ORGANOIRON CHEMISTRY
Annual Survey for the Year 1986*

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* 1985 Survey: J. Organometal. Chem. **318** (1987) 157-229.

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LIST OF ABBREVIATIONS USED

acac	acetylacetonate, $(MeCO)_2CH^-$
An	any arene ring, such as benzene, C_6H_6
Ar	an aryl ring, such as 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
DMF	N,N-dimethylformamide
DMPE	1,2-bis(dimethylphosphino)ethane
DMPM	bis(dimethylphosphino)methane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPM	bis(diphenylphosphino)methane
Et	ethyl, C_2H_5-
Fp	cyclopentadienyldicarbonyliron, $CpFe(CO)_2-$
Fp'	cyclopentadienyl(carbonyl)(triphenylphosphine)iron
Fp*	(pentamethylcyclopentadienyl)dicarbonyliron
Ft	the tricarbonyliron group, $Fe(CO)_3$
HMP	hexamethylphosphorictriamide
L	a 2-electron donor ligand such as a phosphine
LAH	lithium aluminum hydride
M	any transition metal
Me	methyl, CH_3-
MTHF	2-methyltetrahydrofuran
NMP	N-methyl-2-pyrrolidone
Ph	phenyl, C_6H_5-
Por	any porphyrin ligand coordinated as a dianion
PPN^+	$Ph_3P=N=PPh_3{}^+$
R	any unicovalent organic group such as methyl
TCNE	tetracyanoethene
Tf	trifluoromethanesulfonyl group, F_3CSO_2-
THF	tetrahydrofuran
X	any halogen

1. INTRODUCTION

In this Annual Review, I attempt to cover the organoiron chemistry reported in journals published during calendar year 1986. Organoiron compounds are those compounds which contain at least one C-Fe bond; however Fe-CN compounds are not included in this review, and properties and reactions of the simple iron carbonyls are not described exhaustively. Ferrocenes are treated in Annual Surveys by B. W. Rockett and G. Marr.

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

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

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

2. REFERENCE WORKS

Parts B10 and C7 of the current (8th edition) Gmelin organoiron series have appeared during 1986. These exhaustively cover (trimethylenemethyl)$Fe(CO)_3$ and (η^3 + η^1)$Fe(CO)_3$ complexes and compounds with two π-bound ligands (Part B10)[1] and polynuclear clusters from $Fe_3(CO)_{12}$ on up (Part C7)[2].

3. REACTIONS OF "NAKED" IRON ATOMS AND IONS

In this section, I discuss reactions of Fe^+ and lightly ligated derivatives in the gas phase, as well as matrix reactions of iron atoms.

Reactivity of Fe^+ toward dihydrogen, to form FeH^+ and H•, has been found to depend heavily on the electronic state of the ion. Fe^+ in the ^6D ground state ($4s^13d^6$) is only one-eightieth as reactive as in the ^4F ($3d^7$) state, which lies 0.25 eV higher in energy[3]. Fe^+ (state not specified) underwent insertion into C-C bonds of alkanes up to decane; reactivity of a particular bond was found to correlate inversely with the ionization potentials of the two radicals formed by breaking the bond[4]. With alcohols, Fe^+ reacted by C-O insertion (dehydration), C-H or O-H insertion (dehydrogenation), and C-C insertion[5]. The latter predominated with alcohols $>C_5$, but dehydration won out with ethanol, propanol, and tertiary alcohols. Decarbonylation of acetaldehyde by Fe^+, to form $FeCO^+$ and methane, has been studied by crossed-beam methods[6]. Reaction of Fe^+ with organosilanes gave, *inter alia*, $Fe{=}SiH_2^+$. Insertion into the Si-Si bond of hexamethyldisilane also was postulated[7].

Photodissociation of organic ions $Fe\text{-}Y^+$ (Y = C, CH, CH_2, CH_3, O, S, V, C_6H_6, and C_4H_6) in the gas phase has been studied, allowing estimation of the bond energies in these species[8]. The bond energies, D^o, for $Fe^+\text{-}CH_2$, -CH, and -C were found to be 82(5), 101(7), and 97(7) kcal/mol. The value for the iron-methylene bond is lower than the earlier value of 96(5) kcal[9]. Ab initio calculations on $Fe\text{-}H^+$ led to a bond length of 1.65 A and a bond energy of 48 kcal/mol, to be compared with experimental values of about 56 kcal[10]. Calculations on $Fe\text{-}Cl^+$ indicated a sigma-bonded species; experimental studies showed it to be unreactive toward saturated hydrocarbons[11]. $FeOH^+$ reacted with branched alkanes and with hexane (though not with simpler hydrocarbons) predominantly by C-H insertion and loss of water. Cyclopropane and cyclobutane reacted with C-C insertion[12]. FeS^+ gave alkene complexes, by C-H insertion followed by H_2S loss, upon reaction with hydrocarbons. D^o (Fe^+-S) was estimated to be 65 kcal/mol[13].

Metal dimers and trimers, including Fe_2^+, $FeCo^+$, and $FeCo_2^+$, were found to abstract oxygen atoms from ethylene oxide, giving oxide clusters $M_2O_2^+$ and $M_3O_3^+$. Carbonylated clusters such as $Fe_2(CO)_4^+$ similarly formed oxide clusters upon reaction with dioxygen[14]. $FeCO^+$ formed FeC_nH_{2n-2} products (n = 3-8) upon reaction with alkynes and dienes in the high-pressure source of a tandem mass spectrometer. Structures were postulated based on comparison of collisionally activated fragmentation patterns with those from reference alkynes and dienes[15].

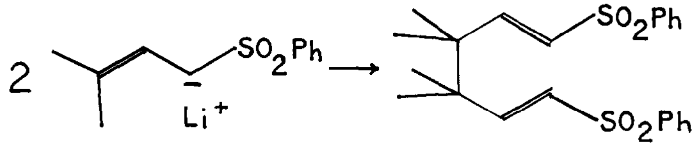
Addition of alkenes to iron atom-C_2D_4 matrices at 77 K resulted in exchange of D into the alkenes, apparently by addition of Fe-D species to double bonds, followed by bond rotation and elimination of Fe-H species[16]. A reactor has been described which allows direct synthesis of $Fe_3(CO)_{12}$ in gram quantities by reaction of iron atoms with CO[17]. Condensation of iron atoms with NO gave $Fe(NO)_4$ as the major product, with $Fe(NO)_3$ also detectible[18]. Reaction of iron atoms with CS_2 gave an adduct for which a linear FeSCS structure was favored; the initial adduct decomposed to FeS and CS upon warming[19]. $Fe(C_6H_6)$, $Fe_2(C_6\ H_6)$, and $Fe(C_6H_6)_2$ resulted from co-condensation of Fe atoms with benzene in argon matrices at 14 K. Analogous cyclohexadiene adducts gave FeH_2 and benzene on photolysis[20].

4. COMPOUNDS WITH η^1-CARBON LIGANDS

a. Hydrido-, Alkyl-, and Aryliron Compounds

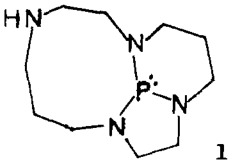
The species $[(bpy)_2FeH_2?]$ which result from reaction of $Fe(acac)_3$ with tri-isobutylaluminum in the presence of ligands such as 2,2'-bipyridyl, which catalyze polymerization of butadiene, have been studied by uv-visible spectroscopy[21]. The configuration of the polymers and the mechanism of the polymerization have been discussed[22].

$FeCl_3$-DMF caused coupling of lithium salts of allylic sulfones, to form principally 1,6-disulfones (Eq. 1)[23]. $Fe(RCOCHCOR)_3$ (R = Ph or t-butyl) were the most effective catalysts for coupling secondary alkyl Grignard reagents with 1-bromo-2-(phenylthio)ethene without rearrangement of the alkyl groups[24].



(1)

Polymerization of active alkenes was initiated by the product(s) of reaction of $[Fe(NO)_2Cl]_2$ with $AgBF_4$ in the presence of phosphines. ESR and IR studies indicated the catalytic species to be radical-cations such as $Fe(NO)_2L_3^+$ (L = phosphine, THF, or $MeCN$[25]. A number of stable $L_2Fe(NO)_2$ species have been reported, having L = PPh_2H or PPh_2R (from protonation or alkylation of (μ-$PPh_2)_2Fe_2(NO)_4$ anions)[26], and L = **1** (from displacement of both

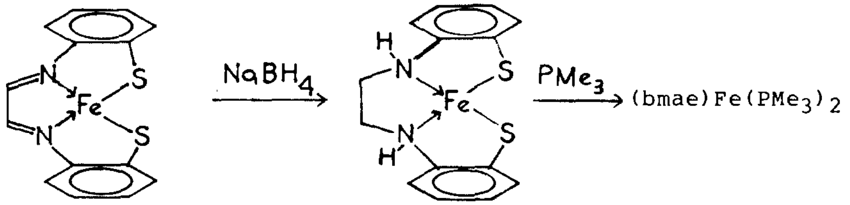


1

CO's from $Fe(CO)_2(NO)_2$ by the phosphine)[27]. The crystal structures of $(ON)_2Fe[PhP(OCH_2CH_2)_2\ddot{N}H]_2$ and its bis-BPh_3 adduct, which show different conformations in the eight-membered rings, have been reported[28]. Reaction of $Fe(NCMe)_6(BF_4)_2$ with DPPE and related triphosphines gave chelates such as $(DPPE)_2Fe(NCMe)_2(BF_4)_2$, which were studied electrochemically[29].

The compounds $[\textit{o}\text{-}C_6H_4(PMe_2)_2]_2FeCl_2(BF_4)_n$ (n = 0, 1, 2) have been studied by EXAFS, which indicated that the Fe-Cl bond lengths decreased with increasing charge, while the Fe-P bond lengths increased[30]. The crystal structures of *cis*-$[P(CH_2CH_2CH_2PMe_2)_3FeX_2$ (X = Cl, Br, I) have been reported[31]. The halides in these compounds have also been replaced by pseudohalides (CN, N_3, and NCS); reduction of the dihalides with LAH gave the halohydro derivatives, (tetraphosphine)FeHX[32]. The UV photoelectron spectra of $Fe(PF_3)_5$ have been reported[33].

Coordinatively unsaturated, insoluble (bmae)Fe was obtainable as shown in Eq. 2; it readily added ligands as shown, but



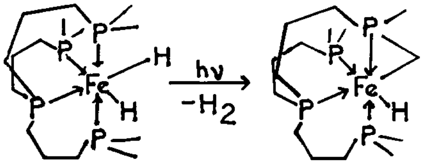
(2)

was not reduced by sodium in liquid ammonia[34]. $(C_6H_{11}N{=}CH\text{-}CH{=}NC_6H_{11})_2Fe$ reacted with dimethyl acetylenedicarboxylate with formation of a ferrole complex, which catalyzed trimerization of acetylenedicarboxylate esters[35].

Whereas protonation of $(DPPE)_2FeHCl$ with Tf_2CH_2 gave free hydrogen and $(DPPE)_2FeCl^+$, $(DPPE)_2FeH_2$ gave $(DPPE)_2Fe(\eta^2\text{-}H_2)H^+$, from which the hydrogen was readily displaced by Me_3P[36]. Another "nonclassical" hydride structure has been found, by means of IR and T_1 measurements on $(R_3P)_3FeH_2(\eta^2\text{-}H_2)$ (R = ethyl, phenyl)[37]. Reaction of the "classical" dihydride $H_2Fe[P(OEt)_3]_4$ with ArN_2^+ at -80° gave $L_4FeH(HN{=}NAr)^+$, **2**, and $L_4Fe(HN{=}NAr)_2^{2+}$. Reaction of the latter with triethylamine gave $ArN{=}N{=}FeL_4^+$, which was characterized by X-ray crystallography. The N=Fe bond length was 1.67(1) Å, in contrast to 1.91(1) Å for 2[38].

Photochemically-induced dissociation of H_2 from L_4FeH_2, to form unsaturated L_4Fe species, has received increased attention during 1986. $(DMPE)_2Fe$ and $(DPPE)_2Fe$, generated by this method, underwent oxidative addition to a C-CN bond of TCNE, forming $(DMPE)_2Fe(CN)[C_2(CN)_3]$[39]. The analogous DEPE species (DEPE = $Et_2PCH_2CH_2PEt_2$) reacted with ethene at low temperatures by C-H bond insertion and by π-complex formation. At room temperature the vinyl hydride complexes isomerized to the π-complex[40]. Similar results were reported for $(DMPE)_2Fe$ and other alkenes and arenes[41].

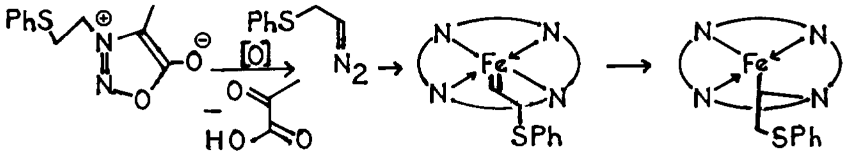
$(DEPE)_2Fe$, formed by reaction of $(DEPE)_2FeHCl$ with Me_2Mg, followed by reductive elimination of methane, underwent reversible oxidative addition to an α-CH bond of an ethyl group[42]. The tetradentate ligand shown in Eq. 3 behaved similarly[43]. A model for the sort of intermediate likely to be involved in these oxidative additions may be found in the X-ray structure of *trans*-$(DMPE)_2FeH(H{\cdots}BH_3)$, which showed an unbridged Fe-H distance of 1.69 Å, and bridged distance of 1.72 Å, and a H---B distance of 1.14 Å, with the Fe-H---B angle 162°[44].



(3)

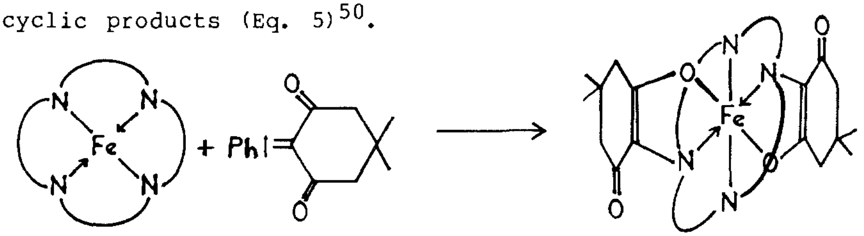
Reduction of (Por)Fe in the presence of alkyl halides resulted in alkylation at the iron. No ring alkylation was observed[45]. σ-Alkyl and -aryliron(III)porphyrins have been studied by Raman spectroscopy, with the conclusion that the iron remained pentacoordinated under all conditions, and that different spin systems (S = 5/2 and 1/2) were present[46]. However, proton NMR studies of low-spin (S = 1/2) (Por)FeAr complexes indicated that imidazoles added to the sixth coordination site of the iron at -60°, and analogous resonances in the spectrum of arylmyoglobin indicated coordination of the histidine imidazole in that species as well[47].

Oxidation of (Por)FePh with bromine at -60° produced the Fe(IV) species, characterized by NMR, which rearranged at room temperature to the iron(II) N-phenylporphyrin[48]. An analogous process has been proposed to account for inactivation of cytochrome P-450 during oxidation of an (arylthio)ethylsydnone (Eq. 4)[49].



(4)

In a related reaction, iron(II) tetraarylporphyrins reacted with an iodonium ylide by bis N-alkylation with formation of metallacyclic products (Eq. 5)[50].

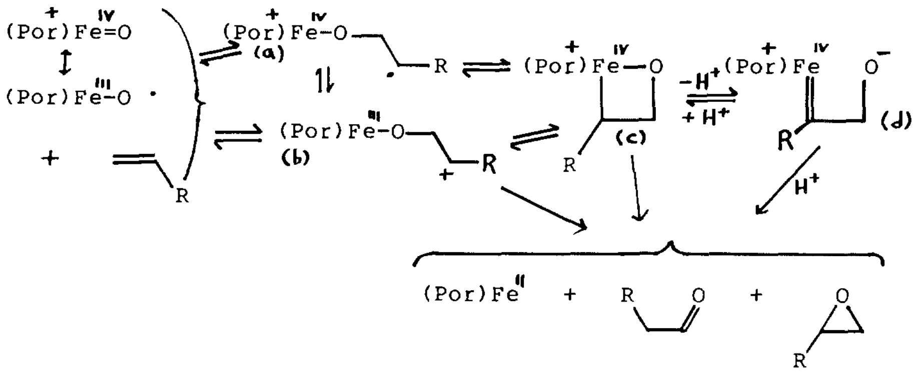


(5)

The mechanism of cytochrome P450-catalyzed alkene oxidations has continued to attract attention. What appears to be generally accepted is the intermediacy of a [(Por)Fe=O]$^+$ species. Extended Hückel calculations on interaction of this species with ethene have suggested a radicaloid reactivity in forming a C-O bond to the alkene[51]. What is of particular interest from the perspective of this review is the question whether a ferraoxetane (c in Scheme I) forms. Collman et al., based on deuterium labelling studies using synthetic porphyrin models, favored formation of the epoxide from the ferraoxetane and the aldehyde from intermediate (a)[52]. Traylor et al. have reported studies of rearrangements in oxidation of cyclooctene and norbornene and favor carbocationic intermediates (b), with little role for (c)[53,54]. Groves et al. have detected an intermediate which may be (c) or a π-complex[55]. Based on hydrogen exchange with solvent during oxidation of propene by actual cytochrome P-450, they have further suggested a carbene intermediate (d)[56]. Such an intermediate would also account very neatly for the formation of N-alkylated byproducts as in Eq. 4.

SCHEME I

Possible Intermediates in Alkene Oxidations by Oxoporphyrins



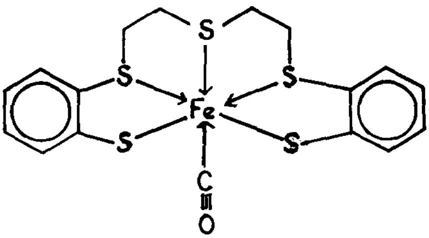
b. Iron Monocarbonyls, e.g. $L_4Fe(CO)$

The majority of such compounds are (Por)FeCO derivatives, studied in connection with binding of CO and O_2 to natural heme systems. The effect of trans-axial phosphine and phospite ligands on such binding in protoporphyrin IX dimethyl ester and in a number of porphyrin models has been studied. With tributyl phosphite, CO binding increased in the order phthalocyanine < dimethylglyoxime < heme[57]. Diamagnetic (Por)FeCNC(=O)R (R = Ph, t-butyl) complexes have been prepared, and the binding of the acyl isocyanide found closely to resemble that of CO; various trans-ligands included pyridines, N-methylimidazole, and tetrahydrothiophene[58]. The effect of thiolate trans ligands (models for the cysteinate trans ligand in P-450) in various heme CO complexes has been studied: CO affinities increased with decreasing porphyrin basicity and with increasing thiolate basicity[59]. Iron-sulfur distances in such complexes have been studied by EXAFS, with the result that RS-Fe distances averaged about 2.33 Å and $R_2S \rightarrow Fe$ distances about 2.40 Å[60].

Synthetic model porphyrins have continued to be elaborated, in order better to understand such factors as strain in the iron-imidazole linkage and cooperativity in CO binding. Examples of current efforts in this area include compounds **3**-**7**[61-65], shown on the next page.

Compound **8** was a key intermediate in the synthesis of hexathiodibenzo[18]crown-6, formed by reaction of **8** with $S(CH_2CH_2Br)_2$, then decomplexation with conc. HCl[66]. Trans-$L_4FeX(CO)^+$ salts [L = trimethyl- and triethylphospite and $PhP(OEt)_2$] have been prepared[67]. Reduction with zinc in acetonitrile gave the hydride analogs. Trans-$[(EtO)_3P]_4FeH(CO)^+$ Ph_4B^- was characterized by X-ray crystallography. It reacted with aryldiazonium cations to give aryldiazene complexes, $ArN{=}NH \rightarrow FeL_4(CO)^{2+}$, from which the diazene ligands were readily displaced by ketones, nitriles, and the like[68].

$Fe(CO)(NO)_2(\eta^2\text{-}H_2)$ was generated by photolysis of $Fe(CO)_2(NO)_2$ in a xenon matrix under 10 atm of hydrogen[69].



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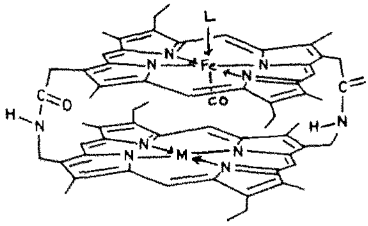
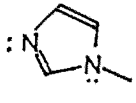
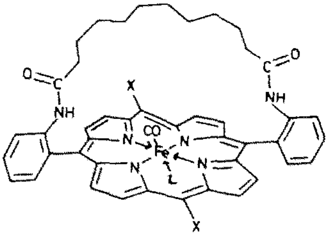


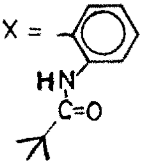
3[61] M = Fe, Cu, H_2

L =

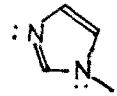


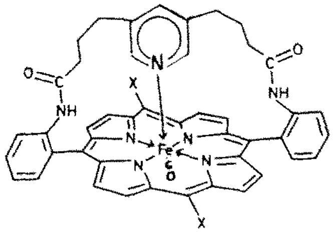


4[62] X =

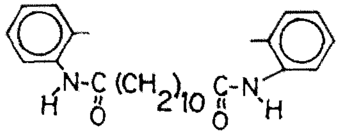


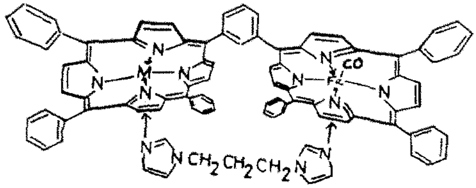
L =



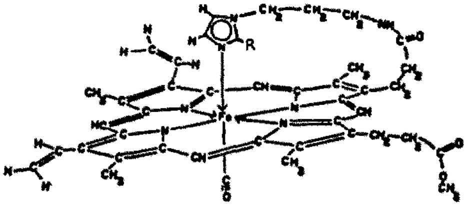


5[63] X~X =





7[65] M = Fe, Zn



6[64] R = H, Me

c. Iron Dicarbonyls, e.g. $L_3Fe(CO)_2$

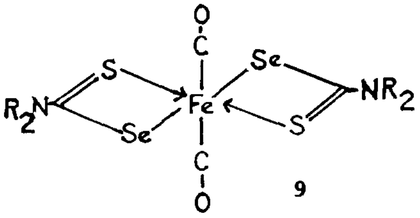
Flowing afterglow studies of $Fe(CO)_2^-$ have revealed addition of hydrogen, to form $(OC)_2FeH_2^-$. Reaction with water gave oxidative addition and CO loss; H_2S and PH_3 likewise gave $(OC)Fe{=}S^-$ and $(OC)Fe{=}PH^-$, respectively[70].

Reaction of a heterocyclic diazonium cation with $(Ph_3P)_2$-$Fe(CO)_3$ gave the cation $ArN{=}\overset{+}{N}{=}Fe(CO)_2(PPh_3)_2$[71]. Cationic $BrFe[PhP(OEt)_2]_3(CO)_2^+$ has also been reported[67]. The crystal structure of $Fe(CO)_2[P(OEt)_3]_3$ showed the expected trigonal bipyramid with one equatorial phosphite[72]. Displacement of CO from $Fe(CO)_5$ by $P(CF_3)_3$ stopped at the relatively inert $[(F_3C)_3P]_3Fe(CO)_2$ stage, in which all three phosphines occupied equatorial positions in the trigonal bipyramid, as shown in the X-ray structure[73].

A kinetic study of the reaction of cis,cis-(diars)$Fe(CO)_2L$-$(Me)^+$ with trimethylphosphite to form (diars)$Fe(CO)L[P(OMe)_3]$-$C({=}O)Me^+$ [diars = $(Ph_2AsCH_2CH_2AsPh_2)$] showed the reaction to be first-order and to be accelerated by bulky ligands L, suggesting an initial methyl migration without nucleophilic assistance[74]. Oxidative addition of $L_2Fe(CO)_2(MeCN)$ [L = tertiary phosphine] to methyl or ethyl iodide gave $L_2Fe(CO)_2RI$; with larger phosphines L (cone angle > 135°), rearrangement to the dihaptoacyl isomers $L_2Fe(CO)(\eta^2\text{-}COR)I$ occurred[75].

Synthesis of $L_2(OC)_2FeSO$ and $L_2(OC)_2FeSO_2$ was achieved by reaction of $L_2Fe(CO)_2^{2-}$ with thionyl and sulfuryl chlorides, respectively [L = $(PhO)_3P$]. The X-ray structure of the SO_2 complex showed a trigonal bipyramid with the SO_2 equatorially bound, and the $FeSO_2$ plane perpendicular to the equatorial $Fe(CO)_2$ plane. The SO complex was oxidized to the SO_2 complex by air[76]. $Fe(CO)_2(\eta^2\text{-}S_2CNMe_2)_2$ resulted when $CpMo(CO)_3[SC({=}S)NMe_2]$ and $Fe_2(CO)_9$ were photolyzed together, using visible light[7] . An analogous sulfur-selenium compound, **9**, has also been reported[78]. The coordinatively unsaturated species (bmae)Fe (Eq. 2) reversibly added two CO molecules to form (bmae)$Fe(CO)_2$, which could also be obtained directly from Na_2(bmae), $FeCl_2{\cdot}4H_2O$ and CO in methanol[34].

Reduction of $(R_3P)_2Fe(CO)_2(\eta^2\text{-}CS_2Me)^+$, **10**, with sodium amalgam gave the thiocarbonyl complex $(R_3P)_2Fe(CO)_2CS$, formation of which was accompanied by phosphine exchange with free phosphines present in solution. A 17-electron intermediate, $(R_3P)_2Fe(CO)_2$-$[-C({=}S)SMe]$, was proposed[79]. An X-ray structure of the thiocarbonyl $(Ph_3P)_2Fe(CO)_2CS$, from reduction of cation **10** with trialkylphosphines, showed an equatorial CS group, with Fe-C and C-S bond lengths of 1.768(8) and 1.563(8) Å, respectively[80].



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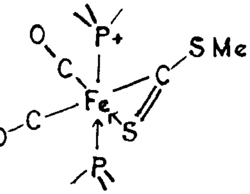


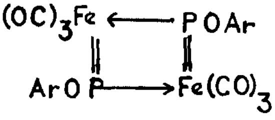
10

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

The reactions of $Fe(CO)_3^{\dot{-}}$ with alcohols and alkyl halides in the gas phase have been investigated. Abstraction of halide to form $Fe(CO)_3X^-$ was the principal reaction in the cases of most of the halides[81]. From the complex nature of the products of reaction of $Fe(CO)_3^{\dot{-}}$ with nitroalkanes, mechanistic conclusions have been drawn[82].

Synthesis and crystal structure of $[CH_2{=}C(PPh_2)_2]Fe(CO)_3$, a square pyramidal molecule with two basal phosphine groups, have been reported[83]. Mono- and dimetallated DPPM iron complexes were formed when the methylene group of $(DPPM)Fe(CNPh)_4^{2+}$ was deprotonated using KOH, and the resulting ylide was allowed to react with Ph_3PAuCl[84]. Reaction of $ArOPCl_2$ [Ar = 4,2,6-Me(t-Bu)$_2C_6H_2$] with $Na_2Fe(CO)_4$ gave the "organometallic cyclobutadiene analog," $(ArOP)_2Ft_2$, **11**[85]. The four-membered ring was rectangular, with P-Fe bond lengths of 2.202(1) and 2.112(1) Å. Another ferracycle, **12**, has been studied electrochemically; reduction in the presence of trimethyl phosphite resulted in displacement of one CO by the phosphite[86].

Pyridine-2-carbaldehyde imines formed N,N-coordinated $Fe(CO)_3$ complexes analogous to the well-studied 1,4-diazadiene complexes[87]. They gave [2.2.2]-bicyclic products, **13**, upon reaction with dimethyl acetylenedicarboxylate in the presence of ligand L (L = ^{13}CO or trimethyl phosphite)[88].



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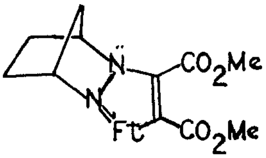

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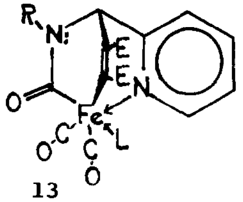


13

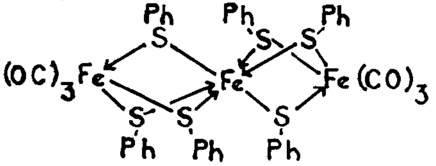
IR studies of trans-$HFe(CO)_3L^-$ M^+ (L = various phosphines, M = Group 1 and tetraethylammonium cations) have indicated two types of ion pairs, having M---O and M---Fe contact interactions, the latter being consistent with the metal-based nucleophilicity observed in reactions of these species with alkyl halides. The crystal structure of Et_4N^+ $HFe(CO)_3PPh_3^-$ indicated a distorted trigonal bipyramidal structure for the anion, with axial phosphine and hydride (not located directly) ligands[89].

Irradiation of $R_3PFe(CO)_4$ in the presence of various silicon hydrides produced *mer*-$R_3PFeH(CO)_3SiR_3$, which on more prolonged irradiation with excess silane sometimes gave bis(silyl) products, $R_3PFe(CO)_3(SiR_3)_2$[90]. An X-ray structure of $HFe(CO)_3(PPh_3)(SiPPh_3)$ confirmed the meridional stereochemistry[91].

The oxidized 17-electron complex $(Ph_3P)_2Fe(CO)_3^+$ retains the D_{3h} symmetry of its neutral 18-electron precursor, based on IR study of its hexafluorophosphate salt. EPR and theoretical studies of the cations were also reported[92]. Kinetics of displacement of CO from $L_2Fe(CO)_3$ cations by pyridines indicated an associative mechanism. The oxidized species with L = PPh_3 is about 10^9-fold more reactive than the neutral[93].

Reaction of halide ions with $[$*o*$-C_6H_4(AsMe_2)_2]Fe(CO)_3Me^+$ caused migration of the methyl group from iron to carbonyl ("insertion"); a kinetic study indicated formation of a cation-halide ion pair intermediate[94].

The bis(tricarbonyliron) compound **14** (X-ray) resulted from direct reaction of NaSPh with $FeCl_2$ under CO, and also from PhSSPh and $Fe(CO)_5$ under irradiation[95].

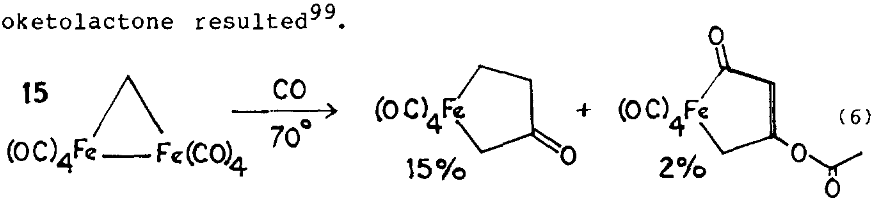


14

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

The mechanism of photolysis of $HFe(CO)_4^-$, to give a solution which catalyzes the water gas shift reaction under 1 atm. CO, has been studied. The initial step was proposed to be CO loss, followed by bimolecular loss of H_2, forming $Fe_2(CO)_7^{2-}$ [96]. Reaction of benzylic halides with $Fe(CO)_5$ under phase transfer conditions produced acyltetracarbonyl anions, $RCOFe(CO)_4^-$, which were described as "the true catalysts" in formation of ketones and carboxylic acids[97]. Direct study of the reaction of Et_4N^+ $HFe(CO)_4^-$ with methyl iodide in acetonitrile revealed the predominant formation of methane and unstable $(MeCN)Fe(CO)_4$; some acetone also formed. A number of lines of evidence favored direct displacement of halide by hydride in formation of the hydrocarbon products[98].

Two ferracycles resulted from reaction of $Fe_2(\mu-CH_2)(CO)_8$, **15**, with CO at 70° (Eq. 6). In the presence of norbornene, a spiroketolactone resulted[99].

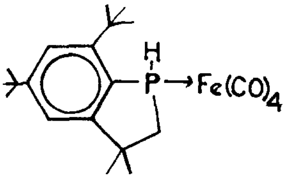


(6)

Treating $C_3F_7Fe(CO)_4I$ with silver fluoroborate in methylene chloride gave $C_3F_7Fe(CO)_4{}^+$ $BF_4{}^-$, into which bromide or chloride were readily introduced by reaction with tetraalkylammonium halides[100]. Reaction of $R_FFe(CO)_4I$ with AgF gave $(R_F)_2Fe(CO)_4$ or, in the presence of arenes, R_FAr[101]. Cis-trans isomerization of $(R_F)_2Fe(CO)_4$ at 80-100° has been studied by IR spectroscopy[102].

Trans-$(ArNC)_4FeCl_2$ (Ar = 2,6-dimethylphenyl), from direct addition of the isonitrile to $FeCl_2$, has been characterized by X-ray crystallography[103]. Photolysis of $(MeNC)_4Fe(CN)_2$ in acetonitrile led to replacement of isonitrile ligands by solvent; the same triplet intermediate was implicated in both direct and sensitized photolysis[104].

Tetracarbonyliron complexes of several novel phosphines have been described. These include $(i\text{-}Pr_2N)_2PH$[105] and phosphole dimers[106]. Contrary to a previous report, the syn and anti isomers of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene gave distinct $Fe(CO)_4$ complexes, in each case with complete retention of configuration at phosphorus[106]. Reaction of ArP=C=O (Ar = 2,4,6-tri-t-butylphenyl) with nonacarbonyldiiron proceeded with oxidative addition of phosphorus to a C-H bond, forming **16**[107]. **17** resulted from reaction of $PhC{\equiv}CPClCMe_3$ with $HFe(CO)_4{}^-$ then $Co_2(CO)_8$[108].



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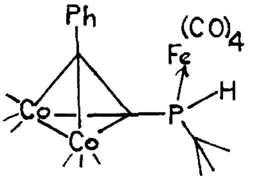

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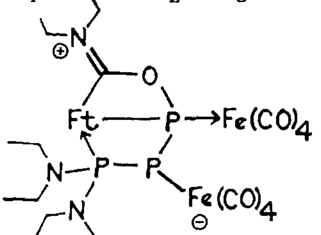
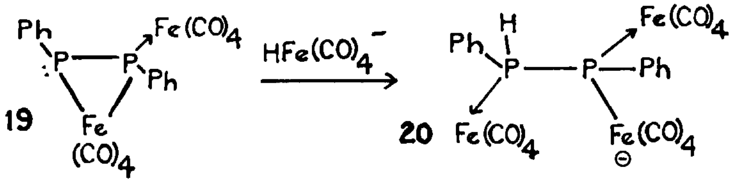


21

Reaction of the unsaturated phosphine, $(Me_3Si)_3C{=}PCp^*$, with nonacarbonyldiiron gave the phosphine→$Fe(CO)_4$ complex; upon photolysis, the pentamethylcyclopentadienyl group migrated to iron[109]. Complexation of the diphosphene, $Fp^*P{=}PAr$ (Ar = 2,4,6-tri-t-butylphenyl) gave the product **18**, with the $Fe(CO)_4$ group coordinated to the Fp^*-bound phosphorus (X-ray)[110]. Reaction of $PhPCl_2$ with $HFe(CO)_4{}^-$ led, depending upon reaction conditions, to $PhPHCl{\rightarrow}Fe(CO)_4$, to the diphosphene complex **19** (X-ray), or to the triiron complex, **20** (Eq. 7)[111]. The related reaction of Et_2NPCl_2 with $Fe(CO)_4{}^{2-}$ gave the rather extraordinary heterocycle **21**[112].



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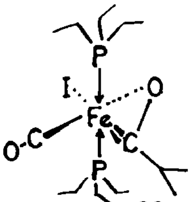
f. Carbene Complexes $R_2C{=}FeL_4$

The acyl anion $Me_3CC({=}O)Li$ was found to attack a carbonyl group of iron pentacarbonyl, to give an acylferrate complex. An X-ray structure of the PPN^+ salt was reported. Electrophiles, E, reacted at the nucleophilic oxygen to form labile carbene complexes, $(OC)_4Fe{=}C(OE)COCMe_3$ [E = Et, $SiMe_3$, COMe][113]. Reaction of $L_2(CO)_2Fe{-}N{\equiv}N{-}FeL_2(CO)_2$ [L = PEt_3] with isopropyl iodide gave the η^2-acyliron complex, **22**, whose X-ray structure showed a Fe=C distance of 1.80(2) Å and a Fe-O distance of 2.19(1) Å, consistent with the oxycarbene structure shown[114]. Another novel synthesis of an oxycarbene occurred upon reaction of $Cp_2Zr(H_2C{=}CH{-}CH{=}CH_2)$ with $Fe(CO)_4L$ [L = CO, PPh_3] to form **23**[116].



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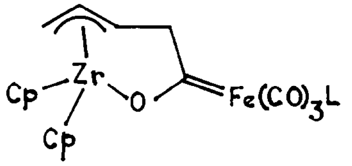

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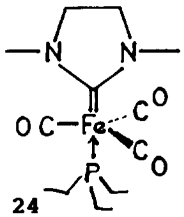
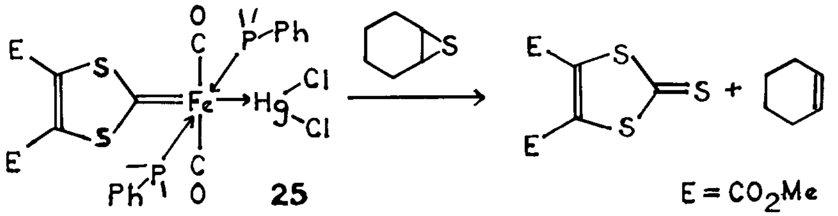


24

Reaction of the aminocarbene complex $Me_2NC(Ph){=}Fe(CO)_4$ with alkynes occurred with CO incorporation to form 2-dimethylamino-5-phenylfurans or, at high CO pressures, 6-dimethylamino-α-pyrones [116]. An X-ray structure of the diaminocarbene complex **24** showed a C=Fe distance of 1.95 Å[117]. The mercury-coordinated dithiocarbene complex **25** showed a C=Fe distance of 1.91 Å; the mercury coordination significantly increased the reactivity of the carbene complex toward cyclohexene sulfide, shown in Eq. 8[118]. The unmercurated carbene complex of **25** underwent protonation at Fe, followed by trans-cis isomerization, hydride migration to the carbene carbon, and sulfur-iron coordination[119].



(8)

A study of inactivation of cytochrome P-450 during oxidation of 3-(phenylthioethyl)sydnones has implicated an iron-carbene species, (Por)Fe=$CHCH_2SPh$, which is converted to the end-product, N-vinylporphyrin[49]. Analogous intermediates in P-450-catalyzed epoxidations [for example, (d) in Scheme I] have also been discussed[56].

Germylene and stannylene complexes (Por)M=$Fe(CO)_4$ [M = Ge, Sn] have been obtained by reaction of (Por)MCl_2 with $Fe(CO)_4^{2-}$, and their electrochemical reduction has been studied[120,121]. Simpler analogs $(ArO)_2M=Fe(CO)_4$ resulted from reaction of the $M(OAr)_2$ with nonacarbonyldiiron; X-ray structures revealed Ge=Fe and Sn=Fe bond lengths of 2.24 and 2.41 Å, respectively, with the germylene and stannylene groups equatorially attached to the trigonal bipyramidal iron[117].

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

Collision of $Fe(CO)_5$ with metastable helium atoms in the gas phase resulted in dissociation to excited Fe atoms, whose emission spectra have been analyzed[122]. The ultrasound-induced disruption of $Fe(CO)_5$ has been found to occur partly in the vapor phase of microbubbles at an effective temperature of 5200 K and partly in the liquid phase after bubble collapse at an effective temperature of 1900 K[123]. The dynamics of 193 nm photofragmentation of $Fe(CO)_5$ have been studied under molecular beam conditions by laser-induced fluorescence spectroscopy[124]. Photochemistry of $Fe(CO)_5$ in alkali halide matrices occurred in a manner consistent with other matrix and solution studies; $Fe(CO)_4$ was initially formed, followed by $Fe_2(CO)_9$ if mobility sufficed[125]. Photolysis of $Fe(CO)_5$ in pentane under varying hydrogen pressures produced $H_2Fe(CO)_4$ and $H_2Fe_2(CO)_8$, along with paramagnetic mono-, di- and trihydrides[126].

The 19-electron radical anion from reduction of $Fe(CO)_5$ readily abstracts hydrogen from R_3SnH to produce the formyl anion species, which decomposed by a radical-chain process[127]. Acyl anion products $X-C(=O)Fe(CO)_4^-$ also resulted from additon of anions to $Fe(CO)_5$ in the gas phase; in some cases, loss of one or two carbonyl ligands was also observed[128]. Effects of solvation of the anions have also been investigated[129].

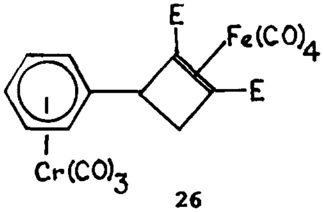
Reaction of 2,6-dimethylphenyl isonitrile (L) with $FeCl_2$ resulted in formation of FeL_5Cl^+ $FeCl_4^-$, which was characterized by X-ray crystallography[103]. $Fe(CO)_5$ and sym-tetrachloroethane caused dimerization and oligomerization of hexachlorocyclopentadiene[130]. $Fe(CO)_5$ also catalyzed reduction of o-nitrostyrenes by CO, to form indoles[131]. The dimers and dimer.ketones formed upon thermal reaction of 7-(benzoyloxy)norbornadienes with $Fe(CO)_5$ have received further study, including X-ray structures which established the stereochemistry of two minor ketone products[132].

5. η^2-ALKENE AND η^3-ALLYL COMPLEXES

Extended Hückel calculations on the conformations of trigonal bipyramidal (carbene)(alkene)$Fe(CO)_3$ complexes have indicated a preference for the carbene ligand to be axially bonded and the alkene to be in the equatorial plane[133]. Photoelectron spectroscopic studies of (alkene)$Fe(CO)_4$ complexes have suggested that the equatorially coordinated alkene is a better π-acceptor and a poorer π-donor than a CO[134]. ^{13}C NMR spectra indicated formation of a labile adduct between ethene and $Fe(NCMe)_6{}^+$ $FeCl_4{}^-$ [135].

The coordinatively unsaturated species (DPPE)Fe and its tetraethyl analog inserted into a C-H bond of ethene without prior formation of the π-complex, but the (DPPE)FeH($CH=CH_2$) product rearranged to the π-complex at room temperature[40,41]. Photolysis of $Fe(CO)_2(NO)_2$ in the presence of 1-butene in liquid xenon at -104 gave $Fe(NO)_2(CO)(\eta^2$-1-butene) and $Fe(NO)_2(\eta^2$-1-butene$)_2$. One of the coordinated butene molecules of the latter was readily replaced by CO at -55° [136].

The novel cyclobutene complex **26** was said to be formed as a minor product when (COT)$Cr(CO)_3$, dimethyl acetylenedicarboxylate, and $Fe_3(CO)_{12}$ were refluxed together in THF[137]. The complex **27** resulted, along with several organic products, from reaction of the ligand with $Fe_2(CO)_9$ or $Fe(CO)_5/h\nu$; ring opening to the diazepine complex was not observed[139]. Temperature-dependent CD spectra of several optically active $Fe(CO)_4$ complexes of 7-oxabicyclo[2.2.1]heptenes have been studied[139]. The crystal structure of **28**, having a novel coordinated ether oxygen, has been reported[140].



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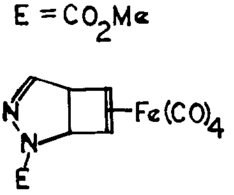

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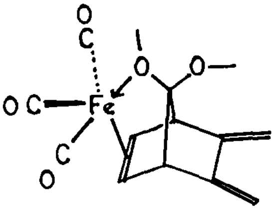


28

Reaction of $[MeSi(CH_2PMe_2)_3]Fe(\eta^4-C_6H_6)$ with diphenylacetylene gave $[MeSi(CH_2PMe_2)_3]Fe(C_2Ph_2)$, in which the alkyne group functioned as a four-electron donor[141].

A detailed comparison has been made of allylation of stable carbanions by (a) $MeCH=CHCH_2OCOR$, catalyzed by nonacarbonyldiiron; (b) $[\eta^2-MeCH=CHCH_2OCOR]Fe(CO)_4$; and (c) $[\eta^3$-MeCH-CH-

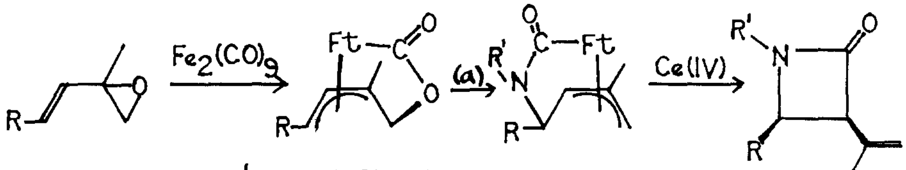
$CH_2]Fe(CO)_4^+\ BF_4^-$. Consistently high stereospecificities and variable regioselectivities were observed[142].

(Allyl)$Fe(CO)_4^+$ complexes have been obtained directly by reaction of allyl alcohol with $Fe(CO)_5$ under irradiation or of butadiene with $Fe_2(CO)_9$, in each case in the presence of HBF_4[143]. Nitrosylation of (allyl)Fe(CO)(NO)(PR_3) with $NOPF_6$ gave the (allyl)$Fe(NO)_2PR_3^+$ cations. The allyl groups underwent rather slow rotation, as shown by spin saturation transfer spectroscopy[144]. Mass spectrometric studies of various allyl-iron complexes containing carbonyl, nitrosyl, and phosphine ligands showed facile loss of CO or allyl from the η^1 complexes, but only CO from the η^3 [145].

Two extensive papers on the reaction of cyclopropenyl cations with $Fe(CO)_3NO^-$ have appeared. The reactions generally yielded (η^3-cyclopropenyl)$Fe(CO)_2NO$ and (η^3-oxocyclobutenyl)Fe-$(CO)_2NO$ products. An X-ray structure of the *t*-butyldiphenylcyclopropenyl complex was reported. The bond distances and the C-H coupling constant of the diphenylcyclopropenyl analog were consistent with a ferratetrahedrane structure[146]. Reaction of the cyclopropenyl complexes with phosphines gave ring expansion with CO insertion to form the oxocyclobutenyl complexes in a number of cases; a nonfluxional η^1-cyclopropenyl intermediate was proposed[147].

Bromo(η^3-2,4-pentadienyl)tricarbonyliron, **29**, [from 1-bromo-2,4-pentadiene and $Fe_2(CO)_9$] was reduced by sodium amalgam or zinc to (1,3-pentadiene)tricarbonyliron and dimeric μ-(1,3,7,9-tetraene)bis(tricarbonyliron)[148]. Reactions of (allyl)$Fe(CO)_3X$ with nucleophiles have been reported; $Ph_2C{=}NLi$ and $HC{\equiv}CMgBr$ displaced halide X from iron, but $PhC(=S)NMeLi$ appeared to have attacked a carbonyl group[149]. Phosphines attacked cationic (allyl)$Fe(CO)_4^+$ salts at the less-substituted end of the allyl group, followed by loss of "$Fe(CO)_4$" to produce allylic phosphonium salts[150].

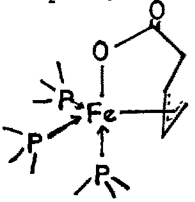
Allylic lactone complexes from reaction of diene monoepoxides with iron carbonyls have proven useful in synthesis of precursors to naturally occurring β-lactams (Eq. 9). Use of chiral amines gave separable diastereomeric mixtures of lactam complexes, which gave optically active lactams upon oxidation[151,152]. A homologous lactone complex, **30**, (X-ray structure)



(9)

(a) $R'NH_2$, $ZnCl_2$, TMEDA

resulted from reaction of the electron-rich (n^4-butadiene)Fe(PR_3)$_3$ with carbon dioxide. **30** reacted with additional carbon dioxide to produce 3-hexene-1,6-dioic acids and with $FeCl_3$ to produce (E,E)-deca-3,7-diene-1,10-dioic acid[153]. Methallyl chloride and $FeCl_2(PR_3)_n$ reacted in the presence of magnesium to produce (η^3-2-methylallyl)$_2$Fe(PR_3)$_2$; use of 2-methylallyl-lithium or -potassium resulted also in formation of the trimethylenemethyl complex, [C(CH_2)$_3$]Fe(PR_3)$_3$[154].



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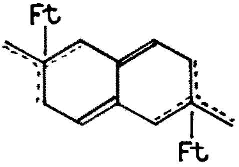
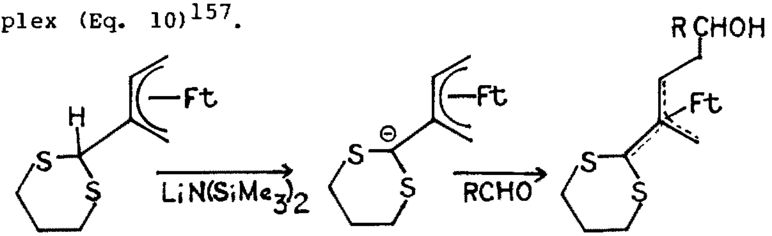


31

6. COMPOUNDS WITH η^4-LIGANDS

a. Trimethylenemethyl Complexes

Formation of [C(CH_2)$_3$]Fe(CO)$_3$ from CH_2=C(CH_2Cl)$_2$ and nonacarbonyldiiron was effectively promoted by ultrasonication, to give a quantitative yield[155]. Semiempirical theoretical methods have been applied to (p-xylylene)bis(tricarbonyliron), and **31** has been proposed as a plausible synthetic goal[156]. Substituted trimethylenemethyl complexes resulted from reaction of aldehydes with the carbanion generated from a dithiane-substituted diene complex (Eq. 10)[157].

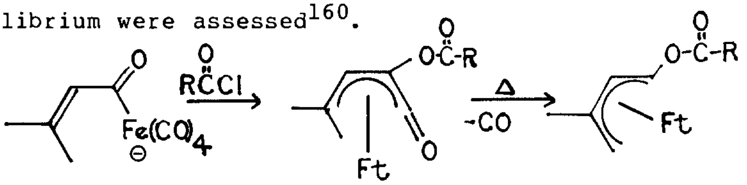


(10)

b. Complexes of Acyclic Dienes, including Heterodienes

Ultrasound was also found useful for preparing diene complexes, e.g. (CH_2=CH-CH=CHOAc)Fe(CO)$_3$[155]. Synthesis of (butadiene)Fe(PEt_3)$_3$ was achieved using $FeCl_2$, PEt_3, and magnesium-butadiene; further reaction with butadiene gave (butadiene)$_2$Fe(PEt_3)[158]. Ketodiene complexes resulted from reaction of alkenoyliron tetracarbonyl anions with electrophiles such as acyl chlorides; an example is shown in Eq. 11[159].

NMR studies have shown that (diene)Fe(CO)$_2$PPh$_3$ complexes existed in solutions as mixtures of isomers having the phosphine group in the axial or basal position of the square pyramidal structure; effects of diene substituents on the position of equilibrium were assessed[160].



(11)

Acylation of [(3-6)η-E-4,5-dimethylhexa-3,5-dien-2-one]tricarbonyliron gave <u>syn</u>-acylation at the unsubstituted 6-carbon. The product could by isomerized to the symmetrical bis(<u>anti</u>-acyl) complex with base[161]. Resolved (2-formylbutadiene)tricarbonyl iron reacted diastereospecifically with organo-lithium and -copper reagents, but gave mixtures with Grignard and titanium reagents. Wittig-type reactions were also reported[162].

Photoelectron spectra of (η^4-α-methylstyrene)- and η^4-1-vinylnaphthalene)tricarbonyliron were obtained and interpreted in terms of a simple MO model[163]. Iron tricarbonyl complexes of methyl 2,4-heptadien-7-ol-1-oate and its methyl ether were used as examples of methods for solving crystal structures of poorly crystalline substances[164].

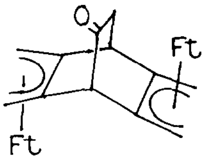
Photochemical reactions of (η^4-1-azadiene)tricarbonyliron complexes have been investigated in solution and in matrices. In the matrix, the N→Fe isomer was identified as the principal photoproduct. In solution, substitution of phosphines or azadienes for CO occurred, presumably via the same intermediate as observed in the matrices. Prolonged photolysis in the presence of RN=CH-CH=NR (R = cyclohexyl) gave $(RN{=}CH{-}CH{=}NR)Fe(CO)_2(ArN{=}CH{-}CH{=}CHPh)$ isomers, having the diazadiene coordinated in each case through the nitrogen lone-pairs, but the azadiene coordinated in one case at N and the other in an η^2 fashion to the C=C bond[165].

Reduction of $FeCl_3$ or $Fe(acac)_3$ with triethylaluminum or isopropylmagnesium bromide in the presence of bipyridyl and a diene produced a reagent [(bpy)Fe(diene) ?] which catalyzed coupling of allylic ethers with dienes[166]. An iron tricarbonyl complex of butadiene-styrene block copolymer, of unknown structure, has been made, and its radiation-induced conductivity studied[167].

c. Complexes of Exocyclic Dienes

Iron tricarbonyl complexes of tetramethylidenebicyclo-[2.2.2]octane derivatives have continued to receive intensive study. The <u>exo</u>,<u>endo</u>-diiron complex, **32**, and the <u>endo</u>-monoiron complex (verified by X-ray crystallography) of 5,6,7,8-tetramethylidenebicyclo[2.2.2]octan-2-one have been studied by CD, which showed behavior consistent with the octant rule[168]. Hydrocarbons from Tebbe methylenation of the ketone **32** and reduction of the resulting alkene were also subjected to CD study[169]. Analogous compounds having the bicyclo[3.2.1]octane skeleton have been acylated, and the X-ray structure of the diacylated derivative determined[170].

Reaction of 1,2,4,5-tetrakis(bromomethyl)benzene with $Fe_2(CO)_9$ was said to have produced the unusual Dewar benzene derivative, **33**[171].



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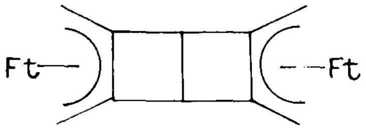

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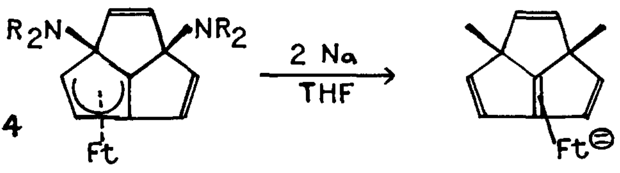
d. Complexes of Cyclic Dienes

Measurement of proton spin-lattice relaxation times in the solid state have led to estimation of the ring rotational barrier of (cyclobutadiene)tricarbonyl iron as 15.1 and 22.1 kJ/mol, depending upon lattice site. Raman measurements gave values in the range 13.9-19.1 kJ/mol[172].

Reaction of 2- and 3-borolenes with $Fe(CO)_5$ under irradiation led to dehydrogenation and complexation, to form borole complexes $(C_4H_4BR)Fe(CO)_3$ [R = Ph, Me, cyclohexyl, or OMe]. A low-temperature X-ray study of the phenyl derivative showed a Fe-B distance of 2.286(2) Å, as compared to Fe-C distances averaging 2.132(2) and 2.077(3) for the alpha- and beta-carbons, respectively[173]. Thus, the structure may be interpreted as a hybrid between an η^4-diene and an η^5-boracyclopentadienyl structure. A number of (η^4-2,5-diphenylsilole)tricarbonyliron complexes have been prepared by direct complexation of the siloles[174].

The novel dihydroacepentalene complex **34** has been prepared by direct complexation of the diamine; reduction with sodium [Eq. 12] did not result in elimination of the amine groups, but rather

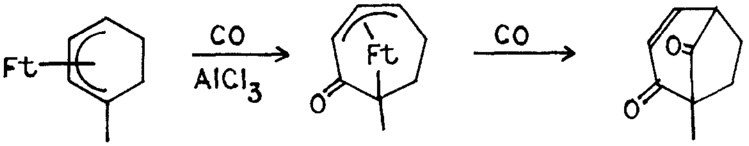
34



(12)

gave the stable (alkene)tricarbonylferrate(2-)[175]. [η^4-Tetrakis(diethylamino)cyclopentadienone]tricarbonyliron has been prepared, and its oxidation reactions have been studied[176].

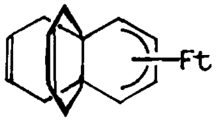
Substituted cyclohexadiene complexes resulted when 4-vinylcyclohexenes were allowed to react with $Fe(CO)_5$, with hydrogen rearrangement. Kinetically-controlled mixtures (predominantly 2-alkyl substituted) resulted from use of $Fe(CO)_5$ alone; thermodynamic mixtures (predominantly 1-substituted) resulted from use of HCl-modified $Fe(CO)_5$[177]. Photoelectron spectra of (1,3-cyclohexadiene)tricarbonyliron, **35**, have been measured as part of a study of C-H activation in dienylmanganese compounds[178]. Thermal electrons in the gas phase gave the (η^2 ?) radical anion of **35**, which predominantly fragmented to $HFe(CO)_3^-$ and $Fe(CO)_3^-$ upon reaction with H atoms [179]. The tricarbonyliron complex of 1-methyl-1,3-cyclohexadiene underwent ring enlargement with $AlCl_3/CO$, after which a second carbonylation and decomplexation could be achieved [Eq. 13] under CO pressure, in the same pot[180].



(13)

An η^4-benzene complex, $[MeSi(CH_2PMe_2)_3]Fe(\eta^4-C_6H_6)$, resulted when the triphosphine displaced the trimethylphosphines from $(\eta^6-C_6H_6)Fe(PMe_3)_2$. It was not fluxional at -60° [141].

Reaction of 1,2,3-triphenyl-3-vinylcyclopropene with nonacarbonyldiiron proceeded with rearrangement, to form the $Fe(CO)_3$ complex of 2,3,4-triphenylcyclohexa-2,4-dienone (X-ray)[181]. The propellatetraene complex **36** has been prepared directly by complexation $[Fe_2(CO)_9]$ of the tetraene[182]. Photoreaction of cyclohexadiene, pentacarbonyliron, and a disilacyclobutene led to formation of **37**[183]. 1-Silacyclohexa-2,4-dienes underwent complexation with iron carbonyl reagents with concomitant hydrogen migrations, giving in some cases isomeric mixtures[184].



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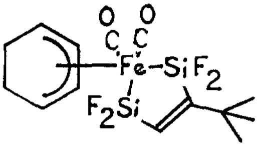

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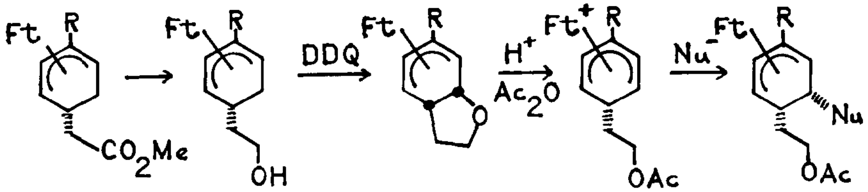
Introduction of two *cis*-1,2-substituents onto the six-membered ring has been achieved as shown in Eq. 14[185]. An analogous sequence applied to cycloheptadiene complexes provided a synthetically useful route to *cis*-1,3-disubstituted products[185].

Addition of the tricarbonyliron group to 2-substituted tro-



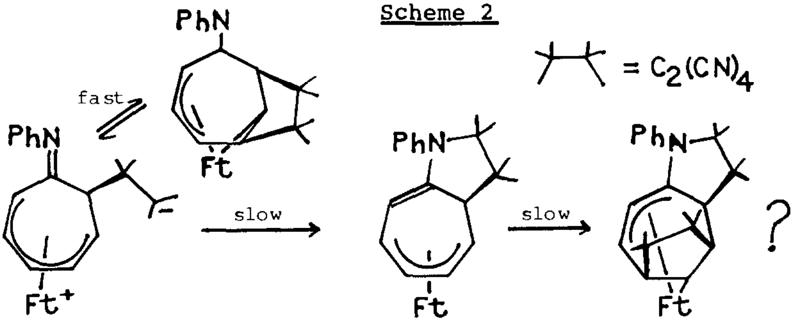
(14)

pones (using $Fe_2(CO)_9$ or $Fe(CO)_5/h\nu$) occurred predominantly at the unsubstituted diene unit (substituent = Me, Ph, OMe, OTs, CN); in only a few cases (Br, OAc, OCOPh) was the (2-5η) complex also observed as a result of equilibration of the two regioisomers. In the 2-Br case, the equilibrium ratio of (4-7η)/(2-5η) complexes was 10:1[186]. For 2-OAc, the ratio was 2:1. Equilibration of the acetoxy complexes involved haptotropic rearrangement of the $Fe(CO)_3$ group [$G^{\ddagger}$ = 25.3 kcal/mol at 50°], not transfer of the acetyl group, as shown by study of resolved material[187].

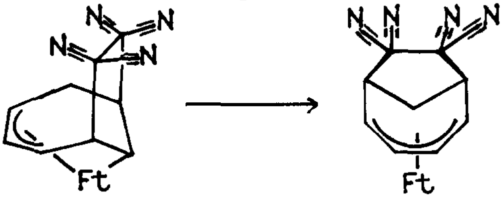
Deprotonation of (η^4-cycloheptatriene)tricarbonyliron, **38**, with KH, followed by acylation, gave exo-C7-acyl derivatives. Treatment with base gave enolates which reacted at oxygen with acyl and silyl chlorides; rapid protonation resulted in formation of C5-acylcyclohept atriene complexes[188].

Reaction of TCNE with N-p-tolyltroponimine has been studied, with results interpretable as shown in Scheme 2[189]. A study of

Scheme 2



the rearrangement of the initial TCNE-**38** adduct to its more symmetrical isomer (Eq. 15) has been reported, along with a crystal structure of the final product. The mechanism was shown



(15)

by kinetic data and solvent effects to involve a concerted, non-synchronous process with some charge separation[189].

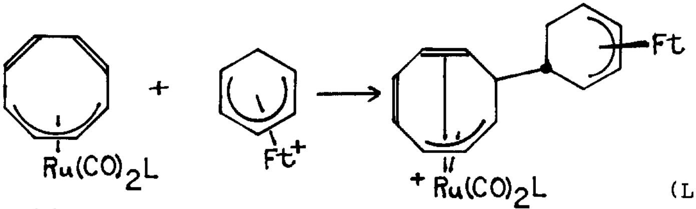
(Cyclooctatetraene)tricarbonyliron was the principal product (82%) of reaction of $(COT)Cr(CO)_3$ with $Fe_3(CO)_{12}$[137]. Photoreaction of trans,trans,cis-1,5,9-cyclododecatriene with $Fe(CO)_5$ gave tricarbonyl iron complexes of the starting triene and also of the all-trans isomer. Photolysis of the latter was reported to yield an $Fe(CO)_3$ complex of dimeric $C_{24}H_{36}$[191].

7. η^5-DIENYL COMPOUNDS

a. Compounds with Open Pentadienyl Ligands

Reaction of tricarbonyl(η^5-hexadienyl)iron fluoborate with trimethyl phosphite resulted in attack at both ends of the coordinated dienyl unit[150]. Reduction of tricarbonyl(2,4-dimethylpentadienyl)iron cation with zinc gave an unisomerized tetraene-bis(tricarbonyliron) dimer (X-ray structure)[192].

Reactions of nucleophiles with (cyclohexadienyl)iron tricarbonyl cations, to give 5-exo-substituted cyclohexadiene complexes, draw continued interest because of their synthetic applicability. Reaction of $(C_6H_7)Fe(CO)_3{}^+$ with partially dried KF/crown ether gave the ether rather than the earlier-reported fluoride, but NaOEt and NaCN gave the expected adducts[193]. This was not the case when a methyl substituent occupied the 1- or 5-position of the cyclohexadienyl moiety; it underwent deprotonation by basic reagents. In such cases, trimethylsilyl cyanide has proven effective in introducing the cyanide group onto the ring[194]. Iodide ion in acetone or nitromethane solution gave predominantly the photosensitive acyl iodide by carbonyl attack, along with some ring attack[195]. (COT)ruthenium complexes functioned as novel nucleophiles in attacking the cyclohexadienyl complex (Eq. 16)[196]. Reaction of dienyl complexes with 2-ethylpyridine has been studied kinetically, with the results indicating a second-order (direct addition) mechanism and a first-order (dissociative mechanism) reversal[197].



(16)

(L = CO, PPh_3)

This chemistry has been applied in total synthesis studies directed toward trichothecenes[198] and macrolide antibiotics[199].

Reactivity of (cycloheptadienyl)tricarbonyliron cations with nucleophiles has also continued to receive attention. Nucleophiles studied have included trimethyl phosphite[150], iodide ion[195], and 2-ethylpyridine; the latter was found to be 1/46th as reactive toward cycloheptadienyl cation as toward cyclohexadienyl[197].

Reaction of (cycloheptadienyl)$Fe(CO)_2L^+$ [L = $P(OPh)_3$] with sulfoximine-stabilized enolates gave chiral products with up to 50% enantiomeric excess[200]. $(C_7H_9)Fe(CO)(L)Me$ has been prepared from the corresponding iodide, and its X-ray structure reported. "Insertion" reactions occurred much more readily than in the analogous FpMe, a difference which was attributed to a facile $\eta^5 \rightarrow \eta^3$ slip in the case of the cycloheptadienyl ligand[201].

Theoretical studies of (cycloalkadienyl)$Fe(CO)_3^+$ ions having ring sizes between C_5 and C_8 have been reported. The effects of ring conformations on the dienyl MO's and on the rotation of the $Fe(CO)_3$ group have been assessed, and the results generally agreed with available structural information[202].

b. <u>(Cyclopentadienyl)dicarbonyliron Hydride and Related Compounds</u>

In this section, I describe recent results on FpH, Fp^-, and on compounds containing bonds between the Fp group and non-metals of Groups 14-17, as well as analogs having one or more CO group replaced by another 2-electron ligand, most commonly a phosphine.

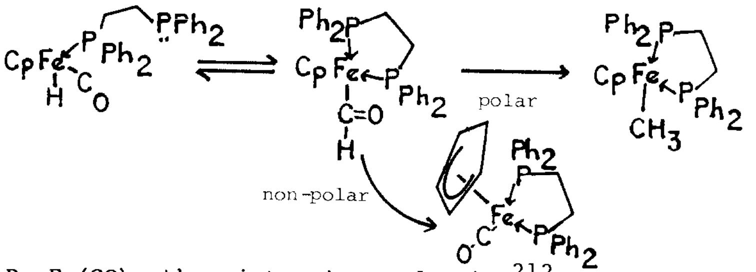
Various cyclopentadienes have been shown to inhibit corrosion of iron samples in 1 N. sulfuric acid, perhaps through formation of surface-bound η^5-cyclopentadienyl groups. Indene was most effective[203].

A short review of Cp^*-iron chemistry has appeared[204]. The use of $Cp^*Fe(acac)$ as starting material for preparation of Cp^*Fe derivatives has been recommended[205]. Photolysis of Fp^*_2 has been studied by fast time-resolved IR spectroscopy, and $Fp^{*\bullet}$ has been directly detected as a primary photoproduct, along with lesser amounts of $Cp^*Fe(\mu\text{-}CO)_3FeCp^*$[206].

The coupling constant $^1J(Fe,H)$ = 9.3 Hz for CpFe(DPPE)H has been measured by an indirect two-dimensional method, which also allowed determination of P-Fe coupling constants[207]. The pK_a values of FpH (19.4) and Fp^*H (26.3) have been determined in acetonitrile by IR measurements[208]. CIDNP results have indicated that the reaction of FpH with 1,3-dienes, to produce substituted allyl-Fp products, occurred by a [Fp$^\bullet$ allyl$^\bullet$] radical-pair mechanism[209].

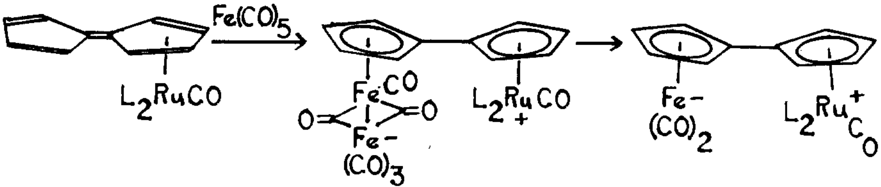
The carbonyl hydride, CpFe(CO)(DPPE)H, existed in equilibrium with the formyl isomer, whose fate was solvent-dependent (Eq. 17)[210].

Reaction of CpFe(DPPE)Br with activated magnesium gave the "inorganic Grignard reagent," CpFe(DPPE)MgBr·2THF[211]. The novel dianion, $CH_2[C_5H_4Fe(CO)_2^-]_2$, was prepared from the dithallium derivative of dicyclopentadienylmethane through reaction with



(17)

$Br_2Fe(CO)_4$ then intensive reduction[212]. A heterobimetallic fulvalene analog was prepared as shown in Eq. 18[213].

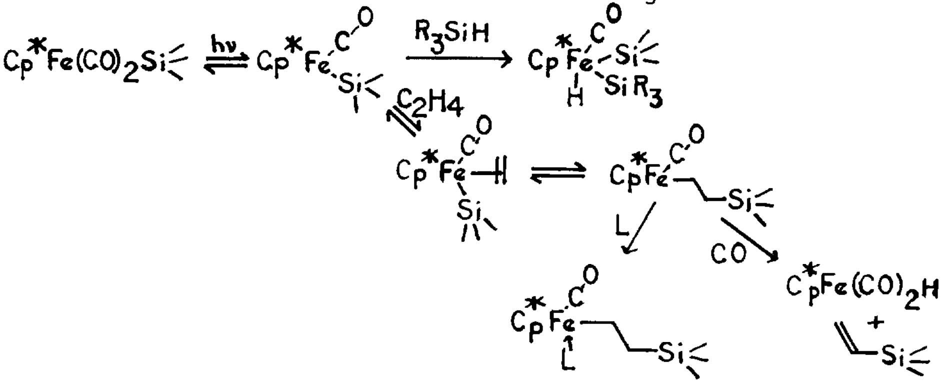


(18)

The crystal structure of the disiloxane meso-$[FpSiMeF]_2O$ showed a linear Si-O-Si linkage, even at 120 K; this phenomenon was probed by extended Hückel MO calculations[214]. The crystal structure of $FpSiMe_2GePh_3$ showed some lengthening of the Si-Ge bond and shortening of the Fe-Si bond compared to model compounds[215]; a small contribution of the structure $Fp{=}SiMe_2^+\ GePh_3^-$ to the ground state may be responsible. Photolysis of di- and trisilyl derivatives of (cyclopentadienyl)dicarbonyliron led to loss of silylene units to form silyl-Fp products. For example, $FpSiMe_2SiPh_3$ gave predominantly $FpSiPh_2Me$[216]. Treatment of the disilyl-Fp compounds with butyl-lithium resulted in migration of the intact disilyl group to the ring after deprotonation[216]. Photochemistry of Fp^*-$SiMe_3$ in matrices has also been studied, with some of the results shown in Scheme 3[217].

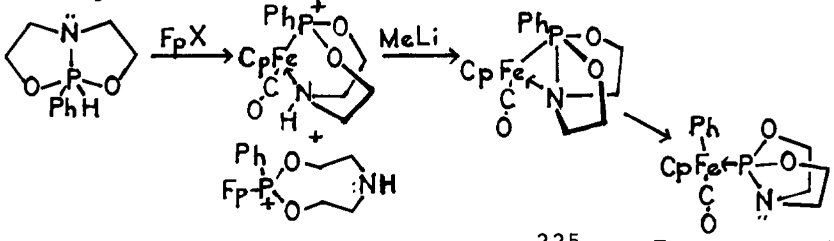
Scheme 3

Photoreactions of Fp^*SiMe_3



NMR spectra of several Fp-L^+ species, in which L = a diazaarene, have shown no evidence of exchange of Fp group between basic nitrogen sites[218]. Irradiation of CpFe(CDPE)(CO)$^+$ under nitrogen gave (μ-N_2)[FeCp(CDPE)]$_2^{2+}$ [CDPE = *cis*-$Ph_2PCH{=}CHPPh_2$]. This reacted with nitrogen nucleophiles to produce CpFe(CDPE)Nu$^+$, where Nu = N_3^- , NH_3, and even N_3H[219].

Fp-L compounds in which L is a ligand containing both nitrogen and phosphorus have received a good deal of attention during 1986. A P-bound cyclotriphosphazene-Fp compound has been prepared and characterized by X-ray crystallography[220]. Fp(PPh_2NHR)$^+$, from direct reaction of Fp(THF)$^+$ with the ligand, reacted further to form CpFe(PPh_2NHR)$_2$(CO)$^+$ under photolysis[221]. Similar compounds bearing a range of ligands, $Ph_{3-n}P(NMe_2)_n$, and also As- and Sb(NMe_2)$_3$, have been prepared; spectroscopic results indicated an increase in electron density on Fe as the number of P-bound NMe_2 groups increased[222]. Use of a bicyclic aminophosphorane led to coordination of both P and N to the iron, and a novel aryl group migration (Eq. 19)[223]. A similar migration of the P-allyl analog gave the Fe-CH=CHMe product; the route proposed involved Fe insertion into a C-H bond, 1,3-H migration, and cleavage of the P-C bond[224]. However, no reaction was observed between "cyclenphosphorane" and Fp_2[225]. Fp^- displaced halide from $R_2NPH(X){\rightarrow}ML_n$ complexes to form Fp-PH(NR_2)$\rightarrow ML_n$ products. These reacted with HX to lose NHR_2, forming Fp-PH(X)$\rightarrow ML_n$, from which the halide X was displaceable by MeOH[226]. Treating Fp*H with Me_2NPR_2 gave the metallophosphine, Fp*-$\ddot{P}R_2$ (R = Ph, Cl)[227]. Reaction of FpPPhN($SiMe_3$)$_2$ with hexafluoro-2-butyne gave a cycloaddition product, **40** (X-ray)[228].



(19)

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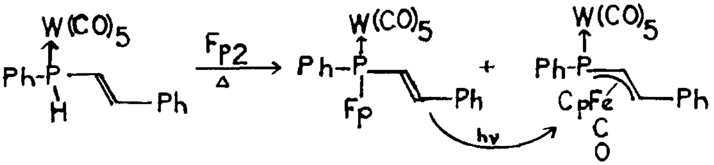
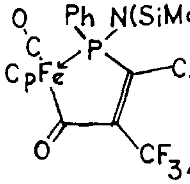
Unsaturated phosphorus ligands have also maintained their popularity. Photolysis of (Me_3Si)$_2$C=P(Cp*)$\rightarrow$Fe(CO)$_4$ occurred with migration of the Cp* group from phosphorus to iron, to form Fp*P=C($SiMe_3$)$_2$ (X-ray)[109]. An analogous product, FpP=C($OSiMe_3$)R, (X-ray) resulted from reaction of FpP($SiMe_3$)$_2$ with acyl chlorides, RCOCl [R = Ph, *t*-Bu, mesityl][229]. Pentamethylcyclopentadienyl derivatives formed analogous phosphaalkenyl products, along with diacylphosphinyl-Fp* products[230]. Related phosphaalkenyliron compounds resulted from reaction of Cp*CO$^+$ with LiP(Ar)$SiMe_3$ (Ar = 2,4,6-tri-*t*-butylphenyl)[231]. Phosphaallyl complexes were formed by reaction of a vinylphosphine-tungsten complex with Fp_2 in refluxing xylene (Eq. 20)[232].



(20)

Cationic indenyl cations $(\eta^5\text{-}C_9H_7)Fe(CO)_2L^+$ have been prepared by oxidation of the dimer with ferricenium ion in the presence of L [L = PPh_3, NCMe, $P(OR)_3$, etc.][233]. The same process has been recommended for producing a wide range of $Fp\text{-}L^+$ cations, including those with L = $AsPh_3$, $SbPh_3$, SMe_2, $SeMe_2$, and $TeMe_2$[234]. An extensive set of phosphine-, arsine-, and stibine-Fp^+ cations have been made by displacement of THF from $Fp\text{-}THF^+$ [235]. Use of $CpFe(CO)(SMe_2)_2{}^+$ or $CpFeAn^+$ gave cations with two or three Group 15 ligands[236]. The bonding characteristics of ligands in $CpFe(CNMe)_2L^+$, $CpFe(CO)(CNMe)L^+$, and $CpFe(CNMe)L_2{}^+$ has been studied by IR and Mössbauer spectroscopy[237]. Synthesis and crystal structure of $Cp^*Fe(CO)(PMe_3)(THF)^+\ PF_6{}^-$ have been published[238].

Reaction of $FpAsMe_2$ with dimethyl acetylenedicarboxylate resulted in a cycloaddition to form **41**, completely analogous to formation of **40**[239]. The first arsaalkenyl complex, $FpAs{=}C(OSiMe_3)CMe_3$, (X-ray) has been prepared by reaction of $FpAs(SiMe_3)_2$ with pivaloyl chloride[240].



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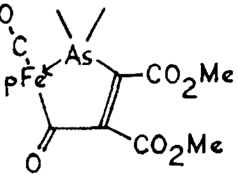
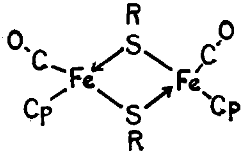


Covalent triflate complexes, Fp^*OTf and its mono-trimethylphosphine analog, were prepared by reaction of Fp^*X (X = H, Cl, Me) with ROTf (R = H, Me, Me_3Si). As might be expected, the triflate ligand was very readily displaced[241]. X-ray structures of Fp- and $Fp^*OP(=O)(SR)_2$ (R = isopropyl), in which the dithiophosphate ligands were monodentate, have been published[242,243]. Crystal structures of the H-bonded dimer, $[FpOC(=O)R]_2H^+\ SbF_6{}^-$, and of $Fp_2Cl^+\ SbF_6{}^-$ have also been determined. The Fe-Cl-Fe angle in the latter was 119.4(2)° [244].

The sulfonium salt, $Fp\text{-}SC_4Me_2H_2{}^+\ Cl^-$, resulted from reaction of FpCl with 2,5-dimethylthiophene[245]. Pyramidal inversion in a series of Fe-Group 16 adducts, including $CpFe(CO)(YMe_2)_2{}^+$ (Y = S, Se, Te) and Fp'SMe_2^+ has been studied by dynamic NMR methods[246]. The disulfide complex, CpFe(CO)[$P(OMe)_3$]S(Me)SMe$^+$ BF_4^- showed sulfur-to-sulfur migration of the iron group upon heating[247]. Coordination of Fp$^+$ groups to 1-3 sulfur atoms of di- and trisulfides was achieved by reaction, in appropriate stoichiometric ratios, of Fp(THF)$^+$ with the ligands. Chelate complexes [CpFe(CO)(η^2-S⁀S)]$^+$ resulted from irradiation of some of the monodentate cations[248]. Reaction of Fp_2 with RSSR (R = N-methyl 4-piperidinyl) gave the cyclic product, **42**, which showed a planar ring and a 3.44 Å Fe·····Fe distance in the X-ray structure[249].

Magnetic and Mössbauer measurements on thioselenocarbamates (such as **9** and CpFe(CO)[η^2-SC(=Se)NR_2] have been compared with those on their dithio- and diseleno-analogs[78]. Fp_2Se was found to react with elemental selenium to form FpSeSeFp[250].

FpCl and Fp_2, in contrast to some other carbonyl complexes, were found to be ineffective at catalyzing alkane halogenation [251]. Reaction of $LiNEt_2$ with CpFe(CO)[PhP$(OEt)_2$]Br rather surprisingly resulted in introduction of the diethylamino group onto the cyclopentadienyl ring (88% yield). The crystal structure of the product showed the iron to have moved away from the ring centroid, resulting in a long (2.30 Å) distance to the amino-bearing carbon. A short (1.33 Å) C$\overset{\cdots}{-}$N distance was consistent with a hybrid structure, **43**[252].



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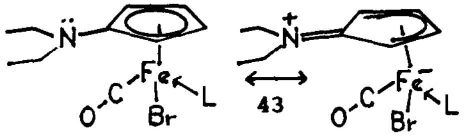

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c. Fp-Acyl, -Alkyl, and -Carbene Complexes

A review of the extensive contributions of the Rosenblum group to the chemistry of FpR systems, including synthetic applications, has appeared[253].

A detailed procedure for preparation of FpCO$^+$ BF_4^- by protonation of $FpCO_2Me$ has been published[254]. MO calculations have been used in conformational analysis of Fp'COMe, which indicated that the acyl oxygen should lie approximately anti-periplanar to the CO ligand as a consequence of steric interactions with phenyl groups on the triphenylphosphine ligand[255].

In the presence of $EtAlCl_2$, H_2C=CHCOFp served as an effective dienophile in Diels-Alder reactions. ^{13}C NMR spectra of the Lewis acid adducts suggested considerable alkoxycarbene character[256]. Coordination of aluminum bromide with FpCOMe in toluene has been studied thermochemically; the heat of coordination was -31(2) kcal/mol, somewhat larger than the values for benzophenone (-24) or N,N-diphenylbenzamide (-27)[257]. Under a CO atmosphere, aluminum bromide promoted "insertion" of CO into the Fe-CH_2 bonds of $FpCH_2Ph$ and $Fp(CH_2)_5Fp$[258]. Aluminum chloride or (better) ferricenium ion catalyzed CO "insertion" into Fe-vinylic carbon bonds in $CpFe(CO)[P(OPh)_3]CR{=}CR_2$ species at -78°. The stereochemistry about the C=C bond was in most cases retained, as supported by X-ray structures of two acyl products[259].

Migration of the *t*-butyl group in *t*-BuFp from iron to CO, to form Fp'CO-*t*-Bu, was faster than methyl migration in MeFp, for reasons of steric bulk. For the same reason, SO_2 insertion into *t*-BuFp failed[260]. A sequence of insertion reactions has been used to convert 3 CO's into the malonic acid skeleton through the sequence $FpCO^+ \rightarrow FpCH_2OMe \rightarrow FpCH_2CO_2Me \rightarrow CH_2(CO_2Me)_2$[261]. In an organometallic *tour de force*, a repetitive sequence of reductions and carbonylations was used to produce pentanoic acid, in which all carbons were derived from CO, starting from $FpPMe_3^+$ [210,262].

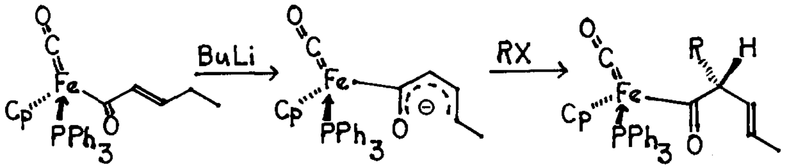
Deprotonation of acyliron compounds to form enolates constitutes the basis of much synthetically important chemistry. Reaction of chiral $Fp'C(=CH_2)O^- \, Li^+$ at -78° with Cp_2ZrCl_2 gave the metallo-enol (X-ray), whereas Ph_3PAuCl gave the metallo-ketone, $Fp'C(=O)CH_2AuPPh_3$ (IR)[263]. A study of the reactions of Fp-acyls with various bases showed competitive removal of the enolic hydrogen and a Cp ring hydrogen. The use of $LiN(SiMe_3)_2$ rather than $LiN(iPr)_2$ resulted in maximum enolate formation. Ring deprotonation was followed by acyl migration from iron to the ring[264].

Chirality transfer from the iron to the organic products in reactions of Fp'-acyls has been intensively investigated. Use of appropriate metals (e.g. Et_2AlCl or $SnCl_2$) to coordinate with the enolate, $Fp'COCH_2^-$, resulted in high diastereocontrol in condensation with carbonyl compounds. The aldol products were dehydrated to form α,β-unsaturated iron acyls, which were subjected to Michael addition/alkylation with high stereoselectivity. γ-Aminoiron acyls resulted from addition of RNHLi to the α,β-unsaturated acyls or from condensation of enolates with imines; these gave β-lactams on low-temperature oxidation with bromine [265].

The Davies group has been exceptionally prolific in exploiting the Fp' group for purposes of stereocontrol. They have prepared Fp'COCH=CHR compounds by Wittig reactions using $Fp'COCH{=}PR_3$ or Peterson reactions using $Fp'COCH_2SiMe_3$[266]. X-ray structure determination of a diastereomer of the (R)-menthyl ether $Fp'COCH_2CH_2OR$ enabled assignment of absolute configurations to Fp'COMe and compounds derived from it[267]. Treatment of the ether with NaH led to the acrylyl acyl, $H_2C=CHCOFp'$, which gave a $ZnCl_2$-induced Diels-Alder reaction with cyclopentadiene; oxidation and iodination gave the iodolactone in 65% chemical yield and better than 95% enantiomeric excess, demonstrating excellent chirality transfer[268].

Quaternary carbon centers resulted stereoselectively from Michael addition of butyl-lithium to $Fp'COC(R)=CH_2$, then alkylation of the enolate; the configuration of the new chiral center was established[269,270]. Chiral discrimination in attack of the lithium enolate from Fp'COEt on *cis*- and *trans*-2-butene oxides has also been studied[271]. These results have been extended to the dienolates which resulted from (exclusive) γ-deprotonation of $Fp'COCH=CHCH_2R$ or $Fp'COCH=CMe_2$. Reactions with electrophiles (MeOH, RX, MeSSMe) occurred regio- and stereoselectively at the α-position (Eq. 21)[272].

X-ray investigations of BF_2-coordinated diacyls **44** have been published. The di-*t*-butyl compound showed a boat-shaped chelate ring, with the Cp ring axial[273]. The compound with R^1 = Me and R^2 = $C(=CH_2)CH_3$ also manifested a boat-like ring, but with the CO axial[274]. The latter compound entered readily into Diels-Alder reactions, to form cyclohexenes with high diastereoselectivity[275]. Treating the enolate $FpCOCH_2^-$ with methyl-lithium resulted in addition to a CO ligand; treatment of the resulting dianion with benzoyl chloride led to ligand coupling to generate an allylic ligand (Eq. 22). Analogous reactions occurred (in poor yield) with vinylic ligands[276].



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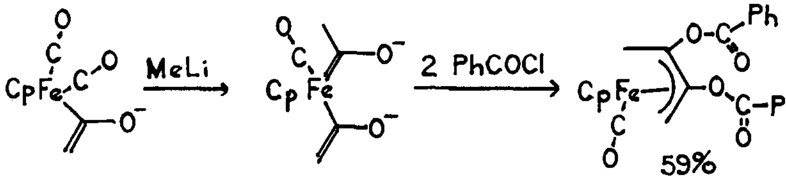

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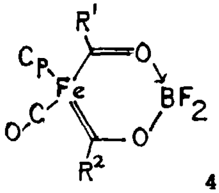
$FpCH_2COCl$ served to acylate various metal anions ML_n^-, including Fp^-, giving products which may be viewed as μ-ketene complexes $FpCH_2COML_n$[277]. An X-ray structure of $FpC(CF_3)_2OH$ showed a relatively normal Fe-C bond length of 2.060(6) Å[278].

One-electron reduction of FpMe was found to be followed by migration of the methyl group to a CO, then migration of the acetyl group to the Cp ring, ultimately forming

$(MeCOC_5H_4)Fe(CO)(THF)^-$ [279]. Cp ring metallation of $FpCH_2Ph$ with BuLi, followed by treatment with ketones or dimethylformamide, gave carbinol- or formyl-substituted cyclopentadienyl rings[280]. Similar reaction of FpMe with BuLi and then FpI produced $(FpC_5H_4)Fe(CO)_2Me$ (X-ray); the same product also resulted from the less obvious reaction of Fp_2 with BuLi and MeI[281].

Reaction of FpMe (and Fp'Me) with N-sulfinylsulfonamides $[RSO_2N{=}S{=}O]$ occurred with initial formation of $FpN(SO_2R)S({=}O)Me$, which rearranged to isolable $FpS({=}NSO_2R)(O)Me$ products. The crystal structure of the S-benzyl analog of the latter was determined[282].



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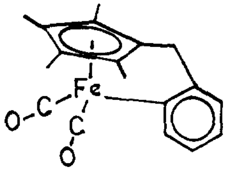

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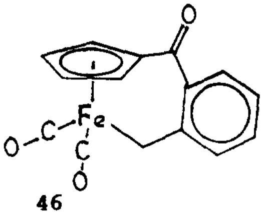

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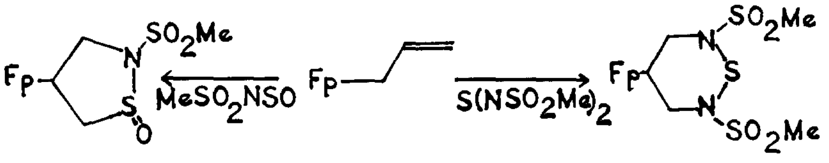
Photolysis of Fp^*Me in an alkane solution containing R_3SiH gave methane and $Cp^*Fe(CO)(SiR_3)_2H$ by a process of CO loss, iron insertion into an Si-H bond, loss of methane, and repeat insertion[217]. Photolysis of $(PhCH_2C_5R_4)Fe(CO)_2Me$ [R = H, Me] also occurred primarily by loss of CO; in the absence of other ligands, the unsaturated iron species underwent oxidative addition to an ortho C-H bond of the benzyl group, forming **45**. Photolysis of **45** under hydrogen resulted in reversal of the oxidative addition to form $(PhCH_2C_5R_4)Fe(CO)_2H$[283]. Another example of ligand coupling, to form **46**, occurred when $PhCH_2Fe(CO)_2(C_5H_4COCl)$ was treated with aluminum chloride[284].

Formation of the vinyl-iron compound MeCH=CHFe(CO)LCp by rearrangement of the organic group from an allylphosphine[224] was previously noted. $CH_2{=}CH{-}Fp$ has been obtained in good yield by reaction of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)$, **47**, with nucleophiles MeCN and NaI[285]. A detailed preparation of $Me_2C{=}CHFp$ by direct reaction of $Me_2C{=}CHCl$ with Fp^- has been provided, as part of a procedure for preparing (isopropene)Fp^+ BF_4^- [285a]. $Fp[C(CF_3){=}CMe(CF_3)]$ was produced upon reaction of $CpFe(CO)(\mu\text{-}SMe)_2FeCp(CO)$ with (hexafluoro-2-butyne)$Co_2(CO)_6$[286]. The reverse process, transfer of ligand from iron to cobalt, occurred when $CpFe(CO)[\mu\text{-}C(CF_3){=}C(CF_3)SMe]FeCp(CO)$ reacted with dicobalt octacarbonyl[286]. The keto group in 3-Fp-2,4-diphenylcyclobutenone was converted to a thioketo group, and the S coordinated to Group 6 metals[287]. The triple bond in $FpC{\equiv}CPh$ reacted normally with dicobalt octacarbonyl, giving the dicobaltatetrahedrane complex (X-ray)[288].

In addition to **39** (Eq. 19), the aryliron compound Fp-p-C_5F_4N

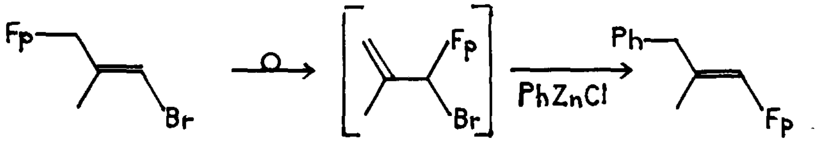
resulted when Fp^- reacted with pentafluoropyridine[289].

A proposed general method for reducing allylic alcohols to 1-propenes involved conversion to the phosphate, displacement by Fp^-, protonation to form the alkene$(Fp)^+$ cation, and demetallation[290]. Cycloadditions of allylic- or propargylic-Fp complexes with N-sulfinylmethanesulfonamide gave [3 + 2] cycloaddition products; with sulfur bis(methanesulfonylimide), propargylic complexes did the same, but allylic ones formed [3 + 3] cycloadducts. An example is shown in Eq. 23. Cyclopropylmethyl-Fp gave both insertion and cycloaddition products[291]. Use of allyl-Fp



(23)

as a nucleophile for carbon-carbon bond formation has been extended to use of allylic iodides as electrophiles, which has been used in syntheses of lavandulol and red scale pheromone[292]. Reaction of (1-bromoallyl)Fp with organozinc nucleophiles surprisingly gave rearranged products; mechanistic investigation implicated radical-induced isomerization of the unreactive vinylic bromide to a reactive allylic one, with rapid S_N2' displacement following (Eq. 24)[293]. FpCp has been shown to function as a



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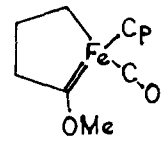
synthetic surrogate for 5-aminocyclopenta-1,3-diene in Diels-Alder reactions; this was achieved by converting the adducts to acyl azides by oxidation in presence of excess azide ion, followed by Curtius rearrangement: RFp → $RCON_3$ → RNH_2[294].

Just as acyliron compounds were reported to manifest oxycarbene character when coordinated to Lewis acids[256], FpMe has been found to rearrange on absorption on alumina to a carbene-like acyl complex, based on ^{13}C CPMAS NMR spectroscopy[295]. Two simpler iron-carbene species, $Fp^*{=}CH_2^+$ and $Fp^*{=}CHOH^+$, were observed after treatment of Fp^*CH_2OH at -90° with Me_3SiOTf[296]. Reaction of Fp^*CH_2OH with Ph_3C^+ at -80° gave the ESR-identifiable radical cation, which lost H· on warming to -20°, forming Fp^*CHOH^+ [296,297]. Fp^*CHOMe^+ formed R_3SiCH_2OMe on reaction with R_3SiH, and $Fp^*(styrene)^+$ on reaction with styrene[297].

2-Fp'-3,3-dimethyltetrahydrofuran (from $NaBH_4$ reduction of the tetrahydrofurylidene-iron cation) underwent epimerization on silica gel, presumably through ring opening to a γ-hydroxycarbene complex followed by reclosure[298]. Neopentylidene-iron species, $Fp{=}CHCMe_2R^+$, prepared by protonation and dissociation of ether groups at -78°, rearranged to η^2-alkene complexes, $Fp(RCH{=}CMe_2)^+$ [299]. Upon photolysis, 1-Fp-1-methoxycyclobutane underwent ring expansion to form the carbene complex **48**. Recarbonylation of **48** at 6.5 atm. CO produced the (trans-β-methoxycyclobutyl)Fp product, which upon irradiation reformed **48**[300]. Similarly, photolysis of the benzocyclobutenyl analog gave ring expansion, with formation of isomeric carbene complexes (Eq. 25). A crystal structure of the major product, **49**, showed a C=Fe distance of 1.83 Å[301].



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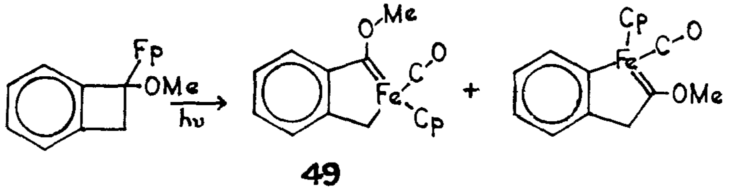

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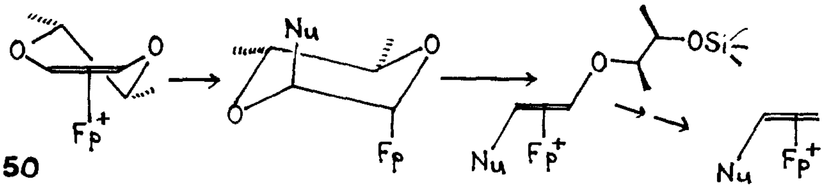
Reactions of the carbene complexes, $Cp(OC)(MeCN)Fe{=}C(SR)_2{}^+$ with metal anions, to form bimetallic species with a bridging $C(SR)_2$ ligand, have been studied[302].

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

Some work involving (alkene)Fp^+ cations from rearrangement of carbene complexes[299], from electrophilic attack on allyl-complexes[290], and from protonation of vinylic complexes[285a], has already been cited.

Direct synthesis of $(C_2H_4)Fp^+\ BF_4{}^-$ from Fp_2, ethene, and ethereal HBF_4 has been reported[303]. Metal carbonyl force constants in a series of ethene complexes, including those with Fp^+, Fp'^+ and related compounds, have been determined and shown to correlate with susceptibility of the coordinated ethene toward nucleophilic attack[304]. The chemistry of (1,2-dialkoxyalkene)Fp^+ salts has received attention from two groups. The salts could be made by alkene exchange with $(Me_2C{=}CH_2)Fp^+$ and the free dialkoxyalkene or by rearrangement of the carbene complex



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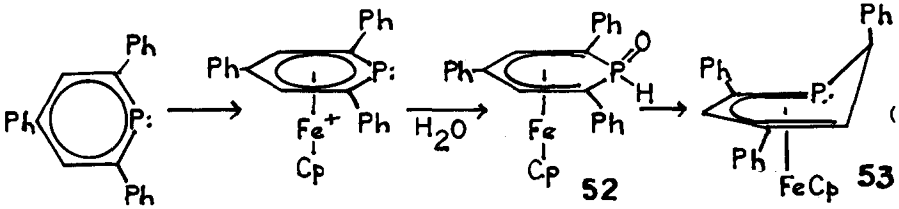
$Fp{=}C(OEt)CH_2OMe^+$. They readily exchanged alkoxy groups with free alcohols; with water, FpCH(OR)CHO resulted[305]. The cyclic dioxin analogs, **50**, reacted stereospecifically with nucleophiles as exemplified in Eq. 26 to give products which could be converted to optically active vinyl ether or alkene complexes of known configuration[306].

Reactions of $CpFe(CO)[P(OPh)_3](MeC{\equiv}CR)^+$ complexes with nucleophiles resulted in a number of different modes of attack. Depending on R and on the nucleophile, examples of addition to the coordinated triple bond, deprotonation to form the propargylic-Fp product, deprotonation to form the allenyl-Fp, and attack at the Cp ring were observed. The allene complex, $CpFe(CO)L(CH_2{=}C{=}CH_2)^+$, in all cases added nucleophiles to form $CpFe(CO)L[\eta^1\text{-}C(=CH_2)CH_2L]$[307].

Irradiation of FpCp and its mono- and di-indenyl analogs at low temperature produced two isomers of $(\eta^5\text{-Cp})Fe(CO)(\eta^3\text{-Cp})$, the more stable of which thermally formed ferrocene with an activation energy of about 58 kJ/mol. The analogous di-indenyl compound required about 91 kJ/mol[308]. Likewise, photolysis of $Fp(\eta^1\text{-}CH_2\text{-}CH{=}CH\text{-}CH{=}CH_2)$ at -20° gave two forms of $CpFe(\eta^3$-pentadienyl), characterized as exo and endo allylic isomers, which underwent further decarbonylation to form the "half-open ferrocene," $CpFe(\eta^5$-pentadienyl)[309].

Dimeric (cyclohexadienyl)FeCp products, **51**, resulted from reduction of $(\eta^6\text{-}C_6H_5X)FeCp$, followed by air oxidation[310]. An X-ray structure of **51** (X = H) was reported[311]. Reaction of 2,4,6-triphenylphosphabenzene with ferrocene and aluminum chloride, then water, gave the oxide complex **52** (Eq. 27), which was reduced by $HSiCl_3$ to three isomeric phosphadienyl complexes, including **53**, whose crystal structure was determined[312].



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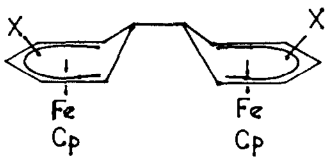
Reaction of $CpFe(C_4H_4BPh)^-$ with $Cr(CO)_3(NH_3)_3$ gave the 30-electron triple-decker complex, **54** (X-ray)[313]. Tetramethylthiophene reacted with ferrocene in the presence of wet aluminum chloride to form $CpFe(\eta^5\text{-}C_4Me_4S)^+$, which could be reduced to the neutral 19-electron complex[245]. Phospholide anions, $C_4R_4P^-$, displaced arenes from $CpFeAn^+$ to form neutral $CpFe(\eta^5$-phosphacyclopentadienyl) complexes[314]. The analogous Cp^*Fe compounds were prepared by displacement upon $Cp^*Fe(acac)(THF)$[315].



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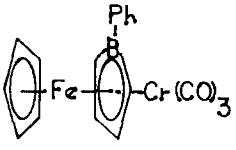

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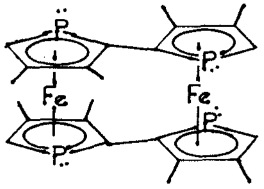

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Bis(phospholyl)iron complexes (diphosphaferrocenes) formed adducts with Lewis acids either at phosphorus (BF_3) or at iron ($AlCl_3$, CuI, AgOTf)[316]. The bis(diphosphafulvalene) complex **55** (and an isomer) resulted from reaction of the diphosphafulvalene dianion with $FeCl_2$[317].

8. COMPOUNDS WITH η^6-ARENE LIGANDS

A comprehensive review of the synthesis and chemical and physical properties of η^6-arene-η^5-cyclopentadienyliron cations and related systems has appeared[318]. The photochemistry of these compounds, and of $CpFeL_3^+$ ions derived from them, has been reviewed, with particular emphasis on possible photochromic applications[319].

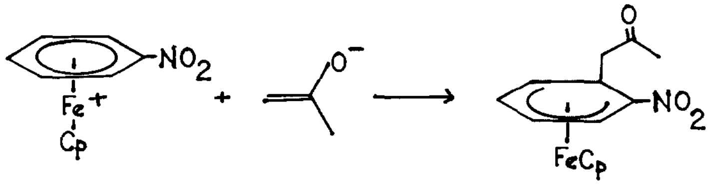
Quantum yields for arene loss from $CpFeAn^+$ as compared to Cp^*FeAn^+ have been reported. For the hexamethylbenzene complexes, the Cp^* compound was found to be less reactive by a factor of 20500, suggesting severe hindrance to solvent (acetonitrile) access to the iron[320]. Photolysis of $Cp(^*)Fe(COT)^+$ in acetonitrile also resulted in formation of $Cp(^*)Fe(NCMe)_3^+$ [321].

Heating cyclopentadienyl-(η^6-fluorenyl)iron at 80° resulted in migration of the CpFe group to the 5-membered ring, to form the dibenzo[a,c]ferrocene[322]. Complexation shifts in ^{13}C NMR spectra of a series of (cyclopentadienyl)([n]paracyclophane)iron$^+$ salts with n = 8, 9, 11, 12, and 15 have been related to the molecular geometries[323]. The temperature dependence of the Mössbauer spectrum of $CpFe(C_6H_5F)^+$ PF_6^- indicated that the cation possessed rotational mobility in the solid at $T > 220$ K[324].

Synthesis of functionalized $AnCpFe^+$ salts has received attention during 1986. $CpFe(\eta^6\text{-}C_6H_5CH_2COR)^+$ (R = Me, OEt, and OH) were made from β-dicarbonyl precursors by deacetylation or decarboxylation[325]. Arene complexes bearing α-methylene groups could be deprotonated and nitrosylated to form α-oximes, which were converted to ketones, alcohols, and amines by conventional synthetic procedures[326]. Methylene groups in the bis($CpFe^+$) dications of 9,10-dihydroanthracene, diphenylmethane, xanthene, and thioxanthene underwent direct oxidation to ketone groups with $KMnO_4$[327]. Similarly sulfide functions attached to the complexed arenes were oxidized to sulfones by use of m-chlorperbenzoic acid[327]. X-ray structures of μ-(phenoxazine)bis(CpFe$^+$) $(PF_6^-)_2$ and (η^6-phenoxathiin)FeCp$^+$ have been published[328].

Pivalyl (Me_3CCO) substituents on either ring of AnFeCp$^+$ underwent rearrangement to the 3-methylbutanoyl group under the influence of strong acids; the organometallic compounds rearranged much faster than $PhCOCMe_3$. Loss of the acyl substituent from $(RCOC_6H_5)FeCp^+$ also occurred[329].

Reactions of AnFeCp+ with nucleophiles, which often result in arylation, have been explored in depth. Reaction of ketone enolates with arene complexes containing an electron-withdrawing group on the arene ring gave products of exo addition of the anion ortho to the substituent (Eq. 28)[330]. Reaction of enolates with $(C_6H_5Cl)FeCp^+$ resulted in phenylation of the enolate[331]. Use of ethanenitronate anion with the same complex gave $(C_6H_5COMe)FeCp^+$ [332], and Ph_3SnLi gave the mono CpFe$^+$ complex of tetraphenyltin[333]. Reactions of (o-dichlorobenzene)FeCp$^+$ with alkoxides could be manipulated to give either mono- or di-substitution; amines and enolates gave only monosubstitution[334]. The nitro group of (nitroarene)FeCp$^+$ could be displaced by O-, S-, or N-based nucleophiles, and the organic ligands liberated by pyrolytic sublimation[335,336].



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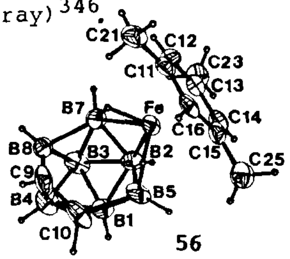
Partial hydrogenation of polycyclic aromatics during introduction of FeCp$^+$ or FeCp^{*+} groups has been investigated. One curious result was that reaction of Fp*Br with anthracene in the presence of aluminum chloride gave the 1,2,3,4-tetrahydroanthracene complex, in contrast to the unmethylated cyclopentadienyl case, which gave complexed 9,10-dihydroanthracene. The general mechanism proposed involved formation of neutral AnFeCp and H-atom transfers[337]. Reduction of AnFeCp$^+$ cations [An = naphthalene, phenanthrene] by sodium has been found by ESR to occur in three stages[338]. Cyclic voltammetric study of such reductions has also been reported: in the presence of donor ligands, the neutral AnFeCp readily lost the arene to form a labile 17-electron intermediate $CpFeL_2$. In the absence of such ligands, ligand exchange reactions led to ferrocene, the amount of which could be increased by addition of cyclopentadiene[339]. Reaction of ferrocene with arenes and aluminum chloride under CO_2 provided AnFe$(C_5H_4COOH)^+$. Reduction of the hexamethylbenzene complex gave the unstable neutral carboxylic acid or the thermally-stable radical-anion, $(C_6Me_6)Fe(C_5H_4CO_2^-)$[340]. Two novel mixed-valence compounds, $CpFe(\mu-C_5H_4-C_5H_4)FeAn$ and $AnFe^+(\mu-C_5H_4-C_5H_4)FeAn$, have been studied by Mössbauer spectroscopy from 4 K to room temperature. The less-symmetrical Cp compound was found to be localized, and the symmetrical bis(arene) compound delocalized, consistent with MO calculations[341].

A review of polyhedral metalloboranes, -carboranes, and -heteroboranes containing the cyclopentadienyliron group has appeared[342]. Salts of $AnFeCp^+$ cation with various cyclic halohydroborate anions have been prepared[343]. Reactions of iron atoms with arenes and nido-2,6-$C_2B_7H_{11}$ led to closo-(arene)iron($C_2B_7H_9$) clusters and, with mesitylene, a nido-$C_2B_7H_{11}$ cluster, **56**[344].

Bis(η^2-ethene)(η^6-toluene)iron was formed by reaction of bis(toluene)iron with ethene at - 60°. Despite its decomposition at temperatures above -20°, an X-ray structure was obtained. The ethene ligands were readily displaced by phosphines to form (toluene)FeL_2[345]. Reaction with the free heterocycle produced **57** (X-ray)[346].



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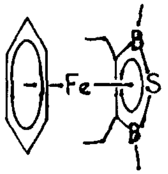

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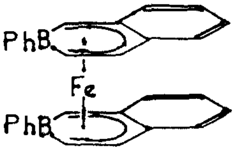

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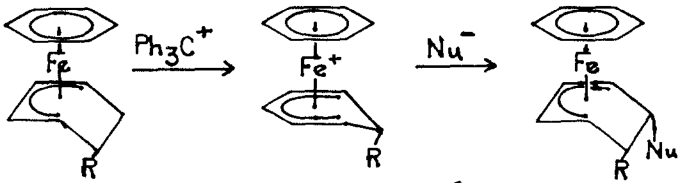
Hydride removal by trityl cation from substituted cyclohexadiene complexes **58** was shown to occur by electron transfer followed by hydrogen transfer[347]. This reaction was a key part of synthetic sequences (Eq. 29 shows one example) which facilitated syntheses of cis-disubstituted 1,3-cyclohexadienes[347,348].

58



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A complex of a diborabenzene, [η^6-1,3-bis(diisopropylamino)-1,3-diborabenzene]tricarbonyliron, was one product of reaction of a bicyclic precursor with $Fe(CO)_5$[349]. The bis(boratanaphthalene)iron compound **59** was prepared from the lithium boratanaphthalene and FeX_2[350].

Bis(arene)iron compounds reacted with the heterocycle at about -80° to give, after warming, **56**[346]. Salts of An_2Fe^{2+} with $B_{12}H_{12}^{2-}$ anion have been prepared using a variety of arenes[351].

High quality crystals of (η^6-C_6Me_6)Fe^{2+} (tetracyanoquinodimethane$^-$)$_2$ were prepared by carefully controlled electrocrystallization[352].

Formation of (η^6-benzene) groups on the catalyst surface has been postulated, to account for the effect of added benzene on product chain length during hydrogenation of CO on iron catalysts[353].

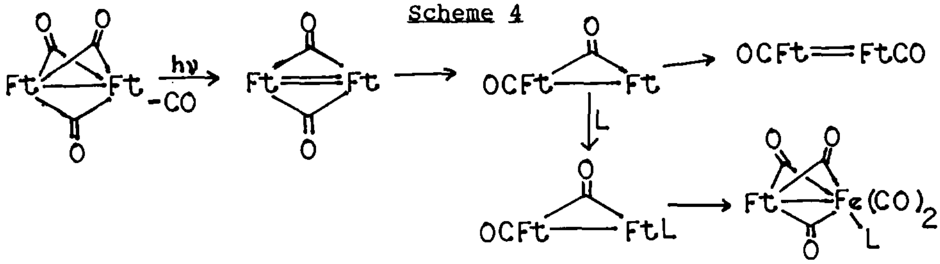
9. BIMETALLIC COMPOUNDS

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

A molecular mechanics simulation using a surface force field model has indicated a crowded ligand environment in $Fe_2(CO)_9$[354]. Its photolysis in argon matrices (Scheme 4) formed the doubly-bridged $Fe_2(CO)_8$ as the primary photoproduct, which isomerized through a singly-bridged intermediate to the D_{2h} unbridged form. The singly-bridged species was found to be the one responsible for reactions with ligands L[355].

The bridged methylene complex $(OC)_4Fe(\mu$-$CH_2)Fe(CO)_4$, **15**, has been synthesized directly from $Fe(CO)_5$ and CH_2Br_2 under phase transfer conditions[356]. FTIR studies in argon and nitrogen matrices (in which the compound adopts the doubly CO-bridged structure of the crystal state rather than the un-CO-bridged structure found in solution), have indicated sp^3 hybridization of the methylene carbon; the $^1J_{C-H}$ value of 147 Hz was smaller than the 161 Hz of cyclopropane[357]. Reactions of **15** with CO were previously described (Eq. 6).

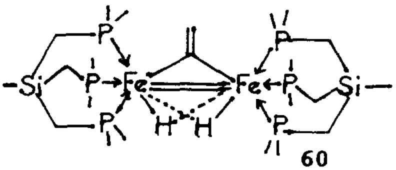
Scheme 4



Bonding in $[\mu$-$SbCH(SiMe_3)_2]Fe_2(CO)_8$ has been discussed, with emphasis on formation of the "closed" (Fe-Fe bonded) rather than "open" structure[107]. The novel product **60** resulted from reaction of (η^4-C_6H_6)FeL with 7 atm. ethene at 50° and also from reduction of $LFeCl_2$ under 2 atm. ethene. [L = $MeSi(CH_2PMe_2)_3$] The Fe=Fe bond distance was 2.428(1) Å.[141].

Reaction of $Fe_3(CO)_{12}$ with DPPM gave *inter alia* $Fe_2(CO)_7(\mu$-DPPM) and $Fe_2(CO)_5(\mu$-DPPM$)_2$[358]. Oxidation of $R_2P[Fe(CO)_4]_2^-$ produced isolable 33-electron species, $(OC)_4Fe(\mu\text{-}PR_2)Fe(CO)_3$, having the odd electron localized on the $Fe(CO)_3$ group (based on ESR and MO results). These readily added CO to form 35-electron $Ft(\mu\text{-}PR_2)(\mu\text{-}CO)_2Ft$, in which the odd-electron was housed primarily on the bridging CO groups[359].

The $(\mu\text{-}B_3H_6)Fe_2(CO)_6^-$ anion, **61**, which resulted from removal of a Fe-H-B bridging proton from its conjugate acid, has been investigated, with particular emphasis on its static hydrogens, which contrasted with the fluxionality of the conjugate acid[360].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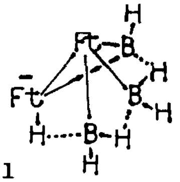
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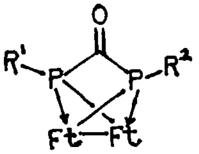
The most common di-iron compounds are those in which two tricarbonyliron (Ft) groups are bridged by two three-electron donors, commonly RS or R_2P. This review will discuss first the Group 15 examples, then the Group 16, then compounds with organic bridging ligands.

The Mössbauer spectra of some N-bridged $Fe_2(CO)_6$ complexes have been reported, including those of $(\mu\text{-}Ph_2C{=}N)_2Ft_2$ and (benzo[c]cinnoline)$Fe_2(CO)_6$[361]. Oxidation of $(\mu\text{-}Me_3CPH)_2Ft_2$ formed the diferradiphosphatetrahedrane (X-ray), whose P-P bond readily added such species as CO, hydrogen, and ethene[362]. An extensive study of reactions of $(ON)_2Fe(\mu\text{-}PR_2)_2Fe(NO)_2$, especially its reduction to a dianion, and the reactions of the latter with electrophiles, has been carried out. The results were compared with those on $Ft(\mu\text{-}PR_2)_2Ft$[26].

When $(OC)_2Fe(\mu\text{-}CO)[\mu\text{-}(RO)_2PN(Et)P(OR)_2]_2Fe(CO)_2$ was dissolved in carbon tetrachloride, the bridging CO was rapidly lost, replaced by a μ-chloronium bridge[363]. Reaction with halogens gave eventually the same product, but an intermediate, $Ft(\mu\text{-}PNP)_2Fe(CO)_2X^+$, could be detected; in the case of X = I, an X-ray structure of the PF_6^- salt of the intermediate was reported[364].

A number of complexes with carbonyl-diphosphinidene ligands (**62**) have been described. **62** ($R^1 = R^2 = CMe_3$) has already been described as resulting from CO insertion into a P-P bond[362]. Another example, $R^1 = Fp^*$, R^2 = 2,4,6-tri-t-BuC_6H_2, (X-ray) resulted from reaction of the diphosphene complex **18** with $Fe_2(CO)_9$[110]. Another example, with $R^1 = R^2 = N(CHMe_2)_2$, resulted in low yield from dehydrochlorination of $(Me_2CH)_2NP(H)Cl{\rightarrow}Fe(CO)_4$[105]. The same compound had previously been obtained from R_2NPCl_2 and $Fe(CO)_4^{2-}$ in ether. In THF, the latter reaction produced mainly the analogous triphosphine derivative, Ft[μ-

P(NR$_2$)P(NR$_2$)P(NR$_2$)]Ft (X-ray) along with other minor products. The di-isopropylamino group on the central (uncoordinated) phosphorus was replaced by Cl upon treatment with HCl[365]. An exotic μ-triphosphine, **63**, was produced by room-temperature decarbonylation of **21**[112].



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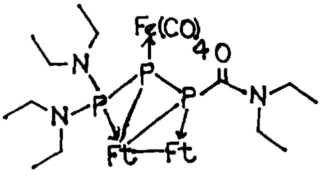
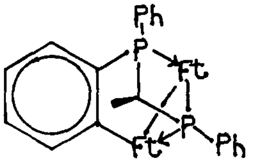


63

Whereas heating (μ-DPPM)$Fe_2(CO)_7$ resulted in P-C bond cleavage to form Ft(μ-PPh$_2$)(μ-CH$_2$PPh$_2$)Ft, the C-methyl analog gave a more complex ortho-metallation process, to form **64** (X-ray)[366]. Heating (μ_3-PPh)$Fe_3(CO)_9$ in the presence of diphenylacetylene led in part to formation of **65**[367]. Benzo analogs of **65** resulted when



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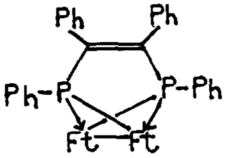
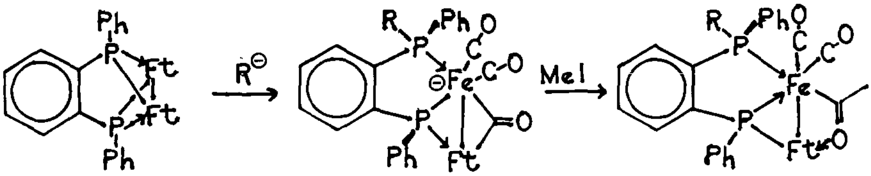


65

o-C$_6$H$_4$(PRCl)$_2$ was allowed to react with nonacarbonyldiiron[368]. These reacted at phosphorus with strong nucleophiles, giving anions which formed μ-acyls on reaction with MeI (Eq. 30)[369].



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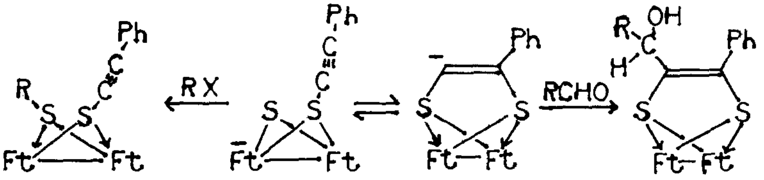
EXAFS studies of the structures of E$_2$Ft$_2$, the dianions E$_2$Ft$_2$$^{2-}$, and the alkylated ($\mu$-ER)$_2Ft_2$ [E = S,Se] confirmed the similar Fe-C, Fe-Fe, and Fe-E distances in all cases, the result of reduction being to break the E-E bond present in the neutral starting material. Similar results were obtained for the nitrosyls E$_2$Fe$_2$(NO)$_4$$^{2-}$ and (μ-ER)$_2$Fe$_2$(NO)$_4$[370]. Conversion of the nitrosyl dianion, picturesquely called "Roussin's red salt," to neutral products by reaction with electrophiles RX, R$_3$SnX, Ph$_3$PbBr, RHgX, and Fp(THF)$^+$ has been studied[371].

Fe$_2$(μ-SPh)$_2$(CO)$_4$L$_2$ formed a BF$_3$ adduct in which the Lewis acid was said to bridge the Fe-Fe bond[372]. However, reaction of the dianion S$_2$Ft$_2$$^{2-}$ with various boron halides produced products

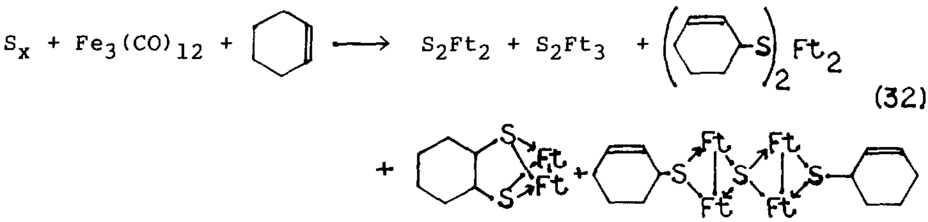
Ft[μ-SB(X)S]Ft, having X = NMe_2, O-t-Bu, halogen, or R, and Ft[μ-SB(X)B(X)S]Ft, with X = NMe_2, Cl, or Br[373]. S-S bridged intermediates were also suggested by the results of alkynyl-lithium attack of (μ-dithio)bis(tricarbonyliron). The resulting anionic products reacted at S with alkylating and acylating agents, but



(31)

at C with H^+ and aldehydes (Eq. 31)[374]. A product with a metal group linking the two sulfurs resulted when the dianion reacted with $MoCl(=NNMe_2)_2(PPh_3)_2^+$ [375]. Bis(μ-mercapto)bis(tricarbonyliron), $(\mu\text{-HS})_2Ft_2$, gave Michael adducts with α,β-unsaturated ketones, esters, and nitriles in the presence of piperidine. With acetylenic substrates, both sulfurs added, to form a one-carbon bridge between them. An X-ray structure of Ft[μ-SCH(CH_2COMe)S]Ft confirmed the structure. Dimethyl acetylenedicarboxylate formed the two-carbon bridged structure, Ft[μ-SCH(E)CH(E)S]Ft [E = CO_2Me][376].

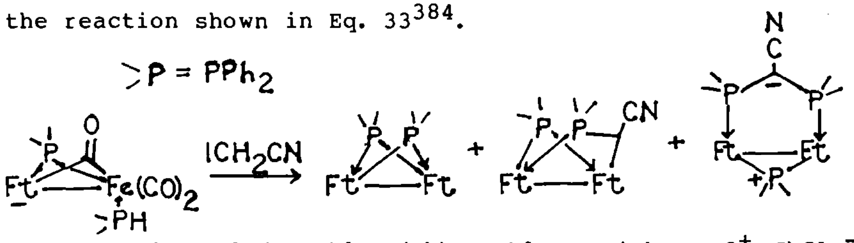
Reactions of sulfur with $Fe_3(CO)_{12}$ and various alkenes also result in formation of derivatives of the S_2Ft_2 system. For example, cyclohexene reacted as shown in Eq. 32[377]. The struc-



(32)

ture of the tetrairon compound was ascertained by S-ray crystallography[377]. A similar reaction using allyltrimethylsilane gave S-S bridged products with bridges derived from 3-trimethylsilylpropane-1,2-dithiol and 2-trimethylsilyl-1,3-propanedithiol[378]. Cyclic dienes gave 1,2-dithiol-derived bridges[379]. Norbornadiene gave isomeric bridged products containing the norbornene and nortricyclene skeletons[379,380].

Reaction of dithioesters with $Fe_2(CO)_9$ gave **66** (X-ray)[382]. **66** reacted with ligands L [$P(OMe)_3$, CNR, Ph_2PH] exclusively by substitution at the iron not bound to carbon[382]. Reactions of $(\mu\text{-CO})(\mu\text{-SR})Ft_2^-$ with alkyl- and aryl-HgX gave the μ-acyl compounds, $(\mu\text{-RCO})(\mu\text{-SR})Ft_2$. However, vinylic and alkynylic mercury reagents reacted with displacement of the CO to form μ-vinylic compounds such as **67**[383]. Organic ligands were also produced in the reaction shown in Eq. 33[384].



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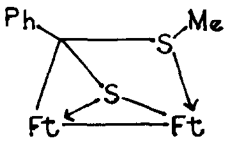
Reaction of (μ-CO)[μ-C(Ph)=CHPh]Ft_2 with Me_3O^+ $SbCl_6^-$ went beyond the expected methylation of the bridging carbonyl group to produce the (μ-Cl) product (X-ray)**68**[385].



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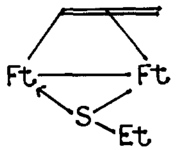

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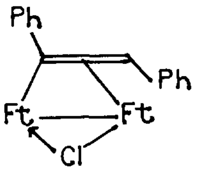

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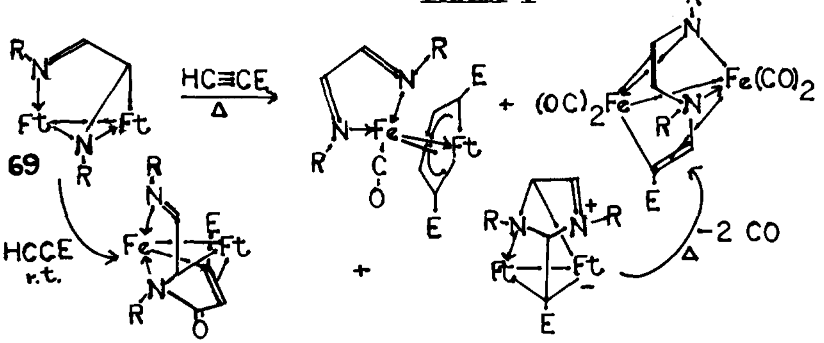
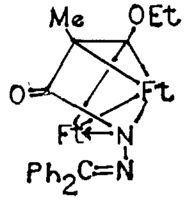
The structures of $Fe_2(CO)_6$ complexes of unsymmetrical diazadienes, $R^1N{=}CH{-}CH{=}NR^2$ have been found to be distinguishable by detection of a four-bond allylic coupling between R^1 and the imine C-H (see structure **69**)[386]. Pyridine-2-carbaldehyde imines reacted with nonacarbonyldiiron to form N,N-bound $Fe(CO)_3$ complexes and diiron hexacarbonyl complexes similar to **69**, with the pyridine nitrogen playing the N-donor role. They thus behaved very similarly to the diazadienes[87]. Reaction of **69** with methyl propynoate resulted in elaborate ligand coupling reactions (Scheme 5)[387].

Scheme 5



Ligand coupling was also the hallmark of reaction of (μ_3-CMe)(μ_3-COEt)Ft_3 with diphenyldiazomethane. The product, **70**, showed loss of one tricarbonyliron group and coupling of both alkylidene fragments with a CO and the diazo compound[388]. Reaction of 1-(diethylamino)propyne with iron carbonyls gave two diiron and two triiron products. One of the former, **71** (X =

Et_2N, R = Me) was an example of the well-known class of "flyover" compounds; the other, **72**, a more novel coordinated dicarbene, was implicated as a precursor to **71**[389].



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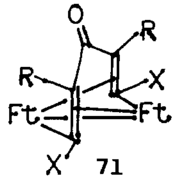

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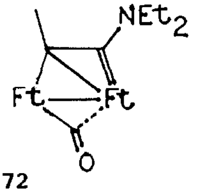
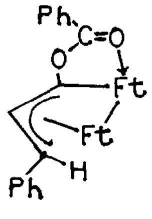


72

The photoelectron spectra of the unsaturated cluster (μ-*t*-BuC≡C-*t*-Bu)Ft_2 have been obtained and interpreted by comparison with SCF calculations on the unsubstituted ethyne analog[390].

Reaction of the ketodiene complex [PhCH=CH-C(OCOPh)=C=O]-$Fe(CO)_3$ with nonacarbonyldiiron (or thermolysis) gave the diiron complex **73**. The ferrole complex **74** (X-ray) (R^1 = OCOPh, R^2 = OMe, R^3 = H) resulted from reaction of $H_2C=C=C(OMe)Li$ with dodecacarbonyltriiron, followed by addition of benzoyl chloride[391]. A benzoferrole complex, **74** (R^1 and R^2 = C_4H_4, R^3 = Ph), resulted from treatment of several different di- and tri-iron complexes of diphenylacetylene with acids, alkylating agents, and oxidizing agents[392]. Detailed NMR studies of benzoferrole complexes **74** have been reported[393]. Photoelectron spectra and MO calculations on "flyover" compound **71** (R = X = Et) have been reported[394]. The fluxional process in **71**, which interconverts the σ- and π-bonded groups at each metal, has been studied by variable temperature NMR. The $G^{\ddagger}$ was about 70 kJ/mol[395].

The dihydroacepentalene complex **75** was the principal product formed when di- and trihalotriquinacenes reacted with nonacarbonyldiiron[175]. Several $Fe_2(CO)_6$ complexes of 2-substituted tropones, which presumably have the bis(π-allyl) structure of the parent, have been prepared[186].



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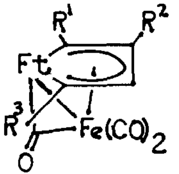

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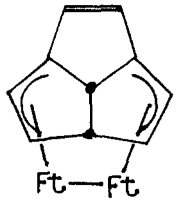
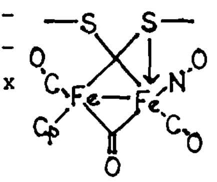


75

b. Derivatives of $Cp_2Fe_2(CO)_4$

Reaction of 6,6-dimethyl-1,2-benzofulvene with nonacarbonyldiiron gave the dimer $[InFe(CO)_2]_2$ (In = η^5-1-isopropylindenyl) and μ-(1-5-η^5:6-η^1-6,6-dimethyl-1,2-benzofulvene)hexacarbonyldiiron(Fe-Fe) (X-ray)[397]. Reaction of (6,6-diphenylfulvene)diiron pentacarbonyl with CN^- resulted in the reaction shown in Eq.

34[396]. The product **76**, with a bridging dithiocarbene ligand, resulted from reaction of a terminal dithiocarbene complex with $Fe(CO)_3NO^-$ [302].



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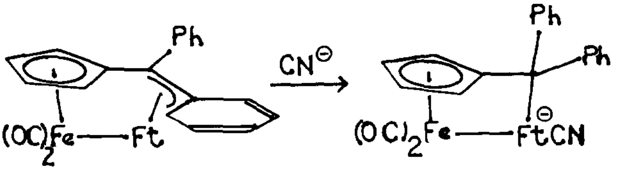


(34)

The borabenzene complex $[(\eta^6\text{-}PhBC_5H_5)Fe(CO)_2]_2$ resulted on irradiation of $(\eta^5\text{-}PhBC_5H_6)Fe(CO)_3$[398]. Fenske-Hall MO calculations were used to compare $[CpFe(NO)]_2$ with cobalt and nickel analogs[399]. Reaction of dicyclopentadiene with $Fe(CO)_5$ in the presence of kerosene as a source of hydrogen gave 33% of the normal Fp_2, along with 7% of a ketone derived from dicyclopentadiene[400]. The cis isomer of $Fp^*{}_2$ was detected in a photochemical study[206]. A 10 µs time-resolved IR study of photosubstitution in Fp_2 indicated that $CpFe(\mu\text{-}CO)_3FeCp$ was the principal intermediate; activation parameters for its reaction with phosphines were reported[401]. Fenske-Hall MO calculations have been used to compare the bonding and reactivity in a series of compounds $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}X)Fe(CO)Cp$ ($X = {>}CO, {>}CH_2, {>}C{=}CH_2,$ and ${>}CH^+$). The conclusions reached on photochemical reactivity of Fp_2 were at odds, however, with the just-cited experimental study on photosubstitution, favoring an open $Fp\text{-}CO\text{-}Fe(CO)Cp$ intermediate[402].

The X-ray structure of trans-$CpFe(NCR)(\mu\text{-}NCR)_2Fe(NCR)Cp$, **77**, [R = 2,6-dimethylphenyl] and the dynamics of its cis-trans isomerization in solution have been studied[403]. **77** (R = Me) underwent facile mono- and dialkylation and protonation on the bridging isonitrile nitrogens[404]. The monoprotonated cation underwent a two-electron oxidation when treated with one equivalent of Ag^+; the products depended on the coordinating ability of the counter-anions[405,406].

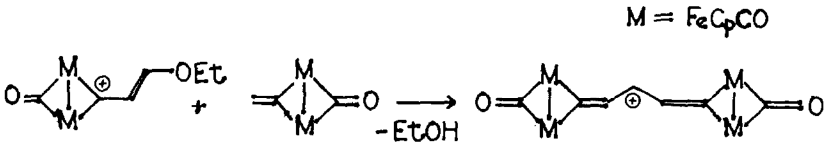
Fp_2 has been found to catalyze addition of halocarbons to alkenes at 40-120° by a non-radical process. $FpC(=O)Fe(R)(X)Cp$ was proposed as the active intermediate[407]. Fp_2 was also an effective catalyst for substitution of CO by L in polynuclear metal carbonyls[408]. Photoreaction of the bridged Fp_2 analog $Me_2Si[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ with DPPM and DPPE has been studied. Formed were monosubstitution products, and products with intramolecular and intermolecular bidentate bridging. Mössbauer spectra were reported[409].

Cis-trans isomerization of $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}CH_2)Fe(CO)Cp$ has been studied by NMR methods. The proposed mechanism involved Fe-

Fe bond cleavage[410]. Bonding in $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}CH_3)Fe(CO)Cp^+$ has been studied by Fenske-Hall MO methods, which indicated a small preference for asymmetric Fe-----H-CH_2-Fe bridging over symmetrical methyl group bridging[411].

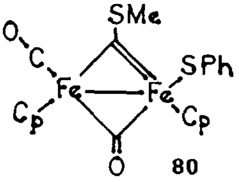
The bridging vinylidene complex $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}C{=}CHR)\text{-}Fe(CO)Cp$, **78** (R = H), functioned as a nucleophile in Michael addition to $HC{\equiv}CCN$, to yield the μ-C=CH-CH=CHCN adduct. Hydride reduction of the adduct occurred at the bridging carbon[412]. Reaction of **78** (R = H) with ethyl diazoacetate/ CuI gave a μ-cyclopropylidene complex which opened on treatment with acid to give **78** (R = CH_2CO_2Et). Photolysis of **78** (R = H) and ethyl diazoacetate gave $Cp(CO)Fe(\mu\text{-}H_2C{=}C{=}CHCO_2Et)Fe(CO)Cp$[413]. The parent μ-allene complex (X-ray) could be obtained by photolysis of the μ-cyclopropylidene; it was also formed from the latter at temperatures above 100°, but decomposed at those temperatures with liberation of allene[414]. Protonation of the μ-cyclopropylidene complex gave the cation $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)Fe(CO)Cp^+$, which deprotonated to form **78** (R = Me). Repetition of the cycle (methylenation, protonation, deprotonation) formed $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}C{=}CMe_2)Fe(CO)Cp$ rather than **78** (R = Et); thus the process fails to model the predominantly linear chain growth observed in Fischer-Tropsch chemistry[415]. The X-ray structure of the μ-(methylcyclopropylidene) complex has been reported[416].

The methylidyne complex $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CH^+)Fe(CO)Cp$, **79**, underwent allylation on treatment with allyltrimethylsilane. Addition reactions of several functionalized alkenes were also reported[417]. Simple alkenes gave μ-alkylidyne products ("hydrocarbation") by attack of the electron-deficient methylidyne carbon at the less substituted end of the alkene[418]. Eq. 35 represents an example where a dimetallocarbyne and a dimetalloethylene react in this manner[419].



(35)

The bridging thiocarbyne species $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CSMe^+)Fe(CO)Cp$ underwent one-electron reduction to form a persistent neutral radical whose CO groups were very labile compared to those of the cation. The radical reacted with PhSSPh to form **80**[421]. Reaction of the methylidene complex $[CpFe(NO)]_2(\mu\text{-}CH_2)$ with Ph_3C^+ salts led to hydride abstraction to form **81**, which in part reacted further, depending on conditions. It abstracted the bridging group from the μ-methylidene complex to form a μ-vinyl complex, along with [CpFe(NO)]$_2$. It was much less electrophilic than the carbonyl analog **79**, and its ^{13}C resonance was 142 ppm to higher field than the carbonyl analog[420]; both phenomena may be attributed to the bridging nitrosyls functioning as four-electron donors as shown in the structure on the right.



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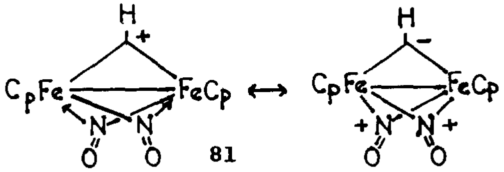
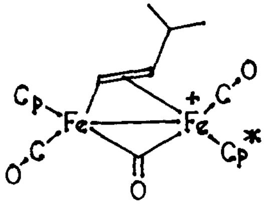


81

Reaction of **79** with vinylcyclopropane, followed by deprotonation with Me$_3$N, gave **78** (R = HC=CH-C$_3$H$_5$). The mono(pentamethylcyclopentadienyl) analog of **79** reacted with isobutene to give the μ-alkenyl complex **82** rather than the μ-alkylidyne; steric and electronic factors influencing the two pathways have been discussed[422]. 1,2-Disubstituted alkenes generally gave equilibrium mixtures of both product types; deuterium labelling studies indicated that the μ-alkylidynes were the kinetic products, which rearranged by hydride shifts to the μ-alkenyls[423]. Reaction of **79** with 1-methylcyclohexene proceeded with alkyl group migration to produce the μ-alkenyl **83**. Analogous migrations were observed with stilbene and other alkenes, and were studied by deuterium labelling[424]. Reaction of μ-vinyl complexes (**47**, **82**, etc.) with acetonitrile produced FpCH=CHR and CpFe(CO)(NCMe)$_2^+$ in a second-order reaction[285].



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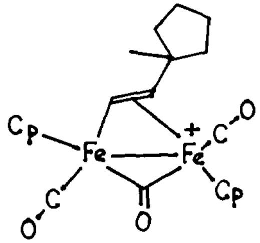


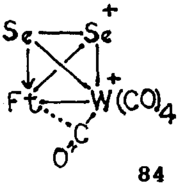
c. Heterobimetallic Compounds

Reaction of Cp$_2$Zr(R)Cl with NaFp produced Cp$_2$Zr(R)-Fp [R = Me, octyl, Cl] with a Fe-Zr bond[425].

The largest group of Fe-M compounds involves Group 6 metals. The simplest such compounds arise when HFe(CO)$_4^-$ donates an electron pair to a M(CO)$_5$ moiety, forming (OC)$_4$Fe(H)-M(CO)$_5^-$. PPN$^+$ salts of the Cr and W compounds, the deprotonated Cr compound, and a trimethylphosphite-substituted W compound have all been studied by X-ray crystallography. Both the hydride and the carbonyl ligands are terminal, and the hydride was believed to be cis to the M(CO)$_5$ group[426]. This was supported by MO calculations based upon the experimental structure of the W compound[427].

Reaction of $Cp(OC)_2M{=}PR_2$ with nonacarbonyldiiron added a $Fe(CO)_4$ group across the P=M double bond, giving a phosphinidene-bridged Fe-M bond[227]. Similar products, $CpFe(\mu\text{-}CO)[\mu\text{-}PH(NR_2)]\text{-}M(CO)_4$, resulted from photolysis of $FpPH(NR_2)\rightarrow M(CO)_5$ [M = Cr, Mo, and W][226]. Reaction of Se_4^{2+} with a mixture of $W(CO)_6$ and $Fe_2(CO)_9$ gave the Se_2-bridged species **84** (X-ray)[428]. A less-symmetrical diselenium-bridged bond resulted when $Fp\text{-}Se_xFp$ (x = 1 or 2) reacted with $[CpCr(CO)_3]_2$ to produce **85** along with the mixed Fe-Cr dimer, $Cp(CO)Fe(u\text{-}CO)_2Cr(CO)_2Cp$[250].

The structure of the novel heterodiene complex **86** (Ar = 2,4,6-tri-*t*-butylphenyl) has been published[429]. (μ-Acyl) compounds have been generated by two different routes. In one, $FpPPh_2$ reacted with $MeMo(CO)_3Cp$ to form $Cp(CO)_2Mo(\mu\text{-}PPh_2)(\mu\text{-}O{=}CMe)Fe(CO)Cp$, whose structure indicated strong oxycarbenoid character (Fe=C and Mo-O bonds) and no formal Fe-Mo bond[430]. In the other case, $Fp(THF)^+$ reacted with $Cp(CO)(NO)Mo{=}C(Ar)OLi$ [Ar = *p*-tolyl] with migration of acyl carbon from molybdenum to iron (Eq. 36). The unstable π-acyl was characterized spectroscopically and shown to rearrange to the final μ-acyl. Byproducts included Fp_2, $CpMo(CO)_2(NO)$, and a trace of FpAr[431].



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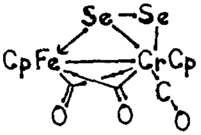

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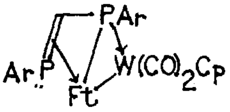

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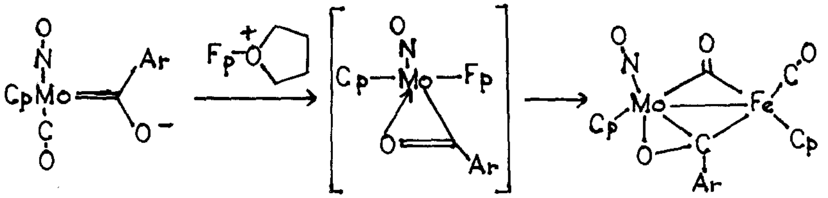
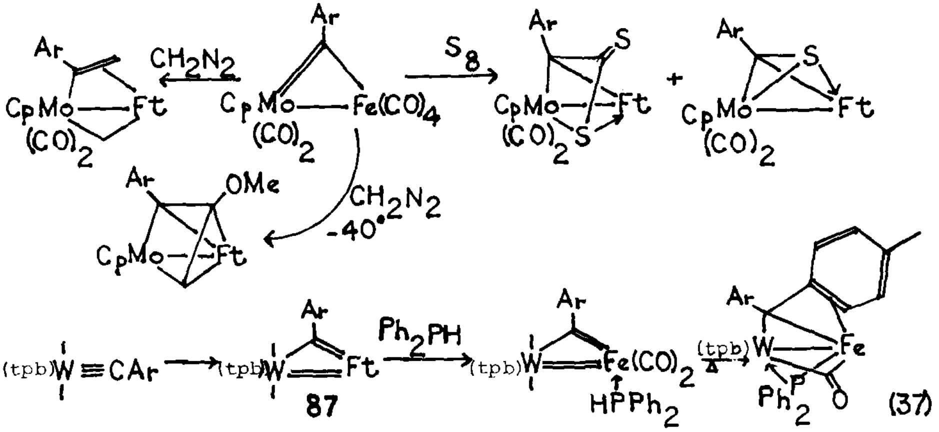


(36)

Additions to the μ-alkylidyne bridge in $Cp(CO)_2Mo(\mu\text{-}CAr)\text{-}Fe(CO)_4$ [Ar = *p*-tolyl] are exemplified in Scheme 6[432]. Addition of diazomethane to $Cp^*(CO)_2W(\mu\text{-}CAr)Fe(CO)_3$ proceeded similarly, with addition of one or two methylene groups across the Fe=W bond[433].

Tris(1-pyrazolylborate) (tpb) analogs of these compounds have also been studied (Eq. 37)[434]. An X-ray structure of **87** showed bond lengths: Fe=W 2.612(2) , W-C 2.025(7), and Fe=C 1.826(6) Å[435]. Reaction of **87** with DMPM gave a μ-DMPM derivative (X-ray)[435].

Scheme 6

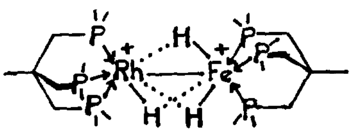


Photolysis of $FpPHNR_2 \rightarrow Mn(CO)_2Cp$ gave $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}PHNR_2)Mn(CO)Cp$[226]. The analogous compound $Cp(CO)Fe(\mu\text{-}CO)_2\text{-}Mn(CO)(SiPh_2Me)Cp'$ was prepared by reaction of the anion $Cp'Mn(CO)_2(SiPh_2Me)^-$ with FpI[436].

The phosphido-bridged mixed-metal compound $(OC)_3Fe(\mu\text{-}PPh_2)_2\text{-}Os(CO)_3$ has been prepared and studied. Hydride reduction gave the osmium-formyl anion, which slowly decarbonylated to the hydride at room temperature[437].

Of possible use as bimetallic catalysts are Fe-M compounds in which the metal-metal bond is reinforced by bridging diphosphine ligands. Several such compounds with Group 9 metals have been described during 1986. Crystal structures of $(OC)_4Fe(\mu\text{-}DPPM)ML_n$, ML_n = Rh(CO)Cl and $PtBr_2$ have been described[438]. The $H_2C{=}C(PPh_2)_2$ analog of the former underwent decarbonylation with Me_3NO to form $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}L)Rh(CO)Cl$[439]. $(OC)_3Fe(\mu\text{-}PPh_2)_2\text{-}Ir(COD)Cl$, from which the 1,5-cyclooctadiene ligand could be displaced by CO's under pressure, has also been prepared. The Fe-Ir distance was 2.703(1) Å, consistent with the expected metal-metal bond[440].

The tris(hydrido)-bridged species **88** has been prepared. It underwent electrochemical reduction to the +1 species[441]. The double-bonded species **89** (M = Co, Rh, and Ir) were made from $Fe(C_6Me_6)_2$ and $Cp^*M(CO)_2$. The iridium compound was converted to the $\mu\text{-}CH_2$ compound with diazomethane[442].



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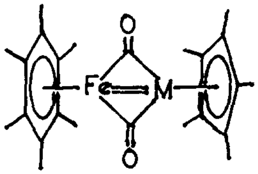
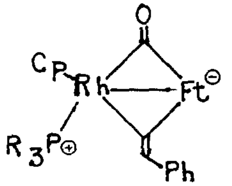


89

Products **90** and **91** resulted from reaction of CpRh(PR$_3$)-(n^{2}HC≡CPh) [R = CHMe$_2$] and Fe$_2$(CO)$_9$[443]. Metal exchange between Co$_2$(CO)$_8$ and Ft(μ-CO)(μ-CH=CHPh)Ft$^-$ produced **92**[444].



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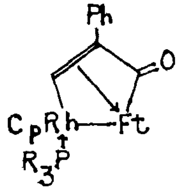

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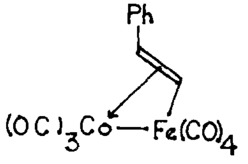


92

Phosphine substitution reactions occurred readily on the rhodium center of (OC)$_2$Rh(μ-C$_7$H$_7$)Fe(CO)$_3$. The Rh(DPPM) compound, unlike the Rh(CO)$_2$, showed a bridging carbonyl ligand; this indicated a η^4-Fe, η^3-Rh mode of bonding to the cycloheptatrienyl ligand, which was verified in the X-ray structure[445]. The structure of (OC)$_3$Fe(μ-COT)Rh(nbd)$^+$ [nbd = η^4-norbornadiene] showed a η^3-Fe, η^5-Rh bonding mode to the biplanar COT ligand[446].

The aforementioned (OC)$_4$Fe(μ-DPPM)PtBr$_2$ reacted with MeI to give (OC)$_3$Fe(μ-DPPM)(μ-I)PtI, which was also formed from (DPPM)-Fe(CO)$_4$ and (COD)PtI$_2$[447].

10. TRINUCLEAR CLUSTER COMPOUNDS

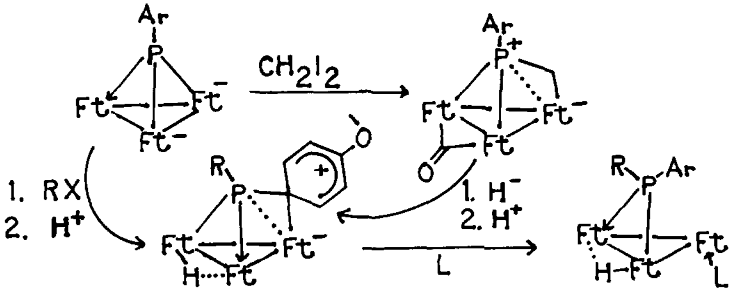
a. Fe$_3$ Clusters

The ^{13}C-NMR of solid Fe$_3$(CO)$_{12}$ has been obtained using magic angle spinning at temperatures down to -93°. This resulted in quenching of fluxional motions and a spectrum consistent with the static (μ-CO)$_2$ structure[448]. Mössbauer spectra of several clusters related to Fe$_3$(CO)$_{12}$, including Fe$_3$(CO)$_{11}{}^{2-}$, mixed Fe-Ru analogs, and phosphine-substituted clusters, have been reported[449]. Adsorption of Fe$_3$(CO)$_{12}$ on hydroxylated alumina has been described in terms of disproportionation reactions which form adsorbed Fe^{2+} Fe$_3$(CO)$_{11}{}^{2-}$, which may undergo decarbonylation to form subcarbonyls[450].

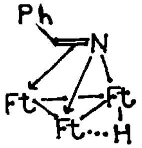
Reaction of Fe$_4$S$_4$(SPh)$_4{}^{2-}$ with *t*-BuLi under CO led to the the tetrahedral cluster (μ$_3$-S)Ft$_3{}^{2-}$, (X-ray structure)[451]. Upon heating, (μ$_3$-NCH$_2$Ph)(μ$_3$CO)Ft$_3$ lost CO and rearranged to **93**. Both were formed upon acidification of a precipitate from reaction of PhCH=N-N=CHPh with Fe$_3$(CO)$_{12}$[452]. The acetonitrile ligand in (MeCN)Ft$_3$, **94**, was synthesized by ligand coupling of the ethylidyne ligand during reaction of Fe$_3$(μ$_3$-CMe)(CO)$_{10}$(NO) with alkynes (which mainly produced ferrole products) and also in reaction of HFe$_3$(μ$_3$-CMe)(CO)$_{10}$ with diphenyldiazomethane (18%) [453].

A phosphorus analog of **94**, (μ$_3$-η^2-RCP)(μ-H)Ft$_3{}^-$ has been reported[454]. Reaction of $Fe_4(CO)_{13}^{2-}$ with PCl_3 produced $Ft_3(\mu\text{-}CO)[\mu_3\text{-}P\rightarrow Fe(CO)_4]$ (X-ray)[455]. Reaction of $(\mu_3\text{-}PAr)Ft_3^{2-}$ [Ar = *p*-C_6H_4OMe] with electrophiles produced several interesting and unusual products, shown in Scheme 7[456]. Photoinsertion of diphenylacetylene into $Ft_3(\mu_3\text{-}PR)(\mu\text{-}CO)$ (R = mesityl and *t*-Bu) has been studied. In each case, **95** was the initial product, which underwent additional thermal (R = mesityl)[457] or photochemical (R = *t*-Bu)[458] changes.

Scheme 7



Reaction of $Bi[Fe(CO)_4]_4^{3-}$ (whose tetraethylammonium salt has been structurally characterized[459]) with acidic methanol produced Ft_3Bi_2 and $Ft_3(\mu\text{-}H)_3Bi$[460].



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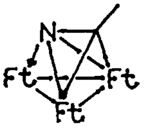

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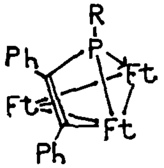
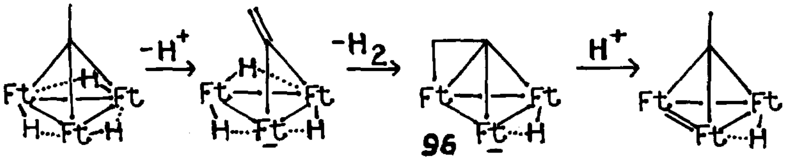


95

The complete series of clusters, $Fe_3(CO)_{10}(\mu\text{-}COMe)(\mu\text{-}MPPh_3)$ [M = Cu, Ag, and Au] has been prepared and characterized. All showed a closed triangle of iron atoms, with $MPPh_3$ and carbyne ligands bridging one bond[461].

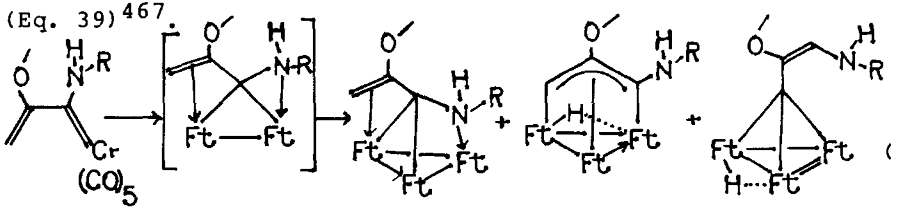
EHMO calculations on Ft_3CCO^{2-} indicated a small energy difference favoring the structure with the CO bridging a C-Fe bond over the linear C_{3v} arrangement; this result was consistent with the known crystal structure[462]. Labelling studies on hydrogenation-dehydrogenation of $Ft_3(\mu_3\text{-}CMe)(\mu\text{-}H)_3$ have indicated the mechanism of Eq. 38[463]. Reactions of terminal alkynes, RC≡CH,



(38)

with $HFe_3(CO)_{11}^{-}$ gave chemistry similar to Eq. 38, in which an intermediate like **96** but with CHR instead of CH_2 lost hydrogen to form an acetylide complex isoelectronic with **94** (C instead of N^+)[464]. **96** itself was obtained in the reaction of acetylene. It readily added CO to form $Ft_3(\mu_3\text{-}CMe)(\mu_3\text{-}CO)^-$, which in solution was in equilibrium with a (μ-CO) form. Reactions of these anions with electrophiles were studied. Ethylation with Et_3O^+ gave $Ft_3(\mu_3\text{-}CMe)(\mu_3\text{-}COEt)$, which formed $EtOCH_2CH_2CH_3$ on hydrogenation[465].

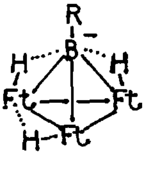
Electroreduction of $Ft_3(\mu_3\text{-}\eta^2\text{-}C_2Et_2)$, which has the alkyne ligand in the perpendicular orientation, gave a dianion in which the parallel orientation was indicated spectroscopically[466]. Reaction of $H_2C{=}C(OMe)C(NHR){=}Cr(CO)_5$ with nonacarbonyldiiron resulted in transfer of the vinylcarbene ligand to iron clusters (Eq. 39)[467].



(39)

Reactions of the boron-capped Ft_3 cluster **97** (R = H, Me) with Lewis bases in low concentrations proceeded with displacement of dihydrogen, giving **98**, rather than CO. At high ligand concentration, cluster fragmentation predominated[468,469]. Structures and spectra of **97** have been described in detail[470].

Turning now to bicapped Ft_3 triangles, one sulfur bridge in $(\mu_3\text{-}S)_2Ft_3$, **99** (Y = Z = S), was oxidized by peracid to give **99** (Y = S, Z = SO)[471]. The disulfide reacted with Me_2NH by substitution of the amine for a CO at a terminal iron atom[472]. The crystal structure of Ft(μ-TeFe(Cp)(NO)Te)Ft has been reported[473].



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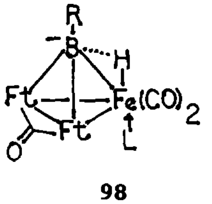

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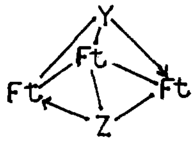


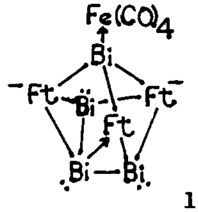
99

The product from reaction of azobenzene and $Fe_3(CO)_{12}$, originally proposed to have an o-semidine-like structure, has now been characterized as **99** (Y = Z = NPh)[474]. The same compound was also produced in "very small amounts" from nitrosobenzene[475]. **99** [Y = Z = $PN(CHMe_2)_2$] was a minor product of reaction of $Fe(CO)_4{}^{2-}$ and $(Me_2CH)_2NPCl_2$[365].

Electron-transfer catalysis induced facile ligand substitution of **99** (Y = Z = PPh), with one trimethylphosphite lig and being readily introduced into the coordination sphere of each iron[476]. The mechanism proposed, based on ESR evidence, involved slippage of a (μ_3-PPh) ligand to μ_2 in the radical anion, providing a labile 17-electron site[475,476]. More intensive reduction gave a dianion, which was protonated at -78° to produce $Ft_3(\mu_3$-$PPh)(\mu$-$PHPh)^-$ [478].

Reaction of the dibismuth analog **99** (Y = Z = Bi) with $Fe(CO)_4^{2-}$ gave a dianion with one bismuth coordinated to a terminal $Fe(CO)_4$ group[479]. Methylation of $Ft_3(\mu_3$-$Bi)(\mu_3$-$CO)^-$ with MeOTf gave the μ_3-OMe product[460]. The crystal structure of $Bi_4Fe_4(CO)_{13}^{2-}$, **100**, and MO calculations dealing with its bonding, have been reported[480].

Reactions of $Fe_2(CO)_9$ with various L_nM-PX_3 compounds produced derivatives of the closed cluster $Ft_3(\mu_3$-$P)_2$, in which each apical phosphorus was coordinated to an additional ML_n fragment [such as $Cr(CO)_5$ or $Mn(CO)_2Cp$]. Arsenic and antimony analogs were also prepared[481]. Thermally reversible photochemical addition of alkynes to $Ft_3(\mu_3$-$PAr)_2$ gave, along with **65**, products **101**. These also resulted when **65** reacted with $Fe_2(CO)_9$[367]. Thermal decarbonylation of **95** formed **102**[458].



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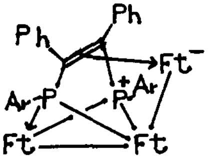

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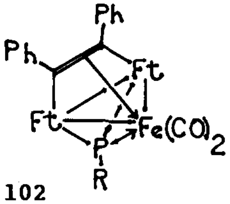
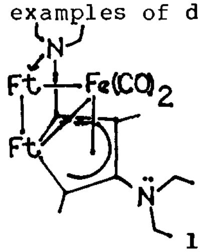


102

Among the products of reaction of 1-(diethylamino)propyne with iron carbonyls (**71** and **72** were previously mentioned) were two triiron compounds. **103** was the more novel, having resulted from head-to-tail coupling of two alkynes; head-to-head coupling gave a less exotic ferrole product, $[(OC)_2Fe(CNEt_2CMeCMeCNEt_2)]$-$Ft_2$[389]. Fp_2 effectively catalyzed ligand substitution reactions at both iron sites in the tetraphenylferrole complex $(Ph_4C_4)Fe_3(CO)_8$[408].

Theoretical considerations have led to an inquiry as to why no examples of dianion **104** appear to have been reported[482].



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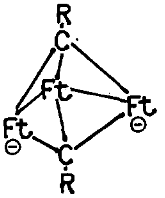

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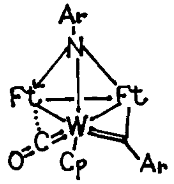


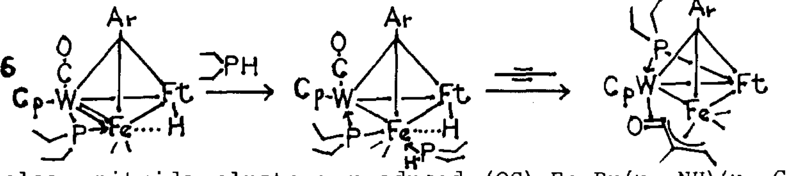
105

b. Fe_2M Clusters

Introduction of nitrogen into the cluster $Cp(CO)_2WFt_2(\mu-CO)(\mu_3-CAr)$ [Ar = p-tolyl] was achieved by reaction with $PPN^+ NO_2^-$ to form $CpW(CO)(NO)Ft_2(\mu_3-CAr)^-$, in which both the CO and the NO were semibridging. Protonation produced $CpW(CO)Ft_2(\mu-CAr)(\mu_3-NOH)$. A very similar product, **105**, resulted when the same starting material reacted with ArN_3[483]. The coordinatively unsaturated cluster **106** (Eq. 40), from thermal decarbonylation of a heptacarbonyl precursor, readily added ligands such as CO, R_2PH, and alkynes[484].

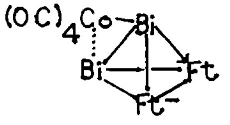
$Fe_2Ru(CO)_{12}$ was among the products of reaction of $Fe(CO)_4^{2-}$ with $[Ru(CO)_3Cl_2]_2$ in aqueous solution[485]. Protonation of tetranuclear nitrido clusters produced $(OC)_9Fe_2Ru(\mu_3-NH)(\mu_3-CO)$ and a mono(trimethyl phosphite) derivative; a crystal structure of the latter was reported[486].

106



(40)

The tetrahedral cluster$(OC)_3CoFt_2(\mu-CO)(\mu_3-CAr)$, in which the aromatic ring was rotationally locked at -80°, resulted from reaction of $(OC)_4Co-W(CO)_4\equiv CAr$ with $Fe_2(CO)_9$[487]. A tricarbonyl iron group in Ft_3Bi_2 was replaced by a tetracarbonylcobalt upon reaction with $Co(CO)_4^-$, giving **107**[479]. Similarly, $Cp(OC)CoFt_2(\mu-H)(\mu_3-COMe)$ and $CpNiFt_2(\mu_3-CO)(\mu_3-COMe)$ resulted from reaction of $Ft_3(CO)(\mu-H)(\mu_3-COMe)$ with appropriate CpM compounds[488]. Reaction of the same starting material with $[CpRh(CO)]_2$ gave **108**, which was characterized as having a "semi-μ_3" alkylidyne ligand, the Fe-C distances averaging 1.87 Å, and the Rh-C 2.21[489].



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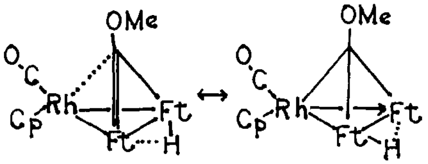


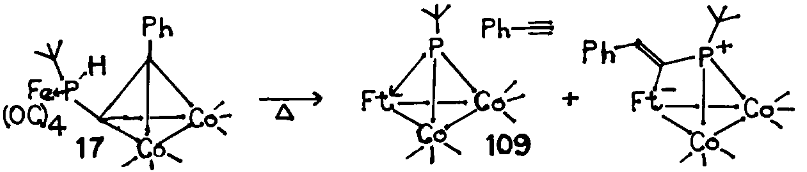
108

c. FeM_2 Clusters

The linear "cluster" $FpHgPt(PPh_3)_2C_6Cl_5$ arose by metathesis between homoleptic mercury compounds[490].

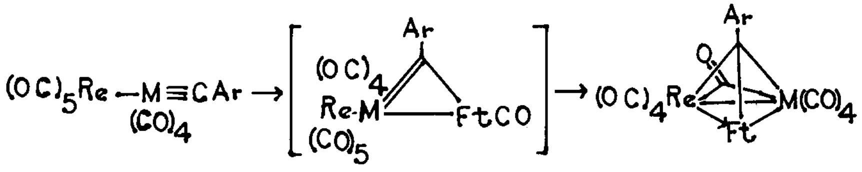
The great majority of trimetallic clusters with which I deal have triangular arrays of metal atoms capped by a non-metal to form a tetrahedral cluster. An unusual μ_3-oxo capped cluster,

$[Cp^*Mo(CO)_2]_2Ft(\mu_3O)$, resulted from co-photolysis of $[Cp^*Mo(CO)_2]_2$ and $Fe_2(CO)_9$ in oxygenated toluene[491]. Reaction of nitrobenzene, $Fe_3(CO)_{12}$ and $Co_2(CO)_8$ produced $[Co(CO)_3]_2Ft(\mu_3\text{-}NPh)$ [along with $Ft_3(\mu_3\text{-}NPh)_2]$[492]. An analogous phosphinidene cluster, **109**, was the main product of the thermolysis reaction (41)[108]. Reaction of **109** with $Na_2Ru(CO)_4$ led to replacement of one $Co(CO)_3$ vertex by an $HRu(CO)_3$ unit, giving a chiral CoFePRu cluster[493].



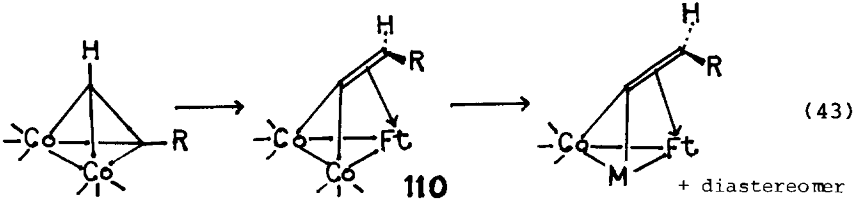
(41)

The acetylene-dicobalt complex $(FpC{\equiv}CPh)Co_2(CO)_6$ lost a carbon atom and a CO ligand (as CO and CO_2) upon reaction with oxygen, resulting in formation of $Cp(CO)Fe[Co(CO)_3]_2(\mu_3\text{-}CPh)$, in which the acetylene ligand was converted in part to an alkylidyne[494]. The chiral alkylidyne clusters $CpM(CO)_2[Co(CO)_3](FtH)\text{-}(\mu_3\text{-}CR)$ [M = Mo, W; R = Me, Ph, CO_2Me, etc.] resulted from replacement of a tricarbonylcobalt unit from the Co_2M precursor, using $K_2Fe(CO)_4$[495]. Addition of a tricarbonyliron unit to an unsaturated precursor (Eq. 42) has also been used to generate a chiral alkylidyne cluster[487].



(42)

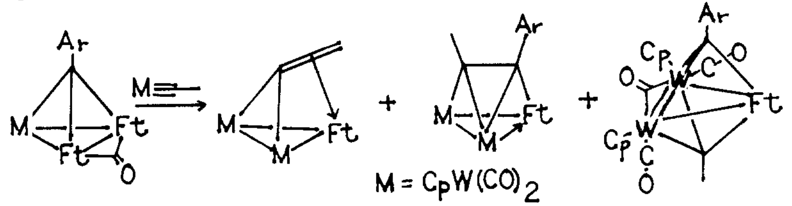
An alkyne ligand was converted into an alkylidene when the dicobaltatetrahedrane $(RC{\equiv}CH)Co_2(CO)_6$ [R = Me, Ph, t-Bu] was expanded using $Fe_3(CO)_{12}$ (Eq. 43). Replacement of a $Co(CO)_3$ unit in **110** was indiscriminate in the case M = NiCp, somewhat selective in the cases M = $Mo(CO)_2Cp$ and R = Me or Ph, and completely selective for M = $Mo(CO)_2Cp$ and R = t-Bu[496].



(43)

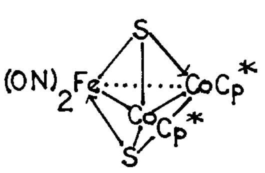
Reaction of a μ_3-alkylidyne complex with a terminal alkylidyne complex produced a gamut of products (Eq. 44), including ethylidene, alkyne, and bis(alkylidyne) complexes[497]. Heterotrimetallic alkyne clusters with the alkyne parallel to an edge of a

FeCoNi triangle have been synthesized, and the orientation of the alkyne has been discussed[98].



(44)

A few examples of bicapped heterometallic triangular clusters have also appeared. V_2Fe clusters with two μ_3-S bridges have been prepared and studied structurally[499]. Reaction of $[Fe(NO)_2]_2(\mu\text{-}S)_2{}^{2-}$ with $Cp^*Co(CO)I_2$ gave the cluster **111** (X-ray)[371]. The arachno-cluster $Cp(CO)_2Mo[\mu\text{-}Te\text{-}Mo(CO)_2Cp\text{-}Te]Fe(CO)_3$ added acetylene to form **112**[500]. Reaction of a Fe-Rh-W alkylidyne cluster with 2-butyne likewise produced **113** [tpb = tris(pyrazolyl)borate; Ar = p-tolyl] [501].



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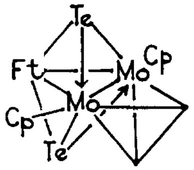

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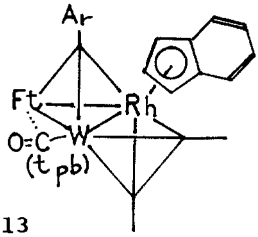
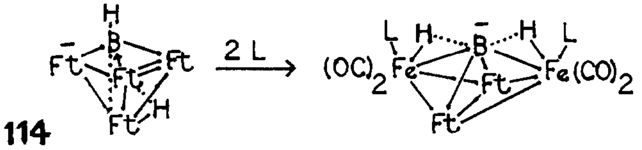


113

11. TETRA- AND POLYNUCLEAR CLUSTER COMPOUNDS

Electrochemical and spectroscopic studies of $[CpFe(CO)]_4$ dissolved in $BuNC_5H_5{}^+$ $AlCl_4{}^-$ showed little effect of coordinated Lewis acid on the oxidation potential of the cluster[502]. Mössbauer studies on $Fe_4(CO)_{13}{}^{2-}$ and related carbido- and alkylidyne-Fe_4 clusters showed a rough correlation between calculated effective nuclear charge and isomer shifts[503].

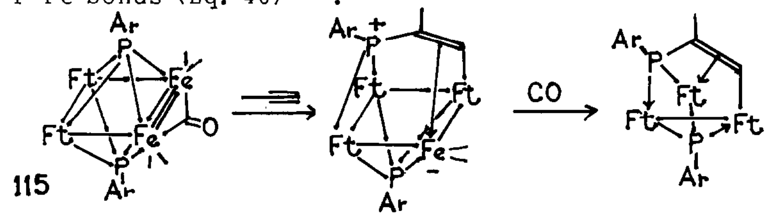
Cluster expansion of **97** produced the "butterfly" cluster, **114**, $(\mu\text{-}H)Fe_4(CO)_{12}BH^-$ [504]. This compound, isoelectronic with the known $(\mu\text{-}H)Fe_4(CO)_{12}CH$, underwent substitution by one or two phosphines at the wingtips, with consequent hydride migration (Eq. 45)[505]. Auration of **114** with excess Ph_3PAuCl gave Fe_4-



(45)

$(CO)_{12}[AuPPh_3]_2BH$, in which both gold groups bridged the same wingtip Fe-B bond. This dissimilarity to Ft_4BH_3 was said to "violate the H/$AuPR_3$ structural analogy"[506]. Attack of electrophiles Me^+ and Ph_3PAu^+ on the carbido cluster Ft_4C^{2-} has been assessed by molecular mechanics calculations, which indicated that deformation of the metal framework must be allowed for if reasonable interaction energies are to be obtained[507].

The unsaturated clusters **115**, $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PR)_2$, were found to add ligands readily. Such additions, interspersed with removal of CO by exposure to vacuum, allowed introduction of four trimethyl phosphite or three CN-*t*-Bu ligands. The X-ray structure of the **115**-trimethyl phosphite adduct showed severe ligand crowding[508]. Reaction of **115** with propyne led to an insertion into P-Fe bonds (Eq. 46)[509].

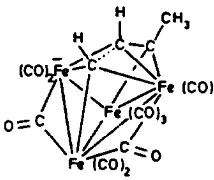


115

(46)

New iron-phosphorus cluster types were sought by oxidation or photolysis of $Ft_2(\mu\text{-}PHR)_2$, and by reactions of P-X compounds with $Fe(CO)_4{}^{2-}$ or $Fe_2(CO)_8{}^{2-}$. These produced such previously described compound types as **99** (Y = Z = PR) and **115**, and also dimers $[Ft_2(\mu\text{-}RPPR)]_2$ with octabisvalene skeletons[510].

Some remarkably complex structures can result when alkynes undergo insertion into clusters; a current example is **116**, obtained from $(\mu_3\text{-}CMe)Ft_4{}^-$ [511]. **117** was obtained by expansion of the alkyne adduct **102** using $Fe_2(CO)_9$[458].



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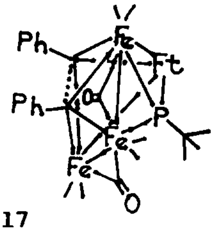


117

The structure and properties of the Fe-S cluster $(CpFe)_4(\mu_3\text{-}S)_2(\mu_3\text{-}S_2)^{n+}$ (n = 2, 1, 0) have been studied as a function of oxidation state[512]. The heterometallic clusters $(CpMo)_2[Fe(CO)_4]_2(\mu\text{-}S)_2$ and $(CpMo)_2Ft_2(\mu_3\text{-}S)_4$ have been found to be effective catalysts for hydrogenation of CO selectively to form ethane[513]. The crystal structure of $(CpMo)_2Ft_3(\mu_3\text{-}Te)_2(\mu_4\text{-}Te)$ has been reported; two Te atoms bridge the triangular faces of the Fe_2Mo_2 "butterfly," and one bridges all four metals[514].

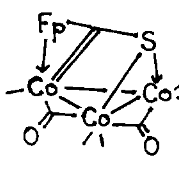
A practical synthesis of $H_2Fe_2Ru_2(CO)_{13}$, by reaction of $Fe(CO)_4{}^{2-}$ with $[Ru(CO)_3Cl_2]_2$, and its crystal structure have been described[485]. Reaction of the tetracarbonylferrate(2-) anion with $(MeCN)_2M_3(CO)_{10}$ [M = Ru, Os] constituted an improved synthesis of $M_3Fe(CO)_{13}H^-$ anions, which were isolated as PPN^+ salts in yields of 55-60%[515]. The same anions were formed on magnesia surfaces by deprotonation of the neutral dihydrides by surface OH groups; $FeCo_3(CO)_{12}^-$ was formed similarly[516].

Protonation of $FeRu_3N(CO)_{12}^-$ in a CO atmosphere gave tri-, tetra- and pentanuclear species, including only small amounts of $HFeRu_3N(CO)_{12}$. Protonation of $FeRu_3N(CO)_{10}L_2^-$ [L = $P(OMe)_3$] (X-ray structure) occurred initially at N, but ultimately gave an $FeRu_2$ product[486]. The clusters $Co_2Fe(MCp)(CO)_8(\mu\text{-}AsMe_2)(\mu_3\text{-}S)$ were obtained as mixtures of two structural isomers, which equilibrated slowly in solution[517]. Reaction of FpC(=S)SFp with octacarbonyldicobalt gave $CpFeCo_3(CO)_9CS$, **118**. The structure showed a cobalt-carbenoid interaction (bond length 1.90 Å)[518].

Reaction of $Ft_3(\mu_3\text{-}PPh)_2^{2-}$ with $[Cp^*RhCl_2]_2$ produced the unsaturated bicapped cluster $(Cp^*)RhFe_3(CO)_8(\mu_4\text{-}PPh)_2$, which reversibly added CO or underwent two-electron reduction. Structures of the unsaturated octacarbonyl and the saturated nonacarbonyl showed minimal differences in the $RhFe_3P_2$ framework[519]. Reaction of $CpM(CO)_2$ [M = Rh or Ir] with trimetallic clusters $M_3(\mu_3\text{-}PR)$ gave several expanded tetranuclear and pentanuclear clusters, in many cases as mixtures of isomers[520].

Reaction between $FeCo_3(CO)_{12}^-$ and Ph_3PCuCl gave $FeCo_3(CO)_{12}$-$(\mu_3\text{-}CuPPh_3)$, from which excess PPh_3 displaced the $FeCo_3$ anion back[521]. Reaction of Pb(II) salts with $Fe(CO)_5$/KOH produced the cluster anion $Ft_2(\mu\text{-}CO)_2[\mu\text{-}Pb(Fe(CO)_4)_2]$ (X-ray) [522]. The novel half-open cluster **119** was characterized by X-ray[481].

Use of extended Hückel calculations in understanding the bonding in clusters has been defended, with results on Fe_5 clusters being presented[523]. Nitrosyl clusters were prepared by reaction of $Fe_5C(CO)_{15}$ with $Fe(CO)_3(NO)^-$, and the structures of $Fe_5C(CO)_{13}(NO)^-$ and $Fe_6C(CO)_{13}(NO)_2^{2-}$ were determined[524]. Coupling of two C_2H_3 ligands occurred when $Ft_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)^-$ and $[Rh(CO)_2Cl]_2$ reacted in the presence of Tl(I), to produce **120**[525].



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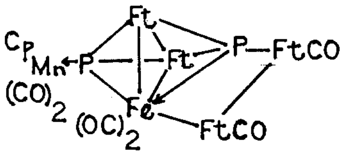

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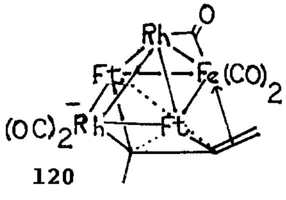

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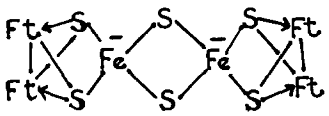
Although the paramagnetic anion $Fe_3(CO)_{11}^-$ doesn't dimerize, the monoruthenium analog does. The structure of the dimeric $[Fe_2Ru(CO)_{11}]^{2-}$ showed a rather long Ru-Ru bond [2.916(1) Å][526]. Reaction of $(OC)_4Fe(\mu\text{-}GeH_2)_2Fe(CO)_4$ with octacarbonyldicobalt gave $Co_4Ge_2Fe_2(CO)_{21}$, in which a $Fe_2(CO)_7$ unit was bridged by two μ-Ge[$Co_2(CO)_7$] units[527]. An even more extended cluster was $Fe_6S_6(CO)_{12}^{2-}$, **121**, having an "inorganic" Fe_2S_2 center and "organometallic" Ft_2S_2 termini[528]. Planar copper-iron clusters $Cu_3[Fe(CO)_4]_3^{2-}$, $Cu_5[Fe(CO)_4]_4^{3-}$, and $Cu_6[Fe(CO)_4]_4^{2-}$, have been described in full[529]; the structure of the Cu_5Fe_4 "raft" is shown here as **122**.

The synthesis and structure of the 88-valence-electron trianion, $Fe_3Rh_3(CO)_{17}^{3-}$, have been described[530]. Electrochemical oxidation and reduction of $Fe_6C(CO)_{16}^{2-}$ have been studied. Irreversible oxidation eventuated in formation of $Fe_5C(CO)_{15}$, and reduction to $Fe_5C(CO)_{14}^{2-}$ [531]. Reactions of the latter with $Pt(PPh_3)_4$ and $[Rh(CO)_2Cl]_2$ led to formation of MFe_5C clusters[532]. The hexa-anion $Tl_6Fe_{10}(CO)_{36}^{6-}$ was obtained as a minor product of slow decarbonylation of $Tl[Fe(CO)_4]_2^{-}$ in methanol solutions, along with a thallium-iron carbonyl tetra-anion[533].



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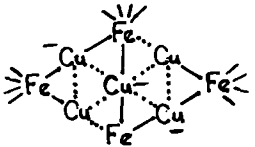

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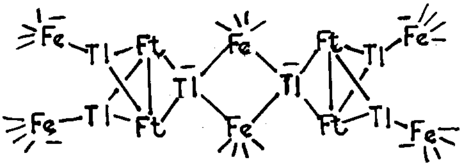

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Thermal decomposition of $H_2FeM_3(CO)_{13}$ [M = Ru or Os] or $HFeCo_3(CO)_{12}$ adsorbed on magnesia produced, after hydrogen treatment at 400°, small bimetallic particles whose composition was the same as the precursor clusters[534]. Fused iron catalysts were used in reactions of phenylacetylene with CO and H_2 to give hydrocarbons $PhCH_2CH_2R$ [R = H, Me, vinyl, Pr, and Bu] and alcohols[535].

<u>POST-SCRIPT</u>: The 1983, 1984, and 1985 organoiron reviews covered 393, 399, and 423 references, respectively. This 1986 review has covered 536. Although this sharp increase may attest to the vigor of the subject, this reviewer finds it daunting.

As has typically been true, the top three journals account for more than half of the total publications in the field of organoiron chemistry. These are J. Organometal. Chem. (121 citations), Organometallics (89), and J. Am. Chem. Soc. (71), followed by Inorg. Chem. (48) and J. Chem. Soc., Chem. Comm. (34). The most prolific authors during 1986 were Mathieu, Davies, Vahrenkamp, and Casey.

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