\text{H}_5)$ at $60\text{-}80^\circ$ afforded (300) the functionalised gel as shown in Scheme 6. Reaction of the functionalised gel with $\text{Fe}_2(\text{CO})_9$ gave cyclopentadienyl dicarbonyl iron hydride derivatives, but these, on heating did not eliminate hydrogen to give bimetallic species. However, reaction of $\text{Fe}_2(\text{CO})_9$ with $\text{Si}(\text{OEt})\text{R}_2(\text{C}_5\text{H}_5)$ (R = Me or OEt) gave $[\text{Fe}(\text{CO})_2\{\text{C}_5\text{H}_4\text{Si}(\text{OEt})\text{R}_2\}]_2$ which could then be attached to the silica gel affording bimetallic species as shown in Scheme 6.

Reaction of $\text{Fe}_2(\text{CO})_9$ with 6,6-dicyclopropylfulvene afforded the bimetallic species 75, which contains η^5 -cyclopentadienyl and η^3 -allyl groups (301).

Scheme 6



Ethyl(tetramethyl)cyclopentadiene reacted with $\text{Ru}_3(\text{CO})_{12}$ giving (302) $[\text{Ru}(\text{CO})_2(\text{C}_5\text{Me}_4\text{Et})]_2$ whose structure was determined crystallographically. The rings were mutually trans, there were two bridging CO groups, and Ru-Ru = 2.76 Å. The complex reacted slowly with CHX_3 giving $\text{Ru}(\text{CO})_2(\text{C}_5\text{Me}_4\text{Et})\text{X}$ (X = Cl or Br).

Photolysis of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2\text{SiMeR}$ gave $\text{Fe}_2(\text{CO})_3(\text{C}_5\text{H}_5)_2(\mu_2\text{-SiMeR})$ (R = H, Cl), containing one bridging CO group and a bridging SiMeR^{2-} ligand (303). Treatment of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ with $\text{P}(\text{CF}_3)_2(\text{OCH}_2\text{CH}_2\text{Cl})$ afforded $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\{\text{P}(\text{CF}_3)_2\}$ and other unidentified products (304).

ESCA studies and MO calculations have been made of $[\{\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)\}_2\text{-}\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]^{\text{m}+}$ (n = 1,2; m = 0,1), and it appeared (305) that oxidation of the neutral species involved removal of electrons from a non-binding Fe-Fe-based orbital, rather than removal of electrons from a metal-metal σ bond.

Electron-impact mass spectral studies have been made of $[\text{Fe}(\text{CO})(\text{CS})(\text{C}_5\text{H}_5)]_2$ and $\text{Fe}_2(\text{CO})_3(\text{CS})(\text{C}_5\text{H}_5)_2$ (306). Appearance potentials for most of the metal-containing fragments were determined, and it was found that fragment ions resulting from the loss of CO were much more abundant than those resulting from loss of CS. Reaction of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]^-$ with $(\text{PhO})_2\text{CS}$ gave (307,308) the cis- and trans-isomers of $\text{Fe}_2(\text{CO})_3(\text{CS})(\text{C}_5\text{H}_5)_2$ (containing $\mu_2\text{-CS}$). These isomers interconverted in solution, and reacted with alkylating agents giving $[\text{Fe}_2(\text{CO})_2(\mu_2\text{-CO})(\mu_2\text{-CSR})(\text{C}_5\text{H}_5)_2]^+$ (R = Me, Et) (307). The structure of the cis-cation, as a BF_4^- salt with R = Me, was determined crystallographically. Sodium amalgam reduction of $\text{Fe}_2(\text{CO})_3(\text{CS})(\text{C}_5\text{H}_5)_2$ afforded $[\text{Fe}(\text{CO})(\text{CS})(\text{C}_5\text{H}_5)]^-$ (308), which reacted with MeI affording a species described as $\{\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)(\text{CS-Me})\}$ of unknown structure. Reaction of the anion with SnClPh_3 gave $\text{Fe}(\text{CO})(\text{CS})(\text{C}_5\text{H}_5)\text{SnPh}_3$ which further reacted with NH_2Me and ethylenediamine giving $\text{Fe}(\text{CO})(\text{CNMe})(\text{C}_5\text{H}_5)\text{SnPh}_3$ and the carbene species $\text{Fe}(\text{CO})(\text{CNHCH}_2\text{CH}_2\text{NH})(\text{C}_5\text{H}_5)\text{SnPh}_3$, respectively. Halogenation of $\text{Fe}_2(\text{CO})_3(\text{CS})(\text{C}_5\text{H}_5)_2$ gave a mixture of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{X}$ and $\text{Fe}(\text{CO})(\text{CS})(\text{C}_5\text{H}_5)\text{X}$ in low yields, while the HgCl , and O_2 and HBF_4 $\text{Fe}_2(\text{CO})_3(\text{CSHgCl}_2)(\text{C}_5\text{H}_5)_2$ and $\text{Fe}_2(\text{CO})_3(\text{CSFe}(\text{CO})_2(\text{C}_5\text{H}_5))(\eta\text{-C}_5\text{H}_5)_2$ were apparently formed, albeit in low yield. Methylation of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\{\text{C}(\text{:S})\text{OPh}\}$ afforded the carbene species $[\text{Fe}(\text{CO})_2\{\text{C}(\text{SMe})\text{OPh}\}(\text{C}_5\text{H}_5)]^+$ which underwent elimination of methanethiol and phenol in methanol, giving $[\text{Fe}(\text{CO})_2\{\text{C}(\text{OMe})_2\}(\text{C}_5\text{H}_5)]^+$ (308).

A IR spectral study has been made of the tautomeric equilibria of $\text{Fe}_2(\text{CO})_3(\text{CNR})(\eta^5\text{-dienyl})_2$ (dienyl = C_5H_5 , $\text{C}_5\text{H}_4\text{Me}$, C_9H_7 ; R = alkyl or benzyl) in solution (309). The studies revealed the presence of four isomers which had structures based on cis- and trans- $\text{Fe}_2(\text{CO})_2(\mu_2\text{-CO})_2(\text{C}_5\text{H}_5)_2$. In two of these isomers, the CNR ligand replaced a $\mu\text{-CO}$ group, while in the others it had replaced a terminal CO ligand. The equilibria between the various forms were a function of steric hindrance, electronic effects, solvent and temperature.

UV irradiation of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ with $\text{NMe}(\text{PF}_2)_2$ gave $\text{Fe}_2(\mu_2\text{-CO})_2(\mu_2\text{-F}_2\text{PNMePF}_2)(\text{C}_5\text{H}_5)_2$ (Fe-Fe bond) and $\text{Fe}_2(\mu_2\text{-PF}_2)(\mu_2\text{-MeN:PF}_2)\text{-}$

$(\mu_2\text{-F}_2\text{PNMePF}_2)(\text{C}_5\text{H}_5)_2$ (310). The structure of the latter was established by X-ray methods and the inter-iron distance, 3.65 Å, was judged to be non-bonding.

Cationic Species. Chloride extraction from $\text{Ru}(\text{CO})\text{L}(\text{C}_5\text{H}_5)\text{Cl}$, using AlCl_3 or $\text{BF}_3 \cdot \text{OEt}_2$, in the presence of CO gave $[\text{Ru}(\text{CO})_2\text{L}(\text{C}_5\text{H}_5)]^+$ (L = PPh_3 , PEt_3 , C_3H_6 , $\text{c-C}_6\text{H}_{10}$, NH_3 , CNMe); $[\text{Ru}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{C}_5\text{H}_5)]^+$ was also prepared (311).

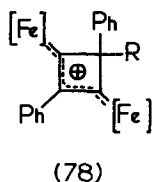
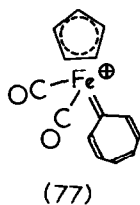
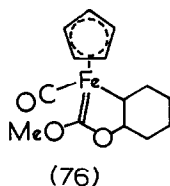
Reaction of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]^-$ with CS_2 , followed by addition of MeI , gave $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\{\text{C}(\text{:S})\text{SMe}\}$ which, on treatment with HCl , and NH_4PF_6 , provided a convenient route to $[\text{Fe}(\text{CO})_2(\text{CS})(\text{C}_5\text{H}_5)][\text{PF}_6]$ (312).

Anionic Species. Reaction of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]^-$ with CO_2 gave (313) $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ and carbonate ion. When $^{13}\text{CO}_2$ was used, ^{13}CO was observed in the iron complex. When $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]^-$ was dissolved in liquid SO_2 at -78°C , a red solution was formed which, on treatment with MeI , gave (314) both $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\{\text{S}(\text{:O})_2\text{Me}\}$ and $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$. It was suggested that $[\text{Fe}(\text{CO})_2(\text{SO})_2](\text{C}_5\text{H}_5)]^-$ was an intermediate in this reaction and on warming solutions believed to contain this species, followed by chromatography, $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2(\mu_2\text{-SO}_2)$, $[\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)]_2(\mu\text{-CO})(\mu\text{-SO}_2)$, and $[\text{Fe}(\text{CO})_2(\text{SO}_2)(\text{C}_5\text{H}_5)]_2$ were isolated.

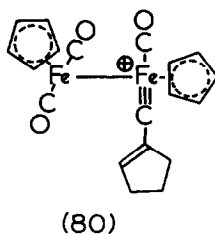
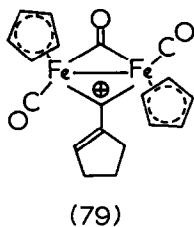
Carbene and Vinylidene Complexes. Treatment of $[\text{Fe}(\text{CO})(\text{CNR})_2(\text{C}_5\text{H}_5)]^+$ with $\text{NH}_2\text{R}'$ ($\text{R}, \text{R}' = \text{Me}, \text{Et}, \text{Pr}^+$) gave $[\text{Fe}(\text{CO})(\text{CNR})\{\text{C}(\text{NHR})(\text{NHR}')\}(\text{C}_5\text{H}_5)]^+$ (315). Similar idenyl complexes were obtained, and $[\text{Fe}(\text{CO})(\text{CNMe})_2(\text{C}_5\text{H}_5)]^+$ was readily converted to a mixture of $[\text{Fe}(\text{CO})(\text{CNMe})\{\text{C}(\text{NHMe})(\text{NHR}')\}(\text{C}_5\text{H}_5)]^+$ and $[\text{Fe}(\text{CO})(\text{CNR})\{\text{C}(\text{NHMe})_2\}(\text{C}_5\text{H}_5)]^+$. Treatment of $\text{Fe}(\text{CO})(\text{PR}''_3)(\text{C}_5\text{H}_5)\text{CN}$ ($\text{R}'' = \text{Me}, \text{Ph}$) with RX gave $[\text{Fe}(\text{CO})(\text{CNR})(\text{PR}''_3)(\text{C}_5\text{H}_5)]^+$ (R as above), and these species were also readily converted to carbene complexes. $\text{Fe}(\text{CO})(\text{CNR})(\text{C}_5\text{H}_5)(\text{CN})$ afforded $\text{Fe}(\text{CO})\{\text{C}(\text{NHR})(\text{NHR}')\}(\text{C}_5\text{H}_5)(\text{CN})$ more slowly than the cationic species. Rotational isomerism was observed about the $\text{Fe-C}(\text{NHR})(\text{NHR}')$ bond.

Treatment of 76 with acid at low temperature gave (316) the coordinatively unsaturated $[\text{Fe}(\text{CO})\{\text{C}(\text{OMe})(\text{OC}_6\text{H}_{11})\}(\text{C}_5\text{H}_5)]^+$ which took up CO giving $[\text{Fe}(\text{CO})_2\{\text{C}(\text{OMe})(\text{OC}_6\text{H}_{11})\}(\text{C}_5\text{H}_5)]^+$. Under ethylene pressure at -20° , the mono-carbonyl afforded $[\text{Fe}(\text{CO})(\text{C}_2\text{H}_4)\{\text{C}(\text{OMe})(\text{OC}_6\text{H}_{11})\}(\text{C}_5\text{H}_5)]^+$, the coordinated olefin being readily displaced by coordinating solvents. Two conformers of the ethylene complex were detected in solution, their existence probably being due to restricted rotation about the metal-carbene bond. Reaction of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$ with LiC_7H_7 afforded the σ -cycloheptatrienyl complex $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(\eta^1\text{-C}_7\text{H}_7)$ which underwent hydride abstraction (317) to give the cycloheptatrienyldiene species 77. Protonation of $\text{Fe}(\text{CO})\text{L}(\text{C}_5\text{H}_5)\text{C}_2\text{Ph}$ (L = CO or PPh_3) gave (318) the previously observed $[\text{Fe}(\text{CO})\text{L}(\text{C}_5\text{H}_5)(\text{C}=\text{CHPh})]^+$ (319). Reaction of this with methanol afforded (318) $[\text{Fe}(\text{CO})\text{L}(\text{C}_5\text{H}_5)\{\text{C}(\text{OMe})\text{CH}_2\text{Ph}\}]^+$ which rearranged in methanol to give $\text{Fe}(\text{CO})\text{L}(\text{C}_5\text{H}_5)\text{COCH}_2\text{Ph}$. This last species was also formed by direct attack of OH^- on $[\text{Fe}(\text{CO})\text{L}(\text{C}_5\text{H}_5)\text{C}=\text{CHPh}]^+$. Addition of $\text{HBF}_4 \cdot \text{OME}_2$ to $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{C}_2\text{Ph}$ in dichloromethane gave, however, the bimetallic carbene

species 78 ($R = H; [Fe] = Fe(CO)_2(C_5H_5)$). Similarly, methylation using $MeOSO_2F$ gave 78 ($R = Me$). The mechanism of this reaction was thought to involve the intermediacy of the species $[Fe-C(=CHPh)CPh=CFe]^+$.

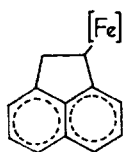


Reaction of $Na[Fe(CO)_2(C_5H_5)]$ with ethyleneoxide gave $[Fe(CO)_2(C_5H_5)CH_2CH_2O]^-$ which ultimately deoxygenated to $[Fe(CO)_2(C_2H_4)(C_5H_5)]^+$ via either $[Fe(CO)(C_5H_5)\{CH_2CH_2OC:O\}]^-$ or its tautomer $Fe(CO)\{C(O^-)OCH_2CH_2\}(C_5H_5)$ as intermediate. Using $Li[Fe(CO)_2(C_5H_5)]$ the rate of this reaction was significantly enhanced (320). However, the reaction with cyclopenteneoxide was different. If the reaction time was kept short, on acidification $[Fe(CO)_2(\eta_2-C_5H_8)(C_5H_5)]^+$ was obtained. Over a longer reaction period, however, 79 was produced which, on heating was converted to the cis-isomer via the carbyne intermediate 80. Exo-norbornene epoxide behaved similarly. Treatment of $Fe(CO)_2(C_5H_5)CH_2Ph$ with $Li[Fe(CO)_2(C_5H_5)]$ followed by acidification gave $[Fe_2(CO)_2(\mu-CO)(\mu-CCH_2Ph)(C_5H_5)_2]^+$, and similar species $[Fe_2(CO)_2(\mu-CO)(\mu-CR)(C_5H_5)_2]^+$ ($R = Me, Bu^N$ or Ph) were prepared by reaction of $[Fe(CO)_2(C_5H_5)]_2$ with LiR and HBF_4 . Addition of $Li[Fe(CO)_2(C_5H_5)]$ to $[Fe(CO)_2\{C(OMe)(OC_6H_{11})\}(C_5H_5)]^+$ gave $Fe_2(CO)\{C(OMe)(OC_6H_{11})\}(\mu_2-CO)_2(C_5H_5)_2$.

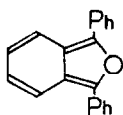


Protonation or methylation of $\text{FeLL}'(\text{C}_5\text{H}_5)\text{C}_2\text{R}$ ($\text{L} = \text{L}' = \text{CO}$, $\text{R} = \text{Ph}$; $\text{L} = \text{CO}$, $\text{L}' = \text{PPh}_3$, $\text{R} = \text{CO}$; $\text{LL}' = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $\text{R} = \text{H}$, Me) gave (321) the vinylidene complexes $[\text{FeLL}'(\text{C}_5\text{H}_5)=\text{C}=\text{CRR}']^+$ ($\text{R}' = \text{H}$ or Me). A similar ruthenium complex $[\text{Ru}(\text{PPh}_3)_2(\text{C}_5\text{H}_5)\text{CCHR}]^+$ ($\text{R} = \text{Me}$, Ph , C_6H_5 , CO_2Me) was prepared (322) from $\text{Ru}(\text{PPh}_3)_2(\text{C}_5\text{H}_5)\text{Cl}$, RC_2H and NH_4PF_6 . Deprotonation of the vinylidene complex readily afforded $\text{Ru}(\text{PPh}_3)_2(\text{C}_5\text{H}_5)\text{C}_2\text{R}$.

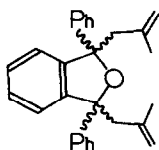
Olefin Complexes. Treatment of the acenaphthylene complex $[\text{Fe}(\text{CO})_2(\eta^2\text{-C}_{12}\text{H}_8)(\text{C}_5\text{H}_5)]^+$ with NaBH_3CN gave (323) the η^1 -acenaphthenyl complex $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{C}_{12}\text{H}_9)$, **81** ($\text{Fe} = \text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$). Thermal decomposition, either in vacuo or in refluxing toluene, afforded $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$, acenaphthene, acenaphthylene, bis(acenaphthenyl) and some polymer. The reaction involved conventional β -elimination, Fe-C bond homolysis to give acenaphthenyl radicals, and also hydrogen abstraction from the cyclopentadienyl ring by an undetermined pathway.



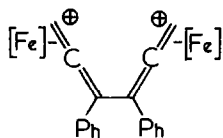
(81)



(82)

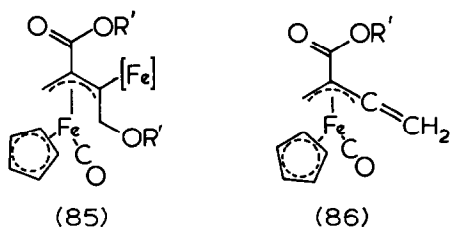


(83)



(84)

Oxidative coupling by Ag^+ of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\text{CR}=\text{CR}'\text{CR}''$ afforded (324) three complexes, $[\{\text{Fp}\}(\eta^2\text{-CH}_2=\text{CR}'\text{CR}''\text{CR}'\text{R}'\text{CR}=\text{CH}_2)]^+$, $[\{\text{Fp}\}(\text{CH}_2=\text{CR}'\text{CR}''\text{CR}'\text{R}'\text{CR}=\text{CH}_2\{\text{Fp}\})]^{2+}$, and $[\{\text{Fp}\}(\eta^2\text{-CH}_2\text{CR}'\text{CR}''\text{H})]^+$ ($\text{Fp} = \text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$). Treatment of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\text{CMe}=\text{CH}_2$ with **82** in the presence of Ag^+ and then I^- led to formation of **83** and $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$. Oxidation of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\text{C}_2\text{Ph}$ by two moles of Ag^+ gave **84** ($\text{Fp} = \text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$). Hydride abstraction by Ph_3C^+ from $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\text{C}_2\text{CH}_2\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$ gave (325) the bimetallic $\eta^2:\eta^2$ -butatriene complex $[\{\text{Fp}\}(\text{CH}_2=\text{C}=\text{C}=\text{CH}_2)\{\text{Fp}\}]^{2+}$, **A** ($\text{Fp} = \text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$). Reaction of **A** with OH^- afforded $\text{Fp}(\text{C}(\text{OMe})=\text{CH}_2)$, whereas bicarbonate caused formation of this and also $\text{FpCH}_2\text{COC}(\text{Fp})=\text{CH}_2$, **B**. Acetate, phenolate and p-nitrophenolate (OR^-) reacted with **A** giving $[\{\text{Fp}\}(\eta^2\text{-CH}_2=\text{C}=\text{C}(\text{OR})\text{CH}_2\text{Fp})]^+$ whereas alkoxide gave **85**, **86** and cis- and trans- $\text{Fe}_2(\text{CO})_3(\eta^2\text{-CH}_2=\text{C}(\text{CO}_2\text{R}')\text{CH}=\text{CHOR}')(\text{C}_5\text{H}_5)_2$ ($\text{R}' = \text{Me}$, Et , Pr^1). Reaction with $[\text{O}^-\text{Bu}^t]$ gave only $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$. Treatment of **B** with Et_3O^+ gave $[\text{FpCH}_2\text{C}(\text{OEt})\text{CFp}=\text{CH}_2]^+$.



Complexes containing M-C σ -Bonds. Thermolysis of $\text{Me}_2\text{Si}\{\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{C}_5\text{H}_{11}\}_2$ and $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_{11})$ gave pentene, the yield from the former being higher than from the latter (326). $\text{Me}_2\text{Si}\{\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2(\text{CH}_2)_5\text{Fe}(\text{CO})_2\text{C}_5\text{H}_4\}\text{SiMe}_2$ and $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{CH}_2)_5\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$ behaved similarly indicating that β -elimination did not occur in two sequential steps. The pentene products were the 1- and *cis*- and *trans*-2-isomers, and pentane was also detected.

Cyclopropenium salts, $[\text{C}_3\text{R}_2\text{R}']\text{X}$ ($\text{R} = \text{Ph}$, $\text{R}' = \text{Ph}$, H ; $\text{R} = \text{Bu}^t$, $\text{R}' = \text{Me}$; $\text{X} = \text{BF}_4$, Br , ClO_4) reacted (327) with $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]$ giving the cyclopropene derivative $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CR}'\text{CR}=\text{CR}$. The cyclopropenyl cation salt $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\overline{\text{C}=\text{CR}=\text{CR}}][\text{ClO}_4]$ ($\text{R} = \text{NPr}^i$) was obtained from $[\text{C}_3(\text{NPr}^i)_3\text{Cl}][\text{ClO}_4]$. Treatment of bis(diisopropylamino)triafulvene with $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$, followed by addition of KClO_4 , led to the isolation of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\overline{\text{C}=\text{C}(\text{NPr}^i)}_2]\overline{\text{C}(\text{NPr}^i)=\text{C}(\text{NPr}^i)}][\text{ClO}_4]$ (328).

The cyclopropyl halides $\text{C}_3\text{H}_5\text{CH}_2\text{X}$ ($\text{X} = \text{Br}$, I) reacted (329) with $\text{Na}[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]$ at 0° in THF to give $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\text{C}_3\text{H}_5$ and $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\text{CH}=\text{CH}_2$. With the bromide, the ratio of the two species was 70:30, whereas when $\text{X} = \text{I}$ it was >97:>3; the reaction with $\text{C}_3\text{H}_4\text{CH}_2\text{I}$ involving radical pathways to a significant degree. Chemical or electrochemical oxidation of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{R}$ ($\text{R} = \text{Me}$, CH_2Ph or $\text{CH}_2\text{CH}_2\text{Ph}$) in dichloromethane in the presence of Cl^- afforded $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{Cl}$ and RCl (330). The reaction was believed to occur via $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{R}]^+$ and $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$.

Electron-impact mass spectral studies of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\text{OMe}$ showed that the major fragments were $[\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)\text{CH}_2\text{OMe}]^+$ and $[\text{Fe}(\text{C}_5\text{H}_5)\text{CH}_2\text{OMe}]^+$ (331) and that $[\text{Fe}(\text{CO})_n(\text{C}_5\text{H}_5)\text{CH}_2]^+$ was present only in low abundance. However, when NH_4^+ , C_2H_5^+ , CH_5^+ or H_3^+ was added, the abundance of the "carbene" species rose significantly. Indeed $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{CH}_2)]^+$, in the gas phase, reacted with cyclohexene giving $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]^+$ and norcaradiene, whereas $[\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)(\text{CH}_2)]^+$ afforded $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_6\text{H}_{10})]^+$ and $\text{CH}_2=\text{C}=\text{O}$, suggesting that a ketene rather than a carbene moiety was present in the "monocarbonyl" fragment.

UV photolysis of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\text{OMe}$ in the presence of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) gave (332) $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{CH}_2\text{OMe}$, and treatment of this with HBF_4 in acetic anhydride apparently gave $[\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{CH}_2]^+$. However, attempts to recrystallise this from acetonitrile gave $[\text{Fe}(\text{dppe})(\text{NMe})(\text{C}_5\text{H}_5)]^+$, whose structure was determined crystallographically. Reaction of $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{CH}_2\text{OMe}$

with HBF_4 in the presence of cyclohexene afforded norcarane in low yield. Photolysis of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CH}_2\text{OMe}$ with PPh_3 gave $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\text{CH}_2\text{OMe}$ which behaved like its dppe analogue when acidified in the presence of cyclohexene.

Treatment of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$ with $\text{Ph}_3\text{P}=\text{CHR}$ ($\text{R} = \text{H}, \text{Me}$) in THF gave $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\{\text{CHR}(\text{PPh}_3)\}]^+$ (333), and reaction of $[\text{Fe}(\text{CO})_3(\text{C}_5\text{H}_5)]^+$ with $\text{Ph}_3\text{P}=\text{CHR}$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}$) afforded $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{COCR}=\text{PPh}_3)$ (334). Reduction of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{COR}$ ($\text{R} = \text{Ph}, p\text{-MeOC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4$) with LiBHET_3 in THF at low temperature afforded $[\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)(\text{CHO})(\text{COR})]^-$ (335).

Thermolysis of (+)- and (-)- $\text{Fe}(\text{CO})(\text{PPh}_2\text{R})(\text{C}_5\text{H}_5)\text{COMe}$ ($\text{R} = \text{NMeCHMePh}$) gave $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{Me}$ and PPh_2R before epimerisation at the Fe centre occurred (336). The equilibrium

$$\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\text{COMe} \rightleftharpoons \text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{Me} + \text{PPh}_3$$

was readily attained starting from either side, and decarbonylation of $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\text{COMe}$ to $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\text{Me}$ could be attained only by photolytic means.

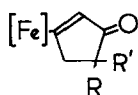
The structures of (+)- $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\text{CH}_2\text{OR}^*$ and $\text{Fe}(\text{CO})(\text{PPh}_3)_2\{\text{CH}_2\text{C}-(\text{:O})\text{OR}^*\}$ ($\text{R}^* = \text{menthyl}$) were determined crystallographically (337), the former having S and the latter R conformation. From these results it was possible to determine the absolute configuration of a large number of related species of the type $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\text{X}$. The X-ray structural determination of the configuration of (R)-(-)- $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\{\text{C}(\text{:O})\text{OR}^*\}$ was also reported (338).

Reaction of $\text{Fe}(\text{CO})_2(\eta^5\text{-dienyl})\text{CH}_2\text{CR}=\text{CR}'\text{R}''$ ($\text{dienyl} = \text{C}_5\text{H}_5, \text{C}_5\text{H}_4\text{Me}, \text{C}_5\text{Me}_5, 1,3\text{-Ph}_2\text{C}_5\text{H}_3$; $\text{R}, \text{R}', \text{R}'' = \text{H}, \text{Me}, \text{Ph}$) gave $\text{Fe}(\text{CO})_2(\eta^5\text{-dienyl})\text{SO}_2\text{CH}_2\text{CH}=\text{CR}'\text{R}''$ and $\text{Fe}(\text{CO})_2(\eta^5\text{-dienyl})\text{SO}_2\text{CR}'\text{R}''\text{CR}=\text{CH}_2$ (339,340,341). The reaction appeared to proceed via a metal- η^2 -alkene-sulphinate Zwitterion, $[\{\text{Fp}\}^+(\eta^2\text{-CH}_2=\text{CR}'\text{R}''\text{SO}_2^-)]$ ($\text{Fp} = \text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$), (339,341). This species could be trapped by addition of Me_3O^+ or Ph_3C^+ , which afforded, for example, $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\{\eta^2\text{-CH}_2=\text{CHCH}_2\text{S}(\text{:O})_2\text{R}\}]^+$ ($\text{R} = \text{Me}$ or Ph_3C) (339). The formation of the rearranged sulphinate $\text{Fe}(\text{CO})_2(\eta^5\text{-dienyl})\text{SO}_2\text{CR}'\text{R}''\text{CR}=\text{CH}_2$ was promoted by the use of neat SO_2 at low temperature, and by organic solutions of SO_2 . However, formation of the unrearranged sulphinate was promoted by increasing methylation of the cyclopentadienyl ring (340). The threo-1,2-dideuteriophenethyl complex $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CHDCHDPh}$ reacted with SO_2 giving the corresponding S-sulphinate with inversion of configuration (342). This was consistent with an $\text{S}_{\text{E}}2$ (inversion) process. When treated with PPh_3 in acetonitrile, the threo-phenethyl complex formed a threo-acyl derivative, $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\text{COCHDCHDPh}$ via 1,2-migration of the alkyl group from the metal to a coordinated CO ligand. The conformation of (S)-(-)- $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\{\text{S}(\text{:O})_2\text{CH}_2\text{Pr}^i\}$ was determined crystallographically (343), the structure confirming the view that the stereochemistry of SO_2 "insertion" reaction involved retention of configuration at the iron.

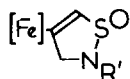
Reaction of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{R}$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}$) with $\text{R}'\text{S}(\text{:O})_2\text{NSO}$ ($\text{R}' = \text{Me}$ or

p-MeC₆H₄) gave Fe(CO)₂(C₅H₅)[N{S(:O)R}{S(:O)₂R'}] (344). This species rearranged on storage to give Fe(CO)₂(C₅H₅){S(:O):NS(:O)₂R'} and could be oxidised by perbenzoic acids to give Fe(CO)₂(C₅H₅)[N{S(:O)₂R'}]{S(:O)₂R'}]. Treatment of Fe(CO)₂(C₅H₅)R (R as above) with MeS(:O)₂NSNS(:O)Me gave Fe(CO)₂(C₅H₅)-[N{SR:NS(:O)₂Me}{S(:O)₂Me}].

The species 87 ([Fe]=Fe(CO)₂(C₅H₅); R = Me, Ph, CH₂[Fe]; R' = Ph, Bu^t; R' = Ph, CN) and 88 (R = Me, Ph or CH₂[Fe]; R' = Ph or *p*-MeC₆H₄SO₂) were obtained (345) by cycloaddition of Ph₂C=C=O, Bu^t(NS)C=C=O, PhNSO and *p*-MeC₆H₄SO₂NSO to Fe(CO)₂(C₅H₅)CH₂C₂R (R = Me, Ph or CH₂Fe). Treatment of Fe(CO)₂(C₅H₅)Me with SeO₂ gave Fe(CO)₂(C₅H₅){Se(:O)₂Me} (346).



(87)



(88)

Compounds containing Group IVA Ligands other than C. Mass spectra data have been obtained (347) from Fe(CO)₂(C₅H₅)QR₃ (Q = Si, R = Me; Q = Sn, R = Me, Ph, Cl), and bond dissociation energies calculated for the Fe-Si and Fe-Sn bonds. Reaction of [Fe(CO)₂(C₅H₅)₂] with CH₂=CHSiCl₂Me gave Fe(CO)₂(C₅H₅){SiClMe(CH:CH₂)}, (348). Attack by [Fe(CO)₂(C₅H₅)] on silacyclobutane MeClSiCH₂CH₂CH₂ afforded (349) the σ-silyl complex Fe(CO)₂(C₅H₅)(SiMeCH₂CH₂CH₂). Photolysis of this species caused loss of the silyl group, whereas halogenation gave Fe(CO)₂(C₅H₅)X and MeXSiCH₂CH₂CH₂ (X = Cl or Br). UV irradiation in the presence of PMePh₂ gave Fe(CO)_x(PMePh₂)_{2-x}(C₅H₅)(SiMeCH₂CH₂CH₂) (x = 1,2) whereas HCl caused generation of Fe(CO)₂(C₅H₅)H, Fe(CO)₂(C₅H₅)(SiMePrⁿCl) and ClMeSiCH₂CH₂CH₂. With KOH in methanol, the iron silyl complex afforded [Fe(CO)₂(C₅H₅)]⁻ and (SiMePrⁿO₂)²⁻, and in the presence of traces of [Pt(C₂H₄)Cl₂]₂, [(SiMe{Fe(CO)₂(C₅H₅)}CH₂CH₂CH₂)]_n was formed. Fe(CO)₂(C₅H₅)(SiMePrⁿCl) reacted with water giving Fe(CO)₂(C₅H₅)-{SiMePrⁿ(OH)}.

Photolysis of Fe(CO)₂(C₅H₅)SiMe₂, with CNC₆H₁₁ afforded (350) in sequential reaction, racemic Fe(CO)(CNC₆H₁₁)(C₅H₅)SiMe₃ and Fe(CNC₆H₁₁)₂(C₅H₅)SiMe₃. The mono-isocyanide was also obtained by irradiation of a mixture of the dicarbonyl and bis(isocyanide) species. No evidence was found for insertion into the Fe-Si bond.

Treatment of (S)-(+)-MePh(np)GeCo(CO)₄ with [Fe(CO)₂(C₅H₅)₂] gave (351) racemic Fe(CO)₂(C₅H₅)GeMePhnp (np = 1-naphthyl). Fe(CO)₄ reacted with LiGePh₃ giving (351) [Fe(CO)₄GePh₃]⁻, isolated as an [NEt₄]⁺ salt. Insertion of GeCl₂, SnCl₂ and SnBr₂ into the Fe-C bond in Fe(CO)₂(C₅H₅)R (R = Me, Et, Prⁿ, *p*-MeOC₆H₄CH₂, PhCH₂, *p*-F₃C₆H₄CH₂) afforded (352), in a radical chain process, Fe(CO)₂(C₅H₅)MX₂R (M = Ge, X = Cl; M = Sn, X = Cl, Br). Similarly, Fe(CO)₂(C₅H₅)MX₂(allyl) was prepared (353) from the η¹-allyl complex

$\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(\eta^1\text{-allyl})$ (allyl = C_3H_5 , $\text{CH}_2\text{CMeCH}_2$, CH_2CHCHMe). This insertion reaction was inhibited by small amounts of radical scavengers.

Treatment of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{SnX}_3$ (X = Cl, Br) with NaS_2CNR_2 (R = Me, Et; NR_2 = piperidinyl) afforded (354) $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\{\text{SnX}_2(\text{S}_2\text{CNR}_2)\}_2$.

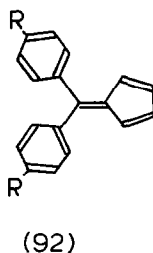
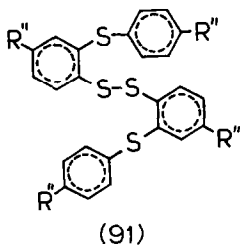
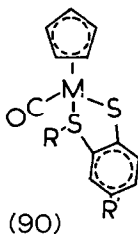
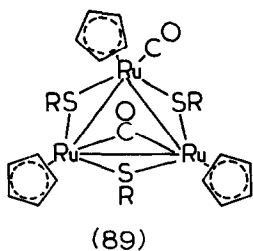
Complexes containing Sulphur Ligands. Methylation of a mixture of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$ -NCS and its S-bonded isomer with MeOSO_2F , followed by treatment of the product with BH_4^- , gave small amounts of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{CN}$ and $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{SMe}$ (355).

The structures of the previously described (356) $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{SET}$ and $\{\{\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\}_2\text{SET}\}\text{BF}_4$ have been determined crystallographically (357). The Fe-S bond distances and Fe-S-C bond angles were virtually identical in the two compounds, the latter containing $\{\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\}$ units bridged by a single SET bridge. In this species the C_5H_5 rings were cis to the FeSFe plane, and the molecule was fluxional.

UV irradiation of $[\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ with E_2R_2 (E = S, R = Me, CH_2Ph , Ph; E = Se, R = Ph) gave $\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5)\text{ER}$ and $[\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5)(\mu\text{-ER})]_2$, the former being converted into the latter on further uv irradiation (358). With $(\text{S}_2\text{Bu}^t)_2$, a mixture of $\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{SBu}^t)$, $\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{S}_2\text{Bu}^t)$ and $\text{Ru}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2(\mu\text{-SBu}^t)(\mu\text{-SBu}^t)$ was produced. The binuclear species had non-planar Ru_2E_2 rings, and existed as isomers in which the C_5H_5 rings were cis and trans with respect to the Ru_2E_2 ring. Additional isomerism arose by virtue of the relative orientation of the R groups. Interconversion of the cis- and trans-isomers occurred on irradiation or on heating, the relative stabilities of the isomer formed depending on the ER group. Isomers varying only in the orientation of the R group, however, could be interconverted on the n.m.r. timescale. On photolysis of $\text{Ru}(\text{CO})_2(\text{C}_5\text{H}_5)\text{SR}$ (R = Me or Ph), small amounts of $\text{Ru}_3(\text{CO})_2(\text{C}_5\text{H}_5)_3(\text{SR})_3$, 89, were produced. Irradiation of $\text{Ru}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2(\text{SBu}^t)(\text{S}_2\text{Bu}^t)$ in the presence of PhSSPh, in an attempt to induce SR-group exchange, afforded instead 90 (M = Ru, R = Ph, R' = H). Photolysis of $(p\text{-R}''\text{C}_6\text{H}_4\text{S})_2$ (R'' = H, Me) gave 91 which reacted (359) with $[\text{M}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ (M = Fe, Ru) giving $\text{M}(\text{CO})_2(\text{C}_5\text{H}_5)\{\text{S}(\text{C}_6\text{H}_3\text{R}''\text{SC}_6\text{H}_4\text{R}'')\}$ (S ligand = 91), and 90 (M = Fe, Ru, R = p-R''C₆H₄; R' = R'' = H, Me). The structure of 90 (M = Ru, R = p-MeC₆H₄; R' = Me) was determined crystallographically. Photolysis of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ with $(\text{PhS})_2$ gave a third isomer of a species which may be $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(\mu\text{-SR})]_2$ (360) or, more probably, 90 (M = Fe, R = Ph, R' = H).

Reaction of thiobenzophenones with $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]^-$ afforded fulvenes under anhydrous phase-transfer conditions (361). Thus $(p\text{-RC}_6\text{H}_4)_2\text{CS}$ was converted into 92 (R = H, Me, OMe) and $[(p\text{-RC}_6\text{H}_4)\text{HCS}]_2$, and $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5\text{Me})]_2$, but not $[\text{Fe}(\text{CO})_2(\text{C}_5\text{Me}_5)]_2$, also effected this transformation.

Magnetic susceptibility and high-field Mossbauer spectral studies have been made of $[\text{Fe}(\text{C}_5\text{H}_5)\text{S}]_4^{n+}$ (n = 0, 1, 2) (362) and it was shown that the unpaired electron in the monocation was predominantly in a liquid-base MO, whereas the dication was essentially diamagnetic.



Halide and Related Complexes. Mossbauer spectral studies have been made (363) of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCO}, \text{NCS}, \text{SCN}, \text{SeCN}, \text{CN}$), $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\text{X}$ ($\text{X} = \text{Br}, \text{I}, \text{NCS}, \text{SCN}, \text{CN}$), $[\text{Fe}(\text{CO})_3(\text{C}_5\text{H}_5)]^+$ and $[\text{Fe}(\text{CO})_2(\text{PPh}_3)(\text{C}_5\text{H}_5)]^+$. It has been established that the primary process in the photolysis of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{X}$ ($\text{X} = \text{Br}, \text{I}$) was dissociation of CO (364). In benzene solutions saturated with ^{13}CO , $\text{Fe}(\text{CO})(^{13}\text{CO})(\text{C}_5\text{H}_5)\text{X}$ was formed, and in the presence of PPh_3 , $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\text{X}$ was produced with high quantum efficiency. The linkage isomers $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{SCN}$ and $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{NCS}$, interconverted on irradiation in THF, and each underwent CO displacement by PPh_3 . Photolysis of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(\text{NCS})$ with AsPh_3 gave only $\text{Fe}(\text{CO})(\text{AsPh}_3)(\text{C}_5\text{H}_5)\text{NCS}$.

Reaction of $\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)\text{R}$ ($\text{R} = \text{I}, \text{Me}$) with (*S*)-(+)- $\text{PPh}_2\text{NMeCHMePh}$ gave $\text{Fe}(\text{CO})(\text{PPh}_2\text{NMeCHMePh})(\text{C}_5\text{H}_5)\text{X}$ ($\text{X} = \text{I}, \text{COMe}, \text{Me}$) as pairs of diastereoisomers (365). ^{57}Fe complexes were made via $^{57}\text{FeI}_2$, $^{57}\text{Fe}(\text{CO})_4\text{I}_2$ and $^{57}\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$.

Treatment of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{Cl}$ with $\text{MeN}(\text{PF}_2)_2$ afforded $\text{Fe}(\text{CO})(\text{F}_2\text{PNMePF}_2)(\text{C}_5\text{H}_5)$ in ether, $\text{Fe}(\text{F}_2\text{PNMePF}_2)_2(\text{C}_5\text{H}_5)\text{Cl}$ in boiling hexane and $\text{Fe}(\text{CO})(\text{F}_2\text{PNHMe})(\text{C}_5\text{H}_5)\text{Cl}$ in benzene/methanol mixtures (366). Reaction of $\text{Ru}(\text{CO})_2(\text{C}_5\text{Me}_4\text{Et})\text{Cl}$ with AsPh_3 gave $\text{Ru}(\text{CO})(\text{AsPh}_3)(\text{C}_5\text{Me}_4\text{Et})\text{Cl}$ (367).

Complexes containing Group IIA, IIIB, and Transition Metals. Magnesium metal reacted with $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{Br}$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) in THF giving (368) the "inorganic Grignard" reagent $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{Mg}(\text{THF})_2\text{Br}$. This species, whose structure was determined crystallographically thereby confirming the existence of the Fe-Mg bond, reacted with water, ethanol, acetone or cyclohexene oxide giving $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{H}$, with CO_2 or $(\text{CF}_3\text{CO})_2\text{O}$ (in the presence of AgBF_4) giving $[\text{Fe}(\text{CO})(\text{dppe})(\text{C}_5\text{H}_5)]^+$ and with O_2 regenerating $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{Br}$. The compound

was generally a weak nucleophile but readily reacted with organic bromides by a single electron transfer process, as shown by formation of cyclic products from 5-hexenyl bromide. Thus, with MeOTs (TS = tosylate), PhCOCl and MeCOBr, $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{Me}$, $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{COPh}$ and $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{Br}$ are formed and with RX (R = Bu^n , CH_2Ph), $\text{Fe}(\text{dppe})(\text{C}_5\text{H}_5)\text{R}$, (R-H) and R_2 were produced.

Reaction of $\text{Na}[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]$ with TiR_2Br (R = Me, Ph) or TiCl_3 gave only $\text{Ti}[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_3$ (369).

Photolysis of a 1:1 mixture of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ with $[\text{M}(\text{CO})_3(\text{C}_5\text{H}_5)]_2$ (M = Mo or W) gave (370) the metal-metal bonded species $\text{FeM}(\text{CO})_5(\text{C}_5\text{H}_5)_2$. The electronic spectra of these species were measured, and photodissociation caused regeneration of the starting materials. Photolysis of the mixed metal complexes in CCl_4 afforded $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{Cl}$ and $\text{M}(\text{CO})_3(\text{C}_5\text{H}_5)\text{Cl}$.

Treatment of $\text{C}_5\text{H}_5\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{X})$ (X = $\text{O}_3\text{SC}_6\text{H}_4\text{Me}$, Cl) with $\text{Na}[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]$ gave $\text{C}_5\text{H}_5\text{Fe}\{\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\}$ (371). Hydride abstraction from this species gave $[\text{Fe}(\text{CO})_2\{\eta^2\text{-CH}_2=\text{CHC}_5\text{H}_4\text{Fe}(\text{C}_5\text{H}_5)\}\{\text{C}_5\text{H}_5\}]^+$ which was also formed in an alkene exchange reaction involving $[\text{Fe}(\text{CO})_2\{\eta^2\text{-CH}_2=\text{CMe}_2\}(\text{C}_5\text{H}_5)]^+$ and $\text{C}_5\text{H}_4\text{Fe}(\text{C}_5\text{H}_4\text{CH}=\text{CH}_2)$. Iodination of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\{\eta^1\text{-C}_5\text{H}_4\text{Mn}(\text{CO})_3\}$ caused cleavage of the Fe-C σ -bond (372) giving $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$ and $\text{Mn}(\text{CO})_3(\text{C}_5\text{H}_4\text{I})$. The analogous $\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_5\text{H}_5)\{\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3\}$ behaved similarly, but reaction of the dicarbonyl iron species with $[\text{MeCO}][\text{BF}_4]$ in acetonitrile afforded $[\text{Fe}(\text{CO})_2(\text{NCMe})(\text{C}_5\text{H}_5)]^+$, $\text{Mn}(\text{CO})_3(\text{C}_5\text{H}_5)$ and $\{\text{Mn}(\text{CO})_3\}_2(\text{C}_5\text{H}_4)_2$. Mercuration via $\text{Hg}(\text{OCOMe})_2$ of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\{\eta^1\text{-C}_5\text{H}_4\text{Mn}(\text{CO})_3\}$ occurred at the α -cyclo-pentadienyl ring (373), and treatment of the product with thiosulfate gave HR_2 (R = $\text{Fe}(\text{CO})_2\text{-}(\text{C}_5\text{H}_5)\{\text{C}_5\text{H}_3\text{Mn}(\text{CO})_3\}$).

DIENYL COMPLEXES

^{13}C n.m.r. spectral studies coupled to MO calculations of atomic charges have indicated (374) that there is an alternation of charge along the dienyly chain in $[\text{Fe}(\text{CO})_3(\eta^5\text{-dienyl})]^+$, C(1), C(3) and C(5) being less electron-deficient than C(2) and C(4). The site exchange of CO ligands was also investigated.

Protonation of the ψ -*exo* and ψ -*endo* forms of $\text{Fe}(\text{CO})_3\{\eta^4\text{-MeCHCHCRCHCHMe}(\text{OH})\}$ afforded (375) the *syn,syn* and *syn,anti* acyclic dienyly cations $[\text{Fe}(\text{CO})_3\{\text{MeCH-CH-CR-CH-CHMe}\}]^+$ with >97% stereospecificity, and quenching of these species with methanol caused regeneration of the precursor diene complexes, again with >98% stereospecificity. It was shown that *syn,anti*- $[\text{Fe}(\text{CO})_3\{\text{MeCH-CH-CMe-CH-CHMe}\}]^+$ was configurationally stable in FSO_3H and H_2SO_4 for hours.

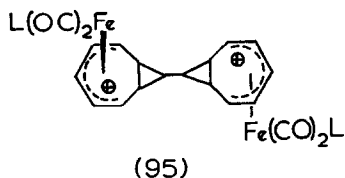
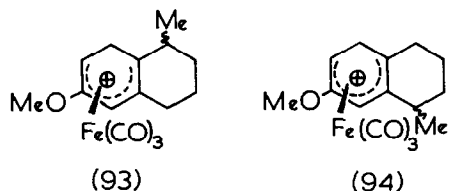
Treatment of $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]^+$ with KX (X = F, Cl or Br) in acetonitrile in the presence of 18-crown-6 gave (376) the 5-halo-cyclohexa-1,3-diene complex $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_7\text{X})$, whereas with KI, $\text{Fe}(\text{CO})_2(\eta^5\text{-C}_6\text{H}_7)\text{I}$ was also formed. In

contrast, $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]^+$ reacted with $\text{CsF} \cdot 1.5\text{H}_2\text{O}$ giving the ether-like species $(\text{OC})_3\text{FeC}_6\text{H}_7\text{OC}_6\text{H}_7\text{Fe}(\text{CO})_3$ (377).

Ring-coupling occurred when $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]^+$ or $[\text{Fe}(\text{CO})_2(\text{CNEt})(\eta^5\text{-C}_6\text{H}_7)]^+$ was treated with $[\text{Fe}(\text{CO})_3(\text{C}_7\text{H}_7)]^-$ (378). The products were $\text{Fe}(\text{CO})_2\text{L}\{\eta^4\text{-C}_6\text{H}_7\text{C}_7\text{H}_7\text{Fe}(\text{CO})_3\}$ (L = CO or CNEt), and attack of $[\text{Cr}(\text{CO})_5(\text{CN})]^-$ on the cyclohexadienyl cations gave $\text{Fe}(\text{CO})\{\eta^4\text{-C}_6\text{H}_7\text{NCCr}(\text{CO})_5\}$.

The dienyl complexes **93** and **94** (*exo* or *endo*-Me) were obtained from appropriate dihydronaphthalenes and $\text{Fe}(\text{CO})_5$ followed by hydride abstraction (379), and their reactions with CN^- and $[\text{CH}(\text{CO}_2\text{Me})_2]^-$ investigated. The presence of *exo* methyl substituents suppressed addition of the nucleophile to the angular terminus, and *endo* methyl substituents caused formation of mixtures of angularly and non-angularly substituted products.

Oxidation of $\text{Fe}(\text{CO})_2\text{L}(\eta^4\text{-C}_8\text{H}_8)$ by $[(\text{p-BrC}_6\text{H}_4)_3\text{N}]^+$ or Ag^+ occurred in a one-electron step (380), and was followed by dimerisation to give $[\text{Fe}_2(\text{CO})_4\text{L}_2\text{-}(\text{C}_{16}\text{H}_{16})]^{2+}$, **95** (L = CO, PPh_3 or $\text{P}(\text{O}Ph)_3$). The structure of **95** (L = $\text{P}(\text{O}Ph)_3$) was determined crystallographically. When $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_7\text{H}_8)$ was similarly oxidised, $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]^+$ was produced, via $[\text{Fe}(\text{CO})_3(\text{C}_7\text{H}_8)]^{\bullet}$ to which hydrogen radical added.



ARENE AND RELATED COMPLEXES

Complexes of Benzene and Other Aromatic Hydrocarbons. MO calculations have been made (381) on $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)]^+$, $\text{Fe}(\eta\text{-C}_5\text{H}_5)_2$ and $[\text{Fe}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^+$ which provided evidence for an appreciable diminution in the aromatic character of benzene when it was complexed.

Treatment of ferrocene with 9,10-dimethylantracene (382) and with phenanthrene and its 9,10-dimethyl derivative (383) afforded $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^6\text{-arene})]^+$, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^6\text{-areneH}_2)]^+$, $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\eta^6, \eta^6\text{-arene})]^{2+}$ and

$[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\eta^6, \eta^6\text{-areneH}_2)]^{2+}$, hydrogenation occurring at the 9,10-positions in each hydrocarbon. In the bimetallic species, $\text{Fe}(\eta\text{-C}_5\text{H}_5)$ units were coordinated to opposite sides of the rings. Similar coronene complexes $[\text{Fe}(\eta\text{-C}_5\text{H}_4\text{R})\text{-}(\eta^6\text{-coronene})]^+$ ($\text{R} = \text{H}$ or Me), in which the metal fragment is bound to an outer ring of the hydrocarbon, have also been reported (384). INDO SCF calculations have been made on $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)]^z$ ($z = 0, +1$) and it was predicted (385) that the unpaired electron in the reduced (neutral) species occupied a predominantly ligand based MO. Reduction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-arene})]^+$ (arene = naphthalene (386), tetralin (386,387), toluene (387), biphenyl (387,388), phenanthrene (387), fluorene (387)) with sodium amalgam in dimethoxyethane or THF afforded the paramagnetic $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-arene})$. Some of these species exhibited esr spectra, and all were readily reoxidised by air or I_2 . $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_5\text{Ph})$ reacted with benzene giving $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)$ (388).

Reaction of benzene, C_6D_6 and C_6F_6 with Fe atoms on co-deposition without diluents at -77°K , or in Ar matrices at 10°K , gave η -arene complexes whose nature was not fully established (389). However, Ru vapour reacted with benzene to give $\text{Ru}(\eta^4\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{H}_6)$ (390). Complexes were also formed in the same way with C_2H_4 , cycloocta-1,5-diene, and cyclopentadiene, but only $\text{Ru}(\eta\text{-C}_5\text{H}_5)_2$ could be identified. With $\text{NMe}_2(\text{PF}_2)$, $\text{Ru}\{\text{NMe}_2(\text{PF}_2)\}_5$ was isolated (390). The species $\text{Ru}(\text{C}_6\text{Me}_6)_2$ was fluxional, a VT n.m.r. study revealing (391) that the rings underwent interchange of the η^4 - and η^6 -bonding modes. The ^1H n.m.r. spectral behaviour was altered by AlMe_3 which also suppressed the catalytic hydrogenation by this species of benzene to cyclohexene. Reaction of $\text{Ru}(\eta^4\text{-C}_6\text{H}_6)\text{-}(\eta^6\text{-C}_6\text{H}_6)$ with acetylenes RC_2R afforded $\text{Ru}(\text{C}_6\text{R}_6)_2$ and $\text{Ru}(\text{C}_6\text{H}_6)(\text{C}_6\text{R}_6)$ ($\text{R} = \text{Ph}$, CO_2Me , Me) (392). With PhC_2H and $\text{HOCH}_2\text{C}_2\text{CH}_2\text{OH}$, the species $\text{Ru}(\eta^4\text{-C}_6\text{H}_3\text{Ph}_3)\text{-}(\eta^6\text{-C}_6\text{H}_3\text{Ph}_3)$ and $\text{Ru}(\text{C}_6\text{H}_6)\{\text{C}_6(\text{CH}_2\text{OH})_6\}$ were isolated.

Reduction of the bis(durene)dication, $[\text{Fe}(\eta^6\text{-C}_6\text{H}_2\text{Me}_4)]_2[\text{PF}_6]_2$ with $\text{Na}_2\text{S}_2\text{O}_4$ or Na/Hg gave the monocation $[\text{Fe}(\text{C}_6\text{H}_2\text{Me}_4)]_2[\text{PF}_6]$, whereas treatment of the durene species of $[\text{Fe}(\text{C}_6\text{H}_6)]_2[\text{PF}_6]_2$ with NaBH_4 gave cyclohexadienyl species in which H^- attack occurred at only one of the benzene rings (393).

Addition of stoichiometric amounts of $\text{CNC}_6\text{H}_{11}$ to $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2]_2$ in refluxing benzene gave (394) $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{CNC}_6\text{H}_{11})\text{Cl}_2$, whereas other isonitriles in excess caused benzene ring displacement, giving $\text{Ru}(\text{CNR})_4\text{Cl}_2$ ($\text{R} = \text{Ph}$, $\underline{p}\text{-MeC}_6\text{H}_4$). The cymene ring in $[\text{Ru}(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2]_2$ was displaced by hexamethylbenzene (395), affording $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]_2$ which reacted with PPh_3 giving $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{-}(\text{PPh}_3)\text{Cl}_2$. Treatment of this last with sources of H^- gave $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{PPh}_3)\text{HCl}$, corresponding mesitylene complexes being made similarly. Related benzene and *p*-xylene complexes rapidly decomposed. These hydrido complexes were catalysts for the hydrogenation of benzene to cyclohexane, and for the hydrogenation of olefins using either H_2 or secondary alcohols. The hydrogenation was slow but the catalyst was fairly stable, there being no evidence for the production of cyclohexadienes or cyclohexenes.

Methylation of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2]_2$ was achieved (396) using HgMe_2 , and addition of (R)-(+)- $\text{Ph}_2\text{PNHCMePh}$ (L^*) afforded $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{L}^*\text{MeCl}$ and some $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{L}^*\text{Cl}_2$. The diastereomers were separated and reacted with SnCl_2 giving $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{L}^*\text{MeSnCl}_3$ with partial epimerisation despite diastereomeric purity of the starting material.

Treatment of $[\text{Ru}(\eta^6\text{-arene})\text{Cl}_2]_2$ (arene = C_6H_6 or $\text{C}_6\text{H}_3\text{Me}_3$) with NaS_2PR_2 ($\text{R} = \text{Me}, \text{Ph}, \text{OMe}, \text{OEt}$) gave $\text{Ru}(\eta^6\text{-arene})\text{Cl}(\text{S}_2\text{PR}_2)$ and $\text{Ru}(\eta^6\text{-arene})(\text{S}_2\text{PR}_2)\text{-}\{\text{SP}(\text{:S})\text{R}_2\}$ (397). Reaction of the former with L ($\text{PMePh}_2, \text{P}(\text{OMe})_3, \text{pyr}, \text{SbPh}_3$) in the presence of NH_4PF_6 gave $[\text{Ru}(\eta^6\text{-arene})\text{L}(\text{S}_2\text{PR}_2)][\text{PF}_6]$, and the pyridine adduct was also obtained by reaction of $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{pyr})\text{Cl}_2$ with NaS_2PMe_2 . $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}(\text{S}_2\text{PPh}_2)$ reacted with TCNE and NaBPh_4^- giving $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{NCBPh}_3)\text{-}(\text{S}_2\text{PPh}_2)$. All of these complexes were stereochemically rigid.

Addition of CsCl in HCl solution to $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2]_2$ gave $\text{Cs}[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_3]$ which converted in aqueous solution into $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{H}_2\text{O})\text{Cl}_2$ (398). Treatment of the trichloro-anion with Lewis bases L ($\text{Me}_2\text{SO}, \text{pyr}, \text{PPh}_3, \text{PMePh}_2$) afforded $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{LCl}_2$. However, $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2]_3$ rearranged in methanol containing NH_4PF_6 , giving $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\eta^6\text{-C}_6\text{H}_6)][\text{PF}_6]$. Treatment of this μ -chloro species with Lewis bases ($\text{pyr}, \text{SEt}_2, \text{AsPh}_3, \text{PPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph}$) afforded $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{L}_2\text{Cl}]^+$. Electrochemical studies of $[(\eta^6\text{-C}_6\text{H}_3\text{R}_3)\text{Ru}(\mu\text{-X})_3\text{Ru}(\eta^6\text{-C}_6\text{H}_3\text{R}_3)]^+$ ($\text{X} = \text{Cl}, \text{OH}; \text{R} = \text{H}, \text{Me}$) revealed (399) that in acetonitrile, the dimers underwent two ($\text{X} = \text{Cl}$) or three ($\text{X} = \text{OH}$) irreversible oxidation processes. Reaction of $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{-OH})_3\text{Ru}(\eta^6\text{-C}_6\text{H}_6)]^+$ with aqueous NH_4PF_6 afforded (400) $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{NH}_3)_3]^{2+}$, whereas in refluxing alcohols, $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{-OR})_3\text{Ru}(\eta^6\text{-C}_6\text{H}_6)]^+$ ($\text{R} = \text{Me}, \text{Et}$) also formed from $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2]_2$ and NaOR , was obtained. The μ -hydroxo species did not react with PR_3 .

Reduction of $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{LCl}_2$ in the presence of L' , or of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{LL}'\text{Cl}]^+$ with sodium naphthalenide, gave (401) the $\text{Ru}(0)$ species $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{LL}'$ ($\text{L} = \text{L}' = \text{PMe}_3, \text{P}(\text{OMe})_3; \text{L} = \text{PMe}_2\text{Ph}, \text{L}' = \text{PMe}_3$ or $\text{P}(\text{OMe})_3$). Treatment of $\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{LL}'$ with NH_4PF_6 or $\text{CF}_3\text{CO}_2\text{H}$ afforded $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{LL}'\text{H}]^+$, and with methyl iodide, $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{LL}'\text{Me}]^+$ was isolated.

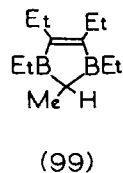
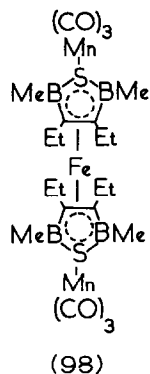
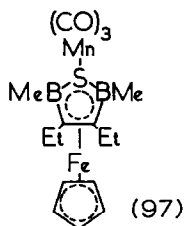
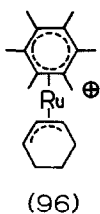
Reduction of $[\text{Ru}(\eta^6\text{-arene})\text{Cl}_2]_2$ (arene = $\text{C}_6\text{H}_6, \text{C}_6\text{H}_3\text{Me}_3, \text{C}_6\text{Me}_6$) by Zn dust in the presence of cycloocta-1,5-diene or cyclohexa-1,3-diene afforded $\text{Ru}(\eta^4\text{-diene})(\eta^6\text{-arene})$ (402). $\text{Ru}(\eta^3\text{-C}_6\text{H}_8)(\eta^6\text{-C}_6\text{Me}_6)$ was also obtained from cyclohexa-1,4-diene, and $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]_2$ reacted with cycloheptatriene and Na_2CO_3 giving $[\text{Ru}(\eta^5\text{-C}_7\text{H}_9)(\eta^6\text{-C}_6\text{Me}_6)]^+$. Reaction of $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]_2$ with ethylene and aqueous ethanolic Na_2CO_3 gave $\text{Ru}(\text{C}_2\text{H}_4)_2(\eta^6\text{-C}_6\text{Me}_6)$, in which there was a high barrier to rotation about the Ru -ethylene bonds. Reduction of $[\text{Fe}(\eta^6\text{-C}_6\text{Me}_6)_2]^{2+}$ with Na/Hg or $\text{K}_2\text{C}_8\text{H}_8$ gave $\text{Fe}(\text{C}_6\text{Me}_6)_2$ which reacted further with dienes and trienes giving $\text{Fe}(\eta^4\text{-diene})(\eta^6\text{-C}_6\text{Me}_6)$ (diene = 1,3- $\text{C}_6\text{H}_8, 1,5\text{-C}_8\text{H}_{12}, \text{C}_7\text{H}_8$). Protonation of $\text{Fe}(\eta^4\text{-C}_7\text{H}_8)(\eta^6\text{-C}_6\text{Me}_6)$ afforded $[\text{Fe}(\eta^5\text{-C}_7\text{H}_9)(\eta^6\text{-C}_6\text{Me}_6)]^+$, whereas attempts to abstract H^- from the cycloheptatriene complex

using Ph_3C^+ afforded instead $[\text{Fe}(\eta^5\text{-C}_7\text{H}_8\text{CPh}_3)(\eta^6\text{-C}_6\text{Me}_6)]^+$. Protonation of $[\text{Ru}(\text{C}_6\text{H}_8)(\eta^6\text{-C}_6\text{Me}_6)]^+$ gave $[\text{Ru}(\text{C}_6\text{H}_9)(\text{C}_6\text{Me}_6)]^+$, which in the solid appeared to be coordinatively unsaturated, 96, but in solution appeared, from ^1H n.m.r. spectral studies, to be $[\text{Ru}(\eta^4\text{-C}_6\text{H}_8)(\eta^6\text{-C}_6\text{Me}_6)\text{H}]^+$.

Complexes derived from Heterocyclic Rings. An exchange reaction between $\text{Co}(\text{C}_5\text{H}_5\text{BR})_2$ and $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ afforded (403) the mixed borinato "sandwich" complex $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5\text{BR})$ ($\text{R} = \text{Me}, \text{Ph}$). Oxidation and Friedel-Crafts acylation of this species caused loss of the BR group and formation of $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{R})]^+$ and $\text{Fe}(\text{C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_5\text{Me})$, respectively. Acylation of $\text{Fe}(\eta^5\text{-C}_5\text{H}_5\text{BMe})_2$ afforded $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5\text{BMe})(\eta^6\text{-C}_6\text{H}_5\text{Me})]^+$ as well as acylated borinato complexes (403). A cyclic voltammetric study of $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{R})(\eta^5\text{-C}_5\text{H}_5\text{BR}')$ ($\text{R} = \text{R}' = \text{Ph}; \text{R} = \text{H}, \text{R}' = \text{Me}, \text{Ph}$) and of $\text{Fe}(\eta^5\text{-C}_5\text{H}_5\text{BR}')_2$ revealed (404) that the complexes oxidised with varying degree of reversibility, the mixed "sandwich" species oxidising at potentials ca. 200 mV more cathodic than their bis-borinato analogues. $\text{Fe}(\text{C}_5\text{H}_5\text{BR})_2$ could be reduced, in a one-electron step, either electrochemically or using Na/K alloy, to give paramagnetic $[\text{Fe}(\text{C}_5\text{H}_5\text{BR})_2]^-$. The lithium phosphacycle $\text{Li}[\text{PCHCMeCMeCH}]$ reacted with FeCl_2 giving (405) the ferrocene analogues $\text{Fe}(\eta^5\text{-PCHCMeCMeCH})_2$, and in boiling xylene, $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ reacted with $\text{Bu}^+\text{PCHCMeCMeCH}$ to afford (406) the mixed ring species $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-PCHCMeCMeCH})$. Reaction of the last compound with $\text{Fe}_2(\text{CO})_9$ gave a bis-iron species in which an $\text{Fe}(\text{CO})_4$ group was bonded to the P atom (406).

Reaction of the *p*-cymene complex $[\text{Ru}(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2]_2$ with tetramethylthiophene in the presence of AgPF_6 afforded $[\text{Ru}(\eta^4\text{-SC}_4\text{Me}_4)(\eta^6\text{-MeC}_6\text{H}_4\text{CHMe}_2)]^{2+}$ (407).

A mixture of $\text{Mn}_2(\text{CO})_{10}$ and $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ reacted (408) with 2,5-dimethyl-3,4-diethylthiadiborolene giving 97. Treatment of this benzene, AlCl_3 and Al caused replacement of the C_5H_5 ring by C_6H_6 , affording $[(\text{OC})_3\text{Mn}(\text{SB}_2\text{Me}_2\text{C}_2\text{Et}_2)\text{Fe}(\eta^6\text{-C}_6\text{H}_6)]^+$, and thermolysis of this gave the "tetradecker sandwich" species 98.



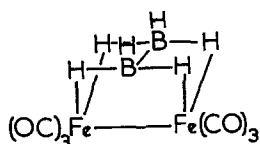
Three mole equivalents of $\text{Co}(\text{CO})_2(\text{C}_5\text{H}_5)$ reacted with two mole equivalents each of $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)]_2$ and 99 giving (409) the mixed metal "triple-decker sandwich" complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[\mu\text{-MeC}(\text{BEt})_2(\text{CEt})_2]\text{Co}(\eta\text{-C}_5\text{H}_5)$.

COMPLEXES OF POLYHEDRAL BORANES AND CARBORANES

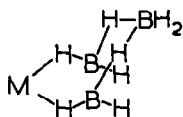
Borane Species. Reaction of $\text{Fe}(\text{CO})_5$ with B_5H_9 in the presence of LiAlH_4 in ether afforded (410) unreacted starting materials, $\text{Fe}_2(\text{CO})_6(\text{B}_2\text{H}_6)$, 100, and $\text{Fe}(\text{CO})_3\text{B}_4\text{H}_8$. The compound could be viewed as containing $\text{B}_2\text{H}_6^{2-}$ as an 8-electron donor to $\text{Fe}(\text{CO})_6^{2+}$, or as an analogue of B_4H_8 in having 12-skeletal electrons in a four-atom cage. Treatment of $\text{K}_2\text{Fe}(\text{CO})_4$ with $\text{BH}_3\cdot\text{THF}$ gave $\text{K}[\mu\text{-Fe}(\text{CO})_4\text{B}_2\text{H}_5]$ (411) in which one of the bridging H atoms in diborane is replaced by an $\text{Fe}(\text{CO})_4$ group.

Photolysis of low temperature of a mixture of $\text{Fe}(\text{CO})_4\text{Br}_2$ or $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$ with $[\text{Me}_4\text{N}][\text{B}_3\text{H}_8]$ gave $\text{Fe}(\text{CO})_3\text{H}(\text{B}_3\text{H}_8)$ and $\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)(\text{B}_3\text{H}_8)$, respectively (412). These species contained the chelating unit 101 ($\text{M} = \text{Fe}(\text{CO})_3\text{H}$ or $\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)$).

The electronic structure of $\text{Fe}(\text{CO})_3\text{B}_4\text{H}_8$ has been probed (413) by a combination of SCF- $\chi\alpha$ -SW MO theory and UVPE spectroscopy. He(I) and Ne(I) UVPE spectral studies of $\text{Fe}(\text{CO})_3\text{B}_4\text{H}_8$, $\text{Fe}(\text{CO})_3\text{B}_5\text{H}_9$, $\text{Fe}(\text{CO})_5\text{B}_5\text{H}_3$, $\text{Fe}(\text{CO})_3\text{C}_2\text{B}_3\text{H}_5$ and $\text{Fe}(\text{CO})_3\text{C}_2\text{B}_3\text{H}_7$ have been reported (414). A comparison of data obtained from $\text{Fe}(\text{CO})_3\text{B}_4\text{H}_8$, B_5H_9 and $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_4)$ revealed that the electronic structure of the borane is a good model for the ferraborane. The characteristics of the spectra of $\text{Fe}(\text{CO})_3\text{B}_5\text{H}_9$ suggest a close relationship with B_6H_{10} , while observations on $\text{Fe}(\text{CO})_5\text{B}_5\text{H}_3$ suggested that two CO groups are bonded to the cage in an exo-polyhedral position.



(100)



(101)

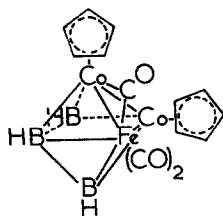
Reaction of $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$ with $[\text{B}_5\text{H}_8]^-$ afforded $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(2\text{-B}_5\text{H}_8)$, in which the metal atom was σ -bonded to a basal B atom of the square pyramidal B_5 unit (415). Reaction of this metallaborane with KH gave $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)(2\text{-B}_5\text{H}_7)]^-$ and addition of more $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{I}$ afforded $\{\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\}_2(2,4\text{-B}_5\text{H}_7)$, the new Fe unit also being σ -bonded to a basal B atom.

Carborane Complexes. Photolysis of $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_4)$ in the presence of B_5H_9 gave $\text{Fe}(\text{CO})_3(\text{C}_4\text{BH}_5)$, 102 (416). A comparative MO study has been made of $\text{Fe}(\text{C}_5\text{H}_5)_2$ and $(\eta\text{-C}_5\text{H}_5)\text{FeC}_2\text{B}_9\text{H}_{11}$ (417).

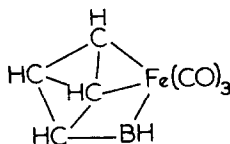
Reaction of $\text{Ru}(\text{PPh}_3)_3\text{HCl}$ with $[7,9\text{-C}_2\text{B}_9\text{H}_{12}]^-$ gave $2,2\text{-}(\text{PPh}_3)_2\text{-}2,2\text{-H}_2\text{-}2,1,7\text{-RuC}_2\text{B}_9\text{H}_{11}$, whereas with $[7,8\text{-C}_2\text{B}_9\text{H}_{12}]^-$, $3,3\text{-}(\text{PPh}_3)_2\text{-}3,3\text{-H}_2\text{-}3,1,2\text{-RuC}_2\text{B}_9\text{H}_{11}$ was obtained (418). These species were regarded as containing formally 7-coordinate

Ru(IV). The 2,1,7-isomer was found to eliminate hydrogen reversibly on heating *in vacuo*, giving 5-coordinate Ru(II). Both isomers reacted with HCl and with CO affording 2,2-(PPh₃)₂-2-H,2-Cl-2,1,7-RuC₂B₉H₁₁ and the corresponding 3,3-substituted-3,1,2-isomer, and 2,2-(PPh₃)₂-2-CO-2,1,7-RuC₂B₉H₁₁ and its 3-substituted carbonyl analogue. Reaction of Ru(PPh₃)₃HCl with Na[9-pyr-7,8-C₂B₉H₁₀] gave 3,3-(PPh₃)₃-3-H-7-pyr-3,1,2-RuC₂B₉H₁₀.

UV irradiation of a mixture of Co(η^5 -C₅H₅)B₄H₈ with Fe(CO)₅ afforded Fe₂(CO)₉, Re₃(CO)₁₂, Fe₂(CO)₉Co(C₅H₅) and 1,2,3-(C₅H₅)₂Co₂(CO)₄B₃H₃, an octahedral Co₂FeB₃ cage, 103 (419). The structure of 1,8-(C₅H₅)₂-1-Fe-8-Co-2,3-C₂B₇H₉ has been determined crystallographically (420). Although the cluster is one electron short of the ideal 2n + 2 configuration for a *c*loso polyhedral framework, the molecule had a *c*loso 11-vertex octadecahedral geometry with C₅H₅Fe having a connectivity of 6 (C₂B₄) and C₅H₅Co a connectivity of 5 (CB₄).



(103)



(102)

Polyhedral expansion of 3,1,2-(C₅H₅)FeC₂B₉H₁₁ by reaction with NaC₅H₅ and FeCl₂ gave (421) three diamagnetic electron-deficient 13-vertex *c*loso-clusters: 4,5-(C₅H₅Fe)₂-2,3-C₂B₉H₁₁, [4-(η^5 -C₅H₅)-5-(η^5 -1,2-C₂B₉H₁₁)-4,5-Fe₂-2,3-C₂B₉H₁₁]⁻ and 1-0H-3,6-(C₅H₅Fe)₂-1,2-C₂B₈H₉. The second species is related to the first by replacement of a C₅H₅⁻ ring by η^5 -C₂B₉H₁₁²⁻. Reaction of 1-(C₅H₅Fe)-2,3-C₂B₈H₁₀ with [Fe(η^5 -C₅H₅)(η^6 -C₆H₆)]⁺ gave ferrocene and (C₅H₅Fe)₂C₂B₈H₁₀ (421).

The structure of 1,14-(C₅H₅Fe)₂-2,5,9,12-Me₄C₄B₈H₈ has been established by X-ray techniques (422). The 14-vertex *c*loso-cage had a bicapped hexagonal antiprismatic geometry, the C₅H₅Fe groups occupying the two high-coordinate vertices at opposite ends of the molecule. The four cage C atoms were arranged in staggered fashion in the two equatorial rings such that the mutual C-C separations were maximised.

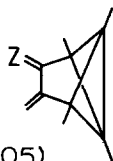
SYNTHETIC AND CATALYTIC REACTIONS

Synthetic Reactions. In refluxing hexane, Fe₂(CO)₉ caused 1,2- and 1,3-shifts (423) of the double bond in the bicyclo[6.1.0]nonene, 104. Fe(CO)₄ complexes of the two products could be isolated. Thermal degradation of {Fe(CO)₄}₂-(1,5-C₈H₁₂) gave initially 1,5-cyclooctadiene and Fe₃(CO)₁₂, but on continuous

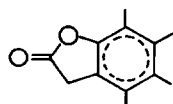
heating, rearrangement to the 1,3-diene occurred. Photolysis of the hydrocarbon 105 ($Z = 0$) with $\text{Fe}(\text{CO})_5$ caused rearrangement to the lactone 106 (424), but when $Z = \text{CH}_2$, only an $\text{Fe}(\text{CO})_3$ complex could be obtained. In benzene, $\text{Fe}_2(\text{CO})_9$ reacted with the azirine 107 to give 108, 2,4,5-triphenylpyrrole, 1-benzoyl-2,4,5-triphenylpyrrole, 2,4,5-triphenyl-3-benzoylpyrrole (main product) and 2,3,5,6-tetraphenylpyridine (425). The formation of the pyridine was unusual, implying the loss of an O atom, and a mechanism was discussed.



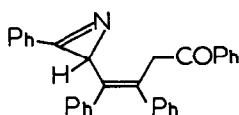
(104)



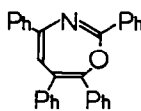
(105)



(106)



(107)

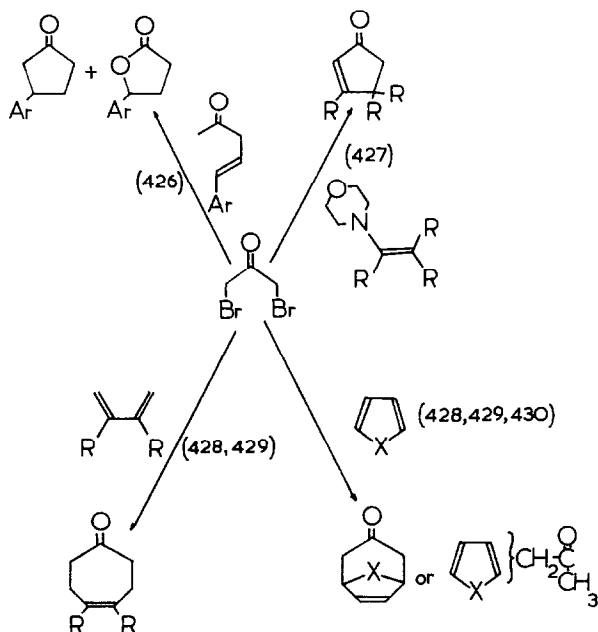


(108)

Iron carbonyls promoted the addition of α,α' -dibromoketones to aromatics olefins (426), enamines (427), 1,3-dienes (428,429), and to pyrroles (429) giving 3-arylcyclopentanones, cyclopentenones, 4-cycloheptenones and species related to tropane alkaloids (see Scheme 7). Mechanistic aspects of the reactions of α,α' -dibromoketones with iron carbonyls, were discussed (431), and an oxyallyl $\text{Fe}(\text{II})$ complex was identified as being the reactive intermediate.

Treatment of $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5$ dioxane with $\text{Fe}(\text{CO})_5$ in THF gave $\text{Na}_2\text{Fe}_2(\text{CO})_8 \cdot x\text{THF}$, and after removal of THF and stoichiometric addition of acetic acid, $[\text{Fe}_2(\text{CO})_8\text{H}]^-$ was obtained (432). This was isolated as Li^+ , PPN^+ , and $[\text{Na}(\text{dicyclohexyl-18-crown-6})]^+$ salts. The bimetallic hydride was used for mild, high-yield and selective reduction of only the olefinic bond in α,β -unsaturated esters, ketones, aldehydes, amides, lactones and nitriles. Comparison of the efficacy of this reagent was made with mixtures of $\text{Na}_2\text{Fe}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ and acetic acid and of $\text{Fe}(\text{CO})_5$ with NaOH . There was a detailed discussion of the mechanism of reduction which was thought to involve concerted reversible and regiospecific addition of $[\text{Fe}_2(\text{CO})_8\text{H}]^-$ to $\text{RCH}=\text{CHCOR}'$, giving $[\text{Fe}_2(\text{CO})_8\text{CH}(\text{COR}')\text{CH}_2\text{R}]^-$ followed by the competing rate-determining steps of Fe-Fe bond cleavage and photolysis to give $\text{RCH}_2\text{CH}_2\text{COR}'$. Under ^{13}C O, there was no detectable labelled carbonyl uptake by $\text{Na}[\text{Fe}_2(\text{CO})_8\text{H}]$ after 3 min., but with PPh_3 , $\text{Na}[\text{Fe}(\text{CO})_4\text{H}]$, $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, $\text{Fe}(\text{CO})_4\text{PPh}_3$ and $\text{Fe}(\text{CO})_5$, but no $\text{Na}[\text{Fe}(\text{CO})_3(\text{PPh}_3)\text{H}]$ were formed. ESR signals were observed in THF solutions containing $\text{Na}[\text{Fe}_2(\text{CO})_8\text{H}]$ or $\text{Na}_2[\text{Fe}_2(\text{CO})_8]$, which may have been due to $\text{Na}[\text{Fe}(\text{CO})_4]$ or $\text{Fe}(\text{CO})_4\text{H}$. Weak esr signals were also observed in solutions of $\text{Na}[\text{Fe}(\text{CO})_4\text{H}]$ and $[\text{NH}_4\text{Et}_3][\text{Fe}_3(\text{CO})_{11}\text{H}]$.

Scheme 7



Catalytic Reactions. Selective hydrogenation of CCl_4 , MeCCl_3 and $\text{CH}_2\text{ClCCl}_3$ by SiHR_3 to CHCl_3 , MeCHCl_2 and $\text{CHCl}_2\text{CH}_2\text{Cl}$ was catalysed (433) by $\text{Ru}(\text{PPh}_3)_3\text{XC1}$ ($\text{X} = \text{H}, \text{Cl}$), $\text{Ru}(\text{PPh}_3)_4\text{H}_2$ and $\text{Ru}(\text{PPh}_3)_3\text{H}(\text{SiMe}_2\text{Cl})$. A reaction pathway involving oxidative addition and reductive elimination steps of the chloro-carbon and silyl reagent to $[\text{Ru}(\text{PPh}_3)_2\text{HX}]$ was proposed.

Treatment of $[\text{L}_3\text{Ru}(\mu\text{-Cl})_3\text{RuL}_3]\text{Cl}$ with AgBF_4 in organonitrile solutions afforded fac- $[\text{RuL}_3(\text{NCR})_3]\text{BF}_4$ ($\text{L} = \text{PMe}_2\text{Ph}, \text{PMePh}_2$; $\text{R} = \text{Me}, \text{Et}, \text{Pr}^n, \text{MeOC}(\text{:O})\text{CH}_2, \text{Ph}$) (434). $[\text{Ru}(\text{PMePh}_2)_3(\text{NMe})_3]^+$ reacted with NaBH_4 giving mer- $\text{Ru}(\text{PMePh}_2)_3\text{H}(\text{H}_2\text{BH}_2)$ which was an active catalyst for the hydrogenation of olefins in the presence of NEt_3 . Treatment of $\text{Ru}(\text{PMePh}_2)_3\text{H}(\text{H}_2\text{BH})$ with CO gave $\text{Ru}(\text{CO})\text{-}(\text{PMePh}_2)_3\text{H}_2$, and reaction of $[(\text{PMePh}_2)_3\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{PMePh}_2)_3]\text{Cl}$ with KOH in ethanol afforded $\text{Ru}(\text{CO})(\text{PMePh}_2)_3\text{H}_2$. UV irradiation of $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\text{Cl}_2$ afforded a catalyst which could assist in the homogeneous hydrogenation of linear and branched aliphatic and aromatic aldehydes (435). $\text{Ru}_4(\text{CO})_{12}\text{H}_4$, $\text{Ru}_4(\text{CO})_{12-x}\text{L}_x\text{H}_4$ ($\text{L} = \text{PPh}_3, \text{PBu}_3^n$; $x = 3, 4$) and $\text{Ru}_4(\text{CO})_8\{(-)\text{-DIOP}\}_2\text{H}_4$, have been tested as hydrogenation catalyst (436).

Treatment of silica with RuCl_3 or $\text{Ru}_3(\text{CO})_{12}$ afforded a catalyst which afforded ammonia from $\text{CH}_4/\text{H}_2\text{O}/\text{N}_2$ mixtures (437). Impregnation of silica, alumina or magnesia with $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$ or $\text{Os}_6(\text{CO})_{18}$, followed by heating under Ar or CO, gave CO_2 , hydrogen and various hydrocarbons, depending on temperature, the nature of the starting cluster and the support, and the water content of the support. The hydrocarbons included CH_4 , C_2H_6 , C_3H_8 , C_3H_6 , C_4H_{10}

and C_5H_{12} . The conversion of CO to CO_2 by water was certainly, and the formation of CH_4 possibly, catalytic.

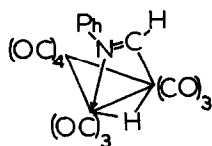
The effectiveness of mixtures of $Fe(CO)_5$ and NaOH in n-butanol or of $Ru_3(CO)_{12}$ and KOH either in methanol or 2-ethoxyethanol as catalysts for the water-gas shift reaction has been investigated (439). The reactions were studied under CO pressure by ir spectroscopy. It was shown that $[PPN][Fe(CO)_4H]$ in an anhydrous THF under CO pressure was converted to $Fe(CO)_5$ at 60° , but that on cooling $[Fe(CO)_4H]^-$ was regenerated. The ability of $Ru_3(CO)_{12}$, $FeRu_3(CO)_{13}H_2$, $Ru_4(CO)_{13}H_2$, $Ru_4(CO)_{12}H_4$, and $Ru_6C(CO)_{17}$ as water-gas shift reaction catalysts was also studied (440). For systems based on tri- or tetra-ruthenium carbonyls, it seemed that the major species present under the conditions used was $[Ru_4(CO)_{13}H]^-$. Mixtures of $Fe(CO)_5$ and $Ru_3(CO)_{12}$ in alkaline solution were much more effective as catalysts in comparison to the carbonyls on their own.

Catalytic reduction of aromatic nitro compounds to amines was achieved (441) by CO and H_2 under pressure in the presence of $Fe(CO)_5$ in aqueous glyme containing an excess of NEt_3 , or using $Ru_3(CO)_{12}$, $Ru_4(CO)_{12}H_4$, $Os_3(CO)_{12}$, $Os_3(CO)_{10}H_2$ or $Os_4(CO)_{12}H_4$ in THF containing NEt_3 .

The species $[Fe(CO)_4H]^-$ or $[Fe_3(CO)_{11}H]^-$ (as PPN^+ salts) catalysed the conversion of CO_2 , H_2 and ROH into alkylformates at high temperature (442). Simultaneous carbonylation and homologation of Me_2O , and homologation of methylacetate to ethylacetate was effected (443) by mixtures of $Ru(CO)_4I_2$, MeI and NaI or of $Ru(acac)_3$ and MeI under H_2/CO or HI and a low partial pressure of H_2 .

In refluxing N,N-dimethylaniline, $Os_3(CO)_{12}$ or $Os_4(CO)_{12}H_4$ catalysed the formation of $(p\text{-}Me_2NC_6H_4)_2CH_2$ (444), and a similar reaction occurred with PhNHMe. Formation of $Os_3(CO)_9(\mu_3\text{-}CH)H_3$ during these reactions implied methyl transfer from N to Os which may be the key step in the catalysis. The formation of the μ_3 -carbyne species also implied generation of $PhN=CH_2$ which could be stabilised by bonding to the cluster, e.g. as 109 and although this was not isolated from reactions with $PhNMe_2$, it was from those with PhNHMe, together with $Os_3(CO)_{10}(\mu_2\text{-}NHPh)(\mu_2\text{-}H)$.

Coupling between $PhMgBr$ and $PhCH_2Cl$ was catalysed by $FeL_2(\eta\text{-}C_5H_5)X$ ($L = PMe_2Ph$; $LL = Me_2PCH_2CH_2PMe_2$; $X = Br$ or Ph) and may have involved one-electron transfer processes (445).



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REVIEWS AND DISSERTATION ABSTRACTS

Reviews. The following reviews of relevance to the organometallic chemistry of iron, ruthenium and osmium have appeared during 1978:

- "Metal carbonyls", by E.W. Abel (446).
- "Substitution reactions of metal and organometal carbonyls with Group V and Group VI ligands", by D.A. Edwards (447).
- "Reactions of Fe(II) macrocycle ligand complexes with CO", by M.H. Park (448).
- "Group VIB derivatives of the iron triad carbonyls", by A. Bonny (449).
- "Thiocarbonyl and related complexes of the transition metals", by P.V. Yaneff (450).
- "Organometallic compounds containing metal-metal bonds", by N.G. Connelly (451).
- "Activation of transition-metal carbonyl clusters", by B.F.G. Johnson, J. Lewis and D. Pippard (135).
- "Metallocarbenes, metallocarbynes, ylides, clusters, metallocarboranes and some applications", by J. Tirouflet and P. Braunstein (452).
- "Nitrosyl complexes of ruthenium", by F. Bottomley (453).
- "Reactivity of the nitrosyl group in transition metal complexes", by Yu.N. Kukushkin, L.I. Danilina and N.S. Panina (454).
- "Complexes containing metal-carbon σ bonds", by B.L. Booth (455).
- "Preparation of π -alkenyl and σ -organometallic compounds of transition metals and their properties", by B.A. Dolgoplosk and 8 colleagues (456).
- "Organic reactions of selected π -complexes (an annual report for 1977)", by G. Marr and B.W. Rockett (457).
- "Complexes of butatrienes with hexacarbonyldi-iron and tetracarbonyl iron", by A. Zimniak (458).
- " π -Cyclopentadienyl, π -arene and related complexes", by W.E. Watts (459).
- "Triple-layered complexes with boron heterocycles", by W. Siebert (460).
- "The carbaboranes, including their metal complexes", by T. Onak (461).
- "Noble metal compounds", including ruthenium compounds and recent topics on synthetic reactions by application of ruthenium compounds as catalysts, by J. Tsuji, K. Yamamoto and I. Ojima (462).
- "The noble metals, Part 1. Ruthenium, osmium, rhodium and iridium", by J. Evans and D.W. Clack (463).
- "Elements of the first transitional period. Part 1. Manganese and iron", by R. Davis, C.A. McAuliffe and D.M. Johns (464).

- "Organometallics in synthesis", by D.J. Thompson and K. Smith (465).
- "The organic chemistry of iron", by E.A. Koerner von Gustorf, W.F. Grevels and I. Fischler (466).
- "Transition metal derivatives in organic synthesis (Annual Survey for 1977)", by L.S. Hegedus (467).
- "Organic syntheses by means of metal clusters", by Y. Ishii (468).
- "The role of organic transition metal compounds in organic chemical syntheses", by B. Heil (469).
- "Aspects of the organometallic chemistry of transition metals, Part 1. Synthesis and reactivity", by J. Tirouflet and P. Braunstein (470).
- "Organometallic chemistry, Part 1. The transition elements", by R. Pearce, D.J. Thompson and M.V. Twigg (471).
- "Organometallic compounds", by D.J. Cardin and K.R. Dixon (472).
- "Iron carbonyls", by N. von Kutepow (473).
- "Reactivity of monoolefin ligands in transition metal complexes", by M.I. Rybinskaya (474).
- Dissertation Abstracts. "Formation and reactions of lithium pyridinyl carbonyl tetracarbonylferrate", by K. Ueno (475).
- "The synthesis and study of iron and cobalt carbonyl tri-fluorophosphine compounds", by M.A. Krevalis (476).
- "Preparation and stoichiometric and catalytic chemistry of low-valent iron complexes of phosphine and phosphite ligands", by T. van Harris (477).
- "Organometallic synthesis on insoluble macroreticular poly(styrene-divinylbenzene) supports, and preparation, characterisation and some reactions of bis(chlorozinc)tetracarbonyliron", by R.C. Winterton (478).
- "Studies of the tetracarbonylferrate(2-) ion, a strong nucleophile; the preparation and characterisation of $K[Fe(CO)_4B_2H_6]$ ", by G.F. Medford (479).
- "Transition metal carbonyl hydride cluster complexes: stepwise reduction of nitriles on the face of a tri-iron nonacarbonyl cluster. Synthetic, mass spectrometric and X-ray crystallographic studies", by M.A. Andrews (480).
- "Reactions of unsaturated triosmium carbonyl clusters", by M. Tachikawa (481).
- "Synthesis, structure and bonding of new types of iron and cobalt nitrosyl clusters containing tri-, tetra- and penta-coordinated S and/or N atoms", by C.T.-W. Chu (482).

"Selective trapping of dienes by benzylideneacetone iron tricarbonyl. Attempted synthesis of ZZZZ-cyclononatetraenyl iron tricarbonyl cationic and anionic complexes", by C.R. Graham (483).

"Selective trapping of dienes as iron tricarbonyl complexes by enone iron tricarbonyl compounds. Characterisation and reactions of the tautomeric compounds 1,3,5-cyclooctatrienone iron tricarbonyl and bicyclo[4.2.0]octa-2,4-dienone iron tricarbonyl", by G.O. Nelson (484).

"Intramolecular trapping of cyclobutadiene iron tricarbonyl systems", by T.A. Pancoast (485).

"Synthesis and reactions of a thiocarbonyl bridged complex $[(C_5H_5)_2Fe_2(CO)_2(\mu-CO)(\mu-CS)]$ ", by M.H. Quick (486).

"Some aspects of organo-iron chemistry", by N.J. Grice (487).

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