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Annual Survey for the Year 1990

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LIST OF ABBREVIATIONS USED

An	any arene ring, such as benzene or naphthalene
Ar	an aryl ring, such as p-tolyl, MeC_6H_4-
Cp	cyclopentadienyl, C_5H_5
Cp'	methylcyclopentadienyl, C_5H_4Me
Cp^*	pentamethylcyclopentadienyl, C_5Me_5
DMF	N,N-dimethylformamide
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	1,2-bis(dimethylphosphino)methane
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
E	an ester group, usually carbethoxy or carbomethoxy
Et	ethyl, C_2H_5
Fp	cyclopentadienyldicarbonyliron, $CpFe(CO)_2$
Fp'	cyclopentadienyl(carbonyl)(triphenylphosphine)iron
Fp^*	(pentamethylcyclopentadienyl)dicarbonyliron, $Cp^*Fe(CO)_2$
Ft	a tricarbonyliron group, $Fe(CO)_3$
L	a two-electron donor ligand, such as a phosphine
M	any transition metal
Me	methyl, CH_3
Nu^-	a nucleophile
Ph	phenyl, C_6H_5, also shown as φ in structures
Por	any porphyrin ligand, coordinated as a dianion
PPN^+	$Ph_3P=N=PPh_3^+$
Pr	propyl, $CH_2CH_2CH_3$
R	any unicovalent organic group such as methyl
TCNE	tetracyanoethylene
Tf	trifluoromethanesulfonyl group, F_3CSO_2
X	any halogen
[XRC]	X-ray crystal structure reported for this compound

1. INTRODUCTION

In this Annual Review I attempt to cover the organoiron chemistry reported in journals published during calendar year 1990. 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 elsewhere in the Annual Surveys.

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 compounds. However, for purpose of brevity, many reactions of dimers such as dicyclopentadienyltetracarbonyldiiron [Fp_2, $Cp_2Fe_2(CO)_4$], in which they undergo fission into monoiron products, are treated alongside those of their monomeric derivatives such as FpR. Likewise, FeM_n clusters are treated as a group with other metal clusters of like nuclearity; however, metals of Groups 11 and 12 are treated as counterions rather than as cluster partners. For example, $(Ph_3PAu)_2Fe(CO)_4$ is treated with other derivatives of $Fe(CO)_4{}^{2-}$ rather than with trimetallic clusters.

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

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

2. REFERENCE WORKS AND REVIEW ARTICLES

Two additional volumes of the Gmelin organoiron series were published during 1990, one in two parts. Volume B16a[1] covers compounds with an η^5 ligand and a carbenoid ligand. Volume B16b[2] covers compounds with an η^5 ligand and an η^2 ligand, and having 0 or 1 CO ligand. Volume B17[3] covers compounds with η^5 and η^2 ligands and two carbonyls (mostly Fp derivatives), and compounds with η^5 and η^{3-5} ligands other than ferrocenes.

No other general reviews of organoiron chemistry as a whole appeared during 1990. However, several reviews of specific types of compounds were published. Brunet reviewed the properties of tetracarbonylhydridoferrates, M^+ $HFe(CO)_4^-$, especially their uses in synthesis and catalysis[4]. Volume 2 of *Organometallics in Organic Synthesis* included three reviews of organoiron compounds: Salzer reviewed his group's work on dieneiron complexes, especially their Wittig reactions[5]; Vogel and Roulet reviewed iron tricarbonyl complexes of exocyclic dienes[6]; and Zenneck's group from Heidelberg described addition reactions of highly reactive arene complexes prepared by iron atom co-condensation[7]. The use of bis(arene)iron compounds as precursors to various exotic organoiron species was also reviewed by Zenneck in *Angewandte Chemie*[8]. Conformational analysis of ligands bound to the chiral auxiliary $CpFe(CO)(PPh_3)$ [Fp'] was reviewed by Davies and coworkers[9].

3. REACTIONS OF "NAKED" IRON ATOMS AND IONS

Reactions of unligated metal atoms with all manner of substrates in the gas phase have received continued attention. The reactions of first-row transition metal ions with 2-methylbutanenitrile, Me_2CHCH_2CN, studied by use of Fourier transform ion cyclotron resonance mass spectrometry with isotope labeling, were used to elucidate general patterns of reactivity. Early transition metal ions (Ti^+ and V^+) reacted mainly by dehydrogenation, whereas the closed d-shell late transition metal ions Cu^+ and Zn^+ reacted through initial formation of ion-dipole complexes. Cr^+ was unreactive. Reaction of Fe^+ occurred mainly with C-C bonds[10]. Kinetic isotope effects were used to study ethene loss from (4-octyne)M^+. In the case of the iron complex, ethene loss from $(C_2H_4)FeH(C_6H_9)^+$ was the rate-determining step, the intermediate having been formed primarily through C_6H_9-Fe-Et^+ [11]. Reaction of Fe^+ with 1-heptyne similarly resulted in release of propene. Labeling studies showed that the propene resulted very predominantly from C1-C3 of the 1-heptyne, requiring three hydrogen transfers from the butyl group of C4-C7. As in the previous case, slow dissociation of $(C_4H_6)Fe(C_3H_6)^+$ resulted in release of the propene product[12].

Similarly, site-specific oxidative addition to unstrained C-C bonds in RNH_2-Fe^+ [R = 2-ethylbutyl or 2,2-dimethylbutyl] was found to be responsible for loss of butene. Also observed were loss of dihydrogen, methane, ethane, and ethene. Labeling experiments led to suggested mechanisms for these processes[13]. Loss of ethene in reaction of Fe^+ with 1,7-octadiene also resulted from activation of internal C-C bonds rather than from a metathesis-like coupling of terminal methylene groups. The intermediate $(C_3H_5)_2Fe(C_2H_4)^+$ was implicated[14].

Fe^+ reacted with benzene derivatives by coordination to the most electronegative atom in the substituent, followed by oxidative addition into a bond to that atom. With nitrobenzene, a C_5H_5 ligand was produced.Lower limits for bond dissociation energies for Fe^+-X were estimated as: 247 kJ/mol for benzyne; 116 kJ/mol for ethene; 155 kJ/mol for cyclopentadienyl[15]. A different group obtained a much higher value, 370 ± 30 kJ/mol for D° Fe^+-C_5H_5. They studied the reaction of Fe^+ with cyclopentene and then propane, finally to form $CpFe(C_3H_5)^+$. Photoreaction of this species produced $Fe(C_8H_8)^+$ and $Fe(C_6H_6)^+$; the latter resulted from a higher energy process which was favored at low total pressure. Dehydrogenation of cyclopentene by Fe^+ was found to be exothermic by about 140 kJ/mol[16]. Further studies of reactions of Fe^+ with cycloalkanes and cycloalkenes indicated that dehydrogenation and double-dehydrogenation processes occurred with statistical energy partition, showing absence of a barrier to the reverse association of Fe^+ with the alkene products[17].

Beams of $CpFe^+$ from electron-impact ionization of ferrocene could be collisionally reduced to neutral FeCp, which could in turn be reionized in a second collision step. Some of the gas phase properties of the neutral and ionic FeCp were characterized[18]. The ionization energy of Fe^+ was lowered by at least 300 kJ/mol when one or two Cp ligands was attached. Naked Fe^{2+} was formed in an excited state[19].

Reaction of $C_6H_4Fe^+$ with alkenes in the gas phase has been studied. Reaction with ethene produced Fe^+ and (benzocyclobutene)Fe^+; the latter was explained by ethene coordination, ligand coupling to form a ferraindane intermediate, and rearrangement to the coordinated benzocyclobutene. A hydrogenated product, $C_6H_6Fe^+$, also formed; it was the predominant product with cyclohexene and cyclopentene. Propene and isobutene gave (PhMe)Fe^+, by a process which involved oxidative addition to a vinylic C-H bond. Butadiene gave (naphthalene)Fe^+ [20]. $(C_2H_4)Fe^+$ reacted with chlorobenzene by oxidative addition to the C-Cl bond, insertion of the ethene into the resulting C-Fe bond, and HCl elimination, to form (styrene)Fe^+. The analogous reaction of (propene)Fe^+ occurred selectively to form complexed β-methylstyrene[21].

Gas phase analogs of the classical Meerwein-Ponndorf-Verley reaction were observed when $FeOMe^+$ [from reaction of Fe^+ with nitromethane] reacted with acetone to form $Fe(OCHMe_2)^+$ and $Fe(OCMe_3)^+$. The reaction was studied by Fourier transform ion cyclotron resonance, using isotope labeling[22]. An Fe^+-catalyzed oxidation of ethene by nitrous oxide to acetaldehyde in the gas phase has been studied by FT-ICR. Intermediates FeO^+, $(C_2H_4)Fe^+$, and *cyclo*-$FeOCH_2CH_2^+$ were detected, and rate constants determined[23]. Activation of methane by FeO^+ in the gas phase, to form methanol and Fe^+, has also been studied. As above, inclusion of nitrous oxide to reoxidize the latter produced a catalytic cycle[24].

Gas-phase reactions of ketone-Fe^+ complexes resulted in elimination of dihydrogen and of ethylene, by relatively specific "remote functionalization" processes, which were studied by isotope labeling, including determination of kinetic isotope effects[25]. With silicon compounds Me_3Si-Y-$SiMe_3$ [Y = CH_2, NH], Fe^+ reacted by abstraction of methanide ion, forming neutral FeMe and Me_3Si-Y-$SiMe_2^+$ [26]. The functional groups in 7-(trimethylsilyl)heptanenitrile functioned cooperatively in reaction with Fe^+, resulting in regiospecific C-H bond activation. Activation of C-C bonds, observed in the monofunctional analogs, was absent in the bifunctional compound[27].

Formation of metallic clusters $Fe_{1-3}(CO)_{4-9}^+$ by reaction of $Fe(^{13}CO)^+$ with $Fe(CO)_5$ has been studied. Loss of the ^{13}CO ligand during cluster formation was favored, showing non-fluxionality in the cationic clusters. This was interpreted in terms of decreased back-bonding as a consequence of the positive charge[28]. Formation and reactions of (benzyne)Fe_2^+ in the gas phase were studied by laser desorption-Fourier transform mass spectrometry. With chlorobenzene, (Ph-C_6H_4)Fe^+ and FeCl resulted. With ethene, competitive processes resulted in formation of Fe_2^+ and benzocyclobutene or (benzocyclobutene)Fe^+ and Fe. Alkanes predominantly reduced the benzyne complex to (benzene)Fe_2^+, in contrast to their unreactivity toward naked Fe_2^+ [29].

Neutral Fe atoms [d^6s^2], in contrast to the cations, were unreactive toward alkanes and alkenes in the gas phase, a consequence of the filled *s*-subshell[30]. *Ab initio* theoretical studies of the interactions of Fe, Fe^+, and HFe with H, CH, CH_2, CH_3, and Cp have been carried out. Bond dissociation energies calculated with large basis sets reproduced experimental trends fairly well. HFeX species [X = H, Me, Cp] were calculated to have quintet ground states and linear geometries[31]. Theory was also applied to ground and excited states of oxaferretane, $\overline{FeOCH_2CH_2}$, in order to interpret its photochemical rearrangement to (ethene)-Fe=O and (C_2H_3)FeOH, observed in matrices. The latter isomer was found to be most stable[32].

4. COMPOUNDS WITH η^1-CARBON LIGANDS

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

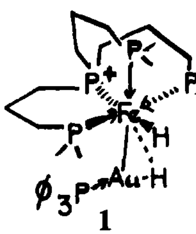
In this section I discuss not only well-characterized organometallic compounds having iron-carbon sigma bonds (but no carbonyl groups), but also a number of low-coordinate or low-valent iron species which, in the absence of iron-carbon bonds, are not organometallics by strict definition. They are included here because of their utility in synthesis of organometallics and because of their intrinsic interest to organometallic chemists. Also included are some transient species thought to have iron-carbon bonds and some results on reactions which may involve intermediates with iron-carbon bonds.

The dihydride complex $(dmpe)_2FeH_2$ and its ethyl and propyl analogs, $(depe)_2FeH_2$ and $(dppe)_2FeH_2$, were synthesized by lithium aluminum hydride reduction of the bis(diphosphine)iron dichlorides, so long as alcohols or compounds of comparable acidity were avoided during workup. The dihydrides existed as mixtures of cis and trans isomers in solution, and the cis isomers were fluxional on the nmr time scale[33]. Borohydride reduction of $(dmpe)_2FeHCl$ or treatment of $(dmpe)_2FeH_2$ with THF-borane led to formation of $(dmpe)_2FeH(BH_4)$. Rapid internal motion of the BH_4 moiety led to exchange among the free B-H bonds and the open Fe-H-B bridge. The barrier to exchange was lower in more hindered (and less stable) analogs containing depe and dppe[34].

cis-$(dmpe)_2FeH_2$ and analogous compounds reacted readily with N-H bonds of primary amides, to form *trans*-$(dmpe)_2FeH(NHCOR)$.The reaction was thought to have proceeded by protonation of the iron hydride to form $(dmpe)_2$-$FeH(H_2)^+$, then displacement of the dihydrogen ligand by the amidate[35]. A completely analogous reaction occurred with thiols, forming $(dmpe)_2FeH(SR)$ and $(dmpe)_2Fe(SR)_2$. The cyclic product from 1,2-ethanethiol was the subject of an X-ray crystallographic study[36].

The dihydride $(PP_3)FeH_2$ [$PP_3 = P(CH_2CH_2CH_2PMe_2)_3$] was protonated by alcohols to form $(PP_3)FeH(H_2)^+$, previously thought to be $(PP_3)FeH^+$. The protonated compound was fluxional, but the exchange was slowed at low temperatures in isotopically labeled compounds, to show the separate hydride and dihydrogen ligands[37]. Inelastic neutron scattering was used to determine the vibrational spectrum of *trans*-$(dppe)FeH(H_2)^+$ BF_4^- in the solid state. The results indicated a double-minimum potential for rotation of the dihydrogen ligand, with a barrier of 9.6 kJ/mol[38]. Neutron diffraction study of $L_3FeH_2(H_2)$ [$L = EtPPh_2$] indicated a *cis, mer* structure, similar to that previously determined for the dinitrogen analog. The barrier for rotation of the dihydrogen ligand was only about 4 kJ/mol. Extended Hückel calculations suggested an attractive interaction between the dihydrogen and hydride ligands, due to electron-donation from the filled Fe-H σ-orbital into the σ^* H-H orbital[39].

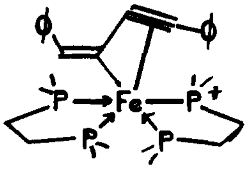
The T_1 criterion for classifying polyhydrides as having all M-H bonds or having η^2-H_2 ligands (so-called "non-classical hydrides") has been tested on a set of compounds having known solid-state structures. The relaxation times have been found to depend predominantly on dipole-dipole relaxation, and correlate well with values calculated on that basis. Included in the set studied were $(Ph_2EtP)_3FeH_2(H_2)$ and $(dppe)_2FeH(H_2)^+$ [40]. Electrochemical properties of hydrides were assessed as a structural diagnostic. Oxidation of $(PP_3)FeH_2$ gave unstable mono- and dications, which did not deprotonate. $(PP_3)FeH(H_2)^+$ underwent one-electron reduction in THF to form $(PP_3)FeH_2$. ESR was used to characterized paramagnetic monohydrides[41]. Also proposed for distinguishing "classical" and "non-classical" dihydrides was reaction with phosphine-gold reagents. Thus, $(PP_3)FeH_2$ was aurated by Ph_3PAu^+ to form **1**[42].



1

The dihydrogen ligand in $(dmpe)_2FeH(H_2)^+$ underwent ready displacement by acetonitrile, carbon monoxide, dinitrogen, and ethene. CO_2 and CS_2 also inserted into the C-H bond, to form formate and dithioformate complexes. Phenylacetylene reacted to form an acetylide product, whereas methyl propynoate reacted in the presence of borohydride to form a cyclic alkenyl complex, $(dmpe_2)Fe[-CH{=}CH{-}C(OMe){=}O]^+$ [43].

Reagents prepared *in situ* at -78° by reaction of methyl-lithium with ferrous chloride were used to alkylate 2-cyclohexenone. The most effective reagent had the stoichiometry of Me_2Fe, and gave 87% of 3-methylcyclohexanone[44]. Similarly, inorganic iron salts were treated with dimetallated organics at low temperatures to form spirocyclic organoiron species. For example, $Li(CH_2)_4Li$ and $FeBr_2(THF)_2$ reacted to form a $Li_2[(CH_2)_4]_2Fe$ solvate, which was said to be stable in solution at room temperature[45]. The reaction of $(dmpe)_2FeCl_2$ with phenylacetylene formed *trans*-$FeCl(C{\equiv}CPh)(dmpe)_2$ [XRC] and the η^3 species **2**[46]. Reaction of terminal acetylenes with $(dmpe)_2FeH_2$ resulted in formation of acetylide and diacetylide complexes, such as *trans*-$(dmpe)_2Fe(C{\equiv}CPh)_2$ [XRC], formed along with styrene, by dissolving the dihydride in neat phenylacetylene[47].



2

Lithium triethylborohydride in methylene chloride transferred an ethyl group to (Por)FeCl [Por = tetraphenylporphyrin] to form the alkylated (Por)FeEt. Reduction by the same reagent in benzene/THF gave the diamagnetic $(Por)Fe(II)Et^-$, which was readily reoxidized by atmospheric oxygen. Electron exchange between the neutral and anionic (Por)FeR species was rapid[48]. Reaction of 1,4-dilithiobutane with (Por)FeCl produced the alkane-bridged species, $(Por)Fe(CH_2)_4Fe(Por)$; the μ-phenylene species was prepared analogously. Unlike simple (Por)FeAr species, the phenylene species was ESR silent at 80 K. Both bridged dinuclear species reacted rapidly with oxygen to form $[(Por)Fe]_2O$[49]. Aryliron species (Por)FeAr reacted with oxygen at room temperature to form phenoxide complexes (Por)-FeOAr. At -30°, (Por)FePh also gave some $(Por)FeOC_6H_4OH$ and $(Por)FeO\text{-}C_6H_4OFe(Por)$. The mechanism of these reactions was proposed to involve insertion of O_2 into the Fe-C bond, then rapid homolysis of the resulting peroxide bond to form (Por)Fe=O and ·OAr radicals. In chloroform at -60°, oxygen converted (Por)FeAr into the cation and (Por)FeCl, with no phenoxide complex formed. The chloro product arose from reaction of the solvent with superoxide ion[50].

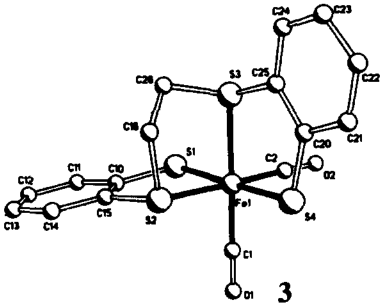
One reason for the interest in these porphyrin species is as models for biological oxidation catalysts such as cytochromes. The suicide inactivation of cytochrome P-450 by 1-alkenes has been modeled by use of synthetic hemins, in studies of the branching ratio between epoxidation and hemin N-alkylation by substituted styrenes. The ratios were fairly insensitive to the steric requirements of the porphyrin and the electronic properties of the alkene. An oxaferretane intermediate remains a viable possibility for the epoxidation and N-alkylation reactions[51]. The role of iron in lipoxygenase catalysis has also received further attention, the latest workers[52] favoring a non-covalent pentadienyl-Fe(II) intermediate rather than Corey's covalent (η^1-pentadienyl)iron(III) species. The role of the iron-containing enzyme in clavulanic acid biosynthesis has also been discussed, with an organoiron intermediate being favored at present[53].

Epoxidation of alkenes by iodosylbenzene in the presence of Fe(III) complexes of tri- and tetradentate ligands as catalysts has been studied[54]. A system which included an iron(III) complex, zinc powder, acetic acid, and 2,2'-bipyridyl, and using hydrogen peroxide as oxidant, was used to convert unactivated aliphatic hydrocarbons to (primarily) secondary alcohols, e.g. adamantane to 2-adamantanol[55]. Several continuing studies on the closely related Gif oxidizing systems have appeared. Oxidation of terminal alkenes to formaldehyde and ketone or aldehyde has been taken as evidence for an iron(V)-oxenoid system reacting through formation of an oxaferretane[56]. Modified Gif^{III} and Gif^{IV} systems gave been used to convert unactivated C-H bonds into C-SPh and C-X bonds, with intermediate R-FeL$_n$OH species favored[57]. Conversion of cyclohexane to cyclohexanone in 90% yield was achieved by use of ferrous picolinate and hydrogen peroxide in pyridine solution. Use of [Fe(salen)]$_2$O [(salen) = N,N'-bis(salicylideneimine)] as catalyst in the presence of $HSCH_2CH_2OH$ allowed oxidation of α-dialkylaminoketones, $RCOCH_2NR_2$, to α-oxoamides by molecular oxygen; in the presence of sodium sulfide, α-oxothioamides were formed[59]. The mechanisms of alkane functionalization by non-heme iron complexes have been investigated[60].

4b. Iron Monocarbonyls, e.g. L$_4$Fe(CO)

Thermal decarbonylation of **3** [XRC] resulted in coupling of the resulting unsaturated fragments in such a way that fragments of like chirality coupled, to form **4** [XRC]. A CO ligand in **4** could be substituted by NO$^+$, but treatment with NO or Me$_3$P resulted in cleavage of the bridges and formation of derivatives of **3**, $[SC_6H_4SCH_2CH_2SC_6H_4S]Fe(NO)_2$ and $[SC_6H_4SCH_2CH_2SC_6H_4S]Fe(CO)$-

(PMe$_3$), respectively. Treatment of **4** with methyl-lithium resulted in cleavage of the ethano bridges, resulting in formation of [SC$_6$H$_4$S]$_4$Fe$_2$$^{2-}$ [61].



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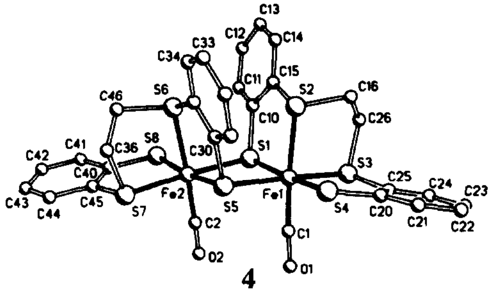


4

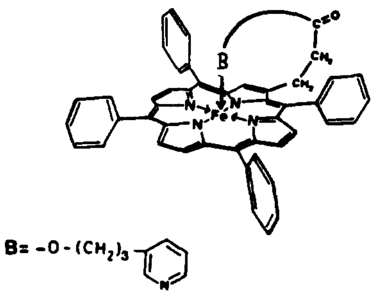
Carbonyl complexes of iron(II)-phthalocyanine and -(salen) were observed by infrared studies of low-temperature matrices. In order of decreasing carbonyl frequency were dicarbonyl, carbonyl-dioxygen, carbonyl-water, and monocarbonyl derivatives of these L$_4$Fe compounds[62]. The antibiotic bleomycin coordinates to an Fe(II) by use of heterocyclic amine, β-aminoalanine, and amide sites as ligands, forming an L$_5$Fe entity. The structure of (bleomycin-A$_2$)Fe(CO) in solution has been probed by two-dimensional NMR methods.[63].

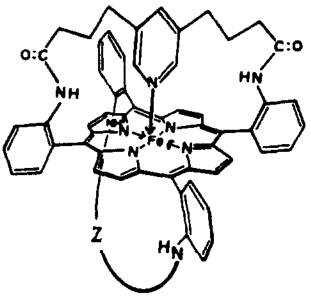
The invention and synthesis of heme models capable of discriminating between CO and O$_2$ binding analogous to that of natural hemes is a matter or continuing interest. The iron porphyrins shown in Chart I have been prepared, and the temperature dependence of CO and O$_2$ binding studied by laser flash photolysis. A double energy barrier, due to steric hindrance on the distal side in addition to the normal barrier to bond formation. The free energy changes among the different porphyrins were about the same for CO and O$_2$, indicating no steric discrimination in the transition states[64]. ^{57}Fe NMR chemical shifts have been found to be quite sensitive to deformations in the porphyrin geometry in various model systems like those in Chart I. "Ruffling" of the porphyrin as a consequence of strain introduced by bridges was found to be able to invert d-orbital energy levels[65].

Time-resolved resonance Raman measurements have been used to probe microsecond-range quaternary structure changes in photolyzed carboxyhemoglobin[66]. Similar structural rearrangements in photodissociated carboxymyoglobin have been studied by picosecond time-resolved circular dichroism measurements[67]. The effect of pressure on attachment of small ligands to sperm whale myoglobin and protohemes has been investigated by flash photolysis. Only for CO was bond formation involved in the rate-determining step. Escape of the ligands from the heme pocket of the myoglobin was accompanied by a volume increase, ascribed to a conformational change akin to the opening of a gate[68].

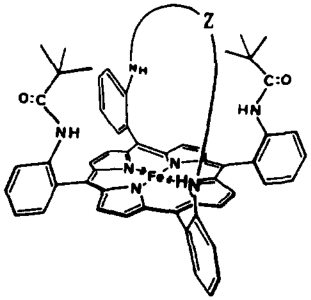
Carbon monoxide inserted into the Fe-C bond of σ-alkyl porphyrins, but the increased Fe-C bond strength of σ-aryl analogs apparently prevented the insertion

CHART I





$Z = CO-(CH_2)_{10}-CO$

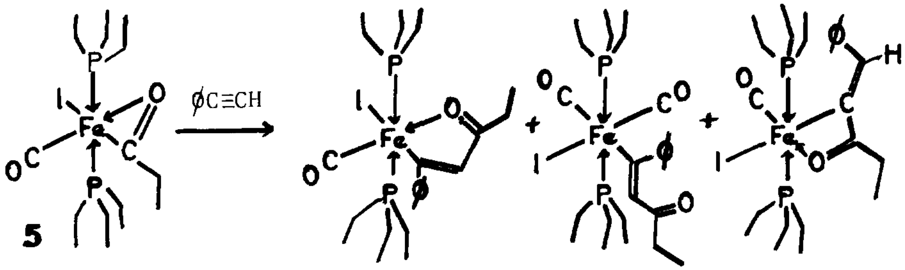


$Z = CO-(CH_2)_{10}-CO$
$Z = CO-(CH_2)_8-CO$
$Z = CO-(CH_2)_8-CO$

reaction. With (Por)Fe-CMe_3, insertion occurred in the anionic Fe(II) species, but the neutral Fe(III) species underwent homolysis, (Por)Fe(CO) being formed. With primary alkyl groups, insertion occurred in the Fe(III) oxidation state. Rates were measured electrochemically[69].

Dynamic ^{13}C NMR experiments on $(Ph_2PMe)_2Fe(^{13}CO)[\eta^2\text{-}^{13}C(=O)Me]I$ have shown rapid equilibration in solution with the isomeric alkyl $(Ph_2PMe)_2Fe(^{13}CO)_2(Me)I$. The acyl was favored at equilibrium, and kinetic and thermodynamic parameters for the reaction were reported[70]. Acyl complexes (diars)Fe$(CO)_2L(COMe)$ [diars = $Me_2AsC_6H_4AsMe_2$; L = various phosphines and phosphites] underwent thermal decarbonylation to the corresponding alkyls. Treatment of the latter with a second phosphine resulted in migratory insertion to reform acyls. The stereochemical outcome was governed by the strong trans-labilizing influence of the acyl ligand[71].

Reaction of the η^2-propanoyl complexes 5 with phenylacetylene produced a mixture of products [Eq. 1]. Curiously, the isobutanoyl homolog reacted under similar conditions by insertion of the phenylacetylene into the O=C-CHMe$_2$ bond, giving a η^2-[C(=O)-C(φ)=CHCHMe$_2$] product[72].



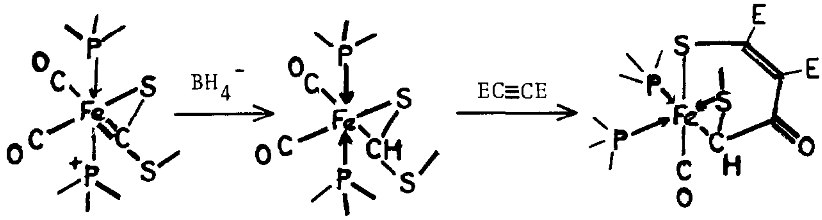
(1)

4c. Iron Dicarbonyls, e.g. L$_3$Fe(CO)$_2$

trans-Fe(CO)$_2$(PMe$_3$)$_3$ has been prepared directly by reduction of anhydrous FeCl$_2$ with sodium sand under a carbon dioxide atmosphere in the presence of trimethylphosphine[73]. *cis*-H$_2$Fe(CO)$_2$L$_2$ [L = trimethyl-, triethyl-, and triphenylphosphite] were obtained in over 90% yield by reaction of KHFe(CO)$_4$ with the phosphite in aqueous THF at room temperature[74]. Treating *cis,cis*-(dppe)Fe(CO)$_2$H(SiMe$_3$) with R$_3$SnH [R = Me, Ph] produced the stannyl iron hydride product; the bis(trimethylphosphite) analogs were prepared similarly. Reaction of the L$_2$Fe(CO)$_2$H$_2$ compounds with SnCl$_4$ gave the (trichlorostannyl)iron hydrides, L$_2$Fe(CO)$_2$H(SiCl$_3$). Deprotonation of the hydrides with KH gave a reactive anion, which readily underwent alkylation with MeI or stannylation with R$_3$SnX[75].

Already cited (Section 4b) were dicarbonyls of iron coordinated to tetradentate, 6-electron ligands: phthalocyanines[62] and 1,2-bis[(2-mercaptophenyl)thio]ethane, 3[61]. One or both of the terminal sulfur atoms of the ligand in 3 underwent coordination to Group 6 metal pentacarbonyl groups when 3 reacted with (THF)M(CO)$_5$. The chromium compound was also prepared by reaction of (OC)$_5$CrSC$_6$H$_4$SCH$_2$CH$_2$SC$_6$H$_4$SCr(CO)$_5$$^{2-}$ with ferrous chloride. Crystal structures of the monochromium and ditungsten adducts were reported[76].

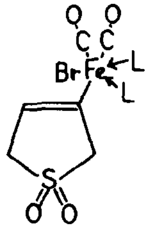
The Lewis base character of sulfur was also shown in coordination of the thiocarbonyl group in (Ph$_3$P)$_2$Fe(CO)$_2$(η^2-CS$_2$) by Re(CO)$_5$$^+$ [77]. Reaction of the



(2)

cations $(Me_3P)_2Fe(CO)_2(\eta^2\text{-}CS_2R)$ with borohydride produced thioformate and thioformaldehyde complexes. The former reacted with electrophilic alkynes as shown in Eq. 2[78]. A more straightforward example of ligand coupling occurred when methylamine consecutively attacked two isonitrile ligands of (dppe)Fe-$(CNPh)_4^{2+}$, forming $(dppe)Fe(CNPh)_2[C(=NPh)NMeC(NHPh)]^+$. This was protonated on the imine nitrogen by conc. aq. perchloric acid; heating caused opening to the carbene complex **6**, *mer*-$(dppe)Fe(CNPh)_3[C(\underset{H}{N}Ph)(\underset{H}{N}Me)]^{2+}$[79].

Equilibration of $(Ph_2PMe)_2Fe(CO)_2MeI$ with the η^2-acyl[70] in solution was described in Section 4b, as was migration of the methyl group from carbon to iron upon decarbonylation of $(diars)Fe(CO)_2(PR_3)[C(=O)Me]$[71]. A rather unexpected alkyl, **7**, [XRC] resulted from reaction of a mixture of thiophene 1,1-dioxide and 4-bromo-4,5-dihydrothiophene dioxide with $N_2[Fe(CO)_2L_2]_2$ [L = trimethyl phosphite][80].



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

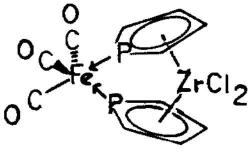
Salts of $HFe(CO)_3PR_3^-$ reacted with Ph_3PAuCl with partitioning to form the dihydride $H_2Fe(CO)_3PR_3$ and the gold derivatives $(Ph_3PAu)_2Fe(CO)_3PR_3$ [R = OMe, OEt, OPh, Me,Ph]. The crystal structure of the triphenyl phosphite compound showed attractive interactions between the two gold atoms (distance 2.87 Å and 70° Au-Fe-Au angle)[81]. Crystal structures of the PPN^+ salts of anions LFe-$SiCl_3(CO)_3^-$ [L = Ph_3P, $(PhO)_3P$] have been determined; both were trigonal bipyramidal with trans silyl and phosphorus groups[82]. The anion $Fe(CO)_3NO^-$ has been employed as a carbonylation reagent in reactions with primary and secondary alkyl, benzylic and allylic halides, converting RX into RCO_2Me after treatment with iodine and methanol[83].

The reaction of PPN^+ $RFe(CO)_4^-$ [R = Me, Et, $PhCH_2$] with iodine in methylene chloride induced alkyl group migration to carbon, with formation of the acyl anions *cis, mer*-$RCOFe(CO)_3I_2^-$ [XRC, R = Me]. The same product resulted from iodination of the acyl $RCOFe(CO)_4^-$ and from reaction of $(PPN^+)_2$ $Fe_4(CO)_{13}^{2-}$ with methyl iodide[84].

The cubane cluster $Fe_4S_4Cl_4^{2-}$ reacted with excess *t*-butylisonitrile in THF to form $Fe_4S_4Cl_2(CNCMe_3)_6$, with an intact Fe_4S_4 cubane cluster. Two iron vertices were coordinated to three isonitriles each, and two remained "inorganic" [XRC][85].

Synthesis of tricarbonylbis(phosphine)iron compounds by direct displacement from iron pentacarbonyl has been found to work especially well in cyclohexane, from which the desired products precipitated cleanly[86]. Mixed compounds $LL'Fe(CO)_3$ [L, L' = different phosphines or phosphites] were prepared by allowing $LFe(CO)_3HSiPh_3$ to react with L', displacing triphenylsilane. With unhindered L', some $L'_2Fe(CO)_3$ was also formed, presumably by exchange in the starting material[87]. The ligand tris(sodium *m*-sulfonatophenyl)phosphine has been introduced for the purpose of generating water-soluble complexes. Reaction of the phosphine with $Fe_2(CO)_9$ gave seven products, including $(Ar_3P)_2Fe(CO)_3$ and $Ar_3PFe(CO)_4$[88].

Two new chelating diphosphines with large bite angles have been used to prepare, by reaction with (benzylideneacetone)tricarbonyliron, $Fe(CO)_3$ complexes. *trans*-1,2-Bis(diphenylphosphinomethyl)cyclopropane gave a trigonal bipyramidal complex, with the diphosphine coordinated to two equatorial positions [P-Fe-P angle 124°]. 2,2'-Bis(diphenylphosphinomethyl)biphenyl showed a distorted square pyramidal geometry with the P-Fe-P angle 152° and the basal OC-Fe-CO angle 142°. A plot of geometric parameters of eighteen $L_2Fe(CO)_3$ compounds showed a continuous transition between trigonal bipyramid and square pyramid along the Berry coordinate[89]. [1,1'-Bis(diphenylphosphino)ferrocene]$Fe(CO)_3$ has been prepared independently by two groups, one[90] using $Fe(CO)_5$ and $NaBH_4$ in refluxing butanol (33% yield), and one[91] using excess $Fe(CO)_5$ in refluxing benzene (20%). Mono- and di-$Fe(CO)_4$ complexes were also formed. A crystal structure of the chelate $Fe(CO)_3$ complex showed axial-equatorial coordination of the diphosphine in a distorted trigonal bipyramid[91]. A more exotic diphosphine-$Fe(CO)_3$ complex, **8**, was obtained by coordinating the lone pairs on the phosphole ligands of a diphosphazirconocene derivative, by reaction with $Fe_2(CO)_9$. The crystal structure showed axial-equatorial coordination, with P-Fe-P angle 81°.



8

Photochemical reaction of 2-(diphenylphosphinomethyl)pyridine with $Fe(CO)_5$ gave first the phosphorus-coordinated $LFe(CO)_4$ complex, then *trans*-$L_2Fe(CO)_3$. Prolonged irradiation produced the chelated $LFe(CO)_3$ complex[93]. Similar photoreaction with diphosphinoamines X_2PNRPX_2 [X = OCH_2CF_3, OAr, Ph; R = Me, Ph] yielded four-membered ring chelate $Fe(CO)_3$ complexes and bimetallic products[94]. Treatment of the cationic complexes $(dppm)FeL(CNPh)_3^{2+}$ [L = PPh_3, CNPh] or $(dppm)FeX(CNPh)_3^+$ with KOH resulted in deprotonation of a methylene group of the chelated dppm ligand. Gold derivatives of the resulting carbanion were formed by reaction with Ph_3PAuCl, $(C_4H_8S)AuCl$, and $(C_4H_8S)_2Au^+$. The crystal structure of $(PhNC)_3FeCl[Ph_2PC(AuPPh_3)_2PPh_2]^+$ PF_6^- showed a short Au-Au contact[95].

Deprotonation of *mer*-$Ph_3PFe(CO)_3(H)SnR_3$ [R = Me, Ph] with KH gave anionic products which were readily methylated or stannylated. The crystal structure of *mer*-$Ph_3Fe(CO)_3(SnMe_2Cl)_2$ [from reaction of K^+ $Ph_3PFe(CO)_3SnMe_3^-$ with excess Me_2SnCl_2] showed no interaction of the chlorodimethylstannyl groups in the solid state, but in solution a second isomer was indicated by NMR; a structure with Sn-Cl-Sn bridges was suggested. Attempts to displace R_6Sn_2 or R_6SiSn from iron by reaction with phosphines succeeded only in the case of hexamethyldistannane; other compounds evolved tetramethylstannane or $Me_3SnOSiMePh_2$ instead[75].

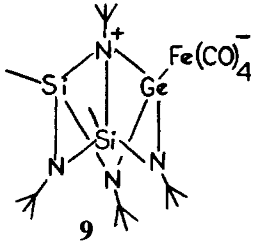
4e. Iron Tetracarbonyls, e.g. $LFe(CO)_4$ and $R_2Fe(CO)_4$

Photolysis of $Fe(CO)_5$ has been studied in polymer films at 12-298 K. At the lowest temperatures, $Fe(CO)_4$ and $Fe(CO)_3$ were detected by IR; recombination with CO occurred at 80 K and 60 K, respectively. Products from reactions of the unsaturated species with the polymer medium or with monomers or solvents incorporated into the films were also observed at temperatures below 140 K. Examples included adducts of $Fe(CO)_4$ with polyvinyl chloride and dichloroethane (probably coordinated through chlorine) and with C-H bonds of hexane and polyethylene[96].

Uses of $HFe(CO)_4^-$ in synthesis and catalysis have been reviewed[4]. Variable temperature ^{13}C NMR spectra of PPN^+ and Et_4N^+ $HFe(CO)_4^-$ in the solid state have been studied using magic angle spinning. The activation energy for axial-equatorial exchange in the tetraethylammonium salt was estimated as 29(3) kJ/mol, with a higher barrier in the PPN^+ salt. A hydrogen tunneling mechanism was proffered[97]. Reaction of $HFe(CO)_4^-$ with $RMo(CO)_3Cp$ [R = Me, CH_2CHMe_2] to form principally RH and RCHO has been studied[98]. Acrylic acid was converted to methylmalonic acid by reaction with $HFe(CO)_4^-$, generated *in situ* from calcium hydroxide and $Fe(CO)_5$, in aqueous isopropyl alcohol at 70° under one atmosphere of CO. A catalytic mechanism was proposed[99]. Ethanolic $HFe(CO)_4^-$ efficiently brought about the condensation of succinaldehyde with primary amines to form pyrrolidines. Similarly, phenylenediamines formed arylpyrrolidines in moderate yields under CO pressure[100].

Reduction of $Fe(CO)_5$ with "Super-hydride," Li^+ Et_3BH^-, studied by variable temperature IR over the range -80° to room temperature, showed three distinct acid-base complexes of the formyl anion $HCOFe(CO)_4^-$, with BEt_3 and lithium in a contact ion pair, with BEt_3 alone, and in a tight ion pair with Li^+. Equilibria among the various species were studied. With L-selectride as reducing agent, the hindered trisiamylborane did not coordinate to the formyl oxygen, and only the lithium ion pair was observed[101]. Reaction of tetraethylammonium hydroxide with $Fe(CO)_5$ at -78° in THF containing 0.35% methanol produced both $(OC)_4Fe$-$COOH^-$ and $(OC)_4FeCOOMe^-$, the former predominating. Addition of lithium triflate shifted the equilibrium strongly toward the methoxycarbonyl species[102].

The novel species **9** resulted from reaction of the precursor germanium ylide with $Fe_2(CO)_9$[103]. Several tin-iron salts, $R_3SnFe(CO)_4^-$, were prepared by reaction of $HFe(CO)_4^-$ with R_3SnCl [R = Ph, *p*-MeC_6H_4]. $SnCl_4$ gave predominantly $Cl_2Sn[Fe(CO)_4]^{2-}$, characterized by a partial crystal structure of the PPN$^+$ salt[104]. Reaction of the tetraethylammonium salt with $ClHgMo(CO)_3Cp$ afforded the linear heptametallic species $Hg[Fe(CO)_4SnCl_2Fe(CO)_4^-]_2$. The crystal structure showed a cis relationship of tin and mercury groups about the internal $Fe(CO)_4$ groups, and considerably shorter Sn-Fe bonds to the terminal $Fe(CO)_4$ groups (2.496 Å) than to the internal (2.593 Å)[105].

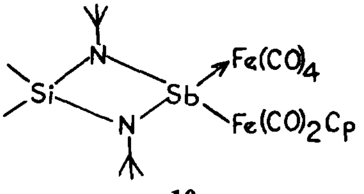


9

Direct synthesis of $LFe(CO)_4$ [L = phosphines, phosphites, $AsPh_3$, $SbPh_3$] from $Fe(CO)_5$ and the ligand has been catalyzed by CoX_2, Fp_2, or Fp^*_2[106,107]. P-coordinated [2-(diphenylphosphinomethyl)pyridine]$Fe(CO)_4$ was the initial product of reaction of the ligand with $Fe(CO)_5$ under irradiation[93]. Diferrocenylphenylphosphine and triferrocenylphosphine were converted to $Fe(CO)_4$ complexes by reaction with $Fe_3(CO)_{12}$[108]. Mono and bis-$Fe(CO)_4$ complexes also formed from 1,1'-bis(diphenylphosphino)ferrocene upon reaction with $Fe(CO)_5$ and Me_3NO[90] or excess $Fe(CO)_5$ alone[91]. The monoiron complex was converted to bimetallic complexes by coordination of the free phosphine group with, for example, a $Mo(CO)_5$ moiety[90,109]. The dangling diphenylphosphino group of $Cp_2Mo_2(\mu\text{-}\sigma,\Pi\text{-}CNCMe_3)(\eta^1\text{-dppm})(CO)_3$ was coordinated to an $Fe(CO)_4$ moiety through reaction with $Fe_2(CO)_9$[110].

The halogenated diphosphines $RXPCH_2PXR$ [R = hindered aryl groups, NEt_2, NPh_2, OAr, etc.] reacted with $Fe_2(CO)_9$ with initial formation of mono- and bis-$Fe(CO)_4$ complexes, but dehalogenation to form diphosphirane complexes ensued. Under more vigorous conditions Fe_2 and Fe_3 cluster compounds formed[111]. Reduction of $(RPCl_2Fe(CO)_4$ with zinc in the presence of tributylphosphine resulted in formation of diphosphene complexes, $(OC)_4FeP(R){=}PBu_3$. Aldehydes ArCHO, reacted with these "phospha-Wittig reagents" to form unstable phosphaalkene complexes $(OC)_4FeP(R){=}CHAr$, which were trapped by methanol to form phosphinite complexes, $(OC)_4FeP(R)(OMe)(CH_2Ar)$[112]. Displacement of chloride from $Me_2Si(NR)_2SbCl$ [R = CMe_3] by Fp^- gave the Sb-Fp derivative. Other Sb-and Bi-coordinated analogs were prepared similarly. The lone pair on Sb underwent coordination to an $Fe(CO)_4$ unit upon reaction with $Fe_2(CO)_9$, giving **10**. The Sb$\rightarrow$$Fe(CO)_4$ bond in **10** was shorter (2.530 Å) than the Sb-Fp bond (2.547 Å)[113].

Tetracarbonyl(dimethyl sulfide)iron has been prepared as precursor to $Fe(CO)_4$ groups in solution. It was formed in 50% yield by thermal reaction of Me_2S with $Fe_2(CO)_9$ or 80% by low temperature photolysis with $Fe(CO)_5$. It was



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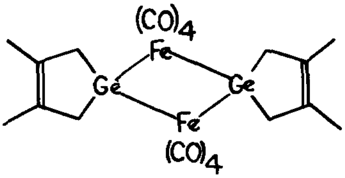
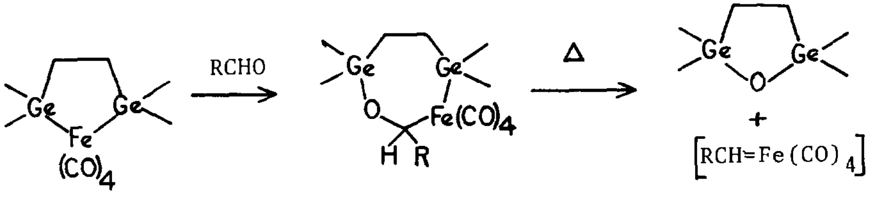


11

isolable, but labile in solution in the absence of excess dimethyl sulfide[114]. An analogous compound, $(OC_4H_8N)_2S \rightarrow Fe(CO)_4$, was formed upon thermal reaction of thiobis(morpholine) with $Fe_2(CO)_9$. It was unstable, and decomposed in solution with formation of $S_2Fe_3(CO)_9$. The latter was formed directly when thiobis(morpholine) reacted photochemically with $Fe(CO)_5$[115].

The spirocyclic product **11** [XRC] formed in 94% yield from reaction of $Na_2Fe(CO)_4$ and 1,1-dibromo-3,4-dimethylgermacyclopent-3-ene[116]. As shown in Eq. 3, ferradigermacycles inserted aldehydes into the Fe-Ge bond with ring expansion. Thermal decomposition of the adducts produced alkylidene intermediates trapped by triphenylphosphine to form $Ph_3P^+CH(R)Fe(CO)_4^-$ or which formed alkenes RCH=CHR[117].



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Dimethylsilylferrocene reacted thermally with iron pentacarbonyl to form $ArSiMe_2Fe(CO)_4SiMe_2Ar$ [Ar = ferrocenyl]. An intramolecular analog, $[\eta^2\text{-}Me_2SiC_5H_4FeC_5H_4SiMe_2]Fe(CO)_4$, was formed similarly, from 1,1'-bis(dimethylsilyl)ferrocene[118].

Reaction of perfluorosuccinyl or -glutaryl dichlorides with tetracarbonylferrate dianion gave cyclic diacyls [XRC]. Heating of these species led to facile decarbonylation, with eventual formation of the perfluoroferracyclopropane and -cyclobutane tetracarbonyls [XRC][119]. Reaction of 1,8-bis(bromomethyl)naphthalene with $Fe_2(CO)_9$ was said also to produce a cyclic dialkyliron product, $[1,8\text{-}C_{10}H_6(CH_2)_2]Fe(CO)_4$. Treatment with triphenylphosphine allegedly displaced the organic ligand to form $Ph_3PFe(CO)_4$[120].

4f. Carbene complexes $R_2Fe(CO)_4$

Equation 3 showed a rather novel route to a carbene complex[117]. Several examples of carbene complexes $ArC(OEt)=Fe(CO)_4$ have been prepared by the classical Fischer route, reaction of iron pentacarbonyl with an aryl lithium at low temperatures, followed by ethylation with triethyloxonium fluoroborate[121]. Reaction of the ylide $Bu(NMe_2)_2P{=}CHSiMe_3$ with iron pentacarbonyl occurred by addition to a carbonyl group and silyl migration, forming the carbene complex $(OC)_4Fe{=}C(OSiMe_3)CH{=}PBu(NMe_2)_2$ [XRC][122].

The dicationic carbene complex **6**[79] was previously cited in Section 4c. Also highly carbenoid in character is the compound $(Me_3P)_2Fe(CO)_2[\eta^2\text{-}SC(SR)]$, which underwent attack at the carbenoid carbon by borohydride, giving dithioformate complexes, as shown in Eq. 2[78].

Reaction of the diazo compound $PhCH_2CHN_2$ with (Por)FeCl [(Por) = tetra-*p*-chlorophenylporphyrin] led to insertion of benzylcarbene into a Fe-N bond. Reduction with zinc or electrochemically formed the diamagnetic carbene complex, $(Por)Fe{=}CHCH_2Ph$[123]. Reaction of $(Por)Fe{=}CCl_2$ [(Por) = tetraphenylporphyrin] with two moles of $Re(CO)_5^-$ produced $(Por)Fe{=}C{=}Re(CO)_4Re(CO)_5$, whose structure showed a nearly linear (173°) Fe-C-Re linkage[124].

The first neutral carbyne complex of iron, $Ph_3P(OC)_2Fe{\equiv}CN(CHMe_2)_2(OCOCF_3)$, has been prepared by treating iron pentacarbonyl successively with lithium di-isopropylamide, trifluoroacetic anhydride, and triphenylphosphine[125]. A crystal structure of this novel species would be welcome.

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

Reactions in which $Fe(CO)_5$ undergoes conversion to more complex organometallic products are treated in this review according to the product structure. Here we discuss physical properties of $Fe(CO)_5$ and some simple reactions which generate other iron carbonyls or isonitrile derivatives.

The crystal packing in solid $Fe(CO)_5$ has been examined, along with those of several other binary transition metal carbonyls, as part of a study of the factors controlling such packing[126]. The variable temperature ^{13}C NMR of solid $Fe(CO)_5$ obtained by use of magic-angle spinning showed no evidence of axial-equatorial exchange of carbonyl ligands, in contrast to previous broad-line NMR results. The rate of such exchange was found to be less than 10^2 sec^{-1} at -60°, more than two orders of magnitude slower than previous estimates[97]. Matrices containing isolated $Fe(CO)_5$ molecules in alkali halide lattices have been prepared by codeposition from the vapor phase. In these matrices, photolysis led to loss of CO ligands, and to oxidation and reduction due to interaction with light-induced defects and color centers. In aggregated samples, $Fe_2(CO)_9$ was formed[127].

The extended fine structure in the K-shell continuum of gaseous $Fe(CO)_5$ was studied by electron energy loss spectroscopy. The results provide a model for chemisorbed CO[128]. The energy distribution which results in $Fe(CO)_5^+$ upon high-energy collisions with argon atoms has been studied. Both vibrational and electronic excitation mechanisms were indicated[129]. Photoelectron-photoion coincidence spectra for $Fe(CO)_{0-5}^+$ have been measured. These have led to new values of CO dissociation energies for this family of iron carbonyl cations. The data were generally consistent with a mechanism for sequential CO loss in collision-induced fragmentation[130].

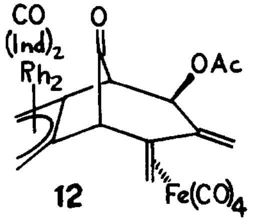
Photolysis of $Fe(CO)_5$ adsorbed on hydrated alumina produced $HFe(CO)_4^-$ and $HFe_3(CO)_{11}^-$, the latter by a sequence which involved B-$Fe(CO)_4$ and adsorbed $Fe_3(CO)_{12}$[131]. $Fe(CO)_5$ adsorbed on NaY zeolite was fifteen times as reactive in photoinduced butene isomerization as when adsorbed on KY zeolite[132].

Carbon monoxide units from $Fe(CO)_5$ were incorporated into heterocyclic rings when $Fe(CO)_5$ and tri(*tert*-butyl)azadiboriridine were photolyzed at -30°[133]. Aryl iodides and $Fe(CO)_5$ reacted under phase-transfer conditions [aq. NaOH/-benzene/Bu_4NBr] and one atmosphere of carbon monoxide to produce benzophenones in good yield; inclusion of cobalt carbonyl improved the yield further[134].

Substitution of up to five ArNC molecules for CO in $Fe(CO)_5$ has been accomplished thermally[135] or, better, with $CoCl_2$ catalysis[136].

5. η^2-ALKENE AND η^3-ALLYL COMPLEXES

The principal species observed in photolyzed samples of $Fe(CO)_5$ in low-density polyethylene at room temperature were (alkene)$Fe(CO)_4$ products formed from adventitious alkene impurities in the polymer[96]. The alkene complex **12** was formed both regio- and stereoselectively as the first product of iron complexation of the rhodium-complexed precursor, using $Fe_2(CO)_9$[137]. Another bimetallic complex having an η^2-$Fe(CO)_4$ group was obtained by complexing the free double bond of (CH_2=CH-CH_2-η^6-C_6H_5)$Cr(CO)_3$ with iron pentacarbonyl under photochemical conditions[138]. A novel η^2-thiophene dioxide complex, $(C_4H_4SO_2)Fe(CO)_2$-$[P(OMe)_3]_2$ [XRC][80] was formed alongside 7, described in Section 4c. An unusual route to an η^2complex was the thermal decarbonylation of tetracarbonyl(perfluorosuccinyl)tetracarbonyliron, which produced at 110° tetracarbonyl(η^2-tetrafluoroethene)iron[119].



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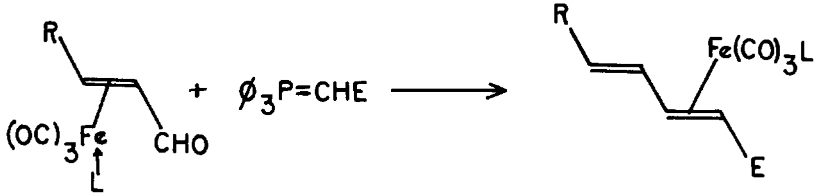


(4)

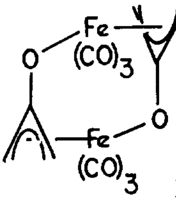
η^2-Complexed α,β-unsaturated aldehydes readily underwent the Wittig reaction with stabilized ylides; however, β-substituents in the original aldehyde led to migration of the iron group (Eq. 4; R = Me, Ph, furyl; L = CO, PPh_3)[139].

Structures of η^2-alkyne complexes, including FeL_3 complexes, have been discussed with the help of extended Hückel MO calculations. The C_s, quasi square pyramidal, structure found has been ascribed to strong bonding arising from four-electron donation by the alkyne. Facile rotation of the alkyne, accompanied by a breathing motion of the ligands of the FeL_3 moiety, was indicated[140].

η^2-Coordination of the B=C bond in [9-fluorenylidene(2,2,6,6-tetramethylpiperidino)borane]$Fe(CO)_3[P(OMe)_3]$ has been observed [XRC][141]. The addition of Ph_3PAu^+ to $(\eta^2\text{-}B_2H_5)Fe(CO)_4^-$ occurred at the iron, forming $Ph_3PAuFe(CO)_4(\eta^2\text{-}B_2H_5)$. Methylation and protonation did not lead to stable products[142].

The principal product of photolysis of $Fe(CO)_5$ in polyvinyl chloride films at room temperature resembled $(\eta^3\text{-}C_3H_5)Fe(CO)_3Cl$ in its IR properties[96]. Two carbonyl ligands of (η^3-allyl)iron tricarbonyl iodide could be displaced by the bidentate ligands 2,2'-bipyridyl or 1,10-phenanthroline to give catalytically active species $(\overset{\frown}{LL})(\eta^3\text{-}C_3H_5)Fe(CO)I$[143].

Bromotricarbonyl(2-hydroxyallyl)iron was prepared by reaction of $CH_2=C(OSiMe_3)CH_2Br$ with $Fe_2(CO)_9$. The pK_a was 5.2, which the authors described as "unexpectedly high acidity," despite previously published pK_a's of OH groups on coordinated ligands which ranged from 3-10. Treatment with pyridine and $AgBF_4$ resulted in dehydrobromination; however the product was a dimer, **13**, of the expected tricarbonyl(propanonediyl)iron. The crystal structure showed the iron farther from the central carbon of the allyl unit [2.27Å vs 2.13Å], the normal consequence of the electron-donating group at that position[144]. Butenediols have been used as starting materials for synthesis of allyliron complexes. Thus, the allyliron lactone **14** was obtained in 73% yield from *cis*-2-butene-1,4-diol and $Fe_2(CO)_9$ in THF, and in 55% yield in benzene using ultrasonication. Under similar conditions in benzene 2-(hydroxymethyl)-2-propen-1-ol gave a 58% yield of the isomeric lactone complex and also 5% of tricarbonyl(trimethylenemethyl)iron. In THF, the latter was the major product (63% yield)[145]. An alternative route to **14** involved the use of the cyclic sulfite, 4-vinyl-1,3,2-dioxathiolane S-oxide as the precursor, with $Fe_2(CO)_9$ and ultrasonication in benzene[146]. Synthesis of the 1- and 4-methyl homologs of



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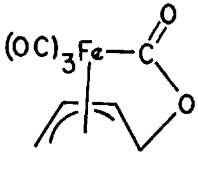
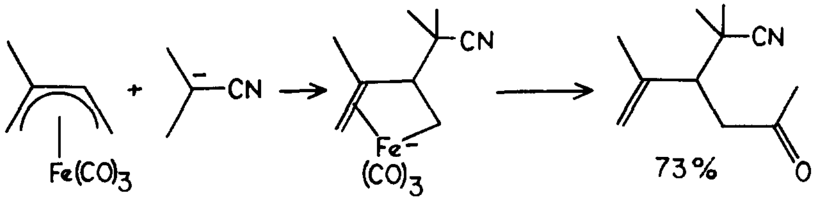


14

14 from the cyclic sulfite played a key role in a total synthesis of avermectin B1a aglycone[147].

Treating the dimer $[(\eta^3\text{-}C_3H_5)Fe(CO)_3]_2$ with tertiary phosphines resulted in disproportionation to $(allyl)Fe(CO)_2L_2^+$ $(allyl)Fe(CO)_3^-$. The labile cations were better prepared from $(allyl)Fe(CO)_3Br$[148]. A more elaborate η^3-allylic cation was **2**, which resulted from coupling of phenylacetylene units in reaction with $(dmpe)_2FeCl_2$ in methanol[46]. The cationic complex $(\eta^3\text{-}C_3H_5)Fe(NO)_2\text{-}[P(OMe)_3]^+$ has been used as an allylating reagent. With $CpRh(\eta^4\text{-}C_8H_8)$, allylation occurred on the cyclopentadienyl ring, followed by proton transfer to the cyclooctatetraene[149]. With $(C_8H_8)M(CO)_2L$ [M = Fe, Ru; L = CO, PPh_3], allylation occurred on the eight-membered ring to give products which will be discussed in more detail in the following section[150].

The structures and fluxional behavior of $(\eta^3\text{-cycloheptatrienyl})M(CO)_3^-$ for the metals of Group 8 have been compared. The coalescence temperatures for the M = Fe, Ru, and Os anions were -150°, -115°, and -65°, respectively[151]. Reaction of the tricarbonyl(η^3-cycloheptatrienyl)iron anion with Ph_3ECl [E = Sn, Pb] resulted in formation of Fe-E bonds, in contrast to the silicon and germanium electrophiles, which gave ring substitution. The tin and lead products showed both haptotropy, in the form of 1,2-shifts of the seven-membered ring relative to the iron group, and carbonyl scrambling[152].



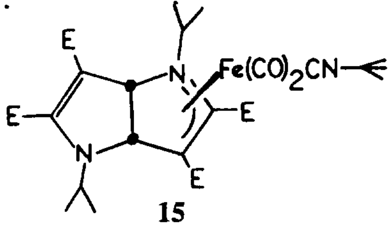
(5)

Methylation of the $(\eta^1,\eta^2\text{-but-3-en-1-yl})Fe(CO)_3^-$ anions formed by attack of nucleophiles on butadiene complexes gave unsaturated ketones. An example is shown in Eq. 5[153].

Reaction of 7-azanorbornadienes with $Fe_2(CO)_9$ led to formation of substituted benzenes, with extrusion of the nitrene moiety. The reaction was most successful with electron-withdrawing groups on both the nitrogen and the 2- and 3-positons of the ring. $\eta^3\text{-}Fe(CO)_3$ complexes of the starting material, with the iron complexed to a double bond and to the nitrogen, were isolated in several cases, and crystal structures were reported for two of them, with $N\text{-}SO_2Me$ and N-Ph substituents[154]. An aza-allyl complex, **15**, [XRC] resulted from reaction of dimethyl acetylenedicarboxylate with $(Me_2CH\text{-}N{=}CH\text{-}CH{=}NMe_2)Fe(CO)_2(CN\text{-}CMe_3)$[155].

Perhaps also construable as a η^3 structure is the *nido*-ferrapentaborane **16** obtained as the principal product of reaction of pentaborane(9) with $(Me_3P)_3Fe$-

(CH_2=PMe_2). **16** appears to have the FeL_3 group replacing a basal BH group of B_5H_9, whereas the previously reported $Fe(CO)_3$ analog has the iron in the apical position[156].



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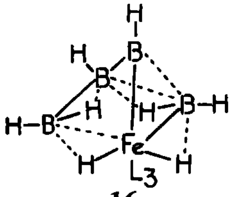

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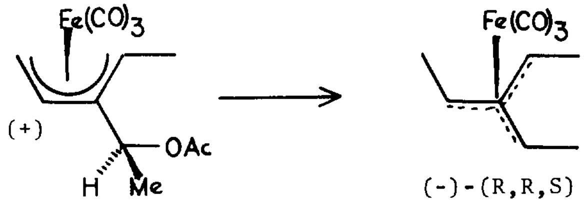
6. COMPOUNDS WITH η^4-LIGANDS

Graph theoretical methods have been used to calculate MO parameters for $Fe(CO)_3$ complexes of various unsaturated hydrocarbons, with results said to be in good agreement with experimental properties[157].

6a. Trimethylenemethyl Complexes

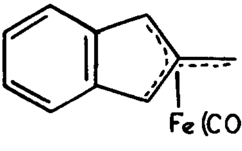
The parent $[C(CH_2)_3]Fe(CO)_3$ was obtained in 63% yield by reaction of 2-(hydroxymethyl)-2-propen-1-ol with $Fe_2(CO)_9$ in THF[145]. Use of the diol appears from this to be superior to use of dihalide precursors for preparing this compound. Stereoselective syntheses of methyl-substituted TMM complexes have been achieved by ionic hydrogenation of 2-acyloxy-1,3-diene complexes using BF_3/Et_3SiH at -78°. Optically active starting materials of known configuration gave products of known configurations, based on the observation that the C-O bond broken was *anti*-periplanar to the β-C-Fe bond. An example of the reaction is



(6)

shown in Eq. 6[158]. A metal-substituted TMM complex, $[Cp(OC)_3W\text{-}CH\text{:-}C(CH_2)_2]Fe(CO)_3$, was prepared by reaction of the allene $Cp(OC)_3W\text{-}CH{=}C{=}CH_2$ with $(\mu\text{-}CH_2)Fe_2(CO)_8$[159].

The formyl-substituted TMM complex, $[(CH_2)_2CCHCHO]Fe(CO)_3$, reacted in a highly diastereoselective manner with organozinc reagents, forming alcohols. By this route, the (+)-aldehyde enantiomer was converted to R-(-)-ipsdienol of high e.e.[160]. The first transition metal-stabilized derivative, **17**, of the highly reactive molecule, isobenzofulvene, has been prepared. It proved to have the coordinated TMM structure shown rather than the isomeric coordinated *o*-xylylene-type structure[161].



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As previously described, an attempt to prepare an oxa analog of TMM-Fe(CO)$_3$, tricarbonyl(η^4-propanone-1,3-diyl)iron, yielded instead the dimer **13**[144]. Greater success attended the reaction of substituted allene episulfides with Fe$_2$(CO)$_9$, which did afford thia-TMM complexes. The tetramethyl derivative, [(Me$_2$C)$_2$CS]Fe(CO)$_3$ was obtained in 16% yield, and the 1,1-diphenyl-3-*tert*-butyl derivative in 29% yield. The crystal structure of the latter showed the Fe-S distance of 2.308 Å[162].

6b. Complexes of Acyclic Dienes, including Heterodienes

A detailed procedure for synthesis of (benzylideneacetone)tricarbonyliron and its use in synthesizing diene complexes under mild conditions has been described[163]. (Methyl 2,4-pentadienoate)Fe(CO)$_3$ has been prepared by Wittig condensation of (η^2-CH$_2$=CH-CHO)Fe(CO)$_4$ with Ph$_3$P=CHCO$_2$Me to form the η^2 product, which lost CO on heating or on treatment with Me$_3$NO to yield the η^4 product[164]. Diastereomeric esters of this acid with S-(-) ethyl lactate were readily separated by silica chromatography. Methanolysis of the pure diastereomers gave methyl esters of high enantiomeric purity, whose absolute configurations could be assigned on the basis of chemical correlations[165].

Highly functionalized diene complexes were obtained in 32-64% yield by treatment of 2,5-dihydrothiophene dioxides with excess Fe$_2$(CO)$_9$ in refluxing toluene. Many of the complexes obtained could not be obtained directly because of polymerization of the free dienes. Substituents included acetyl, carbomethoxy, chloro, cyano, phenylsulfinyl, phenylsulfonyl, and trimethylsilyl groups[166]. Liquid crystals containing (diene)tricarbonyl groups in the backbone have been prepared. The phases and transition temperatures were reported[167]. The Co$_2$(CO)$_6$ complex of hexa-1,3-dien-5-yne, in which the triple bond is coordinated to the dicobalt group, served as a further ligand to a tricarbonyliron group, which was attached by use of "Grevels' reagent," (cyclooctene)$_2$Fe(CO)$_3$, at -40°[168]. A complex of an exocyclic diene was obtained when **12** reacted further with Fe$_2$(CO)$_9$; curiously, the diene complex had the Fe(CO)$_3$ group on the β face, whereas the iron group in the precursor **12** was α[137]. A review of the effects of tricarbonyliron groups on remote reactivity in rigid systems has been published[6].

η^4-Complexes can be prepared by attack of nucleophiles on η^5-dienyl complexes. In the case of (2-methylpentadienyl)Fe(CO)$_3$$^+$, nucleophilic attack occurred mostly at C5, giving substituted diene complexes[169]. Attack of organolithium reagents on (pentadienyl)$Fe(CO)_3^+$ occurred at both C1 and C2; the latter resulted in formation of η^1,η^3-2-pentene-1,5-diyl complexes. These were the principal products when (pentadienyl)$Fe(CO)_2PPh_3^+$ were the substrates of organolithium attack[170]. When diphosphine complexes (pentadienyl)$Fe(PEt_3)_2CO^+$ underwent such attack, again C2 was the primary target, and η^1,η^3-pentenediyl products were the only ones reported[171].

Likewise, attack of $LiMe_2CCN$ on tricarbonyl(2-methylbutadiene)iron occurred at the 3-position, as previously shown, to form an η^1,η^2-butenyl complex (Eq. 5). Methylation of this species resulted in formation of an unsaturated ketone. Methylation under a CO atmosphere resulted in a yield of 73%[153].

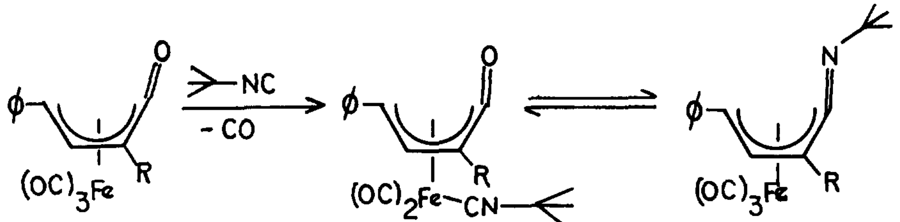
Photochemical studies of (butadiene)tricarbonyliron and several cyclic diene complexes in matrices at 12 K have confirmed previous studies in showing two competing processes, CO dissociation and double bond dissociation. The latter process was responsible for *s-cis*⇌*s-trans* equilibration in the case of the acyclic butadiene complex, and for formation of (η^2-polyene)$Fe(CO)_4$ and $Fe(CO)_5$ in CO matrices[172]. (Diene)$Fe(CO)_2L$ complexes [L = phosphines, phosphites, isonitriles] have been converted photochemically to (diene)$Fe(CO)L^1L^2$ complexes in twenty-three cases. In complexes of prochiral dienes, diastereomeric products were obtained, which could be separated chromatographically. Three crystal structures were reported[173].

Diene aldehyde complexes, (η^4-RCH=CH-CH=CHCHO)$Fe(CO)_3$ [R = Me, CO_2Me] have been resolved kinetically by reaction with a chiral allyl-borane reagent, which transferred the allyl group with high (>100:1) diastereoselectivity. The same reagent attacked one aldehyde group of the meso-dialdehyde with high enantiotopic group and face selectivity[174]. Friedel-Crafts acylation of pure enantiomers of tricarbonyl(η^4-1,3-pentadiene)iron occurred without racemization to form chiral 1-acyl-1,3-pentadiene complexes. These underwent stereospecific attack by alkyl-lithium reagents to form tertiary alcohol complexes. Decomplexation and ozonolysis with reductive workup were used to form α-hydroxyaldehydes of known absolute configuration, based on those of the starting complexes[175]. Friedel-Crafts acetylation of the 2-methyl-1,3-butadiene complex gave a 2:1 ratio of *endo*-4- and 1-acetyl products. Treatment with sodium methoxide converted the *endo* products to the more stable *exo* products, which, contrary to previous reports, underwent a second acetylation reactions to yield dienedione complexes[176]. Conversion of diene complexes to TMM complexes[158] was illustrated in Eq. 6.

A review has described the uses of acyclic diene complexes in synthesis, with emphasis on Wittig reactions[5]. Both enantiomers of (BuCH=CH-CH=$CHCH_2$-PPh_3^+)$Fe(CO)_3$ have been prepared in pure form. Their reaction with a chiral formyloxirane showed a substantial difference in reactivity, yields of the diastereomeric Z-alkene products being 15 and 74%[177]. Reactions with an epoxidized trienal ester were used to prepare tricarbonyliron-coordinated leukotriene analogs[178].

Diels-Alder reactions of free double bonds in η^4-triene and of free diene units in η^4-tetraene complexes have been investigated. The reactions occurred in a highly stereoselective manner, and may be useful for the synthesis of polycyclic products via tandem cycloadditions[179].

Vinylketene complexes were converted into vinylketenimine complexes by heating with isonitriles (Eq. 7)[180]. Both diastereomers of the ketenimine complexes [η^4-PhCH=CH-CMe=C=N-(*S*-CHMePh)]Fe(CO)$_3$ have been obtained in optically pure form. Nucleophilic attack by ethyl-lithium occurred exclusively at C-2, on the *exo* face[181]. In contrast, nucleophiles attacked vinylketene complexes at C-1; those used, in addition to alkyl-lithium reagents, included RNH$_2$, MeO$^-$, and Me$_3$CS$^-$ [182].



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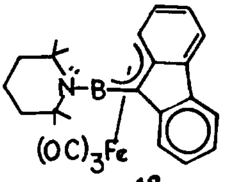
An unusual heterodiene complex, **18**, [XRC] was prepared by photochemical reaction of the free ligand with Fe(CO)$_5$. Phosphorus ligands displaced the arene ring from coordination, leaving the boron-carbon double bond coordinated[141]. Procedures for the preparation of (benzylideneacetone)tricarbonyliron and for its use as a source of tricarbonyliron groups have been described[163]. Significant diastereocontrol in coordination of *ortho*-substituted benzylideneacetophenones having a Cr(CO)$_3$ group on the benzylidene ring, as shown in Eq. 8, has been observed; the relative configurations were established by X-ray crystallography. The meta-substituted analog gave no selectivity[183]. MO calculations have been carried out on (η^4-enone)Fe(CO)$_2$L [L = PH$_3$, P(OH)$_3$, CO] complexes. The



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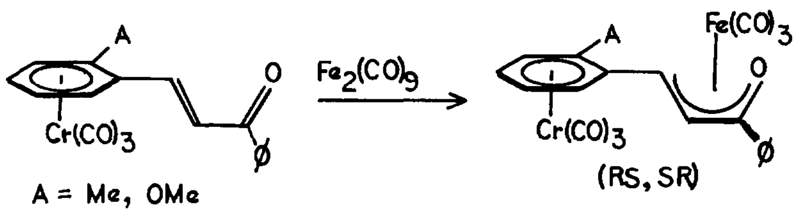

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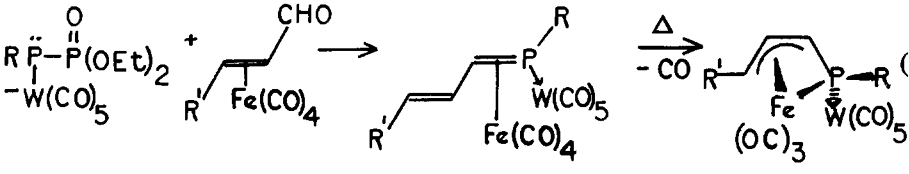
most stable conformation was calculated to have the phosphorus ligand L trans to the central C-C bond of the enone. Bonding was dominated by back-donation from metal to the Π_3 orbital of the ligand, resulting in significant accumulation of electron density on C4[184]. Reactions of dialkyl phosphites with (η^4-enone)$Fe(CO)_3$ complexes have been studied, but this reviewer is unable to discern the results from the available abstract[185].

(η^4-Azadiene)tricarbonyliron complexes have been prepared by reaction of anilines with (η^2-RCH=CHCOR')$Fe(CO)_4$ [R = H, Ph; R' = H,Me][164]. Nucleophilic addition of methyl-lithium to 1-azadiene complexes occurred at C2 when that carbon was unsubstituted; otherwise, addition occurred at a metal carbonyl group, which eventuated in incorporation of a CH_3C atom into the ligand to form substituted pyrrole rings[186]. Reaction of a "phospha-Wittig reagent" with (η^2-RCH=CH-CHO)$Fe(CO)_4$ resulted in formation of a phosphadiene complex [XRC], as shown in Eq. 9 [R = Ph, Me, CMe_3; R' = Ph, Me, furyl][187]. The crystal structure of [η^4-S=C(Ph)-N=$CHCO_2Et$]$Fe(CO)_3$ has been reported[188].



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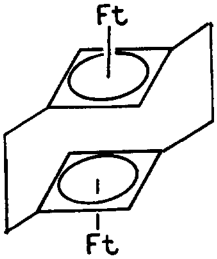
6c. Complexes of Cyclic Dienes

The ultraviolet photochemistry of tricarbonyl(cyclobutadiene)iron in matrices at 12 K has been further investigated. Carbonyl dissociation predominated, but formation of a ferracyclopentadiene was also discussed as a possible route to tricarbonyl(cyclopentadienone)iron, which was formed in a CO matrix. The metal carbonyl groups of the latter, but not the ketone carbonyl, underwent facile photoexchange with external ^{13}CO[172]. Photolysis in supercritical xenon solution at room temperature under a high pressure of N_2 or H_2 let to formation of $(C_4H_4)Fe(CO)_2(N_2)$ (also observed in cryogenic matrices above), $C_4H_4Fe(CO)(N_2)_2$, or $(C_4H_4)Fe(CO)_2(\eta^2\text{-}H_2)$. Decomposition of the latter led to significant amounts of $Fe(CO)_5$[189].

(Tetraphenylcyclobutadiene)dinitrosyliron has been characterized spectroscopically from co-photolysis of $Fe(CO)_2(NO)_2$ and diphenylacetylene. It served as a case in point in a discussion of "the scarcity of two-legged piano-stool complexes."[190]. Reaction of $PhC{\equiv}C\text{-}N_3P_3F_5$ with $Fe(CO)_5$ also formed the cyclobutadiene complex, $[C_4Ph_2(N_3P_3F_5)_2]Fe(CO)_3$. With $Fe_2(CO)_9$, a complex mixture of products, including the cyclobutadiene complex and a cyclopentadienone complex, resulted[191].

A pair of novel double-decker cyclobutadiene complexes, **19** and **20**, both characterized by X-ray crystallography, has been reported. In **19**, synthesized by stepwise construction of the bridges, the ring-ring distance was only 2.7 Å, but the rings were planar[192]. **20** was synthesized by iron carbonyl-induced acetylene dimerization (8% yield) in a precursor having the cyclopentadienylcobalt-complexed ring preformed[193].



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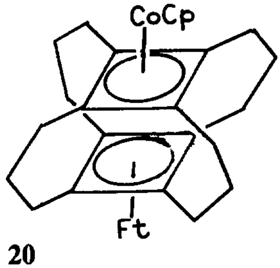

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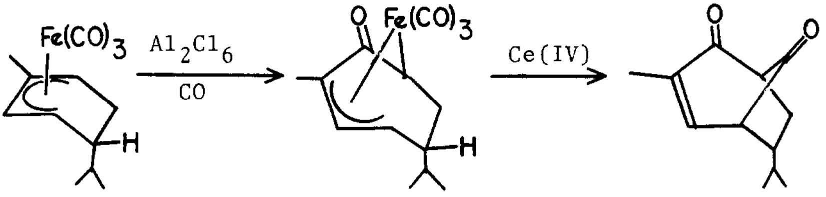
Photolysis of tricarbonyl(η^4-cyclopentadiene)iron in cryogenic matrices has been re-examined. Ring-to-metal hydride migration following carbonyl dissociation produced $CpFe(CO)_2H$ (FpH)[172]. Iron tricarbonyl complexes of the reactive compound thiophene dioxide, and of some phenyl-substituted derivatives, have been prepared [XRC]. Stepwise replacement of carbonyl groups by phosphines could be carried out completely in the case of the parent $(\eta^4\text{-}C_4H_4SO_2)Fe(CO)_3$[80].

Crystal structures of two tricarbonyliron complexes of substituted norbornadienes have been reported. In each case, the ligand occupied one axial and one equatorial site in a distorted trigonal bipyramid, with the more electron-deficient double bond (conjugated with two ester groups) in the equatorial position[194].

Tricarbonyl(η^4-cyclohexadiene)iron, along with a selection of other organometallic species, was studied by inelastic electron scattering, which gave inner shell excitation energies for the species[195]. Isomer ratios obtained in reaction of $Fe(CO)_5$ with 1-alkoxy-4-alkylcyclohexa-1,3- and 1,4-dienes were determined. In most cases, the principal product (over 90% for methoxy and methyl, ethyl, and isopropyl groups) was the tricarbonyl[(1-4-η)-1-alkoxy-4-alkylcyclohexa-1,3-diene]iron. When isopropoxy and *tert*-butyl groups were present, the main product, especially after addition of *p*-toluenesulfonic acid to isomerize the product mixture, was tricarbonyl[(1-4-η)-2-isopropoxy-5-*exo*-*tert*-butylcyclohexa-1,3-diene]iron[196].

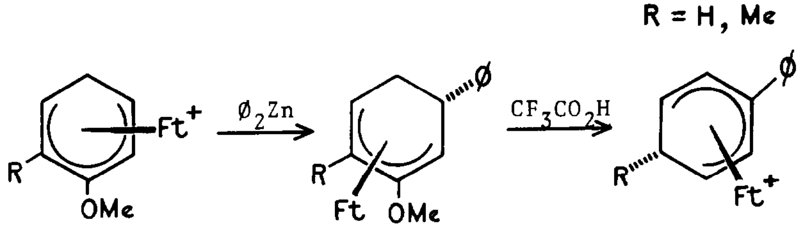
A series of substituted cyclohexadiene complexes has been prepared in order to investigate the stereochemistry of the "carbonylating ring enlargement" reaction, an example of which is shown in Eq. 10. Exo and endo isomers of tricarbonyl(η^4-1,3,5-trimethylcyclohexa-1,3-diene)iron were obtained by reaction of dihydromesitylene with several iron carbonyl reagents. Most selective was $Fe(CO)_5$ in refluxing dibutyl ether, which showed a 5:1 preference for the exo isomer and a 41% combined yield. "Grevels' reagent," $(C_8H_{14})_2Fe(CO)_3$, at low temperature gave the best overall yield (56%), but lower selectivity (2.2:1). Reaction of the two complexes with aluminum chloride under CO pressure gave the respective exo and endo ketones with retention of stereochemistry[197]. Preparation of the exo [shown in Eq. 10] and endo complexes of (R)-(-)-phellandrene and subjection to the ring expansion reaction showed complete retention of chirality in the reaction[198]. This was further demonstrated by reaction of the two enantiomers of tricarbonyl(α-terpinene)iron, which were obtained either by synthesis from precursors of appropriate chirality or by resolution by chromatography on cellulose triacetate[199].



(10)

Treatment of 1,4-cyclohexadienol ethers with sources of $Fe(CO)_3$ groups under mild conditions failed to produce diene complexes, suggesting that prior conversion to 1,3-dienol ether is a necessary first step. Complexes were obtained under more stringent conditions, using $Fe_3(CO)_{12}$, and then converted to cyclohexadienyl complexes using trifluoroacetic acid[200].

Acid-induced demethoxylation of cyclohexadiene complexes was found to be heavily influenced by a phenyl substituent, as shown in Eq. 11. A methyl substituent rather than the phenyl led to a mixture of cyclohexadienyl products[201]. Nucleophilic attack on tricarbonyl(η^5-1-phenylcyclohexadienyl)iron cation was directed by the phenyl to the remote 5-position; the effect of a 4-methoxy substituent was more powerful, however, resulting in attack of malonate ion, for example, at the 1-position of tricarbonyl(1-phenyl-4-methoxycyclohexa-1,3-dienyl)iron cation[202]. Tricarbonyl(η^5-1-methyl-4-menthoxycyclohexadienyl)iron hexafluorophosphate was obtained as a single diastereomer, starting from *p*-menthoxytoluene; attack by nucleophiles at the 1-position provided a synthetic route to optically pure 4-disubstituted cyclohex-2-enones[203]. (R)-1-Acetyl-1,3-cyclohexa-1,3-dien-5-ol was obtained by microbial oxidation of acetophenone; complexation by $Fe_2(CO)_9$ oc-

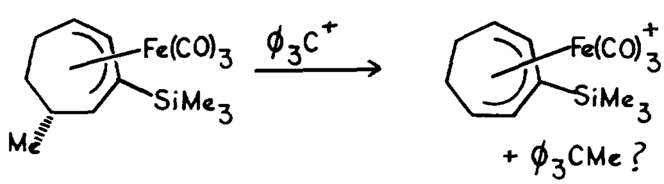


(11)

curred *syn* to the hydroxyl group, providing convenient access to a new family of optically active tricarbonyliron complexes[204].

$(C_6H_7)Fe(CO)_3{}^+$ was used to alkylate the 2-halocycloheptadienone enolate, forming the 2-substituted tropone upon workup[205]. Reaction of the cyclohexadienyl cation with substituted anilines, followed by oxidative cyclization, has been used to synthesize several cytotoxic carbazoles[206].

Hydride abstraction from tricarbonyl[2-(ZMe_3)cyclohepta-1,3-diene]iron [Z = Si, Sn] gave the symmetrical 3-ZMe_3-substituted cycloheptadienyliron cations. The trimethylsilyl-substituted cation reacted as expected with nucleophiles, giving the exo-1 addition product. The trimethylstannyl analog simultaneously underwent partial protodestannylation, giving mixtures of products. A very unusual demethylation reaction (Eq. 12) has also been reported[207]. Photolysis of (cycloheptadiene)-$Fe(CO)_3$ in a cryogenic matrix resulted in loss of CO and hydrogen migration to form (η^5-C_7H_9)$Fe(CO)_2H$[172].



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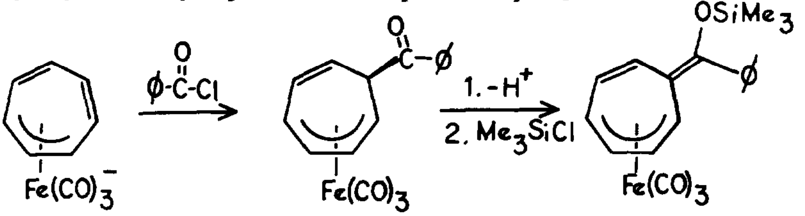
The anion from deprotonation of tricarbonyl(1-4-η-cycloheptatriene)iron reacted readily with electrophiles, including acyl chlorides and BF_3-coordinated aldehydes and ketones, to form 7-exo substituted cycloheptatriene complexes. The acyl products readily rearranged to 5- and 6- substituted isomers. Deprotonation and alkylation of the acyl complexes gave predominantly the 7,7-disubstituted products. "Harder" electrophiles [acyl and silyl chlorides] reacted at oxygen, giving 8-acyloxy or -siloxy heptafulvene complexes [Eq. 13][208].



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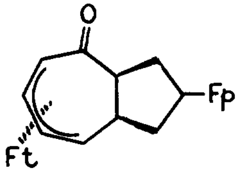
Tricarbonyl(tropone)iron behaved as a dienophile in pressure-induced Diels-Alder reaction with 1-trimethylsiloxy-1,3-butadiene. Two stereoisomeric adducts to the free double bond were obtained in 96% overall yield[209]. Phosphine substitution on the tropone complex, activated by Me_3NO, occurred readily. A crystal structure was reported for the triphenylphosphine substitution product. Recrystallization of the (+)-neomenthyldiphenylphosphine substitution product gave a single diastereomer. The rate of 1,3-shift was increased about 10-fold by the phosphine substitution, but cycloadditions and electrophilic attacks occurred without racemization of the planar chirality[210]. Attack of trimethylsilyl triflate on the tropone complex gave a fluxional mixture of $[C_7H_6(OSiMe_3)]Fe(CO)_3^+$ salts; attack of CH_2=CH-CH_2-Fp and related electrophiles was regiospecific, however, and led to hydroazulenone complexes such as **21**[211]. The homoheptafulvene complex **22** [XRC] and its Z stereoisomer have been prepared from (homotropone)$Fe(CO)_3$[212]. Reaction of optically active tricarbonyl(2-5-η-7-methyltropone)iron with 8-oxoheptafulvene led to formation of the optically active heptafulvalene complex **23**. The *exo-* and *endo*-homotropone complexes likewise gave homoheptafulvalene complexes[213].



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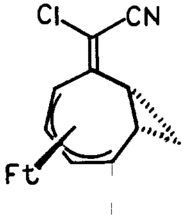

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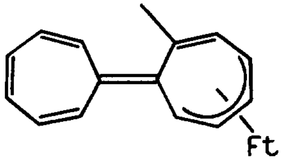

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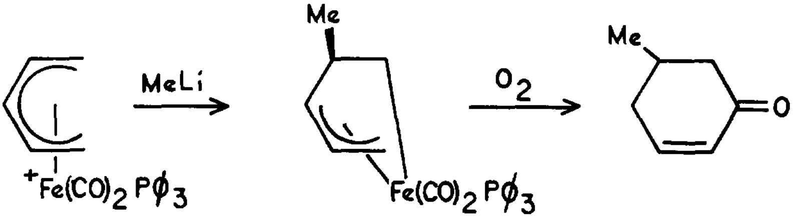
Kinetic study of displacement of 1,5-cyclooctadiene from $(C_8H_{12})Fe(CO)_3$ by triphenylphosphine has indicated the reaction to be first order in complex and zero order in phosphine. A negative entropy of activation led to suggestion of an associative mechanism (?)[214]. Photolysis of $(\eta^4$-$C_8H_8)Fe(CO)_3$ in cryogenic matrices produced both CO and double bond dissociation. The latter led to tub⇌chair rearrangement[172]. The cyclooctatetraene complex $(\eta^4$-COT)$Fe(CO)_2$-$(CNCMe_3)$ reacted with (allyl)$Fe(NO)_2[P(OMe)_3]^+$ to give cationic $[\eta^5$-$C_8H_8(C_3H_5)]Fe(CO)_3^+$ complexes, as a mixture of cyclooctatrienyl and bicyclooctadienyl isomers. Deprotonation gave fluxional allylcyclooctratetraene complexes. Repetition of the reaction sequence gave 1,4- and 1,5- diallylcyclooctatetraene complexes[150].

7. η^5-DIENYL COMPLEXES

7a. Compounds with Open Pentadienyl Ligands

The term "open," as used in this section refers not only to acyclic pentadienyl ligands, but also to cyclohexadienyl and cycloheptadienyl ligands, which do not have a closed cycle of carbon (or hetero) atoms coordinated to iron. Most of the compounds encountered here are cationic $(\eta^5$-dienyl)FeL_3^+ species, whose most important reaction is attack by a nucleophile to give a neutral η^4 product. Accordingly some of these products were also described in the previous sections.

The position of attack of nucleophiles on (η^5-pentadienyl)FeL_3^+ cations is affected by substituents on the pentadienyl ligand and by the nature of the ancillary ligands L. Thus, attack of several nucleophiles on (2-methylpentadienyl)$Fe(CO)_3^+$ occurred predominantly (76-93%) at C5, forming 5-substituted 2-methylpentadiene complexes[169]. Organolithium reagents attacked unsubstituted (pentadienyl)-$Fe(CO)_3^+$ at both C1 and C2, the latter mode of attack giving σ,η^3-pentenediyl products. Replacement of a CO ligand by a triphenylphosphine led to a predominance of C2 attack. The σ,η^3-pentenediyl products formed cyclohexenones on air oxidation (Eq. 14)[170]. The paramagnetic, 16-electron complex (η^5-C_5H_7)Fe-$(PEt_3)_2^+$ [XRC] has been prepared. It readily added CO or RNC ligands to form the 18-electron complex. Consistent with the results on the monophosphine complexes, methyl-lithium attacked C2 of these bis(phosphine) complexes[171]. Attack of the nucleophile $CpMo(CO)_3^-$ on (pentadienyl)$Fe(CO)_3^+$ occurred normally at C1; however the product slowly decomposed to form $[C_5H_7Fe(CO)_3]_2$. With (cyclohexadienyl)$Fe(CO)_3^+$ the dimeric product $[C_6H_7Fe(CO)_3]_2$ was formed directly by one-electron transfer from the molybdenum compound[215].



(14)

The directing effect of a phenyl substituent in forming cyclohexadienyl complexes[201] was illustrated in eq. 11. The phenyl substituent in tricarbonyl(1-phenylcyclohexadienyliron$^+$ directed nucleophiles ($LiCuMe_2$, $NaBH_4$, $NaCHE_2$) so that 85-99% of the reaction occurred at the 5-position[202]. Other related reactions of synthetic interest and utility were described in section 6c.

Reaction of tricarbonyl(η^5-cyclohexadienyl)iron$^+$ with 2-methyl-2-nitrosopropane produced the bis(*tert*-butyl)nitroxyl radical, the intensity of whose ESR signal oscillated with time. Also produced were Ph-N(O·)-CMe_3 and the 3-(*tert*-butylnitroxyl-substituted) tricarbonylcyclohexadienyliron cation[216].

Double addition of carbanions to $(C_6H_6)_2Fe^{2+}$ was facilitated by use of methylene chloride as solvent. Alkyl-lithium and Grignard reagents added to the dication in this solvent at -90° to afford (η^5-$C_6H_6R)_2Fe$, "pseudoferrocenes," in good yields[217]. This result contrasts with previous double additions, in THF, in which both alkyl groups attacked the same ring, giving (arene)(cyclohexadiene)iron products. The crystal structure of bis(η^5-*exo*-6-phenyl-1,3,5-trimethylcyclohexadienyl)iron prepared by this reaction showed a gauche-eclipsed conformation, and variable temperature NMR studies indicated restricted ring rotation[218].

7b. Dicarbonylcyclopentadienyliron Hydride (FpH) and Related Compounds

This section includes results on FpH, Fp·, and Fp⁻ [Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$], and on compounds containing bonds between the Fp group and non-transition elements other than carbon. (Organic derivatives Fp-R are treated in Section 7c.) Derivatives with one or more CO groups replaced by other two-electron ligands or with substituted cyclopentadienyl rings are treated alongside the analogous Fp compounds. Fp-transition metal compounds are treated as bimetallic compounds, in Section 9c.

Despite its reputation as a very labile compound, FpH has been found to be quite stable in the presence of free-radical interceptors such as benzenethiol. It was concluded that the commonly observed decomposition to Fp_2 is the result of a chain process initiated by traces of oxidants. NMR and chemical properties of FpH have been described[219]. Hydrogenation of α-cyclopropylstyrene by FpH was first order in each reactant, and a mechanism involving rate-determining transfer of the first hydrogen to the methylene group, followed by very rapid abstraction of the second hydrogen from another FpH molecule, was proposed. Less than 2% of the product resulted from cyclopropyl ring opening[220].

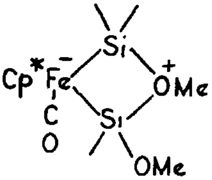
Photolysis of Fp_2 and Fp^*_2 generated primarily the radicals $Fp(^*)\cdot$, as indicated by ESR and spin-trapping results. The iron-centered radicals formed peroxy radicals FpOO· in the presence of oxygen; these gave organic radicals by hydrogen abstraction from solvents. No organic radicals were detected when the photolysis was conducted in carbon tetrachloride. Electron transfer occurred between excited Fp^* and the spin trap, 2-methyl-2-nitrosopropane, generating additional secondary radicals[221]. Photolysis of these dimers in polyvinyl chloride films at room temperature resulted in formation of FpCl by abstraction of chlorine from the polymer[222].

A Fenske-Hall MO study of "two-legged piano stool" structures found, based on a substantial HOMO-LUMO gap, that $CpFe(CO)_2^-$ should be a stable species (as it is), but that CpFe(CO)(NO) and $CpFe(NO)_2^+$ would be reactive due to a smaller energy gap[190].

Indium(I) chloride reacted with Fp_2 in refluxing toluene to form mostly $FpInCl_2$, accompanied by some Fp_2InCl. InI formed only Fp_2InI[223].

Di- and polysilyliron compounds have continued to draw interest, including the synthesis of the indenyl compounds, $(\eta^5\text{-}C_9H_7)Fe(CO)L(SiR_3)$ [L = CO, PPh_3; SiR_3 = $SiMe_3$, Si_2Me_5, $SiMe(SiMe_3)_2$]. The branched trisilyl compounds were obtained by photochemical rearrangement of the linear precursor, $(\eta^5\text{-}C_9H_7)Fe(CO)_2SiMe_2SiMe_2SiMe_3$ in the presence or absence of triphenylphosphine. Crystal structures showed that phosphine substitution led to increased Fe-Si and Si-Si bond lengths, an effect attributed to steric requirements[224]. Photolysis of Fp-Si_2Me_5 having one or two perdeuterio-labelled methyl groups led to complete scrambling of the groups between the two silicon atoms[225]. The crystal structure of $FpSiMe_2SiMe_2Fp$ showed a rather long Si-Si bond (2.39 Å) as compared to that in $MeFe(CO)_2(\eta^5\text{-}C_5H_4\text{-}SiMe_2SiMe_2\text{-}\eta^5\text{-}C_5H_4)Fe(CO)_2Me$ (2.34 Å)[226]. Photolysis of $Fp^*SiMe_2SiMe(OMe)_2$ resulted in formation of **24**, described as a "donor-stabilized bis(silylene)iron compound." The crystal structure showed short Fe-Si bonds (ca. 2.22 Å) and long Si-O bonds (ca. 1.80 Å), consistent with the formal charges shown in the representation of **24** shown here, but taken by the authors as indicating partial double-bond character of the Fe-Si bonds[227].

Lithium reduction of Fp_2GeBr_2 led to formation of $[Fp_2Ge]_n$ oligomers, but in the presence of 2,3-dimethylbutadiene the monomer was intercepted to form the 3,4-dimethylgermol-3-ene heterocycle. Reduction of the 1-bromo-1-Fp-germolene led to coupling, forming **25** [XRC][228]. Displacement of halide from Fp_2GeBr_2 and Fp_2SnCl_2 by sodium azide in acetonitrile formed the bis(azide) products $Fp_2E(N_3)_2$ [E = Ge, Sn] [XRC][229].



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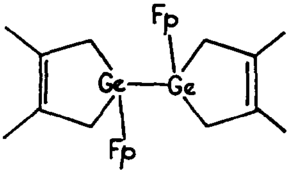

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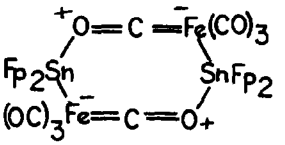

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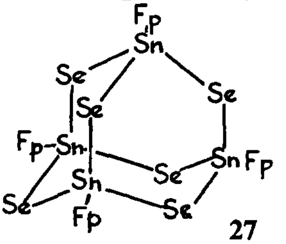
Electrochemical oxidation of $FpSnPh_3$ and Fp_2SnPh_2 in acetonitrile led to cleavage of the Fe-Sn bond, with formation of $Fp(NCMe)^+$ and a solvated tin cation. Reduction of $FpSnPh_3$ produced Fp^- and Ph_6Sn_2; the di-iron compound produced Fp^- and a transient species, characterized by IR, thought to be $FpSnPh_2^-$, which decomposed to $[Ph_2Sn]_n$ oligomers and Fp^- [230]. Fp_2SnCl_2 reacted with disodium tetracarbonylferrate to form a dimer, **26**, of the stannylene complex $Fp_2Sn{=}Fe(CO)_4$ [XRC]. Dissolution in pyridine bifurcated the dimer to form $C_5H_5N^+\text{-}SnFp_2\text{-}Fe(CO)_4^-$ [231]. When Fp_2SnX_2 or $FpSnX_3$ was treated with (bpy)$M(CO)_3(NCMe)$ [M = Mo, W], displacement of a leaving group resulted, forming $FpSnX_2MX(CO)_3(bpy)$[232]. With $Se(SiMe_3)_2$, Fp_2SnCl_2 formed cyclic



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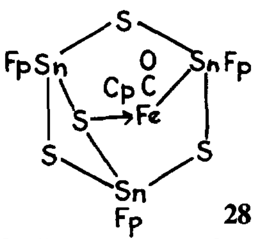

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and polycyclic structures, $[Fp_2SnSe]_2$ and adamantanoid **27** [XRC]. The sulfur compound $S(SiMe_3)_2$ gave a less symmetrical tricyclic cage structure, **28** [XRC]^{233}.

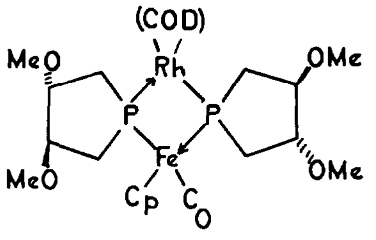
A series of compounds Fp_2SnArX [Ar = Ph, tolyl, chlorophenyl; X = halogen, SPh, SCN, SCNMe, NO_2, ONO_2, N_3] has been compared by partition TLC using liquid paraffin as stationary phase. Increased electron-donating ability of the arene substituents caused the R_f values to increase, as did increasing the electronegativity of X. The results correlated with ultraviolet absorptions of the compounds^{234}. Chemical shift and coupling constant data for a series of lead compounds, including $FpPbR_3$ [R = Me, Et, Ph], Fp_4Pb, and $Fp'PbEt_3$ closely paralleled those of the analogous tin compounds^{235}.

$CpFe(CO)(PPh_3)[N(=O)CMe_3]^+$ was prepared in 75% yield by displacement of THF from $Fp'(THF)^+$ by 2-methyl-2-nitrosobutane. The crystal structure showed a short (1.89 Å) Fe-N bond, and an N-O bond length of 1.23 Å, consistent with strong donor and acceptor roles for the nitrosoalkane, which was not readily displaced by CO, PPh_3, or $CNCMe_3$^{236}.

A crystal structure of the crowded complex $Cp^*(dppe)(NCMe)^+$ PF_6^- has been published^{237}. Photolysis of $(\eta^6\text{-An})Fe[\eta^5\text{-}C_5H_4C(=O)R]^+$ [R = Me, Ph] in the presence of ligands led to displacement of the arene by three ligands, which included acetonitrile, carbon monoxide, trimethyl phosphite, and dppe. Various thermal ligand exchanges in the initial products were also carried out. A crystal structure of $(\eta^5\text{-}C_5H_4COMe)Fe(dppe)(NCMe)^+$ PF_6^- was reported. NMR spectra of the $[\eta^5\text{-4-oxo-4,5,6,7-tetrahydroindenyl}]FeL_3^+$ cations revealed diastereotopic effects in the ligands^{238}. The arene ligands were also readily displaced from the 19-electron complexes AnFeCp, so that it could be used as a catalyst for conversion of $AnFeCp^+$ to $CpFeL_3^+$. Reaction of CpFeAn with stoichiometric amounts of trimethylphosphine gave neutral, 19-electron $CpFe(PMe_3)_3$ in a second-order process. A large, negative activation entropy confirmed an associative mechanism, perhaps occurring through an η^4-arene intermediate. Reduction of the cation $CpFe(PMe_3)_3^+$ by sodium amalgam produced $[CpFe(PMe_3)_2]_2Hg$, whereas use of a sodium mirror gave $CpFe(PMe_3)_2H$. The formation of the 17-electron intermediate $CpFe(PPh_3)_2$ in reaction with triphenylphosphine was indicated by ESR spectroscopy at 10 K^{239}. The sign and magnitude of the P-P coupling constant in $CpFe(PMe_3)_3^+$ have been determined^{240}.

Reaction of the chiral diphosphine ligand "(S)-prolophos," derived from proline, with FpCl gave $CpFe(prolophos)CO^+$ Cl^- as a pair of diastereomers. Precipitation with ammonium hexafluorophosphate and one recrystallization gave a single pure diastereomer. Irradiation in THF generated the reactive $CpFe(prolophos)(THF)^+PF_6^-$ with retention of configuration^{241}. Cationic complexes $CpFe(CO)L_2^+$, with L being the C_2 chiral ligand *trans*-3,4-dimethoxyphospholane, were treated with butyl-lithium and then $[Rh(\eta^4$-1,5-cyclooctadiene$)Cl_2]_2$ to form the bimetallic complex **29**, of interest as a possible enantioselective catalyst[242]. Deprotonation of the methylene group in $CpFe(dppm)CO^+$ gave the ylide complex **30** [L = CO]; under irradiation in the presence of trimethylphosphine, substitution occurred giving **30** [$L = PMe_3$]. The latter underwent C-methylation by methyl triflate to form a mixture of products[243].

The labile diphosphenyl complexes FpP=PAr and Fp^*P=PAr [Ar = 2,4,6-tris(trifluoromethyl)phenyl] were prepared by reaction of $Fp(^*)P(SiMe_3)_2$ with $ArPCl_2$. Not isolable, they were stabilized by formation of $Cr(CO)_5$ adducts. The crystal structure of $Fp^*P[\rightarrow Cr(CO)_5]$=PAr was determined[244]. A similar reaction using $ArAsCl_2$ [Ar = 2,4,6-tri(*tert*-butyl)phenyl] gave, in addition to the arsaphosphenyl complex Fp^*P=AsAr (isolable as the $Cr(CO)_5$ complex), cyclic products $(Fp^*P)_2AsAr$ [XRC], $Fp^*P(AsAr)_2$, and $(Fp^*P)_2(AsAr)_2$ [XRC][245]. Cp^*P=PAr [Ar = 2,4,6-tris(*tert*-butylphenyl)phenyl] gave [2 + 2] cycloaddition reactions with dimethyl maleate and fumarate and fumaronitrile, forming all-*trans*-diphosphetane products; the structure of the dicyano heterocycle **31** was confirmed by a crystal structure[246].



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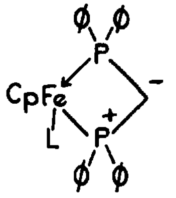

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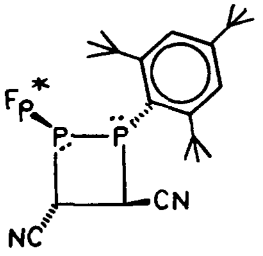

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$Fp_4As^+ Cl^-$ has been prepared by reaction of FpCl and $As(SiMe_3)_3$. Reaction with $NaBPh_4$ in water resulted in formation of $Fp_3As^+ BPh_4^-$ [XRC][247]. Two different iron groups were coordinated to antimony in **10**[113], previously described.

Displacement of acetone from $CpFe(CO)(COMe)(O{=}CMe_2)^{0,+}$ by thioethers at -47° has been followed by square-wave voltammetry. Substitution in the cation was found to occur by an associative ligand-dependent process, and the rate depended on both electronic and steric factors. In the neutral compounds, substitution occurred by reversible predissociation of acetone, giving an overall rate dependent on the steric size of the thioether, but independent of its electronic properties[248]. The THF ligand of $Fp(THF)^+$ was displaced by metal formates L_nMOCHO [L_nM = Fp, $W(CO)_3Cp$, Re(CO)(NO)Cp], giving bimetallic μ-formates $L_nMOCHOFp^+$. Reaction of the μ-formates with iodide depended on M: with W, FpI formed, but with Re, FpOCHO was the product. Reduction with Et_3BH^- formed FpH in all cases[249]. FpO- species were among the products shown by FT-IR to be formed from Fp_2 adsorbed on partially dehydroxylated alumina and silica over the temperature range 30-450°[250].

Spectroscopic studies of the thiocarboxylates FpSC(=O)Ar [Ar = *o*-FC_6H_4, *p*-$C_6H_4NO_2$], $CpFe(CO)(EPh_3)SC(=O)Ar$ [E = P, As, Sb], and (η^5-$Me_3CC_5H_4$)-$Fe(CO)_2SC(=O)Ar$ have suggested that the thiocarboxylate group is a better σ-donor but poorer Π-donor and acceptor than halides or SCN[251]. Decarbonylation of $Fp^*SC(=S)NMe_2$, with chelation of the dithiocarbamate ligand, has been found to occur by a chain mechanism, which could be catalyzed either by oxidation or reduction[252]. The oxidative mechanism had a low coulombic efficiency due to the slow electron transfer from η^1-dithiocarbamate to η^2-cation. The η^1-cation could not be detected by cyclic voltammetry, indicating a very rapid (> 10^7 sec^{-1}) conversion to η^2 with carbonyl loss. Ligand substitutions occurred readily, giving as final products $Cp^*Fe(\eta^2\text{-}S_2CNMe_2)L^+$ [L = PPh_3, THF][253]. A crystal structure of $Fp^*\text{-}SC(=S)NMe_2$ confirmed the monodentate coordination of the dithiocarbamate ligand (Fe-S distance 2.271 Å). The quantum yield for photochelation was about 0.6. Photolysis of $Cp^*Fe(CO)(\eta^2\text{-}S_2CNMe_2)$ in the presence of PPh_3 efficiently produced the expected substitution product $Cp^*Fe(PPh_3)(\eta^2\text{-}S_2CNMe_2)$[254]. Dithiocarboxylate complexes $CpFe(\eta^1\text{-dppm})(S_2CR)$ have been prepared directly by carbon disulfide insertion into the Fe-C bonds of $CpFe(\eta^1\text{-dppm})R$ [R = Me, Ph]. An equilibrium existed in solution between η^2- and η^3- (dithiaallyl) coordination isomers of the dithiocarboxylate ligands. The dithioacetate was predominantly (95%) η^3, whereas the dithiobenzoate was predominantly (70%) η^2 [255]. η^3-Coordination has not been observed for thiocarbamates.

Reaction of $CpFe(dppe)(O{=}CMe_2)^+$ [formed *in situ* by photolysis of the monocarbonyl in acetone solution] with thiirane oxide led to sulfur monoxide transfer, forming $CpFe(dppe)(S{=}O)^+$. $Cp^*Fe(PMe_3)_2(S{=}O)^+$ formed similarly. The less sterically hindered CpFe(dmpe) system gave a binuclear species, $[CpFe(dmpe)]_2S{=}O^{2+}$, however[256]. Cationic mononuclear SO_2 complexes of the Fp, Fp', Fp^*, CpFe(dppe), $CpFe(PMe_3)_2$, and related systems were prepared similarly, by SO_2 displacement of acetone[257].

The thiolate $(MeO)_3SiCH_2CH_2CH_2S^-$ displaced bromide from FpBr or Fp^*Br to form the expected Fp- or Fp^*-SR products. Electrochemical oxidation was followed by loss of RS, giving $Fp(^*)L^+$ [L = PPh_3 or THF][258]. ^{13}C CP-MAS spectra of $FpEMe_2^+$ BF_4^- [E = S, Se, Te] have been obtained and compared[259].

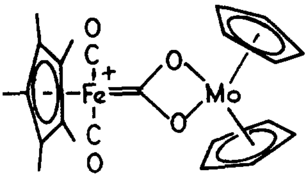
UV Irradiation of FpCl in cryogenic matrices or in polyvinyl chloride films at 12 K formed CpFe(CO)Cl, as the only IR-detectible species[260]. The substituted FpCl analog, chloro(η^5-1,3-di-*tert*-butylcyclopentadienyl)dicarbonyliron, was obtained directly, in 30-40% yield, by reaction of Li^+ $R_2C_5H_3^-$ with $FeCl_2{\cdot}1.5$ THF; also produced in this reaction were the substituted ferrocene and Fp_2

compounds[261]. The highly hindered substituted cyclopentadienides $C_5Ph_4Ar^-$ [Ar = *p*-tolyl, *p*-ethylphenyl, and *p-tert*-butylphenyl] were similarly converted to the FpBr derivatives[262].

Alkyl and aryl iodides were coordinated to iron, forming iodonium species $Fp\text{-}I\text{-}R^+$ [R = *p*-tolyl, Et, Pr, $CHMe_2$, cyclohexyl], when FpI was treated with $AgPF_6$ in the presence of RI in methylene chloride. $Fp\text{-}I\text{-}Me^+$ was formed from Fp_2, Ag^+ and MeI. The coordinated RI species functioned as selective alkylating agents, favoring, for example, C-alkylation of enamines over N-alkylation. Nucleophilic solvents displaced RI from coordination to iron[263]. The crystal structure of CpFe(dppe)I has been reported[264].

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

A [2 + 2] cycloaddition reaction between the cation $Cp'Fe(CO)_3^+$ and the oxo compound $Cp_2Mo{=}O$ formed **32** in 95% yield[265]. A detailed synthesis of $CpFe(CO)_2(CS)^+$ [$FpCS^+$] from Fp_2 via $FpCS_2Me$ has been published[266]. Reactions of nucleophiles with $FpCS^+$ and Fp^*CS^+ occurred in most cases at the thiocarbonyl ligand to form thioacyl products. Azide ion gave $Fp^*N{=}C{=}S$. Methoxide reacted initially at a carbonyl ligand, but migrated over time to the thiocarbonyl. Reduction with sodium hydride gave the dimeric species $Cp^*{}_2Fe_2(CO)_2(\mu\text{-}CS)_2$[267]. The novel η^5 species **33** [XRC], which may be compared with (η^5-indenyl)$Fe(CO)_3^+$ or (η^4-isobenzofulvene)$Fe(CO)_3$, **17**[161], was prepared by complexation of the free ligand with $(C_8H_{14})_2Fe(CO)_3$[268].



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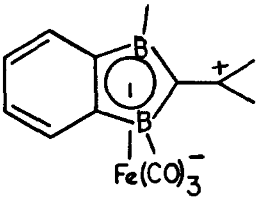


33

FpCN was included in two theoretical studies of chemical shifts of organometallic compounds. A Fenske-Hall approach indicated that the paramagnetic term of the nuclear shielding equation was dominant, in that this term alone gave excellent correlation with ^{13}C chemical shifts of several compounds having a wide range of shifts[269]. An INDO perturbation method was used to calculate ^{13}C, ^{15}N, and ^{17}O chemical shifts; the diamagnetic shielding terms correlated well with the calculated net atomic charges[270].

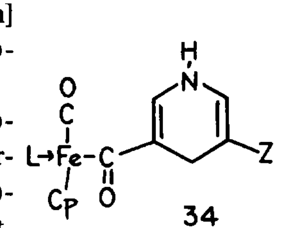
The Lewis acid $Re(CO)_5^+$ added to the thioacyl groups of $FpC({=}S)SMe$ and $FpC({=}S)SFp$ to form isolable $FpC[SRe(CO)_5](SMe)^+$ and $FpC[SRe(CO)_5](SFp)^+$ [XRC][77]. Similar reactions of Group 11 and 12 metal compounds with the cyclic thioacyl Cp(OC)FeC(=S)SC(Fp)S have been studied; the structure of the mercuric bromide adduct was shown by X-ray crystallography to be a dimer[271].

Crystal structures of CpFe(CO)(PPh_3)COMe [Fp'COMe] and Cp'Fe(CO)-(PPh_3)COMe have been published[272]. Fe-P bond lengths for a series of compounds CpFe(CO)(PR_3)COMe have been found to be nearly constant [2.195 ± .015 Å]; however, Fe-P bonds involving phosphites were significantly shorter, as previously known. Steric thresholds dependent on the size of the group R in PR_3 have been detected in rate profiles of five reactions[273]. Conformational analysis of acetyl and formyl ligands has indicated that steric interactions play a dominant role in determining the conformation of the acetyl ligand, but dipolar and electrostatic forces control the formyl conformation[274]. A review of the conformations of Fp' derivatives has appeared[9].

Related to questions of conformation is the chiral recognition observed in reactions of chiral organoiron compounds. The most widely studied series is that employing CpFe(CO)PPh_3 [Fp'] as a chiral auxiliary. Reactions of enolates Fp'$COCH_2^-$ have continued to receive attention. Reaction of the lithium enolate from (*S*)-Fp'$COCH_3$ with racemic $CH_3CHBrCO_2CMe_3$ showed a 40:1 preference for reaction with the (*R*)-enantiomer[275]. A 30:1 stereoselectivity was observed in reaction of the lithium enolate from Fp'$COCH_2OCH_2Ph$ with $CH_3CHBrPh$[276]. Reaction of the aluminum enolate from (*S*)-Fp'$COCH_2CH_3$ with optically pure styrene oxide or propylene oxide, followed by oxidative decomposition, produced optically pure butyrolactones. The (*S*)-aluminum enolate reacted preferentially (100:1) with (*R*)-styrene oxide, so that a product of high stereopurity could be obtained even using racemic styrene oxide[277]. Aldol reaction of the titanium enolate Fp'C(=CH_2)$OTiCp_2Cl$ with benzaldehyde produced Fp'$COCH_2CH(Ph)OTiCp_2Cl$, which was isolated and structurally characterized. Removal of chloride from titanium resulted in formation of a titanium chelate [XRC], which provided a model of the transition state proposed for the aldol reaction[278].

Chiral recognition in additions to the double bond in Fp'COCH=CHR has also been the subject of study. Michael addition of Li^+ $ArCH_2NCHMePh^-$ [Ar = 3,4-dimethoxyphenyl] to Fp'COCH=CHMe proceeded with a 15:1 rate preference for R + R as opposed to S + R addition. Combination of racemic reactants gave a 94% yield of RRR(SSS) racemic product[279]. Treatment of substituted FpCO-CR=CR_2 [R's = H, Me in several combinations] with O-alkylating agents, then with allyltributylstannane resulted in Michael addition of allyl anion. CH_2=CH-$CH_2CR_2CHRCOFp$ were isolated after treatment with NaI in acetone[280]. Activation of the acrylyliron starting material by Lewis acids rather than by alkylation led predominantly to [3 + 2] cycloaddition rather than allylation. The cycloadditions showed high stereoselectivity, rationalized in terms of a synclinal orientation in the allylstannane-acyliron complex[281].

NADH mimics incorporating a Fp' group as a chiral auxiliary on a dihydropyridine have been investigated by determining the enantiomeric excess in the ethyl mandelate [$PhCH(OH)CO_2Et$] product obtained by reducing ethyl benzoylformate. Using **34** [L = PPh_2O-*l*-menthyl; Z = H], a 52% e.e. and a 71% yield were obtained[282]. Using **34** [L = PPh_3; Z = (*R*)-CONHCHMePh] gave 89% e.e.[283]. Using **34** [L = PPh_3; Z = (*R*)-$CONHCH(CHMe_2)CH_2OH$] gave 98% e.e.[284].



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Reaction of the lithium enolate from (*S*)-$Fp'COCH_3$ with chlorodiphenylphosphine at low temperature led to formation of the new chiral ligand (*S*)-$Fp'COCH_2PPh_2$. It was used to form η^1 and O,P-chelating η^2 complexes with palladium compounds[285]. The chiral complex $CpFe(CO)(COMe)(Ph_2POH)$ reacted with $[Rh(C_8H_{12})_2Cl]_2$ to form bidentate complexes with the $Rh(C_8H_{12})$ unit coordinated to the acyl and hydroxyl oxygens [XRC]. Use of this chiral bimetallic complex in hydrogenation of *Z*-α-*N*-acetamidocinnamic acid gave significant asymmetric induction[286].

Synthetic procedures for preparation of FpCOMe, Fp'COMe, and the μ-acyl species Fp(')-C(Me)=O-Fp^+ have been described in detail[287]. The chemistry of the μ-ketene species $FpCH_2COFp$ have been studied, the compounds serving as models for surface-bound ketene species. Electrophiles underwent ready attack by the acyl oxygen, giving several examples of trimetallic species $FpCH_2$-$C(OML_n)Fp^+$. Reaction of $FpCH_2COFp$ with bromine in methanol led to methyl bromoacetate (87%) and a little dimethyl malonate (5%)[288].

Reaction of FpMe with chiral diphosphines, (+)-glyphos and (-)-diop, formed the acyl complexes $R^*PPh_2FeCp(CO)(COMe)$ as pairs of diastereomers differing in the iron configuration. The diastereomers were separable by column chromatography. At high temperatures, epimerization of the iron configuration occurred in solution, along with reversion to FpMe and free diphosphine[289].

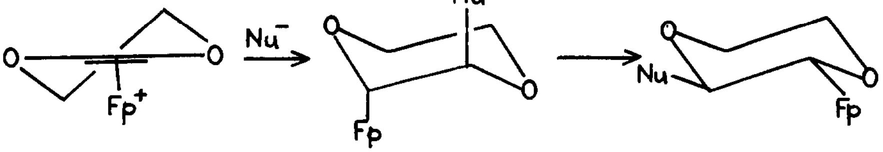
A series of Fp analogs containing the pentaphenylcyclopentadienyl ligand has been prepared. Potassium dicarbonyl(η^5-pentaphenylcyclopentadienyl)ferrate [K^+ $Fp^{\#-}$], prepared by reaction of $Fp^{\#}Br$ with potassium under ultrasonication, gave $Fp^{\#}Et$ in 80% yield upon reaction with EtI. Despite the steric hindrance, this ethyl compound reacted normally with Ph_3C^+ to form the η^2-ethene complex[290]. Cp^*FeL_2Cl [L = PMe_3, dmpe] were prepared by reaction of $Fe(acac)_2$ with $LiCp^*$ in the presence of L, followed by treatment of the intermediate $Cp^*FeL(acac)$ with $ClSiMe_3$. Reaction of $Cp^*Fe(PMe_3)(acac)$ with Grignard reagents in the presence of PMe_3 gave alkyl products $Cp^*Fe(PMe_3)_2R$ [R = Me, Et]; in the absence of the PMe_3, ethylmagnesium bromide formed $Cp^*Fe(PMe_3)(C_2H_4)H$. With *tert*-butyl, allyl and benzyl Grignard reagents, $Cp^*Fe(PMe_3)_2X$ formed instead of the alkyls. $Cp^*Fe(PMe_3)_2CH_2Ph$ and $Cp^*Fe(PMe_3)(\eta^3$-$C_3H_5)$ resulted from reaction of the corresponding Grignard reagents with $Cp^*Fe(PMe_3)_2X$[291].

A number of bromoalkyl complexes $Fp(CH_2)_nBr$ [n = 6-10] and $Fp^*(CH_2)_m$ [m = 3-5] have been prepared and then converted to iodoalkyl complexes by reaction with sodium iodide[292]. The latter were in turn converted to dimetallic compounds by displacement reactions with transition metal nucleophiles, $CpM(CO)_3^-$ [M = Mo, W], $CpRu(CO)_2^-$, and $Re(CO)_5^-$. $Fp^*(CH_2)_3Fp$ was also prepared[293].

A dimetallic compound also resulted when $FpCH_2CH{=}CH_2$ and $CpMo(CO)(NO)(\eta^3\text{-}C_3H_5)$ reacted to form two diastereomers of $Fp(\mu,\eta^2,\eta^2$-1,5-hexadiene)-$Mo(CO)(NO)Cp^+$ [294]. Cycloaddition reactions between $FpCH_2CH{=}CH_2$ and its propargyl and allenyl analogs and tricarbonyl(η^5-tropylium)iron cations have been used to synthesize the hydroazulene skeleton, for example in **21**[211].

The cyclopentadienyl ring of $FpCH_2Ph$ was deprotonated by butyl-lithium and iodinated using C_3F_7I, to form $(\eta^5\text{-}C_5H_4I)Fe(CO)_2CH_2Ph$ in 71% yield[295]. Palladium-catalyzed coupling of the iodocyclopentadienyl ligand of $(\eta^5\text{-}C_5H_4I)Fe(CO)_2Me$ with ethynyltrimethylstannane gave the (ethynylcyclopentadienyl) product. Stannylation followed by coupling to another (iodocyclopentadienyl)metal compound resulted in formation of a series of heterobimetallic compounds[296]. Synthesis of a related series of bimetallic compounds was achieved from $(\eta^5\text{-}C_5H_4C_2H)Fe(CO)_2Me$ by conversion to the iodoacetylene using base and N-iodosuccinimide, diimide reduction to the iodovinyl compound $(\eta^5\text{-}C_5H_4CH{=}CHI)Fe(CO)_2Me$, and palladium-catalyzed coupling with, for example, $(C_5H_4C_2SnMe_3)Fe(CO)_2Me$ in DMF. This sequence yielded 1,3-butenyne-1,4-diyl-bridged bis[(cyclopentadienyl)metal] species[297]. Also related to these compounds is the previously described tetramethyldisilanediyl-bridged species $[MeFe(CO)_2(C_5H_4SiMe_2\text{-})]_2$[226].

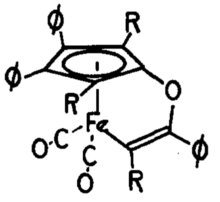
$CpFe(CO)LR$ [L = CO, (*S*)-$Ph_2PNMeCHMePh$; R = Me, C(=O)Me] and its η^5-indenyl analog have been used to catalyze hydrosilylation of acetophenone with diphenylsilane. Only racemic $PhCH(OSiHPh_2)Me$ was formed. The indenyl compounds were more effective catalysts than the cyclopentadienyl, and the methyl compounds better than the acetyl[298]. The single adducts which resulted from addition of nucleophiles [phthalimide, N-methyltoluenesulfonamide, $PhCH_2SH$] to a dioxin-Fp^+ complex (Eq. 15) underwent dyotropic rearrangements, inverting both asymmetric centers, at room temperature in solution. Crystal structures of both phthalimide adducts were obtained[299].



(15)

NaFp displaced halide from $(\eta^6\text{-}p\text{-}C_6H_4FX)Cr(CO)_3$ [X = H, Me, Cl, OMe] to produce chromium-coordinated aryl-Fp products. These bimetallic products gave stable radical-cations on electrochemical oxidation[300].

Reaction of PhC≡CR [R = $P_3N_3F_5$] with nonacarbonyldiiron produced "a plethora of products," including cyclobutadiene, cyclopentadienone, and ferrole complexes, and the vinylic product **35**[191]. The mechanism of the thermal reaction of diphenylacetylene with Fp-Ph or FpCOPh in refluxing decalin, to form 2,3-diphenyl-1H-inden-1-one, has been investigated by deuterium labeling. A mechanism involving coordination of diphenylacetylene, migration of phenyl to form a triphenylvinyl ligand, migration of the latter to CO, and reductive elimination of a $CpFeL_n$ species, was proposed. Phenyl and diphenylferrocenes were formed as byproducts[301]. The analogous reaction of (2-thienoyl)Fe$(CO)_2$Cp with diarylacetylenes has been reinvestigated, and the mechanism was found to be consistent with that resulting from the deuterium labeling studies[302]. Reaction of *ortho*-fluorophenyllithium with FpI gave the aryliron product **36**, characterized by means of a crystal structure of its tricarbonylchromium complex[303].



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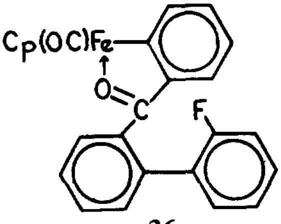

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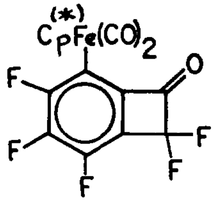
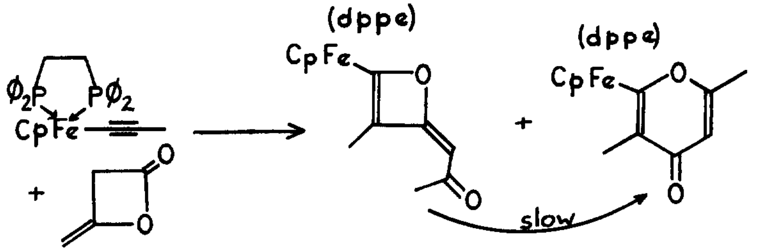


37

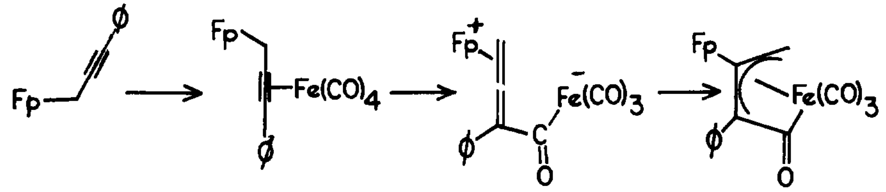
NaFp displaced vinylic chloride from 3-chloro-2-cyclohexenones and 3-chloroindenones to form vinylic-Fp compounds. FpC≡CCO_2Et was also prepared[304]. Likewise, Fp^- and Fp^{*-} displaced a vinylic fluoride from octafluorocyclooctatetraene to produce $C_8F_7Fp(^*)$ [XRC]. The monocyclic products interconverted with the heptafluorobicyclo[4.2.0]octatrienyl-Fp isomers, and chromatography of $C_8F_7Fp(^*)$ produced the perfluorobenzocyclobutenone **37**. Displacement of CO by triphenylphosphine gave pairs of heptafluorocyclooctatetraenyl-Fp' diastereomers, which did not interconvert at room temperature, indicating very slow ring inversion. Reaction of C_8F_7Fp with additional Fp^- led to 1,5-disubstituted $C_8F_6Fp_2$ [XRC][305].

Reaction of Me_3Si-C≡C-C≡CLi with FpCl, followed by desilylation with tetrabutylammonium fluoride, gave butadiynyl-Fp. Deprotonation and reaction with FpCl and other transition metal halides gave bimetallic species Fp-C≡C-C≡C-ML_n, in which the two metal centers showed significant interactions[306]. Several cycloaddition reactions of alkynyl-Fp compounds and phosphine-substituted analogs with ketenes and other reactive alkenes have been investigated. An example is shown in Eq. 16[307]. The triple bond of Fp-C≡C-R [R = Me, Ph, *tert*-butyl] formed



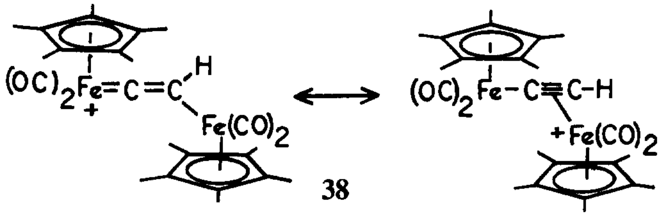
(16)

hexacarbonyldicobalt complexes, which reacted with oxygen to form trimetallic clusters[308]. Reaction of $FpCH_2C{\equiv}CPh$ with $Fe_2(CO)_9$ resulted not just in coordination of the triple bond, but also to rearrangement, as in Eq. 17[309].



(17)

Ethynyl-bridged complexes, $CpW(CO)(\eta^2\text{-}C_2Ph_2)(\eta^2\text{-}HC_2FeL_2Cp)^+$ [L = PMe_3, $P(OMe)_3$] resulted from reaction of $CpFeL_2C{\equiv}CH$ and $CpW(CO)(\eta^2\text{-}C_2Ph_2)Cl$ in the presence of $TlBF_4$. Deprotonation gave ethynediyl-bridged $CpW(\eta^2\text{-}C_2Ph_2)(CO)C{\equiv}CFeL_2Cp$[310]. A related series of diiron μ-acetylide complexes $Fp_2(CCPh)^+$ having Fp and Fp* groups [XRC] were made by complexation of Fp(*)CCPh [XRC]. A hybrid structure, **38**, was indicated by the crystal structure of $Fp^*_2(CCH)^+$. A fluxional process interchanged the two iron groups, for which process an intermediate vinyl cation $Fp(^*)_2C{=}CR^+$ [R = H, Ph] was proposed. Deprotonation of **38** gave the μ-ethynediyl complex, $Fp^*C{\equiv}CFp^*$ [311].



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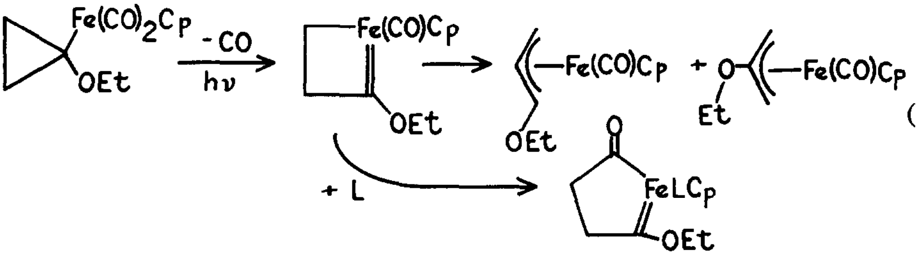
38 is an example of a carbenoid complex. Simpler methylene complexes $Fp^*{=}CH_2^+$ and $Cp^*Fe(CO)(PPh_3){=}CH_2^+$ have been observed by NMR at -80°, after being formed from $Cp^*Fe(CO)LCH_2OMe$ by reaction with HBF_4 or Me_3SiOTf. The triphenylphosphine-substituted complex was stable in solution up to -10°. The methylene protons, nonequivalent at -80°, coalesced at -45°; a methylene rotation barrier of 46 kJ/mol was indicated. Reaction with styrene gave phenylcyclopropane. Thermal decomposition of $Fp^*{=}CH_2^+$ formed $FpCO^+$ and $Fp(\eta^2\text{-}C_2H_4)^+$, whereas trapping with triphenylphosphine gave the expected adduct,

$Fp^*CH_2PPh_3^+$ [XRC][312]. Neutral carbene complexes $CpFe(CO)(SnPh_3)$-$=C(OEt)Ph$ were prepared by consecutive reaction of $FpSnPh_3$ with phenyl-lithium and triethyloxonium fluoborate. The ethoxy group was readily replaced by amines, and the stannyl ligand by iodine. A crystal structure of $CpFeI(CO)=C(OEt)Ph$ showed the carbene ligand coplanar with the iron carbonyl[313]. A cyclic analog, $CpFeI(CO)=\overline{C(OCH_2CH_2C}H_2)$, resulted from reaction of $FpCH_2CH_2CH_2Br$ with NaI in THF[314]; curiously, the identical reaction carried out in acetone solution apparently produced only S_N2 displacement of bromide[292]. The crystal structure of the cyclic carbene complex showed two different conformers within the unit cell, which differed by a 160° rotation of the tetrahydrofuranylidene ligand about the Fe=C bond.

A common route to carbene complexes is by reaction of an acyl complex with an electrophile. Previously cited carbene complexes generated by this route have included $FpCH_2C(OR)=Fp^+$ and $FpCH_2C(OML_n)=Fp^+$ [288], $Fp^*=C(SMe)_2$ and $Fp^*=C(OMe)SMe^+$ [267], $Fp=C(Me)OFp^+$ [287], $Fp=C(SEl)SRe(CO)_5^+$ [El = Me, Fp][77], and the species 32[265].

Reactions of the stabilized alkylidene complex $Fp=CHAr^+$ [Ar = 4-C_6H_4OMe] with nitrosobenzenes and azobenzene have been investigated. The product of reaction with nitrosobenzene was $FpON(Ph)=CHAr^+$ [XRC]; with azobenzene, the analogous $FpN(Ph)N(Ph)=CHAr^+$ formed. Exposure of acetone solutions of these products to light resulted in formation of PhN=CHAr[315].

The alkylidene complex $Fp^*=CHCMe_2Ar$ [Ar = η^6-$C_6H_5FeCp^+$], observable by NMR at -80°, underwent intramolecular C-H insertion at -40° to form the cyclopropane $ArCMe(CH_2)_2$. Some ArC(Me)=CHMe also formed[316]. Rearrangement of a series of (1-methylcycloalkyl)methylene complexes, $(CH_2)_nCMe$-$CH=Fp^+$ [n = 2-5], produced by protonation of precursor ethers, has been studied as a function of ring size. The cyclopropyl, cyclobutyl, and cyclopentyl compounds [n = 2-4] underwent ring expansion to form 1-methylcycloalkenes, whereas the cyclohexyl compound formed ethylidenecyclohexane, a result interpreted in terms of differences in strain energies between the alkylidene complex and the rearranged carbocation[317]. The cyclopropyl complex $FpC(OEt)(CH_2)_2$ lost CO upon photolysis, and the resulting 16-electron intermediate restored itself to 18-electron status by ring expansion ("α-elimination") to form the ferracyclobutene. In the absence of additional ligands this opened to an allyl complex; in their presence, it expanded to a ferracyclopentenone (Eq. 18). Similar studies were also carried out on the α-(phenylthio)-, β-fluoro-, and β-methylcyclopropyl Fp complexes[318]. The (1-bicyclo[2.2.1]hept-2-enyl)$CH=Fp^+$ cation rearranged to 2-bicyclo[3.2.1]oct-3-enylidene$=Fp^+$, which underwent attack by nucleophiles selectively at the *exo*-4 position[319].



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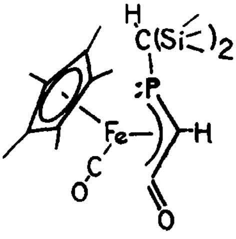
7d. Cyclopentadienyliron Derivatives of η^2- to η^5-Ligands

Detailed procedures for synthesis of $Fp(\eta^2\text{-}CH_2{=}CMe_2)^+ BF_4^-$, from Fp_2 via Fp^- and $FpCH_2C(Me){=}CH_2$, have been made available[320]. Displacement of water from $Fp^*OH_2^+$ by alkenes and alkynes has been used to prepare a number of η^2 Fp^* complexes[321]. A kinetic study of the addition of methoxide to the ethene ligand of $Fp(C_2H_4)^+$ has been carried out. The reaction was found to be first order each in methoxide and in complex, and was characterized by a $\Delta H^{\ddagger}$ of 52(1) kJ/mol and $\Delta S^{\ddagger}$ of -15(5) J/K-mol. Nucleophilicity toward this substrate decreased in the order $RNH_2 > MeO^- > Ar_3P >$ pyridine[332]. Generation of $CpFe(CO)(\eta^3\text{-allyl})$ species from a ferretene[318] has been illustrated in Eq. 18. An η^3-phosphaallyl complex, **39**, was synthesized by reaction of $Fp^*P{=}C(SiMe_3)_2$ with $Me_2S(O){=}CH_2$. Coordination of the phosphorus atom of **39** to a $Cr(CO)_5$ group led to rearrangement, yielding $Fp^*CH{=}P[Cr(CO)_5]CH(SiMe_3)_2$ [XRC][323]. Crystal structures of both the *syn* and *anti* isomers of **39** were determined[324]. η^3-1,3-Dithia-allyl complexes $CpFe(PPh_2R)(\eta^3\text{-SCMeS})$ have been found in equilibrium with the more common η^2-S,S'-dithiocarboxylate complexes, and in one case characterized by a crystal structure[255].



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Reaction of methyl sorbate with $Fp^*(THF)^+$ under photochemical conditions led to formation of $Cp^*Fe(CO)[\eta^4\text{-}MeCH{=}CH\text{-}CH{=}CHE]^+$ [XRC]. Nucleophiles [BH_4^- and MeO^-] attacked the diene ligand at the 5-carbon[325].

Azaferrocene has been synthesized in 61% overall yield by photoreaction of sodium pyrrolide with FpI and decarbonylation of the intermediate $Fp\text{-}NC_4H_4$. N-methylation of azaferrocene by methyl iodide occurred readily[327]. Azaferrocene also coordinated readily to both axial sites of a cobalt(II) porphyrin, in contrast to pyridine[328], and to alkylcobaloximes[329]. Irradiation of a $(\eta^1\text{-azaferrocene})\text{-}Co(Por)(\eta^1\text{-}O_2)$ with visible light at 200 K led to ejection of triplet oxygen, although the pyridine-coordinated analog was photostable[330].

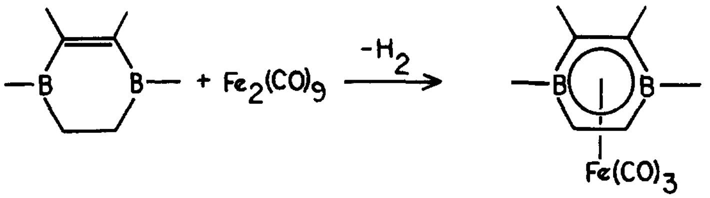
Bis(pyrrolyl)iron compounds (1,1'-diazaferrocenes) were prepared by reaction of pyrrole and methylated pyrroles with $FeCl_2$, followed by hydrolysis[331]. Electrochemical oxidation and reduction of diazaferrocenes in acetonitrile have been studied[332].

Displacement of *p*-xylene from $CpFe(\eta^6\text{-}C_6H_4Me_2)^+$ by 4,5-diphenyl-1,3-diphospholide anion formed 4,5-diphenyl-1,3-diphosphaferrocene [XRC].[333] Laser desorption/Fourier transform mass spectrometry has been used to study the pentaphosphaferrocene, Cp^*Fe(*cyclo*-P_5)[334]. Cothermolysis of Fp^*_2 with yellow arsenic, As_4, produced the homologous pentaarsaferrocene, Cp^*Fe(*cyclo*-As_5). Reaction with $CpFe(C_6H_6)^+$ under irradiation led to a stacking reaction, forming the 30 valence-electron triple decker, $Cp^*Fe(As_5)FeCp^+$ [XRC][335]. Theoretical calculations on decaphosphaferrocene, Fe(*cyclo*-P_5)$_2$, are not encouraging with respect to its preparation: η^1 coordination of the P_5 rings was calculated to be energetically preferable to η^5 [336]. Extended Hückel calculations have been applied to three- and four-decker complexes, some involving *cyclo*-P_5 and -As_5 ligands and also *cyclo*-$C_3B_2H_5$ ligands[337]. Electrochemical properties of multidecker compounds such as $CpFe(C_3B_2R_5)MCp$ have been investigated by use of cyclic voltammetry[338].

The Raman spectrum of the dicarbollide $Fe(\eta^5\text{-}1,2\text{-}C_2B_9H_{11})_2$ has been measured and compared with other metal dicarbollides[339]. The vibrational spectra of metal dicarbollides, including the iron compound, have been analyzed using a rigid pseudoatom model for the ligands[340].

The crystal structure of (η^5-1,3,5-trimethyl-6-*exo*-phenylcyclohexadienyl)-(cyclopentadienyl)iron, synthesized by addition of phenyl-lithium to the (η^6-mesitylene) cation complex, showed similar iron-ring distances for the two rings[341]. The carbanion derived from chloromethyl phenyl sulfone attacked $CpFe(C_6H_5X)^+$ [X = Cl, Br, CN, NO_2] at the 2-position, affording isolable adducts. These did not undergo base-induced elimination, however[342]. The properties of CpFe(2-6-η^5-cyclohexadienonyl) have been investigated by NMR methods. Broad peaks were observed for the cyclohexadienonyl protons in aprotic solvents, but addition of a protic component produced sharpened peaks with the expected couplings. Chemical shifts were also dependent on concentration of the protic cosolvent (D_2O) in a manner consistent with a 1:1 complex between carbonyl group and water. The carbonyl group did not manifest typical ketone reactivity. Equilibration between the η^5-cyclohexadienonyl and an η^6-phenoxide complex was suggested[343]. The structure of the complex obtained upon two-electron reduction of $(Cp^*Fe)_2(\mu\text{-}C_6H_5\text{-}C_6H_5)^{2+}$, which was stable at 20° in contrast to the Cp analog which decomposed above -50°, was shown by NMR and Mössbauer spectroscopy, to be (μ-η^5,η^5-bicyclohexadienylidene)$(FeCp^*)_2$. The mixed-valence 37-electron monocation, made by comproportionation of dication and neutral, was also investigated by ESR and Mössbauer spectroscopy, which indicated an averaged valence, delocalized structure[344].

A 1,4-diborine complex has been prepared (Eq. 19) by reaction of a diboracyclohexene with $Fe_2(CO)_9$. Dehydrogenation also accompanied the reaction of the diboracyclohexene with $Fe(\eta^6\text{-}PhMe)_2$, which formed $(\eta^6\text{-}B_2C_4Me_4H_2)Fe(\eta^6\text{-}PhMe)$, and with Fp_2, which formed the triple-decker complex $CpFe(B_2C_4Me_4H_2)FeCp$[345]. A benzodiborine-$Fe(CO)_3$ complex resulted (69% yield) from reaction of 2,3-diethyl-1,4-dimethyl-1,4-dihydro-1,4-diboranaphthalene with "Grevels' reagent" in hexane. The crystal structure showed unsymmetrical coordination of the iron relative to the heterocyclic ring, with Fe-B distances of about 2.30 Å, and Fe-C distances of 2.19 Å to C2 and 2.32 Å to the benzo carbons[268].



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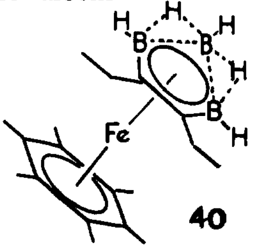
Deprotonation and alkylation of the metallacarborane **40** resulted in introduction of alkyl groups [Me, Et, $CH_2C_6H_4Me$] onto the middle borane (B5). Further cycles of deprotonation/alkylation led to the 4,5-dimethyl and then the 4,5,6-trimethyl derivatives[346]. Use of bis(haloalkyl)arenes with **40** gave xylidene-bridged dimetallic species, $[(C_6Me_6)Fe(Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2\text{-}C_6H_4$. Reaction of these dimetallic species with $(\eta^6\text{-}cyclooctatriene)Fe(Et_2C_2B_4)$ resulted in complexation of the phenylene ring, giving a trimetallic species[347]. Both the C_8H_{10} ligand and the iron were displaced from the aforementioned cyclooctatriene complex by carborane anions, to form higher condensed carboranes, upon thermal reaction at 150° [348]. Photolysis of $(\eta^5\text{-}C_2B_9H_{11})Fe(CO)_3$ in benzene led to replacement of the three carbonyl ligands by a η^6-benzene ligand [XRC][349].



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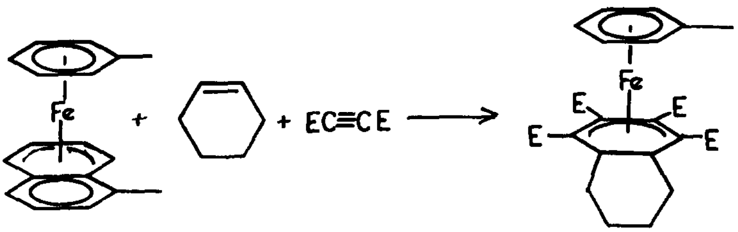
The use of reactive $(\eta^4\text{-}arene)Fe(\eta^6\text{-}arene)$ complexes, obtained by iron atom-arene cocondensation reactions, in promoting low-temperature cycloaddition reactions, e.g. Eq 20, has been reviewed[7].

Fenske-Hall MO calculations have been used to assess the stability of possible "two-legged piano stool" complexes, many of which appear to be as unstable as the physical object they are named for. Cited as a stable example, however, based on a calculated wide HOMO-LUMO gap, was $(\eta^6\text{-}benzene)Fe(CO)_2$[190]. Curious-



(20)

ly, this substance has not been reported, to this reviewer's knowledge.

Reaction of bromopentaphenylcyclopentadiene with zinc dust and iron pentacarbonyl gave, as expected, $(C_5Ph_5)_2Fe$; however, the product formed was not decaphenylferrocene, but rather a zwitterionic coordination isomer, $(\eta^5\text{-}C_5Ph_5)Fe^+(\eta^6\text{-}C_6H_5)\text{-}C_5Ph_4^-$ [350]. Coordination of 2,3-dimethylindole with a $CpFe^+$ group resulted in η^6 attachment to the six-membered ring, which did not change on deprotonation or N-complexation with borane[351]. A crystal structure of $CpFe(\eta^6\text{-thianthrene})^+ PF_6^-$ showed two types of cations, one with the $CpFe^+$ group *exo* and one *endo* with respect to the folded thianthrene ligand[352]. The salt $CpFe(\eta^6\text{-}C_6H_6)^+ PF_6^-$ has been found to form inclusion compounds with cyclodextrins, and the crystal structure of the 1:2 compound with α-cyclodextrin was determined. The cation was encapsulated in the cavity formed by two cyclodextrin units and stabilized by hydrogen bonding between the two units[353].

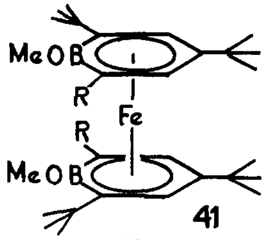
Substituent effects in the Mössbauer spectra of $CpFeAn^+$ compounds have been determined and compared to those observed in ferrocenes and An_2Fe^{2+} compounds. In $CpFeAn^+$, electron-withdrawing substituents on the arene and electron-donating substituents on the cyclopentadienyl decreased the quadrupole splitting, a result interpreted in terms of the primary roles of Cp as donor and an as acceptor in these cations[354]. Patents for use of $CpFeAn^+$ salts in admixture with dicyanobutadienes as visible light-sensitive photopolymerization films[355] or deposited with a siloxy-substituted polystyrene on a silicon substrate as a photosensitive recording medium[356] have been issued.

The properties of $CpFe^+(C_6H_5O^-)$, which may be viewed as a phenoxide complex but more closely resembles a 1-oxocyclohexadienyl[343], have been mentioned in Section 7d. Complexes $(\eta^6\text{-PhR})FeCp^+$ [R = Me, CH_2Ph, $CHPh_2$] and $(\eta^6\text{-fluorene})FeCp^+$ were deprotonated to form neutral complexes. Oxidation with Ag^+ or $SbCl_5$ gave Fe(III) complexes, whose structures were probed by ESR spectroscopy[357].

Addition of nucleophiles to the arene ring of $CpFeAn^+$ to form neutral cyclohexadienyl complexes was mentioned in Section 7d, where the structures of the phenyllithium-(mesitylene)$FeCp^+$ adduct[341] and sulfonyl carbanion-(PhX)Fe-Cp^+ adducts[342] were described. Attack of hydride and carbanion nucleophiles on disubstituted arene complexes in THF has also been examined. The directive effects of substituents were rather small compared to those observed in some other classes of arene complexes such as $AnCr(CO)_3$ and $AnMn(CO)_3^+$. Nonetheless, some new reactions were observed, such as attack of Me_2CCN^- on CpFe[*o*-$C_6H_4(OMe)_2]^+$ to give, after hydrolysis and decomplexation, 4-(α-cyanoisopropyl)-1,2-dimethoxybenzene[358]. $CpFe(\eta^6\text{-}PhNH_2)^+$ and related aniline complexes functioned as a nucleophile toward epoxides, forming $CpFe[PhNHCH_2CH(OH)\text{-}Me]^+$ with propylene oxide, for example[359].

Displacement of the arene ligand from $AnFeCp^+$ by metallophilic nucleophiles has previously been cited as a route to a number of $(RCOC_5H_4)FeL_3^+$ complexes (by photochemically induced displacement)[238] and $CpFeL_3^+$ complexes (by reductively induced displacement)[239].

A crystal structure of a 37-electron mixed-valence bimetallic compound, $Cp^*Fe(\mu\text{-}C_6H_5\text{-}C_6H_5)FeCp^{*\,+}$, showed a nearly planar biphenyl unit, structurally little changed from the 36-electron dication. Thus, the structural organization and stabilization that accompany formation of the neutral 38-electron compound occur in the second reduction step[360]. As previously described, that compound has a $Cp^*Fe(\mu,\eta^5,\eta^5$-bicyclohexadienylidene)$FeCp^*$ structure. Extensive electrochemical, ESR, and theoretical studies of the reduction steps of both the Cp and Cp^* compounds have been carried out[344]. Another bimetallic series was entered through reaction of $Fp^*{=}CHOMe^+$ with $CpFe(\eta^5C_6Me_5{=}CH_2)$. The initial adduct, $[Fp^*CH(OMe)CH_2C_6Me_5]FeCp^+$, was treated with Me_3SiOTf at -80°; in the presence of trimethylphosphine this resulted in formation of $[Fp^*CH{=}CHC_6Me_5]FeCp^+$ [361].



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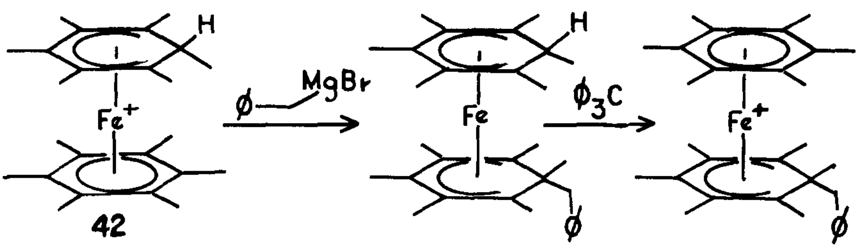
Reaction of hindered boratabenzenes with $FeCl_2$ gave the sandwich compounds **41** [R = H, $CHMe_2$, $SiMe_3$]. An X-ray structure of **41** [R = H] showed η^6 coordination, with the Fe-B distance slightly longer (2.37 Å) than the Fe-C (2.09-2.24 Å)[362]. The structure of $(\eta^6\text{-}C_6H_3Me_3)_2Fe^{2+}$ $\{C_3[C(CN)_2)_3^-\}_2$ has been reported, and used to interpret magnetic and ESR behavior of the solid salt[363]. The ESR behavior was also independently studied by a different group[364].

Attack of carbanions on An_2Fe^{2+} in dichloromethane led to formation of bis(cyclohexadienyl)iron products, in accord with the Davies-Green-Mingos generalizations, but in contrast to the AnFe(cyclohexadiene) products earlier observed in THF[217]. In order to avoid electron transfer products in reaction of $(C_6Me_6)_2Fe^{2+}$ with carbanions, hydride was used as a "protecting group," forming **42**. The hydride addition product underwent nucleophilic attack by carbanions as shown in Eq. 21. The product shown was further functionalized by deprotonation of a 1-methyl group and reaction with benzoyl chloride[365]. The electron-rich compound $(C_6Me_6)_2Fe$ was converted by oxygen to (5,6,7,8-η^4-1,2,3,4-tetramethyl-*o*-xylyl-



(21)

ene)Fe(η^6-C_6Me_6). The exocyclic methylene groups of the latter product exhibited significant nucleophilic character, reacting for example with two moles of benzoyl chloride. **42** also reacted with oxygen, by a process characterized as involving electron transfer, followed by deprotonation by the superoxide ion; an analogous mechanism probably accounts for formation of the xylylene complex. The control of electron-transfer vs. bond-formation processes by judicious choice of temperature was emphasized[366].

A review of the use of bis(arene)iron compounds, obtained by metal atom methods, as synthetic precursors to other organoiron species has been published[8].

9. BIMETALLIC COMPOUNDS

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

The ESR spectrum of the $Fe_2(CO)_8^-$ radical adventitiously trapped in the crystal lattice of PPN^+ $HFe_2(CO)_8^-$ indicated that the radical retained the symmetry of the host anion, and thus had two bridging CO groups. The orientation of the components of the g-tensor agreed with theoretical prediction that the unpaired electron resided in an Fe-Fe antibonding b_2 orbital[367]. The crystal structure of $(Ph_4P^+)_2$ $Fe_2(CO)_8^{2-}\cdot 2$ MeCN showed two apically joined, staggered, trigonal bipyramidal $Fe(CO)_4$ units, as previously found for the PPN^+ salt[368]. The crystal structure of the aurated dianion, $Ph_3PAuFe_2(CO)_8^-$, as its tetraethylammonium salt, showed two bridging carbonyl ligands and a somewhat unsymmetrical bridging $AuPPh_3$ moiety, with Au-Fe distances of 2.62 and 2.70 Å[369]. Reaction of $(NEt_4^+)_2$ $Fe_2(CO)_8^{2-}$ with L_nMHgCl [L_nM = Fp, $Co(CO)_4$, $Mn(CO)_5$, $Mo(CO)_3Cp$, etc.] led to mercury-bridged $(OC)_3Fe(\mu\text{-}CO)_2(\mu\text{-}HgML_n)Fe(CO)_3^-$ anions, analogous to the gold compound previously described[370].

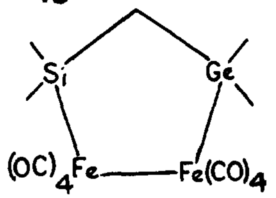
$HFe_2(CO)_8^-$ served as a reducing agent, transferring hydride ion to $(H_2BCo(CO)_4)_2\cdot THF$[371]. Reaction of $Me_2SFe(CO)_4$ with Me_2SBH_3 provided an improved route to the ferraborane $Fe_2(CO)_6B_2H_6$[114].

Revised extended Hückel MO calculations on $Fe_2(CO)_9$, with FMO analysis, has led to revision of previous conclusions on the question of Fe-Fe bonding. After separating out the contributions of bridging C-Fe bonds, this analysis revealed a direct through-space two-electron two-orbital interaction between the two iron nuclei. However, repulsive through-bridge interactions might dominate the direct bond energetically[372]. Packing of $Fe_2(CO)_9$ and other metal carbonyls in crystals indicated that each CO contributed a fairly constant amount to the packing energy, and revealed a preference for orthogonal carbonyl groups in neighboring molecules[126].

$Fe_2(CO)_8(\mu\text{-}CH_2)$ transferred the elements of $(CH_2)Fe(CO)_3$ to the allenyl complex $CpMo(CO)_3CH{=}C{=}CH_2$ to form a trimethylenemethyl-$FeCO)_3$ complex[159]. Formation of propene (or, if CO loss is difficult, cyclopropane) from *cyclo*-$(CH_2)_3Fe_2(CO)_8$ [octacarbonyldiferrolane] has been studied by extended Hückel methods. The favored mechanism involved CO loss, β-hydride elimination to form $H(OC)_3Fe\text{-}Fe(CO)_4CH_2CH{=}CH_2$, hydride migration, and reductive elimination[373].

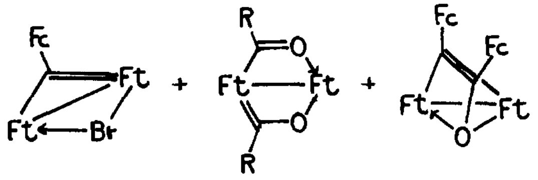
$(\mu\text{-}GeHR)_2Fe_2(CO)_7$ and $(\mu\text{-}GeRH)_3Fe_2(CO)_6$ [R = Me, Et] were among the products tentatively identified from among the products of reaction of $RGeH_3$ with $Fe_3(CO)_{12}$. $RSiH_3$ probably reacted similarly, but the products were less stable[374]. Cyclic product **43** was formed by photoreaction of $Fe(CO)_5$ and $HSiMe_2CH_2GeMe_2H$. A number of reactions were reported, including substitution of phosphines for carbonyls, and reaction with oxygen or sulfur. The latter reactions produced O- or S-containing heterocycles, probably via transient $Me_2E{=}O$ and $Me_2E{=}S$ species [E = Si, Ge][375].

43



A number of di-iron products resulted from reaction of ferrocenyl-lithium with dibromotetracarbonyliron (Eq. 22). **45** was also preparable by methylation of

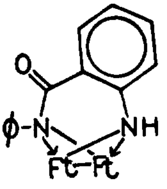
$$FcLi + Br_2Fe(CO)_4 \longrightarrow \qquad (22)$$



44 (R = Fc) **45**

$FcCOFe(CO)_4^-$. Attack of FcLi on a bridging carbonyl of $Fe_2(CO)_9$ followed by methylation produced $(OC)_4Fe[\mu\text{-}C(OMe)Fc]Fe(CO)_4$[376]. Another diacyl complex, **44** [R = $(OC)_5ReCH_2CH_2$], resulted from nucleophilic attack of $Fe_2(CO)_8^{2-}$ on two equivalents of the ethene complex $(OC)_5Re(C_2H_4)^+$ [XRC][377]. The characteristic four-band pattern in the terminal CO region of the infrared spectra of complexes of type **44** has been interpreted in terms of qualitative group theoretical arguments[378].

46, a compound obtained in low yield by photoreaction of $Fe(CO)_5$ with azobenzene in refluxing toluene, has been characterized by means of a crystal structure. A short Fe-Fe bond (2.40 Å) was indicated[379]. Thermal reaction of 2-(diphenylphosphinomethyl)pyridine [PN] with $Fe_2(CO)_9$ gave first $(PN)Fe_2(CO)_7$, which showed bridging carbonyls in the IR. Attachment of both phosphorus and nitrogen to one iron was suggested. Further thermal reaction or decarbonylation with additional $Fe_2(CO)_9$ led to $(PN)Fe_2(CO)_6$, for which structure **47** was suggested[93]. The action of $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)^-$ on L_nMHgCl [same L_nM as in the first paragraph of this section] led initially to the neutral ($\mu\text{-}HgML_n$) product, which spontaneously redistributed ligands to form $Hg(ML_n)_2$ and **48**[370]. The μ_2-benzylidyne complex **49**, $(OC)_3Fe(\mu\text{-}CPh)[\mu\text{-}P(OEt)CMe_3]Fe(CO)_3$ [XRC] was produced upon thermolysis of a (μ_3-benzylidyne)Fe_3 precursor[380]. The cationic binuclear species $(OC)_4Fe(\mu\text{-}PPh_2)Fe(CO)_4^+$ has been synthesized by oxidation of $Ph_2P[Fe(CO)_4]_2^-$ with Ph_3C^+. Reactions with nucleophiles gave doubly bridged species, $(OC)_3Fe(\mu\text{-}X)(\mu\text{-}PPh_2)Fe(CO)_3$ [X = Cl; η^2-acyl (from reaction with NaOMe or LiCu(CN)Me; $\mu,\eta^{1,2}$-CCPh (from reaction with $Li^+PhC{\equiv}CCu^-CN$)][381]. The latter acetylide complex reacted with cyclohexylamine by addition to the coordinated triple bond and hydrogen rearrangement, forming **50**[382]. The phosphido-bridged μ-ethenyl compound $(OC)_3Fe[\mu,\eta^1,\eta^2\text{-}CPh{=}CHPh](\mu\text{-}PPh_2)Fe(CO)_3$ [XRC] has been prepared by reaction of Ph_2PCl with $Fe_2(CO)_7(\mu\text{-}CPh{=}CHPh)^-$ and Tl^+ and also by reaction of $Fe_2(CO)_7(\mu\text{-}PPh_2)^-$ with diphenylacetylene and trifluoroacetic acid[383].



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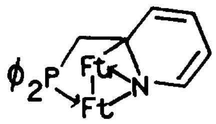

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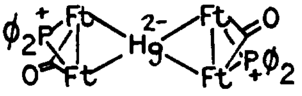

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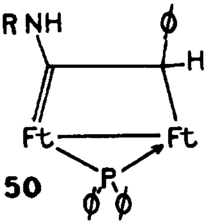

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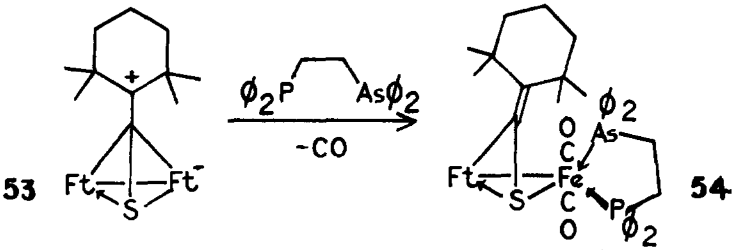
Photoreaction of $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}dppm)Fe(CO)_3$ with ethyl diazoacetate led to replacement of the bridging CO ligand by a bridging carbethoxymethylidene ligand. Heating led to deep-seated ligand rearrangement/combination, splitting out ethyl acrylate and leaving $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$[384]. Reactions of bis(halophosphino)methanes $RXPCH_2PXR$ [R = hindered aryl groups, NEt_2, NPh_2, OAr, etc.] with $Fe_2(CO)_9$ have led to a multitude of products. The initially-formed $Fe(CO)_4$ and bis-$Fe(CO)_4$ complexes reacted further to produce, in addition to diphosphene and diphosphirane complexes, diiron complexes, $(OC)_3Fe(\mu\text{-}PRCH_2PR)Fe(CO)_3$, **51**, in which the bridging ligand contributed 6 electrons overall[111]. Keto analogs, $[\mu\text{-}P(NR_2)\text{-}CO\text{-}P(NR_2)]Fe_2(CO)_6$ resulted from reaction of $Na_2Fe(CO)_4$ with hindered R_2NPCl_2 compounds, along with triphosphine-bridged $(R_2NP)_3$-$Fe_2(CO)_6$. The keto groups showed normal organic reactivity toward $NaBH_4$ and organolithium reagents, but $LiAlH_4$ caused rearrangement to form ($\mu,\eta^{1,2}$-$R_2NPCHPHNR_2)Fe_2(CO)_6$ [XRC, R = $CHMe_2$]. Reaction of the keto compounds with HBr resulted in loss of the keto group, with formation of $(OC)_3Fe[\mu$-$P(NR_2)Br](\mu$-$PHBr)Fe(CO)_3$. Reduction with sodium amalgam cleaved a P-N bond[385]. The anion so formed, (μ-$R_2NPCOP)Fe_2(CO)_6^-$, reacted with electrophiles [Me_3SnCl, R_2NPCl_2[385], R_2PCl] at the unsubstituted phosphorus. The crystal structure of [μ-P(N-*i*Pr_2)COP(PR_2)]$Fe_2(CO)_6$ [R = *tert*-butyl] was determined[386]. A comparison of the Mössbauer spectra of $Fe_2(CO)_6$ complexes bridged by two RPH units, RPSPR, and RPSSPR [R = *tert*-butyl] indicated little change in electron density or distribution as a result of sulfur incorporation[387].

Photochemical or Me_3NO-induced reactions of diphosphinoamines with $Fe(CO)_5$ led to formation of bridged-bidentate complexes, [μ-$P(OR)_2NPh$-$P(OR)_2]_2(\mu$-$CO)Fe_2(CO)_4$ [R = CH_2CF_3, Ph][94]. The new cluster **52** [XRC] has been prepared by reaction of arsine with $Fe_2(CO)_9$ at 70°[388].

Reaction of the thioketene complex **53** with phospine and arsine nucleophiles has been studied. 1,2-Bis(dimethylarsino)benzene and $Ph_2PCH_2CH_2AsPh_2$ (arphos) displaced a carbonyl group and the carbon-carbon double bond from one iron, forming products of type **54** (Eq. 23). On heating, **54** lost a (arphos)$Fe(CO)_3$ group and dimerized[389]. Reactions of the useful intermediates Et_3NH^+ $(OC)_3Fe(\mu$-$CO)(\mu$-$SR)Fe(CO)_3^-$ [R = Et, Ph, CMe_3] with several organic reagents, including vinylic halides, acyl chlorides, and alkynes, have been used to generate μ-vinyl and μ-acyl products (Eq. 24)[390-3]. Thus, β-bromostyrene gave **55** [R = Et, Ph, CMe_3; R^1 = H; R^2 = Ph], and β-chlorovinylketones gave **55** [R = Et, Ph; R^1 = MeCO, PhCO; R^2 = H][390]. *trans*-Crotonyl chloride gave **55** [R = Et, CMe_3, allyl; R^2 =



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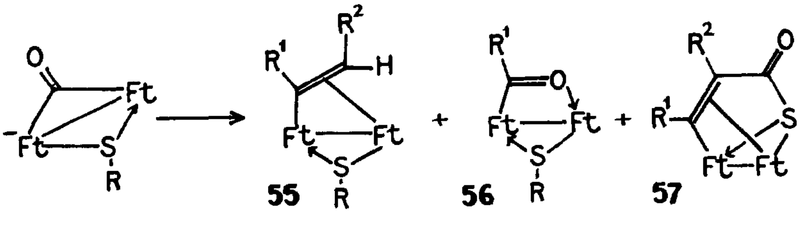
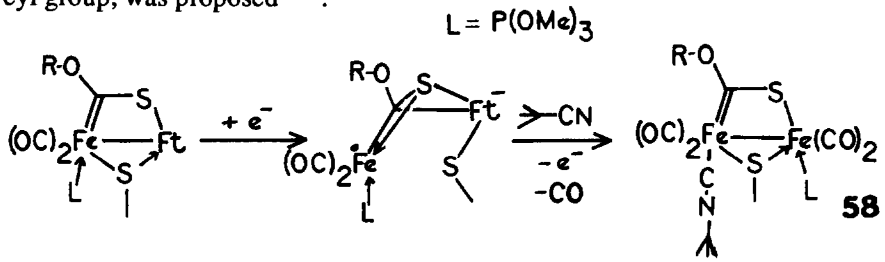


(24)

Me; R^1 = H] and **56** [R = Et, CMe_3; R^1 = MeCH=CH]. Extrusion of CO from the acyl complexes to form alkenyl complexes was found to be kinetically first order[391]. Aroyl and saturated acyl chlorides gave, of course, only acyl complexes **56**, whereas acrylyl chloride gave the unsubstituted μ-vinyl product[392]. Alkynes reacted variously, depending on the substituents. When both substituents were electron-withdrawing groups, **57** was formed. When the two groups differed in electronic character, the vinylic product **55** had the better electron-donating group at R^1. Acyl complexes **56** [R^1 = vinylic group] formed with some internal alkynes; these underwent decarbonylation in refluxing THF[393]. Iron carbonyl substitution by triphenylphosphine or triphenylarsine occurred, however, in refluxing benzene with retention of the μ-acyl structure[394]. Electron transfer-catalyzed displacement of a CO from thioacyl analogs of **56** resulted in introduction of a ligand [$P(OMe)_3$ or Me_3CNC] at the carbon bearing the carbenoid ligand. Substitution of the other ligand formed **58** (Eq. 25) regardless of the order of substitution; an intermediate having the carbene carbon bound to both irons, which allowed rotation of the thioacyl group, was proposed[395].



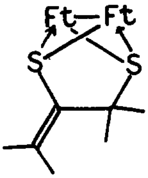
58

(25)

Photochemical reaction of the cluster $(OC)_3Fe(\mu,\eta^2;\eta^2\text{-}S_2)Fe(CO)_3$, **59**, with alkenes led to insertion of the alkene into the S-S bond. The reaction products of several 1- and 2-alkenes[396] and cycloalkenes[397] have been characterized spectroscopically and, in the case of the cyclohexene adduct, crystallographically. One thiolate sulfur in the latter adduct was oxidized to a sulfenate group[397]. Reaction of **59** with Grignard reagents led to formation of $Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}S)^-$ MgX^+; these could be oxidized by sulfuryl chloride to the bridged cluster complexes $(\mu\text{-}SR)Fe_2(CO)_6(\mu\text{-}S\text{-}S\text{-}\mu)Fe_2(CO)_6(\mu\text{-}SR)$. Reaction of the latter with Grignard reagents cleaved the bridging disulfide bond[398]. Addional examples of bridge cluster complexes resulted when the Grignard adducts $Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}S)^-$ MgX^+ were treated with α,α'-dibromoxylenes to generate the link. The *meta* isomer was the subject of a crystal structure[399]. Reaction of **59** with VCp'_2 formed the paramagnetic product $Fe_2(CO)_6(\mu_3\text{-}SVCp'_2)_2$[400]. With $Cp^*Cu(THF)$ at -78°, **59** reacted by insertion of the carbenoid copper fragment to form $Cp^*Cu(\mu_3\text{-}S)_2Fe_2(CO)_6$. The product, stable at -78°, underwent reversible one-electron reduction by sodium naphthalene or methyl-lithium. It decomposed at room temperature[401].

A significant product of the reaction between tetramethylallene episulfide and $Fe_2(CO)_9$, in addition to the previously cited tricarbonyl(η^4-propane-2-thione-1,3-diyl)iron, was **60**[162]. Photochemical reaction of "tetrathiofulvalene" with $Fe(CO)_5$ led principally to addition of an $Fe_2(CO)_6$ moiety across a C-S bond, forming **61** [XRC][402]. The triple bond of $Fe_2(CO)_6(\mu\text{-SR})(\mu\text{-SC}\equiv\text{CPh})$ was readily complexed to a $Co_2(CO)_6$ unit[403].

Refluxing μ-thiolate complexes $Fe_2(CO)_6(\mu\text{-SR})(\mu\text{-SR'})$ with triphenylphosphine or -arsine in benzene or toluene led to displacement of one or two carbonyl groups[404]. The crystal structure of the bis(triphenylphosphine) adduct, $(\mu\text{-SBu})(\mu\text{-SCH}_2\text{CH}_2\text{CO}_2\text{Me})[Fe(CO)_2(PPh_3)]_2$ was reported[405]. The bis(ethylthiolate) analog has been used as a catalyst for carbonyl substitution reactions of $Ru_3(CO)_{12}$[406].



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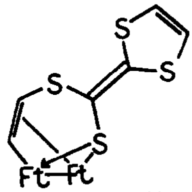

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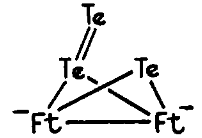
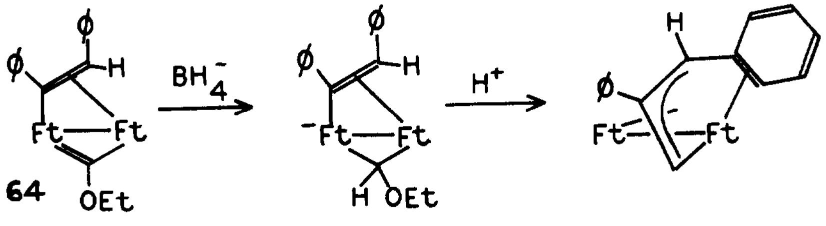


63

Insertion of a methylene group into the Te-Te bond of $Fe_2(CO)_6(\mu\text{-Te}_2)$, **62**, was the result of reaction with diazomethane at room temperature[407]. Reduction of **62** with $LiEt_3BH$ at -78° gave the reactive dianion $Fe_2(CO)_6(\mu\text{-Te})_2^{2-}$, which reacted with metal dihalides [R_2SnCl_2, Cp_2TiCl_2, $(PPh_3)_2MCl_2$; M = Ni, Pd, Pt] to form $Fe_2(CO)_6(\mu\text{-TeMR}_2\text{Te})$ or $Fe_2(CO)_6[\mu\text{-TeM(PPh}_3)_2\text{Te}]$. Similar products were also formed by direct addition of unsaturated metal fragments [$Ru_3(CO)_{11}$, $Os_3(CO)_{11}$] into the Te-Te bond of **62**[408,409]. With $Ru(CO)_4(C_2H_4)$, the trimetallic cluster $Fe_2Ru(CO)_9(\mu_3\text{-Te})_2$ formed, but this reacted in turn with $Pt(PPh_3)_4$ to replace the ruthenium by platinum, forming $Fe_2(CO)_6(\mu\text{-TePt(PPh}_3)_2\text{Te})$[410]. The novel product **63** was formed in the reaction of (η^4-butadiene)tricarbonyliron with excess K_2Te_4, and isolated as the $K[2.2.2\text{-cryptand}]_2^+$ salt [XRC][411].

Reduction of $(OC)_3Fe(\mu\text{-COEt})(\mu,\eta^1,\eta^2\text{-CPh=CHPh})Fe(CO)_3$, **64**, by BH_4^- occurred at the carbyne carbon (Eq. 26) [XRC]. Protonation of the resulting anion resulted in ligand coupling to form a diphenylallylene unit. Protonation in the

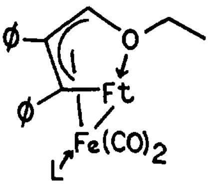


(26)

presence of a phosphine produced an analogous diphenylallylene product, but with the phosphine coordinated in place of the η^2-phenyl ring shown in Eq. 26^{412}. Direct reaction of **64** with triphenylphosphine in boiling hexane led to formation of $(PPh_3)_2Fe(CO)_3$. But $PhPMe_2$, in contrast, induced ligand coupling to form **65** [L = $PhPMe_2$]. Ligand coupling was also observed in reaction of the unsubstituted vinyl analog of **64** with triphenylphosphine, which formed $(Ph_3P)(OC)_3Fe[\mu,\eta^1,\eta^3\text{-}(EtO)CCHCH_2]Fe(CO)_3$. Protonation produced $(OC)_4Fe[\mu,\eta^1,\eta^2\text{-}CH(Me)\text{-}C(OEt)]Fe(CO)_3(PPh_3)$^{413}.

Electron density deformation maps from X-ray diffraction data on $(Me_3C\text{-}C{\equiv}C\text{-}CMe_3)Fe_2(CO)_6$ have been calculated and interpreted. The interactions between the two tricarbonyliron groups were concluded to occur predominantly occur through the alkyne ligand and a semibridging carbonyl ligand, with no accumulation of electron density directly between the two iron atoms^{414}.

Photochemical reaction of pentacarbonyliron with allene and phenylallene produced $(OC)_4Fe[\mu\text{-}\eta^1,\eta^3\text{-}C(=O)C(CH_2)(CHR)]Fe(CO)_3$ [R = H, Ph]. Warming led to decarbonylation, which could be reversed under CO pressure. Insertion of alkynes into the allylene complexes gave ketene complexes such as **66**, which were shown to be fluxional. Insertion of allenes was also investigated. Thermolysis of **66** gave two products, [2,3-diphenyl-4-methyl-1,1,1-tricarbonylferrole]$Fe(CO)_3$ and 2,3-diphenyl-4-methylene-2-cyclopenten-1-one. The latter cyclocarbonylation product was the sole product when the thermolysis was conducted under CO pressure^{415}.



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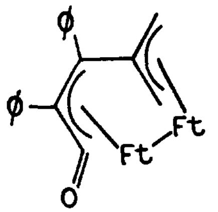

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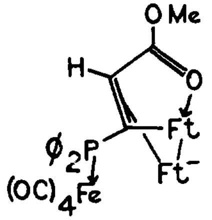
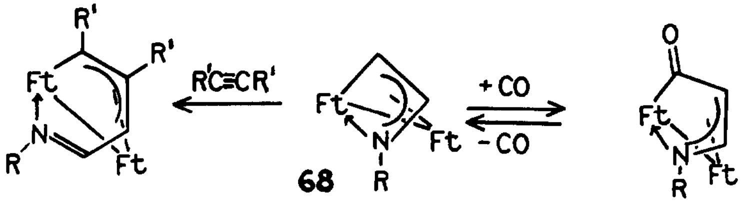


67

Reaction of $Ph_2P\text{-}C{\equiv}C\text{-}CO_2Me$ and $HFe_3(CO)_{11}^-$ initially gave a product, **67** [XRC], with the alkyne ligand intact. Heating resulted in formation of a tri-iron complex containing independent diphenylphosphido and vinylidene ligands^{416}. Reaction of the $HFe_3(CO)_{11}^-$ with simpler alkynes, e.g. diphenylacetylene, followed by quenching with triethyloxonium fluoroborate, led to **65** [L = CO]. A crystal structure of the product from 1-phenylpropyne was reported^{417}.

A ferraazetine complex, **68** [R = ferrocenyl, Fc], resulted when $(\mu\text{-}CH_2)Fe_2(CO)_8$ and $RN{=}PPh_3$ were allowed to react. The additional carbon presumably came from a CO, and Ph_3PO was also formed. Reversible insertion of CO into the Fe-C bond of **68** [R = Fc] gave a ferrapyrrolinone complex (Eq. 27).



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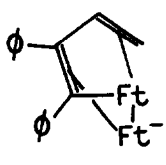
The CO-dependent electrochemistry of **68** [R = Fc] was studied as the basis for a carbon monoxide sensor[418]. Substituted ferrapyrrolinone complexes were also formed upon reaction of $Fe_3(CO)_{10}(\mu_3\text{-NPh})$ or $H_2Fe_3(CO)_9(\mu_3\text{-NPh})$ with alkynes. Photosubstitution by Me_3CNC occurred at the η^3-bound iron. Reaction of the bis(imido) cluster $Fe_3(CO)_9(\mu_3\text{-NPh})_2$ with diphenylacetylene gave a mixture of products, which included the tetraphenylferrole complex and the triphenylferraazetine complex[419]. Interconversion of ferraazetine and ferrapyrrolinone was not noted in this work, but may account for the different products obtained from the mono- and bis(imido) clusters. Photochemical reaction of ferraazetine complexes with alkynes led to insertion into the Fe-C bond to form ferrapyridine complexes, as shown in Eq. 27 [XRC, R = R' = Ph]. With terminal alkynes, the substituted carbon [R' = Ph, $SiMe_3$, CMe_3] was specifically located adjacent to iron. The ferrapyridine complexes formed 2-pyridones in good yield upon decomposition under 600 psi of CO at 160°[420].



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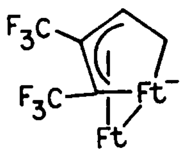

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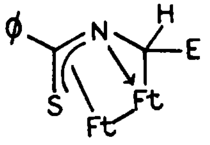
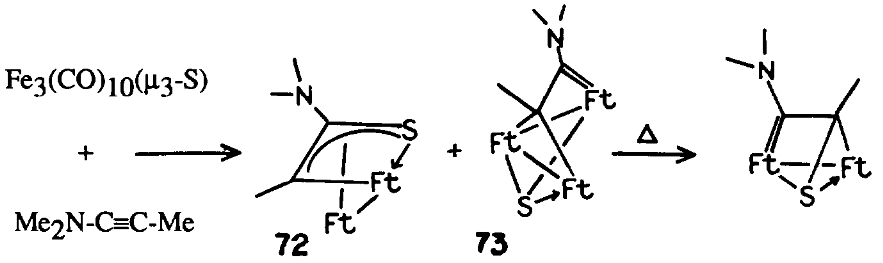


71

Insertion of diphenylacetylene into the Fe-C bond of $Fe_2(CO)_6(\mu\text{-CO})(\mu\text{-}CH{=}CH_2)^-$ led to an acyl-coordinated product $[C(Ph)\text{-}C(Ph)\text{-}C(CH{=}CH_2){=}O]Fe_2(CO)_6^-$, having a structure analogous to that of **67**. Also formed was $[C_2Ph_2CHCH_2]Fe_2(CO)_6^-$, assigned structure **69**. Use of hexafluoro-2-butyne instead of diphenylacetylene gave only a product with composition analogous to that of the latter product, to which, however, a different structure, **70**, was assigned[421]. Crystal structures of these products would be welcome. A crystal structure of **71**, formed along with an $Fe(CO)_3$ complex from the free ligand, has been reported[188].

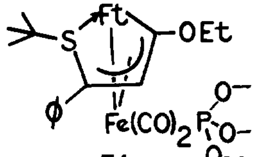
The reaction between $MeC{\equiv}C\text{-}NMe_2$ and $Fe_3(CO)_{10}(\mu_3\text{-S})$ yielded a bimetallic and a trimetallic product, **72** and **73**. Heating the latter caused conversion to another bimetallic product, isomeric with **72** (Eq. 28). The structures were based



72 **73**

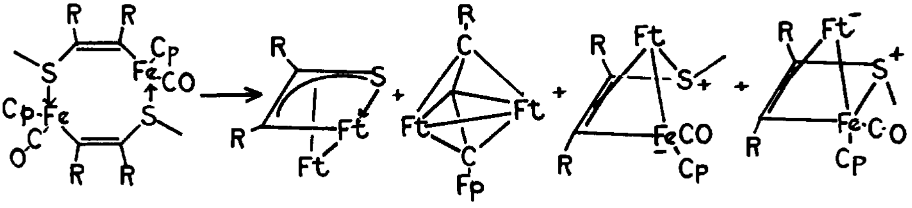
(28)

on spectroscopic data and crystal structures of Ru and Os analogs[422]. **72** is a ferrathiete complex, isoelectronic with the ferraazete complexes of type **68**. Chemical reactions of several ferrathiete complexes have been reported. Thus, reaction with $Pt(PPh_3)_4$ resulted in insertion of $Pt(PPh_3)_2$ into the S-C bond of the 3-phenylferrathiete complex. Reaction of the ferrathiete complex with triphenylphosphine or trimethyl phosphite gave mono- and di-substitution products, which revealed rapid exchange between the two iron centers[423]. The substitution reactions proceeded optimally with electroreductive catalysis, whose mechanism was studied. Reaction of the 3-phenylferrathiete complex with *tert*-butyl-lithium and trimethyl phosphite gave not only catalysis of the exchange reaction, but also addition at sulfur and carbonyl insertion; alkylation of the resulting anion formed **74** [XRC]. CO Insertion [cf. Eq. 27) was also catalyzed by sodium amalgam reduction. Heating the carbonyl-inserted complex resulted in decarbonylation, restoring the ferrathiete starting material[424].



74

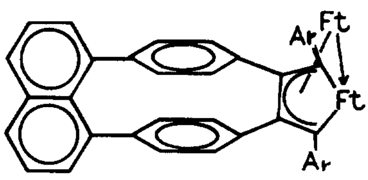
A ferrathiete complex was one of several products which resulted when $Cp(OC)Fe[\mu\text{-}C(CF_3)=C(CF_3)\text{-}S(Me)]_2Fe(CO)Cp$ and $Fe_3(CO)_{12}$ were allowed to react under various conditions (Eq. 29; R = CF_3). Also formed were **55** [R = Me; $R^1 = R^2 = CF_3$] and trinuclear products to be discussed in Sect. 10a[425].



(29)

The benzoferrole complex **75** [Ar = *p*-tolyl, *p*-*tert*-butylphenyl] was prepared from the preorganized diacetylene precursors by reaction with $Fe(CO)_5$[426]. An intermolecular coupling of CO with two molecules of $PhC\equiv CP_3N_3F_5$ during reaction with $Fe_2(CO)_9$ also led, *inter alia*, to a ferrole complex[191], as did pyrolysis of **66**, which formed the 2,3-diphenyl-4-methylferrole complex[415]. Reaction of $(OC)_4Fe(\mu\text{-}CH\text{-}CH=NHR^+)Fe(CO)_4$ [R = Ph, CMe_3] with phenylacetylene formed the ferrole complex **76**[427] [XRC], whose initially proposed structure had a fluorine atom in place of the hydroxyl group[428].

The electronic structure of butatriene complexes $(\mu,\eta^3,\eta^3\text{-}R_2CCCCR_2)Fe_2(CO)_6$ has been investigated by Fenske-Hall calculations and electrochemical studies. Monoanions were found to be stable, but dianions were not[429]. A diiron complex **77**, a well-known type of pentafulvene complex, was obtained as a by-product of the synthesis of **17**[161].



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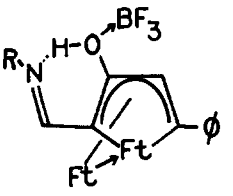

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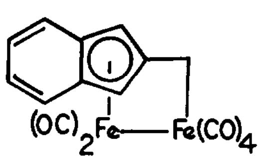

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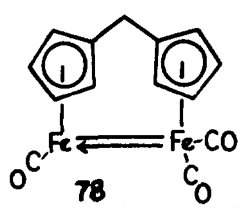
9b. Diiron Compounds, Derivatives of $Cp_2Fe_2(CO)_4$ [Fp_2]

The reaction of FpX with $HFe(CO)_4^-$ and diphenylacetylene led to a successful synthesis of $CpFe(CO)(\mu\text{-}CO)(\mu,\eta^1,\eta^2\text{-}CPhCHPh)Fe(CO)_3$ [XRC][430].

A highly hindered derivative of Fp_2 was prepared by reaction of lithium 1,3-di(*tert*-butyl)cyclopentadienide [from reaction of methyl-lithium with 2-(*tert*-butyl)-6,6-dimethylpentafulvene] and $FeCl_2$ at -80° under CO pressure. The substituted ferrocene, $(C_5H_3R_2)_2Fe$, and $(C_5H_3R_2)Fe(CO)_2Cl$ were also formed[261]. *Tert*-butyl substituents have been found to play important roles in the structural and bonding properties of Fp_2 derivatives[251].

Solid-state ^{13}C NMR studies of *cis*- and *trans*-Fp_2 showed that relaxation of terminal and bridging carbonyls occurred via dipolar interaction with Cp protons and was accordingly affected by rotation of the rings. Variable temperature studies of proton and carbon spin-lattice relaxation times showed different rotation rates for the crystallographically non-equivalent Cp rings in the *cis* isomer, which showed activation energies of 7.2 and 15.8 kJ/mol. The results agreed well with those from crystallographic data and from theoretical calculations[431]. A similar study of 70% deuterated *trans?*-Fp_2 in the solid state, by deuterium NMR, indicated an activation energy for ring rotation of 12.5 kJ/mol[432].

The electronic spectrum of *trans?*-Fp_2 has been scrutinized. The crystal field splitting energy was calculated using the energies of the d→d transitions observed[433]. Photochemistry of Fp_2 and its methylene-bridged analog $[CH_2(C_5H_4)_2][Fe(CO)_2]_2$ have been studied in cryogenic matrices at 12 K. Low energy photolysis led to rupture of the *trans*-carbonyl bridges. Photolysis at the absorption maximum of the unbridged species led to dissociation, forming Fp·, and formation of a small amount of triply-bridged $CpFe(\mu\text{-}CO)_3FeCp$. The latter was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formed directly by photolysis at the absorption maximum of Fp_2. The methylene-bridged analog showed no evidence of carbonyl bridge opening upon photolysis. Carbonyl ejection, with formation of **78**, was suggested as the principal chemical process following photoexcitation[434]. Photolysis of Fp_2 or Fp^*_2 in polyvinyl chloride film at room temperature resulted in formation of $Fp(^*)Cl$ by chlorine abstraction from the film[222]. Photolytic scission of the Fe-Fe bonds in Fp_2 and Fp^*_2 has been studied by ESR and use of spin trapping reagents, which provided evidence of secondary radicals formed by hydrogen abstraction from solvents and from single-electron transfer processes[221]. Sonolysis of Fp^*_2 in the presence of nitrosodurene resulted in formation of the nitrosodurene radical-anion; no RN(O)Ar radicals were detected[435].

Catalysis of the addition of halocarbons to alkenes by Fp_2 has been studied using kinetics, including crossover studies using halocarbon mixtures and Fp_2-Fp^*_2 mixtures. It was concluded that catalysis involved an intact dinuclear species, probably $CpFe(\mu\text{-}CO)_3FeCp$, reacting with RX to form $Cp_2Fe_2(CO)_3X\cdot$ and $R\cdot$ [436]. Fp_2 and Fp^*_2 have also been used to catalyze exchange of Group 15 donor ligands into $Fe(CO)_5$[106]. Fp_2 was not reduced by $HW(CO)_4[P(OMe)_3]^-$ [437]. Fp_2 adsorbed on partially dehydroxylated alumina or silica surfaces formed adducts with Lewis acidic surface sites, as indicated by FT-IR[230].

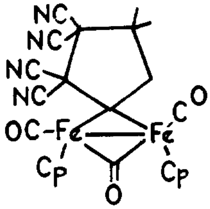
The photoelectron spectra of $CpFe(\mu\text{-}NO)_2FeCp$ and its Cp^* analog have been measured. Comparison with results of Fenske-Hall calculations and results on related metal systems allowed assignment of all valence ionizations. Occupancy of metal-metal antibonding orbitals was said to counterbalance occupancy of bonding orbitals, leaving no net direct metal-metal bonding[438]. Phosphido-bridged species $CpFe(CO)(\mu\text{-}H)(\mu\text{-}PR_2)Fe(CO)Cp$ were prepared by reaction of secondary phosphines with Fp_2 in refluxing toluene, using chiral cyclic phosphines "diopholane" and "tarpholane." The *trans*-bis(phosphido) complexes, synthesized from FpI and PR_2^-, existed as diastereomers differing only in the configuration of the iron atoms. Both mono- and bis-phosphido diiron compounds underwent cis-trans isomerization on irradiation in solution, probably via CO dissociation[439].

$Cp(OC)Fe(\mu\text{-}SR)_2Fe(CO)Cp$ [R = 3-(trimethoxysilyl)propyl], produced by reaction of RSH and Fp_2, was isolated in two isomeric forms. Oxidation by ferricenium ion gave an isolable radical-cation; electrochemical oxidation also formed a dication[258]. The crystal structure of the radical-cation salt $CpFe(CO)(\mu\text{-}SPh)_2Fe(CO)Cp^+$ $TCNQ^-$, formed by one-electron transfer between the neutral reactants, has been reported[440]. The paramagnetic trication $(CpFe)_4(\mu_3\text{-}S)_4{}^{3+}$ has been prepared for the first time by bulk electrolysis of the neutral $(CpFe)_4(\mu_3\text{-}S)_4$ in 83% yield. The mono- and di-cations were also preparable in this manner using the appropriate potentials[441].

Cis-trans isomerization of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ was shown to occur by an acid-catalyzed process, which followed second-order kinetics and exhibited a very high kinetic isotope effect $[k_H/k_D = 70\text{-}105]$. The proposed mechanism involved protonation at iron, bridge opening to form $FpCH_2FeH(CO)Cp^+$, rotation, reclosure, and deprotonation[442]. μ-Isocyanide complexes $Cp(OC)Fe(\mu\text{-}CO)[\mu\text{-}C{=}NC({=}O)SR]Fe(CO)Cp$ [R = Me, Et] were formed as mixtures of *cis* and *trans* isomers by insertion of cyanate ion into the C-S bonds of $[\mu\text{-}CSR]^+$ precursors. A crystal structure of the *cis* isomer [R = Et] was reported. Protonation or alkylation on nitrogen led to aminocarbyne complexes, $Cp(OC)Fe(\mu\text{-}CO)[\mu\text{-}CN(R')C({=}O)\text{-}SR]Fe(CO)Cp^+$ [R' = H, Me, Et]. These in turn added H^- or CN^- to the carbyne carbon, forming μ-carbene complexes. The crystal structure of the carbene complex $Cp(OC)Fe(\mu\text{-}CO)[\mu\text{-}C(CN)NMeC({=}O)SMe$ showed retention of the *cis* geometry of the original isocyanide complex[443].

Reaction of the alkylidene complex $Cp(OC)Fe(\mu\text{-}CO)(\mu\text{-}C{=}CHMe)Fe\text{-}(CO)Cp$ with TCNE resulted in tricyanovinylation, forming the $[\mu\text{-}C{=}C(Me)\text{-}C(CN){=}C(CN)_2$ product. However, the $\mu\text{-}C{=}CHCHMe_2$ homolog reacted instead by addition to form **79** [XRC][444]. The μ-methylidyne complex $Cp(OC)Fe(\mu\text{-}CO)(\mu\text{-}CH^+)Fe(CO)Cp$ was silylated by treatment with $PhSiMe_2Li/CuI$, and other nucleophiles $[HFe(CO)_4^-, MeCuCN^-]$ reacted similarly with arylcarbyne and ethylidyne analogs. Hydride removal from $Cp(OC)Fe(\mu\text{-}CO)(\mu\text{-}CMe_2)Fe(CO)Cp$ produced the μ-isopropenyl cationic complex[445].

The hexafluorobutyne complex **80** resulted from thermal decomposition of isomers of $(C_4F_6)Fe_2(CO)_4Cp(SMe)$, shown in Eq. 29[425]. The mass spectrum of **81** was obtainable using laser-desorption Fourier-transform mass spectrometry, although electron-impact methods failed. Disorder had also prevented characterization of **81** by a crystal structure[334].



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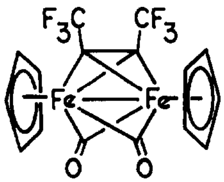

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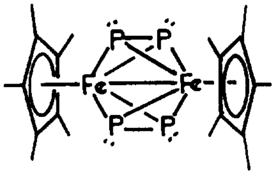
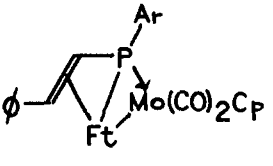


81

9c. Heterobimetallic Compounds

The carbyne complexes $(dmpe)W(CO)_2({\equiv}CAr)X$ [Ar = *p*-tolyl; X = Cl, Br, NCS] reacted with $Fe_2(CO)_9$ in toluene to form unstable $(OC)_4Fe(\mu\text{-}CAr)W\text{-}(dmpe)(CO)_2X$ products, having a $Fe(CO)_4$ group coordinated to the W≡C triple bond, which decomposed above -10°[446]. Coordination of the $Fe(CO)_4$ group to a Mo=P double bond resulted when $PhCH{=}CHP(OAr){=}Mo(CO)_2Cp$ [Ar = 2,4,6-tri-*t*-butylphenyl] reacted with $Fe_2(CO)_9$, also in toluene. The double bond in the initial product, $(OC)_4Fe[\mu\text{-}P(OAr)(CH{=}CHPh)]Mo(CO)_2Cp$, displaced a carbonyl ligand upon heating at 60°, forming **82** [XRC]. The Cp^* analog formed directly upon reaction with $Fe_2(CO)_9$[447]. Reaction of the unsaturated $(OC)_4Fe(\mu\text{-}CAr)W(CO)_2Cp^*$ [Ar = *p*-tolyl] with phosphaalkynes $RC{\equiv}P$ [R = CMe_3, $CHMe_2$] in the cold yielded **83** [XRC, R = CMe_3]. $(OC)_2(Me_3P)Fe(\mu\text{-}CAr)M(CO)_2Cp$ [M = Mo, W] formed similar products upon reaction with the phosphaalkynes, but they isomerized in solution to form **84** [XRC, M = Mo; R = CMe_3][448]. A molybdenum-coordinated ferrole complex, $(Et_2NCS_2)_2Mo(\mu\text{-}CO)[\eta^5\text{-}C_4Ph_4Fe(CO)_3]$ [XRC], resulted from reaction of $(Et_2NCS_2)_2Mo(PhC{\equiv}CPh)_2$ and related acetylene complexes with $Fe_2(CO)_9$[449]. Synthesis of $(C_5H_5\text{-}C_5H_4)W(CO)_3Me$ has led to the opportunity to bind the free cyclopentadienyl ring to a variety of metals to form bimetallic $(\mu,\eta^5,\eta^5$-fulvalene) complexes. Those synthesized included $(OC)_3W(C_5H_4\text{-}C_5H_4)Fe(CO)_2$(*Fe-W*)[450].



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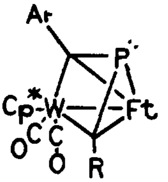

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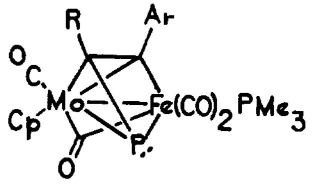
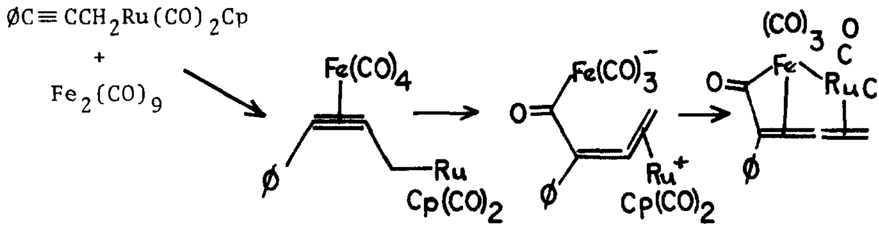


84

Reaction of $Re(CO)_5^-$ with $Fp'(EtC{\equiv}CEt)^+$ resulted predominantly in displacement of the alkyne, forming $Fp'\text{-}Re(CO)_5$. $Fp\text{-}Re(CO)_5$ likewise resulted from reaction of $Fp(MeC{\equiv}CMe)^+$ [451].

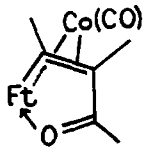
The crystal structure of $(Ph_4P^+)_2\ FeRu(CO)_8^{2-}\cdot MeCN$, prepared by reaction of $Ru(CO)_5$ with $Fe(CO)_4^{2-}$, showed an unbridged Fe-Ru bond, with a structure similar to that of the diruthenium dianion, but with some metal-metal disorder[368]. Reaction of $CpRu(CO)_2H$, $Fe_2(CO)_9$, and an alkyne afforded bimetallic μ-ethenyl complexes, of which $CpRu(CO)(\mu\text{-}CO)(\mu,\eta^1,\eta^2\text{-}CPhCHPh)Fe(CO)_3$ was the subject of a crystal structure. The reaction was proposed to involve activation of the alkyne by formation of an $Fe(CO)_4$ complex, which then inserted into the Ru-H bond. Similar chemistry was observed with FpH[452]. A possibly related reaction, of $CpRu(CO)_2CH_2C{\equiv}CPh$ with $Fe_2(CO)_9$, proceeded more eventfully (Eq. 30). The result may be contrasted with that in Eq. 17 for the all-iron system[309].

Bimetallic clusters such as **85** [XRC] resulted from reduction of $FeCo_2(CO)_9(RCCR)$ followed by treatment with alkylating agents. The acetylene ligand was converted into an acylalkenyl ligand, and the trimetallic cluster underwent fragmentation[453]. **85** may be compared to the similar **67**. A μ_2,η^2-SiO



(30)

bridge resulted when $(\eta^1\text{-dppm})Fe(CO)_3Si(OMe)_3^-$ was allowed to react with $Rh_2(CO)_4Cl_2$, forming **86**. The anion formed (μ-dppm)-bimetallic species also with HgCl and $CuAsPh_3$ groups, but these lacked the SiO bridge found in **86**[454]. Reactions of $(dppm)_2RhCl$ with iron anions formed $(OC)_2Fe(\mu\text{-}H)(\mu\text{-dppm})_2\text{-}Rh(CO)$, in which both dppm ligands unwrapped from the rhodium atom and bridged the two metals, and $CpFe(CO)(\mu\text{-dppm})Rh(\eta^2\text{-dppm})$, in which one remained chelated to rhodium[455].



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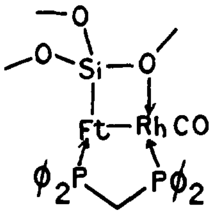

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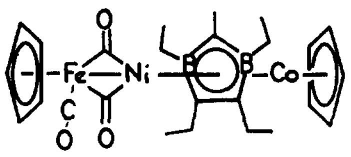
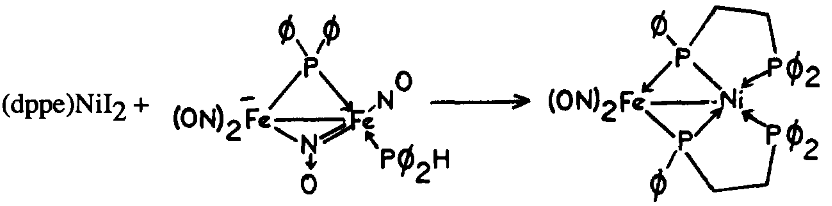


87

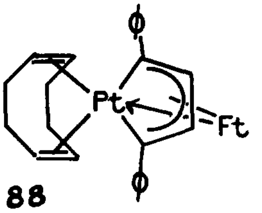
A number of iron-nickel compounds have been obtained by reactions of iron anions with $CpNi(PPh_3)Br$. Use of $HFe(CO)_4^-$ and HC≡CE in combination led to formation of $(Ph_3P)(OC)_3Fe[\mu,\eta^1,\eta^2\text{-}C(E){=}CH_2]NiCp$; EC≡CE formed $(Ph_3P)\text{-}(OC)_2Fe[\mu\text{-}C(E){=}CHC(OMe){=}O]NiCp$, an analog of **85** having a carbomethoxy group coordinated to iron through the acyl oxygen. The same products were formed from the preformed anions $(OC)_3Fe[\eta^3\text{-}CHR{=}C(E)CO]^-$ [R = H, E] and the nickel reagent. Diphenylacetylene, upon treatment with $HFe(CO)_4^-$ and the nickel reagent, gave $(Ph_3P)(OC)_3Fe[\mu,\eta^1,\eta^2\text{-}CPh{=}CHPh]NiCp$ [XRC][430]. An $Fe(CO)_3$ group inserted into a nickel-cyclopentadienyl unit when the triple-decker compound $CpNi[\mu\text{-}(CEt)_2(BEt)_2(CMe)]CoCp$ reacted with $Fe_2(CO)_9$ to form **87**[456]. A novel



(31)

bridging ligand was generated in reaction of $Fe_2(NO)_4(PPh_2)(PPh_2H)^{2-}$ with (dppe)NiI_2 (Eq. 31)[457].

$R_2PFe(CO)_4^-$ and *trans*-$(Et_3P)_2PtHCl$ reacted to form $(OC)_3Fe(\mu\text{-}H)(\mu\text{-}PR_2)Pt(PEt_3)_2$ [R = cyclohexyl]. Protonation with HBF_4 gave a cation with two bridging hydride ligands. However, reaction with $Me_2NC(OH)Me^+$ Cl^- resulted in loss of hydrogen and formation of $(OC)_3ClFe(\mu\text{-}PR_2)Pt(PEt_3)_2$ [XRC][458]. Reaction of $Fe_2(CO)_8(\mu\text{-}CH_2)$ with $(C_2H_4)Pt(PPh_3)_2$ resulted in displacement of the ethylene ligand by the carbene complex $(OC)_4Fe{=}CH_2$, forming $(OC)_4Fe(\mu\text{-}CH_2)Pt(PPh_3)_2$ [XRC][459]. A platinole complex **88** resulted from reaction of a Pt_5Fe_2 cluster with phenylacetylene[460].



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10. TRINUCLEAR CLUSTER COMPOUNDS

10a. Tri-iron Compounds

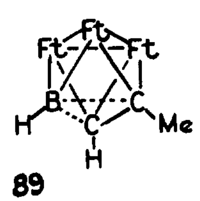
Photolysis of $Fe(CO)_5$ adsorbed on hydrated alumina produced adsorbed $HFe(CO)_4^-$, based on IR measurements. The sequence of reactions presumably involved $Fe(CO)_4$ coordinated to a basic site, trimerization to $Fe_3(CO)_{12}$, and photolytic conversion to the hydrido anion[131]. Multisubstituted isonitrile derivatives of $Fe_3(CO)_{12}$ have been prepared by a number of routes. The disubstituted compound $Fe_3(CO)_{10}(CNCMe_3)_2$ was found in the crystal to have both isonitrile ligands attached to the unique unbridged iron atom, one axial and one equatorial. Reaction of $Fe_3(CO)_9(\mu_3,n^2\text{-}CNCMe_3)$ with ligands [RNC, $P(OEt)_3$, PMe_2Ph] gave trisubstituted derivatives, which had the original isonitrile axially attached to the unique iron, and the two new ligands axially attached to the other two irons[461]. Direct substitution reactions have been used to prepare $Fe_3(CO)_{11}(PFcPh_2)$ and $Fe_3(CO)_{10}(PBuFcPh)_2$ [Fc = $CpFeC_5H_4$-][108].

Two further studies of the dynamic behavior of $Fe_3(CO)_{12}$ in the solid state and in solution have supported the view that the fluxional behavior and isomerization processes are best interpreted in terms of the ligand polyhedron model, in which the Fe_3 unit librates within the enclosure of the $(CO)_{12}$ polyhedron[462,463].

Photochemical reaction mechanisms of $Fe_3(CO)_{12}$ have been reviewed and interpreted in terms of a unified model. In this model, high energy photolysis results in expulsion of a CO, giving the unsaturated cluster $Fe_3(CO)_{11}$, which can react readily with nucleophiles, including CO. Low energy photolysis breaks an Fe-Fe bond of the cluster, leaving a bridging CO. The resulting species, also unsaturated, may undergo nucleophilic attack or fall apart, leading to cluster fragmentation[464]. The kinetics and mechanism of Me_3NO-induced substitution on

$Fe_3(CO)_{11}(YPh_3)$ [Y = P, As, Bi] have been studied[465].

Use of $(C_8H_{14})_2Fe(CO)_3$ as the source of iron carbonyl groups for preparation of $HFe_3(CO)_9(BH_4)$ and $HFe_4(CO)_{12}(BH_2)$ has been reported[114]. Reaction of $Fe_4(CO)_{13}^{2-}$ with Me_2S-BH_2Br at 75° produced a complex mixture from which the unexpected product **89** has been isolated in low yield and characterized crystallographically[466]. The triply-bridging CO group of $Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}CMe)^-$ was replaced by a bridging phosphido unit in $Fe_3(CO)_9(\mu\text{-}PPh_2)(\mu_3\text{-}CMe)$ [XRC], which resulted from reaction of the anion with Ph_2PCl and $TlBF_4$, in 46% yield[467]. Reaction of the phenylimido cluster $Fe_3(CO)_{10}(\mu_3\text{-}NPh)$ with alkynes to form ferrapyrrolinone-$Fe(CO)_3$ complexes was previously described in Sect. 9a. With other unsaturated ligands, cyclohexadiene and allene, the integrity of the Fe_3N cluster was maintained, the organic ligands replacing CO ligands. Thus, cyclohexadiene replaced two CO's on one iron, which then shared CO bridges with both its neighbors; allene formed its tetramethyleneethene dimer, which bridged two irons as a μ,η^3,η^3- ligand, replacing three CO's[419]. Reaction of the phosphinidene clusters $Fe_3(CO)_{10}(\mu_3\text{-}PR)$ [R = $CHMe_2$, CMe_3] with cyanate ion led to formation of anionic clusters; quenching with Et_3O^+ led to several products, three of them shown in Eq. 32[468]. In both **90** and **91**, the phosphorus is well beyond normal bonding distance of one iron atom (2.57 and 2.54 Å, respectively). In **91**, the P-O distance is appreciably shortened (1.53 Å, compared to 1.67 Å in **90**) due presumably to electron pair donation from O to P in the ylide-like structure. A detailed synthesis of $Fe_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}S)$ [structurally analogous to **92**] has been described[469].



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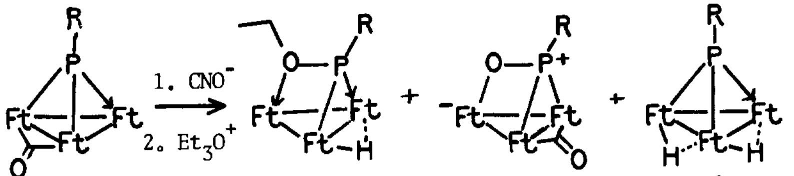
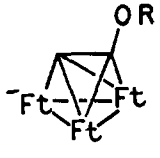


90 **91** **92**

(32)

The ketenylidene cluster $(OC)_9Fe_3(\mu\text{-}CCO)^{2-}$ was converted to acetylide clusters **93** [R = Et, C(=O)Me, C(=O)CF_3] by reaction with appropriate electrophiles [EtOTf, MeC(=O)Cl, and $(CF_3CO)_2O$, respectively]. The acetate and trifluoroacetate groups could be displaced by phosphines to form $(OC)_9Fe_3(CCPR'_3)$ products. Triphenylarsine reacted similarly with the more reactive trifluoroacetate. NaFp also displaced acetate or trifluoroacetate, to form $(OC)_9Fe_3(CCFp)^-$, the PPN^+ salt of which was the subject of a crystal structure[470]. The ethoxy cluster **93** [R = Et] reacted with Ph_2PMe by addition rather than displacement, forming the acetylene cluster $(OC)_9Fe_3[Ph_2P(Me)C{\equiv}COEt]^-$ [XRC, PPN^+ salt]. Protonation of the latter with HOTf led to loss of ethanol, consummating the displacement process and forming $(OC)_9Fe_3(CCPPh_2Me)$ [XRC]^{471}.



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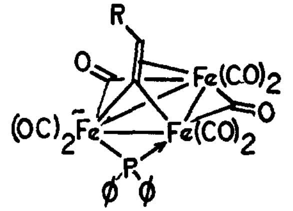

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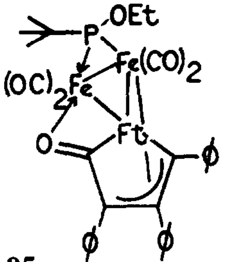

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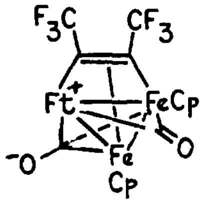
The compound **67** underwent cluster expansion and ligand fission upon heating in acetone to form **94** [XRC, R = CO_2Me]. **94** [R = H] was formed similarly when the product of reaction of $Ph_2P\text{-}C{\equiv}CH$ and $HFe_3(CO)_{11}^-$, $Fe_3(CO)_9(\mu_3\text{-}Ph_2P\text{-}C{=}CH_2)^-$, was heated in ethyl acetate^{416}. Insertion of diphenylacetylene into the benzylidyne cluster $Fe_3(CO)_8(\mu\text{-}CO)[\mu\text{-}P(OEt)(CMe_3)](\mu_3\text{-}CPh)$ by thermal reaction led to formation of **95** [XRC]. 2-Butyne gave a pair of analogous regioisomers, which differed in the sequence of alkyne- and carbyne-derived units in the five-membered ring^{380}.

The fluorines in $(OC)_9Fe_3(\mu_3\text{-}CF)_2$ were exchanged for bromines upon reaction with BBr_3 in methylene chloride. Reduction of the dibromide with tributyltin hydride gave the parent bis(methylidyne) complex^{472}. More highly substituted derivatives, $(OC)_9Fe_3(\mu_3\text{-}COMe)(\mu_3\text{-}CR)$ [R = ferrocenyl, OMe, $O(CH_2)_4OMe$] were formed by reaction of ferrocenyl-lithium with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ in THF, followed by methylation with Me_3O^+ ^{376}. Silicon and germanium analogs $Fe_3(CO)_9(\mu_3\text{-}SiFp)_2$ [XRC] were obtained in one-step reactions by heating (for example) SiH_4, $Fe(CO)_5$, and Fp_2 together at 150°^{374}.

The trigonal bipyramidal complexes $(OC)_9Fe_3(\mu_3\text{-}CH)(\mu_3\text{-}Z)$ [Z = As, Bi] have been prepared by reaction of the carbido cluster $Fe_5C(CO)_{15}$ with the elements in the presence of sulfuric acid or water. Elemental antimony did not react similarly, but the antimony analog was preparable from $SbCl_5$. The uncoordinated electron pairs on the As and Sb atoms in the clusters were coordinated to a variety of transition metal groups to form $(OC)_9Fe_3(\mu_3\text{-}CH)(\mu3\text{-}Z\text{-}ML_n)$ [ML_n = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, and $Mn(CO)_2Cp'$] and $M(CO)_4[AsFe_3(CO)_9]_2$ [M = Cr and Mo]^{473}. Reaction of AsH_3 with $Fe(CO)_5$ at 110° provided an improved synthesis of $(OC)_9Fe_3(\mu_3\text{-}As)_2$^{388}.

Terminal alkynes inserted regiospecifically into Fe-C bonds of $(OC)_9Fe_3(\mu_3\text{-}CF)_2$ to form $(OC)_9Fe_3(\mu_3\text{-}CF)(\mu_3\text{-}CF\text{-}CH\text{-}CR)$ [R = Me, Ph, OEt, $SiMe_3$, CF_3, SF_5]. Internal alkynes formed similar products, but as pairs of regioisomers^{474}. Alongside the myriad of dinuclear cluster products shown in Eq. 29, two trinuclear products also formed; one was shown to be **96** by a crystal structure, and the other was determined to be a stereoisomer of **96** in which the $Fe(CO)_3$ group and one FeCp group exchanged positions[425].



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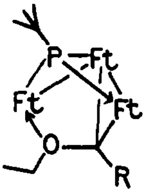

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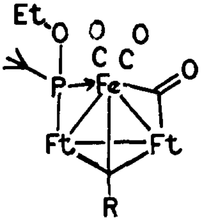

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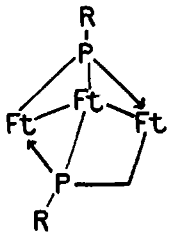
Subjection of $Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}PCMe_3)$ to conditions of the Fischer carbene synthesis [alkyl-lithium followed by ethylation] gave two products, one with a terminal carbene [=CR(OEt)] ligand, and one, **97**, with a bridging carbene ligand. In the latter, the alkoxy group functioned as a ligand toward the third iron atom in the cluster, resulting in an open, 50-electron cluster. Irradiation of **97** resulted in migration of the ethoxy group to phosphorus and restoration of the closed, 48-electron cluster in **98**[475].

Treating **51** with $Fe_2(CO)_9$ added a $Fe(CO)_3$ group to form $(OC)_9Fe_3(\mu_3\text{-}RPCH_2PR)$. Heating this product resulted in cleavage of the ligand and formation of the 50-electron cluster **99**[111]. The well-known 50-electron cluster $Fe_3(CO)_9(\mu_3\text{-}S)_2$ was formed by desulfurization of N,N'-thiobis(morpholine) upon photochemical reaction with $Fe(CO)_5$[115]. Compound **73** (Eq. 28) illustrates another sulfur-bridged 50-electron cluster[422]. The ditellurium cluster $(OC)_9Fe_3(\mu_3\text{-}Te)_2$ transferred tellurium atoms to ruthenium upon reaction with $Ru_3(CO)_{12}$[408].



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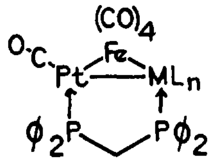
10b. Heterotrimetallic Clusters, Fe_2M and FeM_2

The clusters described in this section are arranged in order of increasing electron count rather than by periodic table group. It is intended that this facilitate comparisons of electronically similar species.

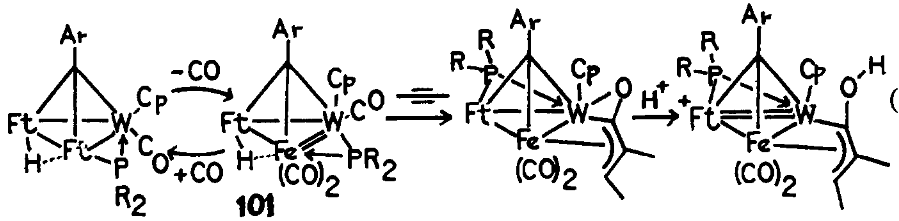
Reactions of $(dppm)PtCl_2$ with various iron carbonyl reagents have been used to prepare electron-deficient clusters **100** [XRC, ML_n = $Fe(CO)_3$, Pt(CO)]. The Fe_2Pt cluster was best obtained using $Fe_2(CO)_9$; the $FePt_2$ using $Fe(CO)_3(NO)^-$. Use of Collman's reagent favored formation of $FePt_2(\mu\text{-}dppm)_2(CO)_6$. Analogous palladium clusters were also prepared, along with mixed trimetallic species, $FePdPt(\mu\text{-}dppm)_2(CO)_4$, from reaction of $PdPt(\mu\text{-}dppm)_2Cl_2$ with Collman's reagent. This



100

reaction initially produced an isomer with a terminal palladium carbonyl, but at equilibrium an equivalent amount of the terminal platinum carbonyl isomer existed in solution[476]. (1,5-Cyclooctadiene)$PtFe_2(CO)_8$ was formed as a byproduct in the reaction of $Pt(cod)_2$ with $Fe(CO)_5$; the main products were six- and seven-metal clusters to be discussed in Section 11[460].

Equation 33 [Ar = *p*-tolyl, R = Et, Ph] shows an interesting sequence of interconversions between 46- and 48-electron trimetallic clusters. All structures were supported by crystal structures of at least one example. The hydride ligand in **101** occupied a bridging position, as shown, in the crystal, but spectroscopic data indicated a terminal hydride in solution[477]. Reaction of **101** with $PhPMe_2$ resulted in addition of the phosphine to the unsaturated iron. At -40°, the adduct existed as two stereoisomers having the phosphine equatorial or axial with respect to the Fe_2W plane; at room temperature these isomers interconverted, but isomerization to the more stable **102** [Ar = *p*-tolyl; L = $PhPMe_2$] also occurred. Further ligand exchange reactions of **102** are summarized in Eq. 34. The two unsaturated decarbonylation products did not interconvert at room temperature, and only one of them readily took up CO to reform **102**. Neither reacted with $PhPMe_2$ at room temperature, but both gave the same unsaturated product upon reaction in refluxing toluene[478].



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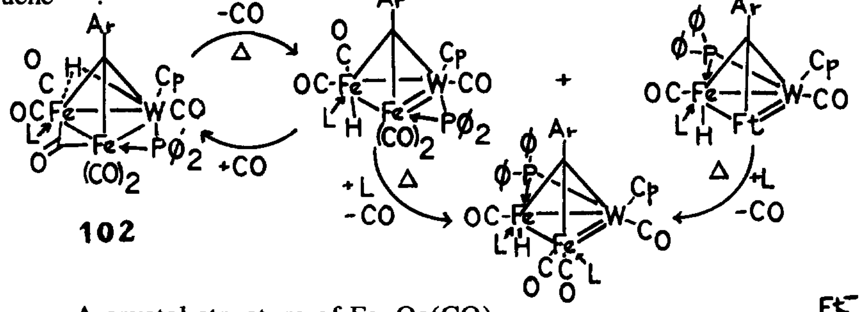

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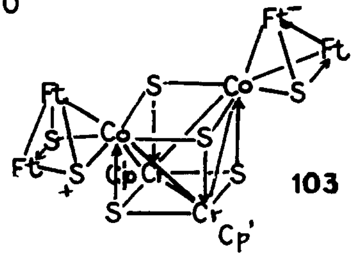
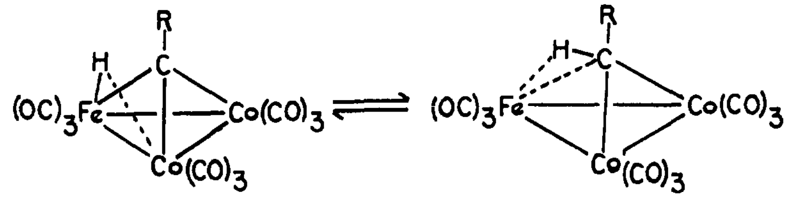


A crystal structure of $Fe_2Os(CO)_{12}$ showed significantly less disorder than has been found in $Fe_3(CO)_{12}$, and its solution shed some light on the problems accompanying solution of the latter[479]. Detailed syntheses of two μ_3-bridged trinuclear clusters,

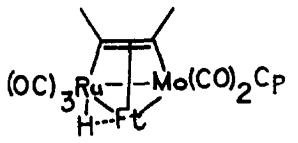
$FeCo_2(CO)_9S$ and $FeCo_2(CO)_9(PPh)$ have been described[480]. The related "super-cluster" **103** [XRC] was prepared by photoreaction of $S_2Fe_2(CO)_6$ with the butterfly cluster $(Cp'Cr)_2S_3Co_2(CO)_4$[481].

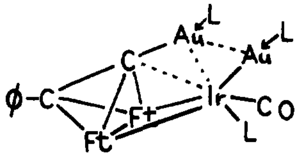
The carbon nucleophile $Ph_3P{=}CHR$ [R = H, $SiMe_3$, COPh, CO_2Et] attacked the carbon electrophile $FeCo_2(CO)_9(\mu_3,\eta^2\text{-}C{=}CH_2)$ to form a C-C bond in the zwitterionic product, $^{-}FeCo_2(CO)_9(\mu_3,\eta^1\text{-}CCH_2CH(R)PPh_3^{+})$ [XRC, R = CO_2-Et][482]. $[CpFe(CO)][Co(CO)_3]_2(\mu_3\text{-}CPh)$ was formed in a non-destructive reaction of $(FpC{\equiv}CPh)Co_2(CO)_6$ with atmospheric oxygen. Based on labeling studies, the "lost" carbon was converted to a carbonyl group, which was largely retained in the product[308]. Rates and equilibria in interconversion of two tautomers of $FeCo_2(CO)_9(CHR)$ in solution (Eq. 35) have been measured, using NMR and IR methods. For the reaction as shown at room temperature, K_{eq} was about 9 for R = Me, and 1.7 for R = Ph[483].



(35)

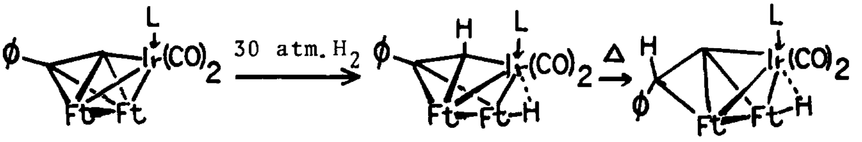
Radical anions of $FeCo_2(CO)_9(\mu_3,\eta^2\text{-}RC{\equiv}CR)$ were formed by reduction with cobaltocene. Treatment with alkylating agents led to cluster fragmentation to form **85**. Isoelectronic clusters **104** were formed by metal exchange methods from an $RuCo_2$ precursor[453]. The $Fe(CO)_3$ moiety in **104** was in turn exchanged for a $Rh(CO)_3$, with accompanying loss of the hydride ligand[484].



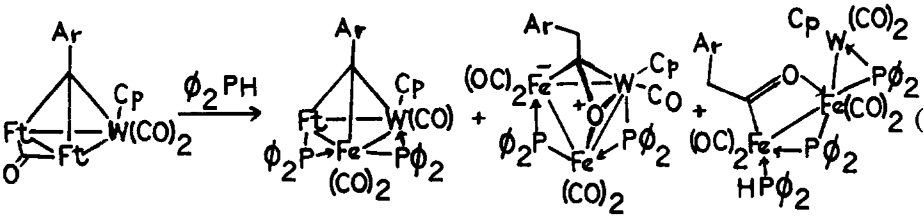


104 **105**

Reaction of $[Fe(CO)_3]_2[Ir(CO)_2L](\mu_3,\eta^2\text{-}CCPh)$ with $(LAu)_3O^{+}$ [L = PPh_3 in both reagents] in the presence of $PPN^{+}\ Co(CO)_4^{-}$ as a reducing agent led to formation of **105** [XRC]. The 48-electron structure of **105** was taken as a model for an intermediate stage in hydrogenation of the starting alkynyl complex. However, hydrogenation (Eq. 36) occurred with retention of all carbonyls, in contrast to the auration, which resulted in loss of one carbonyl[485].


(36)

An extensive set of reactions of $[(OC)_3Fe]_2(\mu\text{-}CO)[W(CO)_2Cp](\mu_3\text{-}CAr)$ [Ar = *p*-tolyl] with phosphines, especially Et_2PH and Ph_2PH, has been described. An example of the transformations observed is presented in Eq. 37. All structures


(37)

shown are derived from crystal structures. The first product shown resulted from loss of dihydrogen from the diphenylphosphines, forming two bridging diphenylphosphido units. In the other products, the hydrogens became attached to the cluster carbon, and the resulting benzylic group migrated to a carbonyl ligand, forming in one case an open, 50-electron cluster[486].

The dianion $Fe_2(NO)_4(PPh_2)(HPPh_2)^{2-}$ (illustrated in Eq. 31) reacted with $CpCo(CO)I_2$ to form the 50-electron open cluster $CpCo(CO)Fe_2(NO)_4(\mu\text{-}PPh_2)_2$, having the diphenylphosphido groups spanning the Fe-Fe bond and the non-bonded Fe-Co edge[457]. $Fe_2Ru(CO)_9(\mu_3\text{-}Te)_2$ formed rapidly and cleanly in the room-temperature reaction of $(C_2H_4)Ru(CO)_4$ and $Fe_2(CO)_6Te_2$ (**62**). A terminal position for the $Ru(CO)_3$ group in the open cluster was indicated by its ready removal using sodium methoxide followed by acidification, and by its replacement by a $Pt(PPh_3)_2$ group upon room temperature reaction with $Pt(PPh_3)_4$[410].

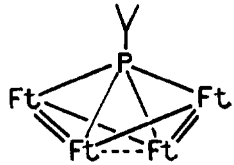
11. TETRA- AND POLYNUCLEAR CLUSTER COMPOUNDS

The effectiveness of iron-ruthenium tri- and tetranuclear clusters [e.g. $H_2FeRu_3(CO)_{13}$] at catalyzing the water-gas shift reaction in the presence of 2,2'-bipyridyl and other diamines has been studied. In general, activity decreased with increasing iron content[487].

Detailed procedures for synthesis of Et_4N^+ $FeCo_3(CO)_{12}^-$ and $Ph_3PAuFeCo_3(CO)_{12}$ have been published[488]. The tetraethylammonium salt and also the protonated clusters $HFeCo_3(CO)_{10}L_2$ [L = CO, PMe_3, PPh_3] exhibited optical limiting through reversible saturable absorption[489]. The anion $FeIr_3(CO)_{12}^-$ has been obtained by reduction of an equimolar mixture of $Fe(CO)_5$ and $Ir_4(CO)_{12}$ in alcohol containing NaOH under one atmosphere of CO, or by degradation of $FeIr_4(CO)_{15}^{2-}$ under a CO atmosphere. The crystal structure of the PPN^+ salt showed the expected closed tetrahedron of metal atoms, with three bridging carbonyl groups in the $FeIr_2$ basal plane. The anion in NEt_4^+ $Fe_2Ir_2(CO)_{12}^{2-}$ showed a very similar structure, with three bridging carbonyls around the Fe_2Ir plane. Formation of the monoaurated derivative of the latter, however, resulted in some changes in carbonyl orientations: the gold coordinated to a $FeIr_2$ face, which then showed the three bridging carbonyls, leaving an unbridged $Fe(CO)_3$ group at the apex[490].

The very stable tetramer $(CpFe)_4(\mu_3\text{-}CO)_4$ was a major product of thermal decomposition of Fp_2 adsorbed on partially dehydroxylated alumina or silica[250].

The trigonal-bipyramidal complex $Fe_4(CO)_{12}(\mu_4\text{-}PCHMe_2)$, **106**, has been obtained as a byproduct from reaction of $Fe_3(CO)_{10}(\mu_3\text{-}PCHMe_2)$ with KOCN, followed by Et_3O^+ BF_4^- (cf. Eq. 32). Described by the authors as "a triple-decker complex of the 2Π ligand $RPFe_2(CO)_6$," the 60-electron complex does not show the expected closed tetrahedral structure, but rather a butterfly arrangement of the four tricarbonyliron groups. The Fe-Fe distance along the "body" of the butterfly was 2.71 Å, whereas all others were in the range 2.55-2.57 Å[491]. Given these data, and the fact that the compound is electron-deficient for a butterfly, the structure **106** should be considered as a significant contributor. A closely analogous case is the μ_4-vinylidene clusters $Fe_4(CO)_{12}[C{=}C(R)OMe]$ [XRC, R = Me, OMe] which resulted from methylation of $Fe_4(CO)_{12}[C\text{-}C({=}O)R]^-$. The vinylidene ligand can contribute at most four electrons to the cluster bonding, resulting in an unsaturated 60-electron butterfly, with a partial double bond between the cluster carbon and the C(R)OMe group [bond length 1.44 Å][492]. By analogy to **106**, **107** may be suggested as an important contributing structure.



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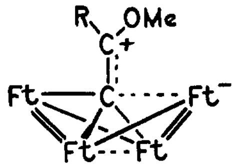

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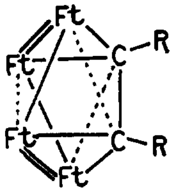
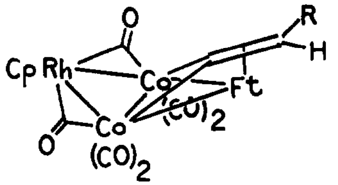


108

Alkyne-bridged tetranuclear clusters, $[Fe(CO)_3]_4(RCCR)$ and related 60-electron cluster derivatives containing $Ru(CO)_3$, NiCp, $Co(CO)_{2-3}$, and CpMo(CO) vertices have been synthesized by cluster expansion of trinuclear alkyne clusters with $Fe_2(CO)_9$ under photochemical conditions. Further clusters containing CpRh vertices were obtained by reaction of $CpRh(CO)_2$ with trinuclear alkyne clusters. Crystal structures were reported for Fe_4 and Fe_3Rh clusters. In the former, the Fe-Fe distance along the butterfly "body" was 2.73 Å, while all other Fe-Fe distances were 2.52-3 Å[493], and again contributing structures **108** are suggested. Expansion of vinylidene clusters $FeCo_2(CO)_9(\mu_3\text{-}C{=}CHR)$ [R = H, Me, Ph, CMe_3] using $CpRh(CO)_2$ occurred predominantly with rearrangement of the vinylidene ligands to alkyne ligands, forming two isomers of $CpRhFeCo_2(CO)_8$-(HCCR), structurally related to **108**. One isomer had both cobalt atoms at the wingtips, and the other had the iron and a cobalt at the wingtips. Also formed in some cases was the electron-precise butterfly compound, $CpRhFeCo_2(CO)_9(C{=}CHR)$, **109** [XRC, R = H]. Metal exchange of either cluster type with $CpMo(CO)_3^-$ led principally to the tetrahedral vinylidene cluster **110** [XRC, R = Me][494].

The 60-electron alkyne cluster $FeCo_3(CO)_{10}(PhCCPh)^-$ underwent two consecutive one-electron reductions, whereas the tetrahedral cluster $FeCo_3(CO)_{12}^-$ showed two steps only in the presence of good electron donors (DMF or PPh_3); in solvents such as 1,2-dichloroethane or propylene carbonate, a single two-electron reduction was observed[495].



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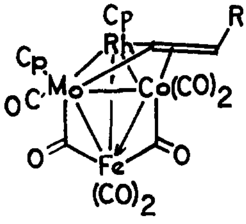

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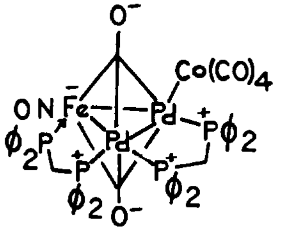
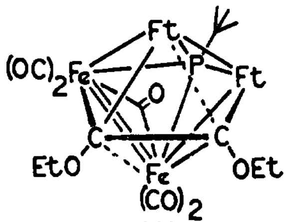


111

Reaction of metal carbonyl anions such as $Co(CO)_4^-$ with trinuclear clusters such as $Pd_2Fe(CO)_2I(NO)(\mu\text{-}dppm)_2$ led to appending the new metal moiety to the trinuclear cluster, displacing the halide and forming spiked triangular clusters, of which **111** is an example. Isomeric clusters did not interconvert at ordinary temperatures[497].

Insertion of ruthenium carbonyl units into **62**, using $(C_2H_4)Ru(CO)_4$, gave first $Fe_2Ru(CO)_9(\mu_3\text{-}Te)_2$ and then the 62-electron cluster $[Fe(CO)_3]_2Te_2$-$Ru_2(CO)_5$ [XRC][498]. Another unsaturated 62-electron cluster, **112**, was a by-product in the reaction of $Fe_3(CO)_{10}(\mu_3\text{-}PCMe_3)$ with an alkyl-lithium followed by ethylation. The di(ethoxy)acetylene ligand resulted from reductive coupling of two carbonyl groups, and electron donation from the ethoxy groups into the cluster may



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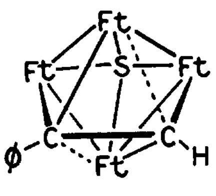

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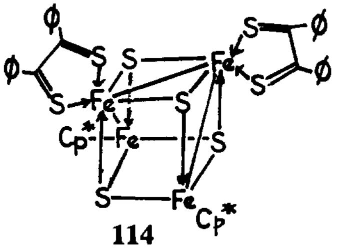


114

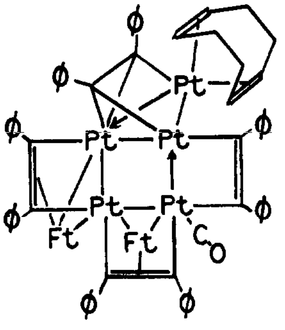
alleviate the formal electron deficiency of the system[475]. A closely related sulfur analog of **112**, **113** [XRC], had a more conventional alkyne constituent, and an additional carbonyl group, resulting in the 64-electron count expected for this geometry[423].

Reaction of Fp^*_2, sulfur, and diphenylacetylene in refluxing xylene led to generation of the mixed-ligand Fe_4S_4 cubane cluster **114**, whose crystal structure showed three bonding Fe-Fe interactions (2.71-2.79 Å) and three non-bonding (> 3.25 Å), consistent with the 66-electron count and the structure shown. Cyclic voltammetry indicated five accessible oxidation states, with net charges ranging from -2 to +2[499]. The isoelectronic heterometallic species $(CpMo)_2[Fe(CO)_3]_2S_4$ [XRC] has also been prepared, by reaction of $[CpMo(CO)_2]_2(SMe)_2$ and iron carbonyls[500]. Bulk electrolysis of $[CpFeS]_4$ at the appropriate potential has been used to prepare mono-, di-, and tri-cations in good yield[441].

Substitution of three $PhPMe_2$ ligands into the square-base pyramidal cluster $Fe_5C(CO)_{15}$ has been carried out. One phosphine substituted for a carbonyl on each of three basal irons. As a result of the increased electron density in the trisubstituted cluster, the carbide carbon lay 0.2 Å out of the basal plane, as compared to 0.09 Å in the unsubstituted cluster and 0.18 Å in $Fe_5C(CO)_{14}^{2-}$ [501].

The reaction of $Pt(C_8H_{12})_2$ with $Fe(CO)_5$ has been used to prepare a number of novel hexa- and hepta-metallic clusters, including $[Pt(CO)]_3[\mu\text{-}Fe(CO)_4]_3$ and $Pt_5(CO)_4(COD)_2[\mu\text{-}Fe(CO)_4]_2$ [both XRC]. Reaction of the latter with diphenylacetylene produced **115**, whereas phenylacetylene reacted to produce **88**[460].

Reaction of four equivalents of $(CpCr)_2(\mu\text{-}SCMe_3)_2S$ with $Fe_2(CO)_6(\mu\text{-}SPh)_2$ produced the cubanoid $(CpCr)_3(FeSPh)(\mu_3\text{-}S)_4$, but use of only two equivalents resulted in formation of the supercluster **116** [XRC], the largest iron-containing cluster reported in 1990[502].



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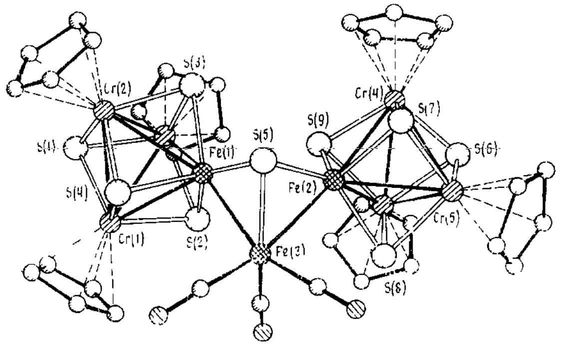
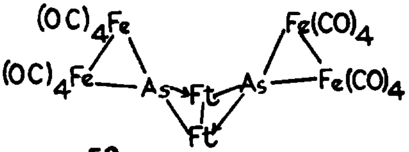


116

Theoretical studies of dissociation of CO on an iron(100) surface (modeled using an Fe_{12} cluster) have suggested that a four-fold site which allows both C and O to bridge between two surface Fe atoms was energetically optimum[503]. A study of benzene hydrogenolysis on an iron surface found that incorporation of carbide from the iron, to form toluene and xylenes, accompanied the intended hydrogenolysis reactions[504].

POST-SCRIPT: This 1990 review includes somewhat fewer references overall than the 1989 version. It is not clear whether this reflects diminished research activity in organoiron chemistry or random fluctuation.

Publishing habits of chemists in this research area remain rather consistent despite the several new journals dedicated to various aspects of organometallic chemistry. Thus, Journal of Organometallic Chemistry (97 citations) has maintained its numerical primacy, followed by Organometallics (84), Journal of the American Chemical Society (44), and Inorg. Chem. (39). All other journals together account for fewer than half of the papers cited.



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(Inadvertently omitted from Section 9a)

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