IRON, RUTHENIUM AND OSMIUM

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Contents

METAL CARBONYLS

Simple Carbonyls and Carbonylate Anions

Two papers have appeared outlining the use of extended Hückel theory modified to include 2-body repulsion on a variety of iron carbonyl complexes as well as other first row carbonyl complexes. It proved possible to reproduce bond lengths fairly accurately in most cases [1]. The second paper calculated enthalpies of activation and/or reaction for a number of dissociative processes of metal carbonyl complexes [2]. Multiple scattering Xα methods have been used to make a comparative study of $[Fe(CO)_4]^{2-}$ and $[Fe(N_2)_4]^{2-}$ as well as $Ni(CO)_4$, $[Co(CO)_4]^-$, $Ni(N_2)_4$, and $[Co(N_2)_4]^-$. Although for $Ni(CO)_4$ backbonding is more important than with the $Ni(N_2)_4$, with the cobalt and iron complexes backbonding is about the same for the CO and N_2 complexes [3]. Molecular orbital calculations have been carried out on a number of classes of molecules containing iron, ruthenium and osmium. In detail, the $Fe_3(CO)_9$ fragment was considered followed by a number of M_3L_9 (ligand) complexes [4].

Using a fixed-frequency argon ion laser, the photoelectron spectra of $[Fe]^-$, $[FeCO]^-$, $[Fe(CO)_2]^-$, $[Fe(CO)_3]^-$, $[Fe(CO)_4]^-$ have been measured. The electron affinity of each of the respective neutral species of this series was also reported and interpreted in terms of the bonding and geometry of these complexes [5]. A new method of calculating bond energies using bond energy-bond length relationships has been applied to $Fe(CO)_5$ and $Fe_2(CO)_9$. The C-O and M-C bond energies for the terminal ligands in $Fe_2(CO)_9$ are 947

± 16 and 241 ± 10 kJ. mol^{-1}, respectively and 869 ± 20 and 166 ± 8 kJ. mol^{-1} for the bridging carbonyls. For $Fe(CO)_5$ the value of $\underline{E}$(C-O) = 963 ± 12 kJ. mol^{-1} and $\underline{E}$(Fe-C) = 230 ± 10 and 220 ± 10 kJ. mol^{-1} for its axial and equatorial bonds, respectively, were determined [6].

The natural abundance ^{17}O NMR spectra of a variety of metal carbonyl complexes including many of iron have been reported. The range of chemical shifts is nearly 100 ppm. The trends for CO, ^{17}O chemical shifts are generally opposite those for the ^{13}C chemical shifts as explained by pi-backbonding arguments [7]. The natural abundance ^{17}O NMR spectra of $Fe(CO)_5$ and other neutral carbonyls have also been reported. The difficulty in obtaining data was reported to be similar to that experienced with ^{13}C NMR [8].

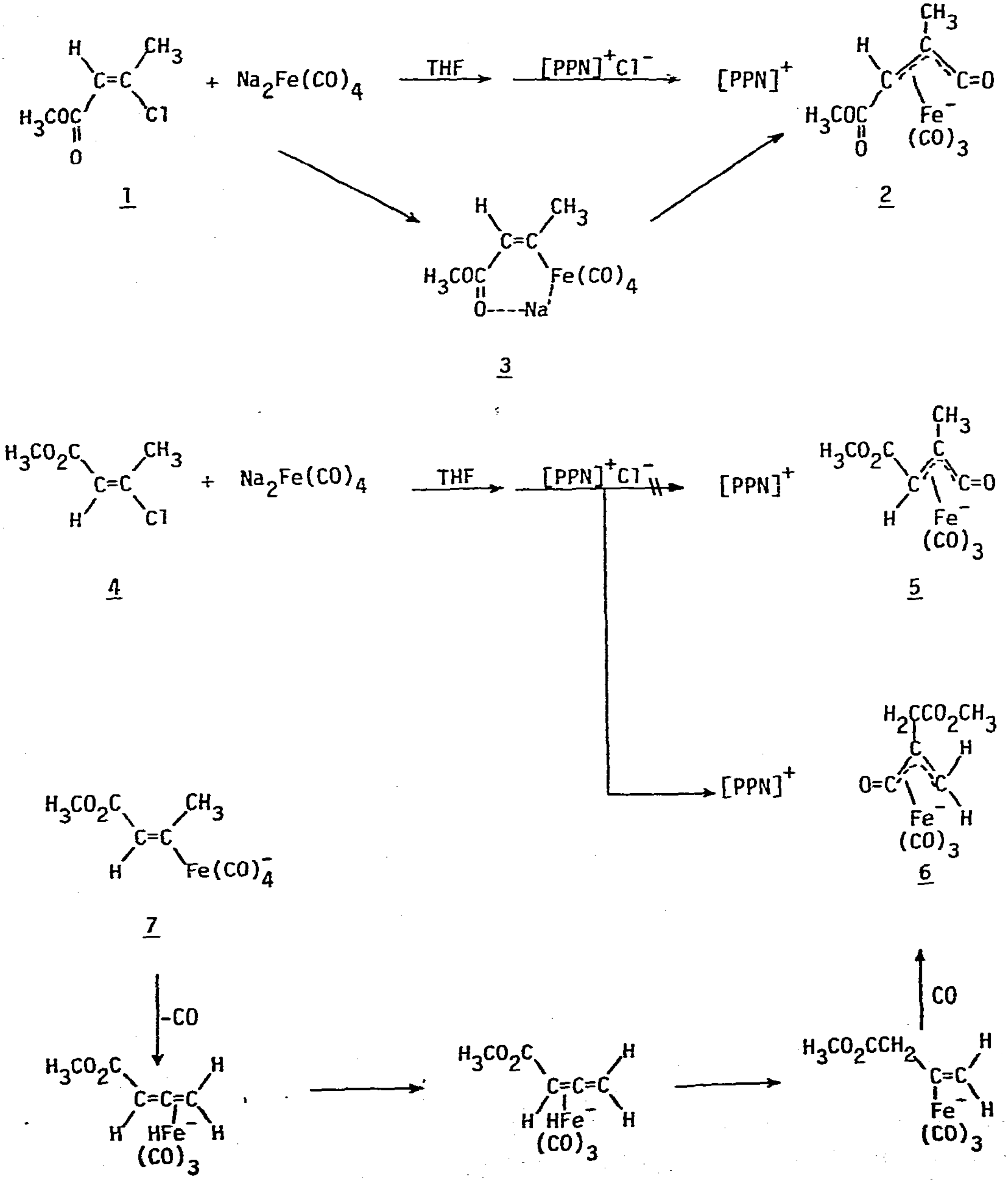
Iron carbonyl compounds have been used to prepare highly dispersed iron supported on Al_2O_3. The carbonyl complexes are physiosorbed on the alumina followed by heating in a helium stream at 120°C. The species present are best described as subcarbonyl species [9]. Temperature-programmed decomposition spectroscopy has been used to determine the properties of $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ supported on λ-Al_2O_3. At low activation temperatures ($<$ 150°C), zerovalent subcarbonyl species are formed. At higher temperatures, extensive oxidation of the iron by reaction with surface hydroxyl groups of the Al_2O_3 takes place [10]. The three binary iron carbonyl compounds have been introduced into a dehydrated HY type zeolite. Although these metal carbonyls retain their molecular structure during absorption, $Fe(CO)_5$ and $Fe(CO)_9$ looses an equivalent of CO upon vacuum treatment to yield $Fe(CO)_4$ bonded to the zeolite. Additional physical and chemical studies were reported [11]. $Fe(CO)_5$ as well as ferrocene has been used to prepare zeolite matrix materials with ultrafine iron oxide controlled particles within the cage structure [12].

$Fe(CO)_5$ has been shown to react with rhodium(I) complexes such as Wilkinson's complex with resultant transfer of carbonyl groups to the rhodium. Thus, the interaction of $Fe(CO)_5$ with $(PPh_3)_3RhCl$ yields $Fe(CO)_4(PPh_3)$, $Fe(CO)_3(PPh_3)_2$ and $Rh(PPh_3)_2COCl$ and with $(butadiene)_2RhCl$ to yield $Fe(butadiene)(CO)_3$ and a rhodium(I)-CO complex containing a bridging butadiene ligand [13].

A detailed discussion of the interaction of $[Na]^+$ with various transition metal carbonylate and cyanocarbonylate anions, including a number of iron compounds, has been presented [14]. The reaction of diaryliodonium salts and $[RCOFe(CO)_4]^-$ (R=Me, Bu^n, Ph) in a THF/pentane mixture yields the corresponding ketone in excellent yield [15]. An aqueous $Fe(CO)_5$-NaOH system in benzene in the presence of a phase-transfer catalyst has been shown to be useful in the preparation of ketones from alkyl halides analogous to the chemistry of $Na_2Fe(CO)_4$ but avoids the preparation of this air sensitive complex [16].

The cis compound 1 reacts with $Na_2Fe(CO)_4$ to yield 2, presumably via 3 as shown in Scheme 1. 2 was isolated as the $[PPN]^+$ salt. Surprisingly the trans

SCHEME 1

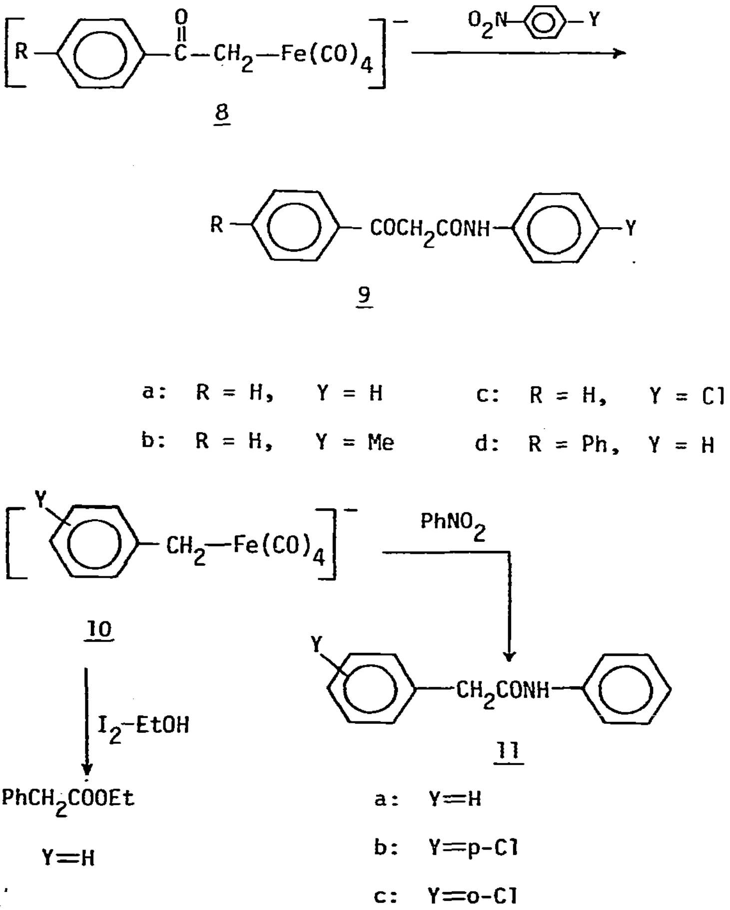


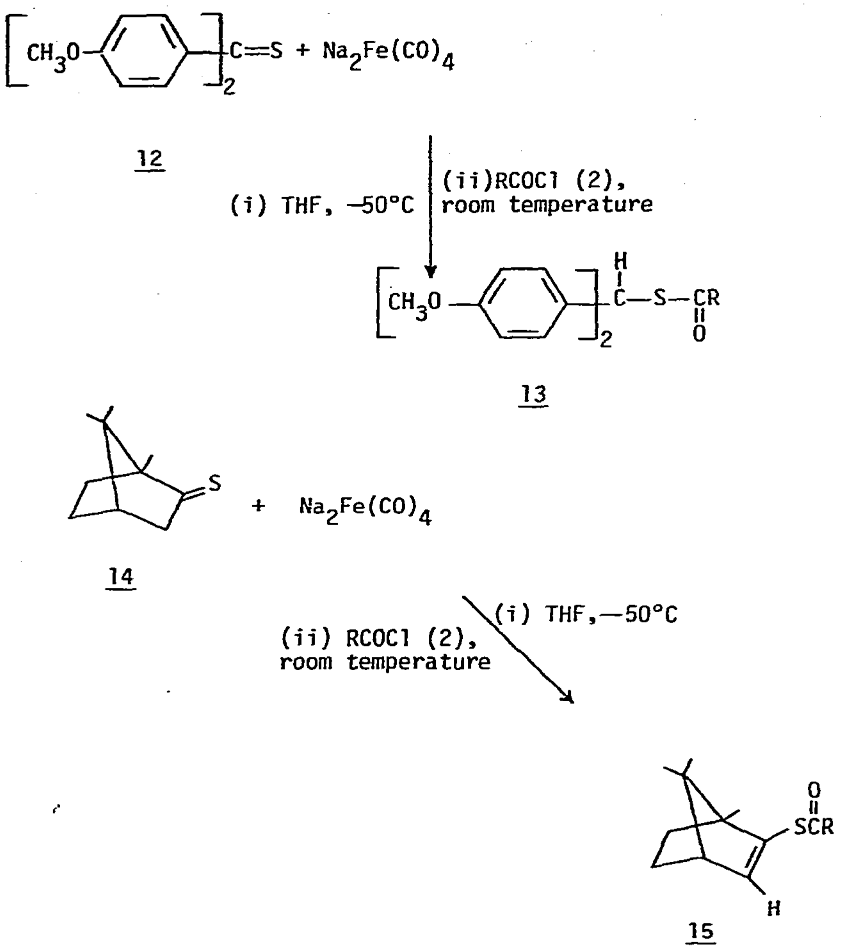
isomer 4 reacts with $Na_2Fe(CO)_4$ to yield 6 and not 5. 6 was again isolated as the $[PPN]^+$ salt. 6 is believed to form from 7 as shown in the Scheme. If correct, this would represent the first 1,3-hydrogen shift to take place through a η^2-allene intermediate [17].

The complexes 8, formed from the reaction of $[Fe(CO)_4]^{2-}$ with α-haloacetophenones, react with nitro compounds as shown in the first reaction of Scheme 2 to yield complexes 9. Complexes 10, formed as with 8 using benzyl chloride, reacts with the nitro compounds to form 11. [18].

The reaction of 12 and $Na_2Fe(CO)_4$ followed by RCOCl produces 13 in modest yield. In a similar reaction of 14 yields 15. [19]

SCHEME 2





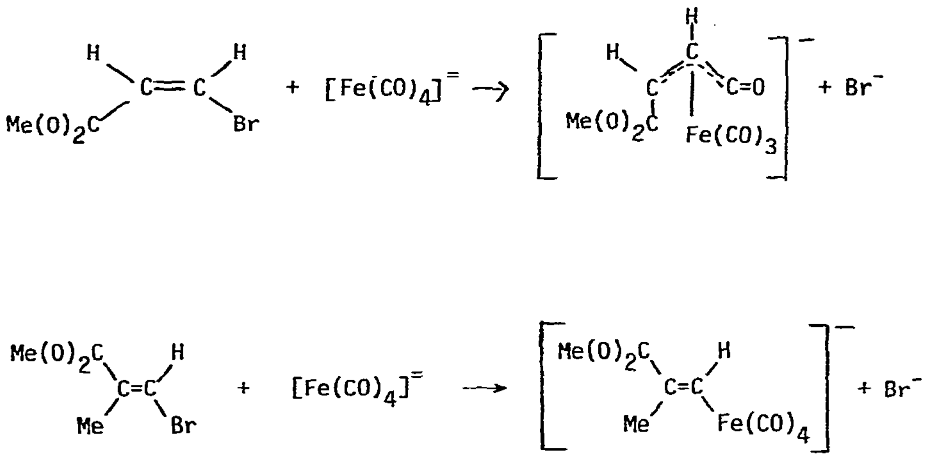
The reaction of $Na_2Fe(CO)_4$ with activated vinyl halides yields various products depending on the starting halide as shown in Scheme 3. The protonation reaction of either product yields $(h^2$-olefin$)Fe(CO)_4$ complexes [20].

Acetyltetracarbonylferrates have been shown to react with imidazole chlorides to yield mesoionic 1,3-oxazol-5-ones as shown in Scheme 4. These complexes are useful for the synthesis of a^{3}amino acid derivatives [21].

Complexes with group IV ligands

An extensive new series of Ru(IV)-SiR_3 complexes have been reported. Thus $RuH_3(SiR_3)L_n(R_3{=}F_3$, MeF_2, $(OEt)_3$, $ClMe_2$, HPh_2, $MePh_2$, Ph_3; L= PPh_3, $AsPh_3$, $P(C_6H_4Me\text{-}p)_3$; n=2,3), are formed in the reaction of excess $HSiR_3$ with RuH_2L_4, $RuHClL_3$, $RuCl_2L_3$ or $RuCl_3(AsPh_3)_3$ and complexes of the type $RuH_2X(SiR_3)L_3$ (X=Cl, I) from the reaction of the chlororuthenium(II) com-

SCHEME 3



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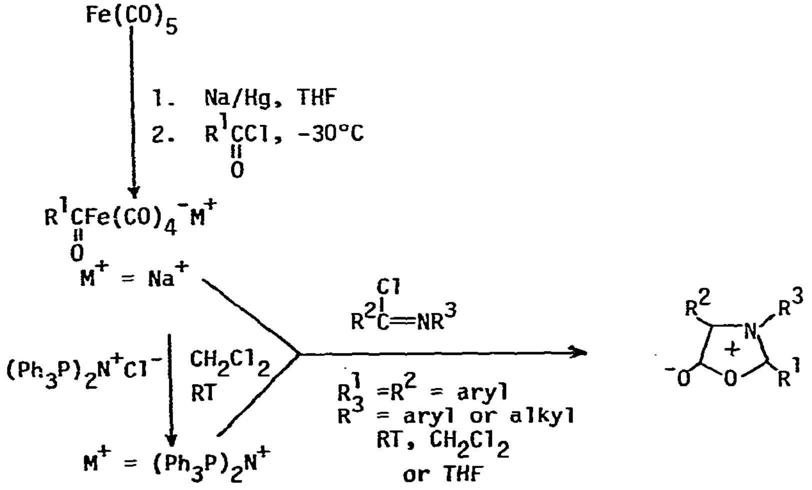
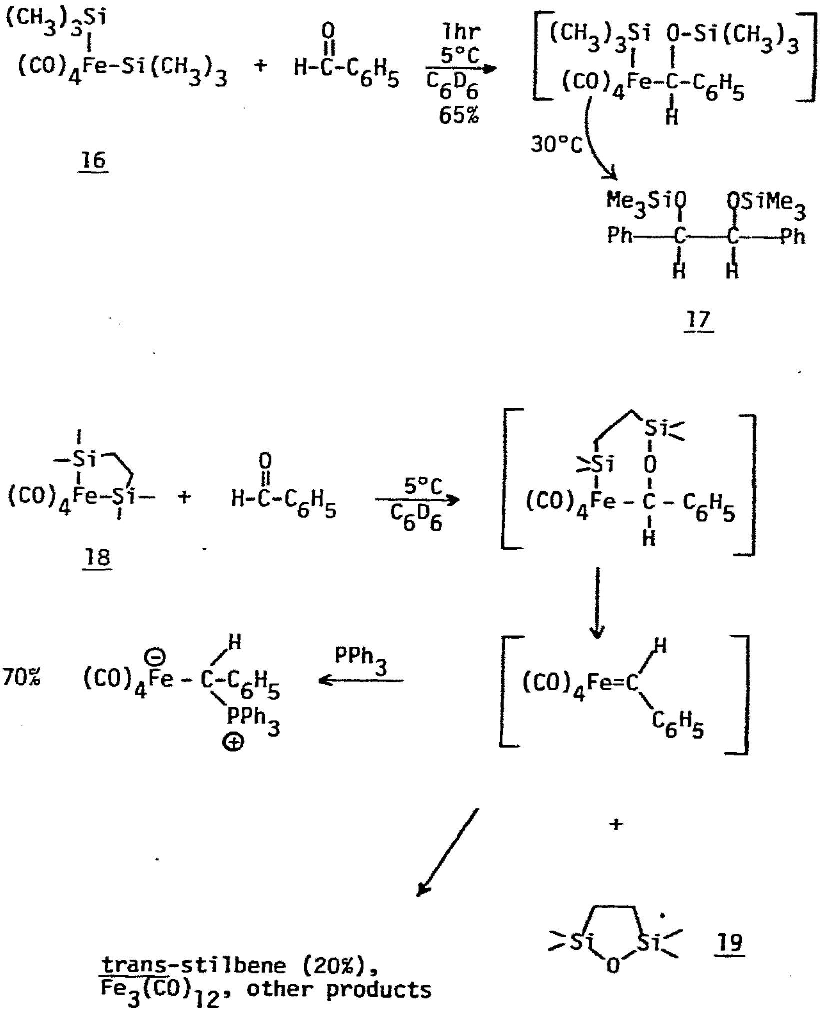


plexes with $HSiCl_3$ or $RuH_3[Si(OEt)_3](PPh_3)_3$ with $CDCl_3$ or I_2 [22]. Ultraviolet irradiation of $Ru_3(CO)_{12}$ in hexane with excess of $SiCl_3H$ and CO gas yields cis-$Ru(CO)_4(SiCl_3)_2$. The method also works for iron and osmium analogs. The new complex reacts with PPh_3 to form mer-$Ru(CO)_3(PPh_3)(SiCl_3)_2$ showing $SiCl_3$ has a larger trans effect than CO [23].

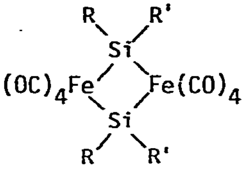
The reaction of 16 with benzaldehyde proceeds as shown in Scheme 5 to produce 17 presumably by the intermediate shown. The complex 18 yields 19 in high yield as also shown in Scheme 5. A metal-carbene intermediate is believed to form and can be trapped by PPh_3 [24].

SCHEME 5



Mössbauer spectroscopy has been used to follow the reaction of Fe(O) and Fe(II) tertiary phosphine complexes with silanes. Although products were difficult to purify, complexes such as trans-$[Fe(SiR_3)_2(dppe)_2]$ were thought to form [25]. The complexes $[Et_4N][(CO)_4FeSiClRR']$(R=Me, Cl, Ph; R'=Me, cyclohexyl, Ph, Cl) are prepared by the UV irradiation of a mixture of HSiClRR' and $Fe(CO)_5$ followed by treatment with CO and Et_4NCl. These complexes can be converted to 20 by treatment with $AlCl_3$ and 20 can be converted to 21 using UV irradiation [26]. Complex 22 was prepared by the reaction of 23 and $Fe_2(CO)_9$ [27]. The reaction of $HMe_2SiSiMe_2H$ and $Fe_3(CO)_{12}$ yields $(\mu\text{-}SiMe_2)_2(\mu\text{-}CO)Fe_2(CO)_6$ [27a].

The reaction of the dimethylstannacycloalkane, 24, with $Fe_2(CO)_9$ yields the highly air sensitive ring expansion product 25 [28].



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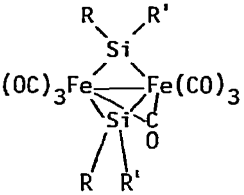

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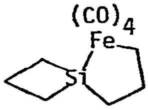

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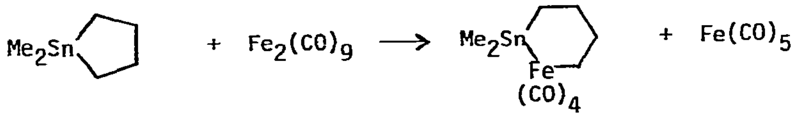

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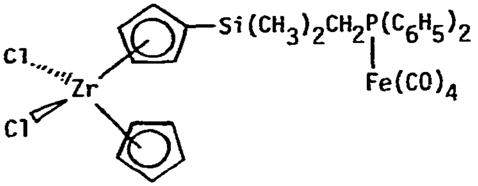
The reaction of $[Mn(CO)_5]^-$ with $(Ge_2H_5)_2Fe(CO)_4$ produces $(Ge_2H_5)Mn(CO)_5$ implying that $[(Ge_2H_5)Fe(CO)_4]^-$ had formed in the reaction. This was demonstrated by mixing this anion in situ with GeH_3Br to produce $(GeH_3)(Ge_2H_5)Fe(CO)_4$ [29]. The reaction of zinc with $(ClHg)_2Fe(CO)_4$ in refluxing diglyme led to the formation of the solvated species $(ClZn)_2Fe(CO)_4 \cdot C_6H_{14}O_3$. This compound, which is stable in air for several hours, was useful in metathesis reactions with R_3SnCl compounds to form $(R_3Sn)_2Fe(CO)_4$ derivatives [30].

Complexes of Group V Ligands

A convenient synthetic procedure for the preparation of $LFe(CO)_4$ complexes (L = PPh_3, $P(OPh)_3$, $P(OMe)_3$) from $Fe(CO)_5$ in which the frequent problem of disubstitution is avoided has been developed. A simple iron carbonyl anion catalyst is generated in situ in the reaction mixture by the addition of sodium benzophenone ketyl. It was shown that polynuclear anions form and act as the catalyst in the substitution reaction [31].

The reaction of $Fe_3(CO)_{12}$ with $P(Bu^t)_3$ in methanol yields $Fe(CO)_4[P(Bu^t)_3]$ whereas in diethyl ether $Fe(CO)_3[P(Bu^t)_3]_2$ is produced. In a like manner, $Ru(CO)_4[P(Bu^t)_3]$ is produced in the reaction of $Ru_3(CO)_{12}$ with this phosphine in butanol whereas $Ru(CO)_3[P(Bu^t)_3]_2$ is produced in methanol [32]. The interesting mixed zirconium-iron complex 26 has been reported [33].



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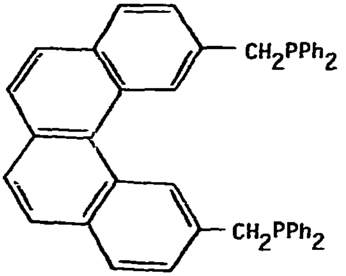

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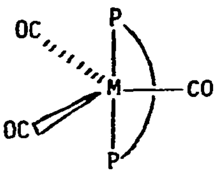

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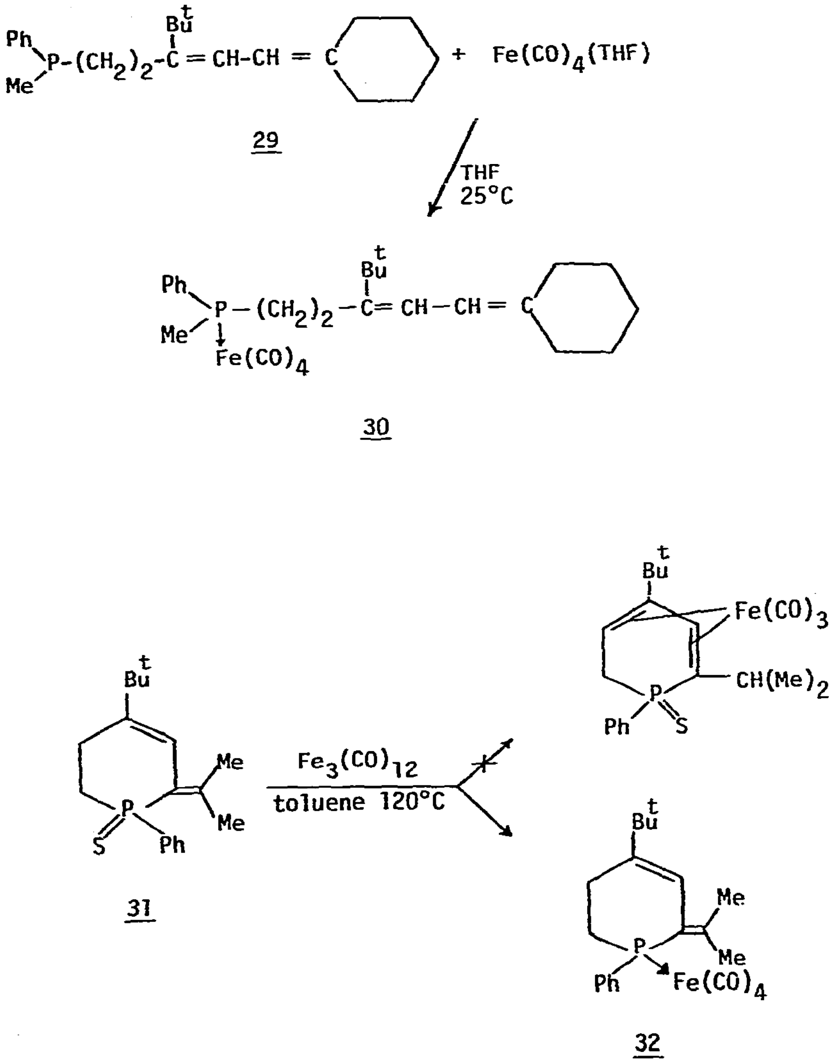
The complexes $[M(CO)_3(L)]$(M = Fe, Ru) where L is 27 have been prepared. For comparative purposes the complexes $[M(CO)_3(dppe)]$ were also prepared. The structures of the $[M(CO)_3(L)]$ complexes are believed to be as shown in 28 with the phosphine atom occupying the apical sites [34]. The four coordinate complex [RuClNO(L)] and three five coordinate Ru(I) complexes of ligand 27 have also been prepared. The structure of [RuCl(CO)(NO)(L)] was determined crystallographically. The coordination around the metal atom is a distorted trigonal bipyramid with the phosphorus atoms in the axial positions [35].

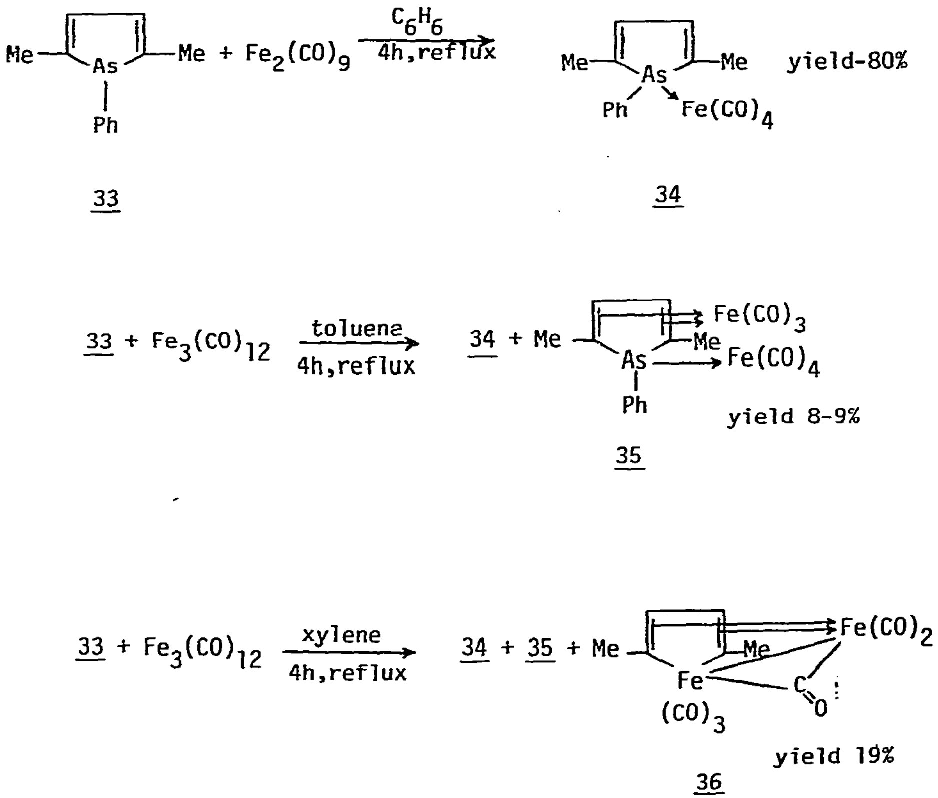
The phosphine 29 was prepared and characterized as the $Fe(CO)_4$ complex 30 as shown in Scheme 6. 31 reacts with $Fe_3(CO)_{12}$ to form 32 as shown in Scheme 6 [36].

SCHEME 6

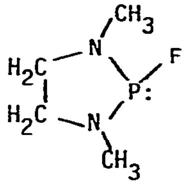


The reaction of 33 and $Fe_2(CO)_9$ proceeds as shown in Scheme 7. With $Fe_3(CO)_{12}$ in refluxing toluene, 34 and 35 are produced. In refluxing xylene, 34, 35, and 36 are produced [37].

SCHEME 7



Reaction of the complex $FLFe(CO)_4^-$ (37, FL = 38) with PF_5 results in F^- removal to yield $[(L)Fe(CO)_4]^+$ (39, L = 40). The neutral complex 37 will not undergo rapid CO exchange whereas 39 does as studied by variable temperature NMR. It was proposed that the CO lability in this cationic complex was due to possible chelation of the phosphine ligand using one nitrogen lone pair [38]. The reaction of $(CH_3)_2NPF_2$ with iron atoms using metal vapor synthesis produces $Fe[PF_2N(CH_3)_2]_5$. A similar reaction with $CH_3N(PF_2)_2$ yields $Fe[(PF_2)_2NCH_3]_4$, a molecule containing one bidentate and three monodentate $CH_3N(PF_2)_2$ ligands [39]. The ligand exchange reactivity of $Fe(PF_3)_5$ has been studied using (positive) chemical ionization mass spectroscopy in which the new ligand is used as the reagent gas. In most cases, the reactivity studied



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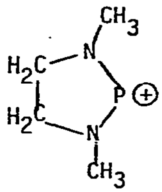

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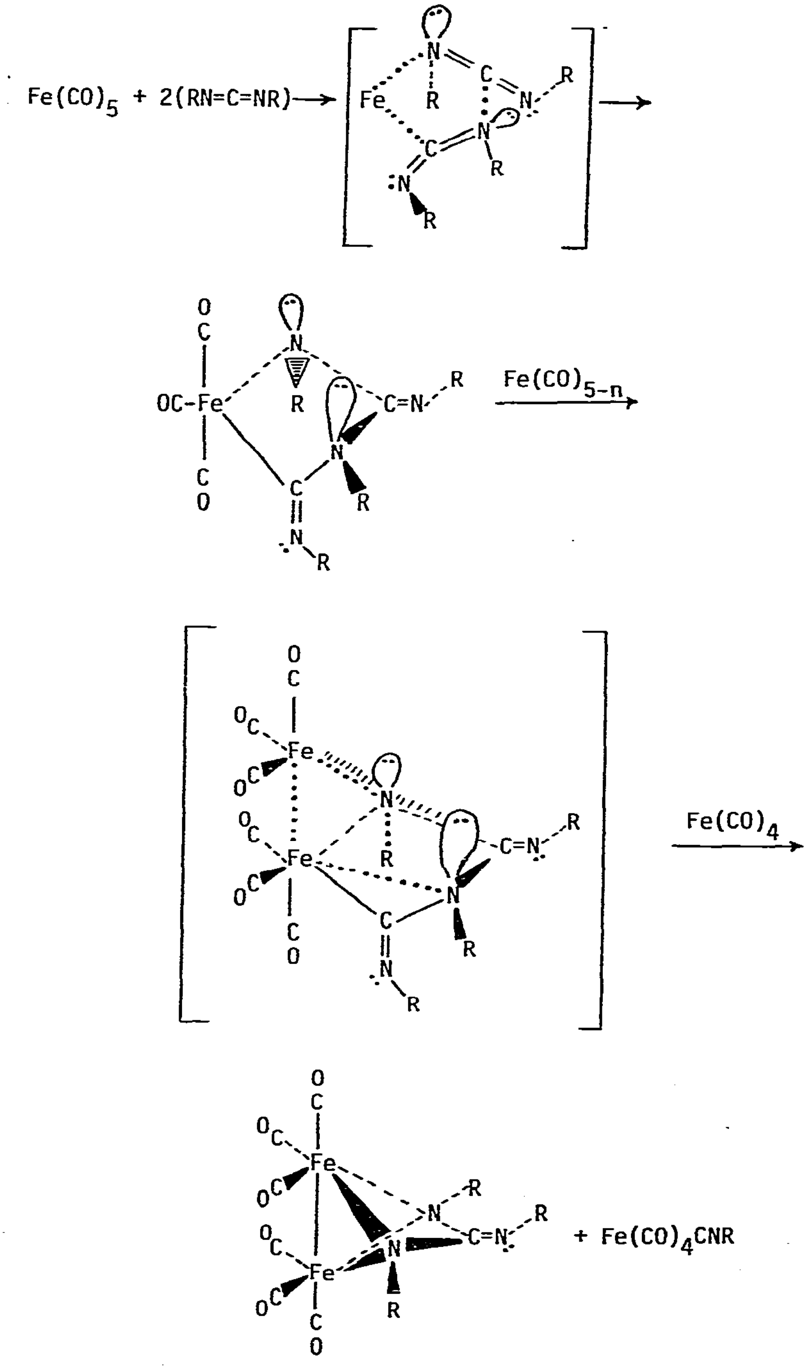
nder these conditions parallels laboratory scale experiments. Thus, ligands uch as CO and CH_3CN exchange readily as is known for chemical experiments ut ligands such as PCl_3 and N_2 do not exchange in either type of experient. Interestingly, hydrocarbons such as isobutane associate with iron. hese reactions must involve either C-C or C-H bond rupture. Acetone was nique because both in the mass spectrometer and under photolytic laboratory xperiments, PF_2 groups were seen. For example, $Fe_2(PF_2)_2(PF_3)_6$ was isoted in a photochemical laboratory scale experiment [40].

A reasonable mechanism has been proposed for the carbodiimide rearrangeents in the presence of iron carbonyls as shown in Scheme 8 [41]. Comlexes of the type $R_3N{\cdot}Fe(CO)_4$ which have proven difficult to prepare preiously have now been prepared in fair to good yield as shown in Scheme 9. he reactivity of these new complexes was briefly described [42]. In order to elp solve the controversy that has arisen over the structure of $(Me_2N)_3P$, the ructure of $[(Me_2N)_3P]_2Fe(CO)_3$ was determined crystallographically. The erall geometry is trigonal-bipyramidal with the aminophosphine ligand occupyg the axial positions. Interestingly, the two $(Me_2N)_3P$ ligands adopt differt conformations. One possesses approximately C_s symmetry while the other s roughly C_3 symmetry [43].

The iron-57 Mössbauer of a series of complexes of the formula $Fe(CO)_4L$, $_2(CO)_7L$ and $Fe_2(CO)_6L$ (L = cyclic diazene ligand) have been reported and e data compared to analogous organophosphane complexes [44].

The reaction of $Ru_3(CO)_{12}$ and $SbPh_3$ yields $Ru(CO)_4(SbPh_3)$ which was own to have a distorted trigonal bipyramidal structure with the $SbPh_3$ group an equatorial site [45]. Heating $[Ru(NH_3)_5N_2]^{2+}$ supported on a Y-type olite yields a highly reactive ruthenium species which reacts with CO, NH_3 d NO. From the position of the carbonyl stretching bands in the infrared at 32 and 2054 cm^{-1}, it was proposed that the CO reaction product was obably small clusters of low charge with 2CO groups on a ruthenium atom 6]. The oxidation of $[Os(NH_3)_5CO]^{2+}$ in acidic solution using Ce^{4+} yields $Os(NH_3)_4CO)_2N_2]^{4+}$. The overall stoichiometry of the reaction was

SCHEME 8



SCHEME 9

$$R_3N + Fe_2(CO)_9 \xrightarrow[\text{R.T.}]{\text{hexane or THF}} R_3N{\cdot}Fe(CO)_4 + Fe(CO)_5$$

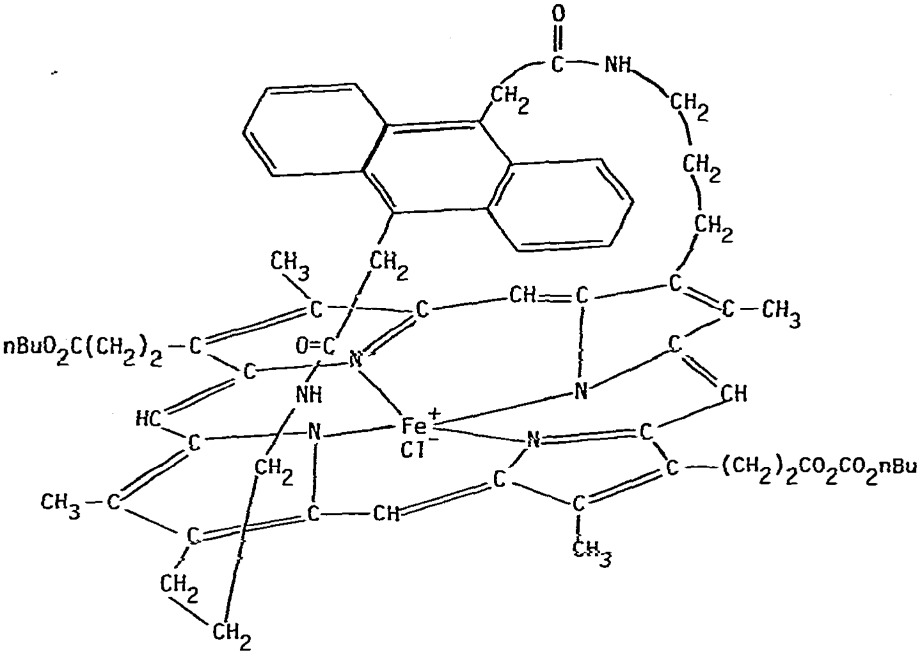
$R = Me, Et, Pr^n, Bu^n$, etc.

determined. An intermediate in the reaction is $[Os(NH_3)_5CO]^{3+}$. Also, Os(IV) and Os(V) species (the latter being possibly $[Os(NH_3)_4CON]^{2+}$ which couples to give the product) are believed to be involved [47].

Meso-tetraphenylporphyrin iron derivatives bearing sidechains with a terminal imidazole group have been prepared and studied for the coordination of the imidazole group with and without the presence of CO [48]. Iron tetraphenylporphyrin, Fe(II)TPP, reacts with CCl_3COOEt and CCl_3CN in the presence of a reducing agent to prepare stable iron (II)-carbene complexes of CClA(A = COOEt and CN). The structure of these complexes was delineated using a combination of IR, ^1H, ^{13}C NMR and mass spectroscopy techniques [49]. The one electron oxidation of the vinylidine complex $[Fe(TPP)(C{=}C(p\text{-}ClC_6H_4)_2)]$ by $CuCl_2$ or $FeCl_3$ yields $[Fe(TPP)(C{=}C(p\text{-}ClC_6H_4)_2)][Cl]$. The spectral properties of this complex and catalases were compared [49a]. The CO stretching frequency for some iron(II) porphyrin complexes has been reported and the origin of the relatively high stretching frequency values discussed [50].

The structure of an iron(II) porphyrin carbonyl complex has been determined crystallographically and is thought to be an analog of cytochrome P-450 [51]. The structure of [bis(tert-butylisocyanide)(meso-tetraphenylporphyrinato)iron(II)]-bis(toluene) has been determined crystallographically. The isocyanide geometry was essentially linear with the geometry about the iron atom approximately tetragonal [52].

Two cyclophane porphyrin ligands have been synthesized as models for steric hindrance of CO ligation in hemoproteins. The interaction of complex 41 with CO was studied and proved to have a greatly reduced affinity for a second CO ligand [53]. The photochemical properties of $[Fe(TIM)(CH_3CN)\text{-}CO]^{2+}$ (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) complexes have been investigated by laser and flash photolysis. The complicated photodissociative mechanism shown in Scheme 10 explained the results under various conditions [54]. The rates of CO dissociation from a series of chelated heme compounds have been measured. For unstrained chelated hemes having attached proximal bases, these compounds react reversibly with CO in a fashion similar to fully ligated (R-state) hemoglobin [55].



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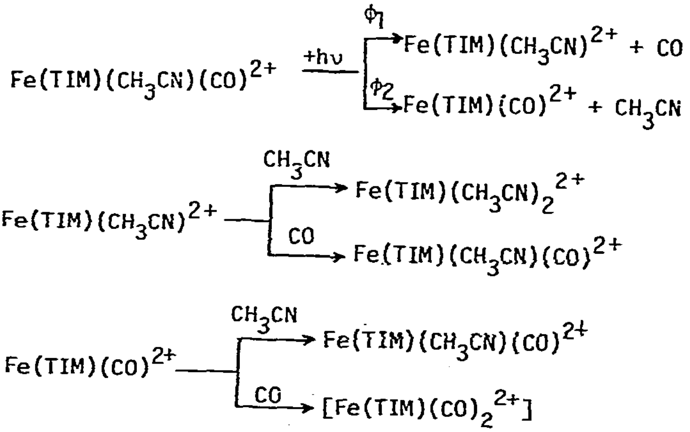
SCHEME 10



$$\mathrm{Fe(TIM)(CH_3CN)(CO)^{2+}} \xrightarrow{+h\nu} \begin{cases} \xrightarrow{\phi_1} \mathrm{Fe(TIM)(CH_3CN)^{2+} + CO} \\ \xrightarrow{\phi_2} \mathrm{Fe(TIM)(CO)^{2+} + CH_3CN} \end{cases}$$

$$\mathrm{Fe(TIM)(CH_3CN)^{2+}} \begin{cases} \xrightarrow{\mathrm{CH_3CN}} \mathrm{Fe(TIM)(CH_3CN)_2{}^{2+}} \\ \xrightarrow{\mathrm{CO}} \mathrm{Fe(TIM)(CH_3CN)(CO)^{2+}} \end{cases}$$

$$\mathrm{Fe(TIM)(CO)^{2+}} \begin{cases} \xrightarrow{\mathrm{CH_3CN}} \mathrm{Fe(TIM)(CH_3CN)(CO)^{2+}} \\ \xrightarrow{\mathrm{CO}} \mathrm{[Fe(TIM)(CO)_2{}^{2+}]} \end{cases}$$

$$\mathrm{Fe(TIM)(CH_3CN)_2{}^{2+} + CO \rightarrow Fe(TIM)(CH_3CN)(CO)^{2+}}$$

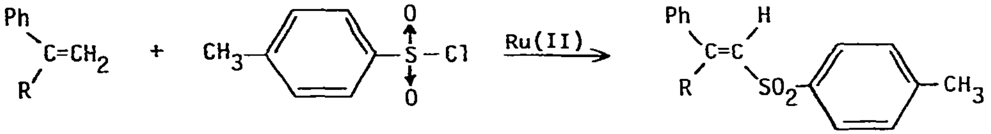
$$\mathrm{[Fe(TIM)(CO)_2{}^{2+}] + CH_3CN \rightarrow Fe(TIM)(CH_3CN)(CO)^{2+}}$$

The ligands t-butylisocyanide and PR_3 (R = Ph, Et, Me) react with Ru(TPP)CO (TPP = <u>meso</u>-tetraphenylporphinate dianion) to yield $[Ru(TPP)(L)_2]$ complexes. The electrochemistry of these new complexes was investigated [56]. A ^{13}C NMR investigation of ^{13}C and ^{15}N labelled alkyl isocyanide complexes bound to ^{57}Fe labelled myoglobin and other porphyrin iron(II) complexes has been reported. ^{13}C chemical shifts and ^{15}N-^{13}C coupling constants are sensitive to changes in these molecules whereas one-bond ^{13}C-^{57}Fe coupling is not [57]. The reaction of $Fe(CO)_5$ with $o\text{-}C_6H_4(CN)_2$ in DMF followed by addition of CO yields the phthalocyanine (PC) complex Fe(PC)(CO)(DMF). The DMF group can be replaced by THF [58].

M(II) phosphine Complexes Containing Hydrido, Halo and Other Ligands

The complex $Ru(PPh_3)_2Cl_2$ catalyzes the reaction shown in Scheme 11. The reaction was both regio- and stereoselective as shown [59]. The reaction of $Fe(THF)_2X_2$ with alkyl phosphites, P, proceeds as shown in Scheme 12. The FeP_3X_2 complexes are reduced by Na amalgam in the presence of excess phosphite to yield FeP_5. This electron rich Fe(O) species is readily oxidized to yield Fe(II) complexes by a number of reagents [60].

SCHEME 11



R: H, Me, Ph

SCHEME 12

$$Fe(THF)_2X_2 \overset{P}{\rightleftarrows} FeP_3X_2$$

$$FeP_3X_2 \rightleftarrows [FeP_3X]^+X^-$$

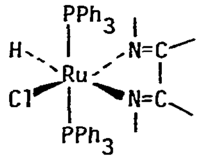
$$FeP_3X_2 \overset{P}{\rightleftarrows} FeP_4X_2$$

$$FeP_4X_2 \overset{P}{\rightleftarrows} [FeP_5X]X$$

$$[FeP_5X]X \overset{P}{\rightleftarrows} [FeP_6]X_2$$

$RuH_2(PPh_3)_4$ or $RuH_4(PPh_3)_3$ reacts rapidly with one equivalent of RSH (R = Ph, $PhCH_2$) to yield $RuH(SR)(PPh_3)_3$ complexes. An analogous complex is formed in the reaction of $RuH_2(PPh_3)_4$ and MeSSMe. These complexes were proposed to have a trigonal bipyramidal structure with the PPh_3 ligands in the equatorial sites [61]. A mixture of $RuCl_3$ and excess $P(Bu^t)_2R$ (R = Me, Et) heated under reflux in 2-methoxyethanol yields $RuHClCO(PBu^t{}_2R)_2$. The R = Et complex reacts with MeNC to yield $RuHCl(CO)(MeNC)(P(Bu^t)_2Et)$ [62]. The complex $RuH_2(PPh_3)_4$ has been treated with a variety of neutral mono-or di-functional acids. The new compounds were characterized by I.R. and NMR (^1H and ^{31}P) and structures were proposed [63]. Single-step syntheses of $HRuCl(CO)(PCy_3)_2$ and $Ru(CO)_3(PCy_3)_2$ have been reported [64]. An X-ray crystallographic determination of $HRuCl(diop)_2$ has shown that this molecule has a distorted octahedral structure with trans stereochemistry in the solid state. Normal application of ^{31}P and ^1H NMR would have predicted a cis-structure but the NMR data can be explained by assuming that the solution structure is the same as the solid structure [65].

The preparation of 42 from $RuHCl(PPh_3)_3$ and the imine ligand was reported. A preliminary account of the chemistry of this new complex was reported [66]. The reaction of $LiNR_2$ (R = Me_3Si) with $RuH(Cl)(PPh_3)_3$ yields $RuH(NR_2)(PPh_3)_2$. Because of the failure to prepare analogous NMe_2 complexes, these results support the contention that β-elimination pathways have a role in metal-amide as well as metal-alkyl complexes [67]. The reaction of FeX_2 (X = Cl, Br, I) and $FeY_2 \cdot 6H_2O$ (Y = BF_4, PF_6) with HPR_2 (R_2 = MePh, EtPh, Et_2) in alcohol yields $[FeX(HPR_2)_4]^+$ and $[Fe(HPR_2)_5]^{2+}$ complexes. The magnetic properties of these complexes were described. These complexes react with CO to yield $[FeX(CO)_2(HPR_2)_3]^+$ and $[Fe(CO)_2(HPR_2)_4]^{2+}$ complexes [68].



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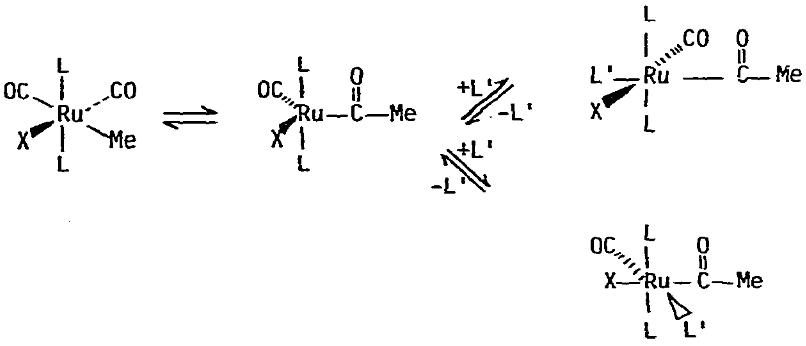
Mössbauer parameters on the two series of complexes $[FeHL(dppe)_2][BPh_4]$ (L = CO, $PhCH_2NC$, $P(OMe)_3$, N_2, PhCN, MeCN, NH_3) and $FeHX(dppe)_2$ (X = CN, NO_2, NCS, NCO, Cl, N_3, Br, I) have been reported and the results interpreted in terms of the bonding properties of the ligands L and X [69].

The complexes $RuX_3(PPh_3)_2L$, $RuX_2(EPh_3)_2L_2$ and RuX_2L_4 (X = Cl, Br; E = P, Sb; L = CNC_6H_4Me-p) were prepared and their electronic, IR and ESR spectra reported [70]. The new complex trans-$[Fe(dppe)(MeCN)_2][ClO_4]_2$ has been prepared and investigated by electrochemical techniques. Reactions in the presence of CO were also reported [71].

The structure of the complex $RuCl_2(PO)_2$ (PO = o-(diphenylphosphino)-anisole) has been determined crystallographically. This six-coordinate molecule has a trans chlorine and cis phosphorus donor atoms arrangement around the Ru. The Ru-O bond is weak. This complex can be oxidized with $NOBF_4$ to its monocation. Reactions with CO and t-BuNC are described. This PO ligand, containing a strong and a weak donor atom is called hemilabile by the authors and is compared to similar ligands used by the Monsanto group in the catalytic L-Dopa synthesis [72]. The complexes $[Ru(CO)_2XMeL_2]$ (X = Cl, Br, I; L = PMe_2Ph, $AsMe_2P$) react rapidly with ligands (L' = CO, PMe_2Ph, etc.) to form the acyl products $[Ru(CO)X(COMe)L_2L']$. Initially a trans isomer forms which generally equilibrates with a thermodynamically more stable isomer as shown in Scheme 13 [73].

SCHEME 13



Following experiments with $W[P(OMe)_3]_6$, the species $Fe[P(OMe)_3]_5$ was shown to react with H_2 with photochemical activation to yield $H_2Fe[P(OMe)_3]_4$. This reaction is slow if light is excluded [74]. The interaction of (η^4-cycloocta-1,5-diene)(η^6-cycloocta-1,3,5-triene)Ru(O) with hydrogen in the presence of trivalent phosphorus ligands leads to new $H_2Ru(PR_3)_4$ complexes with hydrogenation of the cyclopolyene groups. The structure, as determined crystallographically, of the complex $H_2Ru(Ph_2PCH_2CH_2PPh_2)_2$ was reported [75]. The preparation of the new ruthenium(II) complexes $[Ru(NH_3)_4(P(OR)_3)_2]X_2$(X = PF_6^-, $CF_3SO_3^-$; R = methyl, isopropyl, or n-butyl) and $[Ru(NH_4)_4P(OEt)_3P(OR)_3][CF_3SO_2]_2$ (R = methyl, isopropyl, n-butyl or phenyl) has been reported [76]. The bridge cleavage reaction shown in Scheme 14 takes place readily in refluxing benzene to yield the mixtures shown. The mixtures could not be separated. Direct preparations of the $RuYCl_2L_3$ complexes were presented as well as rearrangement reactions in polar solvents [77]. The reaction of cis-$[OsX_4(CO)_2]^{2-}$ (X = Cl, Br, I) with pyridine yields cis-$[Os\overset{*}{X_2}(py)_2(CO)_2]$ (* = ligands in trans-position) showing the strong trans-effect of the carbonyl ligands [78].

SCHEME 14

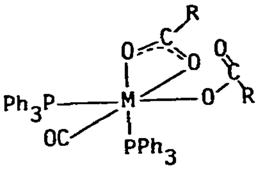
$$Ru_2(Y)Cl_4(PPh_3)_4 \xrightarrow[L]{} RuCl_2L_n + RuYCl_2L_3$$

(Y = CO, CS) n = 3 or 4

$L = PPh_2OR(R = Me, Et)$ or $PPh(OMe)_2$

The reaction of p-tolylisocyanate (RNCO) with $MHXCO(PPh_3)_3$ (M = Ru, Os; X = Cl, Br),$MH_2CO(PPh_3)_3$ and $RuH_2(PPh_3)_4$ or $OsH_4(PPh_3)_3$ yields a mixture of isomers of complexes containing a formamido (RN⋯CH⋯O), ureylene (RN-C(O)-NR) and formamidinato (RN⋯CH⋯NR) ligand, respectively [79, 80]. The reaction of $RuH(Cl)(CO)(PPh_3)_3$ with $Pr^iN{=}C{=}NPr^i$ yields a $Ru(Cl)(CO)(PPh_3)_2$-$(Pr^iN{\cdots}CH{\cdots}NC(Me){=}CH_2)$ complex, as shown by x-ray crystallography, formed from insertion of the carbodiimide moiety into the Ru-H bond and loss of H_2 from one of the isopropyl groups [81].

The intramolecular monodentate-bidentate carboxylate ligand exchange in complexes 43 (M = Ru, R = Me, CF_3, C_2F_5, C_6F_5; M = Os, R = Me, CF_3) have



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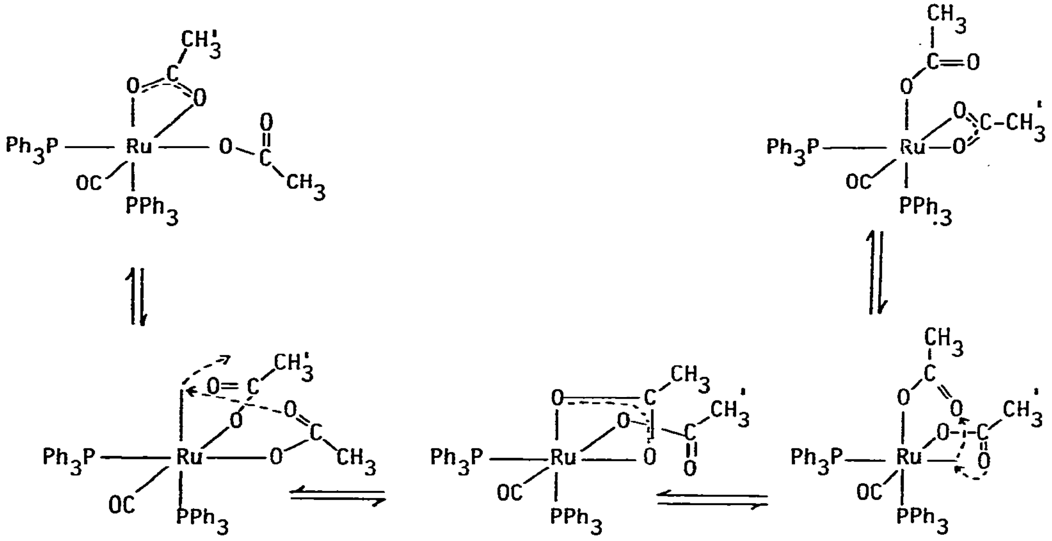
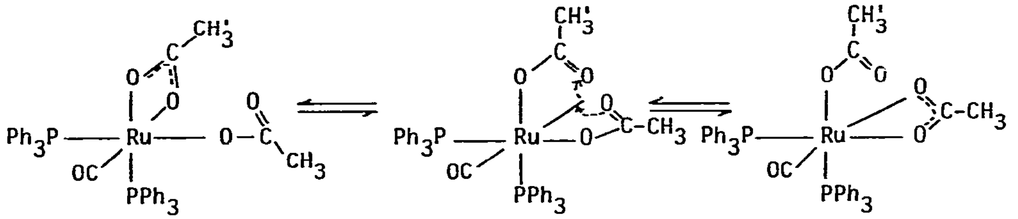
been investigated by standard variable temperature NMR means. Actually, two separate processes were established as shown in Schemes 15 and 16 for the M = Ru, R = CH_3 case. The process shown in 15 is the lower energy one. If methanol is added to these solutions, intermediates in which the methanol is coordinated to the metal complicate the rearrangement processes [82]. Interaction of $Ru_2(CO_2Me)_4Cl$ with Na/Hg in THF containing PMe_3 and LiCl yields trans-$RuCl_2(PMe_3)_4$. At reflux, $[(Me_3P)_4Ru(\mu\text{-}Cl)_2Ru(PMe_3)_4]^{2+}$ is obtained. Reaction of $Ru_2(O_2CMe)_4Cl$, PMe_3 and $(2\text{-}MeOC_6H_4)_2Mg$ yields $[RuCl(PMe_3)_4]^+$ [83].

SCHEME 15. Mechanism for Interchange of Phosphine Ligands but Not Acetate Ligands In $[Ru(O_2CMe)_2(CO)(PPh_3)_2]$.



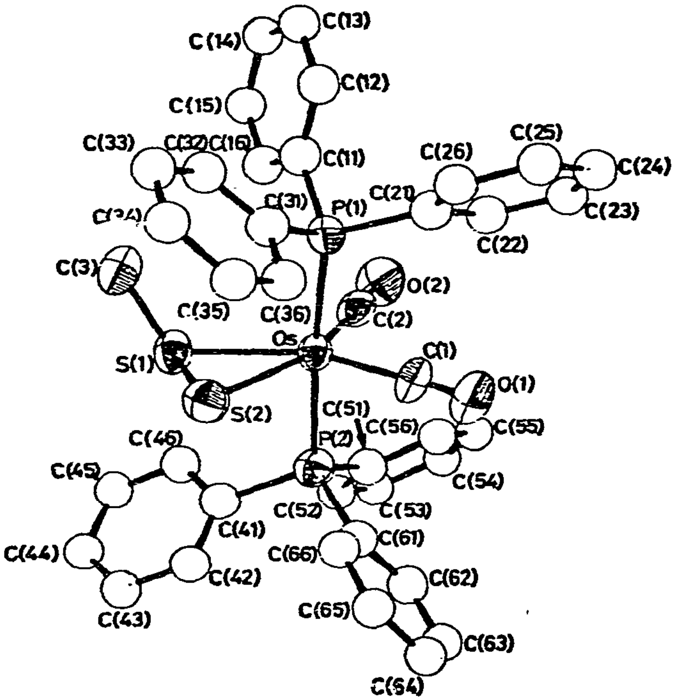
SCHEME 16. Mechanism for Interchange of Phosphine Ligands and of Acetate Ligands in $[Ru(O_2CMe)_2(CO)(PPh_3)_2]$.



Complexes with Sulfur or Selenium Ligands

A mixture of $Fe_2(CO)_9$ and L in CS_2 solution (L = PR_3, $P(OR)_3$, CNR) yields $Fe(CO)_2L_2(\eta^2-CS_2)$ complexes. For L = CNMe or $CNBu^t$, $Fe(CO)L_3(CS_2)$ and a carbonyl-free complex can be isolated. Ligand exchange reactions are also reported. These η^2-CS_2 complexes alkylate readily at the uncoordinated sulfur atom to yield $[Fe(CO)_2L_2(CS_2R)]^+$ salts [84]. Alkylation of the uncoordinated sulfur atom of $Fe(CO)_2(\eta^2-CS_2)L_2$ (L = $P(OMe)_3$, PPh_3, PMe_2Ph, PMe_3) with CH_3I yields $[Fe(\eta^2-CS_2Me)(CO)_2L_2]^+$ cations. For the cases where L is the strong donor ligand PMe_3 or PMe_2Ph, the iodide displaces a CO group to yield $Fe(\eta^2-CS_2CH_3)I(CO)L_2$ complexes [85]. The reaction of

FIGURE 1

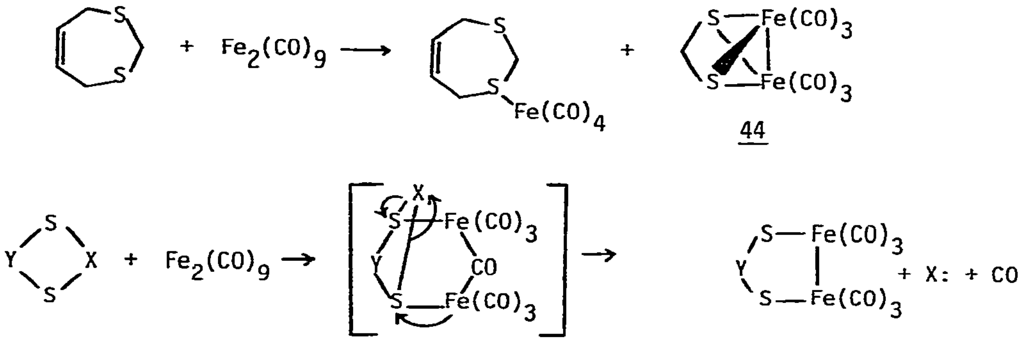


$Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2$ with CF_3CO_2H yields $Fe(\eta^1\text{-}OCOCF_3)(CO)_2(PR_3)_2$ complexes. These react with $(NO)PF_6$ in CH_3CN to yield $[Fe(\eta^1\text{-}OCOCF_3)\text{-}(NCCH_3)(CO)_2(PR_3)_2]PF_6$ and NO [86]. The crystal structure of $[Os(\eta^2\text{-}CS_2CH_3)(CO)_2(PPh_3)_2]ClO_4\cdot\frac{1}{2}C_6H_6$ has been determined and is shown in Figure 1 [87].

The complexes $Fe_2(CO)_6(\mu\text{-}X)_2$ (X = S, Se) react with phosphine ligands (L) to yield simple mono- and bi-substituted derivatives and also more complex polynuclear clusters $Fe_3(CO)_{9-y}L_yX_2$ (y = 0,1,2). A mechanism for the formation of the various products from the initial formation of an $Fe_2(CO)_6LX_2$ adduct is proposed [88]. The reaction of red selenium with $Os(CO)_2(PPh_3)_3$ or $Os(CO)(CNR)(PPh_3)_3$ yields $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$ or $Os(\eta^2\text{-}Se_2)(CO)\text{-}(CNR)(PPh_3)_2$, respectively. The X-ray crystal structure of the dicarbonyl complex was reported. These $\eta^2\text{-}Se_2$ complexes and the analogous $\eta^2\text{-}S_2$ complex react with alkylating reagents to yield cations of the type $[Os(\eta^2\text{-}Se_2Me)(CO)_2(PPh_3)_2]^+$. This cation was reported to react further with borohydride to yield complexes of the type $Os(H)(\eta^1\text{-}Se_2Me)(CO)_2(PPh_3)_2$ [89].

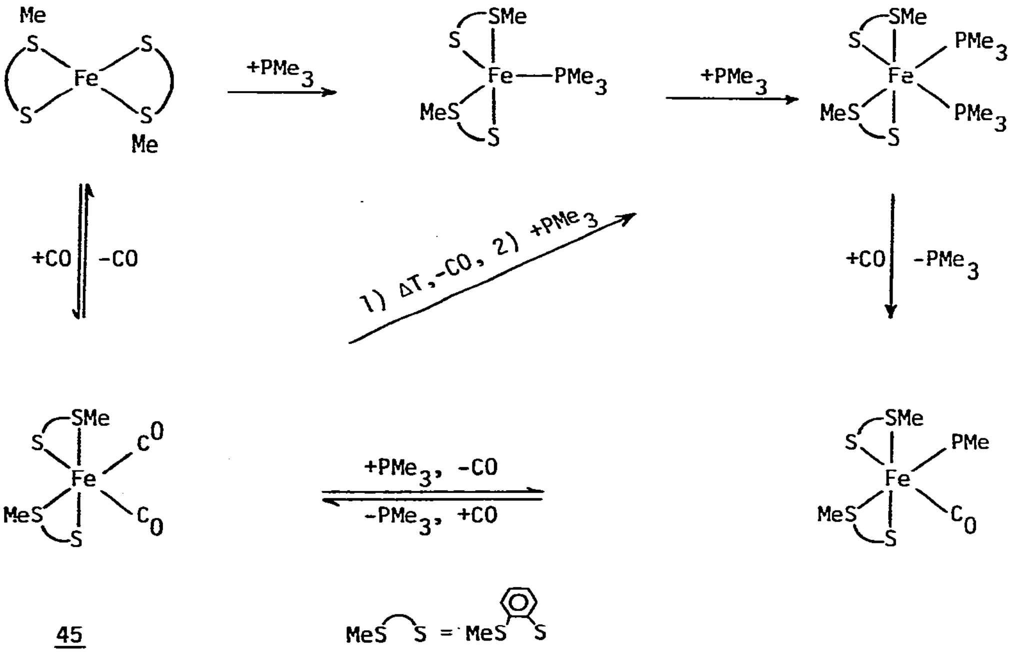
$Fe_2(CO)_9$ has been shown to react with a variety of cyclic organosulfur compounds to yield new products in which two carbon-sulfur bonds must be cleaved. A specific example of the general reaction type is shown in Scheme 17. The structure of 44 was verified crystallographically. A general scheme for the formation of the new complexes was proposed as outlined in Scheme 17 [90].

SCHEME 17



The reaction of thiourea with $Fe_2(CO)_9$ yields diaminocarbenetetracarbonyliron [91]. A variety of reactions of 45 have been reported as outlined in Scheme 18 [92].

SCHEME 18



Carbonyl Halide, Hydride and Cyanide Complexes

The complexes $Na_2[Fe(CN)_5L]$ where L = monodentate, monoprotonated diamines of general formula $NH_2(CH_2)_n\overset{+}{N}H_3$ have been prepared [93]. The complex $[Fe_2(CN)_{10}NH_3]^{4-}$ has been prepared by mixing $Fe(CN)_6{}^{3-}$ and $Fe(CN)_5NH_3{}^{2-}$. X-ray crystallographic techniques have shown the molecule to be bridged by a linear CN group and contain hydrogen bonded water molecules [94].

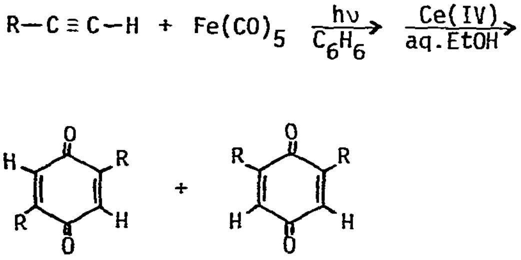
The ^{13}C chemical shifts of a variety of $M(CN)_n$ complexes have been reported. Included are $Fe(CN)_6{}^{-4}$ (δ 177.2), $Ru(CN)_6{}^{-4}$ (δ 162.3) and $Os(CN)_6{}^{-4}$ (δ 142.5). As free CN^- resonates at δ 166.2 (D_2O), the iron complex was the only one in the study to resonate at lower field. These data were interpreted in terms of the σ component of the M-CN bond dominating in general with the iron complex being an exception where π backbonding also has a major contribution. Note that in $M(CO)_n$ complexes, the π component generally dominates. Relaxation time measurements were also reported and it is felt that scalar relaxation of the second kind is generally dominant [95]. *Multiple-pulse NMR techniques on solid samples of* $H_2Os_3(CO)_{10}$, $H_4Os_4(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ have been used to obtain estimates of the proton chemical shift tensors for the hydrogen atoms in these metal clusters. Only the $H_4Ru_4(CO)_{12}$ molecule was shown to have a temperature dependent spectrum in the temperature range of 178-333°K indicating the presence of proton motion [96].

The rates of deprotonation and pKa values of a number of Fe, Ru, and Os carbonyl hydride compounds have been determined. $H_2Fe(CO)_4$ is a stronger acid than $H_2Os(CO)_4$ and metal clusters such as $H_4Ru_4(CO)_{12}$ are even more acidic [97]. The standard enthalpies of formation for $(\eta^3\text{-}C_3H_5)Fe(CO)_3I$, $\eta^4\text{-}C_8H_8Fe(CO)_3$ and $Fe(CO)_4I_2$ have been measured by microcalorimetric measurements of their heats of thermal decomposition and iodination. Also calculated were the bond enthalpy contribution of the various metal-ligand bonds [98]. The complexes $Fe[Fe(CN)_5X]\cdot xH_2O$ ($X = H_2O$, NH_3, CO) have been studied by I.R., Mössbauer and X-ray photoelectron spectroscopy [99].

Photochemical Reactions

Photochemical reaction of $Fe(CO)_5$ with a variety of alkynes followed by treatment with Ce(IV) yields the quinones shown in Scheme 19 [100]. Irradiation of solutions of $Fe(CO)_3(P(OPh)_3)_2$ complexes leads to a new red complex that could not be isolated. Addition of neutral ligands to these solutions yielded $Fe(CO)_2(P(OPh)_3)_2L$ complexes (L = CO, phosphines, *phosphites, isocyanides*, CS_2, SO_2, $C_2(CN)_4$, acetylenes). Various X-Y compounds (H-H, H-Cl, Cl-$SnCl_3$) when mixed with these red solutions yield $Fe(CO)_2(P(OPh)_3)_2(X)(Y)$ complexes. The red intermediate is best formulated

SCHEME 19



as an ortho-metalated Fe(II) hydride complex [101].

The mononuclear species $Fe(CO)_5$ and $Ru(CO)_4(PPh_3)$ undergo photodissociation reactions of a CO group with high quantum yields whereas the cluster complexes $Fe_3(CO)_{12}$ and $Ru_3(CO)_9(PPh_3)_3$ undergo substitution reactions to form $Fe(CO)_4L$ and $Ru(CO)_3PPh_3L$ (L = CO, PPh_3) in low quantum yield. It is suggested that for these clusters, M-M bond cleavage is the primary result of light absorption and the low quantum yields can be explained by rapid reformation of the M-M bond dominating over dissociative and/or associative processes that would lead to mononuclear products. Interestingly, in the photocatalyzed isomerization of 1-pentene by these complexes, the initial ratio of trans- to cis-2-pentene depends on the catalyst precursor used. Thus for example with $Ru(CO)_4(PPh_3)$ and $Ru_3(CO)_9(PPh_3)_3$, the actual catalytic species must be different. The authors conclude from the results that the cluster precursors yield cluster active species [102].

The photocatalytic behavior of phosphinated polymer-anchored iron carbonyl species has been studied with the main goal being the determination of whether the iron species remains coordinated to the polymer during the catalysis. Thus the isomerization of 1-pentene and the reaction with $HSiEt_3$ was studied with a PPh_2 derivatized styrene-1% divinylbenzene resin (PAPh-PPh_2) that yielded a mixture of $(PAPh\text{-}PPh_2)_{5-n}Fe(CO)_n$ (n = 3,4) species when loaded with $Fe(CO)_5$. Also studied were $Fe(CO)_n(PPh_3)_{5-n}$ (n = 3,4,5) complexes. All the complexes were active and quantum yields for the 1-pentene isomerization exceeded unity. It was found that the polymer was a photoinert anchor to the $Fe(CO)_n$ group. Thus different trans- to cis-2-pentene ratios were observed depending on the catalyst precursors. In fact, the ratios obtained for the polymer catalyst resemble closely that expected for a mixture of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$. Also, the irradiation of $Fe(CO)_4PPh_3$ with $P(OMe)_3$ yields no IR bands common to those observed when irradiating $Fe(CO)_5$ and $P(OMe)_3$ [103].

The photochemistry and electronic structure of $[MCp(CO)_2]_2$ (M = Fe, Ru) have been reported. The ruthenium complex, which is known to exist in solution as approximately a 1:1 mixture of bridged and non-bridged forms, exhibits a remarkably temperature and solvent-sensitive absorption spectrum. The bridged isomer is favored at low temperatures and in the more polar solvents. A band at 300 nm is assigned to the $\sigma \to \sigma^*$ excitation for the nonbridged form and one at 265 to the analogous excitation for the bridged form. Presumably, this transition is at higher energy for the bridged complex because of a shorter M-M bond distance. Each complex undergoes M-M bond cleavage when photolyzed in CCl_4 solution to yield $MCp(CO)_2Cl$. Irradiation of $[CpFe(CO)_2]_2(Fp_2)$ in the presence of excess PPh_3 yields $[Fe_2Cp_2(CO)_3PPh_3]$ whereas in the presence of $P(OCH_3)_3$ two primary products are formed, $Fe_2Cp_2(CO)_3P(OCH_3)_3$ and $Fe_2Cp_2(CO)_2(P(OCH_3)_3)_2$. These results are interpreted in terms of photogeneration of $[FeCp(CO)_2]$ radicals. The bridging CO groups do not seem to have a major effect on the M-M bond homolysis [104]. Fp_2 and $Co_2(CO)_6(P(OPh)_3)_2$ react under photolytic conditions to cleave the M-M bonds and form $[Fe(Cp)(CO)_2Co(CO)_3(P(OPh)_3)]$. The isomerization of 1-pentene with these dimers under photolytic conditions with and without added $HSiEt_3$ was studied [105].

ISOCYANIDE AND CARBENE COMPLEXES

A number of Ru complexes react with electron-rich olefins such as 46 to yield complexes containing an ortho-metallated N-arylcarbene ligand as shown in Scheme 20. A large number of new complexes were reported. Two were characterized crystallographically. An interesting feature shown by the structural work was a weak interaction of the ortho-hydrogen atom on the carbene-phenyl group not ortho-metallated to the ruthenium atom [106].

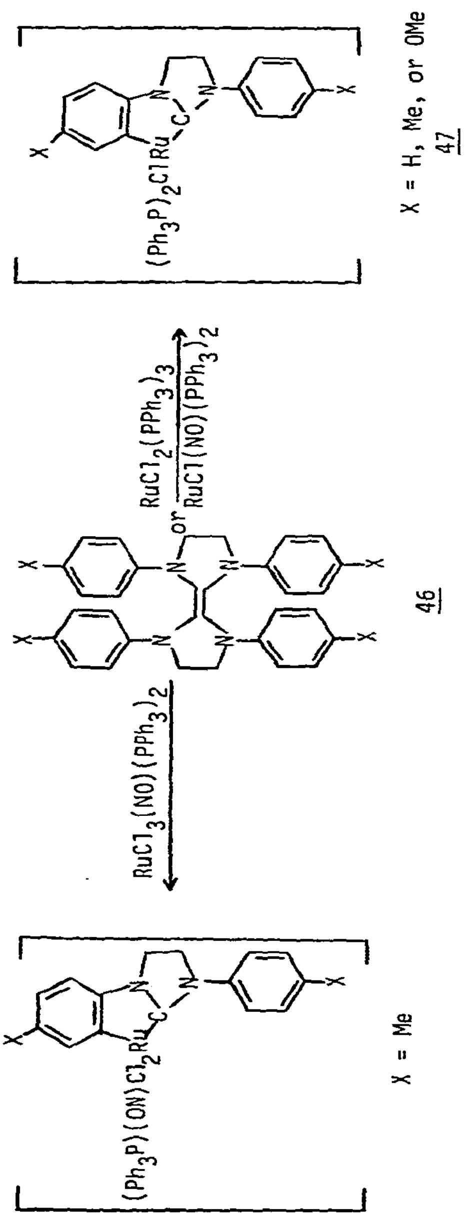
The reaction of $(PPh_3)(CO)_3Fe(C(C_6F_5)OEt)$ with CH_3COOH in the presence of PPh_3 yields $Fe(CO)_3(PPh_3)_2$ and $C_6F_5C(O)C_2H_5$ [107]. High performance liquid chromatography has been shown to be useful for the purification of organometallic iron carborane π- complexes [108].

A series of new low-valent iron and ruthenium complexes with isocyanide ligands has been prepared by reduction of M(II) halide complexes. For example, the complexes $[Ru(CNBu^t)_4(PPh_3)]$ and $[Fe(CNBu^t)_5]$ were characterized crystallographically. Both structures contain isocyanide ligands that show substantial bending, attributed to the considerable backbonding expected for these low valent metal complexes [109].

NITROSYL COMPLEXES

A mechanistic study of ligand substitution reactions of $RuCl_3NOL_2$ (L = $AsPh_3$, $SbPh_3$) with ligands (L') such as PPh_3 or $P(OMe)_3$ to yield $RuCl_3NOL'_2$

SCHEME 20



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complexes has been carried out and the set of reactions shown in Scheme 21 proposed for the transformation [110].

SCHEME 21

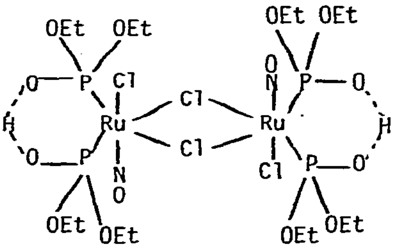
$$\mathrm{RuCl_3NOL_2} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{RuCl_3NOL + L}$$

$$\mathrm{RuCl_3NOL + L'} \xrightarrow{k_2} \mathrm{RuCl_3NOLL'}$$

$$\mathrm{RuCl_3NOLL'} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{RuCl_3NOL' + L}$$

$$\mathrm{RuCl_3NOL' + L'} \xrightarrow{k_4} \mathrm{RuCl_3NOL'_2}$$

The reaction of $RuCl_3 \cdot 3H_2O$, excess triphenylphosphite and commercial Diazald yields the dimeric complex di-μ-chloro-bis{chloro[bis(diethylphosphonito)]nitrosylruthenium(II)} the structure of which was solved crystallographically as shown in 48 [111]. The complexes $M(CO)_2(PR_3)_2X(CONH_2)$(M = Fe, Ru, Os; X = Cl, Br; R = Ph, cyclohexyl) and $Os(CO)(NO)(PPh_3)_2(CONH_2)$ are formed by reactions of $[M(CO)_3(PR_3)_2X]^+$ and $[Os(CO)_2(NO)(PPh_3)_2]^+$ with NH_3 [112].



48

Structural verification of the protonation of a metal coordinated nitrosyl has been provided by the X-ray structure of $OsCl_2(CO)(HNO)(PPh_3)_2$, the product of the reaction of $OsCl(CO)(NO)(PPh_3)_2$ with HCl and is shown in Figure 2. The proton NMR of this molecule showed a resonance at 21.2δ assigned to the HNO proton [113]. The reaction of $Os_3(CO)_{10}(NO)_2$ and trimethylamine oxide yields $Os_3(CO)_9(NO)_2(NMe_3)$ shown to have to have the structure in Figure 3 crystallographically [114].

FIGURE 2

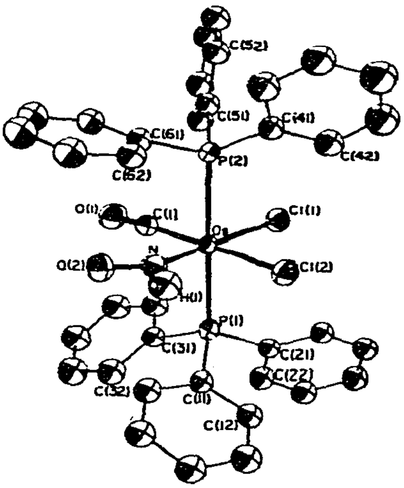
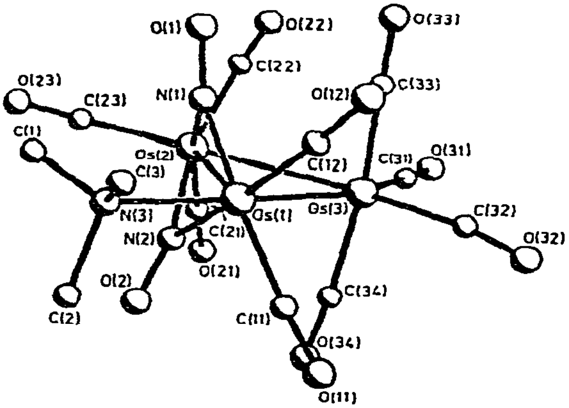


FIGURE 3

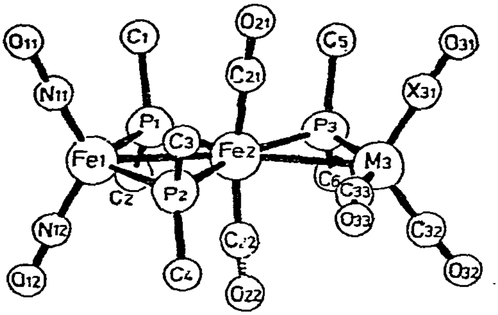


The osmium thionitrosyl complexes $OsClX_2(NS)L_2$(L = $AsPh_3$, PMe_2Ph, 1/2 bipy, py; X = Cl or Br) have been prepared by the reaction of the nitride complexes OsX_3NL_2 with S_2Cl_2. The ν(N-S) bands in the IR spectra are in the range 1120-1280 cm^{-1} and the L groups are trans [115].

The complexes $Fe(CO)_2P_2(\eta^2-CS_2)$(P = tertiary phosphine) react with $NOPF_6$ to displace the CS_2 ligand rather than a CO group. This is thus a good synthetic route to $[Fe(CO)_2P_2(NO)]PF_6$ complexes. The reaction is believed to follow this course because of an initial interaction of the nitrosyl cation with the uncoordinated sulfur atom [116].

The reaction between metal complexes containing a PR_2H ligand and η^3-allyl cluster complexes has been shown to lead to metal clusters with the elimination of propane. The complexes $Fe_3(PMe_2)_3(CO)_4(NO)_3$ and $Fe_2Co(PMe_2)_3(CO)_5(NO)_2$ have been prepared in this way and their structures determined crystallographically as shown in Figure 4 [117]. The reaction of $NOPF_6$ and $[Fe(CO)(L)(NO)(\eta^3\text{-allyl})]$ (L = PPh_3, $P(OMe)_3$, allyl = C_3H_5, 1 - MeC_3H_4, 2-MeC_3H_4) yields $[FeL(NO)_2(\eta^3\text{-allyl})]PF_6$. Reaction of these cations with hydrides and other nucleophiles leads with displacement of the allyl group to yield $[FeL_2(NO)_2]$. The fluxional behavior of the new allyl cations was briefly investigated [118].

FIGURE 4



The molecular stuctures of $[(\mu\text{-}PPh_2)Fe(NO)_2]_2$ and $[(\mu\text{-}PMe_2)Fe(NO)_2]_2$ have been determined crystallographically and have been compared to other similar molecules [119].

The active catalyst $Fe(NO)_2(solvent)_n$ has been generated in THF using both electrochemical means and Zn reduction of $[Fe(NO)_2Cl]_2$ in THF. In both cases, the catalyst was active towards cyclodimerization of dienes. The two electrochemical processes shown in Scheme 22 are believed to account for the generation of the catalysts. Thus at the greater potential needed for the C wave to take place, the system was twice as active [120].

The gas phase X-ray photoelectron spectra of $Fe(CO)_2(NO)_2$ and $Fe(CO)_5$ have been reported and compared to spectra of isoelectronic molecules containing various numbers of CO and NO ligands. The conclusions were that backbonding to a CO group is affected by competitive backbonding to NO groups but backbonding to NO groups is independent of the relatively weakly π-bonding CO groups [121].

SCHEME 22

reduction
B wave: $Fe(NO)_2ClS_n \xrightarrow{e^-} Fe(NO)_2S_n + Cl^-$

$Fe(NO)_2ClS_n + Cl^- \rightarrow [Fe(NO)_2Cl_2]^-$

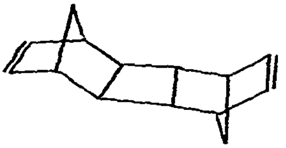
C wave: $[Fe(NO)_2Cl_2]^- \overset{e^-}{\rightleftarrows} [Fe(NO)_2Cl_2]^{2-}$

$[Fe(NO)_2Cl_2]^{2-} \rightarrow Fe(NO)_2S_n + 2Cl^-$

CLUSTER COMPOUNDS

Binuclear Species (excluding η^5-C_5H_5 compounds)

A variety of dinuclear Fe clusters and mixed Fe-Co clusters such as $Fe(CO)_3(\mu\text{-}AsMe_2)(\mu\text{-}CO)CoCO(PMe_3)_2$ have been shown to catalyze the dimerization of norbornadiene. The reaction can be directed to produce either the exo-trans-exo (49) or Binor-s (50) dimers. The intermediate $(CO)_4Fe(\mu\text{-}AsMe_2)Co(CO)_2C_7H_8$ was isolated and characterized by an X-ray crystal structure analysis as shown in Figure 5 [122].



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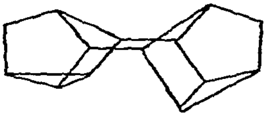


50

The basicity of various dibridged $Fe_2(\mu\text{-}A)(\mu\text{-}A')(CO)_4L_2$ (A = A' = CPh_3, PPh_2, PMe_2; A = SPh, A' = PPh_2 and L = $P(Me_3)_{3-n}(Ph)_n$ n = 0-3) derivatives has been determined by data on the reversibility of the protonation of these complexes. The replacement of the first SPh bridge by a PPh_2 bridge markedly increased the basicity of the M-M bond. IR and ^1H NMR were used to determine the structure of various complexes [123]. The reaction of $P(CF_3)H_2$ with $Fe_2(CO)_9$ at room temperature yields $Fe(CO)_4\{P(CF_3)H_2\}$. IR analysis showed that this complex exists as both possible axial and equatorial isomers. These interconvert fast on the NMR time scale. Pyrolysis of this mixture yields 2 isomers of $Fe_2(CO)_6\{P(CF_3)H\}_2$. The structure of one isomer was elucidated by X-ray means as shown in Figure 6. The crystals were separated by hand. The isomers interconvert in solution [124].

FIGURE 5

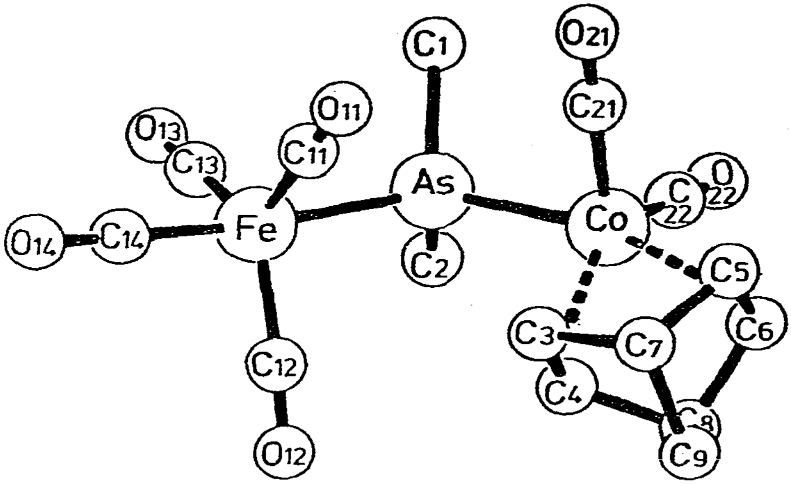
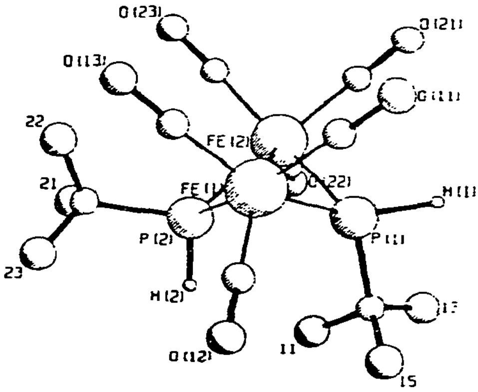
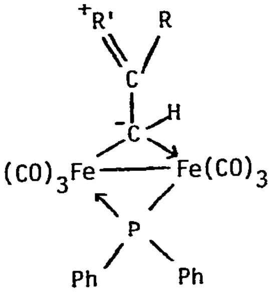


FIGURE 6

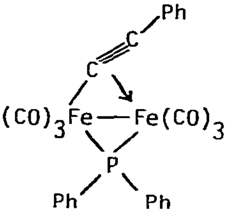


The structure of $[Na(2,2,2\text{-crypt})]_2[Fe(CO)_6(\mu\text{-}PPh_2)_2]$ has been determined crystallographically. Most notable is the change in M-M distance from the neutral precursor, $Fe_2(CO)_6(\mu_2\text{-}PPh_2)_2$, from 2.623Å to 3.630Å in this new complex and the complete flattening of the highly bent Fe_2P_2 core. Thus this study shows that the lowest unoccupied molecular orbital of the neutral dimer possess large antibonding dimetal orbital character. Note also that the cyclic voltammogram of the neutral molecule shows a single two-electron reversible reduction wave [125]. The structures of the complexes $[Fe_2(CO)_5(C(O)R)(\mu_2\text{-}PPh_2)_2]^-$ as the $[Na(THF)_2]^+$ and $[(Ph_3P)_2N]^+$ salts for R = Me and as the $[Li(THF)_3]^+$ salt for R = Ph have been determined crystallographically. The overall structures are geometrically similar to $Fe_2(CO)_6$-$(\mu_2\text{-}PPh_2)_2$ with an equatorial carbonyl replaced by the acyl ligand. For the Li and Na salts, there is an interaction of the alkali metal with the acyl oxygen atom and in addition for the Na salt with a carbonyl oxygen atom. A detailed discussion of the various interactions is presented [126].

Compounds of type 51 (R = Ph, R' = NMe_2, NEt_2, NPr^n_2, etc.) can be synthesized by simple addition of a primary or secondary amine to 52. 51 reacts with $AgClO_4$ to yield 53, as verified by an X-ray crystal structure of the R' = NHMe derivative. Thus the Ag^+ has acted as a Lewis acid, accepting electrons from the electron rich metal center [127]. Complexes of type 54 have been prepared by addition of HX to 51 (X=Cl, Br, I, HCOO, CH_3COO, C_2H_5COO and CF_3COO; Y = PPh_2) [128]. The reaction of 56 (Scheme 23) with



51



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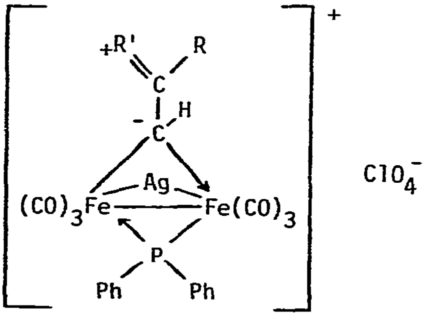
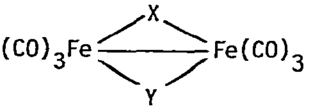


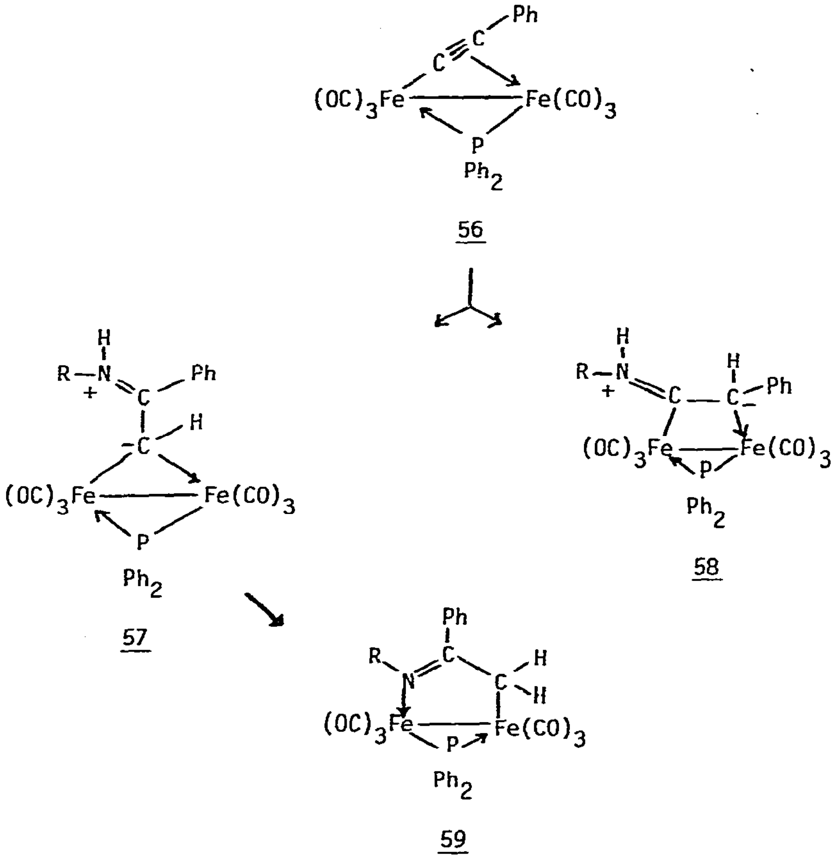
53



54

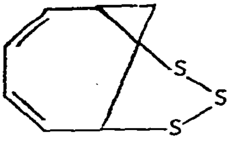
$MeNH_2$ or $EtNH_2$ (1 equiv) yields both 57 and 58. Florisil catalytically converts 57 to 59, the structure of 59 being determined crystallographically [129].

SCHEME 23

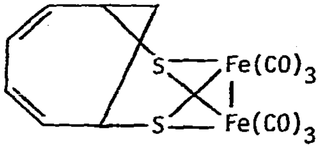


Calculations on M_2L_9 complexes including a number of iron complexes have appeared [129a].

One of a number of products in the reaction of 60 with $Fe_2(CO)_9$ in THF is 61 as shown by X-ray crystallography [130]. The complex 62, containing both



60



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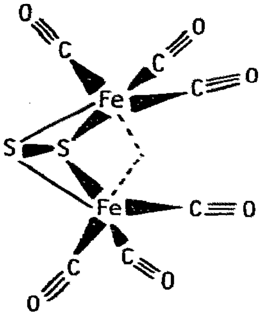
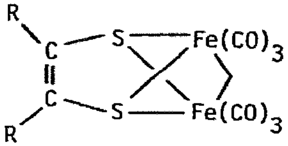
an S-S and Fe-Fe bond reacts with RC≡CR(R = CO_2Me, CF_3) to yield the S-S insertion product 63 [131].

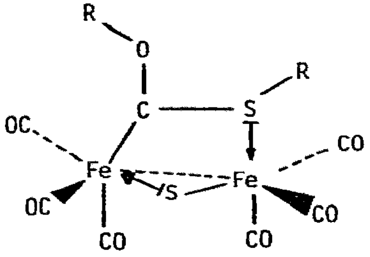


62



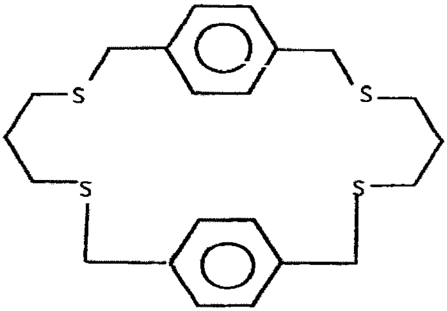
63

The reaction of S-alkyl xanthates of complex organic molecules with $Fe_2(CO)_9$ yields 64 with the ligand acting as a 6 electron donor [132]. The reaction of $Fe_2(CO)_9$ with R-N=S=N-R (R = t-C_4H_9, 4-$CH_3C_6H_4$) leads to a variety of products as indicated in Scheme 24. The structures of 65b, 66a and 67b were established by X-ray techniques [133].

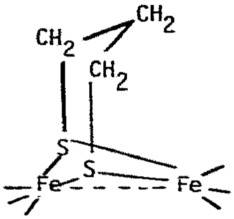


64

The reaction of the sulfur substituted cyclophane 68 with $Fe(CO)_5$ yields 69 in which a 1,3-propanedithia unit has been extracted from 68 [134].

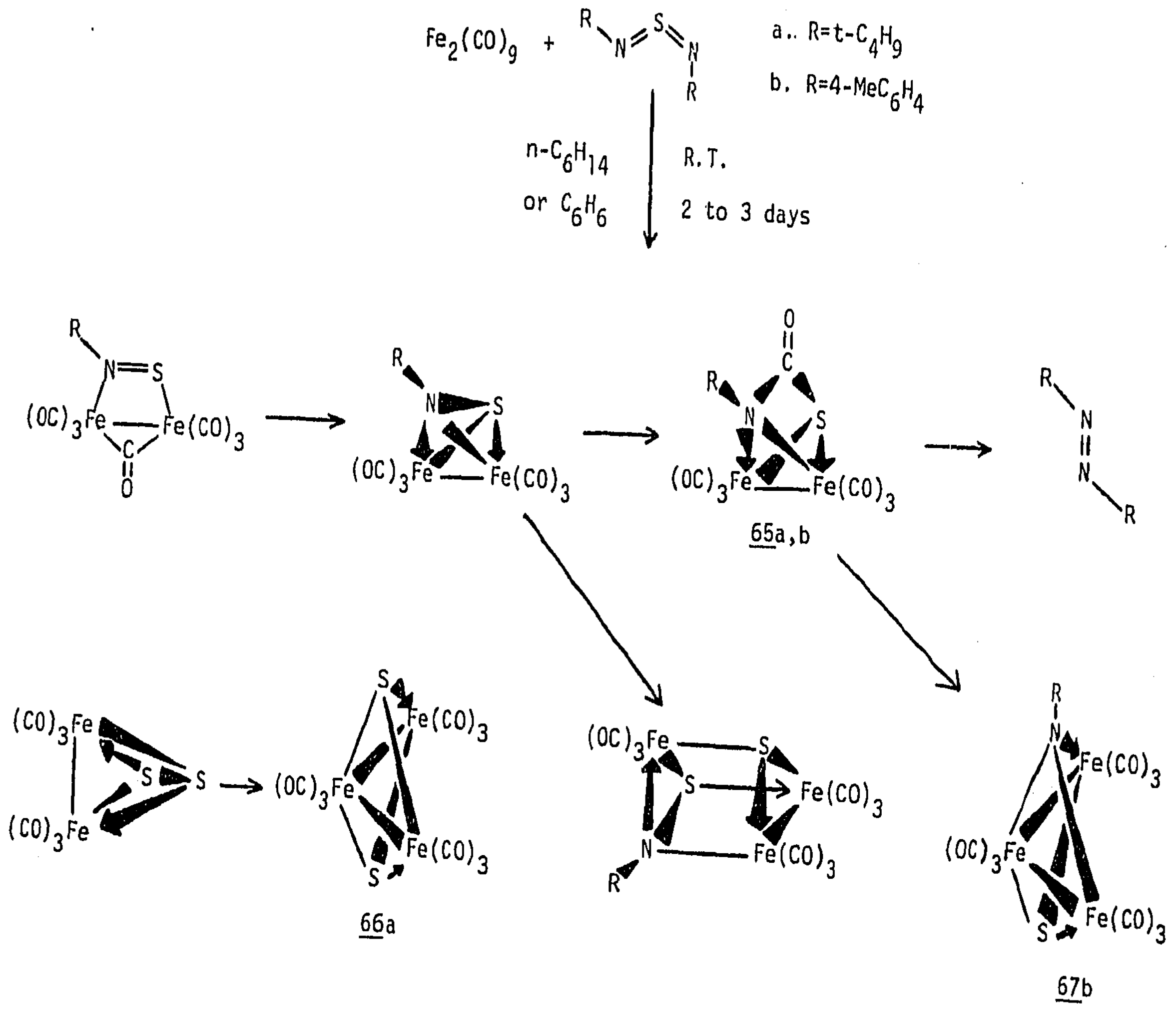


68

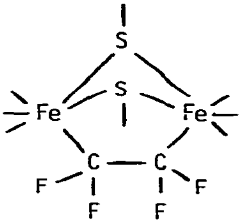


69

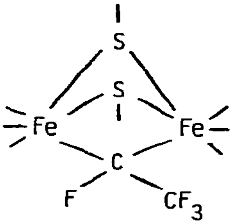
Scheme 24


Fe$_2$(CO)$_9$ + R–N=S=N–R
a.. R=t-C$_4$H$_9$
b. R=4-MeC$_6$H$_4$
n-C$_6$H$_{14}$
or C$_6$H$_6$
R.T.
2 to 3 days
65a,b
66a
67b

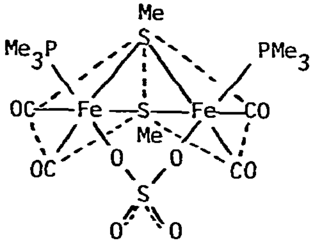
Irradiation of a mixture of C_2F_4 and $[(\mu\text{-}CSCH_3)Fe(CO)_3]_2$ in benzene at 20°C leads to the complex $(\mu\text{-}SCH_3)_2(\mu\text{-}C_2F_4)Fe_2(CO)_6$ (70). At 35°C a different product, $(\mu\text{-}SCH_3)_2(\mu\text{-}FCCF_3)Fe_2(CO)_6$ (71) is formed. Both structures were elucidated crystallographically [135]. The reaction of $[(\mu\text{-}SCH_3)Fe(CO)_2L]_2$ (L = PMe_3, PMe_2Ph) with SO_2 in toluene yields $[(\mu\text{-}SCH_3)Fe(CO)_2L]_2SO_2$. No reaction occurs in the cases where L = PPh_2CH_3 and PPh_3. The new SO_2 complex (L = PMe_3) reacts with O_2 to yield the complex 72, a proposed structure of which was suggested [136].



70



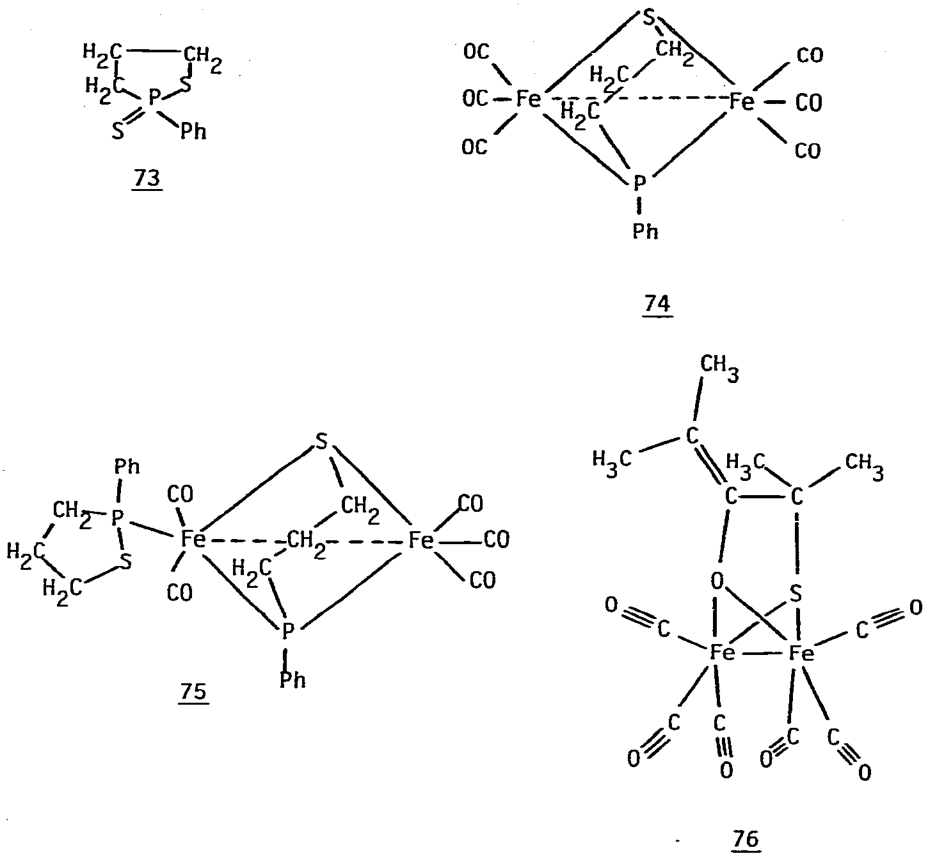
71



72

The reaction of $Fe_2(CO)_9$ with the cyclic dithiophosphinate 73 yields 74 and 75 as proven crystallographically. Complex 75 was shown to arise from the reaction of 73 and 74 [137]. Complete details of the structural characterization of complex 76 has been published [138].

The reaction of the tridentate ligand bis-[2-(diphenylphosphino)ethyl]-phenylphosphine (ppp) with Fe(II) and H_2S yields $[Fe_2(\mu\text{-}SH)_3(ppp)_2]^+$ cations. The structure of one member of the series was determined crystallographically as shown in Figure 7 [139]. The complex $Fe_2S_2(CO)_6$ reacts with diazomethane in Et_2O to give $H_2CS_2Fe_2(CO)_6$, $(H_2C)_2S_2Fe_2(CO)_6$, $(H_2C)_3S_2Fe_2(CO)_6$ and $Me_2S_2Fe_2(CO)_6$ [140]. The structure of $Fe_2(CO)_6(\mu\text{-}Se_2)$ has been determined crystallographically and is, as expected, very similar to the previously determined structure of $Fe_2(CO)_6(\mu\text{-}S_2)$ [141]. The structure of bis(tricarbonyliron) heptalene has been solved by X-ray means and is shown schematically as 77 [142].



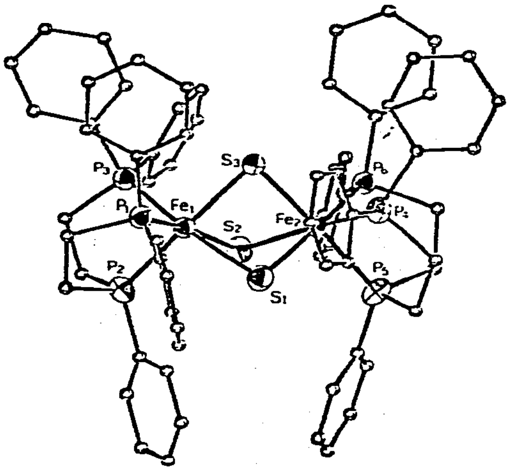
73

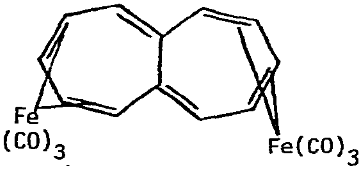
74

75

76

FIGURE 7

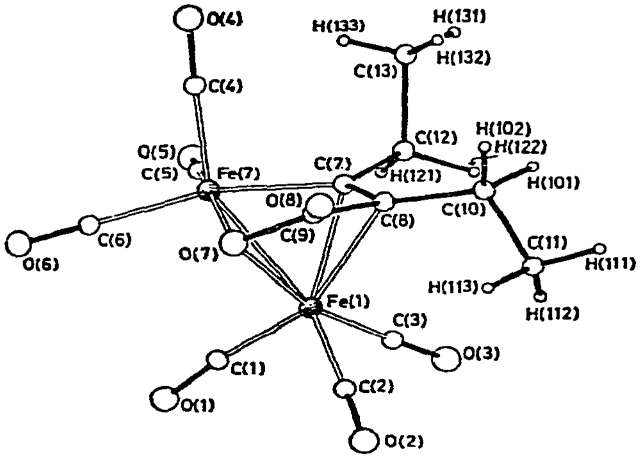




77

The reaction of $Fe_3(CO)_{12}$ with 3-hexyne yields the complex $Fe_2(CO)_6$-$\{C(Et){=}CEt(CO_2)\}$ shown crystallographically to have the structure as in Figure 8 [143]. Heating a heptane solution of $Fe_3(CO)_{12}$ and 3-hexyne leads

FIGURE 8



to the isolation of $[Fe_2(CO)_6\{C_4(OH)_2Et_2\}]$ shown to have the structure in Figure 9 by crystallographic techniques. The same reagents were also mixed in alkaline methanolic solution to produce $[Fe(CO)_4\{(CO)_2C_2Et_2\}]$ shown to have structure in Figure 10 crystallographically [144].

The ^1H NMR spectra of substituted derivatives of $[Fe_2(CO)_6SR]_2S$ and $(C_5H_4R)_4Fe_4S_6$ demonstrate that these molecules have rigid chiral frameworks in solution [145]. High resolution ^{13}C NMR in the solid state of $(COT)_2Ru_2$-$(CO)_4$ at ambient and low temperature has been used to study directly the chemical exchange occurring in the solid state. At 27°C the ring carbon atoms shown as a single resonance but became quite complex at -180°C [146].

The reaction of $[Ru_3O(O_2CMe)_6(H_2O)_3](O_2CMe)$ with Me_2Mg in the presence of excess PMe_3 yields $(Me_3P)_3Ru(\mu\text{-}CH_2)_3Ru(Me_3P)_3$ the structure of which has been determined crystallographically as shown in Figure 11. The Ru-Ru

FIGURE 9

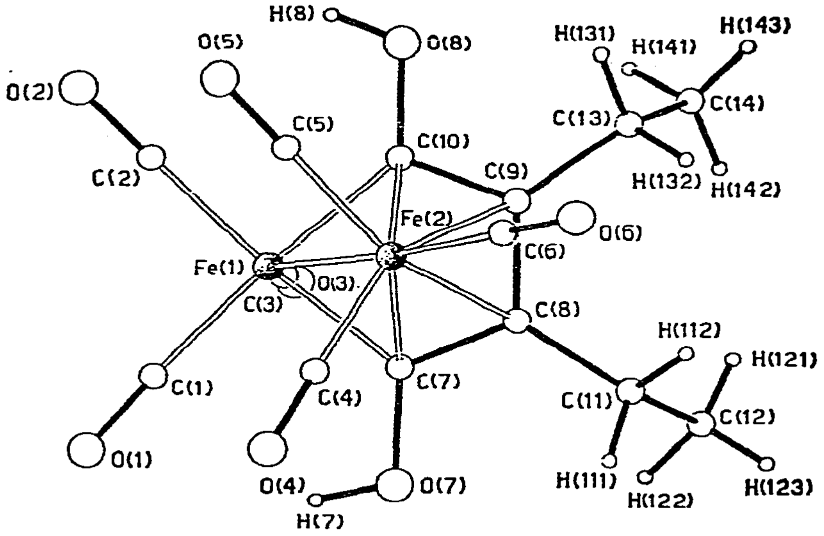
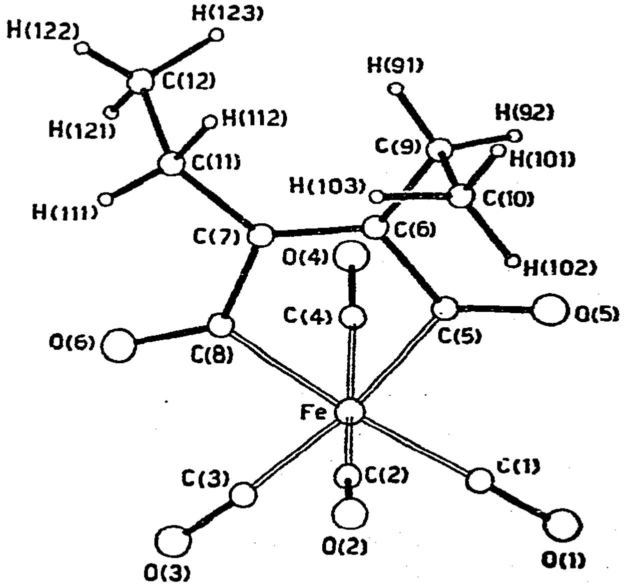


FIGURE 10



distance is 2.650A indicating the occurrence of a metal-metal bond as required for the observed diamagnetism. It was proposed that it formed in some type of α-hydrogen transfer process. Protonation of this complex (or strangely) reaction with one equivalent of Ph_3CBF_4 in THF) with one equivalent of HBF_4 yields $[(Me_3P)_3Ru(\mu\text{-}CH_2)_2(\mu\text{-}CH_3)Ru(PMe_3)_3]BF_4$ as shown by spectroscopic

FIGURE 11

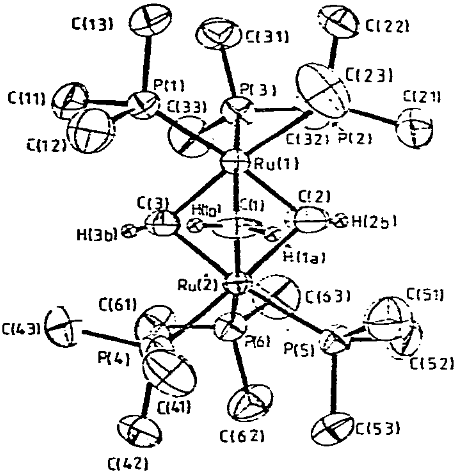
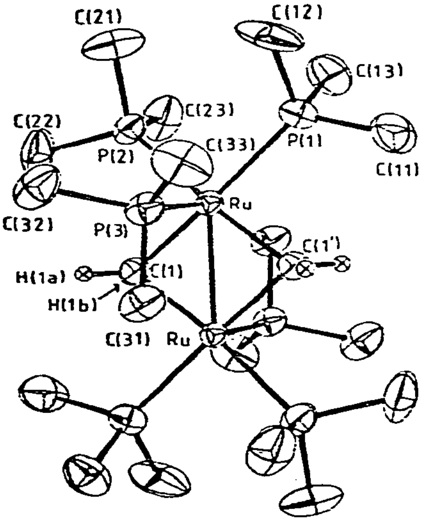
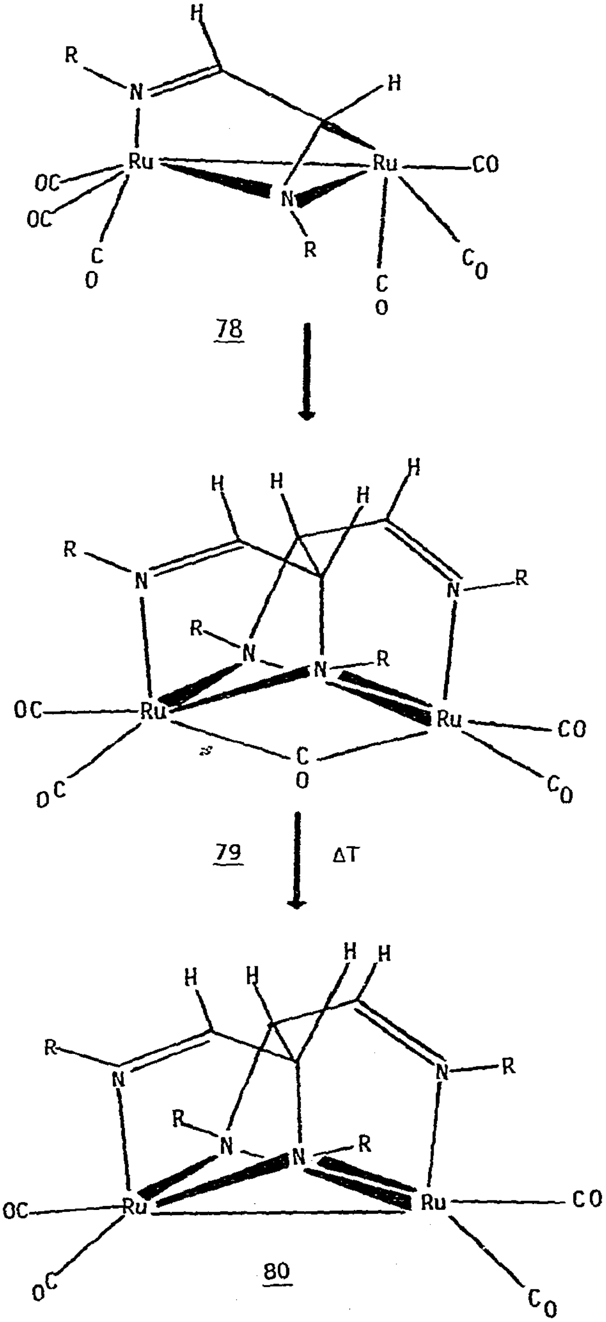


FIGURE 12



and crystallographic (of low quality due to probable orientational disorder) techniques. The reaction of two equivalents of HBF_4 yields $[(Me_3P)_3Ru(\mu\text{-}CH_2)_2Ru(PMe_3)_3][BF_4]_2$ as shown again crystallographically as in Figure 12.



78

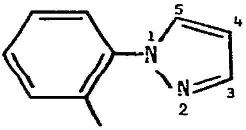
79

ΔT

80

The Ru-Ru distance of 2.641 indicates again a metal-metal bond. A very short Ru-H interaction with one of the phosphine methyl groups of 2.30Å indicates a bonding interaction [147].

DAB(1,4-diazabutadiene) reacts with $Ru_3(CO)_{12}$ to yield complex 78 analogous to an iron complex previously characterized crystallographically. Addition of excess DAB yields 79 in which the ligand has coupled and heating 79 yielded 80 [148]. The reaction of $RuCl_3 \cdot 3H_2O$, CO and the compounds 81, 82, and 83 yield the dimeric compound $[\{RuCl(C\text{-}N)(CO)_2\}_2]$ (C-N = 81, 82, or 83). Further reaction with Hacac and other ligands leads to new monomeric complexes [149].



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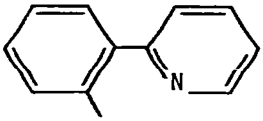

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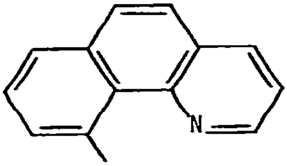
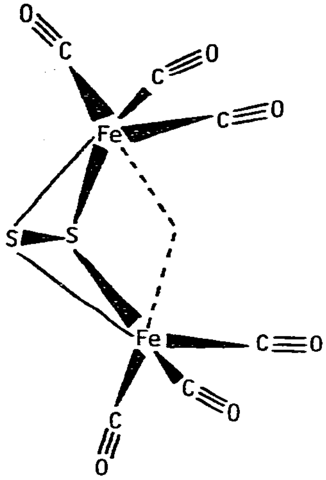


83

The electrochemical behavior of thio and phosphido complexes of iron (I): $Fe_2XY(CO)_{6-n}L_n$ (X = Y = SR, PR_2 and X = SR, Y = PR_2; L = PR_3) on platinum and mercury electrodes has been studied. Large differences were observed between the oxidation potentials on mercury and platinum because the Hg inserts into the M-M bond [150]. Preliminary results on the electrochemical behavior of a variety of triple-bridged diruthenium complexes have been reported establishing with various ligands the entire redox series $[RuCl_3Ru]^{z+}$ z = 1, 2, 3, 4 [151]. In order to compare with these results a variety of monomeric ruthenium complexes, $RuCl_3L_3$, were also studied [152]. Reduction of the known compound 84 yielded the dianion 85 in solution which when treated with CH_3I yields the two known isomers of 86. The monoanion 87 could also be produced from reaction of 84 with RLi [153].

Trinuclear Species (all same metal)

Heating $(\mu\text{-}H)_2Os_3(CO)_{10}$ at reflux in CS_2 yields $H_2CS_2[HOs_3(CO)_{10}]_2$, the structure of which was determined crystallographically as shown in Figure 13 [154]. The cluster $(\mu\text{-}H)_2Os_3(CO)_9[PMe_2Ph]$ reacts with CS_2 differently than $(\mu\text{-}H)_2Os_3(CO)_{10}$ to yield $(\mu\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_9(PMe_2Ph)$, the structure of which was determined crystallographically as shown in Figure 14. If this complex is heated in refluxing hexane it loses one mole of CO to form $(\mu_3\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_8(PMe_2Ph)$ as shown crystallographically in Figure 15 [155].



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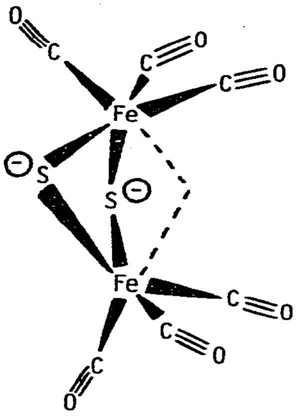

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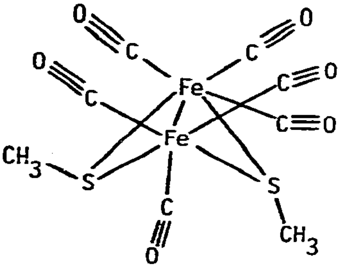
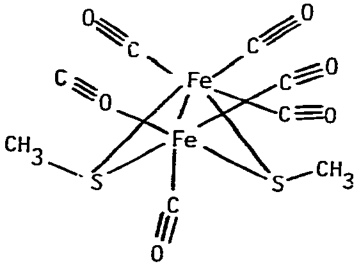


86a



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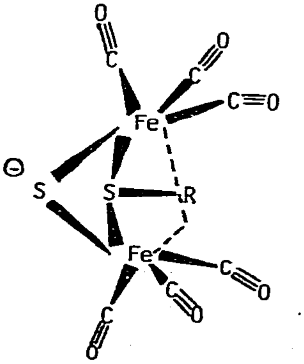

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FIGURE 13

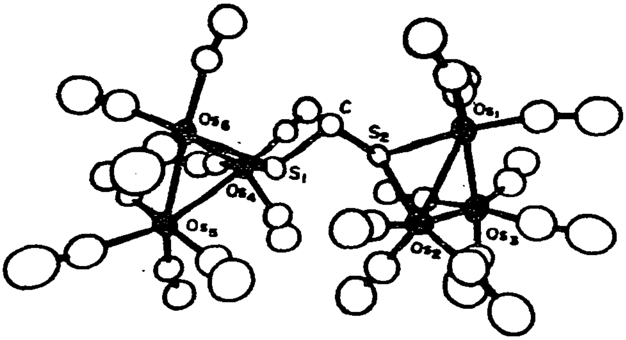


FIGURE 14

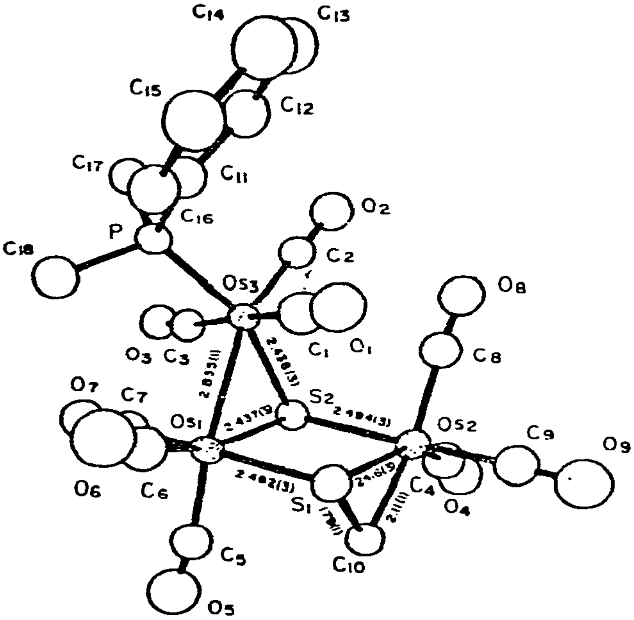
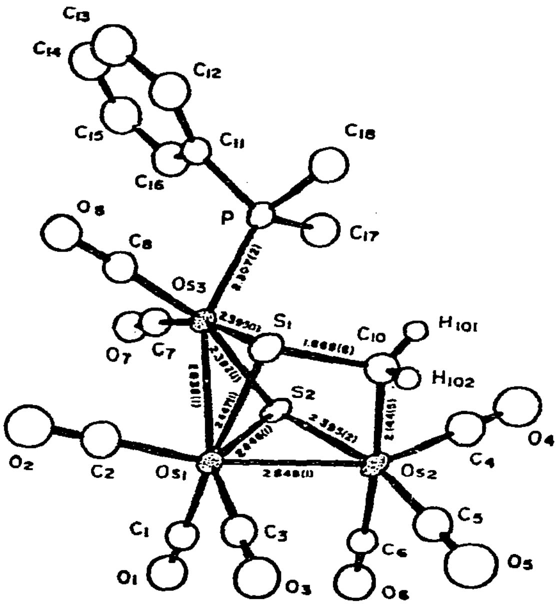
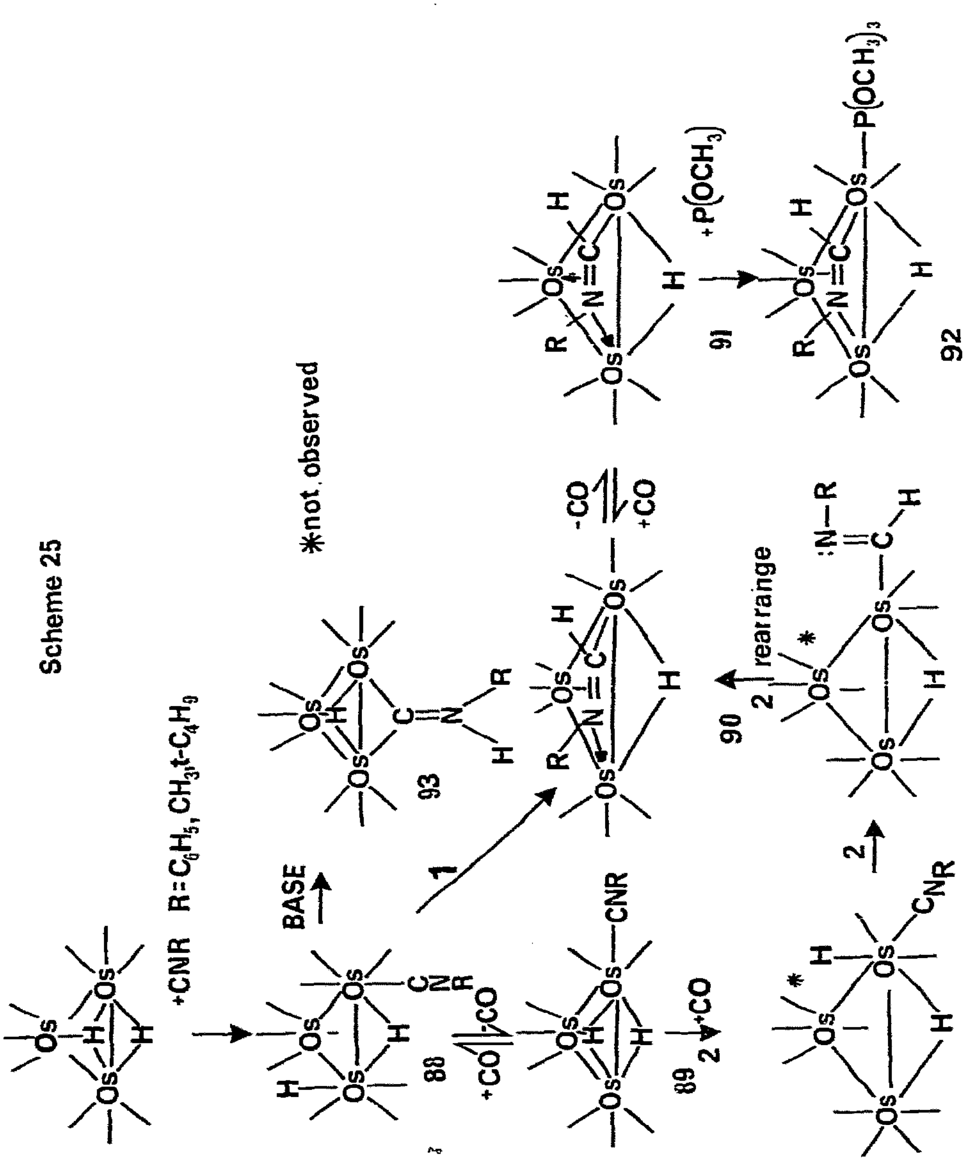


FIGURE 15



The reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ and isocyanide ligands (CNR, R = C_6H_5, CH_3, Bu^t) yields $(H)(\mu\text{-H})Os_3(CO)_{10}(CNR)$(88, Scheme 25) complexes. The structure of the R = Bu^t derivative was determined crystallographically. Heating these molecules in poor donor solvents yields $(\mu\text{-H})_2Os_3(CO)_9(CNR)$ (89) as shown crystallographically for the R = Bu^t derivative. Continued heating for the R = Me or Ph derivatives yields $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC} = NR)Os_3(CO)_{10}$ (90) which then loses a CO ligand to form $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC} = NR)Os_3(CO)_9$(91). The structure of the R = Ph derivative was determined crystallographically. 91 reacts with $P(OMe)_3$ to yield $(\mu\text{-H})(\mu\text{-}\eta^2\text{-HC} = NR)Os_3(CO)_9P(OMe)_3$ (92) as shown crystallographically for the R = Ph derivative. In donor solvents, thermolysis of 88 yields $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C} = N(H)R)Os_3(CO)_{10}$ (93) complexes as shown crystallographically for the R = Bu^t derivative. Scheme 25 shows this information. Two pathways for the formation of 90 are shown with the pathway marked 2 believed to be more likely. It is important to note that the formation of 90 represents insertion of the isocyanide ligand into the Os-H bond in a fashion which is opposite to that taking place in the reaction to form 93. In 90 the hydrogen atom is transferred to the C atom whereas in 93 it is transferred to the N atom of the isocyanide ligand [156]. Complete details of the structure of $(\mu\text{-H})(\mu\text{-}\eta^1\text{-C} = N(H)(Bu^t)\text{-}Os_3(CO)_{10}$ (93) have been reported [157]. Complete details of the structure

Scheme 25


+CNR
R = C_6H_5, CH_3, t-C_4H_9
BASE
*not observed
88
89
90
91
92
93
+CO
-CO
1
2
2 +CO
rearrange
+$P(OCH_3)$
$P(OCH_3)_3$
CNR
:N—R
*

of (μ-H)(H)$Os_3(CO)_{10}$(CN-Bu^t) (88) and (μ-H)$_2Os_3(CO)_9$(CNBu^t) (89) have also been reported [158]. The reaction of (μ-H)$_2Os_3(CO)_{10}$ with PhNC also yields small amounts of $H_3(\mu$-η^2-$C_6H_4)(\mu$-η^2-$HCNC_6H_5)Os_3(CO)_8$ shown by X-ray crystallography to contain a bridging benzyne and μ-phenylformimidoyl ligand as shown in Figure 16 [159]. One molecule of an aryl isocyanate or isothiocyanate adds to (μ-H)$_2Os_3(CO)_{10}$ with the transfer of one hydrogen to the carbon atom of the isocyanate group to produce an N-aryl-formanido or thioformamido ligand. This was proven by the structure, determined by crystallography means, of (μ-p-$CH_3C_6H_4$NC(H)O)(μ-H)$Os_3(CO)_{10}$ as shown in Figure 17 [160].

The compound (μ-H)$_2Os_3(CO)_9(PPh_3)$ was prepared by the reaction of (μ-H)$_2Os_3(CO)_{10}$ and PPh_3. Initially $H_2Os_3(CO)_{10}PPh_3$ forms which loses a CO group when heated. The structure was determined crystallographically to compare to (μ-H)$_2Os_3(CO)_{10}$. The structures are very similar with the PPh_3 group substituted for a carbonyl on one of the osmium atoms involved in the short Os-Os bond and is the presumed location of the bridging H atoms [161].

The structure of $Os_3(CO)_9H_2(S)$, formed in the reaction of $Os_3(CO)_{12}$ with H_2S has been resolved using a combination of X-ray and neutron defraction data and is shown in Figure 18 [162]. The reaction of $Os_3(CO)_{12}$ and NO gas in n-octane at 126°C yields the complex $Os_3(CO)_9(NO)_2$. Although it did not prove possible to grow crystals of this complex for an X-ray analysis, the

FIGURE 16

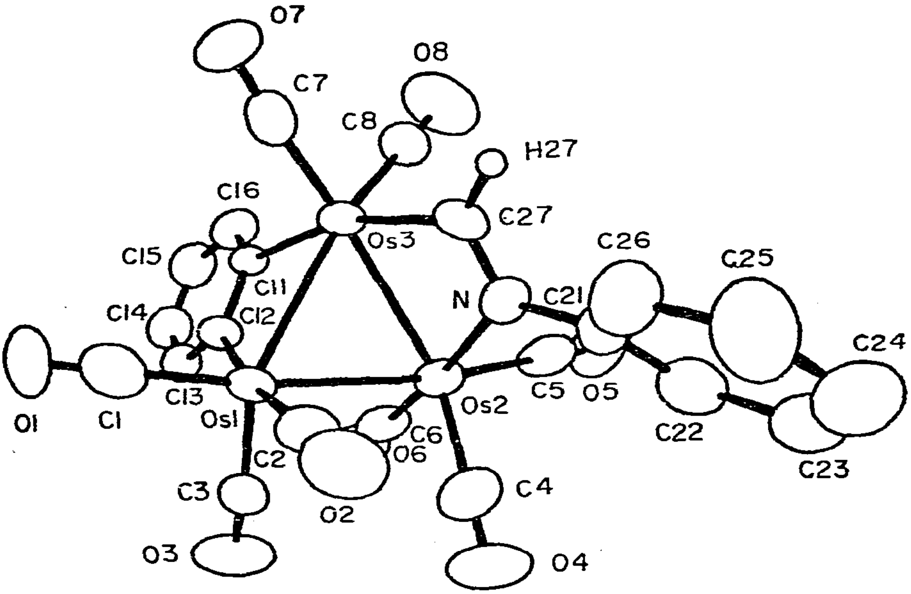


FIGURE 17

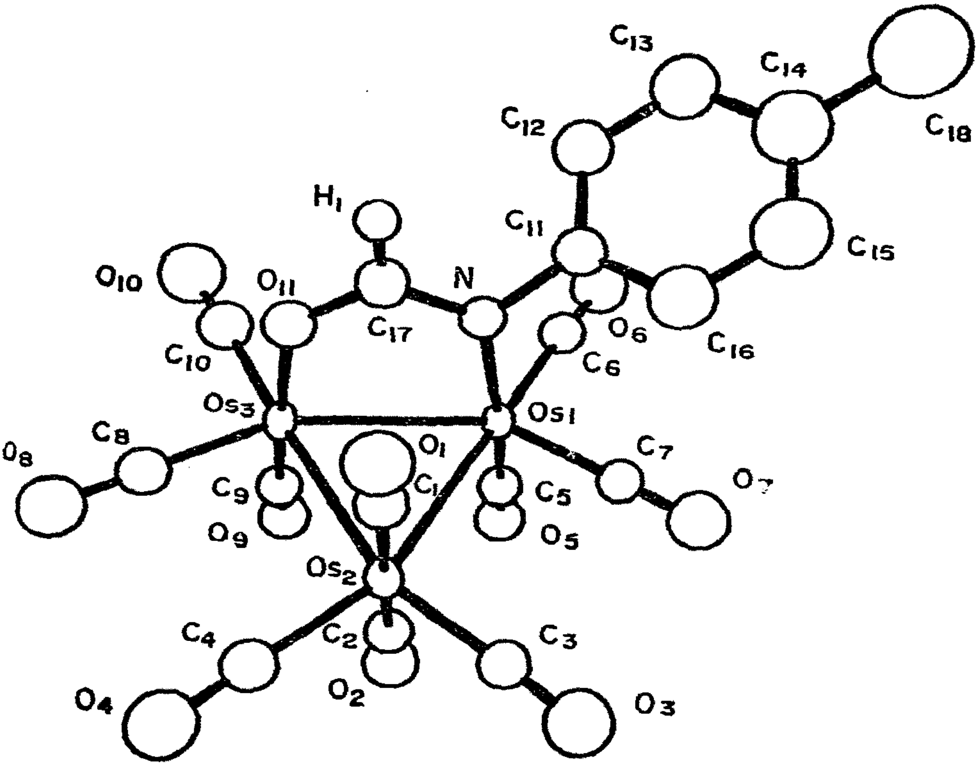
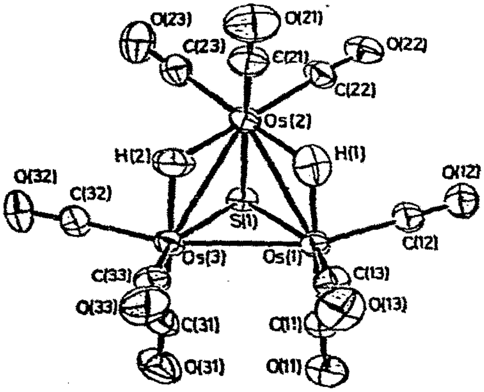
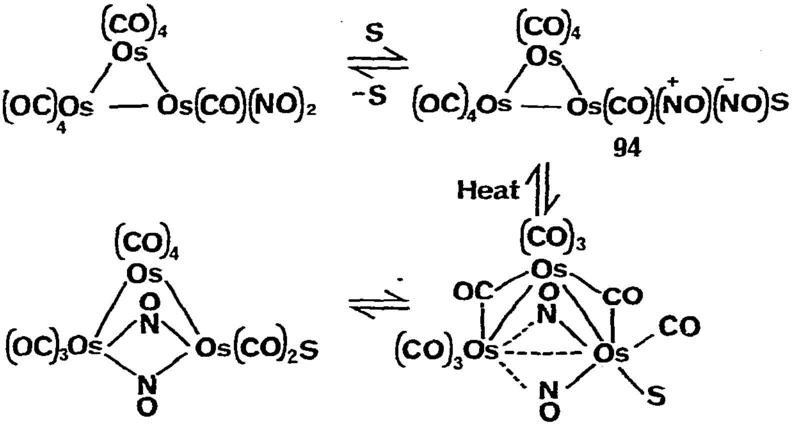


FIGURE 18



derivative $Os_3(CO)_8P(OMe)_3(NO)_2$ was crystallized. The structure of this molecule was shown by X-ray means to have two terminal NO groups bound to the same Os atom. IR data of the parent compound indicated it has an analogous structure. This molecule shows stereodynamic behavior which was explained by the process shown in Scheme 26 in which S is the solvent. Intermediates of type 94 could be observed when $Os_3(CO)_9(NO)_2$ was mixed with the donor ligands NH_3 or $NEtH_2$ [163].

Scheme 26



The structure of the molecule $(\mu\text{-}H)Os_3(CO)_{10}(CHCH = NEt_2)$ produced along with equivalent amounts of $(\mu\text{-}H)_2Os_3(CO)_{10}$ in the reaction of $Os_3(CO)_{10}(NCMe)_2$ and Et_3N has been determined by X-ray means as shown in Figure 19. The H and $CHCH = NEt_2$ ligands bridge the same osmium atoms causing a shortening of the M-M distance. This trend appears to be general as is the general lengthening of single unsupported, μ_2-hydride ligand bridges. The bridging ligand is best viewed as a 1,3-dipolar species ($\rangle\bar{C}H\text{-}CHN^{+}Et_2$) [164].

The X-ray crystal structure of $Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$ has been determined as shown in Figure 20. The dibridged Os-Os distance is 2.846 and is about the same as the other two Os-Os distances. Thus, the general expansion of the M-M bond frequently encountered with bridging H is counterbalanced by the bridging chloride ligand [165]. The structure of $(\mu\text{-}H)(\mu\text{-}Br)Os_3(CO)_{10}$ has been determined crystallographically and conforms to the triangular array of Os atoms shown for many other members of this series and was surprisingly similar to the μ-Cl analog [166].

The structure of $(\mu\text{-}H)_2Os_3(CO)_{10}$ (95) previously determined by X-ray means has been determined by neutron diffraction methods and is shown in Figure 21 [167]. The neutron diffraction study of $(\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}CH_2)$(96) for which a previous study of a partially deuterated sample had

FIGURE 19

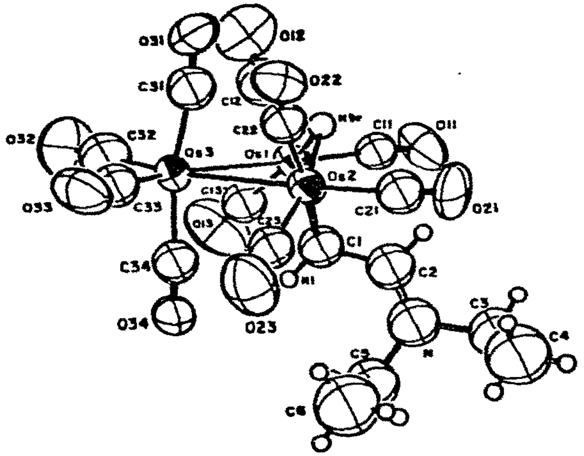
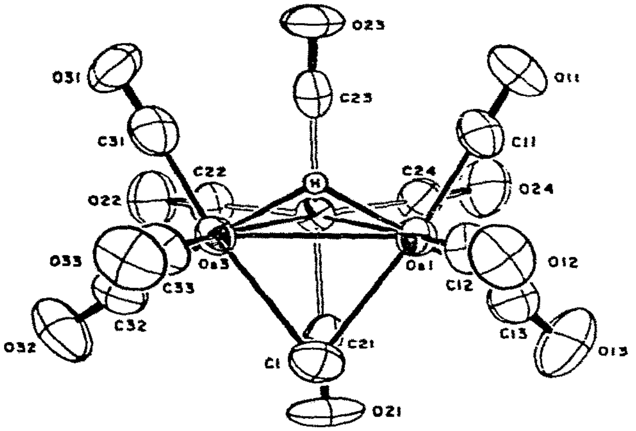


FIGURE 20



been carried out has been reported as shown in Figure 22. A qualitative M.O. scheme was proposed for both molecules which uses a 4-c, 4-e bond for the Os_2H_2 part of molecule 95 and a similar one for 96 (with the carbene carbon atom sp^2) which also includes 2 electrons in the remaining pπ type orbital on the carbene carbon atom making the Os(μ-H)(μ-C) fragment a 4-c, 6-e bond [168].

FIGURE 21

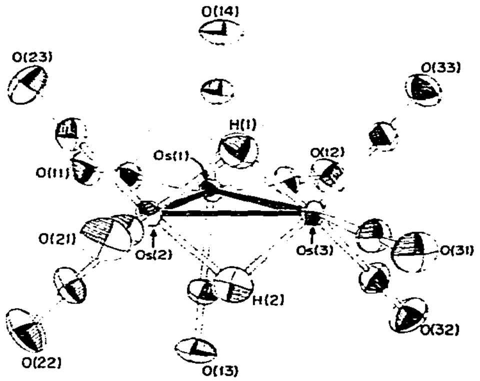
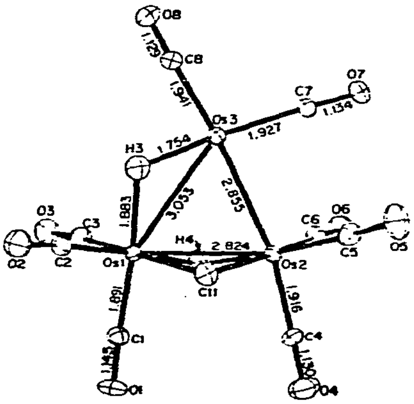


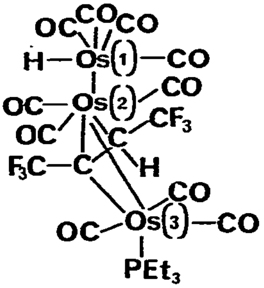
FIGURE 22



The reaction of $Os_3(CO)_{12}$ with cyclohexanone yields $H_2Os_3(\mu^3\text{-}C_6H_8O)\text{-}(CO)_9$, formed by double metallation of a CH_2 α to the ketone. Other aldehydes and ketones react in a similar manner [169]. The reaction of $Os_3(CO)_{12}$ with various diene ligands yields a variety of products, some such as $H_4Os_4(CO)_{12}$, that contain only hydrogen atoms from the diene and others in which the carbon skeleton is bound to the osmium clusters [170]. The reaction of $HOs_3(CO)_{10}(CF_3CCHCF_3)$ and PEt_3 in hexane yields $HOs_3(CO)_{10}\text{-}(PEt_3)(CF_3CCHCF_3)$ shown to have the structure <u>97</u> crystallographically [171].

The negative-ion mass spectra of $Os_3(CO)_{12}X_2$ and $Os_3(CO)_{10}X_2$ (X = Br, I) have been reported. As is typical for negative ion mass spectra of metal carbonyls, the molecular ion (M) is absent but $(M-CO)^-$ peaks are observed. This (M-CO) peak is weak in the spectra of the linear $Os_3(CO)_{12}X_2$ molecules but very intense for the cluster $Os_3(CO)_{10}X_2$ molecules indicating that this form of spectroscopy is useful for structural information [172].

The reaction of $Ru_3(CO)_{12}$ with $NaBH_4$ in THF yields nearly quantitatively $[Ru_3H(CO)_{11}]^-$. The structure, shown as 98, was determined crystallographically. The fluxional properties of this molecule were investigated by ^{13}C NMR [173]. The reaction of $Na[HRu_3(CO)_{11}]$ and $[Me_3O]BF_4$ yields $HRu_3(CO)_{10}$-$(COCH_3)$ the structure of which has been determined crystallographically as shown in Figure 23. Several dynamic processes were investigated using variable temperature ^{13}C NMR spectroscopy. The data taken as a whole indicated that the μ_2-$COCH_3$ group can be best represented as a μ_2-carbyne ligand [174].



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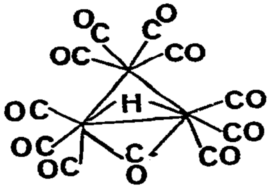


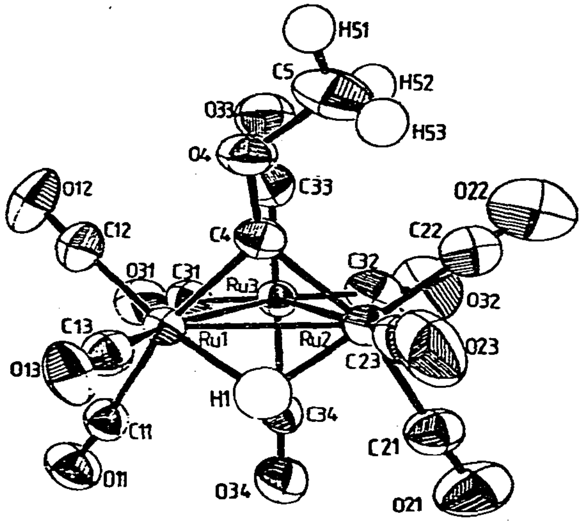
98

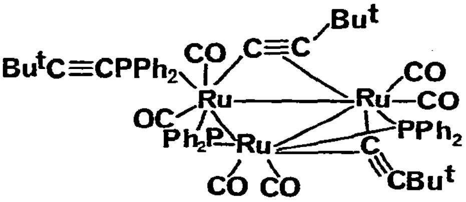
The reaction of $Ru_3(CO)_{12}$ and $Ph_2PC{\equiv}CBu^t$ in refluxing CH_3CN yields first $Ru_3(CO)_9(PPh_2PC{\equiv}CBu^t)_3$ then $Ru_3(CO)_6(\mu_2\text{-}C_2Bu^t)(\mu_2\text{-}\eta^2\text{-}C_2Bu^t)(PPh_2)_2$-$(Ph_2PC_2Bu^t)$, a complex shown to have the structure 99 crystallographically [175].

The reaction of $HRu_3(CO)_9C_2C(CH_3)_3$ (for structure see 100) and either 2-cis, 4-trans-hexadiene or 1,5-hexadiene yields the same product, HRu_3-$(CO)_7(C_6H_9)(C_6H_{10})$. The structure of this product was determined crystallographically as shown in Figure 24 [176]. The reaction of $Ru_3(CO)_{12}$ and isopropenylacetylene yields $Ru_3(CO)_8(C_{10}H_{12})$, the structure of which is shown in Figure 25 as determined crystallographically [177]. The same alkyne reacts with $HRu_3(CO)_9C_2Bu^t$ to yield $Ru_3(CO)_8(C_{16}H_{22})$, the structure of which is shown in Figure 26 as determined crystallographically [178].

The reaction of substituted cyclooctatetraenes and cyclooctatrienes with $Ru_3(CO)_{12}$ or $Ru_2(SiMe_3)_2(CO)_8$ yields a variety of products, some of which contain pentalene ligands. For certain cases an equilibrium such as shown between 101 and 102 was demonstrated in solution [179]. The structures of

FIGURE 23

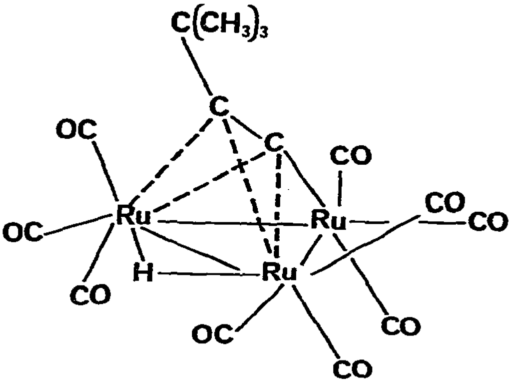




99

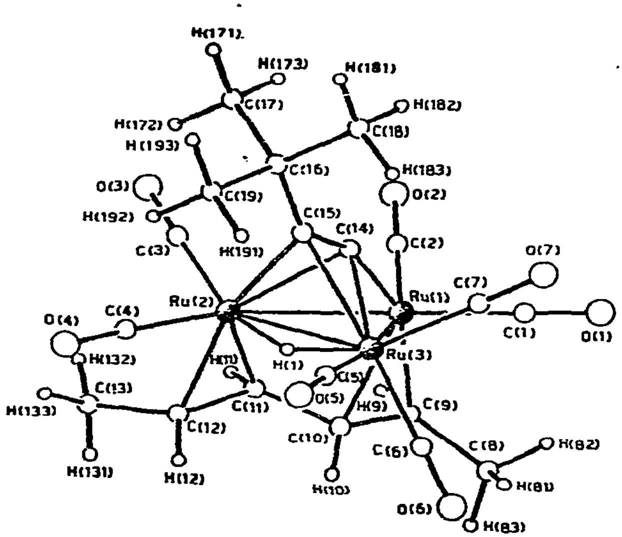
101 and 102 were verified for 2 different isomers of $Ru_3(CO)_9\{C_8H_3(SiMe_3)_3\}$ crystallographically [180].

Reaction of $Ru_3H(CO)_9(\mu_3\text{-}SBu^t)$ with cycloheptatriene in refluxing heptane yields 103 and 104(a). The structure of 103 was determined crystallographically and represents the first example of a molecule containing a facebonded C_7H_7 ligand. Th structure of 104a was assigned by comparison to the known halide complexes 104b [181]. The reaction of Bu^tNC and $Ru_3(CO)_{12}$ yields $Ru_3(CO)_{11}(CNBu^t)$, the structure of which was solved crystallogaphically. The CO groups remain equivalent in the ^{13}C NMR even at -100°C. A second CO can be replaced by using excess Bu^tNC. The cluster hydride $H_4Ru_4(CO)_{12}$ also affords the substitution products $H_4Ru_4(CO)_{12-n}(CNBu^t)_n$(n = 1,



100

FIGURE 24



2, 4) [182]. The reaction of $Ru_3(CO)_{11}(CNBu^t)$ with dihydrogen at one atmosphere of pressure in refluxing cyclohexane yields five products. The major product is proposed to be compound 105 containing a formimidoyl ligand. Another product, $HRu_3(CO)_8(CNBu^t)(HC{:}CBu^t)$, is proposed to have a similar structure. The other three products are $H_4Ru_4(CO)_{12-n}(CNBu^t)_n$(n = 0-2) [183].

The reaction of cyclopentadiene with $Ru_3(CO)_{12}$ yields, in addition to $[Ru(n^5\text{-}C_5H_5)(CO)_2]_2$, a new complex $[\{Ru(n^5\text{-}C_5H_5)(CO)_2\}_2Ru(CO)_4]$ shown to have structure 106 crystallographically [184].

FIGURE 25

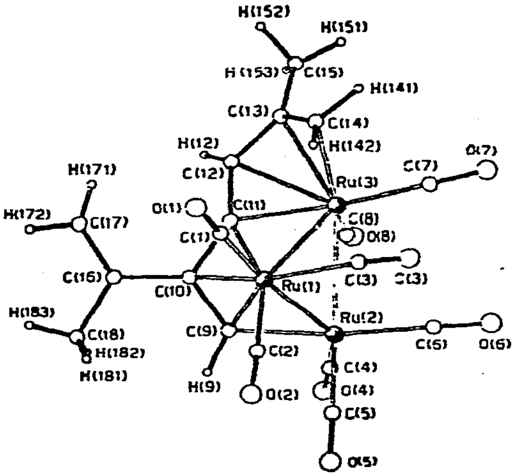
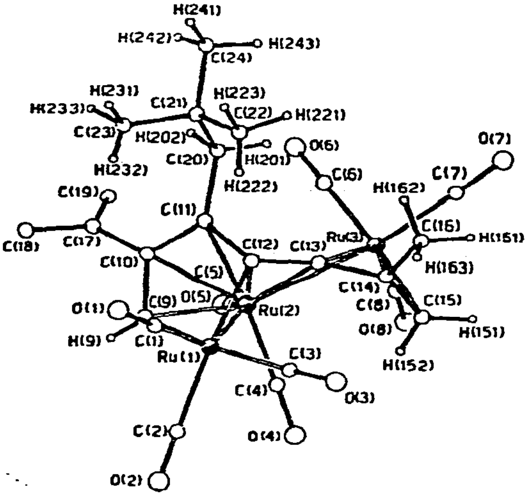
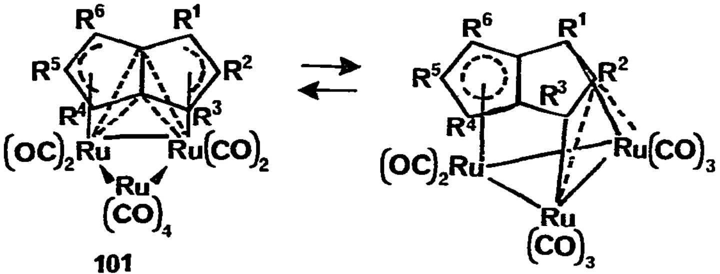


FIGURE 26

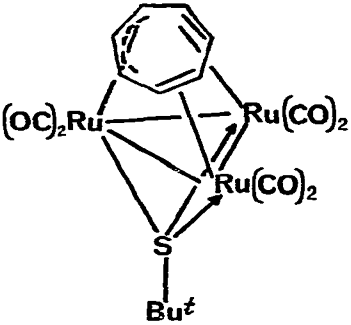


A series of four papers [185-188] has appeared on the reaction of iron carbonyl anions with moist nitriles. The results of the work are summarized in Scheme 27. The structures of 107, 108, and 109 were determined crystallographically. Of particular significance is the demonstration of the stepwise reduction of a carbon-nitrogen triple bond to a single bond (109 → 107 → 108 → 110) while the ligand was bonded to the face of a triiron cluster and thus

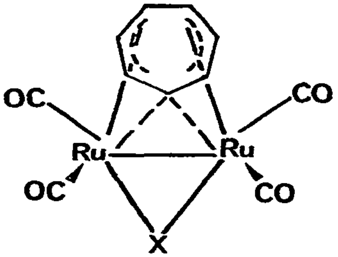


101

102

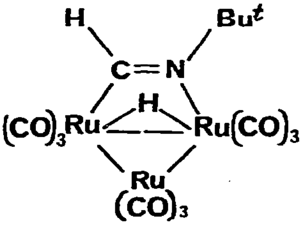


103

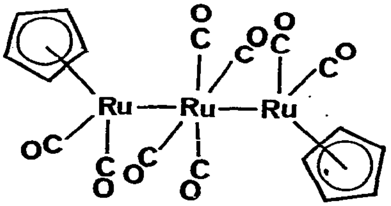


a; X=SBu^t
b; X=Cl,Br,or I

104



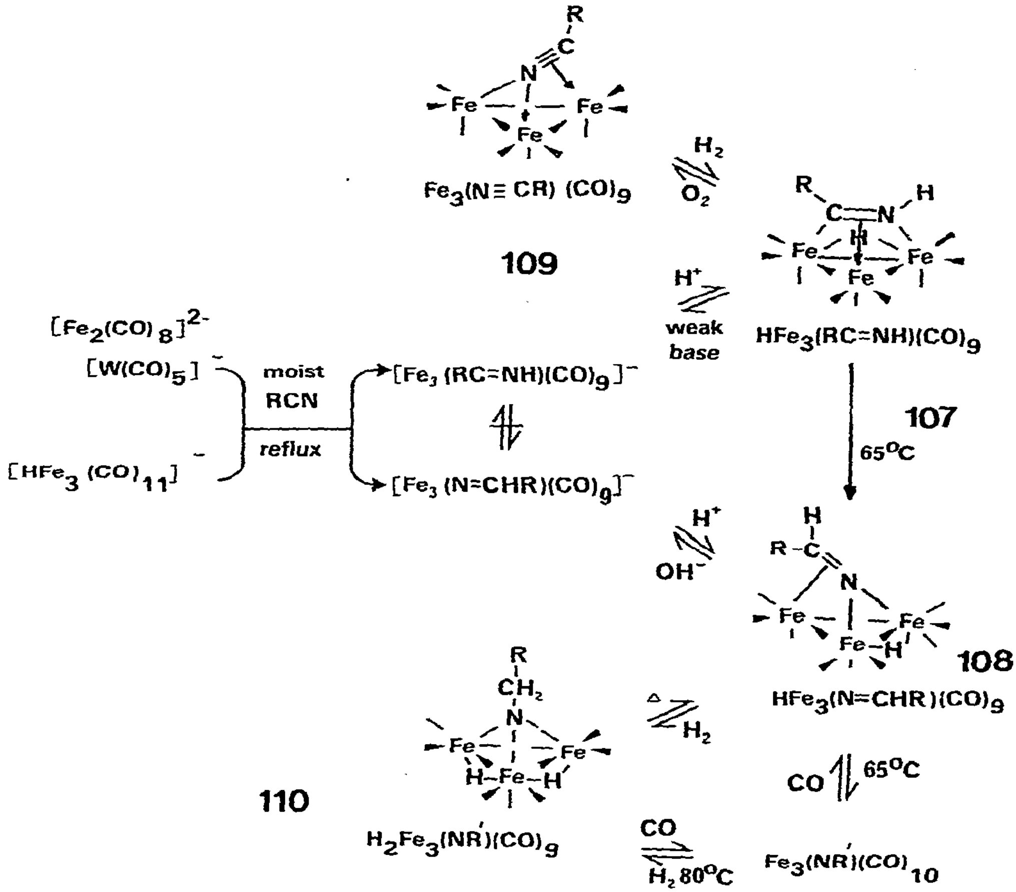
105



106

rovides a detailed model for the steps that might be involved in such a reluction at a metal surface.

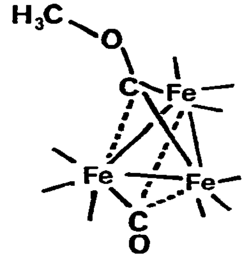
SCHEME 27



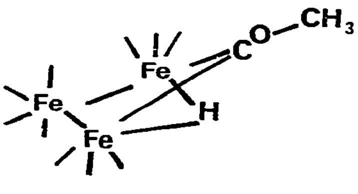
Irradiation of $Ru_3(CO)_{12}$ in hexane in the presence of triphenylphosphine gives $Ru_3(CO)_{11}(PPh_3)$ in addition to $Ru(CO)_4PPh_3$ and $Ru(CO)_3(PPh_3)_2$. The trimer was shown crystallographically to be a single isomer with a triangle of Ru atoms with the PPh_3 group equatorially substituted with no bridging CO group [189].

The reaction of $[Fe_3(CO)_{11}]^{2-}$ with electrophiles R = CH_3^+, $CH_3CH_2^+$, and $CH_3C(=O)^+$ yields $[Fe_3(CO)_{10}COR]^-$ complexes. IR and ^{13}C NMR support structural 111 for these complexes. Protonation of the (R = CH_3) anion yields 112, the X-ray crystal structure of which has been reported previously.

Variable temperature ^{13}C NMR results indicate that these molecules have several different CO permutation rates within each molecule. Also, the alkyl or acyl carbon in $[Fe_3(CO)_{10}COR]^-$ reacts with PhS^- to yield $[Fe_3(CO)_{11}]^{2-}$ [190].



111



112

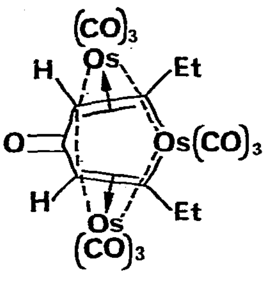
The anion $[HFe_3(CO)_{11}]^-$, which is readily prepared in the reaction of $Fe(CO)_5$, Et_3N and Et_4NCl, selectively reduces nitroarenes to amines, α,β-unsaturated carbonyl compounds to the corresponding saturated compounds and converts some organic halides to dehalogenated products [191].

The reaction of $Fe_3(CO)_{12}$ and chloroformiminium chlorides ($[R_2N = CHCl]Cl$, R = Me, Et) yields mononuclear carbene complexes $R_2NCHFe(CO)_4$ and trinuclear complexes $HFe_3(CO)_{10}CNR_2$ [192].

Both He(I) photoelectron spectroscopy and CNDO calculations agree that the highest occupied molecular orbitals (HOMO) for the $Ru_3(CO)_{12}$ trimer are the Ru-Ru bonding orbitals [193]. The U.V. photoelectron spectra of $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Os_6(CO)_{18}$ have been recorded. The lowest energy band for the Os_6 cluster is only 0.3 eV less than the Os_3 cluster but all three are nearly 3 eV higher than the work functions of the corresponding metals. Therefore, the electronic properties of these small clusters are quite different from the bulk metal [194].

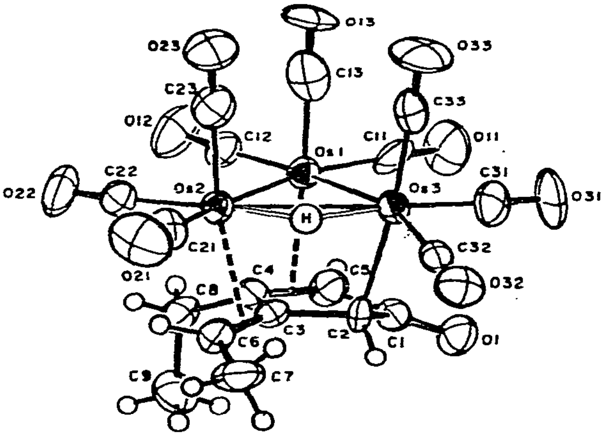
The complexes $Ru_3(CO)_9L_3$($L = PBu^n_3$, $P(OPh)_3$) and the $L = PPh_3$ derivative studied earlier undergo thermal fragmentation to form mononuclear products by three pathways: (1) CO dissociation, (2) L dissociation and (3) metal cluster fragmentation. The major pathway was shown to be CO dissociation. A detailed analysis of the kinetics was presented [195].

Pyrolysis of <u>113</u> has been shown by X-ray methods to produce $(\mu\text{-}H)Os_3(CO)_9[CHC(=O)CH = CEtC(=CHMe)]$ as shown in Figure 27 [196]. The carbyne cluster $HM_3(\mu_2\text{-}COMe)(CO)_{10}$ has been prepared by methylation of $[HM_3(\mu_2\text{-}CO)(CO)_{10}]^-$. The X-ray structure of the M=Ru complex was carried out as shown in Figure 28. The new carbyne clusters react wth H_2 under



113

FIGURE 27



mild conditions to yield $H_3M_3(\mu_3\text{-COMe})(CO)_9$, the structure of which is proposed to be as shown in Figure 29. Reductive cleavage of the COMe group can be achieved for the M=Ru complex at 30°C and $CO{:}H_2$ (1:1, 500 lb/in^2) to produce dimethylether and $Ru_3(CO)_{12}$ [197]. A variety of complexes of the type (cis-diazene)$M_3(CO)_9$ (M=Fe, Ru; cis-diazene=2,3-diazanorbornene, 4-phenyl-3,3-bis(methoxycarbonyl)-1-pyrazoline) have been prepared from free diazene and $Fe(CO)_5$ or $Ru_3(CO)_{12}$ and photochemically from (cis-diazene)-$Fe_2(CO)_6$ and $Fe(CO)_5$. In these molecules the N=N group coordinates to three metal atoms. The dynamic behavior of these molecules was also reported [198].

Polynuclear Clusters

The recently described high yield preparation of $Os_4(CO)_{12}H_4$ has permitted a detailed investigation of its chemistry. The molecule reacts with olefins as

FIGURE 28

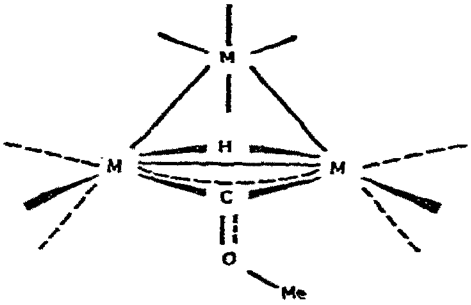
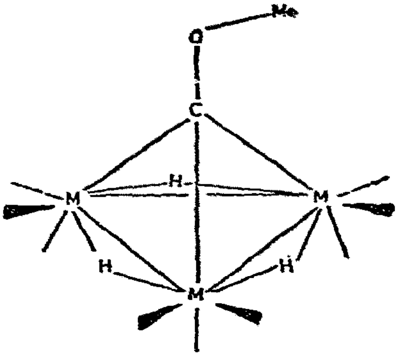
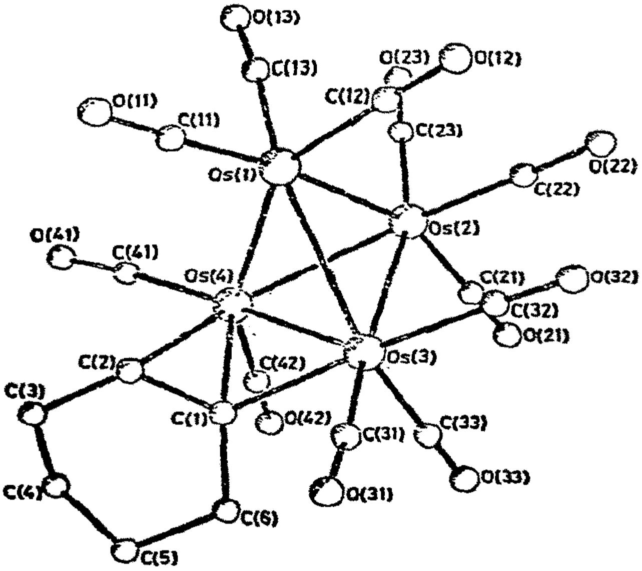


FIGURE 29

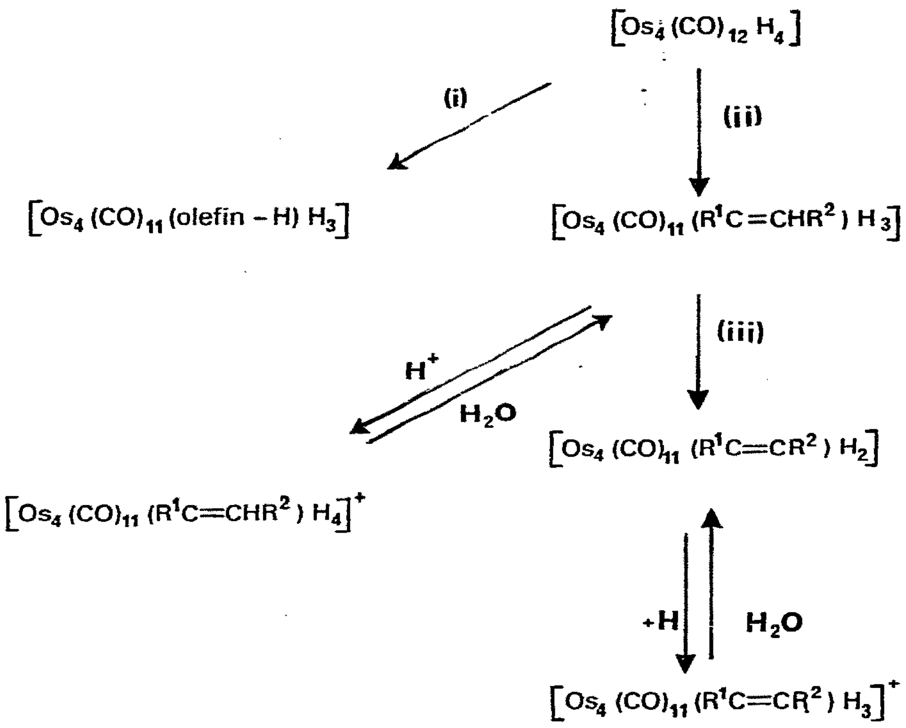


shown in Scheme 28. An X-ray crystal structure has been carried out on the complex $Os_4(CO)_{11}(C_6H_9)H_3$ and is shown in Figure 30. Note that in all cases

FIGURE 30



Scheme 28



(i) Cyclic olefin; (ii) R^{1}CH=CHR^2(R^1=H; R^2=H, Ph, or CMe$_3$; R^1=R^2=Ph); (iii) heat,—H$_2$

the Os_4 tetrahedral unit is maintained [199]. Reactions of $Os_6(CO)_{18}$ have been used to illustrate the reactivity created by the presence of donor metal to metal bonds. Nucleophiles react at donor metal-metal bonds and the opening-out of the cluster that results from this reaction is very important to the course of the over-all reaction [200].

The reaction of base with $Os_5(CO)_{16}$ follows the expected course to produce $[Os_5(CO)_{15}]^{2-}$ whereas the clusters $Os_6(CO)_{18}$, $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$ yield the cluster fragmentation products $[Os_5(CO)_{15}]^{2-}$, $[Os_6(CO)_{18}]^{2-}$ and $[Os_7(CO)_{20}]^{2-}$, respectively. Protonation of these anions produced the expected dihydrido clusters. It was noted that the only cluster which did not undergo fragmentation, $Os_5(CO)_{16}$, was the only electron-precise regular geometry species [201].

Reaction of $H_2Os_5(CO)_{15}$ with OH^- or Me^- results in deprotonation of the cluster to produce $[HOs_5(CO)_{15}]^-$ or $[Os_5(CO)_{15}]^{2-}$ depending on the solvent. I^- reacts to yield $[H_2Os_5(CO)_{15}I]^-$ and $P(OMe)_3$ and CO react to yield $H_2Os_5(CO)_{15}L$ adducts. The structure of $Bu_4N[H_2Os_5(CO)_{15}I]^-$ and $H_2Os_5(CO)_{15}P(OMe)_3$ were shown by crystallography to be as shown in Figures 31 and 32, respectively [202]. The reaction of $[HOs_3(CO)_{11}]^-$ with $Os_5(CO)_{16}$, $Os_7(CO)_{21}$ and $Ru_6C(CO)_{17}$ yields the CO_2 bridged species $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_5(CO)_{15}]^-$, $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_7(CO)_{20}]^-$ and $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Ru_6C(CO)_{16}]^-$, respectively [203].

FIGURE 31

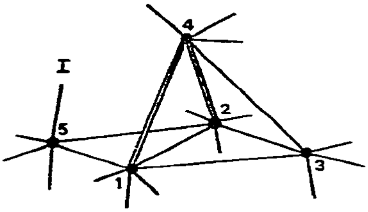
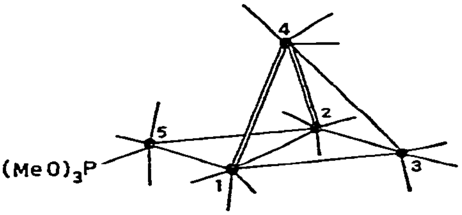


FIGURE 32



A preliminary report of the reduction of $Os_6(CO)_{18}$ to $[Os_6(CO)_{18}]^{2-}$ by iodide has been reported. The best explanation of this chemistry is shown in Scheme 29 [204].

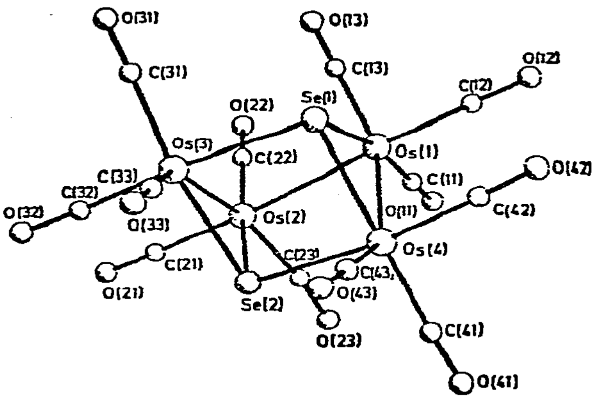
SCHEME 29

$$Os_6(CO)_{18} + I^- \rightleftarrows [\text{Intermediate}]^-$$

$$[\text{Intermediate}]^- + I^- \xrightarrow[\text{slow}]{} [Os_6(CO)_{18}]^{2-} + I_2$$

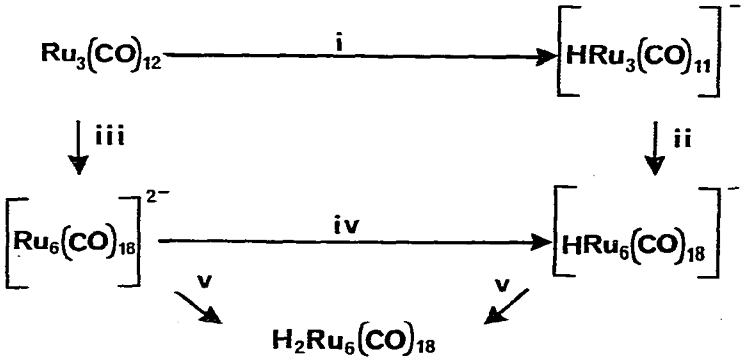
The new clusters $Os_3(CO)_9H_2X$, $Os_3(CO)_9X_2$ and $Os_4(CO)_{12}H_2X_2$ have been prepared by the reaction of $Os_3(CO)_{12}$ with X_n (X=S,Se,Te) in n-octane under reflux. The complexes $Ru_3(CO)_9H_2X$ and $Ru_3(CO)_9X_2$ are also reported but these preparations needed to be carried out under a CO/H_2 pressure of 35 atm. The structure of $Os_4(CO)_{12}H_2Se_2$ was determined crystallographically as shown in Figure 33 [205]. The full report of the X-ray structural determination of $Os_5(CO)_{15}(CH_3OP)$ has been reported [206]. Three $Ru_6(CO)_{18}$ clusters can be easily prepared as shown in Scheme 30. The structure of the dianion was determined crystallographically. The metals are arranged in an

FIGURE 33



octahedral array with two μ_2-bridging CO groups [207]. For the first time, the metal-hydrogen stretching absorptions of interstitial hydrogen ligand have been observed. It occurs near 825 and 600 cm^{-1} for $[HRu_6(CO)_{18}]^-$ and $[DRu_6(CO)_{18}]^-$, respectively. Although a broad doublet at 298°K, the $[HRu_6(CO)_{18}]^-$ complex gives rise to two sharp bands of almost equal intensity at 806 and 845 cm^{-1} at 95°K [208].

Scheme 30

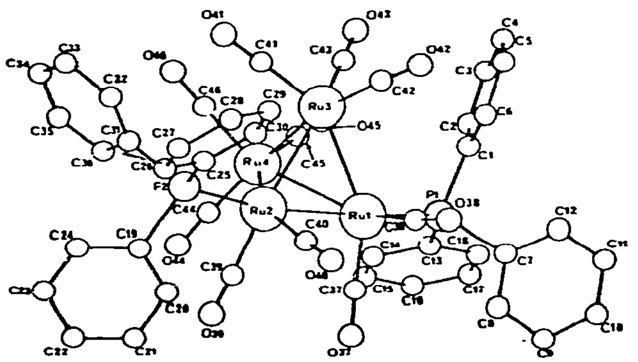


i, KOH-MeOH; ii conc. H_2SO_4 ; iii, $Ru_3(CO)_{12}$-THF added to saturated KOH-H_2O solution; iv, acidification in THF by conc. H_2SO_4; v, acidification in CH_2Cl_2 by conc. H_2SO_4.

The pyrolysis of $Os_3(CO)_{12-X}(CNR)_X$ (R = Bu^t, X = 1,2) in refluxing octane leads to a series of hexanuclear products $Os_6(CO)_{18-X}(CNBu^t)_X$(X = 1-5). Possible structures are discussed [209].

The structure of $H_4Ru_4(CO)_{10}(PPh_3)_2$ has been determined crystallographically as is shown in Figure 34. The hydrogen atoms were not located but are believed to lie above four of the six Ru-Ru bonds. The two bonds not bridged by hydrogen atoms are those connecting the pairs of similar Ru atoms [210]. The reaction of $H_4Ru_4(CO)_{12}$ with one equivalent of KH yields $H_3Ru_4(CO)_{12}^-$. With two equivalents of KH, $H_2Ru_4(CO)_{12}^{2-}$ is produced and with three equivalents of KH an equimolar mixture of $H_2Ru_4(CO)_{12}^{2-}$ and $Ru_4(CO)_{12}^{4-}$ is formed presumably from $HRu_4(CO)_{12}^{-3}$ [211]. The oxidation of $[Fe_6C(CO)_6]^{2-}$ in methanol proceed as shown in Scheme 31 to yield the interesting product $[Fe_4(CO)_{12}C{\cdot}CO_2Me]^-$containing a μ_4-carbomethoxymethylidyne ligand [212].

FIGURE 34



Heterometallic Clusters

The reaction of Cp_2NbH_3 and $Fe(CO)_5$ yields $Cp_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$, the structure of which has been shown crystallographically to be as in Figure 35. NMR data indicate that the two Cp rings are nonequivalent in solution despite the fact that the $Fe(CO)_4$ group shows only one carbonyl ^{13}C resonance [213]. The complex <u>114</u> has been shown to act as a ligand. Thus <u>115</u> forms when <u>114</u> is mixed with $Fe_2(CO)_9$ in THF under CO [214].

The carbamoyl complex <u>116</u> is transaminated with either piperidine or pyrrolidine to yield <u>117</u> and <u>118</u>. These three complexes react with $NiBr_2$ to form <u>119</u> - <u>121</u>. The structure of <u>119</u> as shown in Figure 36 was solved crystallographically [215].

Scheme 31

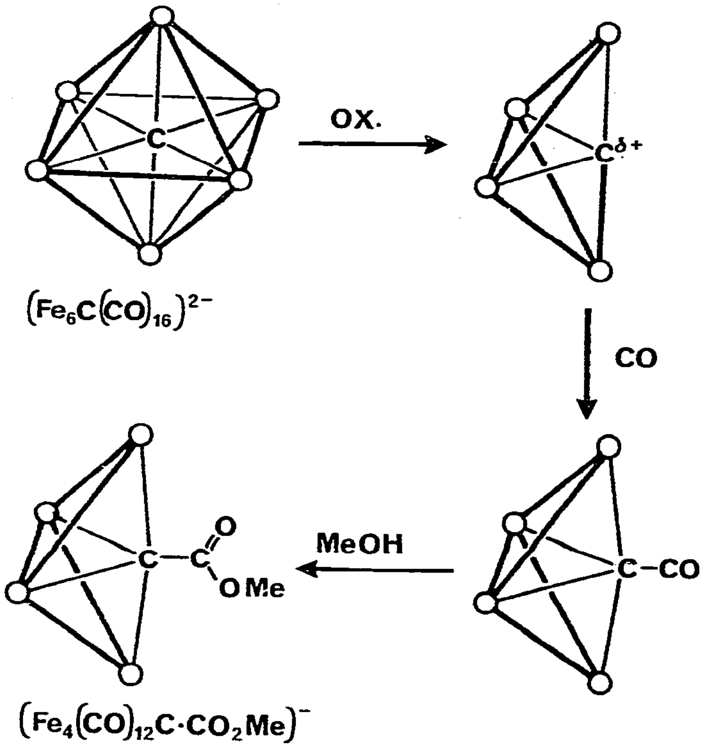
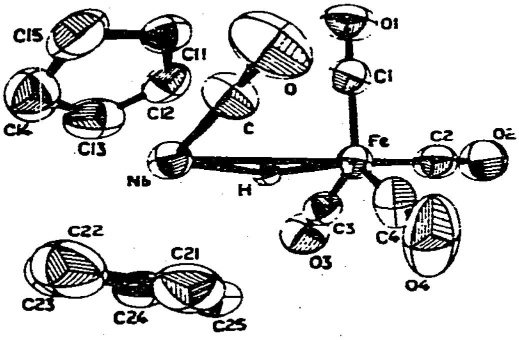
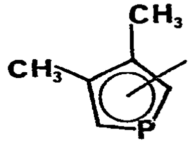
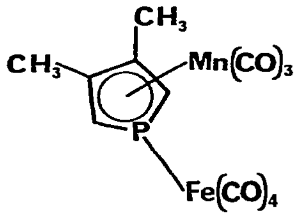


FIGURE 35

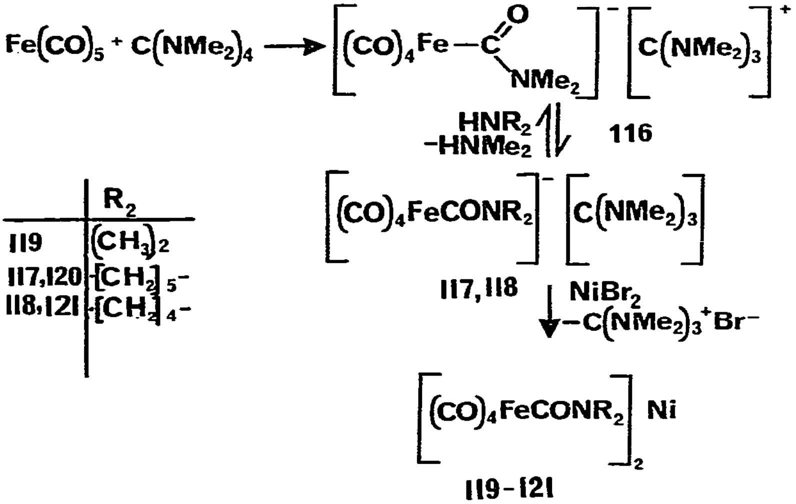




114

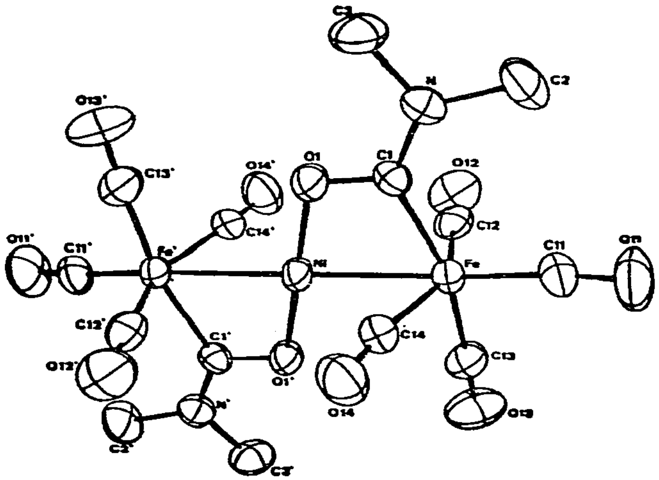


115



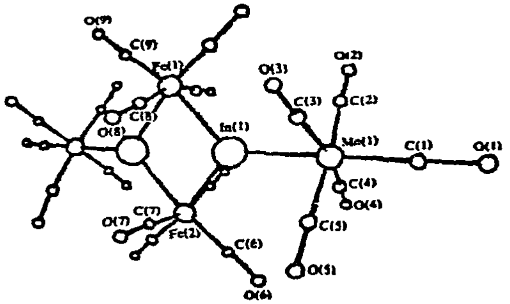
	R_2
119	$(CH_3)_2$
117,120	$-[CH_2]_5-$
118,121	$-[CH_2]_4-$

FIGURE 36



The interaction of $Fe(CO)_5$, In metal and $Hg[Mn(CO)_5]_2$ in a bomb tube reaction yields $Fe_2(CO)_8[In\ Mn(CO)_5]_2$, the structure of which was determined crystallographically as shown in Figure 37. The molecule contains a planar In_2-Fe_2 metal ring with the $Mn(CO)_5$ groups bonded to the In atoms [216].

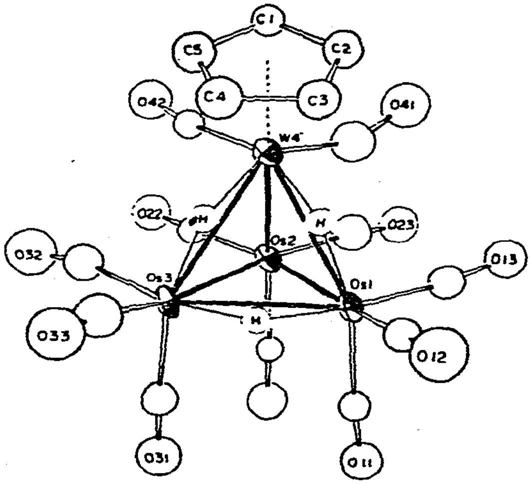
FIGURE 37



The reaction of $Na_2[Fe(CO)_4]$ and $RCCo_3(CO)_9$($R=CH_3$, C_2H_5, C_6H_5) followed by acid workup yields new alkylidyne clusters $RCFeCo_2(CO)_9H$. Modes of formation of these clusters and their possible structures were discussed [217].

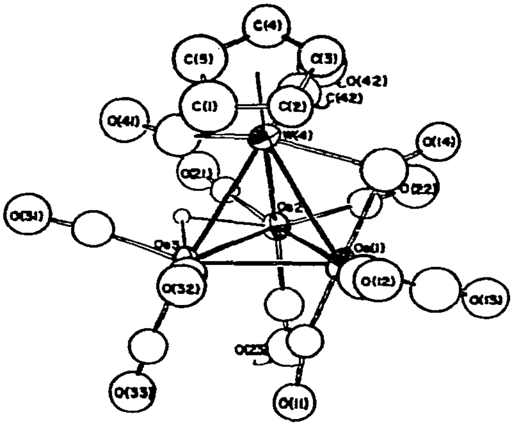
The complex $(\mu\text{-}H)_3Os_3W(CO)_{11}(Cp)$, prepared by the reaction of Os_3-$(CO)_{10}(CNMe)_2$ and $HW(CO)_3(Cp)$ or by H_2 and $(\mu\text{-}H)Os_3W(CO)_{12}(Cp)$, has the structure shown in Figure 38 as determined by X-ray methods [218].

FIGURE 38



The structure of $(\mu\text{-}H)Os_3W(CO)_{12}(Cp)$ also produced in the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $HW(CO)_3(Cp)$ has been determined by X-ray means and is shown in Figure 39. Although not located unambiguously, the hydride ligand location was inferred from the overall structure [219].

FIGURE 39

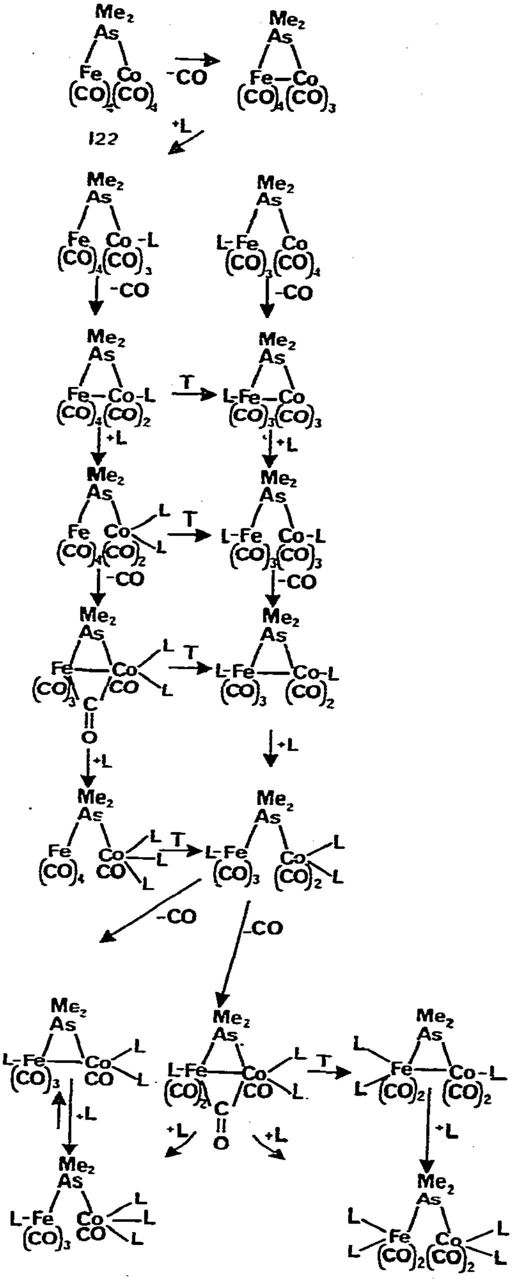


A large number of dimeric complexes as shown in Scheme 32 can be prepared from <u>122</u> by the sequence of formation of a M-M bond with elimination of CO followed by addition of a phosphine ligand (L = PMe_3, $P(OMe)_3$) with cleavage of the M-M bond. The ligand initially adds to the cobalt atom but can be transferred to the iron atom. Mixed L, L' complexes were also reported [220]. Similar reactions take place for <u>123</u> and the new complexes listed in Scheme 33 have been prepared (L = PMe_3, $P(OMe)_3$). Once again, the phosphine ligands initially add to the manganese atom and can be transferred to the iron [221].

The structures of $CrFe(CO)_7(AsMe_2)_2$ and $Fe_2(CO)_6(AsMe_2)_2$ have been determined crystallographically. The M_2As_2 framework of each is folded as shown in Figure 40 for the latter molecule. The fluxional behavior of these molecules is also discussed [222].

A series of new phenylphosphine bridged tetrahedral clusters containing two or three different metal atoms has been prepared. Of particular interest is the chiral complex <u>124</u>, $(PhP)FeCoMoCp(CO)_8$ [223]. The structures of $Fe(Co)_2(CO)_9(PPh)$, a complex having closed electron shells, and $Co_3(CO)_9$-(PPh), a cluster containing one extra electron than required by the 18 - electron rule, have been determined crystallographically. The lengthening of the M-M bonds in the latter of these triangular clusters containing a tri-

Scheme 32



Scheme 33

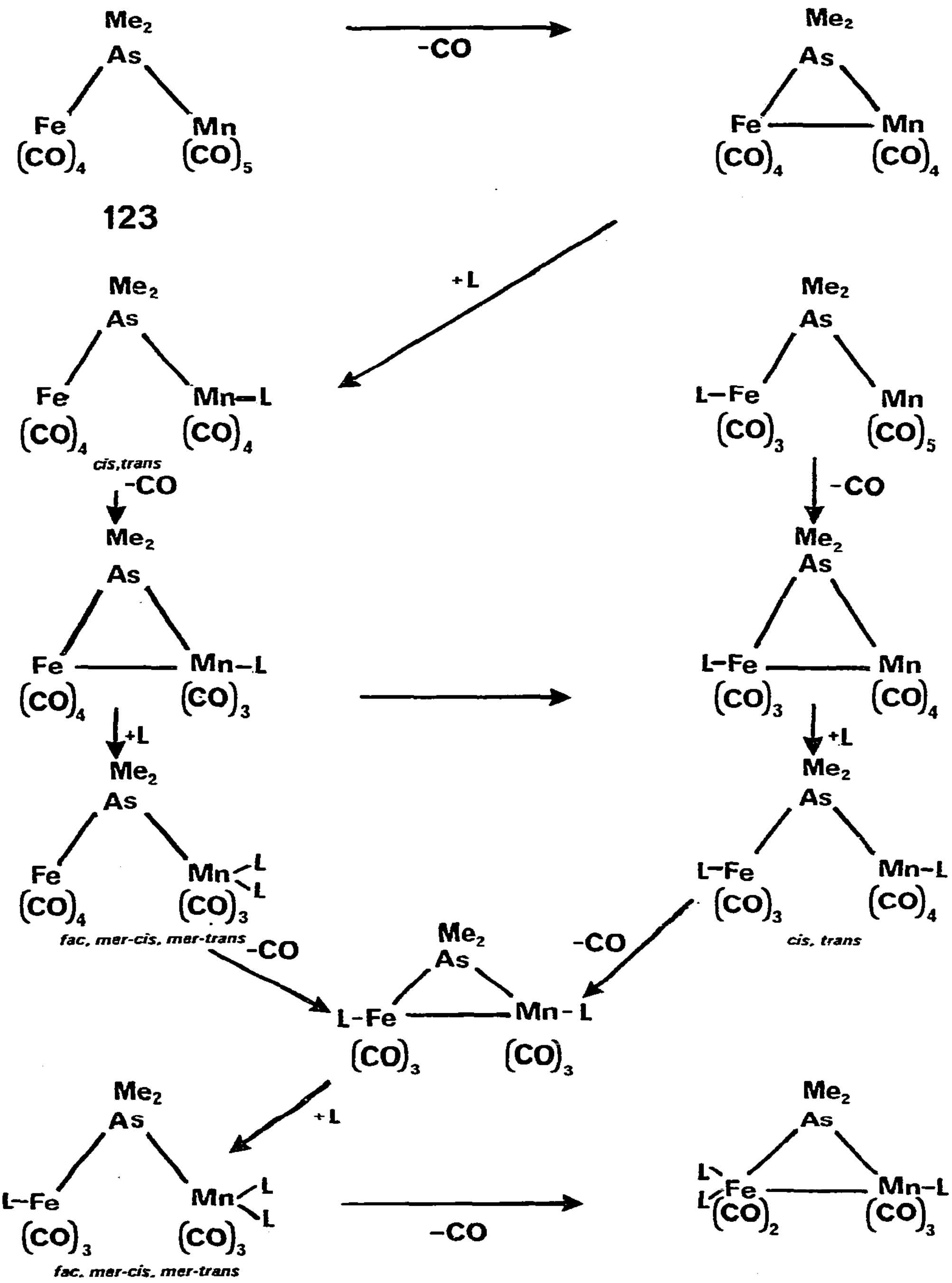
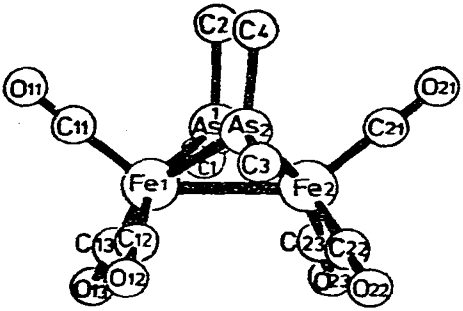
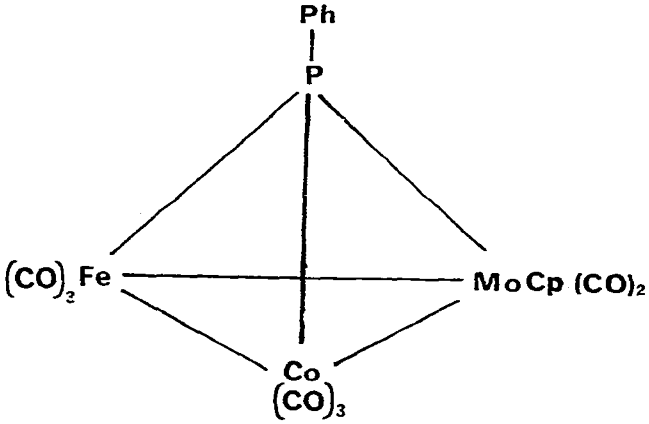

123
-CO
+L
cis,trans
-CO
-CO
+L
+L
fac, mer-cis, mer-trans
-CO
-CO
cis, trans
+L
fac, mer-cis, mer-trans
-CO

FIGURE 40

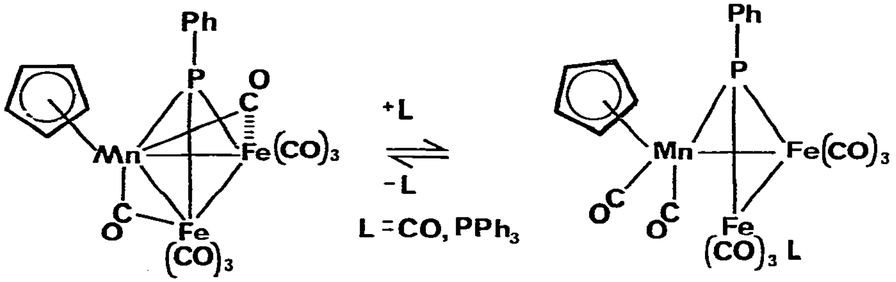




124

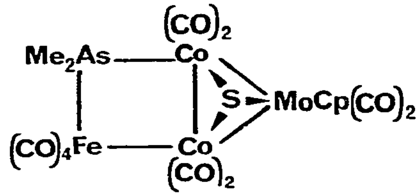
bridging PPh ligand shows that the odd electron is in an orbital antibonding with respect to the MM interaction. The redox behavior and ESR data support this conclusion [224]. The transformation 125 → 126 takes place under mild CO pressure and is reversed in a N_2 atmosphere. A similar reaction takes place with PPh_3 [225].

The first cluster compound containing four different metal atoms has been systematically synthesized. Thus compound 127 (characterized crystallographically) undergoes elimination to form 128 and aggregation to form 129 (characterized crystallographically). Also reaction of 128 with $CpW(CO)_3$-$AsMe_2$ yields 130, the structure of which was assigned by analogy to 129 [226].

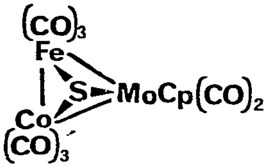


125

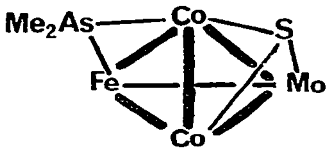
126



127

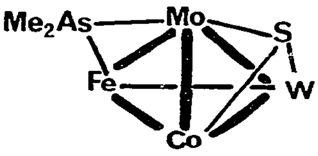


128



$FeCo_2MoS(AsMe_2)Cp(CO)_8$

129



$FeCoMoWS(AsMe_2)Cp_2(CO)_7$

130

The reaction of $[CpNiCO]_2$ with $HRu_3(CO)_9C_2Bu^t$ in refluxing octane yields $CpNiRu_3(CO)_9CC(H)Bu^t$, the structure of which is shown in Figure 41 [227]. Treatment of $[CpNi(CO)]_2$ with $HRu_3(CO)_9(C_6H_9)$ leads to the molecule $CpNiRu_3(CO)_8(C_6H_9)$, the structure of which was determined crystallographically as shown in Figure 42 [228].

The low-frequency Raman spectra of $Os_xRu_{(3-x)}(CO)_{12}(x=0,1,2,3)$ and of $[Os_3(CO)_{12}]_n[Ru_3(CO)_{12}]_{1-n}(0 < n < 1)$ have been reported. It was shown that intermolecular vibrational coupling could be neglected [229].

FIGURE 41

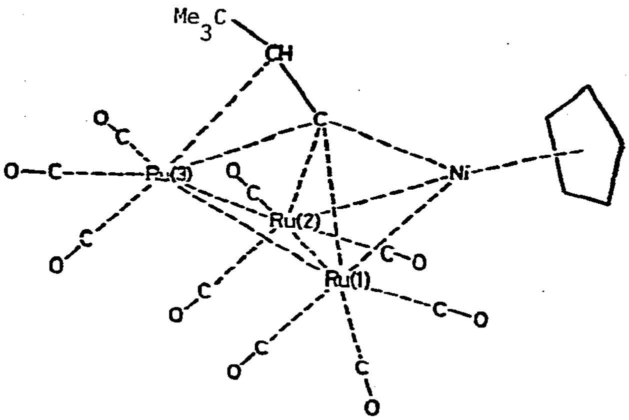
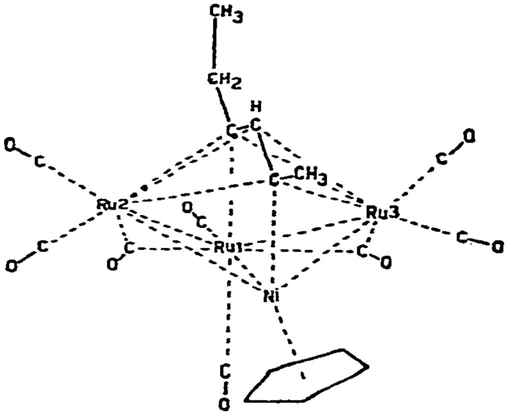
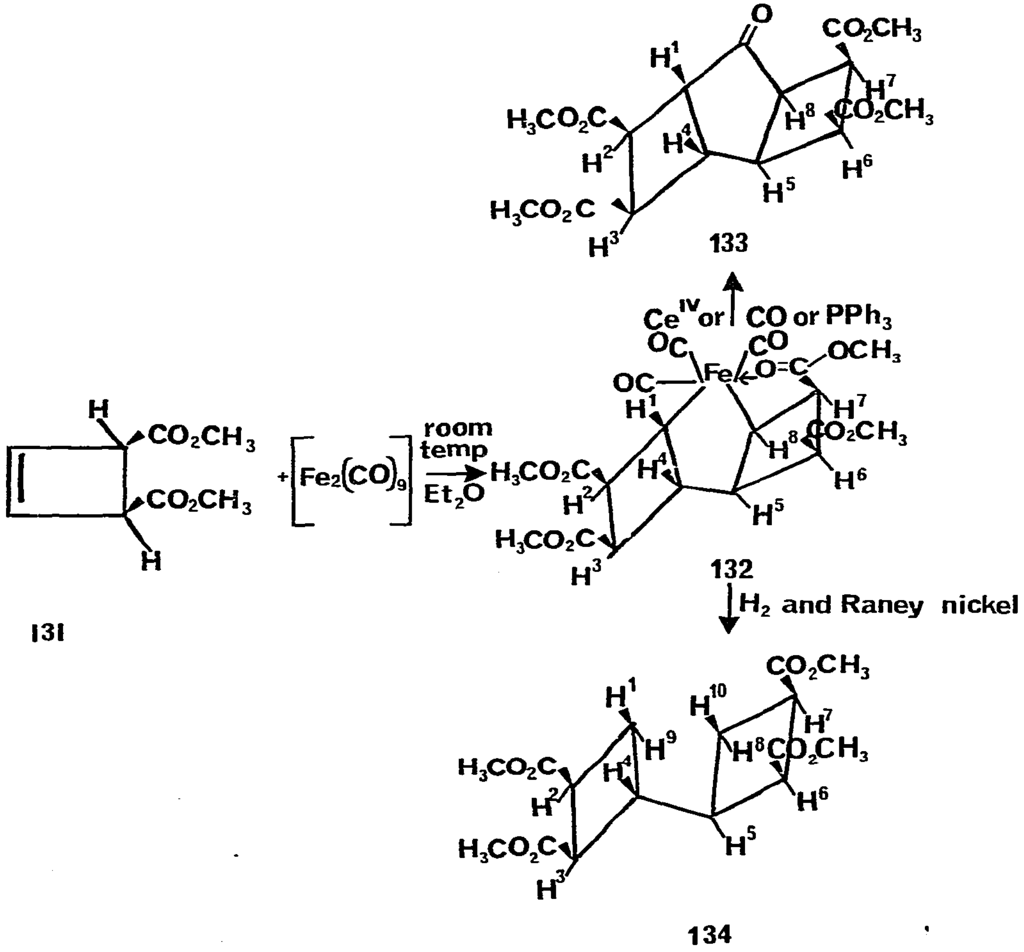


FIGURE 42



Metal Alkyl Complexes

Mixing 131 and $Fe_2(CO)_9$ at room temperature in Et_2O leads to 132. 132 is cleaved by either Ce(IV), CO or PPh_3 to yield 133 and reacts with H_2/Raney nickel to form 134. An analogous photochemical reaction of 131 and $Fe(CO)_5$ leads to similar compounds but different isomers. A mechanism for the formation of these products is proposed [230]. The structure of $Fe(CO)_4(CH_2CH_2CH_2SiCl_2)$ has been reported. The iron atom has a distorted octahedral coordination and the 5 membered ring is in a chair configuration [231].



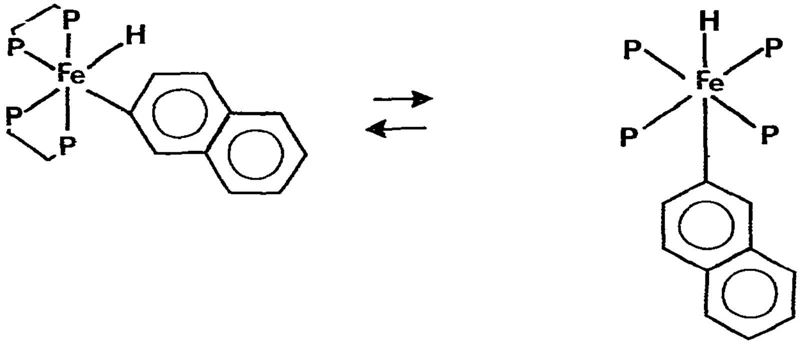
133

131

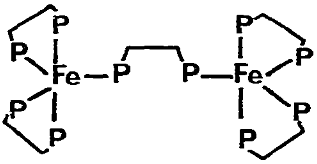
132

134

The reduction of $Fe(dmpe)_2Cl_2$ in THF using sodium naphthalenide yields cis-135 and trans-135 and 136. 135 can be converted into 136 by addition of dmpe. 135 reacts with sp^3 C-H bonds, aromatic C-H bonds and sp^2 C-H bonds [232]. A more detailed paper of the reaction of $HMNp(dmpe)_2$(Np=2-naphthyl, M=Fe,Ru) with various compounds containing sp^2 C-H bonds has appeared. For example, the iron compound reacts with C_6D_6 to produce $DFeC_6D_5(dmpe)_2$ and HNp. The analogous Ru complex reacts much more slowly. A number of substituted benzene derivatives were studied and the products in the isomeric mixtures that generally formed established. In general, product stability is favored by electron - withdrawing substituents and inhibited by electron donors. Benzaldehyde reacts with the Fe complex to yield 137 with no evidence of reaction with the aromatic hydrogen atoms. Methacrylonitrile gave the π-complex to produce 138. Summarizing on this and earlier work it was pointed out for metal complexes to be reactive toward C-H cleavage the complexes must have a high electron density on the metal. It is clear that both steric and electronic effects are important in determining the

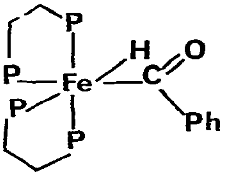


cis-135 **trans -135**



136

reactivity of a given substrate. In the absence of activating or large steric effect the reactivity of C-H bonds is sp > sp^2 > sp^3. This order of reactivity may well be determined by the strength of the M-C bonds thus formed. The main mechanistic pathway for these reactions involves reductive elimination of naphthalene as a rate-determining step followed by oxidation additon of the substrate. An exception is HCN which must react by an electrophilic attack [233].



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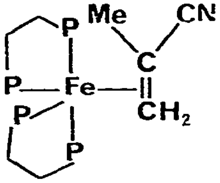


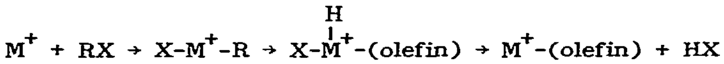
138

A number of iron complexes containing σ-cyclohexylethynyl ligands have been reported. For example, the reaction of [(SCN)$_2$Fe(PPh)$_2$] with KC≡C-C$_6$H$_{11}$ in NH$_3$/ether yields (PPh$_3$)$_2$Fe(C≡C-C$_6$H$_{11}$)$_2$ [234].

Although isolated Fe atoms do not react with a methane matrix, Mössbauer data show that the dimer Fe$_2$ does react to form species containing Fe-H linkages as shown by IR spectroscopy. Fe-CH$_3$ and possibly Fe=CH$_2$ linkages are also formed [235].

Ion cyclotron resonance spectroscopy has shown that Fe$^+$ will react with alkanes to cleave C-C bonds as well as C-H bonds. With i-C$_4$H$_{10}$, the C-C bond cleavage products make up 85% of the reaction mixture [236]. Ion cyclotron resonance spectroscopy has been used to study the reaction of Fe$^+$ with CH$_3$I, C$_2$H$_5$I, i-C$_3$H$_7$Cl, CH$_3$OH, C$_2$H$_5$OH, i-C$_3$H$_7$OH and appropriately deuterium labeled isotopomers. The Fe$^+$ atoms insert readily into the R-X bonds. For cases in which β hydrogen atoms are present, the process shown in Scheme 34 takes place readily.

SCHEME 34

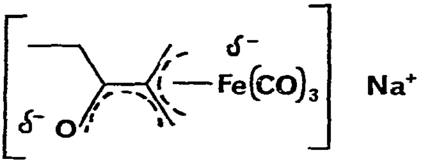


$$M^+ + RX \rightarrow X\text{-}M^+\text{-}R \rightarrow X\text{-}\overset{\overset{\displaystyle H}{|}}{M}{}^+\text{-(olefin)} \rightarrow M^+\text{-(olefin)} + HX$$

The reaction of alkyl halides with Fe(CO)$_n^+$ species and also with the ions formed from electron impact on the alkyl halides and alcohols with Fe(CO)$_n$ species is also described [237].

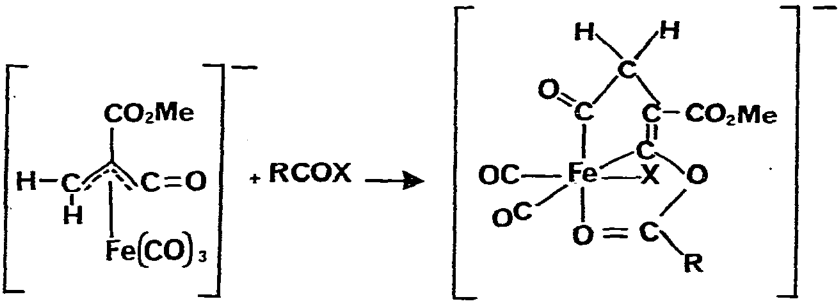
Formyl, Acetyl and Related Complexes

The mechanism of the formation of α,β-unsaturated ketones from the interaction of $Na_2Fe(CO)_4$ with alkyl bromides and allene has been investigated. The key intermediate, 139 (alkyl=ethyl), formed from the insertion of allene into the iron-acyl bond has been isolated and shows substantial delocalization of the negative charge [238]. The rate of CO insertion for $RCH_2Fe(CO)_4^-$ (R=cyclohexyl, n-heptyl, and phenyl) has been studied. Electron withdrawing groups slow the reaction. Extrapolations to the formation of formyl or pyruvoyl complexes indicates that these substituents would migrate very slowly [239]. The reaction of the η^3-acryloylferrate 140 with acyl halides produces the ferracyclopent-2-en-5-one complex of proposed structure 141 as shown in Scheme 35 [240].



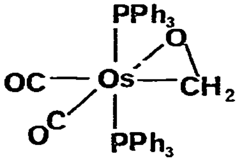
139

Scheme 35



140 **141**

The structures of two dihapto-acyl derivatives of Ru(II), Ru[η^2-C(O)CH_3]I(CO)$(PPh_3)_2$ and Ru[η^2-C(O)p-tolyl]I(CO)$(PPh_3)_2$ have been determined crystallographically [241]. The reaction of $Os(CO)_2(PPh_3)_2$ with formaldehyde yields Os(η^2-CH_2O)$(CO)_2(PPh_3)_2$, the structure of which was determined crystallographically as shown in <u>142</u>. Heating this complex yields Os(CHO)H$(CO)_2(PPh_3)_2$ which decomposes to $Os(CO)_3(PPh_3)_2$ and H_2. Addition of HCl to <u>142</u> yields $Os(CH_2Cl)Cl(CO)_2(PPh_3)_2$ [242].



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A general discussion of the synthesis and properties of iron-formyl complexes of the type $[(ArO)_3PFe(CO)_3CHO]^-$ has appeared. Although these formyl complexes thermally decompose to $[(CO)_4FeH]^-$, the reverse reaction was not observed [243]. The reaction of $LiBH(C_2H_5)_3$ with $Os_3(CO)_{12}$ leads to spectroscopically detectable formyl complexes. A similar product could not be observed in an analogous reaction with $Ru_3(CO)_{12}$ [244].

Fischer-Tropsch and Water Gas Shift Reaction Chemistry

The hydrogenation of CO to methanol and methyl formate has been shown to take place over soluble ruthenium complexes. The only ruthenium species observed in the reaction mixture, as monitored by IR, was $Ru(CO)_5$ and this monomer is believed to be the active catalyst. The methanol/methyl formate ratio was 4/1 but could be increased by enriching the CO/H_2 mixture with additional H_2 or addition of PPh_3 to the catalytic system [245]. Treatment of $Ru_3(CO)_{12}$ with a 15-fold excess of AlH_3 in THF produces rapidly a mixture of methane, ethene, ethane, propene and propane (1:1.7:0.5:0.2:0.1). About 10% of the CO present in the starting Ru complex is converted into hydrocarbon. Acidification of these solutions produced methane, ethane and propane (19:5:1) so that now 30% of the CO overall was converted to hydrocarbon. The group VIB metal carbonyls proved to be more selective yielding mainly ethene [246]. Although solutions of $Ru_3(CO)_{12}$ have been shown to be catalysts for the Fischer-Tropsch reaction, a careful study has shown that the active catalyst is heterogeneous. Solutions of $Ru_3(CO)_{12}$ are not active unless some decomposition takes place [246a].

A general discussion on the use of iron, ruthenium, osmium, and other metal carbonyl complexes as catalysts for converting CO and H_2O into CO_2 and H_2 in the presence of base has been published. The conversion of propene into a mixture of butanal and methylpropanal and nitroarene into aminoarene derivatives was also discussed [247].

$Fe(CO)_5$ in the presence of base has been studied as a water gas shift reaction catalyst. A mechanism for the reaction is shown in Scheme 36 [248].

SCHEME 36

$$HFe(CO)_4^- + CO \rightleftarrows Fe(CO)_5 + H^-$$

$$H^- + H_2O \rightarrow OH^- + H_2$$

$$OH^- + Fe(CO)_5 \rightarrow Fe(CO)_4C(O)OH^-$$

$$Fe(CO)_4C(O)OH^- \rightarrow HFe(CO)_4^- + CO_2$$

A number of metal cluster carbonyl complexes, mainly of ruthenium and iron, have been shown to be active homogeneous catalysts for the water gas shift reaction under alkaline conditions. In the ruthenium system, $H_3Ru_4(CO)_{12}^-$ and $HRu_3(CO)_{11}^-$ are the principal species present. A catalyst prepared from both iron and ruthenium carbonyls was the most active. Possible mechanisms for the reaction were discussed [249].

Analysis of the infrared spectra in the $\nu(CO)$ region of $[HFe(CO)_4]^-$ prepared from $Fe(CO)_5$ as shown in Scheme 37 using both ^{18}O-labeled and unlabeled NaOH showed that the same products (containing no signficant $C^{18}O$) were produced. Therefore, the rate of $Fe(CO)_4COOH^-$ proceeding to $Fe(CO)_4H$ and CO_2 is rapid relative to the reversible loss of OH^- as shown in Scheme 37.

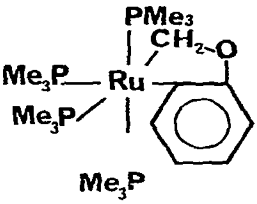
SCHEME 37

$$Fe(CO)_5 + OH^- \rightleftarrows [Fe(CO)_4COOH]^- \rightarrow Fe(CO)_4H^- + CO_2$$

This result was supported by carrying out the reaction under phase transfer conditions in which the OH^- concentration would be low [250].

Aryl Complexes and o-Metallation

$Ru_2(CO_2Me)_4Cl$ reacts with $MgPh_2$ in the presence of PMe_3 to yield $RuPh_2(PMe_3)_4$. This complex, shown to have cis stereochemistry, partially dissociates one phosphine in solution. An analogous reaction with the diarylmagnesium compound of 2-methoxyphenyl is complex but 143 was isolated and shown to have the structure indicated [251]. The reduction of $RuCl_2(PPh_3)_3$ in THF-CH_3CN produces the ortho-metallated complex $RuH(C_6H_4PPh_2)(MeCN)(PPh_3)_2$. The intermediates in the reaction were studied as was the reaction in pyridine and in the presence of 2,2-bipyridyl [252]. The complexes 144 in which the overall charge and thus the oxidation state of the iron is varied from n = -1,0,1 have been prepared [253].



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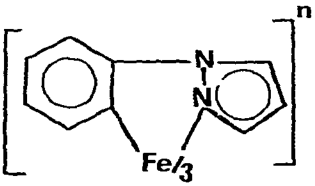

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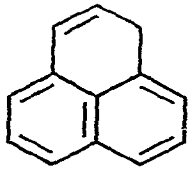
MONOALKENE COMPLEXES

Two iron complexes of phenalene (145) have been reported. $Fe_2(CO)_9$ reacts to yield 146 and Fp^- reacts with the epoxide of 145 to yield 147 [254].



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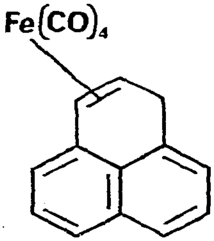

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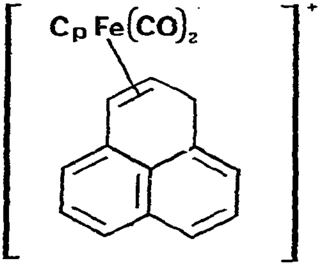

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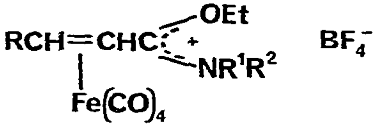
The photoelectron spectrum of (ethylene)$Fe(CO)_4$ was redetermined and found to be similar to that reported previously which indicated, surprisingly, that the $Fe(CO)_4$ group did not greatly perturb the energy levels of the ethylene. For comparison, tetramethylallene$Fe(CO)_4$ was run and compared to tetramethylallene. In this run, the organic ligand was greatly perturbed by the $Fe(CO)_4$ group. This, coupled with mass spectral data that indicated that $(C_2H_4)Fe(CO)_4$ was not stable under the conditions of the photoelectron experiment led the authors to propose that $(C_2H_4)Fe(CO)_4$ decomposes to ethylene and probably $Fe_3(CO)_{12}$ in the photoelectron spectrometer and that the true photoelectron spectrum of $(C_2H_4)Fe(CO)_4$ is still unknown [255].

A variety of alkene and alkyne ligands react with $[(NH_3)_5RuOH_2]^{2+}$ to form new π-complexes. Complete characterization is reported with correlations of spectral properties with the backbonding capabilities of the ligands. The structure of the fumeric acid (HOOCCH = CHCOOH) complex was determined crystallographically [256].

Reactions of <u>148</u> with $Et_2O{\cdot}BF_3$ proceeds as shown in Scheme 38. <u>149</u> readily reacts with one equivalent of primary amines to yield <u>150</u>. A second equivalent of amine converts <u>150</u> into <u>151</u>. The reaction is reversible. Compound <u>151a</u> isomerizes to <u>152</u> [257]. A similar reaction of $Et_2O{\cdot}BF_3$ with the aldehyde complex <u>153</u> yields <u>154</u> as shown in Scheme 39. <u>154</u> reacts with one equivalent of amine producing <u>155</u> which react further to yield <u>156</u> with a second equivalent of amine. The structure of <u>156a</u> was proven crystallographically [258]. The reaction of <u>157</u> with $R^3{}_2NH$ gave <u>158</u> while reaction of <u>157</u> with Et_3N gave <u>159</u> [259].



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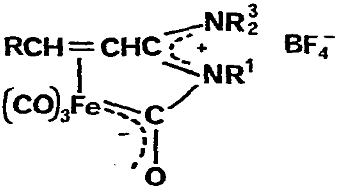

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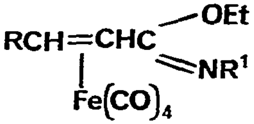

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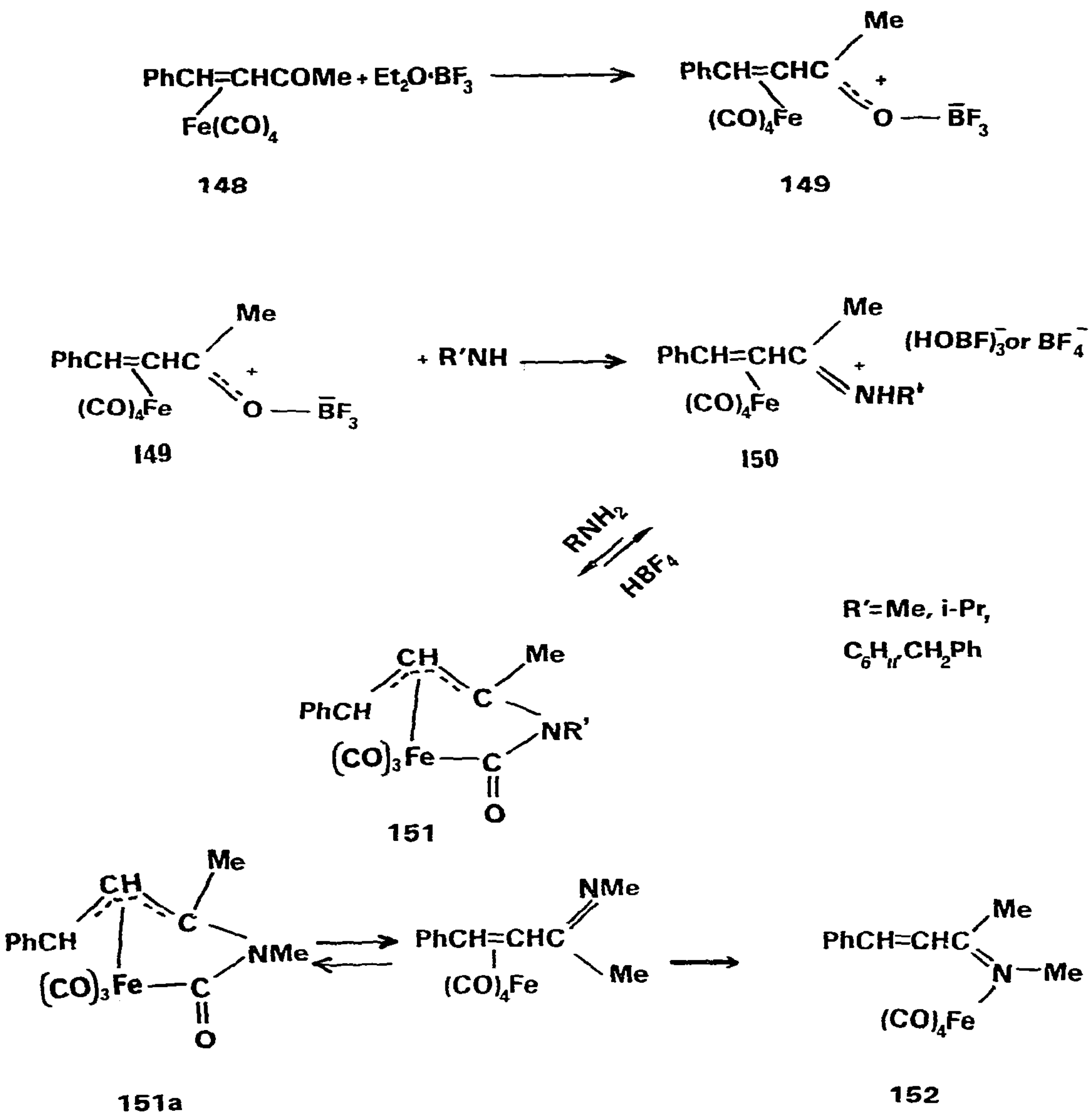
ALLYL COMPLEXES

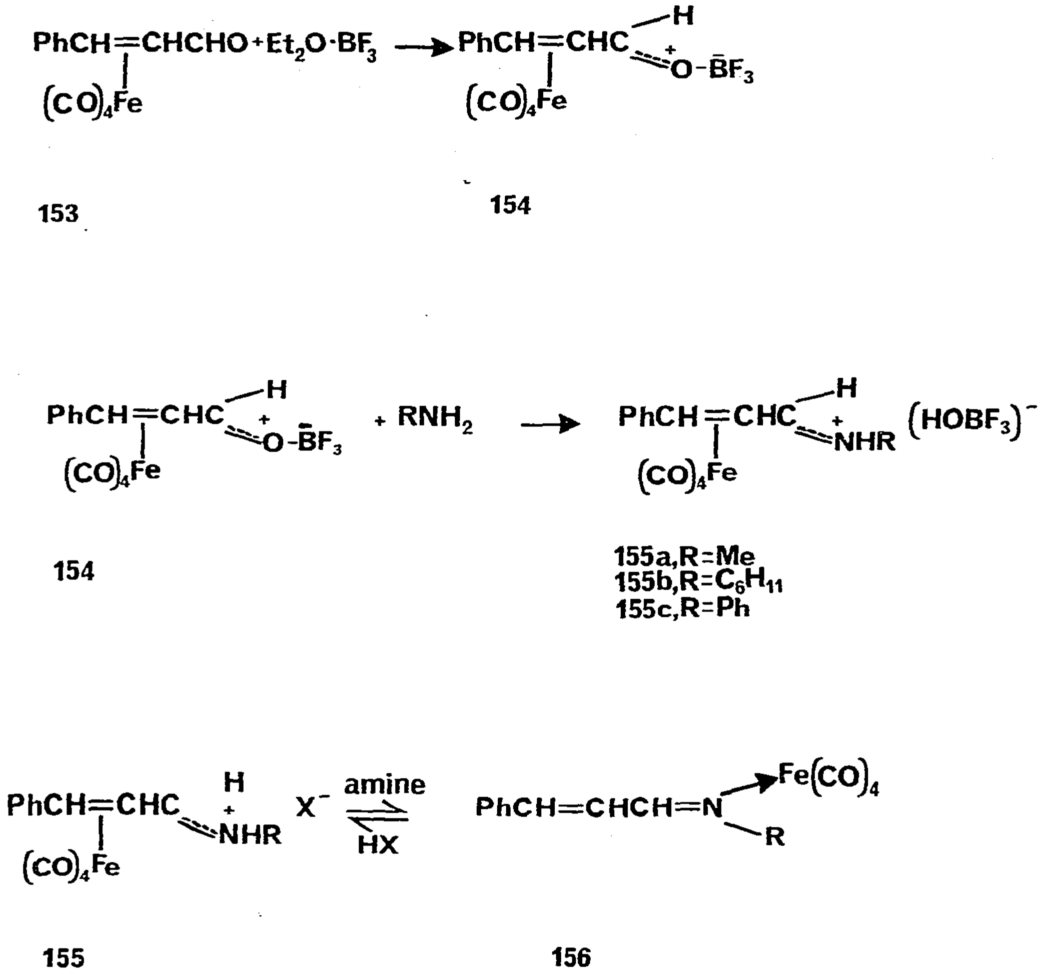
A detailed study has determined whether $(\eta^3\text{-allyl})Fe(CO)_3X$(X=Cl,Br,I,-NCO) complexes have an endo (<u>160</u>) or exo (<u>161</u>) structure as the major isomer in solution. The endo isomer for the X=NCO complex was clearly shown to be the dominant isomer using both shift and relaxation reagents. Because of the

Scheme 38



similar properties of all four complexes it was reasonably argued that this result also holds for the halide complexes. The barrier to interconversion of the two isomers was measured using spin saturation transfer methods. As the <u>anti</u> protons of the major isomer only equilibrate with the <u>anti</u> protons of the

Scheme 39



153 154

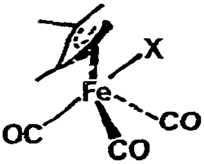
154 155a,R=Me 155b,R=C_6H_{11} 155c,R=Ph

155 156

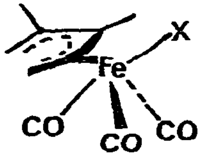
minor isomer, a σ-π mechanism could be ruled out in favor of a simple rotation mechanism [260].

As shown in Scheme 40, the neutral π-allyl complex 162 reacts with stabilized anions such as malonate anion to yield 163 and the appropriately monoallylated organic products. With unsymmetrical η^3-allyl ligands the less substituted carbon was preferentially alkylated [261].

The structure of the 17 electron species $Fe(\eta^3-C_8H_{13})(P(OMe)_3)_3$ has been determined crystallographically and compared to the 16 electron species $[Fe(\eta^3\text{-cyclooctenyl})(P(OMe)_3)_3]BF_4$ and the 18 electron species $Co(\eta^3$-cyclo-

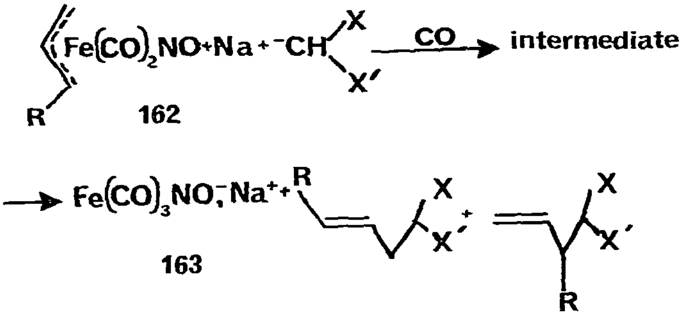


160(endo)



161 (exo)

Scheme 40

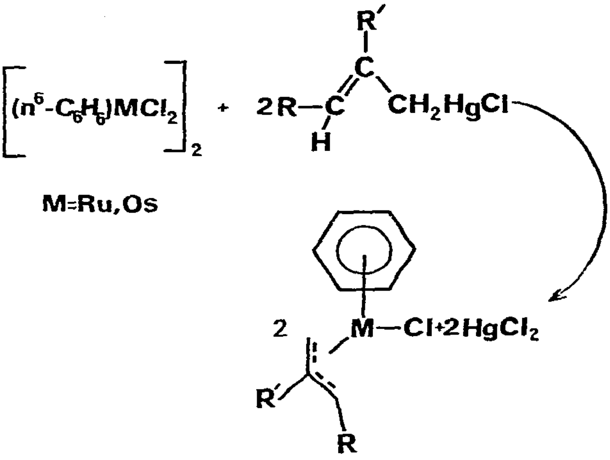


$R = H, CH_3, C_6H_5$

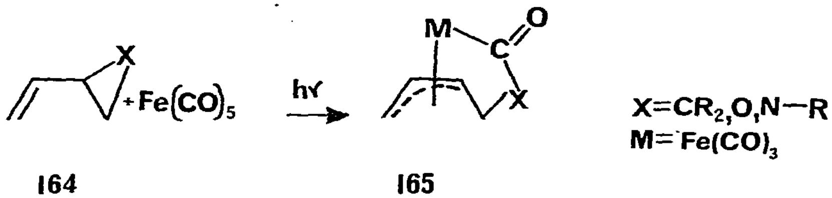
octenyl)(P(OMe)$_3$)$_3$. As with the 16 electron species, there is an interaction of a ring hydrogen atom with the metal, an interaction missing in the coordinatively saturated 18 electron species. An extended Hückel calculation as well as a discussion of fluxional processes for this 17 electron iron species was presented [262]. A series of π-allyl complexes of ruthenium and osmium have been synthesized as shown in Scheme 41 [263].

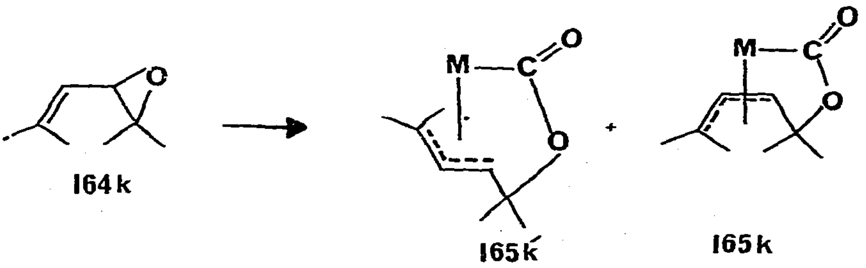
The complex (PPh$_3$)$_4$Ru(π-CH$_3$CN)·CH$_3$CN isomerizes allylbenzene to cis-and trans-β-methylstyrene. Two intermediate hydrido-η^3-1-phenylallyl-Ru complexes have been detected by NMR during the reaction and the main intermediate, (PPh$_3$)$_2$RuH(η^3-C$_3$H$_4$C$_6$H$_5$)CH$_3$CN, isolated. The observation of these intermediates indicates that the isomerization reaction is initiated by oxidative-addition of Ru(O) to an allylic C-H bond [264].

Scheme 41

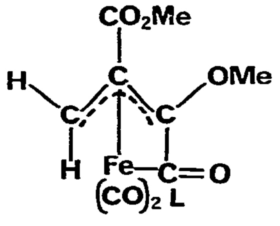


Reaction of $Fe(CO)_5$ and vinyloxiranes 164 under photolytic conditions yields isomers of the ferralactones 165. For the starting material 164k, the two isomers 165k and 165k' were characterized crystallographically. The reactions of these ferralactones with various nucleophiles was investigated [265]. The reaction of 166 ($L=PPh_2Me$ or $PPhMe_2$) with an additional





equivalent of ligand (L' = PPh_2Me, $PPhMe_2$, CO) leads to the formation of 167. The structure of the L=$PPhMe_2$, L'=CO molecule was determined crystallographically [266]. The reaction shown in Scheme 42 leads to two



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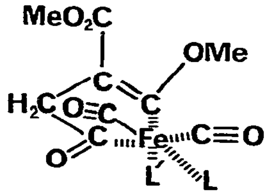
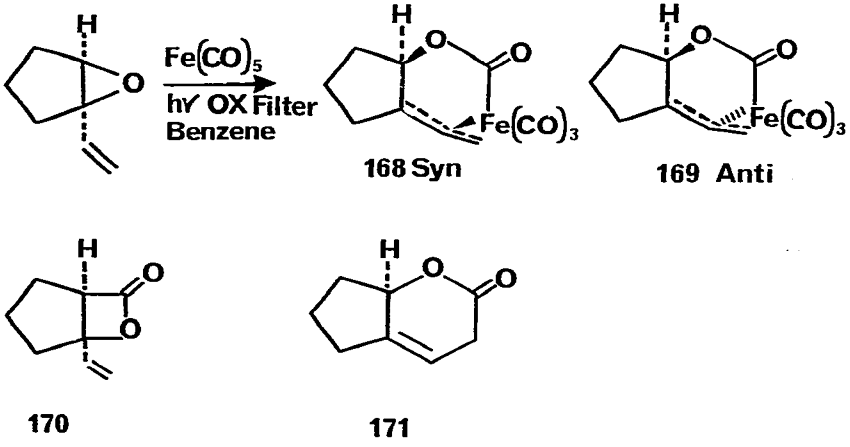
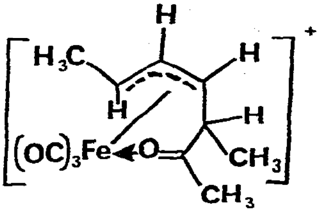


167

separable products as shown in a ratio of 6:1 (syn/anti). Both products were characterized crystallographically. Oxidation of 168 with Ce^{4+} leads to a 1.8/1 mixture of 170 and 171 whereas oxidation of 169 yields 171 [267]. The structure of 172 has been determined crystallographically [268].

Scheme 42





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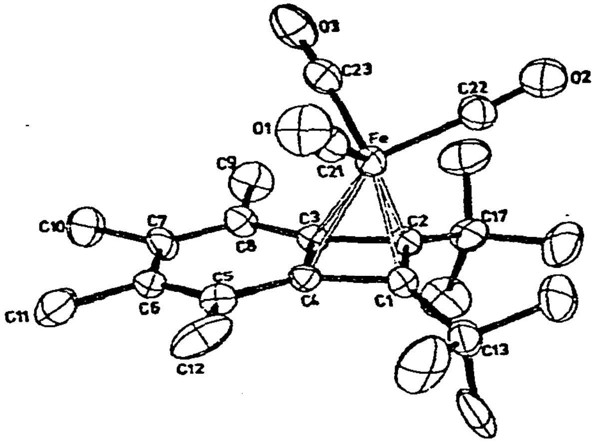
CYCLOBUTADIENE AND TRIMETHYLENEMETHANE COMPLEXES

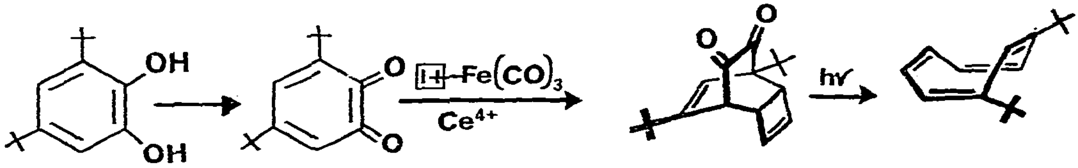
The cyclobutadiene complex shown in Figure 43 has been prepared from the reaction of $Fe_2(CO)_9$ and the respective free benzocyclobutadiene and its structure determined crystallographically [269]. The complex

FIGURE 43



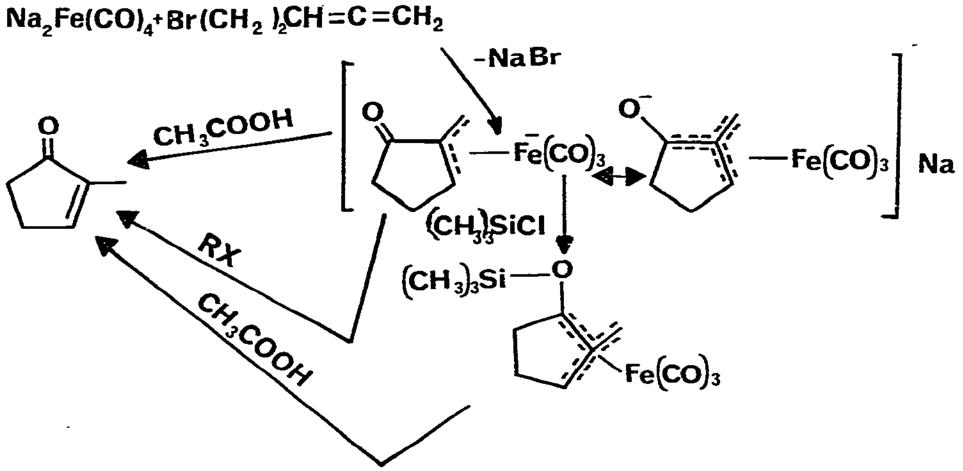
$(\eta^4-C_4H_4)Fe(CO)_3$ was used to deliver cyclobutadiene in the synthesis of 1,3-disubstituted cyclooctatetraenes as shown in Scheme 43 [270].

Scheme 43



The reaction of $[Fe(CO)_4]^{2-}$ with $Br(CH_2)_2CH{=}C{=}CH_2$ followed by various reagents proceeds as in Scheme 44. Although yields are generally low, $[Fe(CO)_4]^{2-}$ can also be used to convert alkenyl halides into cyclic ketones [271].

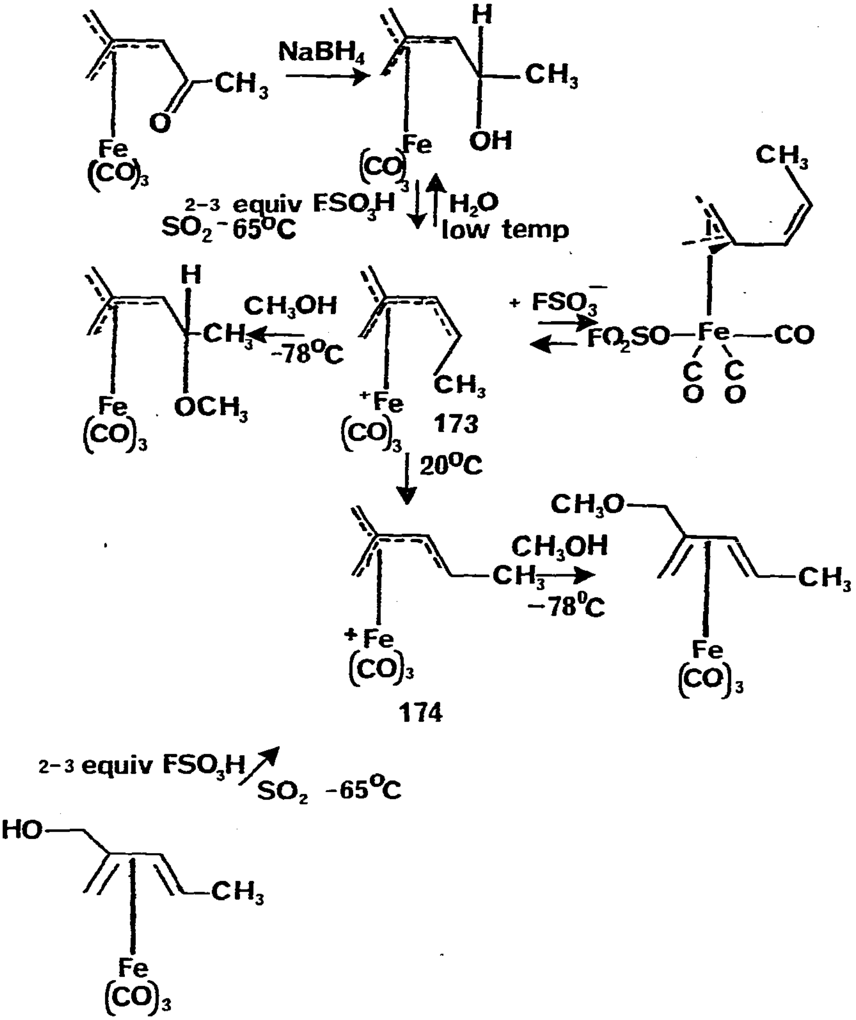
Scheme 44



The (cross-conjugated dienyl)tricarbonyliron cations 173 and 174 have been generated by protonation of the appropriate alcohol as shown in Scheme 45. The 4-anti-methyl cation 173 coordinates fluorosulfonate ion reversibly but slowly whereas the 4-syn-methyl cation 174 does not. There is rotation about the C_2-C_3 bond for 173 and 174. This evidence points to a lack of coordinative unsaturation in these complexes and rules out a n^3-allyl type structures predicted by the simplest Frontier orbital model [272].

The electronic structure of $[ML(CO)_2N_2]$ and $[ML(CO)_3]$($ML{=}Fe(\eta^4\text{-}C_4H_4)$, $Fe\{C(CH_2)_3\}$) has been investigated using the CNDO/2 formalism and compared to analogous complexes where $ML{=}Cr(\eta^6\text{-}C_6H_6)$ and $Mn(\eta^5\text{-}C_5H_5)$. The results are compared to experimental CO and N_2 stretching frequencies. Going across the series from Cr to Fe, π-backbonding becomes less important. Also, as expected, CO interacts more strongly with the metals than N_2 [273]. The Fenske-Hall nonempirical molecular orbital method has been used to study cyclobutadieneiron tricarbonyl. The calculations show clearly that the molecule is better viewed as a C_4H_4Fe fragment interacting with 3 CO groups than a $Fe(CO)_3$ fragment interacting with the C_4H_4 group. A main factor causing this is the near equality in energy of the interacting C_4H_4 and Fe orbitals.

Scheme 45

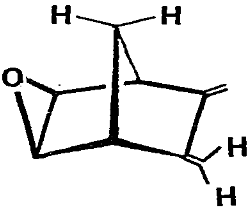


Having established this, the idea of "metalloaromaticity" was introduced because the C_4H_4Fe fragment can be viewed as having 6 π type orbitals (4 p orbitals on carbons and 2 metal π orbitals, d_{xz}, d_{yz}) holding 6 electrons. This system is not greatly perturbed by the 3 CO ligands because these ligands interact mainly with d_{z^2}, $d_{x^2-y^2}$ and d_{xy} metal orbitals. This result is supported by the fact that the C_4H_4 ring in $C_4H_4Fe(CO)_3$ undergoes aromatic substitution reactions readily [274]. The perturbation energies of the π orbitals introduced by the tricarbonyliron moiety have been determined from the photoelectron spectra of cyclobutadiene- and trimethylenemethane-iron tricarbonyl by comparison of eight other 4 π-electron hydrocarbons and their tricarbonyliron complexes [275].

DIENE AND HIGHER OLEFIN COMPLEXES

Acylic Diene Species

The reaction of 175 with iron and ruthenium carbonyls yields mainly the exo-$M(CO)_3$ complexes of the type 176 as shown for the $Fe(CO)_3$ complex by X-ray crystallography. Reaction of these complexes with acid was reported [276].



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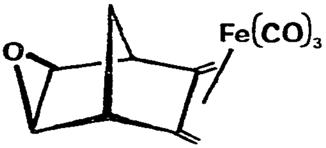

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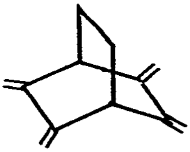
The reaction of 177 with $Fe_2(CO)_9$ yields two (η^4-1,3-diene)$Fe(CO)_3$ isomers and two bimetallic isomers $(C_{12}H_{14})[Fe(CO)_3]_2$. The monomers are a 2:3 mixture of the exo and endo isomers, the structure of the endo isomer was determined crystallographically. The bimetallic isomers are a 4:5 ratio of endo-exo and diexo isomers. 177 also reacts with $Ru_3(CO)_{12}$ to yield mainly endo-$(C_{12}H_{14})Ru(CO)_3$ and endo,exo-$(C_{12}H_{14})[Ru(CO)_3]_2$ [277]. The reaction of 178 with $Fe_2(CO)_9$ or $M(CO)_3(CH_3CN)_3$ (M=Mo,W) leads to complexes 179-184, respectively. The reaction of 179 with $Mo(CO)_3(CH_3CN)_3$ yield 185. The



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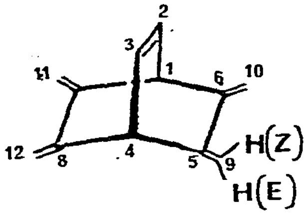
structure of 179 was confirmed crystallographically. It was reported that the "free" diene system in these and related compounds undergo reaction with a dienophile with a rate essentially the same as the free ligand [278].



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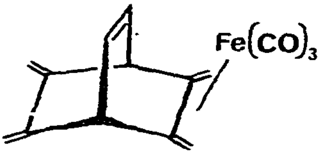

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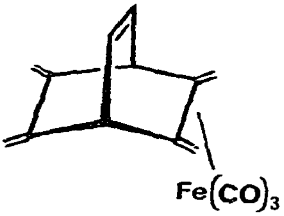

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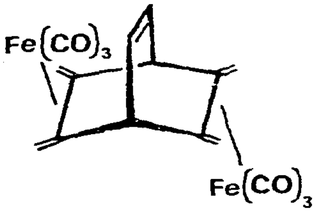

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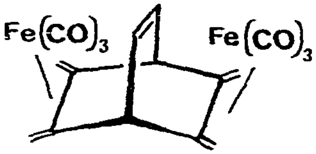

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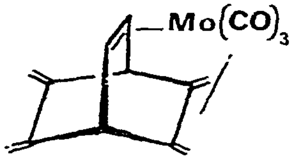

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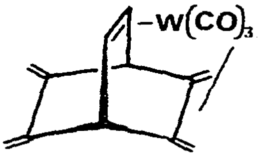

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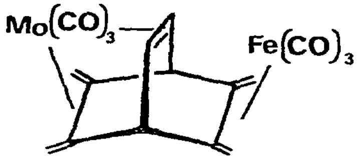

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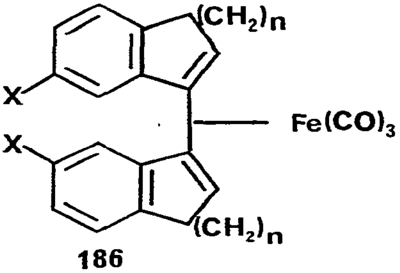
The reaction of $LFe(CO)_3$(L=isoprene, 1,3-cycloheptadiene, 2,5-dimethyl-1, 3-hexadiene) and $NaN(SiMe_3)_2$ yields the new anions $[LFe(CO)_2CN]^-$ [279].

Complexes of the general formula 186 were prepared from $Fe(CO)_5$ or $Fe_2(CO)_9$ and the appropriate diene. The Mössbauer spectra of these new complexes as well as reactions with $AlCl_3$ were reported [280].



186

n = 1,2,3

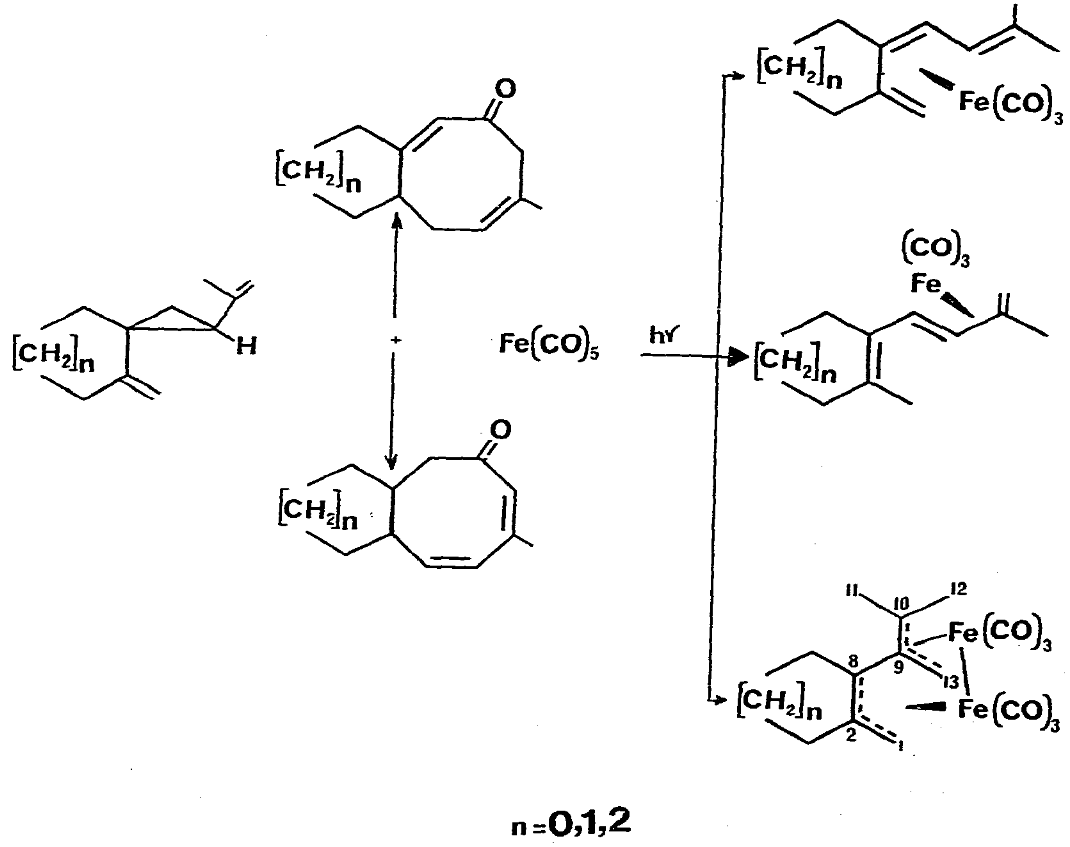
X = H,CH_3,CH_3O

An extensive investigation into the use of metal vapor synthesis to prepare iron diene-phosphite complexes has been reported. A large number of complexes were prepared, many of which are fluxional. As expected, undesirable byproducts are frequently encountered in these reactions but by careful consideration of the experimental conditions these problems can be minimized. In the preparations, C-H bond cleavage and hydrogen atom migration ractions are not unusual but once 18-electron complexes do form they are kinetically stable. The fluxional behavior of these molecules was investigated by temperature-dependent $^{31}P\{^1H\}$NMR; analysis of these spectra was presented in order to ascertain the nature of the rearrangement process [281]. Careful NMR line shape analysis has shown that the best mechanism to explain the intramolecular exchange in Fe(diene)L_3(L=P(OMe)$_3$; diene = butadiene, isoprene, and 2,3-dimethylbutadiene) is best described as diene rotation which would allow cyclical exchange of the three phosphorus ligands [282]. The protonation of (η^4-diene)iron(P(OR)$_3$)$_3$ complexes using acids of noncoordinating counterions yields (η^3-alkenyl)-iron complexes in which a hydrogen atom on the ligand also bonds the iron. The reactions proceed through a hydridoiron intermediate to give an η^3-enyl complex. The hydrogen transfer is believed to take place endo with respect to the metal. These complexes give rise to unusual NMR parameters and dynamic properties were also studied using variable temperature NMR [283].

The relative reactivities for a series of substituted dienetricarbonyliron complexes towards acetyl chloride under Friedel-Crafts conditions have been determined. Although substituent effects are generally small, substituted carbon atoms are not attacked and acyl groups are strongly deactivated [284].

The photolysis of trans-1-isopropenyl-4-methylenespiro [2-x] alkanes (x=4, 5, or 6) in the presence of $Fe(CO)_5$ yields three products as shown in Scheme 45A as well as the organic materials shown. Mechanistic pathways for the formation of these complexes were proposed [285]. The photolysis of (1,4-diaza-1,3-diene)$Fe(CO)_3$ with dienes yields : (1,4-diaza-1,3-diene)(1,3-diene)-FeCO complexes. The photoreaction consists of two consecutive steps, the first of which is thermally reversible [286]. The negative ion mass spectra of a family of (diene)$Fe(CO)_3$ complexes has been reported using a gas phase electron attachment setup [287].

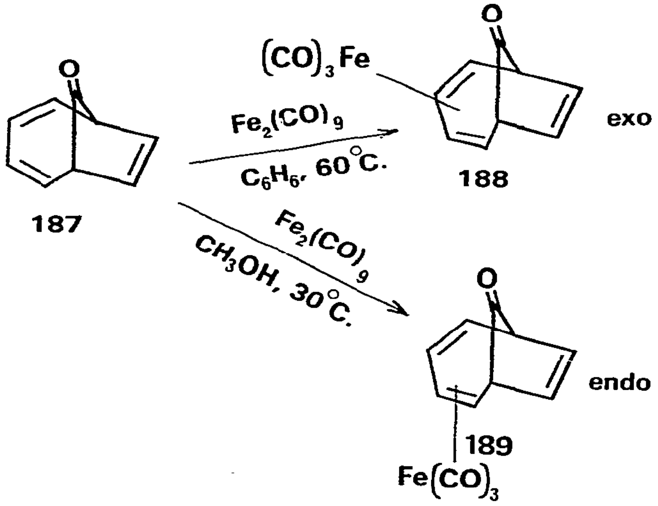
Scheme 45 A



Cyclic Diene and Higher Olefin Species

The reaction of 187 with $Fe_2(CO)_9$ yields either the endo or exo product depending on the reaction conditions as shown in Scheme 46. The free olefinic double bond of both 188 and 189 can be hydrogenated under mild conditions. In contrast, only 189 reacted with $NaBH_4$ to give the corresponding alcohol [288].

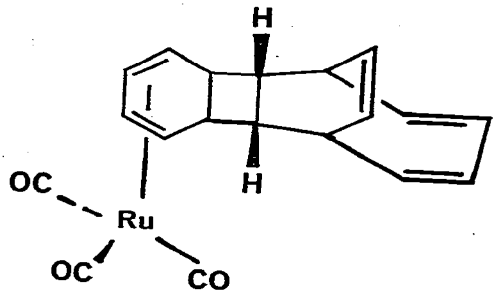
Scheme 46



Two more products have been identified crystallographically from the reaction of $Ru_4H_4(CO)_{12}$ and COT. They are 190 and 191, and 191 is fluxional as shown [289]. The reaction of hexafluorobut-2-yne and (η^4-cycloheptatriene)$Fe(CO)_3$ yields after replacement of a CO ligand with $P(OCH_2)_3CMe$ (in order to obtain good crystals) $Fe(CO)_2\{P(OCH_2)_3CMe\}(C_7H_8)(C_4F_6)_2$, the structure of which was solved by X-ray means. The structure of the tricarbonyl precursor thus established is shown in Scheme 47 along with a proposed mechanism for the formation of this complex [290].

A variety of metal atoms, including iron, have been reacted with 192. As expected, 193 is formed although it was shown that surface catalyzed reactions were occurring. Although a variety of other strained ring compounds did not react, 194 reacted to yield the four products shown in Scheme 48. Complex 195 also reacted to yield two products as shown in the Scheme [291].

A series of 8-alkoxyheptafulvene-$Fe(CO)_3$ complexes, 196, have been prepared. Cycloaddition reactions with $C_2(CN)_4$ lead to 8+2 cycloaddition products [292]. Although the reaction of methylenetriphenylphosphorane with 197 yielded an isomeric mixture of 198 in which a formal (1,9)-hydrogen sigma-



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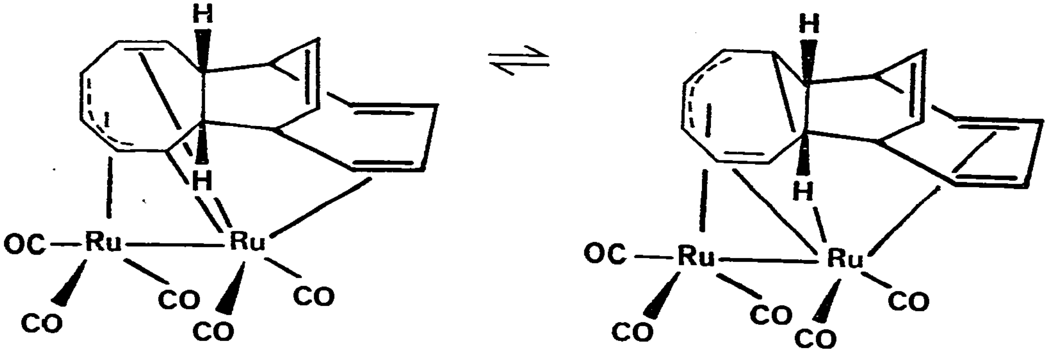
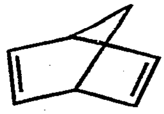


a

b

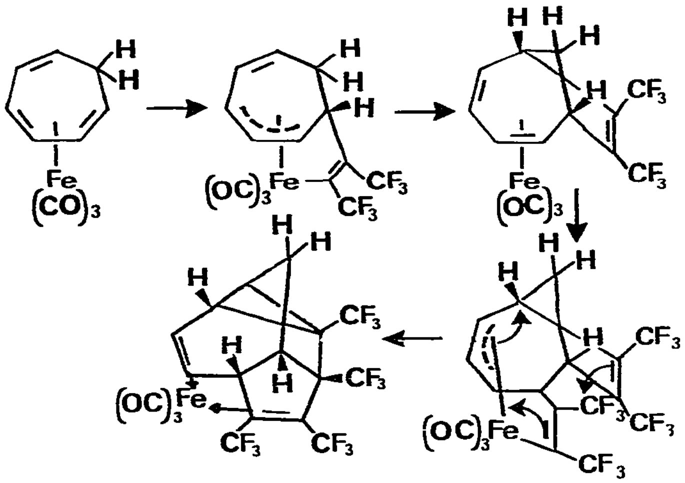
191

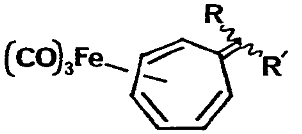
192



193

Scheme 47





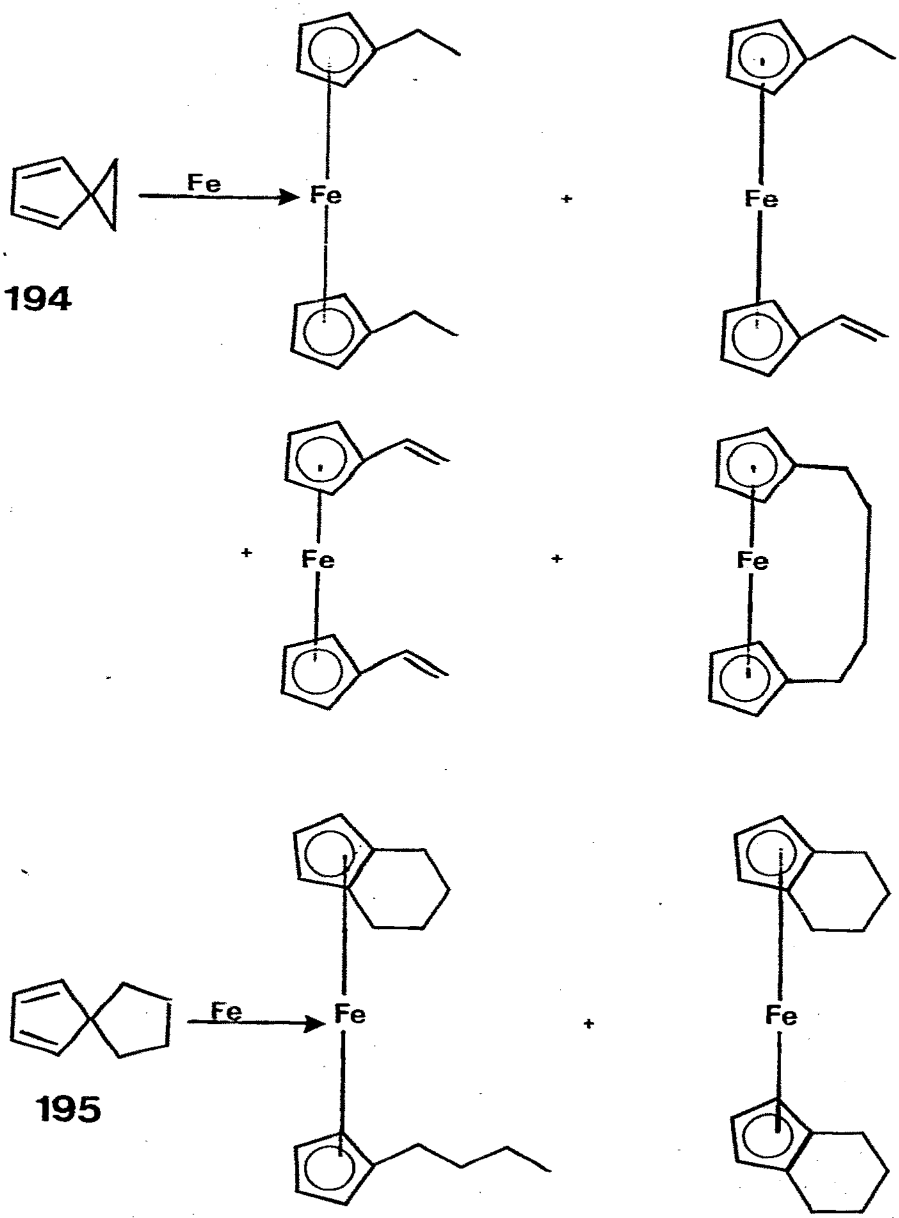
(R=H,Ph;
R'=OMe,OEt)

196

tropic shift has taken place, reaction with substituted phosphoranes yields the products 199. For X=Ph some of the cis isomer was also present. The complexes 199 do not rearrange to complexes analogous to 198, presumably because of the loss of extended conjugation. The complex 199 reacts with TCNE to yield 200, the 4+2 adduct [293]. Methanolysis of (5-cyano-η^4-1,3-cyclohexadiene)Fe$(CO)_3$ converts the cyano group into a C(:NH·HCl)OMe group which can be cyclized with diamines [294].

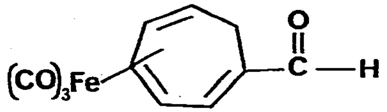
As shown in Scheme 49, the reaction of $(\eta^4\text{-}C_8H_8)Fe(CO)_{3-n}(P(OMe)_3)_n$ with $[N_2C_6H_4R\text{-}p]BF_4$ in CH_2Cl_2 yields 201 whereas in acetone 202 is formed. Both 201 and 202 can be deprotonated to yield 203 and 204, respectively. The organic ring in 203 was cleaved by standard means [295].

Scheme 48



194

195



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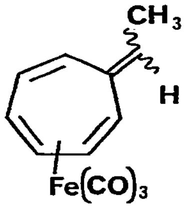

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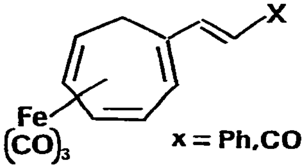
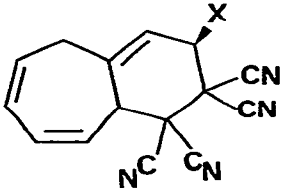


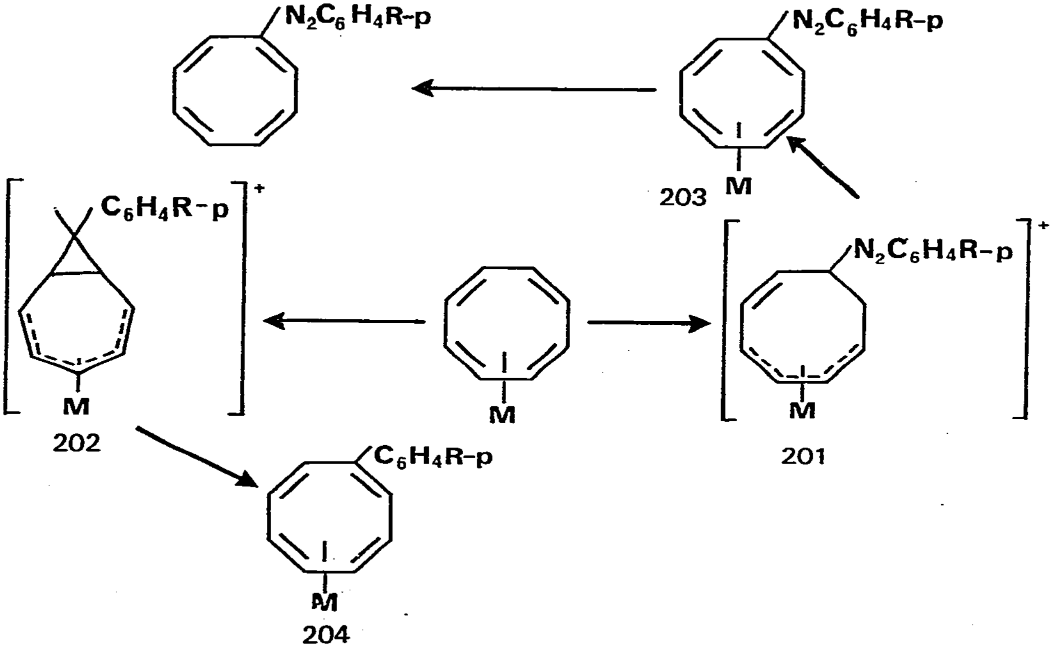
x = Ph,COOR,CN

199



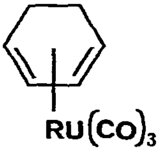
200

Scheme 49



The complexes $[M(C_6H_7)(CO)_3]BF_4$ (M=Fe, Ru, Os) react with NN-dimethylaniline (RH) to yield $M(C_6H_7R)(CO)_3$ complexes. The rates of various reactions were reported [296]. The interaction of aluminum trihalides with polyolefin$Fe(CO)_3$ complexes leads to the formation of Lewis acid adducts at the iron atom as shown by IR [297].

The reaction of $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ with halo- and dihalocyclohexenes has been investigated as a route to 1,3-cyclohexadiene$Fe(CO)_3$ via an elimination reaction. 3-Bromocyclohexene, 3,4-dibromocyclohexene and 3,6-dibromocyclohexene were effective but yields were low [298]. The reaction of $Ru_3(CO)_{12}$ with 1,3-cyclohexadiene leads mainly to the mononuclear species 205 and also to small amounts of materials thought to be 206 and 207. If a large excess of 1,3-cyclohexadiene is used (or treatment of 207 with excess cyclohexadiene) the product is $Ru_4(CO)_9(C_6H_6)(C_6H_8)$, shown to have the structure in Figure 44 by crystallographic techniques [299]. The heptalene-bis($Fe(CO)_3$) complex 209 is readily formed from heating 208 with (benzylideneacetone)$Fe(CO)_3$. X-ray analysis [142] demonstrates that the $Fe(CO)_3$ groups are located on the same side of the heptalene ligand. Reaction of 209 and phosphorus oxide chloride in DMF yields the free ligand 210 [300].



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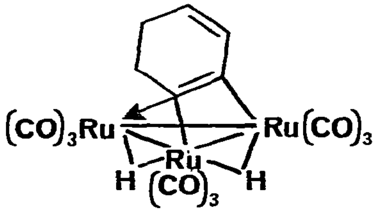

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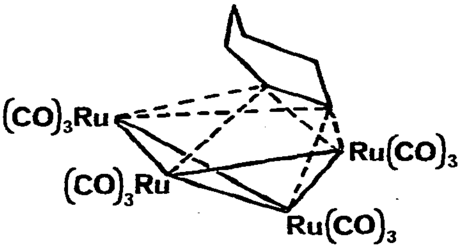
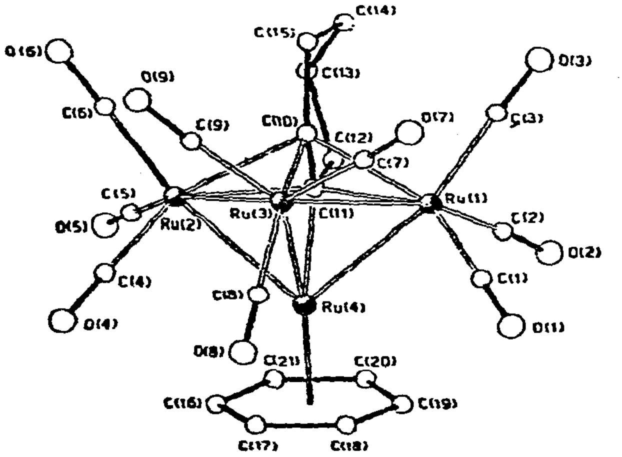
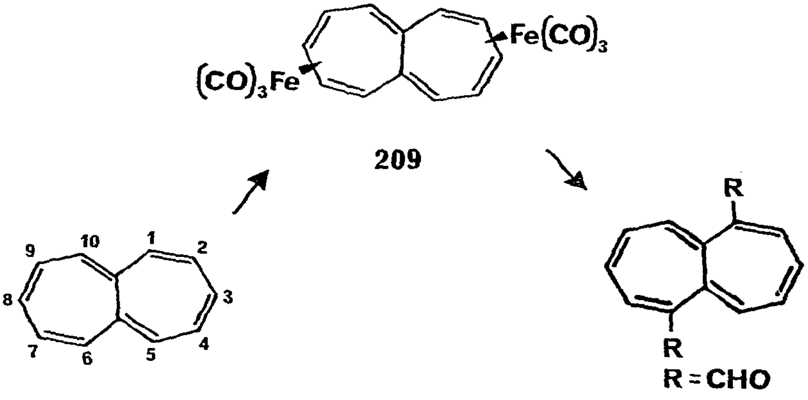


207

FIGURE 44





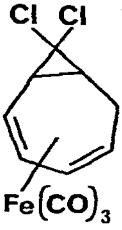
208

209

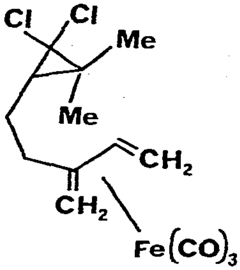
210

The reaction of cycloheptatrieneFe(CO)$_3$ and myrceneFe(CO)$_3$ with CCl$_2$ leads to the cyclopropyl derivatives 211 and 212 [301]. The products formed from the reaction of Fe$_3$(CO)$_{12}$ and gasoline have been studied [302].

The negative ion mass spectrum of (η^4-cycloheptatriene)Fe(CO)$_3$ has been reported and molecular ions are observed. A possible 18 electron di-radical was proposed as a possible structure for the species observed in the mass spectrum experiment [303].



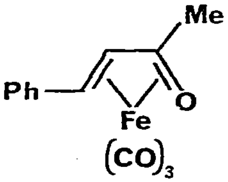
211



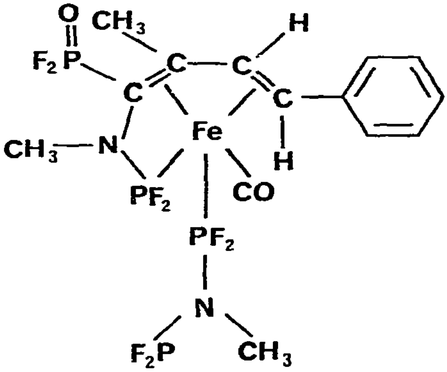
212

Heterodiene Species

The reaction of 213 with a variety of acyclic conjugated dienes yields diene$Fe(CO)_3$ complexes in moderate yield. The non-planar, tub-shaped ligands 1,3- and 1,5-cyclooctadiene are unreactive. Competition studies determined the relative rate of reaction of various dienes [304]. The reaction of $CH_3N(PF_2)_2$ with 213 did not yield the simple displacement product expected but yields instead 214, as shown by X-ray crystallographic techniques [305].

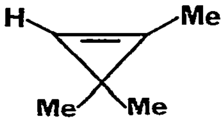


213

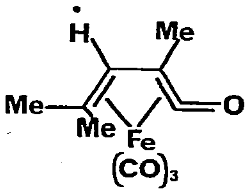


214

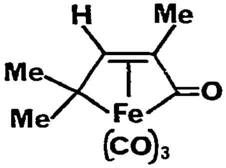
The complex $C_6H_{10}COFe(CO)_3$ previously reported in low yield from the reaction of $Fe_3(CO)_{12}$ with 215 is prepared from $Fe_2(CO)_9$ in much higher yield. An X-ray crystal structure shows that this product contains a vinylketen unit that is best represented as a resonance hybrid of 216a and 216b [306].



215



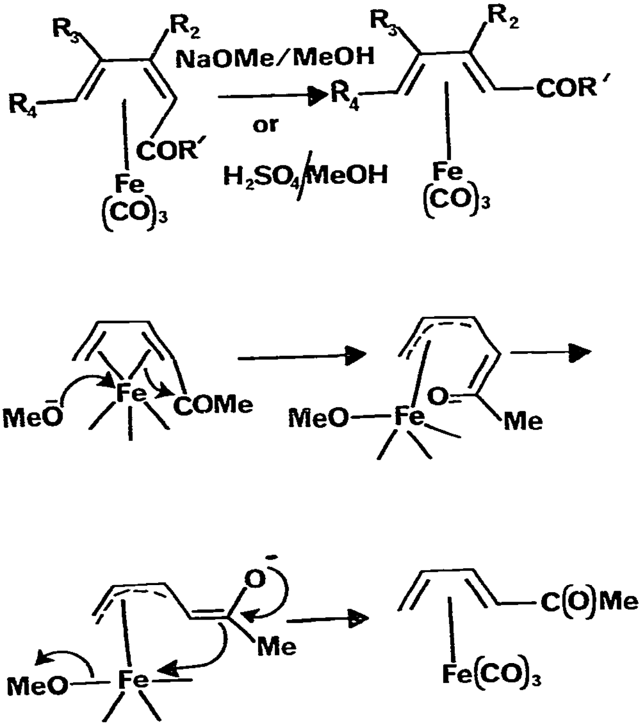
216a



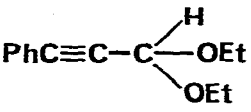
216b

Both the acid- and base-catalyzed anti to syn isomerization of (dienone)tricarbonyliron complexes has been investigated mechanistically (see Scheme 50). In methanol, the reactions are first order in methoxide or methyloxonium ion. Although changes in the various R groups have only a small effect on the rate, substitution of a CO group with PPh_3 slows the rate substantially. In CH_3OD the reaction proceeds with ca. 40% deuterium incorporation α to the carbonyl group. No deuterium is incorporated back into starting material. The conclusion is that rate-determining nucleophilic attack of methoxide (or methanol) at iron takes place as shown in the Scheme [307].

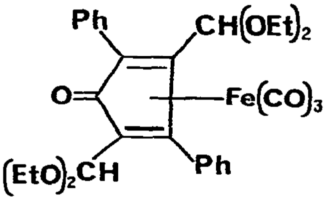
Scheme 50



The reaction of $Fe_2(CO)_9$ and 217 yields 218 [308]. The reaction of 219

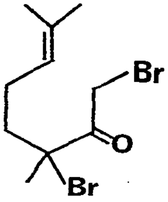


217

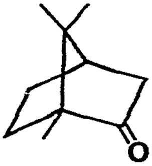


218

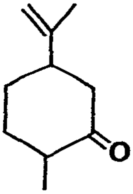
with $Fe_2(CO)_9$ yields 220 (54%) and 221 (20%) and other products in low yield. This intramolecular [3 + 2] ring closing reaction worked for other similar materials although the reaction is affected by the substitution pattern around the double bond [309].



219



220



221

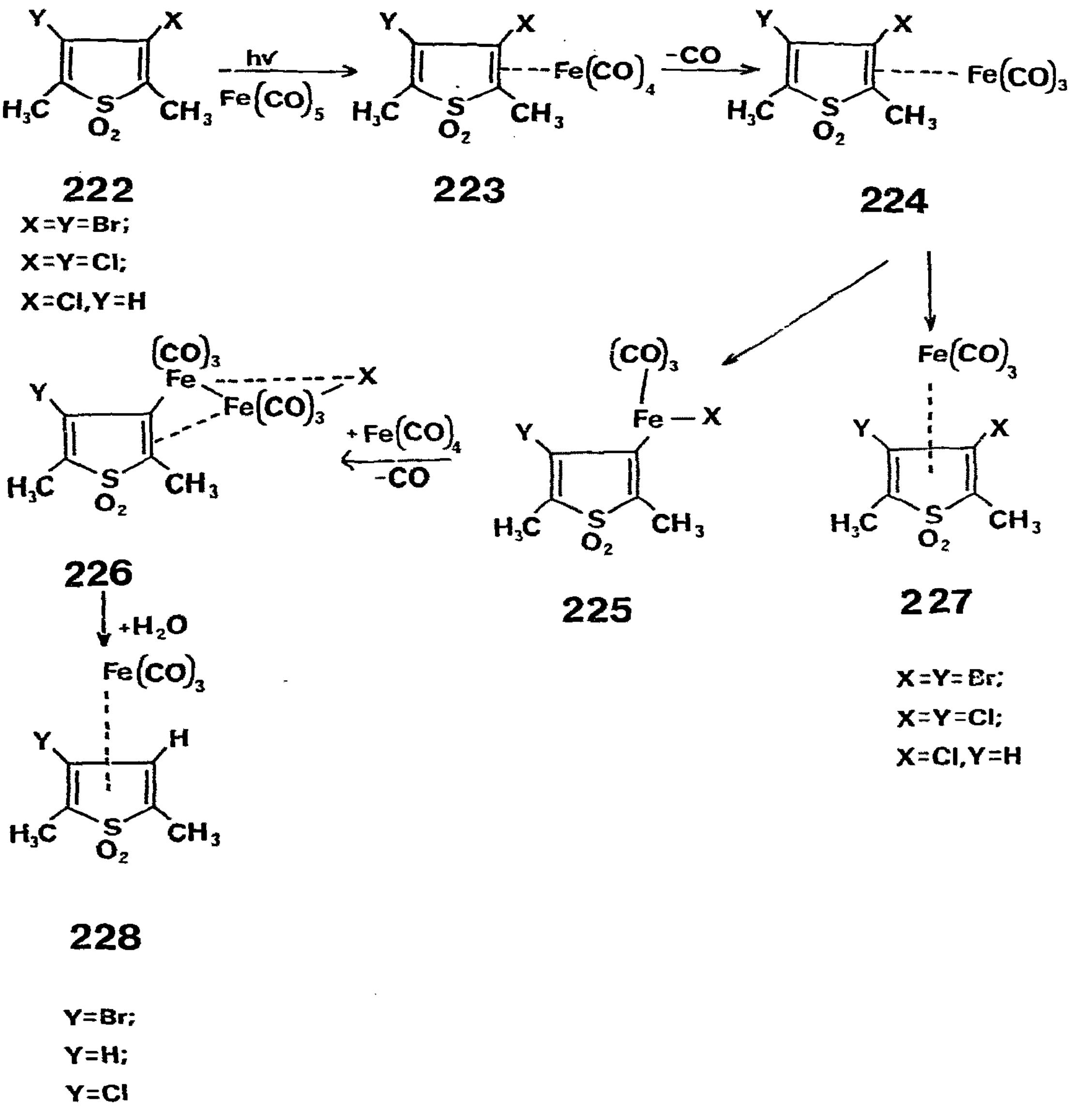
The irradiation of $Fe(CO)_5$ in the presence of various halo-substituted 2,5-dimethylthiophene-1,1-dioxide derivatives (222) yields a number of products (227 and 228) as shown in Scheme 51. 223 to 226 are proposed intermediates in the formation of the new complexes [310].

The complex 3-(trifluoromethyl)-1-phenyl-4-fluoro-1-azabuta-1,3-diene-2,4-diylbis(CpFe(CO)$_2$) has been prepared by the reaction of $[CpFe(CO)_2]^-$ and N-phenylbis(trifluoromethyl)ketenimine. The product was characterized crystallographically [311].

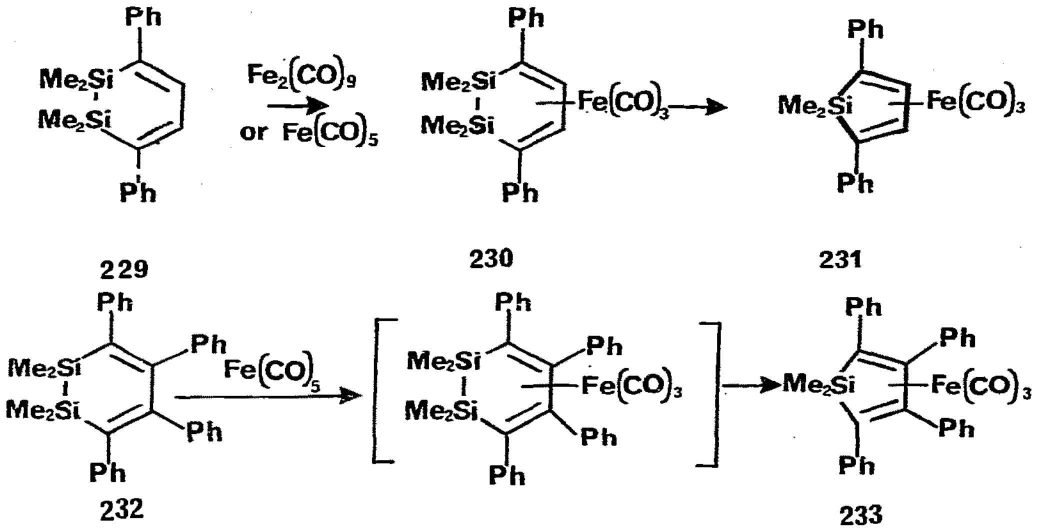
As shown in Scheme 52, the reaction of 229 and $Fe_2(CO)_9$ or $Fe(CO)_5$ at 130°C yields 230. Heating 230 at 160°C yields 231. A similar reaction with 232 yields 233 directly [312].

Complete characterization of the products of the reaction of $Fe(CO)_5$ with substituted silacyclohexa-2,4-dienes as shown in Scheme 53 has been reported [313]. The reaction of bis(trimethylsilyl)butadiyne ($Me_3SiC_4SiMe_3$) and $Fe(CO)_5$ yields 234 as shown crystallographically [314].

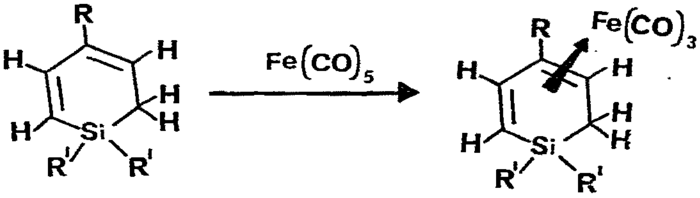
Scheme 51

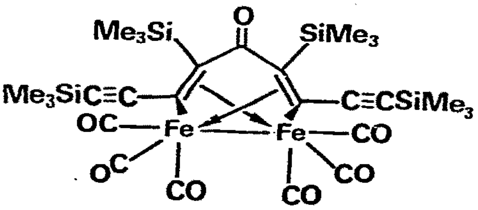

hν
Fe(CO)5
-CO
+Fe(CO)4
-CO
+H2O
222
X=Y=Br;
X=Y=Cl;
X=Cl,Y=H
223
224
225
226
227
X=Y=Br;
X=Y=Cl;
X=Cl,Y=H
228
Y=Br;
Y=H;
Y=Cl

Scheme 52



Scheme 53





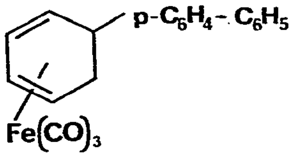
234

DIENYL COMPLEXES

The fluxional behavior and substituent rate preference of the iron in cationic monosubstituted tropyliumiron tricarbonyl complexes has been studied in detail. The results suggest that relatively little of the positive charge resides on the ring carbon atoms [215].

The reaction of many $[Fe_2(\eta^5\text{-dienyl})_2(CO)_{4-n}(CNR)_n]$ (R=alkyl or benzyl; n=1,2; dienyl = C_5H_5 or C_9H_7) complexes with strong acids produces the cations $[cis - Fe_2(\eta^5\text{-dienyl})_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNHR)]^+$ and $[cis - Fe_2(\eta^5\text{-dienyl})_2(CO)_2(\mu\text{-}CNHR)_2]^{2+}$. The X-ray crystal structure of $[cis - Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNHMe)]BF_4$ is reported [316].

$[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ and $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]^+$ are both reduced in solution by CH_3CN, probably by a free radical pathway [317]. The allegedly inert BPh_4^- anion reacts readily with $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ to yield the biphenyl species 235. It is believed that the reaction is initiated by an attack on a boron phenyl group by the iron starting material [318].

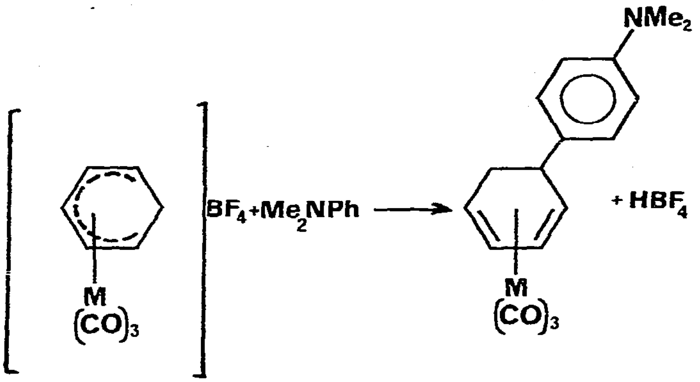


235

The reactions of (pentadienyl)$Fe(CO)_3$ cations with $NaBH_4$, $NaBH_3CN$ and $LiHBEt_3$ have been reported. To explain the fact that the products are different for $LiHBEt_3$, an initial attack on a coordinate CO is proposed for this reactive hydride source whereas direct attack takes place for $NaBH_3CN$. $NaBH_4$ is intermediate between these two and reacts by both mechanisms [319]. The complex $(Ph_3GeC_7H_7)Fe(CO)_3$ undergoes endo proton abstraction when reacted with t-BuOK to yield $[(Ph_3GeC_7H_6)Fe(CO)_3]^-$. Preliminary reaction of this anion as well as variable temperature NMR data were discussed [320].

A detailed kinetic study of the reactions shown in Scheme 54 (M=Fe,Ru) has been carried out. The rate law is bimolecular in both cases suggesting that both reactions take place by direct addition at the dienyl rings. The rate was greater for the iron complexes suggesting that the $Ru(CO)_3$ group is a more effective overall electron donor than $Fe(CO)_3$ [321]. A variety of tertiary phosphines and phosphites react with iron dienyl complexes such as $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$ to yield the phosphonium adduct complexes $[(\eta^4\text{-}C_6H_7\text{-}PR_3)Fe(CO)_3]BF_4$. The rate and activation parameters indicate that the Lewis

Scheme 54



bases add directly to the dienyl rings [322]. The reactions of $(\eta^5\text{-}C_6H_7)\text{-}Fe(CO)_2I$ and $(\eta^5\text{-}C_7H_9)Fe(CO)_2I$ with PBu_3^n and PPr_3^i have been shown to occur by the stepwise reaction shown in Scheme 55 in which the phosphine initially reacts with the diene ligand [323].

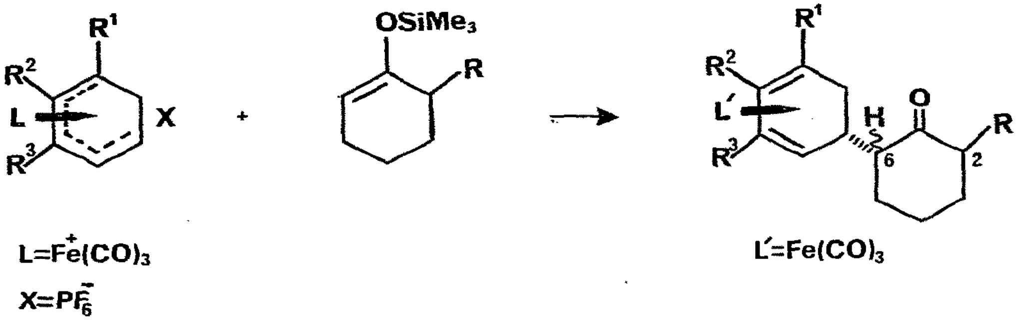
SCHEME 55

$$\begin{tikzcd}
{[Fe(dienyl)(CO)_2I] + PR_3} \arrow[r, "k_1"] & {[Fe(R_3P\cdot diene)(CO)_2I]} \arrow[d, "PR_3"] \\
& {[Fe(R_3P\cdot diene)(CO)_2(PR_3)]I}
\end{tikzcd}$$

The reaction of various $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ cations (236) with trimethylsilyl ethers takes place as shown in Scheme 56 [324]. The reaction of 236 with phenylamine derivatives in CH_3CN at room temperature yields 237 (R=H, Me, OMe). If 236 is added dropwise to a refluxing CH_3CN-aniline solution, C-alkylation takes place to yield mainly 238. Other derivatives were tested [325].

The complexes 239 with a variety of R and R' groups were not stable and converted to 240. The mechanism of this reaction was investigated [326]. The organic spiro compound 241 was prepared in eight steps using the intermediate 242 [327].

Scheme 56



236= $R^1=R^2=R^3=H$

$R^1=R^3=H$, $R^2=OMe$

$R^1=COOMe$, $R^2=H$,

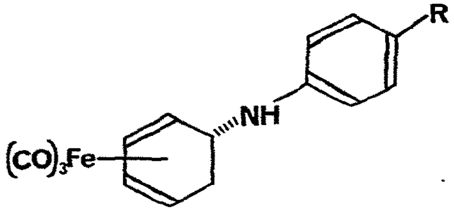
$R^3=Me$

$R^1=R^2=R^3=H$

$R^1=R^3=H$, $R^2=OMe$

$R^1=COOMe$, $R^2=H$,

$R^3=Me$



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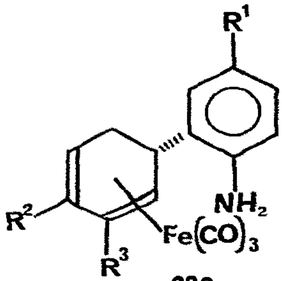

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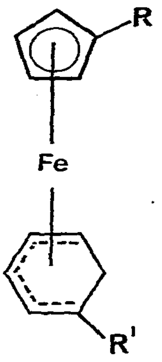

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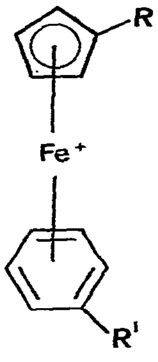
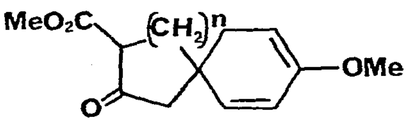


240



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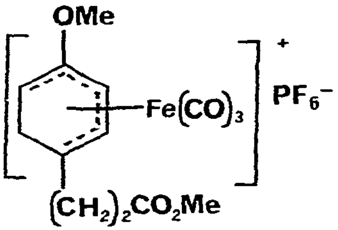


242

CYCLOPENTADIENYL COMPLEXES

Binuclear Species

A variable temperature NMR investigation of $Cp_2Fe_2(CO)_2(CNBu^t)_2$ has revealed that this molecule exists as a mixture of $Cp_2Fe_2(\mu\text{-}CO)_2(CNBu^t)_2$ and $Cp_2Fe_2(\mu\text{-}CO)(\mu\text{-}CNBu^t)(CO)(CNBu^t)$ *in solution*. These isomers interconvert by two different pathways [328]. The complexes $Cp_2Ru_2(CO)_3(CNR)(R{=}Me,Et,Pr^i,Bu^t)$ exists as cis/trans mixtures of bridged and terminal isonitrile isomers. These molecules are fluxional and obey the scrambling mechanism previously proposed for analogous iron complexes by Adams and Cotton [329]. In a study aimed at the effect of substitution of various ligands on CO-bridged and non-bridged isomers in solution, various new $(\eta^5\text{-dienyl})FeCo(CO)_5L$ complexes have been prepared (η^5-dienyl=C_5H_5, MeC_5H_4, C_9H_7; $L = PR_3$, AsR_3). In the solid state, some are bridging and some are non-bridging isomers. In solution, many exist as complex equilibrium mixtures. Overall the trends are as expected in that the non-bridging isomers are favored by high temperature, bulky ligands and for the η^5-dienyl series $C_9H_7 > MeC_5H_4 > C_5H_5$ [330].

The complex $[(CH_3)_5C_5Ru(CO)_2]_2$ has been prepared in good yield from the reaction of $Ru_3(CO)_{12}$ with pentamethylcyclopentadiene in boiling n-decane [331]. The known complex $Cp_2Fe_2(CO)_3(PPh_3)$ can be prepared in modest yield by reaction of $Cp_2Fe_2(CO)_4$ with excess PPh_3 in refluxing benzene. In the purification by column chromatography, the column was cooled to 10°C to prevent decomposition. This complex decomposes in a sealed tube to $Cp_2Fe_2(CO)_4$ but in an open tube to a mixture of this product and $Cp_4Fe_4(CO)_4$. In fact this tetrameric material can be prepared in good yield by the reaction of $Cp_2Fe_2(CO)_4$ with PPh_3 [332].

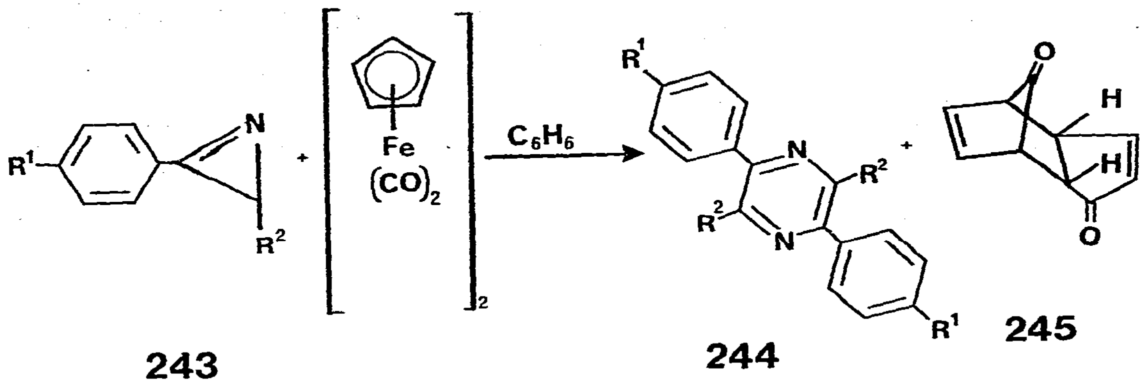
The structure of $Cp_2Fe_2(CO)_3CS$ has been determined crystallographically. The CS group is in a bridging position as expected from earlier work showing CS to prefer bridging sites over CO. The molecule contains cis-Cp groups and terminal CO ligands [333].

The reaction of Fp_2 with a series of 2-arylazirines (243) yields 244 and 245 as shown at the top of Scheme 57. 245 is believed to form as shown in the bottom of the Scheme [334].

The reaction of two equivalents of $[CpFe(CO)_2]^-$ and hexafluorocyclotriphosphazene (246) yields 247 and 248 as shown. Although 247 has only tentatively been characterized, the X-ray crystal structure of 248 was reported [335]. Irradiation of a solution of $[CpFe(CO)_2]_2$ and excess $PhN(PF_2)_2$ yields 249. Reaction of $PhN(PF_2)_2$ with $Fe(CO)_5$ under irradiation or $Fe_3(CO)_{12}$ upon heating yields $[PhN(PF_2)_2]_2Fe_2(CO)_5$ [336].

Results have been presented that point to the mechanism in Scheme 58 being operable in the photolytic substitution of $[CpFe(CO)_2]_2$ with phosphine and phosphite ligands. Thus the bridging CO group greatly influences the reactivity when compared with $Mn_2(CO)_{10}$ which reacts first by dissociation of the M-M bond to give monomers [337]. A detailed analysis of the electron impact induced decomposition of 250 has been reported using both high resolution techniques and ^{2}H-labeling [338]. Molecular orbital calculation on trans-$[CpFe(CO)_2]_2$ and bridged $Fe_3(CO)_{12}$ indicate that there is no direct metal-metal interaction. Instead, the short M-M distance is better described as arising from multicentered linkages between the metal and the bridging carbonyl ligands [339].

Scheme 57



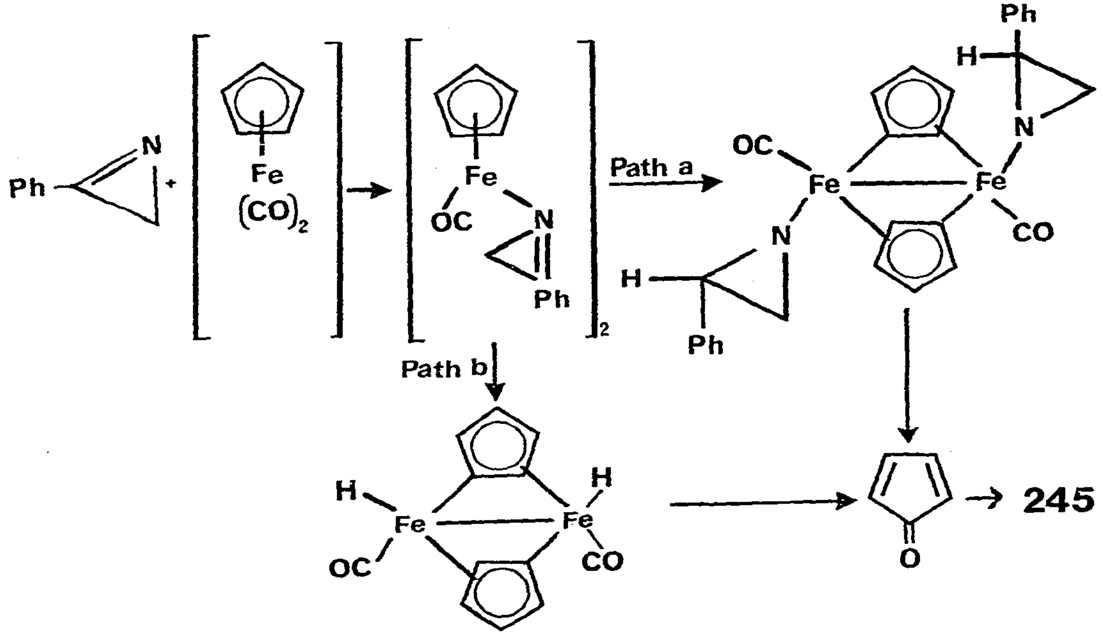
243 **244** **245**

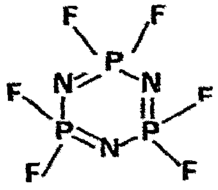
$R^1 = R^2 = H$

$R^1 = CH_3, R^2 = H$

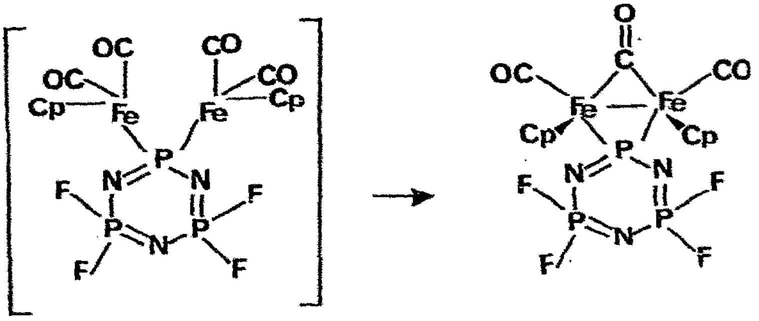
$R^1 = Br, R^2 = H$

$R^1 = H, R^2 = CHO$

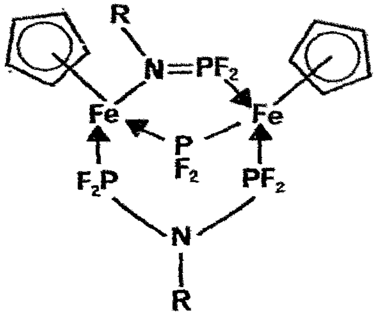




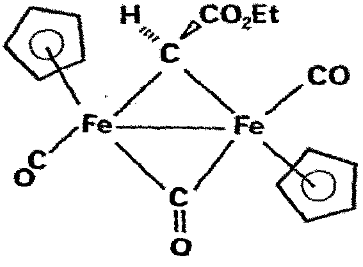
246



247 **248**

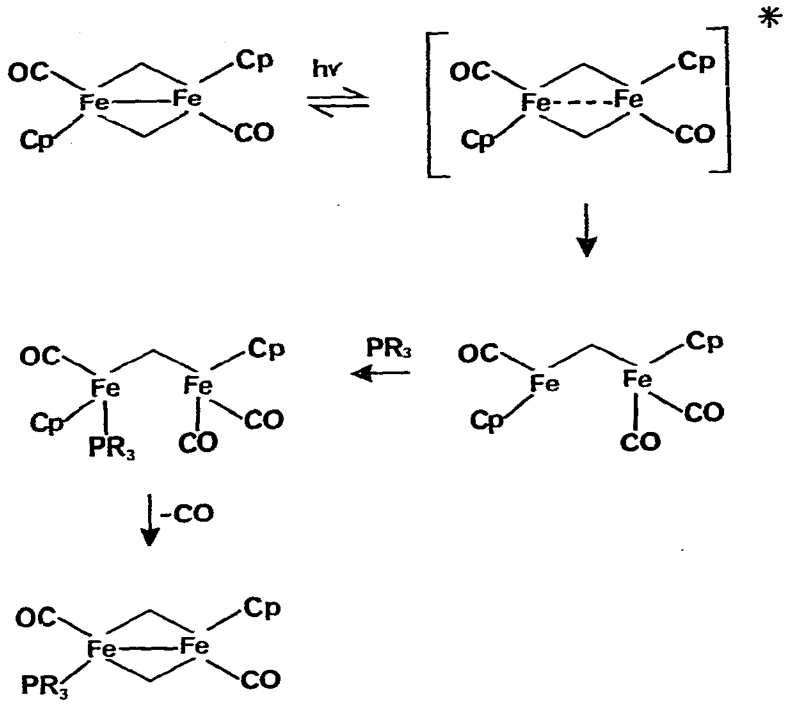


249



250

Scheme 58



Anionic and Cationic Species

A variety of metal carbonyl dimers, including $[CpFe(CO)_2]_2$, have been shown to react with trialkylborohydrides to produce rapidly the transition metal monoanion $[CpFe(CO)_2]^-$. Although quite good for most dimers, $[CpFe(CO)_2]_2$ proved not as reactive [340]. The reaction of Fp^- with various imidoyl chlorides has been reported. The photolytic decarbonylation of the new complexes was also reported [341]. The reaction of a number of organometallic anions with $ClCH_2COCl$ has been reported. For $[CpFe(CO)_2]^-$, the major product was Fp_2 [342].

The reaction of $[CpFe(CO)_2]^-$ with Ph_3E(E=Al,Ge,In) yields $[Ph_3EFe(CO)_2$-$Cp]^-$derivatives which were isolated as their Et_4N^+ salts. The solid state structure of the Ph_3Al derivative is shown in Figure <u>45</u>. The Fe-Al bond length of 2.510A° is in the range appropriate for a Fe-Al single bond [343]. Triphenylborane and $Et_4N[FeCp(CO)_2]$ in Et_2O form the Lewis acid-base adduct $Et_4N[Ph_3BFeCp(CO)_2]$. From dilute solutions a second compound precipitates slowly and was shown crystallographically to be a dimer product similar to cis-$[FeCp(CO)_2]_2$ in which the Ph_3B group has migrated to the η^5-C_5H_5 ring as shown in Figure 46 [344].

FIGURE 45

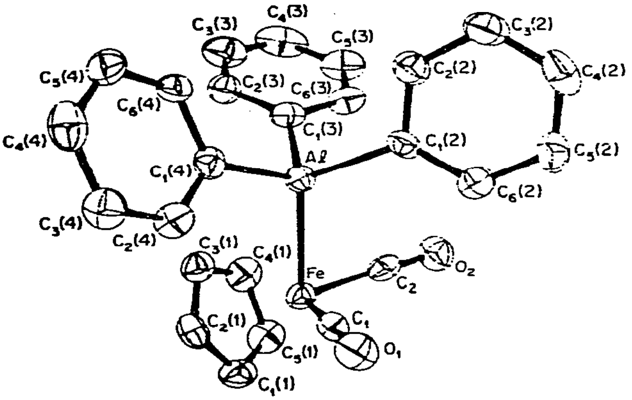
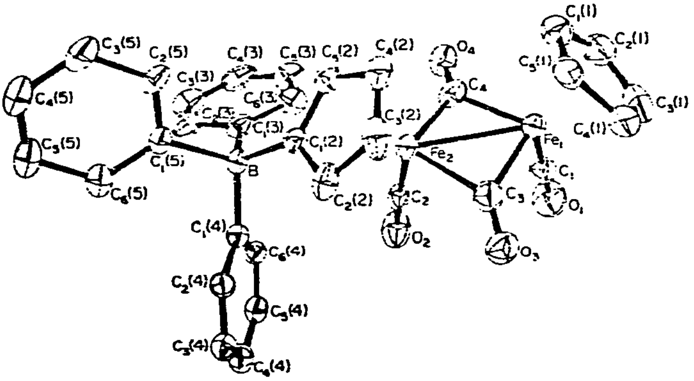


FIGURE 46



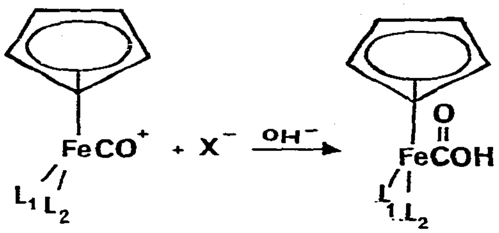
A series of substituted cyclopentadienyl iron carbonyl cations reacts with base as shown in Scheme 59. For the $L_1=L_2=CO$ case, the metallocarboxylic acid derivative is unstable but it can be isolated for the case in which one of the ligands is PPh_3. Interestingly, $CpFe(CO)(PPh_3)(COOH)$ is amphoteric toward acids and bases and, depending on the condition, many ionize in two ways as shown below.

$$MCO^+ + OH^- \rightleftarrows MCOOH \rightleftarrows MCOO^- + H^+$$

The ester derivative, $CpFeCOPPh_3COOMe$, prepared from a similar reaction with OMe^-may also be induced to ionize to MCO and OCH_3^- [345].

The reaction of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2L]^+$(L = CO, MeCN, MeNC, PPh_3, PEt_3) and $[CpOs(CO)_3]^+$ with NH_3 yields $CpRu(CO)(L)(CONH_2)$ and $CpOs(CO)_2$-$(CONH_2)$ complexes. NH_3 also adds to $[CpRu(CO)_2(\eta^2\text{-}C_2H_4)]^+$ to yield

Scheme 59

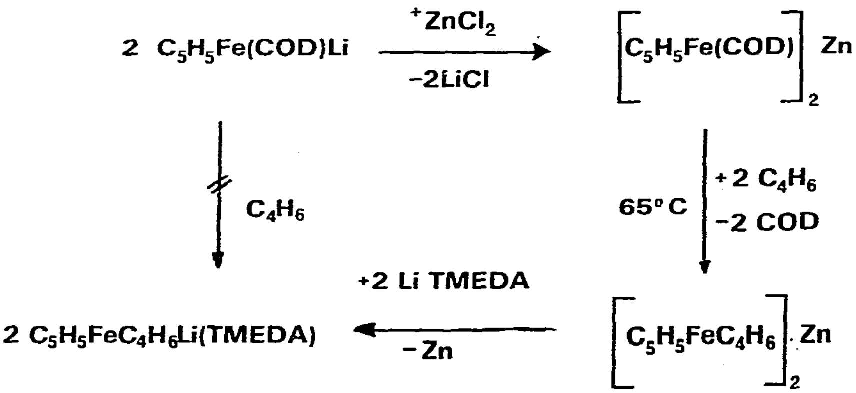


$[CpRu(CO)_2(CH_2CH_2NH_3)]^+$ [346]. The structure of $CpRu(CO)_2CONH_2$ was determined crystallographically [347].

Methylation of $Fp\text{-}CH_2SCH_3$ proceeds smoothly to prepare $[FpCH_2S(CH_3)_2]^+$. This reagent reacts with a variety of olefins to form cyclopropane derivatives. The reaction on cis and trans olefins is stereospecific [348].

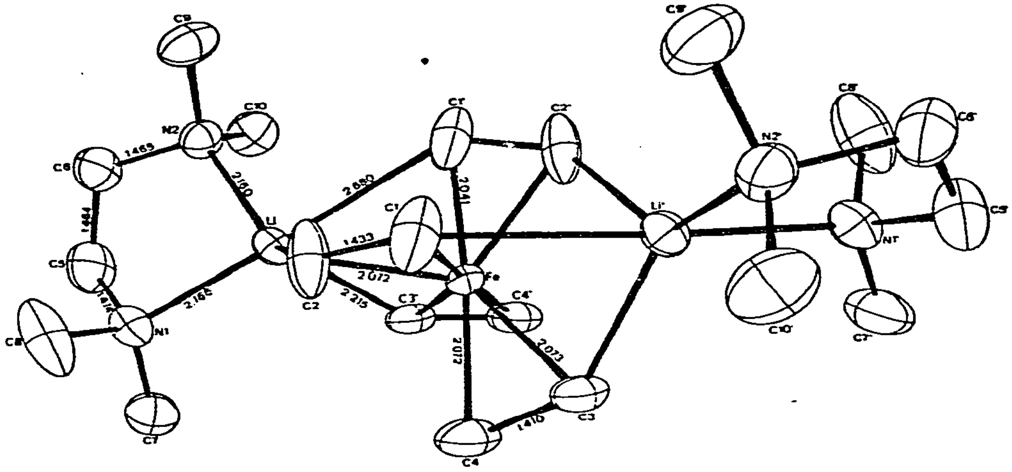
As shown in Scheme 60, reaction of ferrocene, lithium sand and 1,5-cyclooctadiene (COD) or C_2H_4 leads to CpFe(COD)Li or $CpFe(C_2H_4)_2Li$ which can be crystallized as TMEDA adducts. These complexes can be converted into other polynuclear complexes as shown. Also, CpFe(COD)Li reacts with Ph_3CCl to yield the 17 electron radical monomer CpFe(COD) [349]. Use of excess lithium in the reaction with ferrocene in the presence of C_2H_4 followed by

Scheme 60



addition of TMEDA leads to the isolation of $(C_2H_4)_4FeLi_2(TMEDA)_2$, the structure of which was solved crystallographically as shown in Figure 47. This complex reacts with COD to form $(COD)_2FeLi_2(TMEDA)_2$ [350]. The high pressure reaction of CO with a 1/3/1/1 mixture of ferrocene /$AlCl_3$/Al/H_2O in heptane produces $[CpFe(CO)_3]Cl$ in good yield [351]. The structure of $[CpFe(CO)\{(Ph_2P)_2CH_2\}]BPh_4$ has been determined crystallographically [352].

FIGURE 47



The kinetics of the addition of $Bu^n{}_3P$ and PPh_3 to the ethylene ligand in $[Fp\text{-}\eta^2\text{-}C_2H_4)]^+$ has been reported. The rate law as well as the negative ΔS^* is consistent with direct addition [353].

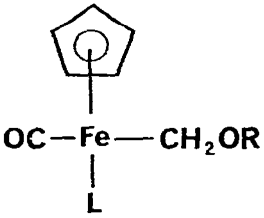
In a general article on $CpM(CO)_2$-ligand complexes, the electronic structure of $CpFe(CO)_2$-alkyl, carbene, alkyne and alkene complexes has been analyzed with emphasis on conformational preferences and rotational barriers. The structure of the methylene complex is predicted to be that which places the H-C-H fragment in the symmetry plane of the $CpFe(CO)_2$ fragment because a better π-backbonding orbital on the metal of appropriate symmetry can interact with the empty p orbital on the methylene carbon. For similar reasons the acetylene and ethylene complexes are predicted to have the structure with the ligand bisecting the symmetry plane of the molecule. Here backbonding into the π^* orbital of the ligand is maximized [354]. Similar calculations on $[CpFe(CO)_2(\eta^3\text{-}C_3H_5)]^+$ show the endo configuration to be slightly more stable than the exo isomer. Interestingly, a simple rotation of the π-allyl ligand to interconvert these two isomers has a high barrier (46 kcal/mol). Other mechanisms such as a π-σ-π rearrangement must be operative [355].

The Mössbauer - effect isomer shifts for a family of cyclopentadienyliron cations containing CO, PPh_3, CNMe and $C(NHMe)_2$ ligands has been reported. The results show an increase in ($\sigma + \pi$) bonding in the order $L = PPh_3 < CNMe \cong C(NHMe)_2 < CO$. The indenyl derivatives were also studied [356].

Carbene and Vinylidene Complexes

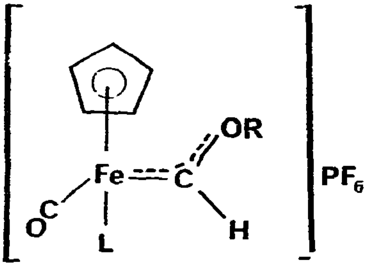
Neutral and cationic complexes of the formula CpFe(CO)(CNR)(L)(L = CN, CNR; R = Me, Pr^i) react with dimethylamine to form new trisubstituted diaminocarbene complexes. These complexes all readily revert to starting material and exist totally in one isomeric conformation [357].

Hydride can be abstracted by $Ph_3C[PF_6]$ from alkoxymethyl iron complexes 251 to give alkoxycarbene salts in 252. The phosphine substituted complexes are more stable as expected. It was hoped that complexes 252 would dealkylate with iodide to yield η^1-formyl complexes. Reaction of 252 with I^- yielded instead, $[CpFe(CO)(L)CO]^+$ and $CpFe(CO)LCH_2OR$. A mechanism was proposed in which the iron-formyl complex did form but then reacts rapidly with the starting material [358].



251

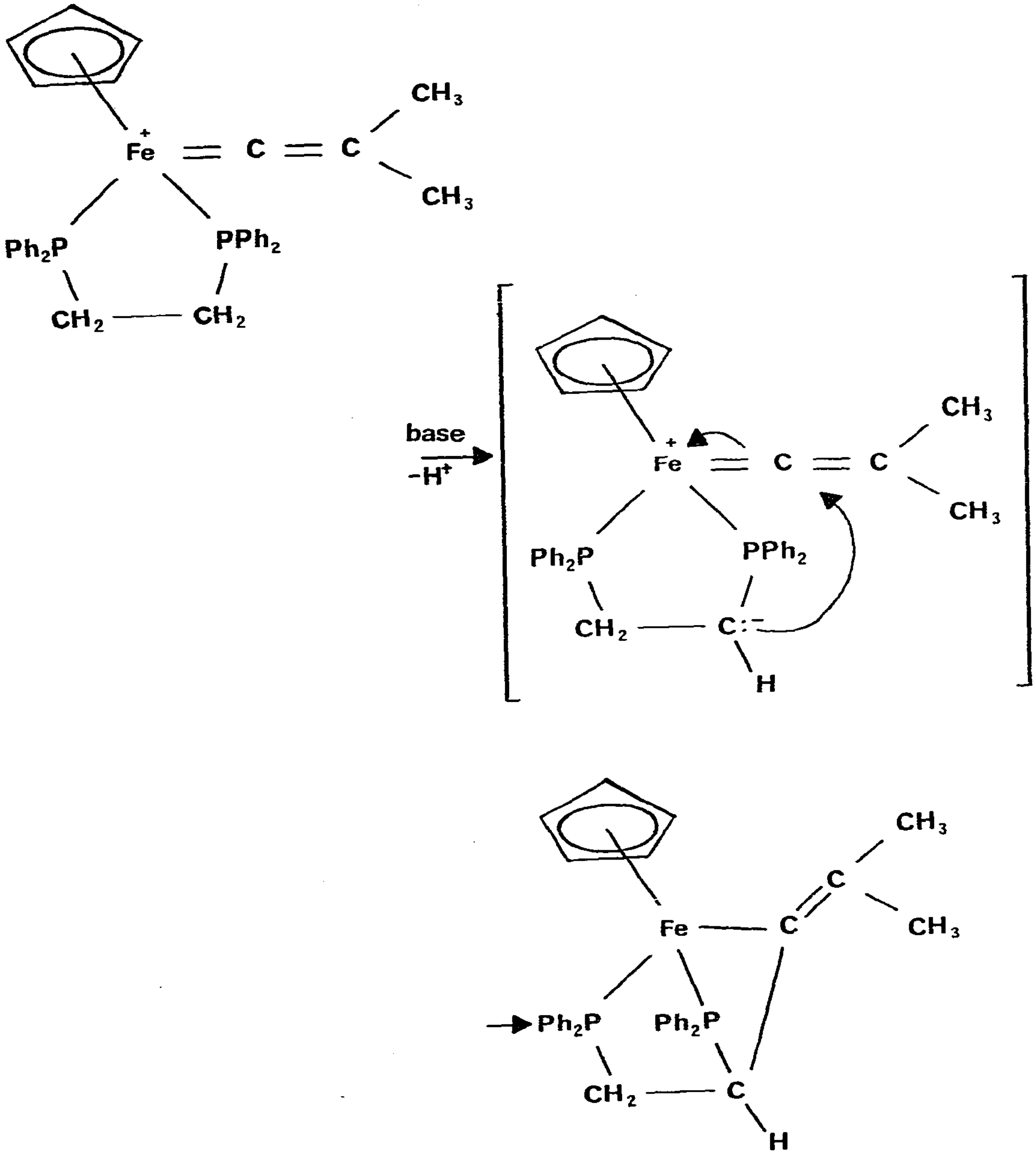
L=CO,PPh_3
R=Me,Et



252

The reaction of CpFe(dppe)Cl with $CH_3C{\equiv}CLi$ followed by methylation with CH_3OSO_2F yields the vinylidene complex $[CpFe(dppe)(C{=}C(CH_3)_2)](SO_3F)$ shown in Scheme 61. This complex reacts with base by deprotonation of the ligand followed by a cyclization reaction with the vinylidene ligand to yield 253, characterized by NMR and crystallographic techniques [359]. The alkynyl complex 254 reacts with $C_2(CN)_4$ to yield the cyclic product 255, presumably through the dipolar intermediate shown in Scheme 62. With the PPh_3 derivative, 256, a mixture of 257 and 258 is observed. Similar reactions with

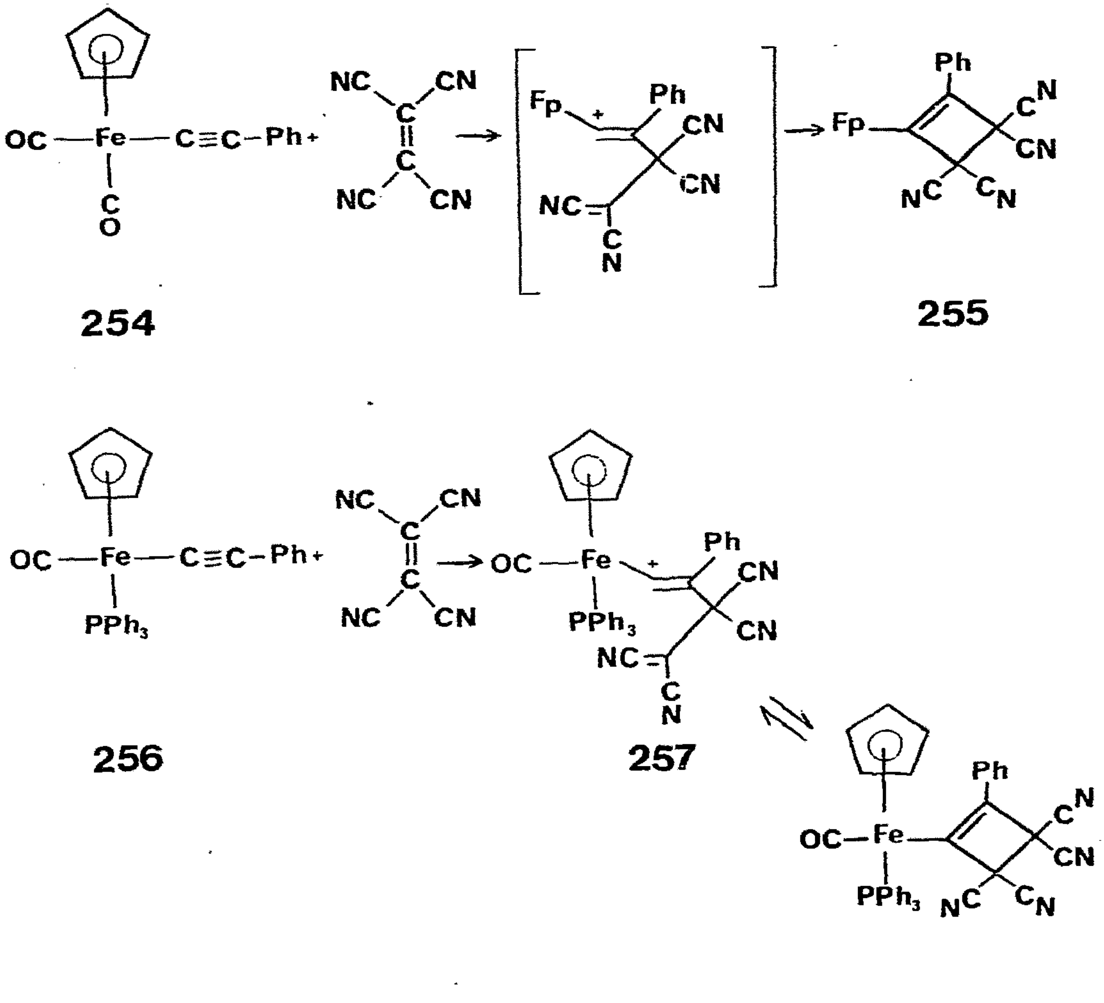
Scheme 61



253

$(CF_3)_2C{=}O$ were reported. Ring expansion products such as 259 were observed along with simple adducts in the dicarbonyl system whereas only the simple adduct 260 was formed in the PPh_3 system [360].

Scheme 62



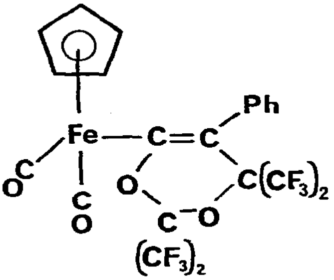
254

255

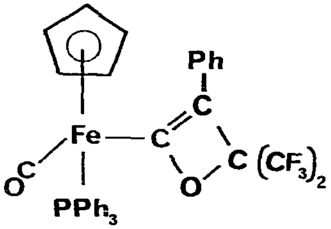
256

257

258



259



260

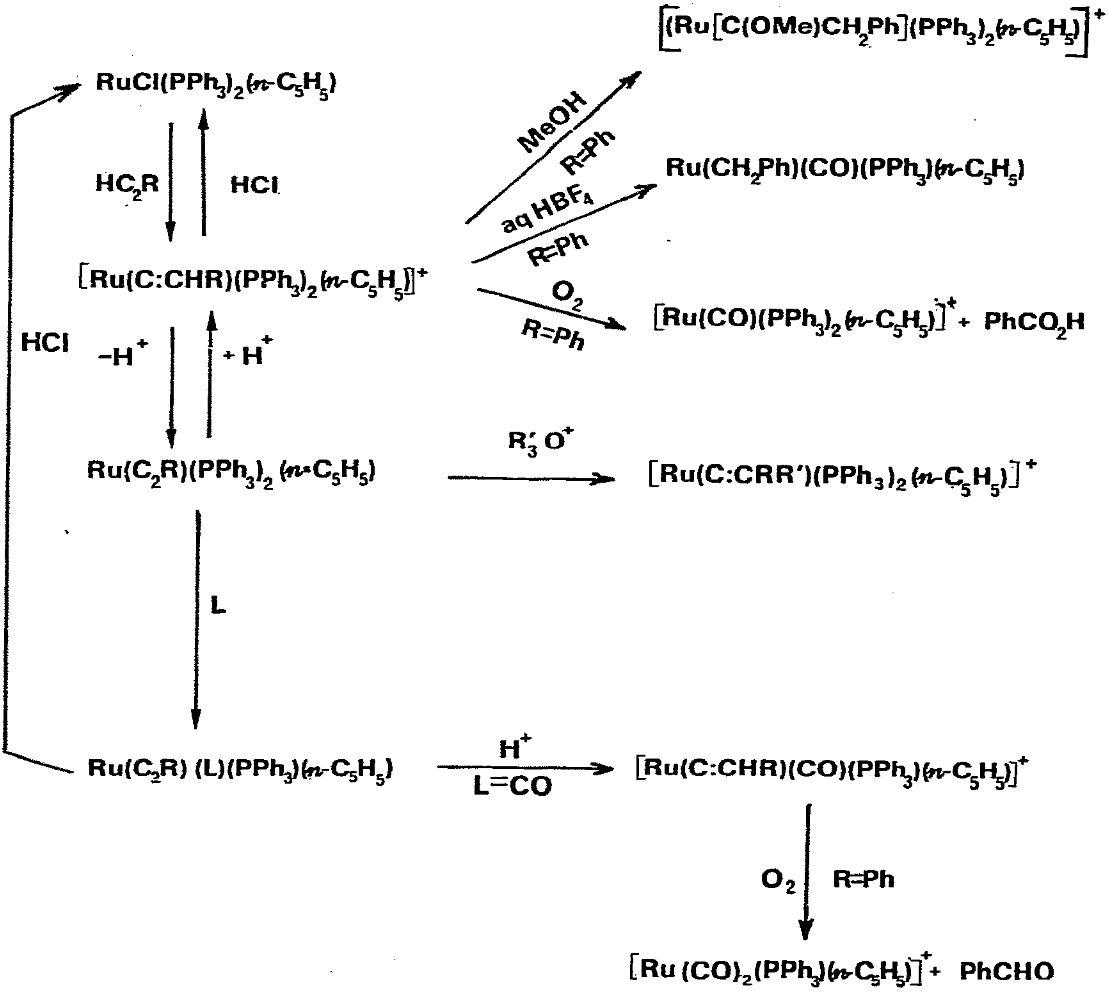
The reactions shown in Scheme 63 for the vinylidene complex $[CpRu(PPh_3)_2C{=}CHR]^+$ have been reported [361]. A full report of this work including analogous osmium chemistry also has appeared [362].

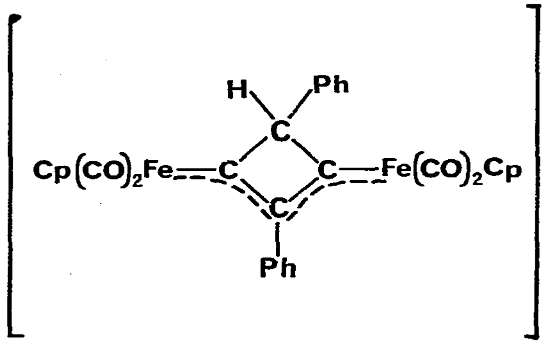
The reaction of $CpFeCO(PPh_3)$(acyl) complexes with trifluoromethanesulfonic anhydride leads to cationic vinylidene complexes via the intermediacy of cationic carbene complexes [363]. As reported also by Davison and Solar, the reaction of Fp-C≡CPh with strong acids yields 261 [364]. The structure of 261 was confirmed crystallographically [365]. This complex can also be prepared by the reaction of Et_3N with 262 [366].

Alkene and Alkyne Complexes

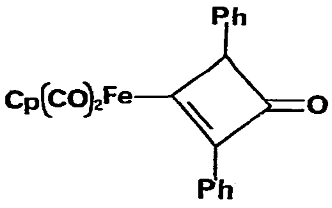
A general route for the preparation of $[CpFeCOL(\text{ligand})]BF_4$(L=CO, PPh_3, $P(OPh)_3$) complexes where the main ligands studied were alkenes and internal alkynes has been reported as shown in Scheme 64. The new L=$P(OPh)_3$ complexes have comparable stability to L=CO derivatives, both of which are more stable than the new L=PPh_3 complexes. The alkyne complexes all react readily with hydride reagents such as $NaBH_3CN$ as shown in the Scheme. This reaction for the L=PPh_3 and $P(OPh)_3$ complexes is much cleaner than for the L=CO complexes (Fp_2 forms) and the new alkenyl products are more stable. In fact, the alkenyl products in the L=PPh_3 system would not undergo β-elimination reactions as observed previously for the analogous alkyl complexes. Also stable are the alkyl derivatives in the $P(OPh)_3$ system, prepared both from addition of hydride to η^2-alkene complexes and direct reaction of the iron-halide with alkyllithium reagents. Attempts to prepare η^2-alkene complexes with cyano-substituted alkenes leads to N-bound cations [367, 368]. The complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)(\eta^2\text{-ligand})]BF_4$ (L=PPh_3, $P(OPh_3)$; η^2-ligand=ethylene, symmetrical alkyne) show an averaged NMR spectra at room temperature, but these spectra collapse to the limiting static spectra at low temperature. The barriers for this rotation were reported.

Scheme 63


RuCl(PPh3)2(π-C5H5)
HC2R
HCl
[Ru(C:CHR)(PPh3)2(π-C5H5)]+
HCl
−H+
+H+
Ru(C2R)(PPh3)2(π-C5H5)
L
Ru(C2R)(L)(PPh3)(π-C5H5)
MeOH
R=Ph
[(Ru[C(OMe)CH2Ph](PPh3)2(π-C5H5)]+
aq HBF4
R=Ph
Ru(CH2Ph)(CO)(PPh3)(π-C5H5)
O2
R=Ph
[Ru(CO)(PPh3)2(π-C5H5)]+ + PhCO2H
R′3O+
[Ru(C:CRR′)(PPh3)2(π-C5H5)]+
H+
L=CO
[Ru(C:CHR)(CO)(PPh3)(π-C5H5)]+
O2
R=Ph
[Ru(CO)2(PPh3)(π-C5H5)]+ + PhCHO

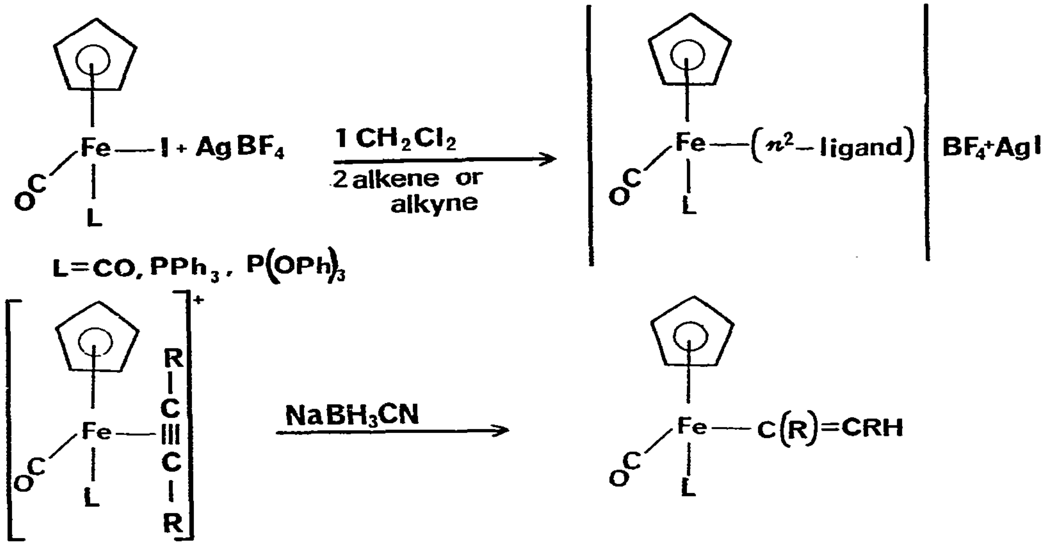


261



262

Scheme 64



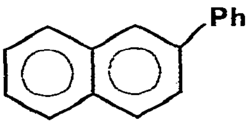
The alkyne complexes have a barrier to rotation of about 5 kcal/mole higher than the ethylene complexes [369]. Note also reference 354 in which calculations on the orientation of the alkene group in these complexes were reported.

The complexes $[CpFe(CO)_2(\eta^2\text{-alkyne})]BF_4$(alkyne = diphenylacetylene, 3-hexyne) have also been prepared by an exchange reaction with $[CpFe(CO)_2(\eta^2\text{-isobutylene})]BF_4$. A similar reaction with phenylacetylene leads to a low yield of 263. Deuteration studies exclude a mechanism involving a vinylidene complex. Another terminal alkyne, methylpropiolate, also does not yield a simple substitution product but leads to a complex reaction producing a variety of products [370].

The reaction of $CpFe(CO)_2CH_2CH{=}CHMe$ with Ph_3CBF_4 yields $[CpFe(CO)_2(\eta^2\text{-}C_4H_8)]BF_4$ instead of the expected cationic butadiene complex [371].

Complexes Containing M-C σ-bonds

Reaction of $[CpFe(CO)_2]^-$ with a variety of methylene-iminium ions preceeds at low temperature to yield $Fp\text{-}(\eta^1\text{-}CH_2NR_2)$ complexes. Substituted iminium ions containing no α-hydrogen atoms yielded analogous products but if α-hydrogens were present (e.g. $[(CH_3)_2CHCH = N(CH_2CH_2)_2O]^+$) only Fp_2 could be isolated. A number of the methylene-iminium complexes show complex infrared νCO stretching patterns with up to six bands observed in some cases. These absorptions were attributed to a specie such as 264, a very surprising 20 electron species. The iminium complexes react with Lewis acids such as H^+ or CH_3^+ to yield new complexes such as $[Fp\text{-}CH_2N(CH_3)_3]^+$ and with species such as CH_3COCl to yield $Fp\text{-}CH_2Cl$. Photolysis of the $CH_2N(CH_3)_2$ complex leads to displacement of a CO group to yield $CpFe(CO)(\eta^2\text{-}CH_2N(CH_3)_2)$, very analogous to know η^3-allyl species. This new complex reacts with PPh_3 to yield $CpFe(CO)(PPh_3)(\eta^1\text{-}CH_2N(CH_3)_2)$ [372].



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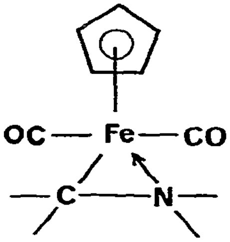
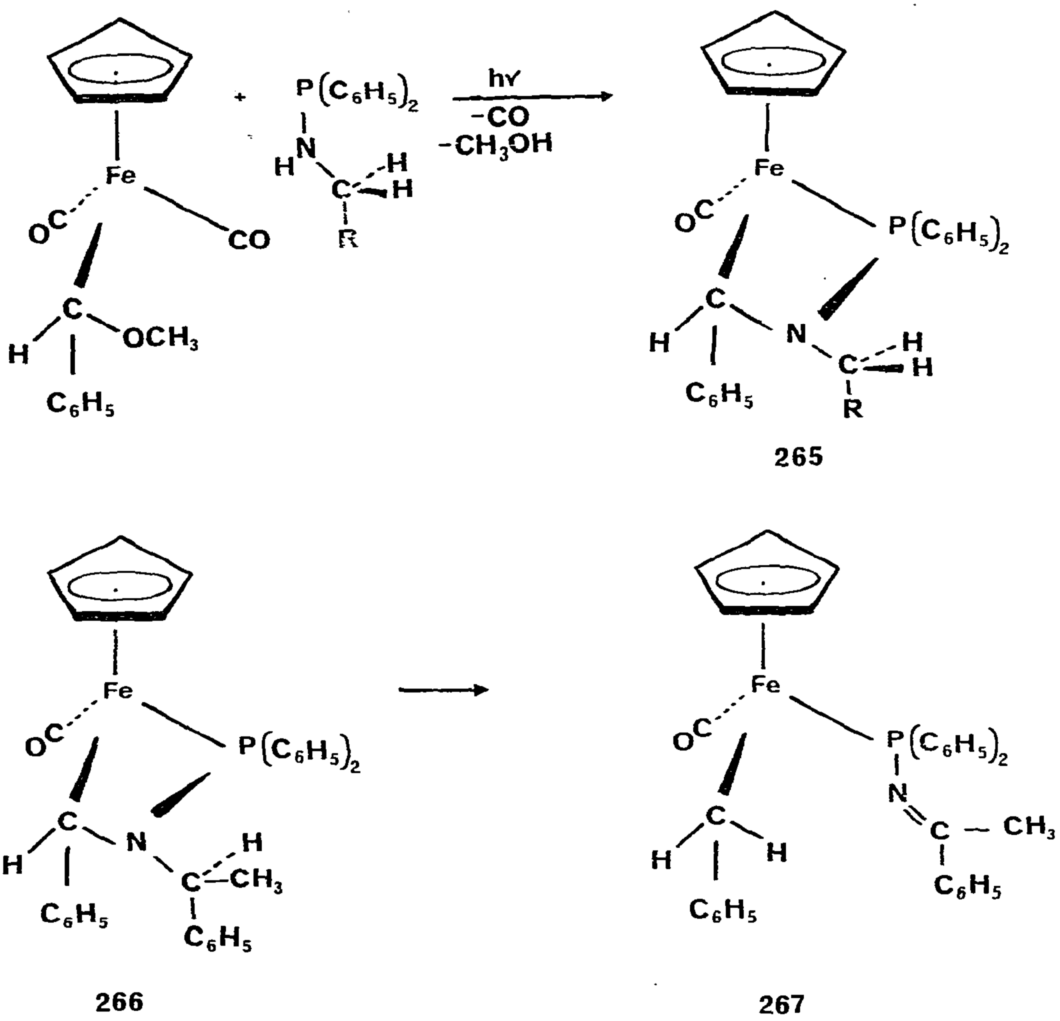


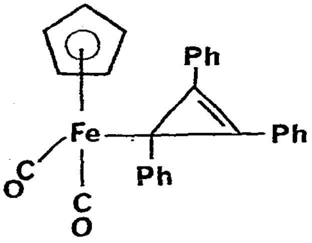
264

In an attempt to prepare an optically active CpFe(CO)(L)(C(H)(Ph)OR) complex, the reaction shown at the top of Scheme 65 was carried out and the unexpected product 265 was obtained (R=Et,Ph). A similar reaction with $PPh_2N(H)CH(CH_3)(Ph)$ yields 267 presumably from rearrangement of 266 [373].

Scheme 65



The complex 268 has been prepared by the reaction of Na[CpFe(CO)$_2$] with 269. The X-ray crystal structure of 268 was reported. Reactions of 268 with a variety of reagents indicates that it does not display the reactivity pattern expected for a cyclopropenyl anion [374]. The reaction of Na[CpFe(CO)$_2$] with 270 produces the stable complex 271 which did not rearrange to 272 as was shown to occur with analogous Co complexes. This contrast was explained by the inertness of 271 toward thermal loss of a terminal CO ligand [375].



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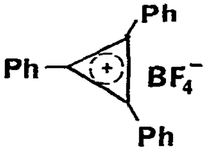

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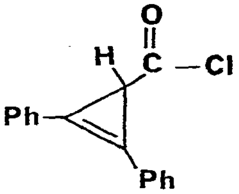

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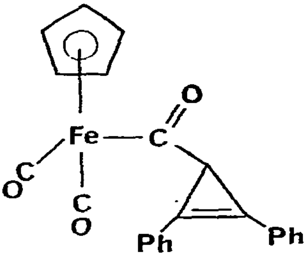

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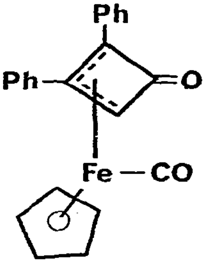

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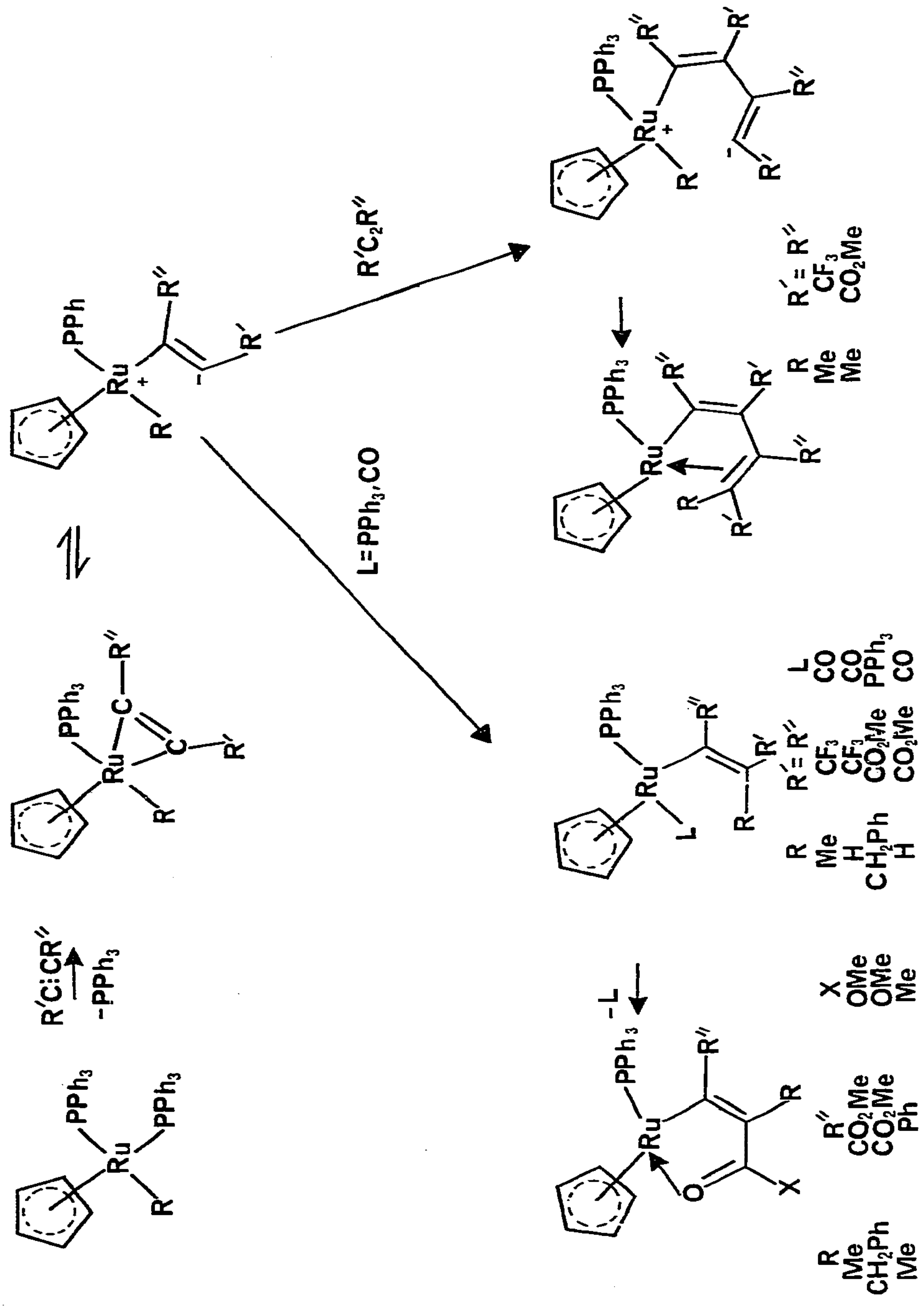
CpFe(dppe)H reacts with alkynes to yield CpFe(dppe)CR=CHR(R=CF_3, COOH) complexes, shown by NMR methods for the R=CF_3 case to have cis stereochemistry. Reaction of the hydride with CS_2 yields CpFe(dppe)S_2CH. CpFe(dppe)Me adds SO_2 to yield CpFe(dppe)SO_2CH_3 [376].

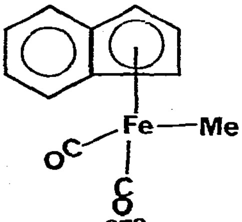
Further studies of the reaction of CpRu(PPh_3)$_2$R (R=Me,CH_2Ph) with disubstituted acetylenes bearing electron withdrawing groups have been reported. Both mono-and di-insertion products were obtained. Scheme 66 shows many of the products and possible routes to these complexes [377]. As shown also for molybdenum, the indenyl complex 273 reacts with acetylenes to yield the vinyl ketone complexes 274 [378].

The reactions shown in Scheme 67 have been reported [379]. The X-ray structure of (cis-[σ-C(F)=C(CF_3)$COOC_2H_5$])Fe(η^5-C_5H_5)$(CO)_2$ has been reported. The Fe-C distance is 0.15A° shorter than expected for a single bond [380]. Note also the preparation of CpFe(CO)(L)(σ-alkenyl)(L=CO,PPh_3, $P(OPh)_3$) derivatives from the reduction of π-alkyne cations [367, 368].



Scheme 66

R′C:CR″
−PPh3
PPh3
Ru
R
C
R′
R″
+
PPh
−
R′C2R″
L=PPh3,CO
L
−L
O
X
R R′ = R″ L
Me CF3 CO
H CF3 CO
CH2Ph CO2Me PPh3
H CO2Me CO
R R′ = R″
Me CF3
Me CO2Me
R R″ X
Me CO2Me OMe
CH2Ph CO2Me OMe
Me Ph Me



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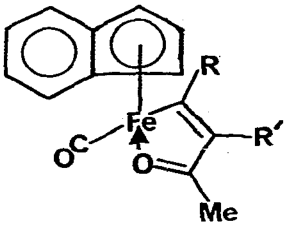

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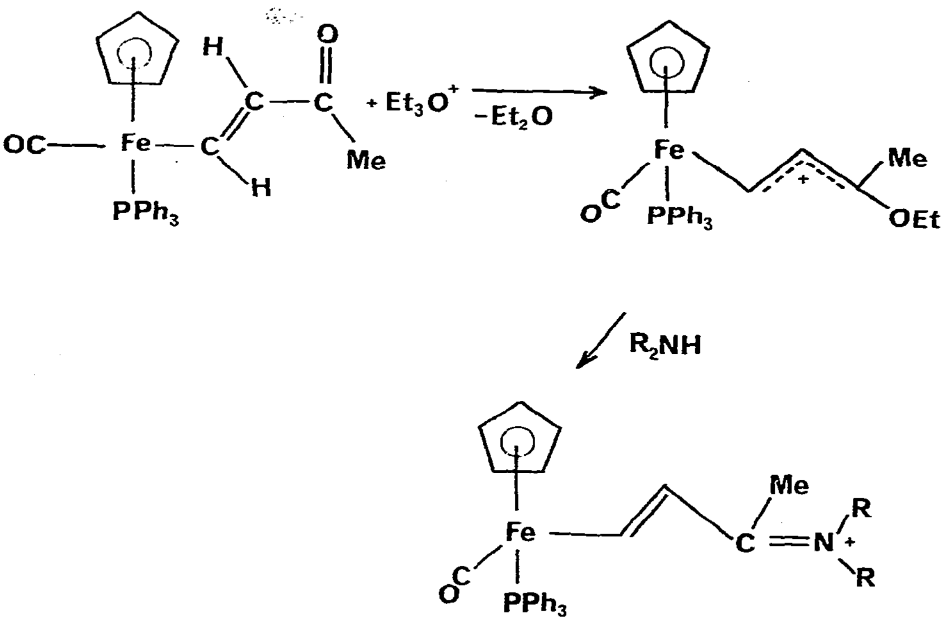
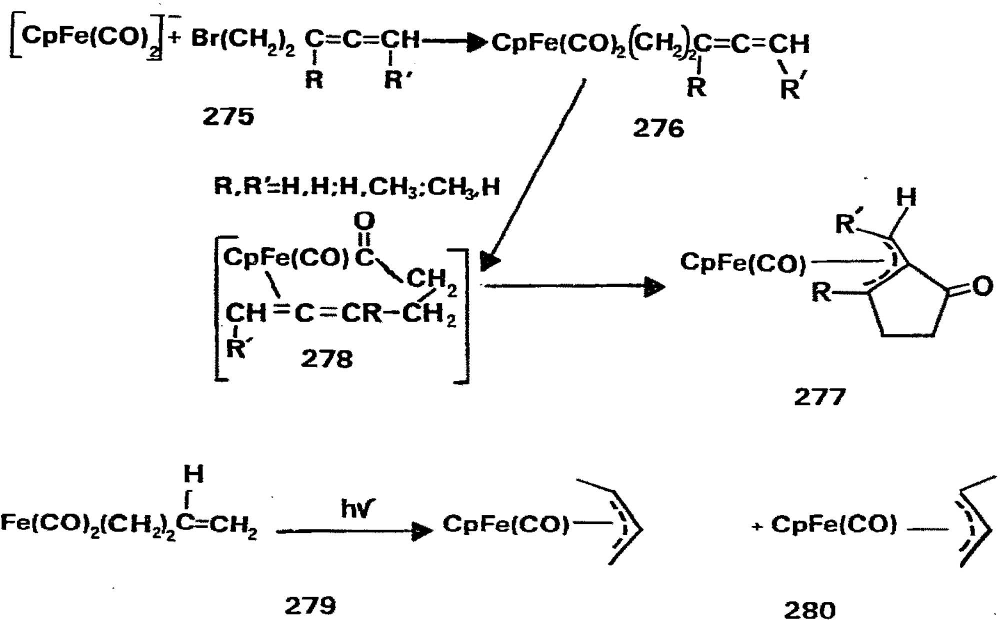
R=R′=Me
R=H,R′=Bu^t

Scheme 67



The complex $[CpFe(CO)_2]^-$ reacts with 275 to yield 276 as shown in Scheme 68. Heating this complex leads to 277 presumably via 278. Photolysis of 279 yields the syn and anti isomeric of 280 [381].

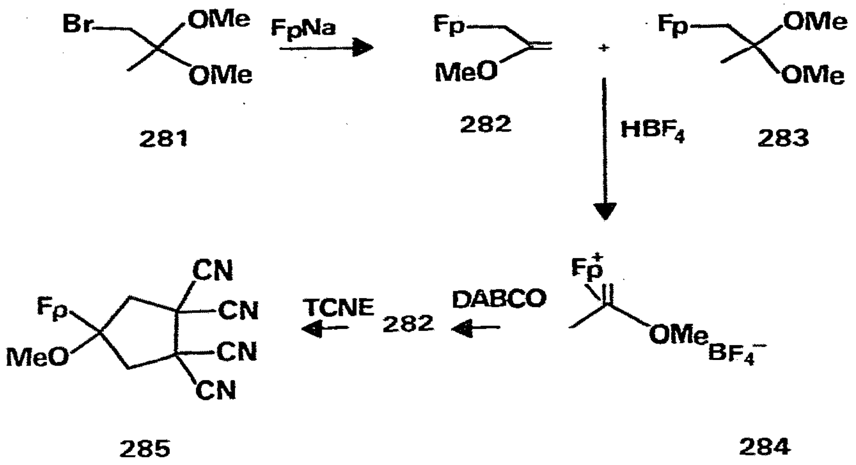
Scheme 68

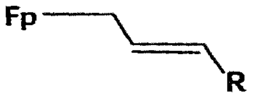


The reactions of $[CpFe(CO)_2]^-$ and 281 leads to a mixture of 282 and 283 as shown in Scheme 69. Treatment of this mixture with acid leads to 284 which can be converted to 282 by reduction. 282 undergoes a cyclization reaction with $C_2(CN)_4$ to yield 285 [382]. A communication of this work has also appeared [383]. The reaction of electron deficient olefins with 282 and 286 has been reported. The 2-methoxy compound is more reactive but yields a variety of products. Reactions with an alkyne were also presented [384].

The complexes π-$C_3H_5CpFe(CO)$ and σ-$C_3H_5(Cp)Fe(CO)_2$ can be prepared from $CpFe(CO)_2Br$ and C_3H_5Br in a reaction containing base carried out in a two phase system of CH_2Cl_2 or benzene and H_2O using phase transfer reaction conditions. Bis-π-$C_3H_5Fe(CO)_2$ was also prepared in a similar manner from π-$C_3H_5Fe(CO)_3Br$ [385]. Reaction of 287 with $[\{(PPh_3)_2PtCl\}BF_4]_2$ yields 288, a new CS_2 bridged dimetallic complex. Complex 289 is prepared similarly from 287 and $PtCl_2$ [386].

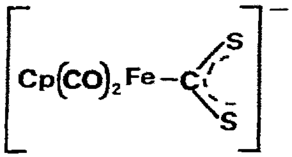
Scheme 69





R = H, OMe

286



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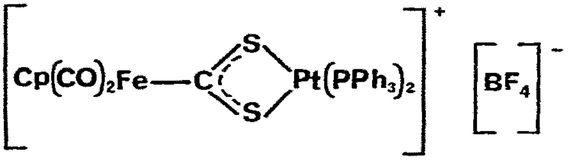

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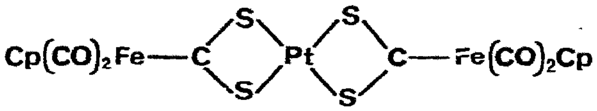

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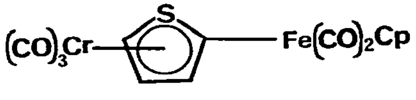
The complexes 290 and 291 were prepared by treating the appropriate RFeCp$(CO)_2$ compound with $Cr(CO)_6$ [387]. Reaction of 292 and 293 with diphenylacelylene yielded 294 and 295 respectively [388].



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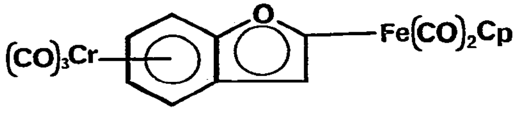

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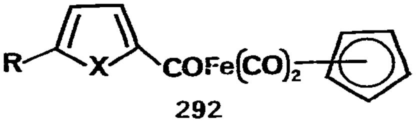

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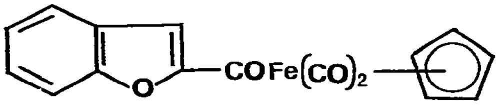

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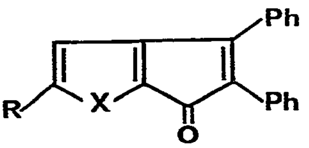

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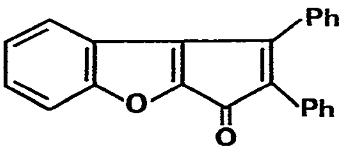
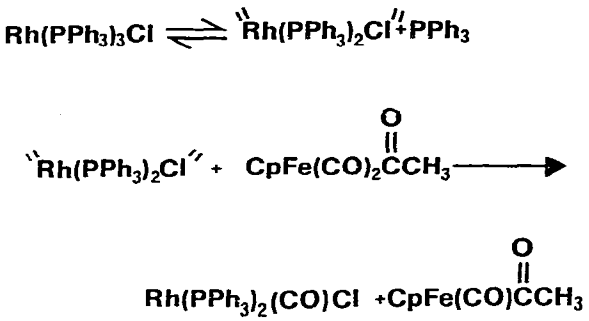
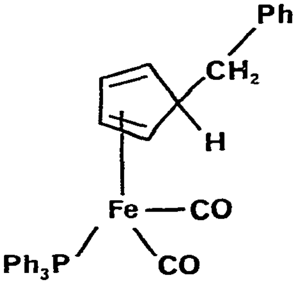


295

The dimeric complex $[Rh(PPh_3)_2Cl]_2$ has been shown to decarbonylate CpFe$(CO)_2$(acyl) complexes to the corresponding alkyl complexes without the omplication of PPh_3 substitution at iron [389]. A detailed investigation of the decarbonylation of CpFe$(CO)_2C(O)CH_3$ has been reported. Rate data and a eries of reactions with substituted iron complexes led the authors to propose he mechanism shown in Scheme 70 in which direct attack by "$Rh(PPh_3)_2Cl$" on a terminal carbonyl is rate determining. Note also in the decarbonylation of CpFe$(CO)_2$(p-$C(O)C_6H_4(CO)H$) that the main product arises from decarbonylaion of the metal to yield CpFeCO(PPh_3) (p-$C(O)C_6H_4(CO)H$) and only small mounts of CpFe$(CO)_2C(O)C_6H_5$ [390]. X-ray crystallography has been used to show that the product of the photochemical reaction of $(\eta^5$-$C_5H_5)Fe(CO)_2$-$CH_2Ph)$ with PPh_3 is 296 in which the benzyl group is exo implying that the eaction is intermolecular. Reaction of 296 with $C_2(CN)_4$ yields the salt $(\eta^5$-$C_5H_5)Fe(CO)_2(PPh_3)][(NC)_2CC(CN)C(CN)_2]$ [391].

Scheme 70





296

The reaction of $[CpRu(CO)_2]_2$ with $P(OR)_3$(R=Me,Et,Bu^n) yields, surprisingly, $CpRu(CO)_2R$ complexes. These complexes were difficult to purify and were treated with PPh_3 to yield isolated $CpRu(CO)(PPh_3)R$ complexes. Reaction of the ruthenium dimer with $P(Pr)_3$ leads to the formation of $Cp_2Ru_2(CO)_3(PPr_3)$ and, in addition, $CpRu(CO)(PPr_3)Cl$. This second product is formed from $CpRu(CO)(PPr_3)H$ which is converted to the chloride in the work-up involving CH_2Cl_2 [392].

Strong evidence has been presented to show that $CpFe(CO)_2(\eta^1\text{-}C_5H_5)$ reacts with $P(OPh)_3$ (and other phosphine and phosphite ligands) to yield $[CpFeCO(P(OPh)_3)(\eta^1\text{-}C_5H_5)](Fp'\text{-}Cp)$ by a radical pathway as shown in Scheme 71. Although the reaction is not accelerated by light, if Fp_2 is added, irradiation substantially enhances the reaction due to the process $Fp_2 \xrightarrow{h\nu} 2Fp\cdot$ which helps initiate the reaction. This reaction pathway is for complexes containing unsaturated alkyl groups and not saturated alkyls because the homolytic displacement step would only be facile in the former case. Fp(allyl) complexes were shown to react in a similar manner. The results of crossover experiments supported the key alkyl transfer step [393].

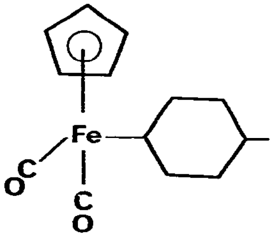
SCHEME 71

$$\begin{aligned} &Q\cdot + FpCp \rightarrow QCp + Fp\cdot \\ &Fp\cdot + L \xrightarrow{fast} F\acute{p}\cdot + CO \\ &F\acute{p}\cdot + FpCp \rightarrow F\acute{p}Cp + Fp\cdot \end{aligned}$$

A full paper reporting complete details of studies designed to elucidate the stereochemical consequences of electrophilic cleavage reactions of the Fe-CH_3 bond in (η^5-1-CH_3-3-C_6H_5-C_5H_3)Fe(CO)(PPh_3)CH_3 has appeared. The insertion of SO_2 is essentially stereoselective supporting the well established intermediate $M^+O_2SR^-$ contact ion pair. Eliminative cleavage of the alkyl complex by HI, I_2 and HgI_2 to yield (η^5-1-CH_3-3-C_6H_5-C_5H_3)Fe(CO)(PPh_3)I proceeds with variable stereospecificity and unreacted alkyl undergoes epimerization during the reaction. The X-ray crystal structure determinations of CpFe(CO)(PPh_3)C(O)-CH_3 and 297 were used to elucidate the stereochemistry of these reactions. The best overall mechanism is that shown in Scheme 72 [394].

Reaction of $CpFe(CO)_2Br$ with $Ph_2P(CH_2)_3MgCl$ leads to the metallocycle complex $Cp\overline{Fe(CO)PPh_2(CH_2)_2C}H_2$. This complex readily inserts SO_2 into the M-C sigma bond to yield $Cp\overline{Fe(CO)PPh_2(CH_2)_3S}O_2$ [395].

The reaction of both cis and trans 298 with DCl and CF_3CO_2D proceeds with retention of configuration at the α-carbon atom suggesting an intermediate like 299 is formed followed by reductive elimination [396]. Cleavage of the



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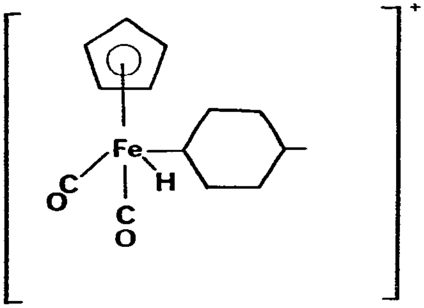

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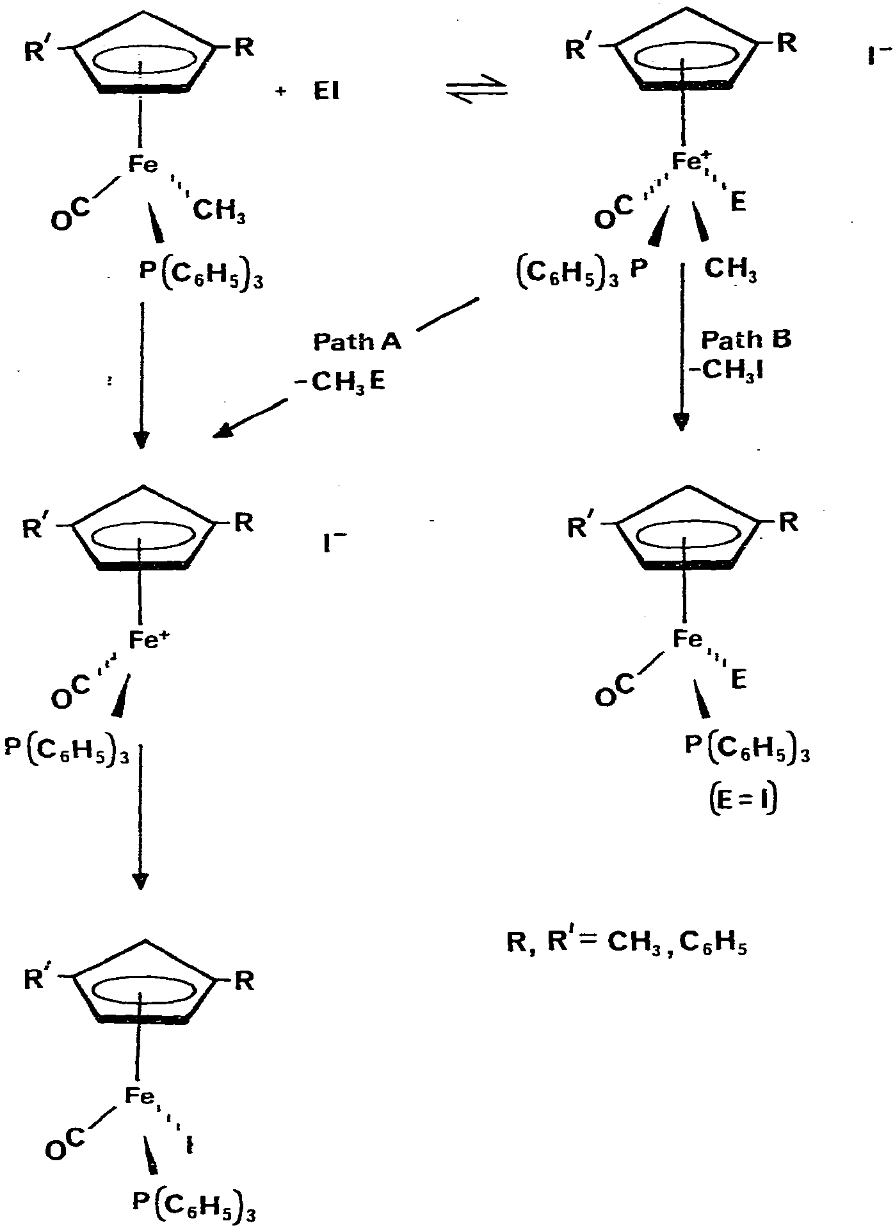
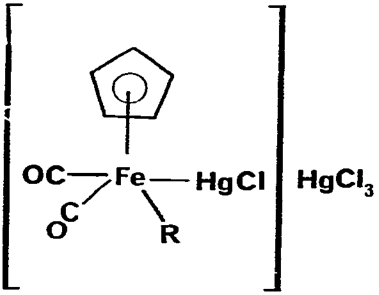
Scheme 72



$R, R' = CH_3, C_6H_5$

297

Fe-C bond in threo-PhCHDCHDFe(CO)$_2$Cp by HgCl$_2$ proceeds with retention of configuration at the α- carbon atom. An intermediate 300 similar to that proposed by others was invoked as the intermediate in the reaction followed by reductive elimination with retention of configuration at iron. Interestingly, although an analogous tungsten complex also reacts with HgCl$_2$ with retention of configuration at the α-carbon, the complex cis-(threo-PhCHDCHD)Mn(CO)$_4$-PEt$_3$ is cleaved with inversion. This was explained in terms of the energy gap between the HOMO and the M-C σ-bonding orbital in each compound [397].



300

Supporting earlier work, the cleavage of Fp-alkyls with CuX$_2$ as shown in the top equation of Scheme 73 has been shown to proceed by an S_{E2} (oxidative) process as shown in the Scheme. The final step is abstraction of halide from the solvent (if halocarbon) or from a second equivalent of CuX$_2$ [398].

SCHEME 73

$$\text{Fp-CH}_2\text{PH} + 2\text{CuX}_2 \rightarrow \text{Fp-X+PhCH}_2\text{X} + 2\text{CuX}$$

X=Cl,Br

$$\text{Fp-CH}_2\text{Ph+CuX}_2 \rightarrow [\text{Fp-CH}_2\text{Ph}]^+ + [\text{CuX}_2]^-$$

$$[\text{Fp-CH}_2\text{Ph}]^+ + \text{CuX}_2^- \rightarrow \text{Fp}\cdot + \text{PhCH}_2\text{X} + \text{CuX}$$

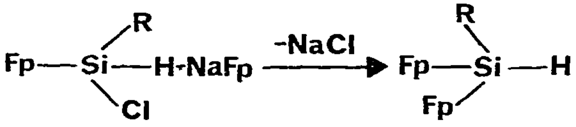
The photolytic decomposition of FpCH$_2$R(R=1-azulenyl, Ph, 1-naphthyl, 1-acenaphthenyl) in solution proceeds via homolysis of the Fe-CH$_2$ bond [399].

The ^{13}C chemical shifts of both the terminal and acyl carbonyl carbon atoms in CpFeCOLC(O)R complexes (L=CO, phosphine, phosphite, CH$_3$NC; R=CH$_3$, p-C$_6$H$_4$OCH$_3$) has been reported. The acyl carbon atom has a greater shift range (25 ppm) than the terminal carbonyl (~6 ppm) over this series of complexes. The reasons for this were discussed [400].

Compounds Containing Group IVA Ligands Other Than C

Transition metal substituted silanes have been prepared as in Scheme 74. Placing these new complexes in CCl_4 results in the conversion of the Si-H group into a Si-Cl group with the remainder of the molecule still the same. These chlorinated derivatives further react with $AgBF_4$ to yield the analogous fluorosilyl complexes [401]. The σ-π bimetallic complex $[\eta^6\text{-PhSiMe}_2\text{Fe(CO)}_2\text{-Cp}][\text{Cr(CO)}_3]$ can be prepared by the reaction of $PhSiMe_2Fe(CO)_2Cp$ and $Cr(CO)_6$ and also $[\eta^6\text{-PhSiMe}_2\text{Cl}][\text{Cr(CO)}_3]$ with $NaFe(CO)_2Cp$. In a like manner, $[\eta^6\text{-PhSiMe}_2\text{CH}_2\text{Fe(CO)}_2\text{Cp}][\text{Cr(CO)}_3]$ was prepared [402].

Scheme 74



R=CH_3,Cl

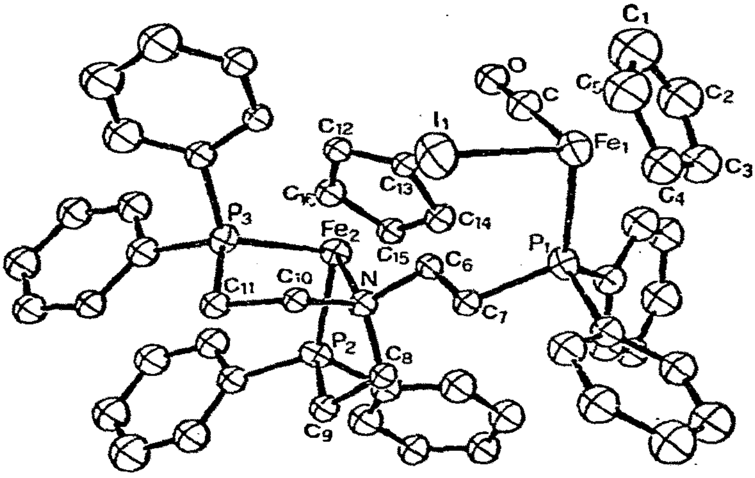
Compounds Containing Group VA Ligands

The reaction of $[CpFe(CO)_2NH_3][PF_6]$ with acetone yields $[CpFe(CO)_2\{NH{=}C(CH_3)_2\}]PF_6$. This reaction was shown to be general for other similar metal-amine complexes [403]. The reaction of $CpFe(CO)_2I$ with the tripod poly-tertiary phosphine ligands(L) tris(2-diphenylphosphinoethyl)amine or tris(2-diphenylphosphinoethyl)phosphine yields $[CpFe(CO)I\text{-L-}FeCp]^+$ as shown crystallographically for the first ligand in Figure 48 [404].

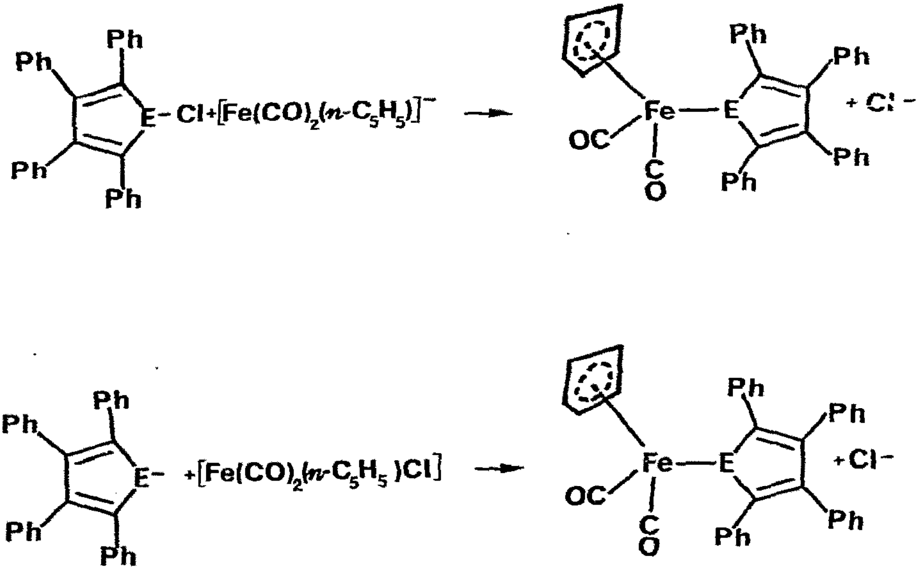
The new complexes $CpFe(L)(RN_3R')$ ($L=PPh_3, P(OMe)_3, P(OPh)_3$, CO; R, R' = $p\text{-MeC}_6H_4$ or $p\text{-ClC}_6H_4$) have been prepared from the appropriate iron halide and $Ag(RN_3R')$ [405].

Phosphole, arsole and stibole complexes of iron have been prepared by the two reactions shown in Scheme 75 [406]. Heating the complex $CpFe(CO)_2$-($\sigma\text{-EC}_4Ph_4$)(E=P, As) converts it into the π complex <u>301</u> [407]. The anion <u>302</u> reacts with $CpFe(CO)_2I$ to yield <u>303</u>. Heating this complex at 150°C yields <u>304</u> and <u>305</u> [408].

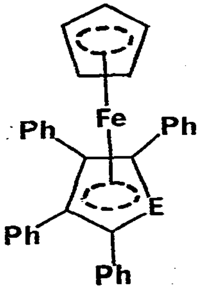
FIGURE 48



Scheme 75



E=P, As, or Sb



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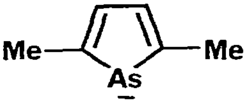

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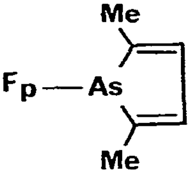

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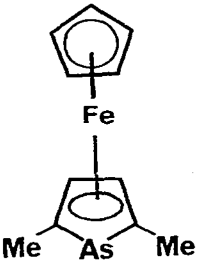

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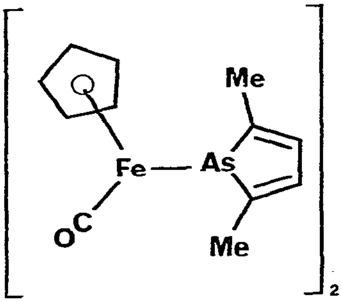

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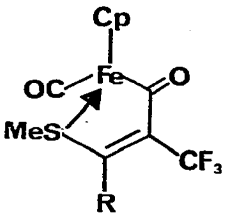
Complexes Containing Sulfur Ligands

The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2H_2O]BF_4$ with $Na[S(O)_2OR]$ $(R{=}CH_3, C_2H_5)$ yields $(\eta^5\text{-}C_5H_5)Fe(CO)_2SO_2OR$ complexes. The R groups may be interconverted by the use of the appropriate alcohol, a reaction which is accelerated by HBF_4. Use of an optically active alcohol in the exchange reaction has shown that the O-C linkage of the alcohol is not broken. A mechanism was proposed for the exchange [409].

Dithiocarbene complexes $[CpFe(CO)_2(C(SR)SR')]^+$ are readily prepared from the alkylation of the dithioester group in $CpFe(CO)_2(C(=S)SR)$ complexes. The ^1H NMR of the R = R' = Me derivative shows as a singlet for the 2 Me groups but at -55°C they become nonequivalent. The equivalence at room temperature is presumably due to rapid rotation around the C(carbene)-S bonds. The dimethyl derivative was shown to react with a variety of amines [410].

The reaction of $CpFe(CO)_2SMe$ with $F_3CC\equiv CH$ yields 306, 307, 308, and 309 (R=H). An analogous reaction with $F_3CC\equiv CCF_3$ yields <u>306</u> ($R=CF_3$), <u>309</u> ($R=CF_3$), <u>310</u> and <u>311</u>. $CpRu(CO)_2SMe$ reacts with $F_3CC\equiv CCF_3$ to yield <u>312</u> [411]. The reaction of $CpFe(CO)_2SR$(R=Me, iso-Pr) with $CF_3C\equiv CCF_3$ or



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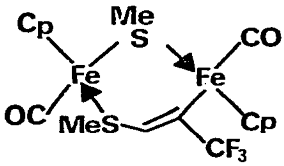

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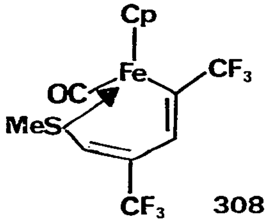

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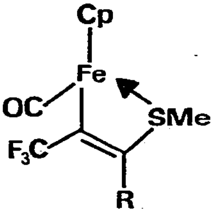

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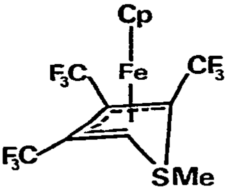

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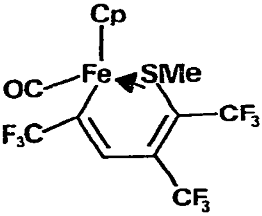

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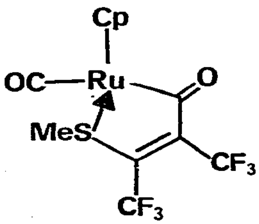

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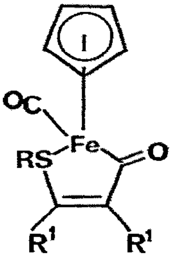
$MeO_2CC{\equiv}CCO_2Me$ yields complexes 313 ($R^1{=}CF_3$, CO_2Me) [412]. $CpFe(CO)_2$-(SMe) reacts with $CF_3C{\equiv}CH$ to yield 314a as shown crystallographically. The same reaction with $CF_3C{\equiv}CCF_3$ yields 314b. Irradiation of 314a produces 315 and this reacts with $CpFe(CO)_2SMe$ to yield 316 as characterized crystallographically [413].



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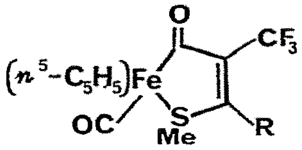

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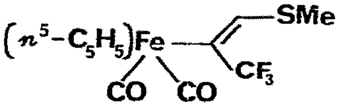
a; R = H
b; R = CF₃



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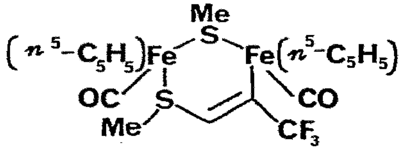

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Halide, Cyanide and Isocyanide Complexes

The complex $[CpFe(dppe)(NCCH_3)]Br$ was prepared on a large scale by the irradiation of $CpFe(CO)_2Br$ and dppe in acetonitrile. It reacts readily with a variety of anionic ligands (X=CN, SCN, SPh, I, Br, CH_3, and H) to yield CpFe(dppe)X complexes [414]. The oxidation of $Fe(\eta^5\text{-}C_5H_5)(dppe)X$ complexes with $AgPF_6$ yields the 17 electron complexes $[Fe(Cp)(dppe)X]PF_6$. $[FeCp\{P(OPh)_3\}_2I]PF_6$ was formed in an analogous reaction. These results were predicted by cyclic voltammetry experiments. The 17 electron complex

FeCp(dppe)S_2O_3 was also reported [415]. A variety of CpFe$(CNR)_2$Br complexes have been prepared as shown in Scheme 76. If excess CNR is used the cationic [CpFe$(CNR)_3$]Br derivatives can be prepared. The cationic complexes [CpFe$(CO)_{3-n}(CNR)_n$]PF_6 (n=1,2) can be prepared from [CpFe$(CO)_2$-(THF)]PF_6 and the appropriate amount of isocyanide. Cyclic voltammetry was used to study the neutral halide complexes. One electron waves were observed. There is a good correlation between the $E_{\frac{1}{2}}$ data and Hammett substituent group parameters for substituted CNPh ligands [416].

SCHEME 76

$Fe(C_5H_5)(CO)_2Br + 2\ CNR \rightarrow Fe(C_5H_5)(CNR)_2Br + 2\ CO$

(R = C_6H_5, p-C_6H_4Me, p-C_6H_4OMe, m-C_6H_4OMe, p-C_6H_4F, m-C_6H_4Cl, m-$C_6H_4CF_3$, p-$C_6H_4NO_2$)

The complexes CpFe(CO)(CN)(CNR) can be alkylated with primary, secondary, and tertiary alkyl iodides (R'I) to produce new mixed cationic bisisocyanide complexes, [CpFe(CO)(CNR)(CNR')]I. The use of chiral alkyl iodides produces configurationally labile diastereomers [417]. The complexes CpFe$(CO)_2CNBH_3$ and $[CpFe(CO)_2CNBH_2NMe_3]^+$ have been reported along with detailed IR and NMR characterization of these complexes [418]. The reaction of $[(\eta^5\text{-}C_5Me_4Et)Ru(CO)_2]_2$ with halogens yields a series of new complexes. In the case of Br_2, the reaction proceds to an unusual Ru(IV) derivative, the structure of which was confirmed crystallographically [419]. Reaction of $CpRu(PPh_3)_2Cl$ with a variety of nitriles yields new $[CpRu(PPh_3)_2(NCR)]^+$ complexes. A similar reaction takes place when this ruthenium complex is mixed with $P(OMe)_3$ and $NaBPh_4$ to yield $[CpRu(PPh_3)_2P(OMe)_3]^+$. In the absence of the $NaBPh_4$ salt, $CpRu(P(OMe)_3)_2Cl$ forms. Similar products formed with chelating bis-phosphine ligands. Reaction of $CpRu(PPh_3)_2Cl$, bisphosphine and NH_4PF_6 yields [CpRu(bis-phosphine)PPh_3]PF_6. Osmium complexes were less reactive. Heating $CpOs(PPh_3)_2Br$ with $P(OR)_3$ briefly yields $CpOs(PPh_3)(P(OR)_3)Br$. Excess phosphite and the reaction conditions of refluxing decalin were required to form $CpOs(P(OR)_3)_2Br$ [420].

ARENE AND RELATED COMPLEXES

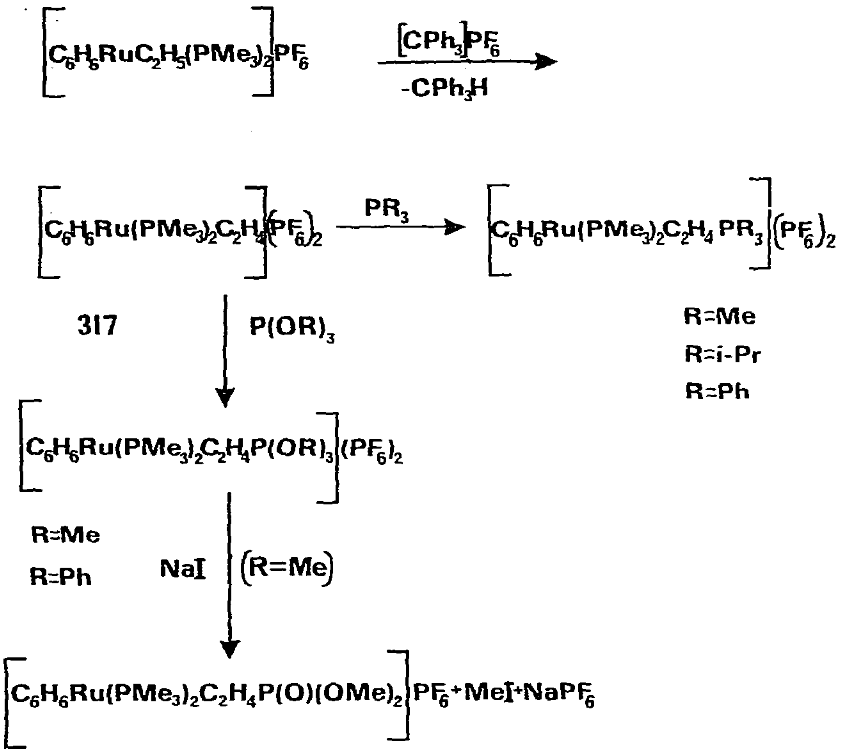
The metal evaporation synthetic method has been used to prepare $Fe(\eta^6\text{-arene})L_2$(L= phosphorous ligand) and $Fe(\eta^6\text{-arene})(\eta^4\text{-diene})$(diene=1,3- and 1,5-cyclooctadiene, cycloheptatriene and cyclooctatetraene). Protonation and alkylation reactions of these new complexes were discussed [421]. A molecular orbital treatment of benzene-$Fe(CO)_2$ has been presented and compared to other similar molecules. Also discussed was butadiene-Fe(CO)$_2$, and the Fe(CO)$_4$ fragment in two configurations [422].

In addition to reviewing the area of exchange of free arene with arene-transition metal complexes, data were presented indicating that (η^6-C_6H_6)-Ru-1,5-COD does not exchange with free arene at temperatures up to 97°C but will exchange slowly if CH_3CN is also present [423]. The d^8, allyl complex η^3-$C_3H_5Ru(\eta^6$-$C_6H_6)Cl$ reacts with hydrogen with exclusive hydrogenation of the allyl ligand to produce propylene irreversibly. For this and other η^6-arene complexes, the arene ligand is not hydrogenated indicating that η^4-arene binding is critical in the catalysis of arene hydrogenation [424].

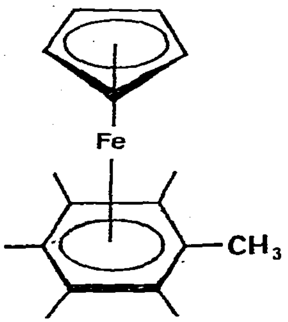
The complex $(C_6H_6)Ru(C_2H_4)PMe_3$ is formed by $NaC_{10}H_8$ reduction of $[(C_6H_6)RuCl(C_2H_4)PMe_3]PF_6$. This new complex can be both alkylated and protonated to yield the respective $[(C_6H_6)Ru(X)(C_2H_4)PMe_3]PF_6$ complexes. Reaction of the X=H complex with PMe_3 yields $[(C_6H_6)RuC_2H_5(PMe_3)_2]PF_6$ whereas for X=CH_3, $[(C_6H_6)RuCH_3(C_2H_4PMe_3)PMe_3]$ is formed [425]. The preparation of analogous $[C_6Me_6Ru(X)(CO)PMe_3]PF_6$ (X=H,CH_3) complexes was also reported starting from $[C_6Me_6RuCl_2]_2$ [426].

The di-cationic Ru-η^2-ethylene complex 317 can be prepared as shown in Scheme 77. Various reactions of this complex are also shown [427]. The reaction of $[(\eta^6$-$C_6H_6)RuCl_2]_2$ with one equivalent of the bidentate ligands (L-L) $Ph_2E(CH_2)_nEPh_2$(E=As, n=2; E=P, n=2,3,4) yields the dimeric complexes (u-L-L)$[(\eta^6$-$C_6H_6)RuCl_2]_2$. If two equivalents of the ligand are used, $[(\eta^6$-$C_6H_6)Ru(L$-$L)Cl]Cl$ complexes are isolated. Using an excess of the ligands leads to displacement of the benzene ligand [428]. The 19 electron species 318 reacts instantaneously with O_2 in dry air at room temperature to produce 319 and H_2O. At -78°C, H_2O_2 and 319 are formed in an analogous reaction. Complex 319 can also be prepared from the reaction of $[CpFe(C_6Me_6)]^+$ with Bu^{t}OK. 319 reacts with water to produce 320 and with CO_2 or CS_2 to produce 321a or b, respectively. The benzene, toluene or xylene derivative of 318 reacts with O_2 at -30°C to yield the dimer 322. It was proposed that the reaction of 318 with O_2 preceeds first by electron transfer to produce $O_2^{\cdot-}$ and $[CpFe(C_6Me_6)]^+$ followed by deprotonation to yield 319 [429]. In a second paper the preparation of 318 was presented along with the structure of this molecule as determined crystallographically. It is a true sandwich complex with planar rings. The M-Cp distance is the longest Fe-Cp bond ever measured by X-ray. ESR and Mössbauer data were reported on this complex and similar derivatives. The authors called these sandwich complexes "electron reservoirs" because of their ability to reversibly hold one electron. This fact has been utilized by showing that 318 is a redox catalyst for the electroreduction of NO_3^- to NH_3 in aqueous 0.1N LiOH at a potential for which 318$^+$ is reversibly reduced to 318 [430]. An analogous series of $[(\eta^5$-$C_5H_5)$-

Scheme 77



(η^6-arene)Fe]$^+$ complexes has been electrochemically reduced to the corresponding neutral 19 electron species. These authors also reported that these neutral species quickly reduce nitrate ions to NH_3 in water [431]. In two related papers a variety of $[(\eta^6\text{-arene})(\eta^5\text{-Cp})Fe]^+$ complexes containing an α-carbon substituent with hydrogen atoms on the arene ligand can be deprotonated with base. The reactivity of these zwitterionic complexes with nucleophiles is presented [432, 433]. Despite an earlier reference to the contrary, the reaction of Cp_2Fe and $PhNH_2$ in the presence of $AlCl_3$ yields $[(C_6H_5NH_2)CpFe]^+$. Also prepared were $[(C_6H_5XH)CpFe]^+$(X=O,S) complexes. All three new compounds could be deprotonated at the heteroatom [434]. Molecular orbital calculations on the cations $[(C_6H_5X)Fe(C_5H_5)]^+$ (X=H,Me,OMe,COOMe) have been carried out in order to provide support for recent proposals concerning the location of nucleophilic attack on complexes containing even or odd hapticity of the π-hydrocarbon ligand [435].



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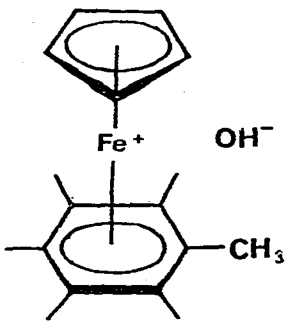

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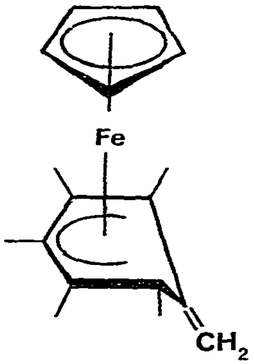

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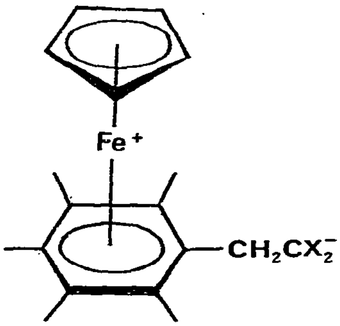


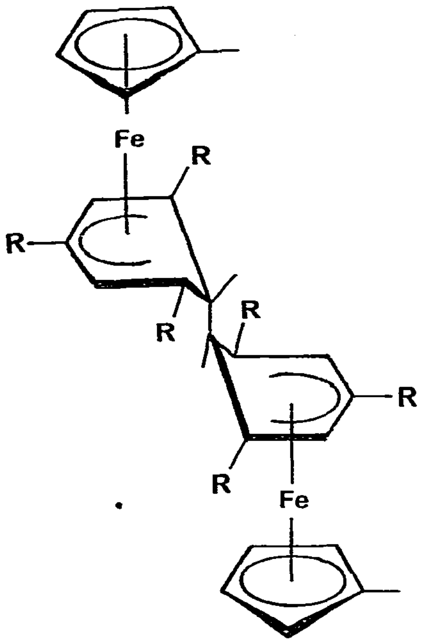
321

a X=O
b X=S

Rate studies on the activation by π-coordination to $[CpFe]^+$ of halogenobenzenes towards replacement of halide by methoxide has been compared to other π-complexes [436]. Detailed ESR measurements on various arene-FeC_5H_5 complexes have been reported and discussed [437].

The addition of a variety of phosphines to $[(C_6H_6)_2Fe](PF_6)_2$ yields 323 [438].

The complexes 324 can be readily prepared by the protonation with HBF_4 of equimolar mixtures of $[M(arene)X_2(C_5H_5N)]$ and $[M(arene)X(C_5H_5N)_2]PF_6$ in methanol [439]. The reaction of $[RuCl_2(\eta^6\text{-arene})]_2$ with $AgPF_6$ in acetone produces $[Ru(\eta^6\text{-arene})(OCMe_2)_3](PF_6)_2$. These compounds slowly are converted in solution to $[Ru_2(u\text{-}PO_2F_2)_3(\eta^6\text{-arene})_2](PF_6)$ complexes. The first



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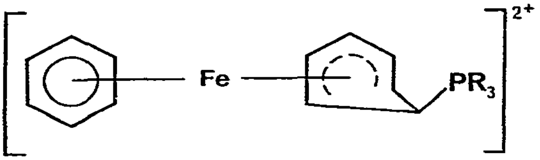

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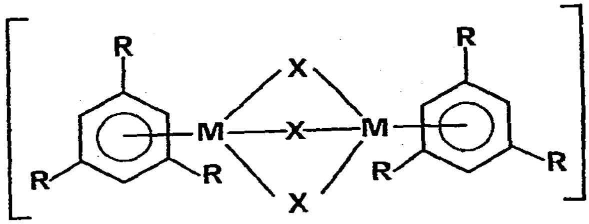
step in this reaction seems to involve an aldol condensation between two of the acetone molecules to yield 325. The structure of the mesitylene derivatives was determined crystallographically [440]. The treatment of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with aqueous Na_2CO_3 in propan-2-ol yields 326. 326 reacts with a variety of olefins. Also, 326 is a very active homogeneous hydrogenation catalyst for arenes. For example, under mild conditions (50°C, 50 atm H_2 for 36 hours in benzene) ca. 9000 molecules of benzene are reduced to cyclohexane per molecule of catalyst [441]. A straightforward general preparation of $[Ru(arene^1)(arene^2)]Y_2$ ($arene^1=C_6H_6$, mesitylene, C_6Me_6, $arene^2$=many



M=Ru,X=Cl,Br;R=H or Me

M=Os,X=Cl;R=H

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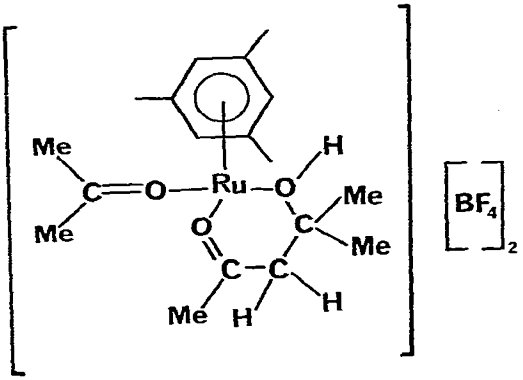

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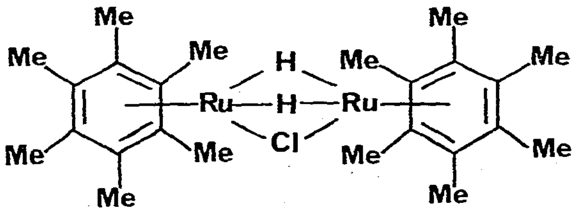

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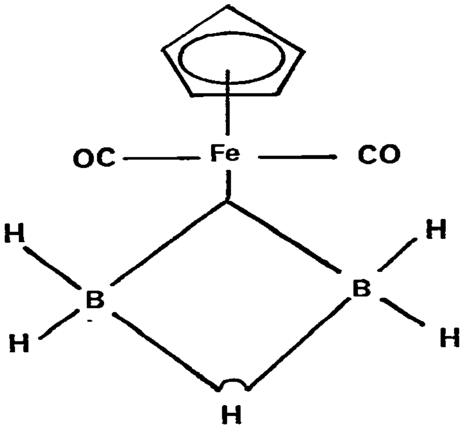
aromatic compounds; Y=BF_4^- or PF_6^-) complexes from the treatment of [$RuCl_2$-(η^6-arene^1)]$_2$ in acetone with $AgBF_4$ or $AgPF_6$, acid (HBF_4, HPF_6), and arene^2 has been published [442].

BORANE AND CARBORANE

The reaction of B_2H_6 with FpK yields the novel complex Fp-(η^2-B_2H_5), isoelectronic and presumably a structural analog of [Fp(η^2-C_2H_4)]$^+$. Two bonding descriptions, 327 using 3-center, 2-electron bonds and 328 using a comparison to metal-olefin bonding were discussed [443].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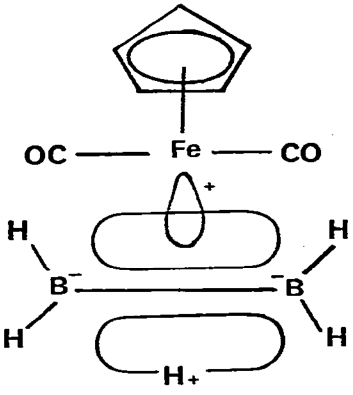
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The complex $Cu(PPh_3)_2B_5H_8Fe(CO)_3$ (329) was prepared by the reaction of $B_5H_9Fe(CO)_3$ (330) and KH followed by $Cu(PPh_3)_3Cl$. The structure of 329 was determined crystallographically as shown in Figure 49 [444]. Using a special hot-cold reactor, 330 can be prepared in low yield from $Fe(CO)_5$ and B_5H_9 [455]. In order to compare the bonding capabilities of a {BH} unit when compred to a $Fe(CO)_3$ unit in cluster compounds, self consistent charge calculations on B_5H_9 and 1- and 2-[$Fe(CO)_3B_4H_8$] have been carried out [446].

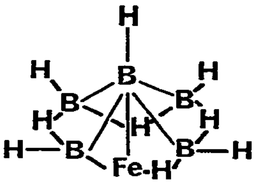
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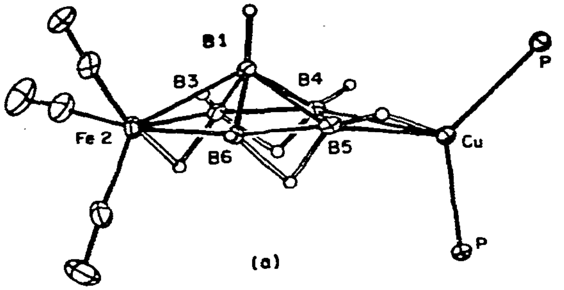
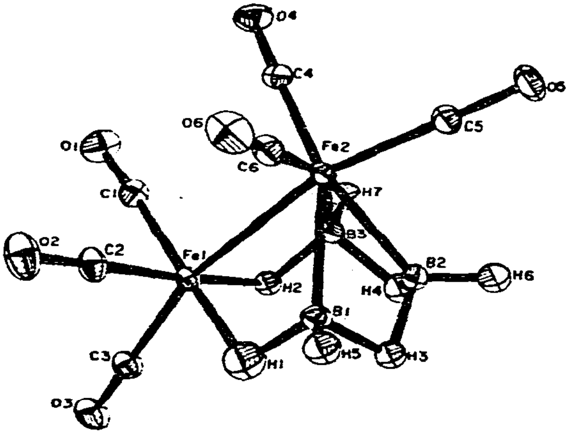
FIGURE 49

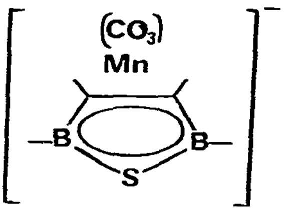


The diiron analog of pentaborane(9), $B_3H_7Fe_2(CO)_6$ has been prepared by the reaction of B_5H_9, $Fe(CO)_5$ and $LiAlH_4$ in 1,2-dimethoxyethane at 60°C. The compound was definitively characterized crystallographically as shown in Figure 50 [447]. The UV photoelectron spectra of $Fe_2(CO)_6B_2H_6$ and $Fe_2(CO)_6S_2$ have been reported. Surprisingly, the band tentatively assigned to the metal-metal bonding orbital was only ca. 0.4eV lower than bands arising from iron nonbonding orbitals. Thus it was proposed, counter to calculations previously published, that these dimers approach the situation of larger organometallic clusters in which the highest occupied orbitals are basically non-bonding with respect to the cluster [448].

FIGURE 50



The tetra-decker complex 332 is prepared from the reaction of the anion 331 with $FeCl_2$. The NMR data indicates that conformational isomers of 332 exist. Reaction of 333 with $FeCl_2$ yields 334 as shown crystallographically



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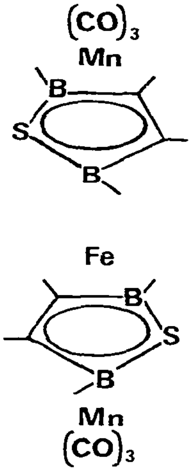

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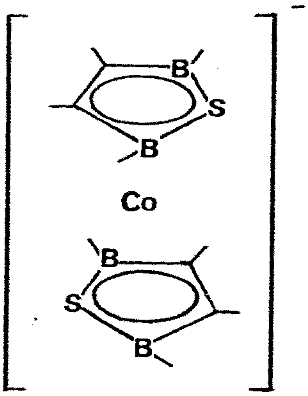
[449]. The structure of $[2,3\text{-}(CH_3)_2C_2B_4H_4]_2FeH_2$ has been reported as shown in Figure 51. The two hydrogen atoms were not directly located but are believed to lie between the two polyhedra on the side of the complex furthest away from the C-CH_3 groups [450].

The reaction of $Tl(C_5H_5B\text{-}C_6H_5)$ and $[RuC_6H_6Cl_2]_2$ yields the new cationic borabenzene complex $[Ru(C_6H_6)(C_5H_5B\text{-}Ph)]^+$ [451]. The molecule bis(borabenzene) iron has been prepared as shown in Scheme 78 [452].

The mild bromination of $CpFeC_2H_2B_9H_9$ yields $CpFeC_2H_2B_9H_8$-Br-8 whereas more rigorous conditions yield $CpFeC_2H_2B_9H_7$-Br_2-8,9 and $CpFeC_2H_2B_9H_6$-Br_3-8,9,12 [453]. The reaction of Cpπ-(3)-1,2-dicarbollyliron and $Tl(O_2CCF_3)_3$ yields 8-(trifluoroacetoxy)-π-Cp-(3)-1,2-dicarbollyliron, as characterized crystallographically [454].



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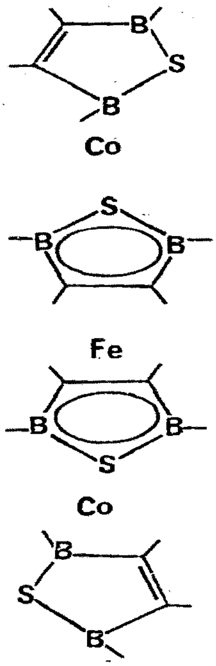

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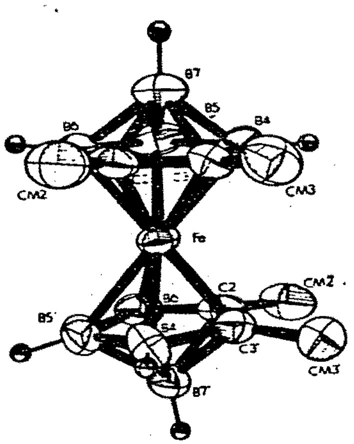
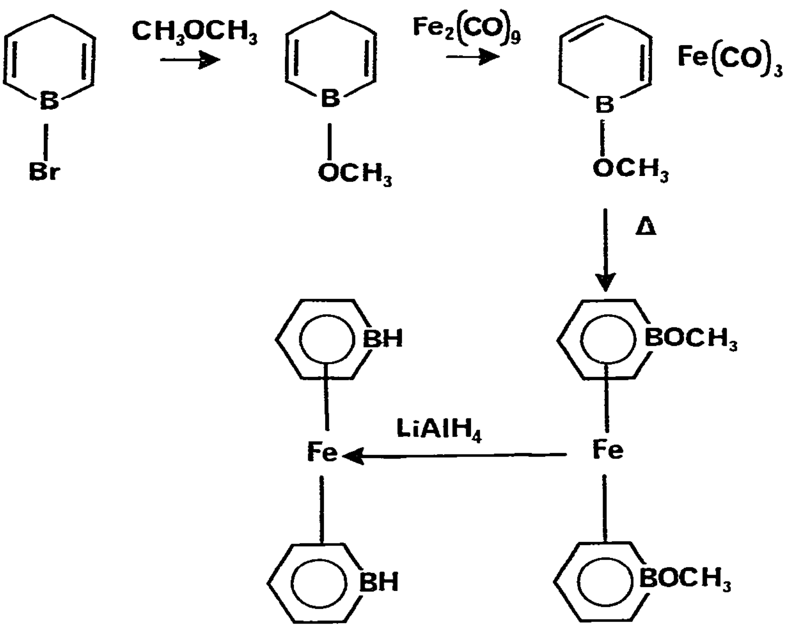
FIGURE 51



Scheme 78



ORGANOMETALLIC SPECIES IN SYNTHESIS AND CATALYSIS

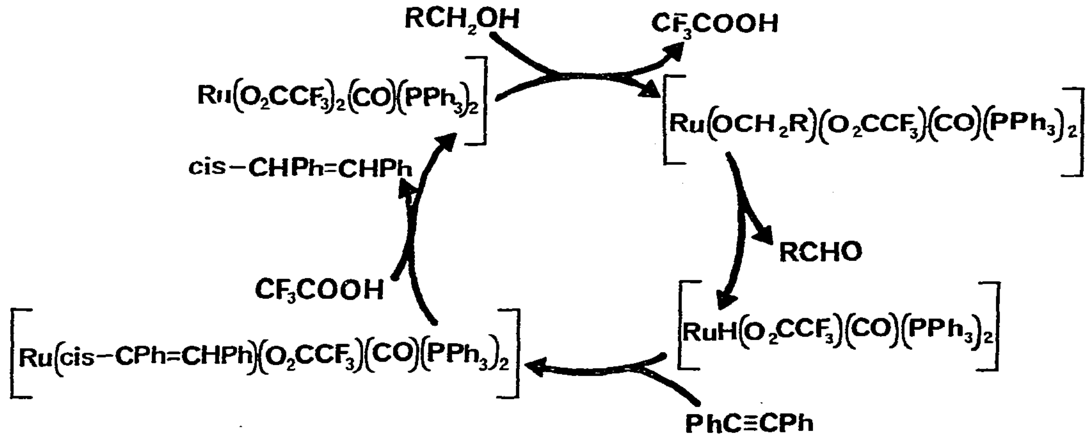
Hydrogenation, Hydroformylation, Hydrosilation and Isomerization

The complexes $RuCl_2(PPh_3)_3$, $RuH_2(CO)(PPh_3)_3$ and $Ru(CF_3CO_2)_2(CO)$-$(PPh_3)_2$ have been shown to be effective hydrogenation catalysts for bulky aliphatic, aromatic and cyclic ketones [455]. Three ruthenium(II) complexes containing PMe_3 ligands have been shown to be active hydrogenation catalysts in the presence of $Me_2NH{\cdot}BH_3$ and ROH [456].

A variety of iron, ruthenium, and osmium clusters have been placed on polymer and silica supports containing PPh_2 groups. Two of the polymer-bound clusters, $[Fe_2Pt(CO)_8(Ph_2PPol)_2]$ and $RuPt_2(CO)_5(Ph_2PPol)_3]$(Pol= polystyrene divinylbenzene), were shown to be very active catalysts for the hydrogenation of ethylene [457].

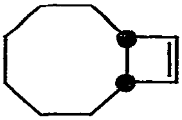
The tetrameric cluster $[(\eta^5\text{-}C_5H_5)Fe(u_3\text{-}CO)]_4$ is an active catalyst for the hydrogenation of alkynes to alkenes at 100-130°C and 100-1000 psi of H_2. Terminal alkynes could be reduced to alkenes in the presence of the alkenes or internal alkynes. It is believed that the cluster remains intact during the reaction [458]. Interaction of diphenylacetylene with $[M(H)(O_2CCF_3)(CO)(PPh_3)_2]$ (M = Ru, Os) yields $[M\{C(Ph)=CHPh\}(O_2CCF_3)CO(PPh_3)_2]$. Cleavage with CF_3CO_2H yields cis-stilbene and $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$ which can be recycled to starting material with primary alcohols yielding also aldehydes thus completing the cycle shown in Scheme 79. A similar reaction with the terminal acetylene PhC≡C-H yields for M=Ru the complex $Ru(C_4HPh_2)(O_2CCF_3)CO(PPh_3)_2$, the structure of which was determined crystallographically [459]. The catalytic hydrogenation of 1-pentyne and 2-pentyne in the presence of phosphine and phosphite derivatives of $H_4Ru_4(CO)_{12}$ has been studied. The ligands improved the selectivity for producing ene products when compared to $H_4Ru_4(CO)_{12}$ [460].

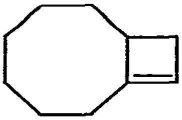
Scheme 79

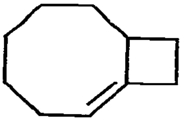


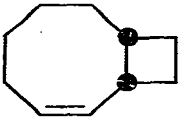
The complex $Ru_2Cl_4((-)\text{-DIOP})_3$ has proved of limited use as a hydrogenation catalyst in converting acetophenone into optically active 1-phenylethanol [461]. The same complex is more successful in the hydrogenation of unsaturated esters. Optical yields on a number of acid and ester substrates were reported [462].

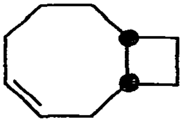
The results of a detailed investigation into hydrogenation and isomerization reactions using the trimeric catalyst precursor $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$ in dimethylformamide has been reported. Two trimeric catalysts were identified in these reactions. An important result is the proposal that only one ruthenium in the clusters is responsible for the coordination of both hydrogens and the olefin and in transfering the hydrogens to the olefin [463]. The influence of the solvent on the isomerization of 1-pentene with $H_4Ru_4(CO)_{11}L$ (L = $P(OEt)_3$, $P(OPh)_3$, PPh_3) and $H_4Ru_4(CO)_{10}(P(OEt)_3)_2$ has been determined. The results indicate that the first step of the reaction is the displacement of a CO ligand by the solvent followed by a standard isomerization via a metal-alkyl intermediate [464]. The isomerization of the cis complex 335 to a mixture of 336-339 by $Fe_2(CO)_9$ produced cis products showing that the rearrangement of simple olefins by iron carbonyls is stereoselective [465].


335


336


337


338

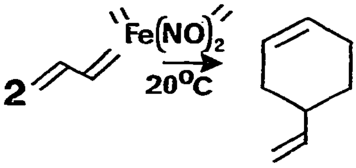

339

A number of metals including iron, catalyze the hydrosilylation of isoprene when co-condensed as metal atoms to yield specifically trans-1-triethoxysilyl-2-methyl-2-butene [466].

C-C Bond Formation

$RuCl_3 \cdot 3H_2O$ and $RuCl_2(PPh_3)_2$ were tested in various alcohol solvents for the polymerization of cyclopentadiene and norbornene [467]. An iron catalyst prepared by electrochemical reduction of $FeCl_3$ in the presence of NO selectively cyclodimerizes 1,3-diolefins as shown in Scheme 80 for butadiene [468].

Scheme 80



A catalytic system containing $RuCl_3 \cdot 3H_2O$, Na_2CO_3 and PPh_3 in EtOH has been reported to convert benzyl chloride into toluene in good yield [469].

Iron chloride reacts with lithium in ethereal solvents in the presence of 5-10% naphthalene as an electron carrier to yield highly reactive iron powder. This powder reacts vigorously with allyl bromide at room temperature to yield 1,5-hexadiene [470]. A system containing $LiAlH_4$, $Fe_3(CO)_{12}$ and HCl causes the reductive dimerization-deoxygenation of 1,5-hexadiene derivatives [471]. The coupling reaction of (neophyl)MgBr in the presence of $FeCl_3$ and $FeCl_2$ has been studied [472]. Another paper followed these experimental results by exploring the symmetry requirements for reductive elimination of dialkylmetal complexes [473]. Two papers have appeared studying a complicated system containing iron stearate complexes in the presence of alkyl aluminum reagents as models for Ziegler-Natta systems [474, 475].

REVIEWS AND DISSERTATION ABSTRACTS

Reviews

A carefully written review of "The Hydrido-Transition Metal Cluster Complexes" by A. P. Humphries and H. D. Kaesz has appeared. It covers the literature between the middle of 1972 and 1977 and extensively reviews iron, ruthenium and osmium clusters [476].

A review of the chemistry of thiocarbonyl complexes by S. Rajan has appeared [477].

A review of π-arene complexes of the Group VIII transition metals by R. G. Gastinger and K. J. Klabunde has appeared which stresses the use of metal vapor synthesis in this rapidly developing area [478].

J. R. Norton has reviewed his excellent work on the thermal decomposition pathways available for $Os(CO)_4RR'$($R = R'$=Me; $R = R' = H$; $R =$ Me, $R' = H$) complexes. Included are a number of important generalizations relating to metal alkyl chemistry [479].

"Transition Metal Complexes of Cyclic Polyolefins" by G. Deganello [480].

"Catalytic Codimerization of Ethylene and Butadiene" by A. C. L. Su [481].

"Hydrogenation Reactions Catalyzed by Transition Metal Complexes" by B. R. James [482].

"The Fischer-Tropsch Reaction" by C. Masters [483].

"The Preparation and Reactions to Tetracarbonylferrates" by Y. Watanabe and Y. Gosei [484].

"Iron, Ruthenium and Osmium. Annual Survey Covering the Year 1976" by J. A. McCleverty [485].

"Structures of Transition-Metal Hydride Complexes" by R. Bau; R. G. Teller, S. W. Kirtley and T. F. Koetzle [486].

"Organic Synthesis via the Polybromo Ketone-Iron Carbonyl Reaction" by R. Noyori [487].

"Catalytic Hydrogenation of Aromatic Hydrocarbons" by E. L. Muetterties and J. R. Blecke [488].

"Reactions of Nitric Oxide Coordinated to Transition Metals" by J. A. McCleverty [489].

"Organometallic Intramolecular-Coordination Compounds Containing a Nitrogen Donor Ligand" by I. Omae [490].

"Clusters and Surfaces" by E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker and W. R. Pretzer [491].

"Mechanistic Features of Catalytic Carbon Monoxide Hydrogenation Reactions" by E. L. Muetterties and J. Stein [492].

Dissertation Abstracts

"Some Thermal Isomerizations by Cyclic Polyolefin Iron Tricarbonyl Complexes" by K. J. Karel [492].

"Synthesis, Electrochemistry and Reactivity of Electron-rich Cyclopentadienyl Iron Complexes with Isocyanide and Phosphine Ligands" by M. C. Molzahn [494].

"Synthesis, Chemical and Structural Characterization of Several Cobalt and Iron Carbonyl Clusters" by R. E. Ginsburg [495].

"Transition Metal Chemistry" by D. J. Fauth [496].

"Synthesis, Reactions and Dynamic NMR Study of Iron Alkene and Alkyne Complexes" by C. J. Coleman [497].

"Transition Metal Chemistry" by A. Gabrielli [498].

"Metal Assisted Cycloaddition Reactions; Hydration of $C_5H_5Fe(CO)_2$(allene) Cations" by P. T. Klemarczyk [499].

"Reactions of Methylenecyclopropane Derivatives and Vinyl Halides with Diiron Enneacarbonyl" by W. L. Lin [500].

"Hydrogenation of Aromatic Ligands During the Synthesis of η-arene-η-cyclopentadienyliron Mono- and Dications: Evidence from ^1H and ^{13}C magnetic resonance Studies" by W. J. Pannekoek [501].

"I. Enantiomeric Recognition with Iron (O). II. Iron Carbonyl Complexes of Dicyclopropylfulvene" by G. A. Page [502].

"Reactions of σ-bonded-η^5-cyclopentadienyl Dicarbonyliron Allyl, Propargyl and Related Complexes" by P. S. Waterman [502].

"The Synthesis and Properties of Borabenzene Derivatives and Their Iron Complexes" by H. F. Sanford [504].

"The Chemistry of Low Valent Polyolefin Complexes in Strong Acids" by J. M. Crockett [505].

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