ORGANOIRON CHEMISTRY
Annual Survey for the Year 1983

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CONTENTS

LIST OF ABBREVIATIONS USED

acac	acetylacetonate, $(MeCO)_2CH^-$
An	any arene ring, such as benzene, C_6H_6
Ar	an aryl ring, such as naphthyl, $C_{10}H_7-$
bpy	2,2'-bipyridyl
COT	1,3,5,7-cyclooctatetraene
Cp	cyclopentadienyl, C_5H_5
Cp'	pentamethylcyclopentadienyl, C_5Me_5
D	a 2-electron donor ligand such as a phosphine
DME	1,2-dimethoxyethane, sometimes called "glyme"
DMPE	1,2-bis(dimethylphosphino)ethane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPM	bis(diphenylphosphino)methane
Et	ethyl, C_2H_5-
Fp	cyclopentadienyldicarbonyliron, $CpFe(CO)_2-$
Fp'	(pentamethylcyclopentadienyl)dicarbonyliron
HMP	hexamethylphosphorictriamide
LAH	lithium aluminum hydride
M	any transition metal other than iron
Me	methyl, CH_3-
MTHF	2-methyltetrahydrofuran
NMP	N-methyl-2-pyrrolidone
Ph, ϕ	phenyl, C_6H_5-
Pn	a pnicogen such as P, As, or Sb
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	triflate, F_3CSO_2O-
THF	tetrahydrofuran
X	any halogen

1. INTRODUCTION

In this Annual Review, I attempt to cover the organoiron chemistry reported in journals published during calendar year 1983. 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 G. Marr and B. W. Rockett.

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. For conciseness, dimers such as dicyclopentadienyldiirontetracarbonyl [Fp_2, $Cp_2Fe_2(CO)_4$] are treated alongside their monomeric derivatives such as FpR, however, and FeM_n clusters are treated with other metal clusters.

2. REVIEWS AND BOOKS

Along with many reviews and books, not detailed here, dealing with general organometallic chemistry, appeared a review on uses of iron-arene complexes in organic synthesis[1]. Part B11 of the current Gmelin organoiron series, dealing principally with CpFe(CO)DX, CpFe(CO)DR, and $CpFe(CO)_2X$ compound types, was published[2].

3. REACTIONS OF "NAKED" IRON ATOMS AND IONS

Ground state ($3d^6 4s^2$, $^5D_4$) iron atoms do not react with methane matrices, nor do Fe_2 molecules. Excitation (300 nm) of Fe atoms to the $3d^7 4p^1$, $^5D_4$ state leads to rapid formation of CH_3FeH at 12 K[3]. Analogous photoinsertion into C-H bonds occurs with ethane and propane, but cyclopropane in argon matrices forms ferracyclobutane by C-C insertion[4].

Iron atoms react in an ethylene matrix at <18 K to form $Fe(C_2H_4)$ at low concentrations and oligomers $Fe_n(C_2H_4)_n$ [n = 2,3,..] at higher concentrations. Propene gives analogous results[5]. Co-condensation of iron atoms with alkynes RC≡CR' results in formation of benzenes $C_6R_3R'_3$, cyclooctatetraenes 1,2,4,7-$C_8R_4R'_4$ and ferrocenes $FeC_{10}R_5R'_5$; the latter may be formed via metal-carbyne intermediates[6].

Solvated iron atoms in MTHF at 140 K reduce $Mn_2(CO)_{10}$ to form $Fe(MTHF)_n^{+2}$ $[Mn(CO)_5^-]_2$. In methylcyclohexane, Fe atoms react preferentially with toluene, forming $(PhMe)_2Fe$, rather than with $Mn_2(CO)_{10}$. But in MTHF, reaction 1 occurs slowly:

$$(PhMe)_2Fe + Mn_2(CO)_{10} \longrightarrow (PhMe)_2Fe^{+2} + 2\ Mn(CO)_5^- \qquad (1)$$

$[CpMo(CO)_3]_2$ is reduced analogously[7].

An iron slurry from Li reduction of $FeCl_2$ in THF or DME reacts readily with C_6F_5X (X = Br, I) to yield solvated $(C_6F_5)_2Fe$ and Fe_2. The former reacts with CO to give $(C_6F_5)_2Fe(CO)_2(DME)_2$[8].

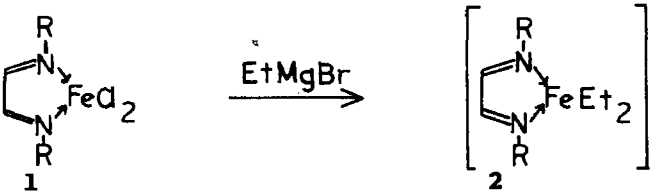
Reactions of Fe^+ ions with organics in the gas phase have been studied by ion-beam[9], Fourier transform mass spectrometry[10-12], and ion-cyclotron resonance methods[13]. Reactions with H- and C-labelled alkanes reveal such processes as C-H and C-C bond insertions, β-alkyl and hydride transfers, and ferracyclobutane formation. Secondary and subsequent reactions of FeH^+, $Fe(CO)_n{}^+$, $Fe(alkene)^+$ and $Fe(butadiene)^+$ with hydrocarbons have also been studied[12-14].

4. COMPOUNDS WITH η^1-CARBON LIGANDS

a. Alkyl- and aryliron compounds

Reaction of phenyllithium with $FeCl_3$ gives $[Ph_4Fe]^{-4}[LiOEt_2{}^+]_4$ which reduces dinitrogen[15]. α-Naphthyllithium, in contrast gives $[(C_{10}H_7)_4Fe]^{-2}[LiOEt_2{}^+]_2$, which is unreactive toward dinitrogen[16]. Both tetraaryliron compounds were characterized by X-ray crystallography. The active Fe(0) compound has rectangular planar coordination of the four phenyl groups; the inactive Fe(II) compound shows distorted tetrahedral coordination of the α-naphthyl groups.

Dimesityliron(II) shows Lewis acid character, undergoing coordination with one (2,6-dimethylpyridine) or two (pyridine, benzonitrile) moles of Lewis base[17]. Reaction of 1 with triethylaluminum or ethylmagnesium bromide gave species, possibly from 2, capable of catalyzing Diels-Alder additions of dienes to alkynes and alkyne trimerization[18].



1 2

R = 2,4-dimethyl-3-pentyl

(2)

A number of alkyl- and aryliron compounds have been prepared by reaction of tightly-coordinated iron chloride derivatives with alkyl- or aryllithium or Grignard reagents[19-21]:

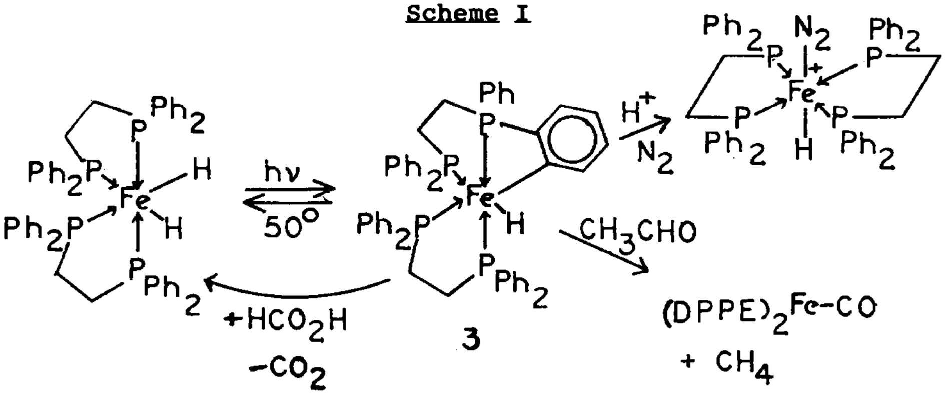
$$(Por)FeCl + RLi \longrightarrow (Por)Fe{-}R \longleftarrow RX + (Por)Fe^- \qquad (3)$$

$$(Por)FeCl + PhMgBr \longrightarrow (Por)Fe{-}Ph \qquad (4)$$

Reaction of hemoglobin or myoglobin with arylhydrazine, followed by separation from the protein matrix, gives the same aryl-iron porphyrin as reaction (4)[20]. Reaction of various D_4FeCl_2 derivatives with methyllithium in ether gives $D_4Fe(CH_3)_2$; the donor ligands include trimethylphosphine, and $R_2PCH_2CH_2PR_2$ (R = Me, DMPE; R = Ph, DPPE). Both cis and trans dimethyl compounds form, depending upon the "bite" of the diphosphine ligand[21].

Irradiation of cis-$H_2Fe(DPPE)_2$ results in evolution of hydrogen, with formation of 3 (Scheme I)[22].

Scheme I



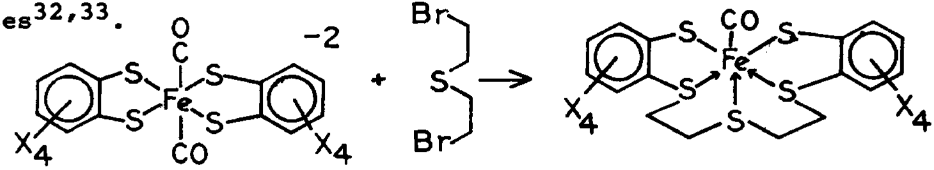
The reactivity of 3 may indicate coexistence with a small amount of highly reactive, coordinatively unsaturated $Fe(DPPE)_2$.

4b. Iron monocarbonyls, e.g. D_4FeCO

Reduction of trans-$FeH(CO)(DPPE)_2^+$ by pulse radiolysis in methanol gives a persistent 17-electron species in which one DPPE ligand is monodentate[23].

Rates and equilibria for CO binding to iron(II) porphyrin models (Scheme II) have been studied extensively, in order better to define the effects of cavity size[24], axial base[25,26], Fe-CO bond strength[27], and electronic structure[28,29] on the carbonylation of oxygen-carrier hemoproteins. A T_1 study of ^{13}CO in 4 has been reported[30]. Photodissociation of CO from 4 and other (Por)-Fe(CO) generates a voltage, which may be useful in solar energy conversion[31].

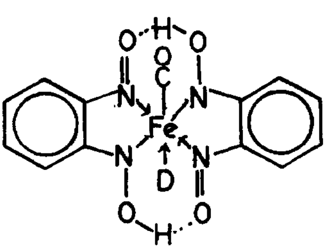
A number of polydentate macrocyclic sulfur ligand-Fe(CO) complexes have been prepared by alkylation of coordinated dithiolates (Eq. 5). The CO ligand can be displaced by various Lewis bases[32,33].



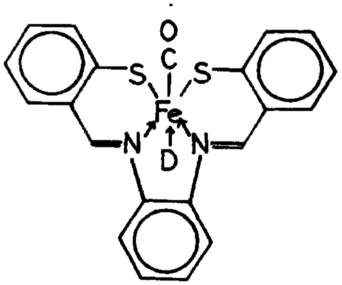
(5)

Protonation of $Fe(CO)_3(NO)^-$ in the presence of excess triphenylphosphine gives, inter alia, $(Ph_3P)_2FeH(CO)(NO)$[34], the crystal structure of which reveals a distorted trigonal bipyramid with the phosphines axial, but bent toward the hydride ligand[35].

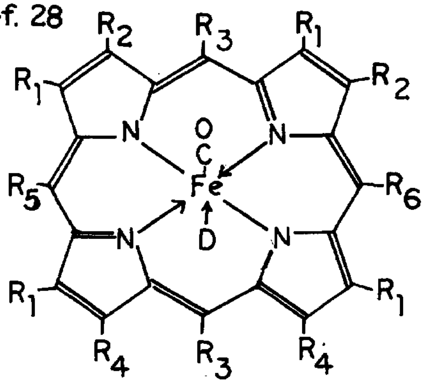
Scheme II Porphyrin Structures

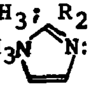


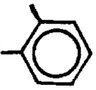
D = Various; Ref. 28

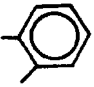


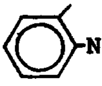
D = C_5H_5N; Ref. 29

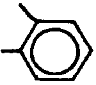


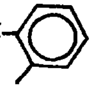
4, $R_1 = CH_3$; $R_2 = CH{=}CH_2$; $R_3 = R_5 = R_6 = H$; $R_4 = CH_2CH_2CO_2CH_3$;
D = CH_3N  N: Ref. 30

$R_1 = R_2 = R_4 = H$; $R_3 = R_5 = R_6 = (CH_3)_3CCONH$–  ; D = Various

$R_1 = R_2 = R_4 = H$; $R_3 = R_6 = (CH_3)_3CCONH$– 

R_5 + D =  $NHCO(CH_2)_4N$  N:

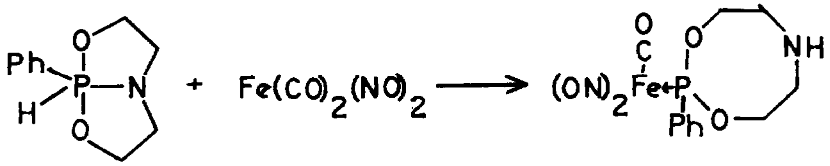
$R_1 = R_2 = R_4 = H$; $R_5 = (CH_3)_3CCONH$– 

$R_3 = R_6 = 1,3,5\text{-}C_6H_3(CH_2)_{1-3}CONH$– 

Refs. 24,25,27

$R_1 = R_2 = R_4 = H$; R_3 + D = $o\text{-}C_6H_4NHCO(CH_2)_4]_2CHN$  N;
$R_5 = R_6 = o\text{-}C_6H_4NHCO(CH_2)_5\text{-}]_2$ Ref. 26

Reaction of $Fe(CO)_3NO^-$ with $Ph_2PNRCHMePh$ and ArN_2^+ gave the diastereomers of $PhCH(Me)NRPPh_2Fe(CO)(NO)(NNAr)$, with a chiral iron atom[36]. A similar compound (with Ph_3P) results from reaction of $(Ph_3P)_2Fe(CO)_2NNAr^+BF_4^-$ with $PPN^+NO_2^-$ [37]. Displacement of CO from $Fe(CO)_2(NO)_2$ by a bicyclic aminophosphorane gives the monocyclic phosphine adduct (eq. 6).



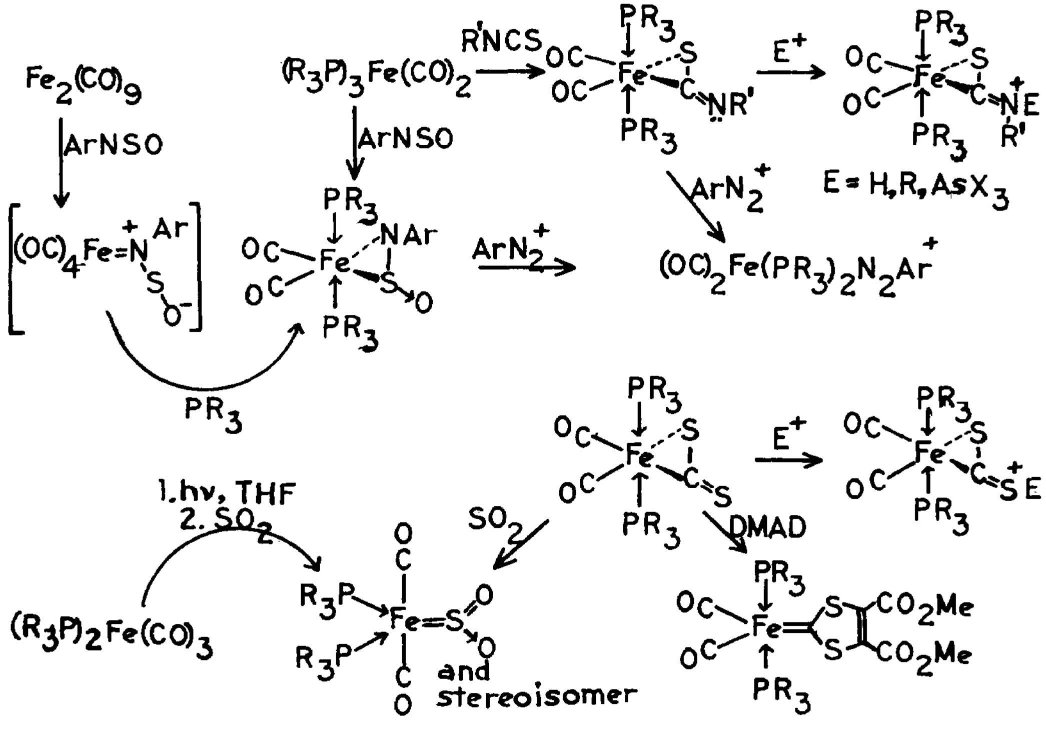
(6)

Likewise, $Ph_2PNHPPh_2$ gave $HN[PPh_2Fe(CO)(NO)_2]_2$[39].

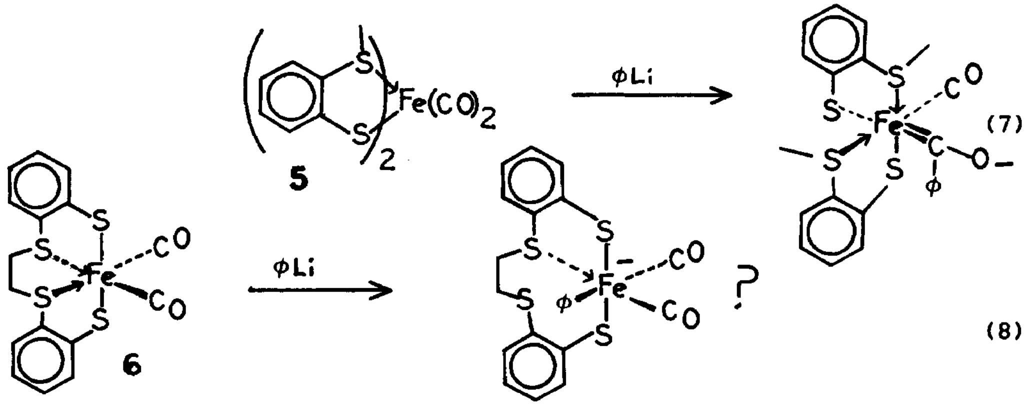
4c. Iron dicarbonyls, e.g. $D_3Fe(CO)_2$

Much of the interest in compounds of this type lies in the novelty of the ligands D. A number of compounds $(R_3P)_2Fe(CO)_2D$ with heterocumulene ligands have been reported on during 1983. The ligands have included isothiocyanates (RNCS)[40], carbon disulfide[41], sulfinylanilines (ArNSO)[42], and sulfur dioxide[43]. All but the latter show η^2-coordination, using the C=S or N=S bond. Some of the observed reactions are summarized in Scheme III.

Scheme III Reactions of (Heterocumulene)$Fe(CO)_2(PR_3)_2$[40-43]



Displacement of triphenylphosphine or CO from $(Ph_3P)_2Fe(CO)_2Br_2$ by isocyanides has been studied; reduction by sodium amalgam in the presence of excess ligand D gave $(Ph_3)_2Fe(CO)_2D$[44]. Reaction of lithium 2-(methylthio)benzenethiolate with $Ph_3PFe(CO)_3I_2$ gives $[\underline{o}-C_6H_4(SCH_3)S]_2Fe(CO)_2$, **5**, and its monophosphine analog. Although phenyllithium attacks a CO group of **5**, it attacks the Fe atom of a macrocyclic analog **6**. (eqs. 7 and 8)



5

6

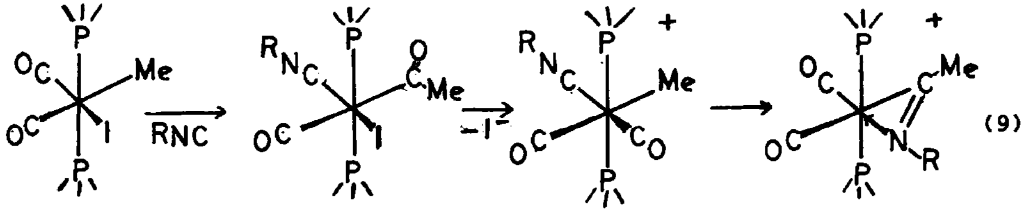
(7)

(8)

$Li^+HBEt_3^-$, however, converts **6** to a formyl compound[45].

Mössbauer studies of $(Por)Fe(CO)_2$ have been reported[46]. A series of $(Por)Fe(CNR)_2$ have been prepared, including a polymeric one from use of $p-C_6H_4(NC)_2$[47].

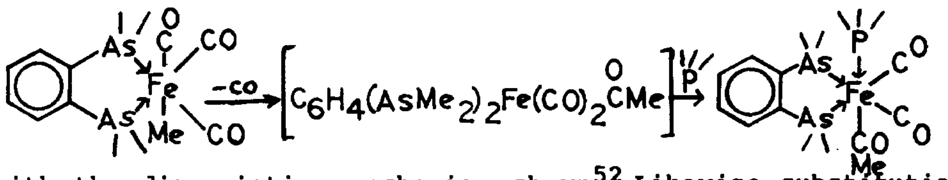
"Insertion" reactions of $(Me_3P)_2Fe(CO)_2(Me)X$, **7**, have been studied by different groups, sometimes with different results. Reaction of **7** (X = I, CN, CH_3, $CNBPh_3$) with ^{13}CO was reported to give the product with ^{13}CO cis to the acetyl group in one case[48] and trans in another case, with X = CN[49,50]. With X = I, the initially formed product rearranges via ionization[48,50]. "Insertion" of Me_3NC proceeds as in eq. 9; the η^2-iminoacyl product was crystallographically characterized[51].



(9)

4d. Iron tricarbonyls, e.g. $D_2Fe(CO)_3$

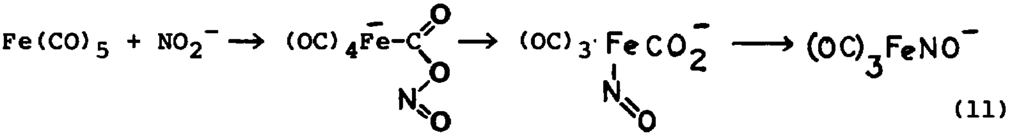
"Insertion" reactions of the ionic complexes $(Me_3P)_2Fe(CO)_3CH_3^+$ occur less readily than in the just-discussed neutral $(Me_3P)_2Fe(CO)_2(CH_3)X$ and are accompanied by ligand exchange of D for CO[50]. For reaction 10, kinetic study shows first-order dependence on the substrate and zero order in phosphite, consistent

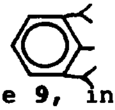


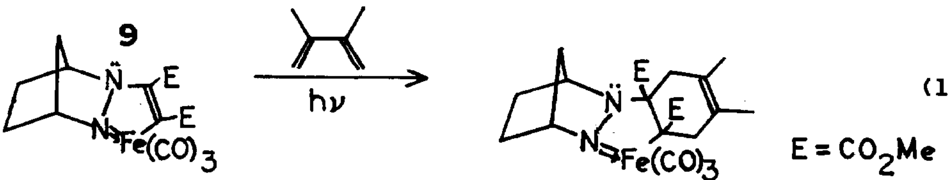
with the dissociative mechanism shown[52]. Likewise substitution of CO for D in $D_2Fe(CO)_3$ at temperatures above 100° occurs by initial dissociation of D, with lability order $Ph_3As > Ph_3P > (PhO)_3P > CO$[53]. Conditions for separating $D_2Fe(CO)_3$ and $D_3Fe(CO)_2$ mixtures (D = various trialkylphosphites) by HPLC have been optimized[54].

The 17-electron radical-cation $(Ph_3P)_2Fe(CO)_3{}^{\cdot +}$ has been generated electrochemically and studied by ESR. In coordinating solvents it disproportionates to $(Ph_3P)_2Fe(CO)_3$ and solvated Fe^{++} [55].

Reaction of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with $PPN^+NO_2{}^-$ in THF at room temp. affords a convenient synthesis of $PPN^+Fe(CO)_3NO^-$ and certain other metal nitrosyl carbonyls[37,56]. The route of eq. 11 was suggested.



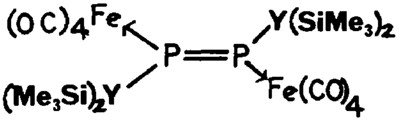
The crystal structures of $PPN^+Fe(CO)_3NO^-$ [57], $(CH_3NC)_2Fe(CO)_3$[58], (RN NR)$Fe(CO)_3$, **8**, R = ,[59] have been reported. Cycloaddition of the diazaferrole **9**, in which the diazene functions as a 3-electron ligand, to dienes occurs as in eq. 12[60].



E = CO_2Me

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

A number of species $DFe(CO)_4$ have been prepared and characterized, which have novel phosphine ligands. These include substances with D = $PhPCl_2$[60], $F_2PN(CH_3)PF_2$[61], CH_3NHPF_2[61], $(RO)_xPF_{3-x}$ [x = 1-3, R = $C(CF_3)_2CN$][62], and $(OC)_3Mo(F_2PNPh)_3P$[63]. Reaction of $Cl_2PN(SiMe_3)_2$, $Cl_2AsN(SiMe_3)_2$, and $Cl_2PCH(SiMe_3)_2$ with $Na_2Fe(CO)_4$ gave the phosphinidene (or the arsinidene) complexes,



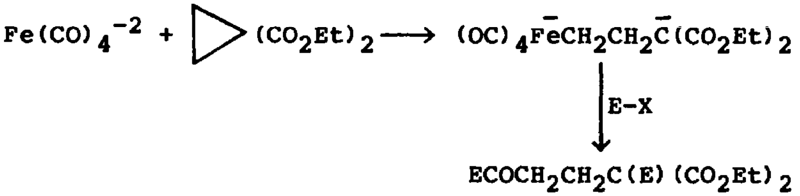
Y = N, CH

which were characterized by X-ray crystallography[64,65]. (η^1-DPPE)Fe(CO)$_4$ has also been characterized crystallographically[66]. Axial-equatorial isomerism in solutions of $Ph_3PnFe(CO)_4$ and $(RO)_2PFFe(CO)_4$ have been studied[62,67].

The photoelectron spectra of $H_2Fe(CO)_4$[68] and $Br_2Fe(CO)_4$[69] have been interpreted by means of the Green's function formalism. Photodissociation of $H_2Fe(CO)_4$ has been interpreted through state correlation diagrams[70].

$(Me_3SiNC)_4FeI_2$ has been prepared and characterized[71]. $(CF_3CF_2CF_2)_2Fe(CO)_4$ results from reaction of $C_3F_7Fe(CO)_4I$ with $Hg[N(CF_3)_2]_2$ and from pyrolysis of $C_3F_7Fe(CO)_4OCOCF_3$. Reaction of the iodide with HgF_2 produces $[C_3F_7Fe(CO)_4]_2Hg$ and $C_3F_7Fe(CO)_4HgC_3F_7$[72]. Mild reduction of $[MFe(CO)_4]_x$ polymers (M = Zn, Cd, Hg) gives $M[Fe(CO)_4]_2^{-2}$, which are further reduced to $Fe_2(CO)_8^{-2}$. The crystal structures of $[Na(THF)_2]_2^+$ $M[Fe(CO)_4]_2^{-2}$ have been determined. $Zn[Fe(CO)_4]_2^{-2}$ reacts with $HgCl_2$ to yield $Fe(CO)_4(HgCl)_2$[73].

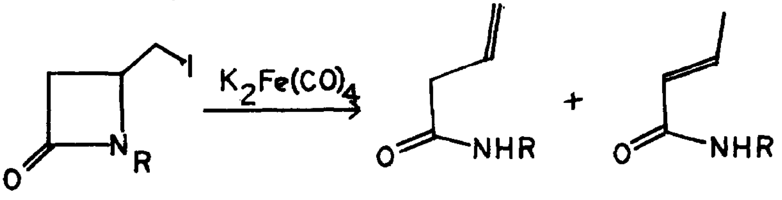
The $HFe(CO)_4^-$ ion can be incorporated in an ion-exchange resin and used to reduce nitroarenes and 1,2-dibromoalkanes[74]. The bimetallic formyl complexes $M_2(CO)_9CHO^-$ (M = Mn, Re) reduce $Fe(CO)_5$ to $Fe(CO)_4CHO^-$ [75]. $Na_2Fe(CO)_4$ opens the ring of diethyl 1,1-cyclopropanedicarboxylate (eq. 13)[76].



(13)

E-X = H-OAc, CH_3-I

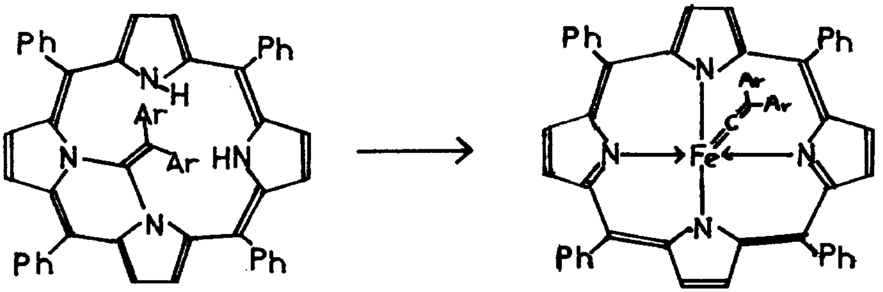
Ring opening also results upon reaction of 4-(iodomethyl)azetidine-2-ones with $K_2Fe(CO)_4$, probably as a result of single electron transfer[77].



(14)

4f Carbene complexes, e.g. $R_2C=Fe(CO)_4$

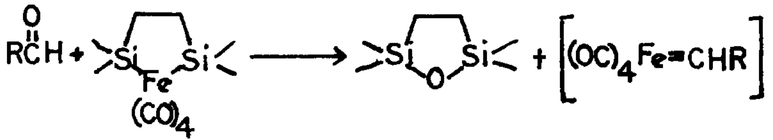
Reaction of the N,N'-bridged tetraphenylporphyrin **10** with $Fe_3(CO)_{12}$ results in migration of the vinylidene group from the nitrogens to the iron (eq. 15)[78]. Electrochemical reduction of $(Por)Fe=C=CR_2$ and (Por)FeCS leads to vinyl and thioformyl com-



(15)

plexes. $PorFe{=}CCl_2$ undergoes dehalogenation to give $(PorFe)_2{=}C$, which reduces in turn with cleavage of the Fe=C bonds[79]. SCF molecular orbital calculations on $(OC)_4Fe{=}CHOH$ predict a 2.00 A. bond length for the Fe=C bond, and a 37 kcal/mol bond strength, with the carbene ligand preferentially in the axial position of the iron trigonal bipyramid. Electrophilic reactivity is frontier orbital-controlled[80].

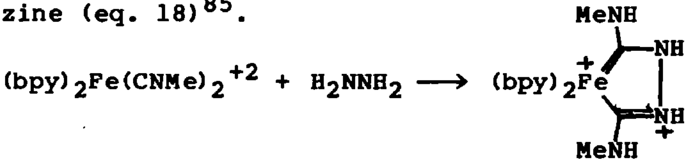
Aldehydes can be converted to carbene complexes (trapped as phosphine adducts) in one step by reaction with a ferradisilole (eq. 16)[81]. Cyclopropanes were not formed in the presence of excess isobutylene[81]. Alkylation of $(OC)_4Fe{=}C(R)O^-$ to form alkoxycarbene complexes has been studied systematically; O-alkylation is favored by ethyl rather than methyl alkylating agent, hard leaving groups, and HMP in the solution[82]. But methylation of $(OC)_4FeCO_2Me^-$ with methyl triflate at -78° gives the Fe-Me product, which decomposes to methyl acetate at room temp.[83] Reaction of alkoxycarbene complexes with alkenes results in formation of one new C-C bond rather than two (eq. 17). Mechanistic possibilities include a ferracyclobutane[84].



(16)

$$(OC)_4Fe{=}C(OEt)Ph + CH_2{=}CHR \longrightarrow PhCH(OEt)CH{=}CHR + PhC(OEt){=}CH_2R \qquad (17)$$

The dithiocarbene complex previously shown in Scheme III decomposes thermally or on reaction with I_2 to a tetrathiafulvalene. A dicarbene-FeD_3 is a possible intermediate[41]. A novel dicarbene complex arises when $(bpy)_2Fe(CNMe)_2^{+2}$ reacts with hydrazine (eq. 18)[85].

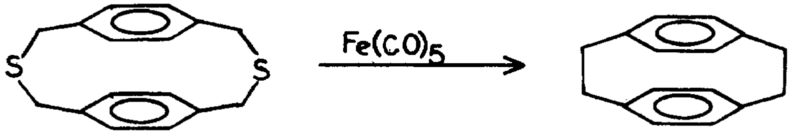


(18)

4g. Selected organic reactions of iron carbonyls

Most reactions involving simple iron carbonyls are discussed in this survey under the heading appropriate to the products. Here, I discuss some miscellaneous reactions and properties of iron carbonyls, which do not fit into other sections but deserve to be noted.

Iron pentacarbonyl in refluxing toluene has been used to desulfurize a dithiaparacyclophane (eq. 19)[86], and to couple benzoyl chloride to cis and trans $[PhCOOC(Ph)=]_2$[87]. Under phase transfer conditions, benzyl halides have been carbonylated to form arylacetic acids in the presence of iron pentacarbonyl[88].



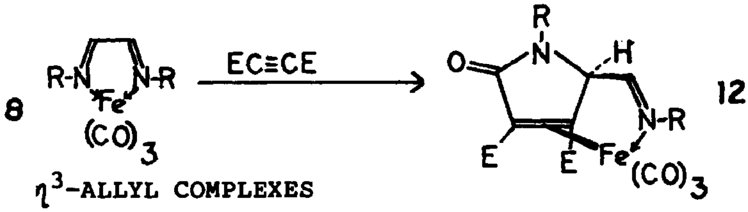
(19)

γ-Radiolysis of $Fe(CO)_5$ in MTHF at 77 K gave $Fe(CO)_5{}^{\bullet -}$ and $Fe(CO)_4{}^{\bullet -}$. $Fe_3(CO)_{12}$ likewise gave its radical-anion[89]. Reduction of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with azole anions gave $Fe_2(CO)_8{}^{\bullet -}$ [90]. Ultrasonication of iron carbonyl solution induces substitution of CO by ligands such as phosphines, probably via coordinatively unsaturated intermediates[91]. Pulsed UV photolysis of $Fe(CO)_5$ in the gas phase, with infrared detection, has allowed identification of $Fe(CO)_x$ transients (x = 2-4)[92]; the $Fe(CO)_4$ appears to have the same C_{2v} geometry as previously found in matrix studies. Photoreaction of $Fe(CO)_5$ with CCl_4 in the presence of Ph_3P has been followed by ESR[93]. $Fe(CO)_5$ catalyzed, under photolytic conditions, isomerization of $CH_2{=}CH(CH_2)_nNR_2$ to the enamines $CH_3(CH_2)_{n-1}CH{=}CHNR_2$ (n = 1,3; R = Me_3Si)[94].

5. η^2-ALKENE COMPLEXES

The X-ray photoelectron spectrum of (ethylene)tetracarbonyliron, **11**, has been reported and interpreted as showing negative charge on the ethylene[95]. Fenske-Hall calculations on **11** have been reported[96]. Photolysis of **11** in alkane matrices at 77 K produces the unsaturated (ethylene)tricarbonyliron. Alkenes with allylic hydrogens give the $HFe(CO)_3(allyl)$ products instead. Warming of the matrices results in formation of dinuclear species $[C_2H_4(OC)_3Fe{=}]_2$, which actively catalyze hydrogen shifts in added alkenes[97].

Reaction of $Fe(acac)_3$ with Et_2AlOEt in the presence of $PhPMe_2$ at low temp. gave the bis(ethylene)trisphosphineiron(0) product[98]. Reduction of $Fe(CO)_2(PPh_3)_2Br_2$ with sodium amalgam in the presence of diphenylacetylene gave the η^2-alkyne complex $Ph_2C_2Fe(CO)_2(PPh_3)_2$ [44]. A series of (cycloalkene)tetracarbonyliron complexes has been prepared for study of the carbonyl group exchange process[99]. The diazadiene complexes **8** (R = Me_2CH and others) react with dimethyl acetylenedicarboxylate to give pyrrolinone complexes such as **12**[100].



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6. η^3-ALLYL COMPLEXES

Reaction of $(C_3H_5)Fe(CO)_3I$ with salts of di- and triazoles gives a variety of products, including in several cases coordinated N-allyl azoles such as **13**[101]. Reaction of $(C_3H_5)Fe(CO)(NO)D$ derivatives with sodium borohydride gives propene derivatives along with $Fe(NO)_2D_2$ and salts such as $Fe(CO)(NO)D_2^-$ [102]. Reaction of substituted allyl-$Fe(CO)_4$ cations (from protonation of diene-$Fe(CO)_3$ complexes in the presence of excess CO) with phosphines gives allylic phosphonium salts useful in synthesis[103].

Reaction of bicyclo[5.1.0]octadienyl-$Fe(CO)_2D^+$ with iodide ion results in ring-opening to form (3-5)η^3-cyclooctatrienyl-$Fe(CO)_2DI$ (D = trimethylphosphite)[104]. Reaction of dimethylaniline with $C_4H_4Fe(CO)_2NO^+$ gives an η^3-cyclobutenyl complex with an exo-4-dimethylaminophenyl substituent, characterized crystallographically[105].

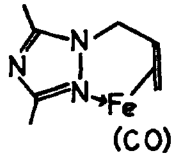
A complete report on the first η^3-cyclopropenyl complex of iron, $Ph_3C_3Fe(CO)_2NO$, including an X-ray structure, has now appeared[106].

7. COMPOUNDS WITH η^4-LIGANDS

a. Compounds with non-contiguous η^4-coordination

(η^5-Cycloheptadienyl)$Fe(CO)_2PPh_3^+$ reacts with methyllithium at C-2, giving **14**. Me_2CuLi causes methylation at C-1[107]. A crystal structure of **15** has been published[108].

13



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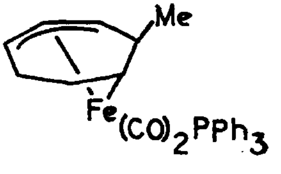

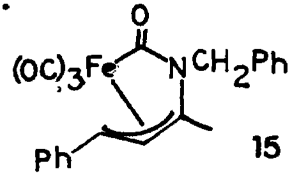

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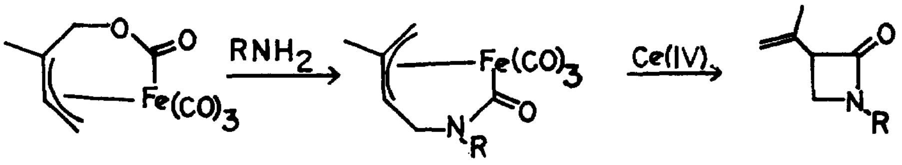
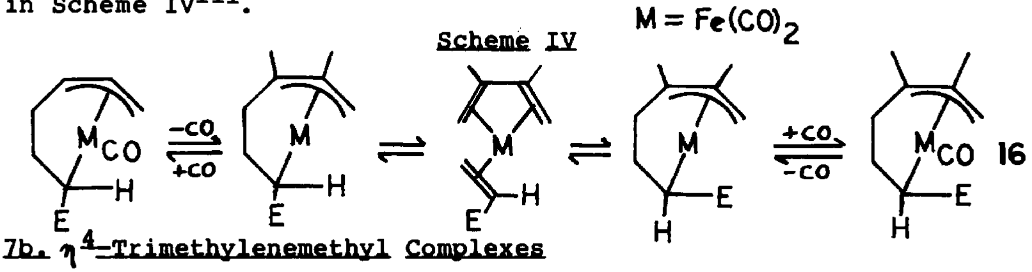
A lactam complex homologous with **15** was obtained by reaction of a lactone complex with benzylamine (eq. 21)[109]. Oxidative de-



(21)

composition gave a β-lactam. Triphenylphosphine attacks the tricarbonyl(1-3:5,6)η^5-cyclooctadienylium cation at C-5, forming a (1-3,6)η^4-coordinated phosphonium ion[110]. A study of photocleavage and isomerization of 16 has indicated the reactions shown in Scheme IV[111].

Scheme IV



7b. η^4-Trimethylenemethyl Complexes

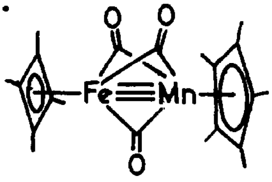
The mechanism of oxidative demetalation of (2-methylenecyclopentane-1,3-diyl)tricarbonyliron has been studied, with the conclusion that the free ligand is generated and trapped in its triplet ground state; at higher concentrations some trapping product may derive from interception of an oxidized iron intermediate[112]. Green's function calculations on $[(CH_2)_3C]Fe(CO)_3$, $C_4H_4Fe(CO)_3$, 17, and other organometallics in the ground and ionized states have been reported[113].

7c. η^4-Cyclobutadiene Complexes

MO Calculations on 17 have been undertaken, for the purpose of better understanding C-C bond alternation[114] and the ionic states observed in photoelectron spectroscopy[113,115]. Nematic-phase NMR studies of $(C_4H_3X)Fe(CO)_3$ indicate transient rhombic deformations of a time-average square planar ligand[116].

Photolysis of $C_4Me_4Fe(CO)_3$ gives a dimer with a triply CO-bridged Fe-Fe triple bond. Photolysis of a mixture containing $C_5Me_5Mn(CO)_3$ gave the analog with a Fe-Mn triple bond, 18[117]. 19 results upon methylation of the corresponding oxocyclobutenyl complex[106].

18



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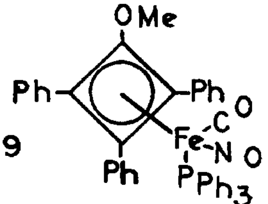
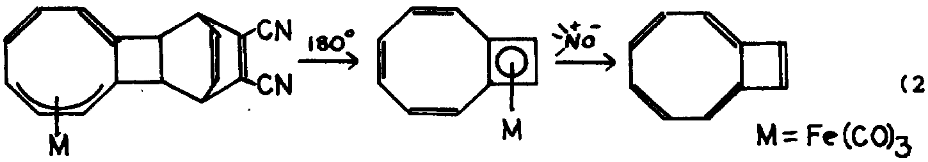


An X-ray structure of (benzocyclobutadiene)Fe(CO)$_2$PPh$_3$ has been published[118]. Free bicyclo[6.2.0]decapentaene has been obtained through its Fe(CO)$_3$ complex (eq. 22)[119].



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7d. η^4-Cyclopentadiene Complexes

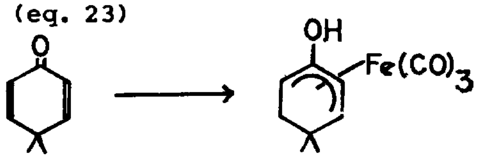
P-H coupling constants can be used to determine the stereochemistry of $(5\text{-}RC_5H_5)Fe(CO)_2PPh_3$ and related complexes[120]. CpFe(DPPE)CHO rearranges at 90° to $(\eta^4\text{-}C_5H_6)Fe(DPPE)CO$[121].

Field-desorption mass spectrometry of (cyclopentadienone)$Fe(CO)_3$ and other organometallics reveals intense molecular ion peaks[123]. A novel cyclopentadienone complex was obtained, *inter alia*, from reaction of the diacetylene $(PhC{\equiv}CC_6H_4)_2PPh$ with iron carbonyls[122].

Iron tricarbonyl complexes of 1,1-dimethylsilole, 1,1,3,4-tetramethylsilole, and 1,1-dimethylgermole have been obtained by reaction of the heterocycles with iron carbonyls[124,125].

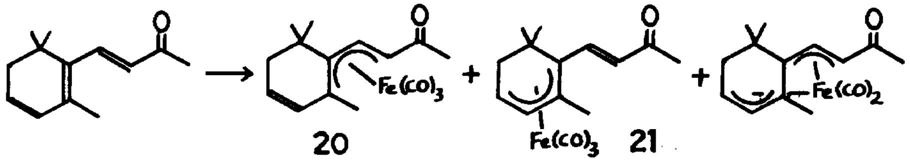
7e. η^4-Cyclohexadiene Complexes

Tertiary allylic cyclohexenols have been converted directly to (cyclohexadiene)tricarbonyliron complexes upon reaction with iron pentacarbonyl in refluxing dibutyl ether[126]. Cross-conjugated cyclohexadienones yielded cyclohexadien-2-ol complexes upon treatment with $Fe_2(CO)_9$ in benzene/THF containing water and hydroxide ion[127]. (eq. 23)



(23)

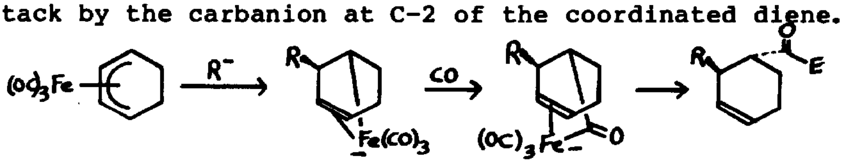
The $Fe(CO)_3$ complex of 6-methoxy-2-pyrone resulted from reaction of 2-methoxyfuran with $Fe_2(CO)_9$[128]. Dehydro-β-ionone gave two iron tricarbonyl products and an unusual iron dicarbonyl (eq. 24).



(24)

Product **20** was favored kinetically; **21** thermodynamically[129].

Reactions of (cyclohexadiene)iron tricarbonyl with carbanions have been intensively studied; the intermediates can be protonated to give substituted cyclohexenes as mixtures of isomers, but trapping with other electrophiles was not generally successful. Alkyllithium reagents attacked carbonyls rather than the coordinated diene[130]. Nucleophilic attack in the presence of CO led to carbonylated products (eq. 25) in good yields[131], suggesting attack by the carbanion at C-2 of the coordinated diene.



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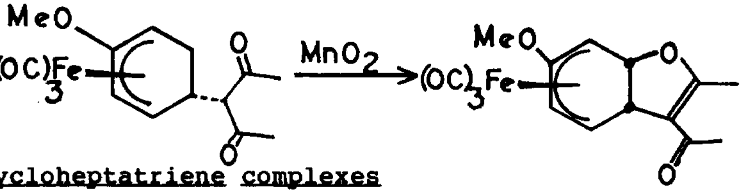
Substituted cyclohexadiene complexes are often produced by quenching a (cyclohexadienyl)tricarbonyliron salt with a nucleophile, a reaction much studied for its synthetic potential. That such nucleophilic attacks may be less straightforward than they seem is suggested by evidence that reaction of $C_6H_7Fe(CO)_3{}^+$ with hydroxide ion to give the 1,3-cyclohexadien-5-ol complex occurs through a $(C_6H_7)Fe(CO)_2CO_2H$ intermediate[132]. Carbanionic nucleophiles whose reactions with cyclohexadienyliron cations have been reported include $BrZnCH_2CO_2Me$[133], aryltrimethylsilanes, stannanes and the like[134], enolates such as $KCH(CO_2Me)_2$[135] and trimethylsilylethyl ester enolates[136], from which the ester group is readily removed. An intramolecular nucleophilic attack (eq. 26) gave a product whose structure has been confirmed[137]:



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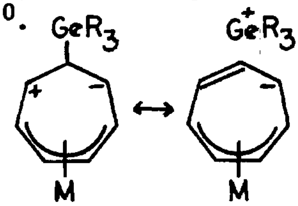
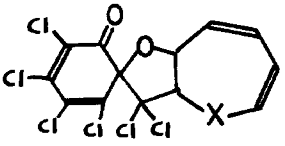
7f. Cycloheptatriene complexes

Fluxional behavior of (η^4-cycloheptatriene)tricarbonyliron derivatives has continued to draw interest. An X-ray structure of the 7-*exo*-(triphenylgermyl) derivative ($G^{\neq}$ for fluxional shift 74 kJ/mol) has shown the $Fe(CO)_3$ group shifted away from C-1 as a consequence of the electron-donating effect of the C-Ge bond[138]. The fluxional shift appears to involve a symmetrical intermediate which may be considered a 2-5 η^4-structure, **22**, stabilized by interaction with the germyl group[139]. He I and II photoelectron spectra have been interpreted in terms of strengthened diene-iron interaction in the ground state due to the electron-donating effect of the germyl group, and comparative isolation of the free double bond[140].

22

M=Fe(CO)3





23

Complexation of 3,7,7-trimethylcycloheptatriene with iron carbonyls gives only the 1-4 η^4-$Fe(CO)_3$ product. Reaction with TCNE gives adducts across the 4,6- and 1,6-positions, in 4:1 ratio. Reaction with diphenylketene gives a [2 + 2] adduct[141]. These results may be readily interpreted in terms of zwitterions resulting from electrophilic attack at C-6.

Phase transfer-generated dichlorocarbene adds to the *anti* faces of the free double bonds of (cycloheptatriene)- and (N-carbethoxyazepine)tricarbonyliron. Reaction of the cyclopropane products with *o*-chloranil gave spiroheterocyclic products **23**, probably as a result of single electron transfer, cyclopropane ring opening, chloranil insertion, and decomplexation[142]. Heating substituted (4-7)η-1-vinylcycloheptatriene)tricarbonyliron complexes resulted in disproportionation to *anti*-bis $Fe(CO)_3$ complexes; only the styryl compound gave a bond-shift isomer[143]. (Cycloheptatriene)tricarbonyliron reacts with *p*-nitrobenzenediazonium salts in the manner of other electrophiles, giving the η^5-cycloheptadienylium salt by attack at C-6. Deprotonation gave the *syn*- and *anti*-arylhydrazones of (tropone)tricarbonyliron[144].

7g. Cyclooctatetraene complexes

^{13}C-NMR magnetization transfer experiments on $COTFe(CO)_2D$, having D = $NCCHMe_2$, indicated the Woodward-Hoffmann allowed mechanism for 1,2-shifts in this fluxional species[145]. Photolysis of $COTFe(CO)_3$, **24**, in a methane matrix at 12 K gives species thought on the basis of FT IR studies to be (η^2-COT)$Fe(CO)_3$, which can return to **24** or an isomer with a chair conformation of the COT ring. (COT)$Fe(CO)_2$ was also detected; a η^4- structure rather than the closed-shell η^6-structure was indicated[146]. Reaction of **24** with arenediazonium ions led to (8-arylbicyclo[5.1.0]octadienyl)$Fe(CO)_3^+$, which was deprotonated to give arylated **24**. In contrast, derivatives of **24** having one or two CO's replaced by trimethylphosphite gave arylazocyclooctatrienyl complexes. Arylation was proposed to result from initial electrophilic attack at Fe, and azo coupling from initial attack on the ring[147].

A compound assigned the structure (3,4,7,8-tetrachlorocycloocta-1,5-diene)tricarbonyliron has been reported as formed (along with the expected diene complex) upon reaction of *trans,trans*-1,4-dichlorobutadiene with $Fe(CO)_5$[148].

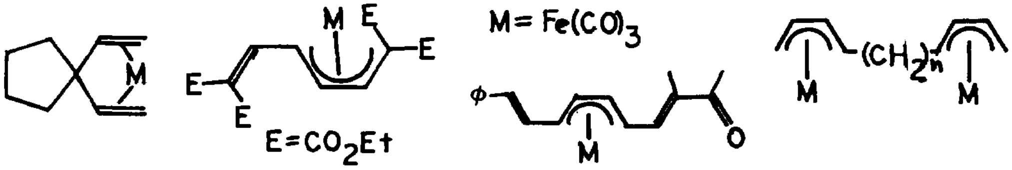
7h. Acyclic diene complexes

Vibrational spectra of butadienetricarbonyliron have revealed discrete rotamers in the liquid state[149]. $Fe(CO)_3$ complexes of several dienes (Scheme V) have been obtained by reaction of the corresponding dienes with iron carbonyls.

Other diene complexes have been obtained in reactions invol-

Scheme V

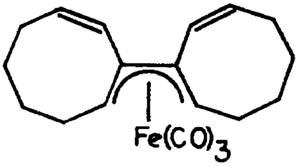
Some Newly Reported Diene Complexes

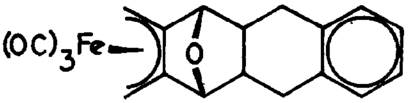


Ref. 150 Ref. 151 Ref. 152 Ref. 153

ving hydrogen rearrangements. Thus, reaction of bi-2,7-cyclooctadienyl with $Fe_3(CO)_{12}$ gave 25[154], and reaction of *cis*-polybutadiene with $Fe(CO)_5$ gave a polymer with 1,3-diene units in the chain[155,156]. A number of studies dealing with complexation of derivatives of 1,2-dimethylenecyclohexane have appeared. Reaction of 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene with $Fe_2(CO)_9$ proceeded with dimerization and deoxygenation to give 26[157]. The presence of $Fe(CO)_3$ groups coordinated to the *cis*-butadiene units of tetramethylenebicyclo[2.2.2]octene[158], tetramethylenebicyclo[2.2.2]octan-2-ol and -2-one[160,159], and hexamethylenebicyclo[2.2.2]octane[160] has curious and sometimes unpredictable effects on the stereochemical outcomes and rates of reactions. An example is given in reaction 27[159].

25





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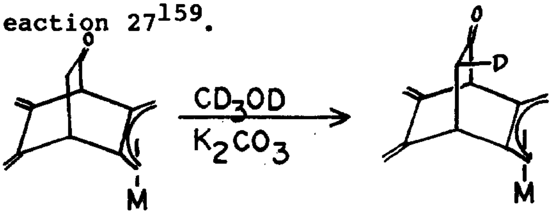

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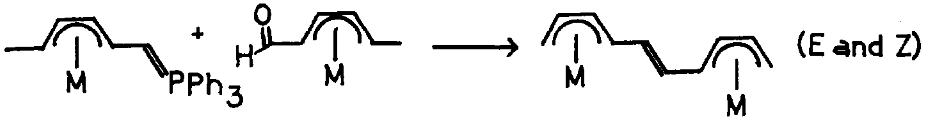
The use of alkaline hydrogen peroxide in methanol has been recommended as a mild method for decomplexation of diene complexes[161]. Wittig reactions have continued to be used to elaborate diene complexes, as in eqs. 28[103,162] and 29[163].



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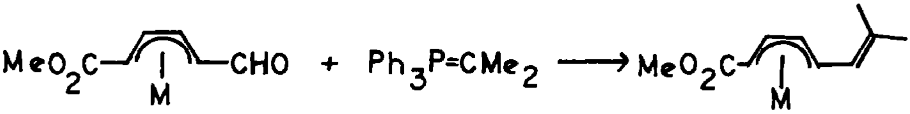


(29)

Reaction of butadiene complexes with reactive carbanions R^- under CO pressure, gives 3-R cyclopentanones in good yield[164]. The mechanism involves R^- attack on the 2-position of the coordinated diene.

Photolysis of 8 in Ar or CO matrices at 10 K results in formation of the heterodiene π-complex[165]. Irradiation of $DFe(CO)_4$ or $D_2Fe(CO)_3$ (D = various phosphines) in the presence of benzylideneacetone in benzene gave (benzylideneacetone)carbonylphosphineiron[0] complexes, two of whose crystal structures have been determined[166].

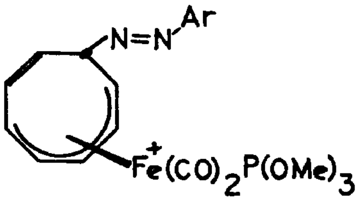
8. η^5-DIENYL COMPLEXES

a. Compounds with open pentadienyl ligands

A molecular orbital study has compared the cyclopentadienyl-, cyclohexadienyl-, and cycloheptadienyl-tricarbonyliron cations' rotational conformations and ligand planarity[167]. A number of reactions of (cyclohexadienyl)$Fe(CO)_3$ cations with nucleophiles, to give cyclohexadiene complexes, were already mentioned in Section 7e. To enhance the synthetic utility of these reactions, two groups have undertaken resolution of (2-methoxycyclohexadienyl)-tricarbonyliron cation, by means of attachment of a chiral nucleophile, forming separable diastereomeric diene complexes, from which the resolved salt could be regenerated[168,169]. The salt could also be methylated by an indirect sequence, giving the enantiomerically pure (2-methoxy-5-methylcyclohexadienyl)tricarbonyliron cation[170].

Nucleophiles attack the (1-3:5,6 η^5-cyclooctadienyl)tricarbonyliron cation variously at C-5 or at the iron[110]. Halide ions attack a methyl group of the cyclooctatrienyl cation 27, giving a coordinated phosphonate ion[104].

27



A full paper on synthesis and properties of bis(pentadienyl)-iron and several methylated derivatives has appeared[171]. The red, air-stable compounds resemble ferrocenes. An X-ray structure shows a gauche, eclipsed ligand conformation. Reaction with PF_3 gave $Fe(PF_3)_5$[172].

8b. Cyclopentadienyldicarbonyliron hydride and related compounds

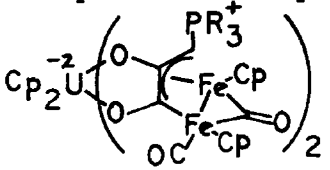
The remainder of Section 8 of this Review deals with the extensive families of compounds containing the cyclopentadienyldicarbonyliron (Fp) group, along with the closely related compounds in which one or both CO ligands is replaced by a phosphine or phosphite and/or the Cp ligand is replaced by a C_5Me_5. These are discussed together in this Section, ordered according to the other element to which the Fp group is attached. This section will discuss consecutively compounds of the types Fp-H, Fp_2, Fp-metal, and then compounds with bonds from the Fp group to elements of groups IV, V, VI and VII, respectively. Section 8c. will deal with organic derivatives, FpR, and cyclopentadienyliron compounds with organic ligands of higher hapticity.

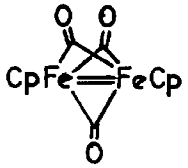
^{57}Fe chemical shift and $^{57}Fe-^{13}C$ coupling constant data have been reported for a number of FpX compounds (X = halogens and organic groups)[173].

Reduction of $Fp'CO^+$ with aq. $NaBH_4$ at 0° or aq. THF at 20° gave Fp'H, **28**[174]. The same hydride could be obtained by protonation of $Na^+Fp'^-$ with acetic acid[175]. One CO of **28** is readily displaced by Me_3P; the resulting hydride is deprotonated by the ylide $Me_3P=CH_2$[175]. LAH reduction of $CpFe(DPPE)CO^+$ gives CpFeH(CO)(DPPE), which disproportionates to DPPE and $(DPPE)[FeH(CO)Cp]_2$. The latter loses H_2 upon photolysis or heating to 90° [176,177].

Differential thermal analysis has been applied to the thermolysis of the dimer Fp_2 at 170-270° [178]. Fp_2 catalyzes exchange of isonitrile ligands for CO in FpX derivatives and other organometallics[179]. The ylide $Cp_3UCH=PR_3$ reacts with Fp_2 by attack at and reductive coupling of carbonyls, giving **29**[180]. Reaction of Fp_2 with strong acids HX in acetonitrile results in cleavage to $FpNCMe^+X^-$ or FpX[181]. In methylene chloride, isolable $Fp-H-Fp^+X^-$ results[182]. Sulfuryl chloride, SO_2Cl_2, in benzene converts Fp_2 to $FpCO^+FeCl_4^-$ [183].

Photolysis of Fp_2 in matrices at 12 K results in formation of triply-bridged **30**[184]. (cf. **18**) Formation of **30** would economically explain the formation of monosubstitution products $Cp_2Fe_2(CO)_3PR_3$ on photolysis of Fp_2 in the presence of phosphines, but a recent mechanistic study has instead suggested an open intermediate, FpC(O)Fe(CO)Cp[185]. Photoreaction of Fp_2 with chlorinated solvents to give FpCl involves Fp• radicals.

29




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Isonitriles displace all four CO ligands from Fp_2 in boiling xylene; the μ-CNR ligands are quite basic[186]. Mössbauer studies of Fp_2, and its μ-CNR and $\mu-CNHR^+$ analogs reveal the $\mu-CNHR^+$ ligand to be a powerful acceptor[187]. Oxidation with silver ion of Fp_2 and its isonitrile substitution analogs has been studied in acetonitrile and THF[188].

Two analogs of Fp_2 having the cyclopentadienyl rings joined by bridges have been reported. One has a $-SiMe_2CH_2CH_2SiMe_2-$ bridge[189], and the other a $-SiMe_2-$ bridge[190,191]. The reactions reported are qualitatively normal. X-ray structures of the diiodide from the latter[190], as well as structures of two diphosphine-bridged substitution products[191], were reported.

Reaction of K^+Fp^- with Cp_2ZrXCl gave Cp_2ZrXFp (X = Me, O-t-Bu)[192]. Reaction with Fp_2M (M = Zn, Cd, Hg) gave Fp_3M^- salts; the tetrabutyl ammonium zincate salt was characterized by X-ray crystallography[193].

Displacement of chloride from chlorosilanes has continued to find use for preparation of silyl-Fp compounds. Thus, $RSiHCl_2$ gives FpSiHRCl, which reacts with CCl_4 to give $FpSiRCl_2$. The latter forms $FpSiRF_2$ upon reaction with $AgBF_4$[194]. The crystal structure of $FpSiMe_2SiPh_3$ shows a slightly elongated Si-Si bond [195]. The iron-silicon bond of $FpSiMe_3$ is cleaved using fluoride ion in THF[196]. Reaction of $FpSiMe_2Cl$ with $LiNMe_2$ gave the expected $FpSiMe_2NMe_2$ and also the dimeric $(C_5H_4SiMe_2NMe_2)_2Fe_2(CO)_4$, from an anionic shift of the aminosilyl group from the iron to the cyclopentadienyl ring. Several additional examples of such shifts were adduced[197]. Reaction of $FpSnCl_3$ with Na_2WO_4 in the presence of NaH_2PO_4 resulted in displacement of the chlorides from the silicon to give a complex phosphotungstate, $(FpSn)_2W_{10}PO_{38}^{-5}$ [198]. Electrochemical reduction of $FpMPh_3$ (M = Si, Ge, and Sn) gave esr-observable anion radicals; further reduction led to cleavage of the Fe-M bonds[199]. Reaction of Fp_2 with GeF_2 gave Fp_2GeF_2[200].

An X-ray study of N3-Fp 1,2,3-triazole cation has been reported[201]. Photolysis of $Fp_2P(OH)_2^+$ in aqueous solution gave the compound 31, whose X-ray structure has been determined[202]. Heating 32 in xylene resulted in CO loss, with formation of 2,5-diphenylphosphaferrocene in low yield[203]. Photolysis of $FpCO^+$ in acetonitrile solutions containing 3,4-dimethyl-1-phenylphosphole gave the cyclopentadienyltris(phosphole)iron cation[204]. Analogous cations have resulted from reaction of Fp(isobutylene)$^+$ with chelating tri- and tetraphosphines, followed by thermolysis or photolysis. Reduction with LAH gave Fe-H species[205]. X-ray structures of $FpPPh_3^+$ and $CpFe(CO)(DPPE)^+$ have been published[118].

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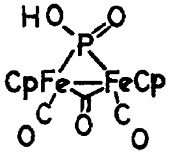

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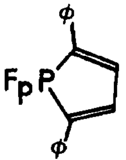


Several compounds with cyclotriphosphazene-Fp linkages have been reported, including crystal structures[206,207].

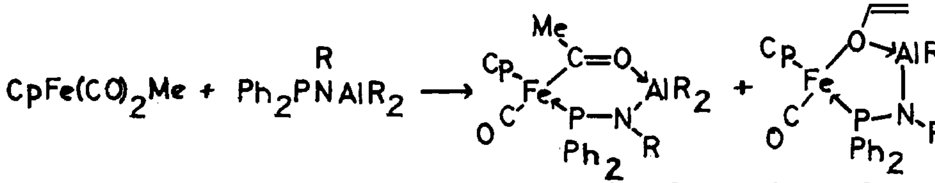
Reaction of NaFp and NaFp' with $ClAsR_2$ (R = Me, Me_3C) gave the metathetical products Fp(')AsR_2. Several reactions demonstrated the expected Lewis base character of the products[208]. Reaction of $Cp(CO)(PMe_3)FePnMe_2$ with (norbornadiene)$Mo(CO)_4$ gave the diastereomeric products $[Cp(CO)(PMe_3)FePnMe_2]_2Mo(CO)_4$, with Pn = As, Sb, and Bi[209]. $FpSbBr_2$ shows Lewis acid character in its reaction with PMe_3, forming $FpSbBr_2PMe_3$, which was crystallographically characterized[210].

Crystal structures of $FpOH_2^+$ Ph_4B^- [211] and $Fp'OSO_2CF_3$[212] have been reported. Oxidation of FpSPh or Fp'SPh gave $FpS(Ph)S(Ph)Fp^{2+}$ or the Fp' analog, which could also be obtained directly from PhSSPh and $Fp(THF)^+$ [213]. Ethylation of $CpFeCO(PR_3)SPh$ with EtBr gave the expected sulfonium salts $CpFeCO(PR_3)S(Ph)Et^+$ Br^-, which underwent slow conversion to $CpFeCO(PR_3)Br$ and PhSEt. In the case of FpSPh and Fp'SPh, the FpBr was formed directly[214]. Organoiron polysulfides FpS_xFp were prepared from NaFp and SCl_2 or S_2Cl_2, Fp_2 and elemental sulfur, and other methods. The X-ray structures of the tri- and tetrasulfides were determined[215].

Photochemical reaction of FpI with trialkyl phosphites gave $CpFe[P(OR)_3]_2I$[216]. γ-Radiolysis of FpCl or FpI at 77 K gave radical-anions with large hyperfine couplings to the halogens, indicating population of the Fe-X π^*-orbitals. Annealing appeared to give Fp· [217].

8c.Fp-Acyl, Alkyl, and Carbene Complexes

Carbonylation of $CpFe(CO)(PPh_3)Me$ to form the acetyl-Fe product is very strongly catalyzed by oxidizing agents; a mechanistic study has revealed that methyl migration is at least 10^7 faster in the oxidized Fe(III) species than in the Fe(II)[218]. Thermal reaction of FpMe with $RPPh_2$ (R contains an aza-crown ether grouping) gave the acetyl-iron product, whereas photoreaction gave the methyl-iron product. A comparison of binding constants for the two compounds implicated the acyl oxygen as a significant participant in cation binding[219]. Reaction of FpMe with $Ph_2PNRAlR_2$ proceeded as shown in eq. 30[220]. Further illustration of the Lewis base property of FpCOMe comes from the formation of stable $FpC(Me)O\text{-}Mo(CO)_3Cp^+$ salts (X-ray) from reaction of either FpMe or FpCOMe with $CpMo(CO)_3^+$ [221,222].



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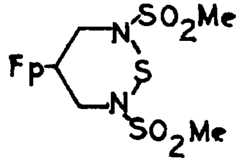
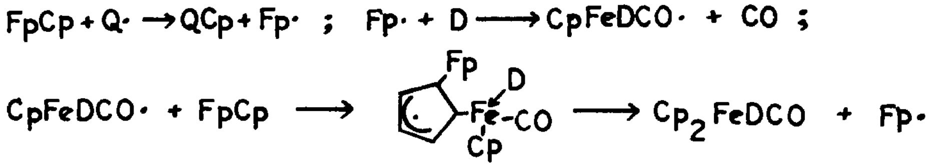
Below -20°, BF_3-promoted carbonylation of CpFe(CO)DMe [D = PPh_2NMe-(S)-CHMePh] proceeds stereospecifically, with methyl migration to the CO group[223]. Stereochemistry of CO insertion in optically active $CpFe(CO)(PR_3)Et$ derivatives has been found to depend on solvent: in nitromethane only formal alkyl migration was observed, but in HMP formal CO migration predominated[224]. Reaction of Me_3P with $CpFe(NO)Me_2$ resulted in methyl migration to the coordinated nitrosyl group, giving $CpFe(PMe_3)(ONMe)Me$[225].

Cycloaddition of $FpCH_2CH=CH_2$ with $MeSO_2N=S=NSO_2Me$ gives the novel 6-membered ring product 33, as verified by an X-ray structure[226].

33



Photochemical introduction of a phosphite ligand into $FpCH_2C(OMe)=CH_2$ enhances its reactivity in cycloadditions with electron-deficient alkenes, as expected from the accepted zwitterion mechanism[227]. FpCp enters readily into (metal-assisted?) Diels-Alder reactions, forming *syn*-7-Fp-bicyclo[2.2.1]heptene products (X-ray); Ce(IV) oxidation in methanol introduces an ester group in place of the Fp group, making FpCp a useful synthetic surrogate for 5-carbomethoxy-1,3-cyclopentadiene[228]. Reaction of FpCp with phosphines and phosphites results in ready CO substitution involving a radical chain mechanism:[229]

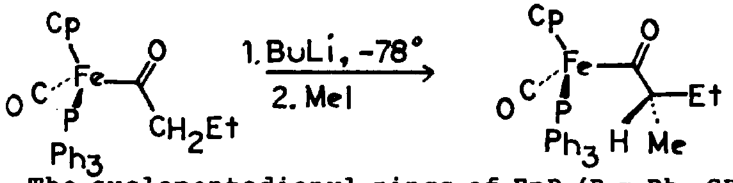


$$FpCp + Q\cdot \rightarrow QCp + Fp\cdot \;;\; Fp\cdot + D \longrightarrow CpFeDCO\cdot + CO \;;$$

$$CpFeDCO\cdot + FpCp \longrightarrow \;\cdots\; \longrightarrow Cp_2FeDCO + Fp\cdot \quad (31)$$

With PMe_3, the product was the ionic $CpFe(CO)(PMe_3)_2^+Cp^-$. $CpFe(CO)(PPh_3)COCH_2COR$ undergoes a similar heterolysis to the cation $FpPPh_3^+$ and the carbanion $RCOCH_2^-$ [230].

Carbamoyl complexes $CpFe(CO)(PMe_2Ph)CONHMe$ result from reaction of methylamine with $FpPMe_2Ph^+$[231]. Isoelectronic carbanions result from low-temperature deprotonation of the acyls $CpFe(CO)(PR_3)COCH_2R$[232-234]. Examples of C-alkylation, acylation, and aldol reactions of these carbanions have been reported. High diastereoselectivity was reported in alkylation reaction 32[234].



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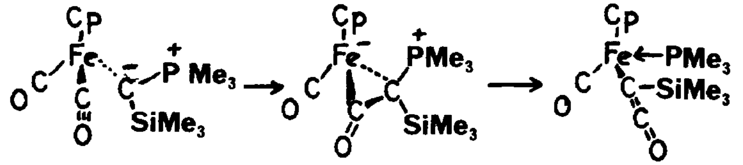
The cyclopentadienyl rings of FpR (R = Ph, CH_2Ph, Fp) underwent metallation with BuLi in THF at -78°, allowing preparation of alkylated and silylated derivatives[235]. Fp^- displaced a fluoride ion from octafluorocyclooctatetraene, giving FpC_8F_7[236]. X-ray structures of $FpCH_2C(=Y)Fc$ [Y = O[237] and $C(CN)_2$ [238]] have been reported.

Matrix photolysis of FpCOMe gave CpFe(CO)COMe, which still showed a η^1-acetyl group, despite its coordinative unsaturation[239]. Reduction of $FpCO^+$ with $NaBH_3CN$ gave $FpCH_2OH$, which decomposed to Fp_2 and formaldehyde when treated with phosphines[240]. Likewise, $NaBH_4$ reduction of $Fp'CO^+$ in methylene chloride gave $Fp'CH_2OH$[174]. $FpCH_2Cl$ gave phosphonium salts $FpCH_2PR_3^+$ on reaction with phosphines[241]. The stereochemical outcome of alkylation of chiral CpFe(D)(CO)CH_2Cl with prochiral nucleophiles has been examined[242].

$Fp'CO^+$ reacted with two moles of $Me_3P{=}CH_2$ to form the ylide $Fp'C(O)CH{=}PMe_3$, which could be alkylated at the ylide carbon[243]. Deprotonation of the phosphonium salt $FpCH(SiMe_3)PMe_3^+$, however, produced a ketenyl complex by rearrangement (eq. 33)[244].



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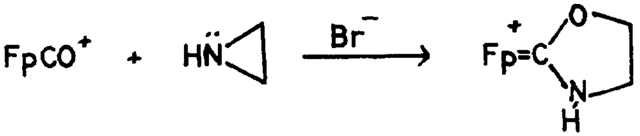
The acetylide complexes such as $CpFe(DPPE)C{\equiv}CMe$ are readily methylated to form vinylidene complexes $CpFe(DPPE)C{=}CMe_2^+$[245]. Methylation of the vinyl complexes $CpFe(CO)(PR_3)C(OMe){=}CH_2$ gave a mixture of carbene complexes $CpFe(CO)(PR_3){=}C(OMe)R^+$ having R = Me, CH_2Me, and $CHMe_2$, as a consequence of acid-base equilibria between vinyl and carbene complexes during reaction[246]. The vinyl complexes resulted from methylation and then deprotonation of acyls; $Fp'C(OMe){=}CH_2$ were also obtained in this manner[247].

Carbene complexes (derivatives of $FpCH_2^+$) have continued to draw intense interest. $FpCH_2^+$ itself has been shown to react with CO at -80° to give the ketene complex $Fp(\eta^2\text{-}CH_2CO)^+$[248]. New routes to alkylidene complexes or their precursors have been reported, including reaction of RLi with $FpCHOMe^+$[249], and borohydride reduction of O-methylated acyl-iron compounds[250]. The resulting α-methoxyalkyls are converted to reactive alkylidene complexes upon reaction with Me_3SiOTf at -78°. These rearrange on warming to the more stable alkene-Fp^+ ions; the ethylidene complex, however, gives $FpCH_2CH^+CHMeFp$). Generation of the alkylidene complexes in the presence of alkenes gives cyclopropanes[250,251]. Use of chiral $CpFe(CO)(PPh_2R)CHMe^+$ complexes gave high optical yields of chiral cyclopropanes[252].

Reactions of the thiocarbene complex $FpCHSMe^+$, **34**, with nucleophiles, especially phosphines[253] and amines[254], have been studied. Reaction of **34** with water gives $FpCO^+$ and $FpCH_2SMe$, via an intermediate formyl, FpCHO. **34** reacts with diazomethane to form $FpS(Me)CH{=}CH_2^+$[253]. $FpC({=}S)SFp$ and other $FpC({=}S)SML_n$ react with $M'(CO)_5(THF)$ (M' = Group VI metal) to form trimetallic species such as $FpC[SM'(CO)_5]SFp$; an X-ray structure for the example with M' = W was reported[255]. More conventional diheterocarbene complexes were obtained by reaction of $FpCO^+$ or $FpCS^+$ with aziridine[256]:



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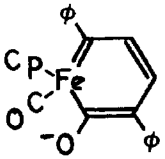
Reaction of FpI with 1,4-dilithio-1,4-diphenylbuta-1,3-diene gave the cyclic carbene complex **35**; reaction with trimethyloxonium fluoborate gave 1,3-diphenyl-2-methoxyferrocene[257]. Protonation of cyclooctatetraenyl-Fp at -40° gave the partially homoaromatic carbene complex **36**, which rearranged to Fp(COT)⁺ at 0° [258].

35



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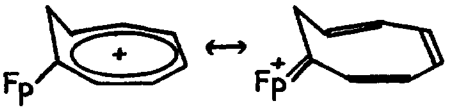
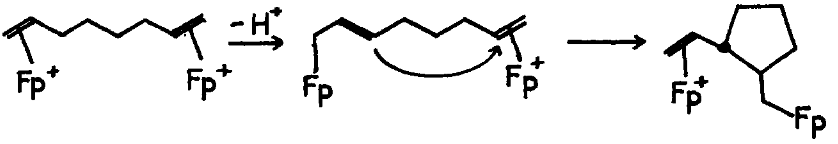


8d. Cyclopentadienyliron derivatives of η^2 to η^5 ligands

The tetrahydroindenyldicarbonyliron group has been transferred from its isobutylene complex to double bonds in dienes for use as a protecting group[259]. Decomplexation of styrene-Fp⁺ occurs upon treatment with tetrabutylammonium fluoride or hydroxide; styrene and Fp_2 result[196].

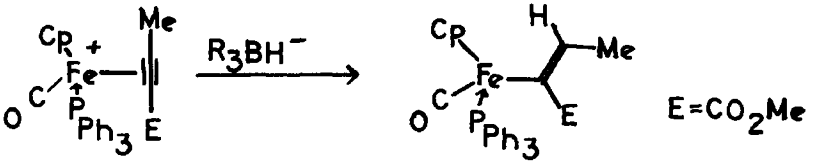
Dicationic bis(alkene) complexes result when the bridged dianion $Me_2Si[C_5H_4Fe(CO)_2^-]_2$ is treated consecutively with allylic chlorides then acid. Alkene exchange from the bis(isobutylene) complex to other alkenes proved unsuccessful[260]. Complexes $[FpCH_2CH{=}CH(CH_2)_nCH{=}CH_2]Fp^+$ (n = 4,3), which can be formed by deprotonation of the doubly complexed dienes or protonation of the bis-allyls, cyclize by attack of the nucleophilic Fp-allyl group on the electrophilic coordinated alkene (reaction 35); the stereochemical effects have been extensively investigated[261].



(35)

The stereochemistry of attack by prochiral nucleophiles on chiral $CpFe(CO)(PPh_3)(CH_2{=}CH_2)^+$ has also been studied[242].

Although attack of nucleophiles on (alkyne)Fp⁺ and related complexes generally gives the product with the nucleophile and the Fp group trans, an apparent exception has been reported:



(36)

Labelling studies revealed that the initial hydride attack was on the *exo* face of the cyclopentadienyl ring, after which the *endo* hydrogen was transferred to the coordinated alkyne[262]. Attack by organocuprates follows the more conventional pattern of *trans*-attack; in the case of coordinated 1-phenylpropyne, the nucleophile attacks the 1-carbon[263]

Reaction of $FpC(O)CH_3$ with MeLi then lithium tetramethylpiperidide results in inter-ligand bond formation, which gives the η^3-allyl dianion, $CpFe(CO)[CH_2C(O^-)CMeO^-]$, which can be acylated or silylated to form neutral η^3-allyls[264]. An X-ray structure of $[\eta^3$-$CH_2C(Fc)C(CN)_2]Fe(CO)Cp$ has appeared[238].

The pentakis(carbomethoxy)cyclopentadienyl anion coordinates Fe(II) with the carbonyl oxygens, not the cyclopentadienyl rings[265]. Reaction of $CpFe[\eta^5$-$B_9H_9CHCCHO]$ with vinylic Grignard reagents then acid gave allylic cations stabilized by the (cyclopentadienyl)(η^5-(3)-1,2-dicarbollyl)iron group[266]. A triple-decker sandwich compound, **37**, was formed in minor amounts from reaction of $CpCo[\eta^5$-$cycloC_2Et_2(BMe)_2CH]^-$ with FpI[267]. The isoelectronic **38** resulted from reaction of 1-phenyl-4,5-dihydroborepin with Fp_2[268]. Photoelectron spectra of several CpFe(cyclohexadienyl) complexes have been reported and interpreted[269].

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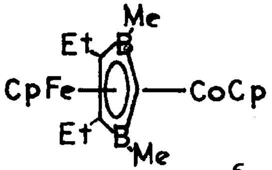

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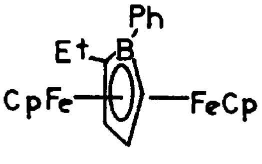


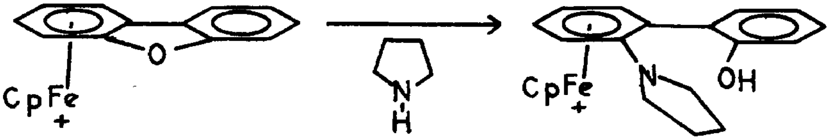
9. COMPOUNDS WITH η^6-TRIENE AND ARENE LIGANDS

A unique $Fe(CO)_2$ complex of a conjugated triene has been obtained, along with more conventional $Fe(CO)_3$ complexes, **20** and **21**, by reaction of dehydro-β-ionone with iron carbonyls (eq. 24), and also by reaction of **21** with HO_2^- in methanol. An X-ray crystallographic study verified the structure, and supported its formulation as a bis-(allyl)-$Fe(CO)_2$[129]. Photolysis of $Cp'Fe(CO)_3^+$ in the presence of cyclooctatetraene gave $Cp'Fe(\eta^6$-$COT)^+$ [204]. An η^6-cyclooctatriene complex, **39**, $(C_8H_{10})Fe(Et_2C_2B_4H_4)$ has been obtained from treatment of $FeCl_2$ with $C_8H_8^{-2}$ and $Et_2C_2B_4H_5^-$ in THF[270].

Theoretical studies of $CpFeAn^{+1}$ and their reduced, neutral forms have been reported[271,272]. The latter are well regarded as 19-electron species, since the added electron occupies an orbital 83% metallic in character[272]. Haptotropic rearrangements of the CpFe group in polycyclic arene complexes have received elegant theoretical treatment[273].

The arene group was readily displaced from $CpFeAn^+$ by three trimethylphosphite ligands, with reductive electron transfer catalysis[274]. Added salts hinder the reaction of $CpFeC_6Me_6$ with oxygen to give $CpFe(\eta^5\text{-}C_6Me_5CH_2)$[275]. Photolysis of CpFe(*p*-xylene)$^+$ in acetonitrile produces $CpFe(NCMe)_3{}^+$, which decomposes to ferrocene and Fe^{+2} at room temperature, and from which the acetonitrile ligands can be readily displaced by phosphines at -40° [276]. Quantum yields for xylene displacement are highly solvent and counterion dependent[277]. $CpFeAn^+$ groups have been attached to polymers for possible use as redox catalysts[278].

Reaction of Fp'Br and $AlCl_3$ with anthracene gave principally the $Cp'Fe^+$ complex of 1,2,3,4-tetrahydroanthracene, whereas FpCl gave the 9,10-dihydroanthracene complex[279]. The latter could be oxidized to CpFe(anthraquinone)$^+$ using $KMnO_4$, as could other methylene groups alpha to arene rings in $CpFeAn^+$ [280]. Nucleophilic ring opening (eq. 37) occurred readily with phenolate, but not thiophenolate or anilide, leaving groups[281]. The $CpFe^+$-complexed heterocycles were obtained by ligand exchange between ferrocene and the heterocycles; with excess ferrocene some dicoordinated products were also obtained[282].



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A CpFe complex of 1-phenyl-2-methylborabenzene was formed along with 38[268]. An $Fe(CO)_3$ complex results from reaction of 1,4-diferrocenyl-1,4-diboracyclohexa-2,5-diene with iron carbonyl; an upfield shift of the boron resonance relative to the free ligand implied η^6-coordination as a diborabenzene ligand[283]. MO calculations on the conformation and reactivity of bis(borabenzene)iron have been carried out[284].

The cyclooctatriene complex 39 reacted with arenes over $AlCl_3$ to give $(\eta^6\text{-arene})Fe(Et_2C_2B_4H_4)$[285], an example of which could also be obtained by reaction of iron atoms with toluene and 2,3-$Et_2C_2B_4H_6$[286]. Reaction of phosphorus nucleophiles with arene ligands in An_2Fe^{+2} has been studied[287]. Bis(paracyclophane)Fe^{2+} complexes have been prepared[288].

10. BIMETALLIC COMPOUNDS

a. Derivatives of nonacarbonyldiiron

Formation of $(bpy)Fe_2(CO)_7$ from bpy and $Fe_2(CO)_9$ does not occur by direct substitution, but rather through the intermediate $(bpy)Fe(CO)_3$, analogous to 8[289]. The compound $Ge[Fe(CO)_4]_4$ (2Fe-Fe) results on reaction of iron carbonyls with vinylgermanes[290] or with $Ge[=Mn(CO)_2(C_5H_4Me)]_2$[291]. Both papers have reported X-ray structures.

The most numerous group of organodiiron compounds related to nonacarbonyldiiron is those in which the three bridging carbonyl groups are replaced by bridging ligands (most commonly two) which contribute a total of six electrons to the $Fe_2(CO)_6$ cluster. If the two bridging atoms Y and Z are mutually bonded, a tetrahedral $YZFe_2$ cluster results; if not, a "butterfly" structure is formed.

A well-known simple example is the cluster compound $S_2Fe_2(CO)_6$, **40**, which has been the subject of Hartree-Fock-Slater calculations[292]. Multiphoton dissociation/ionization of **40** gave rise to species such as Fe^+, FeS^+, and $Fe_2S_{0-2}^+$ [293]. Insertion of styrene into the S-S bond of **40** to give **41** (R = Ph) has been reported[294]. Reaction of trimethylvinylsilane with S_8 and $Fe_3(CO)_{12}$ gave **40**, **41** (R = Me_3Si) (X-ray structure reported) and a number of cyclic sulfur compounds[295]. **40** reacted with alkynyllithium reagents with opening of the S-S bond; the resulting anionic species could be trapped with various electrophiles (RX, MeCOCl, MeHgCl) to yield **42** (Y = $PhC\equiv CS$; Z = MeS, MeC(O)S, MeHgS)[296]. X-ray structures of **42** (Y = Z = MeHgS) and the closely related $(\mu\text{-}MeHgS)_2Fe_2(NO)_4$ have been determined [297]. Reaction of trithia[3]ferrocenophane with $Fe_3(CO)_{12}$ gave **42** (YZ = $SC_5H_4FeC_5H_4S$)[298]. Ph_2PCl reacted with $Fe_3(CO)_9(\mu_3\text{-}SR)^-$ to give **42** (Y = RS, Z = Ph_2P) along with trinuclear products[299]. An analogous heterobridged product resulted from reaction of *ortho*-$C_6H_4(SH)(PHPh)$ with $Fe_2(CO)_9$; two-electron reduction opened the Fe-S bond rather than the Fe-Fe bond. Similar results were obtained for the dithia and diphospha analogs[300].

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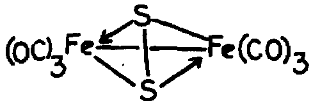

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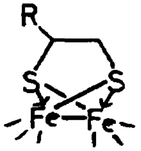

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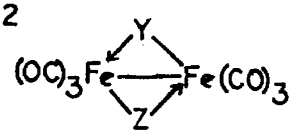
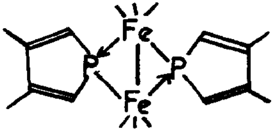


Reaction of $PhPCl_2$ with $Fe_2(CO)_9$ gave, in addition to the $Fe(CO)_4$ complex, two diiron hexacarbonyls **42** (Y = PhPCl; Z = Cl, PhPCl) whose crystal structures were determined[61]. Similarly, $CpMn(CO)_2PBr_3$ gave **42** [Y = Z = $P{=}Mn(CO)_2Cp$][301]. Symmetrical complexes **42** having phosphido and arsenido bridges have been obtained by reaction of iron carbonyls with appropriate diphosphines and diarsines. Thus, 3,3',4,4'-tetramethyl-1,1'-biphospholyl gave **43**, in addition to derivatives in which one or both rings were coordinated as dienes to $Fe(CO)_3$ groups[302]. And tetraphenyldiarsetene formed **44** upon reaction with $Fe_3(CO)_{12}$[303].

43



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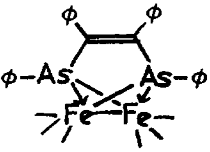
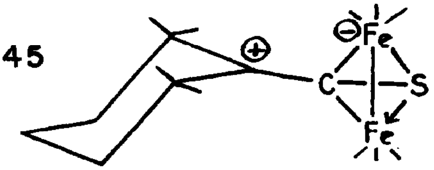
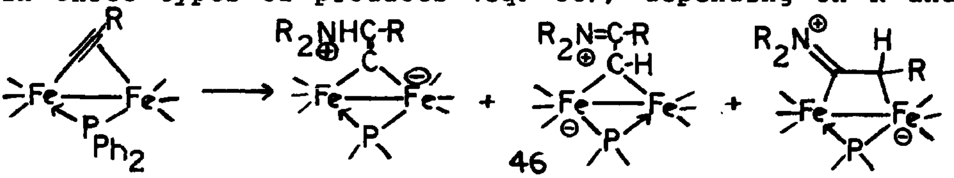


The symmetric (C_{2v}) isomer of **42** (Y = Z = MePH) has been isolated, and its nmr spectra extensively analyzed[304]. Reduction of the analog having diphenylphosphido groups, **42** (Y = Z = Ph_2P), with Et_3BH^- gave a species with one Fe-P bond ruptured, but further reduction gave the known (μ-$Ph_2P)_2Fe_2(CO)_6{}^{-2}$ with no formal Fe-Fe bond. Alkylation of the first species gave a product with a μ-acylbridge[305]. A P-P bond was introduced into **42** (Y = Z = Me_3CPH) by proton removal using MeLi, then oxidation with 1,2-dibromoethane. A crystal structure of the resulting diferradiphosphatetrahedrane was reported[306].

$Fe_2(CO)_6$ complexes with carbon in the bridge are of especial interest. Thioketene complex **45** (X-ray structure reported) added triphenylphosphine to an iron atom, with rupture of the Fe-C bond; photolysis restored the bond with loss of CO[307]. The reactions of the μ-η^2-acetylides **42** (Y = C≡CR, Z = PPh_2) with amines result in three types of products (eq. 38), depending on R and the amine[308]. The product **46** added a silver ion across the Fe-Fe bond (X-ray structure)[309].

45





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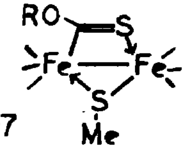
Displacement of CO from the μ-thioacyl complexes **47** by trimethylphosphite has been studied. Under thermal or electrochemical activation, displacement occurs most readily at the carbon-bearing iron atom[310,311], as supported by a crystal structure[312].

Two related instances of carbon-iron bond formation resulting from ylide generation in a bridge have been reported. Deprotonation of **42** (Y, Z = SCH_2S) with $LiNR_2$ followed by alkylation with bromoacetone led to the product **48** (R = CH_2COCH_3, in which an alkyl dithioformate functions as a 6-electron ligand. An isomer **49** was obtained by reaction of MeCOC≡CH with **42** (Y = Z = SH), and X-ray structures were reported for both **48** and **49**[313]. Similar

47



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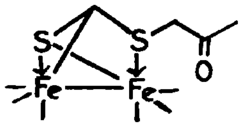

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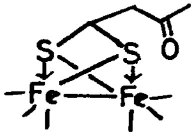
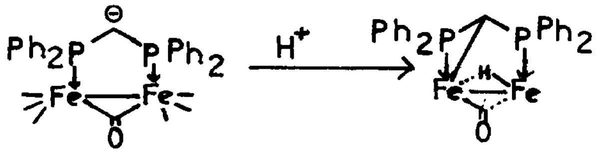


chemistry resulted from deprotonation of a μ-DPPM complex (eq. 39)[314]. Deprotonation of **48** (R = Me) followed by methylation produces a product analogous to **45**, but with a dimethylsulfonium cation rather than a carbenium ion adjacent to the tetrahedral $CSFe_2$ cluster[315] (X-ray structure).



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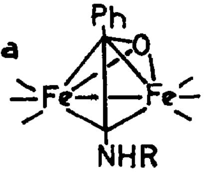
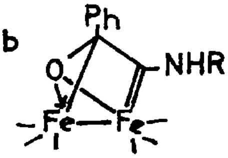
A curious structure was obtained by reaction of $(OC)_5Cr{=}C(COPh)NHR$ with $Fe_2(CO)_9$[316]. An X-ray structure was reported, and the result was represented as **50a**. Two of the Fe-C bonds shown in **50a** were, however, extraordinarily long (2.46 and 2.48 A); accordingly **50b** (which lacks these bonds and the consequent pentavalent carbon) may be a more satisfactory interpretation of the structure. In **50b** the ligand is shown as a ketocarbene. Reaction of 1,2,3-thiadiazoles with $Fe_2(CO)_9$ gave, along with similar thioketocarbene-$Fe_2(CO)_6$ complexes, a new type of thioketoimine complex, **51**, for which an X-ray structure was reported[317].

50a

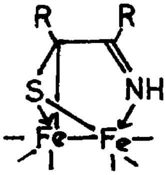


50b



The mass spectra of several types of product from reactions of iron carbonyls with imines and azines have been reported[318]. The products included **42** (Y = Z = N=C(R)Ar) and **52** (R = Ph), from reaction of PhCH=NPh with $Fe_3(CO)_{12}$[319]. **52** (R = Me_2CH) was also obtained by reaction of $Fe_2(CO)_9$ with $(OC)_5W{=}C(Ph)NHCHMe_2$[316].

51



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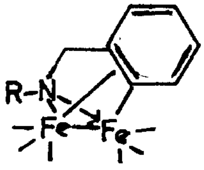
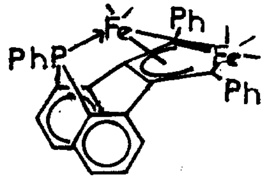


Mass spectroscopic investigations of the well-known ferrole complexes, in which a 1,3-butadiene-1,4-diyl ligand bridges the $Fe_2(CO)_6$ unit, have been reported[123,320]. A ferrole complex **53**

53



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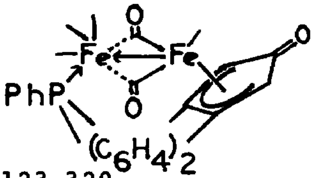
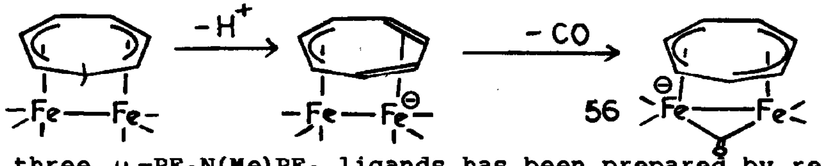


and a related product **54** were obtained upon reaction of $PhP(o\text{-}C_6H_4C{\equiv}CPh)_2$ with iron carbonyls[122]. Butatriene complexes, $(R_2C{=}C{=}CR_2)Fe_2(CO)_6$, were obtained as byproducts from reaction of $(RC{\equiv}CR)Co_2(CO)_6$ with $Fe(CO)_5$[321]. Reaction of 2-alkoxyfurans with $Fe_2(CO)_9$ gave ferracyclic products **55**[128].

Proton removal from (cycloheptatriene)$Fe_2(CO)_6$ gives a reactive anion, $C_7H_7Fe_2(CO)_6^-$, which forms fluxional **56** (X-ray structure) by facile decarbonylation (eq. 40)[322]. A $Fe_2(CO)_3$ complex bearing three μ-$PF_2N(Me)PF_2$ ligands has been prepared by reaction of the aminobisphosphine ligand with $Fe_3(CO)_{12}$ under photolytic conditions[62a].



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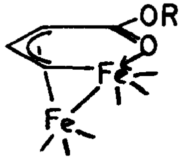

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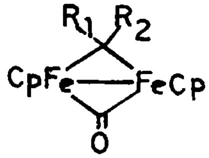
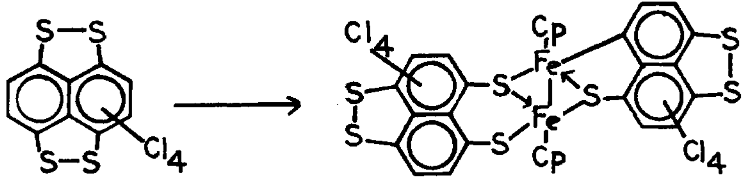


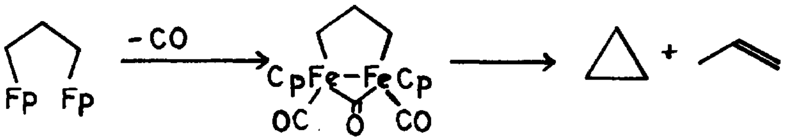
10b. Derivatives of Dicyclopentadienyldiirontetracarbonyl

Reaction of Fp_2 with a tetrachlorotetrathiolene (eq. 41) resulted in desulfurization and formation of an Fe-aryl bond[323].



(41)

Compound **57** (R_1 = R_2 = H) from Fp^- and $FpCH_2Cl$) yielded a small amount of propene on reaction with ethene at 350 psi and 150°. $Fp(CH_2)_3Fp$ gave an 80% yield of cyclopropane upon decomposition at 120°. A diferracyclopentane intermediate has been inferred in these reactions[324].



(42)

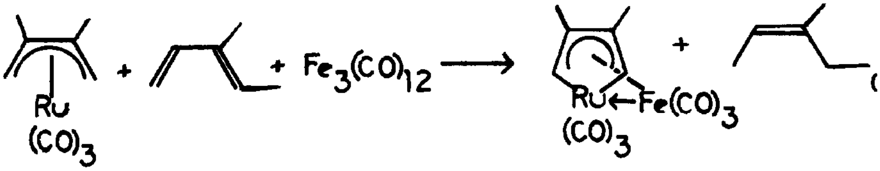
Reaction of Fp_2 with MeLi then trifluoroacetic acid at low temperature afforded the μ-vinylidene products (**57**, R_1,R_2 = $=CH_2$, which were reversibly protonated with HBF_4 to form the μ-ethylidyne cation[314]. Crystal structures of the μ-vinyl and -ethylidene (**57**, R_1 = H, R_2 = Me) have been reported[325]. The rates of rearrangement of the (μ-alkylidyne)$Fe_2(CO)_3Cp_2$ cations to μ-alkenyl cations were highly dependent on the alkyl substituents[326]. The μ-methylidyne cation further revealed carbenium ion character in electrophilic attacks on alkenes (eq. 42)[327]. μ-Alkenyl cations predominantly added H^- to the β-carbon on reduction by $NaBH_4$, giving μ-alkylidene complexes[328].

Reaction of CpFe(1,5-cyclooctadiene) with 2-butyne gave the electron-deficient, fluxional $Cp_2Fe_2(C_6Me_6)$, whose X-ray structure has been published[329].

10c. Heterobimetallic compounds

Reaction of toluene-solvated iron atoms with $Mn(CO)_5^-$ gave $FeMn(CO)_9^-$ [7]. $Me_2NP(H)Fe(CO)_4$ was attacked by $Mn(CO)_5^-$ to produce 58; similar reactions with other transition metals were also reported[330].

Reaction of 25 with $Ru_3(CO)_{12}$ (or of the analogous ruthenium complex with $Fe_3(CO)_{12}$) gave a ruthenole-$Fe(CO)_3$ complex (X-ray). Hydrogen was transferred to other unsaturated molecules[154]:

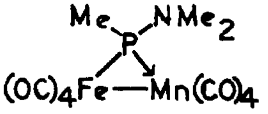


(43)

Similarly, reaction of the cobaltoles $R_4C_4Co(PPh_3)Cp$ with $Fe_2(CO)_9$ gave the CpCo-coordinated ferrole products[331].

An X-ray structure of $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$, from reaction of $Ph_2PFe(CO)_4^-$ and trans-$IrCl(CO)(PPh_3)_2$, showed a long (2.96 A) Fe-Ir bond[332]. Reaction of $(MeC{\equiv}CCH_2OH)Co_2(CO)_6$ with $Fe(CO)_5$ gave 59[321]. The neutral heterometallic compound $Fe(CO)_4(\mu\text{-vinyl})Co(CO)_3$ was obtained from reaction of $Fe_2(CO)_7(\mu\text{-vinyl})^-$ with dicobaltoctacarbonyl. Heating gave several trinuclear clusters[333].

58



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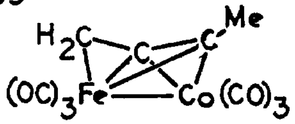


11. TRINUCLEAR CLUSTER COMPOUNDS

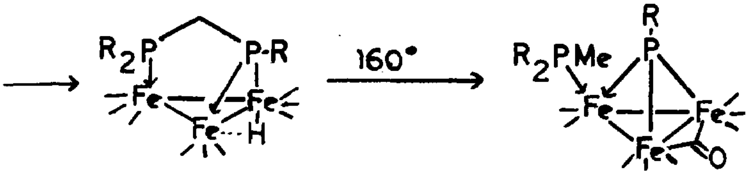
a. Triiron clusters

The dihydrides Cp_2MH_2 (M = Mo or W) reduced $Fe_2(CO)_9$ to form Cp_2MH^+ $HFe_3(CO)_{11}^-$ [334]. The interactions of the anion, triangulo-(μ-carbonyl)decacarbonyl(μ-hydrido)ferrate(1-), with cations and solvents have been studied by IR and by crystallographic study of the diisopropylammonium salt[335].

Acylation of a bridging carbonyl of $Fe_3(CO)_{11}^-$, followed by reductive cleavage of the acylate anion left $[Fe_3(CO)_9CCO]^{-2}$, whose X-ray structure showed the ketenylidene unsymmetrically bound to the Fe_3 cluster. The structure may be described as a carbide-carbonyl having a semibridging carbonyl joining the carbide carbon to one Fe. Reaction with electrophiles displaced the carbonyl to a Fe-Fe bridging position, forming [$Fe_3(CO)_{10}(\mu_3$-CE)]$^-$ (E = H, Me)[336]. The facile migration of the CO to and from the carbide provides an exceptionally apt model for Fischer-Tropsch chemistry.

Likewise, the [$Fe_3(CO)_9(\mu_3$-O)]$^{-2}$ dianion, which has been prepared and characterized[337], provides a model for a metal surface-adsorbed oxygen. The isoelectronic μ_3-NPh species has been implicated as an intermediate in reduction of nitrobenzene to aniline by polymer-bound $HFe_3(CO)_{11}^-$ [338]. Reaction of $Fe_3(CO)_{12}$ with NaSR resulted in formation of the trinuclear $Fe_3(CO)_9(SR)^-$, in which the sulfur functions as a five-electron ligand. The alkyl group R was readily displaced on heating in polar solvents, forming $Fe_3(CO)_9S^{-2}$ [339].

Reaction of diphosphines R_2PCH_2PHR with $Fe_2(CO)_9$ under vigorous conditions gave Fe_3 clusters in which the diphosphine ligand had undergone cleavage (eq. 44)[340]. $HFe_3(CO)_{11}^-$ reacts with ethene at room temperature to form a μ-acyl species **60** (R = Et), which gives ethane and propanal under 15 atm. hydrogen[341]. Protonation of **60** (R = Me) gives a neutral product with a μ-hydrido ligand bridging Fe(1) and Fe(2). Methylation forms **61** or **62** under slightly different conditions[342]. Two-electron reduction of **62** occurred with loss of methanol to give the acetylide complex **63**[343]. The related species (μ_3-η^2-RCCR)$Fe_3(CO)_9$ have been examined by CNDO calculations in connection with photoelectron spectra[344].



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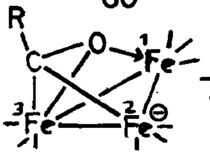

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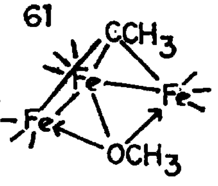

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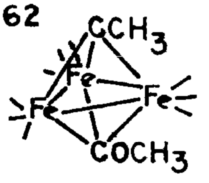

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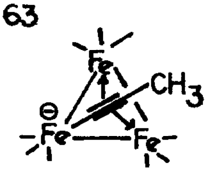
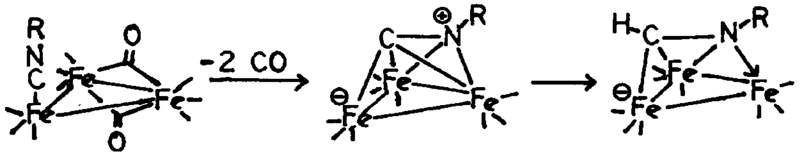


$Fe_3(CO)_{11}$(*ax*-NCR) lost CO on heating at 100°, with the isonitrile ligand assuming the role of a six-electron ligand (eq. 45); reduction with R_3BH^- occurred at the carbon[345]. The methoxymeth-



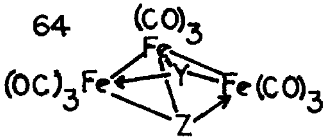
(45)

ylidyne cluster $HFe_3(\mu\text{-COMe})(CO)_{10}$ (from methylation of $HFe_3(CO)_{11}^-$) underwent reversible hydrogen addition to form the symmetrical product $H_3Fe_3(\mu_3\text{-COMe})(CO)_9$[346].

The vinylidene complex **57** (R_1, R_2 = $=CH_2$) formed the cluster $(CpFe)_3(\mu\text{-CO})_3(\mu_3\text{-CMe})$ on refluxing in dibutyl ether, or upon reaction with $Fe_2(CO)_9$, then with cyclopentadiene in refluxing toluene [347].

Syntheses and properties of the nido clusters **64** has received considerable attention during 1983. **64** (Y = Z = S) and their dihydro derivatives have been studied by photoelectron spectroscopy, as illuminated by theory[348]. Reduction of an analog of **64** having a dithiocarbene ligand in place of a terminal carbonyl has been studied[349]. The ditellurium cluster **64** (Y = Z = Te) has been prepared and used as a precursor to an extensive group of iron-tellurium clusters[350]. Reaction with $CpRh(CO)_2$ gave **42** [Y,Z = TeRh(Cp)(CO)Te] , which gave two isomeric hexacarbonyls on decarbonylation with Me_3NO[351]. The mixed clusters **64** (Y = S, Z = PR) were prepared by reaction of $RP(=S)Cl_2$ with $Na_2Fe(CO)_4$, and X-ray strctures for aryl derivatives were reported[352,353]. The sulfur atom in these complexes maintained sufficient Lewis basicity to form adducts with $M(CO)_5$ groups, where M = Cr, W[354]. Photolysis of **64** (Y = Z = PhP) in acetonitrile gave products with one or two acetonitrile ligands replacing CO's. An X-ray structure showed two basal CO's from the same iron atom to have been replaced[355].

64



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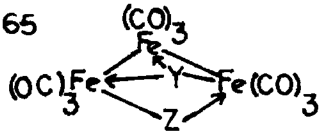
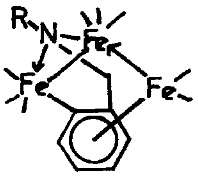


Reaction of the closo anion $Fe_3(CO)_9(\mu_3\text{-SR})^-$ with ZCl (Z = R_2Pn, RS, RSe) gave the reduced clusters **65** (Z as above, Y = SR)[299]. Reaction of **52** (R = PhCH=N-) with $Fe_3(CO)_{12}$ gave the open cluster **66**[356]. The novel linear triiron "cluster" **67** (X-ray structure) resulted from reaction of benzothiadiazole with $Fe_2(CO)_9$[357].

11b. Fe_2M Clusters

A linear trimetallic cluster, **68**, similar to **67** resulted from reaction of $Mo(SCMe_3)_4$ with $Fe_2(CO)_9$[358].

66



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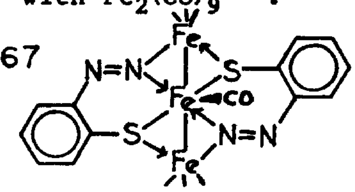

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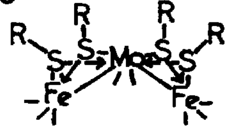
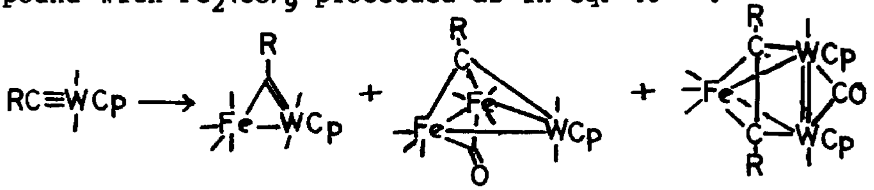


Reaction of PhC≡CM(CO)$_2$Cp (M Cr, Mo, W) with $Fe_2(CO)_9$ gave MFe_2 clusters with a 5-electron bridging alkynyl ligand, **69**[359].

The same type of product resulted from the less obvious reaction of $RC\equiv W(CO)_2Cp$ with $HFe_3(CO)_{11}^-$ [360]. X-ray structures were reported in both cases. Reaction of the alkylidyne-tungsten compound with $Fe_2(CO)_9$ proceeded as in eq. 46[361].



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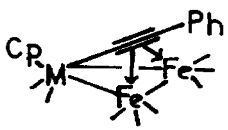
Reactions of the cluster 70 with various 2-electron ligands occurred with reversible opening of a Fe-Mn bond[362]. Reaction of the vinylidene complex 57 (R_1, R_2 = $C{=}CH_2$) with $Mn_3(\mu\text{-}H)_3(CO)_{12}$ gave $(CpFe)_2Mn(CO)_3(\mu_3\text{-}CMe)(\mu\text{-}CO)_3$[347]. A Fe_2Co cluster, 71,

69



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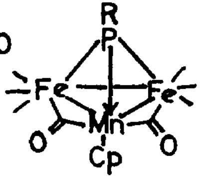

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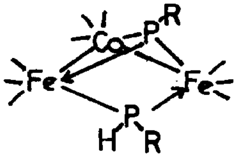

resulted from reaction of $Fe_2(CO)_6(PHR)_2$ with $Co_2(CO)_8$[363]. The mixed cluster $Fe_2Rh(CO)_{11}^-$ was the initial product from reaction of $Rh_2(CO)_4Cl_2$ with $HFe(CO)_4^-$, but reacted further to form higher clusters[364]. The Pt-bound CO in $Fe_2(CO)_8[\mu\text{-}Pt(PPh_3)CO]$ was readily replaced by phosphites and other 2-electron ligands[365].

11c. FeM_2 clusters

Mueller and Vahrenkamp have published four papers during 1983 dealing with synthesis of trimetallic clusters bearing μ_3-PR phosphinidene caps[330,366-368]. The tetrahedral clusters reported included examples with $Co(CO)_3$, $Ru(CO)_3$, $Mn(CO)_4$, $Cr(CO)_2Cp$, and other apical metal groups, in addition to the $Fe(CO)_3$ and PR groups. Metals could be exchanged into existing clusters; for example, a $Co(CO)_3$ group in $FeCo_2(CO)_9(\mu_3\text{-}PR)$ could be replaced by a CpNi group upon reaction with $(CpNiCO)_2$[368].

Photoreaction of multiply-bonded $[CpCr(OR)_2]_2$ with $Fe(CO)_5$ gave the Cr_2Fe cluster 72[369]. An X-ray structure of $FeRu_2(\mu\text{-}OH)_2(CO)_8(PPh_3)_2$ has been published[370].

Exchange of a CpFeCO group for a $Co(CO)_3$ group in (alkylidene)$Co_3(CO)_9$ clusters has been achieved using $HgFp_2$, with electron-transfer catalysis[371]. The analogous imido cluster, $FeCo_2(\mu_3\text{-}NH)(CO)_9$, (X-ray) resulted from reaction of $FeCo_3(CO)_{12}^-$

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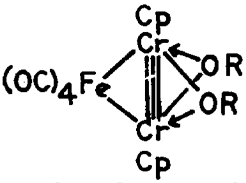
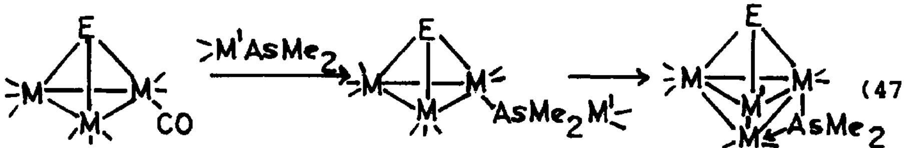


with NO^+ [372]. A $(OC)_3Fe(CoCp)_2$ cluster capped with two PhC ligands has been characterized by X-ray crystallography[373]. A Pt_2Fe cluster compound resulted from reaction of $[(DPPM)PtCl]_2$ with $Na_2Fe(CO)_4$, as did an analogous PdPtFe compound[374].

12. TETRA- AND POLYNUCLEAR CLUSTER COMPOUNDS

The reactions of hydrogen with a variety of previously characterized cluster compounds containing alkyne and vinylidene ligands, and including Ru, Os and Ni in the cluster in addition to Fe, have been studied. Results included hydrogenation of the ligand and disruption of the cluster[375].

Many new tetranuclear tetrahedral clusters have been prepared by a general process summarized in eq. 47. The parent trinuclear clusters included examples with $FeCo_2S$, $FeCo_2PR$, FeCoMoS, and FeCoWS cores. M' was either CpMo(CO) or CpW(CO) . X-ray crystallography was used to characterize the CoFeMoWS and Co_2FeMoS cluster products, and ligand fluxionality was examined[376].



(47)

Two isomeric $Fe_2(CpMo)_2S_2(CO)_8$ clusters resulted from reaction of **40** with $Cp_2Mo_2(CO)_4(Mo\equiv Mo)$. Each is composed of two $FeMo_2S$ tetrahedra sharing the Mo-Mo edge; they differ in the stereochemical orientation of the two tetrahedra[377]. A discussion in the context of electron-counting emphasized that the bitetrahedral structures are electron-precise, in contrast to a hypothetical octahedral isomer, which would be electron-deficient[378]. An analogous compound $[(MeC_5H_4)MoS_2Fe(CO)_3]_2$, having two additional μ_3-S ligands in place of two μ -CO ligands, was obtained by reaction of $[(MeC_5H_4)Mo(\mu\text{-S})(\mu\text{-SH})]_2$ with $Fe(CO)_5$ and Me_3NO[379].

A Fenske-Hall calculation of $HFe_4(CO)_{12}(\eta^2\text{-CH})$ has provided a rationale for the tilted orientation of the CH moiety[380]. The isoelectronic $HFe_4(CO)_{12}BH_2$ has been prepared and characterized crystallographically. Two strong Fe-H-B three-center interactions involving the "wingtip" irons of the Fe_4 butterfly were indicated[381]. Octahedral clusters having two ArP groups capping square planar $Fe_4(CO)_{12}$ or $Fe_2Co_2(CO)_{11}$ arrays were obtained by treating $Fe_2(CO)_6(PHR)_2$ with $Fe_3(CO)_{12}$[363]. $(CpFeCO)_4$ formed a stable adduct with an alumina surface[382]. Mossbauer spectra of many polynuclear iron clusters, including $FeRu_3$, Fe_4[382], Fe_5C, Fe_5N, and Fe_6C clusters, have been reported [383,384]. Rates and equilibria in deprotonation of $H_4FeRu_3(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$, including pK_a's, have been reported[385]. Reaction of $RuCo_2(CO)_{11}$ with the capping reagent $FpC\equiv CPh$ gave the product 73[386]. Fluxionality of the carbonyl ligands in $HFeCo_3(CO)_{12}$, **74**, and its conjugate base has been examined with use of ^{13}CO-enriched material[387]. **74** reacts with alkynes in hexane to give $FeCo_3(CO)_9(RCCR)(RCCHR)$, whose structure has been determined. In acetone or other polar solvents, $FeCo_2(CO)_9(RCCR)$ was the predominant product[388]. The μ-vinyl complex 57 (R_1,R_2 = $=CH_2$) affords compound 75 on reaction with $Co_2(CO)_8$[347]. Several new Fe-Rh anionic carbonyl clusters

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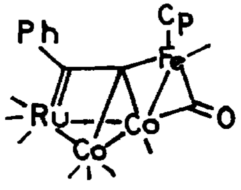

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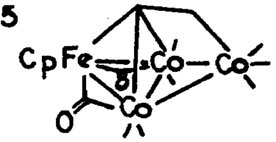
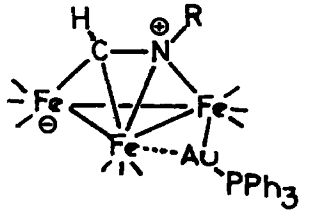


have been prepared, and their fluxional properties examined[364]. The product $Fe_2Rh_2(\mu\text{-}PPh_2)_4(CO)_8$ (from reaction of $Fe(CO)_4PPh_2H$ with $Rh_2(C_3H_5)_4Cl_2$) showed an unusual linear Fe-Rh-Rh-Fe structure[389].

Cluster expansion and contraction reactions of $(CpNi)_2Fe_2(CO)_6(C_2Ph_2)$ have been studied[390]. The Fe_3 cluster anion shown in eq. 45 underwent auration with Ph_3PAuCl to give **76**, in contrast to the protonation result[391]. The structures of $[Fe(CO)_4Au_2(DPPM)]_2$ and $[Fe(CO)_4Au_2(DPPE)]_2$ differed significantly, the former showing a Au_4 rhomboid with two μ-$Fe(CO)_4$ bridges, and the latter isolated Au_2Fe triangles[392]. $SFe_3(CO)_9{}^{-2}$ underwent auration to give 77[392].

76



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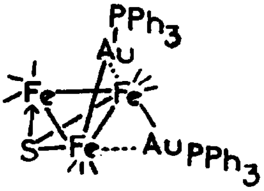

POST-SCRIPT Insofar as the list of references to this 1983 survey represents publication habits in the field of organoiron chemistry as it is currently practiced, it may be of interest to note that, of about 400 references, J. Organometal. Chem. (95 citations), Organometallics (70), and Inorg. Chem. (50) together account for more than half of the published work. Next in order come J. Am. Chem. Soc. (44), J. Chem. Soc., Dalton Trans. (28), J. Chem. Soc., Chem. Comm. (17), and Angew. Chem. (14), followed by many others.

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