ORGANOIRON CHEMISTRY
Annual Survey for the Year 1988*

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CONTENTS

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LIST OF ABBREVIATIONS USED

acac	acetylacetonate, $(MeCO)_2CH^-$
An	any arene ring, such as benzene, C_6H_6
Ar	an aryl ring, such as p-tolyl, MeC_6H_4-
bpy	2,2'-bipyridyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl, C_5H_5
Cp'	methylcyclopentadienyl, $C_5H_4CH_3$
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
E	an ester group, usually carbethoxy or carbomethoxy
El^+	an electrophile
Et	ethyl, C_2H_5-
Fp	cyclopentadienyldicarbonyliron, $CpFe(CO)_2$-
Fp'	cyclopentadienyl(carbonyl)(triphenylphosphine)iron
Fp*	(pentamethylcyclopentadienyl)dicarbonyliron
Ft	the tricarbonyliron group, $Fe(CO)_3$
L	a 2-electron donor ligand, such as a phosphine
LAH	lithium aluminum hydride
M	any transition metal
Me	methyl, CH_3-
Nu^-	a nucleophile
Ph	phenyl, C_6H_5-, also shown as Ø in structures
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
TMEDA	tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$
X	any halogen

1. INTRODUCTION

In this Annual Review, I attempt to cover the organoiron chemistry reported in journals published during calendar year 1988. 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 dicyclopentadienyltetracarbonyldiiron [Fp_2, $Cp_2Fe_2(CO)_4$], in which they undergo fission into monoiron products, are treated alongside those of their monomeric derivatives such as FpR. Likewise, FeM_n clusters are treated as a group with other metal clusters of 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 pair donation and consequent formal charges. Otherwise, formal charges are shown explicitly.

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

2. REFERENCE WORKS, REVIEWS, AND GENERAL STUDIES

In an effort to assess empirically the difference (if any) between X$\rightarrow$Fe and X-Fe bonds, this reviewer has collected all of the reported crystallographic bond length data for bonds between Group 15 and 16 elements and iron, reported in the 1986 and 1987 reviews of organoiron chemistry. This data base produced over 350 relevant data, and by far the greatest number dealt with iron-phosphorus bonds. The bonds were divided into those clearly of coordinate-covalent nature [typically, $R_3P\rightarrow FeL_n$] or of "pure" covalent nature [typically, R_2P-FeL_n, R_4P-FeL_n, or $R_2P(\rightarrow M)-FeL_n$]; data for hybrid cases [such as $(\mu-R_2P)_2Fe_2(CO)_6$] and phosphite complexes (known to have P→Fe bonds significantly shorter than those of phosphines) were excluded. Histograms of the bond length distributions of the two types are shown as Figure I. The data suggest an empirical distinction between P-Fe (average bond length 2.26 Å) and P→Fe (2.21 Å).

The shorter bonds in the latter case can be interpreted in terms of enhanced back-bonding through donation of electron density from formally negative iron into acceptor orbitals (3d or σ^*) made more accessible by the positive charge on phosphorus. This rationale is supported by the fact that the P-Fe compounds having bond lengths in the short end of the range (< 2.23 Å) generally also involve formally positive phosphorus.

Just as impressive as the statistical case is the fact that structures containing both P-Fe and P→Fe in the same unit regularly show the latter to be shorter than the former. A few particularly clear examples from 1988 data (not included in the statistical analysis) will be pointed out in the course of this article.

Data for the other elements are shown in Table I, along with average deviation and number of data for each case. The coordinate-covalent bond shortening observed for phosphorus is not found for nitrogen and oxygen, consistent with inability of those elements to engage in back-bonding. Indeed, in the absence of back bonding, the coordinate-covalent bonds in the nitrogen (and oxygen?) compounds are rather longer than the "pure" covalent bonds.

TABLE I

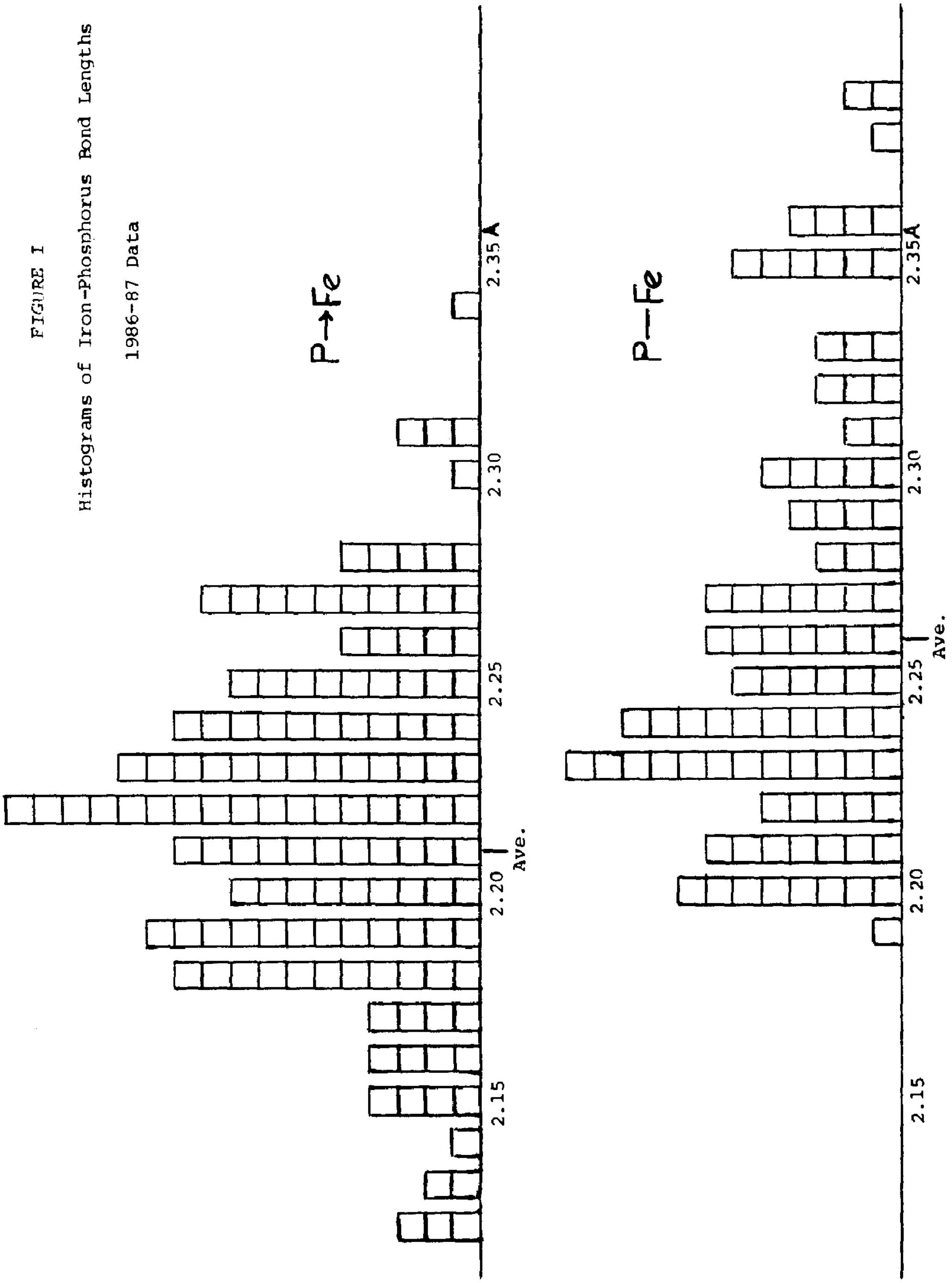
Average Bond Lengths of Y-Fe Bonds as a Function of Bond Type

Y	Y-Fe (A)	#	Y→Fe (A)	#
N	1.96(4)	15	2.01(5)	28
P	2.26(6)	96	2.21(5)	136
As	2.35(9)	2	2.23	1
Sb	2.56(1)	8	--	0
O	1.95(4)	3	1.97(8)	5
S	2.27(7)	43	2.26(4)	25
Se	2.44(1)	4	--	0

FIGURE I

Histograms of Iron-Phosphorus Bond Lengths

1986-87 Data



With sulfur the effect is marginal or nonexistent, suggesting little back-bonding in sulfur-iron bonds as well. Why sulfur and phosphorus should behave so differently is not clear to this reviewer.

Volume B13 of the ongoing Gmelin organoiron series appeared during 1988. This volume covers FpR compounds in which the group R contains a carbocyclic or heterocyclic ring or a carbonyl group, or in which R is a vinylic or alkynyl group[1]. The November, 1988 issue of Chemical Reviews featured many useful and interesting reviews in organometallic chemistry; two which focussed on organoiron chemistry were by Didier Astruc [Nineteen-Electron Complexes and Their Role in Organometallic Mechanisms][2] and Alan Cutler [Carbon Monoxide and Carbon Dioxide Fixation: Relevant C_1 and C_2 Ligand Reactions Emphasizing $(\eta^5\text{-}C_5H_5)Fe$-Containing Complexes][3]. Stephen Davies has also provided an overview of the use of Fp' compounds as chiral auxiliaries in asymmetric synthesis[4].

3. REACTIONS OF "NAKED" IRON ATOMS AND IONS

Iron atoms in argon matrices have been found to react with diazomethane to form CH_2FeN_2 and CH_2Fe. Upon UV photolysis, CH_2Fe was converted to HFeCH, which could be reversed by long-wavelength (>400 nm) photolysis. CH_2Fe added hydrogen and water to form CH_3FeH and CH_3FeOH, respectively. CH_2FeN_2 was even more rapidly hydrogenated to form $CH_3Fe(H)N_2$[5].

Reaction of Fe^+ with isonitriles in the gas phase has been studied. In contrast to the case with nitriles, both end-on and side-on (η^2) coordination have been inferred to occur. With simple isonitriles, side-on coordination led to cleavage of the R-NC bond. With larger nitriles, that process was accompanied by H_2 loss from remote locations, analogous to the process which occurred with long-chain nitriles, which presumably involved in both cases end-on coordination of Fe^+ [6]. Reaction of Fe^+ with 8,8-dimethylnonanenitrile resulted *inter alia* in loss of methane, 90% of which originated in the *t*-butyl group. The process involved end-on coordination to the N, oxidative addition to a remote C-C bond, and β-H migration[7]. With 4-octyne, Fe^+ reacted cleanly to generate ethene, while other metal ions gave additional products. The mechanisms were investigated by deuterium labelling[8].

FeO^+ reacted with ammonia to form $FeNH^+$ and H_2O. A study of ion-molecule reactions of $FeNH^+$ indicated a bond dissociation energy D_0 for Fe^+-NH of about 230 kJ/mol, consistent with a single bond, as in FeO^+. $FeNH^+$ transferred NH to ethene and benzene, possibly via a cyclic azaferretane intermediate[9].

Collision-induced decomposition studies of $Fe(CO)(OH_2)^+$ have been described[10]. Laser-ion beam photodissociation of mass-resolved $Fe(CO)_x{}^+$ [x = 1-5] ions has been studied[11].

Gas-phase ligand substitution reactions of the 17-electron negative ions $(OC)Fe(NO)_2{}^-$ and $Fe(CO)_4{}^-$ have been studied, with an extensive variety of neutral nucleophiles. Associative mechanisms were generally favored[12,13].

Fourier transform mass spectrometric studies of reactions of Fe_2D^+ with alkenes showed that ethene reacted to produce Fe_2H^+ and C_2H_3D, indicating significant barriers to hydrogen exchange during the lifetime of the $Fe_2C_2H_4D^+$ intermediate. In contrast, propene reacted with Fe_2D^+ to produce $FeC_3H_5{}^+$ having 65% of one D, indicating facile reversible reaction of allylic C-H bonds[14]. Photodissociation studies of $Fe_2(CO)_{0-6}{}^+$ and $Fe_3(CO)_{0-4}{}^+$ have also been reported; loss of two carbonyl groups per event were common, with formation of $Fe_2(CO)_3{}^+$ from $Fe_2(CO)_5{}^+$ particularly favored[11].

4. COMPOUNDS WITH η^1-CARBON LIGANDS

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

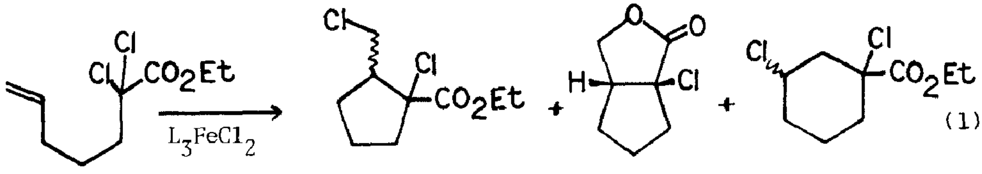
In this section I discuss not only organometallic compounds having only a single iron-carbon sigma bond, but also a number of low-coordinate or low-valent species which, lacking iron-carbon bonds, are not strictly organometallic compounds. They are included herein because of their utility in synthesis of organometallics and because of their intrinsic interest to many organometallic chemists.

Bis[bis(trimethylsilyl)amido]iron(II), $Fe[N(SiMe_3)_2]_2$ has been prepared by reaction of $(THF)_2FeBr_2$ with $LiN(SiMe_3)_2$. Gas phase electron diffraction indicated a linear N-Fe-N geometry, and photoelectron spectra suggested a high-spin $^2B_1$ configuration[15].

Addition of one equivalent of benzyl chloride or bromide to a solution of $Li(TMEDA)^+$ $CpFe(COD)^-$ produced ferrocene and $(TMEDA)Fe(CH_2Ph)_2$. The latter, notwithstanding its paramagnetism, was characterized by NMR methods, which indicated a pseudotetrahedral structure. It reacted rapidly with excess benzyl halide to form bibenzyl and constitutes a useful structural model for the intermediates in iron-induced coupling reactions[16]. Such a coupling reaction has been used to combine ketal-containing Grignard reagents with RC(=O)SPh to form jasmone and derivatives[17]. Carbonylation of (DIPPE)FeR$_2$ [DIPPE = 1,2-bis(diisopropylphosphino)ethane; R = CH$_2$CMe$_3$] yielded the ketone RC(=O)R, along with (DIPPE)Fe(CO)$_3$[18]. Carbonylation of (DIPPE)FeRX gave mono- or bi-dentate acyls, depending on conditions[18]; these are described in Section 4b below.

Addition of DIPPE to FeX$_2$ produced the adduct (DIPPE)FeX$_2$; the dichloride was characterized by X-ray crystallography as a tetrahedral monomer, and EPR showed a high-spin configuration[19]. Likewise, (DPPE)FeX$_2$ [X = Cl and I] and (OPDP)$_2$FeX$_2$ [OPDP = 1,2-C$_6$H$_4$(PPh$_2$)$_2$ have been prepared. The latter existed in a high-spin, trans octahedral form for X = Cl, but for X = Br and I, ionic, low-spin five-coordinate forms also existed[20]. Crystal structures of (DEPE)$_2$FeI$_2$, (OPDP)$_2$FeCl$_2$·THF, (OPDP)$_2$FeI$_2$(MeCN)$_2$, and (OPDP)$_2$FeI$^+$ I$^-$ ·1.85 CH$_2$Cl$_2$ were determined, and interpreted in terms of transition from low-spin octahedral to high-spin octahedral to pentacoordinate as steric requirements of the diphosphine ligands increased[21]. The same interpretation was applied by a different group of workers to comparison of the structures of (DEPE)FeCl$_2$ and (DPrPE)FeCl$_2$[22]. [DPrPE = Pr$_2$PCH$_2$CH$_2$-PPr$_2$].

(Et$_3$P)$_2$FeX$_2$ were used as starting materials for preparation of iron-sulfur clusters[23]. Tris(triethyl phosphite)iron dichloride has been used to induce cyclization reactions of α,α-dichloroesters; an example is shown in Eq. 1[24].



(1)

Complexes of dihydrogen with diphosphine-coordinated iron have received extensive attention in 1988. Reduction of (DMPE)$_2$-FeCl$_2$ and analogs with ethyl and isopropyl groups with LAH gave *cis*-(DMPE)$_2$FeH$_2$, which was protonated by alcohols to form *trans*-(DMPE)$_2$FeH(H$_2$)$^+$, 1. The dihydrogen was readily displaced by nucleophiles[25], and the standard literature preparation of (DMPE)$_2$FeHCl was found to occur by chloride displacement on 1[26].

In contrast, protonation of *trans*-(DEPE)$_2$FeHX or (DPPE)$_2$FeHX with HBF$_4$ in THF resulted in loss of a (protonated) diphosphine ligand, with formation of (DEPE)FeX$_2$ and H$_2$, the pathway to the latter being proposed to involve metal protonation[27]. Protonation of (DEPE)$_2$FeH(N$_2$) followed a similar mechanism, but substitution of nucleophiles (CO, RCN) for nitrogen required dissociation of N$_2$[28].

NMR methods (T$_1$ determinations) have been applied to measurement of the H-H bond length in *trans*-$(DPPE)_2FeH(H_2)^+$, for which the value of 0.86(2) Å has resulted[29]. The barrier to exchange of hydrogen atoms between the terminal H and the η^2-H_2 increased in the curious order $Et_4 < Ph_4 < Et_2Ph_2$, and the H-H distance decreased in the same order, based on T_1 values[30]. The T_1 method has been applied in a broad survey to distinguish "nonclassical" hydrides (those containing η^2-H_2 moieties) from those having only M-H bonds. L_3FeH_4 [L = $EtPPh_2$] was represented as $L_3FeH_2(H_2)$ based on these measurements and IR data[31].

cis-$(PP_3)FeH_2$ [PP_3 = $P(CH_2CH_2CH_2PMe_2)_3$] was prepared by LAH reduction of the dichloride. Protonation with HBF_4 gave the fluxional $(PP_3)FeH^+$ cation; no $(PP_3)FeH_3^+$ was detected by these workers. Neutral ligands (N_2, CO, MeCN) readily replaced one hydride ligand, and photolysis resulted in loss of H_2 and insertion of the unsaturated iron into a C-H bond of a ligand methyl group[32]. A different group succeeded in preparing "exceptionally stable" *cis*-$(PP_3)FeH(H_2)^+$ by reducing $(PP_3)FeCl^+$ BPh_4^- with $NaBH_4$ under a hydrogen atmosphere. In the solid state and in solution at low temperature, the H and H_2 ligands occupied cis octahedral positions, but at ambient temperature the complex was described as trigonal bipyramidal, with an axial "H_3" unit[33].

The linear tetraphosphine $Ph_2P(CH_2CH_2PPh)_3Ph$ allowed formation of $(tetraphos)FeH(H_2)^+$ by reaction of the dihydride with HBF_4. The H and H_2 ligands were trans to each other and did not exchange. Use of HBF_4 in D_2O gave a single isomer of $(tetraphos)FeH(HD)^+$ [34].

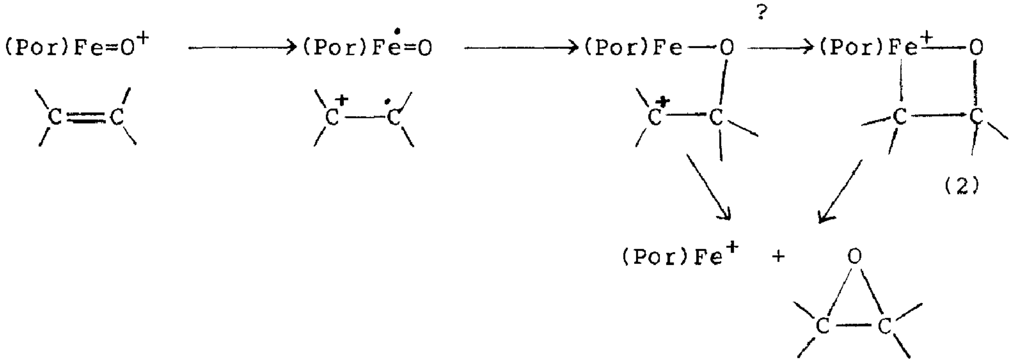
Ab initio calculations on $(H_3P)_4Fe(N_2)$ suggested a strong preference for end-on bonding and a principal role for back-donation. Only unattainable side-on bonding would lead, according to these calculations, to nitrogen activation[35].

$(Nitrilotriacetate)(H_2O)FeMe^-$ underwent Fe-C bond homolysis with an equilibrium constant of 8×10^{-4}, according to pulse radiolysis studies. Methyl radicals formed ethane by methyl abstraction at diffusion-controlled rates[36]. Ferrous nitrilotriacetate complexes formed Fe-C bonds upon reaction with CO_2^- in aqueous solutions; the kinetics and mechanisms were studied by pulse radiolysis methods[37].

The mechanism of reaction of iron porphyrins [(Por)Fe and $(Por)Fe^{-1}$] with alkyl bromides, i.e. S_N2 vs. electron transfer routes, has been discussed[38]. A reactive trimethylsilyliron(III) porphyrin has been synthesized by reaction of trimethylsilyllithium with (Por)FeCl. It underwent insertion of propylene oxide into the Fe-Si bond and homolysis of the Fe-Si bond. A diamagnetic $(Por)FeSiMe_3^-$ was formed similarly from (Por)Fe(HMPA)[39]. σ-Aryl compounds resulted from reaction of (Por)Fe with diaryliodonium salts in the presence of excess iron powder as reducing agent[40]. σ-Alkyl iron(II) phthalocyanines, first reported some time ago, have now been synthesized by reduction and alkylation of iron phthalocyanine and more fully characterized[41].

The magnetic behavior of various (Por)FeR [R = alkyl, aryl, or perfluoroaryl groups) has been studied. Perfluoroaryl ligands and low temperatures favored the high-spin state of the iron-(III)[42]. "Insertion" reactions of CO and CO_2 into the Fe-C bonds of (Por)FeR, to form acyl- and carboxylato-iron products, respectively, have been studied. A homolytic mechanism was favored for these atypical "insertion" reactions[43].

Reaction of diaryliodonium salts with hepatic cytochromes P-450 in the presence of reducing agents (NADPH or dithionite) gave σ-aryliron productslike those obtained with synthetic porphyrins[40]. The role, if any, of species containing carbon-iron bonds in cytochrome P-450-catalyzed oxidation reactions remains contentious. The rate of epoxidation of alkenes in such reactions has been found to correlate with the ionization potential of the alkene, and a mechanism (Eq. 2) has been suggested[44]. Extensive data in support of the acyclic carbocation shown in Eq. 2 resulted from detailed studies of the products from oxidation of *cis*- and *trans*-stilbenes by C_6F_5IO, catalyzed by (Por)FeCl[45].



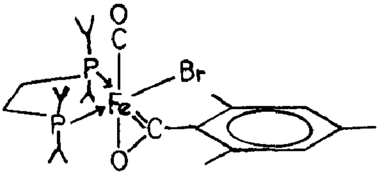
(2)

The reaction of diazoacetophenone with (tetraphenylporphyrinato)iron(II) was found to form the N-phenacyl product (X-ray), with no evidence to support the intermediacy of an Fe-CHR-N intermediate[46]. These authors concluded that "it is unlikely that carbene-insertion ..... intermediates will be detected during the N-alkylation of cytochrome P450 by diazo ketones." A contrasting set of results and conclusions will be discussed in Section 4f.

4b. Iron Monocarbonyls, e.g. $L_4Fe(CO)$

Distortions of heme-CO complexes from perfect Fe-C-O linearity and perpendicularity to the heme ring plane have been studied by resonance Raman and infrared methods. The data generally favored linearity, but significant tilting from the perpendicular and/or buckling of the heme were supported. The results were inconsistent with an EXAFS analysis of myoglobin carbonyl, which had indicated a Fe-C-O angle of 127° [47]. The kinetics of attachment of CO, isonitriles, and other small ligands to myoglobins on a picosecond time scale have been studied[48]. Metal to porphyrin back-bonding in (octaethylporphyrin)Fe(CO)(pyridine) and other six-coordinate porphyrin derivatives has been studied by resonance Raman spectroscopy[49].

Carbonylation of (DIPPE)FeRX [DIPPE = 1,2-bis(diisopropylphospino)ethane; R = neopentyl] gave, depending on CO pressure, (DIPPE)Fe(η^2-C(=O)R)(CO)X or the η^1-acyldicarbonyl. With R = mesityl, only the η^2-acyl, **2**, (ν_{CO} 1525 cm^{-1}) formed, even with excess CO. The crystal structure of **2** [Fe-C 1.85 Å, Fe-O 1.99 Å] suggested the carbenoid structure shown[18]. Carbonylation of iron(II) halides in argon matrices gave $X_2Fe(CO)_x$, whose IR spectra suggested different bonding modes for the CO, one possibly analogous to that in **2**[50].



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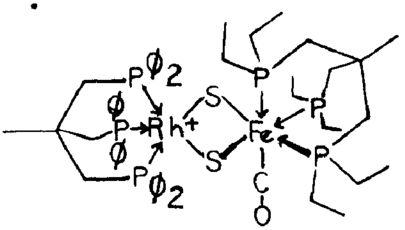
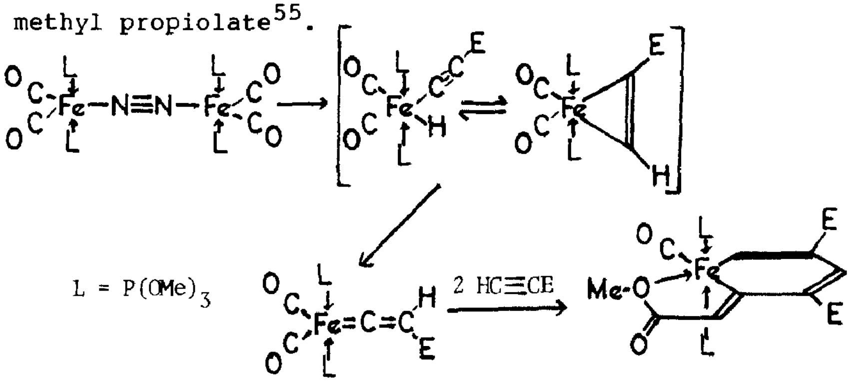


3

A process described as "demolition of the dithiocarbonate ligand" occurred when (triphos)Rh(S_2C=O)$^+$ was allowed to react with (etriphos)Fe^{2+} to form **3**[51]. Pentadentate YS_4 ligands [Y = O, S, NH] have been built up by template alkylation of *cis*-$Fe(CO)_2(1,2\text{-}S_2C_6H_4)_2{}^{2-}$ with $(BrCH_2CH_2)_2Y$ to form (YS_4)FeCO products[52,53]. With Y = S, a meso form resulted; with Y = O or NH, a trans form. Displacement reactions of the CO by phosphines and the like were studied[52].

Photoreaction of (DPPE)$Fe(CO)_2H_2$ or (DPPE)$Fe(CO)_2H(SiR_3)$ with R_3SiH [R = OMe, OEt, Me, Ph] gave fluxional products (DPPE)Fe(CO)$H_3(SiR_3)$. The hydrogens were not located in an X-ray structure of the product with R = OEt, but a *fac* arrangement of R_3Si, H, and H_2 ligands was indicated[54].

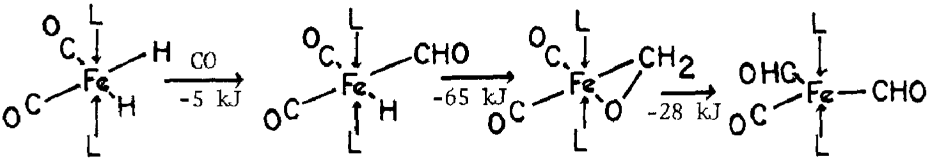
Reaction of methyl propiolate with (μ-N_2)$[Fe(CO)_2L_2]_2$ proceeded to form the bicyclic product (X-ray structure) as shown in Eq. 3[55]. Ethyne and phenylethyne gave the η^2-alkyne products, which underwent reversible conversion to the alkynyl hydride products shown, but did not give further addition as found for methyl propiolate[55].



(3)

4c. Iron Dicarbonyls, e.g. $L_3Fe(CO)_2$

Carbonyl "insertion" reactions of the compounds *cis*-FeMeX-$(CO)_2(PMe_3)_2$ [X = I, CN] have been studied by means of ^{13}CO labelling. The results in all cases supported migration of the methyl group to a cis carbonyl group with the entering CO occupying the vacated coordination site[56]. *Ab initio* calculations on *trans*-$L_2Fe(CO)_2$ [L = PH_3] having hydrido, formyl, and η^2-formaldehyde ligands have favored a hydrogenation process as outlined in Eq. 4, with the key step intramolecular reduction of a CO ligand by hydrogen migration from the bound formaldehyde[57]:

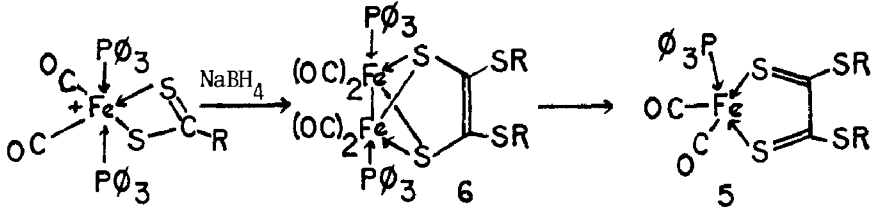


(4)

Reaction of $L_2Fe(CO)_2(MeCN)$ [L = various phosphines], made by reduction of the dihalides $L_2Fe(CO)_2X_2$ with sodium amalgam in acetonitrile, with methyl or ethyl iodide gave simple oxidative addition products $L_2Fe(CO)_2(R)(I)$ with unhindered phosphines. With bulkier phosphines, η^2-acyl products analogous to **2** resulted. A crystal structure of $(Ph_2MeP)_2Fe(CO)(\eta^2\text{-COMe})I$, **4**, gave results similar to those on **2** as far as the Fe=C and C-O bond lengths (1.83 and 1.23 Å) were concerned, but the O-Fe bond length (2.25 Å) was considerably longer than that in **2**. The iodide ligand was trans to the carbon, and the phosphine ligands mutually trans[58].

Dialkyltetrathiooxalate complexes **5** resulted from reaction of diiron complexes **6** with sodium amalgam or Lewis acids in the presence of air (Eq. 5)[59]. Multinuclear NMR studies of *cis*-Fe-

$(S_2CNR_2)_2(CO)_2$ have resulted in correlation of the ^{13}C NMR chemical shifts of the CO groups and the CO stretching force constants with the basicity of R_2NH. Substantial C═N double bond character was indicated[60].

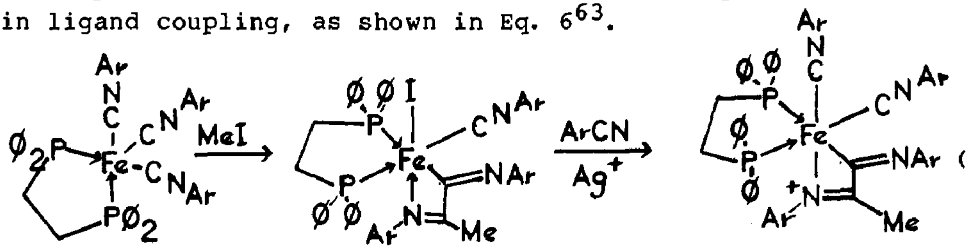


(5)

^{15}N NMR study of $PhN{=}N{=}Fe(CO)_2(PPh_3)_2^+$ and other diazenido complexes have provided criteria for bending about the nitrogens in the diazene ligands[61]. The HNC ligands in $(HNC)_2Fe(ophen)_2^+$ were functionalized by reaction with dicyclohexylcarbodiimide, giving the derivative having two :C≡N-C(=NR)NHR ligands [R = cyclohexyl][62].

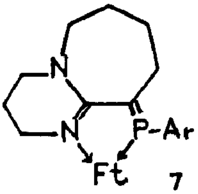
4d. Iron Tricarbonyls, e.g. $L_2Fe(CO)_3$

The "very air-sensitive" complexes $(DPPE)Fe(CNAr)_3$ and $(DPPM)Fe(CNPh)_3$ have been prepared, and their reactions with electrophiles studied. Protonation with NH_4^+ and reaction with Ph_3SnCl gave *mer*-$(DPPE)Fe(CNAr)_3El^+$; with El = H, the *fac* isomer readily formed on heating. Reaction with methyl iodide resulted in ligand coupling, as shown in Eq. 6[63].



(6)

A selective, high-yield synthesis of bis(phosphine)tricarbonyliron compounds, involving reaction of pentacarbonyliron with the phosphine in the presence of sodium borohydride in refluxing butanol, has been reported. The reaction sequence involved $Fe(CO)_4CHO^-$, $HFe(CO)_4^-$, and $HFe(CO)_3PR_3^-$ [64].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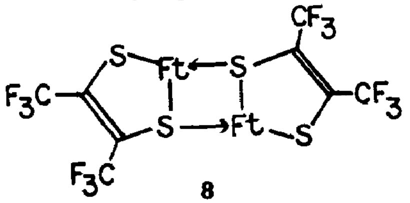
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The novel chelate complex 7 resulted from direct complexation of the free ligand[65]. The X-ray structure of $(\eta^2\text{-}Ph_2P\text{-}NEt\text{-}PPh_2)Fe(CO)_3$ has been reported[66]. The product of reaction of

3,4-bis(trifluoromethyl)-1,2-dithiete with iron carbonyls was, at least in the crystal, a dimer, **8**, of the expected (F_3C-C(=S)-C(=S)-CF_3)Fe$(CO)_3$. This contrasts with the closely related **5**, which is monomeric in the crystal, as are phosphine-substituted derivatives of **8**[67].

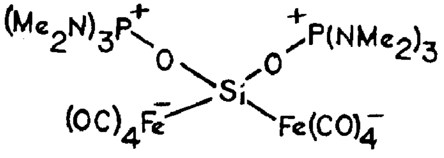
Bu_4N^+ Fe$(CO)_3(NO)^-$ has been used as a catalyst in nucleophilic displacement reactions of optically active allylic carbonates by malonate ion. Good enantioselectivity was obtained in this reaction, which presumably involved (η^3-allylic)Fe$(CO)_2$(NO) intermediates. These are further discussed in Sect. 5.

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

T_1 measurements have confirmed the "classical" structure (i.e. no direct H-H interaction) of H_2Fe$(CO)_4$[31]. Likewise, Mossbauer studies of the ^{57}Fe and ^{197}Au nuclei in $(R_3PAu)_2$-Fe$(CO)_4$ [R = cyclohexyl] indicated localized Au-Fe bonds without significant direct Au-Au interactions[68]. Further auration, to form $(R_3PAu)_3Fe(CO)_4^+$, was concluded to result in delocalized cluster bonding[68].

K^+ $HFe(CO)_4^-$, generated _in situ_ in methanol from K_2CO_3 and Fe$(CO)_5$, specifically catalyzed (up to 18 cycles) reduction of aryl iodides under one atmosphere of CO[69]. Iodide ion was found to react with $Fe_3(CO)_{12}$ to form $IFe(CO)_4^-$ [70].

Two examples of "donor-stabilized silylene complexes," which look to this reviewer like rather normal tetracovalent silicon compounds, have been reported. One, $(Me_2N)_3P^+OSi(OR)_2$-$Fe(CO)_4^-$ [R = _tert_-butyl], resulted from reaction of $(RO)_2SiCl_2$ with $Na_2Fe(CO)_4$ in THF, followed by addition of hexamethylphosphoramide. It showed a Si-Fe bond length of 2.29 Å in the crystal structure[71]. The analogous reaction of $SiCl_4$ produced **9**, with Si-Fe distances of 2.34 Å and Si-O 1.75 Å[72].



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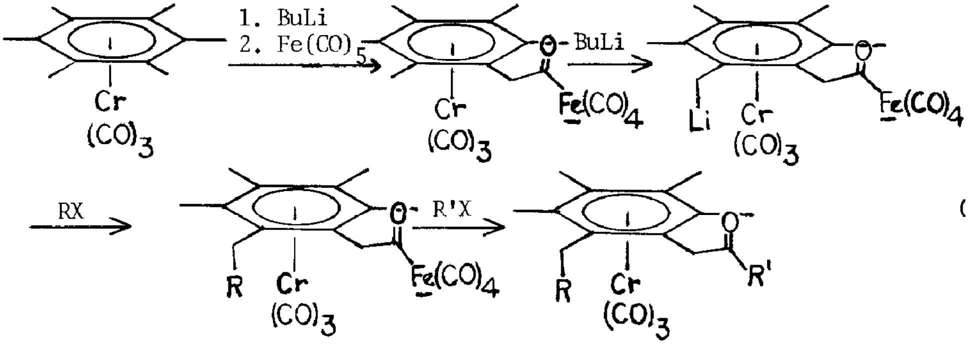
$Na_2Fe(CO)_4$ displaced chloride from (η-C_6H_5Cl)Cr$(CO)_3$ to produce the coordinated aryl-$Fe(CO)_4^-$ anion. Reaction of (ArLi)Cr$(CO)_3$ with Fe$(CO)_5$ produced the aroyliron products, [ArC(=O)$Fe(CO)_4^-$]Cr$(CO)_3$, which gave ketones on reaction with alkyl halides[73]. Use of organoiron intermediates (Eq. 7) resulted in introduction of substituents onto _ortho_-methyl groups of coordinated hexamethylbenzene[74].

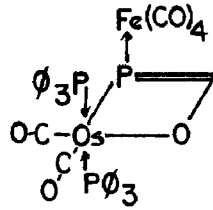
Reaction of $(Me_3Si)_3P{\rightarrow}Fe(CO)_4$,**10**, with methanol gave the unsubstituted phosphine complex $H_3P{\rightarrow}Fe(CO)_4$, which could be deprotonated using butyl-lithium[75]. The crystal structure of **10** showed the expected axial phosphine substitution, but with a sterically-lengthened P→Fe bond distance of 2.34 Å[76]. Reaction of $ArPCl_2$ [Ar = 2,4,6-*tert*-$Bu_3C_6H_2$-] with $Na_2Fe_2(CO)_8$ afforded, along with dinuclear products, $ArPH_2{\rightarrow}Fe(CO)_4$[77]. Similarly, $PhC{\equiv}CPHR{\rightarrow}Fe(CO)_4$ [R = N(*i*-Pr)$_2$, NMe_2, Me] was produced by reaction of $PhC{\equiv}CPRCl$ with $HFe(CO)_4^-$[78]. Cluster products (see Sect. 10c) resulted from its reaction with $Co_2(CO)_8$.



(7)

Trimethylamine oxide-induced reaction of $Fe(CO)_4(CS)$ with phosphines resulted in preferential replacement of a CO ligand to yield $(OC)_3Fe(CS)(PR_3)$ (two isomers in the infrared) and $(OC)_2$-$Fe(CS)(PR_3)_2$[79]. The cyclopentadienyl ligand in $(OC)_4FePPh_2C_5H_5$ did not form a Diels-Alder dimer[80].

New $Fe(CO)_4$ complexes of unsaturated phosphorus compounds have continued to be synthesized. **11** was prepared by reaction of the free metallacycle with $Fe_2(CO)_9$[81]. RCH=CH-CR=P[→Fe(CO)$_4$]-NR_2 [R = $SiMe_3$] was made similarly[82]. Complexation of Fp*P=P-Ar [Ar = 2,4,6-tri-*t*-BuC_6H_2] resulted in coordination of $Fe(CO)_4$ to the phosphorus bearing the Fp* group[83]. A more complex doubly-coordinated diphosphene, **12**, resulted when $ArPCl_2$ [Ar = 2,5-dimethyl-1,2,3-diazaphospholyl] reacted with $HFe(CO)_4^-$. Small amounts of $ArPH_2{\rightarrow}Fe(CO)_4$ and $ArPHCl{\rightarrow}Fe(CO)_4$ were also ob-



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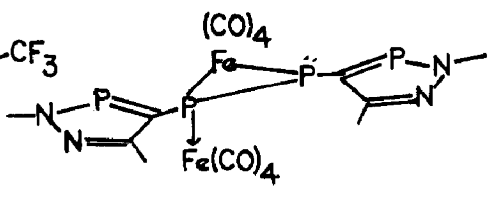

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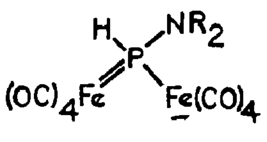

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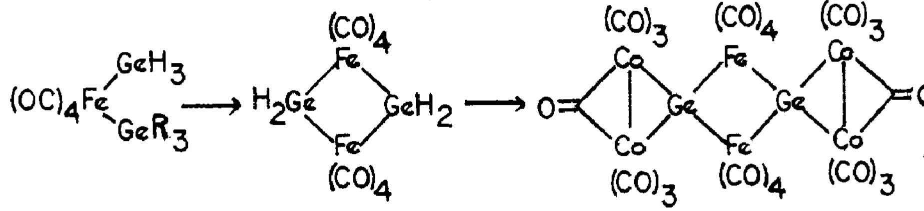
tained[84]. Unfortunately, although a crystal structure was reported for **12**, the Fe-P bond lengths were not reported. With $(R_2N)_2PCl$ [R = Me, Et, i-Pr], $HFe(CO)_4^-$ reacted to form **13**[85].

Reaction of $ROC(=O)-Fe(CO)_4^-$ with methyl bromoacetate gave isolable $RO_2CFe(CO)_4CH_2CO_2Me$ [R = Me, CMe_3], which decomposed thermally under a CO atmosphere to form malonate esters and iron pentacarbonyl. These observations may be relevant to the carbonylation reactions of active organic halides to form esters[86]. Reaction of $Na_2Fe(CO)_4$ with tetrabromodurene [1,2,4,5-$(BrCH_2)C_6H_2$] was reported to produce the isolable bis-(ferracycle), which decomposed at 40° to a bis(diene) complex[87].

Mixed tetracarbonyldigermyliron derivatives, $R_3GeFe(CO)_4$-GeR'_3, having 1-5 methyl groups attached to germanium, have been described[88]. The tendency to eliminate a methylgermane (Eq. 8) increased dramatically with increasing number of methyl groups. Diferradigermetanes (Eq. 8) resulted[89]. Related diferradistannetanes, having Cl and $W(CO)_5^-$ groups on the cyclic tin atoms, have also been prepared, and the crystal structure of the disodium salt has been determined[90].



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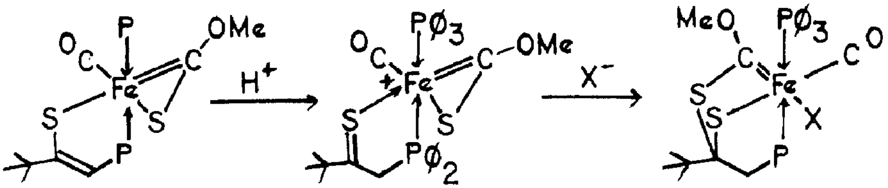
(8)

$(PhS)_2Fe(CNR)_4$ [cis and trans isomers, R = cyclohexyl] were synthesized by addition of RNC to $Fe(SPh)_4^{2-}$. The cis isomer was able to coordinate a $Mo(CO)_4$ group through the two sulfur atoms[91]. Hydroisocyanation reactions of $Fe(CN)_2(CNH)_4$ with reactive alkenes proceeded to form hexa(alkyl isocyanide) complexes, $Fe(CNR)_6^{2+}$ [92].

4f. Carbene Complexes $R_2C=Fe(CO)_4$

Two examples of η^2-acyl complexes, **2**[18] and **4**[58], having significant carbenoid character, have already been described. Reactions of an analogous η^2-thioacyl compound, in which the carbenoid thioacyl group is retained, are shown in Eq. 9. The X-ray structures of both products shown were reported[93].



(9)

A cyclopropenylidene complex, $(Ph_3P)(OC)_3Fe{=}C_3Ph_2$, resulted from reaction of $(Ph_3P)(OC)_3FeSiMePh_2^-$ with 3,3-dichloro-1,2-diphenylcyclopropene[94], presumably a consequence of elimination of a chlorosilane from the initial adduct. It has been reported (if Chemical Abstracts is to be trusted) that $(OC)_4Fe{=}C(OEt)C_6Cl_5$ resulted when (isoprene)$Fe(CO)_3$ was treated with pentachlorophenyllithium followed by triethyloxonium fluoroborate[95].

Reaction of $(OC)_4Fe{=}C(R)OEt$ [R= Me, Ph] with allenes $R'CH{=}C{=}CH_2$ [R' = H, OMe, Ph] resulted in formation of trimethylenemethyl complexes, $C(CH_2)(CHR')[C(R)OEt]Fe(CO)_3$, 15[96]. Reactions of the dioxycarbene $(OC)_4Fe{=}\underline{COCH_2CH_2O}$ have been studied. The complex decomposed thermally to form ethylene and carbon dioxide, but with trimethylamine oxide formed ethylene carbonate. Hydrogenation gave 1,3-dioxolane[97].

Reaction of Fe(II) porphyrins with diazopropiophenone gave $(Por)Fe{=}C(Me)C({=}O)Ph$; an analogous ketocarbene complex was also obtained using an iodonium ylide. Reaction with acids or oxidizing agents caused the carbene complexes to rearrange to N-(ketoalkyl)porphyrins[98]. This result contrasts markedly with that reported in Sect. 4a, that reaction of (Por)Fe with diazoacetophenone gave N-phenacyl porphyrin directly[46]. The results could be reconciled with the assumption that $(Por)Fe{=}CHC({=}O)Ph$ in the former study had rearranged to the N-phenacyl product before isolation.

Reduction of DDT [Ar_2CHCCl_3, Ar = 4-ClC_6H_4-] by (tetraphenylporphinato)iron(II) in the presence of excess stoichiometric reducing agent gave a red complex, shown by crystallography to be $(Por)Fe{=}C{=}CAr_2$, with Fe=C and C=C bond lengths of 1.699 and 1.336 Å, respectively[99]. This contrasts with the previously proposed N-vinylporphyrin structure, and further supports the possibility of intervention of carbene complexes in cytochrome-catalyzed reactions.

A very similar Fe=C bond distance [1.70(1) Å] was found in the structure of $L(pc)Fe{=}C{=}Fe(pc)L$ [pc = phthalocyaninato dianion, L = axial 1-methylimidazole], prepared from (pc)Fe and CI_4, with subsequent attachment of the imidazole ligands[100]. Mössbauer spectra of several μ-carbido derivatives of iron phthalocyanines and porphyrins, including some cytochrome enzymes, have been obtained and analyzed[101].

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

A relatively compact and accurate basis set for calculations on organometallic species has been proposed, based on studies including total geometry optimization on $Fe(CO)_5$ and other representative compounds[102]. The lowest excited state of $Fe(CO)_5$ has been explored theoretically through use of Complete Active Space SCF wavefunctions, and mechanisms of photochemical reactions discussed[103].

Electrochemical reduction of $Fe(CO)_5$, using microelectrodes in cyclic voltammetry, has been reinvestigated. Initial two-electron reduction to form $Fe(CO)_4^{2-}$ was followed by rapid reaction of the latter with $Fe(CO)_5$ ($k_2 = 6 \times 10^6\ M^{-1}sec^{-1}$) to form $Fe_2(CO)_8^{2-}$; contrary to earlier assumptions, dimerization of the radical-anion $Fe(CO)_4^-$ was not an important route to the di-iron dianion[104].

The electron transmission spectrum of $Fe(CO)_5$ has been measured by two groups of workers, whose measurements and interpretations appear generally to be consistent with each other and with theory[105,106].

$Fe(CO)_5$ could be used catalytically for carbonylation of benzyl bromide to form $(PhCH_2)_2C{=}O$ or $PhCH_2CO_2H$ under liquid-liquid phase transfer conditions. Effects of experimental variables on yields of ketone or acid were studied, and a double catalytic cycle proposed[107]. Co-thermolysis of "homohypostrophene" and $Fe(CO)_5$ gave four diastereomeric dimer ketones, whose structures have been assigned spectroscopically. A mechanism was proposed[108].

5. η^2-ALKENE AND η^3-ALLYL COMPLEXES

This review has already described η^2-$Fe(CO)_4$ complexes of a diphosphene, **12**, η^2-acyl complexes, **2** and **4**, in which the acyl group functions as a three-electron donor, and the similar thioacyl complexes in Equation 9.

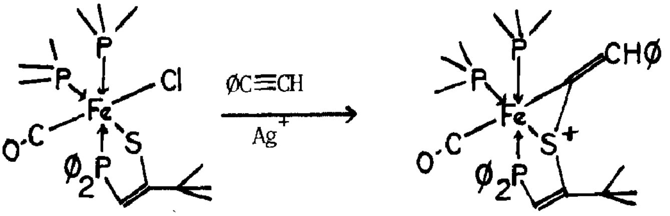
Equation 4 outlined the results of some *ab initio* calculations on hydrogenation of CO in the coordination sphere of iron, which included $(\eta^2\text{-}CH_2O)Fe(CO)_2(PH_3)_2$ as a probable intermediate[57]. Further calculations by the same group have explored the effect of the other ligands on the $(\eta^2\text{-}CH_2O)Fe$ interactions, specifically in the $Fe(CO)_4$ and $Fe(PH_3)_4$ cases. The importance of Fe $d_{xz} \rightarrow$ formaldehyde π^* donor interaction in bonding was emphasized[109]. The calculations were also extended to η^2 complexes of acetone and of thioformaldehyde[110].

In the experimental realm, $(\eta^2\text{-}RCH{=}O)Fe(PEt_3)_2(CO)_2$ [R = H, Ph] have been prepared by replacement of the dinitrogen ligand from $(\mu\text{-}N_2)[Fe(PEt_3)_2(CO)_2]_2$. The results (bond lengths in Å) of the X-ray crystallographic study of the benzaldehyde complex[111] are compared with the theoretical results [57,109,110] below:

	THEORY	EXPERIMENT
	$(\eta^2\text{-}CH_2O)Fe(CO)_2(PH_3)_2$	$(\eta^2\text{-}PhCHO)Fe(CO)_2(PEt_3)_2$
Fe-C	1.952	2.04
C-O	1.311	1.29
Fe-O	1.971	1.96

Considering the effects of the ethyl and (especially) phenyl substituents, the comparison is fairly satisfactory.

A η^2 complex of an alkylated thioketene resulted from the reaction shown in Equation 10[112]. The reaction was proposed to involve intramolecular sulfur attack on a transient phenyvinylidene-iron intermediate. A η^2-coordinated carbon-boron double bond occurred in **16**, despite substantial steric bulk. The Fe-B and Fe-C bond lengths were 2.125 and 2.190 Å, respectively[113].



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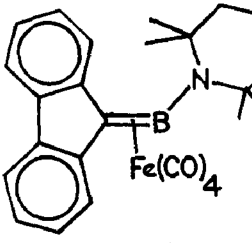
Photochemical formation of $(\eta^2\text{-ethene})Fe(CO)_4$ in low-temperature nitrogen or ethene matrices has been studied by Mössbauer spectroscopy[114]. Ultraviolet photolysis of $Fe(CO)_5$ physisorbed on porous Vycor glass under a 1-pentene atmosphere led to $(\eta^2\text{-1-pentene})Fe(CO)_4$. Continued photolysis led to an active intermediate[$(\eta^2\text{-pentene})Fe(CO)_3$ or $(\eta^3\text{-pentenyl})Fe(CO)_3H$] capable of efficiently promoting alkene isomerization[115].

Thermal or photochemical exchange reactions of $L_2Fe(CO)_3$ [L = η^2-*trans*-cyclooctene] with other alkenes gave diastereomeric mixtures of $(\eta^2\text{-alkene})LFe(CO)_3$, some of which could be separated by fractional crystallization. Crystal structures [alkene = *trans*-cyclooctene and dimethyl fumarate] showed trigonal bipyramidal structures with equatorial alkenes[116].



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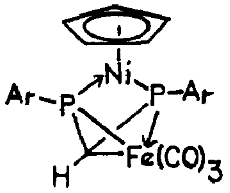

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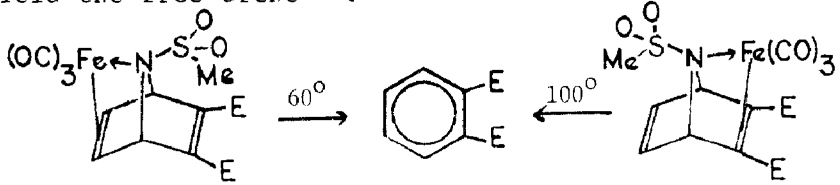
Equation 3 showed, for the case of ethyl propiolate, formation of η^2-alkyne complexes and their reversible conversion in solution into alkynyl hydride complexes. The same [with L =

PEt$_3$] occurred with ethyne and phenylethyne, though no evidence for further cycloaddition via a vinylidene was obtained[117].

Reaction of N-acyl or N-sulfonyl 7-diazabicyclo[2.2.1]heptadienes with Fe$_2$(CO)$_9$ at room temperature gave stable η^3-complexes, which underwent nitrene extrusion at 60-100° (Eq. 11) to yield the free arene[118].



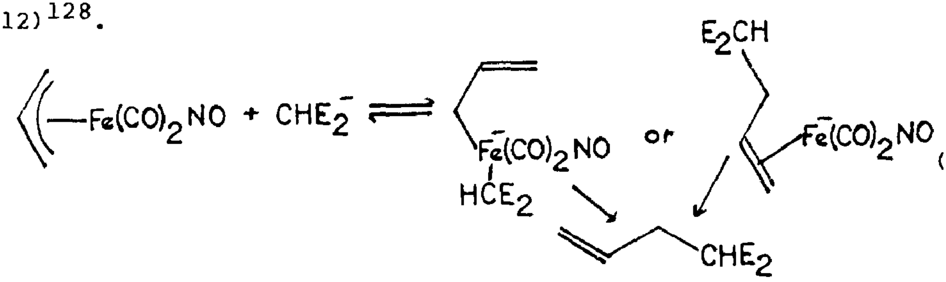
(11)

Reaction of the (η^3-heteroallyl)iron anion, $\mathrm{(ArP\overset{\cdots}{-}CH\overset{\cdots}{-}PAr)}$-Fe(CO)$_3^-$ [Ar = 2,4,6-tri-*t*-BuC$_6$H$_2$-], with nickelocene produced the cyclic η^3 complex, **17**[119].

The EPR spectrum of (η^3-allyl)Fe(CO)$_3$, produced by photolysis of Fe(CO)$_5$ in the presence of propene in pentane at 163 K, showed an iron-centered radical with strong coupling to two protons[120]. (η^3-C$_3$H$_5$)Fe(CO)$_4^+$ was obtained in 18% yield by photochemical reaction of allyl alcohol with Fe$_3$(CO)$_{12}$ in the presence of HBF$_4$. Other cationic allylic complexes were obtained similarly[121]. Cationic complexes (η^3-C$_3$H$_4$R)Fe(CO)$_3$PPh$_3^+$ were obtained by electrophilic attack on (η^4-diene)Fe(CO)$_2$PPh$_3$ complexes. The phosphine plays an important role in directing the electrophilic attack[122].

Electron-rich aromatic and heteroaromatic compounds were sufficiently nucleophilic to attack (η^3-allyl)Fe(CO)$_4^+$, giving allyl-substituted aromatics. The arenes generally reacted at the less highly substituted end of unsymmetrical allyl groups[123]. However, (C$_3$H$_5$)Fe(CO)$_4^+$ reacted with (ethene)Pt(PPh$_3$)$_2$ by transfer of the allyl group, forming (C$_3$H$_5$)Pt(PPh$_3$)$^+$ [and (C$_2$H$_4$)-Fe(CO)$_4$?][124]. Reaction of the cation (C$_3$H$_5$)Fe(NO)$_2$L$^+$ [L = P(OMe)$_3$] with (1,2,5,6-η^4-cyclooctatetraene)CoCp* resulted in C-allylation, with subsequent transannular bonding in the eight-membered ring[125].

A comparison of chemical ionization mass spectra of (η^3-C$_3$H$_5$)Fe(CO)(NO)(PPh$_3$) using both protonating and non-protonating reagent gasses indicated that protonation did not occur on the allyl group[126]. Reactions of *(E)*- and *(Z)*-butenyl mesylates with Na$^+$ Fe(CO)$_3$(NO)$^-$ gave distinct (η^3-butenyl)Fe(CO)$_2$(NO) complexes, which reacted with dimethylmalonyl anion to give *(E)*- and *(Z)*-MeCH=CHCH$_2$CHE$_2$ with retained geometries. Substitution of triphenylphosphine for a carbonyl ligand in either butenyl complex, however, gave only the *syn*-(η^3-butenyl)Fe(CO)(NO)(PPh$_3$)[127]. Mechanistic studies of the reaction of (C$_3$H$_5$)Fe(CO)$_2$(NO) with carbanions has suggested reversibility of the initial attack (Eq. 12)[128].

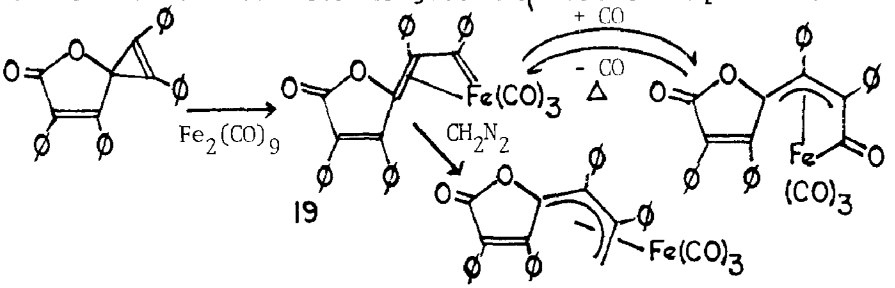


(12)

Reaction of siloxy-substituted allylic complexes, $(Me_3SiO-C(R)CHCH_2)Fe$, with sodium dimethylmalonate and related carbanions has resulted in formation of $RC(=O)CH_2CH_2CHE_2$ and derivatives, again by attack of the nucleophile at the less substituted end of the allyl group[129]. The reaction failed, however, when a 2-alkyl substituent was also present on the allylic moiety[129]. Reaction of siloxyallyl complexes, $(\eta^3-Me_3SiOC(R^1)CHCHR^2)Fe(CO)_2(NO)$ with the electrophile propargyl bromide gave $R^1C(=O)CH_2CH(R^2)CH_2C\equiv CH$ [130].

Alkylation of sodium dimethylmalonate by crotyl and α-methallyl acetates or chlorides in the presence of $Fe(CO)_2(NO)_2$ did not give consistent regioselectivities, ruling out a common η^3-allylic intermediate[131]. Use of $Fe(CO)_3(NO)^-$ to catalyze alkylation of malonate by allylic carbonates resulted in formation of products with high retention of stereochemistry; thus, *(R)*,*(E)*-$PhCH=CHCH(Me)OCO_2Me$ gave *(R)*,*(E)*-$PhCH=CHCH(Me)CHE_2$ in 73% enantiomeric excess[132].

$(\eta^3$-Pentadienyl$)_2FeL_2$, **18**, [L = PMe_3] was produced when two equivalents of K^+ $C_5H_7^-$ reacted with L_2FeCl_2. Depending on the size of L, **18** more or less rapidly underwent intramolecular displacement of L to form $(\eta^3-C_5H_7)(\eta^5-C_5H_7)FeL$[133], further discussed in Section 7a. The vinylcarbene complex **19** (Eq. 13) rearranged to η^4-vinylketene products upon reaction with phosphines or with CO, in a process which was reversed upon heating. Reaction with diazomethane gave a η^4-diene complex[134].



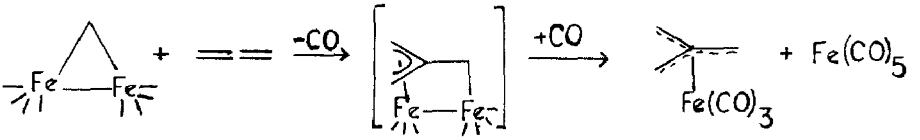
(13)

Reaction of triphenylcyclopropenyl chloride with $Fe(CO)_3(NO)^-$ gave 4% of $(\eta^3-C_3Ph_3)Fe(CO)_2(NO)$; the main product was the oxocyclobutenyl complex, $(\eta^3-C_3Ph_3CO)Fe(CO)_2(NO)$, **20**[135].

6. COMPOUNDS WITH η^4-LIGANDS

6a. Trimethylenemethyl Complexes

The parent complex, $[C(CH_2)_3]Fe(CO)_3$, was formed (Eq. 14) by formal methylene transfer from $(\mu\text{-}CH_2)Fe_2(CO)_8$ to allene[96]. More highly substituted derivatives, **15**, of $TMMFE(CO)_3$ resulted from the related reaction of $(OC)_4Fe{=}C(R)OEt$ with $R'CH{=}C{=}CH_2$[96].

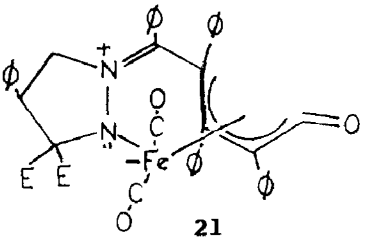


(14)

Several electron-rich $TMMFeL_3$ compounds [L = PMe_3, PMe_2Ph; L_3 = $MeC(CH_2PMe_2)_3$] have been prepared by reduction of a mixture of $CH_2{=}C(CH_2Cl)_2$ and L_2FeCl_2/L with sodium amalgam or magnesium in THF[136]. The complexes were very readily oxidized in a reversible, one-electron oxidation, as shown electrochemically and by reaction with Ag^+ OTf^-. A crystal structure of the stable radical-cation $TMMFe(PMe_3)_3^+$ OTf^- was on the whole quite similar to that of the closed-shell $TMMFe(CO)_3$[136].

6b. Complexes of Acyclic Dienes, including Heterodienes

Anion states of η^4-diene complexes have been investigated by electron transmission spectroscopy. Threshold features showed CO π^* resonances at about 2 eV, similar to $Fe(CO)_5$, and destabilization of higher diene π^* orbitals compared to the free dienes. Attachment of low-energy electrons resulted in dissociation of CO in most cases, as shown by mass spectrometry[106].



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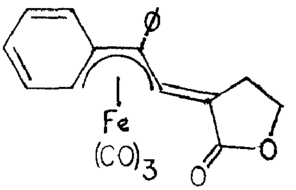

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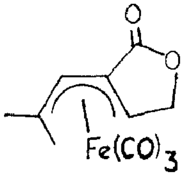
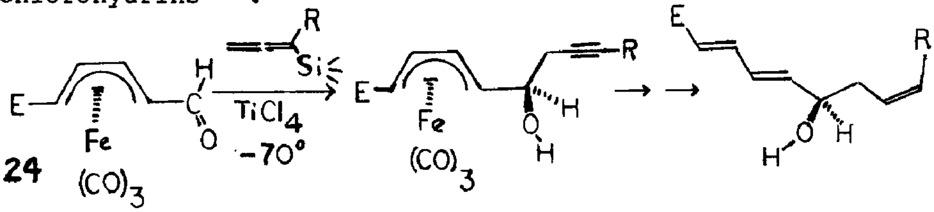


23

The crystal structure of $(\eta^4\text{-}PhCOOCH{=}CH{-}CH{=}CHOCOPh)Fe(CO)_3$ has been reported[137]. The crystal structure and Mössbauer data for vinylketene complex **21**, formed by addition of diphenylacetylene to the cyclic diazene-$Fe_2(CO)_6$ complex, have been reported[138]. The related phenylallene complex **22** (X-ray) was among the products of photolysis of the free ligand with $Fe(CO)_5$; also formed was **23**, by hydrogen rearrangement, and (principally) a diiron complex, **80**[139] (See Section 9a).

Resolution of η^4-diene complexes and their use in asymmetric synthesis are receiving increasing attention. Use of (+)-neomenthyldiphenylphosphine as a ligand to form (diene)Fe(CO)$_2$L led to readily separable diastereomers. Complexes of MeCH=CH-CH=CHCOR [R = H, OMe] and 1-methoxycyclohexadiene were resolved in this manner, and their absolute configurations established by crystallography and CD spectroscopy[140]. $(CH_2=CH-C(CO_2Et)=CH_2)Fe(CO)_3$ was resolved by enantioselective hydrolysis to the acid using pig liver esterase, allowing isolation of each enantiomer of the acid in high optical purity[141].

(1R,4S)-**24** was used as a starting material in enantioselective synthesis (Eq. 15) of leucotriene-B$_4$. The tricarbonyliron group served both to fix the configuration and to protect the double bonds[142]. Addition of a 1-pentenyl group to the aldehyde group of **24** gave an allylic alcohol which, without decomplexation, underwent epoxidation using VO(acac)$_2$ and tert-butyl hydroperoxide in toluene, in 85% yield. Both erythro and threo diastereomers were obtained[143]. Reaction of **24** with ICH$_2$Cl and BuLi in THF at -80° likewise produced a mixture of diastereomeric chlorohydrins[144].

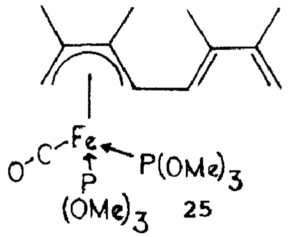


(15)

Friedel-Crafts acylation of (η^4-butadiene)tricarbonyliron complexes bearing 1-trimethylsilyl substituents generally occurred at the 4-position, the silyl group being retained in the product. Only when the 4-position was alkylated did replacement of the silyl substituent occur[145]. Electrophilic attack on diene complexes was facilitated by replacement of one carbonyl ligand by a triphenylphosphine ligand; thus, $(\eta^4-C_4H_6)Fe(CO)_2PPh_3$ was readily protonated to form $(\eta^3-MeCH-CH-CH_2)Fe(CO)_3PPh_3{}^+$[122].

The preparation of the phosphonic ester $(E,E-BuCH=CH-CH=CH-CH_2P(=O)(OMe)_2)Fe(CO)_3$ has been described. The stable sodio derivative reacted readily with unhindered aldehydes in the Wittig-Horner reaction to produce triene complexes, in 45-90% yield[146]. Reaction of bis(η^4-2,3-dimethylbutadiene)Fe(CO) with excess trimethyl phosphite occurred with ligand coupling to form **25** in 87% yield[147].

Electron-rich complexes of o-xylylene, $[1,2,7,8-\eta^4-C_6H_4(CH_2)_2]FeL_3$ [L = PMe$_3$, PMe$_2$Ph, etc.] have been prepared by addition of the Grignard reagents $o-C_6H_4(CH_2MgCl)_2$ or o-



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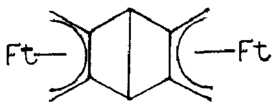

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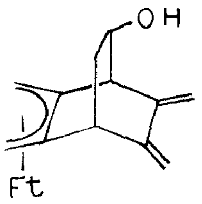
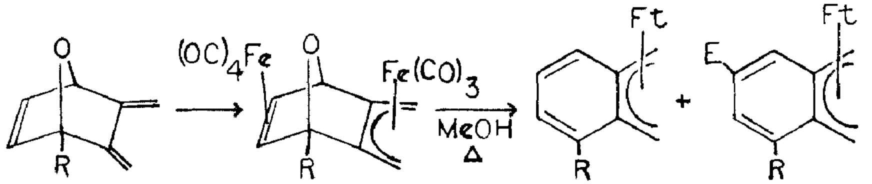


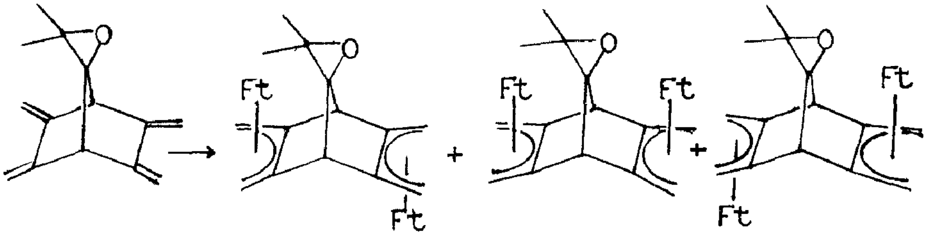
27

$MeC_6H_4CH_2MgBr$ to L_2FeCl_2, or by coreduction of L_2FeCl_2 and $C_6H_4(CH_2Cl)_2$ with magnesium[135]. Reaction of tetrabromodurene with $Na_2Fe(CO)_4$ was claimed to produce **26**[87], but some questions exist on reproducibility of this result. Further *o*-xylylene complexes resulted from deoxygenation of an oxabicycloheptene, as shown in Eq. 16. Oxidation of these complexes resulted in formation of 2-indanones[148].



(16)

Diels-Alder reactions of the free diene unit of **27** and of its tosylate and benzoate derivatives have been studied[149]. Complexation of a related tetraene (Eq. 17) initially incorporated tricarbonyliron groups only on the two exo faces. These exo complexes in turn reacted without facial selectivity to produce the three bis[$Fe(CO)_3$] complexes shown[150].



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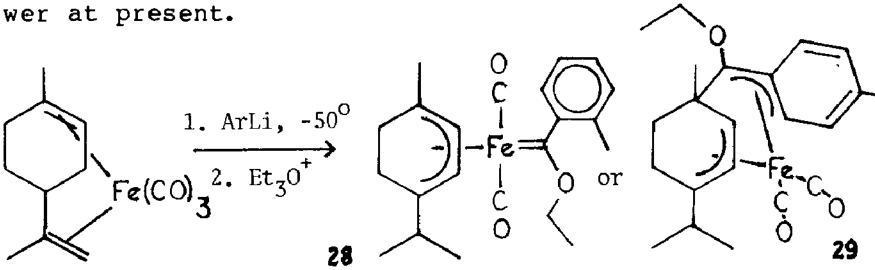
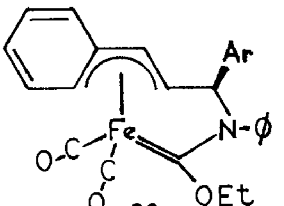
Several papers by chemists from Shanghai have described the rearrangements which have ensued when (diene)tricarbonyliron complexes were treated with aryl-lithium reagents at low temperature to form acylferrates, which were alkylated with triethyloxonium fluoroborate to form (diene)(ethoxyarylcarbene)dicarbonyliron products, which often rearranged to give novel products by ligand coupling reactions. In the case of (η^4-limonene)tricarbonyliron and *o*-tolyl-lithium, the carbene complex **28** (with a rearranged diene) was isolated and characterized by X-ray diffraction; with less hindered aryl-lithiums, rearrangement to a novel bis(η^3) product, **29**, occurred (Eq. 18)[151,152]. Further examples of the latter type of product are discussed in Section 8 of this review. The reaction sequence has been applied to (isoprene)tricarbonyliron, apparently to give rearranged products $[C_5H_8C(OEt)Ar]Fe(CO)_2$[95], but the detailed structures of the products (though probably analogous to **29**) are not available to the reviewer at present.



(18)

Application of this reaction sequence to a heterodiene complex, (η^4-PhCH=CH-CH=NPh)Fe(CO)$_3$, evidently followed a somewhat different course from the one described above, in which the aryllithium attacked a carbonyl ligand. Formation of the product **30** clearly indicates initial attack on the azadiene ligand, followed by migration of nitrogen from Fe to CO. Reaction of **30** with Lewis bases resulted in displacement of the phenyl ring from coordination[153]. Attack of methyl-lithium at -78° on [η^4-PhCH=CH-C(Me)=NPh]Fe(CO)$_3$ was not analogous to the above-described aryl-lithium attack; the eventual product was 2,5-dimethyl-1,3-diphenylpyrrole[154].

Electrochemical oxidation of [η^4-PhCH=CH-C(Me)=O]Fe(CO)$_2$L has been studied[155]. A number of α,β-unsaturated ketones containing a phosphite appendage have been designed, synthesized, and coordinated to iron carbonyl units, to give products such as **31**. **31** [R = Me] underwent nucleophilic attack (Michael addition) by LiCMe$_2$CN in a highly face-selective manner, at least 99% from the lower face as drawn below[156].



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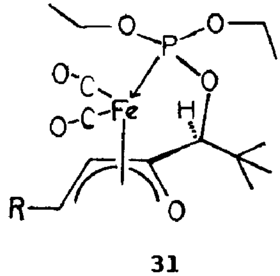

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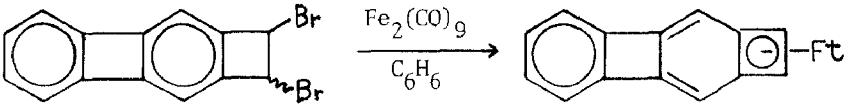
6c. Complexes of Cyclic Dienes

Variable temperature infrared studies of (η^4-norbornadiene)-Fe(CO)$_3$ have revealed coalescence phenomena like those more commonly observed in NMR spectra, but of course on a much faster time scale. Line shape analysis revealed an activation energy of about 6 kJ/mol for CO site exchange[157].

The crystal structure of (η^4-cyclobutadiene)$Fe(CO)_3$ at -45° has been determined, and the ring found to be square within experimental error. A study of the temperature dependence of the PMR spin-lattice relaxation time led to a rotational barrier of 22.6 kJ/mol in the solid state[158]. Electron transmission spectroscopy of $(C_4H_4)Fe(CO)_3$ indicated a significant destabilization of the π_3^* orbital due to interaction with iron 3d orbitals. Attachment of low energy electrons caused a complex process which resulted in loss of C_2[106]. Other (cyclic diene)$Fe(CO)_3$ complexes principally lost CO on electron attachment[106].

Reaction of a linearly annulated dibromocyclobutabiphenylene with $Fe_2(CO)_9$ gave the annulated cyclobutadiene complex (Eq. 19) in unusually high (91%) yield, whereas the angularly fused analog gave no cyclobutadiene complex[159]. A vinylcyclopropene complex,



(19)

$[\eta^2\text{-}CF_2{=}CF\text{-}(C_3Ph_3)]Fe(CO)_4$ rearranged on irradiation to form the substituted cyclobutadiene complex $[\eta^4\text{-}C_4Ph_3(CF_3)]Fe(CO)_3$[160]. A chiral, cationic cyclobutadiene complex $[\eta^4\text{-}C_4Ph_3(OMe)]Fe(CO)(NO)(PPh_3)^+$ was prepared from the η^3-oxocyclobutenyl complex, **20**, by introducing a triphenylphosphine ligand and then O-methylation with trimethyloxonium fluoroborate[135].

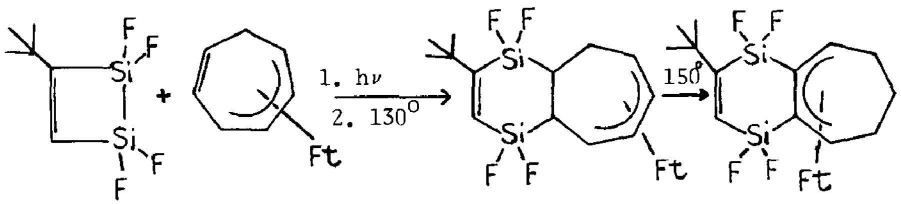
The silicon atom in the silole complex (η^4-1,1-difluoro-2,5-diphenylsilacyclopentadiene)tricarbonyliron accepted a fluoride ion when treated with KF and 18-crown-6. The crystal structure of the resulting pentacoordinate silicate complex and its variable temperature ^{19}F NMR behavior have been reported[161]. Heterocyclic complexes **32** [Y = Se[162], PPh[163]] have been prepared by direct reaction of the free heterocycles [Y = Se] or their dimers [Y = PPh] with iron carbonyls. When an isopropenyl group replaced the C-methyl group, complexation of the diene occurred rather than complexation of the ring heterodiene[163].

[Tetra(<u>tert</u>-butoxy)cyclopentadienone]tricarbonyliron [X-ray structure] resulted from reaction of di-<u>tert</u>-butoxyethyne with $Fe_2(CO)_9$. Treatment with trifluoroacetic acid removed the <u>tert</u>-butyl groups to yield (tetrahydroxycyclopentadienone)$Fe(CO)_3$, which was converted to croconate dianion upon reaction with oxygen under basic conditions[164]. The acidity and fluxionality of $[(HO)_4C_5{=}O]Fe(CO)_3$ would be of interest.

The crystal structure of (η^4-1,1-dichloro-1-silacyclohexa-2,4-diene)tricarbonyliron has been reported[165]. The $Fe(CO)_3$

complexes of ergosteryl and 7-dehydrocholesteryl acetates have been studied by high-field ^1H and ^{13}C NMR methods, which have led to better definition of the anisotropic properties of the $Fe(CO)_3$ moiety[166]. Additional material on cyclohexadiene complexes, involving synthetically important interconversions with cationic cyclohexadienyl complexes, is discussed in the next section of this review.

Photoreaction of a disilete (Eq. 20) with (η^4-cycloheptatriene)tricarbonyliron led to fused cycloheptadiene complexes[167].



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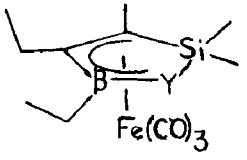
Irradiation of $(Et_3P)Fe(CO)_4$ in the presence of nitrogen, followed by introduction of excess acetylene produced (η^4-tropone)$Fe(CO)_2(PEt_3)$, along with a diiron compound, 77[117] (See Sect. 9a). (η^4-2,3-dihydrotropone)$Fe(CO)_3$[168] and the *exo* and *endo* $Fe(CO)_3$ complexes of homotropone[169] have been resolved by HPLC, and their absolute configurations ascertained by use of theory, X-ray diffraction and CD methods. Protonation of (tropone)$Fe(CO)_3$ with conc. sulfuric acid, and quenching with *l*-menthol, followed by separation of diastereomers, and protonolytic removal of the menthol allowed preparation of optically pure (η^5-2,4-cycloheptadienonium)tricarbonyliron tetrafluoroborate. The (+) enantiomer of the latter was related to the (+) enantiomers of (tropone)- and (dihydrotropone)-$Fe(CO)_3$ by reaction with triethylamine and triethylsilane, respectively[170].



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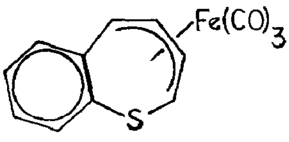

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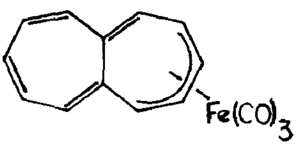


34

Both (tropone)- and (4-7-η^4-2-chlorotropone)tricarbonyliron added diazomethane to the free double bond, forming pyrazoline products, but the regioselectivity was reversed by the presence of the 2-chloro substituent[171]. (η^4-Benzo[b]thiepin)tricarbonyliron, 33, prepared by direct complexation of the free thiepin, could be oxidized successively to the sulfoxide and then the sulfone by *m*-chloroperbenzoic acid at -40°, without disruption of the organometallic group. Treatment of the sulfoxide with Ce(IV) led to decomplexation and formation of naphthalene[172]. (Heptalene)tricarbonyliron, **34**, prepared by partial decomplexation of the previously known bis[$Fe(CO)_3$] derivative, underwent racemization by $Fe(CO)_3$ group migration with an activation energy of 102 kJ/mol in naphthalene-d_8 and 79 kJ/mol in diglyme[173], values comparable to those of (tropone)$Fe(CO)_3$.

Electrochemical reduction of (η^4-cyclooctatetraene)tricarbonyliron has been studied by FT-IR, which led to the conclusion that reversible reduction in aprotic solvents involved population of metal-centered orbitals, while the irreversible reduction observed in protic media involved COT ring orbitals, leading to hydrogenation of a free double bond[174].

7. η^5-DIENYL COMPLEXES

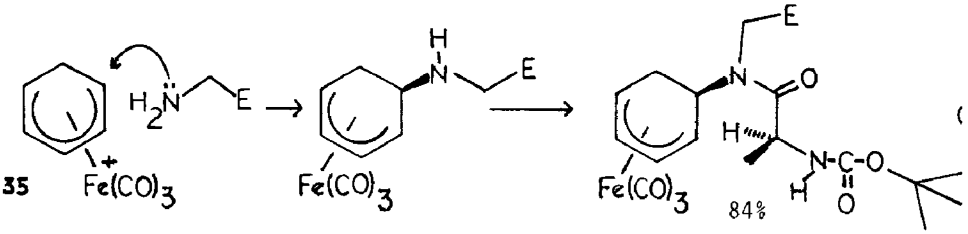
a. Compounds with Open Pentadienyl Ligands

(η^5-C_5H_7)Fe(η^3-C_5H_7)(PR_3) compounds formed upon refluxing **18** in ether [R = Me] or directly from K^+ $C_5H_7^-$ and $(PR_3)_2FeCl_2$ [R = Et, Pr]. With excess PMe_3, the compounds reverted to **18**. Reaction with H^+ or Ag^+, followed by ligands L, resulted in displacement of the η^3-pentadienyl group to form (η^5-C_5H_7)FeL_3^+, which showed dynamic processes in solution involving rotation of the pentadienyl ligand relative to the FeL_3 moiety[133].

Attack of malonate nucleophiles on (η^5-1-R-pentadienyl)Fe-$(CO)_3^+$ cations [R = Me, Et, Pr] occurred at both the substituted and unsubstituted ends of the dienyl moiety; however, with R = CO_2Me, attack occurred exclusively at the unsubstituted end, and with R = Ph exclusively at the substituted end[175].

Nucleophilic attack on cyclohexadienyl cations to form substituted cyclohexadiene complexes continues to attract research attention. The rates of attack of some forty phosphine, amine, and arene nucleophiles on (η^5-C_6H_7)$Fe(CO)_3^+$, **35**, have been determined by stopped-flow kinetic methods, and found to vary by about nine orders of magnitude, from $P[2\text{-}MeOC_6H_4]_3$, the most reactive, to $4\text{-}Me_2NC_6H_4SiMe_3$, the least. Factors affecting nucleophilicity were discussed[176]. Both hindered and unhindered phenoxides added to **35** to form the expected 5-aryloxy-1,3-cyclohexadiene complexes[177]. The use of **35** as a masking group in peptide synthesis (Eq. 21) has been suggested[178].

Replacement of a carbonyl group in **35** by a triphenylphosphine group resulted, not surprisingly, in reduced reactivity toward attack by nucleophiles[122]. Likewise, introduction of a 2-methoxy substituent into **35** reduced its electrophilicity compared to unsubstituted **35**, as shown in a kinetic study of the reversible addition of pyridines[179]. Attack of ketene acetals on (1-methyl-4-alkoxycyclohexadienyl)Fe(CO)$_3^+$ occurred selectively at the methylated terminus[180].



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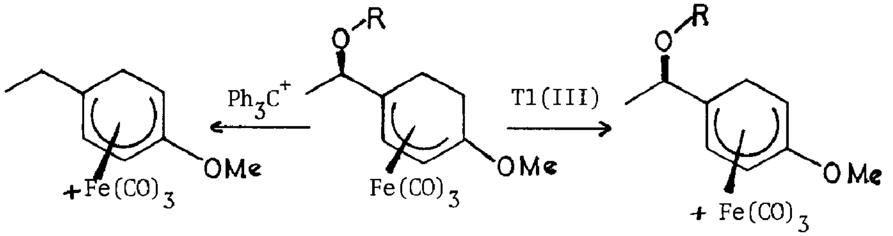
Thallium tris(trifluoroacetate) proved effective in selectively oxidizing some methoxy-substituted cyclohexadiene complexes even in cases when trityl cation preferentially removed an alkoxy group from a side chain (Eq. 22)[181].



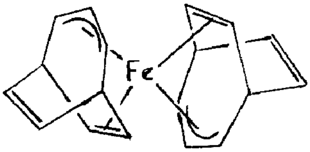
(22)

(*syn*-6-Methoxycyclohexadienyl)Fe(CO)$_3^+$ has been obtained from cyclohexadiene-5,6-diol, available via microbial oxidation of benzene. Alkylation and acid-induced demethoxylation gave *anti*-6-alkylcyclohexadienyl complexes[182]. Application of the same overall sequence (complexation, demethoxylation, reduction, demethoxylation) to the product of microbial oxidation of toluene provided access to enantiomerically pure (η^5-2-methylcyclohexadienyl)Fe(CO)$_3^+$ in 20% yield[183] .

Attack of β-ketoester carbanions on (1-methyl-4-methoxycyclohexadienyl)tricarbonyliron cations has been employed as the key step in syntheses of several heterosteroids[184,185].

(η^5-Cycloheptadienyl)tricarbonyliron cation has been found consistently to be less reactive toward nucleophiles than the cyclohexadienyl analog. This has been explored in detailed mechanistic studies of the reversible addition of 2,6-dimethylaniline[186] and of substituted pyridines[187] to the two cations. Linear Brønsted plots were obtained in the case of the pyridine additions, but deviations revealed steric retardation by 2- and 6-substituents. The cycloheptadienyl system was less electrophilic even than the 2-methoxycyclohexadienyl[179]. Rate data on attack of phosphorus nucleophiles on (η^5-C_7H_9)Fe(CO)$_3^+$ have been obtained. A comparison of nucleophilicities of a variety of species (especially phosphines, amines, and anions) toward the (cyclohexadienyl)- and (cycloheptadienyl)Fe(CO)$_3^+$ cations showed a linear relationship despite the greater reactivity of the former. However, azide ion was anomalously reactive toward $(C_7H_9)Fe(CO)_3^+$ [188].

Two examples of η^5-dienyl complexes in which the dienyl unit is composed of disjoint allyl and alkene systems have been prepared. **36** was prepared directly from the lithiated hydrocarbon and $FeCl_2$ and, despite thermal sensitivity, characterized by X-ray crystallography[189]. Preparation of the lithium salt of dicyclopentadiene at -78° resulted in retro Diels-Alder reaction to form lithium cyclopentadienide and cyclopentadiene; in the presence of $FeCl_2$, the dicyclopentadienide anion could in part be trapped, to form **37** in 20 % yield[190]. Both **37** and **36** are ferrocene analogs having one or two bis(homo)cyclopentadienyl units in place of the usual cyclopentadienyls. Electrochemical studies were reported as well as crystal structures.



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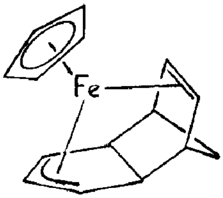

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7b. CyclopentadienyldicarbonylironHydride(FpH) and Related Compounds

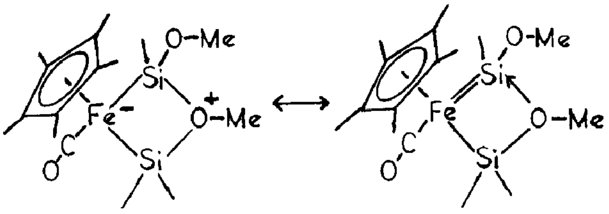
This section includes results on FpH, Fp^- and $Fp^\bullet$, [Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$], and on compounds containing bonds between the Fp group and elements of Groups 14 (except carbon)-17, essentially in that order. Derivatives with one or more CO groups replaced by another 2-electron ligand are included, as are derivatives with substituted cyclopentadienyl rings. Fp-transition metal compounds are treated with other Fe-M bimetallic species in Section 9c.

Density function MO calculations on Fp-H and Fp-Me, along with other metal compounds, have indicated fairly uniform M-H bond strengths across the transition series, but decreasing M-Me bond strengths as repulsions between filled orbitals on the metal and the methyl group come into play, resulting in M-Me bonds becoming weaker than M-H for middle to late transition metals[191]. Reduction of Fp^*CO^+ with sodium borohydride in the presence of water gave only Fp^*H. The hydride was also obtained by $NaBH_4$ reduction of $Fp^*PR_3^+$ at 20° and by reaction of $Fp^*CH{=}O{\rightarrow}BH_3$ with water. Fp^*H itself was found to reduce Fp^*CO^+ and free CO[192].

$ZnFp_2$ has been prepared by metathetical reaction of NaFp with $ZnCl_2$[193]. An improved synthesis of $HgFp_2$ (91% yield) resulted from reaction of FpI with $Hg(GeEt_3)_2$[194].

Electrochemical studies of Fp_2 reduction to Fp^- have indicated a free energy for $Fp_2 \rightleftharpoons 2\ Fp^{\bullet}$ of +92 kJ/mol in acetonitrile at 22° [195]. Na^+Fp^- reacted with cationic allyl complexes of manganese and rhodium by reduction, forming Fp_2[124]. A study of the reaction of Fp^*_2 with TCNE concluded that reaction occurred via $Fp^{*\bullet}$, which underwent one-electron oxidation to form $(Fp^{*+})_2$-$(TCNE^{2-})$. With two equivalents of TCNE, polymeric $[Fp^*(TCNE)]_n$ formed[196].

Treatment of $FpSiPh_2H$ [from NaFp and $ClSiPh_2H$] with LiN(*i*-Pr)$_2$ caused deprotonation of the Cp ring, followed by migration of the diphenylsilyl group to the carbanionic site. Hydrosilylation of phenylacetylene by $FpSiPh_2H$, using chloroplatinic acid, yielded the adduct $FpSiPh_2C(Ph)=CH_2$ in 82% yield; this also underwent metal-to-ring migration on treatment with lithium diisopropylamide[197]. Treatment of $NaFp^*$ with $ClSiMe_2$-$SiMeCl_2$, followed by methanol/ pyridine resulted in formation of Fp^*-$SiMe_2$-$SiMe(OMe)_2$ (32%) and $Fp^*SiMe(OMe)SiMe_2OMe$ (9%). Photolysis of the main product produced a cyclic product, **38**, whose crystal structure showed abnormally short Fe-Si bonds (2.21 Å average) and long Si-O_{ring} bonds (1.80 Å average). Significant silylene character of the ligands, supported by low-field ^{29}Si NMR signals, was suggested[198].



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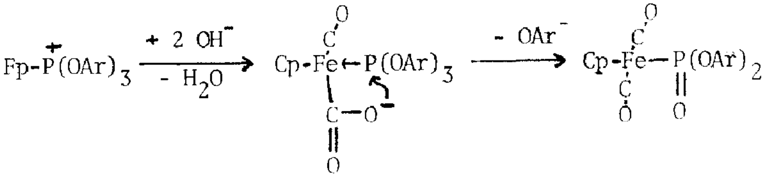
Reaction of Fp_2Hg with $(Et_3Ge)_2Hg$ at 100° resulted in elimination of elemental mercury and formation of $FpGeEt_3$ in 90% yield[199]. Chemical ionization mass spectra of several Fp-ZR_3 compounds [ZR_3 = $SiMe_3$, $GePh_3$, $SnMe_3$, $SnPh_3$] and of FpX have been studied[200]. Photolysis of Fp-ZR_3 [ZR_3 = $SiPh_2Me$, $GePh_3$, $SnPh_2Me$, $SnPh_3$ in the presence of racemic chiral phosphines resulted in formation of diastereomeric $CpFe(CO)(ZR_3)(PR_3)$. Asymmetric induction at iron resulted when the phosphine contained a nitrogen or oxygen heteroatom[201].

The crystal structure of Fp_2SnPh_2 has been reported[202]. ^{17}O NMR data for Fp_2SnR_2 and $FpSnR_2M(CO)_x$ compounds have been utilized as a probe of the electronic environment of the carbonyl oxygens[203].

Organometallic Langmuir-Blodgett films have been prepared from a variety of cationic compounds of general structure $CpFeL_2$-$=N^+=C(R)-(C_6H_4)_{1-3}-C(R)=N^+=N=FeL_2Cp$ $(BF_4^-)_2$ [R = C_3-C_{17} alkyl or alkoxy groups; L = various phosphines and arsines]. Good chemical stability and desirable pyroelectric properties were claimed[204]. Fulvalene complexes $[-(C_5H_4)Fe(DPPE)(NCMe)^+]_2$ resulted from photolysis of $[-(C_5H_4)Fe(C_6H_6)^+]_2$ in the presence of DPPE in acetonitrile. The acetonitrile ligand was readily displaced by CO or Me_3P, and one-electron oxidation of the phosphine adduct gave a delocalized trication[205].

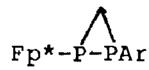
Iron phosphine complexes Fp- or Fp^*-$P(Ph)N(SiMe_3)_2$ have been prepared by direct displacement of chloride from the chlorophosphines. The crystal structure of the Fp compound showed a pyramidal phosphine and a long (2.338 Å) Fe-P bond. Methylation of the phosphorus gave a phosphonium salt $FpP(Ph)(Me)NR_2^+$ $CF_3SO_3^-$ [R = $SiMe_3$] with a shorter Fe-P bond length (2.263 Å)[206]. More highly metallated phosphonium salts Fp_2PPhH^+, $Fp_2PPh_2^+$, and Fp_3PH^+ resulted when $Ph_{3-n}P(SiMe_3)_n$ reacted with FpX, with elimination of Me_3SiX. The crystal structure of $Fp_2PPh_2^+$ I^- showed an average Fe-P bond length of 2.30 Å[207]. Numerous bimetallic compounds $FpPH_2 \rightarrow ML_n$ were produced by protodesilylation of $FpP(SiMe_3)_2 \rightarrow ML_n$ precursors using methanol, water, or acetic acid. $FpPH_2 \rightarrow Fe(CO)_4$ was also produced by treating $LiPH_2Fe(CO)_4$ with FpBr[75], and its crystal structure was reported[207a].

Phosphonate complexes form readily when aqueous base reacted with $Fp-P(OAr)_3^+$ [Ar = phenyl, o-tolyl] or $Fp^*-P(OPh)_3^+$. A mechanism involving initial carbonyl attack, followed by a Wittig-like process, was proposed (Eq. 23)[208]. An X-ray structure



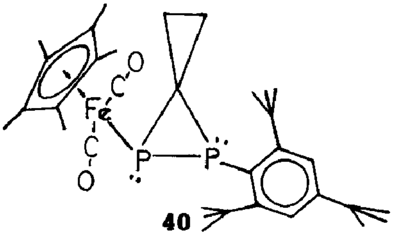
(23)

of the diethylphosphonate analog, $Fp-P(=O)(OEt)_2$, was reported. The latter phosphonate readily added electrophiles to the terminal oxygen to form $FpP(OEt)_2OEl^+$ [El = H, Me, CPh_3][209].

Among the products of reaction of Fp^*-P=PAr [Ar = 2,4,6-$(CMe_3)_3C_6H_2$], **39**, with $Fe_2(CO)_9$ was $Fp^*-P[\rightarrow Fe(CO)_4]=PAr$, whose X-ray crystal structure showed a P-Fp* bond length of 2.302 Å and $P \rightarrow Fe(CO)_4$ bond length of 2.268 Å[83], consistent with the principles described in Section 2 of this review. **39** reacted with sulfur ylides to form diphosphiranes:  Fp*-P-PAr from $Me_2S(O)=CH_2$, and **40** (Fe-P bond length 2.310 Å) from diphenylsulfonium cyclopropanide[210].

Several phosphorus-arsenic heterocycles, having P_2As, PAs_2, and P_2As_2 rings, resulted from reaction of $Fp^*-P(SiMe_3)_2$ with $ArAsCl_2$; the crystal structure of cyclo$(P-Fp^*)_2$AsAr, which showed P-Fe bond lengths of 2.373 and 2.326 Å, was reported[211]. The reactive product $Fp^*P{=}AsAr$ produced in the above reaction was stabilized by reaction with $(\eta^2$-cyclooctene)$Cr(CO)_5$, which produced $Fp^*P[\rightarrow Cr(CO)_5]{=}AsAr$[211]. The isomeric $Fp^*As{=}PAr$ reacted similarly, to produce $Fp^*As[\rightarrow Cr(CO)_5]{=}PAr$; thus the $Cr(CO)_5$ or $Fe(CO)_4$ group coordinated in each case to the atom already bearing the iron group, whether that atom was phosphorus or arsenic. The same result was obtained with $Fp'As{=}PAr$[212] and with $Fp^*As{=}AsAr$, produced by reaction of $Fp^*As(SiMe_3)_2$ and $ArAsCl_2$[213]. The structure of the four-membered ring diphosphadiarsetane formed from $Fp^*As(SiMe_3)_2$ and $ArPCl_2$ has been determined[214]. Reaction of $FpAs(SiMe_3)_2$ with hindered acyl chlorides produced arsaalkenyl complexes, $Fp-As{=}C(OSiMe_3)R$, then, with additional acyl chloride, diacyl compounds $Fp-As(COR)_2$[215].

Displacement of chlorides from $BiCl_3$ by two equivalents of $Cp'Fe(CO)_2^-$ gave $[Cp'Fe(CO)_2]_2BiCl$, which existed in the crystal as a cyclotrimer, **41**, containing a planar ring[216,217]. Three equivalents of the iron nucleophile gave the trisubstituted, pyramidal product, $[Cp'Fe(CO)_2]_3Bi$[217].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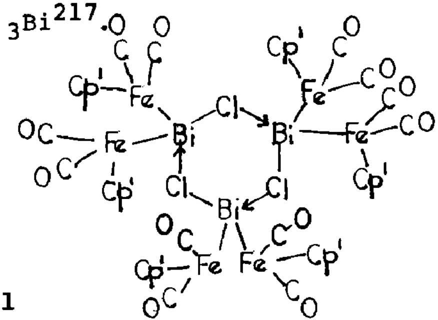
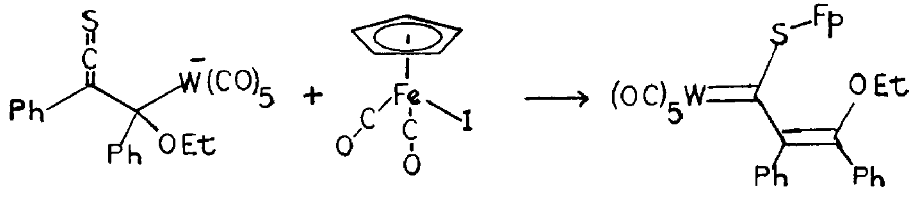


41

Displacement of THF from the $Fp(THF)^+$ adduct by $R_3P{=}S$ [R = Me, Ph, OEt, OPh] occurred readily, to form η^1-$R_3P{-}SFp^+$. The same products could also be prepared by oxidation of Fp_2 in the presence of the ligands[218]. S-Coordinated products were also obtained in the very similar reaction of $Fp(O{=}CMe_2)^+$ with thiosemicarbazide $[H_2NNNC({=}S)NH_2]$ and with thiosemicarbazones[219]. A related but more complex reaction (Eq. 24) occurred when an anionic thioketene complex attacked FpI[220].



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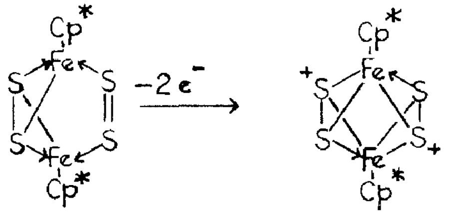
Fenske-Hall MO calculations on Fp-SPh have indicated a HOMO centered largely on the sulfur and having Fe-S antibonding character, and this result was related to the nucleophilicity of the sulfur in FpSR compounds[221]. The same property presumably accounts for the sulfur atom in FpSMe acting as a two-electron donor ligand toward a Co_2C_2 cluster in a recently reported compound[222].

Fp(*)-SC(=S)NMe$_2$ underwent electrocatalyzed chelation in a chain process which occurred efficiently despite an endergonic (> 50 kJ/mol) propagation step[223]. η^1-Xanthate complexes Fp(*)-SC(=S)OEt resulted from reaction of the dimers Fp$_2$ and [-SC(=S)-OEt]$_2$; their structures and their electrochemical reduction have been investigated[224,225]. Photolysis led to loss of CO and formation of chelate complexes[225].

Irradiation of CpFeAn$^+$ [An = p-C$_6$H$_4$Me$_2$] in the presence of excess dimethylsulfide gave the cation CpFe(SMe$_2$)$_3$$^+$; ^{13}C NMR and reactivity of the cation were interpreted in terms of repulsion between sulfur lone pairs and filled metal orbitals[226]. Two groups have independently studied the two-electron oxidation of (Cp*Fe)$_2$S$_4$ (Eq. 25), which is accompanied by rotation of one S$_2$



(25)

unit from parallel with the Fe-Fe axis to perpendicular, and by decrease in the Fe$\cdots$Fe distance by 0.67 Å[227,228]. Cyclic voltammetric study revealed two well-separated one-electron steps[227]. Intercalation of redox-active heterocubane clusters (Cp'Fe)$_4$(μ_3-S)$_4$ into layered MoO$_3$ or FeOCl has been carried out, and the solid state properties of the resulting materials described[229].

The cation SeFp$_3$$^+$ has been prepared as a salt with the Fe$_4$Se$_4$Br$_4$$^{2-}$ dianion [X-ray structure] by reaction of FpBr with Se(SiMe$_3$)$_2$[230]. The same cation was obtained as a byproduct, along with Fp$_2$Se-SeFp$^+$, upon reaction of Fp$_2$Se or Fp$_2$Se$_2$ with (OC)$_5$ReFBF$_3$. With FpSR, the rhenium compound gave FpS(R)Re(CO)$_5$$^+$ BF$_4$$^-$ [R = Me, Ph][231].

X-ray structures of Fp*Cl[217] and of Cp'Fe(CO)LI [L = CNC$_6$H$_3$-2,6-Me$_2$, P(OMe)$_3$, P(C$_6$H$_{11}$)$_3$][232] have been reported. Because of the chiral iron in the latter group of compounds, it was possible to detect and assign ^{13}C resonances for all the ring carbons through use of C-H correlated spectra[233].

The ligand C$_5$Me$_4$R$^-$ [R = CH$_2$CH$_2$CH=CH$_2$] has been used to form organoiron compounds, including the Fp*Br and Cp*Fe(CO)(acac) analogs[234]. Fp_2 reacted very readily with sulfuryl chloride, SO_2Cl_2, giving in polar solvents FpCl and in non-polar solvents $FpCO^+ FeCl_4^-$. Analogous reactions were reported for Cp', η^5-indenyl, and isonitrile-substituted analogs[235].

Photosubstitution reactions of FpI by various ligands have been examined, and the results explained by invoking two competing pathways: heterolysis of the Fe-I bond, and formation of Fp_2 through homolysis, with subsequent disproportionation[236].

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

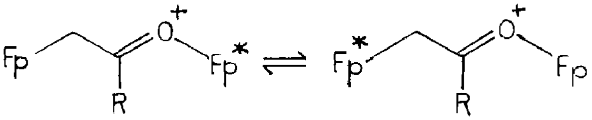
FpC(=S)SH has been prepared by reaction of Fp^- with CS_2 in ether containing HCl; the related μ-dithiocarbonic acid compound was made by protonation of FpC(=S)SFp[237]. Acetylation of FpC(=S)SFp with acetyl chloride gave FpC(=S)Cl and FpSAc, whereas reaction with trifluoroacetic anhydride produced $FpCO^+ CF_3CO_2^-$ and $FpSC(=O)CF_3$. Both reactions involved S-acyl intermediates. Reaction of FpC(=S)SFp with alkylating agents likewise resulted in formation of $FpC(SR)(SFp)^+ X^-$ [R = Me, Et, $PhCH_2$, C_3H_5]. Reaction of the latter cations with I^- resulted in removal of the S-Fp group to form FpC(=S)SR dithioesters[238]. The methyl ester underwent oxidation by m-chloroperbenzoic acid to form the sulfine FpC(=S=O)SMe[239].

^{13}C Chemical shifts for FpCN have been calculated using a new INDO/σ method[240]. Reaction of CpFe(CO)(CN)(CNH) and related compounds with isocyanates and carbodiimides resulted in addition of the N-H bond to the heteroallene to form, for example, CpFe(CO)(CN)[CNC(=NPh)NHPh][62]. $CpFe(DPPE)(CNH)^+ BF_4^-$ added to 2,3-dimethyl-2-butene to form $CpFe(DPPE)(CNCMe_2CHMe_2)^+ BF_4^-$. With less reactive alkenes, formation of $CpFe(DPPE)CNBF_3$ intruded to prevent hydroisocyanation[92]. Tetrachloroferrate(III) salts of cations $CpFe(CO)_{3-n}(CNMe)_n^+$ resulted from reaction of $(CpFe)_2(CO)_{4-n}(CNMe)_n$ with SO_2Cl_2[235].

A low-precision X-ray structure of the indenyl cation, $(\eta^5\text{-}C_9H_7)Fe(CO)_3^+ FeCl_4^-$, has been reported[235]. Reaction of $FpCO^+$ with aryl-lithium reagents at low temperature produced a series of FpC(=O)Ar products[241]. The complete sequence of products of reduction of Fp^*CO^+ by $NaBH_4$ in THF could be observed by controlling the temperature: at -80°, Fp^*CHO was obtained; warming the solution to -60° led to Fp^*CH_2OH; then at 0°, Fp^*CH_3 was produced. Conditions for best obtaining each product were described, as were the reactions among them. Studies of reduction of $Fp^*PR_3^+$ were also carried out[192].

Fenske-Hall MO calculations have been used to interpret structural distortion (slippage of the iron to a position closer to the carbons than to the borons in the C_2B_3 ring) in $(\eta^5\text{-}C_2Me_2\text{-}B_4H_4)Fe(CO)_3$[242].

Reaction of several transition metal anions ML_n^- [including, among others, Fp^- and $Cp'Fe(CO)_2^-$] with $FpCH_2C(=O)Cl$ gave the expected bimetallic μ-ketene products, $FpCH_2C(=O)ML_n$[243]. Other workers, however, failed to obtain $FpCH_2COFp$ by reaction of bromoacetyl bromide with NaFp, only Fp_2 being obtained[244]. $FpCH_2COFp$ (from the acid chloride) underwent carbonylation to form the μ-malonyl product and LAH reduction to C_3 products[243]. Reaction with electrophiles occurred at the acyl oxygen, forming $FpCH_2C(OEl)=Fp^+$ [El = H, Me, $SiMe_3$], whose reactivity with nucleophiles and electrophiles has been studied[243]. Attack of the electrophile $Fp(^*)\text{-}(THF)^+$ on $FpCH_2C(=O)R$ [R = H, Ph, OMe, Fp] occurred similarly, forming $FpCH_2C[OFp(^*)]R^+$. An intramolecular exchange reaction between the terminal C- and O- bound iron groups (Eq. 26) was observable when distinguishable groups were present[245].



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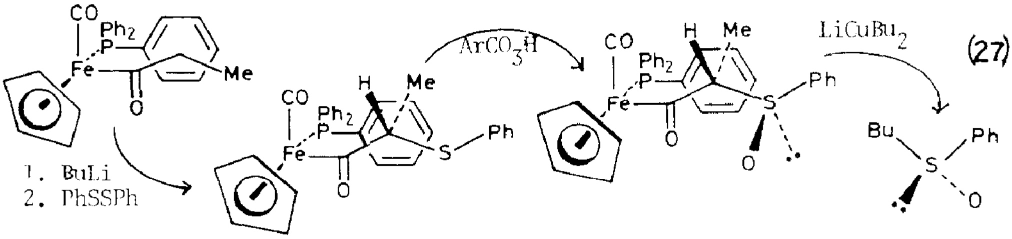
Optically active iron acyls incorporating amino acid units could conveniently be synthesized by protecting the amine with a carbobenzyloxy group, activating the acid group with ClC(=O)O-i-Bu, and displacing the alkyl carbonate with Fp^- [246]. The conformation (**42**) and absolute configuration (S) of (+)-Fp'C(=O)Me were determined by X-ray diffraction methods[247]. Similar conformations were independently found for $CpFe(CO)(PMe_2Ph)COMe$ and for $Fp'CH_2CH(OH)Et$. The high diastereoselectivity in Michael addition to Fp'COCH=CHR acyls was attributed to the effects of the phosphine-bound groups in conformations like **42**[248]. Use of the ligand L = $C_6F_5PPh_2$ led to enhanced stereoselectivity (89-99% de) in enolate reactions of $CpFe(CO)LC(=O)CH_3$[249]. Highly stereoselective reactions of the aluminum enolates of (S)- and (R)-Fp'Ac have been used to prepare both epimers of 1-hydroxypyrrolizidin-3-one from protected L-prolinal[250]. Efficient chirality



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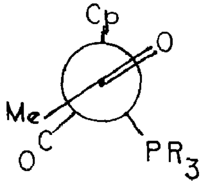
transfer from iron to sulfur resulted in syntheses of homochiral sulfoxides from Fp'C(=O)Et (Eq. 27)[251]. Uses of the Fp' group as a chiral auxiliary have been reviewed[4].

Thermal transformation of Fp'-C(=O)R to FpR and PPh_3 has been studied kinetically; the reaction was faster with bulkier R groups[252]. The reverse reaction, alkyl migration from iron to carbon induced by the presence of excess triphenylphosphine, has been studied in cases involving complex bicyclic alkyl groups[253]. A number of simple organometallics, including FpMe, FpAc, Fp'Me, and Fp'Ac, have been imbedded in polymer films and studied by FT-IR. A polystyrene-acrylonitrile copolymer was particularly useful as a polymer matrix for photolysis studies due to trapping of coordinatively unsaturated species by the pendant nitrile groups[254].

Reaction of Fp^- with $ClCH_2CO_2SiMe_3$, followed by hydrolysis of the silyl group on silica gel, has been recommended as a direct route to $FpCH_2CO_2H$. Conversion of the latter to the acid chloride using oxalyl chloride gave access to numerous acid derivatives[255].



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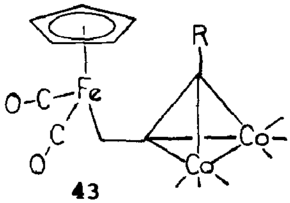

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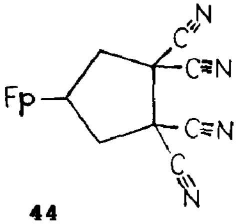


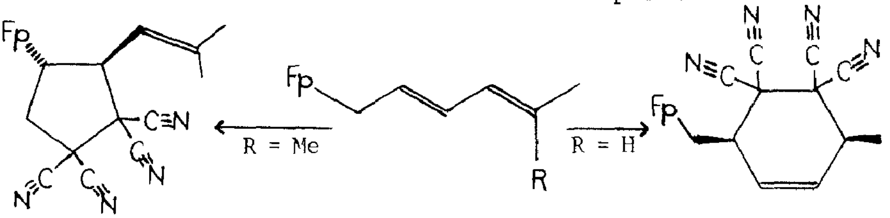
44

Synthesis of the bimetallic species $FpCH_2CH_2CH_2Mo(CO)_3Cp^*$ was accomplished straightforwardly by Fp^- displacement on the corresponding (3-bromopropyl)molybdenum compound[256]. Trinuclear species, **43**, [R = Me, Ph] resulted, also straightforwardly, from complexation of $FpCH_2C{\equiv}CR$ with $Co_2(CO)_8$ [257]. But reaction of the arenecarbonyl cluster $[(OC)_9Co_4]C_6H_5CH_2CH_2Br$ with Fp^- resulted in demetallation of the ring along with the expected bromide displacement, giving $PhCH_2CH_2Fp$[258].

An indirect two-dimensional heteronuclear NMR method has been introduced for extraction of ^{57}Fe chemical shifts and coupling constants using its scalar coupling to nuclei of higher sensitivity. The method has been applied to $CpFeL_2R$ and $CpFeL_2H$, among other organoiron species[259].

Reaction of various Fp-allyls with CCl_4 has been found to occur by a radical chain mechanism initiated by a homolysis of the Fe-C bond. The principal product was CH_2=CH-CH_2CCl_3[260]. Reaction of γ-haloalkyliron compounds, $FpCH_2CH_2CHRBr$, with Ag^+ gave cyclopropanes (73% for R = H), a result which may bear upon the mechanism of cyclopropane formation using "$FpCH_2^+$" and alkenes[261].

The mass spectrum of **44**, which showed negligible parent ion using thermal evaporation in a direct probe, showed abundant parent when a laser evaporation technique was used[262]. Cycloadditions to $FpCH_2CH=CH-CH=CR_2$ have been studied. TCNE gave normal Diels-Alder addition to the diene unit of the unsubstituted pentadienyl or hexadienyl compounds, but added to the 1- and 3-positions of the dimethyl compound (Eq. 28). Dimethyl acetylenedicarboxylate inserted into the Fe-C σ-bond[263]. Maleic anhydride gave Diels-Alder reactions like those of TCNE[264]. Crystal structures of two Diels-Alder adducts were reported[264].



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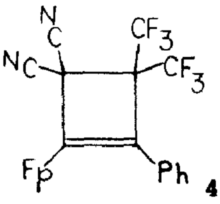
(1Z,3Z)-FpCH=CH-CH=CHBr (X-ray structure) was obtained by reaction of the vinyl-lithium compound with FpI[265]. Reaction of $(\eta\text{-}C_6H_5X)Cr(CO)_3$ with Fp^- or Fp^{*-} proceeded with halide displacement to produce $Cr(CO)_3$-coordinated aryl-Fp(*) compounds. A competitive oxidation-reduction reaction gave Fp_2 and dehalogenated arene complex, but could be minimized by use of chlorides rather than iodides, Fp rather the Fp^*, and avoiding ortho substituents on the ring[266]. Sydnonyl-Fp complexes were produced in 35-40% yields by reaction of lithiated sydnones with FpBr[267]. But formation of the cuprate first, before reaction with FpBr, improved the yield to 75% in the case of 3-phenylsydnone[268]. Similarly, the reaction of $ZnFp_2$ with aryl iodides or bromides, catalyzed by palladium or nickel compounds, appears to provide a very attractive route to aryl-Fp compounds[193].

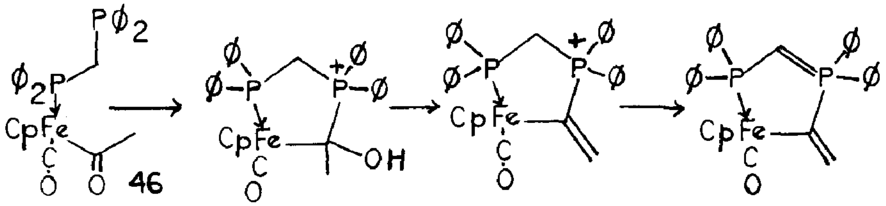
Group 6 $M(CO)_5$ units readily coordinated to the nitrogen of PhCH=C(Fp)-C(Ph)=C(Fp)CN[269]. Reaction of $(F_3C)_2C{=}C(CN)_2$ with FpC≡CPh occurred with formation of the cyclobutenyl-Fp compound, **45**, as the only regioisomer, a result consistent with a dipolar intermediate. In contrast to the tetracyano analog, **45** did not undergo ring opening to form the acyclic diene[270], nor did the perfluoro analog[271]. Consistent with the cyclobutene stability in the latter case, the crystal structures of Fp- and $Fp'\text{-}C_4F_5$ showed short (strong) $CF_2\text{-}CF_2$ bonds[271].



45

Protonation of **46** (produced by reaction of FpMe with DPPM) with HBF_4/Et_2O caused a novel cyclization reaction (Eq. 29) to occur[272]. The cationic cyclic ligand could be deprotonated by

MeLi; however, the phosphorane structure shown for the neutral product in Eq. 29 differs from that proposed by the original authors[272].



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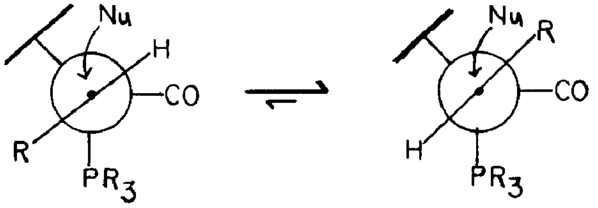
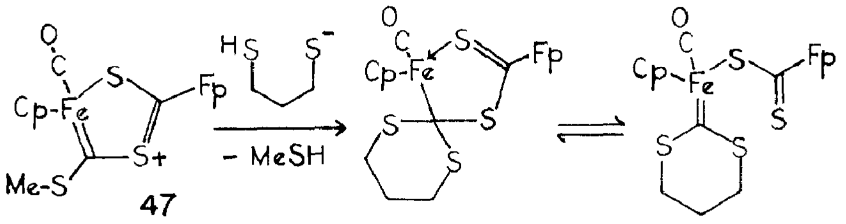
The structures and reactions of carbene complexes of Fp and its derivatives have continued to draw interest. That formation of $Cp^*Fe(DPPE)=CHOMe^+$ by reaction of $Cp^*Fe(DPPE)CH_2OMe$ with Ph_3C^+ PF_6^- involves single electron transfer steps has been clearly demonstrated by isolation and crystal structure determination of paramagnetic $CpFe(DPPE)CH_2OMe^+$ and EPR detection of $CpFe(DPPE)$-$CHOMe^{\cdot}$ [273]. Thus, the reaction appears to occur by (a) electron transfer, (b) proton transfer, and (c) electron transfer. The intermediates are stabilized in the system studied by the combined steric hindrance of the DPPE and Cp^* ligands[273]. The analogous reaction of Fp^*CH_2OMe was monitored by NMR at -80°, which revealed predominant initial formation of the cis isomer of $Cp^*Fe(CO)_2=CHOMe^+$, which isomerized to the more stable trans isomer on warming[274]. $Fp^*=CHOMe^+$ reacted with Et_3SiH and other Si-H compounds by insertion of the methoxycarbene unit into the Si-H bond, forming Et_3SiCH_2OMe; running the reaction in the presence of styrene resulted in trapping of the Fp^{*+} moiety as the η^2-styrene complex[274].

A study of addition of nucleophiles to $Fp'=CHR^+$ [R = Me, Ph] and related phosphine-substituted, chiral, iron carbene complexes indicated that the less abundant synclinal (cis) isomers are much more reactive than the anticlinal (trans). The relative abundances and reactivities of the two isomers were estimated from NMR and product studies[275]. Fluoride ion (from $Me_3SiF_2^-$) attack at the silicon of the extended carbene complex $Fp'=C(OMe)-CH=CH-SiMe_3$ resulted in methyl migration to carbon, forming $Fp'-C(OMe)=CH-CHMe-SiMe_2F$[276].


synclinal anticlinal

Nucleophilic attack on the delocalized carbenoid **47** occurred at the carbenoid carbon bonded to the endocyclic iron (see Eq.

30). In some cases (Nu = H, SMe, CN), simple addition occurred, but in other cases (piperidine and 1,3-propanethiol), methanethiol was displaced. The interconversion of the spiro trithioorthoester with a carbenoid, as shown in Eq. 30, was indicated by the NMR equivalence of the 4- and 6-carbons in the dithiane ring[277].



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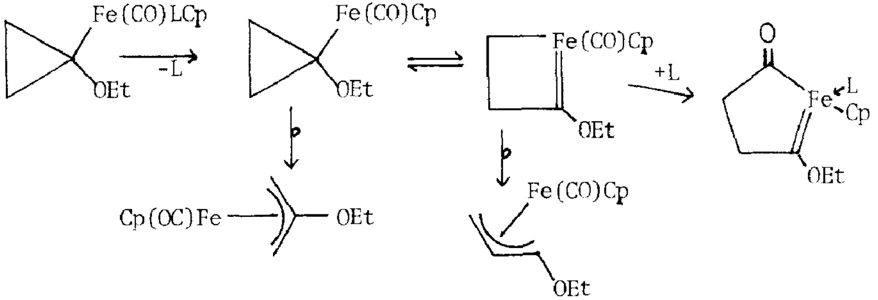
An organometallic Beckman rearrangement ensued when the vinylidene complex Fp'=C=CH$_2$ underwent attack by hydrazines. With Me$_2$N-NH$_2$, for example, the initially formed carbenoid, Fp'-C(Me)=NHNMe$_2$$^+$ lost Me$_2$NH with attendant carbon-to-nitrogen migration of the metal group to form Fp'-N≡CMe$^+$ [278]. Cycloaddition of vinylidene complexes Fp'=C=CR$_2$$^+$ to imines ArCH=NMe gave azetidinylidene complexes, which were oxidized to yield azetidinones[279].

Migration of an alkyl group from carbon to iron was used to generate a reactive ferracyclobutene (Eq. 31); further migration to CO produced a comparatively stable ferracyclopentenone. The first step required photolysis [L = CO] or thermolysis [L = PPh$_3$], whereas the second occurred spontaneously upon addition of L[280]. Two full papers have described in detail the preparation and rearrangement reactions of Fp=CHR$^+$ complexes, in which R is a bi- or tricyclic group whose rearrangement yielded Fp$^+$ complexes of strained alkenes[281,282]. The sequence of products observed by low temperature NMR for the norbornyl case is shown in Eq. 32[282].



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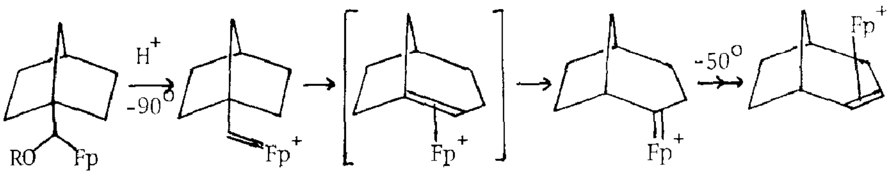

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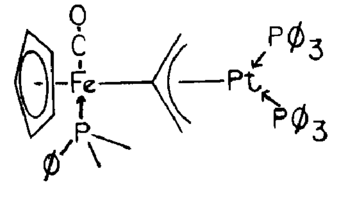
7d. Cyclopentadienyliron Derivatives of η^2- to η^5-Ligands

The fluxional behavior of (η^2-cyclohepta-1,2-diene)Fp^+ and that of its Fp' analog have been studied. The activation energy for the latter was found to be 13-17 kJ/mol higher than for the dicarbonyl (58 kJ/mol), and fluxional interconversion in the phosphine-substituted cation may involve an allylic cation intermediate or transition state[283]. A transition metal-stabilized analog of such an intermediate resulted when $CpFe(CO)L(\eta^2$-$CH_2=C=CH_2)$ [L = $PPhMe_2$, $PHPh_2$] reacted with $(C_2H_4)Pt(PPh_3)_2$ to form **48** (X-ray structure)[284].

Heating $FpCH_2CH_2CH=CH_2$ resulted in coordination of the double bond and metal-to-carbon migration to form (1,4,5-η^3-4-pentenoyl)Fe(CO)Cp. This was converted to chelated alkylidene complexes **49** [R = OEt, H] by standard means[285].

A comparison of theoretical methods as applied to the mechanism of nucleophilic attack on metal-coordinated alkenes, especially $Fp(C_2H_4)^+$, has been made. In contrast to the results of EHMO calculations, INDO methods suggest lowering of the alkene π^* orbital on coordination, and therefore allow direct attack by a nucleophile without mandating slippage of the ethene relative to the metal. Slippage did, however, increase the reactivity. It was pointed out that both methods favored attack of nucleophile (H^-) on CO rather than ethene[286]. Preparation and synthetic uses of $Fp(\eta^2$-1,4-dioxene$)^+$ complexes, including optically active examples, have been described. A variety of nucleophiles added very regioselectively to the trans-5,6-dimethyl-1,4-dioxene complex to form products **50** [Nu = H, Me, CN, Ph, $CH=CH_2$, SCH_2Ph, etc.], perhaps as a consequence of sterically-induced slippage in the cation[287].



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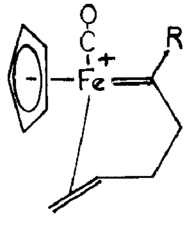

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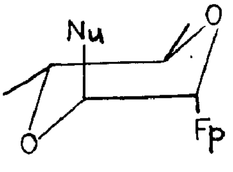

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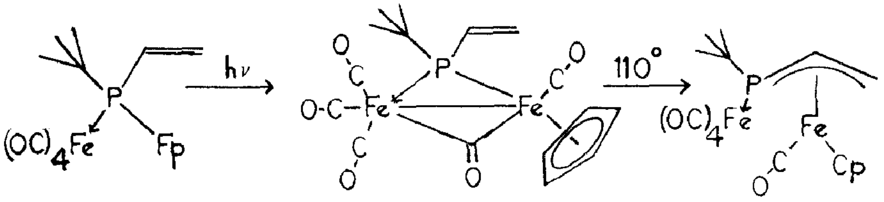
Crystal structures of $CpFe(CO)[P(OPh)_3](\eta^2$-$MeC\equiv CR)^+$ PF_6^- [R = Me, Ph] have been reported. The alkynes were oriented orthogonal to the Fe-Cp vector in the crystal, but rotated in solution; a rotational barrier of 52 kJ/mol was determined for the 2-butyne complex[288]. Nucleophiles attacked the 3-carbon of the (η^2-$MeOCH_2C\equiv CMe$) complex both stereo- and regioselectively, to form $CpFe(CO)[P(OPh)_3][\eta^1$-(E)-$C(CH_2OMe)=CMeNu]$. These products underwent normal metal-to-carbon migration reactions upon treatment with CO and decomposition to form esters when oxidized in alcohol solution. The (η^2-MeC$\equiv$CCHMe$_2$) complex reacted regioselectively at the 3-carbon with MeLi and PhSLi, but indiscriminately with PhLi[289].

Protonation of CpFe(CO)(η^3-C$_3$H$_5$) with HBF$_4$/OR$_2$ at -80° gave the etherate complexes CpFe(CO)(OR$_2$)(η^2-MeCH=CH$_2$)$^+$ BF$_4^-$ [R = Me, Et]. The ether was readily displaced by acetonitrile or triethyl phosphite[290]. CpFe(CO)(PR$_3$)(η^3-C$_3$H$_5$)$^+$ were among the iron complexes whose ^{57}Fe NMR spectra have been obtained by an indirect two-dimensional spectroscopic method[259]. (η^3-1-phosphaallyl) complexes having the phosphorus also coordinated terminally to a Fe(CO)$_4$ or W(CO)$_5$ group (apparently needed to convey kinetic stability) have been prepared as exemplified in Eq. 33[291]. A novel cation, **51**, (X-ray structure) was obtained from a (μ;η^1,η^2-dienyl)diiron complex[292]. Protonation of (η^5-C$_6$H$_7$)FeCp with HBF$_4$/Et$_2$O gave as product (η^4-1,3-cyclohexadiene)FeCp···F···BF$_3$, with a coordinated fluoroborate ion. It is unclear why in this case the fluoroborate occupies an otherwise vacant coordination site on iron, whereas in the previously described case of protonation of the allyl complex, the ether played the role of reluctant ligand. In any case, dimethyl sulfide displaced first the fluoroborate and then the cyclohexadiene ligand, giving CpFe(SMe$_2$)$_3^+$ [293].



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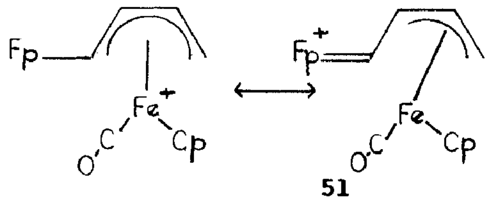
Reaction of CpFe(COD)$^-$ with excess benzyl halide resulted in oxidation-reduction to form bibenzyl and ferrocene. In the presence of DPPE, CpFe(DPPE)CH$_2$Ph formed instead, presumably due to trapping of CpFe(COD)CH$_2$Ph[16].

The pentalene complex **52** resulted from reaction of Cp*Fe(acac) and dilithium pentalenide. A crystal structure of the diamagnetic product showed Fe-shared carbon distances averaging 2.12 Å, and Fe-allyl distances averaging 2.02 Å. Strong through-



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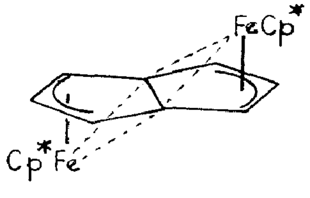

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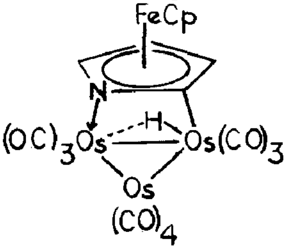
bond interactions of the two Cp*Fe groups were suggested by EHMO calculations[294].

Pentamethylpyrrole displaced dimethylsulfide ligands from CpFe(SMe$_2$)$_3^+$ to form the azaferrocene derivative, CpFe(η^5-C$_4$NMe$_5$)$^+$ [295]. Azaferrocene itself, CpFe(η^5-C$_4$H$_4$N), reacted with Os$_3$(CO)$_{10}$(NCMe)$_2$ to form the oxidative addition product 53[296]. Reaction of Li$^+$ C$_4$Me$_4$N$^-$ with FeCl$_2$ gave 48% of (η^1-C$_4$Me$_4$N)$_2$-Fe·2(THF), which upon treatment with water formed an octamethyldiazaferrocene. In the crystal, each nitrogen of the diazaferrocene accepted a hydrogen bond from an additional tetramethylpyrrole molecule[297].

Tetramethylphosphaferrocene, CpFe(η^5-C$_4$Me$_4$P), has been prepared by reaction of 1-phenyl-2,3,4,5-tetramethylphosphole with Fp$_2$. Reaction of the same phosphole with lithium cleaved the phenyl group off; the resulting anion gave the diphosphaferrocene (η^5-C$_4$Me$_4$P)$_2$Fe upon reaction with FeCl$_2$[298]. A mixture of di-, tri-, penta-, and hexa-phosphaferrocenes was obtained from the reaction of FeCl$_2$ with a mixture of LiCp, Li(1,3-C$_3$R$_3$P$_2$), and Li(1,3,4-C$_2$R$_2$P$_3$) [R = CMe$_3$]. Treatment of a mixture of the di- and triphosphaferrocenes with (THF)W(CO)$_5$ resulted in selective complexation of the P$_3$ compound, forming 54[299]. Co-thermolysis of white phosphorus and Fp$^*_2$ formed the pentaphosphaferrocene, Cp*Fe(η^5-P$_5$)[300]. The same product was formed by reaction of white phosphorus with sodium in THF in the presence of a crown ether, which formed the cyclo-P$_5^-$ anion; this, in combination with LiCp*, formed the pentaphosphaferrocene (27%) by reaction with FeCl$_2$[301]. Reaction of NaP$_5$ alone with FeCl$_2$ gave a black material (decaphosphaferrocene?) with an IR band at 815 cm^{-1} like that of Cp*FeP$_5$[301].



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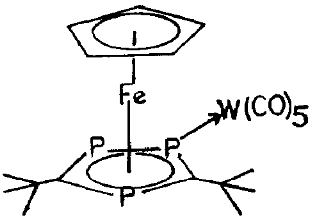

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A 30-electron triple-decker complex, CpFe(μ,η-Cp*)FeCp$^{*\,+}$, has been synthesized by reaction of CpFe(C$_6$H$_6$)$^+$ with decamethylferrocene. Ruthenium and osmium analogs were also reported[302]. Reaction of various carborane anions with FeCl$_2$ followed by air oxidation has continued to be used to fuse the carboranes into larger units, but the presumed bis(carboranyl)iron intermediates have in most cases not been isolated and characterized[303-306].

8. COMPOUNDS WITH η^6-ARENE LIGANDS

Arene complexes $CpFeAn^+$ have commonly been prepared by reaction of ferrocene with the arene in the presence of aluminum chloride. Application of this process to mono- and dialkylnaphthalenes gave mixtures of complexes having the $CpFe^+$ group bound to either of the non-equivalent rings, with slight selectivity[307]. Addition of $TiCl_4$ to the reaction mixture, apparently to function as a Cp acceptor, has appeared in a patent, in which a yield of 71% $CpFe(\eta\text{-}PhCHMe_2)^+$ was claimed[308].

Dicationic complexes of biphenyl, diphenyl ether, phenanthrene, fluorene, and other di- or polycyclic arenes have been prepared by the standard method. In the cases of the condensed ring compounds, the two $CpFe^+$- substituents were trans[309]. Proton and carbon NMR data for many examples of $CpFeAn^+$ have been reported [307,309]. A ^{13}C study of $CpFe(C_6H_6)^+$ AsF_6^- in the solid state indicated three different crystal forms with varying degrees of rotational freedom[310]. Attachment of long aliphatic chains to the arene group in $CpFeAn^+$ via ester, amide and other linkages resulted in organometallic surface-active agents[311].

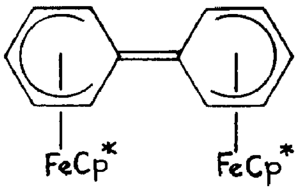
$CpFeAn^+$ [An = chlorobenzene bearing methyl and/or chloro substituents] were used to arylate malonate esters, forming $CpFe(ArCHE_2)^+$, from which the free arylmalonic esters were released by pyrolytic sublimation[312]. Nucleophilic substitution on $CpFe(\underline{m}\text{- or }\underline{p}\text{-}C_6H_4Cl_2)^+$ by β-ketoester and β-diketone anions resulted in displacement of only one chloride ion. The presence of two methyl substituents ortho to chloro or nitro leaving groups created little hindrance to nucleophilic attack by amines, alkoxides, and carbanions in most cases[313]. But hydride ion (from $NaBH_4$), CN^-, and $AcCH_2^-$ added to the unsubstituted ortho-position of $CpFe(2\text{-}MeC_6H_4X)^+$ rather than displace X in most cases. With $2,6\text{-}Me_2C_6H_3X$, addition at all positions was observed, with meta predominant. Steric, electronic, and free valency effects were all considered to play roles in these reactions[314].

Removal of α-protons in $CpFeAn^+$ by bases to form reactive carbanions is also being exploited increasingly in synthesis. Thus, $CpFe(\eta\text{-}PhCHPh_2)^+$ has been treated with $KOCMe_3$, followed by MeI, to form $CpFe(\eta\text{-}PhCMePh_2)^+$ [309]. More dramatically, treatment of $CpFe(C_6Me_6)^+$ with excess $KOCMe_3$ and allyl bromide formed the "tentacle sandwich complex," $CpFe[C_6(CH_2CH_2CH{=}CH_2)_6]^+$ in 75% yield. This could be hydrosilylated or hydroborated to form further hexasubstituted benzene complexes[315]. Deprotonation of $CpFe(\eta^6\text{-tetrahydronaphthalene})^+$ and reaction with chiral menthyl nitrite produced optically active (4-7% e.e.) oxime and, by hydrolysis, ketone[316].

Electronic spectra of the deprotonated complexes $(CpFePh)_2CH^+$ and $(CpFePh)_2CPh^+$ have been obtained and compared with those bearing only one $CpFe^+$-coordinated phenyl ring[317]. A full paper on reaction of reduced, 19-electron CpFeAn [An = mono-hexaalkylbenzene] compounds with O_2 has appeared. In the presence of sodium salts the reaction produced $CpFeAn^+$ and Na_2O_2. Otherwise, reactive CpFe(η^5-benzyl) derivatives, formed by electron transfer to form superoxide ion and deprotonation of the alkylarene by the superoxide, resulted. The benzyl derivatives could be intercepted by reaction with electrophiles at -50°[318].

$CpFe(C_6H_6)$ catalyzed oxidation of methanolic furfural to methyl 2-furoate by aqueous hydrogen peroxide in the presence of visible light[319]. Fluorescence yields of $CpFeAn^+$ at about 520 nm have been determined. Excitation resulted in efficient arene ligand exchange and valence isomerization of hexamethyl Dewar benzene[320].

Electrochemical reduction of CpFe(η^6-fluorene)$^+$, with formation of η^6- and η^5-fluorenyl species, has been studied[321]. Polarographic reduction potentials for two reduction steps of many examples of $CpFeAn^+$ have been measured[322]. Anisotropy in the ESR spectra of CpFe(PhR) [R = $CHPh_2$, $CMePh_2$, OPh] was attributed to interactions of the free phenyl groups with the CpFe moiety[323]. Reduction of binuclear dications such as $CpFePhCH_2PhFeCp^{2+}$ by a sodium mirror at -100° and ESR spectra of the reduction products have been reported[324]. Mössbauer spectra of $CpFeC_6Et_6$ and $Cp^*FeC_6Et_5H$ indicated the extra electron to occupy the e_1^* orbital[325]. The 37-electron systems resulting from one-electron reduction of bis$(Cp^*Fe)^+$ complexes of biphenyl, dihydrophenanthrene, and triphenylene have been characterized by Mössbauer spectroscopy as delocalized mixed-valence systems. The 38-electron neutral systems showed temperature-independent Mössbauer parameters, suggestive of location of the frontier electrons primarily on the polyaromatic ligand, as in 55 326.



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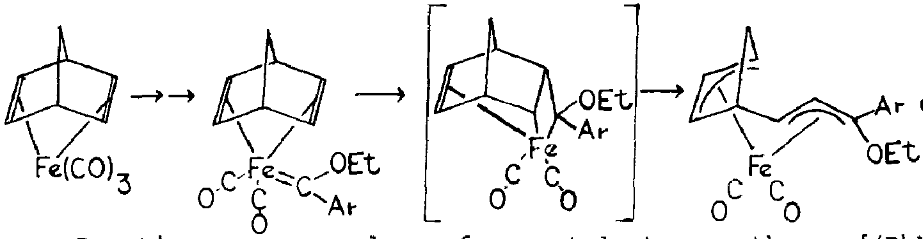
Compound **29** (in Equation 18) is an example of a η^6 bis(allylic)$Fe(CO)_2$ complex produced by intramolecular rearrangement of a carbene complex[151,152]. Application of the standard methodology (addition of aryl-lithium to a carbonyl group, then reaction with Et_3O^+) to (η^4-norbornadiene)$Fe(CO)_3$ proceeded as shown in Eq. 34[327]. However, with (1,5-COD)$Fe(CO)_3$, hydrogen migration occurred, and transfer of the iron to the arene ring, eventually forming product **56**[328,329], an example of a rather rare class of compounds, (η-benzene)dicarbonylirons.



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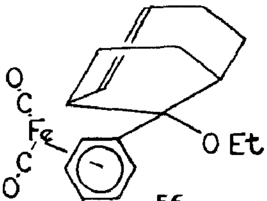
Reactive arene complexes from metal atom syntheses [(PhMe)-$Fe(C_2H_4)_2$, (PhMe)Fe(η^4-1-methylnaphthalene), and (η^4,η^4-C_8H_8)-$(FePhMe)_2$] effectively catalyzed cyclotrimerization of alkynes to arenes[330]. Cocondensation of iron atoms with toluene and thiaboranes led to formation of (η-toluene)thiaferraborane clusters **57** and **58**[331]. Ferracarborane clusters have also been produced by more conventional means, reaction of carborane anions with $FeX_{2,3}$. Thus produced were closo-3-(η-PhMe)-3,1,2-$FeC_2B_9H_{11}$ and the (η-p-xylene) analog[332].



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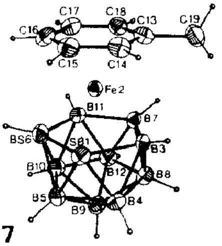

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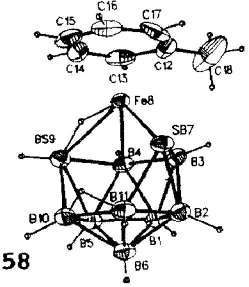

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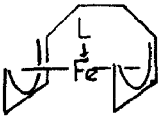
An_2Fe^{2+} salts were monoethylated by Et_3Al to form substituted (6-ethylcyclohexadienyl)$FeAn^+$ salts. Yields improved with the extent of substitution of the arene ring. Absence of transfer of a second ethyl group to the remaining ring was ascribed to an electron transfer mechanism, and lowered reducibility of the monoethylated monocation[333]. Mössbauer parameters of eight $(An)_2Fe^{2+}$ salts have been measured and related to their electronic structure. Electron transfer in An_2Fe^{2+} $B_{12}H_{12}{}^{2-}$ was suggested[334].

The η^8-1,3,7,9-decatetraene complexes **59** were produced by ligand coupling upon refluxing (η^5-pentadienyl)(η^3-pentadienyl)FeL [L = PEt_3, PPr_3] in ether[133].



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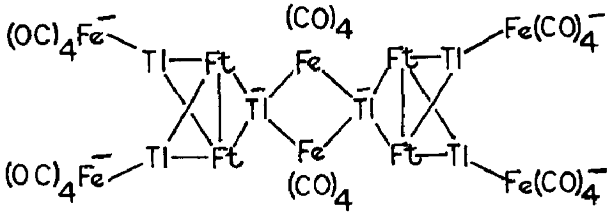
9. BIMETALLIC COMPOUNDS

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

Fenske-Hall electronic structure calculations have been carried out on the systems $(OC)_3Fe(\mu\text{-}CO)_3Fe(CO)_3$ and $(OC)_3Fe(\mu$-

$CO)_2(\mu\text{-}H)Fe(CO)_3^-$ in order to assess the trans effects of bridging ligands[335]. A μ-difluorovinylidene analog of $Fe_2(CO)_9$ has resulted from reaction of $CF_2(COCl)_2$ with $Fe_3(CO)_{11}^-$. A process involving acylation of a bridging carbonyl oxygen and loss of CO_2 was suggested[336].

A whole family of polyanions made up of $TlFe_2$ and Tl_2Fe_2 rings with pendant $Fe(CO)_4^-$ groups resulted from reaction of thallium salts with $KHFe(CO)_4$. The parent of the series, Et_4N^+ $(OC)_4Fe{=}Tl\text{-}Fe(CO)_4^-$, actually existed as a cyclodimer in the crystal. The structure of the most complex member of the series, $Tl_6Fe_{10}(CO)_{36}^{6-}$, is shown as **60**[337]. Improved syntheses of the spiro compounds $Y[Fe_2(CO)_8]_2$ [Y = Si, Ge, Sn] have been developed, the first two from reaction of YH_4 with $Fe_2(CO)_9$ in hexane, the latter from $SnCl_4$ and $Fe_2(CO)_8^{2-}$ in THF. The crystal structure of the silicon compound showed the expected perpendicular $SiFe_2$ rings[338]. $(\mu\text{-}GeH_2)_2[Fe(CO)_4]_2$ reacted with $Co_2(CO)_8$ to form spirogermane **14** (see Equation 8), which in solution slowly lost CO from iron, with formation of a μ-CO bridge between the two iron atoms[89].



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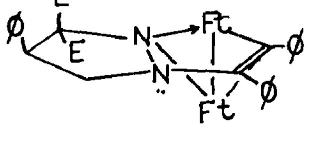
Photosubstitution reactions of $(bpy)Fe(CO)(PBu_3)(\mu\text{-}CO)\text{-}Fe(CO)_4$ havebeen studied at 133 K to avoid problems resulting from thermal instability of the products, in which the last CO of the iron coordinated to the bipyridyl (bpy) had been displaced[339]. Reactions of (cyclic diazene)$Fe_2(CO)_6$ complexes with alkynes have been studied, in which connection Mössbauer data and crystal structures of some of the azaferracyclic products have been reported. Reaction of a (pyrazoline)$Fe_2(CO)_6$ with diphenylacetylene produced, in addition to previously mentioned **21**, the product **61**, in which one nitrogen remained bonded to both irons while the other was displaced by the Ph_2C_2 unit[138].



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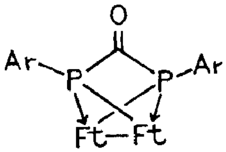
An attempt at rational synthesis of μ-phosphinidene complexes by reaction of $Fe_2(CO)_8^{2-}$ with $RPCl_2$ led to complex mixtures of products. With R = $CH(SiMe_3)_2$, two of the products cocrystallized and were identified by crystallography as $(OC)_3\text{-}Fe(\mu\text{-}OH)(\mu\text{-}PHR)Fe(CO)_3$ and $(OC)_3Fe(\mu\text{-}H)(\mu\text{-}CO)[\mu\text{-}P(OH)R]Fe(CO)_3$.

For R = 2,4,6-tri-t-butylphenyl, ^{31}P NMR of the product mixture indicated the formation of $Fe_2(CO)_6(\mu\text{-PHR})_2$, $RPH_2 \rightarrow Fe(CO)_4$, RPH-PHR, and other products[77].

Substitution reactions of the 33-electron radical $Fe_2(CO)_7(\mu\text{-PPh}_2)$ with tertiary phosphines L have received intensive study. The radical was about 10^5 times as reactive as the diamagnetic analog $Fe_2(CO)_6(\mu\text{-CO})(u\text{-PPh}_2)^-$. The first substitution step cleanly introduced L into the position trans to the PPh_2 bridge on the six-coordinate iron. However, further substitution gave two disubstituted radical products accompanied by 35-electron addition products and disproportionation products. An associative substitution mechanism was indicated by kinetics and electrochemical results, and several crystal structures of both open- and closed- shell species were reported[340].

A revised crystal structure for $LFe(CO)_3[\mu\text{-PPh}(\rightarrow Mn(CO)_2Cp)]Fe(CO)_3L$ [L = Bu_3P] has been reported, based upon revision of the originally reported space group[341].

Reaction of **39**, $Fp^*\text{-P=PAr}$ [Ar = 2,4,6-tri-tert-butylphenyl], with $Fe_2(CO)_9$ gave, along with the previously mentioned $Fe(CO)_4$ derivative, diiron derivative **62**, which features a CO inserted into the original P-P bond[83]. Thermolysis of the diphosphene complex, (PhPPPh)$[\eta^1\text{-Fe(CO)}_4][\eta^2\text{-Fe(CO)}_4]$ (structurally similar to **12**) in refluxing benzene gave the spiro compound **63**, in 70% yield, along with traces of $(\mu_3\text{-PPh})_2Fe_3(CO)_9$[342]. Reactions of $Li^+_2\ (\mu\text{-PPh})_2Fe_2(CO)_6^{2-}$ with various halometal compounds have been used to prepare trimetallic compounds: with FpBr, the product was $(\mu\text{-PHPh})(\mu\text{-PPhFp})Fe_2(CO)_6$; with Group 10 L_2MX_2 compounds, a $P\text{-ML}_2\text{-P}$ bridge was created without disruption of the P_2Fe_2 butterfly framework[343]. Pyridine-catalyzed addition of $(\mu\text{-PHPh})_2Fe_2(CO)_6$ to electrophilic alkynes also built bridges, in



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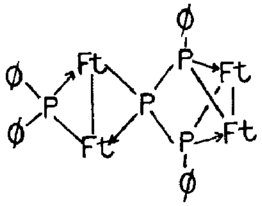

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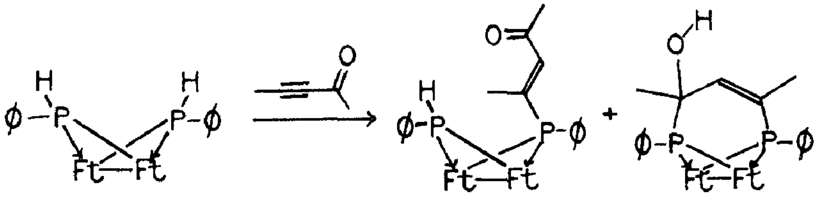


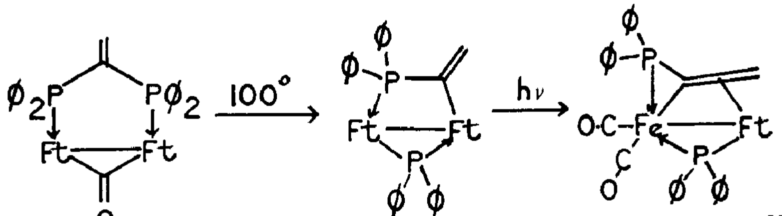
(35)

these cases organic ones, between the phosphorus atoms. Depending on the alkyne, one-, two-, and three-carbon bridges resulted. An example is shown in Eq. 35[344].

An extensive series of reactions of the bridging CO group in $(\mu\text{-}R_2NPC(=O)PNR_2)Fe_2(CO)_6$ [structurally analogous to **62**, but with NR_2 groups on each P; R = isopropyl] has been reported. Whereas $NaBH_4$ reduced the C=O group normally to a CHOH group, reduction with LAH occurred with rearrangement to form $(\mu\text{-}R_2NPH\text{-}CH\text{-}PNR_2)Fe_2(CO)_6$, **64**. Alkyl-lithium reagents added normally. Some reagents (alcohols, HBr) reacted with expulsion of the CO bridge to form bis(phosphido) complexes, $[\mu\text{-}PHNR_2][\mu\text{-}P(OMe)NR_2]Fe_2(CO)_6$ and $[\mu\text{-}PBrNR_2][\mu\text{-}PHBr]Fe_2(CO)_6$[345]. Reactions of triphosphine-bridged complex $[\mu\text{-}P(NR_2\text{-}P(NR_2)\text{-}P(NR_2)]Fe_2(CO)_6$ with similar species occurred with cleavage of the P-N bond at the center, uncoordinated phosphorus atom, giving $[\mu\text{-}P(NR_2)\text{-}PX\text{-}P(NR_2)]Fe_2(CO)_6$ [X = OMe, OEt, Cl, Br, H]. The free phosphorus atom was able to coordinate to neutral metal fragments $[Cr(CO)_5]$, or anionic metal fragments could displace the chloride, giving in either case trimetallic compounds[346].

The bis(diphenylphosphino)ethene ligand in $[\mu\text{-}CH_2{=}C(PPh_3)_2]\text{-}Fe_2(CO)_7$ underwent partial cleavage when the compound was subjected to thermolysis and photolysis (Eq. 36)[347]. Compound **65** in Equation 36 provides an excellent example of the difference in bond length between P→Fe bonds (here, 2.205 and 2.166 Å) and P-Fe bonds (2.268 Å), discussed in Section 2 of this Review.

Reaction of ArP=C=PAr [Ar = 2,4,6-tri-tert-butylphenyl] with $Fe_3(CO)_{12}$ eventuated in hydrocarbation of a C=P bond by an unactivated methyl group, forming **66**[348], a product analogous to the previously described LAH reduction product **64**.

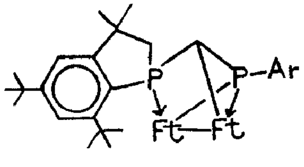


65 (36)

Another ligand rearrangement occurred when $(Ph_2P\text{-}C{\equiv}CR)Fe_3\text{-}(CO)_{11}$ [R = Ph, $CHMe_2$, CMe_3] was pyrolyzed to form $(\mu_2\text{-}\eta^1,\eta^2\text{-}CCR)(\mu\text{-}PPh_2)Fe_2(CO)_6$[349]. Addition of diethylamine to the coordinated triple bond of the product with R = Ph produced zwitterionic **67**[350]. Both the alkynyl complex [with R = CMe_3] and the adduct [with R = Ph] were characterized by X-ray crystallography, along with Ru and Os analogs[349,350].

Loss of an NSN fragment occurred during reaction of the eight-membered heterocycle $RAs(NSN)_2AsR$ [R = CMe_3] with $Fe_2(CO)_9$.

The product was $(OC)_3Fe[\mu\text{-}As(R)N{=}S{=}N\text{-}As(R)]Fe(CO)_3$ (X-ray)[351]. A few additional examples of compounds with mixed Group 15 and Group 16 bridges have been reported. For example, μ-iminoacyl complexes **68** resulted when RSC(=NPh)Ph [R = Me, Et] reacted with



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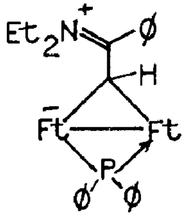

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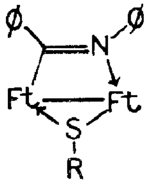
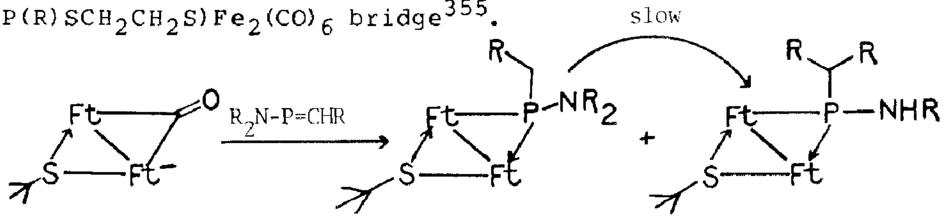


68

$Fe_3(CO)_{12}$, and they were also produced by reaction of PhC(=NPh)Cl with $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}SCMe_3)Fe(CO)_3^-$ [352]. A two-step route from the latter anion involved reaction with PhC≡CBr to form $(\mu\text{-}\eta^1,\eta^2\text{-alkynyl})(\mu\text{-}SR)Fe_2(CO)_6$ complexes, which added aniline to form a homolog of **68**, $(OC)_3Fe(\mu\text{-}CH_2CPh{=}NPh)(\mu\text{-}SCMe_3)Fe(CO)_3$. The alkynyl complex added diethylamine to form the $(\mu\text{-}SCMe_3)$ analog of **67**[353]. Equation 37 [R = $SiMe_3$] shows another use of the above anion to prepare mixed-bridge $Fe_2(CO)_6$ complexes[354]. With $R_2C{=}PCl$, it produced $(OC)_3Fe(\mu\text{-}P{=}CR_2)(\mu\text{-}SCMe_3)Fe(CO)_3$[354]. Reactions of $(\mu\text{-}PRCl)(\mu\text{-}Cl)Fe_2(CO)_6$ with thiols in the presence of base generally resulted in initial displacement of the μ-Cl; with further thiol, the P-Cl also underwent displacement, to form $(OC)_3Fe(\mu\text{-}SR)(\mu\text{-}P(SR)R)Fe(CO)_3$[355]. Ethanedithiol generated a $(\mu\text{-}P(R)SCH_2CH_2S)Fe_2(CO)_6$ bridge[355].



(37)

Reactions of "Roussin esters," $(\mu\text{-}SR)_2Fe_2(NO)_4$, with various nucleophilic anions have been studied. The usual products were paramagnetic ions $Fe(NO)_2X_2^-$ [X = Br, I, N_3, NCO, NO_2], but in the case of SCN^-, $Fe(NO)_2(SR)(SCN)^-$ could be detected as an intermediate in formation of $Fe(NO)_2(NCS)_2^-$ [356]. Crystal structures of the methyl, pentyl, and <u>tert</u>-butyl Roussin esters have been determined; all showed planar Fe_2S_2 rings and trans alkyl groups[357].

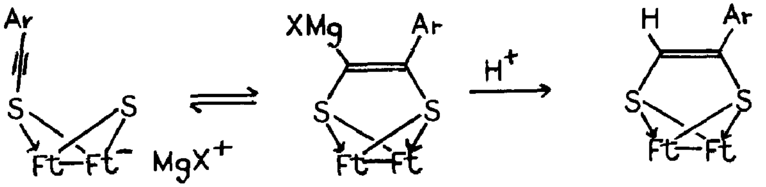
Cyclic $(Me_2Si\text{-}S)_2$ served as a source of sulfur in reactions with iron carbonyls; thus, reaction with $Fe_2(CO)_9$ in hexane gave $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$[358]. Electrochemical reduction of $S_2Fe_2(CO)_6$ cleaved the S-S bond to form the dianion $S_2Fe_2(CO)_6^{2-}$, capable of yielding many derivatives in reactions with electrophiles[359]. For example, reaction of the dianion with $(Me_2N{=}N)_2$-

$Mo(PPh_3)_2Cl^+$ gave $(OC)_3Fe[\mu\text{-}S\text{-}Mo(N{=}NMe_2)_2(PPh_3)\text{-}S]Fe(CO)_3$[360]. The same dianion resulted from reduction of $Fe_4S_4(SPh)_4{}^{2-}$ under one atmosphere of CO, a process which initially formed $Fe_4S_4(CO)_{12}{}^{2-}$ [361]. Also worth mentioning in this context is the formation of **6** (Eq. 5) by sodium borohydride reduction of dithiocarboxylate complexes[59].

Mössbauer spectra of numerous iron-sulfur compounds, including $S_2Fe_2(CO)_6$ and $(\mu\text{-}SR)_2Fe_2(CO)_6$, have been reported. As expected, they showed structurally equivalent iron atoms in all these cases[362]. The kinetics of exo-endo isomerization of the alkyl groups in $(\mu\text{-}SCH_2Ph)(\mu\text{-}SCMe_3)Fe_2(CO)_6$ has been studied by dynamic NMR measurements over the range 35-110°[363]. Reaction of $(\mu\text{-}SCH_2Ph)(\mu\text{-}SCHMe_2)Fe_2(CO)_6$ with excess triphenylphosphine in boiling toluene resulted in displacement of one CO ligand from each iron[365]. Such displacements were accelerated by two-electron reduction in the presence of the ligand; trimethyl phosphite gave consecutively mono- and di-substituted products under such reducing conditions, at room temperature[366].

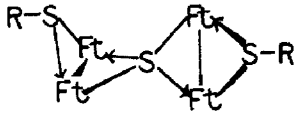
Several papers have reported on reactions of Grignard reagents with $S_2Fe_2(CO)_6$ and interception of the resulting anions, $(\mu\text{-}SR)(\mu\text{-}S)Fe_2(CO)_6{}^-$ MgX^+, with electrophiles. For example, use of p-$MeC_6H_4C{\equiv}CMgBr$ followed by alkylating agents gave rise to eleven new compounds $(\mu\text{-}SC{\equiv}CC_6H_4Me)(\mu\text{-}SR)Fe_2(CO)_6$[367]. The electrophiles used in the second step included α-chloroketones, -esters, and -ethers[368], Michael acceptors[369], and FpI[370]. The crystal structure of $(\mu\text{-}SMe)(\mu\text{-}SFp)Fe_2(CO)_6$ showed the exo,exo-conformer, which was also the only conformer detectible by NMR in solution[370]. Mössbauer spectra of numerous $(\mu\text{-}SR)(\mu\text{-}SFp)Fe_2(CO)_6$ examples were reported[371].

With some electrophiles [CF_3CO_2H, HBr, MeHgCl], however, the product of quenching of the adducts from arylalkynyl Grignard reagents and $S_2Fe_2(CO)_6$ was a bridged species (Eq. 38), which resulted from an equilibrium between open and bridged forms of



(38)

the adducts[372]. Interception of the anions $(\mu\text{-}SR)(\mu\text{-}S)Fe_2(CO)_6{}^-$ MgX^+ with diacid chlorides at -40° gave the expected products having two S_2Fe_2 clusters tethered through the diacyl chain. However, at room temperature, the same reaction produced the μ_4-S products, **69**[373]. Crystal structures of the products with R =



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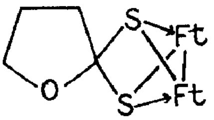

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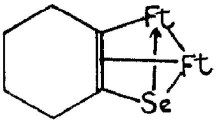
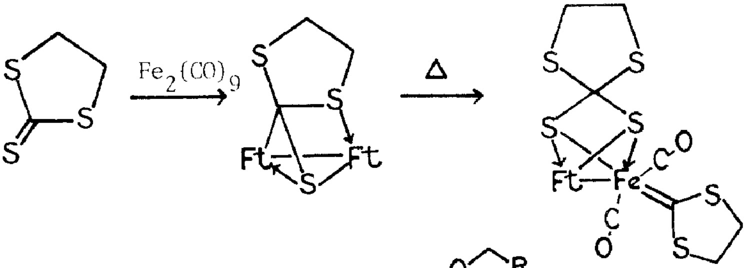


71

Et[373] and CH_2Ph[374] showed similar features. A more extended version of **69**, $(\mu\text{-SR})Ft_2(\mu_4\text{-S})Ft_2(\mu_4\text{-S})Ft_2(u\text{-SR})$ [R = cyclohex-2-enyl] was prepared by reaction of cyclohexene, sulfur, and $Fe_3(CO)_{12}$ at 80°. A crystal structure was reported[375]. A similar reaction in THF produced the tetrahydrofurylene-2,2-dithiolate-bridged species, **70**[376].

Reaction of $Fe_2(CO)_9$ with ethylene trithiocarbonate resulted in coordination of the C=S bond. The product, upon warming, underwent extensive intermolecular redistribution of ligands to form a carbenoid product (Eq. 39)[377]. Another rearrangement to a carbenoid (Eq. 40, R = adamantyl, L = trimethyl phosphite)[378] may be analogous. The structure of the tetrahedral thioacyl complex Ph_4P^+ $(u\text{-RCS})Fe_2(CO)_6{}^-$ [R = 2,2,6,6-tetramethylcyclohexyl] has been reported, as has reaction with NO^+ to form the neutral analog. The structure of $(OC)_3Fe(\mu\text{-RCS})Fe(CO)(NO)(PPh_3)$ was similar to that of the hexacarbonyl anion[379].



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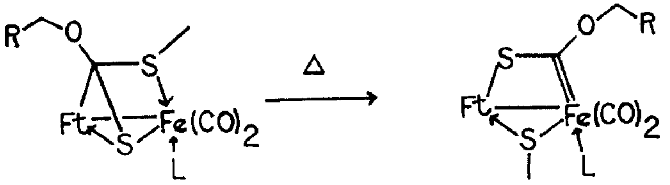
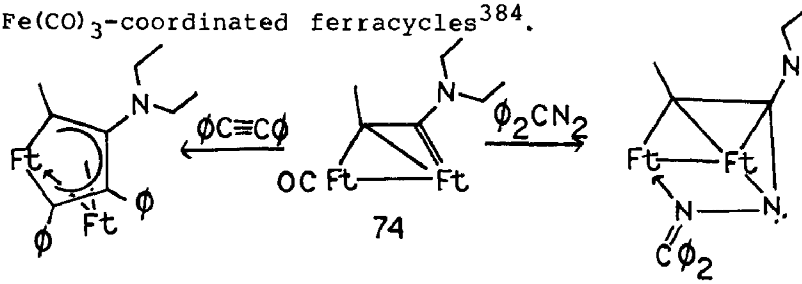


(40)

Oxidation of the selenoketocarbene complex **71** with trimethylamine oxide generated the free selenoketoketene, which could be trapped by alcohols[380].

Reaction of K^+ $Fe(CO)_3NO^-$ with benzoyl chloride produced **72**, (X-ray structure), evidently the product of a rather complex reaction sequence[381]. Displacement of chloride from $Ft(\mu\text{-Cl})(\mu\text{-CPh=CHPh})Ft$ by thiolates produced $Ft(\mu\text{-SR})(\mu\text{-CPh=CHPh})Ft$; the crystal structure of the S-benzyl compound was reported[382]. Reaction of PhCH=NR [R= cyclohexyl, octyl] with $Fe_3(CO)_{12}$ at 80°

produced not only **73** [same R], but also the transbenzylated product, **73** [R = benzyl][383]. Reactions of the cyclic aminocarbene complex **74** (Eq. 41) with diphenylacetylene and diphenyldiazomethane resulted in additions to the Fe=C bond, with formation of $Fe(CO)_3$-coordinated ferracycles[384].



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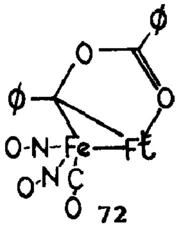
Reactions of thiophenes with $Fe_3(CO)_{12}$ produced thiaferrole complexes such as **75** (the only product from 2-methylthiophene), which at 80° underwent desulfurization to form the 2-methylferrole complex. The benzothioferroles were more stable thermally, but gave benzothiophene at 160° under high CO pressure or upon flash vacuum thermolysis at 280° [385].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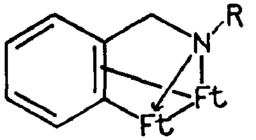
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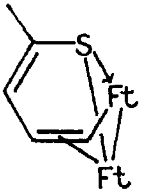
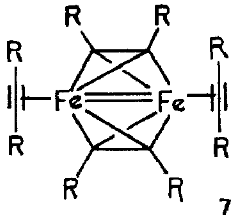

75

^{13}C NMR shifts of μ_2-η^2-bridging acetylides have been reported, and optimum experimental parameters for recording such data recommended[386]. Reactions of alkynes with the reactive (η-PhMe)$Fe(C_2H_4)_2$ resulted in many cases in cyclotrimerization to form hexasubstituted arenes. With bis(trimethylsilyl)acetylene, however, no cyclotrimer was obtained. In the presence of L = trimethyl phosphite, $(Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3)_3FeL_2$ was produced[330]. In the absence of the phosphite, the product was **76** [R = $SiMe_3$]. A sequence was proposed, involving (η-PhMe)$Fe(Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3)_2$, which lost toluene to form $Fe(Me_3Si\text{-}C{\equiv}C\text{-}SiMe_3)_2$. This unsaturated species dimerized to form **76** rather than undergo conversion to a ferrole, as a consequence of the bulky trimethylsilyl groups[387].

Irradiation of $(OC)_4Fe(PEt_3)$ at -70° in the presence of nitrogen, followed by purging with acetylene, produced **77** [L = PEt_3] (5% yield, X-ray structure) and, with excess acetylene, (η^4-tropone)$Fe(CO)_2(PEt_3)$. In solution, **77** was in equilibrium with the μ-vinylidene species, as shown by NMR[117]. The stepwise synthesis of the tropone ligand was clearly revealed by use of the tethered diiron compound, (μ-DPPM)(μ-CO)$Fe_2(CO)_6$. Reaction



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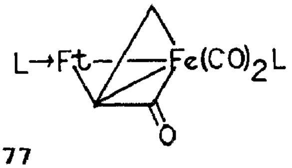

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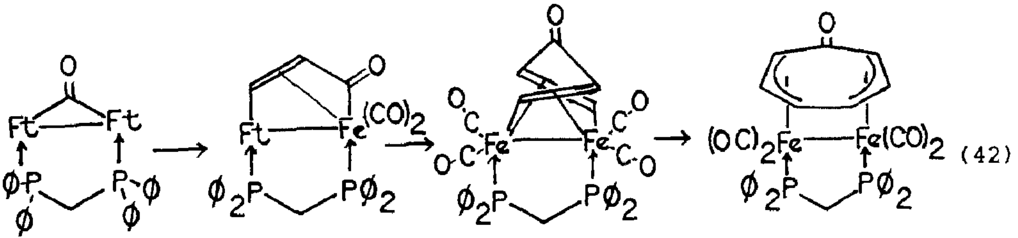
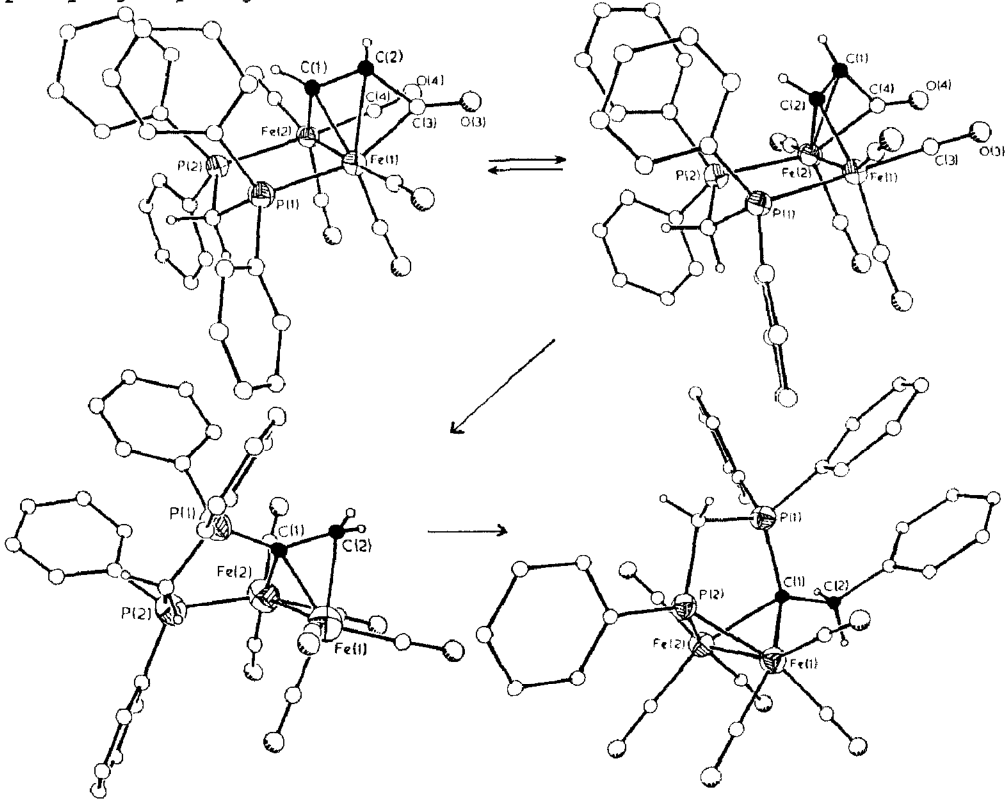
with acetylene under irradiation consecutively produced the sequence of species shown in Equation 42. The tropone complex



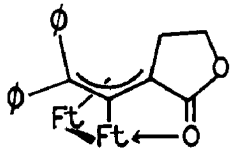
78 **79** (42)

showed a very long Fe-Fe bond distance of 2.95 Å[388]. A beautifully organized and presented set of X-ray structures was used to elucidate the fluxionality of **78** and the migration upon heating of a phosphorus atom from iron to carbon, followed by a phenyl group migration[389]:



The electrochemistry of "flyover bridge" compounds [μ-CR=CR-C(=O)-CR=CR-]$Fe_2(CO)_6$ [R = Me, Et, Ph], structurally analogous to the DPPM-substituted **79**, has been investigated. Reduction of the tetraphenyl compound to the monoanion was said to result in formation of solvated $Fe(CO)_3^-$ and $(Ph_4C_4C{=}O)Fe(CO)_3$, which reverted to the "flyover bridge" compound on reoxidation[390]. Photolysis of the tetraphenyl compound in the absence of ligands eventuated in formation of tetraphenylcyclopentadienone, its $Fe(CO)_3$ complex, and $Fe(CO)_5$. Initial photolytic loss of CO was indicated by efficient formation of phosphine-substituted derivatives of the starting materials when phosphines were present. The "flyover bridge" compounds efficiently catalyzed alkene isomerization in the presence of light[391].

Reaction of iron pentacarbonyl with tribromofluoromethane produced the tetrafluoroferrole complex, [η-$C_4F_4Fe(CO)_3$]$Fe(CO)_3$ [*Fe-Fe*][392]. Photolysis of an allenic lactone and $Fe(CO)_5$ gave as the principal product, in addition to previously mentioned **22** and **23**, **80**[139]. Oxidation of $(Me_2C{=}C{=}C{=}CMe_2)Fe_2(CO)_6$ by Ce(IV) in alcohols ROH [R = Me, Et, $CHMe_2$] gave both $Me_2C{=}C(CO_2R){-}C(CO_2R){=}CMe_2$ and $ROCMe_2C{-}C{\equiv}C{-}CMe_2OR$, via cationic seventeen-electron species[393].



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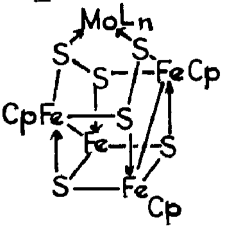
9b. Diiron Compounds, Derivatives of $Cp_2Fe_2(CO)_4$

Reaction of $(CpFe)_4S_6$ with molybdenum carbonyl compounds let to insertion of a MoL_n unit [MoL_n = $Mo(CO)_4$ or $Mo(CO)_2(NCMe)Br$] into a S-S bond, giving **81**. The electronic distribution within the Fe_4S_4 core was little perturbed by the presence of the molybdenum, based on EPR and Mössbauer results[394].



81

Ultraviolet photoelectron spectra of a series of organometallic dimers containing bridging CO, NO, CH_2, and PR_2 groups have been interpreted in terms of the results of discrete variational Xα calculations. The results indicated that low-lying acceptor orbitals on the bridging ligands favored delocalized interactions (concerted back-donations) at the expense of direct metal-metal bonding. Compounds included Fp_2, "where the metal-metal bond is definitely absent"[395]. Comparison of Mössbauer isotope shifts and effective nuclear charge, as obtained from Fenske-Hall calculations, for a series of organoiron carbonyl clusters showed a linear correlation, from which *cis*- and *trans*-Fp_2 deviated as a consequence of reduced 4s orbital populations[396]. Calculations by other workers have indicated that the HOMO of Fp_2 is metal-based and Fe-Fe π^* in character, consistent with the reversible one-electron oxidation observed in electrochemical studies. The LUMO was found to be a strongly antibonding σ^* orbital[397].

IR studies showed that the (μ-CO) ligand of Fp_2 functioned as a hydrogen-bond acceptor toward $(F_3C)_3COH$ and HCl in liquid xenon. Protonation led to hydrogen-bridged dimer species[398]. Fp_2 has been used as a reagent to prepare thin films by pyrolysis and deposition[399] and as a catalyst for ligand substitution reactions of cobalt carbonyl clusters[400].

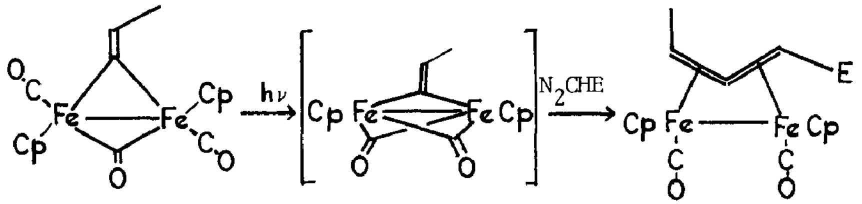
Siloxane-bridged derivatives of *cis*-Fp_2 were prepared by reaction of $Cp\text{-}SiR_2OSiR_2Cp$ [R_2 = Me_2 or Me,Ph] with $Fe(CO)_5$. Oxidation in presence of PPh_3 or reduction by K^+ $OCPh_2^-$ gave the expected tethered derivatives of $FpPPh_3^+$ and Fp^- [401].

Reaction of $InFe(CO)_2Me$ [In = η^5-indenyl] with nucleophilic anions, Fp^- or its indenyl analog, resulted in formation of the stable bimetallic anions $[InFe(CO)](\mu\text{-}CO)_2[\eta^5\text{-}Cp$ or $\text{-}In]Fe(CO)\text{-}(\eta^1\text{-}COMe)^-$. The unsymmetrical compound slowly equilibrated in solution at room temperature by transfer of the acetyl group between irons, but the isomer with the acetyl group on the indenyl-bound iron preferentially crystallized out (X-ray structure)[402].

Reduction of Fp_2 by Ca^{2+} $[H_2Al(OCHMe_2)_2^-]_2$ produced *cis*- and *trans*-$[CpFe(CO)](\mu\text{-}CH_2)(\mu\text{-}CO)[FeCp(CO)]$, **82**. The mechanism proposed involved reduction of a terminal CO and bridge-terminal interchange[403]. Nucleophiles Me_3N, $Ph_2C{=}NH$, $OCMe_3^-$, Br^-, CHE_2, MeLi, and $PhCuCN^-$ added unexceptionally to the electrophilic carbon of $[CpFe(CO)](\mu\text{-}CH^+)(\mu\text{-}CO)[FeCp(CO)]$. Reaction with water occurred with disproportionation of the initial (μ-CHOH) species, giving Fp_2 and **82**. $HFe(CO)_4^-$ reduced the cation to **82**. Ketones added as the enols to afford, after proton loss, $\mu\text{-}CHCHRC({=}O)R$ products[404]. CO also added to the electrophilic carbon of the $\mu\text{-}CH^+$ species to give the $\mu\text{-}CHC{\equiv}O^+$ acylium species, which underwent attack by nucleophiles [$HFe(CO)_4^-$, water, ammonia] to form $\mu\text{-}CHC({=}O)Nu$ products[405].

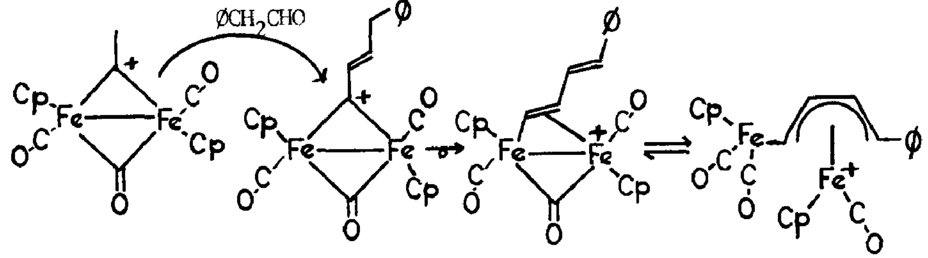
NMR studies of rotational barriers in $[CpFe(CO)](\mu\text{-}C\text{-}CH{=}CH\text{-}C_6H_4NMe_2)(\mu\text{-}CO)[FeCp(CO)]^+$ revealed that rotation of the entire vinylcarbyne ligand had a lower barrier (44 kJ/mol) than rotation of the NMe_2 group (46 kJ/mol) or the aryl group (54 kJ/mol). Fenske-Hall calculations traced the low barrier to vinylcarbyne rotation to maintenance of conjugation throughout rotation as a consequence of use of both orthogonal p-orbitals on the carbyne carbon[406]. $NaCHE_2$ and other nucleophiles [$HFe(CO)_4^-$, MeLi, ArLi, PMe_3] added to the remote vinyl carbon of a vinylcarbyne complex to form the μ-alkenylidene products, $[CpFe(CO)](\mu\text{-}C{=}CH\text{-}CHArNu)(\mu\text{-}CO)[FeCp(CO)]$[407].

Photolysis of (μ-alkenylidene) complexes in the presence of diazo compounds produced (μ-allene) products; an example is shown in Equation 43. Studies with labelled CO indicated formation of a triply-bridged intermediate as shown. The same intermediate was responsible for reactions with hydrogen or Me_3SiH under irradiation. The allenes could be freed upon air oxidation or photolysis under CO[403].



(43)

Thermal reaction of the μ-vinylidene species, $[CpFe(CO)](\mu\text{-}C{=}CH_2)(\mu\text{-}CO)[FeCp(CO)]$, with TCNE proceeded by an electron-transfer process, which resulted in formation of the $\mu\text{-}C{=}CH\text{-}C(CN){=}C(CN)_2$ bridging group (X-ray)[409]. Cationic μ-vinyl complexes $[CpFe(CO)](\mu\text{-}CH{=}CHR)(\mu\text{-}CO)[FeCp(CO)]^+$ [R = H, Pr] underwent nucleophilic attack (Nu = CHE_2^-, $PhSO_2CHE^-$, $MeCuCN^-$) at the β-carbon to form μ-CHCH(R)Nu adducts[410]. In a reaction related to the one that formed **51** (Sect. 7c) upon hydride removal from $[CpFe(CO)](\mu\text{-}CH\text{-}CH_2\text{-}CH{=}CH_2)$, it has been found that condensation of phenylacetaldehyde with the μ-ethylidyne cation led to rearrangement to a η^4-diene complex (Equation 44)[292].



(44)

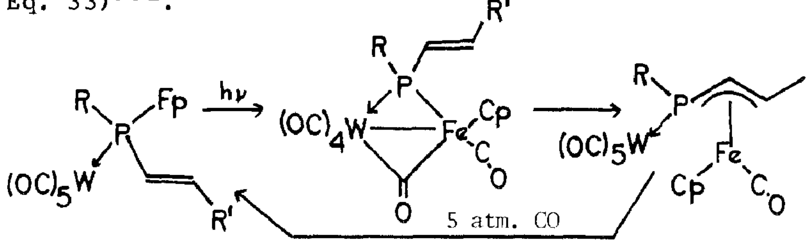
9c. Heterobimetallic Compounds

A wide range of phosphido-bridged Fe-M bonded bimetallic complexes, $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}PR_2)ML_n$, [R = $SiMe_3$; ML_n = $Fe(NO)_2$, $Cr(CO)_4$, $W(CO)_4$, MnCpCO, and CrCpNO] were produced by photolytic decarbonylation of precursors $FpPR_2 \rightarrow ML_n(CO)$[411]. $\mu\text{-}PH_2$ analogs could be prepared either by protodesilylation of the precursors followed by photolysis [ML_n = MnCpCO, MnCp'CO, CrCpNO] or by protodesilylation of the $\mu\text{-}P(SiMe_3)_2$ Fe-M bonded products[75].

Laser generated La^+ reacted with $Fe(CO)_5$ in the gas phase to produce mainly $LaFe(CO)_3^+$, which lost the CO ligands upon collisional activation to give $LaFe^+$. Reaction of the latter with alkanes resulted predominantly in dehydrogenation, but C-C bond cleavage could also be observed in some cases. D° (La^+-Fe) was about 200 kJ/mol[412]. $LaFe^{2+}$ was similarly produced from $LaFe(CO)_2^{2+}$, and reacted with ethane to form hydrogen and $LaFe(C_2H_4)^{2+}$. Dehydrogenation was also the principal reaction with propane[413].

The simple iron-Group 6 compound $Fp-Mo(CO)_3Cp$ was prepared by reaction of $CpMo(CO)_3^-$ with FpX, and its crystal structure determined[414]. Reaction of the heterobimetallic dianion $(OC)_4Fe-W(CO)_5^{2-}$ with electrophiles resulted in attack at iron, giving $E-Fe(CO)_4-W(CO)_5^-$ [E = H, Me, $AuPPh_3$]. The methylated compound was also preparable directly from $MeFe(CO)_4^-$ and $(THF)W(CO)_5$; an X-ray structure of the PPN salt was reported. Reaction with triphenylphosphine revealed an enhanced tendency toward methyl group migration compared to $MeFe(CO)_4^-$; $MeC(=O)-Fe(CO)_3PPh_3^-$ was the sole iron-containing product. With CS_2, methyl migration produced $(OC)_4Fe(\mu-SC(Me)=S)W(CO)_4^-$ [415].

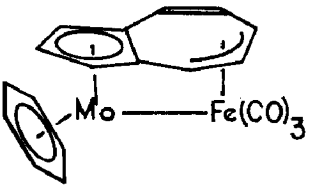
Diiron nonacarbonyl reacted with (η-benzene)Mo(η^6-azulene) to produce **83** (X-ray)[416]. The vinyl group in an iron-tungsten μ-(vinylphosphine) complex displaced the tungsten group from coordination to iron, giving a phospha-allyl ligand (Equation 45, cf. Eq. 33)[291].



(45)

Carbene- and carbyne-bridged bi- and trimetallic species continue to be produced in Bristol, in impressive numbers. For example, the reaction of $Fe_2(CO)_9$ with $CpW(CO)_2{\equiv}CSiPh_3$ produced the novel ketenyl complex, **84**, in which the CO was terminally attached to the bridging carbon rather than bridging the C-Fe bond. The crystal structure showed a very short (2.516 Å) Fe=W bond[417]. The reaction of $(OC)_4Fe(\mu-CH_2)Fe(CO)_4$ with the alkylidyne complexes $CpM(CO)_2{\equiv}CAr$ [M = Mo, W; Ar = *p*-tolyl] afforded the μ-vinyl complexes $Cp(OC)_2M(\mu:\eta^1,\eta^2-CH=CHAr)Fe(CO)_4$, along with trimetallic species. The μ-vinyl complexes reacted with alkynes to form more complex bridging ligands, such as in **85**, formed with 3-hexyne (X-ray structure)[418].

Complexation of the triple bond of the alkylidyne complexes $CpM(CO)_2{\equiv}CAr$ [M = Cr, Mo, W; Ar = *o*-tolyl, 2,6-dimethylphenyl,



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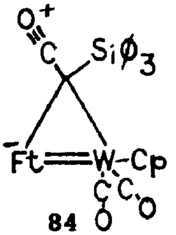

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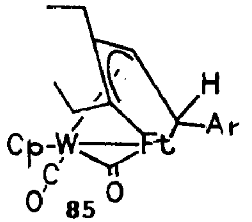
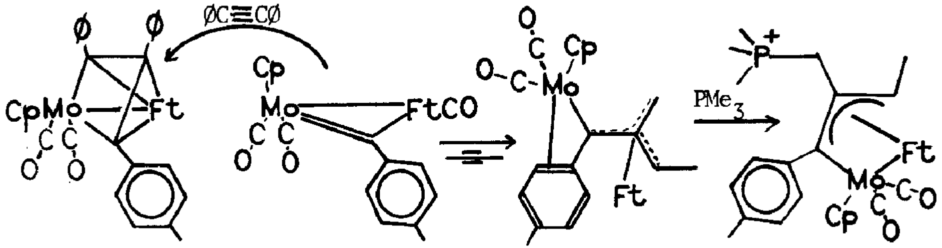


85

2-methoxyphenyl, or *p*-dimethylaminophenyl] by reaction with $Fe_2(CO)_9$ yielded the highly unsaturated species $CpM(CO)_2(\mu\text{-}CR)=Fe(CO)_3$, especially when the 2,6-dimethylphenyl group was present, along with $CpM(CO)_2(\mu\text{-}CAr)Fe(CO)_4$. Interconversion between the two species, depending on CO pressure, was observed in some cases. The structure of $CpMo(CO)_2(\mu\text{-}CC_6H_3Me_2)=Fe(CO)_3$ clearly showed the unsaturation in the form of short bond lengths: Mo=Fe 2.577, Mo-C 1.976, and C=Fe 1.861 Å[419]. Analogous chemistry was also reported for reaction of a series of carborane-coordinated tungsten compounds, $(\eta^5\text{-}Me_2C_2B_9H_9)W(CO)_2\equiv CAr^-$ with $Fe_3(CO)_{12}$ to produce alkylidyne-bridged Fe-W compounds[420].

Insertion of unsaturated organics into carbon-metal bonds of the unsaturated alkylidyne compounds has been studied. Thus, reaction of $Ph_2P\text{-}CH=CH_2$ with $Cp^*W(CO)_2(\mu\text{-}CAr)=Fe(CO)_3$ produced **86**[421]. Reaction with diphenylacetylene occurred in a fairly unexceptional manner, but 2-butyne reacted with substantial hydrogen rearrangement to give the scarcely predictable trimethylenemethyl complex (two geometric isomers were actually obtained) shown in Equation 46[422]. Reaction of the latter complex with trimethylphosphine did expectably result in displacement of the partially-coordinated arene from the molybdenum, but the mode of attack, on the CH_2 group[422], was more surprising. The formation of **87** from reaction of 2-butyne and $CpMo(CO)_2(\mu_3\text{-}CAr)Ft_2$ also manifestly involved substantial hydrogen rearrangements and ligand couplings[422]. Reactions of $CpMo(CO)_2(\mu\text{-}CAr)Fe(CO)_4$ with several additional acetylenes have been reported. The most common product type was **88**, of which ten examples were reported, but each acetylene tended to show its own peculiarities. **88** readily and reversibly inserted CO into the Fe-C(R^1) bond. In several cases, a product with a CO inserted into the C(Ar)-C(R^2) bond of **88** was also obtained[423].



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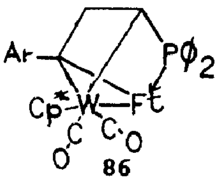

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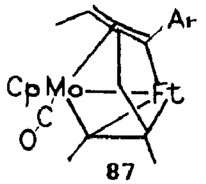

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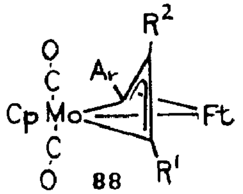
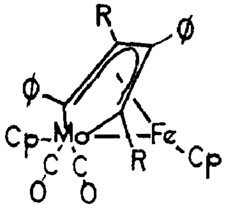


88

Just as **88** is an $Fe(CO)_3$ complex of a molybdenacyclobutadiene, molybdenaferrocenes, **89**, have been obtained, by addition of Na^+ Fp^- to $CpMo(NCMe)(\eta^2\text{-}PhC{\equiv}CR)_2^+$ [R = Me, Ph]. With $CpMo(NCMe)(\eta^2\text{-}Me_3CC{\equiv}CH)_2^+$, however, only dimolybdenum complexes were obtained[424].

A Group 7 analog to some of these Group 6 reactions is the reaction of $(\eta^5\text{-indenyl})Re(CO)_2{\equiv}CAr^+$ with $Fe(CO)_3(NO)^-$ to form $(\eta^5\text{-}C_9H_7)Re(CO)(\mu\text{-}NO)(\mu\text{-}CAr)Fe(CO)_3$, **90**[425]. The crystal structure of the simpler rhenium-iron compound, $CpFe(CO)_2Re(CO)_5$ has been reported, along with the displacement reactions of isonitriles with $(\eta^5\text{-}C_9H_7)Fe(CO)_2\text{-}Re(CO)_5$. Up to three isonitrile ligands were introduced, only onto the rhenium[426]. Introduction of iron into $CpMn(CO)_2(\eta^2\text{-}HC{\equiv}C\text{-}CH_2OH)$ by reaction with $Fe_2(CO)_9$ resulted in formation of **91**, again the product of a complex ligand transmogrification. Other complex processes also involving CO insertion occurred with the analogous phenylacetylene and propargyl methyl ether complexes[427].



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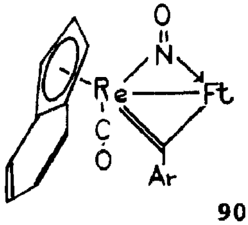

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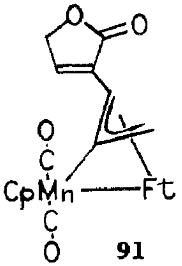
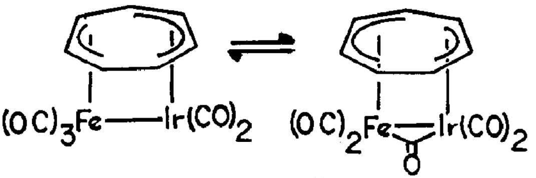


91

Reaction of $(OC)_4Fe(\mu\text{-}PPh_2)Co(CO)_3$ with triphenylphosphine gave a kinetic substitution product with the triphenylphosphine on cobalt, trans to the bridging phosphido group. This converted on standing in solution to the thermodynamic product with the phosphine on iron, $(OC)_3LFe(\mu\text{-}PPh_2)Co(CO)_3$. With PMe_3 the cobalt-substitution product was stable. $P(OMe)_3$ also gave addition products, $LFe(CO)_3{\leftarrow}PPh_2Co(CO)_3L$. Extensive structural and electrochemical studies were reported[340]. Substitution of $PhPMe_2$ into $(OC)_3Co(\mu\text{-}CO)(\mu\text{-}CH{=}CHR)Fe(CO)_3$ resulted in monosubstitution with R = Ph and disubstitution with R = H, with displacement of CO's only from iron.[428]

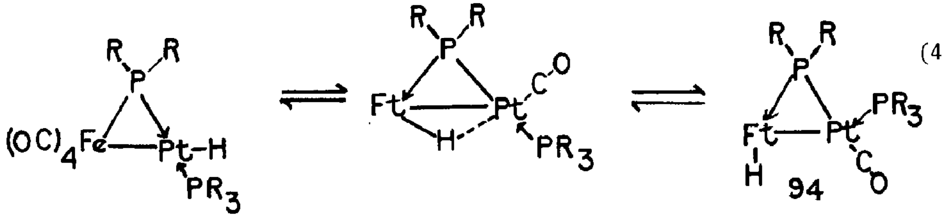
A series of μ-(di-t-butylphosphido)-bridged iron-rhodium compounds has been prepared, and their electrochemistry studied. Crystal structures of $(OC)_2(Me_3P)Fe(\mu\text{-}CO)(\mu\text{-}PR_2)Rh(PMe_3)_2$ and the anion $(OC)_3Fe(\mu\text{-}PR_2)Rh(PMe_3)(CO)^-$ were reported[429]. A crude crystal structure of $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}Ph_2P\text{-}C(=CH_2)\text{-}PPh_2)Rh(CO)Cl$ was obtained from Laue diffraction patterns recorded using a synchrotron light source[430]. Reaction of $CpFe(CO)(COMe)(\eta^1\text{-}DPPM)$ with $Rh_2(CO)_4Cl_2$ resulted in migration of the acetyl group from iron to rhodium, to form $CpFe(\mu\text{-}CO)_2(\mu\text{-}DPPM)Rh(COMe)Cl$. An analogous iridium compound was prepared similarly. Both decarbonylated slowly in solution to produce M-Me products. Protonation of the rhodium acetyl formed acetaldehyde and $[CpFe(\mu\text{-}CO)_2(\mu\text{-}DPPM)RhCl^+]_2$[431].

Reaction of rhodium-vinylidene complexes $CpRh(PR_3)=C=CHR'$ [R = isopropyl; R' = H, Me, Ph] with $Fe_2(CO)_9$ led to complexation of the Rh=C bond to form $CpRh(PR_3)(\mu\text{-}CO)(\mu\text{-}C=CHR')Fe(CO)_3$, **92.** Protonation with HBF_4 occurred at the β-carbon, yielding $\mu\text{-}CCH_2R'$ cations[432]. Oxidative addition of $FpCF_2{}^+$ to $L_2Ir(CO)(Cl)$ [L = $PhPMe_2$] formed the bridging difluorocarbene complex, $CpFe(CO)_2(\mu\text{-}CF_2)Ir(CO)(Cl)L_2{}^+$. The structure showed a symmetrical CF_2 bridge and a semibridging carbonyl[433]. Reaction of $(\eta^3\text{-}cycloheptatrienyl)Fe(CO)_3{}^-$ with $Ir(CO)_3Cl$ produced the highly fluxional $(OC)_3Fe(\mu\text{-}C_7H_7)Ir(CO)_2{}^-$, **93**[434]. The ease of ring rotation may be attributed to the energetic similarity of the two structures:



93

Reaction of $(R_2PH)Fe(CO)_3PR_2{}^-$ with L_2NiCl_2 [R = CMe_3, L = PMe_3] resulted in formation of $LFe(CO)_3(\mu\text{-}PR_2)Ni(L)Cl$[435]. A related reaction saw $(OC)_4FePR_2H$ adding to $R_3PPt(C_2H_4)_2$ initially to form $(OC)_4Fe(\mu\text{-}PR_2)Pt(PR_3)H$, which rearranged as shown in Equation 47[436].



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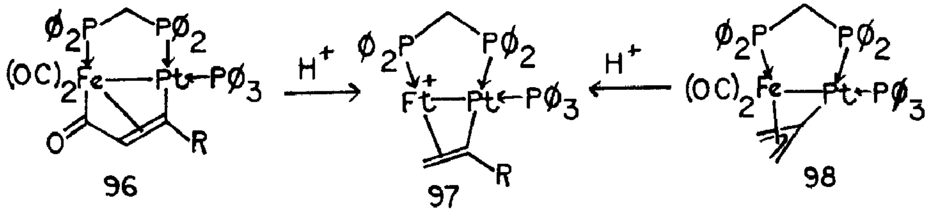
Reactions of $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}DPPM)Pt(PPh_3)$, **95**, with alkynes resulted in insertion of the alkyne into the Pt-CO bond to form **96** [R = H, Me, Ph, CMe_2OH, CO_2Me, etc.]. Protonation of **96** (Eq. 48) broke the CH-C(=O) link to form μ-vinyl cations **97**[437]. Reaction of **95** with allene produced an isomer of **96** [R = Me], $(OC)_3Fe(\mu\text{-}DPPM)(\mu\text{-}C(=O)CH_2C(=CH_2)Pt(PPh_3)$. At 80° a decarbonylated adduct having a dimetallacyclobutane ring, $(OC)_3Fe(\mu\text{-}DPPM)(\mu\text{-}C(=CH_2)CH_2Pt(PPh_3)$ formed. Further heating finally produced the



(48)

metallatrimethylenemethyl complex **98**. Protonation of **98** produced **97** [R = Me][438]. Reduction of the dimetallacyclobutane complex with $LiBEt_3H$ was preceded by migration of the vinyl carbon from the iron to a carbonyl ligand. Reduction of the carbonyl gave a product with a μ-$CH(OH)$-$C(=CH_2)$-CH_2- ligand[439].

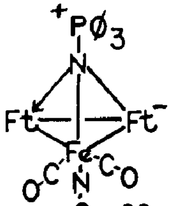
10. TRINUCLEAR CLUSTER COMPOUNDS

a. Tri-iron Compounds

Two studies have discussed the fluxional behavior and crystallographic disorder of $Fe_3(CO)_{12}$ in the solid state. One discussed the relationship between these two aspects in terms of librations involving both the metal triangle and the carbonyl envelope[440]. The other measured and interpreted the unusual temperature effects in the Mössbauer spectrum from 4-295 K, invoking some of the same factors[491]. T_1 measurements for both ^{13}C and ^{17}O nuclei of $Fe_3(CO)_{12}$ in solution have been used to determine ^{17}O quadrupolar coupling constants and correlation times for molecular tumbling[442]. The mass spectrum of $Fe_3(CO)_{12}$ showed only very weak doubly charged ions, but $Fe_3(CO)_8(PhC{\equiv}CPh)$ yielded them in much greater abundance[443].

The kinetics and mechanism of Me_3NO-induced substitution reactions of $Fe_3(CO)_{11}L$ [L = CO, $P(OMe)_3$, $P(OEt)_3$] have been studied. The reactions were significantly retarded by protonic solvents due to hydrogen-bonding to the amine oxide. The rates were first order in cluster and in amine oxide, but zero order in entering ligand, consistent with rate-determining attack of Me_3NO on a carbonyl ligand to afford CO_2 and reactive $Fe_3(CO)_{10}L$[444]. For different ligands L, the relative rates were CO > $P(OMe)_3$ > $P(OEt)_3$[445]. This reaction has been used to prepare $Fe_3(CO)_{11}(NCR)$ at low temperatures, from which the nitrile ligand was readily replaced by CO, phosphines, isonitriles, arsines, and other ligands. The crystal structure of the o-tolunitrile adduct showed the nitrile to be coordinated axially to the unbridged iron atom[446].

Kinetic studies of protonation of $(\mu\text{-}H)Fe_3(CO)_{12}^-$ and its ruthenium and osmium analogs at low temperatures showed no H/D isotope effect in the initial protonation at the bridging carbonyl oxygen, but a large isotope effect in rearrangement to the stable dihydride[447]. The pK_a's of three capped Fe_3 triangles, $(\mu\text{-H})_2Fe_3(CO)_9(\mu_3\text{-PR})$ [R = CMe_3, 4-C_6H_4OMe] and $(\mu\text{-H})Fe_3(CO)_9(\mu_3\text{-}SC_6H_{11})$, in acetonitrile have been found to be 11.4, 9.0, and 16.9, respectively. The capping ligand clearly plays a major role in determining the acidity[448].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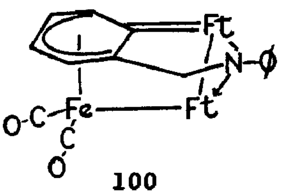
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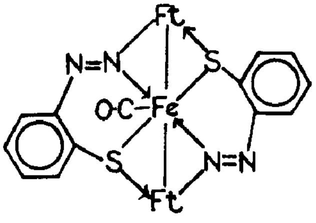
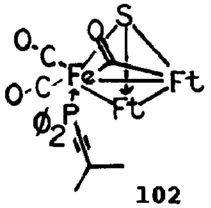

101

Reaction of K^+ $Fe(CO)_3(NO)^-$ with benzoyl chloride in the presence of triphenylphosphine afforded, instead of **72** (formed in the absence of the phosphine), the cluster **99**[381]. A bismuth-capped tri-iron cluster, $(\mu_3\text{-Bi})[Cp'Fe(CO)]_3$, resulted when $[Cp'Fe(CO)_2]_3Bi$ was photolyzed[217]. Compound **100** resulted, along with **73** [R = Ph], from reaction of PhCH=NPh with $Fe_3(CO)_{12}$ at 80°[383]. It could also be made directly from **73** under the reaction conditions[449]. The electrochemical oxidation and reduction of a linear tri-iron cluster, **101**, made from benzothiazole and $Fe_2(CO)_9$, has been studied[450]. Reaction of some phosphine sulfides with $Fe_2(CO)_9$ produced phosphine-substituted sulfur-capped tri-iron products; for example, $(\mu_3\text{-S})_2Fe_3(CO)_7(\mu\text{-DPPM})$ from $Ph_2P(=S)CH_2P(=S)Ph_2$. Use of $Me_2CH\text{-}C{\equiv}C\text{-}PPh_2$ resulted in formation of the bicapped clusters, $(\mu_3\text{-S})_2Fe_3(CO)_9$ and its phosphine-substituted derivative; however the mono-capped **102** (X-ray) was also produced[451].

Isotopic substitution and normal coordinate analysis of trimetal ketenylidene clusters, including $Fe_3(CO)_9(\mu_3\text{-CCO})^{2-}$, **103**, have led to identification of two stretching modes for the ketenylidene moiety[452]. **103** exchanges both ketenylidene and metal-carbonyls with ^{13}CO at room temperature, suggesting a slow exchange of "carbon carbonyl" with iron carbonyl groups[453].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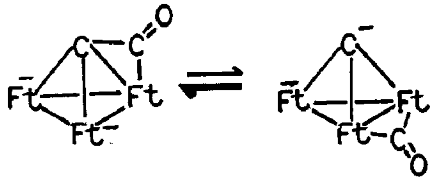
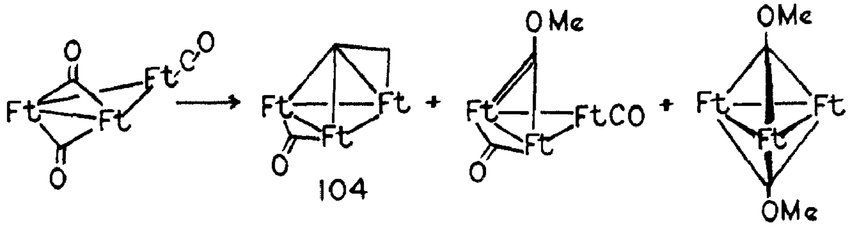

103

Reaction of **103** with sulfur dioxide produced a complex mixture, but $Fe_4(CO)_{12}C^{2-}$ produced a tri-iron ketenylidene cluster somewhat analogous to **103**, $Fe_3(CO)_4(\mu\text{-}CO)(\mu\text{-}SO_2)_2(\mu_3\text{-}CCO)$. The carbon carbonyl group was terminal rather than bridging the C-Fe bond as in **103**, a consequence of the superior electron-accepting ability of the $\mu\text{-}SO_2$ ligands[454].

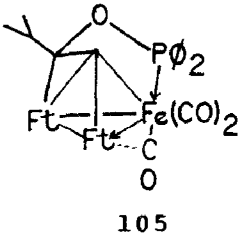
Reduction of $Fe_3(CO)_{12}$ with RLi [R = Bu, CMe_3, or Ph], followed by alkylation with Me_3O^+ gave the three products shown in Equation 49[455]. The latter two derive from $Fe_3(CO)_{11}{}^{2-}$, and



(49)

indeed the bis(μ_3-COMe) product was obtainable from the μ-hydride by deprotonation with BuLi and methylation. Formation of **104** requires some sort of ligand coupling reaction, in which context it is relevant that **104** was produced (19% yield) from the bis(μ_3-COMe) product by reduction with $LiHBEt_3$ followed by protonation [455]. Substituted derivatives of **104**, $(\mu_3,\eta^2\text{-}C{=}CHR)(\mu\text{-}CO)Fe_3(CO)_9$ [R = Ph, CH_2OMe, $SiMe_3$, Et, Pr, Bu] were prepared by reaction of Et_3NH^+ $HFe_3(CO)_{11}{}^-$ with bromoalkynes, $RC{\equiv}CBr$. The structure of the phenyl compound showed C-Fe bond lengths to the unique iron of 2.009 Å (apical carbon) and 2.288 Å (phenylated carbon)[456]. The latter long bond is clearly due to the effect of the phenyl substituent, since unsubstituted **104** had bond lengths of 1.966 and 2.194 Å[455].

Another derivative of **104**, **105**, arose (16% yield) in reaction of $Ph_2P(O)C{\equiv}CCHMe_2$ with $Fe_2(CO)_9$[457], a reaction requiring cleavage of the C-P bond of the starting material. More extensive cleavages are shown in Equation 50, in which the diphosphine ligand in $(\mu\text{-}Ph_2P\text{-}C({=}CH_2)\text{-}PPh_2$ (Eq. 36) has undergone fragmentation into three pieces in the final product[347].



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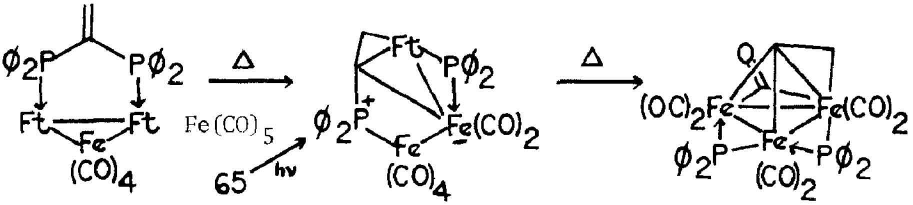
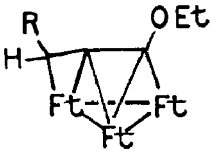


(50)

Ethylation of $Fe_3(CO)_{10}(\mu\text{-}CCH_2R)^-$ [R = Ph, Pr, CO_2Me, COMe] with Meerwein's salt gave the bis(carbyne) products, $Fe_3(CO)_9(\mu\text{-}COEt)(\mu\text{-}CCH_2R)$. Upon two-electron reduction by $Mn(CO)_5{}^-$, these underwent ligand coupling and loss of OEt^- to form the acetylide complexes $Fe_3(CO)_9(\mu\text{-}CCCH_2R)^-$. With the electron-withdrawing ketone or ester groups, however, the major reduction product was allenyl complex **106**[458]. A ^{13}C NMR study of μ_3,η^2-acetylide complexes has shown the alpha carbon (115-220 ppm) consistently downfield of the beta (43-153 ppm)[386]. A precise crystal structure of $Fe_3(CO)_9(\mu_3,\eta^2\text{-}\perp\text{-}C_2Et_2)$ has been reported, and conversion of such complexes to bis(carbyne) complexes has been discussed in light of the structure[459]. Independently, reaction of terminal alkynes with $Fe_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CMe)$ was reported to yield both of these types of complexes, along with a third product, **107**. On heating, **107** underwent rearrangement to a benzoferrole derivative, $(OC)_2Fe(\mu\text{-}CO)[\mu\text{-}(OC)_2Fe\text{-}CH\text{-}C(Et)\text{-}C_6H_4](\mu\text{-}CO)Fe(CO)_2$. Interconversions of the clusters $Fe_3(CO)_9(PR)(RCCR)$ among three isomeric forms have been explored through use of extended Huckel-type calculations on the isolobal system $(BH)_6^{-4}$ [461].



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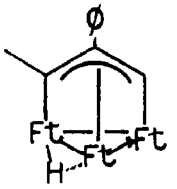

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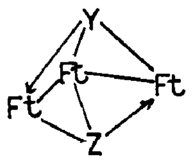


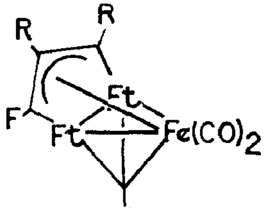
108

Doubly capped Fe_3 clusters, **108** [Y = Z = PNR_2], were formed by reaction of $Na_2[Fe_2(CO)_8]$ with various R_2NPCl_2 compounds, along with $Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}PNR_2)$. The expected di-iron products did not appear to form in significant amounts[462]. Reaction of $R_2As\text{-}N{=}S{=}N\text{-}AsR_2$ [R = CMe_3] with $Fe_3(CO)_{12}$ produced **108** [Y = S, Z = AsR][351].

In an extensive survey of ^{125}Te and ^{77}Se NMR spectra of transition metal derivatives of these elements, **108** [Y = Z = Te], was found to have the highest chemical shifts of all tellurium compounds studied[463]. It reacted with $M(PPh_3)_4$ [M = Group 10 metal] to form $(OC)_3Fe[\mu\text{-}Te\text{-}M(PPh_3)_2\text{-}Te]Fe(CO)_3$ and $(Ph_3P)_2Fe(CO)_3$, in a process whose mechanism has been investigated[464]. Thermal substitution reactions of various examples of **108** [Y and Z = NPh, PPh, S] reacting with trimethyl phosphite have showed the reactivity order S > NR >> PR, presumably reflecting electron-donor ability of the capping groups. The thermal reactivity pattern differs from that observed when the electron-transfer chain-catalyzed mechanism is operative[465].

In a room-temperature reaction catalyzed by sodium benzophenone ketyl, $MeC\equiv CNEt_2$ and $Fe_2(CO)_9$ formed the bis(carbyne) complex, $Fe_3(CO)_9(\mu\text{-}CMe)(\mu\text{-}CNEt_2)$. The different electronic character of the two carbynes led to unsymmetrical bonding, with the MeC unit tightly bonded (1.853 Å) to one carbon and the Et_2NC loosely bonded (2.215 Å) to the same carbon. The other four Fe-C bonds were all in the range 1.93-2.00 Å[466]. Along with the tetrafluoroferrole complex $[\mu,\eta^5\text{-}C_4F_4Fe(CO)_3]Fe(CO)_3$, the bis-(fluorocarbyne) complex $Fe_3(CO)_9(\mu\text{-}CF)_2$ was formed in reaction of $FCBr_3$ with iron pentacarbonyl[392]. Its reactions with symmetrical alkynes resulted in insertion of alkyne into a C-Fe bond, forming **109** [R = H, Me, Ph, E, CH_2Cl][467].

Reaction of $(OC)_3Fe[\mu;\eta^1,\eta^2\text{-}C\equiv CPh](\mu\text{-}SR)Fe(CO)_3$ [R = CMe_3] with $Fe_2(CO)_9$ yielded the open tri-iron cluster **110**, in which the acetylide may be viewed as a five-electron donor. The analogous $\mu\text{-}C\equiv CCMe_3$ compound under similar conditions yielded **111**, (crystal structure), which in solution equilibrated with the analog of **110**[468].



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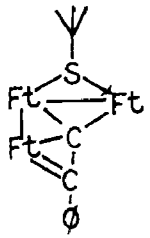

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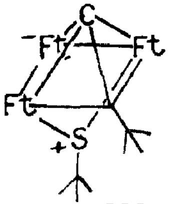
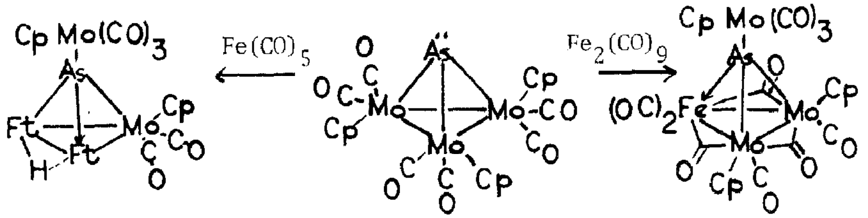


111

10b. Fe_2M Clusters

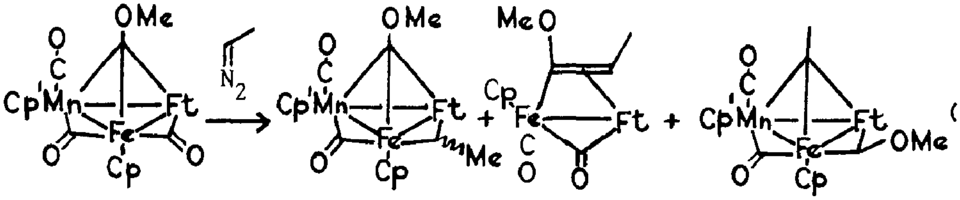
Reactions of $(\mu_3\text{-}As)[MoCp(CO)_2]_3$ with iron carbonyls resulted in insertion of iron carbonyl groups into the cluster with formation of pendant $-MoCp(CO)_3$ groups (Equation 51)[469]. In



(51)

addition to forming the previously described unsaturated bimetallic products, coordination of $CpMo(CO)_2\equiv CAr$ [Ar = 2-MeC_6H_4, 4-($Me_2NC_6H_4$] with $Fe_2(CO)_9$ led to formation of tetrahedral $CpMo(CO)_2(\mu_3\text{-}CAr)Ft_2(\mu\text{-}CO)$[419]. The reactions of these tetrahedral complexes with alkynes have also been studied. With 2-butyne, the previously cited **87** [Ar = 4-MeC_6H_4] resulted; with diphenylacetylene, $CpMo(CO)_2[\mu\text{-}CPh\text{-}CPh\text{-}CAr]Fe(CO)_3$ (pictured in Eq. 46)[422].

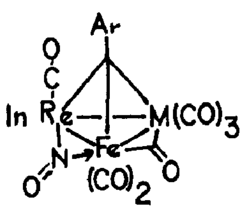
Reaction of a $(\mu_3\text{-}COMe)Fe_2Mn$ cluster with diazoethane produced diastereomeric (μ-CHMe) clusters (Equation 52), which slowly decomposed in solution to form the other products shown. The latter product represents a novel interchange of position between



(52)

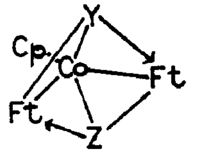
the carbene and carbyne ligands; a mechanism was proposed involving CO loss from the Fe(CO)$_3$ group, migration of hydrogen to the unsaturated iron, and then to the other bridging ligand[470].

Trimetallic compounds **112** [M = Fe, Ru] were formed from the unsaturated iron-rhenium compound **90** by reaction with Fe$_2$(CO)$_9$ or (C$_2$H$_4$)Ru(CO)$_4$[425]. The behavior of Fe$_2$Ru(CO)$_{12}$ on a silica surface has been investigated by infrared methods. When heated in the presence of hydrogen, hydrogenated tri- and tetrametallic carbonyl clusters could be identified[471]. Substitutional reactivity of Fe$_2$Os(CO)$_{12}$ has been studied, with the data indicating dissociation of CO from iron as the rate-limiting step, although substitution of phosphorus ligands on osmium was the result. The Fe$_2$M clusters' reactivity decreased in the sequence Ru > Fe > Os[472].



112

Reaction of (μ-PPh)$_2$Fe$_2$(CO)$_6{}^{2-}$ with CpCo(CO)I$_2$ resulted in displacement of CO as well as iodide ligands from cobalt, forming 113 [Y = Z = PPh][343]. The similar reaction of (μ-S$_2$)Fe$_2$(CO)$_6$ with (C$_5$H$_4$E)Co(CO)$_2$ produced the analog of 113 [Y = Z = S][473]. Replacement of one iron in Fe$_3$(CO)$_9$(μ_3-CCO)$^{2-}$ by cobalt resulted from reaction with Co$_2$(CO)$_8$ under a CO atmosphere. The resulting product, Fe$_2$Co(CO)$_9$(μ_3-CCO)$^-$, showed a semi-bridging carbon carbonyl, with C-CO and Fe-CO distances of 1.29 and 2.46 Å, respectively. Protonation formed Fe$_2$Co(CO)$_9$(μ-CO)(μ_3-CH), and nucleophiles attacked the ketenylidene carbonyl group to form dianionic Fe$_2$Co clusters[474]. Addition of a tricarbonylcobalt group was the outcome of reaction of (OC)$_3$Fe(μ-SR)(μ-C$\equiv$CSiMe$_3$)Fe(CO)$_3$ with cobalt carbonyl; the product was Fe$_2$Co(CO)$_9$(μ-C$\equiv$CSiMe$_3$)[468]. **114** was formed as a minor product, along with **92**, when CpRh(PR$_3$)=C=CHR' [R = CHMe$_2$; R' = H, Me, Ph] underwent complexation with Fe$_2$(CO)$_9$[432].



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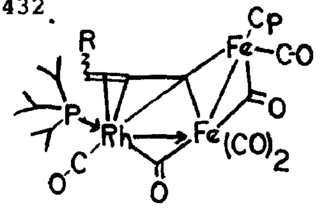

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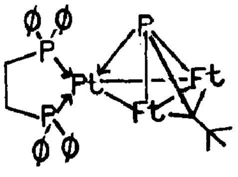
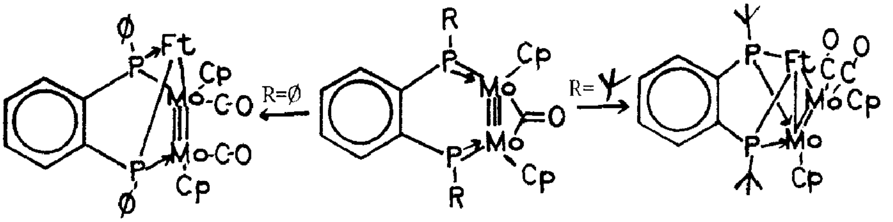


115

Similar complexation of (DPPM)Pt(η^2-$Me_3C-C{\equiv}P$) afforded the trimetallic product **115**[475].

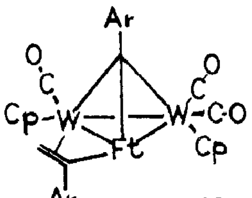
10c. FeM_2 Clusters

The sulfur-capped cluster $[CpW(CO)_2]_2(\mu_3\text{-}S)Fe(CO)_3$ was prepared by reaction of unsaturated $[CpW(CO)_2]_2$ with $(\mu\text{-}S_2)Fe_2(CO)_6$[476]. Other unsaturated ditungsten compounds incorporated the elements of $Fe(CO)_4$ upon reaction with $Fe_2(CO)_9$ to give structures which depended on the organic groups present (Equation 53). The open trimetallic product with the diphenyl-substituted ligand was fluxional, the tricarbonyliron group moving between the molybdenum atoms. The other structure was rigid[477].



(53)

Ligand condensation occurred to form the μ-vinyl ligand in **116** when $(\mu\text{-}CH_2)Fe_2(CO)_6$ reacted with $CpW(CO)_2{\equiv}CAr$ in THF at room temperature[418]. **117** was similarly formed from an unsaturated tungsten-platinum compound; it readily and reversibly added an additional CO, at platinum[417].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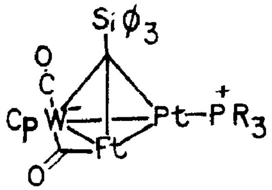
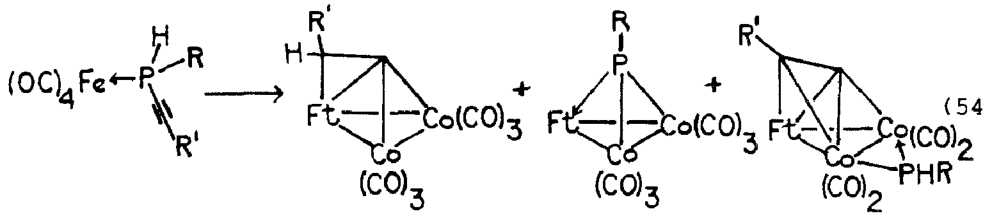
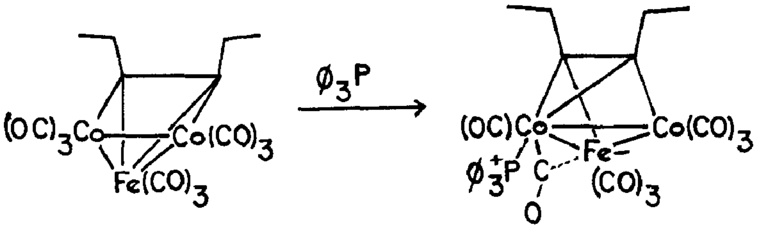

117

The linear trimetallic compound $(OC)_5Re\text{-}Fe(CO)_4\text{-}Re(CO)_5$, Fe-Re bond length 2.855 Å, was prepared by intercepting $Re(CO)_5$ radicals with $Fe(CO)_5$[478].

An array of $FeCo_2$ clusters (Equation 54) resulted, albeit in low yields, from attempts to coordinate the free triple bond of $R'C{\equiv}C\text{-}PHR{\rightarrow}Fe(CO)_4$ [R = NMe_2, Me; R' = Ph, CMe_3] with cobalt


(54)

carbonyl[78]. Phosphine substitution reactions of (μ_3-MeC$\equiv$CMe)-$FeCo_2(CO)_9$ occurred exclusively at cobalt[479]. An independent study found that triphenylphosphine substitution at cobalt in the 3-hexyne complex caused a reorientation of the alkyne ligand from a conformation parallel to the Co-Co bond in the nonacarbonyl starting material to one along the Co-Fe bond in the product (Equation 55)[480].



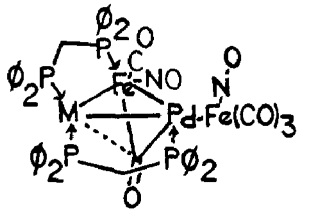
(55)

The solution equilibrium between (μ_3-CPh)(μ-H)$FeCo_2(CO)_9$ and its isomer (μ-CHPh)$FeCo_2(CO)_9$, the latter stabilized by an "agostic" interaction between the C-H bond and the tricarbonyliron group, has been studied by NMR of the ^{13}C-enriched species. A previously reported crystal structure was reinterpreted in favor of the (μ-CHPh) form in the crystal[481]. Reaction of the ketenylidene cation $(\mu_3\text{-}CCO)Co_3(CO)_9^+$ with $HFe(CO)_4^-$ unexpectedly gave the vinylidene cluster $FeCo_2(CO)_9[\mu\text{-}C{=}CHOC({=}O)]CCo_3(CO)_9$[482].

The reaction of $[CpFe(NO)]_2$ with $CpCo(C_2H_4)_2$ produced $Cp_3FeCo_2(\mu_3\text{-}NH)(\mu_3\text{-}NO)$ as the main product[483]. Compound **94** reacted readily with $LPt(C_2H_4)_2$ [L = tricyclohexylphosphine] to form triangular $(OC)_3Fe(PtL)_2$ clusters with dynamic R_2P, CO, and hydride edge-bridges. These in turn formed tetrahedral $FePt_3$ clusters on further reaction[436].

11. TETRA- AND POLYNUCLEAR CLUSTER COMPOUNDS

Open tetranuclear clusters **118** [M = Pd, Pt] were formed by reaction of $PdMCl_2(\mu\text{-}DPPM)_2$ with $Fe(CO)_3(NO)^-$. The pendant $Fe(CO)_3NO$ group was easily displaced, for example by iodide ion[484].



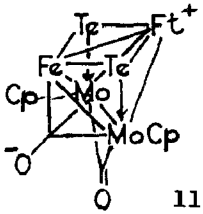
118

A new 60-electron tetrahedral cluster anion, $HFe_3Rh(CO)_{12}^{2-}$, was obained from reaction of $HFe(CO)_4^-$ with $[Rh(CO)_2Cl]_2$. The crystal structure of its tetraethylammonium salt showed three μ-CO groups, two bridging Rh-Fe bonds and one Fe-Fe. The hydride was presumed to bridge the same $RhFe_2$ face[485]. The fate of the $FeCo_3(CO)_{12}^-$ anion upon heating in solutions under hydroformylation conditions has been studied by high pressure IR methods. Its thermal stability decreased with increasing solvent polarity, and decomposition principally formed $Co_2(CO)_8$, $Fe(CO)_5$, and

$Co(CO)_4^-$ salts. The $FeCo_3$ cluster reformed at temperatures below 50° [486]. Various tetralkylammonium salts of $FeCo_3(CO)_{12}^-$ were effective and selective hydroformylation catalysts[487]. Addition of phosphines decreased the reactivity[488]. Thermal decomposition of $HFeCo_3(CO)_{12}$ in the presence of surfactants was used to prepare finely dispersed iron-cobalt alloy particles[489].

Refluxing $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ with $Cp_2Mo_2(CO)_6$ produced **119**. Consistent with its 60-electron count, **119** has a tetrahedral cluster core, with the two Te atoms and a μ_3-CO ligand contributing three additional apices of a norcubane overall structure[490]. The similar reaction of $Cp_2Mo_2(CO)_4$ with $Fe_2(CO)_6(\mu\text{-}S)_2$ produced the 62-electron clusters $(CpMo)_2[Fe(CO)_3]_2(\mu_3\text{-}S)_2(CO)_2$, which were isolated in both planar form [*trans*-μ_3-S bridges and CO's bridging Mo-Fe bonds] and a butterfly form [*cis*-μ_3-S bridges and terminal Mo-CO groups]. The 66-electron cluster $(CpMo)_2[Fe(CO)_3]_2(\mu_3\text{-}S)_4$ expectably showed decreased metal-metal bonding as a consequence of the excess electron count[491].

Protonation of the 62-electron butterfly clusters $MFe_3(CO)_{13}^{2-}$ [M = Cr, W] has been studied by multinuclear NMR methods. The first protonation occurred at the carbide ligand to form **120**, a behavior which contrasted with that of $Fe_4(CO)_{12}^{2-}$, and which was interpreted with the help of Fenske-Hall MO calculations[492].



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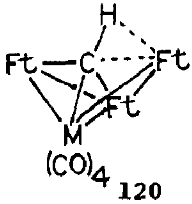
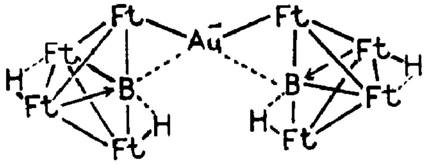


120

The principal activity in butterfly clusters in 1988 dealt with the boride cluster $Fe_4(CO)_{12}B^{3-}$ and its protonation and auration products. Relaxation rates in ^{11}B NMR of these species have been related to electric field gradients at the boron nucleus, as deduced from Fenske-Hall MO calculations[493]. $(\mu\text{-}H)Fe_4(CO)_{12}(\mu\text{-}AuPPh_3)BH$ has been prepared, in which the $AuPPh_3$ fragment bridged a Fe(wingtip)-B bond. Attempted introduction of the $AuPEt_3$ moiety into PPN^+ $Fe_4(CO)_{12}BH_2^-$ resulted in phosphine exchange between the PPN^+ counterion and the gold[494]. In another case, a novel fused metallaborane cluster anion, **121**, resulted from cleavage of $PMePh_2$ or PPh_2Me from the gold reagent[495]. The crystal structure of $(\mu\text{-}H)Fe_4(CO)_{12}(\mu\text{-}AuPEt_3)_2$ showed the hydride ligand bridging the Fe-Fe backbone and the two gold groups formally bonded to the wingtip irons and bridging to the boron [496]. The crystal structure of the tri-aurated species **122** showed deviations from the usual H-AuPR$_3$ structural analogy due to attractive interactions among the gold atoms[497].



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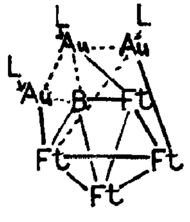
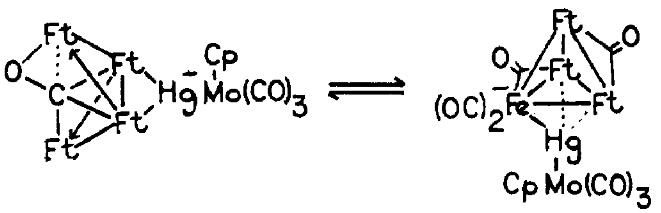


122

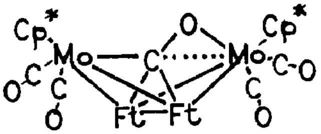
Coordination of Lewis acids ML_nHg^+ [ML_n = CpMo(CO)$_3$ or Fp] to $Fe_4(CO)_{13}^{2-}$ led in solution to an equilibrium mixture of butterfly and tetrahedral isomers (Equation 56). The butterfly

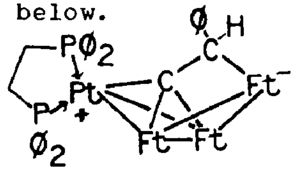


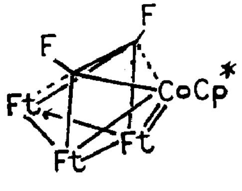
(56)

form was found in the crystal, but from temperature effects the ΔH for Equation 56 was -4 kJ/mol[498]. A heterometallic analog of the butterfly form, **123**, was prepared by cophotolysis of $Fe_2(CO)_9$ and $[Cp^*Mo(CO)_2]_2$[499]. **123** was written in the original paper with a fifth bond to the cluster carbon[499], but this appears gratuitous to the reviewer. The Mo-C and Mo···C distances in the crystal structure were 2.06 and 2.54 Å, respectively, the latter presumably being as far apart as the two non-bonded atoms can get while maintaining bonding to the remainder of the cluster and the oxygen. The same may apply to the $PtFe_3(\mu_4$-vinylidene cluster **124** recently prepared from $Fe_2(CO)_9$ and (DPPE)Pt(μ-CO)(μ-C=CHPh)Mn(CO)Cp[500].

Photochemical reaction of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ with $Cp^*Co(CO)_2$ led to the formation of the difluoroethyne cluster **125**[501], a 60-electron quasioctahedral cluster for which one contributing structure is represented below.

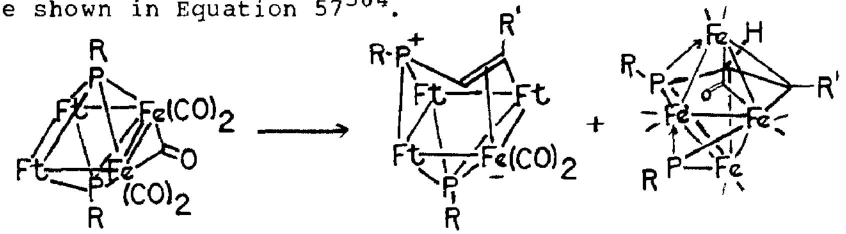






123 **124** **125**

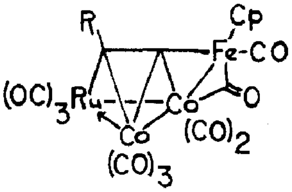
The unsaturated 62-electron octahedral cluster $Fe_4(CO)_{11}(\mu_4\text{-}PPh)_2$ has been prepared by an improved synthesis. The entire family of iron-ruthenium mixed clusters from Fe_4 to Ru_4 has been prepared, separated, and compared. All except the Fe_4 compound added two moles of CO with opening of the cluster[502]. Clusters were linked through *p*-phenylene bidentate ligands[502]. The unsaturated clusters showed two reversible one-electron reductions, and the esr spectra of the monoanions showed strong couplings with the μ_4-phenylphosphine units[503]. Insertion reactions of alkynes into the unsaturated Fe_4P_2 unit gave products such as those shown in Equation 57[504].



(57)

^{13}C NMR studies of polynuclear μ_4,η^2-acetylide complexes have indicated that the resonance of Cα (185-230 ppm) was consistently downfield from that of Cβ (91-165 ppm). Optimum experimental parameters for measuring ^{13}C spectra of these compounds were recommended[386]. An acetylide complex of an open, 64-electron, tetranuclear cluster, **126**, resulted from reaction of FpCl with $RuCo_2(CO)_9(\mu_3\text{-}C\equiv CR)^-$ in the presence of catalytic CuI[505]. Another 64-electron acetylide cluster, **127**, was formed in high yield by reaction of $Fe_2(CO)_6(\mu\text{-}SCMe_3)(\mu\text{-}C\equiv CPh)$ with dicobalt octacarbonyl[468].

A 66-electron cluster, **128**, was the product of thermolysis of the spirane **63** in refluxing xylene. **128** demonstrates in one molecule just about every possible mode of phosphorus-iron bonding. Consistent with the principles discussed at the beginning of this review, the P→Fe bonds averaged 2.197 Å in length, and the P-Fe bonds 2.265 Å. The bonds from the 3-coordinate phosphorus to the irons were particularly long (2.32 Å)[342].



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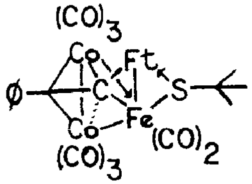
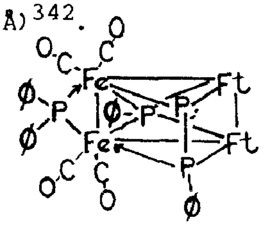


127



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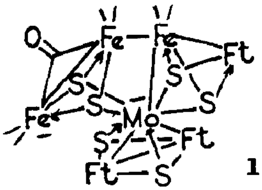
Chemical oxidation of $Fe_5C(CO)_{14}^{2-}$ by Ag^+ in the presence of ligands L [CO, PPh_3, or $P(OMe)_3$] led to efficient formation of $Fe_5C(CO)_{14}L$[506]. MO calculations on $Fe_4(CO)_{12}(\mu_4\text{-}C)^{2-}$ and $Fe_5C(CO)_{15}$ indicated accumulation of significant negative charge on the carbide carbon[507]. Crystal structures of octahedral interstitial carbido clusters $Fe_5RhC(CO)_{16}^-$ and $Fe_5[PtPPh_3]C(CO)_{15}$ have been reported[508]. The biggest characterized organometallic cluster of iron reported in 1988 appears to be $Fe_6MoS_6(CO)_{16}^{2-}$,

129, a possible model for the iron-molybdenum cofactor of nitrogenase. The structure showed a molybdenum atom coordinated by a planar Ft_2S_2 unit and by an unsymmetrical $Fe_4(CO)_{10}S_4$ unit[509].



129

Various iron-rhodium, iron-palladium, and iron-platinum clusters having five to twelve metals have been supported on silica, and the resulting solids found to have high activity for conversion of syngas to methanol and ethanol[510]. Iron-palladium clusters **118** also led to effective catalysts for carbonylation of *o*-nitrophenol to benzoxazolone, when impregnated onto silica and thermally decomposed. Improved catalysis compared to materials prepared from coimpregnation with separate iron and palladium compounds was attributed to bimetallic particle formation[511].

Likewise, the magnetic fluids produced by decomposing $HFeCo_3(CO)_{12}$ in the presence of surfactants have been shown to contain microparticulate iron-cobalt alloys[489]. Chemical vapor deposition of the same cluster has been used to produced mixed-metal alloy and oxide thin films[512].

Addition of iron to palladium zeolite catalysts[513] or to Cr_2O_3 catalysts[514] in each case shifted the selectivity of Fischer-Tropsch-type processes toward production of methanol.

POST-SCRIPT: This 1988 review, with 515 references, covers about the same number of papers as during 1986 and 1987. Considerably more work is coming from China than in previous years, but the total remains nearly constant.

The Journal of Organometallic Chemistry (103 citations) continues to lead, followed by Organometallics (79), Journal of the American Chemical Society (44), J. Chem. Soc., Dalton Transactions (38) and Inorganic Chemistry (38). All other journals together accounted for less than half of the total.

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