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Annual Survey for the Year 1989*

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CONTENTS

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LIST OF ABBREVIATIONS USED

acac	acetylacetonate, $(MeCO)_2CH^-$
An	any arene ring, such as benzene, C_6H_6
Ar	an aryl ring, such as *p*-tolyl, MeC_6H_4-
bpy	2,2'-bipyridyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl, C_5H_5
Cp'	methylcyclopentadienyl, $C_5H_4CH_3$
Cp*	pentamethylcyclopentadienyl, C_5Me_5
DEPE	1,2-bis(diethylphosphino)ethane
DMF	N,N-dimethylformamide
DMPE	1,2-bis(dimethylphosphino)ethane
DMPM	bis(dimethylphosphino)methane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPM	bis(diphenylphosphino)methane
E	an ester group, usually carbethoxy or carbomethoxy
El^+	an electrophile
Et	ethyl, C_2H_5-
Fp	cyclopentadienyldicarbonyliron, $CpFe(CO)_2$-
Fp'	cyclopentadienyl(carbonyl)(triphenylphosphine)iron
Fp*	(pentamethylcyclopentadienyl)dicarbonyliron
Ft	the tricarbonyliron group, $Fe(CO)_3$
L	a 2-electron donor ligand, such as a phosphine
LAH	lithium aluminum hydride
M	any transition metal
Me	methyl, CH_3-
Nu^-	a nucleophile
Ph	phenyl, C_6H_5-, also shown as Ø in structures
Por	any porphyrin ligand coordinated as a dianion
PPN^+	$Ph_3P{=}N{=}PPh_3{}^+$
R	any unicovalent organic group such as methyl
TCNE	tetracyanoethene
Tf	trifluoromethanesulfonyl group, F_3CSO_2-
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$
X	any halogen

1. INTRODUCTION

In this Annual Review, I attempt to cover the organoiron chemistry reported in journals published during calendar year 1989. Organoiron compounds are those compounds which contain at least one C-Fe bond; however, Fe-CN compounds are not included in this review, and properties and reactions of the simple iron carbonyls are not described exhaustively. Ferrocenes are treated in Annual Surveys by B. W. Rockett and G. Marr.

The material is organized more-or-less by the Gmelin system, first by increasing number of conjoined iron atoms, then by increasing hapticity of principal organic ligand. The latter is determined by the principle of last position. Thus, (η^3-allyl)(η^5-cyclopentadienyl)(η^2-ethene)iron would be treated with cyclopentadienyliron compounds rather than with allyl- or alkene-iron species. However, for purpose of conciseness, many reactions of dimers such as dicyclopentadienyltetracarbonyldiiron [Fp_2, $Cp_2Fe_2(CO)_4$], in which they undergo fission into monoiron products, are treated alongside those of their monomeric derivatives such as FpR. Likewise, FeM_n clusters are treated as a group with other metal clusters of the same nuclearity.

In structural drawings, solid lines between nuclei represent electron-pair bonds unless otherwise stated. In cases where the electron pair is considered to originate from one atom, an arrowhead is used in the traditional way to show direction of electron pair donation and consequent formal charges. Otherwise, formal charges are shown explicitly.

This reviewer finds adherence to these conventions to be possible in describing all but the largest clusters and multiple-decker molecules, and I believe that their use provides clarity sometimes lost when lines are used willy-nilly in the same structural drawing to represent electron-pair bonds, partial bonds, and geometrical proximity of unbonded atoms. To minimize clutter in structural drawings (particularly in cluster structures), I am also continuing to use the symbol Ft for the commonly-occurring tricarbonvliron group.

2. REFERENCE WORKS

Two volumes of the ongoing Gmelin organiron series have appeared during 1989. Volume B14[1] covers Fp-R compounds with R a carbocyclic or heterocyclic ring, the Fp$^\cdot$ free radical, and salts of Fp^-, Fp^+, and $Fp\text{-}L^+$. Volume B15[2] covers salts of $FpCO^+$, $(dienyl)Fe(CO)_3{}^+$, and their thiocarbonyl and isonitrile derivatives.

3. REACTIONS OF "NAKED" IRON ATOMS AND IONS

Gas phase reactions of Fe^+ with a variety of organic and inorganic substrates have continued to receive intensive study. The energetics and mechanism of reaction of Fe^+ with 1-pentene have been studied by means of the energy spectrum of the products and collision-induced dissociation studies of plausible intermediates. The ferracyclobutane intermediate, cyclo-$FeC_3H_6^+$, was implicated, and its heat of formation estimated at about 1120 kJ/mol[3]. Reactions of Fe^+ with allenes have been investigated, with emphasis on labelling studies to probe rearrangements, which are prevalent in the $Fe(allene)^+$ systems as compared with the isomeric $Fe(alkyne)^+$ systems[4].

Two groups have studied reactions of halobenzenes PhX with Fe^+. Iodobenzene reacted to form $Ph_{1,2}Fe^+$ [5], but dehydrohalogenation predominated with X = F, Cl, and Br, which formed $Fe(C_6H_4)_n^+$, n = 1-7[5,6]. $Fe(C_6H_4)^+$ reacted with alkanes to give products explicable on the basis of iron insertion into C-C or C-H bonds, followed by migration of alkyl groups or hydrogen onto the benzyne ligand, or by insertion of the benzyne into Fe-C or Fe-H bonds[6]. The bond dissociation energy D^o for $Fe^+-(C_6H_4)$ was determined to be 320 ± 40[6] and 350 ± 10 [5] kJ/mol by the two groups.

Reactions of the anion Fe^- with organosulfur compounds were dominated by insertion into C-S bonds. With thiols, $FeSH_{0-2}^-$ were produced[7]. Fe^+ reacted with ethylene sulfide to generate the sequence of ions FeS_n^+ [n = 1-6][8].

Several studies from Berlin have dealt with the mechanistic details of the reaction of Fe^+ with nitriles, as studied by extensive isotopic labelling. In general the reactions were found to proceed by end-on coordination of the Fe^+ to the nitrile group. Depending on structure and chain length, this is followed by insertion of Fe^+ into a topologically remote C-H bond or into the C-CN bond. The latter process dominates for *t*-butyl cyanide and isocyanide, and is followed by hydrogen transfer to form $(C_4H_8)Fe(HCN)^+$ [9]. With longer chain molecules R_2CHCN, both processes compete, and one chain experiences alkene loss while the other gives hydrogen loss[10-12]. Isotope effects suggested that alkene loss, not oxidative addition to the C-H bond, was the rate-determining step[11]. Unsaturated nitriles have also been studied, with the conclusion that dicoordinate species may form when the double bond is sufficiently remote from the nitrile group; insertion into the distal allylic C-C bond then led to loss of alkene[13]. The phosphorus analogs of nitriles, RC≡P, did not behave similarly to nitriles in reactions with Fe^+; processes which eventuated in loss of methane and ethene dominated[14].

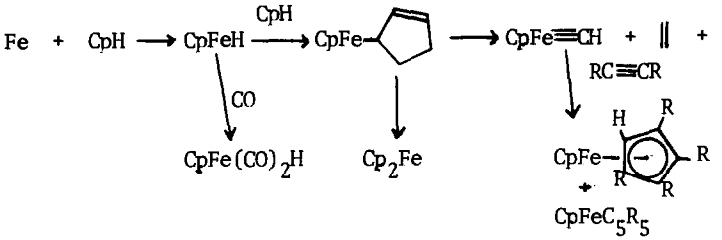
The processes which result in loss of hydrogen and ethene when Fe^+ reacts with 1-alkanols in the gas phase have been studied further by isotope labelling and reinterpreted in terms of remote functionalization analogous to that characterized for nitriles[15,16]. As the result of such a process, the Fe^+-induced loss of ethene from 1-aminopropane was found specifically to involve the 1- and 2-methylenes[16]. Reinterpretations of previous findings on primary alcohols and amines in terms of the remote functionalization mechanism have been offered and supported by extensive isotopic labelling[17].

Reaction of various Fe^+-L species with ammonia resulted in formation of $Fe{=}NH_2{}^+$, for which a strong Fe-N bond strength was indicated[18]. The proton affinity of $Fe{=}CH_2$ was about 930 kJ/mol, from which a $D^o(Fe-CH_2)$ of 360 ±30 kJ/mol was calculated. This may be compared with the $D^o(Fe^+-CH_2)$ of 343 ± 21[19] or an independently determined value of 347 ± 17[20]. For the first-row transition metals from Sc to Cu, the $M^+{=}CH_2$ bond strengths were found to correlate with promotion energies to an s^1d^{n-1} state suitable for formation of the double bond[20].

Although reaction of naked Fe^+ with allyl chloride led principally to the allyl cation, reactions of $Fe(CO)_n{}^+$ resulted in coupling reactions analogous to ones which occur in solution, forming $C_6H_{10}{}^+$ and $FeCl_2$. With $Fe(CO)_2{}^+$, the major product was $(C_3H_5)FeCl^+$; with $Fe(CO)_4{}^+$, $(C_6H_{10})FeCl_2{}^+$, which gave hexadiene radical-cation on collisional activation[21].

The bimetallic ion $ScFe^+$ was unreactive toward alkanes, but reacted with alkenes with scission of C-H bonds. Collisional deactivation of various $ScFeL^+$ species generally resulted in cleavage of the weak Sc-Fe bond, with loss of FeH_{0-2}[22]. $NbFe^+$ resulted from collisional loss of CO ligands from $NbFe(CO)_{2,3}{}^+$, formed from Nb^+ and $Fe(CO)_5$. $NbFe^+$ reacted most efficiently with alkenes having allylic C-H bonds. Extensive reactions of $NbFeL^+$ [L = O, CO, H_2O, alkenes] were studied and compared[23].

Two groups have studied the reactions of Fe atoms with cyclopentadiene in condensed phases. ESR spectra of Fe^{3+} complexes in various spin states were reported, but not the nature of the redox processes which might have led to Fe^{3+} [24]. Cocondensation of iron atoms with cyclopentadiene and various alkynes at 77 K led to substituted ferrocenes; for example, 1,2,3,4-tetramethylferrocene resulted when 2-butyne was used. A mechanism involving $CpFe{\equiv}CH$ (Eq. 1) was proposed[25].



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4. COMPOUNDS WITH η^1-CARBON LIGANDS

a. Hydrido-, Alkyl-, and Aryl-Iron Compounds

In this section I discuss not only organometallic compounds having only iron-carbon sigma bonds, but also a number of low-coordinate or low-valent species which, in the absence of such bonds, are not organometallics, according to strict definition. They are included here because of their utility in synthesis of organometallics and because of their intrinsic interest to many organometallic chemists.

Among these are dihydrogen complexes. Several examples of $L_4Fe(H_2)H^+$ have been reported on during 1989. Reduction of $(DEPE)_2FeCl_2$ with $NaBH_4$ in the presence of dihydrogen and base effectively produced *trans*-$(DEPE)_2Fe(H_2)H^+$; a mechanism involving deprotonation of η^2-dihydrogen intermediates was proposed[26]. Protonation of L_4FeH_2 [L = $(EtO)_3P$, $(EtO)_2PPh$] with HBF_4 at -80° produced $L_4Fe(H_2)H^+$, from which the H_2 ligand was readily displaced. Reaction with aryldiazonium salts led to formation of $L_3Fe(N{=}NAr)_2^{2+}$ and $L_4Fe(ArN{=}NH)(N{\equiv}CMe)^{2+}$ [27]. X-Ray and neutron diffraction studies of $(DPPE)_2Fe(H_2)H^+$ Ph_4B^- indicated a H-H distance of 0.87(3) Å [X-ray] or 0.816(16) Å [neutron]. These studies also showed the hydride ligand to be closer to the metal [1.535(12) Å] than the dihydrogen [1.616(10) Å], and serve to calibrate the NMR T_1 method[28]. A number of new hydride ligand T_1 values shorter than 125 ms have been measured; for example $L_4Fe(H_2)H^+$ [L = $PhP(OEt)_2$] showed T_1's of 60 ms for the hydride and 4 ms for the dihydrogen ligand[29]. $[P(CH_2CH_2PPh_2)_3FeH[X_2]^+$ BPh_4^- [X = H, N] in THF served as a selective hydrogenation catalyst for reducing terminal alkynes to alkenes[30].

Further examples of two-coordinate iron compounds, which owe their stability to the bulkiness of the ligands, have been reported: $Fe[N(SiMe_2Ph)_2]_2$ and $Fe[N(SiMePh_2)_2]_2$. Both have linear structures and high-spin configurations[31]. A compound described as $Fe(NPh_2)_2$ formed ferrocene on reaction with two equivalents of cyclopentadienyllithium. With four equivalents of PhC≡CLi, a compound, characterized as Li^+_2 $(Ph_2N)_2Fe(C{\equiv}CPh)_2^{2-}$ by elemental analysis and magnetic moment determination, was formed. With $Li(CH_2)_4Li$, a product similarly characterized as Li^{+}_{3} $[(CH_2)_4]_2$-$FeNPh_2^{3-}$ resulted[32]. The product from reaction of phenyllithium and $FeCl_2$ at -78° (Ph_2Fe ?) underwent coupling with Me_3SiCH_2Cl to form, after protonolysis, $PhCH_2SiMe_3$ and biphenyl[33].

Reduction of (1,4-diazadiene)$FeCl_2$ with Grignard reagents gave a species [(diazadiene)Fe(0) ?] capable of catalyzing Diels-Alder additions of internal alkynes to norbornadiene[34]. The crystal structure of $(RN{=}CH{-}CH{=}NR)Fe(NO)_2$ [R = CMe_3] has been reported, as a representative of several (diazadiene)irondinitrosyls which were synthesized. Spectroscopic and electrochemical properties were reported[35]. Crystal structures of (DPPE)$Fe(NO)_2$ and (μ-DPPE)$[Fe(NO)_2Cl]_2$ have also been reported[36]. Phosphine adducts $(R_3P)_{1-3}FeCl_3$ have been studied by ESR and crystallographic means. Unstable monophosphine adducts [R = Ph, cyclohexyl] were found to be high-spin tetrahedral compounds. Diphosphine adducts were isolable and more fully characterized. The bis(PPh_3) adduct had long (2.64 Å) axial Fe-P bonds in a trigonal bipyramidal structure and was a high-spin compound, whereas the bis(trimethylphosphine) analog had more normal Fe-P bond lengths (2.335 Å) and a $S = 3/2$ ground state[37].

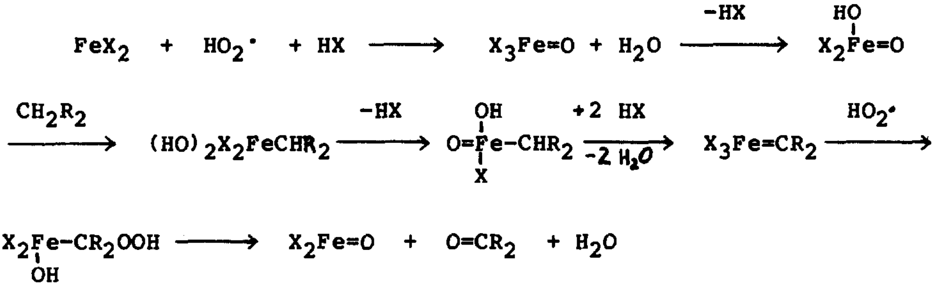
Electrochemically generated Fe[0] porphyrins were found to react readily with alkyl halides to form $RFe(Por)^{-}$, which were isolable with sufficient steric hindrance around the alkyl group. Electrochemistry gave access to formal oxidation states of iron between I and IV, and their relative stabilities were discussed as a function of the alkyl group and the porphyrin ring[38]. Reaction of (Por)FeR with dioxygen has been studied by NMR methods at low temperatures, allowing characterization of the following reaction scheme:

$$\begin{aligned} &(Por)FeCHR_2 + O_2 \longrightarrow (Por)FeOOCHR_2 \\ &(Por)FeOOCHR_2 \longrightarrow (Por)FeOH + R_2C{=}O \qquad (2) \\ &2\ (Por)FeOH \longrightarrow (Por)FeOFe(Por) + H_2O \end{aligned}$$

The first step was photochemically assisted, but was retarded by an axial N-methylimidazole ligand. (Por)FeOH catalyzed the formation of acetaldehyde from ethyl hydroperoxide[39].

Evidence for formation of an organoiron intermediate in biosynthesis of leukotriene A_4 has been adduced by study of lipoxygenase enzymes from different species, which produce different stereochemistry, and by studying the effect of oxygen pressure on the products[40]. The possible role of organoiron intermediates in cytochrome-catalyzed epoxidation reactions, as modeled by use of characterizable porphyrin systems, remains a topic of controversy. The successful epoxidation of adamantylideneadamantane catalyzed by (Por)FeCl [Por in this case is tetraphenylporphyrin] has been held by Traylor[41] to argue against oxaferracycle intermediates. The σ-alkyl porphyrin $(Por)FeCH_2CH(OH)CH_2CMe_3$ has been synthesized by reduction of (Por)FeCl [here Por signifies tetrakis(2,6-dichlorophenyl)porphyrin] in the presence of the bromohydrin or by reduction of the N-alkylated porphyrin with dithionite. Deprotonation of the hydroxyl group resulted in formation of the epoxide, $Me_3CCH_2\overline{CHCH_2O}$, in 80% yield. This result provides a model for cytochrome epoxidation reactions involving organoiron intermediates[42], though it does not prove their necessity in the actual biological reactions. Molecular modeling studies of reaction of the efficient catalyst [tetrakis-(2,6-dibromophenyl)porphinato]iron(III) chloride did not support the formation of oxaferracyclic intermediates[43].

The mechanisms involved in selective oxidation of alkanes using the Gif and Gif-Orsay systems have been discussed, and the role of organoiron intermediates supported. Using the Gif system, involving $(C_5H_5N)_4FeCl_2$, acetic acid, zinc dust, and oxygen, the following symbolic mechanism was proposed[44]:



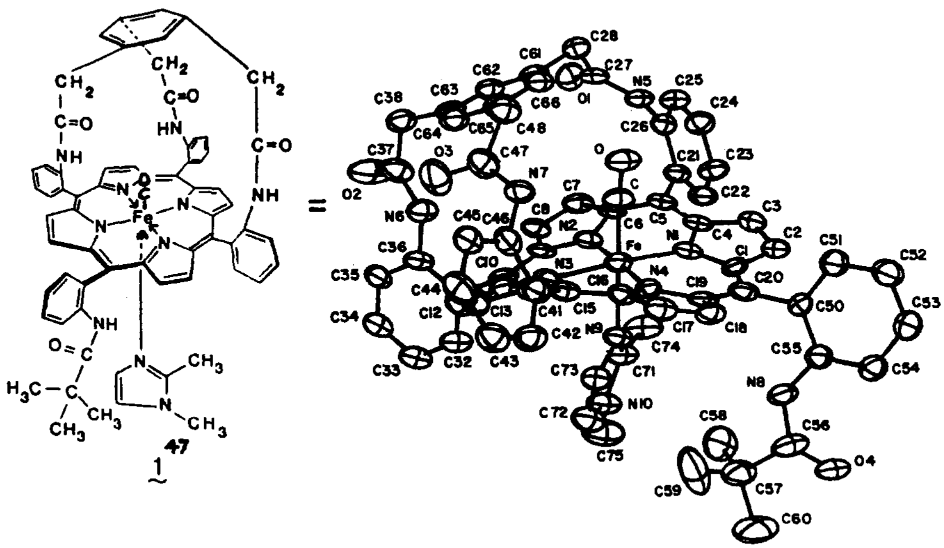
$$FeX_2 + HO_2^{\bullet} + HX \longrightarrow X_3Fe{=}O + H_2O \xrightarrow{-HX} X_2\overset{HO}{\overset{|}{Fe}}{=}O$$

$$\xrightarrow{CH_2R_2} (HO)_2X_2FeCHR_2 \xrightarrow{-HX} O{=}\underset{X}{\overset{OH}{Fe}}{-}CHR_2 \xrightarrow[-2\,H_2O]{+2\,HX} X_3Fe{=}CR_2 \xrightarrow{HO_2^{\bullet}}$$

$$X_2\underset{OH}{Fe}{-}CR_2OOH \longrightarrow X_2Fe{=}O + O{=}CR_2 + H_2O$$

4b. Iron Monocarbonyls, e.g. $L_4Fe(CO)$

The majority of the compounds in this class are iron porphyrin derivatives (Por)Fe(CO), which continue to be studied as models for biological heme systems. A topic of current interest is the basis for discrimination between O_2 and CO as axial ligands. Two independent molecular mechanics studies of several monocapped porphyrin models have suggested that steric considerations play an important role in favoring coordination of O_2 (bent) rather than CO (linear)[45,46]. The crystal structure of a sterically encumbered (Por)Fe(CO) molecule, 1, did show a slight distortion (172.5°) of the Fe-C-O angle from linearity[47]. The significant influence of distortions in the porphyrin ring, induced by shortening the cross-ring strap, upon O_2 or CO dissociation was investigated by resonance Raman spectroscopy[48]. A new class of porphyrins having a strap across one face and two large pendant groups on the other, called "jellyfish" porphyrins, has


CH2
C=O
NH
HN
Fe
NH
O=C
H3C–C
CH3
N
CH3
=
C28
C61
C27
C62
N5
C25
C38
C63
C66
O1
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C64
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N9
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C74
C33
C32
C43
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C71
C54
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C72
N10
C58
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C75
O4
C59
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C60

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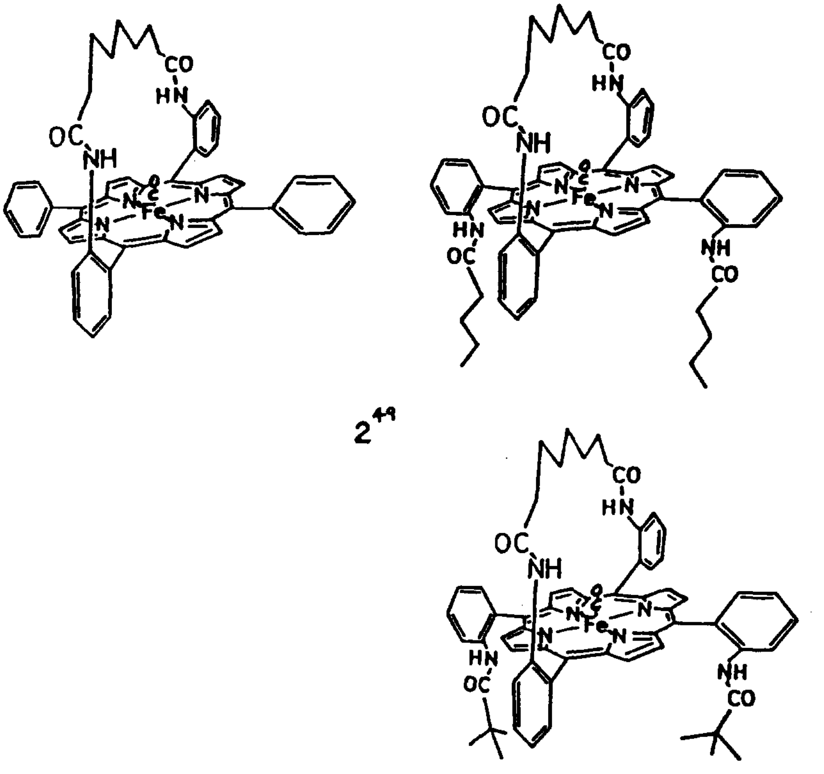

CO
HN
OC
NH
O
C
N
Fe
HN
OC
NH
CO

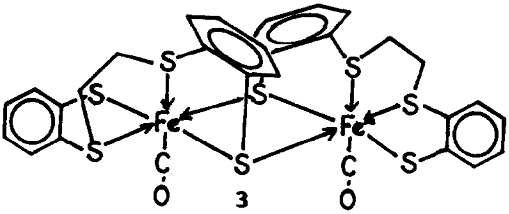
2[49]

been synthesized, and their affinities for O_2 and CO measured[49]. Examples are shown as **2**. Measurements of proton NMR spectra of both O_2 and CO adducts of the "jellyfish" porphyrin having pendant pivalamide groups suggested significant conformational differences in the two adducts[49].

Time-resolved infrared linear dichroism has been applied to study of the CO orientation in carbonylated cytochrome oxidase. The results indicated a Fe-C-O angle of 175° and a 16° deviation of the Fe-C bond from perpendicularity with the mean heme plane[50]. ^{17}O NMR studies of carbonylated heme proteins [sperm whale myoglobin and human and rabbit hemoglobins] showed "surprisingly narrow" lines. Comparison results revealed linear relationships between the chemical shift, the infrared stretching frequency of the CO ligand, and the CO binding affinity of the protein[51]. Reversible CO binding to iron(III) isobacteriochlorins has been studied by ESR spectroscopy, as has binding of Me_3CNC and PF_3[52].

Thermal decarbonylation of $[SC_6H_4SCH_2CH_2SC_6H_4S]Fe(CO)_2$ at 90° in DMF gave the dimeric monocarbonyl product 3, whose structure was ascertained by X-ray crystallography. Only 3 and its enantiomer, of the ten possible stereoisomers, were observed[53].

Photolysis of $(ON)_2Fe(CO)_2$ in hydrogen-doped liquid rare gas solvents produced $(ON)_2Fe(CO)(\eta^2\text{-}H_2)$[54]. An arsine complex, $R_3As\rightarrow Fe(CO)(NO)_2$ [R = CMe_3], along with analogous compounds having silyl, germyl, and stannyl substituents on the arsenic in lieu of the *tert*-butyl groups, were prepared by carbonyl displacement reactions[55].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4c. Iron Dicarbonyls, e.g. $L_3Fe(CO)_2$

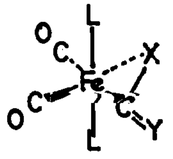
$Fe(CO)_2^-$ reacted in the gas phase with methane and neopentane by C-H bond insertion to form $(OC)_2Fe(R)H^-$. With dimethyl ether, an adduct $Me_2OFe(CO)_2^-$ and a dehydrogenated adduct, thought to be $(OC)_2Fe{=}CHOMe^-$ based on deuterium exchange experiments, formed[55a].

The low-energy electron transmission spectrum of $Fe(CO)_2(NO)_2$ has been analyzed through use of multiple scattering Xα calculations, which indicated four stable anion states[56].

$Fe(CO)_2(NO)_2$ catalyzed the alkylation of allylic carbonates by sodium diethylmalonate more effectively than salts of $Fe(CO)_3(NO)^-$ [57].

Several complexes $(RS)_2Fe(DPPE)(CO)_2$ were synthesized directly from Fe(II) salts by reaction with DPPE and the thiolate under CO. The crystal structure of the bis(benzenethiolate) complex showed the all-cis configuration[58]. The electrochemistry of $[MeC(S)CHC(S)Me]_2Fe(CO)_2$ has been explored; one-electron reduction was followed by rapid loss of both CO's, whereas oxidation resulted in formation of the 3,5-dimethyl-1,2-dithiolium cation *(from the dithioacetylacetonate ligand) and (η^5 ?) [MeC(S)CHC(S)Me]*$Fe(CO)_2^+$ [59].

Reaction of μ-$N_2[FeL_2(CO)_2]_2$ with propionitrile gave the N-coordinated $EtCN{\rightarrow}FeL_2(CO)_2$ [L = $P(OMe)_3$, PEt_3], but diphenylketene and its p-tolylimine gave η^2-coordinated products **4** [Y = CPh_2; X = O, NAr], for which crystal structures were reported. Reactions of compounds **4** [X = Y = S] with alkynes to form isomeric *products, 5 and 6, which can equilibrate in solution, have* been studied by extended Hückel MO methods[61]. Halopropynal acetals, $XC{\equiv}CCH(OR)_2$ [X = Cl, Br, I; R = Me, Et] reacted with the μ-N_2 complex to form $(OC)_2L_2Fe(X)[C{\equiv}CCH(OR)_2]$, but $HC{\equiv}CCH(OR)_2$ gave the carbenoid products **7**, $(OC)_2L_2Fe{=}C{=}CH{-}CHO$. With the chloroalkyne $ClC{\equiv}C\overline{CH(OCH_2CH_2CH_2O)}$, dehydrohalogenation and ligand coupling produced a small amount of **8**[62].



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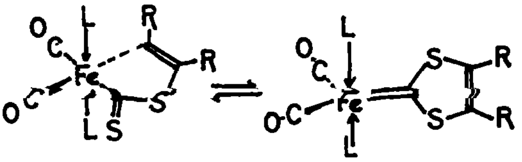
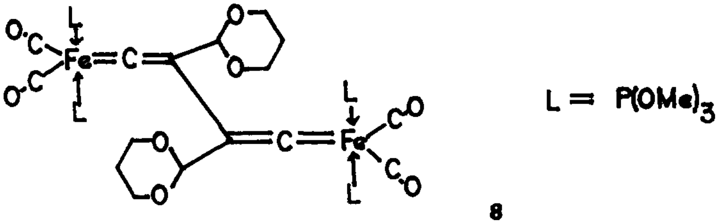


5 **6**



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Reaction of DPPE with $HFe(CO)_4SiPh_3$ gave the bis-hydride $H_2Fe(CO)_2(DPPE)$, also obtainable by photodecarbonylation of $(DPPE)Fe(CO)_3$ in the presence of hydrogen. This product is probably the same as the product previously reported to be $(DPPE)Fe(CO)_2(H)(SiPh_3)$ [63]. An authentic sample of the latter could be prepared by silane exchange. A number of silyl complexes $(OC)_2Fe\{P(OEt)_3\}_2(H)(SiR_3)$ have been prepared by photolysis of the tricarbonyl $(OC)_3Fe[P(OEt)_3]_2$ in the presence of the silane [R = OEt, Ph, R_3 = Ph_2Me]. Triphenylphosphite analogs were better prepared by thermal reaction of the ortho-metallated complex $(OC)_2Fe[P(OPh)_3]_2$. The compounds showed fluxionality at room temperature, and they were deprotonated by KH to form anionic silyl complexes, which gave covalent metallo derivatives $MFe(CO)_2L_2SiR_3$ [M = Ph_3PAu, Me_3Sn, and Me_2ClSn]^{64}.

4d. Iron Tricarbonyls, e.g. $L_2Fe(CO)_3$

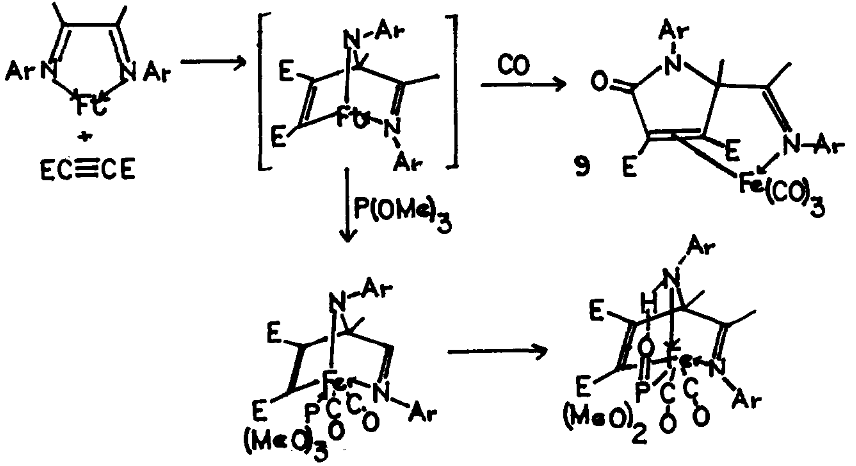
Photolysis of $LFe(CO)_4$ and oxidative addition of the resulting $LFe(CO)_3$ to an Si-H bond have been used to prepare silyl complexes *mer*-$(OC)_3FeL(SiR_3)(H)$ [L = $P(OMe)_3$, $P(OPh)_3$; R = OEt, Ph]^{64}. The anion, $Ph_3PFe(CO)_3SiR_3^-$ reacted with Group 12 halides to form stable -CdCl and -HgBr adducts, but the -ZnCl adduct was unstable. $Hg[Fe(CO)_3(PPh_3)(SiR_3)]_2$ could also be formed by further reaction^{65}. The geometry of the silyl hydride complexes has been found to depend on solvent; in nucleophilic solvents, the triphenylsilyl ligand is coplanar with the meridional CO's, in non-nucleophilic solvents the hydride lies in that plane. The hydride and silyl ligands were mutually *cis* in each case. Reaction of $(Ph_3P)Fe(CO)_3(H)(SiPh_3)$ with R_3P or R_3N resulted in deprotonation of the relatively acidic (pK_a < 9) hydride^{66}.

The highly reduced dianions, $Fe(CO)_3PR_3^{2-}$ [R = Ph, Me], were produced by treatment of the tetracarbonyls with tetraethylammonium hydroxide in methanol to form $HFe(CO)_3PR_3^-$, followed by deprotonation with K(*sec*-Bu)$_3$BH. They are very strong bases, which readily deprotonated acetonitrile. The triphenylphosphine ligand readily exchanged with trimethyl phosphite at room temperature^{67}. The acyliron complexes Na^+ $[RC(=O)Fe(CO)_3PPh_3]^-$, obtained by reaction of alkyl halides with $Na_2Fe(CO)_4$ and PPh_3, reacted readily with aryl iodides in the presence of catalytic $Pd(PPh_3)_4$ and $ZnCl_2$ to form aryl ketones RCOAr. (*S*)-2-bromooctane gave the (*R*)-ketone in high enantiomeric purity^{68}.

Synthesis of tricarbonylbis(phosphine)iron compounds by photolysis of $Fe(CO)_5$ in the presence of two equivalents of phosphine has been described in detail^{69}. $(Ph_3P)_2Fe(CO)_3$ can be obtained free of mono- or tri-phosphine compounds by reaction of triphenylphosphine with $KHFe(CO)_4$ in ethanol^{70}. $(DPPM)Fe(CO)_3$, $(DPPE)Fe(CO)_3$ and other diphosphine-$Fe(CO)_3$ complexes were prepared by reduction of $FeCl_2$ by manganese[0] in the presence of the diphosphine and carbon monoxide^{71}. What appears to be the same reaction could also be achieved by acetone-sensitized photoreduction of $FeCl_2$ in THF also containing triethylamine^{72}.

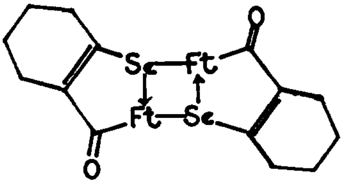
The crystal structure of [*o*-$C_6H_4(PPh_2)_2$]$Fe(CO)_3$ has been reported, along with nitrosylation studies of this and other (diphosphine)$Fe(CO)_3$ complexes[73]. The $Fe(CO)_3$ complex of 1,1'-bis(diphenylphosphino)ferrocene, which resulted from Me_3NO-induced decarbonylation of the $Fe(CO)_4$ complex, was also the subject of X-ray crystallographic study[74]. Mössbauer spectra of trans-$L^1L^2Fe(CO)_3$ *compounds* (L^1 *and* L^2 = *phosphines and phosphites*) have been measured and interpreted in terms of Fe→P back donation[75].

A mechanistic study of the photosubstitution reactions of $[R-N=\overset{|}{C}-\overset{|}{C}=N-R]Fe(CO)_3$ has indicated the presence of two excited states of similar energies. Population of the lowest triplet ligand-field state led to CO dissociation, whereas population of the slightly lower energy metal-ligand state resulted in formation of the η^4 isomer[76]. Similar behavior was also observed for ruthenium analogs and for phosphite-substituted complexes $[R-N=\overset{|}{C}-\overset{|}{C}=N-R]Fe(CO)_2[P(OPh)_3]$; in the latter cases the ligand-field state reacted by photodissociaiton of an Fe-N bond, with rapid reclosure[77]. Thermal reaction of a diazabutadiene complex with dimethyl azodicarboxylate occurred as shown in Eq. 3[78].



(3)

Reaction of tetramethylene-1,2,3-selenadiazole with $Fe_2(CO)_9$ in ethanol produced the dimeric product **10** (X-ray structure)[79]. Bridged complexes **11** resulted when methanolic solutions of Fe^{2+} and arenethiolates were allowed to absorb CO[58].



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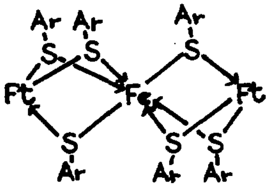

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4e. Iron Tetracarbonyls, e.g. $LFe(CO)_4$ and $R_2Fe(CO)_4$

The homolytic bond dissociation energy of $H\text{-}Fe(CO)_4H$ has been indirectly measured as 250 kJ/mol, using data on pK_a and oxidation potentials in acetonitrile[80]. $Na_2Fe(CO)_4$ reacted with COS to form $Fe(CO)_5$ and sodium dithiocarbonate, $Na_2COS_2^{2-}$, but carbon disulfide did not form $Fe(CO)_4(CS)$. Isothiocyanates RNCS gave isonitrile complexes $Fe(CO)_4(CNR)$ [R = Ph, Me][81]. $Na_2Fe(CO)_4$ displaced chloride from (η^6-PhCl)Cr(CO)$_3$ in THF/N-methylpyrolidinone solution, forming the complexed aryl iron species [η^6-$C_6H_5Cr(CO)_3$]-$Fe(CO)_4^-$ [82].

Metathetical reaction of Et_4N^+ $HFe(CO)_4^-$ with MCl_2 [M = Zn, Cd, Hg] gave $M[HFe(CO)_4]_2$, from which butyl-lithium was able to abstract two protons. A crystal structure of $(PPN^+)_2$ $Hg[Fe(CO)_4]_2^{2-}$ showed a linear Fe-Hg-Fe skeleton with idealized D_{3h} symmetry[83]. An ionic compound, $(Ph_3P)_2Rh[R\text{-}N{=}CH\text{-}CH{=}N\text{-}R]^+$ $HFe(CO)_4^-$, 12, [R = cyclohexyl] was formed (along with covalent Rh-Fe species to be discussed in Section 9c of this review) from interaction of $(Ph_3P)_2RhH_2[RN{=}CH\text{-}CH{=}NR]^+$ and $HFe(CO)_4^-$ [84].

Phase-transfer reactions involving $Fe(CO)_5$ and base have often been supposed to involve either $HFe(CO)_4^-$ or $Fe(CO)_4^{2-}$ as reactive intermediates. Evidence has been presented supporting the latter alternative in a phase-transfer system involving 1 M $NaOH/CH_2X_2/Bu_4N^+$ HSO_4^-: use of preformed $HFe(CO)_4^-$ instead of $Fe(CO)_5$ gave no reaction, whereas $Na_2Fe(CO)_4$ gave reactions identical to those of $Fe(CO)_5$. The reactions observed were formation of $(OC)_4^-FeCH_2PPh_3^+$ in the presence of triphenylphosphine and of μ-$CH_2Fe_2(CO)_8$ in its absence. Reactive alkyl chlorides under 10 atm. CO produced acyl anions $RC({=}O)Fe(CO)_4^-$ [R = benzyl, cinnamyl, cyanomethyl, etc.][85]. Treatment of $ArCHBr_2$ with $Fe(CO)_5$, KOH, and 18-crown-6 in benzene gave (mostly trans) stilbenes ArCH=CHAr in high yields[86]. Use of a $Fe(CO)_5$-$Co_2(CO)_8$ mixture under phase transfer conditions resulted in catalytic conversion of iodobenzene to benzoic acid[87].

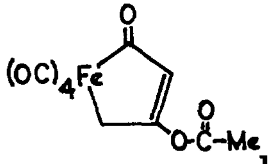
The hydride binding energy of $Fe(CO)_5$ in the gas phase (forming $HC({=}O)Fe(CO)_4^-$) was measured as 230(20) kJ/mol, considerably stronger than those of the Group 6 metal carbonyls; from the available energetics, CO insertion into the $H\text{-}Fe(CO)_4^-$ bond was concluded to be thermodynamically unfavorable[88]. MINDO calculations for hydride migration from iron to CO in $HFe(CO)_4^-$ indicated a barrier of 184 kJ/mol, lower than the barrier for direct hydrogenation of CO[89]. $Fe(CO)_4COOH^-$, from reaction of OH^- with $Fe(CO)_5$, has been characterized by spectroscopic means[90].

Reaction of $KHFe(CO)_4$ with ethyl acrylate in ethanol formed the adduct $EtO_2CCH(Me)Fe(CO)_4^-$, which could be isolated as its

PPN^+ salt. Otherwise, it underwent protonation by solvent to form ethyl propanoate and $Fe(CO)_4$, which formed $(\eta^2\text{-}CH_2{=}CHCO_2Et)\text{-}Fe(CO)_4$, 13. Because of partial cycling of the latter, the overall yield of ethyl propanoate was 270% with respect to iron. $EtO_2CCH_2CH_2C({=}O)CH_2CH_2CO_2Et$ also formed (40% yield)[91]. The stable anion $EtO_2CC({=}O)\text{-}Fe(CO)_4^-$, from reaction of $Fe(CO)_4^{2-}$ with $EtO_2CC({=}O)Cl$, underwent methylation at iron upon treatment with methyl triflate at -50°. The product decomposed at -30° to form $MeCOCO_2Et$ and $MeCOFe(CO)_4CO_2Et$. The latter decarbonylated at +5°, giving $MeCO_2Et$ and $Fe(CO)_5$[92]. The crystal structure of $(Me_2N)_3C^+$ $Me_2NC({=}O)\text{-}Fe(CO)_4^-$ showed the carbamoyl group in the axial position of the iron trigonal bipyramid[93].

The ferracycle **14** (crystal structure) has been isolated from the reaction mixture from carbonylation of $(\mu\text{-}CH_2)Fe_2(CO)_8$. An $(\eta^2\text{-}CH_2CO)Fe(CO)_4$ intermediate was suggested[94]. $(F_3C)_2Fe(CO)_4$ has been prepared in 65% yield by reaction of $Cd(CF_3)_2(MeOCH_2\text{-}CH_2OMe)$ with $X_2Fe(CO)_4$. In acetonitrile the cadmium reagent served to fluorinate rather than trifluoromethylate[95].

A number of compounds having heavier members of Group 14 bonded to $Fe(CO)_4$ groups have been prepared and studied. The products of carbonyl displacement reactions of cis-$HFe(CO)_4MPh_3$ [M = Si, Ge] by phosphines and phosphites were previously described in Section 4d[66]. The silyl and germyl tetracarbonyl hydrides were quite acidic, with pK_a's below 6 in acetonitrile. Reaction of the triphenylsilyl compound with isoprene yielded $(Ph_3Si)_2Fe(CO)_4$[66]. Reaction of bis(dimethylgermyl)methane and -ethane with $Fe(CO)_5$ under ultraviolet irradiation gave rise to cyclic species **15**. The four-membered ring compound decomposed on prolonged irradiation to produce the five-membered ring and other products. Other reactions of these heterocycles, with phosphines, halides, oxygen, and sulfur, were also described[96]. Reaction of $Fe(CO)_4(GeMeH_2)_2$ with cobalt carbonyl, to form a germyl-cobalt species, has been studied[97]. cis-$Fe(CO)_4(SnMe_3)_2$ has been synthesized in high yield from $N(SnMe_3)_3$ and $Fe(CO)_5$; use of $Fe(CO)_4CS$ produced fac-$Fe(CO)_3(CS)(SnMe_3)_2$[98]. The three-coordinate tin and lead complexes $(Et_4N^+)_2$ $M^+[Fe(CO)_4^-]_3$ have been prepared and the crystal structures determined; in both cases the expected trigonal planar structures were found, with average M-Fe distances of 2.55 Å for tin and 2.62 for lead[99]. The crystal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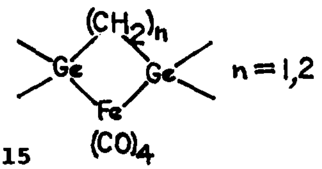

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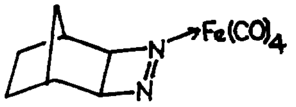
structure of the planar four-membered ring metallacycle [Et_2Pb-$Fe(CO)_4]_2$ has also been reported, with average Pb-Fe distances of 2.73 Å[100]. The shorter distances in the MFe_3 dianions appear to suggest significant double bond character.

The thallium-iron dianion $Tl_2Fe_4(CO)_{16}^{2-}$, which probably exists as $TlFe_2(CO)_8^-$ in solution, has been found to coordinate with diamines to form distorted tetrahedrally coordinated (diamine)$Tl[Fe(CO)_4]_2^-$. Several examples have been prepared and characterized through spectroscopy and crystal structures[101].

Reaction of the diazete with $Fe_2(CO)_9$ produced **16** and a tri-iron compound[102]. Synthesis of $[(Me_3C)_3P]Fe(CO)_4$ has been described in detail[69]. A more complex phosphine-$Fe(CO)_4$ product, **17**, (crystal structure) resulted from reaction of $HFe(CO)_4^-$ with $(R_2N)_2PCl_2$ [R = isopropyl]. In **17** the purely coordinate-covalent P→Fe bond was 2.25 Å long, whereas the bond lengths in the PFe_2 grouping averaged 2.32 Å. Reaction of $HFe(CO)_4^-$ with $(PhPCl_2)W(CO)_5$ gave $(OC)_4Fe$-PPhH-$W(CO)_5^-$ [103].

The trianion $Sb[Fe(CO)_4]_4^{3-}$ was readily prepared by reaction of antimony chlorides with Collman's reagent or $Fe(CO)_5$/KOH/MeOH. The trianion showed a tetrahedral structure in the crystal, with an average Sb-Fe bond length of 2.67 Å. Reaction with $TiCl_3$ or $SbCl_3$ gave $ClSb[Fe(CO)_4]_3^{2-}$ [104]. The same dianion was also produced directly from $HFe(CO)_4^-$ and $SbCl_3$[105] or from $Fe_2(CO)_8^{2-}$ and $SbCl_3$[106]. Use of $BiCl_3$ in these reactions similarly produced the bismuth analog[105,106]. Methylation of the latter afforded **18**[106].



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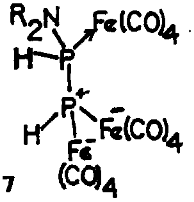

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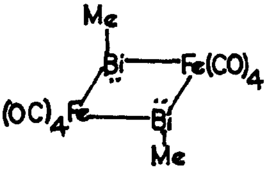

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A series of thiolate complexes, $RSFe(CO)_4^-$, [R = H, Me, Et, Ph] have been synthesized, in the case of R = Ph by reaction of $HFe(CO)_4^-$ with PhSSPh. The bond length between the axial PhS ligand and the iron in PPN^+ $PhSFe(CO)_4^-$ was a fairly long 2.33 Å. Although the formal charge in $PhSFe(CO)_4^-$ resides on the iron, alkylation at low temperature occurred on sulfur, forming labile thioether complexes (PhSR)→$Fe(CO)_4$. Displacement of the thioether by thiolates provided convenient access to other thiolate complexes[107]. Protonation of $MeSFe(CO)_4^-$ at low temperatures formed observable thiol complex $(MeSH)Fe(CO)_4$[107,108]. When a more electron-rich iron was generated by phosphine substitution, then protonation occurred on the iron, forming for instance $HFe(SPh)(CO)_3(PEt_3)$ or the selenium analog $HFe(SeMe)(CO)_3(PEt_3)$.

Protonation of $MeSFe(CO)_3(PEt_3)^-$, however, gave (η^2-MeS-H)Fe-$(CO)_3(PEt_3)$. The site selectivities in these low-temperature protonations were consistent with atomic charges calculated by Fenske-Hall methods[108].

4f. Carbene Complexes $R_2C{=}Fe(CO)_4$

A number of carbene complexes, **6**, **7**, and **8**, were mentioned on previous pages. The electrochemical properties of **6** [R = CO_2Me, L = various phosphines having methyl and phenyl substituents] have been investigated. Oxidation of **6** [R = CO_2Me; L = PPh_3] in acetonitrile resulted in catalyzed decomposition to the carbene dimer, tetrakis(carbomethoxy)tetrathiafulvalene. This apparently involved dimerization of the one-electron oxidation products, followed by ligand elimination[109]. Conjugate addition of butyl-lithium to vinyl sulfide, then addition of the carbanion to $Fe(CO)_4(PPh_3)$ gave the acyl anion complex , which was ethylated with triethyloxonium fluoborate to form the carbene complex, $Ph_3PFe(CO)_3{=}C(OEt)CH(SPh)Bu$. The crystal structure of this compound showed axial phosphine and carbene ligands, and an unusually short Fe=C distance of 1.86 Å. $Ph_3PFe(CO)_3{=}C(OEt)$(o-$C_6H_4NMe_2$) was formed similarly from lithiated N,N-dimethylaniline[110].

8 represents a rather exotic bis cumulated carbene complex. Simpler examples of cumulated carbene complexes are the μ-carbido dimers (phthalocyanine)Fe=C=Fe(phthalocyanine). Examples of these compounds and derivatives with additional axial ligands on the irons have been studied by a battery of spectroscopic and magnetic methods, whose results are consistent with their formulation as containing Fe(IV)[111].

The zwitterionic complex $(Me_2N)_3P^+{-}OSiMe_2{-}Fe(CO)_4^-$, described as a HMPA-solvated silylene complex, has been implicated as an intermediate in reduction of Me_2SiCl_2 to polysilanes by $Fe(CO)_4^{2-}$ in HMPA[112].

4g. Some Reactions and Properties of $Fe(CO)_5$

The optical spectra of $Fe(CO)_5$ and other metal carbonyls were examined with a fast-scan spectrometer, and compared with results of INDO/S calculations including configuration interaction. Near UV absorptions were attributed solely to metal-to-ligand charge transfer[113]. SF_6-Sensitized infrared photodecomposition of $Fe(CO)_5$ proceeded via sequential decarbonylation; in the presence of PF_3, unsaturated iron intermediates were trapped to form $(OC)_nFe(PF_3)_{5-n}$. Without trapping agent, the ultimate product was austenite iron with a mean particle size of 80 Å[114].

The kinetics and mechanism of trimethylamine oxide-induced substitution of triphenylphosphine for CO in $Fe(CO)_5$ have been studied. The reaction was first-order each in iron pentacarbonyl and trimethylamine oxide and zero-order in phosphine, consistent with rate-determining attack of the oxide on a carbonyl group[115]. Photochemical reaction of $Fe(CO)_5$ with nitrosoarenes produced azoxyarenes in high yields, along with small amounts of azoarenes; nitrene complexes $ArN{=}Fe(CO)_4$ may be involved as intermediates[116].

Reaction of $Fe(CO)_5$ with excess 3,5-di-t-butyl-1,2-benzoquinone produced $Fe(O_2C_6H_2R_2)_3$, whereas salts of $Fe_4(O_2C_6H_2R_2)_4{}^{2+}$ resulted with excess iron carbonyl. Both contained high-spin Fe(III)[117]. Co-thermolysis of 2-trimethylsilylnorbornadiene and iron pentacarbonyl produced three isomeric dimeric ketones $[C_7H_7(SiMe_3)]_2C{=}O$, all with the trimethylsilyl groups on the remanent double bonds[118]. [2 + 2]-Cyclobutane dimers resulted when 7,7-ethanonorbornadiene was allowed to react with $Fe(CO)_5$ in the presence of activating ligands such as phosphines, and triethylaluminum as reducing agent[119].

An IR investigation of $Fe(CO)_5$ bonded to surfaces of alumina and zeolites has indicated coordination of a carbonyl oxygen to Lewis acid sites[120].

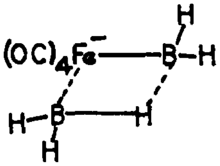
Homoleptic $Fe(CNCF_3)_5$ has been prepared by exhaustive ligand substitution from bis(η^4-butadiene)carbonyliron. NMR spectra revealed rapid fluxional processes even at -100° [121]. Reaction of $[BrC(CHO)_2]_2Fe$ or $[BrC(CHO)_2]_3Fe^-$ [the ligand is the conjugate base of bromomalonaldehyde] with 4-tolyl isocyanate produced $BrFe(CNAr)_5{}^+$ [122].

5. η^2-ALKENE AND η^3-ALLYL COMPLEXES

A new semiempirical SCF MO procedure for calculation of energies and geometries of organotransition metal compounds, called CNDO-S^2, has been developed. For the formation of $(\eta^2\text{-}C_2H_4)Fe(CO)_4$ from ethene and $Fe(CO)_4$, the calculated energy was in reasonable agreement with experiment, but the calculated C-C bond length in the complex was 1.40, as compared to experimental 1.46 Å[123]. EHMO calculations have also been applied to the mechanism of the substitution reaction of iron pentacarbonyl by ethene; the results favored a dissociative mechanism, with the ethene attacking a square planar $Fe(CO)_4$ fragment to form the product[124]. $Fe(CO)_4(B_2H_5)^-$, which is isoelectronic with $Fe(CO)_4(C_2H_4)$, has been formed by reaction of $Fe(CO)_4{}^{2-}$ and $THF\text{-}BH_3$ or $Me_2O{\rightarrow}BH_3$; a diborane-like structure, **19**, was indicated by NMR and Mössbauer spectra[125].

Formation of $(OC)_4Fe(CH_2{=}CHCO_2Et)$, **13**, during reduction of ethyl acrylate by $HFe(CO)_4^-$ [91] was previously noted in Section 4e. Reactions of organolithium or Grignard reagents with $(OC)_4Fe(\eta^2\text{-}CH_2{=}CHCONR_2)$ occurred with acyl transfer from the iron to the organic ligand, to form γ-ketoamides, $R'C(=O)CH_2CH_2CONR_2$, in 52-82% yields[126]. Unusual zwitterionic η^2 complexes **20** (crystal structure for Ar = phenyl) resulted when $(\eta^4\text{-}PhCH{=}CH\text{-}CH{=}N\text{-}C_6Me_2H_3)Fe(CO)_3$ was allowed to react with an aryl-lithium, then alkylated with triethyloxonium fluoborate[127].

Some examples of η^2-ketene complexes, **4** [X = O, Y = CAr_2][60], were previously cited, as was the role of $(\eta^2\text{-}CH_2C{=}O)Fe(CO)_4$ in formation of **14**[94]. A dimeric η^2-complex of a thioketene, **21** [R = CF_3], resulted from photolysis of iron pentacarbonyl and $(F_3C)_2C{=}C{=}S$[128].



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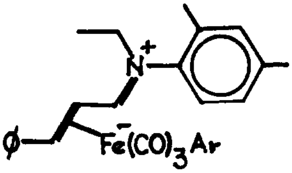

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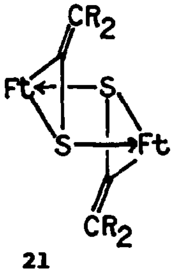

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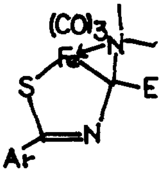
The quantum yields for sequential substitution of *trans*-cyclooctene for CO's in $Fe(CO)_5$ have been measured. The first substitution occurs with high (0.77-0.80) quantum yields at both 302 and 254 nm wavelengths; the second shows a lower quantum yield (0.59) at the longer wavelength, a consequence of partial cyclooctene photodissociation. The novel tris(alkene) complex $(\eta^2\text{-}trans\text{-}C_8H_{14})_3Fe(CO)_2$ was synthesized by irradiation of the bis(alkene) complex in the presence of excess alkene[129].

The product **9** in equation 3 has an η^2-alkene ligand also coordinated to iron through a remote nitrogen atom, generating an overall η^3 attachment. The chemistry of analogous $Fe(CO)_3$ complexes of 7-azanorbornadienes has been described: when the $Fe(CO)_3$ group was coordinated to a double bond bearing two ester substituents, the complex was readily demetallated by trimethylamine oxide, but isomeric complexes with the iron coordinated to an unsubstituted double bond were comparatively resistant to Me_3NO attack[130]. Other examples of products with non-contiguous η^3 coordination, **22**, resulted from complexation of $ArC(=S)\text{-}N{=}C(E)\text{-}NMe_2$ with diiron nonacarbonyl[131].



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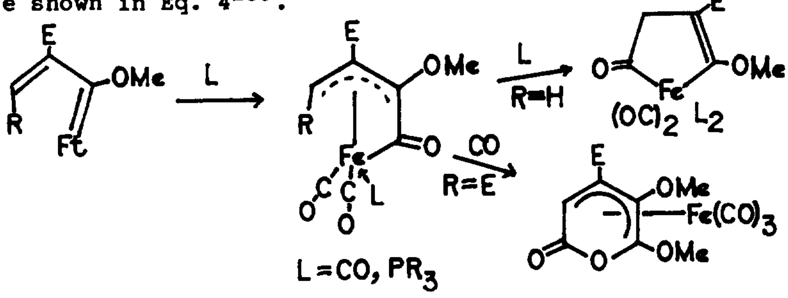
$(\eta^3\text{-}Allyl)$iron tetracarbonyl fluoborate salts have been synthesized directly from allylic alcohols or dienes, $Fe(CO)_5$, and

HBF_4. The parent $(C_3H_5)Fe(CO)_4{}^+ BF_4{}^-$ was obtained in 88% yield using ultraviolet irradiation. $(\eta^3\text{-PhCH}{\overset{..}{-}}\text{CH}{\overset{..}{-}}\text{CH-CH}_2\text{Ph})Fe(CO)_3{}^+ BF_4{}^-$ was obtained in 28% yield from 1,4-diphenylbuta-1,3-diene[132]. The stereochemistry of the (allyl)iron tetracarbonyl cations from these reactions has been studied by spectroscopic means[133].

Neutral allylic complexes $(\eta^3\text{-CH}_2{\overset{..}{-}}\text{CR}{\overset{..}{-}}\text{CH}_2)Fe(CO)_3X$ [R = H, Me; X = Cl, Br] were obtained from the reaction of $Me_2SiFe_2(CO)_8$ with allyl halides[134]. Attack of lithium halides on $(\eta^5$-pentadienyl)tricarbonyliron cations resulted in partial decoordination to form $(\eta^3$-pentadienyl)tricarbonyliron halides. In the case of the 1-phenylhexadienyl cation, attack was unspecific, and both η^3 complexes resulted[135]. ^{57}Fe NMR studies of neutral and cationic (allyl)iron complexes showed chemical shifts in the range 780-1770 ppm[136].

Dienes $RCH{=}CH{-}CR{=}CH_2$ [R = H, Me] underwent 1,4-functionalization upon treatment with MeI, $Fe(CO)_3(NO)^-$, and $R'CE_2{}^-$, resulting in formation of $MeC({=}O)CHR{-}CH{=}CR{-}CH_2CR'E_2$. A likely intermediate in this reaction was $(\eta^3\text{-MeCOCHR-CH}{\overset{..}{-}}\text{CH}{\overset{..}{-}}\text{CH}_2)Fe(CO)_2(NO)$[137]. Analogous allylic intermediates may be implicated in the alkylation of allylic carbonates by malonates in the presence of $Fe(CO)_3(NO)^-$ [57].

Alkylation of $(\eta^3\text{-}C_3H_5)Fe(CO)_3{}^-$ by methyl iodide or benzyl bromide has been followed by low-temperature NMR. Alkylation at iron was followed by rapid alkyl migration to CO upon treatment with triphenyl phosphine, forming $(\eta^3\text{-}C_3H_5)Fe(CO)_2(PPh_3)(COR)$. These reacted further to form $(\eta^4\text{-MeCH=CH-CR=O})Fe(CO)_2(PPh_3)$ products. In acetonitrile solution, the initial iron alkyls were diverted by solvent attack to form $CH_2{=}CH{-}CH_2COR$[138]. Additional reactions which result in conversion of η^3- to η^4-iron compounds are shown in Eq. 4[139].



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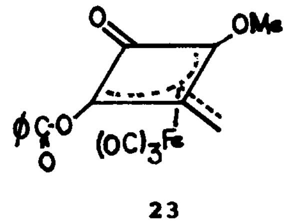
6. COMPOUNDS WITH η^4-LIGANDS

6a. Trimethylenemethyl Complexes

The crystal structure of the $[(CH_2)_3C]Fe(CO)_3$-thiourea inclusion compound, which, unlike the two components, was active in frequency doubling of 1.06 μm laser light, has been determined. The TMMFe(CO)$_3$ "guests" were found to be aligned head-to-tail along thiourea channels[140].



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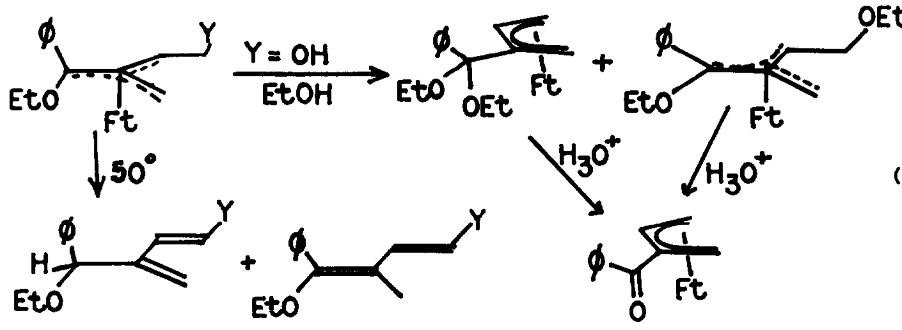
Reaction of (α-methoxyallenyl)lithium with iron pentacarbonyl at -78°, then with benzoyl chloride, produced the novel TMM complex 23. CH_2=C=CYLi [Y = SMe, NMe$_2$] reacted similarly[141]. Carbene complexes (OC)$_4$Fe=C(OEt)Ph and allenes H_2C=C=CH_2R [R = OH, CO_2Et, or CH_2OH] reacted by addition of the allene to the Fe=C bond, forming TMM complexes (OC)$_3$Fe-[C(CH_2)($CHCH_2R$)(CPhOEt)], as a mixture of stereoisomers[142]. These complexes underwent acid-catalyzed rearrangement reactions under mild conditions to form dienes and/or diene complexes (Eq. 5)[143]. Chiral (-)(OC)$_3$Fe[MeCHC(CH_2)$_2$] cleanly rearranged in five minutes in 85% sulfuric acid to (+)-(CH_2=CMe-CH=CH_2)Fe(CO)$_3$[144].



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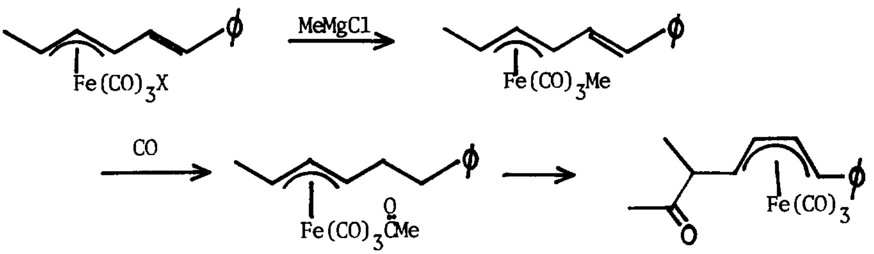
6b. Complexes of Acyclic Dienes, including Heterodienes

Localized MO's for butadiene- and cyclobutadienetricarbonyliron have been presented, and the relationship between the LMO bonding patterns and the symmetry-based bonding description discussed[145].

A general route to (2-acylbutadiene)tricarbonyliron complexes via palladium-catalyzed reaction of acyl chlorides and (2-trialkylstannylbutadiene) complexes has been described[146]. Reaction of an (η^3-pentadienyl)Fe(CO)$_3$X complex with methylmagnesium chloride under CO produced an acylated complex [135]; a mechanism is suggested in Eq. 6. The same product resulted upon reduction of the starting material with sodium amalgam and reaction with acetyl chloride[135]. Synthesis of a large number of dienetricarbonyliron complexes and their ^1H, ^{13}C and ^{57}Fe NMR spectra have



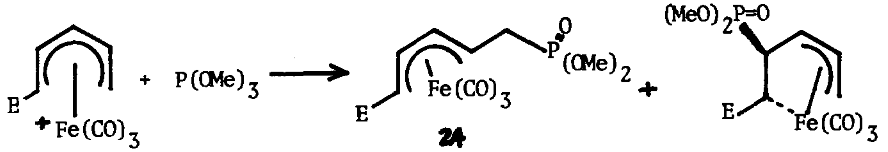
(6)

been reported. Wittig-Horner-type reactions and attack of carbon-nucleophiles at aldehyde, ketone, ester, and nitrile functional groups were used to build up complex organic diene ligands. The ^{57}Fe NMR spectra showed chemical shifts in the range 0-600 ppm[136]. An X-ray structure of [3-6-η(E)-6-methyl-3,5-heptadiene-2-one)]tricarbonyliron showed a twisting of the terminal CMe_2 group[136]. Pseudorotation of the tricarbonyliron group in that compound showed a $\Delta G^{\ddagger}$ of about 50 kJ/mol, as shown by variable temperature ^{13}C NMR study[147].

The circular dichroism spectra of a range of functionalized dienetricarbonyliron complexes have been measured and used to determine the absolute configurations of chiral complexes[148]. Reduction of $[CH_2{=}CH{-}C(CH_2OR){=}CH_2]Fe(CO)_3$ [R = (1S,4R-camphanoyl] with Et_3SiH/BF_3 at -78° gave (isoprene)$Fe(CO)_3$ in 9% yield and 88% e.e. The principal product was the chiral (96% e.e.) TMM complex $[MeCHC(CH_2)_2)Fe(CO)_3$[144].

(Butadiene)tricarbonyliron captured thermal electrons in the gas phase, as shown by pulsed high-pressure mass spectrometry. The free energy for electron capture was -106 kJ/mol, and the reaction was slow, presumably as a consequence of the reduced species having a η^2 structure. The tricarbonyl radical anion lost CO with a thermal activation energy of about 80 kJ/mol, to form (η^4-butadiene)$Fe(CO)_2^-$ [149]. The reaction pathway in multiphoton dissociation of (butadiene)$Fe(CO)_3$ and several related diene complexes has been studied, using pressure-dependent measurements and RRKM theory[150]. A series of solid (diene)tricarbonyliron compounds, when doped with iodine, showed semiconducting behavior. Formation of (diene)$FeI_2(CO)_2$ was indicated by means of Mössbauer, IR and CPMAS NMR spectra[151].

Sorbic acid complexes $[MeCH{=}CH{-}CH{=}CHCO_2H]Fe(CO)_2L$ [L = CO, PPh_3, PEt_3, $P(OPh)_3$] were synthesized from $LFe(CO)_4$ and sorbic acid under UV irradiation; their Mössbauer spectra were discussed in terms of variable back-bonding from iron to L[152]. Two isomeric η^4 phosphonate products resulted from reaction of a pentadienyliron cation with trimethyl phosphite (Eq. 7). Diene complex **24** was also synthesized by BF_3-induced reaction of $(ECH{=}CH{-}CH{=}CH{-}CH_2OAc)Fe(CO)_3$ with trimethyl phosphite, and used in Wit-



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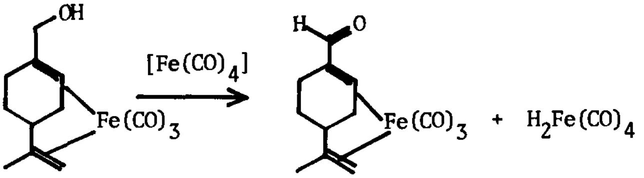
tig-Horner-type chain extensions. Haptomeric mixtures of η^4 triene complexes resulted ^{153}.

Some benzylic and complexed allylic alcohols (Eq. 8) were oxidized to carbonyl compounds by diiron nonacarbonyl, in a process suggested to involve hydride transfer to $Fe(CO)_4$, forming an $RCH{=}OH^+$ $HFe(CO)_4^-$ ion pair, followed by proton transfer. The coordinated $Fe(CO)_3$ group in the example shown facilitated the reaction by stabilizing the intermediate cation^{154}.



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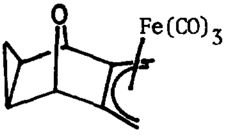
1,3-Dipolar addition of nitrile oxides to the free vinyl group of (η^4-$RCH{=}CH{-}CH{=}CH{-}CH{=}CH_2$)$Fe(CO)_3$ [R = Me, CO_2Me, and $CH_2OSiPh_2CMe_3$] occurred with high (9:1) face selectivity in the isoxazoline products^{155}. The ylide from trimethylsulfonium iodide reacted with the aldehyde group of (η^4-$MeCH{=}CH{-}CH{=}CH{-}CHO$)$Fe(CO)_3$ to form diastereomeric epoxides in 22% combined yield^{156}. (η^4-$MeO_2C{-}CH{=}CH{-}CH{=}CH{-}CHO$)$Fe(CO)_3$ served as the starting material in an asymmetric synthesis of the natural products (-)verbenalol and (-)epiverbenalol. Steps carried out in the presence of the iron tricarbonyl group included condensation of the aldehyde group with Meldrum's acid, followed by conjugate addition of methylmagnesium iodide to the α,β-unsaturated system^{157}. Synthesis of long-chain glycols related to the leukotrienes from (η^4-$Me_3CPh_2SiOCH{=}CH{-}CH{=}CH{-}CHO$)$Fe(CO)_3$ has been carried out, with the key step being diastereoselective hydroxylation (using OsO_4) of C=C double bonds conjugated to the coordinated diene group^{158}.

Reaction of **25** with water under basic conditions led to removal of the metal group and partial hydrogenation of the diene. The free ligand of **25** was reduced by iron carbonyls in the presence of water to the cyclohexenol and the cyclohexadiene derivatives^{159}. A crystal structure of **26** confirmed previous spectroscopic deductions concerning its relative and absolute configurations^{160}. 1-(Dimethoxymethyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene underwent iron carbonyl-induced cyclodimerization during attempted complexation, forming inter alia **27** (crystal structure) and isomers with exo and endo $Fe(CO)_3$ groups and cis and trans $CH(OMe)_2$ groups[161]. Complexation of 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptan-7-one with diiron nonacarbonyl gave exo, exo and endo,exo-bis[$Fe(CO)_3$] complexes. Some mixed complexes with iron tricarbonyl and μ-(CO)bis(indenyl)rhodium groups on separate diene moieties were also prepared[162].



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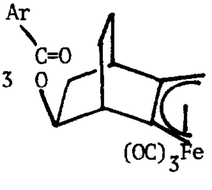

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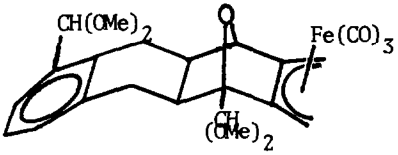
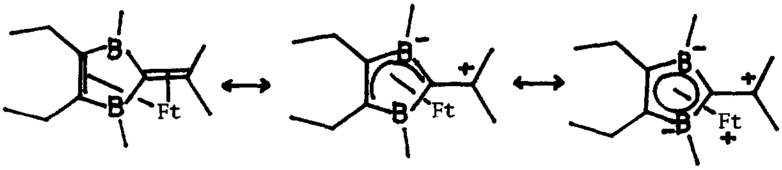


27

The four-electron ligand, 4,5-diethyl-1,3-dihydro-1,3,6,6-tetramethyl-1,3-diborapentafulvene gave an iron tricarbonyl complex, **28**, upon reaction with tricarbonylbis(cyclooctene)iron[163]. Depending upon the degree of bonding between the boron atoms and the iron, the compound can be viewed as anywhere between η^4 and η^6. The extreme deshielding of the 6-carbon in the ^{13}C NMR (230 ppm) was consistent with substantial carbocationic character.



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Formation of enone complexes, $(\eta^4\text{-}MeCH{=}CH\text{-}CR{=}O)Fe(CO)_2\text{-}(PPh_3)$, in 60-90% yields, by reaction of $(\eta^3\text{-}C_3H_5)Fe(CO)_3^-$ with alkyl halides, RX [R = Me, Et, Bu, etc.], followed by PPh_3[138], was previously described in Sect. 5. FAB mass spectra of a number of (enone)$Fe(CO)_3$ compounds have been recorded and discussed[164].

Two groups have independently studied and described reaction of enone complexes with carbanions to form 1,4-diketones, a reaction that evidently involves attack of carbanion at an iron carbonyl, followed by migration of the resulting acyl group to the enone β-carbon[165,166]. Enones used included benzylidene-, ethylidene-, and methylidene-acetone, and the carbanions included Grignard, organolithium, and organocuprate reagents. Treatment of $(PhCH{=}CH\text{-}CMe{=}O)Fe(CO)_3$ with methyl-lithium under a CO atmosphere rather than N_2, however, produced a quite different result: formation of the vinylketene complex $(\eta^4\text{-}PhCH{=}CH\text{-}CMe{=}C{=}O)Fe(CO)_3$

[crystal structure]. In the presence of triphenylphosphine, (η^4-PhCH=CH-CR=C=O)$Fe(CO)_2(PPh_3)$ was obtained. The enal complex (η^4-PhCH=CH-CH=O)$Fe(CO)_3$ did not give a vinylketene complex under CO; instead, a small amount of the triene complex (η^4-PhCH=CH-CH=CH-CH=CHPh)$Fe(CO)_3$ was obtained. Attack of CO or PPh_3 on a vinylcarbene-$Fe(CO)_3$ complex was suggested as a possible mechanism for these novel reactions[167].

Reactions of carbanions with enimine complexes (η^4-PhCH=CH-CR=NPh)$Fe(CO)_3$ [R = H, Me] have also been studied. Ph_2CHLi attacked at the imino carbon, producing PhCH=CH-CH($CHPh_2$)NHPh, and $NCCMe_2CLi$ did likewise[168]. An apparently different result was obtained on addition of aryl-lithium reagents to (η^4-PhCH=CH-CH=N-$C_6H_3Me_2$)$Fe(CO)_3$. Quenching with triethyloxonium fluoroborate at -60° produced **20**, with the aryl group clearly having attacked the iron[127].

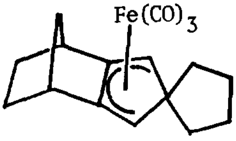
η^4-Diazadiene complexes were formed from the more stable η^2-N,N' structure upon photolysis, especially with long wavelength light[76,77].

6c. Complexes of Cyclic Dienes

X-ray crystal structures of both dicarbonyl(η^4-tetraphenylcyclobutadiene)(trimethylphosphite)iron and the fluoroborate salt of its one-electron-oxidized cation have been determined, allowing an assessment of the structural consequences of removing an electron from the iron-based HOMO. The iron-carbon and carbon-carbon bonds of the cyclobutadiene ligand were little affected, but the iron-phosphorus and iron-carbonyl distances lengthened appreciably, presumably as a consequence of diminished backbonding[169]. Iron tricarbonyl complexes were prepared by direct complexation of tris(*tert*-butyl)trimethylsilylcyclobutadiene and of tris(*tert*-butyl)azacyclobutadiene with diiron nonacarbonyl[170]. Analogous $Fe(CO)_3$ complexes of the cyclobutadiene analogs, diazadiboretidines, $[RBNR']_2$ [R = Me, Et, Pr, Bu, R' = CMe_3; R = R' = $CHMe_2$], have also been prepared[171]. And an $Fe(CO)_3$ complex of 2,4-di-*tert*-butyl-1,3-diphosphacyclobutadiene resulted when $Me_3C-C\equiv P$ reacted with $(C_8H_{14})_2Fe(CO)_3$ or $Fe_2(CO)_9$[172].

Attack of aryl-lithium reagents on tricarbonyl(η^4-cyclopentadiene)iron occurred at a carbonyl group. Quenching of the resulting acyl anion with triethyloxonium fluoroborate occurred by hydride transfer from the cyclopentadiene ligand, to form $CpFe(CO)_2COAr$[173]. The η^4-cyclopentadiene complex **29** was prepared with complete facial selectivity by reaction of the hydrocarbon with $Fe_2(CO)_9$, but use of (benzylideneacetone)$Fe(CO)_3$ resulted in formation of η^5 products with fission of a C-C bond[174]. The cyclophanoid bis[Fe(CO)$_3$] complex **30** also resulted from complexation of the free ligand with diiron nonacarbonyl[175]. The electron-rich pentafulvene complex [η^4-C_5H_4=CPh_2]Fe(PMe_3)$_3$ [from reaction of (benzene)Fe(PMe_3)$_2$ with 6,6-diphenylpentafulvene] showed very high electron density at the exocyclic carbon, which was protonated by methanol[176]. The contrast with the fulvenoid **28** is impressive.

Several Fe(CO)$_3$ complexes of 2,3,4,5-tetraphenylsilacyclo-



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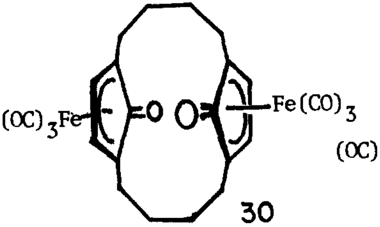

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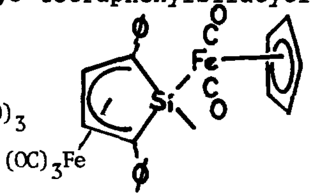

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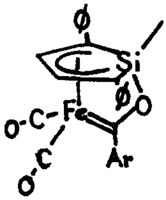
pentadienes having chloro, phenyl, and methyl substituents on the silicon have been prepared[177]. Likewise, **31** was formed by direct complexation. Photolysis of **31** in methanol resulted in replacement (with retention of configuration) of the Fp group by a methoxy group[178]. Other substitution reactions of (η^4-silole)-Fe(CO)$_3$ have been studied. In general, *exo* leaving groups showed enhanced reactivity, and retention of configuration was observed. Attack of organolithium reagents on the *endo*-chlorosilole complex occurred at a carbonyl group, with the acyl anion then displacing chloride intramolecularly to form the carbenoid product **32**[179]. Reaction of (η^1-thiophene)Re(CO)$_2$Cp* with diiron nonacarbonyl gave the η^4 iron complex without disruption of the S→Re bond[180].

Reaction of substituted 4-vinylcyclohexenes with Fe(CO)$_5$ under conditions sufficiently vigorous to result in hydrogen migrations led to mixtures of 1- and 2-substituted cyclohexadiene complexes and complexes of substituted 1-vinylcyclohexenes. The 2-substituted cyclohexadiene complexes were generally favored under conditions of thermodynamic control, but the 1-substituted isomers could be favored by inclusion of ferrous chloride in the reaction mixture[181]. The use of ^{13}C NMR for establishing the structures was recommended, making use of the 15-23 ppm deshielding of carbons of the complexed diene moiety by directly attached alkyl substituents[182].



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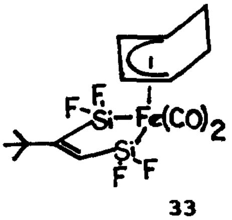

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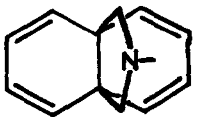
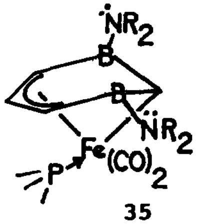


34

A crystal structure of 33 has been reported[183]. A family of complexes having the diene units of the propellane 34 coordinated to *exo* and *endo* $Fe(CO)_3$ and CoCp units in various combinations have been studied[184]. Mass spectra of the three $(C_{13}H_{11}NO_2)[\eta^4\text{-}Fe(CO)_3][\eta^4\text{-}CoCp]$ stereoisomers obtained have been compared and interpreted[185].

Although (η^4-naphthalene)iron tricarbonyl has eluded synthesis, use of arenes or phosphites rather then CO as ancillary ligands has proven conducive to formation of (η^4-naphthalene)iron complexes. Thus, co-condensation of iron vapor, 1,4-dimethylnaphthalene, and triethyl phosphite produced (5-8-η-1,4-dimethylnaphthalene)$Fe[P(OEt)_3]_3$, whose structure was confirmed by X-ray crystallography. But iron vapor, 1,4-dimethylnaphthalene and *p*-xylene gave both 1-4-η and 5-8-η isomers of (η^4-dimethylnaphthalene)Fe(n^6-$C_6H_4Me_2$). And 1-methylnaphthalene gave two isomeric (η^4-methylnaphthalene)Fe(η^6-PhMe) complexes upon reaction with bis(toluene)iron at -50° [186].

The crystal structure of the complex 35, a hetero analog of a η^4-*m*-xylylene complex, showed normal Fe-C bond distances of 2.10-2.19 A, but distortions of the ligand from planarity brought the Fe·····B non-bonding distances up to 2.46 Å[187].



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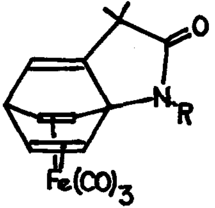

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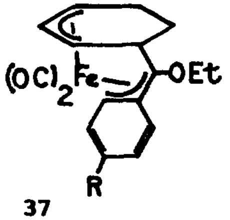
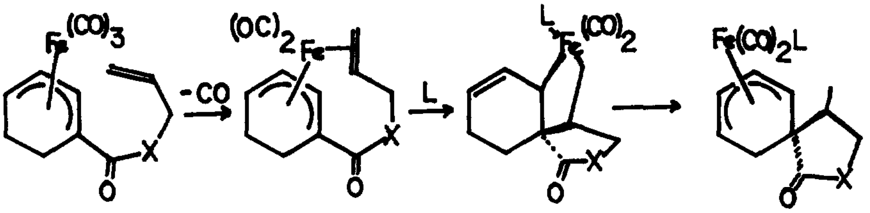


37

Complexes 36 [R = CH_2Ph, Et] have been prepared by photoreaction of the free trienes with $Fe(CO)_5$[188]. An $Fe(CO)_3$ complex of 1,4,5,8-tetrahydronaphthalene was prepared similarly[189].

Reaction of tricarbonyl(η^4-cyclohexadiene)iron with aryllithiums, then alkylation with triethyloxonium fluoborate, produced 37 [R = Me, OMe, CF_3], evidently the result of aryl attack at a carbonyl group and acyl group migration to the ligand[190]. *tert*-Butyl lithium attacked the *exo*-cyano group of (η^4-2-methoxy-5-cyanocyclohexa-1,3-diene)tricarbonyliron to form, after hydrolysis, the ketone. No decyanation was observed[191]. Intramolecular reaction of pendant alkenyl groups with the iron in complexed cyclohexadienes led to C-C bond formation, when the compounds were heated at 140° in the presence of CO or PPh_3, or at 50° with use of trimethylamine oxide to initiate the reaction (Eq. 9)[192]. The tricarbonyliron group was used to protect the cyclohexadiene unit of ergosteryl acetate, allowing functional group manipulations on the side chain. Reactions successfully performed in-



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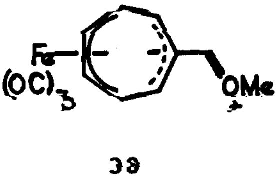
cluded hydroxylation of the side-chain double bond, oxidation of the diol with MnO_2 , reduction of the aldehyde with $Ca(BH_4)_2$, and oxidation of the aldehyde to the acid[193]. Synthesis of the antitumor agent, (+)-taxodiene, from (-)-abietic acid has been carried out, with formation of an iron tricarbonyl complex from abietic acid the first step[194,195]. Many additional examples of cyclohexadiene complexes and their applications to synthesis, which involve interconversion with η^5-cyclohexadienyl complexes, are described in Section 7a of this Review.

Two reactions of (2-5-η-1H-azepine)tricarbonyliron with electrophiles have been reported. Both electrophiles, tropylium ion and dibenzoylacetylene, attacked at the 6-carbon, consistent with previous findings that the azepine complex reacts predominantly as an enamine[196]. Iron tricarbonyl complexes of substituted cycloheptatrienes have been deprotonated, and the anions allowed to displace chloride from 2-chlorotropone, forming [7-(2-troponyl)-6-methoxycycloheptatriene]$Fe(CO)_3$ from the 7-methoxycycloheptatriene *complex, for example*[197]. *The 1,3-haptotropic* rearrangement of the tricarbonyliron group in 8-substituted (1-4-η-heptafulvene)$Fe(CO)_3$ has been studied. The activation barriers $G^{\ddagger}$ for anti→syn rearrangement were 88 kJ/mol for the 8-$CHPh_2$ and 76 kJ/mol for the 8-OMe derivatives [198]. Although the authors, following Brookhart, described the transition state as η^2, this observer considers 38 a more plausible description, supported by the *stabilizing effect of the methoxy group.*



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Reaction of (3,7,7-trimethylcycloheptatriene)$Fe(CO)_3$ with TCNE gave an equilibrium mixture of [2 + 2] and [3 + 2] cycloadducts. Interconversion of the two adducts was studied kinetically, and the results were interpreted in terms of a concerted migration, termed a "[2,2]-sigmahaptotropic rearrangement"[199,200]. A deuterium labelling study of the rearrangement of the [3 + 2] adduct of $(\eta^4-C_7H_8)Fe(CO)_3$ and TCNE into the [6 + 2] adduct showed that it occurred without hydrogen migration; a [4,4]-sigmahaptotropic rearrangement was suggested[201].

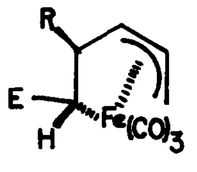
The low-temperature decomposition of $(OC)_3Fe(\mu-C_7H_7)Rh(COD)$ under a hydrogen atmosphere has been used to prepare new iron-rhodium catalysts[202].

Structural changes which accompany reduction of $(\eta^4\text{-cyclooctatetraene})\text{Fe(CO)}_3$ have been studied by FT-IR spectroelectrochemistry[203]. Variable pressure ^{1}H NMR spectroscopy indicated a negligible activation volume for CO site exchange in $(1,3\text{-cyclooctadiene})\text{Fe(CO)}_2(\text{PPh}_3)$, for which a crystal structure was also reported. However, the analogous exchange process in $(2,3,O\text{-}\eta^3\text{-}7,7\text{-dimethoxybicyclo[2.2.1]heptene})\text{Fe(CO)}_2(\text{PPh}_3)$ showed a $\Delta V^{\ddagger}$ of +5 cm^3/mol, possibly due to O⟶Fe bond dissociation[204].

7. η^5-DIENYL COMPLEXES

7a. Compounds with Open Pentadienyl Ligands

Treatment of the epoxide $(\eta^4\text{-MeCH=CH-CH=CH-}\overline{\text{CH-CH}_2\text{O}})\text{Fe(CO)}_3$ with acetic anhydride/HBF_4 resulted in ring opening to form $(2\text{-}6\text{-}\eta\text{-1-acetoxy-2,4-heptadien-6-yl})\text{tricarbonyliron}^+$ BF_4^-. The product of malonate anion attack on the $(1\text{-carbomethoxypentadienyl})\text{-Fe(CO)}_3^+$ cation, previously thought to be the *E,Z*-diene complex, has instead been shown to be **39** [R = CHE_2][205]. Trimethyl phosphite also attacked in part at the 2-position of the same cation, producing **39** [R = P(=O)(OMe)_2] (crystal structure), along with diene complexes from attack at the 5-carbon[153]. Alkynylcuprates selectively attacked 1-R-pentadienyl complexes [R = Me, Ph, E] at the 5-position to produce (*trans, cis*-dienyne)iron tricarbonyl complexes[206].



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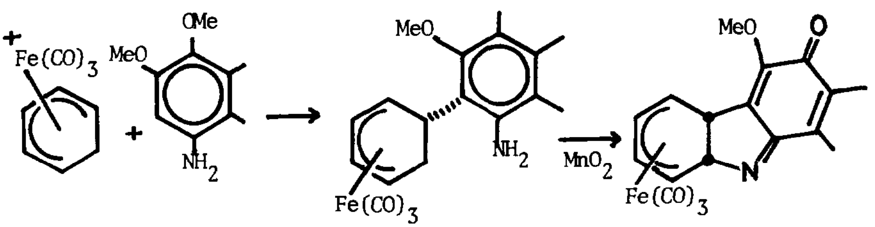
^{13}C and ^{57}Fe NMR studies of bis(pentadienyl)iron and (cyclopentadienyl)(pentadienyl)iron compounds have been reported. These compounds show very deshielded (by 700-1100 ppm) iron in the ^{57}Fe NMR, in comparison to ferrocenes[207]. Photoelectron spectra of these compounds were measured and interpreted with the help of INDO calculations[208].

Reactions of $(\text{cyclohexadienyl})\text{Fe(CO)}_3^+$ cations, including their synthetic applications and the regioselectivities observed in their reactions, have been briefly reviewed[209]. Kinetic studies of the addition of substituted anilines with $(\text{C}_6\text{H}_7)\text{Fe(CO)}_3^+$ showed a linear correlation of rate with basicity, with a Brønsted slope of 1 and a Hammett slope of -3.2, consistent with a transition state having well-advanced C-N bond formation and significant positive charge on the nitrogen[210]. Dimethylaluminum acetylides, $\text{Me}_2\text{Al-C}\equiv\text{CR}$, transferred alkynyl groups to a terminal carbon of the cyclohexadienyliron cation without competing reduction reactions. $(\text{Me}_3\text{SiC}\equiv\text{C})_3\text{Al}$ was the preferred reagent for introducing the trimethylsilylethynyl group[211]. $Re(CO)_5^-$ also added as a nucleophile to the (cyclohexadienyl)iron cation, but the 5-substituted cyclohexadiene complex tended to rearrange to the 2-substituted[212].

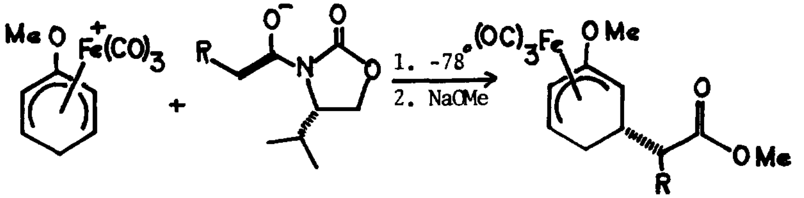
Use of an electron-rich benzene derivative as a nucleophile toward $(C_6H_7)Fe(CO)_3^+$ and oxidative cyclization of the product (Eq. 10) were key steps in a total synthesis of the antibiotic carbazomycin B[213,214].



(10)

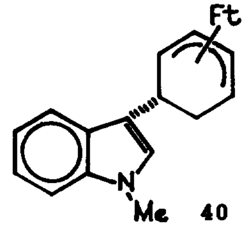
Reaction of nitrosoarenes with $(C_6H_7)Fe(CO)_3^+$ led to formation of free radicals, which have been studied by ESR. Presumably the nitrosoarenes initially attacked the cation as nucleophiles, with the resulting $(OC)_3Fe(C_6H_7{-}N({=}O){-}Ar^+$ cations undergoing subsequent reduction to form the corresponding nitroxyl species or elimination to form $Ph{-}N(-O^\bullet)Ar$[215]. Electrochemical reduction of tricarbonyl(4-methoxy-1-methylcyclohexadienyl)iron cation gave a transient 19-electron species, which dimerized by coupling reactions at C(1) and C(5) to form bis[tricarbonyl(cyclohexadienyl)iron] species[216]. Analogous radical intermediates and dimeric products were formed by treating solutions of $(C_6H_7)_2Fe_2(CO)_4$, which contained some 17-electron $(C_6H_7)Fe(CO)_2$, as shown by ESR, with CO or Ph_3P[217].

The enolates from chiral N-acyloxazolidinones were used as nucleophiles in reactions with (3-methoxycyclohexadienyl)-$Fe(CO)_3^+$, in order to obtain chiral products through asymmetric induction (Eq. 11). With the acetyl derivative [R = H], good

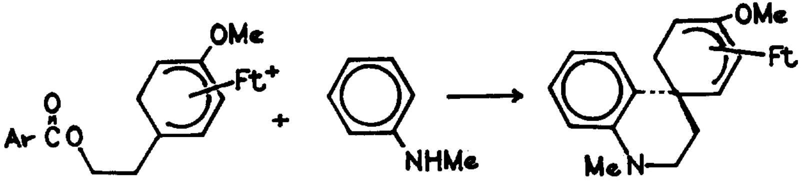


(11)

results (60% e.e.) were obtained, but the propanoyl derivative [R = Me] gave only 11% d.e.[218]. Reaction of the (1-methyl-2-indolyl)cyanocuprate ion with (2-methoxycyclohexadienyl)$Fe(CO)_3^+$ anion resulted in bond formation between the 3-carbon of the indole and the 5-carbon of the cyclohexadiene, forming **40** (71%)[219]. Selective attack at the 5-carbon of the (2-methoxycyclohexadienyl)iron cation was employed in syntheses of two natural products, with cyclopentenyl trimethysilyl ether as the nucleophile[220]. The formation and use of (2-arylcyclohexadienyl)iron tricarbonyl cations, which also reacted with nucleophiles selectively at the 5-position, has been described. An electron-rich aryl group was most effective[221].



Attack of lithium dimethylmalonate and related carbanions on tricarbonyl(4-alkoxy-1-alkyl)cyclohexadienyl)iron$^+$ cations in general resulted in mixtures of products, both 1- and 5-attack being observed[222]. However, N-methylaniline, a reversible and more selective nucleophile, gave a spirocyclic product from ring attack at C5 (Eq. 12)[223]. Selective attack of tin enolates on C1 of tricarbonyl(4-methoxy-1-methylcyclohexadienyl)iron$^+$ was the key step in syntheses of (±)-trichodermol and related natural products[224,225]. Attack of the nucleophile $CH_2{=}C(OMe)OSiMe_3$ on



(12)

tricarbonyl(1,2-dimethoxycyclohexadienyl)iron$^+$ occurred largely at C1, allowing the formation of $(1\text{-}R\text{-}2\text{-}OMeC_6H_5)Fe(CO)_3^+$ [R = CH_2CO_2Me][226]. Hydride removal from tricarbonyl(1,4,5,8-tetrahydronaphthalene)iron gave the expected (cyclohexadienyl)iron cation; less expectedly, reduction with $NaBH_4$ was said to give the starting tetrahydronaphthalene complex back, a surprising attack on the middle carbon of the complexed cyclohexadienyl cation[189].

Hydride abstraction from an equilibrating mixture of isomers led to preferential formation of tricarbonyl(1,3-dimethyl-4-methoxycyclohexadienyl)iron$^+$ [227]. Microbial oxidation of toluene produced homochiral 1-methylcyclohexa-1,3-diene-5,6-diol; this served as the precursor to homochiral tricarbonyl(6-methoxy-1-methylcyclohexadienyl)iron$^+$ cation after methylation, complexation, and hydride removal. This process, it is hoped, will provide a general route to resolved organoiron species of broad synthetic utility[228].

Kinetic studies of reversible addition of substituted anilines to tricarbonyl(η^5-cycloheptadienyl)Fe$^+$ have been described. The results indicated an "ordered transition state mechanism"[229]. Attack of chiral sulfoximine ester enolates, $PhS({=}O)({=}NR)CHE^-$, on the cycloheptadienyl cation and on its triphenylphosphite-substituted analog, gave modest asymmetric induction[230]. Attack of nucleophiles on the 1- and 3-carbomethoxycycloheptadienyliron tricarbonyl cations was generally cleaner and more regioselective than on the unsubstituted cycloheptadienyl cation. Sodiodimethylmalonate, for example, gave clean attack on C2 of the 1-substituted cation, and a mixture of attack at C2 (62%) and C1 (14%) of the 3-substituted cation[231]. The attack at C2 is consistent with the formation of 35 from the open chain pentadienyl cation, $(\eta^5$-$C_5H_6)Fe(CO)_3^+$ [205], reported at the beginning of this section.

7b. Cyclopentadienyldicarbonyliron Hydride (FpH) and Related Compounds

This section includes results on FpH, Fp•, and Fp^-, [Fp = $(\eta^5$-$C_5H_5)Fe(CO)_2$], and on compounds containing bonds between the Fp group and elements of Groups 13-17, essentially in that order. (*Organic derivatives Fp-R are treated in Section 7c.*) *Derivatives* with one or more CO groups replaced by other 2-electron ligands or with substituted cyclopentadienyl rings are included along with the analogous Fp compounds. Fp-transition metal compounds are treated as bimetallic compounds, and appear in Section 9c.

Sodium borohydride reduction of $(\eta^5$-indenyl)$Fe(CO)_3^+$ at -80° produced the formyl product, $(\eta^5$-$C_9H_7)Fe(CO)_2CHO$, which decarbonylated above -55° to the hydride $(\eta^5$-$C_9H_7)Fe(CO)_2H$[232]. The homolytic bond dissociation energy of the Fe-H bond of Fp-H has been estimated as 209 kJ/mol, the weakest metal-hydrogen bond of those measured[80]. Consistent with this finding, reaction of FpH with $Co_2(CO)_8$ was found to produce $HCo(CO)_4$ and Fp-$Co(CO)_4$[233]. The mechanism of the reaction of FpH with dienes to produce hydrometallated and hydrogenated products has been explored. CIDNP effects observed and reaction kinetics were consistent with a mechanism involving initial hydrogen transfer from FpH to diene to form Fp• and an allylic radical. Coupling of the two radicals in the solvent cage formed the hydrometallated product; dissociation led to reaction of the allylic radical with additional FpH to form the hydrogenated product. The dimer Fp_2 was eventually formed from the Fp• radicals[234]. Solutions of FpH could be stabilized *against decomposition to* Fp_2 *and* H_2 *by a trace of* thiophenol[234].

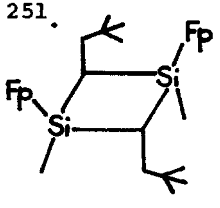
A review of the photochemical reactions of bimetallic species such as Fp_2 has summarized the evidence for 17-electron radical species (Fp•) as intermediates in many of the reactions observed[235]. Picosecond-resolved infrared spectroscopy has been used to elucidate the details of photolysis of Fp_2 in cyclohexane. An unbridged Fp-Fp species appeared to form upon photolysis, with a rise time of 50 ps; this may be eventual precursor to Fp• radicals, but these were not observed within at least 4 ns[236]. Photolysis of Fp_2 in the presence of alkyl halides RX has been proposed as a synthetically useful means of generating alkyl radicals in solution[237], presumably as a consequence of the reaction $Fp^{\bullet} + RX \longrightarrow FpX + R^{\bullet}$.

Fp• was the chain carrier in the thermal chain reaction of Fp_2 with DPPE. These 17-electron radicals reacted with the ligand to form the 19-electron species $Fp(DPPE)^{\bullet}$, which reduced Fp_2, forming $Fp(DPPE)^+$ and the radical anion $Fp_2^{\dot{-}}$. Dissociation of the latter formed Fp^- and $Fp^{\bullet}$, which continued the chain[238].

Sonication has been found to stimulate the reduction of the $[(C_5Me_5)Fe(CO)_2]_2$ dimer, Fp^*_2, by potassium metal[239]. The crystal structure of $Na^+(TMEDA)\ Fp^-$ showed coordinated sodium ions bridging carbonyl oxygens of adjacent $CpFe(CO)_2^-$ units, forming a spiral chain structure[240]. Similarly, the crystal structure of $Fp_2^-\ Na(THF)_4^+$ indicated linear chains formed by coordinated sodium ions joining bridging carbonyl oxygens[240,241]. Reactions of Fp^- with a number of metal carbonyl cations have been examined. Binuclear products, $Fp\text{-}ML_n$, ultimately formed, by a single electron transfer mechanism. However, a two-electron process, formally transfer of CO^{2+}, was also revealed by CO labelling. Thus, reaction of Fp^- with ^{13}CO-enriched $Mn(CO)_6^+$ produced enriched Fp_2. The CO transfer presumably occurred via $Fp\text{-}CO\text{-}Mn(CO)_5$[242]. Unexpected single-electron processes have been invoked to explain the reaction of NaFp with anionic hypervalent silicon and germanium species such as $PhSi(catecholate)_2^-$ [243]. The second order rate constant for reaction of $PPN^+\ Fp^-$ with methyl iodide in THF was about $3 \times 10^6\ M^{-1}sec^{-1}$, 10^3 faster than any other metal carbonyl anion, and it was even faster in acetonitrile[244]. However, NaFp reacted with $CpW(CO)_3CH_2CH_2CH_2COCl$ by deprotonation (with cyclization of the resulting carbanion), rather than by attacking the acyl chloride[245].

The structure of $Fp(B_{11}CH_{12})$, from reaction of $Ag^+(B_{11}CH_{12}^-)$ with FpI, showed a three-center B--H--Fe interaction, with B-H and H-Fe distances of 1.18 and 1.56 Å, respectively, and a B-H-Fe angle of 141°. Thus this weakly nucleophilic anion manages to coordinate significantly to the highly electrophilic Fp^+ moiety [246]. Reaction of Fp^- with $H_3B \leftarrow OR_2$ yielded $Fp(B_2H_5)$, whose crystal structure showed a diborane-like structure analogous to that of **19**, with the Fp group replacing a bridging hydrogen in a three-center two-electron bond. The Fe-B distances were 2.217(3) Å[125]. Fp_3In was formed by reaction of 3 equivalents of Fp^- with $InCl_3$[247]. A compound having a $FpHg^+$ bridging a Ru-Ru bond of an anionic triruthenium cluster has been prepared and characterized by ^{199}Hg NMR[248].

Displacement reactions of chloride from Fp- and Fp^*-SiR_nCl_{3-n} [R = Me, H] by azide have been carried out. Trimethyl phosphite converted the azides into iminophosphoranes such as Fp-$SiMe(N_3)(N{=}PMe_3)$[249]. Migration of the silyl group from iron to the deprotonated cyclopentadienyl ligand upon treatment of CpFe-$(CO)_2SiR_3$ with butyl-lithium has been found to occur with retention of configuration at silicon, by study of (R)-(+)-FpSiMePhNp [Np = 1-naphthyl][250]. Analogous migrations of germyl, stannyl, and plumbyl groups upon treatment of $FpZR_3$ [R = Me, Ph] with lithium diisopropylamide or (less satisfactorily) butyl-lithium have been found. The trimethyl-lead and -tin compounds showed competitive demetallation with formation of Fp^-[251].



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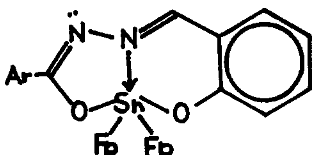
Synthesis of the Fp-silole ligand in 31 was achieved by reaction of the 1-chlorosilole with NaFp. Photolysis produced Fp_2 and 1,4-diphenylbutadiene, rather than a silaferrocene[178]. Reaction of $FpSiMeCl(CH{=}CH_2)$ with *tert*-butyl-lithium eventuated in formation of the disilacyclobutane **41**, a dimer of the hoped-for Fp-$Si(Me){=}CHCH_2CMe_3$. With larger groups R in $FeSiRCl(CH{=}CH_2)$,the *tert*-butyl-lithium attacked a carbonyl group rather than the vinyl group[252].

Photolysis of several disilyl complexes Fp-Si_2R_5 resulted in loss of silylene units, to give Fp-SiR_3 products. Use of mixed phenyl and methyl groups gave results consistent with formation of equilibrating silyl-silylene complexes $CpFe(CO)({=}SiR_2)SiR_3$ as intermediates[253]. In an independent study, another group of workers found that the yield of $FpSiMe_3$ from $FpSi_2Me_5$ improved dramatically when the reaction was carried out under a CO atmosphere rather than with an argon sweep. Lack of crossover products and results with $FpSiMe_2SiMeEt_2$ led to suggestion of the same silyl-silylene intermediate as proposed above[254]. Photolysis of oligosilanes such as $FpSi_4Me_9$ led to redistribution reactions, in this case to produce $FpSi(SiMe_3)_3$. Silylene fragments were not expelled[255]. Cyclosilanyl-Fp compounds have been prepared and characterized by NMR methods, including the first measurement of a ^{29}Si-^{55}Fe one-bond coupling constant, 12.1 Hz in Fp-$Si(Me)(Si_5Me_{10})$[256]. Photolysis of this same compound resulted in rearrangement to $FpSi(SiMe_3)(Si_4Me_8)$[255].

1,1-Fp_2-3,4-dimethylgermacyclopent-3-ene was prepared by chloride displacement from the dichlorogermacyclopentene. Pyrolysis at about 150° produced dimethylbutadiene and, presumably, the germylene Fp_2Ge. The fate of the latter fragment was not apparent[257].

The ^{119}Sn chemical shifts in a series of compounds Cp'Fe(CO)LSnMe$_3$ [L = various phosphines] correlated with the Tolman cone angle of L[258]. Mössbauer spectra of Fp$_2$SnArZ [Z = ONO$_2$, ONO, N$_3$, etc.] have been studied; the iron parameters were little affected by changes in Ar and Z, whereas the tin parameters were affected[259]. Several derivatives of **42** have been prepared, and one of them subjected to a crystal structure determination. The Fe-Sn bond distances were about 2.53 Å[260]. Insertion reactions of R$_2$Y [Y = Sn or Pb; R = CH(SiMe$_3$)$_2$] with FpX yielded FpYR$_2$X. Displacement reactions of iodide or bromide from tin occurred readily. FpSnR$_2$H served as a reducing agent, converting benzoyl chloride to benzaldehyde. The ^{119}Sn chemical shifts of FpSnR$_2$X [X = halogens, H, and OMe] correlated with the Taft σ_I constants for X[261].

Photolysis of FpI in the presence of diisopropylamine as base and succinimide or phthalimide was reported to produce the N-Fp derivatives. Thermal substitution of triphenylphosphine for CO produced the N-Fp' analogs[262]. A more novel route to a Fp-heterocycle lay in cycloaddition of dimethyl acetylenedicarboxylate to CpFeL$_2$N$_3$ [L$_2$ = Ph$_2$P-CH=CH-PPh$_2$]. The azide group behaved like a triaza-allyl group, reacting with migration of the iron group to form **43** (crystal structure)[263].



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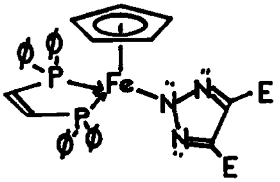

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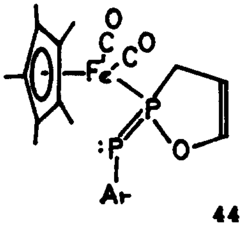
Amino- and diamino-substituted phosphine complexes Fp[P(NR$_2$)(OMe)$_2$]$^+$ and Fp[P(NR$_2$)$_2$(OMe)]$^+$, made by displacement of chloride from FpCl, underwent facile demethylation to form Fp[P(=O)(NR$_2$)(OMe)] or Fp[P(=O)(NR$_2$)$_2$][264]. A crystal structure of similarly-obtained {Fp[P(=O)(NEt$_2$)$_2$]}$_2$FeCl$_2$ showed a rather normal Fp-P bond length of 2.24 Å, and coordination of phosphoryl oxygens to the "inorganic" iron. The latter was displaced from coordination by pyridine[265]. Like the silyl groups previously discussed, the phosphoryl groups in FpP(=O)(OEt)$_2$ and related compounds migrated to the cyclopentadienyl ring upon deprotonation of the latter with lithium diisopropylamide[266].

Fp*-P=N-Ar [Ar = 2,4,6-tri-t-butylphenyl] was prepared from Cl-P=N-Ar and KFp*; the Fe-P bond length was 2.20 Å[267]. The diphosphenyl complex Fp*-P=P-Ar formed Fp*-P(S)=PAr upon reaction with one equivalent of sulfur. Heating caused cyclization to the thiadiphosphirane. Selenium analogs were prepared similarly[268]. Reaction of Fp^*-P=P-Ar with acrolein formed the heterocycle **44**[269].

The effect of the bidentate ligands on the structures of CpFe(DPPM)L^+ and CpFe(DPPE)L^+ [L = CO, NCMe] has been examined. DPPM appeared to cause a shortening of the Cp-Fe distance[270,271]. Photochemically induced exchange of CO and MeCN in CpFe(DPPM)L^+ produced a photochromic system. Electrochemistry of these systems was explored[272]. The cation $(\eta^5\text{-}C_5H_4CHPh_2)Fe(PMe_3)_3{}^+$ was formed by methanol protonation of the electron-rich (6,6-diphenylfulvene)iron tris(trimethylphosphine)[176]. $[\textit{o}\text{-}C_6H_4(PMePh)_2]$-$FeCp(PCl_3)^+$ was obtained by PCl_3 displacement of acetonitrile, and its crystal structure was determined[273].

$[\textit{o}\text{-}C_6H_4(PMePh)_2]FeCp(PH_2Ph)^+$ was deprotonated with butyllithium, and the resultant phenylphosphido group coordinated to a pentacarbonylchromium group. A mixture of diastereomers was obtained, and the stereochemistry of the principal one [(R*,R*),-(R*)] was determined by means of a crystal structure[274]. Likewise, alkylation of the phenylphosphine complex with methyl or ethyl iodide produced predominantly the [(R*,R*),(R*)] diastereomers. At -95°, deprotonation of the methylphenylphosphine cation was stereospecific, and alkylations carried out at that low temperature proceeded with complete stereoselectivity[275]. Similarly the [(R*,R*),(R*)]methylphenylarsine complex was obtained in optically pure form by displacement of acetonitrile by racemic AsHMePh. Deprotonation and ethylation at -65° gave the optically pure complex of ethylmethylphenylarsine, from which the resolved arsine could be obtained by cyanide displacement[276].



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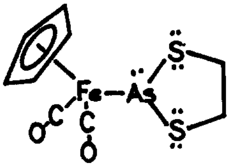

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45 was obtained by displacement of chloride from the 2-chloro-1,3,2-dithiarsolane by Fp^-. NMR gave no indication of pyramidal inversion of the arsenic atom[277]. A crystal structure of the triphenylarsine complex $Fp\text{-}AsPh_3{}^+$ $BF_4{}^-$ has been reported [278]. The diarsene complex Fp^*-As=As-Ar [Ar = 2,4,6-tri-*t*-butylphenyl], prepared by reaction of $Fp^*\text{-}As(SiMe_3)_2$ and $ArAsCl_2$, dimerized *in situ*. The monomeric diarsene could, however, be trapped by reaction with (cyclooctene)chromium pentacarbonyl to form $Fp^*\text{-}As[\rightarrow Cr(CO)_5]{=}As\text{-}Ar$ [crystal structure]. Reaction of $SbCl_3$ with appropriate amounts of NaFp produced Fp_2SbCl and

Fp_3Sb. The crystal structure of the latter showed the expected pyramidal antimony atom[280].

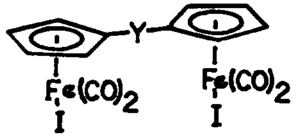
A crystal structure of $CpFe(CO)(O_2CCF_3)$, produced along with FpCl upon protonolysis of $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}CH_2)FeCp(CO)$ with trifluoroacetic acid in methylene chloride, has been reported[281]. $Fp(THF)^+$ salts showed empirical catalytic activity for the Diels-Alder additions of enones, but the nature of the true catalytic species, possibly a trace impurity, remained elusive[282].

Transfer of Fp^+ groups to an electrically non-conducting polymer of 3-methyl- and 3-hexylthiophene, using $(CH_2{=}CMe_2)Fp^+$, gave a product with 10^8-fold increased conductivity. Less than one-tenth of the thiophene rings were coordinated to iron[283]. Thiocarboxylate complexes Fp-SC(=O)Ar were produced by acylation of $Fp\text{-}S_{3,4}\text{-}Fp$. The crystal structure of the *o*-nitrobenzoyl compound was determined[284,285]. Also determined was the crystal structure of benzalthiosemicarbazone S-coordinated to the Fp group, $PhCH{=}N\text{-}NH\text{-}C(NH_2){=}S\text{-}Fp^+\ PF_6^-$. This compound and similar monodentate complexes of thiosemicarbazide and other thiosemicarbazones were prepared by displacement of acetone from $Fp\text{-}O{=}CMe_2^+\ PF_6^-$ [286]. The bidentate dithiocarbamate complexes $Cp^*Fe(S_2CNMe_2)L$ [L = CO, MeCN, THF, etc.] were oxidized to radical cations, which disproportionated or reacted with $Me_2NCS_2^-$ to form $Cp^*Fe(S_2CNMe_2)_2^+$ [287]. Refluxing Fp_2 with EtSH in ether formed $CpFe(CO)(\mu\text{-}SEt)_2FeCp(CO)$[288]. 1,4,7-trithiacyclononane displaced both iodide and carbonyl ligands from FpI to form $CpFe(S_3C_6H_{12})^+$ (crystal structure). This cation gave a reversible one-electron oxidation in acetonitrile[289].

The iron-tellurium compounds $CpFe(CO)L\text{-}Te_{1,2}\text{-}FeCpL(CO)$ [L = Et_3P] were prepared by reaction of Fp_2 with Et_3PTe and excess triethylphosphine. The monotellurium compound reacted with Et_3PTe to form the ditellurium compound. "Low-temperature pyrolysis" of these compounds specifically produced solid-state FeTe and $FeTe_2$, along with CO, Et_3P, and ferrocene[290].

FpX compounds have been found to catalyze the addition reactions of silyl ketene acetal, $Me_2C{=}C(OEt)OSiMe_3$, to aldehydes[291]. Synthesis of [tris(trimethylsilyl)cyclopentadienyl]iron compounds, $[\eta^5\text{-}C_5H_2(SiMe_3)_3]Fe[P(OMe)_3]_2X$, direct from the ligands and FeX_2 has been described[292]. The crystal structures of several highly hindered derivatives of FpX have drawn attention. In $(\eta^5\text{-}C_5Ph_5)Fe(CO)_2Br$, the phenyl substituents were canted by 49-143° from the cyclopentadienyl plane[293]. In $(ArPPh_2)FeCp(CO)I$ the interest lay in the novel ligand, which had a coordinated diphenylphosphino group on the 4-position of a dibenzothiophene[294]. The conformation of $(\eta^5\text{-}Ph_2CHC_5H_4)Fe(CO)(PPh_3)I$ in the crystal had the benzhydryl group *anti* to the triphenylphosphine ligand, and the C-H group oriented toward the carbonyl ligand; NOE experiments in solution indicated the same preferential conformation. The isopropyl analog did not show this effect[295]. Conformational preferences of $(\eta^5\text{-}Me_3C\text{-}C_5H_4)Fe(CO)LI$ in solution were studied by NMR and molecular mechanics methods. The triphenylphosphine compound in the crystal showed the tert-butyl group approximately eclipsed with the carbonyl group, which is believed also to be the most stable conformation in solution[296]. The crystal structure of $(\eta^5\text{-}FpC_5H_4)Fe(CO)_2I$ has also been reported[297].

The bridged compound **46** [Y = C≡C] was further coordinated by reaction with $Co_2(CO)_8$ to produce **46** [Y = $C_2Co_2(CO)_6$] (crystal structure). Reaction of either diiodide with $LiBEt_3H$ gave unstable hydrides[298]. **46** [Y = $CH_2CH_2CH_2$] was prepared by iodination of the polymer formed upon reaction of the trimethylene-bridged bis(permethylcyclopentadiene) with $Fe_2(CO)_9$. Reduction gave the bridged Fp^*_2-type dimer[299].



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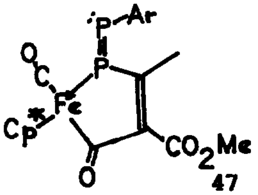
7c. Fp-Acyl, -Alkyl, and -Carbene Complexes

$CpFe(CO)_3{}^+$ [$FpCO^+$] and other electrophilic Fp compounds reacted with the phenoxide complex $(C_6H_5O)Cr(CO)_3{}^-$ by one-electron transfer to form the dimer Fp_2[300]. Photosubstitution reactions of the borole complexes $(\eta^5\text{-}C_4H_4BR)Fe(CO)_3$ [R = Me, Ph], which are isoelectronic with $FpCO^+$, have been studied. Products included $(C_4H_4BR)Fe(CO)_2L$ [L = Me_3P, NCMe, $CNCMe_3$], $(C_4H_4BR)Fe(CO)L_2$ [L = PMe_3 and dienes], and $(C_4H_4BR)FeL_3$ [L = PMe_3, benzene][301]. Self-consistent charge and configuration calculations on $(\eta^5\text{-}B_4C_2H_6)Fe(CO)_3$ and analogous systems indicated that the tricarbonyliron group is weakly bound to the carborane cluster compared to the BH group which it formally replaces[302].

$FpCS_2{}^-$ is more stable and easily studied than $FpCO_2{}^-$, but the assumption that they should possess analogous chemical properties has been questioned as a result of a study of their reactions with electrophilic compounds FpX [X = I, OTf, HgCl], Fp'I and $CpFe(CO)(NCMe)_2{}^+$. Reaction of $FpCS_2{}^-$ with the latter produced $Fp[\mu(\eta^1\text{-}C\text{:}\eta^2\text{-}S,S'\text{-}CS_2)Fe(CO)Cp$, whereas the CO_2 adduct formed no $(\mu\text{-}CO_2)$ species, but only the mixed dimer $CpFe(CO)(\mu\text{-}CO)_2Fe(CO)(NCMe)Cp$. Likewise, reaction of $FpCO_2{}^-$ with Fp'I gave Fp_2 and only traces of FpFp', even though Fp^- and Fp'I gave 50:50 mixtures of the two products. Photolysis of FpOAc produced no dihapto $Cp(CO)Fe(O_2CMe)$ species, only Fp_2 being formed. Thus, the $FpCO_2$ system differed sharply from $FpCS_2$ in giving no μ- or dihapto species[303,304].

The cyclic acyl species **47** (crystal structure) formed upon cycloaddition of methyl 2-butynoate with Fp^*-P=P-Ar [Ar = 2,4,6-tri-*tert*-butylphenyl] at 20°. Analogous species formed with several other electrophilic alkynes as well[305]. **48** resulted when the fused spiro[2.4]heptadiene starting material was allowed to react with (benzylideneacetone)$Fe(CO)_3$. With $Fe_2(CO)_9$, **48** was accompanied by a diiron complex. With the less-strained spiro[4.4]nonadiene starting material, the alkyliron analog of **48** (no CO-insertion) resulted with (benzylideneacetone)$Fe(CO)_3$, and **29** resulted with $Fe_2(CO)_9$[174]. Another novel approach to Fp-acyls (aroyls in this case) involved reaction of $(\eta^4\text{-}C_5H_6)Fe(CO)_3$ with aryl-lithium reagents at -78° and quenching with triethyloxonium fluoborate. In this reaction, the triethyloxonium ion apparently removes a hydride ligand from the ring of the intermediate $(\eta^4\text{-}C_5H_6)Fe(CO)_2{=}C(Ar)O^-$ rather than alkylating the acyl anion to form the carbenoid. The crystal structure of *p*-$CF_3C_6H_4C({=}O)Fp$ from this reaction was determined[173].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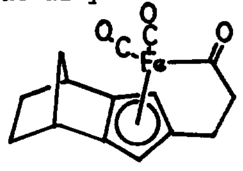
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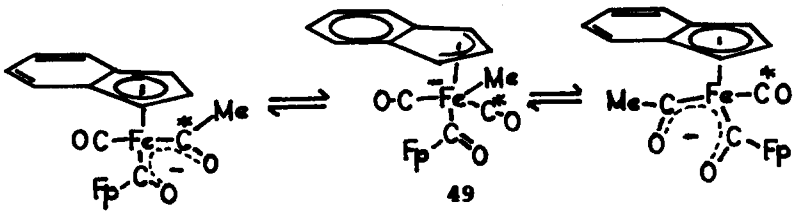
Acylation of $(\eta^5\text{-}C_9H_7)Fe(CO)_2^-$ [C_9H_7 = indenyl = Ind] with $Me^{13}COCl$ at -78° did produce the expected labelled acetyl complex $(Ind)Fe(CO)_2\text{-}^{13}COMe$, but only if all of the $(Ind)Fe(CO)_2^-$ was consumed. If excess anion remained upon warming, or if the acetyl-labelled product was treated with Fp^-, then a large amount of scrambled $(Ind)Fe(CO)(^{13}CO)COMe$ formed. This was the result of attack of the nucleophilic anion at an iron carbonyl group to form the equilibrating mixture **49**[306]:



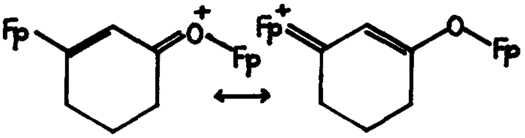
An indirect way of bringing about migration of recalcitrant alkoxymethyl groups, so as to form acyls, has been developed. The alkoxymethyl complex $(Ind)Fe(CO)_2CH_2OR$ [R = Me, Et] was treated with $(Ind)Fe(CO)_2^-$ to form the bimetallic species $(Ind)Fe(CO)(\mu\text{-}CO)_2Fe(Ind)(COCH_2OR)^-$. Reaction with methyl iodide under 1 atmosphere CO formed the desired acyl complex (Ind)Fe$(CO)_2COCH_2OR$ in 50-60% yields. Secondary alkoxyacyl complex (Ind)Fe$(CO)_2$COCHMeOEt was formed similarly. Reversible $\eta^5 \rightleftharpoons \eta^3$ indenyl ring slippage was advanced as an important factor in formation and cleavage of the bimetallic intermediates[307].

The crystal structure of Cp'Fe(CO)(PPh_2Et)COMe has been determined[308]. The space group of the crystal of CpFe(CO)(PPh_3)-COMe has been corrected from a previously reported determination[309]. T_1 values in solution for several acyl compounds, including FpCOR [R = $CHMe_2$, $CHEt_2$] and Fp'COR [same R's], have been studied[310].

Electrochemical oxidation of FpMe in acetone/0.1 M $LiClO_4$ at -86° produced CpFe(CO)(L)$COMe^+$ [L = $OCMe_2$, $OClO_3^-$]. The perchlorate underwent conversion to the acetone solvate. Thioanisole displaced acetone from CpFe(CO)$(OCMe_2)$COMe via a dissociative pathway, whereas the reaction with the perchlorate analog proceeded much faster and via a different mechanism[311]. A study of infrared and electrochemical data for CpFe(CO)LMe, Cp'(CO)L-COMe, and CpFe(CO)LCOMe compounds with a range of phosphorus ligands L has led to classification of phosphorus ligands as pure σ-donors (e.g., R_3P, Ar_3P, R_2POR') and σ-donor + π-acceptors (e.g., $P(OR)_3$ and $P(OR)_2R$). pK_a values of the phosphines provided a reasonable measure of their tendency to function as pure σ-donors[312].

Reaction of Fp'C(=O)CH_2CH_2Ar [Ar = Ph, C_5H_4FeCp] with several electrophiles [$HgCl_2$, I_2, HX, Et_3O^+ BF_4^-] was said to result in fragmentation to $Fp'CO^+$ X^- and ECH_2CH_2Ar[313]. Also leading to alkyl group cleavage was the reaction of $Fp'COCH_2CH_2Ph$ with three equivalents of trimethylsilane or trimethylstannane, which afforded $PhCH_2CH_2CH_2OH$ and CpFeH(CO)$(YMe_3)_2$ [Y = Si, Sn]. $FpCOCH_2CH_2Ph$ and $FpCH_2CH_2Ph$ reacted similarly[314]. Hydrosilylation of FpCOR [R = Me,Et,Pr], Fp^*COMe, and (Ind)Fe$(CO)_2$COMe by dihydrosilanes was catalyzed by $(Ph_3P)_3RhCl$. FpCH$(OSiEt_2H)$R was produced, using Et_2SiH_2. Branched chain acyls reacted sluggishly. With $PhSiH_3$, complete reduction to $FpCH_2R$ resulted. The phosphite substituted analog, CpFe(CO)[$P(OMe)_3$] COMe, was converted to the vinyl compound CpFe(CO)[$P(OMe)_3$]$CH{=}CH_2$ by catalyzed silanol loss. Only di- and tri-hydrosilanes participated in this reaction; Et_3SiH did not[315].

As previously shown, reaction of acyl complexes $FpCH_2COR$ [R = H, OMe, Ph, p-C_6H_4OMe, Fp, Fp^*, etc.] with $Fp(THF)^+$ transfers the electrophilic Fp^+ group to the acyl oxygen. Using ring-labelled Fp groups having methylcyclopentadienyl (Cp') and pentamethylcyclopentadienyl (Cp^*), it has been shown that the iron groups attached to the methylene group and the acyl oxygen exchange intramolecularly, and that the rate of exchange increases with electron-donating power of R[316]. Charge distributions in vinylogous species such as **50** have been investigated by Mössbauer spectroscopy, which indicated "a considerable degree of polarisation"[317]. Crystal structures of $FpCH_2COFp$, $Fp^*CH_2COFp^*$, and $FpCH_2CH_2COFp$ were interpreted to show, by virtue of short CH_2-CO bonds and long acyl C-O bonds in the μ-ketene complexes, some contribution of a π-complex structure[318]. Similar interpretations were made for heterobimetallic analogs $FpCH_2COML_n$ [ML_n = NiCp(CO), $Mn(CO)_5$][319].



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The acetyl complexes $CpFe(CO)(PR_3)COMe$ [R = Me, Et] have been resolved by protonation with camphorsulfonic acid and recrystallization of the diastereomeric salts[320]. Chiral acyls $Fp'C(=O)CH_2R$ underwent stereoselective alkylation upon deprotonation with butyl-lithium and reaction of the enolate with $BrCH_2CO_2CMe_3$. Oxidation led directly to $HOCOCHRCH_2CO_2CMe_3$. The (R) enantiomer was obtained using (R) acyl[321]. This methodology has been applied to the synthesis of the α-pentylsuccinate fragment of the natural product (-)-actonin[322]. Similarly, reaction of the enolate from $Fp'COCH_2OCH_2Ph$ with 2,3-epoxybutanes occurred with a high degree (10:1) of chiral recognition, allowing stereoselective synthesis of disubstituted γ-lactones[323]. Conversion of homochiral $Fp'COCH_2OR$ [R = menthyl] into its lithium enolate, then reaction with Et_2AlCl to form the aluminum enolate, and attack on Me_2CHCHO gave the aldol product Fp'COCH(OR)CH(OH)$CHMe_2$ with good diastereoselectivity. Oxidation with bromine in the presence of ethylene glycol produced (R)-acetal $Me_2CHCH(OH)CH(O_2C_2H_4)$[324].

An asymmetric synthesis of cyclopropanecarboxylic acids has been developed using Fp' reagents. Nucleophilic methylenation of (E)-Fp'COCH=CHR using CH_2I_2/MeLi at -78° produced the trans cyclopropane product in 80-90% chemical yield and 98% diastereoselectivity[325]. With (Z) isomers, Simmons-Smith methylenation using $CH_2I_2/Et_2Zn/ZnCl_2$ produced comparable results[326].

In a search for migration of carbon groups to 16-electron iron species, acyl species FpC(=O)R [R = 1-phenylcyclobutyl and 1-phenylcyclopropyl] have been photolyzed. The cyclopropyl species gave simple decarbonylation to form FpR. The cyclobutyl species also gave some decarbonylation, but accompanied by formation of 1-phenylcyclobutane-1-carboxaldehyde[327].

Synthesis of several Fp^*-alkyls was conveniently achieved by sonochemically-induced reduction of Fp^*_2 with potassium metal, followed by direct addition of alkylating agent: MeI, EtI, or $MeOCH_2X$[239]. $(FpCH_2)_3CH$ has been prepared by three-fold displacement from $(MeSO_2OCH_2)_3CH$. It decomposed rapidly in solution at 25°, giving Fp_2 and the cyclopropylmethyl compound $FpCH_2C_3H_5$. Reaction with two equivalents of Ph_3C^+ proceeded with electron- rather than hydride-transfer, and eventuated in loss of a Fp group and migration of a $-CH_2Fp$ group, forming $(\eta^2\text{-}FpCH_2CH_2CH{=}CH_2)Fp^+$. Photolysis of $(FpCH_2)_3CH$ at 350 nm formed Fp_2 and $CpFe(CO)[\eta^3\text{-}CH_2{\cdots}C(Me){\cdots}CH_2]$[328].

Some differences were revealed in the chemical properties of $FpCH_2CH_2CH_2Si(OMe)_3$ and its Fp^*- analog. Reaction of the Fp-compound with triphenylphosphine in refluxing acetonitrile proceeded with alkyl group migration (so-called "insertion") to form the acyl compound $Fp'C({=}O)CH_2CH_2CH_2Si(OMe)_3$, but the Fp^* analog behaved differently. Electrochemical oxidation of both compounds occurred with rapid migration to form the acyl, accompanied by attack of solvent at the iron. But added triphenylphosphine attacked the iron upon oxidation only in the case of the less-hindered Fp compound[329]. $(Ph_5C_5)Fe(CO)_2Me$ showed only irreversible cyclic voltammetric behavior[330]. Reaction of $Fp(CH_2)_nFp$ [n = 3-7] with phosphines has been shown to occur sequentially, with formation of the monoacyl product $CpFe(CO)L[CO(CH_2)_n]Fp$, then the diacyl[331].

Reactions of $FpCH_2X$ with neutral nucleophiles L [amines, phosphines, sulfides] have been studied. Depending on the halide X, the solvent, and the nucleophile, either $FpCH_2L^+$ or $CpFe(CO)L_2^+$ was formed. In some cases, the latter product was shown to be formed from the former. The normal sequence of halide reactivities was observed, and rates of halide displacement depended on basicity and size of L[332].

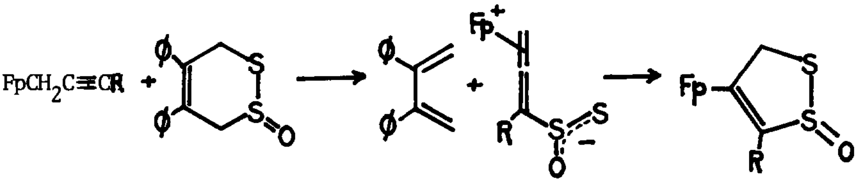
Lithiation of the cyclopentadienyl ring of FpMe followed by reaction with Ph_2PCl produced the diphenylphosphino-substituted derivative. Coordination of the phosphorus to various tungsten groups [$W(CO)_2MeCp$, $W(CO)_2ClCp$, $W(CO)_3Cp^+$] was readily achieved. Also prepared by analogous means was $Me(OC)_3W(\eta^5\text{-}C_5H_4PPh_2\text{-}\eta^1)Fe(CO)Cp(COMe)$[333]. Another route to bimetallic species was reaction of $CpFe(CO)(\eta^2\text{-}CH_2SMe)$, produced by photolysis of $FpCH_2SMe$ at -78°, with reactive transition metal precursors to produce $CpFe(CO)CH_2S(Me)ML_n$ [ML_n = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $MnCp'(CO)_2$][334].

Formation of η^3-benzylic species upon low-temperature photolysis of FpCHRPh [R = H, OMe] has been studied quantitatively.

Formation of the unsaturated η^1 species from the η^3 was found to occur with free energies of activation of 50 and 64 kJ/mol for the unsubstituted and methoxy-substituted species, respectively. CpFe(CO)(η^1-CH_2Ph) collapsed to the saturated η^3 species at a rate of 10^8 s^{-1} at 293 K. Reactions with phosphines to form CpFe(CO)(PR_3)(CH_2Ph) were also studied[335]. Independent flash photolysis experiments by another group gave results consistent with these, and showed that recombination of CpFe(CO)(η^3-CH_2Ph) with external ligands showed low selectivity; the rate ratio between CO and PPh_3 was only 8.9[336].

Fluxionality in substituted compounds Fp(η^1-C_5H_4R) has been studied. The interconversion barrier in Fp(η^1-C_5H_4Me) [56 kJ/mol] was higher than in FpCp [45 kJ/mol], whereas the barrier in Fp(η^1-$C_5H_4CONHSO_2C_6H_4Me$) was lower. The crystal structure of the latter showed the substituent in the 1-position of the ring, not the 5-position as originally proposed to account for the two-fold symmetry in the NMR spectrum[337].

Cycloaddition of dimethyl acetylenedicarboxylate to Fp(C_5H_4-Me) gave two 7-exo-(Fp)norbornadiene products, having the methyl group in the 5-position in the principal product and the 1-position in the minor product[337]. Eq.13 illustrates a formal cycloaddition reaction of S_2O (from metal-assisted retro-Diels-Alder reaction of a dihydrodithiin oxide) with $FpCH_2C{\equiv}CR$ [R = Me, Ph]. The structure of the product with R = phenyl was verified by crystallography[338]. Cycloaddition of TCNE to $FpCH_2$-CH=CH-CH=CMe_2 gave the [3 + 2] (cyclopentane) adduct in moderate yield; the uncoordinated double bond thus remained uninvolved in the reaction[339].



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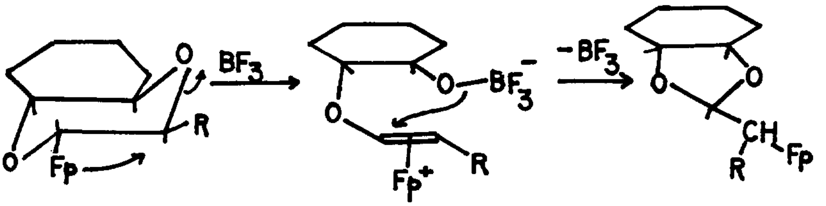

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Cis-fused dioxins (eq. 14) [R = H, CN, Ph], in which the Fp group can occupy a position anti-periplanar to the C-O bond, were found to rearrange readily to dioxolanes upon treatment with BF_3.

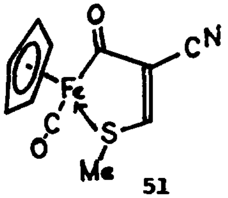
The *trans*-fused isomers, in which the Fp group was held in an axial position, were unreactive unless a phenyl substituent was present to stabilize developing positive charge[340].

In a stereochemical investigation of cyclopropane formation, *threo*-FpCHDCHDCH$_2$SPh was alkylated with methyl triflate. Heating the resultant sulfonium salt to 65° gave *cis*-cyclopropane-d$_2$, showing inversion of configuration of the carbon bound initially to iron[341]. Conformational analysis of Fp'CH$_2$OR and Fp'CH$_2$SR by variable temperature NMR and NOE methods singled out the importance of steric interactions in controlling the preferred conformation(s). In the absence of strong steric effects, solvent polarity played a significant role[342]. Epimerization at the iron center of CpFe(CO)(L)Me [L = (S)-(+)-Ph$_2$PNMeCHMePh] and its (η^5-indenyl) analog has been studied under both thermal and electrochemical conditions. Thermally, the indenyl compound epimerized 10-20 times faster; upon electrochemical reduction, the reaction was very fast. Dissociation of the ligand L was implicated in each case[343]. Chiral analogs of Fp compounds resulted when the cyclopentadienyl ligand was replaced by (η^5-1-*tert*-butyl-2-methyl-1,2-azaborolyl) [Ab]. AbFe(CO)$_2$CH$_2$OR [R = menthyl] diastereomers were separated by HPLC and decomposed with iodine to give homochiral AbFe(CO)$_2$I. Alternatively, reaction of racemic AbFe(CO)$_2$I with triphenylphosphine produced two diastereomers of AbFe(CO)(PPh$_3$)I in 4:1 thermodynamic ratio[344].

Vinylic iron compounds, Ph$_2$C=C(Ar)Fp, from reaction of Ph$_2$C=C(Ar)Li [Ar = phenyl, 1-naphthyl], gave 2-Ar-3-phenylinden-1-ones on thermolysis in decalin. Addition of triphenylphosphine improved the yields to as high as 86%[345]. Electrochemical oxidation of CpFe(CO)LC(Ph)=CPhMe [L = P(OPh)$_3$] has been studied over the temperature range of -78 to 22°. At -60° the *E* and *Z* isomers gave distinguishable oxidation waves, but at temperatures warmer than -20°, rapid conversion of oxidized *E* cation to *Z* caused merger of the waves. Individual oxidation potentials and rates of interconversion were measured. The stereochemical preference of the neutral species for the *E* isomer (ca. 5:1) was dramatically reversed in the cations (1:900)[346].

Reaction of FpSMe with HC≡C-CN produced a number of products: the acetylide Fp-C≡C-CN, Fp-C(CN)=C(SMe)Fp, NCCH=CHSMe, and a cyclic species, **51** (crystal structure). Reaction of the acetylide or its triphenylphosphine-substitution product with TCNE gave cyclobutene products **52**. The triple bond also formed a Co$_2$(CO)$_6$ complex[347] (cf. **46**, Y = C$_2$Co$_2$(CO)$_6$). The triple bond in Fp- and Fp'-C≡CPh reacted with nitrile oxides by 1,3-dipolar addition to form isoxazoles having the iron substituent at the 5-position, next to oxygen. The Fe-C bond length in 2,3-diphenyl-

5-Fp'-isoxazole was a rather short 1.951(3) Å[348]. Reaction of $(OC)_5Re\cdots F\cdots BF_3$ with acetylides Fp-C≡CR [R = Me, Ph] resulted in rearrangement of the Fp group, forming $Fp[\eta^2\text{-}RC{\equiv}CRe(CO)_5]^+$ [349]. Attack of $Et_2C_2B_4H_5^-$ on $Fp'(\eta^2\text{-}MeC{\equiv}CMe)^+$ produced 53, which showed a three-center two-electron bond joining the carborane cage and the β-vinylic carbon. Heating at 110° resulted in loss of Fp'H and formation of *nido*-4,5-Me_2-7,8-$Et_2C_4B_4H_4$[350].



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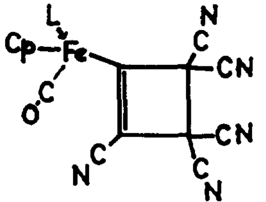

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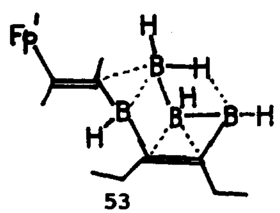

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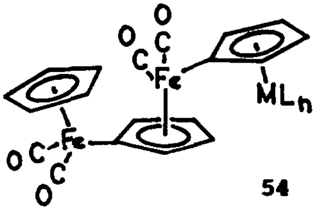
The vinylic fluoride of perfluoro-1-methylcyclopentene was displaced by K^+ Fp^- in THF, giving the vinyl-iron compound in good yield; an addition-elimination mechanism was indicated[351]. Displacement of chloride from chloropentafluorobenzene was also observed[352].

The novel compounds 54 [ML_n = $FeCp(CO)_2Me$, $FeCp(CO)_2CH_2Ph$, $Mn(CO)_5$ (crystal structure)] were prepared by lithiation of $(\eta^5\text{-}C_5H_4Fp)ML_n$ and reaction with FpI. (μ-Arylene)di-iron and tri-iron compounds have been prepared by reaction of di- and tri-(chlorocarbonyl)benzenes with Fp^-, and thermal decarbonylation in refluxing dibutyl ether. Thus prepared were 1,3- and 1,4-$C_6H_4Fp_2$ and 1,3,5-$C_6H_3Fp_3$ (55), and also methylcyclopentadienyl derivatives. A perfluoro analog was prepared directly from 1,4-$C_6F_4Li_2$ and FpI[353,354]. Reaction with $Cr(CO)_6$ produced $(\eta^6\text{-}arene)Cr(CO)_3$ derivatives[354], and $Mo(CO)_3$ and $W(CO)_3$ complexes were synthesized similarly[355]. Cyclic voltammetric studies of several of the chromium complexes showed reversible oxidation, with substantial transfer of charge from iron to chromium. The radical cations were stable even in acetonitrile, allowing isolation in some cases[356].



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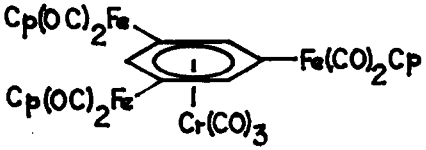

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A simplified, one-flask preparation of the useful cyclopropanation reagent $FpCH_2SMe_2^+$, and of the analogous Fp^* reagent, has been described[357]. Fp^*CH_2SR [R = Me, Ph] underwent facile alkylation at sulfur by Ph_3C^+ or $Fp^*CH_2^+$, and the tritylated sulfonium species served as a cyclopropanating agent^{358}.

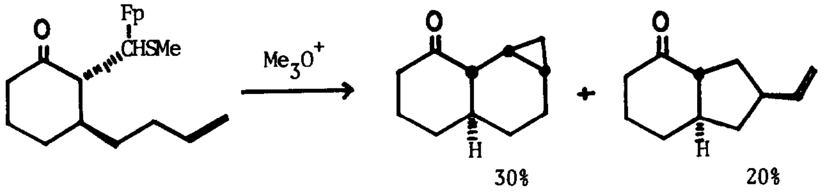
The stabilized carbene complex $Fp{=}\overline{C(OCH_2CH_2O})^+$ gave an unstable radical upon reduction with sodium naphthalenide; the radical rapidly decomposed to Fp_2, CO_2, and C_2H_4. Substitution of phosphines for CO was catalyzed by sodium naphthalenide. Reaction of the cation with nucleophiles produced ring-opened $FpC({=}O)CH_2CH_2Nu$ [Nu = Cl, OMe, etc.]. The sulfur analog, $Fp{=}C(SCH_2CH_2S)^+$, was the subject of a crystal structure. Upon reduction with sodium naphthalenide, it produced insoluble sulfides, little Fp_2, and no CS_2^{359}. Photolysis of $FpC(SMe)_3$ produced $CpFe(CO)[\eta^2\text{-}(MeS)_2C{=}SMe]$, also preparable by thermal reaction of $CpFe(CO)(NCMe)[{=}C(SMe)_2]$ with NaSMe. Variable temperature NMR studies indicated an equilibrium between the η^2 species and the carbene complex $CpFe(CO)(SMe)[{=}C(SMe)_2]$. Reaction with two equivalents of R_3P produced $CpFe(CO)(PR_3)(SMe)$ and $R_3P{=}C(SMe)_2$, and reaction with Me_3O^+ gave $CpFe(CO)(SMe_2){=}C(SMe)_2^{+}$ ^{360}. In contrast, reactions of $CpFe(CO)(\eta^2\text{-}CH_2{=}SMe)$, described earlier in this section, gave no sign of equilibrium with the unstabilized carbene, $CpFe(CO)(SMe)({=}CH_2)$^{334}.

A stable methylene complex, $Cp^*Fe(DPPE)({=}CH_2)^+$, has been prepared by reaction of the methyl ether $Cp^*Fe(DPPE)CH_2OMe$ with HBF_4. Cyclopropanation of styrene was initiated by electron transfer, with a coulomb efficiency of 100^{361}. Benzylidene complexes $Fp{=}CHAr^+$ and $Fp'{=}CHAr^+$ have been studied by variable temperature NMR to determine barriers to ring rotation. Benzylidene transfers to propene formed predominantly *cis*-1-aryl-2-methylcyclopropanes^{362}.

Homochiral acetyl complexes $CpFe(CO)(PR_3)COMe$ [R = Me, Et] were converted to homochiral ethylidene complexes by consecutive reaction with MeOTf, $NaBH_4$, and Me_3SiOTf at -78°. Reaction with vinyl acetate gave cyclopropanes with high (89-97%) enantioselectivity^{320}. By analogous methods, diastereomeric benzylidene complexes $CpFe(CO)(PPh_2R)({=}CHPh)^+$ [R = (S)-2-methylbutyl] were prepared and used to transfer benzylidene moieties to propene and vinyl acetate. The phenylcyclopropanes were formed with 43-92% enantioselectivity via a mechanism involving attack of the synclinal conformer of the benzylidene complex on the alkene and backside attack of the nascent carbocation on the iron-bound carbon^{363}. The latter step is consistent with the stereochemical outcome in cyclopropane formation from $FpCHDCHDCH_2SMePh^+$ ^{341} and likewise in phenylcyclopropane formation from FpCHDCHDCH(OMe)Ph and Me_3SiOTf^{364}.

Photosubstitution of PPh_3 into FpCH(OMe)Ph occurred via [η^3-CH(OMe)Ph], with high diastereoselection of 75:1. The selectivity was the result of thermodynamic preference, achieved through phosphine dissociation and recombination. Photosubstitution of triethylphosphine was studied similarly. Quenching of the benzylidene complexes $CpFe(CO)(PR_3)(=CHPh)^+$ by methoxide ions and of $CpFe(CO)(PR_3)[=C(OMe)Ph]^+$ by hydride in each case gave mixtures of diastereomers[365].

Cationic carbene complexes have been reported to engage in intramolecular electrophilic attacks, as in Eq. 15. When a β-phenylethyl group was present instead of the 4-butenyl group shown in Eq. 15, the insertion product, 2-phenyl-<u>trans</u>-hydrindan-4-one, was formed in 90% yield[366]. In a related intramolecular case, attack of a transient Fp-carbene cation on a double bond resulted in formation of a cyclohexene ring[367].



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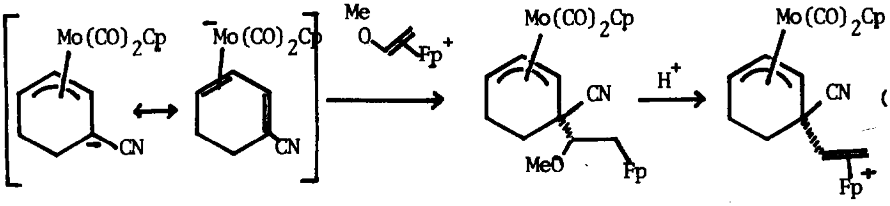
7d. Cyclopentadienyliron Derivatives of η^2- to η^5-Ligands

$(\eta^2\text{-}CH_2{=}CH_2)Fe(CO)_2Cp^+$ $[(C_2H_4)Fp^+]$ has been synthesized directly from Fp_2, ethene, and HBF_4, in 20% yield[132]. The inclusion of an appropriate oxidizing agent would probably further increase the yield. The Fp^+ complex of 2,3-dihydrofuran has been synthesized from 3-bromo-2-methoxytetrahydrofuran by bromide displacement by Fp^- and removal of methoxide. The 3,4-dihydropyran analog was prepared similarly[368]. Their reaction with CHE_2^- resulted in clean addition of the nucleophile next to the oxygen and trans to the Fp group. With enol ethers and indole as nucleophiles, ligand exchange reactions and polymerization competed with the desired addition reactions[369].

Attack of an organometallic nucleophile on $(CH_2{=}CHOMe)Fp^+$ at -78° occurred normally (Eq. 16)[191]. Reaction of $(CH_2{=}CHOMe)Fp^+$ with optically active alcohols gave diastereomeric $(CH_2{=}CHOR)Fp^+$ cations [R = menthyl, bornyl, <u>sec</u>-butyl, etc.], which equilibrated rapidly at room temperature. The greatest diastereoselec-



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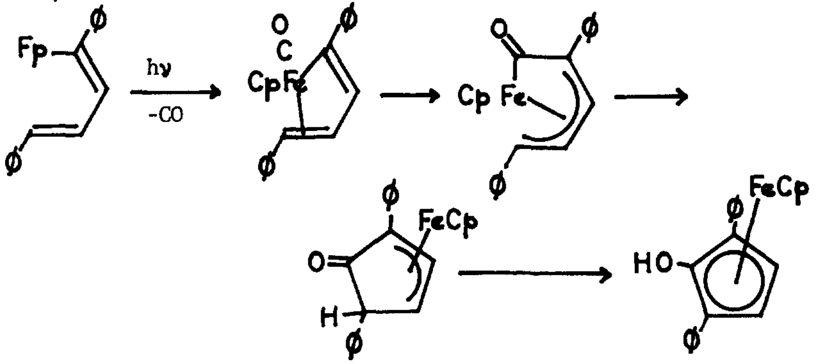
tion (4:1) resulted in the menthyl case, and the absolute configuration of the predominant isomer was determined. Correlation of the circular dichroism spectra and the absolute configurations of these cations and cations (CH$_2$=CHR)Fp$^+$ produced from homochiral epoxides was made[370].

Studies of CpFe(CO)(η^3-CHRC$_6$H$_5$) produced by low temperature photolysis of η^1-benzylic precursors[335,336] have been described in the previous section of this review. Less transient was the product, CpFe(CO)(η^3-CH$_2$CHCHCO$_2$Me), produced in photolysis of FpCH$_2$CH=CHCO$_2$Me, which was characterized by X-ray crystallography. Further photolysis in the presence of phosphines produced CpFe(PR$_3$)(η^3-CH$_2$CHCHCO$_2$Me), but an (η^5-oxapentadienyl) intermediate could not be detected[371]. In comparison, photolysis of three (η^1-1-butadienyl)Fp compounds, which eventuated in formation of hydroxyferrocenes, was shown by low temperature photolysis with IR and NMR monitoring to occur through a sequence of η^3 and η^5 intermediates, shown as Eq. 17[372].



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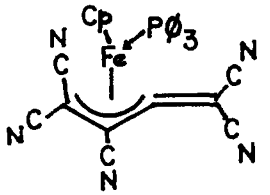
Photolysis of 52 [L = PPh$_3$] resulted in cleavage of a C-C bond to generate the novel η^3-species 56[347]. Ring opening also resulted when (η^1-1-phenylcyclopropyl)Fe(CO)(PPh$_3$)Cp was heated. Expulsion of PPh$_3$ resulted in formation of [η^3-CH$_2$C(Ph)CH$_2$]Fe(CO)Cp[327].



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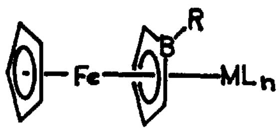

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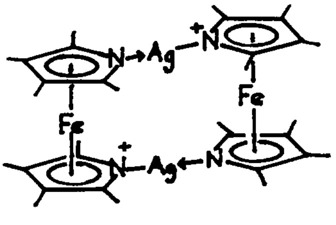
Irradiation of the borole complexes (η^5-C$_4$H$_4$BR)Fe(CO)$_3$ [R = Me, Ph] in the presence of dienes produced several examples of (η^5-C$_4$H$_4$BR)Fe(CO)(η^4-diene), with dienes including butadiene, cyclopentadiene, cyclohexa-1,3-diene, and cycloocta-1,5-diene[301]. Exhaustive photolysis of the cyclopentadiene complex formed

CpFeH(C_4H_4BR). Deprotonation of the latter produced a borataferrocene derivative[301].

Although they are closed-shell species isoelectronic with ferrocene, borataferrocenes have been found to form triple-decker molecules 57 with several metal moieties, through sharing of the borole ring. Examples of ML_n in 57 include Rh(COD)[301], Re(CO)$_3$[373], M(CO)$_4$ [M = Nb[374], Ta[374], and V[375]], and M(CO)$_3^-$ [M = Cr, Mo, and W[375]]. All of these examples are 30-electron triple-deckers, and all were susceptible to degradation by nucleophiles[374,375]. A more boron-rich analog of these triple-deckers is the compound CpFe(μ-$Et_2C_2B_3H_3$)CoCp, a 29-electron species prepared by treatment of (η^6-1,3,5-cyclooctatriene)Fe($Et_2C_2B_3H_4$)$^-$ with sodium cyclopentadienide and cobalt(II) chloride, followed by air oxidation[376]. Similarly, (η^6-C_8H_{10})Fe($R_2C_2B_4H_4$) [R = Et, CH_2Ph] has been converted to the paramagnetic triple-deckers, (η^5-$C_2R_2B_4H_4$)Fe(u-$Et_2MeC_3B_2Et_2$)CoCp and (η^5-$R_2C_2B_3H_5$)Fe(μ-$Et_2MeC_3B_2Et_2$)CoCp. The redox chemistry of these species was investigated[377].

New complex salts of bis(*o*-dicarbollyl)iron(III), (*o*-CB_9H_{11})$_2Fe^-$ with bpy- and 1,10-phenanthroline-coordinated cations such as Na(bpy)$_2^+$ and Fe(bpy)$_4^{2+}$, showed no C-H bands in the IR, suggesting deprotonation of the carborane by the amines[378]. A phenylene-bridged bis(dicarbollide), C_6H_4(η^5-7,8-$C_2B_9H_{10}$)$_2$Fe resulted when the ($C_2B_9H_{11}$)$_2Fe^-$ anion was allowed to react with benzenediazonium ion[379].

1,2,5-Trimethylpyrrole displaced the dimethyl sulfide ligands from CpFe(SMe_2)$_3^+$ to form the η^5-pyrrole complex or azaferrocene, CpFe(n^5-$C_4NMe_3H_2$)$^+$ [380]. The pK_a of CpFe(η^5-C_4Me_4NH)$^+$ (7.2) was similar to that of alkylpyridines. The deprotonated azaferrocene CpFe(C_4Me_4N) readily formed adducts with Lewis acids, including CH_3^+, MeCO$^+$, BH_3 and Fe(CO)$_4$. The crystal structure of the BH_3 adduct, isosteric with pentamethylferrocene, showed eclipsed rings[381]. An analogous bis adduct, (η^5-$C_4Me_4NBH_3$)$_2$Fe, has been prepared from the previously described bis(tetramethylpyrrolyl)iron-tetramethylpyrrole adduct and characterized by crystal structure[382]. Reaction of the adduct with $AgBF_4$ gave the novel bridged species 58[383].

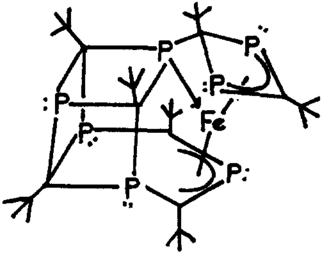


58

A study of acylated phosphaferrocenes in strong acids has indicated that the preferential site of protonation in all cases was the acyl oxygen rather than phosphorus or iron lone pairs[384]. Electrochemical oxidation of phosphaferrocenes and diphosphaferrocenes in the presence of nucleophiles such as chloride, bromide, or bipyridyl showed that the cations are more susceptible to nucleophilic attack than ferrocenium ions[385]. Phosphorus-based unshared electron pairs of the pentaphosphaferrocene, $Cp^*Fe(\eta^5$-P_5, were sufficiently basic to coordinate with transition metals. Thus, reaction with $(THF)Cr(CO)_5$ gave the 1,3-bis[$Cr(CO)_5$] derivative. Up to four $MnCp(CO)_2$ units could be coordinated to the P_5 ring. Irradiation of $Cp^*Fe(P_5)$ with $CpFe(C_6H_6)^+$ gave a 30-electron triple decker complex, $CpFe(\mu$-$P_5)FeCp^{*\,+}$ [386]. An extended Hückel MO study of $CpFe(P_5)$ and related compounds indicated metal-ring bonding as strong as in carbon analogs. The patterns of MO interactions differed in detail, but led to strong bonding[387].

8. COMPOUNDS WITH η^6-ARENE LIGANDS

The large majority of compounds dealt with in this section have arene ligands, but a few show η^6 bonding to a bis(allyl) or triene moiety. An example of a bis(allyl) species is **37**, previously mentioned in Section 6c. A more exotic example is **59**, formed (along with penta- and hexaphosphaferrocenes, $(\eta^6$-$PhMe)Fe(\eta^4$-$\underline{t}Bu_2C_2P_2)$, and polycyclic oligomers) upon reaction of Me_3C-$C{\equiv}P$ with $(\eta^4$-1-$MeC_{10}H_7)Fe(\eta^6$-$PhMe)$. Although formally a 16-electron species, **59** was described as a very stable substance[388].



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Reaction of CO or trimethyl phosphite with $(C_6H_6)Fe(PMe_3)_2$ resulted in displacement of trimethylphosphine ligands and retention of the coordinated benzene ring, whereas $(C_6H_6)Fe(DMPE)$ reacted by displacement of the benzene ring[176]. At -50°, 1-methylnaphthalene reacted with bis(toluene)iron to displace one toluene molecule, forming two coordination isomers of $(\eta^4$-1-$MeC_{10}H_7)Fe(\eta^6$-$PhMe)$. Likewise, co-condensation of iron vapor, 1,4-dimethylnaphthalene, and p-xylene, produced two isomers of $(\eta^4$-dimethylnaphthalene)Fe(p-xylene). Reactions with phosphites resulted in displacement of the η^4 ligands, giving the $(\eta^6$-arene)FeL_2 products[186].

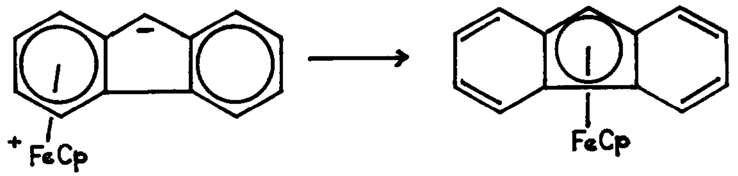
An unusual combination of ligands was assembled in $(\eta^6$-arene)$Fe(\eta^3$-$C_3H_5)(CO)^+$, which formed when $(C_3H_5)Fe(CO)_3Br$ reacted with arenes in the presence of aluminum chloride. The arenes used were benzene, mesitylene, and hexamethylbenzene. Triphenylphosphine attacked a terminal position of the allyl ligand to form $(\eta^6$-An)$Fe(CO)(\eta^2$-$CH_2{=}CHCH_2PPh_3{}^+$, whereas sodium borohydride reduced the benzene ring to a cyclohexadienyl ligand[389].

The most common sort of η^6-arene complex is the widespread family of (arene)(cyclopentadienyl)iron compounds, most commonly encountered as the closed-shell monocations. Examples bearing the 1,2,4-tris(trimethylsilyl)cyclopentadienyl ligand have been prepared directly from Li^+ $C_5H_2(SiMe_3)_3^-$ by consecutive reaction with ferrous chloride, then aluminum chloride and arene[390]. Standard syntheses of several $CpFeAn^+$ and Cp^*FeAn^+ cations, with An a polycyclic aromatic such as phenanthrene, pyrene, triphenylene, perylene and others, have been reproduced or improved. Omission of solvent was found to result in improved yields in some cases[391].

However, reaction of Fp^*Br with hexaethylbenzene in the presence of aluminum chloride gave only the pentaethylbenzene cation, $Cp^*Fe(C_6Et_5H)^+$. The yield was 28% when the reaction was carried out at 80°. At 200°, further dealkylation resulted in formation of tri- and tetraethylbenzene complexes as well. $CpFe(C_6Et_6)^+$ and $Cp^*Fe(C_6Me_6)^+$ could be prepared at moderate temperatures, but higher reaction temperatures here too led to dealkylation[392]. The crystal structure of $Cp^*Fe(C_6Et_5H)^+$ PF_6^- showed all five ethyl groups distal relative to the Cp^*Fe group[393]. $CpFe(C_6Et)^+$ BPh_4^- also showed five distal ethyl groups in the crystal, although the PF_6^- salt had earlier shown four. Clearly, small packing effects can lead to qualitative differences in these sterically crowded ligands[394].

A borole complex, $(\eta^5\text{-}C_4H_4BPh)Fe(\eta^6\text{-}C_6H_6)$, isoelectronic to $CpFe(C_6H_6)^+$, has been prepared by exhaustive photolysis of the (borole)$Fe(CO)_3$ complex in benzene[301].

A mixed-valence salt, $[CpFe(\eta^6\text{-tetralin})^+]_3$ $Fe(SCN)_6^{3-}$ was isolated in the course of treating $CpFe(\eta^6\text{-tetralin})^+$ PF_6^- with thiocyanate[395].



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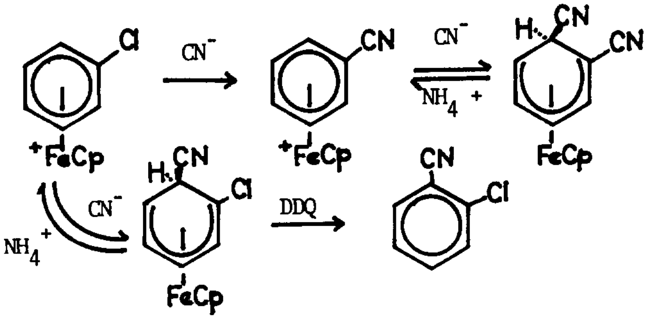
Haptotropic isomerization (Eq. 18) of $CpFe(\eta^6\text{-fluorenyl})$ to dibenzoferrocene occurred at 80-90°. Dibenzoferrocene also resulted in 15% yield when $CpFe(\eta^6\text{-fluorene})^+$ was reduced with sodium amalgam[396], and when $CpFe(C_6H_6)$ was treated with fluorenyl anion, followed by air oxidation[397]. The methyl groups of $CpFe(C_6Me_6)^+$ were deprotonated and alkylated by treatment with KOH and alkyl iodides RI, resulting in formation of $CpFe[C_6(CH_2R)_6]^+$ [R = ethyl, pentyl, $(CH_2)_6OMe$], described as "tentacled iron sandwiches"[398]. Substitution at all four benzylic positions of CpFe(tetralin)$^+$ was achieved by treatment with excess potassium *t*-butoxide and reactive organic halides, to form CpFe($C_{10}H_8R_4$)$^+$ [R = allyl, benzyl, methyl]. By varying the conditions, it was possible to obtain mono- and tri-benzylated compounds. Isolation of the free alkylated ligands was achieved by pyrolytic sublimation[399].

Nucleophilic attack on the arene ring of CpFeAn$^+$ cations constitutes a principal source of their synthetic utility, and several studies and applications of this reaction have appeared. A kinetic study of the reaction of CpFe(PhCl)$^+$ with piperidine in acetone showed that the rate-determining step was the piperidine-induced decomposition of the initial σ-complex[400]. Attack of amine nucleophiles on CpFe$^+$ complexes of the three chloronitrobenzenes gave mixed results. Aniline displaced the nitro group in all cases. Butylamine or pyrrolidine displaced chloride from the *ortho* isomer, but gave mixtures from the *meta* and *para*, with chloride displacement predominating from *meta* and nitrite displacement from *para*[401]. Excess butylamine gave monosubstitution from all three isomers of CpFe($C_6H_4Cl_2$)$^+$, but addition of acetic acid allowed disubstitution. Excess pyrrolidine gave disubstitution in all cases. These results supported the proposal that the deprotonation of primary amine adducts to form CpFe(η^5-ClC_6H_4=NR) was responsible for the lack of reactivity of the remaining chloro substituent[402].

Reaction of CpFe(*m*-$C_6H_4Cl_2$) with substituted phenoxides (protected tyrosines) proceeded sequentially, allowing preparation of complexed diaryl ethers or triaryl diethers[403]. In DMF solution, K$^+$ CHE_2^- and related nucleophiles cleanly displaced chloride from CpFe(*o*-C_6H_4ClMe)$^+$. With the CpFe$^+$ complex of 2,6-dichlorotoluene, the stabilized carbanions and methylamine displaced one chloride, whereas less hindered or stronger nucleophiles ($MeCOCH_2S^-$, MeO^-) displaced both[404]. Reactions of alkylmalonates RCE_2^- with chlorobenzene, dichlorobenzene, and chlorotoluene complexes under different conditions also led in most cases to clean chloride displacement. Use of excess nucleophile allowed displacement of both chlorides from *meta* and *para*-CpFe($C_6H_4Cl_2$)$^+$ [405].

In some cases, nucleophiles attack the coordinated arene ring at sites where there is no displaceable group, giving cyclohexadienyl complexes. The tetralin complex CpFe[$C_6H_4(CH_2)_4$]$^+$ added hydride and carbanion nucleophiles with little regioselectivity, giving mixtures; however, the analogs having four substituents on the benzylic positions showed complete selectivity for adding nucleophiles to the unhindered β-positions[399]. Reaction of $CpFe(C_6H_5Cl)^+$ with NaCN in DMF (Eq. 19) gave both displacement



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and addition, and the net outcome depended upon the method of workup. Addition of aqueous NH_4PF_6 gave only the benzonitrile complex, whereas oxidation with DDQ [2,3-dichloro-5,6-dicyano-1,4-benzoquinone] gave a mixture of o-chlorobenzonitrile and phthalonitrile. Analogous results were obtained from ortho-substituted chlorobenzenes and 2,6-dichlorotoluene complexes[406] and from dichlorobenzene complexes[402].

In an application of these methods to synthesis of an anti-cholesterol agent, $CpFe(p\text{-}C_6H_4Cl_2)^+$ was treated with the carbanion from deprotonation of 3-ethoxy-6-methylpyridazine N-oxide to form an adduct; oxidative decomplexation gave the 2,5-dichlorobenzylated heterocycle[407]. $CpFe(o\text{-}C_6H_4Cl_2)^+$ was converted to mono- and di-substituted cinnolines by means of 3- or 4-step syntheses involving enolate displacements and hydrazine attack with ring closure[408]. Applications of the same o-dichlorobenzene complex to syntheses of several heterocyclic skeletons found in biologically active materials have been described[409].

Liberation of the arene from $CpFeAr^+$ complexes is a necessary final step in a synthetic sequence. Photolysis of the phenoxazine and phenothiazine complexes in methanol, THF, or DMSO has been found to generate the free heterocycles with a quantum yield of 1.0, and has been recommended over the traditional pyrolytic sublimation as the method of choice for liberating arenes[410]. Flash photochemical studies of $CpFeAn^+ Cl^-$ on the 10^{-3} to 10^{-6} sec time scale have been carried out, implicating an intermediate thought to be $AnFeCl^+$. The final products were free arene and ferrocene[411]. Photolysis in the presence of benzonitrile cleanly produced the free arene and $CpFe(NCPh)_3^+$. Two intermediates were detected by time-resolved laser spectroscopy: one, formed from the ion pair, was identified as $CpFe(\eta^4\text{-}An)X^+$, and the other, formed from the free cation, was the unsaturated $CpFe(\eta^4\text{-}An)$[412].

Photolysis of $CpFe(C_6H_6)^+$ in the presence of excess cyclooctatetraene produced $CpFe(\eta^6\text{-}C_8H_8)^+$ in high yield. An X-ray structure showed the uncoordinated double bond of the cyclooctatetraene ligand folded away from the plane of the coordinated C_6 unit[413].

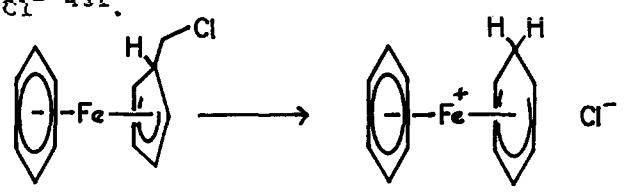
Photolysis of $CpFeAn^+$ Ph_3BR^- salts in THF resulted in electron transfer, then rapid cleavage of the Ph_3B-R bond to form the free radical R· [414]. Visible irradiation of $CpFeAn^+$ in polar solvents was shown by spin trapping to produce Cp· radicals. The excited state of the cations could be quenched by redox quenchers such as methylviologen or by hexamethyl Dewar benzene[415]. The photochemical properties of $CpFeAn^+$ have led to patents suggesting various practical uses of these materials: as photochemical initiators for cationic polymerization[416], as components in photopolymerizable mixtures for coatings, printing inks and the like[417], and for photoresists[418,419].

$CpFeAn^+$ undergo chemical reduction as well as photochemical, and the properties of the resulting 19-electron radicals draw continuing interest. Extended Hückel and SCF-Xα calculations on CpFeAn complexes having polycyclic aromatic ligands have been carried out. Both gave good agreement with experimental spin densities, especially the Xα calculations. The 19-electron radicals were produced from the cations either electrochemically or by reduction with $LiAlH_4$ at low temperature[391]. Carboranyl-substituted compounds $CpFe(C_6H_5\text{-}R)$ [R = m- or p-carboranyl group] have been prepared similarly and studied by ESR spectroscopy[420]. Electrochemical studies of $(C_6H_6)Fe(\eta^5\text{-}Et_2C_2B_4H_4)$ showed a reversible one-electron oxidation[421].

Electroreduction of $CpFe(PhCOPh)^+$ and related compounds with carbonyl groups on the arene ring cleanly led to liberation of the free arenes in yields of 85% or better, without reduction of the carbonyl substituents[422]. $CpFe(C_6H_6)$ reacted with trimethylphosphine in THF solution to form $CpFe(PMe_3)_2H$; in the presence of $NaPF_6$, however, the products were $CpFe(PMe_3)_3^+$ and $(Me_3P)_3FeH(\eta^2\text{-}CH_2\text{-}PMe_2)$[423]. A low temperature spectroscopic study of the reaction of CpFeAn with phosphines and phosphites indicated a fast equilibration of the η^6 19-electron species with a more reactive η^4 17-electron species, which was readily attacked by the phosphorus nucleophile. The toluene complex was 400 times more reactive than the hexamethylbenzene complex[424]. The 19-electron complexes CpFeAn reduced CO_2 to 1/2 $[CO_3^{2-} + CO]$, but in the presence of PMe_3 and $NaPF_6$, the electron-rich species $CpFe(PMe_3)_3$ formed and was converted to $CpFe(PMe_3)_3^+$ and $CpFe(PMe_3)_2(CO)^+$ [425].

The binuclear complexes $CpFe(C_5H_4\text{-}C_5H_4)FeAn^+$ were prepared from biferrocene and the arene [benzene or hexamethylbenzene]. Cyclic voltammetry at -35° in DMF showed four reversibly formed oxidation states. The 35-electron dications were stable, and showed localized, valence-trapped behavior, as did the neutral 37-electron species[426]. Cyclic voltammetric studies of bis-($CpFe^+$) complexes of dibenzo-1,4-dioxin and related heterocycles showed two one-electron reduction steps whose small separation indicated moderate through-space interaction of the two FeCp centers. At slower scan rates, loss of a solvated CpFe(I) group could be observed; this formed ferrocene or, in the presence of CO, Fp_2[427]. The symmetrical binuclear complexes $AnFe(C_5H_4-C_5H_4)FeAn^{2+}$ [An = benzene, toluene, mesitylene, hexamethylbenzene, hexaethylbenzene] showed three reversible reduction waves, whose chemical reversibility increased with the number of methyl groups on the arenes[428]. These dications could be reduced to 37-electron monocations by use of sodium amalgam, $LiAlH_4$, or $CpFe(C_6Me_6)$. The bis(hexamethylbenzene) monocation was isolable at room temperature. Mössbauer spectroscopy showed delocalized valences in the 37-electron species. Further reduction with sodium amalgam gave the 38-electron diradicals, which were revealed by ESR to be localized iron-centered biradicals with comparatively free rotation about the central bond[429]. Effects of external magnetic fields on the Mössbauer spectra of the 36-, 37- and 38-electron species have been determined[430]. Cyclic voltammetric study of $(\eta^5-Et_2C_2B_4H_4)Fe(Ph-Ph)Fe(\eta^5-Et_2C_2B_4H_4)$ showed two reversible oxidation waves[421].

Reaction of the 19-electron species CpFeAn [An = benzene, hexamethylbenzene] with organic halides RX produced $CpFeAn^+ X^-$ salts, $AnFe(\eta^4$-*exo*-$5-R-C_5H_5)$, and $CpFe(\eta^5$-*exo*-$6-R-C_6H_6)$. The (chloromethyl)cyclopentadiene compounds underwent ring expansion (Eq. 20) at room temperature to form $AnFe(\eta^5-C_6H_7)^+ Cl^-$. The isomeric (chloromethyl)cyclohexadienyl compounds similarly solvolyzed at 40° in methanol solution to form $CpFe(\eta^6$-cycloheptatriene$)^+ Cl^-$ [431].



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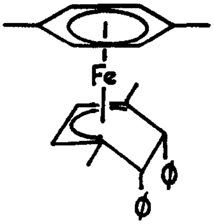
Synthesis of several An_2Fe^{2+} compounds has been reexamined and, in some cases, improved. Reaction with one equivalent of $NaBH_4$ formed $AnFe(\eta^5$-cyclohexadienyl$)^+$ cations. Reactions with C and O nucleophiles resulted in electron transfer rather than covalency formation. Reaction of bis(*p*-xylene)iron^{2+} with two equivalents of phenyl-lithium at -80°, however, gave **60**, albeit in low yield[432]. The stabilities of a series of An_2Fe^{2+} complexes in solution were found to depend on solvent basicity and extent of alkyl substitution on the rings. ^1H and ^{13}C NMR data and ^{57}Fe Mössbauer data were reported and analyzed in terms of charge densities and orbital populations[433]. Use of An_2Fe^{2+} dications in donor-acceptor solids with hexacyanotrimethylenemethyl dianion, $(NC)_2C{=}C[C(CN)_2^-]_2$, has been studied. Crystal structures of the mesitylene and hexamethylbenzene salts showed zigzag linear chains of alternating dications and dianions, with close contacts. The crystal structure of the 19-electron $(C_6Me_6)_2Fe^+\ PF_6^-$ showed little structural change from the 18-electron dication, consistent with the facile charge-transfer interactions shown by these species[434].

Reaction of An_2Fe^{2+} with trimethylaluminum in methylene chloride resulted in chloromethylation, to form **61** in the hexamethylbenzene case[435]. Ring expansions analogous to Eq. 20 were not yet reported.



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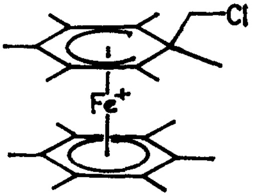


61

Hydride abstractions from $(C_6H_6)Fe(\eta^4\text{-}C_6H_7R)$ [R = benzyl, 2-dithiolanyl, CHE_2 , CN] were investigated. At low temperature, reaction with Ph_3C^+ proceeded by electron transfer, followed by slow hydrogen transfer at -50° in the cases R = benzyl and dithiolanyl, which gave the desired cations $(C_6H_6)Fe(\eta^5\text{-}C_6H_6R)^+$. At higher temperatures or with R = CHE_2 even at -50°, loss of R• led to formation of $(C_6H_6)Fe(C_6H_7)^+$. Addition of CN^- to $(C_6H_6)Fe(\eta^5\text{-}C_6H_6CH_2Ph)^+$ produced an adduct analogous to **60**[436].

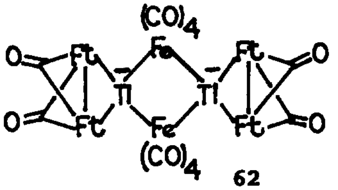
9. BIMETALLIC COMPOUNDS

a. Diiron Compounds. Derivatives of $Fe_2(CO)_9$

$(F_3CCN)_3Fe(\mu\text{-}NCCF_3)_3Fe(NCCF_3)_3$, the trifluoromethylisocyanide analog of $Fe_2(CO)_9$, formed upon spontaneous decomposition of $Fe(NCCF_3)_5$ at room temperature[121]. Visible irradiation of solutions containing $Fe_2(CO)_9$ and $CpW(CO)_3[SC(S)NMe_2]$ resulted in ligand transfer to form $Fe[SC(S)NMe_2]_2$[437]. As previously shown in Eq. 8, $Fe_2(CO)_9$ served as an oxidizing agent toward some reactive benzylic and allylic alcohols, being reduced to $H_2Fe(CO)_4$ in the process[154]. The opposite reaction, reduction of an aldehyde group to a primary alcohol, occurred when RCHO [R = 2-norbornyl, 3-methyl-2-norbornyl] was refluxed in dibutyl ether with $Fe_2(CO)_9$. In refluxing hexane, the ester $RCH_2OC(O)R$ formed, via a novel iron carbonyl-catalyzed Cannizzaro reaction[438].

$Tl_2Fe_6(CO)_{24}^{2-}$ has been prepared by oxidation of $Tl_2Fe_4(CO)_{16}^{2-}$, both as tetraethylammonium salts. The crystal structure of the PPN salt showed the expected structure, **62**. The new Tl_2Fe_6 dianion is a member of a homologous series which includes the already-described Tl_4Fe_8 and Tl_6Fe_{10} dianions[439].

The methylene-bridged complex $(OC)_4Fe(\mu\text{-}CH_2)Fe(CO)_4$ was obtained in high yield from reaction of CH_2X_2 with $Fe(CO)_5$ in a phase-transfer system [1 M aq. NaOH, Bu_4N^+ HSO_4^-][85]. Carbonylation of the methylene complex in the presence of an alcohol, ROH, produced mainly CH_3CO_2R. Byproducts included **14**, and $(OC)_4Fe(\eta^2\text{-}CH_2C{=}O)$ was proposed as an intermediate. Reaction of the methylene complex and CO in the presence of norbornene led to formation of an organic trapping product of the ketene intermediate[94]. The silylene complex $(OC)_4Fe(\mu\text{-}SiMe_2)Fe(CO)_4$ served as a source of iron carbonyl groups in reaction with allyl halides to form $(\eta^3\text{-allyl})Fe(CO)_3X$. Reaction with elemental sulfur produced $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$[134].



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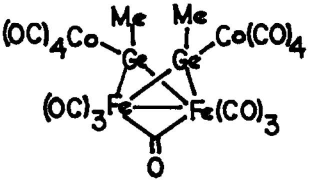

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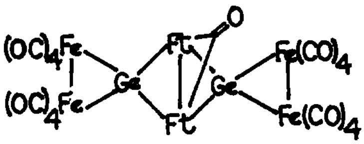
$(OC)_3Fe(\mu\text{-}GeMe_2)_3Fe(CO)_3$ was among the products of prolonged irradiation of **15** [n = 1][96]. Thermal reaction of cyclo$[Fe(CO)_4(GeMeH)]_2$ with $Co_2(CO)_8$ produced **63**, which showed normal Ge-Fe bond lengths (2.45 Å) and a consequentially elongated Fe-Fe distance (2.693 Å)[97]. Reactions of GeH_4 or Ge_2H_6 with $Fe_2(CO)_9$ in refluxing hexane produced, along with the known $(OC)_8Fe_2(\mu_4\text{-}Ge)Fe_2(CO)_8$, the clusters $Ge_2Fe_6(CO)_{23}$, **64**, and $Ge_2Fe_7(CO)_{26}$. Analogous tin clusters were also produced from SnH_4[440].

Mild oxidation of $ClSb[Fe(CO)_4]_3^{2-}$ resulted in formation of $(OC)_8Fe_2(\mu_4\text{-}Sb)Fe_2(CO)_6(\mu_4\text{-}Sb)Fe_2(CO)_8$, a structure analogous to **64** save for the bridging CO in the latter[105]. Similarly, oxidation of $Sb[Fe(CO)_4]_4^{3-}$ produced $(OC)_8Fe_2(\mu_4\text{-}Sb)[Fe(CO)_4]_2^-$, **65**, in which the four-coordinate antimony atom formed part of a $SbFe_2$ ring, and also coordinated two isolated $Fe(CO)_4^-$ units[441]. Reaction of $Fe_2(CO)_8^{2-}$ with $SbCl_3$ or $BiCl_3$ produced **66** [Z-X = $SbCl^-$ or $BiCl^-$], which formed **66** [Z-X = $Sb\rightarrow Cr(CO)_5$ or $Bi\rightarrow Cr(CO)_5$] upon treatment with $(THF)Cr(CO)_5$. Methylation of **66** [Z-X = $BiCl^-$] produced **18**, whereas refluxing it in acetonitrile yielded the



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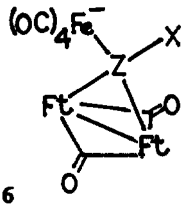


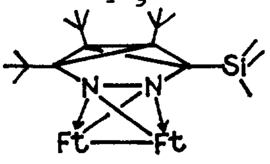
66

previously characterized $Bi_2Fe_4(CO)_{13}^{2-}$. Heating the antimony analog in acetonitrile produced $Sb_2Fe_5(CO)_{17}^{2-}$ [106].

The bridging phosphide salt Et_4N^+ $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3^-$ was obtained in low yield when the $HFe(CO)_3PPh_3^-$ salt was treated with hot ethanol[67]. The ESR spectrum of the neutral 33-electron radical $Fe_2(CO)_7(\mu\text{-}PPh_2)$ trapped in a single crystal of $FeCo(CO)_7(u\text{-}PPh_2)$ has been determined. Spin density was confined to the pentacoordinated Fe nucleus and two of its CO ligands, a result which was consistent with extended Hückel calculations[442].

Spin-lattice relaxation times and nuclear Overhauser enhancement factors in the ^{31}P NMR spectra of several bi- and trinuclear complexes containing phosphine and phosphido groups have been measured. Included among those studied was $(OC)_3Fe(\mu\text{-}PPh_2)(\mu_2,\eta^2\text{-}C{\equiv}CCMe_3)Fe(CO)_3$[443]. This compound and other similar phosphido-bridged ones were also studied in the solid state by CP/MAS ^{31}P NMR spectroscopy. There was a good correlation between the shielding tensor components and the M-P-M bond angle[444].

Reaction of azoalkanes R-N=N-R [R = Et, Pr] with "Grevels' reagent," bis(cyclooctene)$Fe(CO)_3$, or with $Fe_3(CO)_{12}$ produced $(OC)_3Fe(\mu,\eta^2N_2R_2)Fe(CO)_3$ and tri-iron complexes[446]. A structurally similar azo complex, **67**, was obtained (in very low yield) from the diazocyclopropene $[C_3(\underline{t}\text{-}Bu)_3]C(=N_2)SiMe_3$ and diiron nonacarbonyl[9][170].



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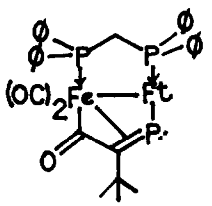

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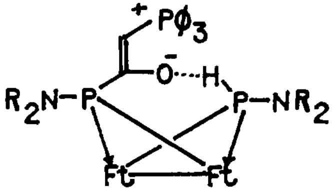

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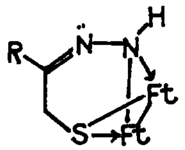
Irradiation of $(OC)_3Fe(\mu\text{-}DPPM)(\mu\text{-}CO)Fe(CO)_3$ and $Me_3C\text{-}C{\equiv}P$ resulted in insertion of the phosphanitrile into the molecule as a four-electron ligand, forming **68**. The fluorophosphine-bridged compound $(OC)_2Fe(\mu\text{-}CO)(\mu\text{-}F_2PNMePF_2)_2Fe(CO)_2$ served as a catalyst in photoassisted hydrosilylation reactions with Et_3SiH. Quenching by added ligands and the wavelength dependence indicated the necessity of carbonyl dissociation[447]. Reaction of $(OC)_3Fe$-

[μ-$R_2NPC(=O)PNR_2$]$Fe(CO)_3$ [R = isopropyl] with dimethylsulfoxonium methylide resulted in insertion of methylene groups into both P-CO bonds. In contrast, triphenylphosphonium methylide attacked the carbonyl group, to form the ylide product **69**[448].

Reaction of 4-R-1,2,3-thiadiazoles with $Fe_2(CO)_9$ in the presence of ethanol, which functioned as a labile ligand and as a reducing agent, produced **70**[79]. Insertion of a $Fe_2(CO)_6$ group into the C-S bond was the net result when $PhCH_2SC(=S)N=C(NMe_2)$-CO_2Me reacted with $Fe_2(CO)_9$, forming $(OC)_3Fe(\mu$-$SCH_2Ph)(\mu$-$C(=S)N=C(NMe_2)CO_2Me)Fe(CO)_3$. This result contrasted with formation of **22** from the thiobenzoyl analog[131].



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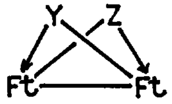

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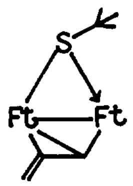

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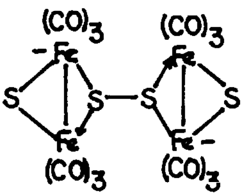
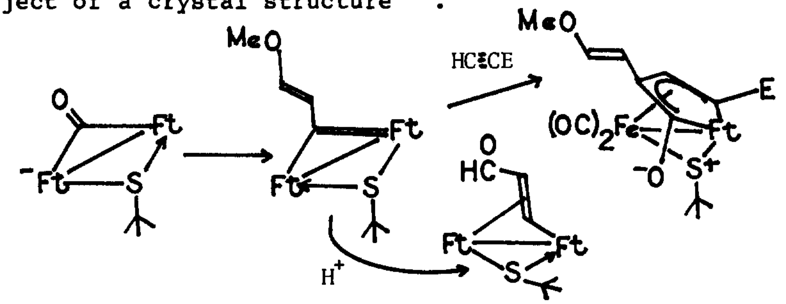
A two-step sequence comprising reaction of $Fe_3(CO)_{12}$ with thiols, RSH, and triethylamine, to form the intermediate Et_3NH^+ $Fe_2(CO)_6(\mu$-$CO)(\mu$-$SR)^-$, then reaction with $PhPCl_2$, produced **71** [Y = SR, Z = PhPCl[449]. Analogous types of products resulted when $Fe_3(CO)_9(\mu$-$CO)(\mu_3$-$PR)$ reacted with R'SeSeR'; about 30% binuclear products **71** [Y = R'Se, Z = PR(SeR')] were obtained, along with trinuclear products. R'TeTeR' reacted similarly[450].

Salts of $(ON)_2Fe(\mu$-S-$SO_3^-)Fe(NO)_2^{2-}$ resulted from reaction of ferrous salts, thiosulfate, and NO or NO_2^-. The crystal structure of the PPN^+ salt showed a planar S_2Fe_2 ring with trans sulfonate groups. The μ-thiosulfate groups were readily displaced by thiols to form $(ON)_2Fe(\mu$-$SR)_2Fe(NO)_2$[451]. Reaction of Me_3CS^- with $(\mu$-S_2-$Fe_2(CO)_6$ produced $(OC)_3Fe(\mu$-$S)(\mu$-S-$SCMe_3)$-$Fe(CO)_3^-$, whereas less bulky thiolates reacted further to form $Fe_4S_4(CO)_{12}^{2-}$, having two [$(\mu$-$S)_2Ft_2$] units linked by a S-S bond[452].



The previously mentioned anions $(OC)_3Fe(\mu$-$CO)(\mu$-$SR)Fe(CO)_3^-$ were useful precursors to species having organic bridging ligands. With the hard electrophile, Et_3O^+, they underwent O-ethylation at the bridging CO ligand, giving μ-carbyne products.

With organic halides capable of forming bridging groups [acyl chlorides, Me$_2$NC(=S)Cl, allyl chloride, propargylic halides], they formed (OC)$_3$Fe(μ-SR)(μ-organyl)Fe(CO)$_3$. Crystal structures of the μ-allyl and the fluxional μ-allenyl [72] products were reported^{453}. Reaction of the (μ-CO)(μ-SR)Fe$_2$(CO)$_6^-$ anions with carbon disulfide gave Ft[μ-S=C(-S$^-$)](μ-SR)Ft anions, which showed strong nucleophilicity of the exocyclic sulfur. μ-S and μ-SO$_2$ products resulted from reactions with sulfur and with sulfur dioxide, respectively^{454}. In an independent report, direct formation of μ-aroyl (μ-SCMe$_3$)(μ-ArCO)Fe$_2$(CO)$_6$ complexes from Fe$_3$(CO)$_{12}$, Me$_3$CSH, Et$_3$N, and aroyl chloride was reported^{455}. A crystal structure of (μ-RCO)(μ-SEt)Fe$_2$(CO)$_6$ [R = CH$_2$=C(Me)-] was reported^{456}. With ArCOCH=CHCl, μ-alkenyl complexes formed ^{457}, one of which, Ft(μ-SPh)(μ-CH=CHC(=O)C$_6$H$_4$Me)Ft, was the subject of a crystal structure^{458}.



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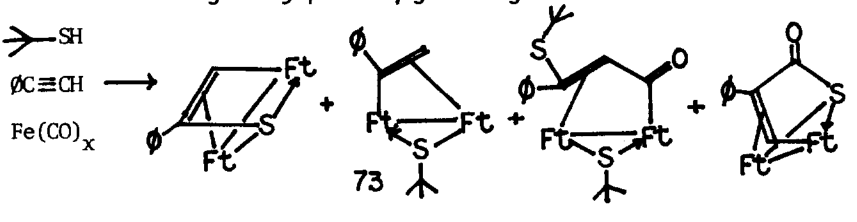
When (μ-CO)(μ-SCMe$_3$)Fe$_2$(CO)$_6^-$ was treated with Hg(C≡CCH$_2$OMe)$_2$ (Eq. 21), a μ-carbyne product formed. Reaction with aqueous acid resulted in hydrolysis of the enol ether, while reaction with electron-deficient alkynes led to insertion reactions, which formed more complex cyclic products^{459}. In what is probably closely related chemistry, a one-pot reaction of Fe$_2$(CO)$_9$ or Fe$_3$(CO)$_{12}$ with Me$_3$CSH and HC≡CPh has been reported to give the products shown in Eq. 22, all characterized by crystal structures. The first two products were also formed in the reaction of Fe$_3$(CO)$_9$(μ-Cl)(μ$_3$-SCMe$_3$) with HC≡CPh^{460}. The pro-



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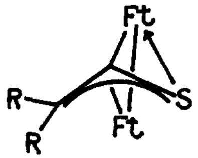
ducts **74** [R = CF$_3$, CO$_2$Et] formed (along with **21** in the trifluoromethyl case) in photochemical reaction of Fe(CO)$_5$ with the thioketenes^{128}.

The very common bis(thiolate) complexes, **71** [Y = Z = SR; R =

H, Me, Et, Ph], resulted when mononuclear thiolate complexes $RSFe(CO)_4^-$ were protonated. Intermediate thiol complexes could be observed in some cases, but these decomposed above -40° to $Ft(\mu\text{-}SR)_2Ft$, molecular hydrogen, and carbon monoxide[107]. Mono- and bis-triphenylphosphine substitution products were obtained by refluxing the reagents together for appropriate lengths of time[461]. $(Ph_3P)Fe(CO)_2(\mu\text{-}SEt)_2Fe(CO)_2(PPh_3)$ has been used as a catalyst for substitution of phosphites into $Fe_3(CO)_{12}$[462]. The crystal structures of eight $Ft(\mu\text{-}SR)(\mu\text{-}SR')Ft$ complexes have been compared in detail; little variation in Fe-Fe and Fe-S distances was apparent[463]. The structure of 73 was also reported[463].

The kinetics of replacement of a CO by another ligand in the thioacyl complexes $(OC)_3Fe[\mu,\eta^2\text{-}C(OR)S](\mu\text{-}SR')Fe(CO)_3$ [R = adamantylmethyl, mesityl; R' = methyl, cyanomethyl] has been studied. Selective substitution occurs at the C-bound carbon, and initial decoordination of the SR' group from there was implicated in the mechanism[464]. Under thermal conditions, the new ligand $[Me_3C\text{-}NC]$ principally entered *cis* to the Fe-thioacyl group; with electron-transfer catalysis, it was found in the *trans* position, which was thermodynamically favored. A second ligand attacked the S-bound carbon in either case[465]. Crystal structures of mono- and bis-isonitrile substitution products were reported[466].



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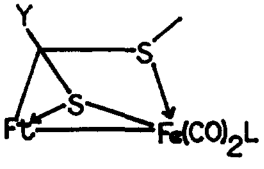

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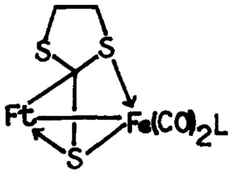


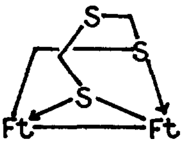
76

Compound 75 [Y = adamantylmethoxy, L = CO] has been obtained as a byproduct in the synthesis of $(OC)_3Fe[\mu,\eta^2\text{-}C(OR)S](\mu\text{-}SMe)Fe(CO)_3$ from $Fe_2(CO)_9$ and ROC(=S)SMe, and is thought to be an intermediate in the formation of the more stable thioacyl product. Reaction of 75 [L = CO] with trimethyl phosphite gave only 75 [L = $P(OMe)_3$] (crystal structure). Curiously, when the latter rearranged to the thioacyl, either thermally or with electron-transfer catalysis, the thioacyl group and the phosphite were bound to the same carbon; migration of the carbon during rearrangement was inferred[467]. Further examples of 75 [Y = CH_2=CH-S, L = CO, $P(OMe)_3$] were obtained by reaction of ethylene trithiocarbonate complexes **76** with strong bases, followed by S-methylation. Again, heating caused conversion to the thioacyl complexes $(OC)_3Fe(\mu\text{-}SMe)[\mu,\eta^2\text{-}S\text{-}C(SCH{=}CH_2)]Fe(CO)_2L$, with migration of the thioacyl carbon[468].

Carbene complexes $(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2[C(OEt)R]$ [R = Ph, Bu] underwent aminolysis with ammonia or dimethylamine to form aminocarbene complexes. Displacement of the carbene ligand by the amine occurred competitively. The crystal structure of $(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2[C(NMe_2)Ph]$ showed the carbene ligand trans to the Fe-Fe bond, with a C=Fe bond distance of 1.97 Å and a C=N distance of 1.32 Å[469]. Reaction of the ethoxycarbene complex with ligands trimethyl phosphite and t-butyl isonitrile resulted in displacement of both a CO (from the tricarbonyliron group) and the carbene ligand. With $LiPPh_2$, the ethoxycarbene complex reacted to form $Fe_2(\mu\text{-}SPh)(\mu\text{-}PPh_2)(CO)_5(PPh_3)$ and $Fe_2(\mu\text{-}SPh)(\mu\text{-}PPh_2)(CO)_4(PPh_3)_2$, the latter being verified by a crystal structure[470].

Irradiation of 1,3,5-trithiane with $Fe(CO)_5$ in THF gave the bridged compound **77** (crystal structure), and 1,3-dithiane gave a similar product with a trimethylene bridge joining the two coordinated sulfur atoms. $(OC)_3Fe(\mu\text{-}SCH_2S)Fe(CO)_3$ was a byproduct in each case. With $CH_2(SMe)_2$, $(OC)_3Fe(\mu\text{-}SMe)(\mu\text{-}CH_2SMe)Fe(CO)_3$ was formed[471]. An unusual stable free-radical complex, **78**, resulted from reaction of 4-phenyl-1,2,3,5-dithiadiazole with iron carbonyls. The Fe-Fe, Fe-S, and S⋯S distances in the crystal structure of **78** were unexceptional. Extended Hückel MO calculations indicated that the unpaired electron was housed in an antibonding MO extending over the CN_2S_2 system[472].

The $(OC)_3Fe(\mu\text{-}SPh)(\mu\text{-}S)Fe(CO)_3^-$ anion attacked the $CpMn(CO)_2{\equiv}CPh^+$ cation at the carbyne carbon, forming $(OC)_3Fe(\mu\text{-}SPh)[\mu\text{-}SC(Ph){=}Mn(CO)_2Cp]Fe(CO)_3$, having a manganese-carbene linkage on the side chain. Similarly formed from $S_2Fe_2(CO)_6^{2-}$ were bis(μ-thiocarbene) complexes of manganese and rhenium[473]. The alkynyl groups in $Fe_2(CO)_6(\mu\text{-}SC{\equiv}CAr)(\mu\text{-}SR)$ readily underwent complexation by $Co_2(CO)_6$ groups[474]. An X-ray structure of $(OC)_3Fe(\mu\text{-}SPr)[\mu\text{-}SC_2Co_2(CO)_6C_6H_4Me]Fe(CO)_3$ showed the S-propyl group equatorial and the $S\text{-}C_2Co_2$ cluster axial with respect to the S_2Fe_2 cluster[475].



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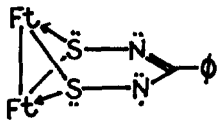

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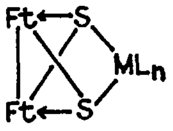
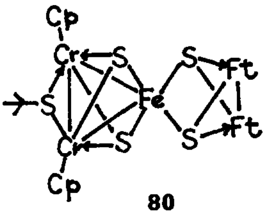


79

The $Fe_2S_2(CO)_6$ cluster is itself capable of serving as a ligand toward other transition metals, as in **79**, and several examples of new compounds in which it plays that role have been described. Reactions of the neutral $(\mu\text{-}S_2)Fe_2(CO)_6$ with various compounds of titanium, iron, cobalt, nickel, palladium, and platinum have been studied. In all cases, an unsaturated metal fragment inserted into the S-S bond of the Fe_2S_2 cluster to form **79**; in some cases Fe-M bonds also formed to satisfy the needs of valency. The crystal structures of **79** [ML_n = $CoCp^*$ and $Cp^*Co(\mu\text{-}CO)_2CoCp^*$] were determined. In the latter, the Fe··Fe distance was 3.35 Å, suggesting little residual interaction[476].

A supercluster, **80**, resulted from reaction of $Cp_2Cr_2(SCMe_3)_3S$ with $S_2Fe_3(CO)_9$. Similar compounds with cobalt and rhodium as central ions were also prepared[477]. Reactions of $M(PPh_3)_4$ [M = Ni, Pd, and Pt] with $E_2Fe_3(CO)_9$ [E = S, Se, and Te], to form **79** [ML_n = $M(PPh_3)_2$] have been explored in detail. Competing mechanisms were indicated, with formation of **79**-type products particularly favored for the larger atoms in each series, especially Te, Pd, and Pt[478,479]. $Te_2Fe_2(CO)_6$ readily added unsaturated triruthenium and triosmium fragments to form $(OC)_6Fe_2(u\text{-}Te_2M_3(CO)_{11}$[479]. A crystal structure of the triruthenium compound may be represented as **81**[480]. Infrared comparison suggested a similar structure for the osmium analog. Heating or irradiating either compound resulted in conversion to $(\mu_3\text{-}Te)_2M_3(CO)_9$[481].



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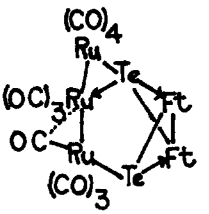

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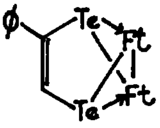


82

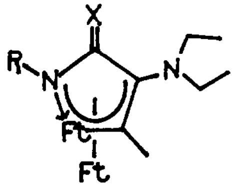
Phenylacetylene added thermally to the E-E bond of $(OC)_3Fe(\mu_2,\eta^2\text{-}E_2)Fe(CO)_3$, to form **82**[482]. The analog with a saturated ethanediyl bridge between the tellurium atoms has also been reported[479].

A group of chemists from Amsterdam has published a series of seven full papers[483-489] on the reactions of bimetallic diazadiene complexes, $[R\text{-}N{=}CH\text{-}CH{=}NR]FeM(CO)_6$ [R = isopropyl, cyclohexyl; M = Fe, Ru], and their benzo analogs, with alkynes, especially methyl propynoate, dimethyl acetylenedicarboxylate, and (N,N-diethylamino)-1-propyne. The diazadiene coordinates to the $FeM(CO)_6$ groups in the starting materials as a six-electron ligand, using both nitrogen electron pairs and one pair of π-electrons. This can readily be expanded to use of eight electrons upon expulsion of a CO ligand, and a panoply of possible products form by coordination of an alkyne, followed by insertion reactions. Much of this chemistry has been reviewed by the original authors[490].

A sense of the transformations involved in these reactions, which commonly occur at room temperature, can be gleaned from Scheme I, which shows intermediates and products in the reaction of $[\text{Me}_2\text{CH-N=CH-CH=N-CHMe}_2]\text{Fe}_2(\text{CO})_6$ and $\text{HC}\equiv\text{CCO}_2\text{Me}$[485] and Scheme II, involving the same diazadiene (and its ruthenium analogs) and $\text{MeC}\equiv\text{CNEt}_2$[489]. Several other systems were studied in depth, and numerous crystal structures were reported.

A series of ferracyclopentadienyl complexes, derivatives of $[\eta^5\text{-C}_4\text{H}_4\text{Fe(CO)}_3]\text{Fe(CO)}_3$ having diazadiene units replacing two carbonyl groups at alternate sites on either iron, have been studied by theoretical methods (Xα calculations) and photoelectron and Mössbauer spectra. It was concluded that replacement of two carbonyls by a diazadiene resulted in increased electron density on the iron, with consequent structural adjustments[491].

When isocyanates RNCX [R = Et, Ph; X = O, S] were allowed to react with $[\mu,\eta^2\text{-MeCCNEt}_2]\text{Fe}_2(\text{CO})_7$, the result was insertion into a C-Fe bond and loss of CO to form a ferrapyrrolidinone ring, **83**[492]. An isomeric ferrapyrrolinone ring **84** was formed by reaction of $(\mu\text{-CH}_2)\text{Fe}_2(\text{CO})_8$ with phosphinimines $\text{Ph}_3\text{P=NPh}$ and $\text{Bu}_3\text{P=N-CMe}_3$ under CO. Loss of CO from the ferrapyrrolinone gave a ferraazetine complex $[\eta^4\text{-}\overline{\text{Fe(CO)}_3\text{-CH-CH-N}}\text{R}]\text{Fe(CO)}_3$. Protonation of **84** led reversibly to $(\text{OC})_4\text{Fe}[\mu_2,\eta^1\text{-CH(CH=NHR)}]\text{Fe(CO)}_4^+$ [493]. Another ferraheterocycle, **85**, resulted as a minor product from reaction of $\text{Ph}_2\text{P-C}\equiv\text{C-CMe}_3$ and $\text{HFe}_3(\text{CO})_{11}^-$ in refluxing ethyl acetate[494].



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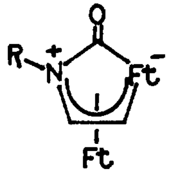

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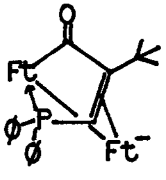
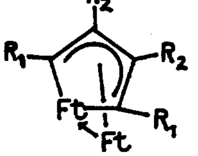


85

A mixture of seven characterized products, five of them $\text{Fe}_2(\text{CO})_6$ derivatives, formed in the reaction of $\text{CH}_2\text{=CH-CH}_2\text{C}\equiv\text{C-NEt}_2$ with $\text{Fe}_3(\text{CO})_{12}$. At 45°, the two products formed represented two common structural types: a ferrole complex, **86** [R_1 = allyl, R_2 = NEt$_2$] and a "flyover" complex, **87** [same R's], both resulting



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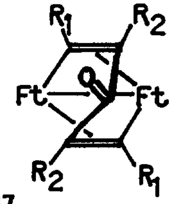
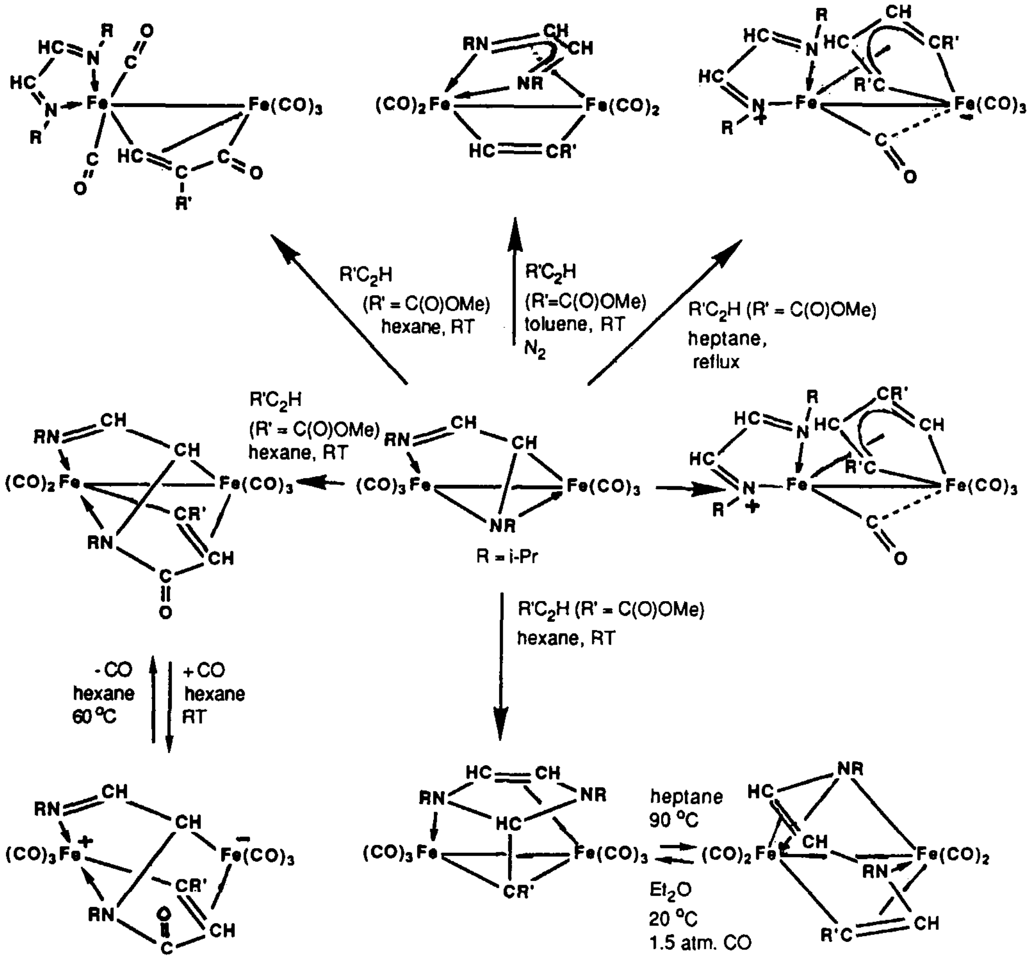


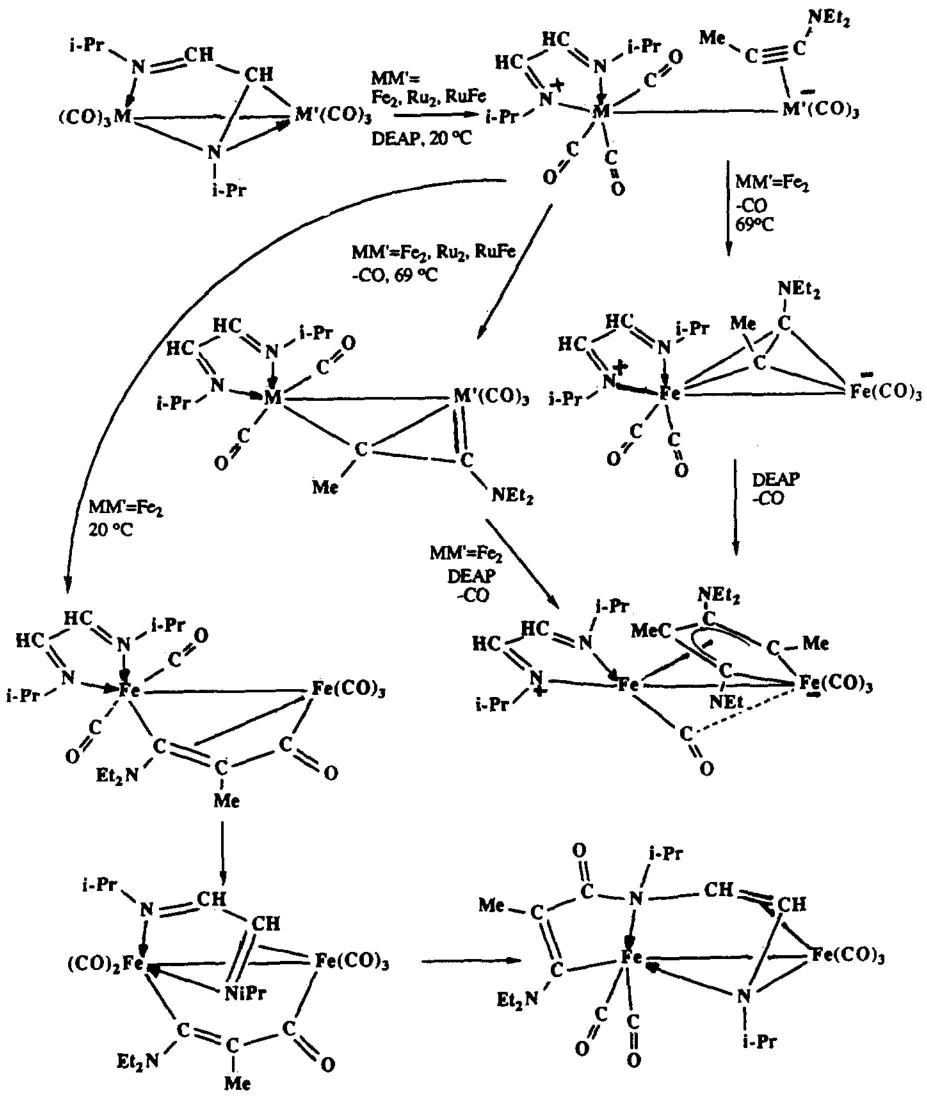
87

from coupling of alkyne ligands. Under more vigorous conditions, these were accompanied by three isomeric $\text{Fe}_2(\text{CO})_6[\text{C}_5\text{H}_5\text{NEt}_2]$ com-

Scheme I. The Reaction Products of $Fe_2(CO)_6(i\text{-}Pr\text{-}DAB)$ with HC≡CR' [R' = C(O)OMe]

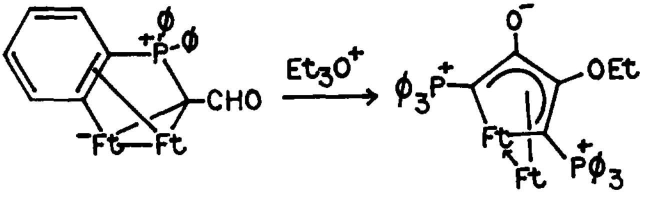


Scheme II. Reactions of $M_2(CO)_6$(*i*-Pr-DAB)[M_2 = Fe_2, FeRu, Ru_2] with $MeC{\equiv}CNEt_2$



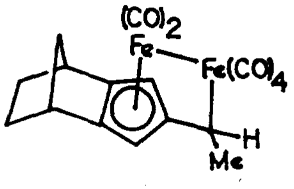
plexes and two tri-iron products. The three isomers differ by hydrogen shifts within the ligand, resulting in three alternate ways of providing six electrons to the $Fe_2(CO)_6$ unit. All were characterized by X-ray crystallography[495]. Two similar products, $(OC)_3Fe[\mu,\eta^2,\eta^3-(EtO)HC{=}CH\overset{\frown}{CHCRCR}]Fe(CO)_3$ and $(OC)_3Fe[\mu,\eta^2,\eta^3-CH_2{=}CH\overset{\frown}{C(OEt)CRCR}]Fe(CO)_3$ resulted when various alkynes $RC{\equiv}CR$ [R = Ph, Me, $SiMe_3$, CO_2Me, etc.] underwent insertion reactions into $(OC)_3Fe(\mu-COEt)(\mu-CH{=}CH_2)Fe(CO)_3$. The former product type, which required hydrogen migration from the vinyl to the ethoxycarbene, formed to a greater extent when bulky R groups were involved[496].

An exceptional degree of ligand coupling resulted in the reaction of $CFBr_3$ with $Fe(CO)_5$ to form inter alia the tetrafluoroferrole complex **86** [$R_1 = R_2 = F$][497]. The tetraethyl and tetraphenyl analogs and the "flyover" complex **87** [$R_1 = R_2 = Ph$] have been studied by solid state ^{13}C CP/MAS NMR spectroscopy[498]. Equation 23 illustrates the formation of a novel ferrole complex in an ethylation reaction accompanied by a long-range proton rearrangement. The starting material in Eq. 23 was obtained as a byproduct of the synthesis of the ketenylidenetriphenylphosphorane complex $(OC)_4\overset{-}{Fe}C(CO)\overset{+}{P}Ph_3$[499].



(23)

The thermal stabilities of four binuclear complexes [e.g. $(OC)_3Fe[\mu,\eta^2,\eta^3-C_6H_4CH_2N(CH_2Ph)]Fe(CO)_3$] and a related Fe_3 complex, all derived from Schiff bases, have been examined, along with their mass spectra[500]. Reaction of the fused spiro[4.2]heptadiene with diiron nonacarbonyl produced, in addition to **48**, the fulvene complex **88**[174]. An analogous structure, **89**, may be suggested as an alternative to the structure originally proposed[163] for the $Fe_2(CO)_7$ complex formed along with **28**. The revised structure receives strong support from the high-field resonance reported for the exocyclic carbon.



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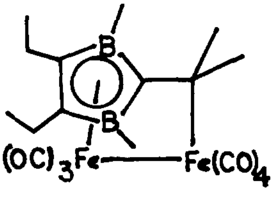


89

A crystal structure of $(\mu,\eta^3,\eta^3-tropone)_{\wedge}$ $Fe_2(CO)_6$ synthesized along with the $Fe(CO)_3$ complex by reaction of tropone with $Fe_2(CO)_9$ in ether, has been reported[501].

9b. Diiron Compounds. Derivatives of $Cp_2Fe_2(CO)_4$ [Fp_2]

A review of the photochemistry of Fp_2[235] and some additional photochemical studies published during 1989[236,237] were described in Section 7b of this review. A crystal structure of the radical anion, $Fp_2^{\dot{-}}$, has been reported[240,241]. Rotations of the cyclopentadienyl ligands in *cis*- and *trans*-Fp_2 in the solid state have been studied by NMR spectroscopy and by potential energy calculations. The results were compared with the anisotropic parameters observed in the X-ray crystallographic structures, which were found to convey information on the librations of the rings[502].

Reaction of the CO_2 adduct $FpCO_2^-$ with Fp'I afforded the symmetrical dimer Fp_2, with only traces of the unsymmetrical $CpFe(CO)(\mu\text{-}CO)_2Fe(PPh_3)Cp$ [FpFp'] formed. In contrast NaFp with Fp'I produced equal amounts of symmetrical and unsymmetrical dimers. $FpCO_2^-$ and $CpFe(CO)(NCMe)_2^+$ formed the mixed dimer $CpFe(CO)(\mu\text{-}CO)_2Fe(NCMe)Cp$, which disproportionated to Fp_2 at room temperature[303].

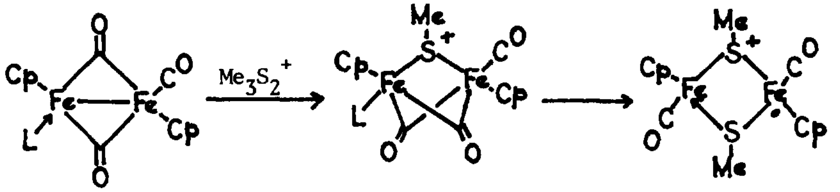
Thermolysis of Fp_2 in a sealed tube at 300° produced ferrocene, biferrocenyl, CO, CO_2, cyclopentadiene, and elemental carbon and iron, whereas thermolysis in refluxing xylene produced mainly the tetramer $(CpFeCO)_4$[503]. Films obtained by chemical vapor deposition using Fp_2 as reagent were essentially iron containing small amounts of carbon and oxygen[504]. Fp_2 was used to catalyze ligand exchanges in $CpRu(CO)_2I$ derivatives[505].

The ring-linked Fp_2 derivative $(OC)Fe[\mu,\eta^5,\eta^5\text{-}C_5H_4CH(NMe_2)\text{-}CH(NMe_2)C_5H_4](\mu\text{-}CO)_2Fe(CO)$, readily prepared from 6-dimethylaminopentafulvene, has been converted to a series of simpler ring-linked derivatives using straightforward synthetic manipulations[506]. The directly linked fulvalene complex $(\mu,\eta^5,\eta^5\text{-}1,3\text{-}R_2C_5H_2\text{-}1',3'\text{-}C_5R_2H_2)Fe_2(CO)_4$ [$R = CMe_3$] was prepared by reaction of the dihydropentafulvalene with $Fe(CO)_5$ in refluxing methylcyclohexane[507]. In contrast to the previous cases, IR showed no evidence of bridging carbonyl groups in the pentafulvalene complex.

The silane hydrogen of $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}SiHCMe_3)Fe(CO)Cp$ was replaced by halogens upon reaction with CCl_4, $CHBr_3$, or I_2; reaction of the chlorosilane with methyllithium gave the methylsilane. The bulkier groups led to formation of some *trans* isomers in equilibrium with the *cis*[508].

Refluxing Fp_2 with ethanethiol in ether produced $CpFe(CO)(\mu\text{-}SEt)_2Fe(CO)Cp$, whose crystal structure was determined[288]. CpFe-

(CO)(μ-DPPM)Fe(CO)Cp was oxidized by Me_2S-SMe^+ to a paramagnetic cation; *a more complex series of events* [Eq. 24; L = $(PhO)_3P$] ensued with a less electron-rich diiron compound[509]. Two isomeric forms of $Cp_2Fe_2S_4$ have been prepared and characterized by X-ray diffraction. One showed two disulfide ligands, one perpendicular and one parallel to the Fe-Fe bond. The other had two η^1,η^2-disulfide ligands. Reaction of the latter with hexafluoro-2-butyne resulted in insertion of the alkyne into S-S bonds to form hexafluorobutenedithiolate ligands[510].



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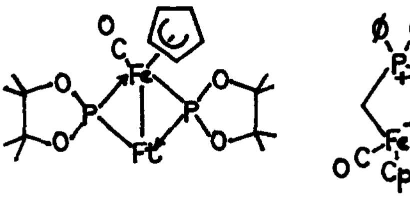
Both cis and trans isomers of the bis(μ-phosphido) complex CpFe(CO)(μ-$POCH_2CMe_2CH_2O$)Fe(CO)Cp have been prepared, the ligands being dimethylphosphorinane rings. Formation of the phosphorolane analogs was accompanied by a small amount of the novel product **90**[511].

Reaction of the phosphorus ylide Ph_3P=CH_2 with $[Cp'Fe(CO)_2]_2$ resulted in replacement of a bridging CO by CH_2. Cp'Fe(CO)-(PPh_3)COMe was also formed. The reaction of Fp_2 with phosphorus ylides proceeded differently, depending on the amount of butyllithium (used to form the ylide) present. Under different conditions, for example, products **91** and **92** formed from Ph_3P=CHPh[512].



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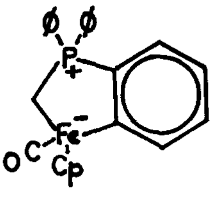

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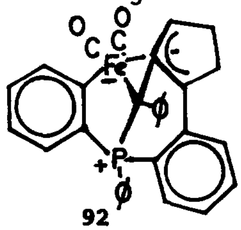

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DV-Xα calculations have been applied to Fp_2, its ring-methylated derivatives, and CpFe(CO)(μ-CO)(μ-CH_2)FeCp(CO), and the results compared with UV photoelectron spectroscopic data. Absence of a direct Fe-Fe bond in these compounds was asserted, based on the theoretical calculations. A localized INDO method was applied to calculations on CpFe(CO)(μ-CH_3)(μ-DPPM)$FeCp^+$; the results indicated coordination of a Fe(1)-methyl C-H bond to Fe(2), and no Fe-Fe bond[514].

Reduction of CpFe(CO)(μ-CO)(μ-CMe)Fe(CO)Cp^+ at a cathode or by cobaltocene led to unstable free radicals, which underwent *disproportionation to μ-vinylidene and μ-ethylidene products*[515].

The vinylidene complex CpFe(CO)(μ-CO)(μ-C=CH$_2$)Fe(CO)Cp underwent protonation in the gas phase (as in solution) at the β-carbon, forming the μ-ethylidyne cation. The proton affinity of the vinylidene complex was measured as 970(10) kJ/mol[516]. Collisionally activated μ-ethylidyne complex decomposed by loss of the three CO's, then acetylene and dihydrogen[516]. In solution, it underwent condensation with *p*-tolualdehyde to form CpFe(CO)(μ-CO)(μ-C-CH=CHAr)Fe(CO)Cp$^+$ in 92% yield. Several other aldehydes and ketones gave analogous condensation products. The initial isobutyraldehyde condensation product rearranged *in situ* to CpFe(CO)(μ-CO)(μ,η^1,η^2-CH=CH-CH=CMe$_2$)Fe(CO)Cp$^+$. Hydride abstraction by trityl cation from alkenylidene complexes CpFe(CO)(μ-CO)[μ-C=C(Me)CH$_2$R]Fe(CO)Cp favored removal from the CH$_2$ group for R = Me and from the methyl group for R = *p*-tolyl[517]. Several alkenylidyne complexes (fluoroborate salts) were tested for non-linear optical properties[518].

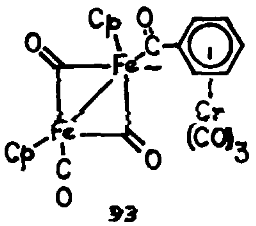
Cuprate reagents Li$^+$ RCuCN$^-$ attacked the bridging ketenyl group of CpFe(CO)(μ-CO)(μ-CHCO)Fe(CO)Cp$^+$, resulting in formation of μ-CH-C(=O)R groups [R = Me, Pr, Ph], which showed low carbonyl stretching frequencies indicative of electron donation from the CFe$_2$ core into the carbonyl antibonding orbital. This was supported by the crystal structure of the benzoyl compound, and by O-methylation with methyl triflate. Double addition to the μ-acylium species by Li$^+{}_2$ Me$_2$CuCN^{2-} directly formed the isopropenylidene species CpFe(CO)(μ-CO)(μ-C=CMe$_2$)Fe(CO)Cp[519].

Thiolate nucleophiles attacked the carbyne complex CpFe(CO)(μ-CO)(μ-CSMe)Fe(CO)Cp$^+$ at the carbyne carbon, giving neutral carbene complexes having a bridging C(SMe)(SR) group [R = CH$_2$Ph, Me, Ph]. PhSe$^-$, PhCH$_2$MgCl, and BH$_4{}^-$ reacted similarly, but 4-dimethylaminopyridine displaced a terminal CO. The carbene complexes CpFe(CO)(μ-CO)[μ-C(SMe)(ZPh)]Fe(CO)Cp [Z = S, Se] underwent rearrangement of the ZPh group with carbonyl loss to form CpFe(CO)(μ-CO)(μ-SMe)Fe(ZPh)Cp[520]. Attack of cyanide ion on the (μ-CSR) cations gave [μ-C(SR)(CN)] cyanocarbene derivatives, whereas thiocyanate led to formation of CpFe(CO)(μ-CO)(μ-CSR)Fe(SCN)Cp[521], probably by a rearrangement process like that demonstrated for the ZPh species above. Irradiation of the [μ-C(SR)(CN)] species led to intramolecular displacement of a CO by the sulfur[521]. Methylation of CpFe(CO)(μ-CO)[μ-C(CN)NMeC(=O)SMe]Fe(CO)Cp with methyl triflate occurred with loss of methyl isocyanate to form a [μ-C(CN)(SMe$_2$)$^+$] product, also obtainable from the [μ-C(CN)(SMe)] cyanocarbene complex. Dimethyl sulfide was readily displaced by nucleophiles, including Me$^-$, NMe$_2{}^-$, H$^-$, OR$^-$, and CN$^-$ [522].

Nucleophilic attack by alkenylidene complexes CpFe(CO)(μ-

CO)(μ-C=CHR)Fe(CO)Cp [R = H, Me, $CHMe_2$] on cyanoethyne led to formation of [μ-C=CR-CH=CHCN] products. The vinylidene complex reacted similarly with dicyanoethyne at -60°, giving the dicyanobutadienylidene product[523]. CpFe(μ-CO)(μ-C=CH_2)(μ-DPPM)FeCp reacted with TCNE to form both a [μ-C=CH-C(CN)=C$(CN)_2$] and a [μ-C=C=C$(CN)_2$] product, with loss of HCN and $CH_2(CN)_2$, respectively[524]. Photochemical insertion of alkynes into Fp_2 has been studied by laser flash photolysis. The results indicated initial loss of CO to form CpFe$(\mu\text{-}CO)_3$FeCp, which irreversibly reacted with alkyne to form CpFe(η^2-RC≡CR)$(\mu\text{-}CO)_2$Fe(CO)Cp, which collapsed to the dimetallacyclopentenone products, CpFe(CO)(μ-CO)-[μ,η^1,η^3-CR=CR-C(=O)]FeCp[525].

Reaction of Collman's reagent with (η^6-FpC_6H_5)$Cr(CO)_3$ led, via some curious and complex mechanism, to formation of 93[82]. This anion resembles some analogs produced by Cutler[307] by reaction of (for example) Fp^- with InFe$(CO)_2$Me, but appears to be the first having simple cyclopentadienyl rings.



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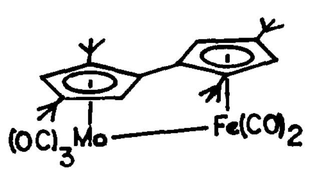
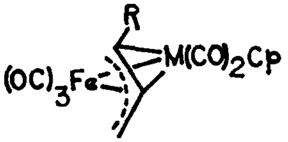
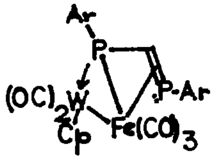
9c. Heterobimetallic Compounds

Reaction of Fp^- with $LnCl_3$ [Ln = Nd, Sm, Gd] in THF produced $FpLnCl_2(THF)_{1,2}$. IR data indicated carbonyls bridging between Fe and Ln[241].

The (μ-pentafulvalene) complex **94** has been prepared by the simple expedient of allowing the dihydrofulvalene to react with equimolar amounts of $Fe(CO)_5$ and $Mo(CO)_6$ and separating the homonuclear and heteronuclear products[507]. Reaction of the propargylic complexes CpM$(CO)_3CH_2C$≡CR [M = Mo, W; R = Me, Ph, p-tolyl] with $Fe_2(CO)_9$ produced CpM$(CO)_2$(μ,η^2,η^3-$RCCCH_2$)$Fe(CO)_3$, **95** (crystal structures for M = W,R = Ph and p-tolyl)[526]. Similar reaction of CpW$(CO)_2$=P(Ar)-CH=PAr [Ar = 2,4,6-tri(t-butyl)phenyl] with $Fe_2(CO)_9$ produced **96**[527]. A (η^4-1-molybda-3-phosphacyclobutadiene)$Fe(CO)_3$ complex resulted from head-to-tail cyclization of Cp*W$(CO)_2$(μ-CAr)$Fe(CO)_3$ (Ar = p-tolyl) with Me_3C≡P[528].







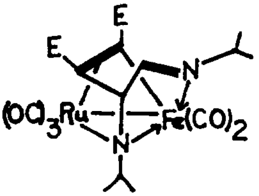
94 **95** **96**

When the anionic dicarborane tungsten complex (η^6-C_2Me_2-$B_{10}H_{10}$)W$(CO)_2$≡CAr^- reacted with $Fe_2(CO)_9$ in THF, the product was

$(\eta^6\text{-}C_2Me_2B_{10}H_{10})W(CO)_2(\mu\text{-}CAr)Fe(CO)_2^-$, whose apparent electron deficiency was relieved by coordination of a B-H bond of the dicarborane ligand with the iron, as revealed in the crystal structure[529].

Reactions of $FpCO^+$ with $Mn(CO)_5^-$ and Fp^- with $Mn(CO)_6^+$ have been investigated mechanistically. The latter reaction produced only Fp_2 and $Mn_2(CO)_{10}$, although labelling experiments showed transfer of CO from manganese to iron via $Fp\text{-}C(=O)\text{-}Mn(CO)_5$. The reaction of $FpCO^+$ with $Mn(CO)_5^-$ produced $FpMn(CO)_5$ in addition to the two dimers[242]. Rhenium-iron μ-formate species were obtained by reaction of CpRe(CO)(NO)OCHO with FpH and Ph_3C^+ or by reaction of FpOCHO with $[CpRe(CO)(NO)]_2OCHO^+$. Iron-tungsten μ-formate species were also produced similarly[530].

Heterobimetallic 1,4-diazabutadiene (DAB) complexes were synthesized by reaction of $(DAB)Fe(CO)_3$ with $Ru_3(CO)_{12}$ or $(DAB)\text{-}Ru(CO)_3$ with $Fe_2(CO)_9$. The structures were analogous to that of the central species in Scheme I, with the iron η^2-coordinated and the ruthenium N-coordinated[531]. $(OC)_3Ru[\mu,\eta^1,\eta^2\text{-}RN{=}CH\text{-}CH{=}NR]\text{-}Fe(CO)_3$ underwent hydrogenation at the ligand C-C bond at 90° to form μ-ethanediyldiamido species, $(OC)_3Fe(\mu\text{-}RNCH_2CH_2NR)Ru(CO)_3$ (cf. **67**)[532]. Reactions of these complexes and their Fe_2 and Ru_2 analogs with hydrogen and with alkynes have been reviewed[490]. Reaction of $(DAB)FeRu(CO)_6$ with allene occurred so as to form a metalla-TMM product, $[\eta^4\text{-}L_4Ru\text{-}C(CH_2)_2]Fe(CO)_3$, L_4Ru indicating a $(DAB)Ru(CO)_2$ group[531]. Chelation of ruthenium by DAB is characteristic of the products of many adducts of $(DAB)FeRu(CO)_6$ with unsaturated organics. Scheme II provides an additional example, addition of $MeC{\equiv}CNEt_2$ yielding the carbenoid product shown, with ruthenium (M) chelated by the DAB ligand[489]. Addition of dimethyl acetylenedicarboxylate to the iron-ruthenium compound produced $(OC)_3Fe(\mu_2,\eta^2\text{-}ECCE)Ru(CO)_2(DAB)$ and **97**. Methyl propynoate yielded **98** (two isomers), which reversibly lost CO to form Fe-Ru bonded tetracarbonyl species[533].



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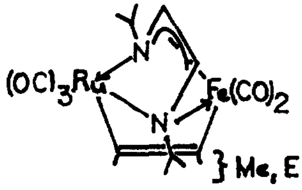

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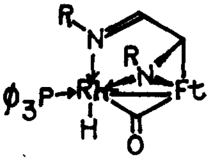

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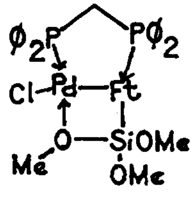
The dihydride complex $(DAB)RhH_2(PPh_3)_2^+$ reacted with $HFe(CO)_4^-$ to form the ionic species **12** and also neutral complexes such as **99**[84].

FpH reacted with $Co_2(CO)_8$ to form $HCo(CO)_4$ and $FpCo(CO)_4$, the latter product in 70% yield[233]. Ligand exchange with triphenylphosphine produced $FpCo(CO)_3PPh_3$ (crystal structure)[534]. Impregnation of $FpCo(CO)_4$ into alumina produced a highly selective catalyst for alkene synthesis from CO and H_2. Mössbauer and magnetic studies indicated retention of the Fe-Co bond in the surface layers[535].

The unsaturated, triply hydride-bridged species $[MeC(CH_2PPh_2)_3\}Rh(\mu\text{-}H)_3Fe\{MeC\{CH_2PEt_2)_3\}^{2+}$ has been reported[536]. Nucleophilic attack of $(OC)_4FePR_2^-$ [R = cyclohexyl] on $ClRh(CO)(PPh_3)_2$ produced $(OC)_3(Ph_3P)Fe(\mu\text{-}PR_2)Rh(PPh_3)(CO)$, whose crystal structure was determined. With $ClRh(COD)_2$, $(OC)_4Fe(\mu\text{-}PR_2)Rh(COD)$ resulted. Additions of CO and phosphines to both compounds were studied[537]. Similar reaction of $(OC)_4FePR_2^-$ with $ClIr(CO)(PPh_3)_2$ produced the more saturated $(OC)_3(Ph_3P)Fe(\mu\text{-}PR_2)Ir(PPh_3)(CO)_2$, which protonated on iridium with loss of a CO ligand. Reaction with $ClIr(COD)_2$ was the same as in the rhodium case. Ligand substitution reactions of the iron-iridium species were also extensively explored[538]. The structure of $(OC)_2Rh(\mu\text{-}Cl)[\mu\text{-}Ph_2PC(=CH_2)PPh_2]Fe(CO)_3$ has been solved by a new Laue photographic method[539].

A product with a novel siloxane bridge, **100**, resulted when trans-$PdCl_2L_2$ [L = PhCN, PPh_3, or L_2 = DPPM] was allowed to react with mer-$Fe(CO)_3H[Si(OMe)_3](\eta^1\text{-}DPPM)$ or its conjugate base. A platinum analog was also synthesized similarly, along with a platinum-hydride compound from $(Ph_3P)_2Pt(C_2H_4)$[540].



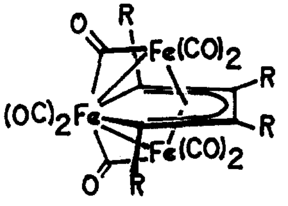
100

10. TRINUCLEAR CLUSTER COMPOUNDS

10a. Tri-iron Compounds

Tri-iron compounds with 46 cluster electrons may be viewed as electron-deficient, since a closed triangular Fe_3 cluster should have 48. Perhaps as a consequence of their unsaturation, $(alkyne)Fe_3(CO)_9$ clusters and their mono- and diphosphine substitution products were found in a study of HPLC separation of cluster compounds to be comparatively strongly bound to silica[541].

Several examples of the well-known 46-electron $(C_4R_4)Fe_3(CO)_8$ clusters **101** (e.g., R = Ph, Et, etc.) have been studied by ^{13}C and ^1H NMR spectroscopy and by cyclic voltammetry. The tri-irom compounds were more easily reduced than the triruthenium analogs, and gave stable mono- and dianions, the latter in consonance with the EAN rule[543]. A new compound of type **101**, with the R's alternating allyl and diethylamino groups, was among the products of reaction of diethyl(pent-4-en-1-ynyl)amine with $Fe_3(CO)_{12}$. Also formed was the closely related 48-electron cluster, in which double bond migration within an allyl group has made two additional electrons available to coordinate to the Fe_3 cluster[495].



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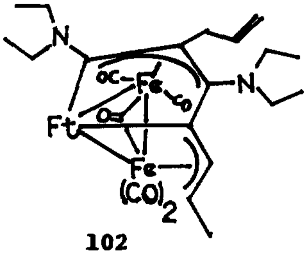

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Phosphorus analogs of **101** (P replacing a CR group in **101**) have been prepared by photoreaction of $Me_3C{-}C{\equiv}P$ with $Fe_3(CO)_9(\mu{-}CP)_2$. The unshared electron pair on phosphorus remained active, coordinating readily to metal groups such as $Cr(CO)_5$[544].

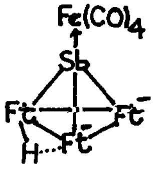
The use of $Fe_3(CO)_{12}$ under three-phase conditions to reduce nitrobenzene to aniline has been researched; an advantage of this method was ease of product isolation[545]. Reduction of ketones by alcohols catalyzed by $HFe_3(CO)_{11}^-$ under phase transfer conditions has been studied, and a mechanism proposed[546]. Studies of $Fe_3(CO)_{12}$ impregnated in alumina used Mössbauer and IR spectroscopy to characterize the species present[547]. Photolysis was used to "graft" $Fe_3(CO)_{12}$ weakly physisorbed on silica to the substrate, in the form of $HFe_3(CO)_{11}^-$ ions[548].

Structures and dynamic behavior in solution of $Fe_3(CO)_{12-n}L_n$ [n = 2,3; L = various trialkyl phosphites or triphenyl phosphite] have been studied by two groups[462,549]. The very facile fluxional processes in these compounds make definition of solution structures difficult, but the results of the two groups showed general agreement. A crystal structure of $Fe_3(CO)_{10}[P(OMe)_3]_2$ showed trans-diequatorial substitution, with bridging carbonyl groups between the unsubstituted iron and one of the substituted ones[549].

Reaction of tin and germanium hydrides with $Fe_2(CO)_9$ produced mixtures of clusters. In addition to **64**, $Ge_2Fe_7(CO)_{26}$ has been isolated and characterized by crystal structure: it proved to be a $Fe_3(CO)_{12}$ derivative having three $Fe(CO)_3$ groups joined in a closed triangle, with the three Fe-Fe bonds bridged by one CO and two $[GeFe_2(CO)_8]$ groups[440]. Also newly obtained, from SnH_4, was another $Fe_3(CO)_{12}$ derivative, $SnFe_5(CO)_{19}$, having one Fe-Fe bond bridged by a carbonyl group and a $[SnFe_2(CO)_8]$ group[550].

Protonation of $Sb[Fe(CO)_4]_4^{3-}$ with one equivalent of trifluoromethanesulfonic acid resulted in carbonyl loss and formation of **103**, a tetrahedral dianion with appreciably shorter Fe-Sb bond lengths than its trianion precursor. Further protonation occurred at an Fe-Fe edge^{104}. The cluster products $(Cp'Fe)_3(\mu$-$CO)_3(\mu_3$-$N\rightarrow O)$ and its Cp^* analog have been identified as byproducts in synthesis of $(CpFeNO)_2$ by reaction of Fp_2 and NO at 100° ^{551}. The analogous bismuth cluster, $(CpFe)_3(\mu$-$CO)_3(\mu_3$-$Bi)$ resulted from photodecarbonylation of Fp_3Bi^{552}.

Reaction of sulfur, cyclohexadiene, and $Fe_3(CO)_{12}$ produced the cluster product **104**, as shown by a crystal structure determination^{553}. In the anion $[PhP$-$C(Me)=CHPh]Fe_3(CO)_9{}^-$, prepared by reaction of Ph_2P-$C\equiv C$-Me with $HFe_3(CO)_{11}{}^-$ at 58°, the phenylphosphido group bridges one Fe-Fe bond while the alkene is π-bonded to the third iron of a closed triangle^{554}. Ph_2P-$C\equiv CPh$ gave an analogous product^{554}, but Ph_2P-$C\equiv CCMe_3$ reacted with still more extensive bond cleavage and hydrogen migration to form **105**, along with **85** in lesser amount^{494}.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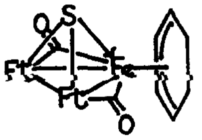
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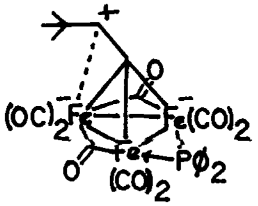
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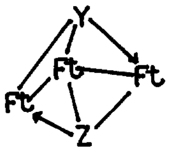
$(PPN^+)_2\ Fe_3(CO)_{11}{}^{2-}$ produced tetrahedral anions $[Fe(CO)_3)_3(\mu$-$CO)(\mu_3$-$COC(=O)R)]^-$ (R = CH=CHMe or CH=CHPh) upon reaction with acyl chlorides, and μ_3-acyl anions $[Fe(CO)_3]_3[\mu_3$-$C(=O)R)]^-$, in which the acyl group acts as a five-electron donor, upon reaction with alkyl halides^{555}.

The azo group which served as a two-electron donor in **16** expanded its coordination to become a six-electron donor in $(\mu_3,\eta^2$-$C_7H_{10}N_2)Fe_2(CO)_6{}^{102}$. No di-iron products (analogous to **67**) formed in the reaction of the fused diazete with $Fe_2(CO)_9$, in contrast to results with other cyclic and acyclic azo compounds. Such a product did form from R-N=N-R [R = Et, Pr], along with $(\mu_3,\eta^2$-$N_2R_2)Fe_3(CO)_9$. This 48-electron species cleaved upon heating to form the open 50-electron species **106** [Y = Z = NR]. The mechanism of formation of **106** was found to involve initial CO loss, rearrangement, and CO reattachment^{446}. Azobenzene gave only the opened product **106** upon reaction with iron carbonyl reagents^{446}.

Photochemical reaction of $[Fe(CO)_3]_3(\mu$-$H)(\mu_3$-$SCMe_3)$ with diphenylacetylene produced **107**^{460}. The trigonal bipyramidal cluster $[Fe(CO)_3]_3(\mu_3$-$CF)_2$ exchanged fluoride for other halogens upon treatment with Al_2X_6 [X = Cl, Br]. Reaction with Al_2Br_6 under a CO atmosphere and then with methanol produced

$[Fe(CO)_3]_3(\mu_3\text{-}C\text{-}CO_2Me)_2$. In benzene solution, treatment with



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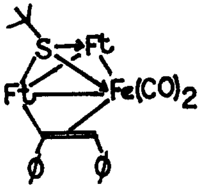

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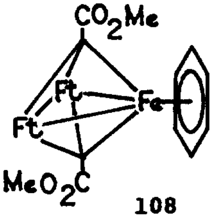

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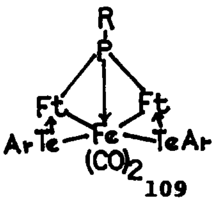
Al_2Br_6 followed by methanol produced **108**[556]. Many additional reactions of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ have been reviewed[497].

Introduction of a chalcogen atom into $[Fe(CO)_3]_3(\mu\text{-}CO)(\mu_3\text{-}PR)$, to form **106** [Y = PR, Z = S, Se, Te] was achieved through treatment with ZCN^- or ArZZAr [Z = Se, Te]. In the latter case, **109** [Ar = mesityl] also formed[450]. Co-photolysis of $Fe_3(CO)_9(\mu_3\text{-}S)_2$ [**106**, Y = Z = S] with $W(CO)_6$ yielded a product in which the Fe_3S_2 cluster remained intact, with one sulfur further coordinated to a $W(CO)_5$ group [i.e.,**106**, Y = S, Z = $S\rightarrow W(CO)_5$)]. With $W(CO)_5(PMe_2Ph)$, the analogous product was accompanied by WFe_2 and WFe_3 cluster products[557]. Reaction of the three dichalcogen complexes, $Z_2Fe_3(CO)_9$, with the three Group 10 $M(PPh_3)_4$ complexes proceeded by more than one mechanism to produce $(OC)_3Fe(\mu\text{-}Z\text{-}M(PPh_3)_2\text{-}Z)Fe(CO)_3$ (especially with Z = Te) and triphenylphosphine-substituted derivatives of $Z_2Fe_3(CO)_9$[478,479]. $Te_2Fe_3(CO)_9$ was also used as a starting material for synthesis of ruthenium-tellurium and cobalt-tellurium clusters[558].

Photocycloaddition of 2-butyne to **106** [Y = Z = $PCHMe_2$, $PCMe_3$] produced **110**. Phenyl- and diphenylacetylene reacted similarly[482]. Phenylacetylene reacted thermally with $(\mu_3,\eta^2\text{-}N_2Et_2)\text{-}Fe_3(CO)_9$ to form **111** and an isomer with the terminal iron bound into a ferrole ring. The two isomers equilibrated upon heating, with **111** the predominant form[559].



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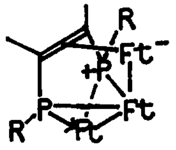

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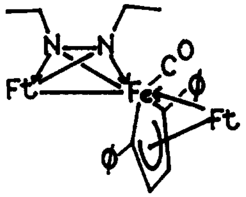

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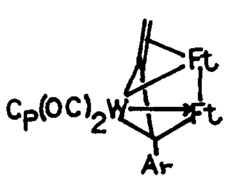
10b. Fe_2M Clusters

The great majority of trimetallic clusters reported are 48-electron *closo* clusters. Two 46-electron exceptions among this year's Fe_2M clusters are $(DPPE)PtFe_2(CO)_8$[560] and $M[Fe(CO)_4H]_2$ [M = Zn, Cd, Hg][83]. In each case, the electron deficiency arises from the presence of a late transition element. The platinum compound showed a closed triangular structure, with the platinum exhibiting a 16-electron configuration[560]. The Group 12 compounds were linear, as shown in the crystal structure of the PPN$^+$ salt of $Hg[Fe(CO)_4]_2^{2-}$ [83].



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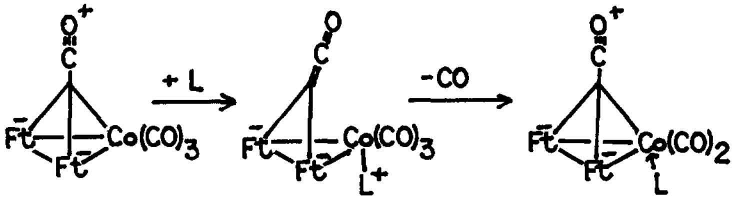
The 48-electron tetrahedral clusters $[Fe(CO)_3]_2[W(CO)_4L](\mu_3\text{-}S)$ [L = CO, PMe_2Ph] were prepared by reaction of $Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ with $LW(CO)_5$ under UV irradiation. The W-Fe bonds in the phosphine-substituted cluster were about 0.04 Å shorter than those in $Fe_2W(CO)_{11}S$[561]. Trinuclear allenyl clusters **112** [M = Mo, W; R = Me, Ph, p-tolyl] were formed along with previously described dinuclear allenyl clusters **95** in the reactions of $CpM(CO)_2CH_2C{\equiv}CR$ with iron carbonyls[526]. The alkylidyne molybdenum complex $(\eta^5\text{-}Me_2C_2B_9H_9)(OC)[P(OMe)_3]_2Mo{\equiv}CAr^-$ [Ar = p-tolyl] reacted with $Fe_2(CO)_9$ to form a μ_3-alkylidyne complex, $MoFe_2(CO)_8(\mu_3\text{-}CAr)(\mu,\eta^5,\eta^1,\eta^1\text{-}Me_2C_2B_9H_7)^-$, in which two B-Fe bonds joined the carborane cap to the $Fe(CO)_3$ groups, allowing the carborane to function as a 6-electron ligand[562]. The analogous tungsten compound formed similarly, although the more hindered aryl group, 2,6-dimethylphenyl, allowed only the formation of a bimetallic product, previously cited[529].

Nitrosobenzene reacted with $Fe_2Ru(CO)_{11}(NCMe)$ in a halide ion-promoted reaction at 0° in THF to form $Fe_2Ru(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}CO)$. The $FeRu_2$ analog was prepared similarly[563].

Substitution of phosphine for CO on PPN$^+$ $Fe_2Co(CO)_9(CCO)^-$ has been found to occur by an associative mechanism, to form cobalt-substituted products, **113**. Activation parameters have been measured, and the reaction has been found to occur more rapidly in more polar solvents[564]. Equation 25 shows a plausible mechanism. The products **113** underwent an exchange reaction between the carbon-carbonyl and cobalt-phosphine ligands, forming $Fe_2Co(CO)_9(\mu_3\text{-}CL)^-$. The rate was decreased by bulky groups [phenyl, cyclohexyl] on the phosphine ligand L, and a bridged transition state leading to pairwise exchange was proposed[565]. The crystal structure of $Fe_2Co(CO)_9(\mu_3\text{-}CPMe_3)^-$ showed a cluster carbon-phosphorus bond length of 1.715 Å, compared to P-methyl bond



(25)

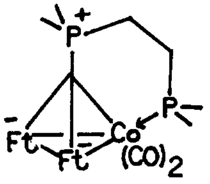
lengths averaging 1.792[566].

Reaction of the ketenylidene cluster $Fe_2Co(CO)_9(\mu_3CCO)^-$ with DMPM resulted in substitution at cobalt and at iron, retaining the μ_3-ketenylidene structure[566]. However, the longer reach afforded in DMPE resulted in reaction to form the ylide-type product **114**. Protonation of **114** occurred on the Fe-Fe bond, with migration of the phospine from cobalt to iron[567].

Low temperature NMR studies showed no sign of hindered rotation of the aryl ring in $Fe_2Co(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CAr)$ [Ar = p-tolyl, 3,4-xylyl], contradicting a previous report[568]. Syntheses of $Cp_3RhFe_2(CO)_4$ by reaction of $CpRh(C_2H_4)_2$ with Fp_2 or of $CpRhBr_2$ with Fp^- have been explored[569].

Reaction of $Cp_2Ni_2(Ph_2P\text{-}C{\equiv}CR)$ [R = $CHMe_2$, Ph] with iron carbo nyls gave inter alia $CpNiFe_2(CO)_6(\mu_3,\eta^2\text{-}CCR)$ and an incompletely characterized $Cp_2NiFe_2(CO)_3(\mu\text{-}PPh_2)(C_2R)$[570]. Use of HPLC for separating these and several other products was investigated[541].

Photocondensation of $Fe_3(CO)_9(\mu_3\text{-}S)_2$ [**106**, Y = Z = S] and $W(CO)_5(PMe_2Ph)$ led to replacement of the middle $Fe(CO)_3$ group in the 50-electron starting material by a isolobal $W(CO)_3(PMe_2Ph)$ group, with retention of the open triangular 50-electron cluster structure. The same product also formed using $Fe_2(CO)_6(\mu\text{-}S_2)$ under similar conditions. Products with one sulfur additionally coordinated to a $W(CO)_4L$ group [L = CO, PMe_2Ph] were also obtained in some of these reactions[557]. Another 50-electron cluster, **115**, resulted from reaction of $CpCo(CO)_2$ with $Fe_2(CO)_6(\mu\text{-}S_2)$[476].



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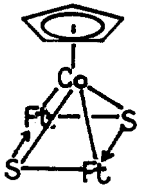

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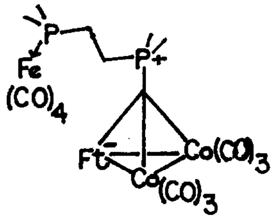

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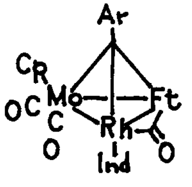
10c. FeM$_2$ Clusters

Vahrenkamp has reviewed the extensive work of his group on the preparation and properties of tetrahedral ZM_3 clusters, especially those which possess framework chirality due to the presence of three different metals[571].

The compounds $Fp\text{-}Hg\text{-}M(CO)_3(bpy)X$ [M = Mo, W; X = halogens, SCN, and N_3] were prepared by insertion of $M(CO)_3(bpy)$, from the acetonitrile adduct, into the Hg-X bond of FpHgX. These 46-electron "clusters" presumably have a linear trimetallic backbone[572].

Reaction of **114** with $Co_2(CO)_8$ resulted in replacement of a $Fe(CO)_3^-$ vertex by a $Co(CO)_3$, with the extruded iron remaining attached through the μ-DPPE group in the product, **116**[567]. μ_3-Ethylidyne clusters $HFeCo_2(CO)_9(\mu_3\text{-}CCH_3)$ and its CoFeMo analog lost H_2 upon heating to form μ_3-vinylidene clusters; the reaction was reversible only with the CoFeMo system, however. Binding of the vinylidene unit to trinuclear clusters was considered to be particularly favorable[573]. Reaction of phosphines with $H[Fe(CO)_3][Co(CO)_3][CpMo(CO)_2](\mu_3\text{-}CMe)$ showed that the cluster was unexpectedly inert to substitution reactions[574].

Reactions of the unsaturated complex $CpMoFe(CO)_6(\mu\text{-}CAr)$ [Ar = p-tolyl] with the reagents $(C_2H_4)_2Pt(PR_3)$, $(Ind)Rh(CO)_2$, and $Cp^*Cu(THF)$ led to formation of trimetallic alkylidyne clusters. The 48-electron rhodium cluster **117** had a closed tetrahedral structure, but the 46-electron platinum product, $[CpMo(CO)_2]$-$[Fe(CO)_3][Pt(CO))PR_3)](\mu\text{-}C\text{-}Ar)$, **118** ?, probably had the μ-C-Ar group bridging the Fe-Mo bond and not attached to the platinum, based on the carbyne carbon resonance at 340 ppm. The structure of the copper product was also not fully deducible from the NMR data[575]. Reaction of $Cp(OC)_2M{\equiv}C\text{-}C{\equiv}C\text{-}CMe_3$ [M = Mo, W] with $Fe_2(CO)_9$ proceeded with ligand coupling to form **119**. In the case of tungsten, a byproduct had an $Fe_2(CO)_6$ group attached to the C≡C bond of the starting material. An analog of structure **117** [$Me_3C\text{-}C{\equiv}C\text{-}C$ instead of Ar-C] was prepared by reaction of $[Cp(OC)_2Mo][(Ind)Rh(CO)](\mu\text{-}C\text{-}C{\equiv}C\text{-}CMe_3)$ with $Fe_2(CO)_9$[576].



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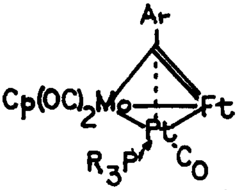

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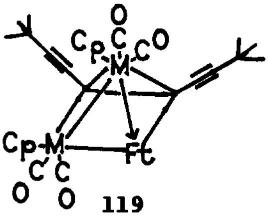

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11. TETRA- AND POLYNUCLEAR CLUSTER COMPOUNDS

A review of tetranuclear clusters containing iron, ruthenium, cobalt, and/or rhodium compared in particular their metal-metal bond distances, NMR properties, and reactivity toward phosphine substitution[577].

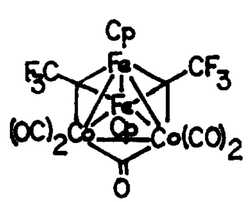
A 58-electron planar Fe_4 "cluster" has been prepared. The structure showed a closed parallelogram of iron nuclei, with the irons alternately being coordinated to four carbonyl groups or to two pyridine molecules. Some degree of bonding between the $Fe(pyr)_2$ groups was suggested by a distance of 2.76 Å across the diagonal between them[578]. An electron-deficient (58-electron) cubane cluster, $(Cp'V)_2[Fe(NO)]_2(\mu_3\text{-}S)_4$, has been prepared. Its structure was compared to those of V_2Co_2 and V_2Ni_2 analogs, with the conclusion that increasing electron density principally increased the M-M bond lengths [Fe-Fe 2.59 Å, Co-Co 2.73 Å, Ni-Ni 3.02 Å (non-bonded][579].

Thermolysis of Fp_2 in boiling xylene produced the well-known 60-electron tetrahedral cluster $[CpFe(CO)]_4$. Thermolysis of the cluster compound at 300° in a sealed tube produced ferrocene, iron, and CO; differences in the products from Fp_2 and $[CpFe(CO)]_4$ have been discussed[503]. The tetranuclear cluster has been oxidized to its radical-cation by air in the presence of acids[580].

Reaction of Fp_2 and $Co_2(CO)_6(\mu,\eta^2\text{-}RCCR)$ [R = CF_3] at 100° produced three 60-electron clusters: 71% $(CpFe)_2[Co(CO)_2]_2(\mu_3\text{-}CO)_2(\mu\text{-}RCCR)$, 7% $(CpFe)_3[Co(CO)_2](\mu_3\text{-}CO)_2(\mu\text{-}RCCR)$, and 14% $(CpFe)_2[Co(CO)_2]_2(\mu\text{-}CO)(\mu_3\text{-}CR)_2$. The structures of the first two were not determined, but the latter proved to have structure **120**, showing fission of the alkyne into two alkylidyne fragments[581].

The effectiveness of $MCo_3(CO)_{12}^-$ [M = Ru, Fe] salts in catalyzing hydroformylation reactions has been assessed, and the iron cluster found to be less effective than the ruthenium cluster, but more effective than $Co_4(CO)_{12}$[582]. Cationic $Cp_4Rh_3Fe_3\mu\text{-}CO)_3^+$ clusters have been synthesized by reaction of $CpFe(PhNO_2)^+$ with $[CpRh(\mu\text{-}CO)]_3$[583].

Addition of two electrons to the closed tetrahedral clusters generally produces a cluster with a "butterfly" skeleton. A number of chalcogen-bridged examples of these have been reported. For example, irradiation of **106** [Y = S, Z = S→$W(CO)_4(PMe_2Ph)$ in the ultraviolet produced **121**[557]. An X-ray crystal structure of the closely related $(CpMo)_2[Fe(CO)_3]_2(\mu\text{-}CO)_2(\mu_3\text{-}S)_2$ has been reported[584]. The tritelluride **122** was prepared by reaction of **106** [Y = Z= Te] with $Cp_2Mo_2(CO)_6$ and also characterized by a crystal structure[585].



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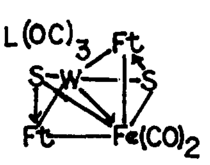

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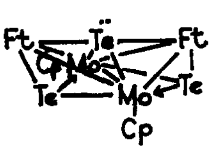

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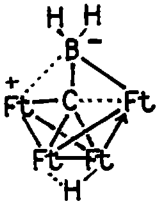
The role of the μ_4-bridging atom in butterfly clusters has been explored by Fenske-Hall calculations on $Fe_4(CO)_{12}Z$ [Z = C^{2-}, N^-, O] The Z to wingtip bonds were found to weaken upon progression from C to N to O. There was little energetic difference in the two isomers of $FeRu_3(CO)_{12}(\mu_4\text{-}N)^-$ [586]. $Fe_4(CO)_{12}[\mu_4\text{-}C\text{-}C(=O)\text{-}R]^-$ [R = Me, CH_2Ph] was found by cyclic voltammetry and bulk electrolysis to undergo ready reduction to a stable dianion-radical. EPR spectra indicated the spin density to reside on the iron carbonyl cluster and to be isolated from the CC(=O)R ligand. This was consistent with the results of Fenske-Hall MO calculations and the results of crystal structure determination of the dianion-radical[587].

The preparation and structure of a borane-substituted carbido cluster, **123**, have been described. The borane group was unreactive toward Lewis bases, indicating effective electron donation by the cluster to the vacant boron p-orbital[588]. Gold-phosphine derivatives of $H[Fe(CO)_3]_4B^{2-}$ have been described. Depending on the phosphine, two different structural types were characterized: one with the hydride bridging from boron to a wingtip and the gold-phosphine groups associated with the other wingtip and an Fe_2B face, and one with the hydride bridging the hinge irons and the two golds bridging from boron to the wingtips. The two isomers interconverted in solution[589].

A butterfly cluster **124** resulted from photoreaction of $Fe_3(CO)_9(\mu_3\text{-}NCPh)$ with $Fe_2(CO)_9$. In **124**, the benzonitrile ligand acts as a six-electron donor, giving an overall 62-electron butterfly. A similar reaction using $Fe_3(CO)_9(MeCCMe)$ produced $[Fe(CO)_3]_4(MeCCMe)$[590]. The butterfly-derived alkyne complexes $[Fe(CO)_3]_4(\mu_4,\eta^2\text{-}RCCR)$ appear to be electron-deficient, having only 60 cluster electrons if the alkyne is taken as a four electron donor. Involvement of the C-C sigma electrons, as suggested in structure **125**, would tend to remedy the deficiency.



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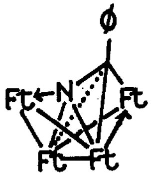

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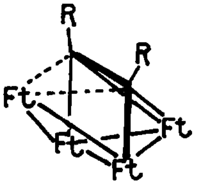

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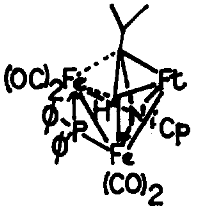
A heteronuclear analog of **125**, $(Cp^*Co)[Fe(CO)_3]_3(\mu_4,\eta^2\text{-}FCCF)$, was characterized by a crystal structure from among the products of reaction of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ and $Cp^*Co(CO)_2$; the Cp^*Co group was at a wingtip position[497]. A more complex mixed-metal analog was $CpNiFe_3(CO)_7(\mu\text{-}PPh_2)(\mu_4,\eta^2\text{-}HC{\equiv}CCHMe_2)$, **126**, one of several products of reaction of $(CpNi)_2(Ph_2PC{\equiv}CCHMe_2)$ with iron carbonyls, which showed the nickel at a hinge position[570]. This reaction also produced the 64-electron species **127**, and separation of such products by HPLC was the focus of a careful study[541]. Cleavage of the C-P bond in $Fe_2Co(CO)_9(\mu_3\text{-}C\text{-}PMe_3)$



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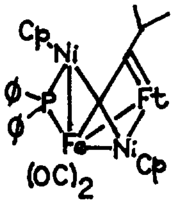

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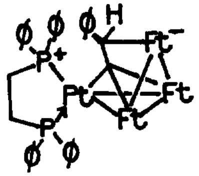

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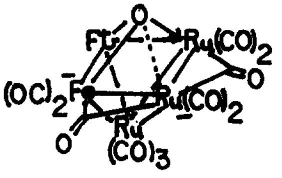
during cluster expansion by reaction with $Co_2(CO)_8$ formed the heteronuclear butterfly carbide product $Fe_2Co_2(\mu_4\text{-}C)(CO)_{11}$-$(PMe_3)$[566]. A novel platinum-containing butterfly cluster, **128**, was formed in high yield from $CpMn(CO)_2(\mu\text{-}CH{=}CHPh)Pt(DPPE)$ and $Fe_2(CO)_9$ in benzene[560].

64-Electron clusters include the octahedral $Fe_2Co_2(CO)_{11}(\mu_4\text{-}PPh)_2$, which has been studied as a hydroformylation catalyst. Entry into the catalytic cycle was proposed to involve initial opening to a nido structure to provide a coordination site[591]. Photolysis of **65** gave the closely related octahedral species $Fe_4(CO)_{12}[\mu_4\text{-}Sb\text{-}Fe(CO)_4^-]_2$, also preparable directly from $Fe_4(CO)_{13}^{2-}$ and $SbCl_3$[441]. The electrochemistry of $(CpFe)_4S_{4-6}$ in benzonitrile has been studied by a battery of techniques[592].

Pentanuclear iron-iridium clusters have been prepared and characterized by means of crystal structures. The 72-electron trigonal bipyramidal anion $Fe_2Ir_3(CO)_{10}(\mu\text{-}CO)_4^-$ was prepared from $Fe(CO)_4^{2-}$ and $Ir(CO)_2Cl_2^-$ and consisted of a triangle of $Ir(CO)_2$ groups capped on each face by a $Fe(CO)_2$ group, with four carbonyls bridging Ir-Fe bonds and mean Ir-Fe bond length of 2.65 Å. The 76-electron dianion, $FeIr_4(CO)_9(\mu\text{-}CO)_6^{2-}$, was a more elongated trigonal bipyramid, with a $Ir_3(CO)_3(\mu\text{-}CO)_3$ triangle surmounted by a $Fe(CO)_3$ group (average Ir-Fe distance 2.94 Å) and a $Ir(CO)_3$ group. The distorted structure was a manifestation of the electron excess[593].

A pentametallic oxo cluster, $Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)^{2-}$, a model for surface-bound oxygen, was prepared from $Fe_3(CO)_9(\mu_3\text{-}O)^{2-}$ and $Ru_3(CO)_{10}(NCMe)_2$. The benzyltrimethylammonium salt showed the anion structure **129**. The unsaturated (62 electron) cluster $Fe_4(CO)_{11}(\mu_4\text{-}PPh)_2$ was expanded by reaction with $CpRh(CO)_2$ to form a 76-electron product, $CpRhFe_4(CO)_{12}(PPh)_2$, in which a $(CpRh)[Fe(CO)_3]_3$ quadrangle was capped by a μ_4-PPh group on one side and a μ_4,η^2-$[(OC)_3Fe{\leftarrow}PPh]$ group on the other[595].



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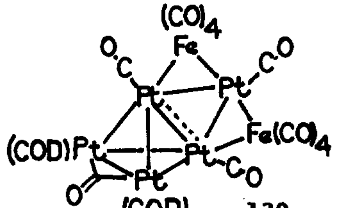
78-Electron clusters analogous to **80**, but having Co and Ir in the middle have been described. The crystal structure of the cobalt compound showed no Fe-Fe bond in the Fe_2S_2 grouping [Fe---Fe distance 3.40 Å], and the existence of two Co-Fe bonds [ca. 2.54 Å]^{477}.

$(Ph_3PAu)_5Fe(CO)_3{}^+$, formally a hexanuclear cluster, resulted from photolysis of a mixture of Ph_3PAuN_3 and any iron carbonyl in THF. Structurally, the cation contained a Au_3Fe tetrahedron, with two additional Ph_3PAu groups capping two Au_2Fe faces^{596}. Reaction of $Fe(CO)_5$ with $Pt(COD)_2$ formed, *inter alia*, a planar cluster $Pt_3Fe_3(CO)_{15}$, which consisted of a triangle of Pt(CO) groups, with $Fe(CO)_4$ groups bridging each edge^{597}. A more complex platinum-iron cluster, $FePt_5(CO)_9(PEt_3)_4$, was synthesized by reaction of $Na_2Fe(CO)_4$ with *cis*-$PtCl_2(PEt_3)_2$. The reaction also produced $Pt_5(CO)_6(PEt_3)_4$, which was converted to the $FePt_5$ cluster by reaction with iron pentacarbonyl. The structure of the $FePt_5$ cluster showed a Pt_4 tetrahedron with one edge-bridging Pt, and an $Fe(CO)_4$ group bridging from that Pt to a vertex of the tetrahedron^{598}. The principal product in the aforementioned $Pt(COD)_2$ reaction was a derivative of the latter, **130**, with two bridging $Fe(CO)_4$ groups^{597}.



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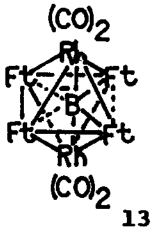

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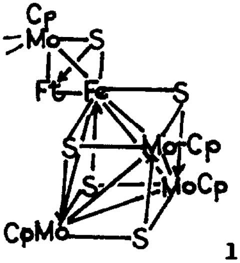
Reaction of $Fe_4(CO)_{12}BH_2{}^-$ with $[Rh(CO)_2Cl]_2$ produced the 86-electron octahedral cluster $Fe_4Rh_2(CO)_{16}B^-$, **131**. This product, with *trans*-rhodium atoms, was formed upon rearrangement of a spectroscopically characterized *cis* isomer. The rearrangement was catalyzed by CO or phosphines, presumably by formation of an intermediate of higher electron count^{600}. A cluster isoelectronic with **131**, $Fe_3RuCoRhC(CO)_{16}$, was prepared from $Fe_5C(CO)_{14}{}^{2-}$ by consecutive treatment with $[Ru(CO)_3Cl_2]_2$, $Co_2(CO)_8$, and $[Rh(CO)_2Cl]_2$. The structure was not determined^{601}. An unexpected product, $[Rh_3(\mu_3\text{-}PMe)(PMe_3)_4(CO)_5]^+$ $[FeRh_5(PMe_3)(CO)_{15}]^-$, was obtained via rhodium-catalyzed carbonylation of allylethylamine in the presence of trimethylphosphine. The source of the iron in the product is obscure. The anion was an 86-electron octahedral cluster^{602}.

Sulfur bridging is found in some of the largest iron-containing clusters. An example is the cluster $MoFe_5S_6(CO)_6L_3$ [L = PEt_3], which showed a $(OC)_6Fe_2S_2$ cluster coordinated to a molybdenum through two S-Mo and one Fe-Mo bond (2.90 Å). The molybdenum was part of a Mo(FeL)$_3$(μ_3-S)$_4$ cubane cluster. The compound is related to **79**, but supplemented by the iron-molybdenum bond[603]. The structure of another capped cubane cluster, **132**, produced upon reaction of $Cp_2Mo_2(CO)_6$ and $Fe_3S_2(CO)_9$ [**106**, Y = Z = S], has been determined[604]. A similar reaction, using $Mo(CO)_3(NCMe)_3$ and $Fe_2(CO)_6S_2$, produced **133**, a nine-metal cluster held together by multiple sulfur bridges[605].



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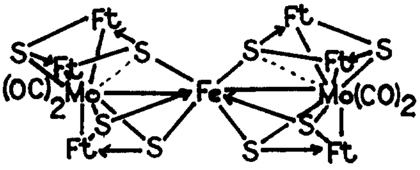

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MINDO calculations have been applied to hydrogenation of CO on an iron surface, modeled as an Fe_{12} unit[89]. Freshly reduced powdered iron with particle size of 2-7 µ has been used to dehalogenate vicinal dibromoethanes, and surface-bound bromoalkyl intermediates were implicated[606].

POST-SCRIPT: At over 600 references, this 1989 review deals with substantially more publications than previous years, which have been averaging about 520 for 1986-88. Some of the increase may be ascribed to more timely coverage of new journals by Chemical Abstracts, but some doubtless arises from increased research activity.

The Journal of Organometallic Chemistry, with 110 citations, maintains a slight lead in number of organoiron papers, with Organometallics second (93 citations), and Journal of the American Chemical Society third (70 citations). All other journals have fewer than 30 citations.

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