ORGANOIRON CHEMISTRY
Annual Survey for the Year 1985*

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CONTENTS

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LIST OF ABBREVIATIONS USED

acac	acetylacetonate, $(MeCO)_2CH^-$
An	any arene ring, such as benzene, C_6H_6
Ar	an aryl ring, such as naphthyl, $C_{10}H_7-$
bpy	2,2'-bipyridyl
COT	1,3,5,7-cyclooctatetraene
Cp	cyclopentadienyl, C_5H_5
Cp*	pentamethylcyclopentadienyl, C_5Me_5
DME	1,2-dimethoxyethane, sometimes called "glyme"
DMPE	1,2-bis(dimethylphosphino)ethane
DMPM	bis(dimethylphosphino)methane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPM	bis(diphenylphosphino)methane
Et	ethyl, C_2H_5-
Fp	cyclopentadienyldicarbonyliron, $CpFe(CO)_2-$
Fp'	cyclopentadienyl(carbonyl)(triphenylphosphine)iron
Fp*	(pentamethylcyclopentadienyl)dicarbonyliron
Ft	the tricarbonyliron group, $Fe(CO)_3$
HMP	hexamethylphosphorictriamide
L	a 2-electron donor ligand such as a phosphine
LAH	lithium aluminum hydride
M	any transition metal
Me	methyl, CH_3-
MTHF	2-methyltetrahydrofuran
NMP	N-methyl-2-pyrrolidone
Ph, ϕ	phenyl, C_6H_5-
Por	any porphyrin ligand coordinated as a dianion
PPN^+	$Ph_3P{=}N{=}PPh_3{}^+$
R	any unicovalent organic group such as methyl
TCNE	tetracyanoethene
Tf	trifluoromethanesulfonyl group, F_3CSO_2-
THF	tetrahydrofuran
X	any halogen

1. INTRODUCTION

In this Annual Review, I attempt to cover the organoiron chemistry reported in journals published during calendar year 1985. Organoiron compounds are those compounds which contain at least one C-Fe bond; however Fe-CN compounds are not included in this review, and properties and reactions of the simple iron carbonyls are not described exhaustively. Ferrocenes are treated in Annual Surveys by G. Marr and B. W. Rockett.

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

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

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

2. BOOKS AND REFERENCE WORKS

Parts B8 and B9 of the current Gmelin organoiron series have been published during 1985. These exahustively cover $^4LFe(CO)_3$ compounds, with ^4L being cyclohexadienes (Part B8)[1] and larger ring dienes (Part B9)[2]. Another useful new reference work is the volume, "Organometallic Compounds of Iron,"[3] which comprises the 2222 organoiron entries from the Dictionary of Organometallic Compounds, with structures, physical properties, Chemical Abstracts Registry Numbers, and key references.

A review of papers published during 1981-2 on the coordination chemistry of iron, which covers carbonyls and related species, appeared during 1985[4].

3. REACTIONS OF "NAKED" IRON ATOMS AND IONS

Reactions of Fe and Fe_2 with organic substances in matrices have been studied. These species reacted with methane in an argon matrix to form $Fe(CH_4)$ and $Fe_2(CH_4)$. The latter was inert to irradiation, but the former underwent photodissociation and rearrangement to MeFeH[5]. With ethene, pi-complexes $Fe(C_2H_4)_n$ (n > 2) and $Fe_2(C_2H_4)_{1,2}$ resulted, along with species in which atomic iron interacts with ethene through a hydrogen atom. The latter species showed a photoreversible C-H insertion process[6]. Analogous chemistry was found between atomic iron and ethyne (Eq. 1)[7].

$$Fe + HC{\equiv}CH \longrightarrow Fe{\cdots}HC{\equiv}CH \xrightarrow{h\nu} H{-}Fe{-}C{\equiv}CH \qquad (1)$$

Monatomic iron reacted with diazomethane to produce $Fe{=}CH_2$ (Fe=C stretch at 624 cm^{-1} compared to 520 cm^{-1} for $HFe{-}CH_3$). At higher iron concentrations, $(N_2)Fe_2CH_2$ formed[8].

Gas phase studies have also continued to produce interesting results. Reactions of Fe^+ with alkanes and alkenes eventuated in formation of $Fe(alkene)^+$ species, as indicated by ion cyclotron resonance and Fourier transform mass spectrometric (FTMS) studies. These underwent deuterium exchange with C_2D_4[9]. Fe^+ reacted with methyl nitrite by insertion into the weak O-N bond, followed mostly by NO loss. From ligand displacement studies, the strength of the Fe^+-NO interaction lies between Fe^+-H [58(2) kcal/mol] and $Fe^+{-}C_2H_4$ [34(2) kcal/mol][10]. Fe^+ appeared to cause a nitro-to-nitrite rearrangement in nitromethane[10] and higher nitroalkanes[11]. Otherwise, reactions of the latter appeared to involve predominant insertions into the N-O and C-C bonds[11].

Collision-induced dissociation of CO from $Fe(CO)_n^-$ gave Fe^-, which could be isolated by double resonance ejection. Bracketing suggested a proton affinity of 339(3) kcal/mol, and thus a D[Fe-H] of 30(3) kcal/mol. Fe^- reacted with $Fe(CO)_5$ by dissociative electron transfer to form $Fe(CO)_4^-$ [12].

Reactions of $FeCH_2^+$ with organics in the gas phase have been studied, principally by FTMS. The principal reaction channel with alkanes involved C-H bond insertion, and methane and ethane were unreactive[13]. With cyclopropane and cyclobutane, insertion into strained C-C bonds to form metallacycloalkanes was the principal initiating step, which was followed by various ring cleavage or expansion reactions or hydrogen losses[14]. Ethene reacted with $FeCH_2^+$ to form Fe^+ and C_3H_6. The occurrence of metathesis-like reactions was indicated by formation of $FeCH_2^+$ from $FeCD_2^+$ and ethene and by formation of $FeC_2H_4^+$ from propene. Reaction of $FeCH_2^+$ with butadiene yielded $CpFe^+$ and $CpHFe^+$, from which a $D(Fe^+-Cp)$ value of at least 93 kcal/mol was deduced[15].

CH_3Fe^+ did not react with ethene; higher alkenes reacted with elimination of methane to give allyliron species. With ethyne, insertion and dehydrogenation resulted in formation of $C_3H_3Fe^+$. With butadiene, the first-formed $C_5H_9^+$ likewise underwent hydrogen loss to form $CpFe^+$ [16].

The bimetallic ion VFe^+ resulted from reaction of V^+ with $Fe(CO)_5$, followed by collision-induced losses of CO. This species was unreactive toward alkanes and n-alkenes, but reacted with some cycloalkenes. Cyclohexene or benzene reacted to form $VFe(C_6H_6)^+$; cycloheptatriene gave $VFeCH_2^+$ [17]. Reactions of $CoFe^+$ were somewhat analogous[18].

Fe(alkene)$^+$ reacted with ferrocene and nickelocene to give $FeMCp_2^+$ (M = Fe, Ni); collisional activation of the latter gave predominantly Cp_2Fe^+. Reaction of $MFeCp_2^+$ (M = Fe, Co, Ni) with additional ferrocene gave mostly the condensation products, $MFe_2Cp_4^+$ [19].

Clusterification resulted from reactions of $Fe(CO)_n^+$ (n = 0, 1, 4) with $Fe(CO)_5$, with $Fe_6(CO)_{18}^+$ being the highest cluster observed. Reactivities of the various intermediate clusters were determined. $Fe_2(CO)_3^+$, $Fe_3(CO)_{5-6}^+$, and $Fe_4(CO)_{8-9}^+$ were comparatively unreactive intermediates, which was rationalized on the basis of multiple Fe-Fe bonding or 4-electron donation by carbonyls in these species[20].

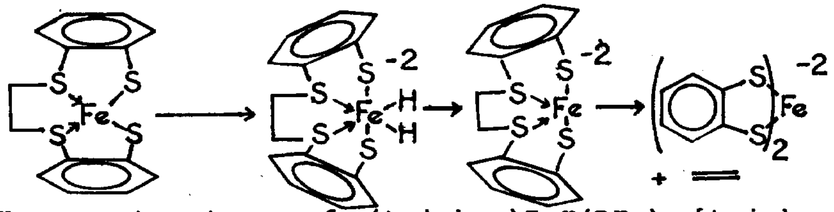
4. COMPOUNDS WITH η^1-CARBON LIGANDS

a. Hydrido-, Alkyl-, and Aryliron Compounds

Reaction of diarylmagnesium reagents, Ar_2Mg, with iron(II) halides has been reported to produce ArFeX, which could be stabilized by coordination with 2,2'-bipyridyl[21]. The analogous dimesityliron was reported to add to alkynes, forming dialkenyliron compounds, $Fe[CR{=}CRAr]_2$, stabilized by coordination to solvent or amine ligands[22]. The product $Li_3(Ar_3FeN_2)$ from reaction of lithium trinaphthyliron[0] with nitrogen has been isolated and characterized by magnetic and IR methods[23].

Reaction of iron(II) acetate with dimethylmagnesium in the presence of DMPM gave *cis*-$FeMe_2(DMPM)_2$, whereas the larger benzyl groups gave the trans analog. An X-ray crystal structure of Fe(DMPM)$_3$ showed a square pyramidal structure with a unidentate DMPM ligand attached to the axial site[24]. In contrast, the crystal structure of Fe(F$_2$PNMePF$_2$)$_4$ revealed a distorted trigonal bipyramid with the single bidentate ligand bridging axial-equatorial positions[25]. Methylation of (DMPE)$_2$FeX$_2$ gave *cis*-Fe(DMPE)$_2$Me$_2$[26]. The analogous alkylation of (1,4-diaza-1,3-diene)$_2$FeCl$_2$ with Grignard reagents or (C$_4$H$_6$)Mg·2 THF gave species which efficiently catalyzed diene cyclodimerization. Use of chiral dad ligands gave good chirality transfer in formation of 4-vinylcyclohexene[27].

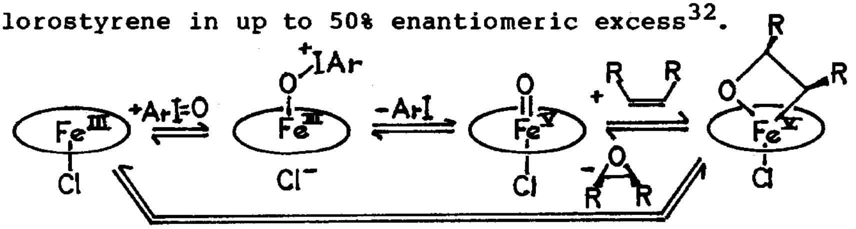
Reduction of Fe(SC$_6$H$_4$SCH$_2$CH$_2$SC$_6$H$_4$S) with LiBEt$_3$H (Eq. 2) gave an apparently unstable dihydride, which reductively eliminated dihydrogen. The resulting Fe[0] species reductively eliminated ethene from the ligand to form the *o*-benzenedithiolate product[28].



(2)

An X-ray structure of (triphos)FeH(BH$_4$) [triphos = CH$_3$C(CH$_2$PPh$_2$)$_3$] indicated a hexacoordinate iron, achieved by bonding to one terminal hydride and two bridging hydrides of the BH$_4$ moiety. The Fe-B distance was 2.16(2) A[29]. Reaction of (DPPE)$_2$FeH$_2$ with one equivalent of strong acid under hydrogen produced *trans*-(DPPE)$_2$Fe(η^2-H$_2$)H$^+$, which was stable to dihydrogen loss up to 50°, and which was characterized by X-ray crystallography of the fluoroborate salt. The dihydrogen ligand was symmetrically coordinated, with Fe-H distances of about 1.54 A[30].

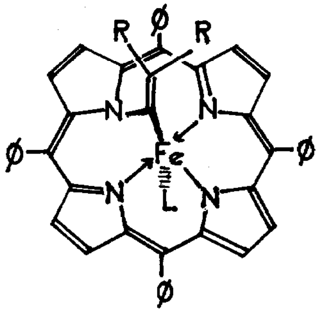
Kinetic studies of the competitive epoxidation of alkenes by C$_6$F$_5$IO in the presence of catalytic PorFeCl [Por = tetrakis(pentafluorophenyl)porphyrin] have provided evidence for the intermediacy of a ferroxetane intermediate (Eq. 3)[31]. If this is also the case for *in vivo* epoxidations by cytochrome-P450 enzymes, then a new area of biological organometallic chemistry will open up. Use of synthetic iron-porphyrins having chiral groups on the side chains as epoxidation catalysts gave asymmetric epoxidation of *p*-chlorostyrene in up to 50% enantiomeric excess[32].



(3)

Substituent effects in formation of σ-aryliron(III)hemoglobin products upon reaction of diazonium salts with hemoglobin have been studied[33]. Stable alkyliron products were not found upon reaction of iron(III)porphyrins with methyl-magnesium species; the initial products were reduced Fe(II) porphyrins, which in turn formed magnesium porphyrins[34]. Study of several new aryliron(III) porphyrins has uncovered some containing high spin (S = 5/2) iron[35]. Na^+_2 $[Fe(phthalocyanine)]^{2-}$ displaced Cl^- from $PhSCH_2Cl$ to form Na^+ $[PhSCH_2Fe(phthalocyanine)]^-$ [36]. Several σ-bonded alkyl- and aryliron porphyrins formed nitrosyls on reaction with NO. The products, (Por)Fe(NO)R, were characterized spectroscopically as compounds of Fe(II)[37].

Extensive NMR studies have been carried out on the previously reported compounds, **1**, having a diarylvinylidene group inserted into the Fe-N bond of various porphyrins[38, 39].



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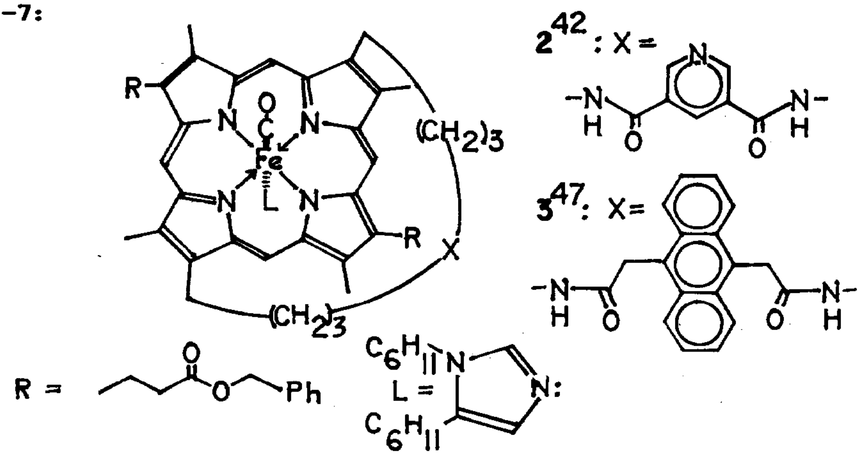
b. Iron Monocarbonyls, e.g. $L_4Fe(CO)$

Two groups have reported ^{57}Fe NMR data for carbonylmyoglobin[40, 41]. Synthetic porphyrins continue to be devised and synthesized in order to study various effects on carbon monoxide and oxygen binding. Some of the newer examples are portrayed as compounds **2–7**:



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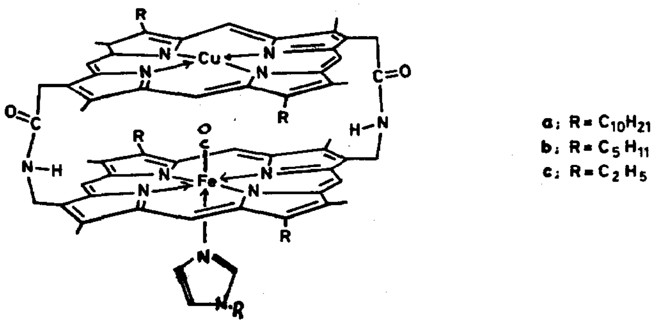

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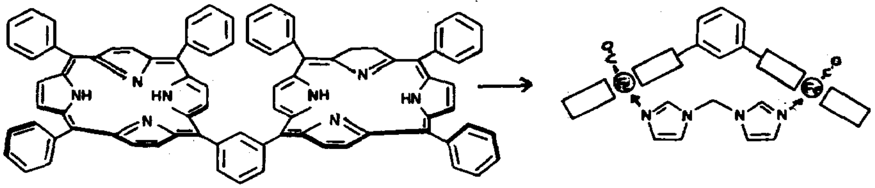

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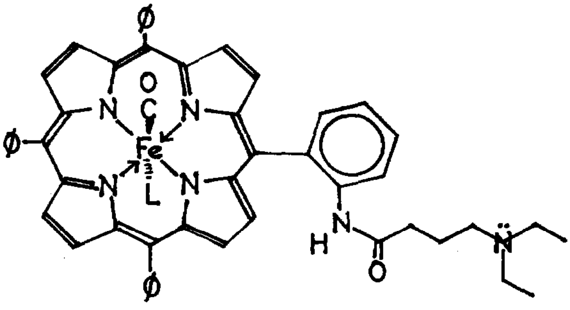
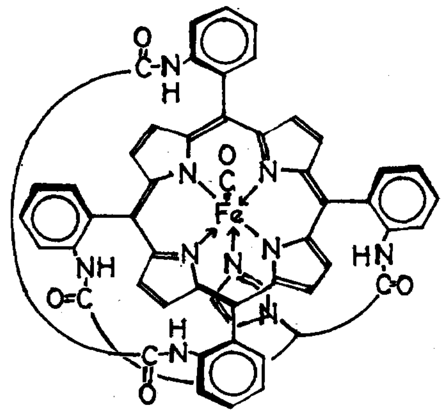


7[45]



The electrochemistry of (tetraphenylporphyrin)FeCSe has been studied, with the result that the CSe, unlike CO, remains coordinated even after oxidation of the iron[48]. Porphyrins bearing axial isonitrile ligands have been studied by IR and ^{13}C NMR[49].

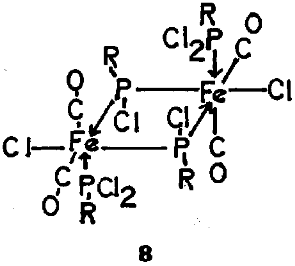
Studies of phthalocyaninatoiron(II) carbonyl complexes have also been reported. These have included equilibrium and rate studies of competition between pyridine, CO, and solvent DMSO for the axial coordination sites[50], and studies of isonitriles as axial ligands[51]. A related (tetraazamacrocycle)iron(II) compound has been used to facilitate transport of CO across a liquid membrane[52].

Bis(*o*-benzenedithiolato)iron(II) takes up CO readily to form a monocarbonyl, and then slowly to form a dicarbonyl[28]. Likewise (DMPM)Fe mono- and dicarbonyls have been characterized[24]. $FeCl_2$ reacted with CO and triethylphosphite in the absence of reducing agents to form $\{Fe(CO)[P(OEt)_3]_2Cl_2\}_2$; in the presence of active metal reductants, mixed Fe(0)-phosphite-carbonyls resulted[53].

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

PRDDO calculations on $(H_3N)_4Fe(CO)_2{}^{2+}$ favored the trans isomer over the cis because of poor back-bonding (which would favor the cis isomer)in this Fe(II) compound[54]. The oxidative addition product **8** (X-ray structure, Fe-Fe distance 3.56 Å) was among the products of reaction of $MePCl_2$ with nonacarbonyldiiron[55].

An electron-diffraction study of gaseous $Fe(CO)_2(NO)_2$ showed the expected tetrahedral geometry, with Fe-N and Fe-C distances of 1.688(3) and 1.883(3) Å, respectively[56]. An X-ray crystallographic structure of $(Ph_3P)_2Fe(CO)_2(NO)^+$ BF_4^- showed a long Fe-P bond [2.280(3) Å)] as compared to the hydride $(Ph_3P)_2FeH(CO)(NO)$ [2.182(7) Å]; a good correlation was found between the Fe-P bond lengths and the CO stretching frequencies in a series of 22 iron compounds containing both carbonyl and triphenylphosphine ligands[57]. Reduction of **9** with sodium amalgam or with sodium borohydride followed by oxygen resulted in ligand coupling to form the tetrathiooxalate compound **10** (X-ray)[58].



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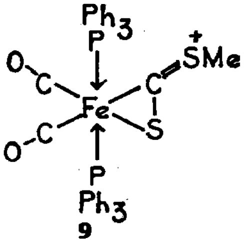

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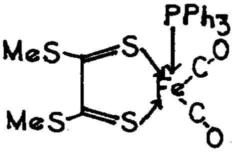


10

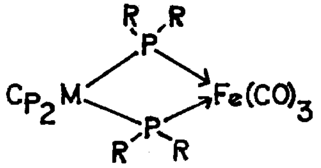
Synthesis of a series of cations $RFe(CO)_2(PMe_3)_2L^+$ having chiral phosphines L resulted in diastereotopic trimethylphosphine ligands with detectible P-P couplings; the configurations of the compounds were determined using ^{31}P and proton NMR[59].

A mixture of two stereoisomers of $(diars)Fe(CO)_2(COMe)(PMe_3)^+$ BF_4^- [diars = *o*-phenylenebis(dimethylarsine)] underwent decarbonylation at 150° in the solid state to give the methyliron product having the methyl group cis to the diars and trimethylphosphine ligands (X-ray)[60]. The similar *o*-phenylenebis(dimethylphosphine) compound, $(pdmp)Fe(CO)_2I(COMe)$, also decarbonylated thermally in solution, and treatment with halide acceptors gave migration of methyl to iron with halide loss, forming $(pdmp)Fe(CO)_3Me^+$. The methyl migration was reversed on treatment of the latter cation with trimethylphosphite; however, the phosphite displaced iodide from $(pdmp)Fe(CO)_2IMe$, and no methyl migration was observed[61]. A study of the carbonylation of $(Me_3P)_2Fe(CO)_2IMe$ using labelled CO indicated formal methyl migration in formation of the acetyl product[62].

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

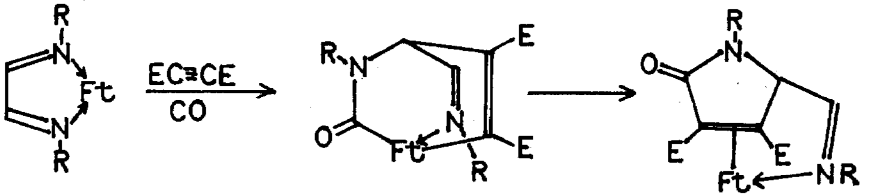
A theoretical study of stabilization of phosphinophosphinidenes, R_2P-P, (and related phosphinidenes and nitrenes) through transition metal complexation indicated that the $Fe(CO)_3$ group might provide optimum stabilization[63].

The entire series of compounds **11** (M = Group 4 metals Ti, Zr, and Hf) has been prepared by two groups of workers, using complementary methods. The Ti and Zr compounds (R = cyclohexyl) resulted from reaction of Cp_2MCl_2 with $Li_2[Fe(CO)_3(PR_2)_2]$[64]; the Hf analog (R = Et) from $Cp_2Hf(PR_2)_2$ with nonacarbonyldiiron[65].



11

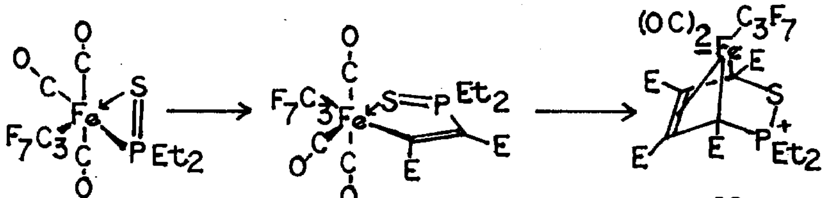
Photoelectron spectra of $(1,4\text{-diazadiene})Fe(CO)_3$ complexes show that replacement of two CO's of $Fe(CO)_5$ by the diazadiene ligands significantly lowers the ionization potential[66]. Reaction of a $(diazadiene)Fe(CO)_3$ with the electrophilic dimethyl acetylenedicarboxylate (DMAD) gave a bicyclic product (Eq. 4), whose structure was deduced from X-ray crystallographic study of the more stable trimethylphosphite-containing analog[67]. Another remarkable insertion reaction of a dialkyl diacetylenedicarboxylate is portrayed in Eq. 5[68].



R = isopropyl, E = CO_2Me

12

(4)



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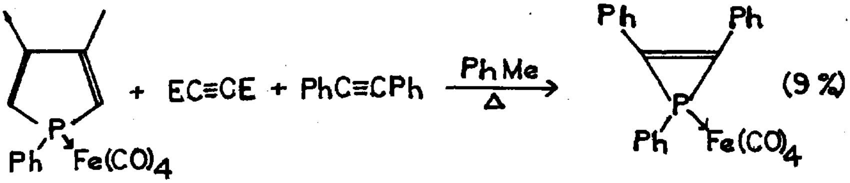
(5)

The full paper on reactions of alkyleneditriflates with $LFe(CO)_3^{2-}$ nucleophiles [L = CO, Ph_3P, or $(MeO)_3P$] has now appeared[69]. Included are isolation and characterization of a number of examples of ferracyclopentanes, including an X-ray structure of $(CH_2)_4Fe(CO)_3PPh_3$, in which the phosphine ligand was shown to be trans to a CH_2 group around an octahedral iron. Liquid SO_2 selectively inserted into the Fe-C bond trans to the phosphine[69].

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

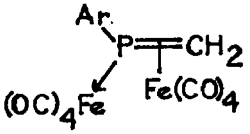
Extended Huckel and *ab initio* calculations on phosphinidene and phosphirene complexes have been carried out, and the results have been compared with photelectron spectral data. Species on which calculations were done included $HP{=}Fe(CO)_4$[70].

Many new examples of (phosphine)$Fe(CO)_4$ complexes having novel phosphine ligands have been prepared. The ligands include $(C_6H_{11})_2NPH_2$ and N-phosphino-2,2,6,6-tetramethylpiperidine[71], *t*-butylphenylphosphine (the complex obtained by reaction of $Cl_2PhPFe(CO)_4$ with *t*-butyllithium)[72], and diphosphadicobaltatetrahedrane clusters[73]. A phosphole-$Fe(CO)_4$ was converted to a phosphirene-$Fe(CO)_4$ by a cycloaddition-cycloreversion sequence (Eq. 6)[74]. Both inversional stereoisomers of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene gave the same $Fe(CO)_4$ complex on reaction with nonacarbonyldiiron[75].



(6)

The unsaturated phosphine, $ArP{=}CH_2$ (Ar = 2,4,6-tri-*t*-butylphenyl), gave predominantly the P-coordinated $Fe(CO)_4$ complex on reaction with one equivalent of nonacarbonyldiiron; with two equivalents, a bis[$Fe(CO)_4$] complex, **14**, resulted[76]. The more complex methylenephosphine in **15a** was also inferred by IR to be axially coordinated[77]. This contrasted with the previously reported equatorial coordination of the still more hindered **15b**.



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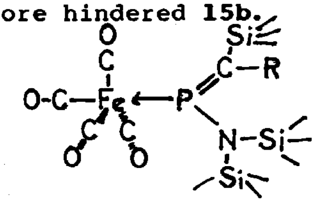


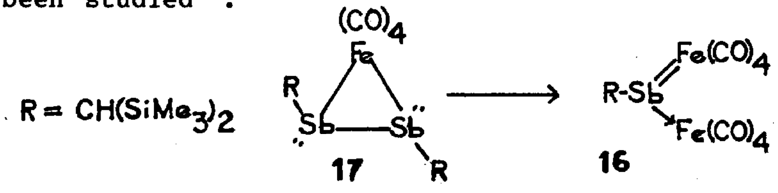
15 a, R = H

b, R = $SiMe_3$

Axial-equatorial isomerization in the series $R_3PnM(CO)_4$ [R = Ph, Me and others; Pn = P, As, and Sb; M = Fe, Ru, and Os] has been discussed. Several compounds showed both axial and equatorial isomers in solution, based on IR data, but ^{13}C NMR indicated very rapid interconversion. Of the group 8 metals, iron showed the least tendency toward formation of equatorial isomers. The ligands' tendencies to give equatorial isomers was in the order Sb>As>P and Ph>Me[78]. ^{13}C NMR studies of a series of R_3P-$Fe(CO)_4$ compounds showed good correlation of the carbon resonances with the donor-acceptor properties of the ligands, but some puzzling trends accompanied successive substitution of CO by phosphines[79].

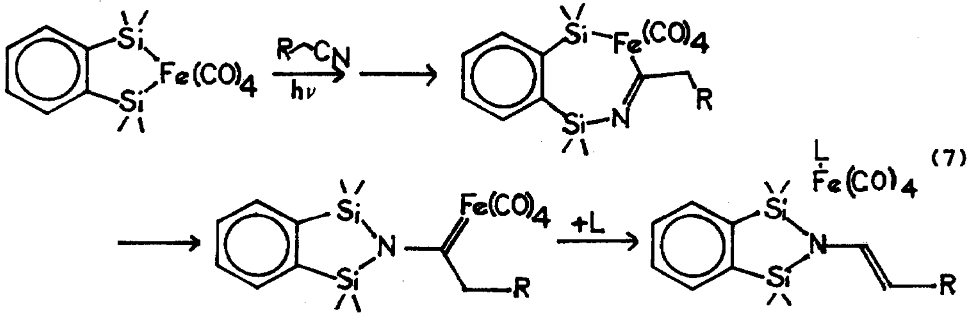
The reaction of the triphosphine, $Me_2PCH_2P(Me)CH_2PMe_2$, with nonacarbonyldiiron under various conditions led to a number of products, including a tris[$Fe(CO)_4$] complex (X-ray), a chelate with the terminal phosphine groups coordinated to an $Fe(CO)_3$ group and the internal to an $Fe(CO)_4$, and a number of cluster compounds[80]. 1,2,3-triphenyl-1,2,3-triphosphaindane likewise formed a 1,3-bis[$Fe(CO)_4$] complex as principal product, along with several clusters, on reaction with iron carbonyls[81].

An unstable compound believed to be **16** was among the products of reaction of nonacarbonyldiiron with the distibene-$Fe(CO)_4$ complex, **17**[82]. The closed diferrastibirane isomer of **16** was stable and is discussed in Section 9a. Reaction of DPPM and DPPE dioxides and several homologs and arsenic analogs with $I_2Fe(CO)_4$ has been studied[83].



^{13}C NMR results have been reported for $HFe(CO)_4^-$ and for $H_2Fe(CO)_4$. Axial-equatorial interconversion for the latter was estimated to require about 8.1 kcal/mol, based on variable temperature results[79]. Molecular orbital calculations on $HFe(CO)_4^-$ and $(OC)_nFeCHO^-$ (n = 3, 4), including potential energy curves for hydride migrations, have appeared[84, 85]. The results underscored the importance of alkali metal coordination to a carbonyl ligand of $HFe(CO)_4^-$ in inducing metal-to-carbon hydride migration. Metal coordination to the formyl oxygen in the product, $(OC)_3FeCHO^-$, was said to stabilize the HOMO and to reduce its C-H antibonding character[85]. The crystal structures of analogous formyl and acetyl salts, *trans*-$(PhO)_3PFe(CO)_3C(=O)R$ (R = H, Me), prepared from $(PhO)_3PFe(CO)_4$ with $(\textit{i}\text{-}PrO)_3BH^-$ and MeLi, respectively, have been published[86]. They were quite similar except for the shorter formyl C=O bond [1.166(4) Å compared to acetyl 1.226(5) Å].

The ^{29}Si NMR spectra of a series of $R_3SiFe(CO)_4H$ and $(R_3Si)_2Fe(CO)_4$ compounds having R = Cl and Me and mixtures thereof have been reported[87]. A chelate bis(silyl)Fe(CO)$_4$ complex has been used to convert nitriles into bis(silyl)enamines, as outlined in Eq. 7[87a].

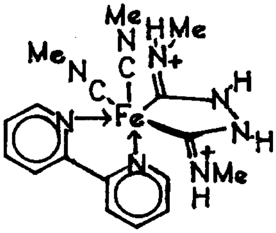


(7)

Synthesis of several ferracyclopentanes by reaction of $Fe(CO)_4^{2-}$ with 1,4-ditriflates has been reported in full[69]. Ketoferracycles [from $-C(=O)-Fe(CO)_4-$ group insertion into strained organics] were converted into diketones upon oxidation with $CuCl_2$[88]. Reaction of $Na_2Fe(CO)_4$ with C_6F_5COCl gave $(C_6F_5)_2Fe(CO)_4$ and $(C_6F_5)(C_6F_5CO)Fe(CO)_4$, and analogous results were also obtained with perfluorobutanoyl chloride[89].

f. Carbene Complexes $R_2C{=}FeL_4$

Little has been reported in this area in 1985. The chemistry of the carbene complex 9[58] has already been mentioned. In addition, addition of hydrazine to the isonitrile ligands of $(bpy)Fe(CNMe)_4^{2+}$ to form the bis(carbene)complex, **18**, has been reported[90].



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

MINDO calculations on iron pentacarbonyl in trigonal bipyramidal and square pyramidal configurations and in intermediate configurations along a pseudorotational path have uncovered no barrier to configurational interconversion[91]. Hartree-Fock Slater calculations on protonation of $Fe(CO)_5$ and $Fe(CO)_4^{2-}$ in comparison with several other metal carbonyls have been reported[92]. Photoelectron spectroscopic results on several isonitrile compounds, $(OC)_4FeCNR$, have suggested that the isonitriles are weaker σ-donors, better π-donors, and weaker π-acceptors than CO[93].

Flash photolysis studies of $Fe(CO)_5$ in benzene-d_6 have provided IR evidence of formation of $(C_6D_6)Fe(CO)_4$, which reacted with CO or $Fe(CO)_5$ through a highly reactive intermediate, possibly a spin isomer[94]. The isomerization of $ArCH_2CH{=}CH_2$ to $ArCH{=}CHCH_3$ using $Fe(CO)_5$ and light has been studied[95]. Use of zeolites in the photoassisted $Fe(CO)_5$-catalyzed isomerization of alkenes has been found to result in altered selectivity[96]. A mechanistic study of $Fe(CO)_5$-catalyzed photohydrogenation of 1-octene has implicated $HFe(CO)_4^{\bullet}$ radicals, formed from the primary photoproduct $Fe(CO)_4$, as the active hydrogenation promoters[97].

Iron pentacarbonyl reacted with the dialkylborane, 9-H-9-BBN, at high temperatures to form a complex mixture of 9-alkyl-9-BBN products, a reaction which has been proposed as a model for the Fischer-Tropsch synthesis[98].

Reactions of $Fe(CO)_5$ with anions in the gas phase have received considerable attention during 1985. Hydride ion reacted at 40% of the collision-limited rate, to produce $HFe(CO)_{3,4}^-$. The hydride affinity of $Fe(CO)_5$ was determined to be 56(4) kcal/mol[99]. Binding energies of a series of anions with $Fe(CO)_5$ (to form acylirontetracarbonyl anions) correlated linearly with the proton affinities and the acetyl cation affinities of the anions[100].

Rates of reaction of $Fe(CO)_5$ with methoxide ion in solution were found to be solvent-dependent; reaction with hydroxide was slower and eventuated in formation of $HFe(CO)_4^-$ by an intramolecular decarboxylation reaction[101]. Introduction of $Fe(CO)_5$ into the phase-transfer system Ph_3P-CH_2Cl_2/aq. $NaOH/(Bu_4N)_2SO_4$ generated tetracarbonylferrate dianion in the organic phase, with

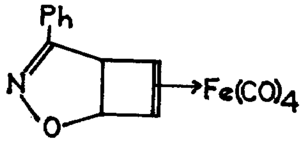
$Ph_3PCH_2Fe(CO)_4$ as the final product[102].

5. η^2-ALKENE AND η^3-ALLYL COMPLEXES

Compounds **12** and **13**, previously mentioned, contain η^2-alkene-iron groupings, derived in each case from insertion of dimethyl acetylenedicarboxylate into simpler organometallics. Compounds **14** and **17** represent η^2-$Fe(CO)_4$ complexes of highly reactive hetero-alkenes.

Simple η^2-complexes of ethene resulted when $LFe(CO)_3{}^{2-}$ salts [L = CO, PPh_3, and $P(OMe)_3$] were allowed to react with the ditriflate, $TfOCH_2CH_2OTf$. An X-ray structure of the triphenylphosphine compound was reported[69]. A mechanistic study of ethene hydrogenation in the gas phase using $(C_2H_4)Fe(CO)_4$ as photocatalyst confirmed the key catalytic role of the coordinatively unsaturated $(C_2H_4)Fe(CO)_3$; recombination of the latter with CO showed an activation barrier of 5.5 kcal/mol. The rate determining step in the catalytic cycle was judged to be a concerted insertion of ethene into a Fe-H bond[103].

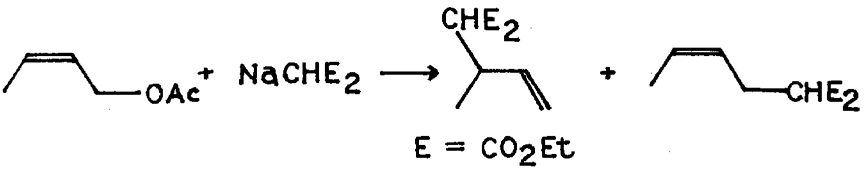
The cyclobutene complex **19** resulted from reaction of the free ligand with nonacarbonyldiiron for a short time. The principal (after five hours the only) product was 2-phenylpyridine, from deoxygenation and rearrangement of the starting material[104].



19

An $Fe(CO)_4$ complex was also obtained from reaction of 1,5-hexadiene with nonacarbonyldiiron[105].

Reaction of (*cis*-2-butenyl acetate)$Fe(CO)_4$ with sodiodiethylmalonate gave the two possible coupled products (Eq. 8) in nearly equal yield. However, the use of catalytic nonacarbonyldiiron to promote coupling of the free *cis*-2-butenyl acetate with sodiodiethylmalonate gave the products in a significantly different (7:3) ratio, suggesting that the catalytic process does not only involve the "obvious" route through the alkene-$Fe(CO)_4$ and $(allyl)Fe(CO)_4{}^+$ intermediates[106].

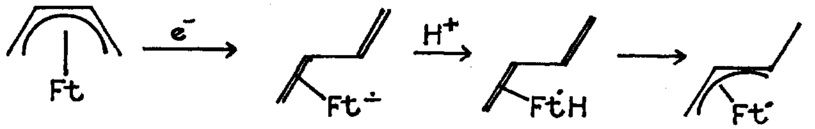


(8)

Interaction between allyl anion and Fe^{2+} has been studied theoretically, using a pseudopotential *ab initio* method[107]. Theory, in this case extended Huckel calculations, has also been applied to cyclohexenyl- and cyclooctenyl-$Fe(CO)_3^+$ cations, with the conclusion that the "agostic" Fe-H-C interaction in these species is best considered as an open system with little direct Fe-C bonding[108].

The negative-ion mass spectra of $(C_3H_5)Fe(CO)_3X$ [X = Cl, Br, I] have been studied[109]. Reaction of various allylic halides with $Fe(CO)_3NO^-$ gave neutral $(allyl)Fe(CO)_2NO$ complexes. Additional such complexes, having 1-acylmethyl groups, could be obtained by reaction of alkyl halides with $Fe(CO)_3NO^-$ in the presence of 1,3-dienes. The allyliron complexes served as allylating agents toward allylic halides (giving 1,5-dienes) and acyl halides (giving allylic ketones)[110].

Irradiation of cold pentane solutions of $Fe(CO)_5$ and 2,3-dimethyl-1- or -2-butene gave intense ESR spectra of $(\eta^3\text{-}C_6H_{11})Fe(CO)_3$ radicals. The $(2\text{-isopropylallyl})Fe(CO)_3$ radical rearranged at -80° to the isomeric $(1,1,2\text{-trimethylallyl})Fe(CO)_3$ [111]. Cyclic voltammetric reduction of $(butadiene)Fe(CO)_3$ in THF at -20° in the presence of acid or alkylating agents gave allylic radicals as in Eq. 9[112].



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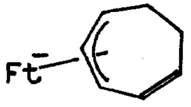
Reaction of $(\eta^5\text{-cycloheptadienyl})Fe(CO)_2^-$, **20**, with CO gave the (presumably η^3) $(cycloheptadienyl)Fe(CO)_3^-$ anion, **21**, which underwent acetylation to give (*exo*-5-acetylcyclohepta-1,3-diene)-tricarbonyliron[113]. Treatment of **20** with acetyl chloride first, followed by CO, gave a different result, to be described with other reactions of η^5-dienyl complexes.

TCNE added across the ends of one allyl ligand in $(C_3H_5)_2Fe(CO)_2$ to form the 16-electron complex, $(\eta^3\text{-allyl})(3,3,4,4\text{-tetracyanocyclopentyl})$dicarbonyliron, which readily added triphenylphosphine[114]. A bis(allyl)dicarbonyliron compound, **22**, resulted (19%) from ligand coupling during reaction of $(2,3\text{-dimethylbuta-1,3-diene})_2FeCO$ with CO, along with $(C_6H_{10})Fe(CO)_3$[115].



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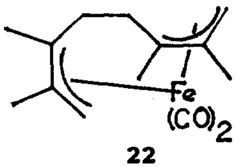

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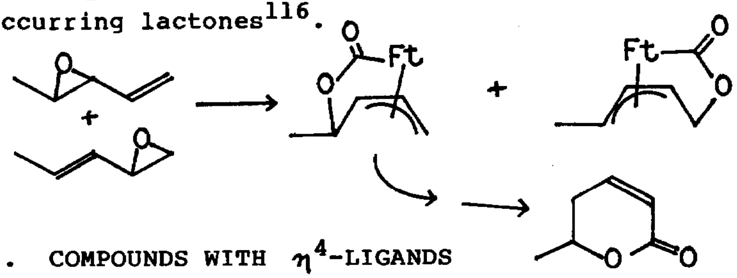
(Allyl)tricarbonyliron lactone complexes have found synthetic utility (Eq. 10) as intermediates in synthesis of naturally occurring lactones[116].



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6. COMPOUNDS WITH η^4-LIGANDS

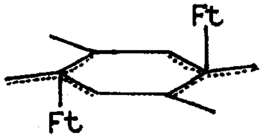
a. Trimethylenemethyl Complexes

Reaction of 1,4-bis(bromomethyl)-2,5-dimethylbenzene with nonacarbonyldiiron gave the *trans*-bis(trimethylenemethyl) complex, **23** (X-ray structure)[117]. Some features of the mass spectra of **23** and related compounds suggested trans ⟶ cis isomerization upon electron impact[118]. Electron-rich $[C(CH_2)_3]Fe(PR_3)_3$ complexes resulted from reduction of $FeCl_2(PR_3)_2$ and $H_2C{=}C(CH_2Cl)_2$ with magnesium in the presence of additional PR_3. The compounds were oxidized by silver ion, and an X-ray crystal structure of the 17-electron tris(trimethylphosphine) cation was described[119].

b. Complexes of Acyclic Dienes, including Heterodienes

Photoelectron spectra of some (1-azabutadiene)tricarbonyliron complexes have been determined and interpreted through use of semi-empirical MO calculations. The involvement of the nitrogen's lone pair in bonding was discussed[120]. A family of 1-oxabutadiene complexes, (benzylideneacetone)$Fe(CO)_2L$ [L = CO and various phosphite and phosphine ligands] has been studied by ^{13}C NMR spectroscopy. The compounds containing the more electron-donating phosphorus ligands, unlike the tricarbonyl compound, were not fluxional at 32°, and the carbons directly bonded to iron showed significant upfield shifts with phosphorus introduction. These effects were interpreted as reflecting increased population of the oxadiene LUMO in the phosphorus-containing compounds[121].

(Diene)tricarbonyliron complexes could be obtained (along with hydrocarbons from reduction of the C-X bond) by reaction of allylic halides and phosphates with $K_2Fe(CO)_4$. For example, geranyl bromide, $Me_2C{=}CH(CH_2)_2CMe{=}CHCH_2Br$, gave the complex **24**[122]. Use of the more conventional nonacarbonyldiiron gave tricarbonyliron complexes of 2,4-hexadiene[104] and of 3-vinyl-1,5-hexadiene[123]. The product of the latter reaction was cationically polymerized to produce a polymer containing dienetricarbonyliron groups. When



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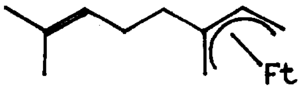

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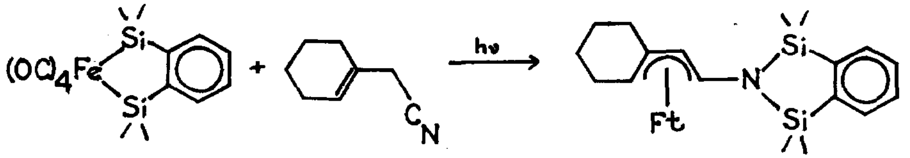
doped with iodine, this and related polymers showed significant conductance[123]. An $Fe(CO)_3$ complex of the 1,4-diene unit of trans-1,4,9-decatriene resulted from photochemical reaction of the triene with pentacarbonyliron. Treatment with Ph_3C^+ BF_4^- then $NaBH_4$ resulted in isomerization to (2-5η-2,4,9-decatriene)tricarbonyliron[124].

Use of allylic nitriles in the reaction shown as Eq. 7 produced a different outcome, the products being complexes of (disilylamino)dienes (Eq. 11)[87a].



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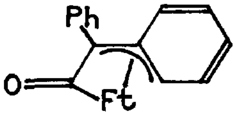
An X-ray structure of (α-methylstyrene)tricarbonyliron has been reported[125]. A single-crystal neutron diffraction structure of (diphenylketene)$Fe(CO)_3$, **25**, has been interpreted in terms of [η^3-benzyl + σ-acyl] coordination of the organic ligand[126].



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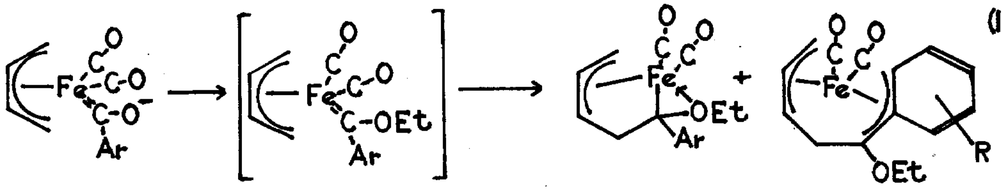
(Butadiene)tricarbonyliron was found to absorb thermal electrons in a flowing afterglow apparatus to form radical-anions $(C_4H_6)Fe(CO)_n^-$ [n = 3,2,1], the amount of CO dissociation increasing with increasing electron energy. The monocarbonyl added H_2 and exchanged up to four hydrogens with D_2[127]. There appear to be similarities between this chemistry and the solution-phase reduction of the butadiene complex (Eq. 9)[112].

Condensation reactions of (MeCH=CH-CH=CH-CH=O)$Fe(CO)_3$ with active methylene compounds have been further studied. In some cases, the $Fe(CO)_3$ group migrated readily into conjugation with the newly introduced electron-withdrawing group[128].

Nucleophilic attack on simple (diene)tricarbonyliron complexes has continued to draw attention. Benzhydryllithium added principally to an internal position of diene complexes to give a homoallylic iron tricarbonyl anion, whose quenching reactions have been studied using CF_3CO_2D. The labelling patterns observed indicated transient ferracyclobutane intermediates[129]. In contrast to the "harder" carbanions studied by the Semmelhack group, aryllithium reagents have been found to add to a carbonyl ligand of (butadiene)tricarbonyliron; interception of the resulting acylmetallate with triethyloxonium fluoroborate gave two types of products (Eq. 12)[130]. Both types were isomers of the ethoxyarylcarbene complexes presumed to have initially formed. The mass spectra of these product types have been studied[131].



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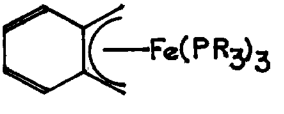
c. Complexes of Exocyclic Dienes

(*o*-Xylylene)triphosphineiron complexes, **26**, resulted from reaction of $FeCl_2(PR_3)_3$ with magnesium and 1,2-bis(chloromethyl)benzene. Yields were in the range 33-45%[119].

Several papers have extended the chemistry of iron tricarbonyl complexes derived from tetramethylidenebicyclo[2.2.2]octene, **27**, and related species. UV photoelectron spectra of *exo*- and



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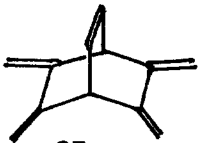
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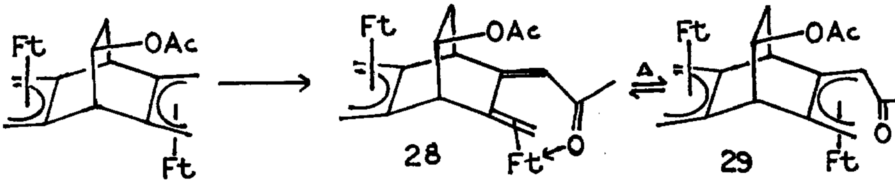
endo-tricarbonyliron and *exo*-,*exo*- and *exo*-,*endo*-bis(tricarbonyliron) complexes have been reported and interpreted with the help of *ab initio* calculations[132]. Acetylation of an acetoxy-substituted diiron derivative proceeded with high regio- and stereoselectivity, as shown in Eq. 13. The structure and absolute configuration of (-)-**29** (from optically pure starting material) were ascertained by X-ray crystallography[133]. The tri-

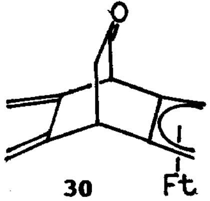


(13)

carbonyliron group anti to the etheno bridge in the pentaene analog of **28** was selectively removed upon mild oxidation. The facial selectivity in Diels-Alder reactions of the free diene units of the product and its Z isomer was found to depend upon the dienophile[134]. Similarly, the stereoselectivity of reduction of the ketone **30** depended upon the hydride reagent. Attack from the coordinated side was always preferred, with the degree of preference being $LiBHEt_3 > LiAlH_4 > HAl(OCH_2CH_2OMe)_2$[135].

d. Complexes of Cyclic Dienes

NMR spectra of (cyclobutadiene)tricarbonyliron in nematic solvents have been studied, and the results interpreted in terms of models of distortion of the four-membered ring[136]. UV-photolysis of the compound at low temperatures gave the dicarbonyl (detectible by IR); in the presence of Et_3SiH oxidative addition occurred to form cis-$(C_4H_4)Fe(CO)_2(H)(SiEt_3)$, with an activation energy of about 11 kcal/mol. The adduct was unstable above 220 K[137]. Reaction of a [3]phenylene with nonacarbonyldiiron gave, besides several diiron products, a small amount of the novel cyclobutadiene complex **31**[138].



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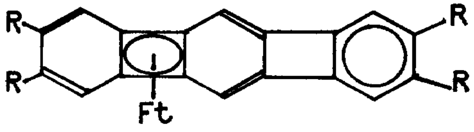
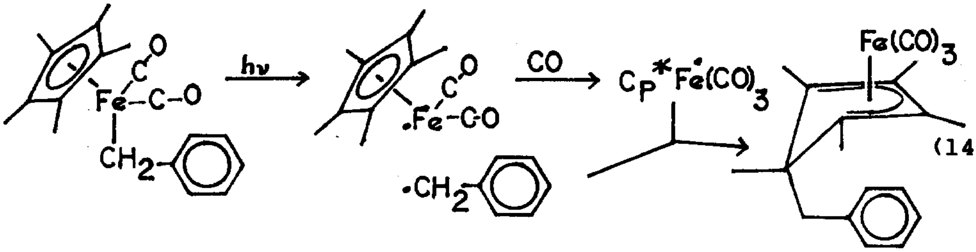


31 R=SiMe$_3$

η^4-Iron tricarbonyl complexes of several siloles and germoles have been reported[139]. Their photoelectron spectra indicated strong electron donation from iron to the ring, possibly conferring some aromatic character[140]. η^4-cyclopentadiene complexes resulted when Cp- or $Cp^*Fe(CO)_2CH_2Ph$ were subjected to UV-irradiation under two atmospheres of CO at room temperature. The exo placement of the benzyl group was shown by X-ray crystallography, and the mechanism of Eq. 14 was suggested[141]. Reaction of 2,2-dimethylspiro[2.4]hepta-4,6-diene with $Fe_2(CO)_9$ gave (besides a predominance of η^5-cyclopentadienyl products resulting from C-C bond rupture) both isomeric η^4-$Fe(CO)_3$ complexes, each in about 18% yield[142].



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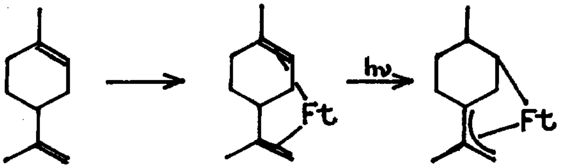
Irradiation of $Fe(CO)_5$ in the presence of limonene has been reported to give the results shown in Eq. 15, but the structures were based only on low-field proton NMR[143]. Reaction of 1,1-dichloro-1-silacyclohexa-2,4-diene with $Fe_3(CO)_{12}$ gave the expected $Fe(CO)_3$ complex, **31**, in 80% yield. The chlorines in **31** underwent normal displacement reactions[144]. The cyclohexadiene complex **32** also resulted in unexceptional manner when the 3a-H-indene was treated with $Fe_2(CO)_9$[145]. Reactions of cross-conjugated cyclohexadienones (and related compounds) with $Fe_2(CO)_9$ in wet organic solvents resulted in reduction of the organic ligand and formation of 1,3-cyclohexadien-2-ol $Fe(CO)_3$ complexes[146]. α-Phellandrene-$Fe(CO)_3$, **33**, arose, along with carbonylation products and p-cymene, upon heating (+)-2-carene with $Fe(CO)_5$[147].



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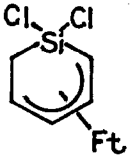

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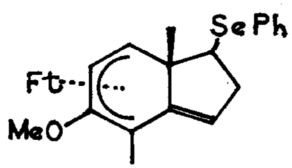

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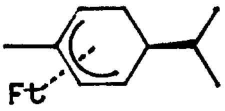

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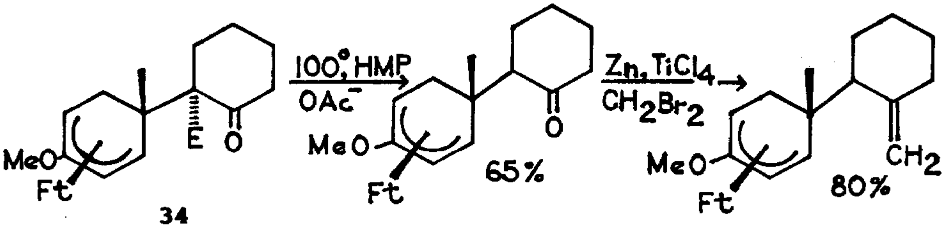
A number of substituted (cyclohexadiene)tricarbonyliron complexes have been converted to triphenylphosphine substitution products by treatment with trimethylamine oxide, followed by the phosphine[148].

Cyclohexadiene complexes are of especial interest in synthetic chemistry because of their ease of conversion to cationic cyclohexadienyl complexes, which in turn react with nucleophiles to regenerate diene complexes. This chemistry is discussed in this section if the emphasis is on a novel cyclohexadiene complex or the chemical reactivity of the diene complex. Otherwise it appears in Section 7a.

The cyclohexadiene complex **34** underwent the transformations shown in Eq. 16. without decomplexation[149]. The same sequence of



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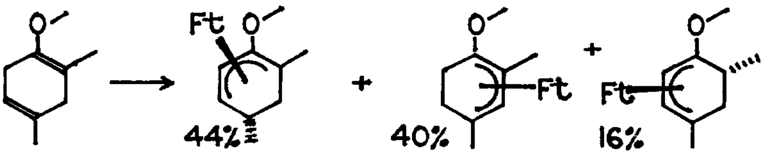
(16)

reactions was also applied to a diene complex which resulted from attack of a more complex enolate on the same (1-methyl-4-methoxycyclohexadienyl)tricarbonyl iron cation[150]. Polycyclic lactones were the ultimate synthetic goals in each case.

(1- and 2-Methoxycyclohexadiene)tricarbonyliron are converted to cyclohexadienyl complexes on treatment with acids through a sequence of protonations, hydrogen transfers, and deprotonations. This process has been studied by use of deuterium labelling, which indicated protonation first at iron, then transfer to a terminal carbon of the coordinated diene, equilibration about the ring if necessary, then loss of methanol from the allylic cation intermediate[151].

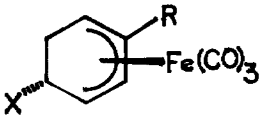
Reaction of 1-methoxy-2,4-dimethyl-1,4-cyclohexadiene with $Fe(CO)_5$ in refluxing dibutyl ether gave a mixture of three isomeric products (Eq. 17). However, treatment of the crude mixture



(17)

with F_3CCOOH at -15° gave only the 2,4-dimethylcyclohexadienyl complex. Likewise, only one product of hydride removal formed, in this case because the isomers with the exo methyl groups were unreactive toward trityl cation[152].

In addition to the extensively-developed carbocation chemistry of cyclohexadiene complexes, the chemistry of carbanions derived from them is also beginning to be explored. Several recent examples have involved deprotonation of diene complexes **35** to form carbanions, which preferentially reacted with electrophiles at the exo face. For example, **35** (R = Me, OMe; X = CN) underwent deprotonation with BuLi/TMEDA then *exo*-allylation, and use of resolved starting material left chiral product of known stereochemistry[153]. Similarly, *exo*-sulfones **35** (X = SO_2Ar) were converted to their endo isomers by deprotonation and reprotonation at low temperature. Treatment with methoxide at room temperature resulted in formation of **35** (X = OMe), and treatment with $NaBH_4$ caused reduction to **35** (X = H)[154]. The *exo*-phosphonio salts **35** (R = OMe, X = PPh_3^+) with bases gave Wittig reagents, which reacted normally



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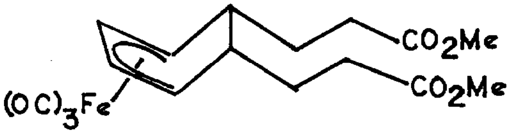

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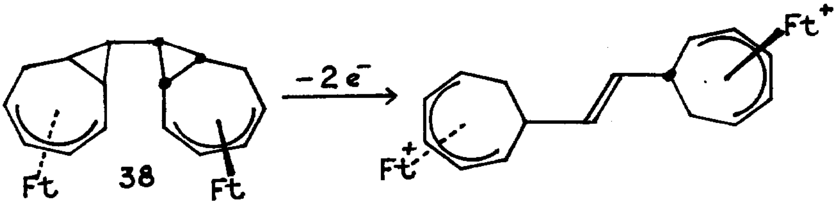
with aldehydes to form alkylidenecyclohexadiene complexes[155].

An unusual alkylation reaction resulted when (cyclohexadiene)tricarbonyliron reacted with (η^2-CH_2=$CHCO_2Me)_2Fe(CO)_3$, **36**, to form the disubstituted product, **37** (X-ray)[156].

Replacement of a CO by triphenyl phosphite in (cycloheptatriene)tricarbonyliron has been found to proceed best (75% yield) in dilute solutions. The product protonated cleanly to form the η^5-cycloheptadienyliron cation[157]. The redox chemistry of the bis(cycloheptadiene)tricarbonyliron compounds **38**[158] and **39**[159] has been reported in detail (Eqs. 18 and 19), including X-ray structures for **38**, **39**, and the tetracycle **40** (Eq. 19). The newly-formed bond in the cyclobutane ring in **40** was unusually long [1.596(4) Å][159].



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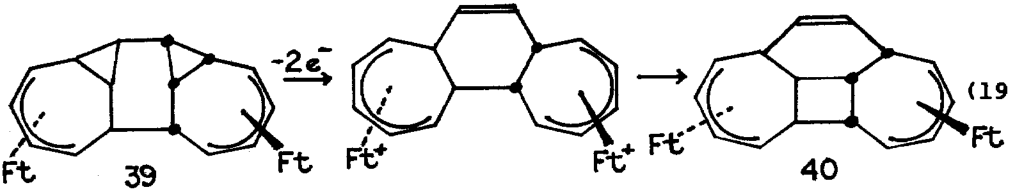

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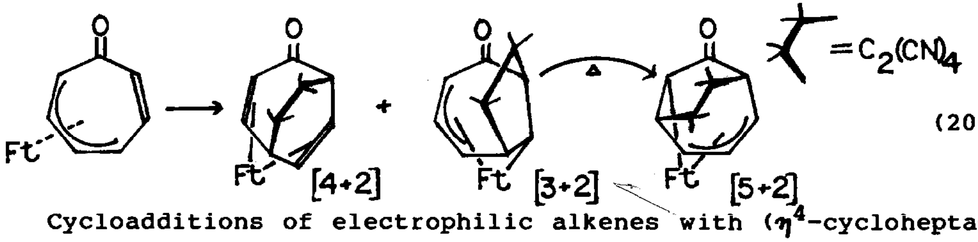
The racemization of tricarbonyl(tropone)iron, which occurs by 1,3-haptotropic shift of the tricarbonyliron group, has been followed in the circular dichroism spectrum, and showed an activation energy of 25.8 kcal/mol, in line with previous estimates[160]. Electrophilic cycloaddition of TCNE to the tropone complex has been reinvestigated, which has revealed a new primary product, a [4 + 2] adduct (4% yield), and rearrangement of the previously characterized [3 + 2] adduct, in what is grandly characterized as a "pericyclic [3,3]-sigmahaptotropic rearrangement," to a formal [5 + 2] adduct[161] (Eq. 20). Although the rearrangement, like the cycloaddition, could be imagined to proceed through a zwitterion, the experimental evidence (solvent effects and $\Delta S^{\ddagger}$) favored a more nearly concerted process, as did MO calculations[161].



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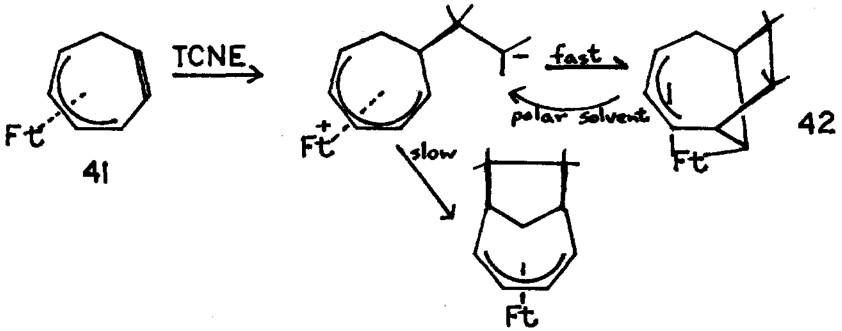
Cycloadditions of electrophilic alkenes with (η^4-cycloheptatriene)tricarbonyliron, **41**, have also received further attention during 1985. Tetracyanoethene has been found to be 682 times as reactive as tricyanoethene toward **41**, a high ratio which has been interpreted as favoring a concerted mechanism leading to the known [3 + 2] adduct, **42**[162]. However, the high reactivity ratio may also be attributed, in the opinion of this reviewer, to an electron-transfer mechanism. Cycloaddition of carbomethoxymaleic anhydride to **41** has been investigated. In contrast to the TCNE case, the product is a [4 + 2] adduct (X-ray structure), a result which has been attributed to secondary orbital interactions in a concerted transition state[163]. Curiously, the [4 + 2] cycloaddition to **41**, previously assessed by Mingos as not allowed, has now been interpreted as allowed based on use of a different Kekule structure for the starting material[163]. The [3 + 2] TCNE adduct, **42**, has been found to rearrange to a formal [6 + 2] adduct in a reaction highly favored by polar solvents (Eq. 21). Oxidation of the rearranged adduct proceeded without rearrangement to give an otherwise-unobtainable [4 + 2] adduct of cycloheptatriene[164].



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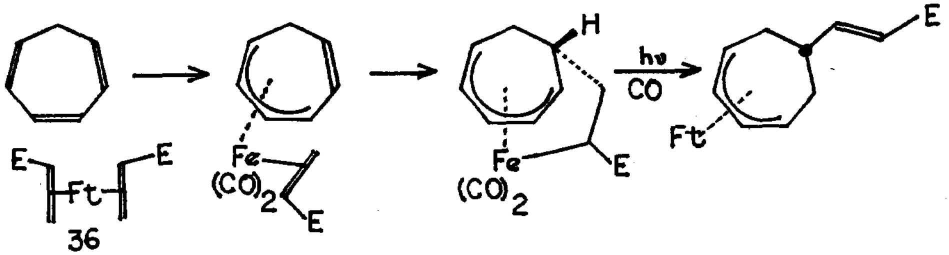
A partial cycloaddition occurred when **36** reacted with cycloheptatriene (Eq. 22) in a reaction reminiscent of those which occur when **41** is irradiated in the presence of alkenes. A similar reaction occurred with (cyclooctatetraene)tricarbonyliron[156].



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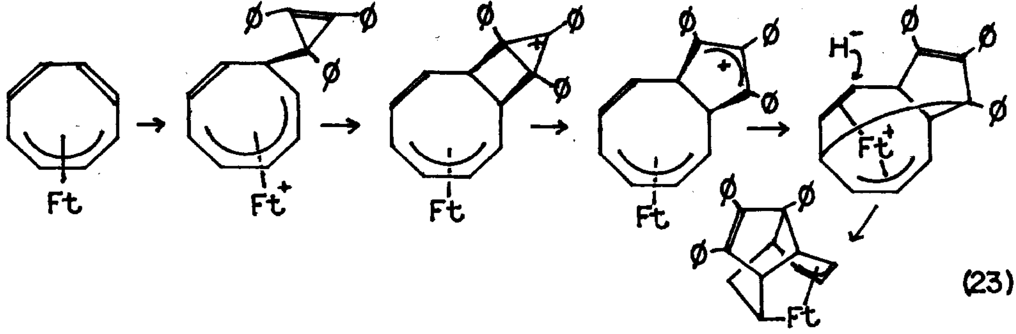
Quantum yields in photosubstitution reactions of $(COT)Fe(CO)_3$ with trimethyl phosphite have been studied as a function of wavelength[165]. Isonitrile-substituted derivatives, $(COT)Fe(CO)_2(CNR)$ [R = Me, i-Pr, t-Bu, Ph] and the trimethyl phosphite derivative have been prepared for studies of their proton, carbon, and phosphorus NMR spectra, which have indicated that the facile haptotropic rearrangements of these compounds proceed according to the

Woodward-Hoffmann-allowed path[166]. Attack of cyclopropenium salts on (COT)Fe$(CO)_3$ was followed by rearrangement to a tricyclic product, which was characterized by X-ray methods[167] (Eq. 23).



Photolysis of *trans, trans, cis* —1,5,9-cyclododecatriene in the presence of Fe$(CO)_5$ has been reported to result in formation not only of the expected (cyclododecatriene)Fe$(CO)_3$ complexes [*trans, trans, cis*- and all-*trans*], but also an Fe$(CO)_3$ complex of a dimer $(C_{24}H_{36})$Fe$(CO)_3$[168].

7. η^5-DIENYL COMPLEXES

a. Compounds with Open Pentadienyl Ligands

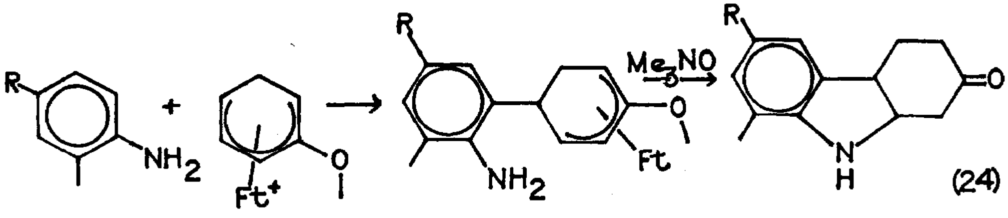
An electrochemical study of bis(2,4-dimethylpenta-2,4-dien-1-yl)iron (an "open ferrocene"), (cyclopentadienyl)(2,4-dimethylpenta-2,4-dien-1-yl)iron (a "half-open ferrocene"), and related ferrocenes has revealed easier oxidation and increased lability with opening of the cyclopentadienyl rings to pentadienyl ligands. INDO calculations have suggested more extensive metal-ligand mixing in the oxidized (pentadienyl)iron species[169].

(Cyclohexadienyl)iron species, and especially derivatives of (cyclohexadienyl)tricarbonyliron$^+$, continue to receive attention as reagents or intermediates in synthesis. The work of the Birch group has been summarized in a review with 64 references[170]. The role of the Fe$(CO)_3$ group in stabilizing intermediates and directing reactions of these complexes has been compared to the roles of enzymes in biological reactions[171].

An extensive theoretical study of nucleophilic attack on (cyclohexadienyl)- and (cycloheptadienyl)tricarbonyliron cations has led to the conclusion that initial attacks, whether orbital-controlled or charge-controlled, should occur at the iron tricarbonyl group[172]. There is evidence for this in some specific cases, but it sheds little light on the course of the more chemically significant processes which eventually result in exo attack on the dienyl ligands.

Many new experimental examples of that attack have been provided, with applications in syntheses of several classes of natural products. In most of these, the (cyclohexadienyl)tricarbonyliron electrophile has been substituted with an alkoxy group in the 2-position. This provides oxygen functionality in the product and directs nucleophilic attack to the 5-position.

Use of substituted anilines as nucleophiles (Eq. 24) has led to a synthesis of tetrahydrocarbazolones[173]. Use of enolates from 2-carbalkoxycyclohexanones led to adducts such as the one shown in Eq. 16[149], with more complex enolates providing routes to steroidal products[150,174]. Intramolecular alkylations have been exploited in synthesis of spirocyclic products (Eq. 25)[175]. Attack of enolates on [1-(2-acetoxyethyl)-4-(isopropoxy)cyclohexadienyl]-tricarbonyliron cation has been studied. Simple malonate and acetoacetate attacked predominantly at the normal 1-position, with small amounts of 5-attack. The cyclic enolate in Eq. 26 also caused deprotonation and activation of the resulting allylic acetoxy group to displacement (Eq. 26) [176]. Nucleophilic attack by benzamide nitrogens on cyclohexadienyliron cations has been claimed, but little structural evidence was proferred[177].



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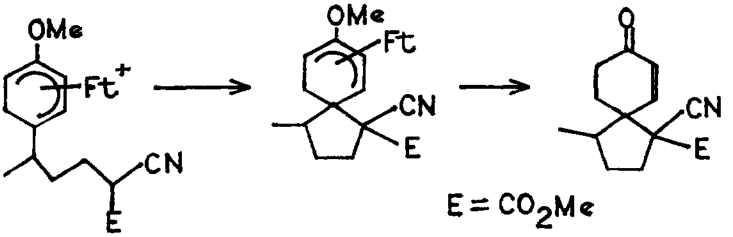

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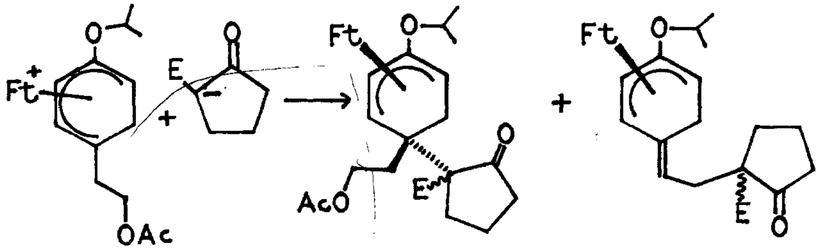

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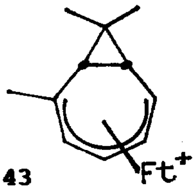
In spite of all this activity on use of (cyclohexadienyl)tricarbonyliron cations in synthesis, Pearson has provided some persuasive examples that dicarbonyl(triphenylphosphine)iron cations offer important synthetic advantages, due to decreased reactivity of the carbonyl ligands and decreased tendency to undergo reduction, compared to the tricarbonyls. For example, reaction with vinylmagnesium bromide led cleanly (98% yield) to the 5-vinylcyclohexadiene complex in the phosphine-substituted case, but only to reductive dimerization in the tricarbonyl[178].

An additional alternative that has been suggested is use of $(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)Fe^+$ cations as electrophiles suitable for C-C bond formation with appropriate carbanionic nucleophiles. MO calculations have suggested that the reactions are orbital-controlled and should lead to attack at the terminal positions of the cyclohexadienyl ligand, and several experimental examples of this mode of reaction have been described[179].

Cycloheptadienyl cations have received less attention than their cyclohexadienyl homologs. A stable cycloheptadienyl cation resulted from attack of triphenylcyclopropenium cation on the 6-carbon of (1-4-η-cyclohepta-1,3,5-triene)tricarbonyliron, in contrast to the extensive rearrangement found in the COT series (Eq. 23)[167]. The bicyclic cycloheptadienyl cation **43** has been found to undergo a circumambulatory rearrangement with migration of both the CMe_2 and $Fe(CO)_3$ groups[180]. Reaction of (η^5-cycloheptadienyl)dicarbonyliron anion with acetyl chloride gave initially the acetyliron compound, which rearranged to the 5-*endo*-acetyl product and then, upon treatment with CO, to (6-*endo*-acetyl-1,3-cycloheptadiene)tricarbonyliron, **44** (45%)[113]. The driving force for the hydrogen migration in the last step is obscure.



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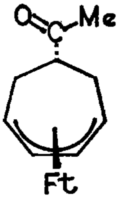

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b. Cyclopentadienyldicarbonyliron Hydride and Related Compounds

Codeposition of iron atoms with cyclopentadiene in an argon matrix resulted in formation of (η-Cp)FeH[181]. Photolysis of Fp- or Fp*R (R = Me, Et[182], or CH_2Ph[141]) led in part to dissociation of the alkyl group, forming Fp$^\cdot$ and ultimately Fp_2 dimer. Under two atmospheres of CO, the 17-electron Fp$^\cdot$ radical apparently formed the 19-electron FpCO$^\cdot$ (Eq. 14)[141]. Photolysis of FpEt in a methane matrix produced FpH[182].

Hydride reduction of $Cp(DPPE)Ru(\mu\text{-}CN)Fe(DPPE)Cp^+$ occurred with cleavage of the N-Fe bond to form Cp(DPPE)FeH[183]. In contrast, reduction of $FpCS^+$ OTf^- with NaH gave only the dimers $[CpFe(CO)(\mu\text{-}CS)]_2$. Photolysis of the $FpCS^+$ salt gave the reactive triflate, CpFe(CO)(CS)OTf, which formed numerous $CpFe(CO)(CS)L^+$ and $CpFeL_2(CS)^+$ cations upon reaction with various ligands L[184].

Reactions of FpI, $Fp(THF)^+$ and the like with phosphites, to form $CpFe(CO)[P(OR)_3]I$ and $CpFe(CO)_{3-n}[P(OR)_3]_n{}^+$ have been studied[185]. The transient $CpFe(NCMe)_3{}^+$ (from photolysis of $CpFeAn^+$ in acetonitrile) has been studied electrochemically at -40° and detected electrochemically at room temperature, at which it rapidly disproportionated to ferrocene and $Fe(NCMe)_6{}^{2+}$ [186]. Reaction of $CpFeAn^+$ with various phosphites proceeded either thermally or (better) photochemically to produce $CpFe[P(OR)_3]_3{}^+$ [187]. UV irradiation of $CpFeAn^+$ in the presence of $CH(PPh_2)_3$ (TPPM) similarly gave $CpFe(TPPM)^+$ with all three phosphorus atoms coordinated to Fe (X-ray). One was readily displaced by a solvent molecule in refluxing acetonitrile[188].

An exceptional case related to the above reactions occurred when $CpFeAn^+$ was irradiated in methylene chloride solution containing excess ethylene oxide. In this case, both the arene and the cyclopentadienyl ligands were displaced, forming $(C_8H_{16}O_4)_2Fe^{+2}$ (X-ray), where the ligands were tetrameric [12]-crown-4 molecules[189].

A novel product, $[\eta^5\text{-}(CEt)_2(BMe)_2S]Fe(CO)_3$, isoelectronic with $CpFe(CO)_3{}^+$, resulted on reaction of the thiadiborolene with $Fe(CO)_5$, along with a $(\text{thiadiborolene})_2Fe(CO)$[190].

The anion Fp^- reduced $(RN{=}CH{-}CH{=}NR)Mn(CO)_3Br$ to dimanganese species, being oxidized to Fp_2 in the process[191]. The anion functioned in part as a source of Cp^- in reactions with thioketones such as ferrocenyl phenyl thioketone, forming 6-ferrocenyl-6-phenylpentafulvene, benzoylferrocene, and other products[192]. Other reactions of Fp^- in this review are discussed according to the nature of the products formed.

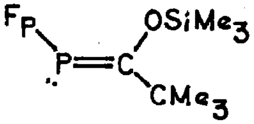
A number of silyl-iron compounds $FpSiMe_{3-n}Cl_n$ have been studied by ^{29}Si NMR[87]. Reaction of FpBr with $LiSi(SiMe_3)_3$ occurred primarily by reduction to Fp_2, only 8% of $FpSi(SiR_3)_3$ having resulted. Use of Fp'Br was little more successful, 10% of the Fp'-Si product being formed[193]. Iron-silicon bonds resulted from reaction of $RSiH_2Br$ (R = Me, Ph) with Fp^-, forming $FpSiH_2R$. Reaction of the latter with $Co_2(CO)_8$ gave $(\mu\text{-}SiFpR)(\mu\text{-}CO)Co_2(CO)_6$[194]. Reaction of $FpSiMe_2R$ (R = Me, Pr, Ph) with strong bases such as butyllithium or lithium di-isopropylamide caused deprotonation of the ring and rapid migration of the trialkylsilyl group, forming $(RMe_2SiC_5H_4)Fe(CO)_2Li$[195].

Reaction of Fp_2GeI_2 with $KCo(CO)_4$ produced the cluster product $FpGeCo_3(CO)_9$ (X-ray) by displacement of a Fp^- group along with two iodides[196]. The tetrahedral $GeCo_3$ cluster reacted with $[CpMo(CO)_3]_2$ to form a tetrahedral $GeCo_2Mo$ cluster, with the Fp group remaining attached to the Ge, unaffected[197].

A number of novel Fp-Group 15 compounds have been studied. The thionitrosyl dication, FpNS^{2+}, resulted from reaction between two cations, FpSO$_2^+$ and NS$^+$. The thionitrosyl ligand was said to be both a better σ-donor and a better π-acceptor than nitrosyl[198]. Reaction of Fp^{*-} with RPCl$_2$ (R = CMe$_3$) at -78° gave Fp*PRCl. The X-ray structure showed the angles at phosphorus to be nearly tetrahedral. Photolysis gave Fp*Cl and (RP)$_n$ (n = 3, 4), and the phosphorus reacted readily with electrophiles[199]. Reaction of LiPPh$_2$ with Fp*CO$^+$ or Fp*Br gave Fp*PPh$_2$. An X-ray structure was quite similar in conformation and bond lengths and angles to that of Fp*PRCl, although the phosphorus was described as a "distorted trigonal bipyramid." A number of other compounds, Fp*PR$_2$ (R = SiMe$_3$, CMe$_3$) were obtained similarly; however, reaction of the tricarbonyl Fp*CO$^+$ with LiP(SiMe$_3$)$_2$ gave the phosphinoacyl, Fp*C(=O)P(SiMe$_3$)$_2$[200].

FpP(SiMe$_3$)$_2$ reacted with RCOCl (R = CMe$_3$) by P-acylation then rearrangement to the phosphaimine complex, **45**. The X-ray structure showed normal Fe-P single bond (2.30 A) and P=C double bond (1.70 A) lengths, and a planar Fe-P-C-O grouping[201]. Fp*P(SiMe$_3$)$_2$ reacted with ArPCl$_2$ (Ar = 2,4,6-tri-*t*-butylphenyl) by condensation to form another complex of an unsaturated phosphorus compound, Fp*P=PAr (X-ray)[202].

The phosphorus atom of Fp*PPh$_2$ reacted as a Lewis base toward sulfur, forming Fp*P(=S)Ph$_2$, and toward BH$_3$, with which it formed an adduct, **46** (X-ray)[203]. Adducts of FpPPh$_2$ with AlMe$_3$, AlBr$_3$, and AlMe$_2$Cl have also been characterized[204]. The analogous acid-base adducts FpPH(NR$_2$)M(CO)$_5$ (R = CHMe$_2$, M = Cr, Mo, W), **47**, resulted directly from reaction of Fp$^-$ with R$_2$NPHX$\rightarrow$M(CO)$_5$. Reaction with HX cleaved the P-N bond, giving FpPHXM(CO)$_5$[205].



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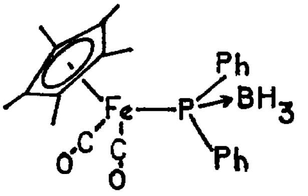

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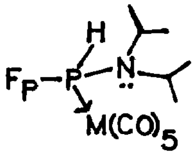

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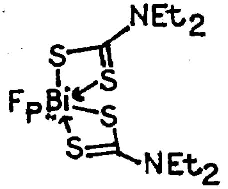
Iron-bismuth compounds, FpBiX$_2$, (X = Br, SC(=S)NEt$_2$, SC(=S)OMe resulted when Fp$_2$ reacted with RBiX$_2$ (R = Me, Ph). The crystal structure ot the bis(dithiocarbamate), **48**, showed chelation of the bismuth by both ligands, resulting in a very unsymmetrically pentacoordinated bismuth. The Fe-Bi bond length was 2.65 A[206].

Reaction of LiCp* with Fe(acac)$_2$ formed Cp*Fe(acac), which served as a useful source of Cp*Fe groups. Thus, reaction with

MeLi under CO gave Fp^*Me and with substituted cyclopentadienide ions gave pentamethylferrocene derivatives[207]. Unidentate carboxylatoiron compounds, FpOC(=O)R (R = H, Me), resulted when FpMe reacted with RCO_2H and HBF_4. They reacted further with $Fp(THF)^+$ or other sources of "Fp^+" to form bridged dimers, $[FpOCROFp]^+$. The latter were susceptible to nucleophilic attack at iron, e.g. by BH_4^-, I^-, or PPh_3[208].

Dithiocarboxylate analogs, FpSC(=S)Fc, [Fc = $CpFeC_5H_4$-] resulted from reaction of $Fp(NCMe)^+$ with ferrocenedithiocarboxylate. On heating, decarbonylation occurred, with formation of the chelate product, **49**. Monodentate dithiophosphate complexes $Fp^*SP(=S)(OR)_2$ resulted from reaction of Fp^*_2 and the disulfide derivative, $[-SP(=S)(OR)_2]_2$[210].



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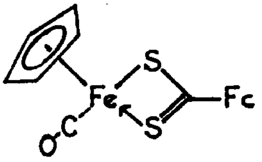

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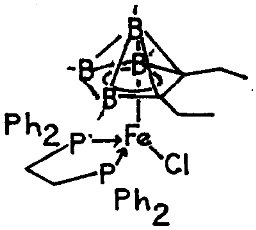

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FpSPh formed acid-base adducts with $AlMe_3$, which underwent displacement by phosphines to form $FpPR_3^+$ $PhS(AlMe_3)_2^-$. The $AlBr_3$ adduct of Fp'SPh reacted with PPh_3 to form the halide, Fp'Br[204]. Displacement of THF from the cation $Fp(THF)^+$ by disulfides RSSR gave $FpS(R)SR^+$ (R = Me, *n*-C_4H_9, CMe_3, Ph). Diselenide- and ditelluride-Fp^+ cations were obtained similarly. Nmr studies indicated a rigid PhSSPh adduct, a dynamic 1,2-shift of the Fp group in the PhSeSePh adduct, and equivalent phenyls (even at -73°) in the PhTeTePh adduct[211].

Reaction of NaFp with Se_2Cl_2 produced Fp_2Se in 60% yield. The Se could be protonated with HBF_4 and alkylated with MeOTf[212]. The selenium atom also showed basic character in coordinating with manganese in the pyramidal $Fp_2Se \rightarrow Mn(CO)_2Cp$ (X-ray)[213].

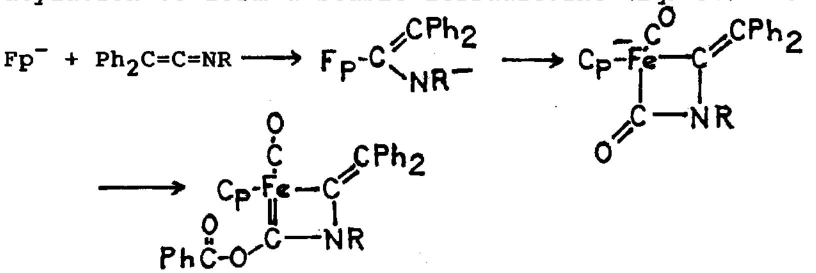
An example of an unsaturated selenium compound coordinated to iron, $[Fp \leftarrow Se{=}SbMe_3]^+$, resulted when $Fp(THF)^+$ reacted with the cyclic $(Me_3SbSe_2)_2$, cleaving the six-membered ring of the reactant in the process[214].

The bis(thiocarbonyl) compound, $CpFe(CS)_2I$, has been prepared by reaction of KI with $CpFe(NCMe)_2(CS)^+$ [184]. An X-ray structure of FpCl has been reported[215]. Fp^*Br has been produced directly by reaction of Cp^*Li with $FeBr_2(DME)$ at -80°, followed by CO addition[216]. An analogous carborane was produced in an analogous reaction, using *nido*-2,3-$Et_2C_2B_4H_5^-$, DPPE, and $FeCl_2$ to produce **50** (X-ray). ESR and magnetic susceptibility measurements indicated the presence of low-spin Fe(III)[217].

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

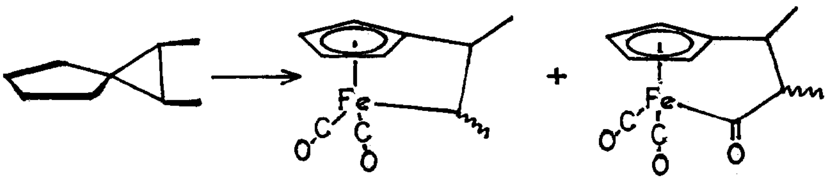
A detailed preparation of the indenyl analog of Fp_2, $[(\eta^5\text{-}C_9H_7)Fe(CO)_2]_2$, has been published, along with syntheses of the acetyl and methyl derivatives of $(C_9H_7)Fe(CO)_2$-. Neither of these showed evidence of enhanced reactivity toward hydrogen as a consequence of the possible formation of stabilized η^3 intermediates[218].

Intramolecular oxide transfer in the metallacarboxylate species $FpCO_2^-$ occurred above -20°, as revealed by studies using labelled CO_2. $FpCO_2^-$ decomposed at room temperature to form formate and carbonate, along with Fp_2 and FpH[219]. Reaction of $FpCO^+$ with $W(CO)_5(CO_2)^{2-}$ proceeded with intermolecular oxide transfer, based on labelling results; however, the $FpCO_2^-$ formed reacted rapidly with $FpCO^+$ to give predominantly Fp_2[220]. Reaction of Fp^- with ketenimines was analogous to the reaction with CO_2, and the initially formed acyl cyclized in a reaction analogous to the intramolecular oxide exchange. In the ketenimine case, however, the four-membered ring intermediate could be intercepted by acylation to form a stable ferraazetine (Eq. 27)[221].



(27)

Reaction of several methylated derivatives of spiro[2.4]hepta-4,6-diene with nonacarbonyldiiron have been investigated. Complex mixtures of products generally formed, which included intramolecular analogs of Fp-acyls and -alkyls. Both the *cis*- and *trans*-2,3-dimethyl spiroheptadienes gave the same mixtures of stereoisomeric products, implicating freely rotating open-chain intermediates (Eq. 28)[142].



(28)

44%, Z/E = 2.2 32%, Z/E = 5.7

Reduction of the diacyl, $Cp(OC)Fe[C(=O)R]_2BF_2$ (R = CMe_3) with sodium amalgam, sodium naphthalene, or electrochemically resulted in coupling of the two pivaloyl ligands, with formation of pivaloin upon workup[222].

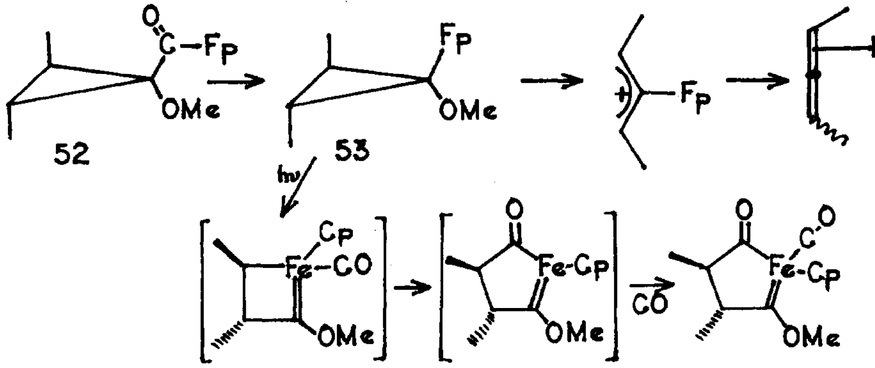
Reaction of Fp'COPh with butyllithium at -40° resulted in deprotonation of the cyclopentadienyl ring and migration of the benzoyl group to form $(\eta^5\text{-}C_5H_4COPh)Fe(CO)(PPh_3)^-$. A carboalkoxy group migrated similarly. Acyls Fp'COR having hydrogens α to the carbonyl group formed only enolates at -78°, but underwent competitive ring lithiation at 20° [223]. The enolate species which result from α-deprotonation of Fp-acyls have drawn a great deal of interest because of their evident synthetic potential. Thus, FpCOMe has been converted to FpCOEt in 84% yield by deprotonation with $LiN(SiMe_3)_2$ and alkylation with MeI[224].

Asymmetric induction in reactions of $Fp'COCH_2^-$, 51, with electrophiles has been a hot topic. Reactions of 51 with monosubstituted epoxides in the presence of Lewis acids occurred with high diastereoselectivity. Thus, reaction of Fp'COMe with BuLi at -78°, followed by propene oxide and Et_2AlCl gave a single racemic mixture, which was found by X-ray crystallography to be (RS,SR)-$Fp'COCH_2CH_2CH(OH)Me$[225]. Similarly, reaction of 51 with aldehydes in the presence of Et_2AlCl gave high diastereoselectivities; in this case, the crystallographic results for $Fp'COCH_2CH(OH)Et$ indicated preferential formation of (RR,SS) racemic mixture[226].

Aldols from condensation of 51 with aldehydes or ketones have been dehydrated by acetylation and treatment with $KOCMe_3$, to produce $Fp'COCH{=}CR_2$[227]. The same result could be obtained by α-silylation-elimination or, in one step, by treatment with NaH and MeI in THF[228]. Convenience and reported yields (90-95%) appear to favor the latter alternative. Another route to the α,β-unsaturated acyls was through C-silylation of 51, then reaction with BuLi and an aldehyde in a "Peterson reaction"[228]. Conjugate addition of nucleophiles (BuLi and LiNHR) to these acyls occurred with high stereoselectivity[229,230]. Thus, reaction of E-Fp'CO-CH=CHMe with BuLi and alkylation of the resulting enolate with MeI selectively produced (RSS,SRR)-Fp'COCHMeCHMeBu[230].

In related carbanion chemistry, ambident behavior of the phosphorus ylides $FpCOC(R){=}PR'_3$ toward MeOTf has been reported. With R = H, R' = Me, C-methylation occurred, to give $FpCOCH(Me)PMe_3^+$, whereas with R = Me, R' = Et, O-methylation gave $FpC(OMe){=}C(Me)PEt_3^+$ exclusively (structure by X-ray diffraction). In other cases mixtures of both types of products resulted[231].

Decarbonylation of acyl complexes, FpCOR, has been used to prepare some novel FpR products. For example, reaction of 52 (Eq. 29) with "Wilkinson's catalyst," $[(Ph_3P)_2RhCl]_2$, produced the cyclopropyl-Fp product 53 in 60% yield. Reaction of 53 with Me_3SiOTf resulted in ring opening to form the coordinated allene. Formation of racemic allene complex from optically pure 53 suggested the occurrence of an achiral intermediate, probably the allyl cation[232]. Photolysis of 52 did not stop at 53, but rather went on with further decarbonylation to produce carbene complexes (Eq. 29)[233]. A similar reaction sequence starting with 7-methoxycycloheptene-1-carbonyl chloride and using photodecarbonylation gave 1-Fp-7-methoxycycloheptene, which formed (η^2-1,2-cycloheptadiene)-(cyclopentadienyl)dicarbonyliron$^+$ upon treatment with Me_3SiOTf[234].



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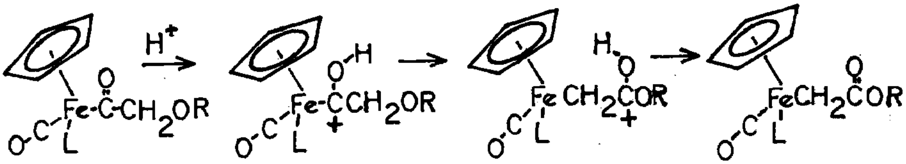
A careful study of conditions for carbonylation of FpMe and related compounds has been made. The reaction is favored by substitution of an indenyl group for cyclopentadienyl or a phosphine for a CO, by use of acetonitrile, nitromethane, or (best of all) trifluoroethanol as solvent, and by including a trace of Brønsted acid. Even under the best of conditions, compounds such as $Fp'CH_2X$ (X = OMe, Ph, CO_2Me) failed to form the acyls[235]. However, reaction of $FpCH_2OR$ with trimethyl phosphite (L) did result in iron-to-carbonyl migration, forming $CpL(CO)FeCOCH_2OR$ in moderate yield. This rearranged upon treatment with acids, as shown in Eq. 30[236].



(30)

Treatment of RFp (R = exo- or endo-2-norbornyl), which had been prepared by photodecarbonylation of the corresponding acyls, with trityl salts caused some carbonylation to RCOFp and some formation of (η^2-exo-norbornene)Fp$^+$. An electron-transfer chain mechanism was proposed for the carbonylation[237].

Two reports have dealt with use of carbanionic reagents to generate Fe-C bonds. Reaction of $PhCH_2Li$, $PhSCH_2Li$ or MeMgCl with $Cp^*Fe(NO)I_2$ [made by iodination of $Cp^*{}_2Fe_2(NO)_2$] gave good yields of the dialkyls, $Cp^*Fe(NO)R_2$[238]. Similarly, reaction of (DPPE)-FeCpBr [from CpLi and $(DPPE)FeCl_2$, followed by LiBr] with a wide variety of Grignard reagents produced (DPPE)FeCpR in 42-93% yield[239].

The nucleophilic properties of Fp^- and its analogs continue to be exploited in synthesis of R-Fp compounds. The nucleophile Fp^- has most commonly been obtained by reducing Fp_2 dimers, but ring-silylated analogs have now been prepared by ring-deprotonation of $FpSiMe_3$, followed by rapid silyl group migration to leave $(Me_3SiC_5H_4)Fe(CO)_2^-$, which could be methylated or silylated normally at iron[195]. Generation of Fp^- or its analogs by phase-transfer methods has also been explored[240]. Reaction of Fp^- with $MeC(CH_2X)_3$ (X = Br, I) formed (1-methylcyclopropyl)methyl-Fp[241].

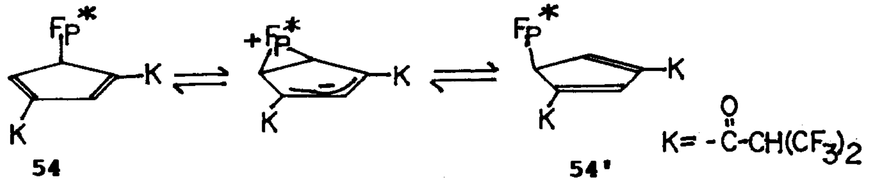
Displacement reactions of $FpCH_2Cl$ have been found to be facilitated by $TlBF_4$. Good to excellent yields resulted when tertiary amines and phosphines and sulfides were used as nucleophiles[242]. The acetoxy ligand in $FpCH_2OCOMe$ (from Fp^- and $BrCH_2OCOMe$) was labile in the presence of acids HX, giving acetic acid and $FpCH_2X$ (X = Cl, OCOR), but not very reactive toward nucleophiles[243]. FpMe reacted with $HMn(CO)_5$ in acetonitrile at 55° to give MeCHO, Fp_2, and $Mn_2(CO)_9(NCMe)$[244].

Conformational analysis of $Fp'CH_2R$ derivatives has become a highly contentious subject[245,246]. Baird has now proferred nuclear Overhauser effect evidence in support of his view, originally based on P-H coupling constants, that the compounds may be treated as pseudotetrahedral, and that the cyclopentadienyl ring is the most sterically demanding substituent[247]. Davies has pressed his view, based primarily on stereochemical results of chemical reactions and extended Hückel calculations, that the compounds must be treated as pseudooctahedral, and that the triphenylphosphine is the most sterically demanding ligand[248].

Photochemistry of FpR (R = Me and Et) in fluid solutions and in matrices has been studied. In solution, both formed Fp_2 on irradiation. In matrices, the unsaturated product of CO ejection, CpFe(CO)R, was readily trapped by CO, N_2, or ethene[182]. With R = $PhCH_2$, the monocarbonyl photoproduct was stabilized by η^3-benzyl coordination. Although the quantum yield for CO loss was much higher than for benzyl group loss, presence of 2 atm. CO suppressed products of the former reaction, allowing the chemistry of Eq. 14 to predominate[141]. Solution photolysis of a glucopyranosyl-Fp compound in the presence of triphenylphosphine gave the expected Fp' product in 85% yield; there was some stereoselectivity at iron, the two diastereomers having been formed in 70/30 ratio[249].

Interesting examples of use of $CH_2=CH-CH_2-Fp$ and related compounds as carbon nucleophiles have appeared. Reaction with the Noyori reagent $[(PhCHBr)_2CO$ and $Fe_2(CO)_9]$ produced 2,6-diphenyl-4-

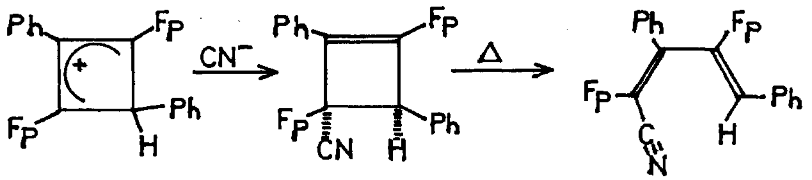
Fp-cyclohexanone, oxidation of which with Ce(IV) gave the 4-carbomethoxycyclohexanone in 46% yield[250]. Reaction of allyl-Fp with $FpCH_2^+$ formed $(FpCH_2CH_2CH{=}CH_2)Fp^+$ [251]. The cycloaddition reaction of Fp^*Cp with dimethyl fumarate to form the expected norbornene cycloadduct was about five times faster than reaction of FpCp. Fp^*Cp reacted with bis(trifluoromethyl)ketene to form 54[252]. The location of the trifluoroacetyl groups in 54 should be optimal for stabilizing the transition state in the 1,2-migration of the iron group, and hence further structural and dynamical studies of 54 would be of some interest.



54 **54'**

O-Ethylation of $CpFe(CO)[P(OMe)_3]CH_2COOMe$ with Et_3O^+, followed by reduction with $NaBH_4$ formed the ethyl-iron product. Reduction with $LiHR_3$ (R = *sec*-butyl) instead gave the $(\eta^2$-$CH_2{=}CHOEt)$ complex and the aldehyde $CpFe(CO)[P(OMe)_3]CH_2CHO$[236].

A series of di-iron compounds $Fp(CH_2)_nFp$ (n = 3-12) has been prepared from the dihalides and Fp^-, and studied by mass spectrometry and differential scanning calorimetry[253]. The cations resulting from hydride removal by trityl salts were studied by NMR, including further variable temperature studies of the previously studied $FpCH_2CHCH_2Fp^+$ [254]. Reaction of the cyclobutenyl analog with cyanide occurred as expected, and the resulting cyclobutene opened on heating to a butadiene (Eq. 31). Both structures were confirmed by X-ray crystallography[255]. Addition of nucleophiles to the cyclopropenium ion, $FpC_3Ph_2^+$, occurred at a phenyl-substituted carbon. Formation of the methyl ether by methoxide attack was reversed by acid, regenerating the cyclopropenium ion[256].



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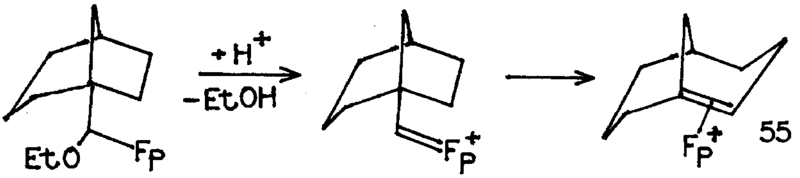
Butadienes bearing Fp groups were found to give Diels-Alder reactions with enhanced rates. However, the regioselectivity in cycloadditions with unsymmetrical dienophiles was not high, and considerable decomposition of the starting material limited the usefulness of the reactions in many cases[257]. 1,4-dibromo-1,4-diphenylbutadiene was partially lithiated and allowed to react with FpI, to form the Fp-substituted bromodiphenylbutadiene. Further lithiation then methylation resulted in formation of a small amount of 1,3-diphenyl-2-methoxyferrocene, possibly by way of a ferrabenzene intermediate[258].

Carbene complexes have continued to attract research activity. The acyls FpCOR and Fp'COR (R = Me, Ph) formed carbene complexes Fp(')C(OMe)R^+ directly and in high yields upon reaction with trimethyl orthoformate[259]. FpC(OEt)R^+ (R = 1-bicyclo[3.2.1]-octyl) was reduced wth $LiBHEt_3$ and then protonated, which resulted in rearrangement to a bicyclo[3.3.1]nonene complex, 55 (X-ray structure) (Eq. 32), which resisted decomplexation with NaI[260].

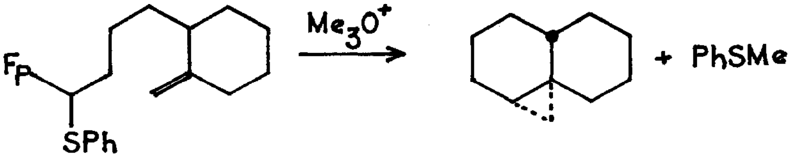


(32)

Reaction of Fp^*CH_2OMe with HBF_4 at -90° produced $Fp^*CH_2{}^+$, as evidenced by trapping with triphenylphosphine or styrene, the latter forming phenylcyclopropane. The analogous $Cp^*Fe(CO)(PPh_3)$-$CH_2{}^+$ could be detected directly by proton NMR at low temperatures; the barrier to rotation of the Fe=C bond could be estimated from coalescence of the two non-equivalent methylene hydrogens as 10.6 kcal/mol[261]. Formation of $Fp'CH_2{}^+$ by protonation of $Fp'CH_2OMe$ was found to be followed by hydride transfer, forming Fp'Me and $Fp'CHOMe^+$[262]. Likewise, Fp- or Fp'-CH_2OMe reacted with the organometallic Lewis acid $CpMo(CO)_3{}^+$ to form Fp(')$CHOMe^+$ (by hydride transfer) and Fp(')Me (by methoxide and hydride transfer)[263].

Rearrangement of the vinylic complexes $CpFeL(CO)C(=CH_2)CH_2R$ [L = $P(OPh)_3$, R = Me, Ph, vinyl, C≡CMe, SPh] in the presence of alumina has been studied using deuterium labelling and found to occur through β-protonation, with formation of intermediate alkylidene complexes[264]. Protonation of $Fp'CMe{=}CH_2$ gave the isopropylidene complex $Fp'CMe_2{}^+$, which was isolable as the fluoroborate salt at room temperature. The analog $FpCMe_2{}^+$, in contrast, rearranged at -11° to the isomeric propene complex. $Fp{=}CMe_2{}^+$ and $Fp{=}CH{-}CH{=}CMe_2{}^+$ reacted with isobutylene, styrene, and cyclooctene to give cyclopropanes[265].

Treatment of $FpCH(OMe)C_3H_5$ (C_3H_5 = cyclopropyl) with Me_3SiOTf gave the carbene complex $Fp{=}CHC_3H_5{}^+$, which was stable up to about -35°, and which gave bicyclopropyls upon reaction with alkenes[266,267]. FpCHMeSPh has been recommended as an ethylidene transfer reagent, capable of forming cyclopropanes in good yield by treatment with an alkylating agent in the presence of an alkene[268]. Analogous intramolecular cyclopropanations have also been reported (Eq. 33)[269]. In addition to several other sulfonium



(33)

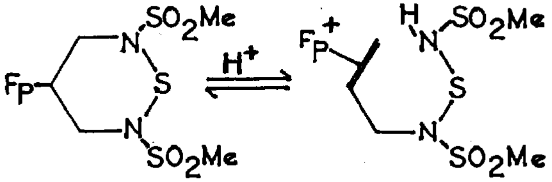
salts previously used, $FpCH_2SPh_2^+$ has been found to convert cyclooctene to bicyclo[6.1.0]nonane[242]. However, reaction of $FpCH_2^+$ with $FpCH=CH_2$ did not give the cyclopropyl-iron product, but rather the highly stabilized cation, $(FpCH_2)_2CH^+$, which evidently arose from a hydride migration in the initially-formed $[Fp=CHCH_2CH_2Fp]^+$ [251].

Crystal structures of $FpCCl_2^+$ and $Fp'CF_2^+$ have been reported. In the former, the plane of the CCl_2 group bisected the OC-Fe-CO angle. Low-temperature NMR study of the CF_2 complex showed rapid rotation of the CF_2 group, and the crystal structure showed an unsymmetrical rotamer[270].

Reduction of $Fp^*PMe_3^+$ with $NaBH_4$ at -60° gave zwitterionic $Cp^*\overset{+}{Fe}(CO)(PMe_3)=CHOBH_3^-$, as a mixture of syn and anti isomers. Further reduction to $Cp^*Fe(CO)(PMe_3)Me$ occurred at -20° [271].

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

Although β-hydride removal from an alkyliron compound has long been a common route to alkene complexes, the reaction has now been achieved using the novel Lewis acid $CpMo(CO)_3^+$ to convert $Fp'CH_2CH_3$ to $Fp'(C_2H_4)^+$ [263]. N-Protonation of the cycloadduct shown in Eq. 34 led to formation of the alkene complex (X-ray) with dissociation of the leaving group; the reaction was reversed by "Proton Sponge"[272].



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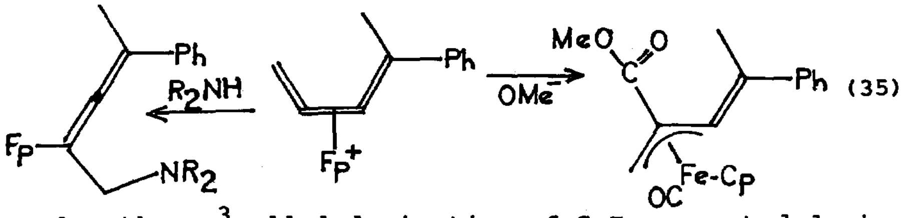
(1,2-Cycloheptadiene)Fp^+, **56**, resulted from demethoxylation of 1-Fp-7-methoxycycloheptene with Me_3SiOTf or Me_3O^+. **56** was fluxional, with E_a 13.9 kcal/mol. Upon heating, it rearranged to the (1,3-cycloheptadiene)Fp^+ complex[234]. Formation of an acyclic allene complex from a cyclopropylidene was shown in Eq. 29[232], as was formation of 55, also from rearrangement of a carbene complex, in Eq. 32[260]. Butatriene complexes resulted from treatment of

$FpCH_2C{\equiv}CR_2OH$ (R = Me, Ph; R_2 = fluorenylidene) with HBF_4 at -50°.

The ethene complex $CpFe(CO)(C_2H_4)Me$ resulted from photolysis of FpMe in the presence of ethene, either in solution or in matrices. Similar photolysis of FpEt, however, gave, along with FpH and Fp_2, the novel dimer, $[CpFe(CO)(C_2H_4)]_2$[182]. An intramolecular photodisplacement of CO by a double bond occurred upon photolysis of $FpCH_2S(Ph)CH_2CH{=}CH_2$[242].

Attack of R^- on $CpFe(CO)L(\eta^2\text{-}CH_2{=}C{=}CH_2)^+$ [L = $P(OPh)_3$] gave alkenyl complexes $CpFe(CO)L[C(=CH_2)CH_2R$ (R = H, Me, Ph, C_2H_3, $C{\equiv}CMe$, and SPh). Reduction of the 2-butyne complex with $LiHBEt_3$ gave a mixture of *E*- and *Z*-isomers of the (2-butenyl)iron product, but use of $LiH(CHMeEt)_3$ gave only the *E*-isomer[264]. The position of attack of nucleophiles on the butatriene complexes $[\eta^2\text{-}CH_2{=}C{=}C{=}CR_2]Fp^+$ has been found to depend upon both R and the nucleophile (Eq. 35)[273].



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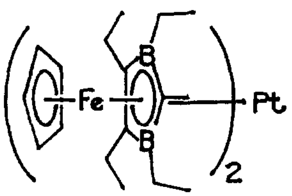
The only other η^3-allyl derivative of CpFe reported during 1985 was the product $(\eta^3\text{-}CH_2C_6H_5)Fe(CO)Cp$, obtained upon photolysis of $FpCH_2Ph$ in rigid alkane matrix at 77 K or in fluid solution with active purging of CO[141].

The electronic effect of the 1-(η-cyclopentadienyl)[η^5-(3)-1,2-dicarbollyl]iron group, as measured by its Taft constants, has been found to be more electron-donating than that of the ferrocenyl group[274]. Reaction of bis(η^5-2,3-dihydro-1H-1,3-diborolyl)-platinum with $CpFe(C_8H_{12})$ yielded the tetradecker complex 57. NMR studies of 57 indicated relatively free rotation of the rings in this symmetrical (X-ray), 42-valence-electron complex[275]. Reaction of $FeCl_2$ in THF with $Et_4C_4B_8H_8{}^{2-}$ ion, followed by addition of $Et_2C_2B_4H_5{}^-$, gave principally paramagnetic $(Et_2C_2B_4H_4)FeH(Et_4C_4B_8H_7)$, for which no specific structure was suggested[276].



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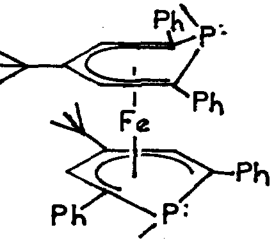

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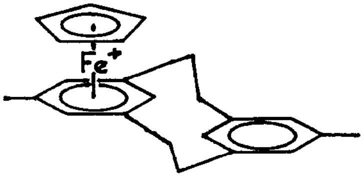
The electrochemistry of free bis(phospholyl)iron compounds and derivatives in which the phosphorus lone pairs were coordinated to one or two $M(CO)_5$ groups (M = group 6 metal) has been studied[277]. Bis(η^5-phosphinine)iron complexes such as **58** have been prepared by reaction of the lithiated phosphinines with $FeCl_2$. The phosphorus atoms displayed normal nucleophilic properties toward acids and methylating agents, MeI giving a monomethyl derivative, and Me_3O^+ a dimethyl derivative[278]. Mössbauer studies indicated the expected similarities to the "open ferrocenes." An X-ray structure of **58** was reported[279].

8. COMPOUNDS WITH η^6-ARENE LIGANDS

The kinetics of addition of nucleophiles to (η^6-cycloheptatriene)$FeCp^+$ has been studied. The relative reactivities of nucleophiles are the same as their reactivities toward other cations and other coordinated polyenes, but the $FeCp^+$ moiety was found to be 11,000 times less potent at activating cycloheptatriene toward nucleophilic attack than $Mn(CO)_3{}^+$ [280]. Kinetically-controlled nucleophilic attack on the cyclohexadienyl ligand of (η-C_6H_6)(η^5-C_6H_7)Fe^+ has been recommended for synthesis of 5-substituted 1,3-cyclohexadiene complexes[179].

Extended Hückel calculations on some extended sandwich compounds (submarine sandwiches?) have led to predictions of some interesting but unknown compounds as possible synthetic targets. Among these are (naphthalene)(pentalene)diiron and the isoelectronic (azulene)(pentalene)diiron[281].

$Cp^*Fe(acac)$ has been used to prepare $Cp^*Fe(C_6H_6)^+$ by reaction with benzene in the presence of aluminum chloride[207]. The crystal structure of $CpFeAn^+$, **59**, in which An is 5,13-dimethyl[2.2]metacyclophane has been reported[282]. ^{13}C chemical shifts for the coordinated ring carbons in CpFe(cyclophane)$^+$ complexes have been found to correlate with the C-Fe distances[283]. A "deltaphane" complex, **60**, has been prepared by exchange of the free ligand with CpFe(p-xylene)$^+$ under irradiation[284].



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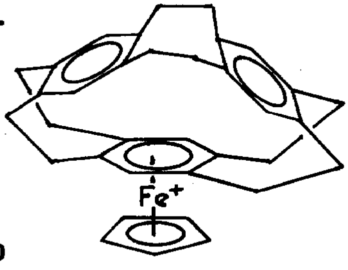

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Reaction of CpFe(1,2-dichlorobenzene)$^+$ with toluene-3,4-dithiol proceeded with consecutive displacements to produce the complex, CpFe(2-methylthianthrene)$^+$. X-ray structures of the thianthrene hexafluorophosphate complex and of CpFe(xanthene)$^+$ $PF_6{}^-$ were reported[285]. The phosphorus atom in $CpFe(C_6Me_5CH_2PPh_2)^+$

has been coordinated with a Rh(1,5-cyclooctadiene)Cl moiety. The product underwent carbonylation and catalyzed hydrogenations[286].

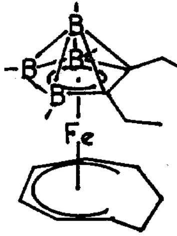
Use of $CpFeAn^+$ cations as sources of $CpFe^+$ groups in ligand exchange reactions has received attention. Photolytic conditions were recommended for preparation of $CpFe[P(OR)_3]_3^+$, as was use of $CpFe(C_6H_5Cl)^+$ in photochemical arene exchange reactions with thiophenes and other arenes[187]. Examples of using the p-xylene[186,188] and toluene[189] complexes to produce $CpFeL_3^+$ have already been described.

Studies of redox properties of CpFeAn systems continue to be of interest. Reaction of $CpFeAn^+ I^-$ (An = mesitylene or hexamethylbenzene) with tetracyanoquinodimethane (TCNQ) in refluxing acetonitrile gave $[CpFeAn^+] (TCNQ)_2^-$, whose crystal structure showed separate one-dimensional stacks of anions and cations[287]. Reaction of neutral $CpFe(C_6Me_6)$ with TCNQ in THF, however, gave the 1:1 salt, $CpFeAn^+ (TCNQ)^-$, or the 2:1 salt, $(CpFeAn^+)_2 (TCNQ)^{2-}$, depending on the ratio of reactants[288]. The electronic spectra of CpFeAn systems in different redox states have been studied, with the conclusion that the outer electrons were held in non-bonding d-orbitals on iron[289].

Reaction of biferrocenyl with one equivalent of hexamethylbenzene and excess aluminum chloride resulted in formation of $(FcC_5H_4)Fe(C_6Me_6)^+$, whose cyclic voltammagram showed four reversibly-connected oxidation states[290]. Reaction of biferrocenyl with two equivalents of hexamethylbenzene produced the dication $[(C_6Me_6)Fe(C_5H_4-)]_2^{2+}$, which could be reduced through three intermediate stages to the dianion. The mixed-valence monocation was found to be delocalized even at 4 K[291]. Use of reduced CpFeAn compounds as "organometallic electron reservoirs" has been reviewed[292].

Carbanion attack on $CpFeAn^+$ compounds activated by presence of electron-withdrawing groups on the arene ring gave stable neutral adducts, which were converted to the substituted benzenes on oxidation with Ce(IV)[293].

The physical and chemical properties of a number of AnFe(carborane) species, analogs of $AnFeCp^+$ in which various formally dianionic η^5-carborane ligands substitute for the more common cyclopentadienyl group, have been studied. The effect of solvents on the ^{11}B NMR spectra of the most common series, $(Et_2C_2B_4H_4)Fe$-(benzene) and -Fe(cyclooctatriene) has been studied[294]. Reaction of tetramethylethylenediamine with $(C_6R_6)Fe(Et_2C_2B_4H_4)$ resulted in removal of the apical BH group to form nido-$(C_6R_6)Fe(Et_2C_2B_3H_5)$. The latter was deprotonated and treated with $FeCl_2/O_2$ to form an 11-vertex cage compound, $(C_6R_6)Fe(Et_4C_4B_6H_6)$. Biphenyl complexes with one and both rings coordinated to $Fe(Et_2C_2B_4H_4)$ moieties were prepared by reaction of the (cyclooctatriene)Fe(carborane), **61**, with biphenyl at 180-200° [295]. (Cyclooctatriene)Fe[$B_4H_4CHC(CH_2$-$CH_2CH_2Ph)$] underwent loss of the cyclooctatriene ligand and complexation of the pendant phenyl group upon treatment with $Al/AlCl_3$, to give a [3]-ferracarboranophane, **62** (X-ray structure).



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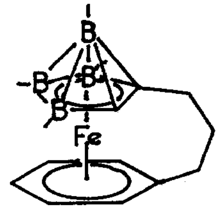

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Similar reaction with the β-phenylethyl substituted carborane gave the bridged dimer rather than the [2]-ferracarboranophane. The apical BH of the [3]-ferracarboranophane was removed by reaction with methanol[296]. $(Et_2C_2B_4H_4)Fe$ complexes of naphthalene and phenanthrene were prepared by displacement of cyclooctatriene from **61**. Phenanthrene gave both central-ring and terminal-ring (X-ray structure) coordination isomers[297]. Icosahedral ferracarboranes resulted when $CpFe(C_8H_{12})$ reacted with 2,3-$C_2Me_2B_9H_9$ in the presence of arenes. The toluene complex (X-ray structure) was also obtained from $(CpFe)_2(\mu$-η-$C_6Me_6)$ and the carborane. Naphthalene could be displaced from its complex by 3 CO's at 50° and 100 bar CO pressure [298].

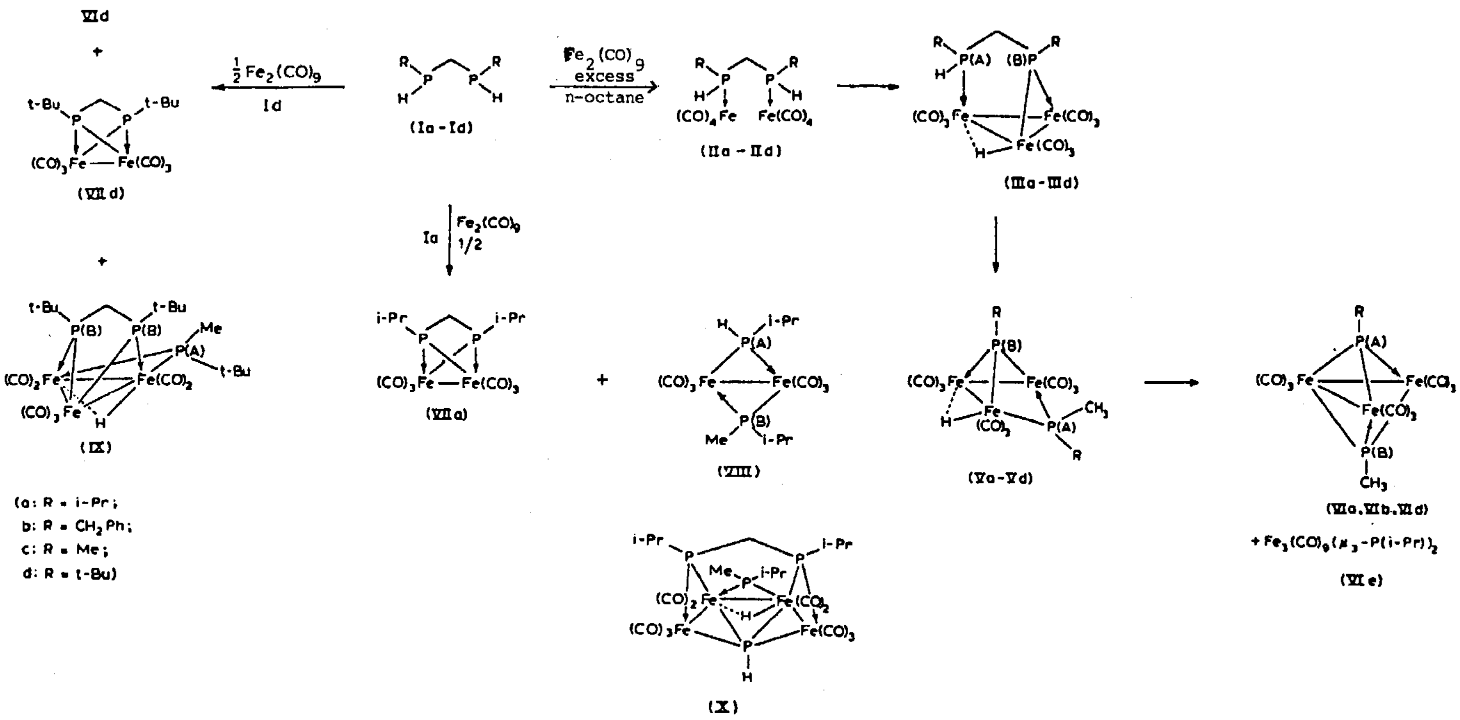
Cocondensation of iron vapor with arenes has been reinvestigated. Naphthalene and 1-methylnaphthalene formed unstable $(\eta^4$-$An)_2Fe$ at temperatures below 77 K and stable, 20-e $(\eta^6$-$An)_2Fe$ above 150 K. Benzene, toluene, and tetralin formed $(\eta^4$-$An)(\eta^6$-$An)Fe$, which were stable up to about 225 K[299]. $(C_6Me_6)Fe$ readily transferred one electron to TCNQ or phenazine[288]. EHMO calculations have predicted stability for $Fe_n(polyacene)_2$[281].

Lastly, a correlation of redox potentials of organometallic sandwich compounds with gas-phase metal ionization potentials has been derived. Examples included all of the foregoing classes of iron compounds, $CpFeAn^+$, An_2Fe, and ferracarboranes[300].

9. BIMETALLIC COMPOUNDS

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

Carbonylation of $(\mu$-$CH_2)Fe_2(CO)_8$ in lauryl alcohol (ROH) gave predominantly the expected lauryl acetate; however, 9% of dilauryl malonate also resulted. The latter also formed upon reaction of $Fe_2(CO)_8{}^{2-}$ with chloroacetyl chloride and lauryl alcohol[301]. The μ-allenylidene complex, $(R_2C{=}C{=}C)Fe_2(CO)_8$ (R = Me_3C), reacted with

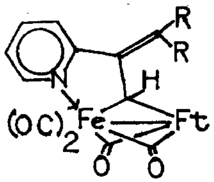


Scheme I

Products of Reaction of $RPHCH_2PHR$ with $Fe_2(CO)_9$

triphenylphosphine by CO displacement, giving the mono- and diphosphine analogs. With pyridine, CO displacement was followed by addition of a pyridine C-H bond across an allylidene double bond, to give **63** (X-ray structure)[302]. A comparative study of products of thermolysis of μ-alkylidene complexes of many metals has appeared; complexes of iron were particularly prone to form carbene-carbene coupling products (alkenes)[303].

The stable, closed stibinidene complex **64** (X-ray structure,) was among the products of reaction of $RSbCl_2$ with $Fe(CO)_4{}^{2-}$, along with its less stable, open isomer **16**[82]. Reaction of RP=NR (R = Me_3C) with nonacarbonyldiiron gave principally **65**, which in turn lost two CO's at 100° to form $(RPNR)Fe_2(CO)_6$[304].



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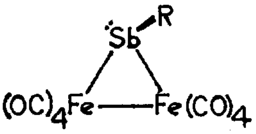

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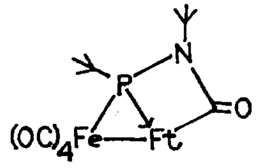
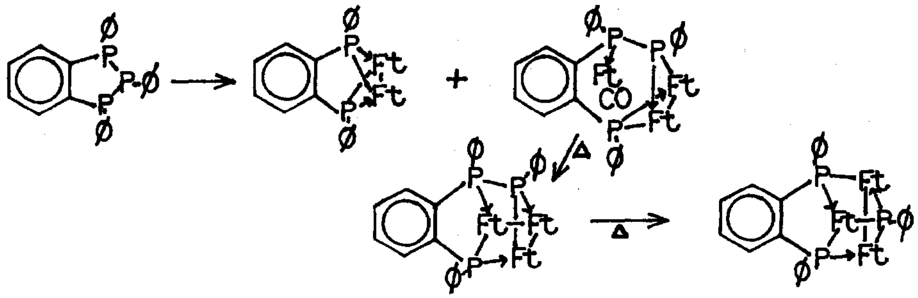


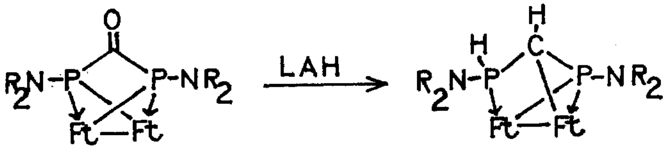
65

UV irradiation of a mixture of pentacarbonyliron and $(DMPM)_3Fe$ resulted in formation of $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}DMPM)$, **66**, and $Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}DMPM)_2$. The crystal structure of the latter showed mirror symmetry and a 2.719(4) Å Fe-Fe distance[305]. Reaction of $RPHCH_2PHR$ with nonacarbonyldiiron under various conditions gave a large variety of products having 2-4 irons per molecule (see Scheme I), several resulting from cleavage to RP, MeP, and RPMe fragments[306]. Reaction of the triphosphine, $Me_2PCH_2PMeCH_2PMe_2$, with five equivalents of nonacarbonyldiiron gave, *inter alia*, an analog of **66** (X-ray structure, Fe-Fe bond length 2.705(1) Å) having a pendant $CH_2PMe_2 \rightarrow Fe(CO)_4$ group[80]. Similarly, 1,2,3-triphenyl-1,2,3-triphosphaindane reacted with iron carbonyls with cleavage of P-P bonds to yield a number of products with doubly bridged $Fe_2(CO)_6$ units (Eq. 36)[81]. An unusual bridging diphos-



(36)

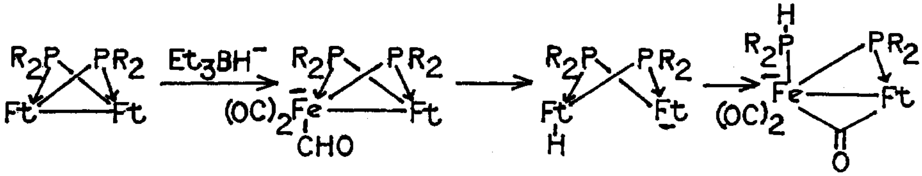
phine unit was generated during reaction of $Na_2Fe(CO)_4$ with R_2NPCl_2 (R = Me_2CH) to form **67** (X-ray structure). **67** reacted with alcohols R'OH to form $(\mu\text{-}R_2NPH)(\mu\text{-}R_2NPOR')Fe_2(CO)_6$. Reduction of the ligand carbonyl group with LAH gave the alcohol and the novel product **68** (Eq. 37)[307].



67 68

(37)

Reaction of $R_2C{=}PCl$ (R = Me_3Si) with $Na_2Fe(CO)_4$ resulted in formation of $(\mu\text{-}R_2C{=}P)_2Fe_2(CO)_6$ (X-ray), in which the C=P double bonds [bond length 1.650(4) Å] remained uncoordinated[308]. Reduction reactions of $(\mu\text{-}PR_2)_2Fe_2(CO)_6$ and $(\mu\text{-}PR_2)_2Fe_2(NO)_4$ have been reviewed[309]. The mechanisms of reactions of bis(μ-phosphido)hexacarbonyldiiron compounds with hydride reagents, and of their dianions with acids and alkylating agents, have been studied, with representative results shown in Eq. 38[310].



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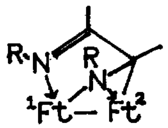
Substitution of CO's in (diazadiene)$Fe_2(CO)_6$, **69**, by trialkyl phosphites has been studied. Thermally, a CO from Fe(1) underwent substitution most readily, but irradiation caused isomerization to the Fe(2)-substituted product. The mechanism was determined by use of unsymmetrically-substituted diazadiene ligands[311].

Reaction of "Lawesson's reagent," $[ArP(=S)S]_2$, with nonacarbonyldiiron gave, along with Ft_3S_2 and $Ft_3(S)(PAr)$, **70** [Y = ArP->Fe(CO)$_4$], for which X-ray structures of two crystalline forms were reported. Photochemical reaction of $[Me_2P(=S]_2$ with pentacarbonyliron gave (u-SPMe$_2$)Fe$_2$(CO)$_6$[312]. Norbornadiene reacted with elemental sulfur and dodecacarbonyltriiron to give **70**, Y = three isomeric forms of C_7H_8, all characterized by X-ray crystallography[313]. Reduction of **9** with sodium borohydride gave the dimeric tetrathiooxalate product **71** (68%) (X-ray structure), in contrast to the trimethylphosphine analog, which added hydride to the ligand carbon. Oxidation of **71** gave **10**[58]. Extended Hückel MO calculations on metal bisdithiolenes and tetrathiolates have led, in the case of iron, to the prediction that the unknown **72** may be more stable than the known **73**[314].



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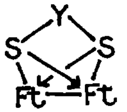

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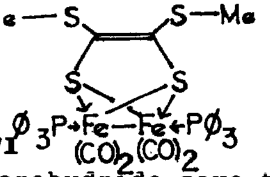

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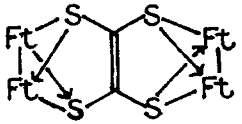

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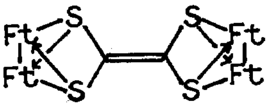

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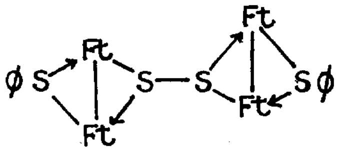
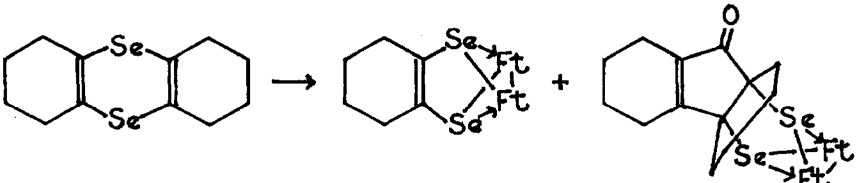


74

Organolithium and -magnesium reagents added to the S-S bond of (μ-S$_2$)Fe$_2$(CO)$_6$ (**70**, Y = bond) at -78°. The resulting monoanions could be alkylated or protonated on the second sulfur atom to give (μ-RS)(μ-R'S or HS)Fe$_2$(CO)$_6$[315]. Reaction of the monoanions with sulfuryl chloride resulted in oxidation with formation of an S-S bonded dimer, **74**, whose X-ray structure showed a long S-S bond, (as might be expected from the formal charges on the sulfur atoms)[316]. Acylation of the monoanions also occurred at S. Reaction of diacyl chlorides with the dianion from two-electron reduction of **70** (Y = bond) gave **70** [Y = CO(CH$_2$)$_n$CO][317].

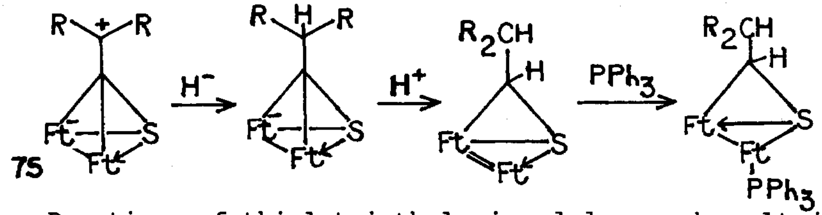
Preparation of (μ-MeS)$_2$Fe$_2$(CO)$_6$ by reaction of Fe$_3$(CO)$_{12}$ with MeSSMe has been proposed as an undergraduate laboratory experiment[318]. This compound and its phosphine-substituted derivatives have been found to catalyze carbonyl substitution reactions; cleavage of the Fe-Fe bond was proposed to account for the catalysis[319]. Mechanistic studies of substitution reactions of (μ-SPh)(μ-SCH$_2$CH=CH$_2$)Fe$_2$(CO)$_6$ by phosphines have found a two-term rate law, and interpreted in terms of direct associative substitution in competition with a preisomerization[320]. Several monophosphine derivatives have been characterized[321].

Reactions of (hydrido)iron carbonyl anions with chalcogen species, including sulfite, polysulfide, and selenite, have been studied. $E_2Fe_2(CO)_6$ (E = S, Se) were formed cleanly from reaction of excess sulfur or selenium with $HFe(CO)_4^-$, but other combinations gave mixtures with several tri-iron species[322]. Reactions of fused-ring 1,4-diselenacyclohexadienes with nonacarbonyldiiron have been found to give a variety of products depending on the size of the fused ring. An example is given in Eq. 39. Reactions of "1,4-diselenafulvenes" were also investigated[323].



(39)

Reactions of $(\mu,\eta^2$-thioketene)$Fe_2(CO)_6$ complexes, **75**, with nucleophiles have been examined. Phosphines, arsines, and stibines attacked an iron, with cleavage of an Fe-C bond. DPPM and DPPE did likewise, but displacement of a CO from the other iron gave a restored cluster with a μ-diphosphine group[324]. Hydride ion attacked the formally cationic carbon of **75**. The resulting anion coordinated symmetrically with Ph_3PAu^+ (X-ray) or Hg^{2+}. Protonation of the anion occurred as in Eq. 40[325].



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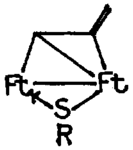
Reactions of thiol-triethylamine-dodecacarbonyltriiron mixtures, the active reagent in which is believed to be $(\mu$-CO$)(\mu$-SR$)Fe_2(CO)_6^-$, with electrophiles have resulted in formation of several types of Ft_2 complexes containing bridging thiolate and organic ligands. Acyl halides gave products with $(\mu,\eta^2$-acyl) ligands, and propargyl bromide gave **76** (X-ray structure). Perhaps most interesting, allyl chloride gave **77**, whose crystal structure showed an average Fe-CH_2 distance of 2.13 Å and an average Fe-CH distance of 2.49 Å. The bonding in the μ-allyl group thus resembled that in $FpCH_2CHCH_2Fp^+$. Thermal decomposition of the di-



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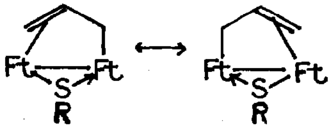
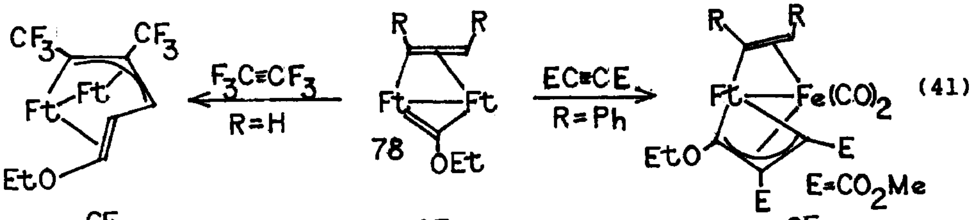


77

acyl compound (μ,η^2-RC=O)$_2$ Fe$_2$(CO)$_6$)(R = nonyl) gave R$_2$, R$_2$C=O, and (RC=O)$_2$. Reactions with MeI and Ph$_3$P were also reported[327].

Reactions of the (μ-carbyne) compound, **78**, with electrophilic alkynes (Eq. 41) have been reported, as shown in Eq. 41. The ethoxy group in the hexafluorobutyne adduct was labile toward nucleophilic substitution[328]. The anionic hexafluorobutyne adduct, **79**, readily lost fluoride ion to electrophiles, as shown in Eq. 42. The fluorines in the resulting difluorovinyl group were also readily replaced by ethoxy groups. The crystal structure of the coordinated ketene acetal group showed very asymmetrical bonding, with Fe-CH and Fe-C(OR)$_2$ distances of 2.15(1) and 2.86(1) Å, respectively. A formally analogous compound, **80**, resulted when **25** reacted with nonacarbonyldiiron[126]. Dehalogenation of (μ-Cl)(μ-Me$_3$CPCl)Fe$_2$(CO)$_6$ with Zn/Mg in the presence of alkynes RCCH led to formation of a coordinated ferraphosphacycle, **81**[330].



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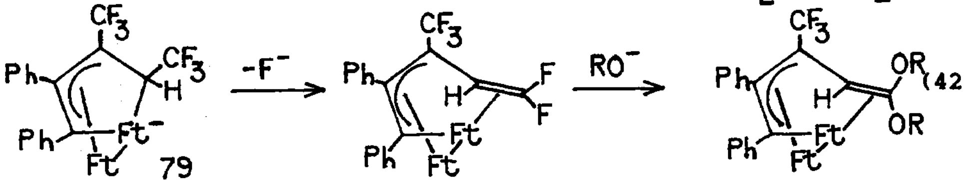

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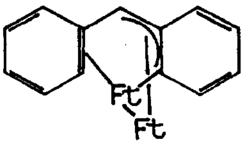
UV Photoelectron spectra and *ab initio* calculations on the very stable ferracycles (μ-C$_4$R$_4$)Fe$_2$(CO)$_6$ have been reported[331]. Some novel examples of this ring system, e.g. **82**, resulted from reaction of a [3]phenylene with excess nonacarbonyldiiron[138] .



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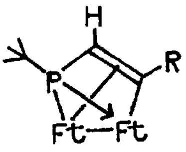

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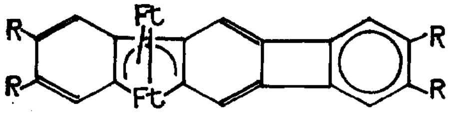


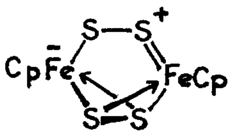
82, R=SiMe$_3$

Derivatives of Cp$_2$Fe$_2$(CO)$_4$

Reaction of (ArNC)Fe(CO)$_4$ with dicyclopentadiene at 140° formed Cp$_2$Fe$_2$(CO)$_3$(CNAr) and Cp$_2$Fe$_2$(CO)$_2$(CNAr)$_2$, but (ArNC)$_2$Fe(CO)$_3$ were unreactive[332]. Oxidation of Fp$_2$ by ferricenium ion in the presence of neutral ligands such as Ph$_3$P was recommended for preparation of cations such as $FpPPh_3^+$ [333]. 355-Nanometer photolysis of Fp^*_2 or Fp^*H in purged hydrocarbon solutions produced $Cp^*Fe(\mu-CO)_3FeCp^*$, which has been found to have a triplet ground state, and a 2.265(1) Å Fe-Fe bond length[334]. Fp_2 resulted when a photolyzed THF solution of $[CpFe(NO)]_2$ reacted with $CpCo(CO)_2$ [335]. Photolysis of $Fp_2Se{\rightarrow}Mn(CO)_2Cp$ occurred even on exposure to room light, with formation of $[CpFe(CO)]_2(\mu-CO)[\mu-Se{\rightarrow}Mn(CO)_2Cp]$ [213].

Photolysis of Fp_2 in the presence of elemental sulfur yielded $(CpFeS_2)_2$, **83**, which has been shown by X-ray crystallography to have two mutually perpendicular S_2 ligands, although another isomer was found also to exist in solution. Reaction with hexafluoro-2-butyne resulted in formation of dithiolate products[336]. Fp^*_2 reacted with sulfur in refluxing toluene to give a product analogous to **83**, also characterized by X-ray crystallography[337].

A good deal of interesting chemistry dealing with μ-alkylidyne complexes $[CpFe(CO)]_2(\mu-CO)(\mu-CCHR_2)^+$, **84**, has appeared during 1985. Depending on the lability of the β-H, these compounds were interconvertible with μ-alkenyl compounds **85**. When the R's were both alkyl groups, the equilibration was facile at room temperature in solution. With one alkyl group, heating to 88° was required. The methyl compound, with both R's = H, did not form the vinyl compound. **84** readily lost a proton to aqueous bicarbonate ion to form μ-alkenylidene complexes, whereas **85** formed alcohols by addition of OH^- to the β-carbon. **85** were fluxional, with E_a 9.8 kcal/mol when $R_2 = (CH_2)_5$ [338]. Alkenylidene-bridged compounds, $[CpFe(CO)]_2(\mu-CO)(\mu-C{=}CR_2)$, underwent hydride abstraction from the R groups with Ph_3C^+, giving alkenylidyne-bridged cations. These added Me_3P to the electrophilic γ-carbon and underwent δ-deprotonation with $LiN(SiMe_3)_2$ to form dienylidene-bridged products, e.g. $[CpFe(CO)]_2(\mu-CO)(\mu-C{=}CH{-}CH{=}CHMe)$ [339]. The ethylidyne-bridged dimer, **84**, R = H, underwent condensation reactions with aldehydes and with acetone to form alkenylidyne-bridged products in high yields. The crystal structure of $[CpFe(CO)]_2(\mu-CO)(\mu-C{-}CH{=}CH{-}C_6H_4Me)$ showed a coplanar C_3Fe_2 unit[340]. Reaction of the electrophilic μ-methylidene complex with the nucleophilic μ-ethenylidene complex occurred as shown in Eq. 43. The crystal structure of the product revealed it as another analog of $FpCH_2CHCH_2Fp^+$, formed by hydride migration after the initial C-C bond formation[341]. Photolysis of the μ-ethenylidene dimer in the



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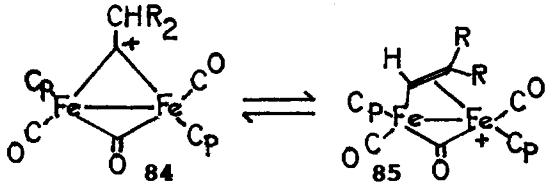
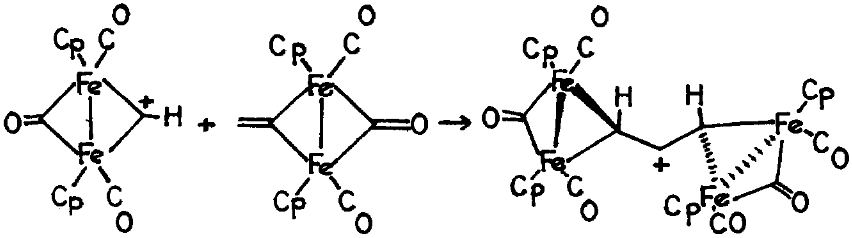
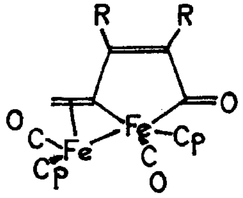


84 **85**



(43)

presence of RC≡CR (R = Me, Ph) and CO gave the ferracyclopentenones **86** (X-ray structure for R = Ph). Photolysis of **86** (R = Ph) caused decarbonylation, with formation of **87**[342].



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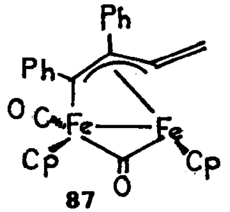

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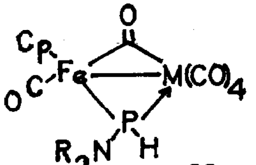
c. Heterobimetallic Compounds

An iron-zirconium compound has been synthesized by reaction of KFp with $CpZrCl(OCMe_3)(\eta^5\text{-}C_5H_4PPh_2)$. Photolysis resulted in displacement of a CO from the iron by the phosphorus[343]. $Cp_2M(CO)H$ reacted with $Fe_2(CO)_9$ to form $Cp_2M(CO)(\mu\text{-}H)Fe(CO)_4$ (M = Ta, Nb)[344].

The hydride species *cis*-$(OC)_4Fe(H)[(M(CO)_5]^-$ (M = Cr, Mo, W) have been found to be active alkene isomerization catalysts, in which the role of the $M(CO)_5$ unit is postulated to be similar to that of other Lewis acids in activating $HFe(CO)_4^-$ [345]. The X-ray structure of the "auralog," Et_4N^+ *cis*-$(OC)_4Fe(AuPPh_3)[W(CO)_5]^-$, showed essentially octahedral iron and tungsten and no gold-tungsten interaction[346]. Synthesis and crystal structure of $Cp_2Mo(\mu\text{-}H)_2FeI_2(NCMe)$ have been reported[347].

Photolysis of $Fe(DMPM)_3$ with $Cr(CO)_6$ produced $(OC)_3Fe(\mu\text{-}DMPM)_2Cr(CO)_3$, whose X-ray structure revealed little effort by iron to relieve the electron-deficiency of the 16-electron chromium (the Fe to Cr distance was 3.111(6) Å)[305]. Reaction of NaFp with $(R_2NPHX)M(CO)_5$ (R = Me_2CH; X = Cl, Br; M = Cr, Mo, W) produced $FpPH(NR_2)M(CO)_5$ by simple displacement. Photolysis resulted in decarbonylation to form **88**[205]. Analogous compounds having CpMn(CO) instead of $M(CO)_4$ groups were also prepared[205]. The tetrahedral cluster **89** (X = Br) has been prepared and crystallographically characterized. The bromide could be removed with Ag^+, and the resulting cation inserted $IrCl(CO)(PPh_3)_2$ into the Te-Te bond[348].



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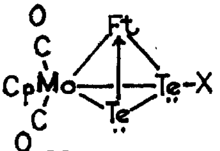

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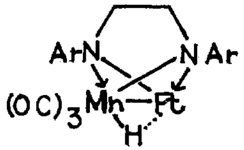
Fp$^-$ displaced acetonitrile from Cp'Mn(CO)$_2$(NCMe) (Cp' = MeC$_5$H$_4$) to give the Fp$_2$ analog, Cp(CO)Fe(μ-CO)$_2$Mn(CO)Cp'$^-$. This compound, like Fp$_2$, existed as interconvertible cis and trans isomers, and underwent methylation on a bridging CO ligand. The resulting (μ-methoxycarbyne) compound decomposed at 65^o in the presence of PPh$_3$ to give Cp'Mn(CO)$_3$ and CpFe(CO)(PPh$_3$)Me, the latter requiring migration of the methyl group from oxygen to iron[349].

Excess HFe(CO)$_4$$^-$ reacted with (ArN=CH-CH=NAR)Mn(CO)$_3$Br to yield, after protonation, the reduced product **90**. The high symmetry of the molecular structure rendered the metals indistinguishable in the crystallographic structure determination; the Fe-Mn bond length was a short 2.539(1) Å.[350]. Similar reaction of LMn(CO)$_3$Br (L = a 2-carboximinopyridine, C$_5$H$_4$N-CH=NCMe$_3$) gave a stoichiometrically analogous product, (μ-H)(μ-L)FeMn(CO)$_6$, **91**; however in this case the C=N bond of the unreduced ligand was coordinated to the iron[351].



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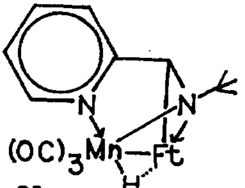

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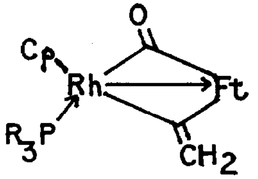
CpFe(CO)(μ-CO)$_2$Ru(CO)Cp has been prepared from NaFp and CpRu(CO)$_2$I. Its crystal structure has been determined (Fe-Ru bond length 2.626(1) Å.), and it has served to provide entree into an extensive chemistry of bridged iron-ruthenium compounds, including examples having vinyl and alkylidene bridges. The chemistry studied qualitatively resembled that of the diiron system, but the Fe-Ru system was often more reactive than either homobimetallic system[352].

Reaction of the phosphazene-bridged Fe$_2$(CO)$_8$(μ-P$_3$N$_3$Cl$_4$) with CpCo(CO)$_2$ resulted in metal exchange to produce primarily (OC)$_4$Fe-Co(CO)Cp(μ-P$_3$N$_3$Cl$_4$), but the analogous Fe-Rh compound did not form[353]. Reaction of Cp(R$_3$P)Rh=C=CH$_2$ (R = Me$_2$CH) with Fe$_2$(CO)$_9$ gave the ethenylidene-bridged product, **92** (X-ray structure)[354]. A "nickelaferrocene", **93**, resulted from reaction of Fp$_2$ with Cp$_2$Ni and diphenylacetylene. The Ni-Fe distance was 2.419(2) A., and the compound underwent reversible one-electron oxidation[355].



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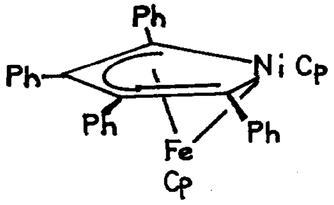

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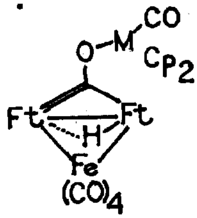
10. TRINUCLEAR CLUSTER COMPOUNDS

a. Fe_3 Clusters

The complex salt, $[Cp_2Mo(CO)H]^+$ $[Fe_3(CO)_{11}H]^-$, (X-ray structure) resulted from photolysis of Cp_2MoH_2 with $Fe(CO)_5$ in benzene[356]. An analogous product, **94**, resulted when $Cp_2M(CO)H$ or $CpMH_3$ (M = Nb, Ta) reacted with $Fe_3(CO)_{12}$; **94** tended to dissociate in THF to $[Cp_2M(CO)(THF)]^+$ $[Fe_3(CO)_{11}H]^-$ [344].

The kinetics of substitution of $Fe_3(CO)_{12}$ by phosphines and phosphites has been studied. Products included $Fe_3(CO)_{12-n}(PR_3)_n$, where n = 1,2,3, and also $Fe(CO)_4PR_3$ and $Fe(CO)_3(PR_3)_2$. CO dissociation was proposed as the rate-determining step[357]. Attack of the hard nucleophile, methoxide ion, on $Fe_3(CO)_{12}$ was suggested to involve formation of $Fe_3(CO)_{11}(CO_2Me)^-$, which fragmented rapidly to $(OC)_4FeCO_2Me^-$; the rate of reaction was studied by stopped-flow techniques[358].



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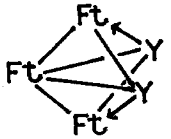
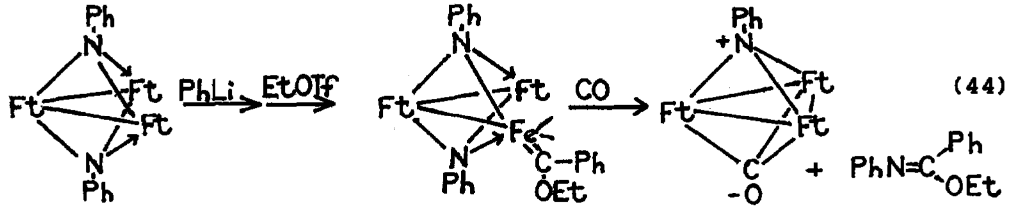


95

Reaction of $Fe_3(CO)_{12}$ with benzylic thiols in a HBF_4/benzene two-phase mixture resulted in efficient desulfurization[359]. Reaction of $HFe_3(CO)_{11}^-$ with sulfite or polysulfide yielded mixtures of the known di- and tri-iron sulfide clusters, including $Fe_3S_2(CO)_9$ (**95**, Y = S), $Fe_3S(CO)_{10}$, and $Fe_3S(CO)_9(SO)$. Reaction of $HFe(CO)_4^-$ with selenite yielded only $Fe_3Se_2(CO)_9$ (**95**, Y = Se)[322]. $Fe_3S_2(CO)_9$ also resulted when $Cp^*{}_2S$ reacted with $Fe_2(CO)_9$[360]. The formation and interconversion reactions of iron-chalcogen carbonyl clusters have been discussed in detail[322].

(2,3-Diazanorbornene)$Fe_3(CO)_9$ showed two reversible one-electron reductions in cyclic voltammetry. Reduction in the presence of trimethyl phosphite induced substitution reactions, with up to three CO's undergoing replacement by the phosphite[361]. Reactions of **95** (Y = NPh) with $LiEt_3BH$ or RLi resulted in attack at a CO of a terminal Ft group, with formation of formyls or acyls. Alkylation of the benzoyl compound with EtOTf gave a carbene complex (X-ray) which slowly eliminated PhN=C(Ph)OEt on exposure to CO (Eq. **44**). The chemistry of the bis(phosphinidene) analogs was generally similar; however, ethylation of the benzoyl anion (from phenyllithium attack) resulted in 37% of the product **96** (X-ray) from carbene insertion into a Fe-P bond[362]. **95** [Y = $SbCH(SiMe_3)_2$] was produced by reaction of **17** with nonacarbonyldiiron[82]. The compound $(\mu_3\text{-Bi})_2Ft_3$, a product of reaction of $NaBiO_3$ with $HFe(CO)_4^-$, has been found crystallographically to have a closed trigonal bipyramidal core with apical bismuth atoms[363].



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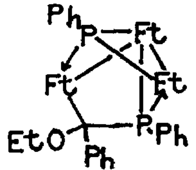
A detailed comparison of the structures of the three clusters $(\mu\text{-H})_2M_3(CO)_8(\mu\text{-PPh}_2)_2$ with M = Fe, Ru, Os has been made. The Fe_3 compound, **97**, showed a long unbridged Fe-Fe bond (2.83 A compared to 2.66 A average for the bridged bonds). **97** reacted with CO to form the bis(phosphinidene) complex, **95** (Y = PPh)[364].



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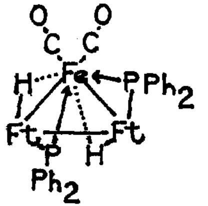

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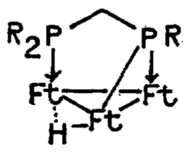

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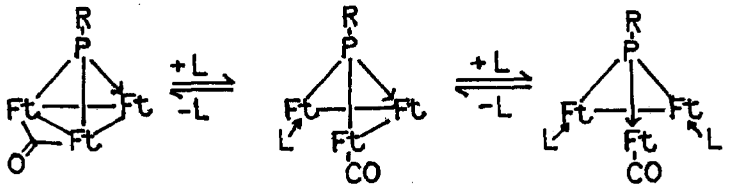
Substitution reactions of the tetrahedral clusters $(\mu_3\text{-RP})Fe_3(CO)_{10}$ have been found to proceed by opening of Fe-Fe bonds, as illustrated in Eq. 45, rather than by CO dissociation[365]. Such



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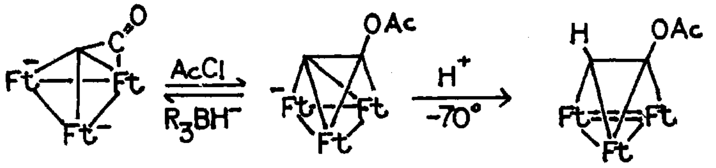
tetrahedral clusters resulted, along with **95** (Y = PR), from decomposition of clusters **98** (themselves made by reaction of R_2PCH_2PRH with nonacarbonyldiiron; see Scheme I[306]) at elevated temperatures[366]. Bridged triiron clusters analogous to **98** also resulted from reactions of the triphosphines, $Me_2PCH_2P(Me)CH_2PMe_2$[80] and

1,2,3-triphenyl-1,2,3-triphosphaindane[81], with excess iron carbonyls.

Extended Hückel MO calculations on bonding of tetrahedral P_4 to transition metals and metal clusters have resulted in the suggestion that $(\eta^3\text{-}P_4)Ft_3$ should be an attractive candidate for synthetic efforts[367]. The Ft_3Bi_4 core of the recently described $Bi_4Fe_4(CO)_{13}{}^{2-}$ anion, **99**, may be considered a related example[368].

Reaction of $CFBr_3$ with iron carbonyls gave 2-3% of $(\mu_3\text{-}CF)_2Ft_3$, whose crystal structure showed the expected trigonal bipyramidal structure with apical CF groups[369]. PPN^+ salts of $Fe_3(CO)_{10}{}^{-}$, $Fe_3(CO)_9CCO^{2-}$, and $Fe_2Co(CO)_9CCO^-$ have been studied by Mossbauer spectroscopy, in comparison with neutral $Fe_3(CO)_{12}$. The results for the anionic clusters were interpreted in terms of increased electron density primarily at the two equivalent Fe atoms, consistent with the nucleophilic reactivity patterns of these clusters[370]. An example of the latter reaction was acylation of the ketenylidene dianion (Eq. 46) to form an acetylide cluster (X-ray structure)[371]. A saturated analog of the latter resulted from reversible carbonylation of the bis(alkylidyne) cluster, $Ft_3(\mu_3\text{-}CMe)(\mu_3\text{-}COEt)$ under 20 atm. CO, or from its reaction with PPh_3, which gave the more stable **100** (X-ray structure)[372]. An extended Hückel MO study of trimetal-alkyne clusters has dealt with the orientation of the alkyne relative to the metal triangle as a function of the donor and acceptor properties of the alkyne and M_3 fragments, with generally good agreement with experimental results[373].



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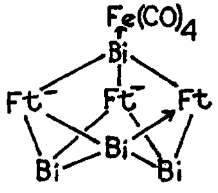

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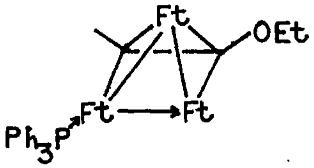

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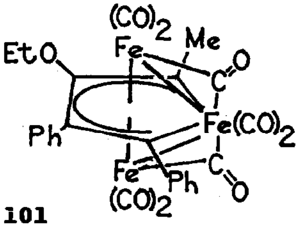

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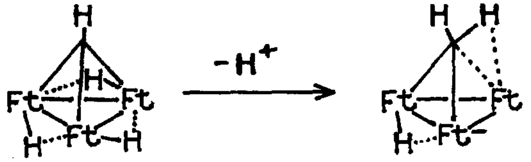
Deprotonation of $(\mu\text{-}H)_3Ft_3(\mu_3\text{-}CH)$ resulted in hydride rearrangements as shown in Eq. 47, whereas deprotonation of the $(\mu_3\text{-}CMe)$ analog resulted in hydrogen elimination, forming $(\mu\text{-}H)Ft_3\text{-}(CCH_2)^-$ [374].

Reaction of the bis(alkylidyne) cluster $Ft_3(\mu_3\text{-}COEt)(\mu_3\text{-}CMe)$ with alkynes such as diphenylacetylene resulted in coupling of the alkylidynes (as in formation of **100**), to produce ferrole-type

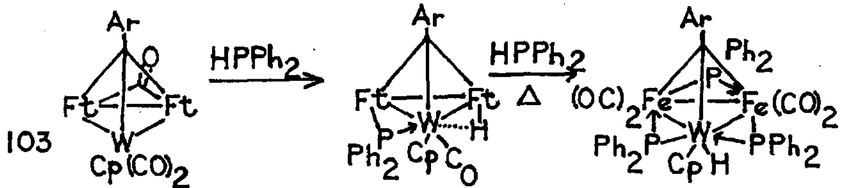


(47)

complexes such as **101**[375]. The electronic structures of these complexes have been investigated by UV photoelectron spectroscopy, in combination with *ab initio* calculations[331].

b. Fe_2M Clusters

The tetrahedral cluster (μ_3-As)[CpMo(CO)$_3$]$_3$ was converted to the AsFe$_2$Mo cluster, **102**, upon reaction with excess Fe(CO)$_5$[376]. Reactions of (μ_3-alkylidyne)Fe$_2$W clusters **103** have received considerable attention. Reaction with Ph$_2$PH in ether resulted in formation of a product with phosphido and hydrido bridges (Eq. 48), and, under more vigorous conditions, a tris(μ-phosphido) cluster[377]. In methylene chloride, the same reactants produced a different result, with products of methylidyne-CO coupling predominating (Eq. 49)[378]. Reaction of **103** with S or Se gave products



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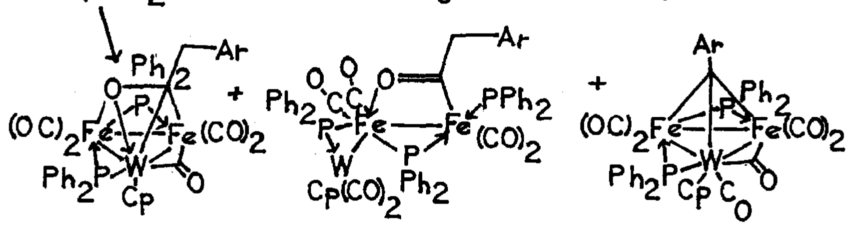
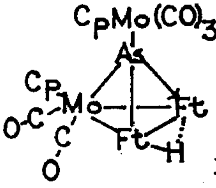


(49)

with a (μ_3-S or -Se) cap and a (μ-CAr) ligand bridging a Fe-W bond. The ethylidyne analog also produced a cluster with a (μ-thioacyl) ligand[379].

The triangular cluster Fe$_2$Mn(CO)$_{12}^-$ was produced by reaction of Fe$_3$(CO)$_{11}^{2-}$ with (MeCN)Mn(CO)$_5^+$ [380]. The tetrahedral clusters, Cp(CO)$_2$MnFt$_2$(μ_3-PR) have been found to react with ligands L rather in the manner of Eq. 45, with opening of an Fe-Mn bond the rate-determining step, with $\Delta H^{\ddagger}$ of about 22 kcal/mol[381]. The similar cluster Cp*Mn(CO)$_2$Ft$_2$(μ_3-S) was formed upon reaction of Cp*Mn(CO)$_2$SCMe$_3$ with Fe$_2$(CO)$_9$[382].

Mixed Fe-Ru catalysts $M_3(CO)_{12}$, supported on alumina, effectively catalyzed CO hydrogenation, ethene homologation, and ethane hydrogenolysis[383]. Reaction of $NaCo(CO)_4$ with $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CSMe)^+$ gave the open $CoFe_2$ cluster **104**, which underwent CO displacement by phosphines from cobalt[384]. The crystal structure of trans-$Pt(NCPh)_2[Fe(CO)_3NO]_2$ has been reported[385].



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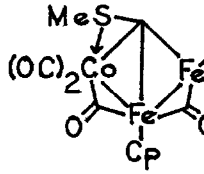

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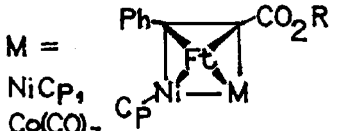
c. FeM$_2$ Clusters

Square pyramidal clusters **105** and **106** have been prepared by insertion of Pt units into tetrahedral clusters, using nonacarbonyldiiron. Both were fluxional on the NMR time scale, by a process tantamount to alkyne rotation[386]. But reaction of the tetrahedral $(\mu_3\text{-}GeR)Co_3(CO)_9$ with $Fe(CO)_4{}^{2-}$ resulted in group replacement to form the $GeCo_2Fe$ cluster, **107**[197].



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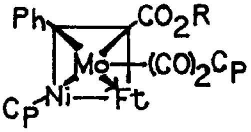

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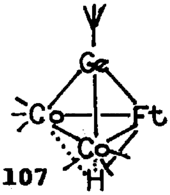

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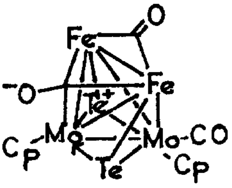
Reaction of $[Cp^*MoS_2]_2$ with iron carbonyls gave new mixed iron-molybdenum-sulfur clusters, based on Mo_2Fe triangular and Mo_2Fe_2 butterfly skeletons[387]. **95** (Y = Te) with $[CpMo(CO)_3]_2$ formed $[CpMo(CO)_2]_2PtTe_2$, in which a $CpMo(CO)_2$ moiety bridged the Te wing tips of a $MoFeTe_2$ butterfly. Thermolysis with $Fe(CO)_5$ gave several Te-capped tetrahedral clusters, including **108**, which showed an exceptionally short (2.43 A) Fe-Fe bond[388].

A new compound with a phosphazene functioning as a four-electron ligand toward a $FeCo_2(CO)_9$ triangular cluster has been prepared[353]. The X-ray structure of $(L_2Cu)_2Fe(CO)_4$, (L = PPh_3), prepared from L_2CuCl and $Fe(CO)_4{}^{2-}$, showed a linear Cu-Fe-Cu skeleton and semibridging CO groups[389].



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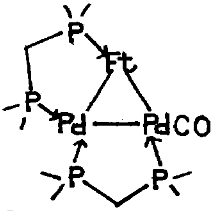


109

The complex **109** was an effective catalyst for reductive carbonylation of *o*-nitrophenol to benzoxazol-2-one[390,391].

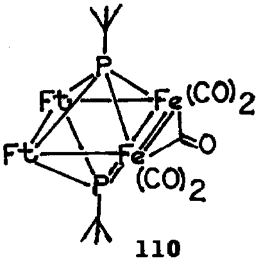
11. TETRA- AND POLYNUCLEAR CLUSTER COMPOUNDS

The trinuclear complex $Ft_3(\mu_3\text{-CMe})(\mu_3\text{-CO})^-$ reacted with Ph_3PMCl (M = Cu, Au) to form tetranuclear adducts; the X-ray structure of the Cu adduct showed a butterfly structure with the Cu at one wingtip. The μ_3-CMe ligand continued to bridge the Fe_3 triangle, but the bridging CO was reduced to μ_2, joining basal and wingtip Fe's[392].

SCF discrete variational $X\alpha$ calculations on bare metal clusters have indicated 12 unpaired electrons on Fe_4. Addition of CO ligands reduced the paramagnetism of the cluster[393]. The crystal structure of $[PPN^+]_2\ Fe_3(CO)_{13}{}^{2-}$ showed one μ_3-CO group, but, in contrast to the previously determined $Fe(py)_6{}^{2+}$ salt, little tendency toward carbonyl bridging in the basal plane[394]. The crystal structure of the PPN^+ salt of the isoelectronic ion, $Fe_3Co(CO)_{13}{}^-$ [the anion resulted from reaction of $Co_2(CO)_8$ with $Fe_4(CO)_{13}{}^{2-}$] showed a tetrahedral framework, with CO's bridging each Fe-Co bond and one terminal CO on the cobalt[380]. Mercuric and gold adducts of $FeCo_3(CO)_{12}{}^-$ have been reported[395]. Interaction of $HFeCo_3(CO)_{12}$ with hydrated magnesia and alumina surfaces gave surface-bound anion $FeCo_3(CO)_{12}{}^-$, but with dehydrated surfaces, cluster decomposition occurred[396].

Reduction of $Ft_2(\mu\text{-Cl})(\mu\text{-Me}_3CPCl)$ with zinc gave a 50% yield of cluster **110**, which could also be obtained as a product of reaction of $(Me_3CPCl)Fe(CO)_4$ with excess $Fe_2(CO)_9$[55]. Electron structures of six-vertex clusters like **110**, having RP, RGe, S, and Te vertices and ML_3 and ML_2 metal groups have been analyzed[397]. The crystal structure of $Fe_2Mo_2Te_2(CO)_7(Cp)_2$ has been determined[398]. The structure of $(Et_4N)_2\ MoFe_3S_6(CO)_6$, prepared by reaction of $Li_2Fe_2S_2(CO)_6$ with $(Et_4N)_2\ Cl_2FeMoS_4$, has been found to be that of **70** with Y = $Fe(\mu\text{-S})_2MoS_2$[399]. Along with several other cluster products (Scheme I), reaction of $RPHCH_2PHR$ (R = Me_2CH) with two equivalents of $Fe_2(CO)_9$ yielded **111**, whose crystal structure has been reported[400].

Reaction of $HFe_4(CH)(CO)_{12}$ with partially dehydroxylated alumina has been studied by EXAFS and IR methods. Initially, the anion, $HFe_4(C)(CO)_{12}{}^-$ became bound to the surface, followed by partial decomposition to form iron or iron carbide species. The resulting material showed some CO-reduction and benzene-hydrogenation activity[401]. Interactive molecular graphics methods have been applied to analysis of steric interactions in $Fe_4(CO)_{12}(CR)^-$ clusters[402]. A number of heterometallic analogs of such clusters have been reported. Thus, reaction of the ketenylidene cluster Ft_3CCO^{-2} with $[Rh(CO)_2Cl]_2$ or $Mn(CO)_5(NCMe)^+$ produced **112** [M = $Rh(CO)_3{}^+$ (X-ray) or $Mn(CO)_4{}^+$]^{403}. The triruthenium ketenylidene cluster $Ru_3(CO)_9(CCO)^{-2}$ reacted with $Fe_2(CO)_9$ to form the carbide cluster analogous to **112**, with the iron tricarbonyl group at a wingtip^{404}. Protonation of these heterometallic carbide clusters produced results similar to those of the parent Fe_4 species.



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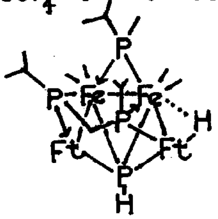
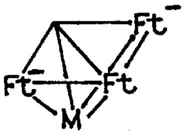
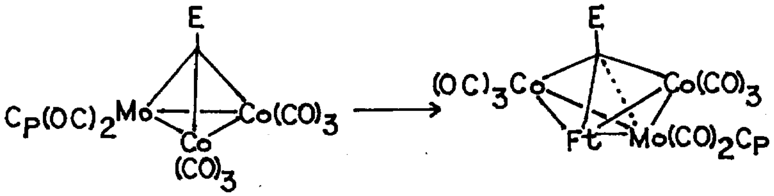


111



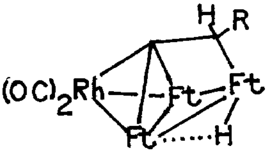
112

Cluster expansion reactions, using $Fe_2(CO)_9$, of $Cp(CO)_2MoM_2$-$(\mu_3$-$CCO_2CHMe_2)$ (M = CpNi or $Co(CO)_3$) gave products of differing structure. The $MoNi_2$ compound gave a pyramidal product with a Ft group spanning a planar $MoNi_2C$ base. The $MoCo_2C$ starting material (Eq. 50) gave a bipyramidal product (X-ray) similar to **112**. Other square pyramidal products incorporating other metal moieties were also reported^{405}.

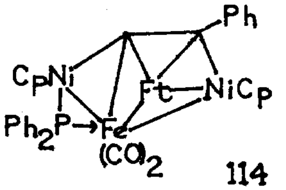


(50)

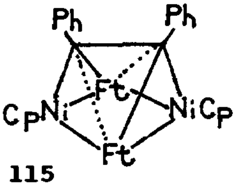
Expansion of $HFt_3(C{=}CHR)^-$ (R = H, Ph) with $[Rh(CO)_2Cl]_2/Tl^+$ gave a $RhFe_3$ cluster whose spectra indicated a μ_4-η^2 mode of bonding for the vinylidene ligand^{406}. Structure **113** may be suggested for the product. It equalled $Rh_4(CO)_{12}$ in hydroformylation catalysis and exceeded it in hydrogenation activity^{406}. Condensation of $[CpNi(CO)]_2$ with $Ft_2(\mu$-$PPh_2)(\mu_2,\eta^2$-$CCPh)$ gave the mixed cluster, **114** (X-ray)^{407}. An X-ray structure of the closely related cluster, $(CpNi)_2Ft_2(\mu_4,\eta^2$-$C_2Ph_2)$, **115**, a 62-electron nido cluster, has also been reported. **115** underwent further cluster expansion reactions with suitable metal reagents^{408}. Reaction of acetylene with $HFe_4(CO)_{13}{}^-$ in refluxing ethyl acetate gave mostly



113



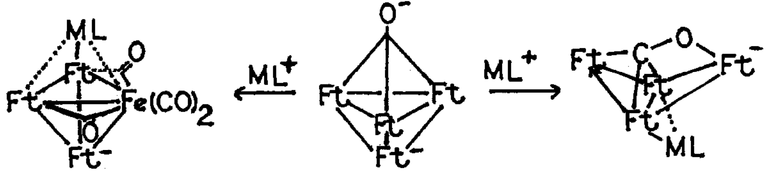
114



115

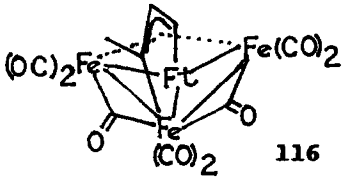
$Fe_4(CO)_{12}(\mu_3\text{-}CMe)^-$, but in refluxing 3-pentanone, **116** was the product. $RC{\equiv}CH$ gave homologs of **116** when R = alkyl, and smaller clusters $Ft_3(CCR)^-$ when R = Ph or CO_2Me[409].

Equilibria between isomeric forms of $Fe_4(CO)_{13}{}^{2-}$ in solution have been studied by reactions with Lewis acid cations such as Et_3PAu^+, Ph_3PCu^+, and $MeHg^+$. (See Eq. 51) In solution two isomers of the adducts existed, and suitable manipulations of conditions led to isolation of examples of each type in crystalline form. Crystal structures were obtained for the tetrahedral form with face-bridging ML group with ML = Ph_3PCu[410,411] and MeHg[411], and for the μ-CO butterfly form with edge-bridging ML, with ML = Et_3PAu. NMR studies were employed to assess the position of equilibria of the two forms in solution, and it was found that increasing Lewis acid strength of ML^+ or electrophilic coordination of the O favored the butterfly form[412].

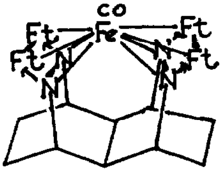


(51)

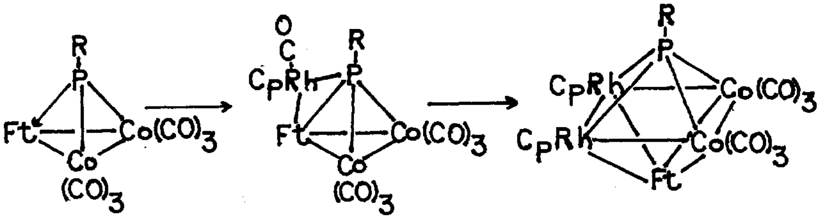
A nearly planar array of five iron atoms stabilized by coordination to a substrate having parallel diazene groups has been found in **117**[413]. Cluster expansion of a tetrahedral Co_2FeP cluster, using $CpRh(CO)_2$, proceeded stepwise as shown in Eq. 52[414].



116



117



(52)

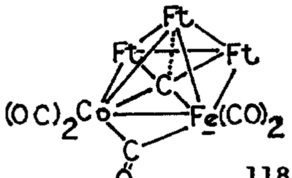
Similar results were obtained with a CoFeRuP cluster.

The electrochemical reduction of the square pyramidal cluster, Ft_5C, has been found to involve transfer of two electrons followed by (slow at low temp.) loss of a CO to form $Fe_5C(CO)_{14}{}^{2-}$. The X-ray structures of these two species and of isoelectronic $Fe_5N(CO)_{14}{}^-$ showed increasing displacement of the carbide or nitride from the basal plane with increasing charge[415]. The heterometallic analog **118**, which resulted from reaction of

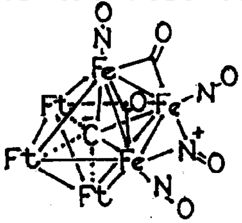
$Co_2(CO)_8$ with the ketenylidene cluster, $[Ft_3CCO]^{2-}$, fit in with this trend[403,416].

Several new heterometallic octahedral clusters with included carbido ligands have been prepared and characterized by X-ray crystallography. The metals involved have included Ni_3Fe_3[403], Fe_4CoRh[416], and Fe_4CoPd[416]. Fe_6 clusters with nitrosyl ligands, $Fe_6C(CO)_{15}(NO)^-$ and $Fe_6C(CO)_{11}(NO)_4$, **119**, have also been reported[417].

A theoretical discussion of triangular M_3L_6 molecules included an analysis of the $Pt_3Fe_3(CO)_{15}{}^{-1,-2}$ systems[418]. Multinuclear NMR studies of the closely related $Cu_3Fe_3(CO)_{12}{}^{3-}$ anion have been reported, along with studies of the more complex $Cu_5Fe_4(CO)_{16}{}^{3-}$ and $Cu_6Fe_4(CO)_{16}{}^{2-}$[419]. The X-ray structure of the latter showed an octahedron of copper atoms with four tetrahedrally-arranged faces capped by $Fe(CO)_4$ groups[389].



118



119

In a theoretical analysis of "How Carbon Monoxide Bonds to Metal Surfaces," Sung and Hoffmann discussed, *inter alia*, bonding to the Fe(110) surface. CO on Fe(100) has been found to exhibit an unusually low CO stretching frequency (1210 cm^{-1}), appropriate to a C-O single bond[421]. The effect of d-band positions on acetylene bonded to Fe(100) has also been studied theoretically[422]. The oligomerization of phenylacetylene on iron catalysts has been studied, and four products characterized[423].

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