ORGANOIRON CHEMISTRY

Annual Survey for the Year 1987*

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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
DEPE	1,2-bis(diethylphosphino)ethane
DMF	N,N-dimethylformamide
DMPE	1,2-bis(dimethylphosphino)ethane
DMPM	bis(dimethylphosphino)methane
DPPE	1,2-bis(diphenylphosphino)ethane
DPPM	bis(diphenylphosphino)methane
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-
NMP	N-methyl-2-pyrrolidone
Ph	phenyl, C_6H_5-
Por	any porphyrin ligand coordinated as a dianion
PPN^+	$Ph_3P{=}N{=}PPh_3{}^+$
R	any unicovalent organic group such as methyl
TCNE	tetracyanoethene
Tf	trifluoromethanesulfonyl group, F_3CSO_2-
THF	tetrahydrofuran
X	any halogen

1. INTRODUCTION

In this Annual Review, I attempt to cover the organoiron chemistry reported in journals published during calendar year 1987. Organoiron compounds are those compounds which contain at least one C-Fe bond; however Fe-CN compounds are not included in this review, and properties and reactions of the simple iron carbonyls are not described exhaustively. Ferrocenes are treated in Annual Surveys by B. W. Rockett and G. Marr.

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

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

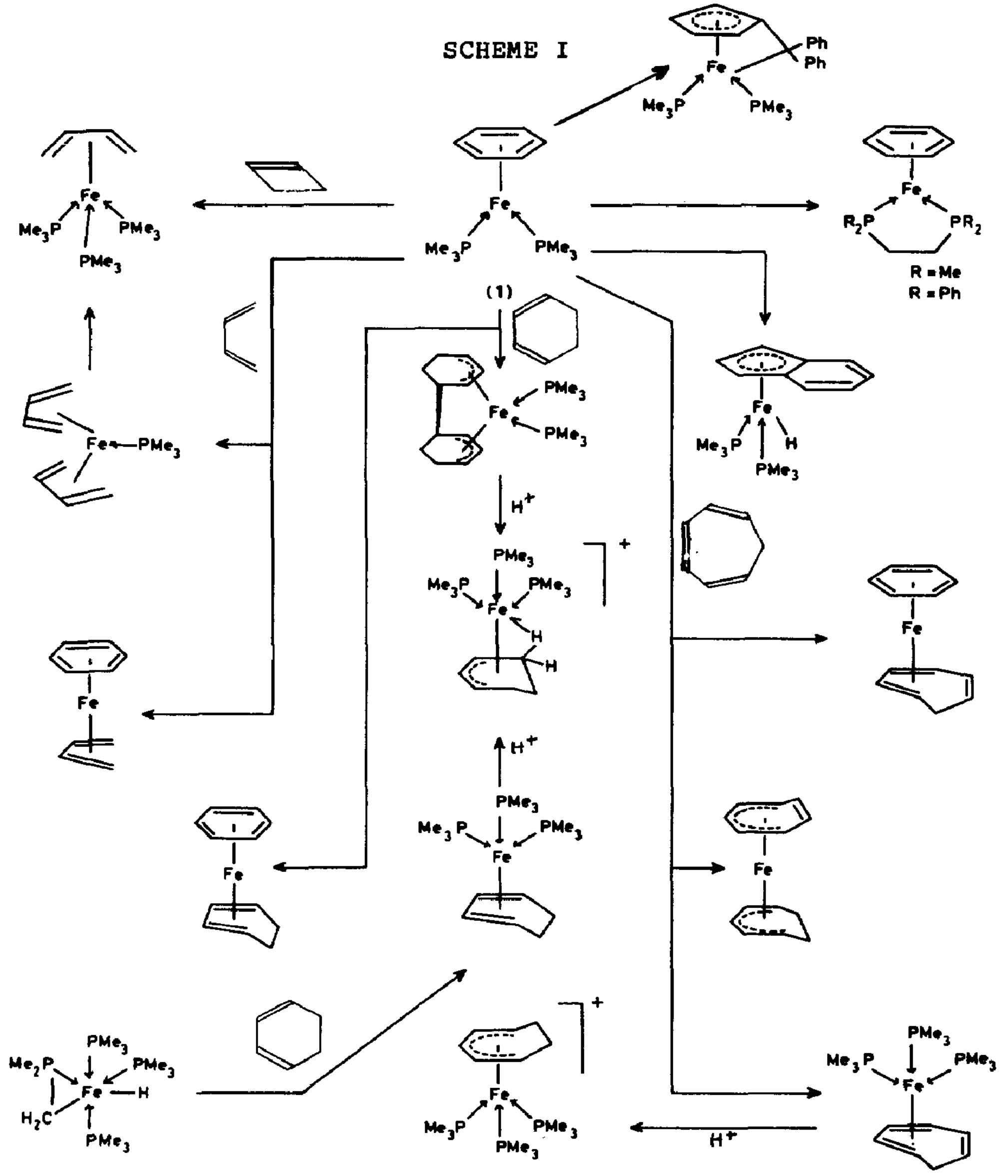
This reviewer finds adherence to these conventions to be possible in describing all but the largest clusters, and believes that their use provides clarity sometimes lost when lines are used willy-nilly in the same structural drawing to represent electron-pair bonds, partial bonds, and geometrical relationships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

2. REFERENCE WORKS, REVIEWS, AND GENERAL STUDIES

Volume 13/9a of the Houben-Weyl *Methoden der Organischen Chemie* contained a very detailed chapter (348 pages) by A. Segnitz on "Methods of Preparation and Transformation of σ-Organoiron Compounds."[1] D. Astruc has contributed a 106-page chapter, with 303 references, on "Use of Organoiron Compounds in Organic Synthesis," to Volume 4 of *The Chemistry of the Metal-Carbon Bond*.[2]

I will also discuss in this section a number of papers which deal with several classes of organoiron compounds. (η-C_6H_6)Fe-(PMe_3)$_2$, 1, available in gram quantities by co-condensation of iron vapor, benzene, and trimethylphosphine[3], has been found to react readily at room temperature with many unsaturated organics to produce a variety of (polyene)iron compounds, as shown in Scheme I[4]. A similarly extensive series of organoiron compounds resulted from reaction of 1 with MeSi(CH_2PMe_2)$_3$ [tmps], to give (η^4-C_6H_6)Fe(tmps), 2, from which the benzene ligand was displaced by a variety of unsaturated organics[5].

SCHEME I



^{57}Fe relaxation mechanisms in a number of organoiron compounds have been studied at different field strengths. Field-dependent chemical shift anisotropy was the dominant factor in most compounds at high field and spin rotation at low field. Trace particles from sample decomposition also affected the transverse relaxation[6].

Multiphoton ionization spectra of several organoiron compounds containing hydrocarbon and fluorocarbon ligands have been studied. Both the nature of the ligand bonding and the intramolecular energy transfer (affected by the ligand vibrational modes) affected the distribution of iron electronic states and thus the electronic states of the photoproducts[7].

Molecular mechanics methods have been used to calculate ligand configurations in diene and cyclopentadienyl π-complexes also containing hydride, halide, and carbonyl ligands. Experimental ligand-metal-ligand angles were said to correlate well with those calculated on the basis of non-bonding interactions among ligands[8].

Compressed disks of several organoiron π-complexes, doped with iodine, showed good semiconducting properties[9].

3. REACTIONS OF "NAKED" IRON ATOMS AND IONS

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

With respect to the latter, theoretical methods have been brought to bear on the interaction of iron atoms with methane and ethylene. Ground-state iron atoms ($3d^6 4s^2$) were found to be unreactive toward oxidative addition to C-H bonds (compared to excited state $3d^6 4s^1 4p^1$) because of closed-shell repulsions, in agreement with earlier experimental results. Similar effects explained the preference of ground-state iron atoms for sigma-coordination with ethene[10]. Reactions of iron atoms with oxirane (ethylene oxide) in matrices have been studied. Insertion into a C-O bond gave a ferraoxetane, which formed (η-ethene)Fe=O upon visible photolysis; the latter was converted to CH_2=CHFeOH by UV irradiation[11].

Gas-phase reactions of Fe^+ with organics continued to attract interest in 1987. Just as with neutral iron atoms, the electronic state of the iron had important effects on reactivity. Use of two distinct iron sources allowed discrimination between the chemical properties of ground-state ^6D ($3d^6 4s^1$) and excited ^4F ($3d^7$) iron ions in reactions with propane. At high kinetic energies, the excited state was more reactive, but at low kinetic energies, the ground state was; this rather surprising result was explained in terms of non-adiabatic behavior at high energy[12]. The often-complicated reactions of transition metal ions, including Fe^+, with alkanes have also been interpreted in terms of the structures of long-lived ion-molecule complexes initially formed[13].

Gas-phase Fe^+ generated by fast-atom bombardment of $FeSO_4$ has been found to display similar reactivity as that generated by electron-impact ionization of iron pentacarbonyl, based upon reaction with hexanonitrile[14]. Reactions of this Fe^+ with 2-octyne have been interpreted in terms of complexation to the triple bond, followed by insertion of the complexed Fe^+ into a remote C-H bond, forming a ferracycle, in contrast to the classical pathway of insertion into a C-C bond then β-H transfers[15]. Use of deuterium-labelled substrates has allowed more complete characterization of the multiple reaction pathways involved in the reactions of Fe^+ with octynes[16].

Similar reactions with nitriles were described in terms of formation of $RC{\equiv}N\text{-}Fe^+$, followed by reaction with remote C-H bonds, depending on chain length[17]. A comparison of Fe^+ and Co^+ reactions revealed greater mechanistic complexity in the iron case[18].

Reactions of MOH^+ (M = Fe and Co) with ammonia produced $MNH_2{}^+$, which reacted with propene or cyclopropane to form $(C_3H_5)M^+$ and ammonia[19]. The species $FeCH_x$ (x = 0-3) were prepared and characterized by neutralization-reionization mass spectrometry. Neither neutral nor ionic $FeCH_{2,3}$ rearranged to hydridometal complexes, but $FeCH^{0,+1}$ did rearrange to $HFeC^{0,+1}$ [20].

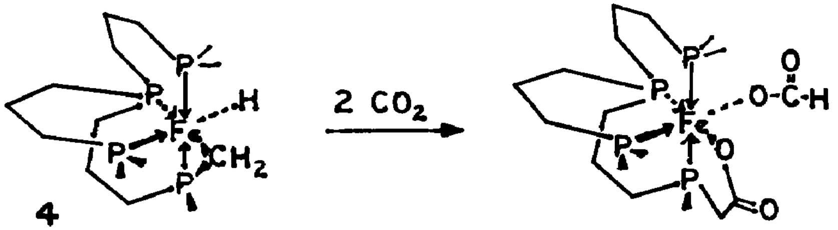
Fe_2 reacted with oxirane in cryogenic matrices by double insertion to form 1,3,2-diferroxolane, based on infrared characterization[11]. Metal dimer ions FeM^+ have been prepared and studied in the gas phase. Photodissociation spectra showed bond energies in the range 200-300 kJ/mol, depending on M. The ions were generally more strongly bound than the neutral dimers FeM; ionization potentials for the latter ranged from 5.4 to 7.4 eV[21]. Reactions of $CuFe^+$ with organics in the gas phase have been studied by FTMS. It was unreactive toward simple alkanes and gave predominantly dehydrogenation of alkenes[22]. Metal carbonyl cluster fragments having 2-4 metal atoms could be obtained by ion-molecule reactions after electron impact ionization of mixtures of metal carbonyls. Reactivities generally correlated with cluster valence electron deficiency, except for anomalies in species able to contain $Fe(CO)_4$ units[23].

4. COMPOUNDS WITH η^1-CARBON LIGANDS

a. Hydrido-, Alkyl-, and Aryliron Compounds

A number of compounds of iron with unusually low coordination numbers, which presumably owe their existence to the presence of unusually bulky ligands, have been characterized in 1987. A two-coordinate, 12-electron iron atom was found to exist in the crystal of $Fe[N(SiMePh_2)_2]_2$; the N-Fe-N angle was 169°, and a close approach of one phenyl group to the iron produced a Fe···C distance of 2.695(5) Å. The [bis(trimethylsilyl)amido]-iron analog was dimeric, with amido bridges[24]. The tris(trimethylsilyl)silyl anion reacted with $FeCl_2$ to produce paramagnetic $[(Me_3Si)_3Si]_2FeCl^-$, whose tetraethylammonium salt showed a Si-Fe-Si angle of 137° and Si-Fe-Cl angles of about 111°. The chloride ligand was readily replaced by triflate or by ether solvents[25]. Reaction of four-coordinate $(DIPPE)FeBr_2$ [DIPPE = $R_2PCH_2CH_2PR_2$, R = isopropyl] with Grignard reagents gave $(DIPPE)FeR_2$ or (with mesityl or neopentyl reagents) (DIPPE)FeRBr. All were high-spin fourteen-electron species, and the crystal structure of $(DIPPE)Fe(CH_2C_6H_4\text{-}p\text{-}Me)_2$ showed a distorted tetrahedral structure with no evidence of intramolecular interactions due to the net electron deficiency; this was plausibly attributed to the lack of vacant d-orbitals in the high spin species[26].

In contrast, $(DMPE)_2Fe$ (from photolysis of the dihydride **3**) readily underwent intermolecular reaction in pentane at -90° to form *cis*-(1-pentyl)$FeH(DMPE)_2$. Further irradiation at -30° led to β-hydride elimination; the resulting 1-pentene reacted with **3** to give *cis*(*Z*-1-pentenyl)$FeH(DMPE)_2$ and $(PrCH{=}CH_2)Fe(DMPE)_2$[27]. Reduction of $[(Me_2PCH_2CH_2CH_2)_3P]FeCl_2$ with lithium metal gave **4** by intramolecular insertion. Addition of trimethyl phosphite trapped the sixteen-electron Fe[0] tautomer. **4** reacted with two equivalents of carbon dioxide, as shown in Eq. 1. Reaction with methanol gave the dihydride[28].

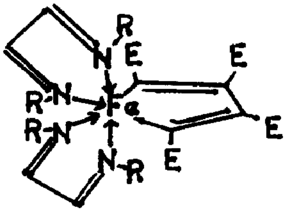


(1)

Reaction of *trans*-$(DPPE)_2FeHCl$ with L and $TlBF_4$ gave *trans*-$(DPPE)_2FeHL^+$ BF_4^- (L = various isocyanates and dinitrogen); electro-oxidation resulted in replacement of H by F[29]. One chloride ligand of $(DMPE)_2FeCl_2$ underwent replacement by nitriles at room temperature, but at reflux in RCN trans-$(DMPE)_2Fe(N{\equiv}CR)_2^{2+}$ formed, as confirmed by the crystal structure of the Ph_4B^- salt. The nitrile ligands of the acetonitrile complex could be reduced to coordinated ethylamine ligands with hydrogen[30]. Trans-$(DEPE)_2FeH(\eta^2\text{-}H_2)$ has been prepared by reaction of $(DEPE)_2FeHCl$ with $NaBPh_4$ and hydrogen and compared with its DPPE analog and ruthenium and osmium analogs. Reaction with deuterium gas gave the η^2-HD isotopomers , which gave temperature-dependent NMR spectra due to intramolecular isotope exchange[31].

Reaction of L_4FeH_2 [L = $PhP(OEt)_2$] with aryldiazonium ions led to formation of bis(aryldiazenido)iron complexes, $L_3Fe(=N=N\text{-}Ar)_2^{2+}$ [32].

Benzildianil [PhN=CPh-CPh=NPh] reacted with CpFe(1,5-cyclooctadiene)$^-$ with disproportionation, giving ferrocene and the dianion, $(PhN{=}CPh{-}CPh{=}NPh)_2Fe^{2-}$ [33]. Reduction of Fe(II) compounds with alkali metals or Grignard reagents in the presence of 1,4-diazadienes gave the paramagnetic, neutral analogs, $(DAD)_2Fe$, **5**. Depending upon the steric bulk of the diazadiene ligand, **5** underwent various addition reactions with CO, isocyanates, nitrosyl chloride, and diazoalkanes. Reaction with dimethyl acetylenedicarboxylate produced a stable ferrole, **6** (X-ray)[34].



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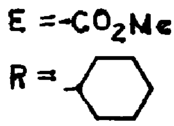
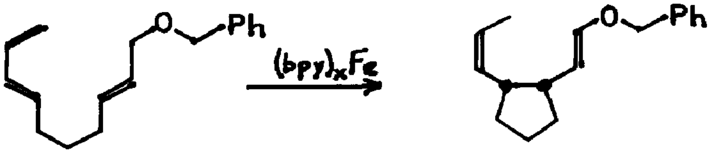


Catalysis of a number of new carbon-carbon bond formation reactions by $(bpy)_xFe(0)$ species has been reported this year. Examples are shown as Equations 2[35] and 3[36]. The catalyst was made by reduction of $Fe(acac)_3$ with triethylaluminum in the presence of 2,2'-bipyridine and furan[35-37]. The catalyst appears to this reviewer to resemble the ferrous naphthenate-1,10-phenanthroline-tri(isobutyl)aluminum catalyst used to polymerize butadiene; the latter has been improved by addition of diethylaluminum chloride [38,39].



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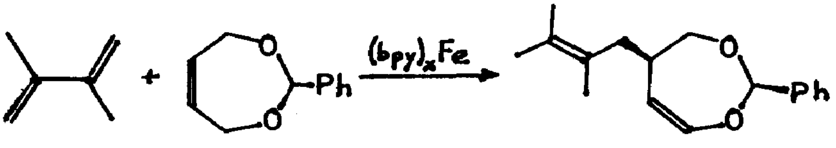
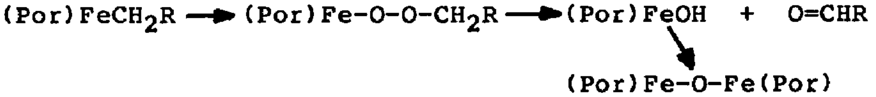


(3)

A new, synthetically-useful, iron-pyrrolyl reagent has been prepared either by reaction of atomic iron with pyrrole or reaction of sodium pyrrolide with $FeCl_2$. It reacted with bipyridine to give $(bpy)_2Fe(NC_4H_4)_2$[40].

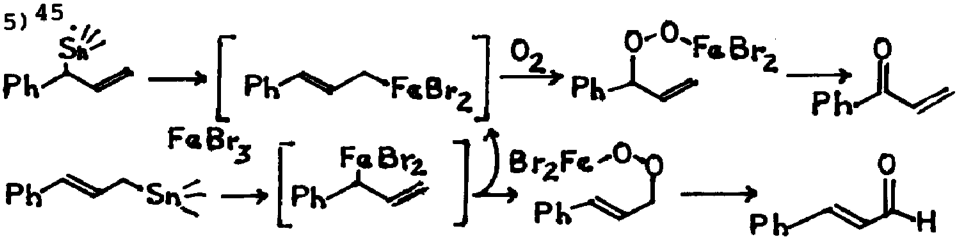
The mechanisms of reaction of hemoglobin with aryldiazonium salts have received further attention, with the finding that diazonium salts having polar substituents undergo electron transfer in the aqueous medium around the hemoprotein, resulting in production of arenes by hydrogen abstraction from a hydrogen-donor cosolvent. On the other hand, diazonium ions having hydrophobic substituents reacted at the hydrophobic protein pocket, eventuating in formation of the Fe-arylated product[41]. (Por)Fe-$CH{=}CR_2$ (from reaction of vinylic Grignard reagents with $(Por)Fe^+ ClO_4^-$) rearranged to N-vinylic porphyrins upon oxidation with $FeCl_3$, and the stereochemistry about the double bond was retained[42].

Reaction of (Por)FeR with oxygen has been studied by NMR, which has indicated the pathways shown in Eq. 4[43]; these reac-



$$\begin{tikzcd}(Por)FeCH_2R \arrow[r] & (Por)Fe\text{-}O\text{-}O\text{-}CH_2R \arrow[r] & (Por)FeOH + O{=}CHR \arrow[d] \\ & & (Por)Fe\text{-}O\text{-}Fe(Por)\end{tikzcd} \qquad (4)$$

tions are possible models for biological reactions involving heme oxygenases. In discussing the enzymatic lipoxygenation of polyunsaturated fatty acids, Corey has favored an organoiron-mediated pathway, based on effects of structure, oxygen pressure, and temperature on rates. Enzyme-induced deprotonation of substrate, in concert with addition of Fe(III) at an allylic position, was proposed; this was followed by oxygen insertion into the Fe-C bond as in Eq. 4[44]. Model studies involving organotin compounds have been offered in support of this proposal (Eq. 5)[45].



(5)

The role of possible organoiron intermediates in epoxidation reactions of alkenes with oxo-iron porphyrins has continued to be studied intensively. Theory has suggested that the most stable structure of the putative oxo-iron poryphyrin involves insertion of O into an Fe-N bond of the porphyrin, and that the resulting distortions favor iron-alkene interaction. Slipping of the alkene toward the oxygen would then generate a ferraoxetane, with reductive elimination of the epoxide the last step[46].

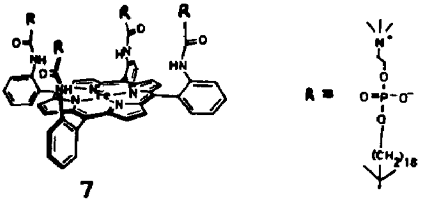
Loss of catalytic activity during such oxidations has been found to result from formation of N-alkylporphyrins. In one tetraarylporphyrin model system, the 1-alkene has been found to be bound at the 2-carbon rather than at the 1-carbon as in actual cyctochrome P-450 systems[47]. Formation of N-alkylporphyrins by acid demetalation of -Fe-O-C=C-N- cyclized porphyrins, and other reactions of the latter cycles, have been reported[48]. Reversible formation of N-alkylhemins during epoxidation of norbornene has been shown[49]. Alkenes known to rearrange upon one-electron oxidation (e.g. hexamethyl Dewar benzene) were found in fact to undergo partial rearrangement during epoxidation with tetraphenylporphyrin/m-chlorperbenzoic acid, implicating electron transfer in the mechanism of epoxidation[50]. This result neither confirms nor denies the possible intermediacy of intermediates having Fe-C bonds.

In the absence of air, cytochrome P-450 is known to reduce C-X bonds of halomethanes. Calculations on halomethyl radicals have been used in support of a proposed enzymatic cycle involving halomethyl-iron intermediates[51]. MCD studies of reduced rabbit liver microsomal cytochromes and their CO complexes have been carried out[52].

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

The majority of such compounds are (Por)FeCO derivatives, studied in connection with binding of CO and O_2 to natural or model heme systems. ^{57}Fe NMR has been used to study such binding; the chemical shift was highly dependent on strength of binding of an axial nitrogen ligand[53]. Electrochemical studies of (Por)FeX (X = Cl, ClO_4) under a CO atmosphere allowed determination of formation constants for carbonyl adducts of (Por)Fe and (Por)FeX$^-$ [54]. Recombination of isocyanide ligands after flash photolysis of protoheme complexes has been found to occur on the picosecond time scale; CO recombination was at least 70 times slower, a fact attributed to CO's lower basicity[55].

Two new synthetic porphyrins, 7[56] and 8[57], have been prepared, and their CO binding studied.



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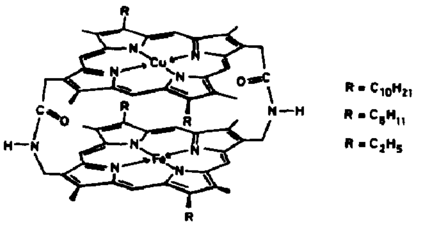

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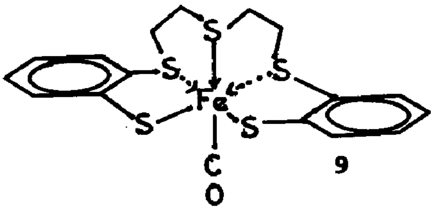
Unsaturated bis(diazadiene)iron complexes, $(DAD)_2Fe$, 5, behaved diversely toward CO. Depending on steric bulk of the diazadiene, some did not add CO, some added it reversibly to form diamagnetic $(DAD)_2Fe(CO)$, and some underwent replacement of a DAD ligand to form $(DAD)Fe(CO)_3$[34].

The meso-diastereomer of 9 has been characterized crystallographically, and t-butyl-substituted analogs have been prepared[58]. Reaction of DPPM with FeI_2 under a CO atmosphere gave 10[59]. A similar reaction of the hexaphosphine eHTP, $[(Et_2PCH_2CH_2)_2P]_2CH_2$, with $FeCl_2$ under CO produced (eTHP)-$FeCl(CO)^+$, with two terminal phosphorus atoms uncoordinated (X-ray structure)[60]. The diazene ligand in $(p\text{-}MeC_6H_4N{=}NH)Fe(CO)$-$[P(OEt)_3]_4^{2+}$ was readily displaced by azide ion, sulfides, amines, and aldehydes[61].



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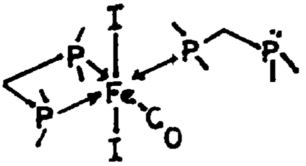

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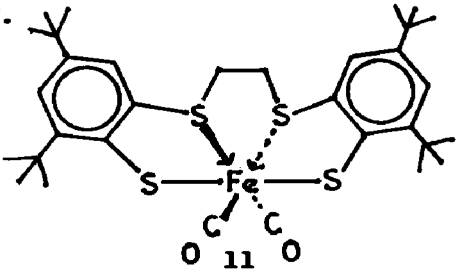
c. Iron Dicarbonyls, e.g. $L_3Fe(CO)_2$

Adsorption of $Fe(CO)_2(NO)_2$ on zeolite-Y under NO was shown by isotope labelling to give a surface-bound $Fe(NO)_3$ group[62]. Reaction of 4 (Eq. 1) with CO gave a mixture of mono- and dicarbonyl derivatives of $Fe[P(CH_2CH_2CH_2PMe_2)_3]$, the latter having one free phosphine group[28].

The bulky ligand, 2-mercapto-3,5-di-tert-butylaniline, LH, reacted with $FeCl_2$ under CO to form $L_2Fe(CO)_2$[63]. The analogous dithiolate complex underwent alkylation by dibromoethane to form 11 (X-ray structure). The free ligand from 11 could be obtained by acid hydrolysis; it gave 11 back upon reaction with Fe^{2+} salts followed by CO[64].



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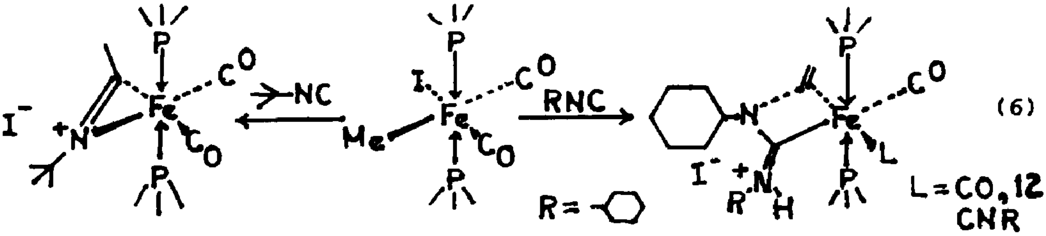
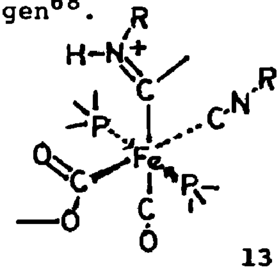
The effect of solvents ranging from cyclohexane to DMF on kinetics and equilibrium of the CO insertion reaction of $(Me_3P)_2$-$Fe(CO)_2(Me)(X)$ [X = CN] has been found to be very small[65]. Results of insertion of isonitriles into the same series of compounds have been found to depend on X and the isonitrile. With X = CN and *tert*-BuNC, the expected acetyl complex, $(Me_3P)_2Fe(CO)(COMe)(CN)(NCCMe_3)$, resulted. With X = I, ionic complexes (Eq. 6) resulted[66]. Reaction of **12** with methanol gave the carbomethoxy complex **13**. The X-ray structure of the Ph_4B^- salt showed a short $Fe-CO_2Me$ bond distance of 1.90(2) A ; dissolutionof **13** in dichloroethane regenerated **12**[67].



(6)

Reaction of $(DPPE)Fe(CNR)_4^{2+}$ with KOH resulted in synthesis of a coordinated CO ligand, with formation of **14**. (X-ray structure, Ar = $4-MeC_6H_4$). **14** underwent protonation at an imine nitrogen[68].



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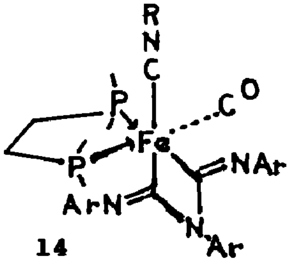

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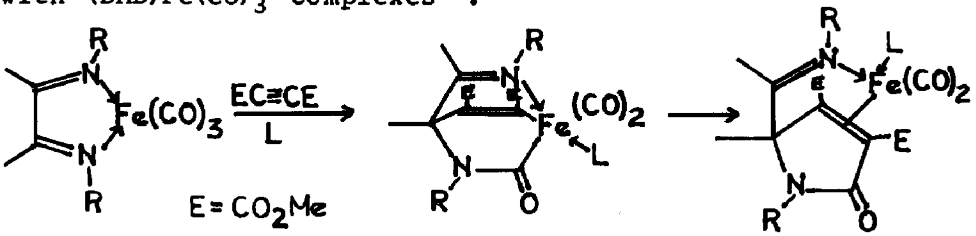
Ab initio calculations have been performed on heterocumulene complexes $(H_3P)_2Fe(CO)_2(\eta^2-Y=C=Z)$ having Y = O, S and Z = O, S, NH, CH_2. The most important bonding interaction was identified as iron to heterocumulene back-bonding, as a result of which η^2-CS coordination was favored over η^2-CO. The relative instability of CO_2 complexes was also consistent with this result[69]. Silylated complexes $(DPPE)Fe(CO)_2(H)(SiR_3)$ (crystal structure reported for R = Me) and $(DPPE)Fe(CO)_2(SiCl_3)_2$ have been prepared by photochemical reaction of (DPPE)iron carbonyls with silanes or silyl iron carbonyls with DPPE[70].

A bicyclic intermediate (Eq. 7) has been detected spectroscopically in the addition of dimethyl acetylenedicarboxylate with $(DAD)Fe(CO)_3$ complexes[71].



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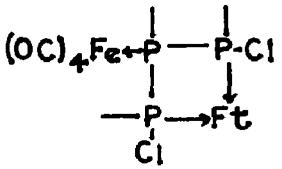
d. Iron Tricarbonyls, e.g. $L_2Fe(CO)_3$

Alkylation of malonate ion by allylic carbonates has been found to be catalyzed by Bu_4N^+ $Fe(CO)_3(NO)^-$, and a σ-allyliron intermediate has been proposed[72].

The P-H coupling constants in *trans*-$HFe(CO)_3PR_3^-$ [R = OMe, OEt, Ph, Et] have been reported to depend strongly on solvent and temperature, as a consequence of changes in H-Fe-CO angle[73]. In contrast to these cases, the anion $HFe(CO)_3[P(OPh)_3]^-$ adopts a structure with the triphenyl phosphite ligand in an equatorial position of the trigonal bipyramid and cis to the hydride, as shown by spectra in solution and by the X-ray structure of the PPN^+ salt[74].

Silyl hydrides $HFe(CO)_3(SiR_3)L$ [L = PPh_3, $P(OPh)_3$] could be deprotonated with sodium or potassium hydride, and the resulting salts reacted with numerous electrophiles. The crystal structure of $Ph_3PAuFe(CO)_3(PPh_3)(SiMePh_2)$ was determined[75]. Similar compounds with bridging DPPE ligands, (DPPE)[*mer*-$Fe(CO)_3(H)(SiR_3)]_2$ and (DPPE)[*mer*-$Fe(CO)_3(SiR_3)_2]_2$ have also been prepared by appropriate ligand-substitution methods[70].

The crystal structure of (DPPE)$Fe(CO)_3$ (from reduction of $FeCl_2$ in the presence of DPPE and CO) has been determined[76]. **15**, with its novel chelating ligand, was one of the products of reaction of $MePCl_2$ with $HFe(CO)_4^-$ [77]. Similarly, the cyclic product **16** was produced, *inter alia*, by reaction of $ArOPCl_2$ with $Na_2Fe(CO)_4$[78]. Other products of these reactions are discussed in the next section.



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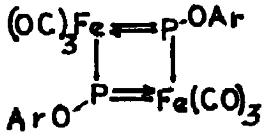


16

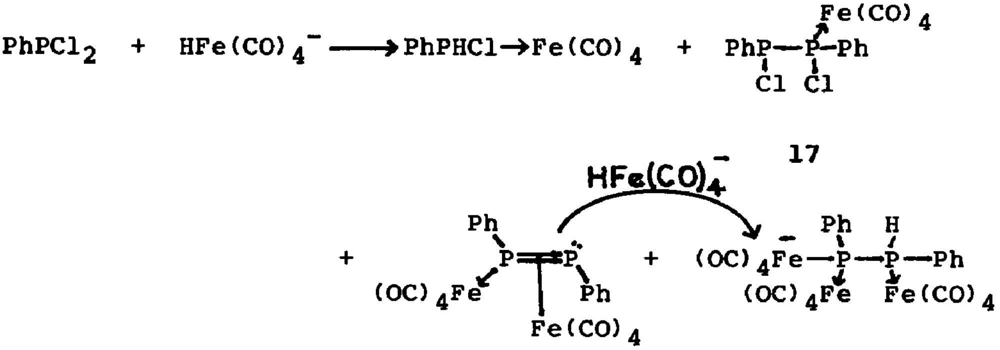
A general synthesis of tris(isonitrile) complexes, $(RNC)_3Fe(PMe_3)_2$, by reaction of $Fe(PMe_3)_4$ with RNC, has been reported. X-ray structures for R = neopentyl, phenyl, and 2,6-xylyl showed axial trimethylphosphine and equatorial isonitrile ligands. Tetra- and penta-isonitrile complexes could be formed with excess isonitrile in solution[79]. Photolysis of the tris(isonitrile) complexes in benzene resulted in formation of aldimines, PhCH=NR, in a process which was catalytic in the presence of low concentrations of isonitrile. The proposed process involved oxidative addition of $(Me_3P)_2Fe(CNR)_2$ to a benzene C-H bond, and isonitrile insertion[80].

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

Rates of proton transfer from $H_2Fe(CO)_4$ (and other metal hydrides) to *para*-substituted anilines gave linear Bronsted plots, and kinetic acidities of the different hydrides generally paralleled the thermodynamic acidities. Self-exchange between $H_2Fe(CO)_4$ and $HFe(CO)_4^-$ was found to involve proton transfer, and little effect of counterion was noted[81]. $HFe(CO)_4^-$ transferred a hydride to the 2-carbon of (η-thiophene)$Mn(CO)_3^+$ [82]. MO calculations have been carried out on the D_{3h} hydrogen-bridged species, $[(OC)_4Fe{\cdot\cdot}H{\cdot\cdot}Fe(CO)_4]^-$ [83].

Reaction of $Na_2Fe(CO)_4$ with CO_2 eventuated in formation of $Fe(CO)_5$ and Na_2CO_3[84]. With N-formylimidazole in the presence of Lewis acids, the tetracarbonylferrate salt gave $(OC)_4FeCHO^-$; other acyltetracarbonylferrates were obtained similarly. The Lewis acid both increased the reactivity of the acylimidazole and scavenged the sodium imidazolate byproduct[85].

Reactions of $HFe(CO)_4^-$ with halophosphines have given rise to an extensive family of novel products, and this chemistry has been briefly reviewed[86]. New results in this area have also appeared: the results of reactions of $RPCl_2$, as affected by R and by reaction conditions, have been described. Equation 8 summarizes the products obtained in the case R = Ph[77]. With R = Me,



$$PhPCl_2 + HFe(CO)_4^- \longrightarrow PhPHCl{\rightarrow}Fe(CO)_4 + PhP(Cl){-}P(Cl)({\rightarrow}Fe(CO)_4){-}Ph \qquad (8)$$

17

18

19

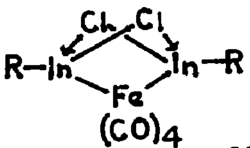
products analogous to **17** and **19** formed, along with **15** (mentioned in previous section). Me_3CPCl_2 gave only $Me_3CPH[Fe(CO)_4]_2^-$, and R_2NPCl_2 [R = isopropyl] gave an analogous product, presumed formed via a phosphinidene intermediate, $XP{=}Fe(CO)_4$[77]. With bulky dichlorophosphines $RPCl_2$ (R = mesityl, Me_3SiCH_2, $(Me_3Si)_2$-CH, $(Me_3Si)_2N$, etc.), the products included **16**, cluster compounds, and diphosphene complexes, $RP[{\rightarrow}Fe(CO_4]{=}PR[Fe(CO)_4]$. Also obtained with R = 2,4,6-tri-*tert*-butyl-C_6H_2 was a product analogous to **18**[78]. The factors which favor this n,π-coordination relative to the more common n,n-coordination in diphosphenebis-

(tetracarbonyliron) complexes remain elusive.

Two full papers on reactions of R_2NPCl_2 with iron carbonyls have appeared. With $Na_2Fe(CO)_4$, a reaction scheme involving formation of $R_2NP{=}Fe(CO)_4$ was proposed; this species underwent electron transfer reactions with $Fe(CO)_4{}^{2-}$ in THF but not in ether. Di- and tri-iron cluster products (see sections 9 and 10 of this review) predominated, but an unstable diphosphenebis(tetracarbonyliron) product, which added water on attempted chromatography to form $[R_2NP(H)OP(H)NR_2][Fe(CO)_4]_2$, was detected in the case R = isopropyl. The major product when R = Et was a heterobicycle having fused FeP_3 and FePOC rings[87]. With nonacarbonyldiiron and Et_2NPCl_2, the simple $Fe(CO)_4$ adduct formed first, with subsequent reactions giving cluster products[88].

Reaction of $HFe(CO)_4{}^-$ with the unsaturated chlorophosphine, $R_2C{=}PCl$ ($R = SiMe_3$), produced a diphosphirane along with its $Fe(CO)_4$ complex, $R_2CHPHCl{\rightarrow}Fe(CO)_4$, and $(\eta^2\text{-}HP{=}CR_2)Fe(CO)_4$[89].

Cyclic $Fe(CO)_4$ complex **20** [$R = C(SiMe_3)_3$] resulted from reaction of $Na_2Fe(CO)_4$ with $RInCl_3{}^-$; the In-Fe bonds averaged 2.63 Å in the crystal structure[90]. The Sn_2Fe_2 rings of **21** were cleaved on treatment with Lewis bases such as pyridine to give monomeric $B^+\text{-}SnCp^*{}_2\text{-}Fe(CO)_4{}^-$ [91]. Photoreactions of **22** with dienes have been studied; the processes observed included substitution of diene for two carbonyl ligands and cycloadditions to form 3,6-disilacyclohexenes[92].



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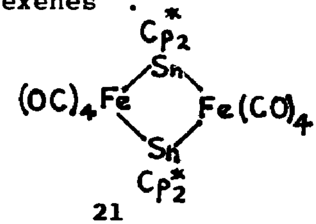

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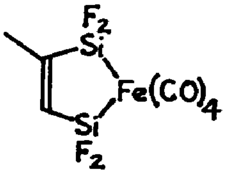

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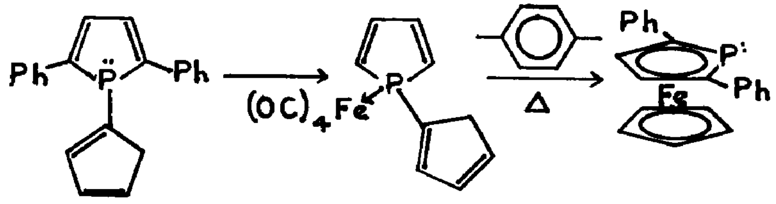
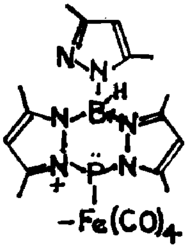
Infrared, Mössbauer, and ^{31}P NMR studies of phosphine- and phosphite tetracarbonyliron complexes have been carried out, and the observations correlated with the donor-acceptor nature of the phosphorus ligand[93]. $Fe(CO)_4$ complexes of several novel phosphorus ligands have been prepared. These include cyclic diacylphosphines (from reaction of $RP(SiMe_3)_2$ with diacid chlorides)[94], phosphazene precursors $Me_3SiN{=}PMe(OCH_2CF_3)CH_2PR_2$ [R = Ph, NMe_2)[95], the sulfodiimide $R_2P{-}N{=}S{=}N{-}PR_2$ (R = tert-butyl)[96], and a



(9)

Mo_2CP tetrahedral cluster[97].

An interesting rearrangement of a cyclopentadienyl group from phosphorus to iron has been reported (Eq. 9)[98]. **24**, described as a "base-stabilized phosphinidene complex," has been prepared and characterized crystallographically, The P-Fe bond length (2.274 Å) indicated a single bond in **24**, which led the authors to disparage the double-bonded structure $RP=Fe(CO)_4$ often drawn in true phosphinidene-metal complexes[99]. However, since a satisfactory double-bonded structure cannot be drawn for **24**, in contrast to true phosphinidene complexes, the basis for this conclusion is unclear.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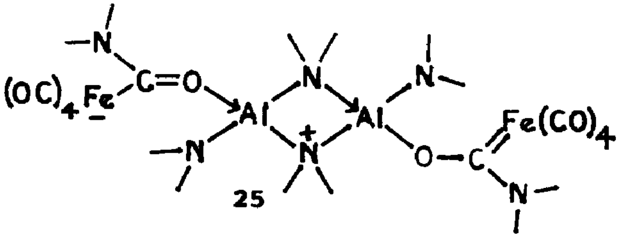
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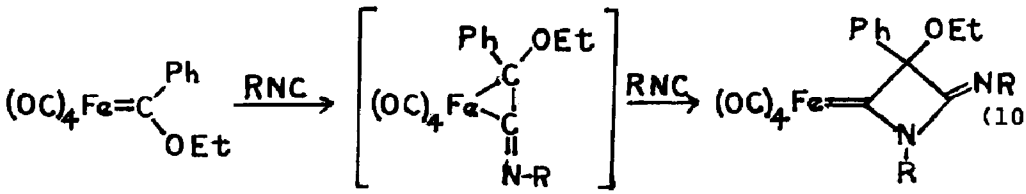
f. Carbene Complexes $R_2C=FeL_4$

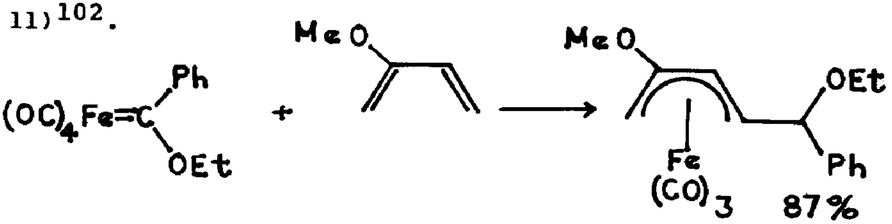
The carbenoid complexes **12-14** have already been discussed. Double protonation of **14** gave the acyclic carbene complex $[(DPPE)Fe(CNPh)_2(CO)=C(NHPh)_2]^{2+}$ [68]. A more complex carbenoid resulted when $Fe(CO)_5$ and $[Al(NMe_2)_3]_2$ interacted to form **25**. The Fe C bond length in **25** [1.998(3) Å][100] showed significant double bond character.

Use of carbene complexes in synthesis has increased. Reaction of $(OC)_4Fe=C(Ph)OEt$ with two equivalents of isonitriles gives first ketenimine complexes (Eq. 10) then iminoazetidinylidene complexes.



(10)

The latter could be oxidized to iminoazetidinones[101]. The same carbene complex reacted with dienes (via ferracyclobutanes?) to form substituted pentadiene complexes (Eq. 11)[102].



(11)

A formal silylene complex, stabilized by interaction with the solvent (THF or HMP), resulted from reaction of $Na_2Fe(CO)_4$ with $(RO)_2SiCl_2$ (R = tert-butyl). The Fe-Si distance in the product $(Me_2N)_3P^+OSi(OR)_2$-$Fe(CO)_4^-$, 2.289(2) Å, may be taken as appropriate for a Si-Fe single bond[103].

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

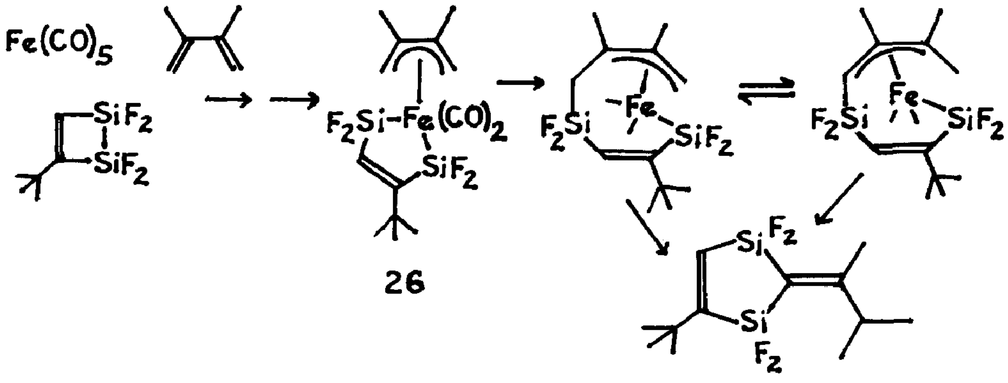
Molecular orbital calculations based on density function theory have been applied to calculation of mean M-CO bond energies and first CO dissociation energies for Group 6, 8, and 10 carbonyls. For $Fe(CO)_5$, the respective values 216 and 185 kJ/mol were calculated[104]. Photofragmentation of $Fe(CO)_5$ at 193 nm under molecular beam conditions apppeared to occur with complete energy randomization before each sequential CO dissociation[105]. MO calculations for $EFe(CO)_5^+$ (E = H, Me) and other E-metal species have been reported; M-Me bonds were found to be weakened in general relative to M-H bonds by filled orbital repulsions; these were less important in the cationic species[106].

Ligand exchange reactions of $Fe(CO)_5$ have been found to be catalyzed by a range of supported metals and metal oxides, and the catalysis inhibited by free radical traps; a radical non-chain process was inferred. The metal effectiveness fell in the order Pd > Pt > Ru > Rh, and species such as $LFe(CO)_4$ and $Fe(CO)_{5-n}(CNR)_n$ (n = 0-5) were readily obtained from $Fe(CO)_5$[107]. Formation of $(OC)_3Fe(CNCMe_3)_2$ was used as a probe reaction to test the efficacy of catalysts for ligand exchanges in general [108]. Use of coupled capillary columns to achieve optimum gas chromatographic separation in the series $(F_3P)_{n-5}Fe(CO)_n$ (n = 0-5) has been recommended[109].

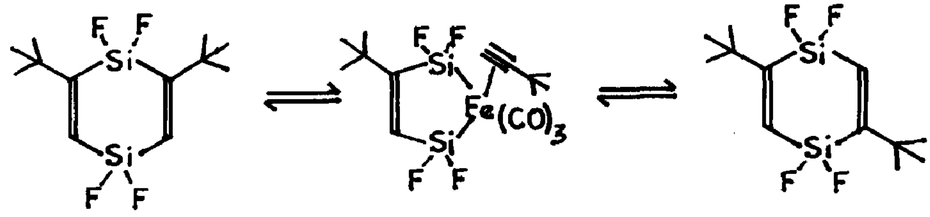
Theoretical calculations on addition of hydride to a carbonyl ligand of $Fe(CO)_5$ have been carried out. The addition was found to be exothermic, and no activation barrier was found[110]. The uncertain fate of solvent molecules in reaction of initially solvated anions with $Fe(CO)_5$ made calculation of entropy effects difficult[111]. KH and $NaBH_4$ promoted the isotopic exchange of ^{13}CO with $Fe(CO)_5$[112].

Cycloaddition reactions of 1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene with butadienes were carried out by photolysis in the presence of $Fe(CO)_5$. The principal products were disilacyclopentene derivatives (Scheme II), but some dienes gave disilacyclohexenes or disilacyclooctadienes instead[92,113]. Similar products were produced from photolysis of **22** and analogs in the presence of dienes. Rearrangements of the various cyclic products occurred in the presence of $Fe(CO)_5$ and ultraviolet

Scheme II



light; an example is given in Eq. 12[114].



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UV photolysis of $Fe(CO)_5$ physisorbed on porous Vycor glass occurred as in solution, giving $Fe(CO)_4$ with a quantum yield of 1. Oxidative addition to adsorbed water and to silanol groups gave products $H\text{-}Fe(CO)_4OM$ [$M = H, Si(OX)_3$]. With further photolysis, dimeric and trimeric iron products formed via a "mobile intermediate," principally $Fe(CO)_3$[116]. The colloidal sols which resulted from oxidation of $Fe(CO)_5$ by hydrogen peroxide have been characterized as non-crystalline iron(III) hydroxoacetates[117].

5. η^2-ALKENE AND η^3-ALLYL COMPLEXES

η^2-$Fe(CO)_4$ complexes of diphosphenes[77,78] and of phosphenes[89] have been described in the previous section of this review, as has theoretical treatment of bonding in $(H_3P)_2Fe(CO)_2(\eta^2\text{-}CO_2)$ and related species[69].

Reaction of $(DMPE)_2Fe$ [from irradiation of **3**] with pentene was found to produce both $(\eta^2\text{-}CH_2{=}CH\text{-}CH_2CH_2CH_3)Fe(DMPE)_2$ and C-H insertion to form (1-pentenyl)FeH$(DMPE)_2$[27]. Reaction of (methyl acrylate)$Fe(CO)_4$, **27**, with alkyl-lithium or Grignard reagents occurred by attack at a metal carbonyl and transfer of the resulting acyl group to the *β*-carbon, to produce 4-ketoesters[118]. Photolysis of **27** in low-temperature matrices proceeded with predominant loss of CO, to produce $[\eta^4\text{-}CH_2{=}CH\text{-}C({=}O)OMe]Fe(CO)_3$ and isomers with the acrylate bonded to iron via double bond and ester OMe group and via the carbonyl group alone[119].

Reduction of $FeCl_2$ with magnesium in the presence of ethene and triethylphosphine gave pseudotetrahedral $(Et_3P)_2Fe(C_2H_4)_2$ (X-ray structure). In the presence of additional phosphine ligands, this unsaturated compound reacted with carbon dioxide to give (after methanolysis) dimethyl methylmalonate or dimethyl succinate, depending on the phosphine used[120].

Irradiation of $Fe(CO)_2(NO)_2$ in liquid xenon containing 1,3-butadiene gave $(\eta^2\text{-}C_4H_6)Fe(CO)(NO)_2$, $(\eta^4\text{-}C_4H_6)Fe(NO)_2$, and $(\eta^2\text{-}C_4H_6)_2Fe(NO)_2$. The latter was considered a likely intermediate in the catalytic dimerization of dienes, since it can isomerize to a η^2, η^4-structure with bending of a NO group[121].

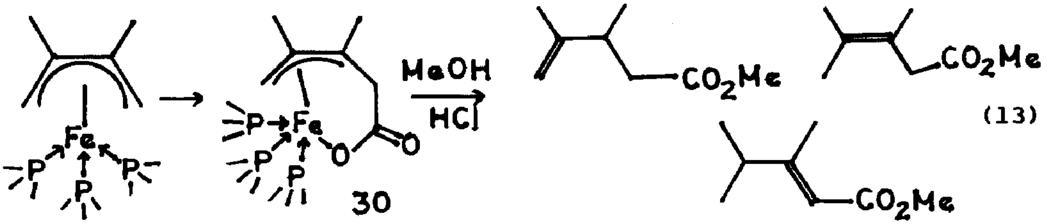
Several studies relevant to catalytic isomerization of alkenes have been reported. Photolysis of $(C_2H_4)Fe(CO)_4$ in low-temperature solutions containing excess ethene produced $(ethene)_2Fe(CO)_3$, **28**, (the species previously assigned di-iron structures) and $(ethene)_3Fe(CO)_2$, **29**. Addition of 1-pentene resulted in rapid isomerization to 2-pentenes, and gradual loss of catalytic activity was accompanied by dehydrogenation of pentene to form $(1,3\text{-pentadiene})Fe(CO)_3$[122]. In the gas phase, **28** reacted with CO via ethene dissociation, to form $(ethene)Fe(CO)_4$. The intermediate $(ethene)Fe(CO)_3$ reacted about 35 times more rapidly with CO than with ethene[123]. Pulsed laser photolysis of mixtures of **28** and ethene produced cis- and trans-**29** and $(ethene)_4FeCO$. Decay constants for the isomers of **29** were measured, and again the unsaturated intermediate $(ethene)_2Fe(CO)_2$ reacted more readily with CO rather than ethene, this time by a factor of 400[124]. Pulsed laser photolysis of a mixture of ethene, hydrogen, and $Fe(CO)_5$ produced a reservoir of **28** in equilibrium with an active hydrogenation catalyst, $(ethene)Fe(CO)_3$. The rate of hydrogenation of ethene was studied as a function of reagent pressures, and a detailed mechanism elucidated[125].

Photolysis of various 1,4-diazadiene complexes, $(dad)Fe(CO)_3$, in the presence of electron-deficient alkenes gave CO-substitution products, $(dad)Fe(CO)_2(\eta^2\text{-alkene})$. Activation energies for alkene rotation in these trigonal bipyramidal products have been measured from low-temperature NMR spectra[126]. Formation of a (η^2-alkene) structure in the analogous reactions of $(dad)Fe(CO)_3$ with alkynes was previously shown in Eq. 7[71].

A comparison of $(RC{\equiv}CR)Fe(CO)_4$ ($R = SiMe_3$) with its ruthenium and osmium congeners showed the iron compound to have the largest ^{13}C NMR coordination shift, and the smallest reduction in C-C stretching frequency on coordination[127]. A series of $(\eta^2\text{-alkyne})Fe[(Me_2PCH_2)_3SiMe]$ complexes has been obtained by reaction of the alkynes with **2**[5]. Reduced cubane clusters such as $Fe_4S_4(SPh)_4^{2-}$ were found to form adducts with ethyne, liberating a phenylthiolate ligand in the process; this displacement may be relevant to reduction of ethyne by nitrogenase[128].

Localized INDO calculations on $(\eta^3\text{-cyclooctenyl})Fe(PH_3)_3^+$ have revealed the interaction of the allylic C-H bond with a nominally vacant iron orbital. The calculated bond orders for the Fe-C and Fe-H interactions were 0.302 and 0.190, respectively[129,130].

η^3-Allyl carboxylates such as **30** were the key intermediates in the reaction of electron-rich diene complexes with carbon dioxide (Eq. 13)[131]. Increased reactivity of indenyl-iron compounds as compared to their cyclopentadienyl-iron analogs has often been attributed to formation of η^3-indenyl intermediates. This has been unequivocally demonstrated in reaction of $(\eta^5\text{-}C_9H_7)Fe(CO)_2^-$ with CO to form the (indenyl)tricarbonyliron anion, whose PPN salt clearly manifested the n_3 structure in the crystal. There was a 22° dihedral angle between the plane of the η^3-allyl group and the plane of the benzene ring. Maintenance of the η^3 structure in solution was indicated by ^{13}C NMR. Methylation of the tricarbonyl anion was thought to occur at iron to produce $(\eta^3\text{-}C_9H_7)Fe(CO)_3Me$, which reverted to an η^5 structure with carbonyl loss[132]. The analogous indenyl radicals, $(C_9H_7)Fe(CO)_2L^{\cdot}$, produced by photolysis of $[(C_9H_7)Fe(CO)_2]_2$ in the presence of ligands L (CO, PPh_3, $PHPh_2$), were also thought to possess the η^3 structure, based on EPR results which indicated an iron-centered radical[133].



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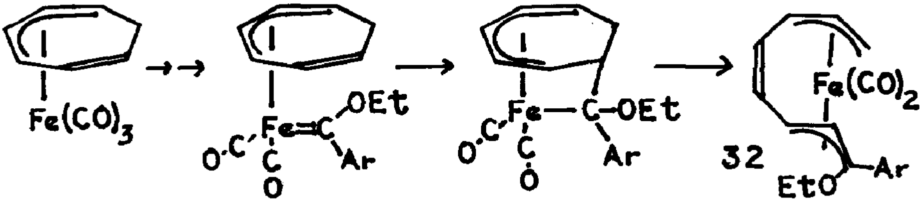
(13)

A number of compounds having an organic ligand bound to iron through two η^3-allylic linkages have been described in 1987. The compound 2-4-n:2'-4'-n-1,1'-bi(cyclohex-3-en-2-yl)bis(trimethylphosphine)iron, produced in reaction of cyclohexa-1,3-diene with **1** (Scheme I) has been characterized by X-ray crystallography[4]. Additional examples of this hitherto unusual structural type have been prepared by low-temperature treatment of various $(\eta^4\text{-polyene})$tricarbonyliron compounds with aryllithium reagents, then alkylation with triethyloxonium fluoroborate, classic conditions for generating "Fischer-type" carbene complexes. The products **31** [from cyclohexadiene-$Fe(CO)_3$][134] and **32** [from cycloheptatriene-$Fe(CO)_3$][135] were characterized by crystal structures; their ori-



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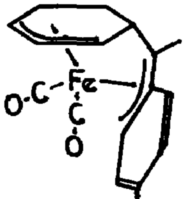
gins may be traced to rearrangements of the initially-formed carbene complexes, as exemplified in Eq. 14[135]. A similar reaction sequence involving COTFe(CO)$_3$ gave, depending on the aryl group, products analogous to **31**, or the isomeric product **33**. Allowing the mixture to warm above -30° before ethylation resulted in formation of **34**[136].



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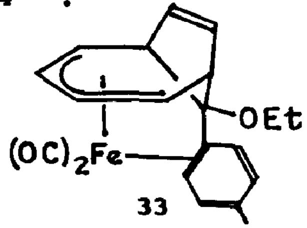

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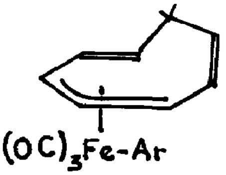

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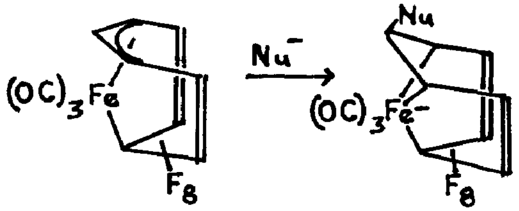
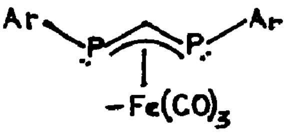
The same reaction sequence applied to (tetrafluorobenzobicyclo[2.2.2]octatriene)tricarbonyliron gave a bis(allyl)Fe(CO)$_2$ product, not unlike **32**, which resulted from breaking a ligand C-C bond[137]. Reaction of $(C_8F_8)Fe(CO)_3$ with nucleophiles resulted in their addition to the internal allylic carbon (Eq. 15)[138].



(15)

A brief review of η^1,η^3-1-phosphaallyliron complexes has been published[139]. The 1,3-diphosphaallyl complex, **35**, has been prepared in 90% yield by reaction of ArP=CH-P(Cl)Ar with $Na_2Fe(CO)_4$ [Ar = 2,4,6-tri(*tert*-butyl)phenyl]; it could also be obtained from Li^+ $(ArP)_2CH^-$ and $Fe(CO)_5$. Alkylation or protonation of **35** occurred on phosphorus to form a η^2,η^1-diphosphapropene complex[140]. The novel heteroallyl moiety in **36** resulted from reaction of $XFe[\eta^2\text{-}C(=S)SR](CO)L_2$ with $NaBH_4$[141].



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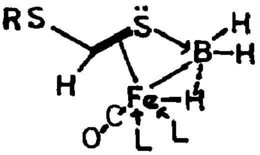
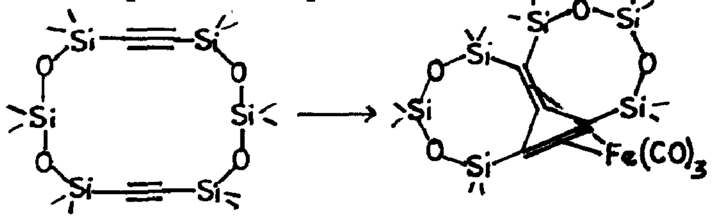


36

6. COMPOUNDS WITH η^4-LIGANDS

a. Trimethylenemethyl Complexes

The first stable transition metal complex of a methylenecyclopropene resulted from rearrangement on reaction of a diyne with nonacarbonyldiiron (Eq. 16)[142].



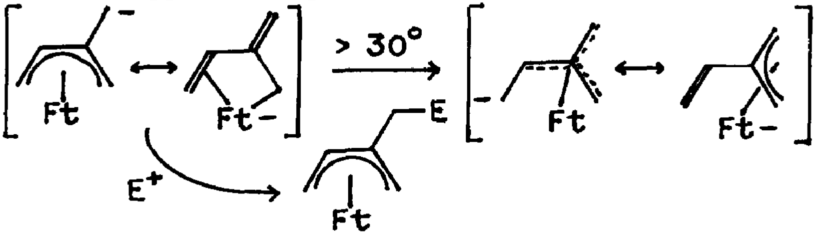
(16)

Photolysis of mixtures of aldehydes [RCHO, R = Me, Et, Ph], allenes [R'CH=C=CH$_2$, R' = H, Ph, Me$_2$CH, PhCH$_2$], and Fe(CO)$_5$ produced substituted trimethylenemethyl complexes, [C(RCH)(R'CH)-(CH$_2$)Fe(CO)$_3$, with loss of CO$_2$. Rotation of substituents around the $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ bonds could be observed at 180° [143]. Reaction of (Me$_3$P)$_2$FeCl$_2$ with potassium 2,4-dimethylpentadienide in equimolar ratio gave rise to [(CH$_2$)$_2$C(CH-C(=CH$_2$)Me]Fe(PMe$_3$)$_3$, as confirmed by a crystal structure[144].

The gas phase ion chemistry of [C(CH$_2$)$_3$]Fe(CO)$_3$ and its butadiene isomer have been studied by high- and low-pressure electron impact mass spectroscopy and flowing afterglow studies of their negative ions. The trimethylenemethyl complex tended to remain attached to iron under conditions where butadiene was displaced. The proton affinity of the TMM isomer was about 20 kJ/mol greater[145].

b. Complexes of Acyclic Dienes, including Heterodienes

A methyl proton was removed from (η^4-isoprene)tricarbonyliron with LiN(i-Pr)$_2$ at -78°, and the resulting anion reacted at the same site with electrophiles (aldehydes, ketones, alkylating agents). At temperatures above 30° the anion rearranged to a trimethylenemethyl-derived anion (Eq. 17), but the rearrangement could be suppressed by addition of zinc bromide[146].



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A number of examples of electron-rich (η^4-diene)tris(phosphine)iron complexes have been reported. These compounds have been prepared by reduction of $FeCl_2$ with magnesia-cyclopent-3-enes or activated magnesium in the presence of dienes and phosphines[5,147]. Bis(η^4-diene)phosphineiron products were also formed[147]. Reactions of these electron-rich diene complexes with CO_2[131] have already been illustrated in Eq. 13.

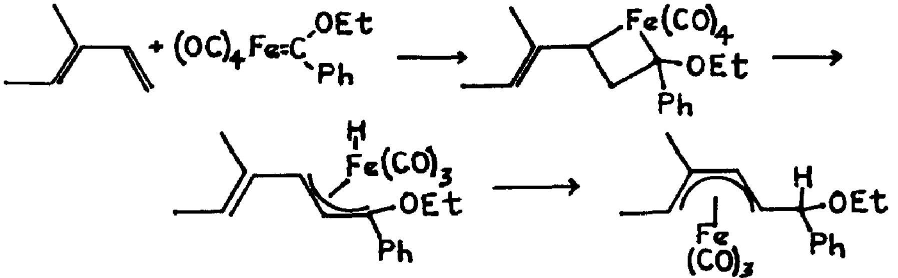
X-ray structures have been reported of two complexes (η^4-MeO_2C-CH=CH-CH=CH-CO_2Me)$Fe(CO)_2L$. Quinoline as ligand L occupied a basal site in the tetragonal pyramid, whereas pyrazine occupied the apical site[148]. Another (η^4-diene)iron dicarbonyl derivative is the previously mentioned **26** (see Scheme II)[92].

Formation of C-C bonds to each diastereomer of (η^4-MeCH=CH-CH=CH-CHR(OAc)$Fe(CO)_3$, using carbon nucleophiles in the presence of Lewis acids, proceeded regio- and stereospecifically[149]. The crystal structures of E,E- and E,Z-[MeO_2C-CH=CH-CH=CH-CHO]$Fe(CO)_3$ have been compared, and no significant difference in C-C or C-Fe bond lengths discerned. The activation energy for thermal conversion of the E,Z-isomer (with the formyl group endo) to the more stable E,E was 120(2) kJ/mol, allowing synthetic use of the E,Z-isomer at temperatures below 60° [150].

Reaction of block styrene-butadiene rubber with $Fe_3(CO)_{12}$ produced copolymer-$Fe(CO)_3$ complexes, presumably involving 1,3-diene units resulting from hydrogen migration(s)[151]. The effects of the $Fe(CO)_3$ on various physical properties of the polymer were studied, and the results interpreted in terms of increased crystallinity of the iron-containing polymer[152]. Thermal decomposition of the complexed polymer was studied by Mössbauer spectroscopy, which indicated formation of iron[0] cross-links between chains at ca. 200°, and decomposition to iron[II] compounds at higher temperatures[153].

Measurement of ^{13}C-^{13}C coupling constants in a number of butadiene-$Fe(CO)_3$ complexes gave values of 43-47 Hz for both terminal and internal C-C bonds, consistent with the similar bond lengths generally observed in crystal structures[154]. The resonances observed in electron transmission spectroscopy of (butadiene)tricarbonyliron have been assigned by use of multiple-scattering $X\alpha$ calculations[155]. Theory (in this case extended Hückel calculations) has been applied to the addition of nucleophiles to diene complexes. In the case of tricarbonyliron complexes, the $HOMO_{Nu}$---$LUMO_{complex}$ interaction, which normally favors C1 attack, is countered by a $HOMO_{Nu}$---$HOMO_{complex}$ repulsion, resulting in preference for C2 attack. Replacement of CO ligands by phosphines would increase this preference still further[156].

Reaction of the electrophilic carbene complex $(OC)_4Fe$=C-(OEt)Ph with dienes resulted in homologation at C1 of the diene, and formation of the diene complex (Eq. 18)[102]. Positional isomers also resulted in some cases. This reaction appears to be the intermolecular analog of those which produced previously described products **31**–**34** by intramolecular attack of carbenes on coordinated dienes, although mechanistic details may differ.



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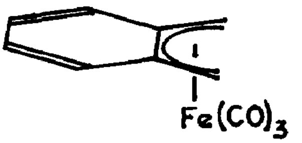
Friedel-Crafts acylation of [2-(trialkylsilyl)butadiene]tricarbonyliron resulted primarily in introduction of 4-*endo*-acyl groups. After isomerization to the *exo*-isomers, these could be acylated a second time on the other terminal carbon[157,158].

The conjugated diene unit of ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4,10-dodecatrienoate was protected by introduction of the tricarbonyliron group before tritium reduction of the remote C=C double bond under homogeneous conditions[159].

The crystal structures of [*E,E*-AcO-CH=CH-CH=CH-OAc]$Fe(CO)_3$[160] and of [*o*-xylylene]tricarbonyliron, **37**[161], have been reported.



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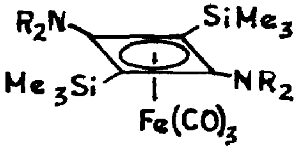

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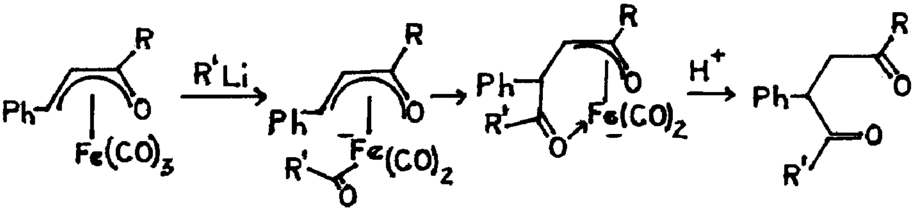
The latter showed the iron slightly closer to the terminal carbons (2.08 A) than to the internal carbons (2.12 A), in contrast to most diene complexes; this is presumably an accommodation to maintenance of a degree of aromatic character in the six-membered ring, which nevertheless showed some bond alternation.

Reaction of (1-oxadiene)tricarbonyliron complexes with organo-magnesium or -lithium nucleophiles occurred with attack at the metal carbonyl moiety, then acyl migration (Eq. 19)[162].



(19)

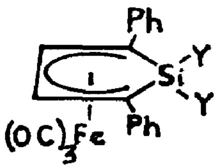
Electrochemical oxidation of (benzylideneacetone)$Fe(CO)_2[P(OPh)_3]$ has been studied by cyclic voltammetry in DMF. The radical cation from one-electron oxidation was found to decompose rapidly, with solvent assistance[163].

c. Complexes of Cyclic Dienes

The oxidative addition of (η-C_4H_4)Fe(CO)$_2$ (from photodissociation of CO from the tricarbonyl) to Si-H bonds has been studied over the temperature range 118-157 K. The activation parameters for the reaction with triethylsilane were $\Delta H^{\ddagger}$ 44(4) kJ/mol and $\Delta S^{\ddagger}$ 47(20) J/mol-K[164]. A novel cyclobutadiene complex, **38**, (X-ray structure for R_2N = piperidino) resulted from reaction of R_2N-C$\equiv$C-SiMe$_3$ with Fe(CO)$_5$[165].

Ultraviolet photolysis of (η^4-cyclopentadiene)Fe(CO)$_3$ complexes at 77 K resulted in loss of CO (quantum yield about 0.1 at 366 nm). The coordinatively unsaturated dicarbonyl restored itself to 18-electron normalcy by migration of an endo substituent to iron, induced by warming or irradiation at longer wavelengths (> 420 nm). An endo-hydride migrated at least 100 times more readily than an endo-methyl group[166].

Corriu and coworkers have continued their exploration of the chemistry of η^4-silole and -germole complexes. New 2,5-diphenylsilole complexes **39**, having vinyl, allyl, and 1-propynyl groups on the silicon, have been prepared by direct complexation of the free siloles with Fe$_2$(CO)$_9$[167]. **39** [Y = OMe] was obtained similarly, in 60% yield[168]. The exo Si-H bond of **39** [Y = H] was preferentially cleaved in reaction with PCl$_5$[168]. Substitution of exo or endo chlorides from 1-chloro-2,5-diphenylsiloles occurred with retention of configuration, with the exo isomers reacting more rapidly[169]. Reaction of [endo-1-chloro-exo-1-methyl-2,5-diphenylsilole]tricarbonyliron with phenyllithium resulted in carbonyl attack, whereupon the resulting enolate was silylated intramolecularly to form carbene complex **40**[170]. Silole and germole complexes without the usual flanking phenyl groups have now been prepared, including Fe(CO)$_3$ complexes of 1,1-dimethylsilole, 1,1,3,4-tetramethylsilole, and 1,1,3,4-tetramethylgermole. The silole complexes underwent photosubstitution of triphenylphosphine for a CO group. Reaction with SnCl$_4$ caused replacement of exo-methyl by chloride, with the resulting chlorides susceptible to further nucleophilic displacements[171].



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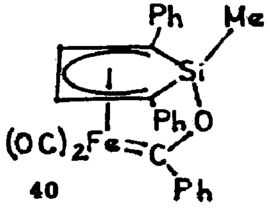

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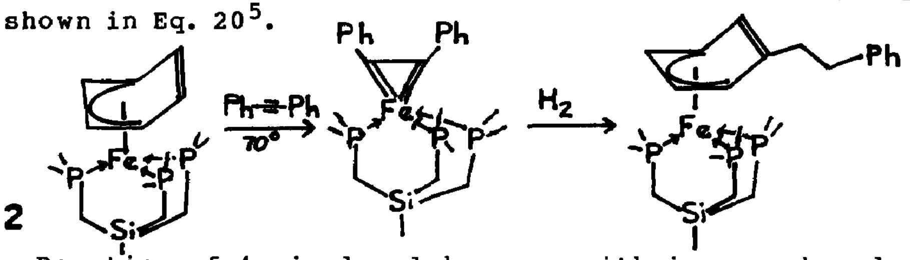
The η^4-benzene complex, **2**, was mentioned in Section 2 of this Review. The benzene ligand of **2** was readily displaced by other unsaturated organics; one particularly interesting sequence is shown in Eq. 20[5].



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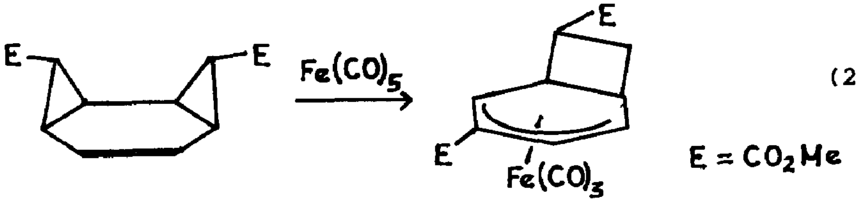
Reaction of 4-vinylcyclohexenes with iron carbonyls gave principally 2-substituted (η-cyclohexadiene)tricarbonyliron products, formed by 1,3-hydrogen shifts in η^2 intermediates[172]. A bicyclo[4.2.0]octadiene complex resulted from reaction of a tricyclic diester with $Fe(CO)_5$ (Eq. 21)[173].



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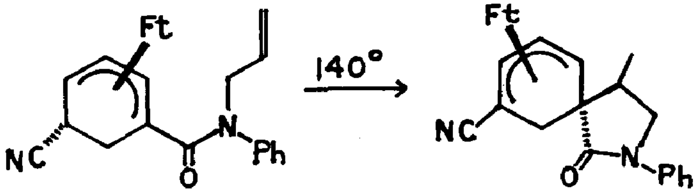
Upon heating at 140°, the iron tricarbonyl complex of ethyl 1,3-cyclohexadien-1-carboxylate underwent racemization through a series of hydrogen transfers, but incorporation of a trans-5-cyano substituent rendered the complex stable under the same conditions[174]. Heating allylic amide or ester derivatives under these conditions gave spirolactam or spirolactone complexes[175] which, with proper substitution, could be obtained enantiomerically pure (Eq. 22)[175].



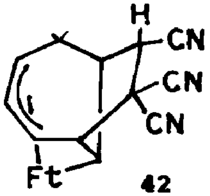
(22)

Interconversion of cyclohexadiene and cationic cyclohexadienyl complexes underlies many synthetic applications of these compounds. The use of thallium(III) trifluoroacetate for hydride removal from cyclohexadiene complexes has been recommended; the reagent was said to provide better yields and (in some cases) complementary regiocontrol compared to trityl cation[176]. Quenching reactions of cyclohexadienyl cations will be discussed in Section 7a.

(1-4-η-Cycloheptatriene)tricarbonyl iron could be functionalized by deprotonation to form the η^3-cycloheptatrienyl anion, then reaction with alkyl chloroformates. The 7-substituted product presumed to be initially formed in the acylation reaction was converted to the 5- and 6-substituted products by base-induced proton transfers; the product with the ester group in the 5-position predominated under these conditions. Photochemical complexation of carbethoxycycloheptatrienes with Fe(CO)$_5$ gave, as previously found, principally the 6-ester[177].

(2-5-η^4-Tropone)tricarbonyliron, **41**, gave separable diastereomers upon replacement of one CO by [+)-neomenthyl]diphenylphosphine. 1,3-Shift of the Fe(CO)PRPh$_2$ group was an order of magnitude faster than that of the Fe(CO)$_3$ group[178], consistent with a dipolar transition state having a η^5-coordinated metal group. The cycloaddition of TCNE to **41** has been studied through the effects of pressure and solvents on rates. Both the volume and the entropy of activation were quite negative, with values of -31 cm^3/mol and -152 J/K-mol, respectively, in acetone solution, consistent with a highly ordered (concerted but not synchronous) transition state[179].

TCNE cycloadditions to Fe(CO)$_3$ complexes of azepines and of 1-cyanocycloheptatriene have also been studied kinetically[180]. The relative rates for (η^4-C$_6$H$_6$Y)Fe(CO)$_3$ in methylene chloride decrease in the order Y = NH >> CH$_2$ > NCO$_2$Et > C=O, and the 6-cyano derivative of (1-4-η^4-C$_7$H$_8$)Fe(CO)$_3$ was about 10^{-4} as reactive as the unsubstituted complex. Replacement of a CO by a triphenylphosphine ligand increased the reactivity of the cycloheptatriene complex about 2000-fold. All of these data bespeak the importance of electron-donation by the coordinated cycloheptatriene to the TCNE. Tricyanoethene has been found to be several hundred-fold less reactive than TCNE, a fact which was interpreted as favoring a highly concerted addition[180], but which is also consistent with an electron-transfer mechanism. The structures of the tricyanoethene adducts have not been determined; this reviewer, based on persistent belief in some dipolar character in these concerted reactions, believes that the correct structure should be **42**, rather than the regioisomer preferred by the original authors[180].



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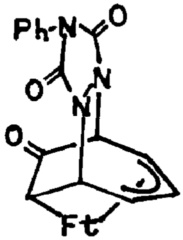
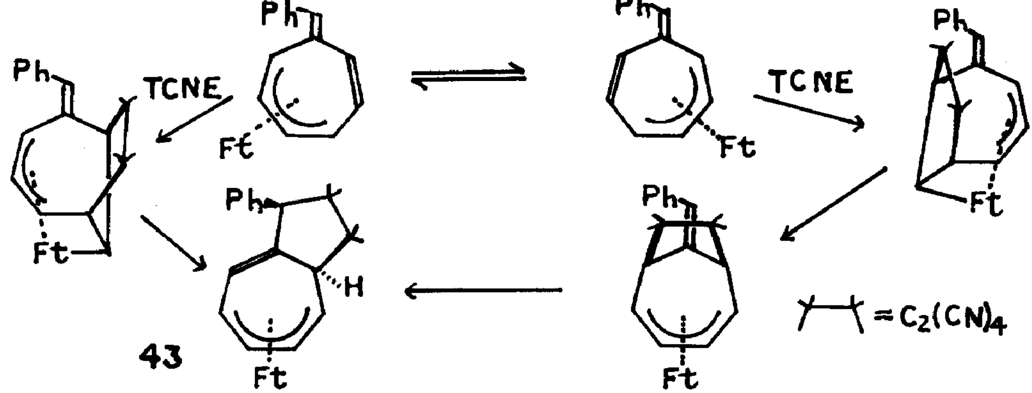


Reactions of TCNE with 7-alkylidenecycloheptatriene complexes have been studied by NMR, with results presented in Scheme III. The structure of the final product, **43**, was confirmed by X-

Scheme III



ray crystallography[181]. Addition of 4-phenyl-1,2,4-triazoline-3,5-dione to **41** has been similarly studied, with kinetic control producing adducts across the 7,5- and 7,4- positions of the complexed tropone ring. Thermodynamic control eventually produced primarily the 7,3-adduct, **44**[182]. Analogous "sigmahaptotropic rearrangements" of the adducts of aryl ketenes with $(C_7H_8)Fe(CO)_3$ have been studied kinetically. The rearrangement was about 40 times faster in methanol than in acetone, allowing partial charge separation in the quasiconcerted transition state[183].

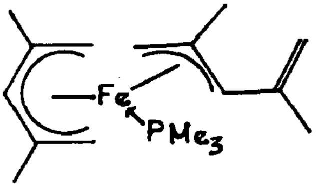
The multifarious products resulting from intramolecular reactions of iron-carbene complexes resulting from reaction of $(\eta^4\text{-COT})Fe(CO)_3$ with aryl-lithium reagents, followed by alkylation with triethyloxonium fluoborate, (e.g. **33** and **34**)[136] were described at the end of Section 5 of this review.

The IR spectra of (norbornadiene)- and (1,5-cyclooctadiene)-tricarbonyl iron at 10-12 K showed three CO stretching bands, consistent with the square pyramidal structure found in the crystal structure of the cyclooctadiene complex. But at room temperature, only two such bands were observed, suggesting dynamic processes on the infrared time scale. The activation energy for tricarbonyliron group rotation in the norbornadiene complex was calculated to be less than 9 kJ/mol, compared to 40 kJ/mol for (butadiene)tricarbonyliron[184].

7. η^5-DIENYL COMPLEXES

a. Compounds with Open Pentadienyl Ligands

The results of reaction of $FeCl_2L_2$ [in this paragraph, L = PMe_3] with potassium 2,4-dimethylpentadienide depended on the ratio of reactants. Use of two equivalents of K^+ $C_7H_{11}^-$ resulted in formation of $(\eta^5\text{-}C_7H_{11})(\eta^3\text{-}C_7H_{11})FeL$ (**44**), use of equimolar amounts gave the previously described trimethylenemethyl derivative, and use of two equivalents of $FeCl_2L_2$ gave $(\eta^5-C_7H_{11})FeL_3^+$ $FeCl_3L^-$. The latter was confirmed by a crystal structure. Protonation of **44** in the presence of trimethylphosphine (L) also gave the $(\eta^5-C_7H_{11})FeL_3^+$ cation. ^{31}P NMR studies of this cation indicated a 48 kJ/mol barrier for ligand rotation[144]. The unsubstituted pentadienyl cation $(\eta^5-C_5H_7)FeL_3^+$ was prepared by protonation of $(\eta^3-C_5H_7)_2FeL_2$ with HL^+. It underwent attack by 2,4-dimethylpentadienide at C-2, to form the unusual product **45** (X-ray structure)[185].



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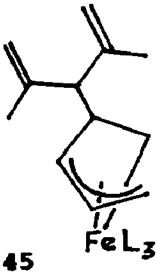

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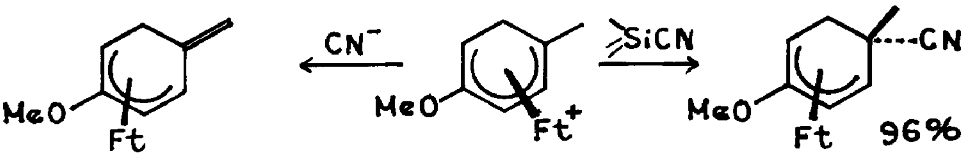
Substituted pentadienyliron cations, $(\eta^5-1-R-C_5H_6)Fe(CO)_3^+$ were prepared from RCH=CH-CH=CHCHO by complexation with $Fe_2(CO)_9$, $NaBH_4$ reduction, and protonation[186]. Reaction of the (2,4-dimethylpentadienyl)tricarbonyliron cation with KI in acetone gave $(C_7H_{11})Fe(CO)_2I$, which showed an unsymmetrical crystal structure[187]. Reduction with sodium amalgam gave a dimer $[(C_7H_{11})Fe(CO)_2]_2$, whose crystal structure was similar to that of *cis*-Fp_2[188]. Reaction of $(\eta^5-C_7H_{11})Fe(CO)_2I$ with Fp^- gave the unsymmetrical dimer, $CpFe(CO)(\mu-CO)_2Fe(CO)(\eta^5-C_7H_{11})$. Reduction of the iodide with excess sodium amalgam gave an anion, which underwent alkylation with methyl iodide to produce unstable $(\eta^5-C_7H_{11})Fe(CO)_2Me$[187]. The chemistry of these (dimethylpentadienyl)dicarbonyliron derivatives was described by the authors as "open Fp chemistry;" perhaps the group can be designated as "Fop"?

Bis(2,3,4-trimethylpentadienyl)iron has been prepared by reaction of the carbanion with $FeCl_2$ at -78° [189]. A crystal structure[190] and photoelectron spectra have been reported, and comparisons with ruthenium and osmium analogs made[191]. Extended Hückel calculations have been performed on bis(pentadienyl)M species, with particular emphasis on the relative configurations of the two pentadienyl ligands[192].

Bis$(\eta^5$-cyclohexadienyl)iron and bis$(\eta^5$-6,6-dimethylcyclohexadienyl)iron have been prepared by reaction of the carbanions with $FeCl_2$. The former underwent isomerization to $(\eta^6$-benzene)$(\eta^4$-1,3-cyclohexadiene)iron[193].

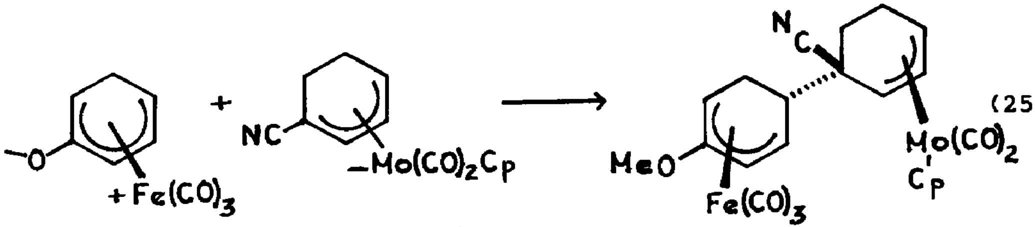
The principal uses of (cyclohexadienyl)iron compounds, especially cationic ones, are in synthesis, where reactions with nucleophiles produce cyclohexadienes. The kinetics of reaction of $(\eta^5\text{-}C_6H_7)Fe(CO)_3^+$ and of its 2-OMe derivative with 4-chloroaniline have been studied. The additions were reversible, and excess aniline was required in order to deprotonate the initial adduct. The 2-methoxy cation was about one-seventh as reactive as the unsubstituted one[194]. Reaction of (η^5-2-methyl-3-methoxycyclohexadienyl)tricarbonyliron cation with (–)α-phenylethylamine was used to prepare separable diastereomers, which were converted to resolved cations for use in asymmetric synthesis[195].

The use of Me_3SiCN in cyanating (cyclohexadienyl)iron cations has been recommended, particularly in cases where use of CN^- results in deprotonation (Eq. 24)[196]. Likewise, tributyltin



(24)

enolates were reported to have advantages over more basic lithium enolates; their use was exploited in a synthesis of (±)-trichodiene [197]. A molybdenum-stabilized carbanion functioned as a novel nucleophile for addition to a (cyclohexadienyl)iron cation (Eq. 25)[198]. Reduction of (η^5-1-carbomethoxycyclohexadienyl)tricarbonyliron cation electrochemically or with zinc dust led to formation of the (19-electron?) free radicals, which coupled with high regioselectivity at the carbomethoxy-bearing termini[199]. Reduction of the corresponding N,N-diallylamide gave ca. 20% of intramolecular coupling analogous to that shown in Eq. 22[199].



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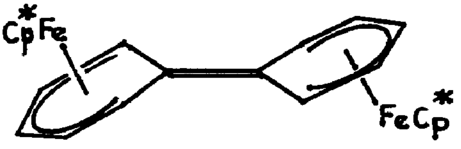
Protonation of the (η^4-benzene) complex 2 occurred with exceptional facility, using $NH_4^+\ PF_6^-$, to form the (η^5-cyclohexadienyl)iron product[5]. (η^5-Methylenecyclohexadienyl)FeCp resulted from deprotonation of (η^6-toluene)$FeCp^+$ with potassium t-butoxide[200]. Similarly, two-electron reduction of $[Cp^*Fe(\eta^6\text{-}C_6H_5)]_2^{2+}$ produced the species **46** (X-ray structure)[201].

Further chemistry reminiscent of "Fp" chemistry involved (cyclohexadienyl)iron compounds. Reaction of $(\eta^5\text{-}C_6H_7)Fe(CO)_2I$ (**47**) with Fp^- at -78° gave a mixed dimer, $(C_6H_7)Fe(CO)(\mu\text{-}CO)_2Fe(CO)Cp$, which gave up a hydride to trityl cation to produce the cationic benzene analog. Unlike Fp chemistry, however, was the ready displacement of benzene from **47** on reaction with triphenylphosphine, which produced trans-$(Ph_3P)_2Fe(CO)_2(H)I$[202].

Consistent with previous results, (η^5-cycloheptadienyl)tricarbonyliron cation reacted more slowly than the cyclohexadienyl analog with 4-chloroaniline[194]. A thoroughly unexpected result was the formation of **48** (X-ray structure) from reaction of (η^4-cycloheptatriene)tricarbonyliron with o-tolyl-lithium, followed by triethyloxonium fluoroborate in methylene chloride at -60° [135]. Some additional η^5-cycloheptadienyl and -trienyl complexes were shown in Scheme I.



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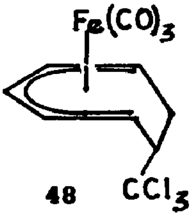
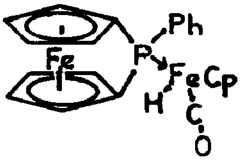


48

b. (Cyclopentadienyl)dicarbonyliron Hydride and Related Compounds

This section includes results on FpH, Fp^-, and Fp•, and on compounds containing bonds between the CpFe group and non-metals of Groups 14-17, essentially in that order. Derivatives with one or more CO groups replaced by other 2-electron ligands are included. Fp-M compounds with covalent Fe-M bonds are treated with other heterobimetallic species in Section 9c.

$Cp^*Fe(DPPE)H$ has been prepared directly from $(DPPE)FeCl_2$, pentamethylcyclopentadiene, and potassium metal in a sonochemically-assisted one-pot reaction. It gave a stable radical-cation on one-electron oxidation[203]. $CpFe(PMe_3)_2H$ resulted directly from reaction of 1 with cyclopentadiene[3], and the (η^5-indenyl) analog was prepared similarly[4].



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Reaction of (1,1'-ferrocenediyl)phenylphosphine with Fp^- gave the novel hydride **49** (X-ray structure) in 40% yield[204]. FpH resulted from protonolysis of $FpThCp_3$ with trifluoroethanol or acetone[205]. FpH reacted with α-cyclopropylstyrene at room temperature to give 1-cyclopropyl-1-phenylethane (83%) and a trace of 2-phenyl-2-pentene. With increasing electron density on the metal hydride, the percent of 2-phenyl-2-pentene increased, to 30% with Fp^*H and 64% with $CpFe(CO)(PMe_3)H$. A hydrogen atom-transfer chain mechanism was proposed[206].

Association of trimethyl phosphite with Fp• (from photolysis of Fp_2 in heptane at room temperature) to form $FpP(OMe)_3^{\cdot}$ has been followed by time-resolved IR spectroscopy, and found to occur with a second-order rate constant of 9×10^8 M^{-1} sec^{-1} [207]. The nineteen-electron species resulting from such associations were found to function as strong reducing agents toward a variety of organic and inorganic substrates; in methylene chloride solution, $FpL^{\cdot}$ reduced $Fp^{\cdot}$ to Fp^-, which with solvent gave $FpCH_2Cl$[208]. Photolysis of Fp_2 with phosphines in micellar phases resulted in reduction of methylviologen in the aqueous phase[209]. The analogous (indenyl)$Fe(CO)_2L^{\cdot}$ radicals reversibly lost L, regenerating the dimer $[(C_9H_7)Fe(CO)_2]_2$; the radicals probably had a seventeen-electron η^3 structure, based on ESR[133].

The anion Fp^- was generated in the gas phase by dissociative electron attachment to Fp_2. The electron affinity of $Fp^{\cdot}$ was estimated at 1.0-1.7 eV. In the gas phase, Fp^- reacted with methyl iodide and triflate, but not with methyl bromide or chloride[210]. Fp^- in solution functioned as a one-electron reductant toward a cationic Mo_2C_3 cluster[211] and also toward $Co(CO)_3(PPh_3)_2^+$ [212].

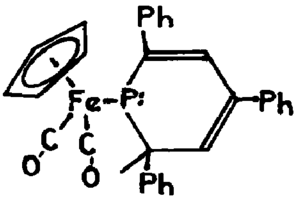
Derivatives of Fp_2 and Fp^- having alkoxysilyl substituents on the cyclopentadienyl rings have been prepared[213]. Electronic spectra of Cp^*FeL_2Y [L = PMe_3, PEt_3, CO; Y = H, X, OR, R, Ar] have been obtained and compared with the Ru analogs[214].

The η^1-silole complex $FpSi(Me)C_4Ph_4$ gave Diels-Alder additions with dimethyl acetylenedicarboxylate or benzyne, forming 7-silanorbornadienyl-Fp products. Thermolysis led to extrusion of FpSiMe, characterized through various addition products[215]. Photolysis of $FpSiMe_3$ in the presence of $RSiH_3$ gave silylene-bridged dimers $(\mu\text{-}CO)(\mu\text{-}SiHR)[CpFe(CO)]_2$[216]. Photolysis of $FpSiMe_2SiMeR_2$ gave monosilyl products $FpSiMeR_2$ and $FpSiMe_2R$, along with ferrocene and Fp_2[217]. The crystal structure of $Fp_2Sn(Ar)Br$ [Ar = *p*-tolyl] has been determined[218].

Reaction of FpN_3 with $[CpMo(CO)_2]_2$ was complex, with Fp_2 the only identifiable iron-containing product[219].

An X-ray structure of the Fp-phosphorin **50** has been published[220]. Reaction of $Fp^*P(SiMe_3)_2$ with $ArPCl_2$ [Ar = 2,4,6-tri-*tert*-butylphenyl] gave the diphosphene product, Fp^*-P=P-Ar, **51**, characterized by X-ray crystallography; Fp'-P=P-Ar was prepared similarly[221]. Reaction of **51** with dimethyloxosulfonium methylide gave the diphosphirane **52**[222]. Sulfur and selenium reacted with **51** to give Fp^*-P(→Y)=P-Ar (Y = S, Se). The stable sulfur derivative was the subject of a crystal structure, but the selenium analog slowly closed to a selenadiphosphirane heterocycle[223]. **51** reacted with acrolein to form the oxaphosphole **53** (X-ray)[224].

K^+ Fp^- displaced chloride from $ClP(=CR_2)_2$ to give $FpP(=CR_2)_2$



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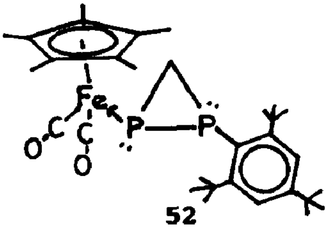

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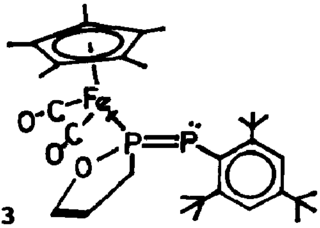
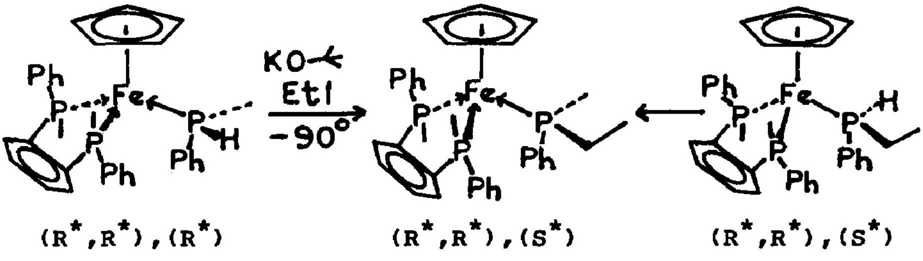


53

[R = SiMe$_3$][225]. Cyclophosphazenes and polyphosphazenes having pendant Fp groups attached to phosphorus have been prepared by straightforward displacement reactions[226].

^{13}C NMR studies of carbonyl ligands in CpFe(CO)$_2$PPh$_n$Y$_{3-n}$ [Y = OMe, Me] have been used to assess electronic effects of the varying phosphorus ligands[227]. [C$_5$H$_4$(SiMe$_2$OEt)]Fe(CO)$_2$PPh$_3$$^+$ resulted from oxidation of the silyl-substituted Fp$_2$ with ferricenium ion in the presence of triphenylphosphine[213]. The same method applied to Fp$_2$ gave Fp[PPh$_2$(CH$_2$)$_n$PPh$_2$]$^+$ and related complexes having monodentate diphosphines, which closed to chelate cations such as CpFe(CO)(DPPM)$^+$ upon photolysis[228]. In turn, photolysis of CpFe(CO)(DPPM)$^+$ in acetonitrile produced CpFe(DPPM)(NCMe)$^+$ [229].

Acetone-sensitized photolysis of Cp*FeAn$^+$ [An = *p*-xylene] led to Cp*Fe[P(OMe)$_3$]$_3$$^+$ [229]. Asymmetric induction in methylation reactions (MeI, Et$_3$N) of the phenylphosphine ligand in (R*,R*)-CpFe[1,2-C$_6$H$_4$(PMePh)$_2$](PH$_2$Ph)FeCp$^+$ was substantial, with a 4:1 preference for formation of the (R*)-PhPMeH ligand[230]. Further alkylation using ethyl iodide and potassium *tert*-butoxide at low temperature (Eq. 26) gave almost complete (99%) selectivity[231].



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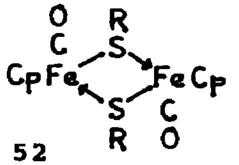
Reaction of BiX$_3$ with two equivalents of Fp$^-$ gave Fp$_2$BiX. The chloride formed trimeric Bi$_3$Cl$_3$ rings in the crystal. Fp$_3$Bi, made using excess Fp$^-$, underwent clusterification upon photolysis[232].

FpOC(=O)C$_7$F$_{15}$ was obtained from FpX and silver pentadecafluorooctanoate[233]. Electrochemical oxidation of Fp*SP(=S)(OR)$_2$ in acetonitrile generated a radical-cation, along with Fp*-NCMe$^+$, Fp*$_2$, and possibly a bridged diiron species[234]. Electrochemical reduction of the same dithiophosphate species (and the Fp analog) at a mercury electrode led to decomposition, with formation of

$Fp^*{}_2Hg$. A wave for reduction of Fp_2 could also be observed[235]. Although FpSC(=S)(OEt) underwent clean carbonyl substitution with phosphines, the Fp^* analog also formed $Cp^*Fe(CO)(\eta^2\text{-}S_2COEt)$. Bidentate xanthates also resulted in either case from photolysis or one-electron oxidation of the monodentate xanthates[236]. Reduction of $Fp\text{-}S_{3,4}\text{-}Fp$ with $LiBEt_3BH$ at low temperature gave FpS_{1-3}^-, which was acylated to form FpSC(=O)R. The same product resulted (along with FpCl) from direct room-temperature acylation of the tri- and tetrasulfides, Fp_2S_n, with RCOCl[237].

Fp_2Se reacted with $Fp(THF)^+$ to form Fp_3Se^+, whose crystal structure revealed a flattened pyramidal structure with Fe-Se bonds averaging 2.44 Å[238]. Thiophene and benzothiophenes displaced isobutene from $Fp(CH_2{=}CMe_2)^+$, to form S-bonded thiophene-Fp^+ complexes. The dibenzothiophene complex showed a pyramidal sulfur and a 2.289 Å Fe-S bond. From ^{13}C NMR study of the benzothiophene complex, the free energy for pyramidal inversion at sulfur was 39 kJ/mol, as compared to 52 kJ in $FpSPhMe^+$. The thiophenes were readily displaced by acetonitrile[239]. The chiral cations $Fp'QMe_2^+$ [Q = S, Se, Te] were prepared by straightforward displacement methods, along with other examples of $CpFe(CO)LQMe_2^+$ and $CpFeL_2QMe_2^+$ [L = $AsPh_3$, $SbPh_3$, PMe_3, $P(OMe)_3$, DPPM, DPPE, etc.). The inversion of the chalcogen atom was investigated by dynamic NMR methods[240]. $CpFe(DPPE){-}S{=}O^+$ has been obtained in reaction of $CpFe(DPPE)(O{=}CMe_2)^+$ with thiirane 1-oxide, and the SO_2 complex from SO_2 directly. Both were η^1-coordinated at sulfur[241]. $Fp\text{-}TePR_3^+$ cations [from reaction of $R_3P{=}Te$ with $Fp(THF)^+$; R = Me, $CHMe_2$, CMe_3, NMe_2] slowly lost elemental tellurium on standing, leaving $Fp\text{-}PR_3^+$ [242].



52

Thermolysis of 52 [R = Et, Ph] produced ferrocene and FpSR[243]. At 300°, under flash vacuum pyrolytic conditions, 52 [R = Me] gave a 78% yield of ferrocene[244].

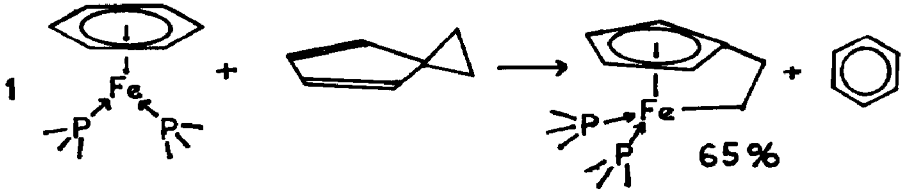
FpCl was produced in high yield upon reaction of Fp_2 with thionyl chloride[245]. Trisubstituted derivatives were produced by reaction of lithium 1,2,4-tris(trimethylsilyl)cyclopentadienide with FeX_2 [X = Cl, Br, I] at -95°, followed by introduction of CO[246]. Treatment of Fp'X and $CpFe(PR_3)_2X$ with $LiNR_2$ generally yielded ring-aminated products $(\eta^5\text{-}C_5H_4NR_2)FeL_2X$, $(\eta^5\text{-}C_5H_4NR_2)FeL_2H$, and dimers Fp'_2, but the results depended on X, the ligands L, and the amide NR_2. In particular, amination was favored by good acceptor character of the ligands L, and bromo derivatives were better than chloro. The crystal structure of $(\eta^5\text{-}C_5H_4NEt_2)Fe(CO)[PPh(OEt)_2]Br$ showed a strong interaction between amino substituent, ring and iron atom, with a coplanar nitrogen, short nitrogen-ring distance, and long substituted carbon-iron distance[247]. FpX derivatives bearing a chiral phenylethylsubstituent on the cyclopentadienyl ring were prepared (from α-phenylethyl)cyclopentadiene via the dimers $[(\eta^5\text{-}C_5H_4\text{-}CHMePh)Fe(CO)_2]_2$. Photolytic displacement of CO by triphenylphosphine produced resolvable 50:50 mixtures of diastereomers. Diastereomers of $(C_5H_4R)Fe(CO)(PPh_3)I$ were stable at room temperature, but equilibrated at 70° [248].

Reaction of FpI with Group 15 donor ligands was catalyzed by $Pd/CaCO_3$, PdO, or Fp_2[249]. The proton NMR spectra of (methylcyclopentadienyl)- and (indenyl)Fe(CO)LI [L = various phosphines and phosphites] have been studied, and ring proton chemical shifts and coupling constants fully assigned[250].

FpI served as a useful reagent for formation of $Fe_4S_4(SH)_4{}^{2-}$ (35%) by reaction with H_2S[251]. Reaction with the anil from salicylaldehyde and 2-(α-aminoethyl)pyridine also occurred with displacement of cyclopentadiene, to give an uncharacterized enantioselective cocatalyst for hydrosilylation[252].

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

$Fp^*[\mu\text{-}(CH_2)_n]Fp^*$ [n = 3-6] and methylcyclopentadienyl analogs [n = 3-10] have been prepared by straightforward displacement reactions of Fp^{*-} or $(C_5H_4Me)Fe(CO)_2{}^-$ with dibromoalkanes[253]. Bridged trinuclear complexes, $MeSi[\eta\text{-}C_5H_4Fe(CO)_2R]_3$ [R = Me, Et, CH_2Ph] were prepared from $MeSiCl_3$ and the ring-lithiated Fp-alkyls, and the crystal structure of the ethyl compound determined[254]. A bridged Fp-alkyl derivative resulted upon reaction of 1 with spiro[2.4]heptadiene (Eq. 27)[3]. Fp^- readily displaced a



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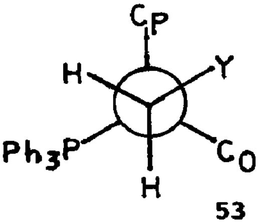
fluoride from 2-(pentacarbonylmanganese)-4,6-difluoro-1,3,5-triazine to give the dimetallated triazine[255]. A more novel, direct synthesis of an aryl-Fp derivative resulted from reaction of $FeCl_2$, DPPE, and PhMgBr to form $(DPPE)FePh_2$, followed by protonolysis of a Fe-C bond by cyclopentadiene at -60°, giving CpFe-(DPPE)Ph in 61% yield[256]. The same method worked with some other phosphines and with Fe-Me and -Et derivatives[256,257]. Syntheses of alkyl derivatives from Li^+ CpFe(cyclooctadiene)$^-$, organic halide RX, and phosphine L have also been reported[257]. A study of the stabilities of ethyl-iron compounds toward β-elimination indicated that they increased with the basicity of the phosphine ligands and decreased with increasing methylation of the Cp ligands[257].

Methylation of $FpCH_2SMe$ gave $FpCH_2SMe_2^+$, a shelf-stable reagent for transfer of methylene to alkenes to form cyclopropanes. The crystal structure of the fluoroborate salt was determined[258]. $FpCH_2CHO$ reacted with organolithium and Grignard reagents in a normal manner to produce alkoxides, $FpCH_2CH(R)O^-$, acidification of which gave alkene complexes[259].

Conformational analyses of Fp'-alkyls have received considerable attention from the Davies group, using NMR and crystallographic studies. Fp'Et was found to occupy exclusively the conformation 53 [Y = Me][260]. $Fp'CH_2OMe$ adopted the same conformation [Y = OMe] in polar solvents, but in non-polar solvent at low temperature, dipolar repulsions favored 54[261]. The bulky trimethylsilyl group in $Fp'CH_2SiMe_3$ was also best accommodated as in conformation 53[262]. The mesityl group in $Fp'CH_2C_6H_2Me_3$, however, forced adoption of a near-eclipsed conformation, 55. Other benzylic compounds showed variations in their $^3J_{PH}$ values consistent with equilibria between conformations 53 [Y = Ar] and 55[263].



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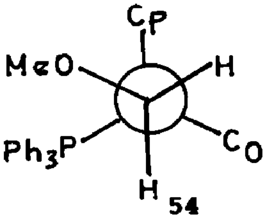

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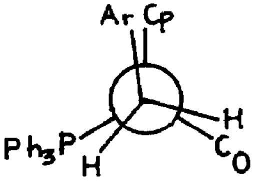

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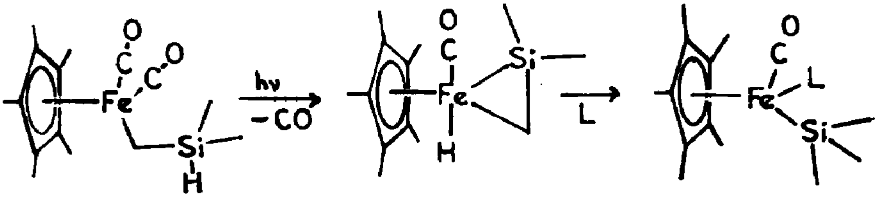
Photolysis of $Fp^*CH_2SiHMe_2$ in the presence of added CO or PPh_3 (L) cleanly produced $Cp^*Fe(CO)(L)SiMe_3$. The mechanism proposed in Eq. 28 was supported by results of matrix photolysis at 77 K[264]. Treatment of $FpCH_2SiMe_2SiMe_3$ with lithium di-isopropylamide at -80°, followed by methyl iodide, led to ring-methylation. At 0°, however, migration and rearrangement of the disilylmethyl group intervened, and the product was $(Me_3SiCH_2SiMe_2\text{-}C_5H_4)Fe(CO)_2Me$[265].



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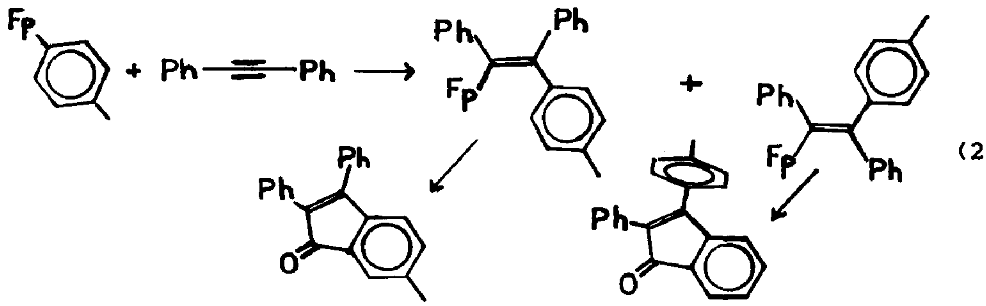
Reaction of FpAr with diphenylacetylene in refluxing decalin led to formation of indenones, probably via initial addition of the elements of Fp-Ar to the acetylene (Eq. 29)[266].



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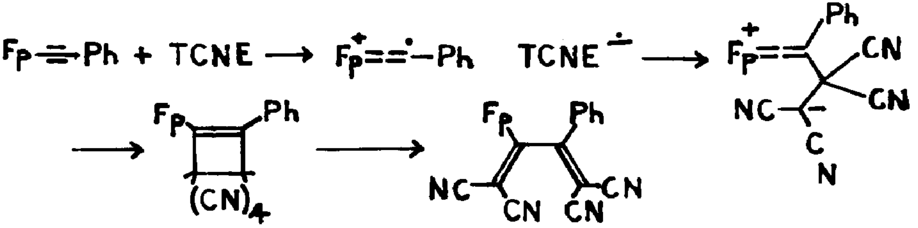
FpH and Fp'H likewise added to the triple bonds of cyano- and dicyanoacetylene, to form *Z*-Fp(')-CY=CHCN [Y = H, CN]. With Fp'H and HC≡C-CN, the reaction was not regiospecific, both *Z*-Fp'CH=CHCN and $Fp'C(CN)=CH_2$ resulting, in 4:1 ratio. (μ-DPPE)-$[FeCp(CO)H]_2$ did add regiospecifically[267].

Condensation of $FpCH_2C(Fc)=OEt^+$ [Fc = 1-ferrocenyl] with ethyl cyanoacetate gave $FpCH_2C(Fc)=C(CN)CO_2Et$, which underwent photodecarbonylation to form $[\eta^3\text{-}CH_2{=}C(Fc){=}C(CN)CO_2Et]Fe(CO)Cp$. $Fp\text{-}CH_2C(Fc)=C(CN)_2$, **56**, was obtained *inter alia* by Fp^- displacement from the chloride[268]. The analogous reaction with the iodide gave principally reduction to $MeC(Fc)=C(CN)_2$, however. **56** reacted with iodine to give the alkyl iodide (58%), FpI (49%), and $[\eta^2\text{-}CH_2=C(Fc)C(CN)_2I]\text{-}Fp^+\ I_3^-$. Reduction of **56** with LAH gave $MeC(Fc)=C(CN)_2$ and Fp_2[269].

High-resolution mass spectra of several aryl- and vinylic-Fp compounds have been discussed in terms of electron-density around the metal and the 18-electron rule[270]. 2,4-Pentadienyl- and 2,4-hexadienyl-Fp have been prepared and studied, along with their $[\eta^3\text{-}C_5H_6R]Fe(CO)Cp$ and $[\eta^5\text{-}C_5H_6R]FeCp$ derivatives[271].

Electrochemical studies of alkynyl-Fp and $\text{-}Fp^*$ and phosphine-substituted derivatives showed one-electron oxidation processes whose reversibility depended on the ligands[272]. The thermodynamics of proton transfer from acidic metal hydrides to $CpFe(CO)(PMe_3)\text{-}C{\equiv}C\text{-}CMe_3$ has been studied by NMR[273]. The product of cycloaddition of TCNE to Fp-C≡CPh, previously assigned a cyclobutene structure, has been shown in fact to be a butadienyl-Fp compound by X-ray crystallography. The mechanism shown in Eq. 30 was suggested[274]. Attempted reaction of Fp-C≡CMe with $EtC{\equiv}W(O\text{-}tert\text{-}Bu)_3$ gave only Fp_2[275].



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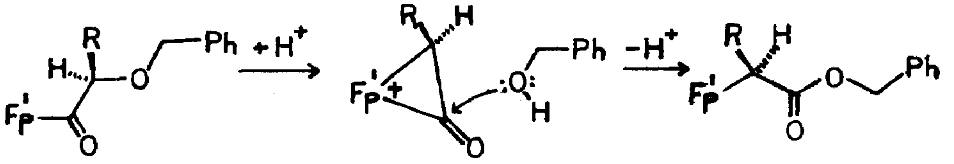
Oxidation of $Cp^{*}Fe(CO)(\eta^{1}\text{-DPPE})Me$ or $Cp^{*}FeL_2Me$ [L = Me_3P, $(MeO)_3P$, or DPPE] with ferricenium ion in THF or methylene chloride gave stable Fe(III) products, which did not undergo hydrogen abstraction, methyl migration, or other reactions[276]. But electrochemical oxidation of $(MeC_5H_4)Fe(CO)_2Me$ in methanol-acetonitrile mixtures produced $(MeC_5H_4)Fe(S)(CO)(COMe)^{+}$, where S is a solvent molecule[277]. Similarly, electrochemical study of alkyl-to-acyl transformation of the methyl group in Fp'Me, in the presence of pyridine nucleophiles, showed that oxidation was followed by rapid association of a pyridine to produce the 19-electron species $CpFe(CO)(PPh_3)(py)Me^{+}$, observable at low temperature, followed by methyl migration to form $CpFe(PPh_3)(py)(COMe)^{+}$. The reactivity of various pyridines correlated with their basicities, indicating the need for a nucleophile to push the methyl group from the iron[278]. Reaction of FpR [R = 2-cyclopropylethyl, neopentyl, 1-norbornylmethyl] with Ph_3C^{+} produced 17-electron Fe(III) cations, but no hydrogen abstraction. Under CO, migratory insertion occurred in each case, accompanied by β-hydride abstraction in the case of $FpCH_2CH_2(cyclo\text{-}C_3H_5)$[279]. Another type of nucleophilic push to induce metal→carbon migration occurred in methylation of $(\eta^{3}\text{-indenyl})Fe(CO)_3^{-}$; the initially-formed $(\eta^{3}\text{-indenyl})Fe(CO)_3Me$ gave rise to mixtures of $(\eta^{5}\text{-indenyl})Fe(CO)_2Me$ and $(\eta^{5}\text{-indenyl})Fe(CO)_2(COMe)$, the yield of the latter increasing with CO pressure[132].

Reaction of the chiral Fp-Me analogs, $(C_5H_4\text{-CHPhMe})Fe(CO)_2\text{-}Me$, with triphenylphosphine, produced a separable 50:50 mixture of diastereomers of $(C_5H_4R)Fe(CO)(PPh_3)(COMe)$. Photodecarbonylation of enriched diastereomers gave partly epimerized $(C_5H_4R)Fe(CO)(PPh_3)Me$, along with epimerically unchanged recovered acetyl compound[248]. "Deinsertion," i.e. C→Fe migration to produce Fp-Me, occurred when $CpFe(CO)PPh_3)COMe$, Fp'COMe, was treated with $(MeCN)_4Cu^{+}$, which functioned as a phosphine-abstractor[280].

The acid-catalyzed rearrangement of $Fp'C(=O)CHROCH_2Ph$ to $Fp'CHRCO_2CH_2Ph$ [R = D, Me] has been found to occur with clean inversion of configuration at carbon, consistent with the mechanism of Eq. 31[281].



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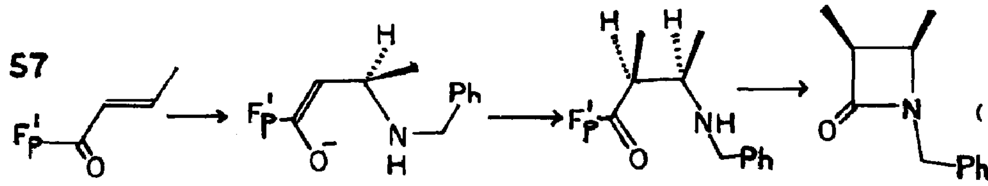
The crystal structure of $FpCS^{+}$ PF_6^{-} showed an Fe-CS distance only slightly shorter than the Fe-CO distances[282]. INDO/GIAO parameters have been adjusted to allow calculation of ^{15}N, ^{17}O, and ^{13}C chemical shifts in metal complexes including $FpCN$[283]. The metal carboxylate $Fp'CO_2{}^-$ was prepared by attack of hydroxides on $Fp'CO^+ I^-$. The potassium salt transferred oxide ion to $Ph_3PMn(CO)_5{}^+$ and Ph_3C^+, but was alkylated by MeX; the lithium salt gave oxide transfer in all cases. Thermolysis of either salt gave mixed dimer Fp-Fp'. Reaction with water gave the anhydride Fp'C(=O)OC(=O)Fp'[284]. The less stable $FpCO_2{}^-$ could be trapped at -80° with $RSiMe_2Cl$ [R = Me, *tert*-butyl] to give silyl esters, $FpCO_2SiMe_2R$. Methylating agents gave only FpMe rather than methyl esters, due to enhanced reactivity toward small equilibrium amounts of Fp^- rather than carboxylate[285].

Direct insertion of CO into Fe-acyl bonds, a much-sought reaction, has been observed as a result of a novel oxidation-NO addition sequence. Fp'COMe was oxidized with ferricenium ion to the 17-electron cation, which rearranged to $CpFe(PPh_3)(NO)(COCOMe)$ when treated with NO gas[286]. The crystal structure of $Fp'COCH_2CH(CH_2)_2$, from reaction of $FpCH_2CH(CH_2)_2$ with triphenylphosphine, has been determined[287].

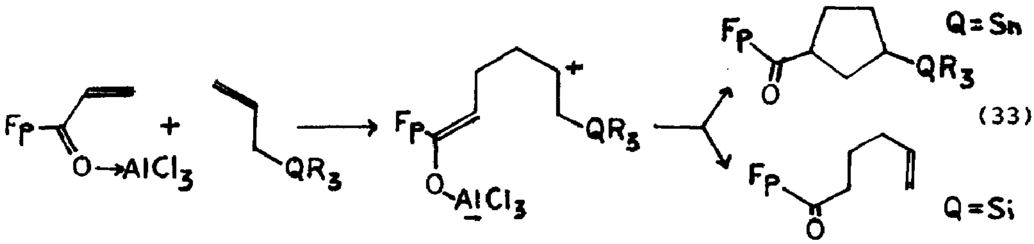
X-ray crystallography of *Z*-Fp'C(=O)CH=CHMe, **57**, showed an *s*-cis conformation of the crotonyl group in the crystal. Deprotonation with butyl-lithium gave a dienolate, which underwent alkylation or protonation α to the carbonyl group, giving (*RS,SR*)-$Fp'C(=O)CHRCH=CH_2$ [R = H, Me, Et, CH_2Ph][288]. Methyl-lithium or butyl-lithium reacted with *E*-**57** (for which an X-ray structure was also obtained) by Michael addition, and trapping of the resulting enolate with methyl iodide gave a single diastereomer of Fp'C(=O)CH(Me)CHMeR [R = Me, Bu]; the same diastereomer resulted when $Fp'C(=O)CH_2CHMe(OMe)$ was allowed to react with two moles of RLi, then methylated with MeI. Michael addition of lithium benzylamide to *E*-**57** led, after methyl iodide quench and decomplexation, to lactam formation (Eq. 32)[289].



(32)

Allylstannanes added to $FpC(=O)CH=CH_2$ in the presence of Lewis acids to give cyclopentanes, whereas allylsilanes gave acyclic products (Eq. 33), perhaps as a consequence of poorer hyperconjugative stabilization of the zwitterionic intermediate[290].

Quenching of the enolate from $Fp'CH_2OCH_2Ph$ with alkyl halides, deuterium oxide, or acetone as electrophiles E gave only



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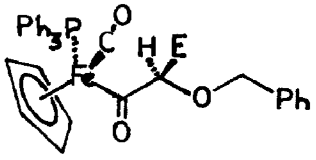
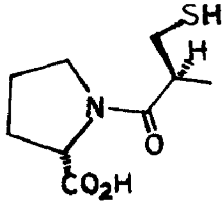
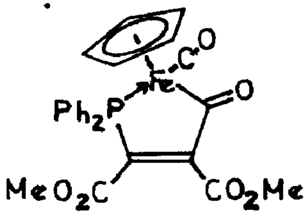
the single diastereomer **58**. Hydrogenolysis of the benzyl group and decomplexation provide an approach to stereoselective synthesis of α-hydroxycarboxylic acids[291]. Alkylation of the enolate from (*R*)-Fp'C(=O)Et with Me_3CSCH_2Br, followed by oxidative decomplexation in the presence of L-proline *tert*-butyl ester then deprotection, gave (-)-Captopril, **59**, in high enantiomeric and diastereomeric purity[292].

$FpPPh_2$ and FpSPh cycloadded dimethyl acetylenedicarboxylate to form cyclic acyl complexes **60**[293,294]. When analogs of FpSPh having CS or CNMe in place of CO were used, the preference for ring incorporation was CNMe > CO > CS[294]. $FpPPh_2$ also added dimethyl maleate and fumarate, reversibly[294].

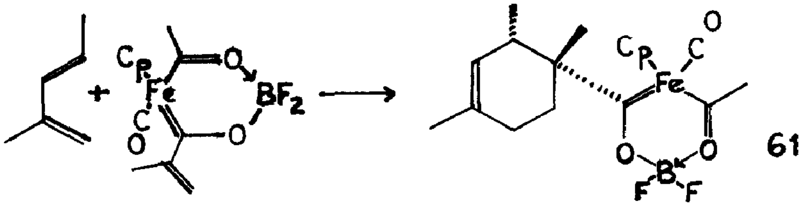






58 **59** **60**

Unsaturated side chains, R^1 and R^2, in $CpFe(CO)(COR^1)(COR^2)BF_2$ functioned as dienophiles. With R^1 = 1-propynyl, cycloaddition to cyclopentadiene gave a norbornadiene. In a competition with R^1 = 1-propynyl and R^2 = 2-propenyl, the latter preferentially added to isoprene[295]. The crystal structure of the adduct from 2-methylpentadiene and the heterocycle with R^1 = Me and R^2 = 2-propenyl revealed the structure **61** (Eq. 34)[296].



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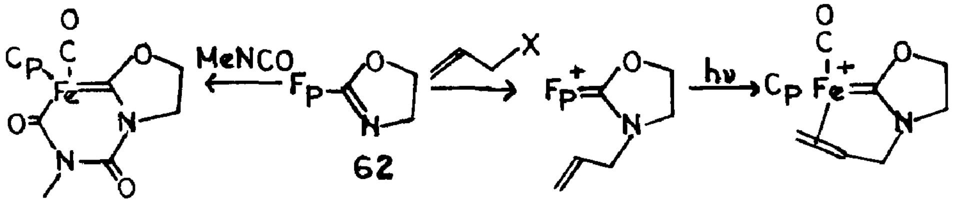
The acyl complex $FpC(=O)C_3H_5$ [C_3H_5 = cyclopropyl] was converted to the α-ether complex FpCH(OMe)R by methylation and reduction. Treating the ether complex with Me_3SiOTf at -78° gave the carbene complex, $Fp{=}CHC_3H_5{}^+$, characterizable by NMR methods, which indicated significant positive charge in the cyclopropane ring. The carbene complex was stable to -40°, and reacted with alkenes to form bicyclopropyl derivatives[297]. Sulfur-stabilized carbene complexes, $Fp{=}CHSPh^+$ and $Fp{=}C(Me)SR^+$ [R = Me, Ph] have been prepared, the former by hydride abstraction from the $FpCH_2SPh$, and the latter by treatment of FpCOMe with Tf_2O and RSH. Crystal structures were reported. Carbon nucleophiles readily formed bonds to the carbene carbons[298].

The oxazoline **62** (Eq. 35) readily underwent N-protonation or alkylation to give aminooxycarbene complexes. Photolysis of the N-allyl derivative gave a cyclic alkene-carbene complex, and methyl isocyanate cycloadded, as shown in Eq. 35[299]. Photolysis of *trans*-1-Fp-2-dimethylaminocyclobutane led to ring expansion to form the cyclic carbene complex, **63** [Y = NMe_2]. Activation parameters for reaction of **63** [Y = OMe] with triphenylphosphine, to form *trans*-1-Fp'-2-methoxycyclobutane by iron-to-carbene alkyl migration, have been determined. Evidence was marshalled to indicate that migration of an alkyl group from saturated carbon to a 16-electron center to give an 18-electron carbene complex is energetically unfavorable in the absence of substantial ring-strain effects[300].



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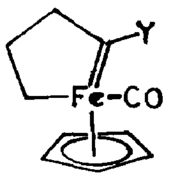
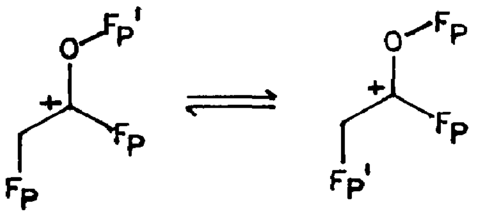


63

Electrophiles (Me, H, $SiMe_3$) reacted at the acyl oxygen of $FpC(=O)CH_2Fp$, **64**, giving $Fp{=}C(OE)CH_2Fp^+$. Reaction of $Fp{=}C(OMe)CH_2Fp^+$ with triphenylphosphine resulted in formation of $FpPPh_3^+$ by displacement of $CH_2{=}C(OMe)Fp$. Reduction with trialkylborohydride produced Fp_2 and $CH_2{=}CHOMe$, presumably via a transient $FpCH_2CH(OMe)Fp$[301]. $Fp(THF)^+$ and $Fp'(THF)^+$ also added to the acyl oxygen of **64**; in the product from the latter case an intramolecular exchange process (Eq. 36) was revealed[302].



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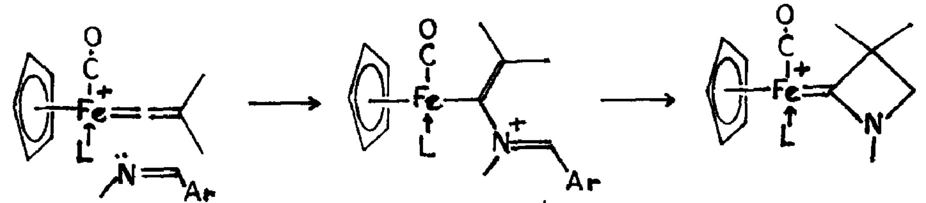
Thermodynamic data for protonation of $CpFeL(CO)-C{\equiv}C-CMe_3$ [L = PMe_3] by acidic metal hydrides, to form $CpFeL(CO){=}C{=}CHCMe_3^+$, have been measured[273]. Related additions of electrophiles to β-carbons of alkynyl-iron complexes have also been described. CpFe(DPPE)-C$\equiv$CR added tropylium ion to form CpFe(DPPE)C=C(R)C_7H_7 adducts, but Fp-C$\equiv$CR underwent oxidation, with formation of $Fp(THF)^+$ [303]. Oxidation of $CpFe^+$(DPPE)=C=CHMe with $Cu(OAc)_2$ or PhIO resulted in loss of hydrogen and dimerization to form the extraordinary bis(vinylidene)iron compound, $CpFe^+$(DPPE)=C=C(Me)-C(Me)=C=Fe^+(DPPE)Cp, whose X-ray structure showed unusually short Fe=C bonds (1.76 Å average)[304]. The vinylidene complexes $Fp'=C=CR_2{}^+$ [R = H, Me] gave stepwise [2 + 2]-cycloaddition reactions with imines (Eq. 37)[305]. Oxidation of the heterocyclic products with iodosylbenzene gave azetidinones[306].



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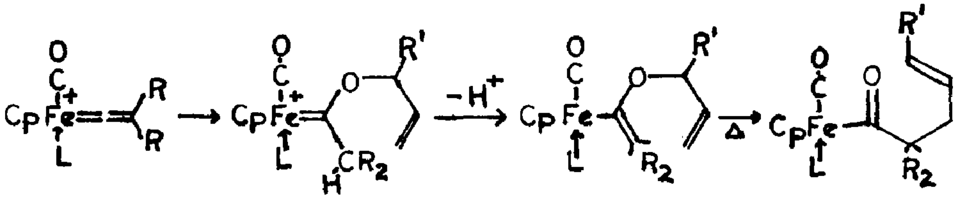
Reaction of $CpFeL(CO)=C=CR_2{}^+$ [L = $P(OMe)_3$] with allylic alcohols gave allyloxycarbene complexes. The allyloxyvinyliron compounds which resulted on deprotonation underwent Claisen rearrangement at about 80° (Eq. 38)[307].



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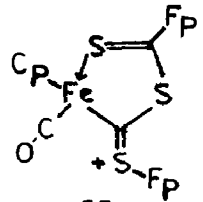
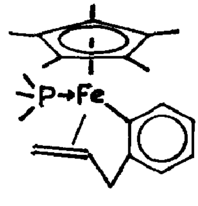
Carbenoid metallacycle **65** resulted when $FpCS^+$ reacted with FpC(=S)SFp. Nucleophiles attacked and removed the thione-bound Fp group. Electrophiles [H^+, R^+, BF_3, HgX^+, and $W(CO)_5$] were readily attached to the free thione group; crystal structures of S-ethyl and S-(pentacarbonyltungsten) derivatives indicated considerable delocalization in the ferradithiolene rings, and carbenoid character of both ring carbons[308].



65

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

The crystal structure of (η^2-1,2-cycloheptadiene)-Fp'^+ showed modest lengthening of the coordinated allenic bond [1.385(6) Å] compared to the uncoordinated one [1.303(7) Å]. The angle at the central carbon of the allene unit was 138°, and the iron was somewhat closer to that carbon than



66

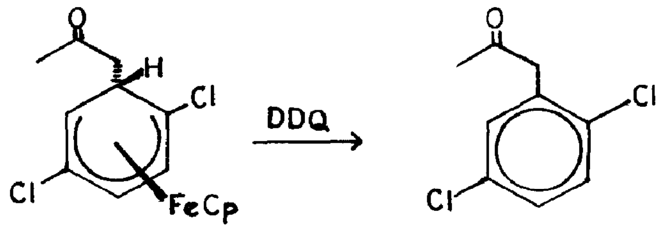
to the external carbon[309]. Also characterized by X-ray crystallography was **66**, produced directly by reaction of $Cp^*Fe(PMe_3)_2Cl$ with *o*-allylphenylmagnesium chloride[257].

Reaction of Grignard or organolithium reagents with $FpCH_2CHO$, followed by acidification of the resultant alkoxides with HBF_4, resulted in synthesis of several (η^2-alkene)-Fp^+ salts in 50-90% yield[259]. The mechanism of attack of hydride ion (as a representative nucleophile) on (η^2-alkene)-Fp^+ cations has been further studied by extended Hückel and INDO theoretical methods. Activation by the Fp^+ group was traced to energy lowering of the π^* orbital in the coordinated ethene[310]. Reactivity of nucleophiles toward $(C_2H_4)Fp^+$ has been used to define a general carbon basicity (pK_c) scale[311]. But reaction of that cation with $NaBH_4$ in acetone at low temperature was found to occur by kinetically-controlled attack at a carbonyl group to form $CpFe(CO)(C_2H_4)CHO$, which decomposed on warming to FpH and ethene, rather than FpEt. On the other hand, the more hindered (η^2-cyclohexene)Fp^+ underwent clean addition of deuterium from $NaBD_4$ to form *trans*-$FpC_6H_{10}D$, consistent with direct *exo* deuteride addition to the coordinated double bond[312].

(η^2-vinyl ether)Fp^+ complexes were readily prepared from α-haloacetals. The unsymmetrical binding of the Fp group led to a low rotational barrier (ca. 80 kJ/mol) around the formal C=C bond. Reactions of the vinyl ether salts with cyclohexanone enolates have been studied; an example is given in Eq. 39[313]. (η^2-vinyl ether)Fp^+ cations reacted with Et_4N^+ CN^- at 0° to form α-cyanoethers, $FpCH_2CR(CN)(OEt)$. Acidification at -78° gave unstable acrylonitrile complexes, (η^2-CH_2=CRCN)Fp^+, which added nucleophiles regiospecifically at the α-carbon, giving $NuCH_2$-$CR(CN)Fp$[314].

Vinyliron compounds Cp^*L_2Fe-CH=CH_2 [L = $Me_nPh_{n-3}P$] reacted with ethene by insertion into the Fe-C bond. After a hydrogen shift, (η^3-crotyl)$FeCp^*L$ resulted[257]. A similar product also formed when $FpCH_2$-*cyclo*-C_3H_5 was heated with triphenylphosphine in hexane[287]. An X-ray diffraction study of CpFe(CO)(η^3-CH_2--CH--CH-CH=CH-CH_3) has been reported. Protonation with HPF_6 gave CpFe(CO)(η^4-2,4-hexadiene)$^+$ PF_6^- (X-ray structure)[271]. A series of analogous salts, $Cp^*Fe(CO)(\eta^4$-diene$)^+$ BF_4^- was prepared by photochemical reaction of $Fp^*(THF)^+$ with dienes. A Bronsted plot involving rates of addition of amines to the cations indicated them to be "soft" electrophiles[315].

(η^5-cyclohexadienyl)FeCp compounds, produced by addition of carbon nucleophiles to $AnFeCp^+$, underwent loss of the elements of HFeCp, giving free arenes, upon treatment with 2,3-dichloro-5,6-dicyanobenzoquinone. An example is shown in Eq. 40[316]. Reaction



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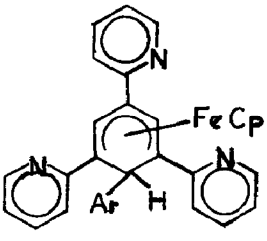
of 2-ethynylpyridine with Fp-Ar under rigorous conditions (refluxing decalin) gave **67** (X-ray)[266].

The rather puzzling product **68** resulted when tricarbonylbis(cyclooctene)iron or (butadiene)tricarbonyliron reacted with the free borole. The electron-deficiency of the iron in **68** might be relieved by means of a 2-electron 3-center interaction with the C-H bond; however, based on spectroscopic similarities to the isoelectronic CpCo(borolene), the hydrogen was taken to be anti to the tricarbonyliron group[317]. A crystal structure would be welcome. With a less highly substituted borolene, the paramagnetic **69** formed[317]. **69**, for which a crystal structure was reported, may be viewed as an ionic salt of high-spin Fe^{2+} with two anions from deprotonation of the (borolene)$Fe(CO)_3$ complex analogous to **68**. A related triple-decker borole complex, $CpFe(\mu,\eta^5$-$C_4H_4BPh)Co(\eta^5$-$C_4H_4BPh)$, has been reported[318].



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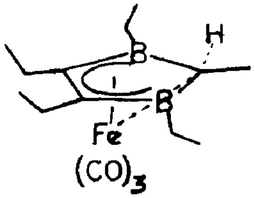

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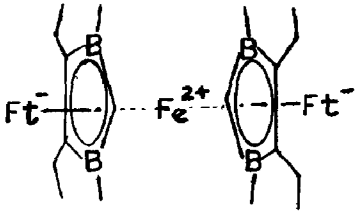


69

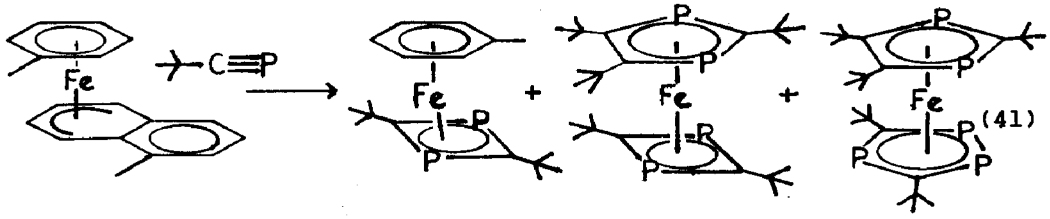
The bis(carborane)iron compounds, $(RR'C_2B_4H_4)_2FeH_2$, **70**, incorporating 2,3-carborane skeletons with R = benzyl and R' = benzyl(tricarbonylchromium), were prepared and oxidized as a means of fusing the carboranes into larger $R_2R'_2C_4B_8H_8$ ones[319]. Extended Hückel calculations on six-vertex ferraboranes have been carried out[320].

Reaction of FpI with pyrrole (and indole) in the presence of di-isopropylamine and sunlight gave the η^1 Fp-NC_4H_4. In refluxing benzene, this was converted to $CpFe(\eta$-$C_4H_4N)$, azaferrocene[321]. Formation of a phosphaferrocene, **29**, was shown in Eq. 9[98]. Another route to phosphaferrocenes involved displacement of arenes from $(\eta^5$-$C_5H_4R)Fe(An)^+$ [R = acyl groups, CO_2H, Me, CH_2NMe_2] with phospholyl anions[322].

Reaction of 1-phenylarsole with $FeCl_2$ and lithium metal produced bis(η^5-arsolyl)iron or diarsaferrocene, $(C_4H_4As)_2Fe$[323]. 1,1'-Diphosphaferrocenes underwent one-electron oxidation with

TCNE in the presence of water; Mössbauer spectra of the neutral and oxidized forms indicated a different frontier orbital in these compounds than in ferrocenes[324]. 3,3',4,4'-Dimethyl-1,1'-diphosphaferrocene underwent Friedel-Crafts acylation at the 2 and 2' positions, and the acyl groups could be protonated with strong acids[325]. When solutions of diphosphaferrocenes in aromatic solvents were treated with aluminum chloride, ring exchange occurred to form $(\eta^5\text{-}C_4R_4P)FeAn^+$ [326].

Reaction of Fp^*_2 with P_4 in xylene at 150° produced $Cp^*Fe(\eta^5\text{-}P_5)$, a pentaphosphaferrocene containing a pentaphospholyl ring[327]. Other phosphorus-rich ferrocenes were prepared by reaction of the 3,5-di*tert*-butyl-1,2,4-triphosphacyclopentadienide ion [from $RC{\equiv}P$ and $P(SiMe_3)_2^-$] with $FeCl_2$. In addition to a 30% yield of the expected hexaphosphaferrocene, $Fe(R_2C_2P_3)_2$, a 10% yield of $(R_3C_3P_2)Fe(R_2C_2P_3)$ was obtained. Both were characterized by crystal structures[328]. The same pentaphosphaferrocene was also obtained directly from $RC{\equiv}P$ (Eq. 41)[329].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8. COMPOUNDS WITH η^6- and η^7-ARENE LIGANDS

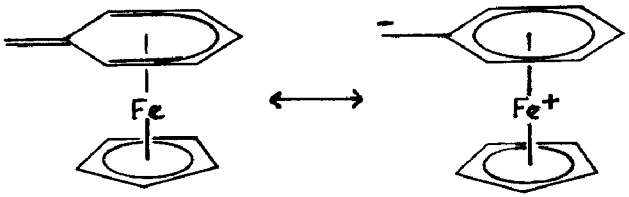
Scheme I summarized the utility of $(\eta^6\text{-benzene})Fe(PMe_3)_2$, **1**, as a precursor to a variety of organoiron compounds, including $(\eta^6\text{-benzene})(\eta^4\text{-diene})$iron compounds[4]. Isomerization of bis(η^5-cyclohexadienyl)iron to (η^6-benzene)(η^4-1,3-cyclohexadiene)iron has been noted[193]. It is amusing to note that this reaction, which formally involves only moving a hydrogen atom from one ligand to the other, constitutes a reduction of the iron from Fe(II) to Fe(0) according to the artificial conventions used to define oxidation states. Hydride abstraction from $(\eta^5\text{-cyclohexadienyl})Fe(CO)(\mu\text{-}CO)_2Fe(CO)Cp$ gave the cationic "mixed dimer" having a (η^6-benzene) ring[202].

A series of 2-substituted biphenyls were converted to $(\eta^6\text{-}C_6H_5\text{-}Ar)FeCp^+$ salts; in all cases, the iron was coordinated to the unsubstituted ring. ^{13}C-NMR and Mössbauer data were obtained and correlated with substituent parameters. The $CpFe^+C_6H_5$- group was found to be comparable to a cyano group as an electron-withdrawing substituent[330]. Variable temperature NMR study of $(\eta^6\text{-hexaethylbenzene})FeCp^+$ revealed multiple stereoisomers resulting from hindered rotation of the ethyl groups[331]. Mössbauer studies of substituted $AnFeCp^+$ have been performed, and the quadrupole splitting correlated with various substituent parameters[332].

Previously mentioned was the displacement of arene rings from $AnFeCp^+$ by phospholide anions to form phosphaferrocenes[321]. Arene displacement from (p-xylene)$FeCp^+$ has also been used to synthesize some complex ferrocene derivatives[333]. The photochemistry of arene displacement reactions, as affected by arene substituents, has been studied in some detail[334].

A more common result of nucleophilic attack on $CpFeAn^+$ is addition of the nucleophile to the arene ring to form a neutral (η^5-cyclohexadienyl)FeCp product. The addition of hydride ion from $NaBH_4$ to fifteen (PhY)$FeCp^+$ cations has been studied by high resolution NMR. With Y = NMe_2, addition occurred exclusively *meta* and *para*. At the other extreme, with Y = NO_2, only *ortho* addition occurred. With other substituents, all three products formed, depending on the electronic character of the substituent[335]. As expected from the above results, cyanide ion attacked ($PhNO_2$)$FeCp^+$ *ortho* to the nitro group. Reaction of cyanide with other arene complexes, including those of polycyclic arenes, generally followed a similar course[336]. Nitronate ions reacted with (η^6-o-$C_6H_4Cl_2$)$FeCp^+$ with displacement of one chloride[337]. 2,5-diphenylphospholide anion likewise displaced chloride from (C_6H_5Cl)$FeCp^+$[322]. β-Diketone and β-ketoester anions generated *in situ* using KF/Celite displaced chloride from chloro- and dichlorobenzene-$FeCp^+$ cations to form arylated products in 73-80% yields[338].

(η^6-Toluene)$FeCp^+$ was deprotonated by $KOCMe_3$ in THF to form 71, which reacted with Me_3SiCl, MeI, and $PhCH_2Cl$ at the exocyclic carbon[200].



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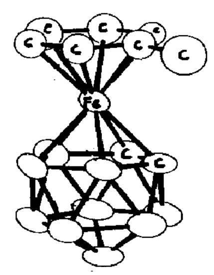
Electrochemical reduction of (μ-η^6,η^6-thianthrene)bis($FeCp^+$) and its monoiron analog have been studied[339]. The neutral, nineteen-electron Fe(I) species Cp^*FeAn have been found to be considerably more stable than the corresponding CpFeAn. ESR studies indicated that CpFe complexes of polycyclic aromatic ligands housed the extra electron in arene π^* orbitals, whereas Cp^*Fe complexes had it localized in an iron-based orbital[340].

Reduction of (μ-η^6,η^6-biphenyl)bis(FeCp* $^+$) electrochemically or with sodium amalgam gave the stable bis(η^5)- product **46**, characterized by a crystal structure[201]. Four reduction stages could be observed starting from (μ-triphenylene)(FeCp*)$^{2+}$. Some stable mixed-valence compounds derived from partial reduction of polycyclic arene-(FeCp$^+$)$_2$ have been isolated[201].

Mössbauer spectra of powder samples of CpFeC$_6$H$_6$ and methylated derivatives over a temperature range of 4-300 K indicated a dynamic Jahn-Teller effect in these nineteen-electron compounds[341]. Solid samples of CpFeAn$^+$ (TCNQ)$_2$$^-$ [An = mesitylene, hexamethylbenzene; TCNQ = tetracyanoquinodimethane] have been studied by a variety of physical techniques, which indicated semiconduction with a temperature-dependent activation energy[342]. The thermal activation was held to involve reverse electron transfer from TCNQ$^-$ to the cation[343].

Controlled-potential reduction of TCNQ in the presence of (η^6-An)$_2$Fe^{2+} [An = C$_6$Me$_6$] allowed formation of a black, conducting An$_2$Fe:4 TCNQ phase, as well as a purple, poorly conducting An$_2$Fe:2 TCNQ phase, depending on reduction potential[344]. Linear chain organometallic phases, (η^6-mesitylene)$_2$Fe^{2+} C$_6$(CN)$_6$$^{2-}$ were prepared by direct combination of the two ions or by electroreduction of hexacyanobenzene in the presence of the An$_2$Fe^{2+}. The crystal structure showed mixed stacks of alternating cations and anions[345].

Reaction of [*nido*-7,8-C$_2$B$_9$H$_{12}$]$^-$ with FeCl$_3$ and Et$_3$N in toluene or *p*-xylene led to formation of mixed *closo*-3- (η^6-arene)-3,1,2-FeC$_2$B$_9$H$_{11}$, **72**, incorporating the solvent as a ligand to iron[346]. Smaller carborane-arene mixed complexes were obtained by arene displacement of cyclooctatriene from (η^6-C$_8$H$_{10}$)Fe(Et$_2$C$_2$B$_4$H$_4$) or by coreaction of Et$_2$C$_2$B$_4$H$_5$$^-$ and arene dianion with FeCl$_2$. Arenes included naphthalene, fluorene, [2.2]-paracyclophane, and 9,10-dihydroanthracene. Reaction with Me$_2$NCH$_2$CH$_2$NMe$_2$ removed the apical BH group, giving *nido*-(η^6-arene)Fe(Et$_2$C$_2$B$_3$H$_5$) (Eq. 42)[347]. Analogs of these complexes having C-benzyl groups rather than C-ethyl groups have also been made by similar methods, and the pendant phenyl rings were successfully coordinated to tricarbonylchromium groups[348].



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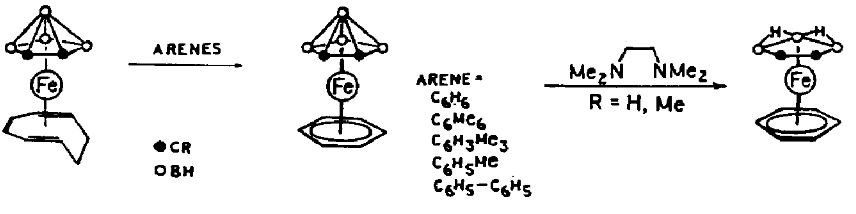

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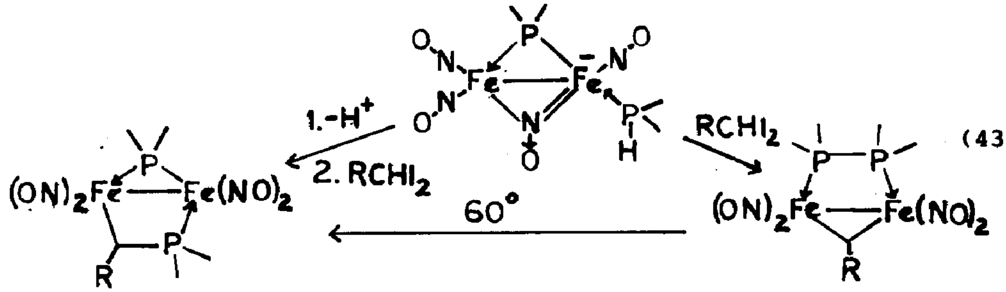
(η^6-cycloheptatriene)FeCp$^+$ yielded up a hydride ion upon reaction with Ph$_3$C$^+$ in solution, to form (η^7-C$_7$H$_7$)FeCp^{2+}, but the dication was not isolable, in contrast to isoelectronic An$_2$Fe^{2+} and to its ruthenium analog[349].

9. BIMETALLIC COMPOUNDS

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

NMR studies of "Roussin esters," (μ-SR)$_2$Fe$_2$(NO)$_4$, examining ^{15}N, ^{13}C, and ^{1}H nuclei, have shown the presence of two isomers in solution, with R groups *cis* (C_{2v}) and *trans* (C_{2h})[350]. For all R groups examined except *tert*-butyl, the two isomers were present in equal amounts; the *tert*-butyl compound favored the C_{2v} form [351]. Reaction of "Roussin esters" with MoS$_4^{2-}$ gave mononuclear species, Fe(NO)$_2$(SR)$_2^-$, Fe(NO)$_2$(S$_2$MoS$_2$)$^-$, and Fe(NO)(S$_2$MoS$_2$)$_2^{2-}$ [352]. Chemical reactions of some phosphorus analogs with diiodides RCHI$_2$ [R = H,Me] have been explored; some of the results are summarized in Eq. 43[353].



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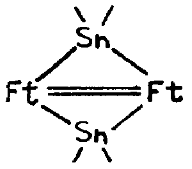
Protonation of (μ-CO)(μ-R$_2$PZPR$_2$)$_2$Fe$_2$(CO)$_4$ [Z = CH$_2$, R = Me, Ph; Z = NEt, R = various alkoxy groups] gave in all cases cations with hydride bridges, (μ-CO)(μ-H)(μ-R$_2$PZPR$_2$)$_2$Fe$_2$(CO)$_4^+$ [354]. Halogenation of the same compounds gave cations with axial Fe-X bonds, which underwent decarbonylation to give halogeno-bridged species analogous to the hydrides[355].

Preparation and characterization of B$_2$H$_6$Fe$_2$(CO)$_6$ and its conjugate base have been described, along with a study of fluxional processes which interconvert terminal and bridging hydrogens in each[356]. Reaction of R$_2$Sn [R = CH(SiMe$_3$)$_2$] with Fe$_3$(CO)$_{12}$ gave (μ-SnR$_2$)Fe$_2$(CO)$_8$, whereas use of Fe$_3$(CO)$_{11}$(NCMe) instead gave the unsaturated cluster (μ-SnR$_2$)$_2$Fe$_2$(CO)$_6$, 73[357]. Reactions of Group 14 compounds [GeI$_2$, Sn(OAc)$_2$, Pb(OAc)$_2$] with Fe$_2$(CO)$_8^{2-}$ gave cluster compounds. With Sn and Pb, dianions QFe$_4$(CO)$_{16}^{2-}$ were obtained, which were reversibly oxidizable to spirocyclic neutral com-



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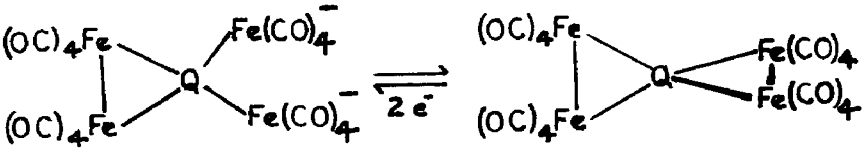
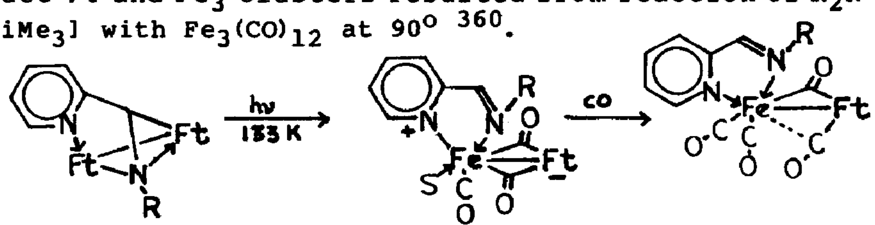
pounds (Eq. 44). With Ge, the spirocycle also formed upon oxidation, but the reduced form was a Fe_3Ge cluster[358].



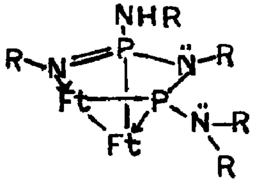
(44)

Photochemical substitution reactions of (bipy)$Fe(CO)_2(\mu-CO)_2Fe(CO)_3$ with phosphines resulted in displacement of a CO from the iron bonded to the (bipy) group. Photolysis of (pyridine-2-carbaldimine)$Fe_2(CO)_6$ complexes at low temperatures resulted in changes in coordination of the organic ligand (Eq. 45)[359]. Product **74** and Fe_3 clusters resulted from reaction of $R_2N-P=NR$ [R = $SiMe_3$] with $Fe_3(CO)_{12}$ at 90° [360].



(45)

Extended Hückel calculations have been performed on M_2E_2 clusters having 5 skeletal electron pairs in order to interpret their preferences for tetrahedral [e.g. $(\mu-C_2R_2)Ft_2$] or butterfly [e.g. $(\mu-P_2R_2)Ft_2$] geometries[361]. **75** [Y = $P(NEt_2)Cl$, Z = Cl] resulted from reaction of $Et_2NPCl_2 \rightarrow Fe(CO)_4$ with nonacarbonyldiiron, along with tri-iron clusters[88]. Reactions of **75** [Y = Z = PPhLi] with various difunctional electrophiles have been investigated. Organic halides alkylated the phosphorus atoms, and dihalides produced organic bridges between them. Deprotonation of the o-xylylene-bridged compound at -20° resulted in displacement of phosphorus from iron by the resulting carbanion (Eq. 46)[362]. **75** [Y = Z = PHPh] gave Michael additions to α,β-unsaturated esters and ketones in the presence of piperidine. With some simple ketones, bridged products resulted from addition of one P-H group to the C=C double bond and the other to the carbonyl group[363]. Reactions of the dilithium salt **75** [Y = Z = PPhLi] with S_2Cl_2 at -10° gave di- and trithio derivatives having one-



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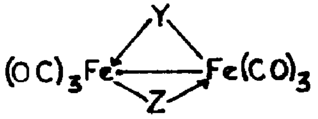

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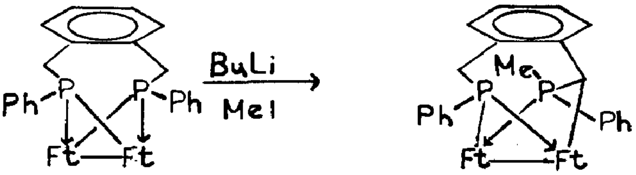


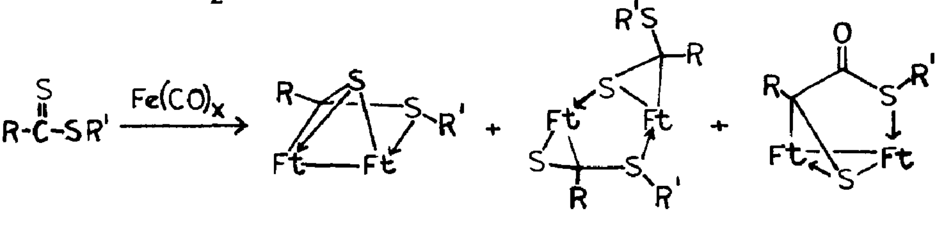
(46)

and two-sulfur bridges, with or without insertion of an additional sulfur atom into a P-Fe bond[364].

Other bridged derivatives of **75** resulted directly from reaction of R_2NPCl_2 [R = Me_2CH] with $Na_2Fe(CO)_4$. In ether, this produced **75** [Y-Z = $-P(NR_2)-C(=O)-P(NR_2)-$], and in THF **75** [Y-Z = $-P(NR_2)-P(NR_2)-P(NR_2)-$][87,365]. These and several related minor products were all characterized by X-ray diffraction[87]. With Et_2NPCl_2 in ether, an initial product $(Et_2NP)_3Fe_3(CO)_{12}$ underwent decarbonylation at room temperature to form **76**[87].

Reaction of $SbCl_3$ with $Fe_2(CO)_8{}^{2-}$ produced **75** [Y = Z = $SbFe_2(CO)_8$, the crystal structure of which was independently determined by two different groups[366,367].

Reaction of S_8 with $HFe_3(CO)_{11}{}^-$ at -70° gave $S_2Fe_2(CO)_6$, **77**, and $S_2Fe_3(CO)_9$. Reaction with thiols RSH gave **75** [Y = Z = RS][368]. Reactions of dithiocarbonates with $Fe_2(CO)_9$ also produced the latter products, $(\mu\text{-}SR)_2Fe_2(CO)_6$, in a complex reaction which resulted in redistribution of thiol groups when unsymmetrical dithiocarbonates were used. **75** [Y = SR; Z = RSCO] were identified as intermediates in some cases[369]. Reactions of dithioesters with iron carbonyls under ultraviolet irradiation led, depending on R, to three classes of products (Eq. 47)[370]. The anion **75** [Y = SPh, Z = SLi] attacked the carbyne complex $CpRe(CO)_2{\equiv}CPh^+$ at low temperature to form **75** [Y = SPh, Z = $SC(Ph)=Re(CO)_2Cp$][371].

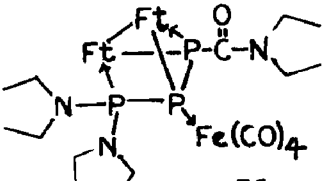


(47)

Bridge formation resulted when ethene inserted into the S-S bond of **77** under photochemical conditions, forming $(\mu\text{-}SCH_2CH_2S)\text{-}Fe_2(CO)_6$. One sulfur atom in the product could be oxidized by peracid to the S-oxide. The (μ-dithiocarbonato) complex resulted from photoinsertion of CO into the S-S bond of **77**[372]. Reaction of **77** with $Pd(PPh_3)_4$ resulted in insertion of a $Pd(PPh_3)_2$ group into the S-S bond[373].

Reaction of propanedithiolato-bridged compound, $(\mu\text{-}SCH_2CH_2\text{-}$

$CH_2S)Fe_2(CO)_6$, with alkyl-lithium reagents, followed by Et_3O^+, gave the carbenoid derivative 78[374]. Reaction of bridging dithiolato complexes with $LiN(CHMe_2)_2$, in contrast, led to deprotonation of the bridges. In the case of the ethano bridge, elimination resulted in formation of 75 [Y = $S-CH=CH_2$, Z = SLi]. In other cases, rearrangements similar to that in Eq. 46 resulted. One sequence is shown as Eq. 48[375]. Deinsertion reactions of alkenes from ethanedithiolato-bridged complexes have been observed when the complexes were treated with oxidizing agents. For example, (μ-$SCH_2CH(SiMe_3)S)Fe_2(CO)_6$, gave trimethylvinylsilane (and 77?) upon treatment with $CuCl_2$ or nitric acid[376].



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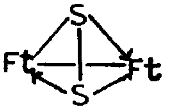

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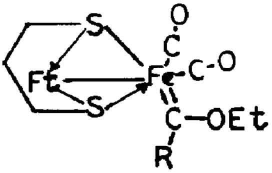

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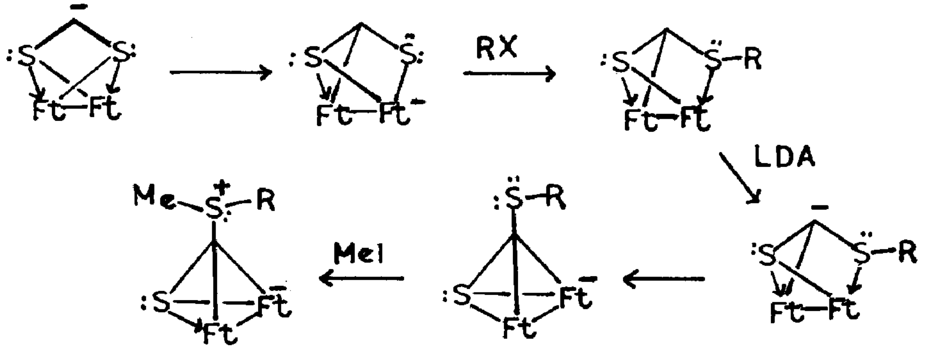


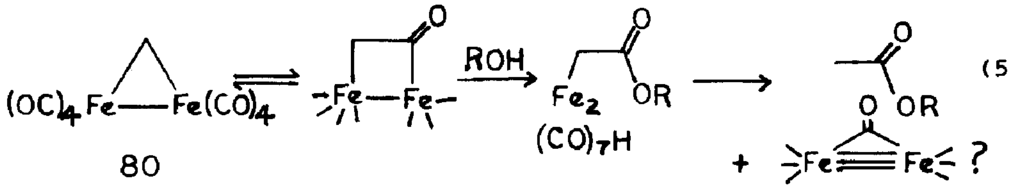
(48)

Some quite elaborate products, such as 79, resulted when triethyl dithiocarbamate was allowed to react with $Fe(CO)_5$ under irradiation[377].

The mechanism of Reppe hydroformylation of ethene in basic $Fe(CO)_5$ solutions has been investigated. The key step in the catalytic cycle was identified as Eq. 49[378]:

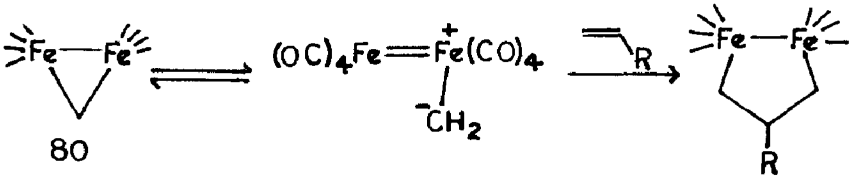
$$RCOFe(CO)_3^- + HFe(CO)_4^- \rightarrow Fe_2(CO)_7^{2-} + RCHO. \qquad (49)$$

Reaction of (μ-$CH_2)Fe_2(CO)_8$, 80, with alcohols and CO has been reported to give 6% malonate esters $CH_2(CO_2R)_2$ along with acetates CH_3CO_2R[379]. Based on work with triosmium clusters, a new mechanism for the formation of the latter products has been proposed (Eq. 50)[380]. Insertion of ethene into a Fe-C bond of 80 has been investigated by means of MO calculations, which led to



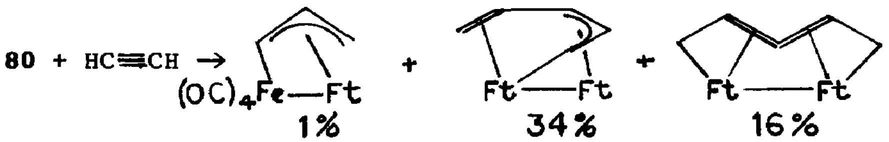
(50)

the scheme shown as Eq. 51^{381}. The cycloaddition step shown appears to the reviewer to be an exact organometallic analog of a



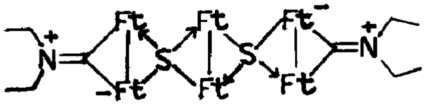
(51)

1,3-dipolar addition reaction. Reaction of **80** with ethyne in toluene gave products of single and double insertion (Eq. 52)^{382}.



(52)

Treatment with $Fe_2(CO)_9$ induced decomposition of 3-azido-1,2,3-triphenylcyclopropene, to form PhCN, PhC≡CPh, PhCOC(Ph)=CH-Ph, and 2,3-diphenyl-1-indenone. A different result, formation of triphenylpyrazole, was obtained upon reaction of the isomer 4,5,6-triphenyl-1,2,3-triazine with $Fe_2(CO)_9$^{383}.



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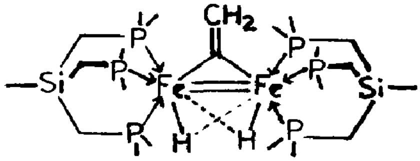
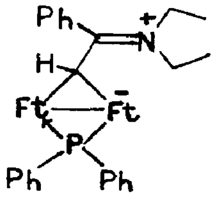


81

Reaction of **2** with ethene at 7 atm. gave the (μ-vinylidene) complex **81**^{5}. Protonation of the zwitterionic (μ-alkylidene) species **82** [made by addition of diethylamine to the (μ-phenylethynyl) precursor] occurred as expected on iron, giving (μ-H)[μ-CH-C(=NEt_2^+)Ph][μ-PPh_2)$Fe_2(CO)_6$^{384}. Reaction of benzoyl chloride with $Na_2Fe(CO)_4$ gave **83**, with a somewhat unusual three-coordinate oxygen atom (X-ray structure)^{385}.

Replacement of two CO ligands in (μ-SMe)[μ-C(OR)S]$Fe_2(CO)_6$ with first trimethyl phosphite and then deuterated trimethyl phosphite gave a mixture of isotopomers, with the deuterated phosphite on each of the iron atoms. This was taken to indicate rotation of the [μ-C(OR)S] bridge relative to the Fe-Fe bond



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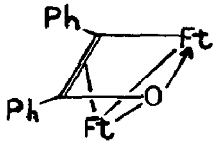

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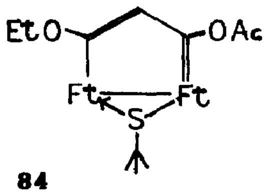
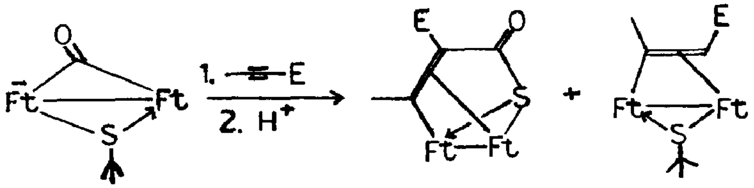


84

during the substitution process[386]. Reactions of Li[(μ-RS)(μ-CO)$Fe_2(CO)_6$ with electron-deficient alkynes have been studied. An exemplary result is presented in Eq. 53[387]. Reaction of the same species with ethoxyacetylene followed by acetyl chloride gave **84**. Under other conditions, products with bridging acyl groups, EtOC(=CH_2)-C(=O)-, formed[388].



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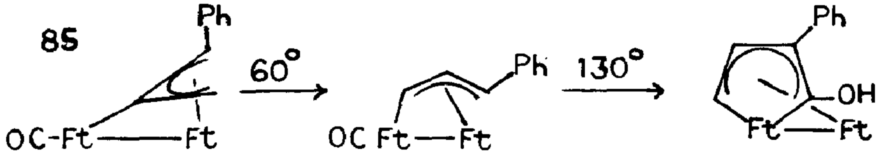
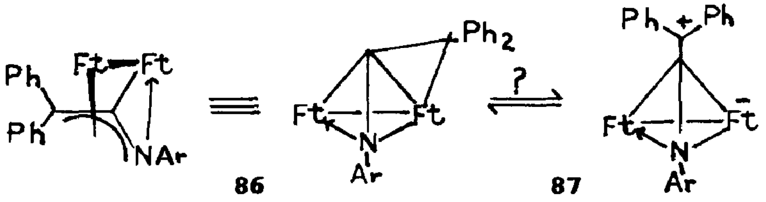
The binuclear "ferratrimethylenemethyl" complex **85**, derived from phenylpropadiene, underwent rearrangements upon heating (Eq. 54), consecutively forming a "ferrabutadiene" and a ferrole com-



(54)

plex[389]. Photolysis of $Fe(CO)_5$ in the presence of triarylketenimines, $Ph_2C=C=NAr$, gave principally organic imidazolidinone

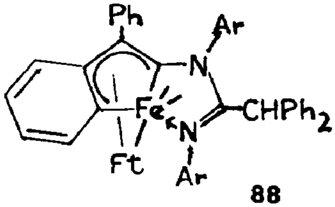


86 **87**

products, accompanied by a 25% yield of **86**[390]. Fluxional interconversion of the two non-equivalent irons in **86** may be interpretable in terms of intermediate **87**. Reaction of **86** with phosphines gave products with the phosphine on the η^3-bound iron. In the case of trimethylphosphine, a benzoferrole product also formed[391].

A more elaborate benzoferrole, **88**, resulted directly from reaction of triarylketenimines with $Fe_2(CO)_9$[390]. Low yields of ferrole complexes were also formed when $Me_3SiC{\equiv}CNEt_2$ reacted thermally with $Fe(CO)_5$; with $Fe_2(CO)_9$, $(Me_3SiCCNEt_2)Fe_2(CO)_6$, with a structure probably analogous to **86**, formed[165]. The electronic structure of the simplest benzoferrole complex $(OC)_3Fe(\mu\text{-}\eta^2,\eta^4\text{-}C_4H_4)Fe(CO)_3$ has been probed by UV photoelectron spectroscopy and theoretical calculations[392].

89 [L = CO] reacted with triphenylphosphine at 20° to form **89** [L = PPh_3]. At higher temperatures, decomposition to $(Ph_3P)_2Fe(CO)_3$ and PhCH=NPh resulted[393]. The crystal structure of **90**, the product of reaction of bis(trimethylsilyl)ethyne with $(\mu\text{-}COEt)(\mu\text{-}CH{=}CH_2)Fe_2(CO)_6$, has been determined[394].



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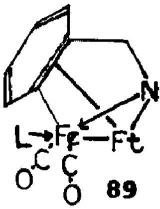

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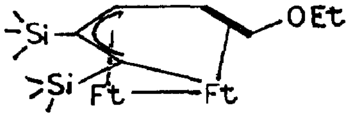
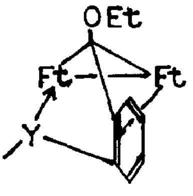


90

Additional examples of unusual products resulting from attempts to generate metal-carbene complexes were production of **91** [Y = O or NMe] from o-$MeYC_6H_4Li$ and $Fe(CO)_5$, followed by Et_3O^+ [374]. Reactions of tungsten-carbene complexes with $Fe(CO)_5$ under photochemical conditions led to hetero- and homo-dimetallic μ-alkylidene complexes. An example is shown in Eq. 55. $(OC)_4Fe{=}C(OEt)CH_2CH_2CH{=}CH_2$ reacted with extensive hydrogen rearrangement to produce a product structurally analogous to those shown first in Equations 52 and 54[395].



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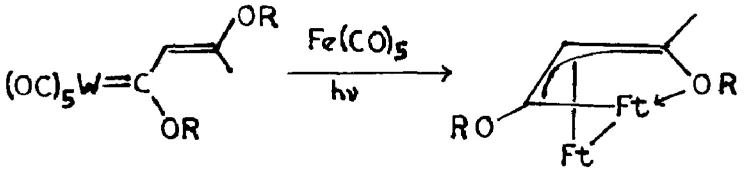


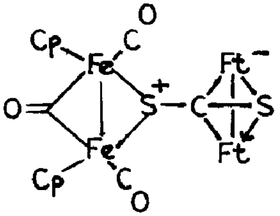
(55)

Reaction of anthracene with $Fe_2(CO)_9$ at -20° with ultrasonic stimulation afforded $(\mu,\eta^3,\eta^3\text{-anthracene})Fe_2(CO)_6$, a tetramethyleneethene derivative, not obtainable by thermal means, nor from the known $(1\text{-}4\eta^4\text{-anthracene})Fe(CO)_3$[396].

b. Derivatives of $Cp_2Fe_2(CO)_4$

The UV photoelectron spectrum of $[CpFe(\mu\text{-}NO)]_2$ has been obtained and interpreted through use of SCF calculations, which indicated that the electron deficiency created by ionization from an iron 3d level was compensated for by transfer of charge from the Cp rings[397]. Electrochemical studies of $[CpFe(\mu\text{-}NO)]_2$ and ring-methylated derivatives have been carried out. Ring methylation made reversible one-electron reduction progressively more difficult. Crystallographic studies showed Fe-Fe distances of 2.326(4) Å in the neutral methylcyclopentadienyl compound, and 2.378(1) Å in the radical-anion, consistent with the odd electron occupying a Fe-Fe antibonding orbital[398].

Reaction of FpC(=S)SFp with $Fe_2(CO)_9$ produced the "double dimer" **92** in 9% yield[399]. Cleavage of Fp_2, and its derivatives having 1-4 CNMe groups replacing CO groups, by halogens and mercuric compounds has been studied. With HgY_2 [Y = X, F, NO_3, BF_4], $CpFe(CNMe)_2Y$ and FpHgY cleanly resulted from $[CpFe(CO)(CNMe)]_2$. Intermediates with the electrophile coordinated to a bridging CO or CNMe group were implicated[400]. Reaction of the same compounds with AgY gave isolable intermediates **93** in the case of the bis(isonitrile) compounds. In general, two-electron oxidative cleavage resulted from treatment of dimers with AgX; in acetonitrile, however, a one-electron process resulted in formation of $CpFe(CO)(L)(NCMe)^+$ and $CpFe(CO)(L)^\bullet$ [L = CO or CNMe], the latter trappable with $CHBr_3$[401]. Reactions of these dimers with Sn(IV) compounds also resulted in isolable adducts analogous to **93** in many cases. In nucleophilic solvents, breakdown to mono-iron products occurred[402].



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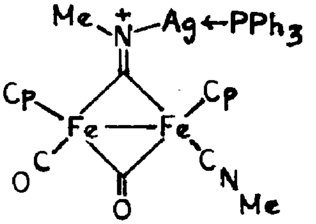
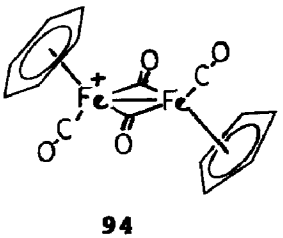


93

Fp_2 and analogs containing one or two isonitriles catalyzed ligand exchange reactions of $Fe(CO)_5$, and the reactivity could be tuned by modifying the number and type of isonitrile(s)[108]. Fp_2 and derivatives have also been used catalytically to incorporate alcohols into triruthenium clusters[403], and as chain transfer agents for molecular weight control in free radical polymerizations[404].

Syntheses of several classes of ring-substituted Fp_2 derivatives, generally by reaction of substituted cyclopentadienes with $Fe(CO)_5$, have been reported. Examples include derivatives with silyl substituents, $-SiMe_2OEt$ and $-CH_2CH_2CH_2Si(OMe)_3$[213], with pinene-annulated cyclopentadienyl rings[405], and the benzannulated (indenyl) compound, $[\eta^5\text{-}(C_9H_7)Fe(\mu\text{-}CO)(CO)]_2$[133]. Photolysis of the latter at 77K in an alkane matrix resulted in CO loss, forming $(\eta^5\text{-}C_9H_7)Fe(\mu\text{-}CO)_3Fe(\eta^5\text{-}C_9H_7)$[133].

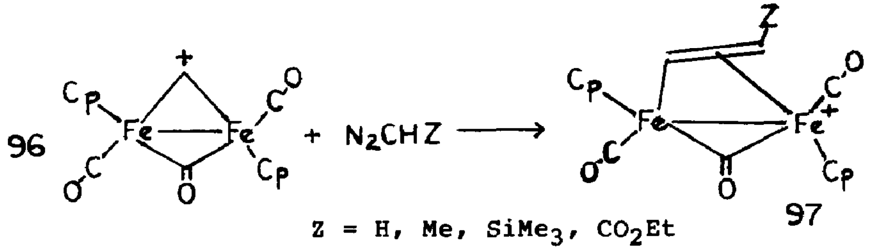
The "open Fp" or "Fop" compound, $(\eta^5$-2,4-dimethylpentadienyl)$Fe(CO)_2I$, has been converted to Fop_2 by reduction with sodium amalgam and to FopFp by reaction with Fp^- [187]. The crystal structure of Fop_2 showed a cis structure similar to that of cis-Fp_2, but with the Fe-Fe bond lengthened by 0.08 A[188]. In a similar manner, $(\eta^5$-cyclohexadienyl)$Fe(CO)_2I$ gave the mixed dimer, $(C_6H_7)Fe(CO)(\mu\text{-}CO)_2Fe(CO)Cp$, along with homodimer $[(C_6H_7)Fe(CO)_2]_2$, on treatment with NaFp. The mixed dimer transferred a hydride ion to Ph_3C^+ to form **94**[202].



94

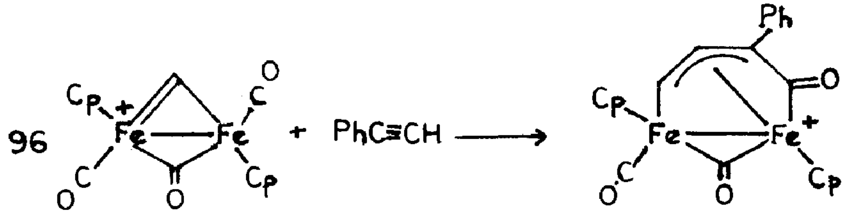
Photolysis of $FpSiMe_3$ in the presence of $RSiH_3$ afforded silylene bridged products, $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}SiRH)Fe(CO)Cp$. The crystal structure of the product with R = tert-butyl was determined[216].

Fenske-Hall MO calculations have been applied to interpreting the reactivity of methylene- and methylidene-bridged bimetallic compounds, including $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}CH_2)Fe(CO)Cp$ (**95**), $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}CH^+)Fe(CO)Cp$ (**96**), and $CpFe(\mu\text{-}NO)_2(\mu\text{-}CH^+)FeCp$[406]. A complex solid state deuterium NMR method applied to **95**-d_2 has indicated the charge on the methylene carbon to be 0 ± 0.17 electron[407]. Reactions of **96** with diazo compounds produced (μ-alkenyl) products **97**, as exemplified in Eq. 56. **97** [Z = CO_2Et] added nucleophiles at the ester-bearing carbon, and underwent reductive dimerization at the same position when treated with aqueous $NaHCO_3$ in acetone[408]. **96** reacted with alkynes to form $(\mu\text{-}\eta^1, \eta^4$-dienonyl) complexes (Eq. 57)[409]. The (μ-propylidyne) complex, $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}CEt)Fe(CO)Cp^+$ reacted with $Me_3Si\text{-}N_3$ under a CO atmosphere to form EtCN, Fp_2, and $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}$



(56)

Z = H, Me, $SiMe_3$, CO_2Et



(57)

C=CHMe)Fe(CO)Cp. Similar reactions were observed for two other alkylidyne complexes[410].

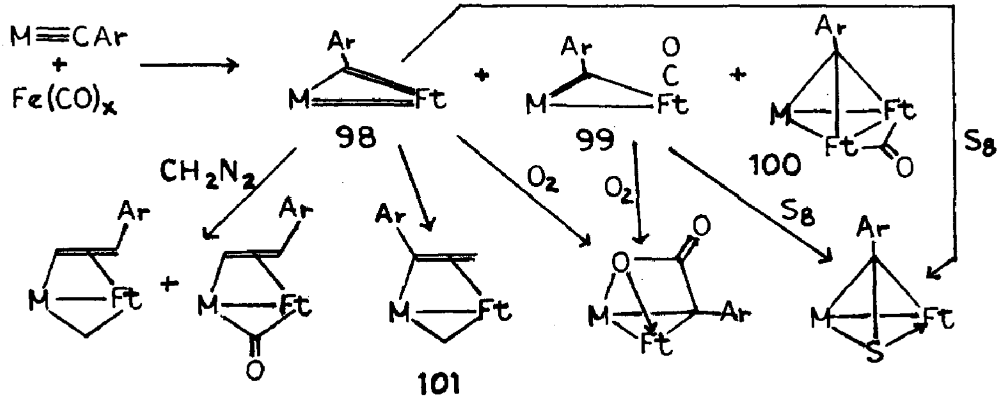
c. Heterobimetallic Compounds

Fp-MCp_3 [M = U, Th] were prepared by reaction of Cp_3MCl with NaFp[205]. The M-Fe bonds were readily protonolyzed by CF_3CH_2OH or acetone, forming FpH[205]. FpH reacted with $Ti(NMe_2)_4$ to afford Fp-$Ti(NMe_2)_3$, which had a Fe-Ti bond length of 2.567(2) Å, and ligand dispositions which suggested some π-character in the Fe-Ti bond[411].

$(OC)_3M(\mu\text{-DPPM})_2Fe(CO)_3$ [M = Cr, Mo, W] have been prepared, and the molybdenum example has been characterized by X-ray crystallography, which indicated a weak Fe→Mo bond of 3.047(5) Å length. Protonation with HBF_4 gave a product with a terminal M-H bond[412]. $(OC)_4Fe(\mu\text{-DPPM})Mo(CO)_4$, like its doubly-bridged analog, also showed a weak [3.024(5) Å] Fe→Mo bond[413].

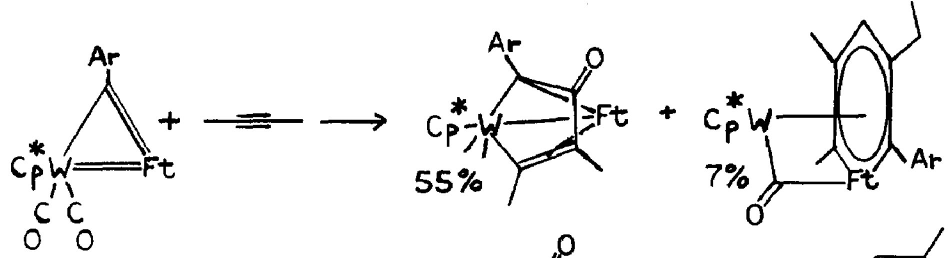
Several full papers from the Bristol group have described the chemistry of compounds derived from coordinating the formal triple bond of $CpM(CO)_2{\equiv}C\text{-}Ar$ [M = Group 6 metal, Ar = p-tolyl] with iron carbonyl groups. Scheme IV summarizes a number of the types of compounds and transformations reported. Formation of **98-100**, and the reactions of **98** were most extensively described for the case M = $Cp^*W(CO)_2$[414]. For the case M = $CpMo(CO)_2$, reaction with $Fe_2(CO)_9$ gave only the more saturated product **99** and the trimetallic cluster **100**.[415] Reaction of **99** with oxygen occurred as shown in Scheme IV; reaction with sulfur gave not only the product shown there, but also an analog of the oxygenation product, with bridging S instead of O[416]. Products **98** and **99** having M = [hydrotris(pyrazolyl)borate]$Mo(CO)_2$ have also been prepared from the alkylidyne precursors[417]. Reaction of **99** [M =

SCHEME IV



$CpMo(CO)_2]$ with trimethylphosphine yielded monosubstitution of phosphine for iron-bound CO. The phosphine-substituted analogs of **98** and **99** interconverted readily with gain or loss of a CO[418].

98 $[M = Cp^*W(CO)_2]$ reacted with diphenylacetylene at 85° to afford $(OC)_3Fe[\mu,\eta^3,\eta^2\text{-}C(Ar)C(Ph)C(Ph)]M$. Reaction with 2-butyne proceeded at 0° as shown in Eq. 58[419], but **99** $[M = CpMo(CO)_2]$ behaved differently (Eq. 59)[420].



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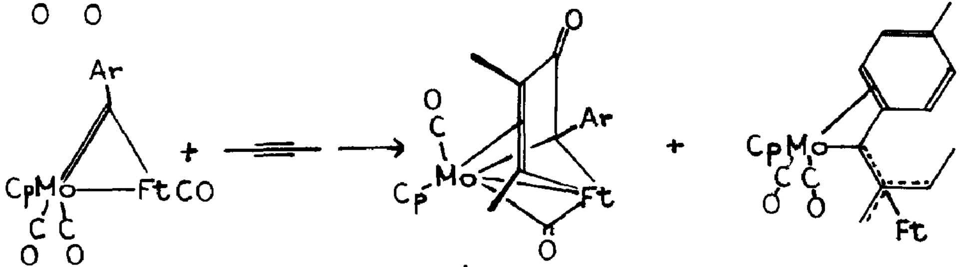
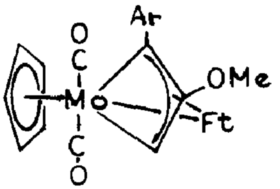


(59)

Reactions of **98** $[M = Cp^*W(CO)_2]$ with diazomethane were shown in Scheme IV[414]. Diazomethane reacted with **99** $[M = CpMo(CO)_2]$ at room temperature to produce **101** (Scheme IV), but at -40°, **102** resulted[421]. The diverse results obtained from the CpMo systems as compared to the superficially similar Cp*W analogs suggest to this reviewer that boring predictability is not yet at hand.

Lending further support to this view are studies of the reaction of anionic $(\eta^5\text{-}Me_2C_2B_9H_9)W(CO)_2{\equiv}CAr^-$ with iron carbonyls. Depending on the aryl group and amount of CO present, products formed included an unsaturated species analogous to **98**, a product with iron σ-bonded to a boron of the carborane ligand, and a trimetallic species with two such Fe-B bonds[422, 423].

The terminal tungsten-carbene complex $(OC)_5W{=}C(OEt)CH{=}CHMe$ was converted to the bridging alkenylidene complex **103** upon photoreaction with $Fe(CO)_5$[395]. Reaction of Se_4^{2+} with $Fe_2(CO)_9$ and $W(CO)_6$ yielded the tetrahedrane-like cluster, $(OC)_3Fe(\mu_2,\eta^2\text{-}Se_2)Mo(CO)_5^{2+}$, characterized by X-ray crystallography[424].



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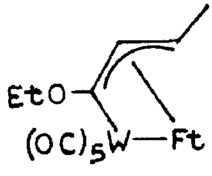

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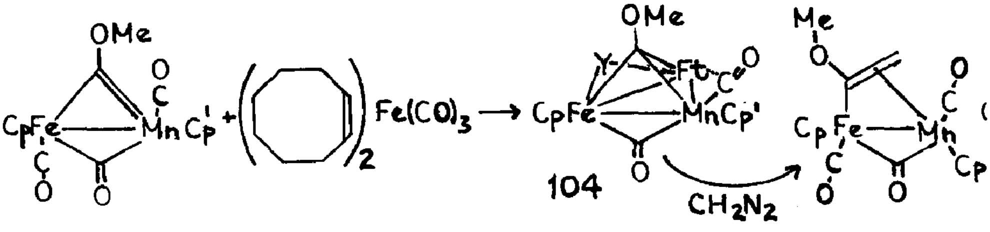
Turning to comparatively straightforward Group 7-iron compounds, $Fe(CO)_4(DPPM)$ was converted to $(OC)_4Fe(\mu\text{-}DPPM)Mn(CO)_3Br$ by reaction with $BrMn(CO)_5$. The product reversibly added CO with rupture of the Fe-Mn bond[413].

Irradiation of $Fp^*\text{-}Mn(CO)_5$ at low temperature led to CO loss, forming (presumably) $Cp^*Fe(CO)(\mu\text{-}CO)Mn(CO)_4$[<u>Fe=Mn</u>]. Reaction with phosphines resulted exclusively in addition to Mn. The resulting $Fp^*Mn(CO)_4PPh_3$ was labile with respect to thermal Fe-Mn bond cleavage[425]. Thermal reaction of RNC [R = *tert*-butyl, 2,4-dimethylphenyl] with $FpMn(CO)_5$ resulted in formation of $CpFe(CO)(CNR)_2^+\ Mn(CO)_5^-$, with substitution on iron rather than manganese, in contrast to the foregoing photochemical results. However, reaction of $FpMn(CO)_5$ with Me_3NO in acetonitrile gave the manganese-substituted product, $FpMn(CO)_4(NCMe)$[426], quite possibly via the analogous unsaturated intermediate, formed upon CO loss. Substitution reactions of the rhenium compound $FpRe(CO)_5$ occurred exclusively at rhenium, whether conducted thermally (90°) or with Me_3NO[427].

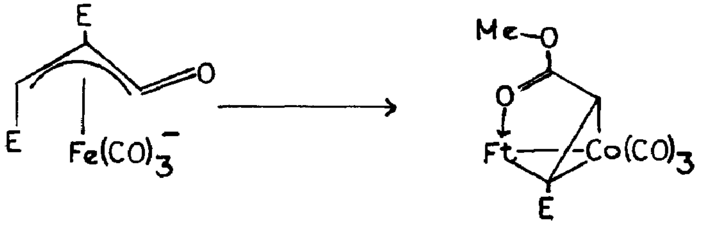
Reaction of $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}COMe)Mn(CO)Cp'$ [$Cp' = C_5H_4Me$] with "Grevels' reagent" (Eq. 60) gave a trinuclear Fe_2Mn cluster, **104** [Y = CO], which upon reaction with diazomethane gave (in part) the (μ-methoxyvinyl) product shown[428]. The overall reaction amounted to addition of a methylene group to the initial C=Mn bond. When $CpMn(CO)_2(\eta^2\text{-}HC{\equiv}CCH_2OH)$ was allowed to react with $Fe_2(CO)_9$, the product was the trimethylenemethyl analog **105** (X-ray structure)[429].



(60)

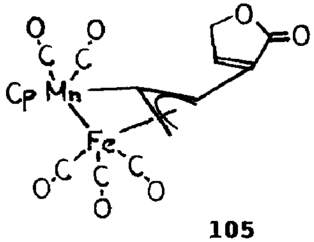
Preparation of the Fp_2 analog, $CpFe(CO)(\mu\text{-}CO)_2Co(CO)(\eta\text{-}C_4H_4BPh)$ has been reported[318]. Equation 61 shows the reaction of a diester-substituted allyliron tricarbonyl anion with $Co_2(CO)_8$ to form a bridged Fe-Co product. The monoester $[\eta^3\text{-}CH_2C(CO_2Me)C{=}O]Fe(CO)_3^-$ reacted to form the simpler (μ-ethenyl) product, $(OC)_4Fe[\mu\text{-}C(CO_2Me){=}CH_2]Co(CO)_3$[430]. Reaction of **70** with $CpCo(CO)_2$ resulted in attachment of cobalt, to form **106**, with a Co→Fe donor bond[431].

Synthesis and structure of $(OC)_4Fe(\mu\text{-}DPPM)Rh(CO)Cl$, **107**, have been reported. The Fe→Rh bond length was 2.699(4) Å[432]. Reaction of the conjugate base of $(R_2PH)_2Fe(CO)_3$ [R = *tert*-butyl] with $[Rh(\eta^4\text{-}1,5\text{-}cyclooctadiene)Cl]_2$ resulted in formation of



(61)

$(R_2PH)(OC)_2Fe(\mu\text{-}CO)(\mu\text{-}PR_2)Rh(COD)$(Fe-Rh). This, upon reaction with phenylacetylene, formed a rhodacyclopentadienyl complex, **108**[433]. Crystal structures of both products were reported; that of the first product was subsequently found to have higher symmetry than originally reported[434].



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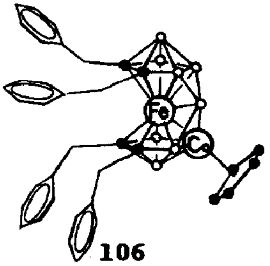

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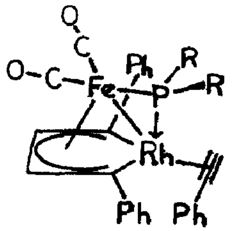

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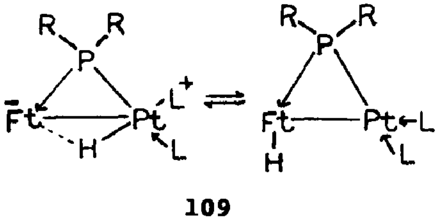
Compounds with formal iron-nickel double bonds resulted when $Na_2Fe(CO)_4$ reacted with $(RPh_2P)_2NiCl_2$, giving $(RPh_2P)_2Ni{=}Fe(CO)_4$ or $(RPh_2P)_2Ni{=}Fe(CO)_3(PRPh_2)$, depending on the mole ratio of the reactants. These unsaturated substances reacted with diphenylacetylene or azobenzene to give 1:1 adducts of uncertain structure[435].

$IFe(CO)_2(\mu\text{-}DPPM)_2PdI$ was formed by reaction of **10** with Pd(dibenzylideneacetone)$_2$. The terminal ligands on iron were readily displaced by acetonitrile, and protonation gave a (μ-H) species[59]. Oxidative addition of $(R_2PH)Fe(CO)_4$ to $L_2Pt(C_2H_4)$ [L = Et_3P, Ph_3P, $(PhO)_3P$] gave **109**, in which equilibration between terminal and bridged hydride could be observed in solution[436]. The synthesis and structure of $(OC)_3Fe(\mu\text{-}DPPM)(\mu\text{-}CO)PtBr_2$ and $(OC)_3Fe(\mu\text{-}DPPM)(\mu\text{-}I)PtI$ have been reported[437]. The electron-rich $(OC)_3Fe(\mu\text{-}DPPM)(\mu\text{-}CO)Pt(PPh_3)$ (made by reduction of the dichloride in the presence of triphenylphosphine) readily added allene or acetylene, forming **110** in the latter case. p-Tolylacetylene added to give both regioisomers[438].



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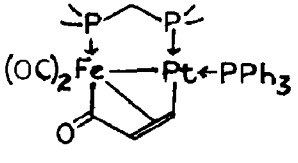

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10. TRINUCLEAR CLUSTER COMPOUNDS

a. Tri-iron Clusters

A statistical analysis of M_3 clusters of Groups 8 and 9 from the Cambridge Crystal Structure Database has shown a very pronounced tendency toward the "magic number" of 48 valence electrons expected for a closed triangular array[439].

The structure of $Fe_3(CO)_{12}$ in solution has been studied by EXAFS. In alkane solution, an all-terminal arrangement of CO's was indicated (mean Fe-Fe distance 2.65 Å), whereas in methylene chloride increased bridging reduced the mean Fe-Fe distance to 2.59 Å[440]. Variable temperature ^{31}P and ^{13}C NMR studies of $Fe_3(CO)_{10}L_2$ [L = $P(OMe)_3$, $P(OPh)_3$] showed several 1,2-isomers. A role was suggested for mobility of phosphite ligands in higher temperature isomerization processes[441]. IR spectra of $Fe_3(CO)_{12}$ impregnated on carbon black have indicated the formation of some $Fe(CO)_5$, but not the $HFe_3(CO)_{11}^-$ commonly formed on silica[442].

Laser-ion beam photodissociation studies of $Fe_3(CO)_{12}$ showed the formation of $Fe_3(CO)_{5-12}^+$ by consecutive losses of CO, with little disruption of Fe-Fe bonds[443]. Likewise 366-nm photolysis of $Fe_3(CO)_{12}$ in 90 K glasses led only to CO loss; the $Fe_3(CO)_{11}$ formed added ethene or triphenylphosphine. At longer wavelength (>540 nm), no photochemistry was observable in glasses at 90 K, but photofragmentation occurred at 298 K in the presence of ethene; the products were $Fe(CO)_n(C_2H_4)_{5-n}$ [n =3-5][444].

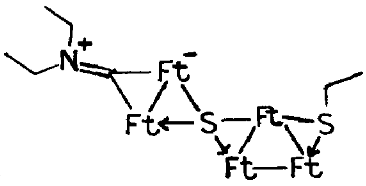
$Fe_3(CO)_{12}$ was reduced to $HFe_3(CO)_{11}^-$ by N-benzyl 1,4-dihydronicotinamide[445]. The stretching frequency of the bridging CO in dialkylammonium salts of that anion has been found to be highly solvent-dependent due to hydrogen-bonding in ion pairs. In the crystal, the di(isopropyl)ammonium salt showed hydrogen bonds to the bridging CO and a terminal CO[446]. The kinetics of deprotonation of $(\mu\text{-H})(\mu_3\text{-SCMe}_3)Fe_3(CO)_9$ by amines, to form ion pairs, has been studied. The fastest rates and largest isotope effects were found for the least hindered bases[447].

It has been suggested that reaction of $Fe_3(CO)_{12}$ with CO to form $Fe(CO)_5$ requires catalysis by electron-transfer; a mechanistic scheme has been proposed[448]. Reductive carbonylation of 2-methyl-2-nitrosopropane and nitronate salts, to form isocyanates via nitrene complexes, also involved radical anion species such as $Fe_3(CO)_{11}^{\cdot -}$ [449].

111 resulted, along with **79**, when $Fe(CO)_5$ and $Et_2NC(=S)SEt$ reacted photochemically[377].

Photodecarbonylation of Fp_3Bi led to the bismuth-capped Fe_3 cluster **112**[232]. Reaction of azoethane with "Grevels' reagent," bis(cyclooctene)tricarbonyliron, gave **113**, in which the azoethane functioned as a six-electron ligand to the closed Ft_3 cluster. Heating **113** at 120° caused rearrangement to the open cluster $(\mu_3\text{-NEt})_2Fe_3(CO)_9$, having two four-electron nitrene ligands, in 75% yield[450].

Several papers from the Huttner group have described the



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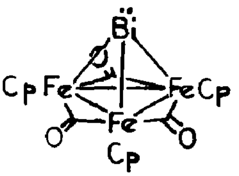

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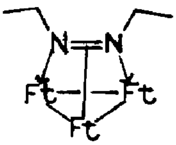

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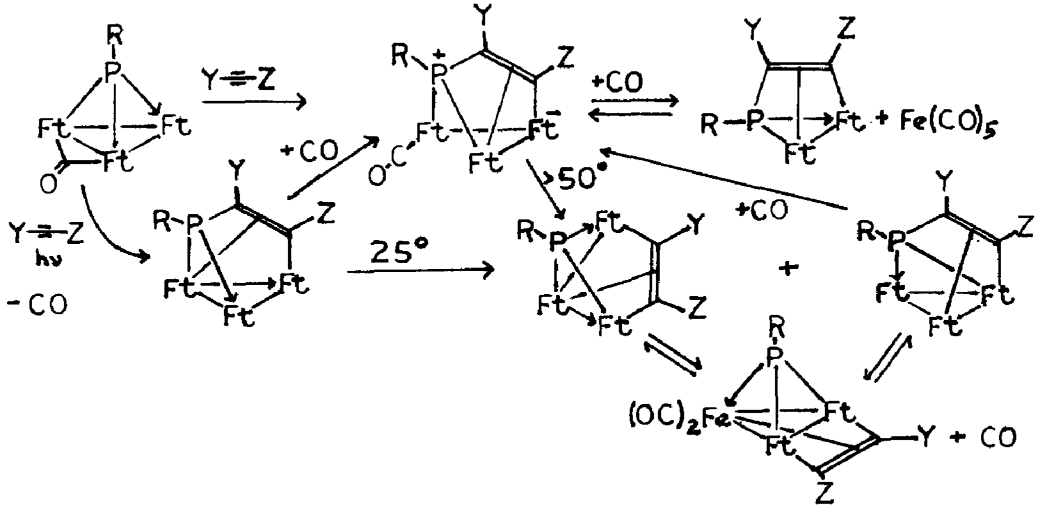
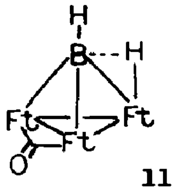
chemistry of $(\mu_3\text{-PR})(\mu\text{-CO})Fe_3(CO)_9$ derivatives, especially reactions with alkynes. They have recommended negative ion mass spectrometry for characterization of metal clusters in general, with examples drawn especially from these $(\mu_3\text{-PR})$ clusters[451]. A summary of many of the transformations which occur in reactions with alkynes appears here as Scheme V. Thermal reactions of terminal alkynes with $(\mu_3\text{-PR})Fe_3(CO)_{10}$ [R and Z = various alkyl and aryl groups; Y = H] gave $(\mu\text{-RP-CH=CZ})Fe_3(CO)_{10}$ products[452]. Photoreaction gave three types of isomeric products, depending on R, Y, Z, and reaction conditions[453]. The initially formed photoproduct shown in Scheme V was stable only for R = mesityl[453] or diethylamino[88]. Interconversions among the various products were described in terms of "tandem isomerization," involving interconversion of pentagonal pyramidal and trigonal prismatic Fe_3C_2P skeletons by movement of pairs of atoms[454]. Reactions of various products with trimethyl phosphite were also described[454].

SCHEME V



Reaction of $B_2H_5Fe_2(CO)_6^-$ with nonacarbonyldiiron gave $H_2BFe_3(CO)_{10}^-$, **114**[356]. $Fe_3(CO)_9CH_4$, **115**, has been found to exist in solution as three tautomers of similar energy. The conjugate base formed by deprotonation of the tautomeric mixture had one $Fe\cdots H\cdots Fe$ interaction. Reprotonation at low temperature formed tautomer **115c**, which most closely resembled the anion in structure[455]. Direct interconversion of $(\mu\text{-}H)_3(\mu_3\text{-}CMe)Fe_3(CO)_9$, **116**, (structurally similar to **115a**) and $(\mu\text{-}H)(\mu\text{-}CO)(\mu_3\text{-}CMe)Fe_3(CO)_9$ under 1-4 atm. of hydrogen or CO has been observed. Indirect conversion also occurred as a consequence of deprotonation of the trihydride, spontaneous H_2 loss from the anion, reprotonation, and carbonylation[456]. UV-Photoelectron spectroscopy of **116** and $(\mu\text{-}H)(\mu_3\text{-}H_3BR)Fe_3(CO)_9$ has been interpreted in light of structural data and Fenske-Hall calculations, and interactions of main group element-iron bonding, hydrogen bridging, and charge assessed[457].



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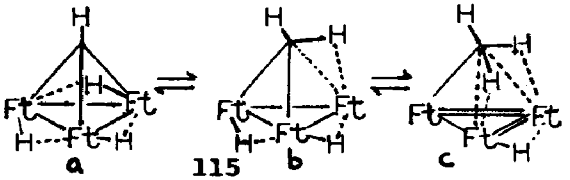

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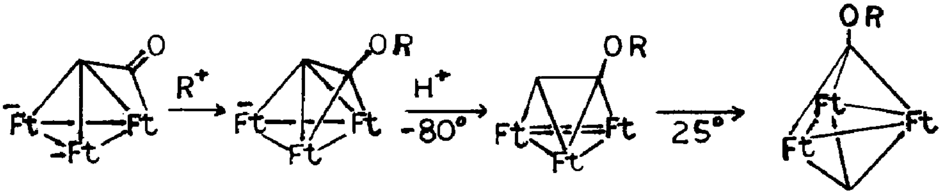
Thermal reaction of **117** [L = CO] with triphenylphosphine gave **117** [L = PPh_3], a displacement reaction rather than the simple addition that might be expected from the unsaturated nature of **117**[458]. Reaction of $Ph_2P(O)C\equiv C\text{-}CMe_3$ with $Fe_2(CO)_9$ proceeded with bifurcation of the C-P bond, to form **118**[459]. The ketenylidene cluster $Fe_3(CO)_9(\mu_3\text{-}CCO)^{2-}$, **119**, reacted with "hard" electrophiles (acetyl chloride, ethyl and methyl triflate) at the bridging CO group (Eq. 62), to form an alkoxyacetylide ligand.



(62)

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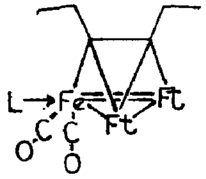
Low temperature protonation gave an unstable, unsaturated alkyne complex, which readily underwent scission upon warming to room temperature to afford a saturated bis(alkylidyne)$Fe_3(CO)_9$ complex[460]. Extended Hückel calculations have been carried out on **119** and its ruthenium and osmium analogs in an effort to understand why the iron and osmium species have the ketenylidene CO bridging the C-M bond, whereas the ruthenium species has three

(μ-CO) bridges and a nearly perpendicular ketenylidene group[461]. The crystal structure of **120** has been determined, and calculations performed on the rotational orientation of the COMe group[462].



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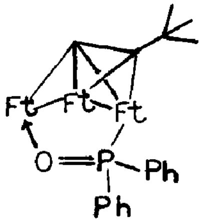

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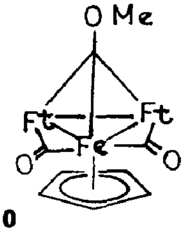

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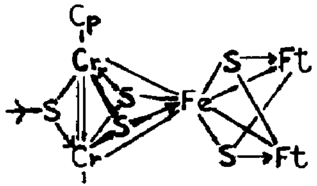
Substitution reactions of the bicapped triangular clusters $(\mu_3\text{-Y})(\mu_3\text{-Z})Fe_3(CO)_9$ **121** [Y, Z = S, Se, NPh, PPh] occurred readily under condition of electron-transfer catalysis. Control of reduction potentials allowed clean selection of mono- or di-substitution of phosphite for CO. Mechanistic details were significantly affected by the nature of Y and Z: in contrast to the phosphinidene clusters, whose radical anions underwent fission of a Fe-P bond, the other clusters showed loss of a CO as the rate-determining step following one-electron reduction[463].

Reaction of **121** [Y = Z = S] with benzotriazole in the presence of oxygen resulted in destruction of the cluster, with formation of $[(C_6H_4N_3)_2FeOH]_n$[464]. Reaction of **121** [Y = Z = S] with $CpCr(\mu\text{-S})(\mu\text{-SCMe}_3)_2CrCp$ resulted in displacement of all three carbonyl groups from one iron, forming **122**[465]. Strong nucleophiles such as Et_3BH^-, alkyl-lithiums, and sodium methoxide attacked a CO group of **121** [Y = Z = NPh] to afford acyl-cluster anions. Ethylation of the benzoyl cluster anion afforded the usual carbene complex (X-ray structure). Exposure of the carbene complex to air resulted in formation of PhN=C(OEt)Ph by formal coupling of carbene and nitrene ligands. The bis(phosphinidene) cluster **121** (Y = Z = PPh) reacted similarly with phenyl-lithium to give the benzoyl cluster anion, but ethylation gave **123** rather than the expected carbene complex[466].

A very low yield of **121** [Y = Z = NPh] was obtained from reaction of azobenzene with $Fe_3(CO)_{12}$[467]; a result which contrasts dramatically with that previously cited, involving use of azoethane and "Grevels' reagent"[450]. **121** [Y = Z = $PNEt_2$], produced by reaction of $(Et_2NPCl_2)Fe(CO)_4$ with $Fe_2(CO)_9$, underwent photochemical addition of diphenylacetylene across the phosphorus centers. Further photochemical substitution incorporated an additional acetylene in place of two CO groups, forming **124**[88].

Reaction of $R_2NP{=}NR$ [R = $SiMe_3$] with $Fe_3(CO)_{12}$ produced, along with the aforementioned **74**, two tri-iron products, **121** [Y = PNR_2, Z = RN=POR] and $(\mu\text{-CO})(\mu_3\text{-PNR}_2)Fe_3(CO)_9$[360]. Bis(phosphini-



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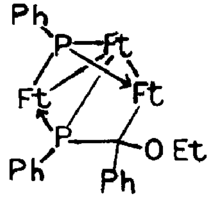

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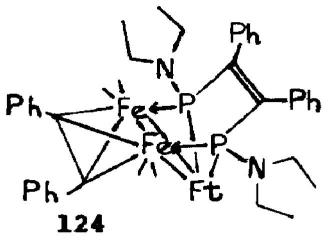
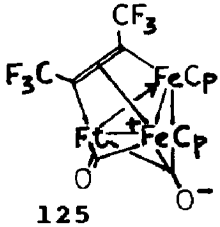


124

dene) complexes **121** [Y = Z = PR] resulted when $RPCl_2$ [R = mesityl or trimethylsilylmethyl] reacted with $Na_2Fe(CO)_4$[78].

Bismuth-containing clusters were prepared by reaction of $Bi[Fe(CO)_4{}^-]_3$ with $BiCl_3$ to form $(\mu\text{-}CO)(\mu_3\text{-}Bi)Fe_3(CO)_9{}^-$ and $(\mu_3\text{-}Bi)(\mu_3\text{-}Bi{\rightarrow}Fe(CO)_4)Fe_3(CO)_9{}^{2-}$. The former anion was oxidized by Cu(II) to **121** [Y = Z = Bi], which underwent reversible reduction with one or two electrons and addition of $Fe(CO)_4{}^{2-}$ to yield the aforementioned $(\mu_3\text{-}BiFe(CO)_4)$ dianion[468].



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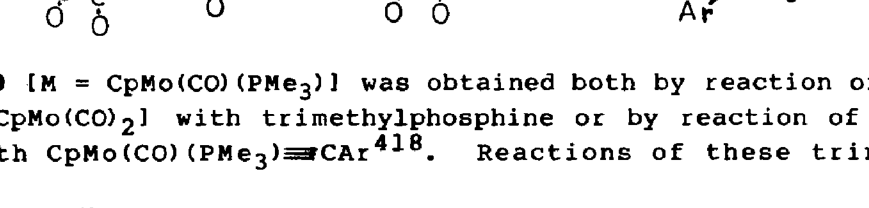
The dianion $(\mu_3\text{-}CO)(\mu_3\text{-}Ge\text{-}Fe(CO)_4)Fe_3(CO)_9{}^{2-}$ was prepared by reaction of GeI_2 with $Fe_2(CO)_8{}^{2-}$. The crystal structure of the tetraethylammonium salt was determined. Oxidation gave the spirocycle $Ge[Fe_2(CO)_8]_2$ (See Eq. 44)[358]. The electronic structure of $(\mu_3\text{-}CF)_2Fe_3(CO)_9$ has been studied by photoelectron spectroscopy and DV-Xα calculations[469]. **125** resulted from reaction of $CpFe(CO)[\mu\text{-}C(CF_3)=C(CF_3)SMe]_2\text{-}FeCp(CO)$ with $Fe_3(CO)_{12}$ in refluxing toluene. Several other products, including Fp_2, FpMe, and $(OC)_3Fe(\mu\text{-}C(CF_3)=C(CF_3)S)Fe(CO)_3$, were also isolated[470].

b. Fe_2M Clusters

Formation of clusters **100** has been described in Scheme IV. As may be expected, the optimum yields of the trimetallic clusters were obtained using excess $Fe_2(CO)_9$ in reaction with M≡CAr [M = $Cp^*W(CO)_2$ or $CpMo(CO)_2$; Ar = p-tolyl][414,416]. Reaction of **100** [M = $CpMo(CO)_2$] with sulfur occurred with insertion of S into metal-metal bonds as shown in Eq. 63[416]. Phosphine-substituted



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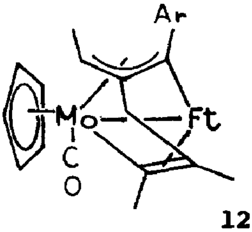
100 [M = $CpMo(CO)(PMe_3)$] was obtained both by reaction of **100** [M = $CpMo(CO)_2$] with trimethylphosphine or by reaction of $Fe_2(CO)_9$ with $CpMo(CO)(PMe_3)$≡CAr[418]. Reactions of these trimetallic clusters **100** with alkynes resulted in cluster fragmentation, with bimetallic FeM clusters the usual products[419,420]. The "flyover" product **126**, from reaction of 2-butyne with **100** [M = CpMo(CO)$_2$], is an example. The compound **127** resulted when (η^5-Me$_2$C$_2$B$_9$H$_9$)-W(CO)$_2\equiv$CR$^-$ [R = Me, Ph, *p*-tolyl] reacted with Fe$_2$(CO)$_9$, demonstrating the role of the carborane as a "non-spectator ligand"[423].

Eq. 60 showed the formation of the Fe$_2$Mn cluster **104** [Y = CO]. Reaction of this product with excess diazomethane gave not only the (μ-methoxyvinyl) product shown in Eq. 60, but also **104** [Y = CH$_2$]. Thermal decomposition of the latter, or reaction with CO or PPh$_3$ resulted in formation of (μ-C(OMe)=CH$_2$) bimetallic complexes[428]. Cycloaddition of Cp'Mn(CO)$_2$ [Cp' = methylcyclopentadienyl] to CpFe(μ-NO)$_2$FeCp gave the μ_3-NO cluster **128** in 76% yield. **128** reversibly underwent one-electron reduction and one-electron oxidation under electrochemical conditions. Attempted preparative oxidation by Ag$^+$, however, yielded only the μ_3-NH$^+$ derivative of **128**, in low yield. Crystal structures of **128** and **128**$^-$ showed an increased Fe-Fe bond length in the reduced form (2.605 Å vs. 2.441 Å)[471].



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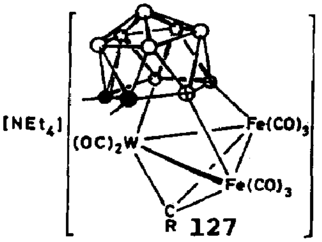

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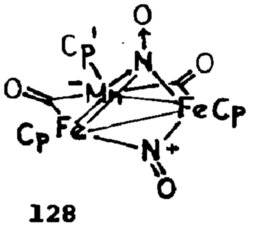

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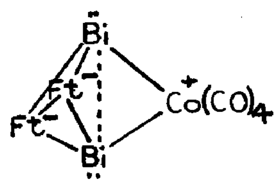
Fe$_2$Ru(CO)$_{12}$ underwent substitution by triphenylphosphine or trimethyl phosphite by a dissociative mechanism, with the first substitution occurring at ruthenium. The mixed-metal cluster was more reactive than either Fe$_3$- or Ru$_3$(CO)$_{12}$[472].

Trimethylphosphine displaced CO from the ketenylidene ligand of Fe$_2$Co(CO)$_9$(μ_3-CCO)$^-$, giving Fe$_2$Co(CO)$_9$(μ_3-C-PMe$_3$)$^-$. Protonation produced a (μ-H)[Fe-Fe] neutral product[473]. Crystal structures of Hg[Fe$_2$M(μ_3-COMe)(CO)$_7$Cp], where M = Co or Rh, differed from each other. In the cobalt compound, the mercury bridged the Ft-Ft bond, and the cobalt held a terminal carbonyl ligand. In the rhodium compound, the mercury bridged one Rh-Ft bond, and a carbonyl group bridged the other. In solution, a polytopal rearrangement of the mercury around the edges of the Fe$_2$Rh triangle was indicated[474]. Reaction of Bi$_2$Fe$_3$(CO)$_9$ [**121**, Y = Z = Bi] with Co(CO)$_4$$^-$ produced the cluster anion **129**[468].

Reaction of **130** [L = CO] with triphenylphosphine resulted in substitution, forming **130** [L = PPh$_3$], rather than addition[458]. **121** [Y = Z = Te] reacted with Pt(PPh$_3$)$_4$ to yield **131**[475].

Electrochemical reduction of $(Ph_3P)(L)PtFe_2(CO)_8$ proceeded similarly to that of $Fe_3(CO)_{12}$, to give a radical-anion and then



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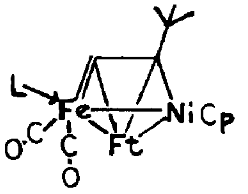

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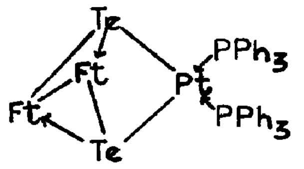
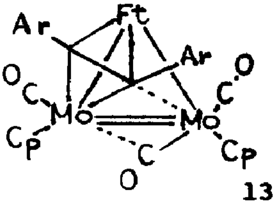


131

a dianion, with the potentials affected by the ligand L bonded to platinum[476]. A number of DPPM-bridged trimetallic clusters have been synthesized by reaction of $(DPPM)PtCl_2$ with $Fe_2(CO)_9$ or $Fe_2(CO)_8{}^{2-}$ [477].

c. FeM$_2$ Clusters

Reaction of $(C_8H_{14})_2Fe(CO)_3$ with two equivalents of $CpMo(CO)_2$ CAr [Ar = *p*-tolyl] at -40° afforded a labile 48-electron complex, $[CpMo(CO)_2]_2(\mu\text{-}ArCCAr)Fe(CO)_3$, which lost CO at temperatures above -20° to form unsaturated **132**[415]. Reaction of **132** with trimethylphosphine resulted in replacement of a Fe-bound CO[418]. A sulfur-bridged $FeMo_2$ cluster, **133**, resulted when $[Cp'MoS(SH)]_2$ reacted photochemically with $Fe(CO)_5$. With FpI, the result was formation of **134**[478].



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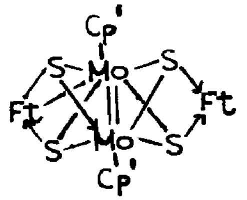

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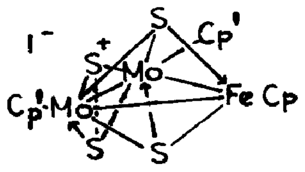
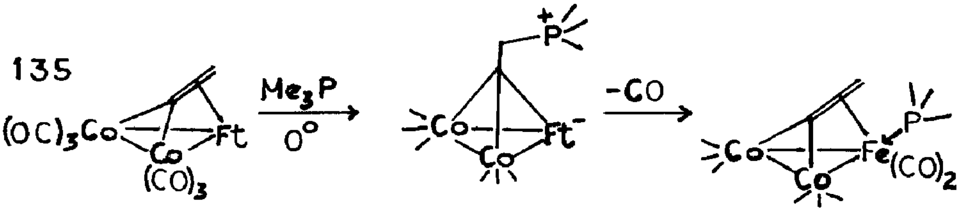


134

CO dissociation occurred more readily from $Ru_2Fe(CO)_{12}$ than from the tri-iron or triruthenium dodecacarbonyls. Trimethyl phosphite or triphenylphosphine reacted cleanly to displace one CO from each Ru[472].

A tricarbonylcobalt vertex of the tetrahedral cluster $(\mu_3\text{-}CPh)Co_3(CO)_9$ was replaced by a tricarbonyliron anion upon reaction with $Fe(CO)_4{}^{2-}$. The structures of the protonated and aurated derivatives of $(\mu_3\text{-}CPh)Co_2Fe(CO)_9{}^-$ showed the proton or Ph_3PAu moiety on a Fe-Co edge [479]. Trimethylphosphine added initially to the vinylidene ligand of $(\mu_3\text{-}C{=}CH_2)Co_2Fe(CO)_9$, **135**, but rearranged to the iron upon warming (Eq. 64)[480]. The same ligand, trimethylphosphine, added to iron and cobalt atoms of $(\mu_3\text{-}PMe)Co_2Fe(CO)_9$ or $(\mu_3\text{-}PMe)CoFeWCp(CO)_8$, to form triangular Fe-P-W or -Co clusters with pendant $Co(CO)_3PMe_3$ groups also coordinated to the bridging phosphorus. Heating in vacuum re-closed the tetrahedral clusters with loss of two CO's or one CO



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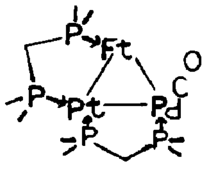
and one Me_3P[481]. A series of chiral (μ_3-vinylidene) clusters conceptually derived from **135** by replacement of a $Co(CO)_3$ vertex by isolobal groups [NiCp, $CpMo(CO)_2$, and $CpW(CO)_2$] have been prepared, as has a group of (μ_3-RCCR)$Co_2Fe(CO)_9$ and (μ_3-RCCR)$Fe(CO)_3(NiCp)_2$ alkyne complexes. Rearrangements of terminal alkynes to vinylidenes on the chiral clusters showed highly variable diastereoselectivities[482].

The 44-electron triangular cluster **136** resulted from reaction of $HFe(CO)_4^-$ with $ClPd(\mu\text{-}DPPM)_2PtCl$[483]. An open cluster, cis-$(Ph_3P)_2Pt(Fp)(Hg\text{-}C_6Cl_5)$, resulted when Fp^- displaced chloride from platinum[484].



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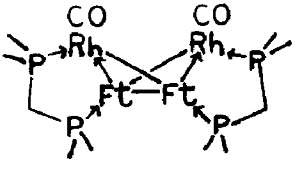
11. TETRA- AND POLYNUCLEAR CLUSTER COMPOUNDS

A statistical analysis of published crystal structures has indicated a strong tendency for tetranuclear clusters of Group 8 and 9 metals to have 60 valence electrons, the "magic number" expected for a closo tetrahedral cluster. An exception was the $M_4(\mu_3\text{-}Y)_4$ cubanoid clusters, which showed no numerical predominance[439].

A clear exception to the "magic numbers" is the 56-electron planar rhombohedral $[Fe(py)_2Fe(CO)_4]_2$ [py = pyridine], obtained from $PyFe(CO)_4$ on dissolution in organic solvents. It reacted with ethylenediamine [en] to form $Fe(en)_3^{2+}$ $Fe(CO)_4^{2-}$, and it reduced CO_2 to CO, forming $FeCO_3$ in the process. It may best be thought of as a mixed inorganic-organometallic substance[485].

A 58-electron "butterfly" cluster, **137**, resulted when **107** was treated with lithium acetate[432]. The corresponding complex incorporating the bridging ligand $CH_2{=}C(PPh_2)_2$ has also been obtained, in this case by treating the analogous starting material with Me_3NO[486].



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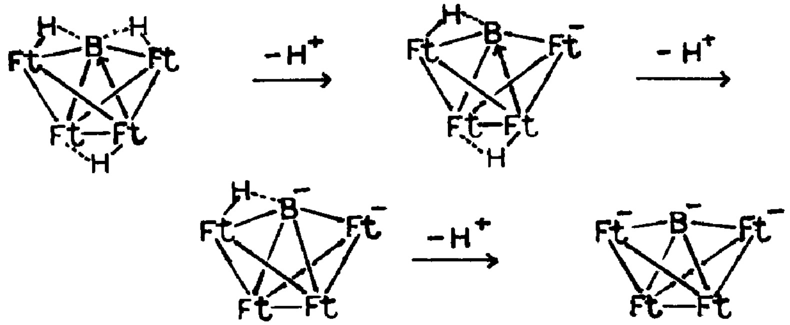
Reaction of $Co_3Fe(CO)_{12}^-$ with phosphines or phosphites resulted in monosubstitution, but $Ph_3PAuCo_3Fe(CO)_{12}$ reacted with trimethyl phosphite to give disubstitution. Several structures were reported[487]. Flash vacuum pyrolysis of Fp_2 at 500° constituted a practical synthesis of $[CpFe(\mu_3\text{-}CO)]_4$[244].

A significant group of 62-electron clusters are the $ZM_4(CO)_{12}$ clusters having a butterfly arrangement of metal atoms with a main-group element, Z, bridging the wingtips. Examples have been described in 1987 having B, C, N, and even O functioning as bridging 6-electron donors. Boron compounds $HFe_4(CO)_{12}BH_2$ and $HFe_4(CO)_{12}BH^-$ resulted from reaction of $B_2H_6Fe_2(CO)_6$ and its conjugate base, respectively, with $Fe_2(CO)_9$[356]. Sequential deprotonation of $HFe_4(CO)_{12}BH_2$ all the way to $Fe_4(CO)_{12}B^{3-}$ (Eq. 65) has been reported[488]. The monoanion in the series was also



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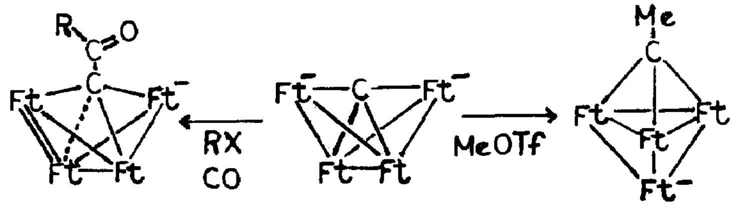
obtained from reaction of $HFe_3(CO)_9BH_3^-$ with $Fe_2(CO)_9$, a reaction which required loss of H_2[489]. Phosphine substitution on the monoanion proceeded at a wingtip; a second substitution at the other wingtip was accompanied by proton transfer from the hinge to the B, producing a product with two B---H---Fe interactions. Extended Hückel calculations were employed in an effort to rationalize the hydrogen positions[489]. The structure of $(Ph_3PAu)_2Fe_4(CO)_{12}BH$ was dissimilar from that of $Fe_4(CO)_{12}BH_3$ in that the two Ph_3PAu groups bridged a common B-Fe edge, as shown in structure 138[490].

An infrared band at about 900 cm^{-1} has been identified as characteristic of the exposed carbide ligand in $Fe_4(CO)_{12}C^{-2}$ [491]. Several analogs of this Fe_4 cluster having isolobal transition metal groups replacing hinge $Fe(CO)_3$ groups have been prepared. The replacement groups included $Cr(CO)_4$, $W(CO)_4$, $Mn(CO)_4^+$, and $Rh(CO)_3^+$ [492]. Reactions of $Fe_4(CO)_{12}C^{2-}$ with alkylating agents took two different courses. With highly cationic agents such as methyl triflate, direct alkylation of the carbide occurred, forming the 60-electron tetrahedral cluster, $(\mu_3\text{-}CMe)Fe_4(CO)_{12}^-$. With alkyl halides, alkylation proceeded by single-electron transfer with CO uptake to form unsaturated butterfly clusters (Eq. 66)[493]. Crystal, molecular, and electronic structures of the latter have been scrutinized[494].

Auration of $Fe_4(CO)_{12}N^-$ and its $FeRu_3$ and Ru_4 analogs have been studied, including the crystal structure of **139**[495]. Reaction of $(\mu_3\text{-O})Fe_3(CO)_9^{2-}$ with $(MeCN)_3Mn(CO)_3^+$ gave **140**, which showed the manganese at a wingtip, in contrast to most MFe_3 butterflies. As might be expected for a 6-electron donor oxygen atom, the metal-oxygen distances were quite short [average 1.89(2) Å][496].



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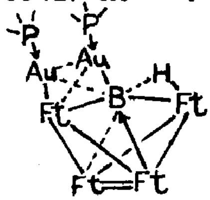

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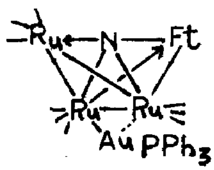

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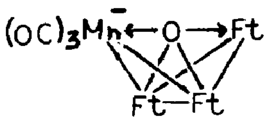
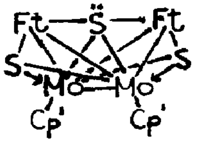


140

Providing a bridge between the butterfly clusters and the cubanoid clusters is **141**, best obtained by reduction of **133** with potassium/graphite[478]. A compound, $Fe_4(CO)_{12}S(SR)_2$, obtained from $(RS)_2$ and $HFe_3(CO)_{11}^-$, is probably a butterfly structure like **141**, with terminal RS- groups at the wingtips[368]. Formal addition of a fourth sulfur atom and deletion of two CO groups from **141** maintains the electron count at 62, but generates a cubanoid cluster, **142**, whose metal-metal bonding maintains the butterfly pattern. MO calculations have been carried out on **142**, and the nature of the metal-metal bonding discussed. Consistent with the valence bond structure shown, the bond orders decreased in the order Mo-Mo > Mo-Fe > Fe-Fe, and reduction was accompanied by loss of Mo-Fe bonds without disrupting the overall structure, which is maintained by the MS_3 interactions even in the absence of metal-metal bonds[497]. The selenium analogs, $(CpFe)_4Se_4^{n+}$ [n = 0-4] have been prepared by reaction of Fp_2 and elemental selenium and electrochemical oxidation. The crystal structure of the trication was determined, leading to the finding that the average Fe-Fe distance uniformly decreased with increasing charge, as expected for removal of electrons from orbitals with metal-metal



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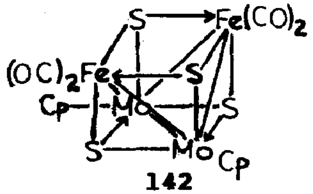

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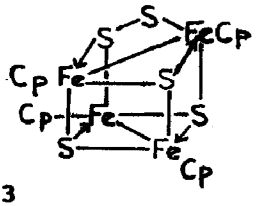
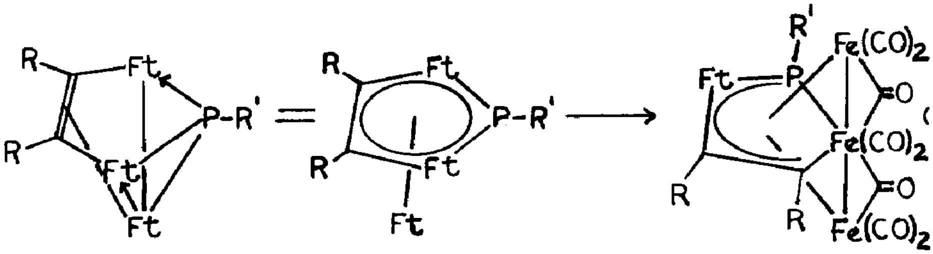


143

antibonding character[498]. The sulfur-rich cluster **143** has been studied electrochemically, which allowed characterization of six different oxidation states, $(CpFe)_4S_5^n$, n = −2 to +3[499].

The clusters $(\mu_3\text{-}PR')(\mu_3\text{-}RCCR)Fe_3(CO)_9$ (see Scheme V) were able to coordinate another iron upon reaction with $Fe_2(CO)_9$, to form triple-decker complexes (Eq. 67)[500]. The 64-electron octahedral cluster $(\mu_4\text{-}PPh)_2Co_2Fe_2(CO)_{10}(\mu\text{-}CO)$ underwent attack by nucleophiles (Et_3BH^-, MeLi) selectively at a cobalt-bound terminal carbonyl group. The formyl compound lost CO at -30° to form $(\mu_4\text{-}PPh)_2Co_2Fe_2(CO)_{10}(\mu\text{-}H)^-$ [501].



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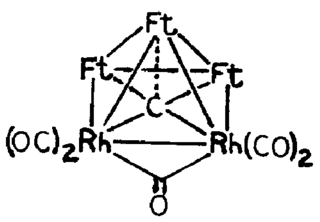
A statistical analysis of published crystal structures of pentanuclear compounds of the Group 8 and 9 metals showed no clear preference for a specific "magic number" of electrons. The hexanuclear clusters did show a clear predominance of 86-electron clusters[439].

Redox condensation reaction of $Fe_3Rh(CO)_{12}C^-$ with $Rh(CO)_2Cl_2$ gave **144**; a presumably related cluster, $Cr_2Fe_3(CO)_{16}C^{2-}$, of unknown structure, was prepared similarly. Variable temperature NMR studies were used to assign the structures of **144** and several tetranuclear clusters[492]. Rhodium-iron bimetal hydroformylation catalysts were prepared by supporting $FeRh_4(CO)_{15}^{2-}$ on metal oxides; EXAFS and Mossbauer studies of the resulting materials indicated increased oxidation states for the iron compared to the starting material[502,503]. The mixed iron-rhodium catalysts were far more active than monometallic ones[503]. Mössbauer studies have been carried out on a number of well-defined anionic penta- and hexanuclear iron-rhodium and iron-Group 10 clusters[504].



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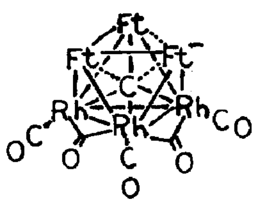

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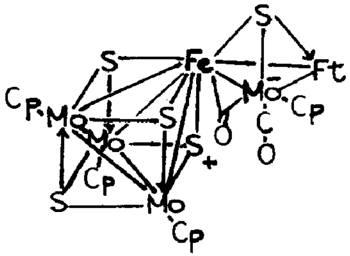


146

Crystal structures of two salts of $Fe_3Rh_3(CO)_{15}C^-$, **145**, have been determined[492,505]. Interconversion of various iron-rhodium clusters during hydroformylation showed conversion of $Fe_5Rh(CO)_{16}C^-$ to $Fe_4Rh_2(CO)_{16}C$ and $Fe_4Rh(CO)_{14}C$. The latter in turn underwent conversion to **145**[505].

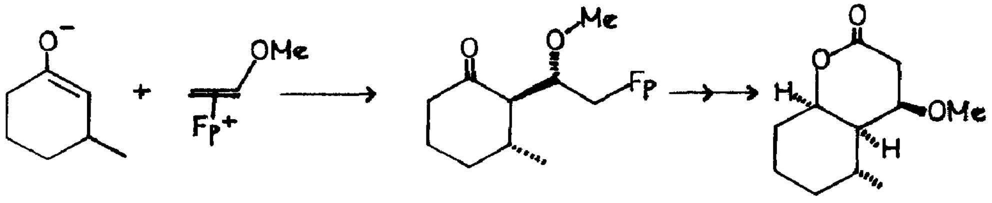
Reaction of $Cp_2Mo_2(CO)_6$ with $(\mu_3\text{-}S)_2Fe_3(CO)_9$ gave the curious double cluster **146** (X-ray structure)[506].

Carbon-carbon bond formation occurred during reaction of diazomethane with CO adsorbed on an iron surface, based on X-ray PES evidence[507]. Iron-iridium bimetallic catalysts favored methanol production in reduction of CO with H_2[508]. Iron-copper alloy catalysts, which suppressed carbon deposition during Fischer-Tropsch reaction, have been produced by decomposition of $Fe(CO)_5$ in a fluidized-bed reactor containing small copper particles[509].

POST-SCRIPT: At 509 references, this 1987 review covers slightly fewer papers than the 1986 one (536). Both of the last two years show substantially more activity than 1983-5, which averaged just over 400 references.

The majority of the organoiron chemistry has continued to be published in one of three journals: J. Organometal. Chem. (117 citations), Organometallics (91 citations), or J. Am. Chem. Soc. 70 citations). Following in frequency are J. Chem. Soc., Chem. Comm. (37 citations), Inorg. Chem. (35 citations), and J. Chem. Soc., Dalton Trans. (34 citations). No other journal had more than 12 citations.

Eq. 39 (inadvertently omitted from Section 7d):



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