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Organoiron chemistry. Annual survey for the year 1991 *

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1. Introduction

In this Annual Survey I attempt to cover the organoiron chemistry reported in journals published during calendar year 1991. 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, as judged from the quantity of work reported, deserve a comprehensive annual survey of their own; due to the current unavailability of such a survey, however, I am including some selected ferrocene chemistry in this Survey.

The material is organized more-or-less by the Gmelin system, first by increasing number of conjoined iron atoms, then by increasing hapticity of principal organic ligand. The latter is determined by the principle of last position. Thus, (η^3-allyl)(η^5-cyclopentadienyl)(η^2-ethene)iron would be treated with cyclopentadienyliron compounds rather than with allyl- or alkene-iron compounds. However, for purpose of

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

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

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

2. Reference works and review articles

Three additional volumes of the Gmelin organoiron series were published during 1991. Volume A10 of the ferrocene series describes mononuclear di- and tri-substituted ferrocenes, especially disubstituted compounds containing phosphorus, arsenic, or a metal substituent [1]. Volume B18 covers monoiron compounds with η^6 ligands, particularly benzene and monosubstituted benzenes [2]. Volume C6a covers Fe_3 compounds with η^1-ligands only, and up to nine carbonyls, i.e. $Fe_3(CO)_xL_{12-x}$ ($x = 3$–9). Included are compounds with μ_3 bridges of Groups 14–16 [3].

A collective volume on *Organic Synthesis via Organometallics* [4] incorporated several chapters emphasizing organoiron methodology: these included chapters by D. Astruc [OrganoIron Complexes in Aromatic Synthesis], P. Eilbracht [Stereoselective Synthesis of Seven-Membered Ring Compounds via Metal-Induced C–C Bond Cleavage], H.-J. Knölker [Applications of Iron-Diene Complexes to Natural Product Synthesis], and G.R. Stephenson [Regiocontrolled Applications of Transition Metal π-Complexes].

A review of multiply-bonded phosphorus compounds emphasized how $HFe(CO)_4^-$ could be used to stabilize unsaturated phosphorus compounds without diminishing their reactivity [5]. A survey of ^{13}C spin–lattice relaxation in organometallic complexes showed large variations for cyclopentadienyl and carbonyl carbons, depending particularly on field strength, temperature, and solvent. Included among the compounds studied were several organoiron compounds: (butadiene)tricarbonyliron, ferrocene, decamethylferrocene, (η^5-cyclohexadienyl)(cyclopentadienyl)iron, and (η^6-benzene)(cyclopentadienyl)iron cation [6]. The crystal packing of organometallic and inorganic molecules and ions has been studied. Based on calculated volumes and surface areas, entities were classified according to degree of spheroidal, discoidal, and cylindrical character. Calculated packing coefficients for essentially spherical cations and anions fell in a narrow range of 65–72%. Cations included in this study were tricarbonyl(cyclopentadienyl)iron, ferrocenium, decamethylferrocenium, and $(CpFe)_4S_4^+$; the anions included $HFe(CO)_4^-$, $Fe(CN)_6^{3-}$, and $(FeNO)_4S_4^-$ [7].

3. Reactions of "naked" iron atoms and ions

A theoretical study of the reactions of first- and second-row transition metal atoms, including Fe, with alkanes has suggested that the barrier to C–C bond insertion is 58 to 84 kJ higher than that for C–H bond insertion; second-row metals were predicted to be more reactive [8]. Theory has also been applied to interpreting the differences in gas-phase bond dissociation enthalpies of M^+–H and M^+–Me in terms of metal electronegativity and hardness [9].

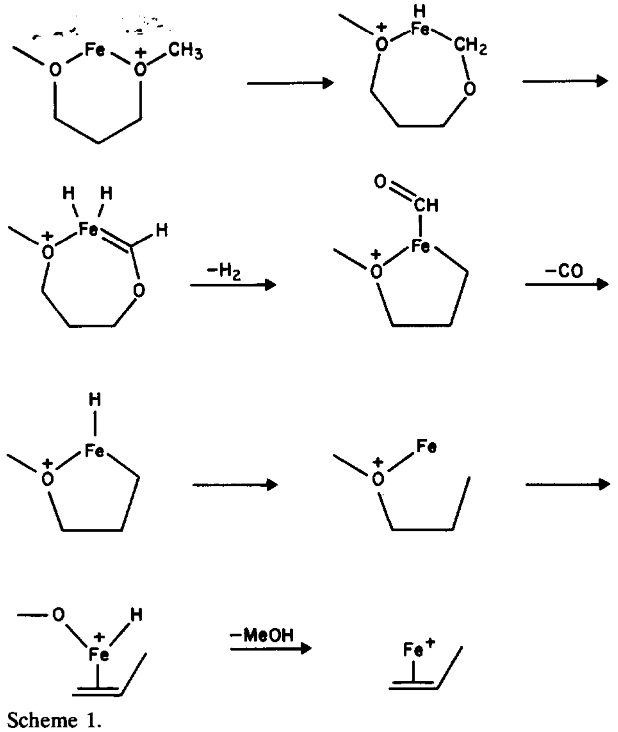
Reactions of first-row transition metal ions with halobenzenes, PhX, have been studied by Fourier transform mass spectrometry. Dehydrohalogenation occurred with several ions, including Fe^+, but only with Fe^+ did reaction result in spontaneous oligomerization to form $(C_6H_4)_n^+$. Oligomerization could be induced by collisional activation in the cases of $M(C_6H_4)_n^+$ (M = Co, Ni), but not with early transition metals. The lower limit for $D^0(Fe^+–C_6H_4)$ was found to be 339 kJ mol^{-1} [10].

The reaction of Fe^+ with pentanenitrile has been studied by Fourier transform ion cyclotron resonance methods, using extensive deuterium substitution. Loss of dihydrogen was attributed to the remote functionalization mechanism, but loss of ethene was from internal positions, resulting in formation of $[MeFeCH_2CN]^+$. Loss of C_3H_6 resulted in formation of $Fe(MeCN)^+$ in low abundance. Equilibration of the 2- and 4-positions was attributed to reversible formation of the cyclic species $(Me)(NC)FeCH_2CH_2CH_2^+$. Structures assigned to intermediates were inferred from low-energy collision-induced dissociation experiments [11]. A metastable ion-mass spectrometric study of reactions of Fe^+

with alkanedinitriles, NC(CH$_2$)$_n$CN (n = 1–10) also indicated that loss of dihydrogen and of ethene proceeded by different mechanisms. The shorter chain homologs reacted principally by redissociation of the intact dinitrile, or by loss of HCN. The longer ones showed loss of ethene, ethyl or vinyl radical, and dehydrogenation. The effect of chain length on reaction outcome was interpreted in terms of Fe$^+$-mediated interaction of the two functional groups [12]. Chain length effects also played a prominent role in the reactions of Fe$^+$ with diethers MeO(CH$_2$)$_n$OMe (n = 2–9). Scheme 1, a sort of retro-Fischer–Tropsch process, provides a rationale for the unique 1,1-elimination of dihydrogen from a methoxy group in the case $n = 3$. Other reactions observed included losses of formaldehyde, methanol, methyl, and methane [13].

Reaction of Fe$^+$ with ethyne resulted in oligomerization to form Fe(C$_{2x}$H$_{2x}$)$^+$, in a sequence which has been studied by neutralization-reionization mass spectrometry. For $x = 2$, the intermediate was assigned the structure Fe(C$_2$H$_2$)$_2^+$, with negligible cyclobutadiene or ferrole formation. But addition of a third ethyne molecule resulted in some cyclotrimerization, forming (C$_6$H$_6$)Fe$^+$. The fourth ethyne did not cause ring expansion to cyclooctatetraene, Fe(C$_2$H$_2$)(C$_6$H$_6$)$^+$ remaining unchanged [14].

A mixture of Fe(C$_n$H$_{2n}$)$^+$ ions from reaction of Fe$^+$ with pentane underwent ligand exchange with the notorious fullerenes, C$_{60}$ and C$_{70}$, to form Fe(C$_{60}$)$^+$ and Fe(C$_{70}$)$^+$. Collision-induced dissociation to form C_{60}^+ suggested that the iron was bound externally to the fullerene [15]. Fe$^+$ reacted with the fullerene predominantly by charge transfer to form C_{60}^+ [16].



Scheme 1.

Elimination of CH$_3$CD$_3$ resulted when Fe$^+$ reacted with the labeled silazane CD$_3$N(SiMe$_3$)$_2$. Migration of a β-methyl group to iron, followed by reductive elimination, was postulated. Reactions of Fe$^+$ with other silazanes and silanes were also investigated [17].

Threshold collisional activation barriers for decomposition of the ion-induced dipole complex Fe$^+$–C$_3$H$_8$ have been measured in a guided ion-beam mass spectrometer. The lowest energy processes involved loss of methane and loss of dihydrogen; dissociation to Fe$^+$ and propane was a major process, with a collisional activation threshold of about 79 kJ mol^{-1} [18]. Partially coordinated iron complexes HFe(CO)$_n^+$ and CpFe(CO)$_2^+$ also formed adducts with methane in the gas phase. With ethane, CpFe(CO)$_2^+$ (Fp$^+$) reacted to form Fp(C$_2$H$_4$)$^+$, presumably by insertion into a C–H bond and concerted dihydrogen loss [19].

FTICR studies of the interaction of Fe$^+$ and FeL$^+$ (L = ethene, propene, or butadiene) with ketones have revealed a rich chemistry. Ketone complexes formed by ligand substitution generally had too little energy to show fragmentation or multiple dehydrogenation processes, and only loss of a single dihydrogen was observed. The site selectivity of dihydrogen loss (remote functionalization) increased with decreasing energy content [20]. Bond dissociation energies for successive carbonyl loss from Fe(CO)$_5^+$ have resulted from guided ion-beam mass spectrometric study using collision-induced dissociation [21].

Rate constants of gas-phase reactions of neutral Fe(CO)$_3$ [from 351 nm photolysis of Fe(CO)$_5$] with ethene and dihydrogen have been measured, including data for formation of the crucial proposed intermediate in Fe(CO)$_3$-induced hydrogenation of ethane, H$_2$Fe(CO)$_3$(C$_2$H$_4$). The latter intermediate was stable for at least 100 μs. Additions to Fe(CO)$_3$ were generally fast, but additions to LFe(CO)$_3$ (L = CO, C$_2$H$_4$) were much slower, probably because of the triplet nature of LFe(CO)$_3$ [22].

Reactions of Fe(CO)$_2^-$ ions with hydrocarbons have been studied by two groups. With alkanes, insertion into C–H bonds was the dominant initial process, with loss of dihydrogen the sequel. With higher alkanes, the resulting alkene complexes rearranged further to allylic (OC)$_2$FeH(C$_n$H$_{2n-1}$)$^-$ products. Cycloalkanes behaved similarly [23]. Formation of (C$_4$H$_6$)Fe(CO)$_2^-$ from 1-butene came about through coordination of the double bond, hydrogen migrations to form first (1-butenyl)FeH(CO)$_2^-$ then (butadiene)FeH$_2$(CO)$_2^-$, and finally dihydrogen loss. Acetylene reacted by carbonyl displacement, forming (C$_2$H$_2$)$_2$Fe$^-$ as terminal product [24]. Reaction of $Fe(CO)_3^-$ with ^{13}CO revealed both substitution (29%) and addition (71%) reactions. The high rate constant for addition suggested that both $Fe(CO)_3^-$ and $Fe(CO)_4^-$ had the same multiplicity, presumably both doublets [25].

The diatomic species $MgFe^+$ has been prepared in the gas phase, and its reactions with various organics studied. Alkenes displaced magnesium from association with iron, forming $Fe(alkene)^+$. Alcohols, however, formed $(ROH)Mg^+$. Reaction with cyclohexene resulted in dehydrogenation, resulting first in formation of $MgFe(C_6H_6)^+$ and then in magnesium displacement to form $(C_6H_6)Fe(C_6H_{10})^+$. Ion molecule reactions suggested an upper limit of 140(20) kJ mol^{-1} for $D^0(Fe^+\text{–}Mg)$, whereas theory gave a binding energy of 123 kJ, based on a Fe(4s)–Mg(3s) σ-bond and a sextet ground state [26].

Some insights into iron-reagent-induced oxidation of hydrocarbons may be gleaned from FTICR studies of reactions of $OFe(OH)^+$ and alkanes in the gas phase. For example, reaction with ethane produced (a) $FeOH^+$ and ethanol, (b) $HFe(OH)_2^+$ and ethene, and (c) $(C_2H_4)FeOH^+$ and water [27].

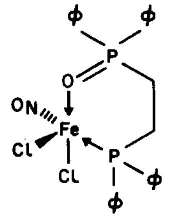
4. Compounds with η^1-carbon ligands

4.1. *Hydrido-, alkyl-, and aryliron compounds, R_nFe*

This section includes not only well-characterized organometallic compounds having iron–carbon σ-bonds (and no carbonyl groups), but also a number of low-coordinate or low-valent iron species which, lacking iron–carbon bonds, are not organometallics by strict definition. They are included here because of their utility in synthesis of organometallics and because of their intrinsic interest to organometallic chemists. Also included are some transient species thought to have iron–carbon bonds and some results on reactions (especially oxidations involving iron reagents) which may involve intermediates with iron–carbon bonds.

Crystal structures of the Fe^{II} amides $Fe(NR_2)_2$ (R = Ph, $SiMe_3$) showed dimeric structures, $R_2NFe(\mu\text{-}NR_2)_2FeNR_2$, with three-coordinate iron. The acid-base adduct $(THF)Fe[N(SiMe_3)_2]_2$ also showed a trigonal planar three-coordinate iron. At 30°C in solution $Fe[N(SiMe_3)_2]_2$ existed as a monomer, with increasing dimerization at lower temperatures [28]. Reaction with $HPAr_2$ (Ar = mesityl = 2,4,6-trimethylphenyl) produced phosphorus-bridged dimers, $R_2NFe(\mu\text{-}PAr_2)_2FeNR_2$. Like the dimeric amides, these cyclic species showed short terminal Fe–N bonds (1.91 Å average), suggesting multiple bonding. The Fe–P bonds, however, were quite long (2.39 Å average). Reaction of $Fe[N(SiMe_3)]_2$ with $HAsAr_2$ resulted in formation of As_2Ar_4 rather than a μ-$AsAr_2$ product [29]. Reaction of the bis(trimethylsilyl)amide with 2,4,6-tri(tert-butyl)phenol resulted in formation of $(Me_3Si)_2NFe(OAr)$ or $Fe(OAr)_2$, using one or two moles of phenol, respectively. Crystal structures showed aryloxy-bridged dimers in both cases. Variable temperature NMR spectroscopic study of $Fe(OAr)_2$ in solution revealed a strong tendency to remain dimerized, with association energy at least 60 kJ mol^{-1}. Reaction of the bis(trimethylsilyl)amide with triphenylmethanol in THF formed the solvated monomer, $(Ph_3CO)_2Fe(THF)_2$, whose crystal structure showed a distorted tetrahedral structure [30].

Reaction of dppe with $Fe_2(NO)_4Cl_2$ yielded (μ-dppe)$[Fe(NO)_2Cl]_2$. With an excess of dppe, halogen displacement resulted in formation of (dppe)$Fe(NO)_2$, accompanied by oxidation of a phosphino group by NO, to form **1**. Similar results were obtained with unsaturated analogs of dppe [31]. Powdered iron reacted with $PhPMe_2Br_2$ at room temperature to form $(PhPMe_2)_2FeBr_3$, which showed in the crystal a trigonal bipyramidal structure with axial phosphines [32]. Based on Mössbauer studies of a series of (diphosphine)$_2$FeXY compounds, partial quadrupole splittings (p.q.s.) have been assigned to ligands, based on assumed additivity, and discussed in terms of the bonding properties of the ligands. Cl, H_2, and N_2 showed the highest p.q.s. values on a scale with the value for H set at zero [33].



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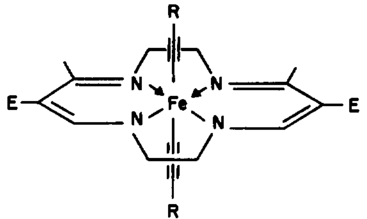


2

Iron complexes of 1,2-benzenedithiolate, $(C_6H_4S_2)_2Fe(PMe_3)_n$ (n = 1, 2) and NMe_4^+ $(C_6H_4S_2)_2Fe(PMe_3)_2^- \cdot MeOH$, have been prepared, and their crystal structures determined. The neutral diphosphine showed distorted octahedral coordination, with a planar FeS_4 unit comprising two long (2.30 Å) and two short (2.19 Å) Fe–S bonds, and a P–Fe–P angle of 160°. The anion was more regularly octahedral, with Fe–S bonds in the range 2.25–2.27 Å. The five-coordinate monophosphine was a tetragonal pyramid, with all four basal Fe–S bonds on the short side (2.18 Å average). The pattern of variation of Fe–S bond lengths was interpreted in terms of variable sulfur π-donation to iron. Electrochemical and spectroscopic results were cited in evaluating these compounds as models for [FeS] centers in redox enzymes [34].

Reaction of Li_2^+ $FeMe_4^{2-}$ with vinylic bromides, CH_2=CRBr, was accelerated by the presence of -OH,

-OMe, and -CN groups on the group R. With the alcohol groups, methane was evolved, signaling the formation of alkoxyiron intermediates [35].

Reaction of phenylhydrazine with equine myoglobin forms, as previously shown, a phenyl-iron product. Rearrangement of this product in the presence of acid and oxygen results in formation of all four possible N-phenylated rearrangement products. These have been isolated and identified, and the effects of reaction conditions on the amounts formed have been assessed [36]. Tetraarylporphyrinatoiron(III) chloride complexes [(Por)FeCl] have been found to catalyze the reduction of styrene by sodium borohydride to form ethylbenzene (in protic solvents) and 2,3-diphenylbutanes. A σ-alkyl complex, (Por)FeCHMePh, was considered a likely intermediate [37]. However, (Por)FeCl-catalyzed oxidation of *cis*-stilbene by tert-butyl hydroperoxide was found not to involve an alkyl-iron intermediate [38].

Bis(alkynyl)iron species **2** resulted from reaction of alkynyl lithium reagents, $LiC{\equiv}CR$ [$R = CMe_3$, Ph, 4-ClC_6H_4, $SiMe_3$, $Si(i\text{-}Pr)_3$, $SiPh_3$] with the (macrocycle)FeI precursor. The shifts in the visible absorption suggested a significant π-acceptor ability of the silyl substituents. Alkynyl complexes $RC{\equiv}CFePc^-$ (R = Ph, Pr; H_2Pc = phthalocyanine) also resulted, as pyridine or THF solvates, from reaction of $RC{\equiv}CBr$ with Na_2^+ $FePc^{2-}$ [40].

Bis(diphosphine)iron diacetylides have been prepared by two groups of chemists. One group used reaction of, for example, $(dmpe)_2FeH_2$ with $RC{\equiv}CH$ in methanol to form *trans*-$(dmpe)_2Fe(C{\equiv}CR)_2$ (R = Me, Ph, p-$C_6H_4C{\equiv}CH$, and others). Crystal structures of three examples showed Fe–C bond lengths of about 1.94 Å [41]. In the other case, treatment of $(depe)_2FeCl_2$ with $PhC{\equiv}CSnMe_3$ produced *trans*-$(depe)_2Fe(C{\equiv}CPh)_2$. Use of $Me_3SnC{\equiv}C$-p-C_6H_4-$C{\equiv}CSnMe_3$ produced a rigid rod-like polymeric species [42].

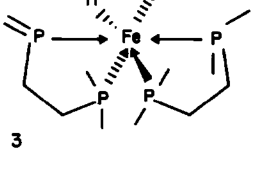
The kinetics of rearrangement of the fluxional hydride, $H_2Fe[\eta^4\text{-}P(CH_2CH_2CH_2PMe_2)_3]$, have been studied by an inversion-transfer-recovery NMR method. The activation energy for positional exchange of the hydride ligands was 64 kJ mol^{-1} at 260 K [43]. Photolysis of $(dmpe)_2FeH_2$ in liquid xenon solution containing methane afforded a mixture of *cis*- and *trans*-isomers of $(dmpe)_2FeHMe$, which equilibrated photochemically at −100°C. Replacement of the solvent by toluene, followed by warming, led to evolution of methane at 0°C [44].

Effects of hydride ligands on coordination of dihydrogen have been investigated by means of *ab initio* theoretical studies on $(H_3P)_4FeH(H_2)^+$. The presence of the hydride ligand favored coordination of dihydrogen either *cis* or *trans* to itself, as compared to a phosphine ligand. A significant attraction was found between the hydride and a suitably oriented *cis*-dihydrogen ligand [45].

Protonation of *cis*-$(dppe)_2FeH_2$ gave *trans*-$(dppe)_2FeH(H_2)^+$, which was also preparable by reaction of *trans*-$(dppe)_2FeHCl$ with $NaBPh_4$ under 1 atm of hydrogen. *trans*-$(Depe)_2FeH(H_2)^+$ was prepared similarly or by use of *cis*-$(depe)_2FeCl_2$ and an excess of $NaBPh_4$ in the presence of 1 equiv. of base. In the series of Group 8 $(diphosphine)_2FeH(H_2)^+$ complexes, the M–H stretching frequency and the phosphorus chemical shifts increased regularly going down the series. In several types of NMR measurements, however, the value for ruthenium did not lie between those of iron and osmium: $^1J_{H,D}$ for the HD compounds, chemical shift difference $\delta(H_2) - \delta(H)$, and T_1 values. The lability of the H_2 ligand increased as Os < Fe < Ru, indicative of the strengths of the M–H_2 bonds. H-atom exchange between the hydride and dihydrogen ligands was also measured by variable-temperature NMR spectroscopy [46].

Deprotonation of $(Ph_2PEt)_3FeH_2(H_2)$ with copper-alkoxides resulted in formation of cuprated analogs. The crystal structure of $(Ph_2PEt)_3Fe(\mu\text{-}H)_3CuPPh_2Et$, formed in this manner, showed an approximately tetrahedral array of three phosphines and copper around the iron (P–Fe–P angles 101–108°, Cu–Fe–P angles 109–116°) and a Fe–Cu distance of 2.32 Å. The hydride ligands, formally bonded to iron, lay in the P_2Cu faces of the tetrahedron [47].

Reaction of $(dmpe)_2FeH(H_2)^+$ with cyclopropene formed cyclopropane and free dihydrogen, but no identifiable iron complex. 3,3-Dimethylcyclopropene, however, yielded predominantly 3-methyl-2-butene, along with small amounts of dimethylcyclopropane. Allene and 1,1-dimethylallene reacted to form organoiron products, **3**, stabilized by an "agostic" hydrogen and suggestive of an intermediate in the insertion of an alkene into a Fe–H bond. Reaction of **3** (R = Me) with acid produced 2-methyl-2-butene. Reaction of $(dmpe)_2FeH(H_2)^+$ with phenylacetylene resulted in coupling of the acetylenes, with formation of an η^3-bound organoiron product [48], to be described in Section 5.



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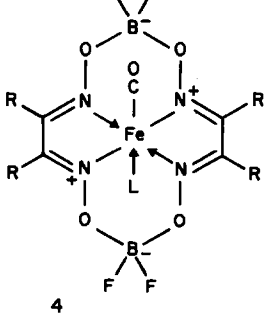
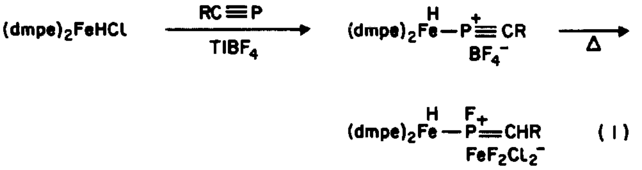


4

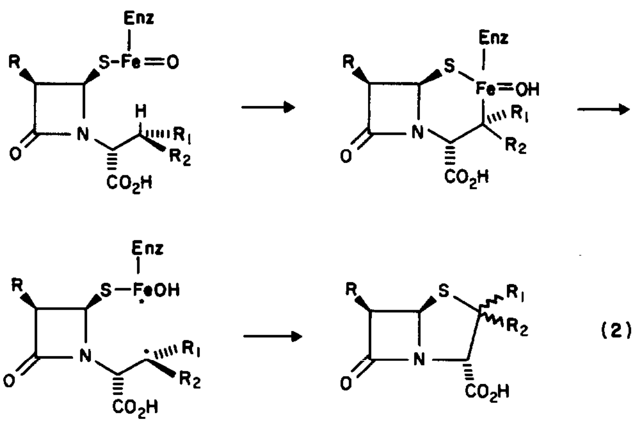
The unstable product $(dmpe)_2Fe(N_2)$ resulted from displacement of dihydrogen from $(dmpe)_2FeH(H_2)^+$ by dinitrogen, followed by deprotonation. Treatment with hydrochloric acid yielded "significant amounts" (2–12%) of ammonia. It was suggested, based on these results, that iron rather than molybdenum or vanadium may be at the active site of nitrogenases, with the role of the other metals being reduced to that of nitrogen-trappers [49].

Equation (1) shows the formation of a novel L_5FeH^+ species by disproportionation of a phosphaalkyne precursor, with addition of HF to the triple bond. The crystal structure of the product was reported [50].



(1)

Oxidation of alkanes to form alcohols and/or ketones using iron reagents has continued to attract research interest. A study of a "Gif-type" oxidation of cyclodecane to cyclodecanone, using $FeCl_3 \cdot H_2O_2$ in pyridine–acetic acid, showed that the oxygen in the ketone product came predominantly from molecular oxygen. This result, along with results of radical-trapping and selectivity studies, was held to support a free-radical mechanism for these oxidations [51]. The combination of [tris-(2-pyridylmethyl)amine]FeX_2^+ ClO_4^- (X = Cl, Br, N_3) and tert-butylhydroperoxide formed a useful reagent for oxidative functionalization of alkanes, and a model for iron-mediated functionalization in β-lactam biosynthesis. The reagent converted cyclohexane into $C_6H_{11}X$ in 70–80% yield at room temperature when used stoichiometrically. Use of the radical scavenger BHT did not alter the result. The mechanism proposed involved displacement of one X from the iron by peroxide, loss of Me_3CO^- to form an oxo species, hydrogen abstraction from alkane by the latter, and rebound abstraction of the remaining X from the iron by the alkyl radical [52]. Stereochemical studies on a synthetic tripeptide using *isopenicillin N synthase*, a non-heme iron enzyme, suggested a similar but not identical route [eqn. (2)] involving insertion of an iron species into the C–H bond before forming the organic radical [53].



(2)

Some μ-oxo diiron species having various ancillary ligands on the irons have been synthesized and tested for oxidative activity. *In situ* conversion to oxo species was considered the key to reactivity in hydroxylation of alkanes [54]. An excess of imidazole was found to increase the activity of binuclear and trinuclear iron oxo species such as $(phenanthroline)_4Fe_2O^{4+}$, a result which would be consistent with stabilization of mononuclear oxo species by imidazole [55].

Oxidation of cyclohexane by a number of binuclear iron species, using hydrogen peroxide/oxygen as oxidants, has been studied. [Tris-(1-methylimidazol-2-ylmethyl)amine]$_2Fe_2(\mu\text{-}O)(\mu\text{-}OAc)^{3+}$ $(ClO_4^-)_3$ was the most catalytically effective of the compounds used. Cyclohexyl hydroperoxide was isolated as a reactive intermediate from the reaction mixtures. These results, along with effects of radical inhibitors and removal of oxygen, led to postulation of a free radical mechanism involving hydrogen abstraction from cyclohexane by an oxo-iron species, oxygen addition to the radical, and chain continuation by further hydrogen transfer. Studies on toluene and adamantane suggested some additional role for hydroxyl radical as a less selective additional chain carrier [56]. Studies using $(bpy)_2Fe_2(\mu\text{-}O)(\mu\text{-}OAc)_2(H_2O)_2$ to oxidize methane, ethane, and cyclohexane also supported the key role of a mononuclear iron-oxo species in these oxidations [57].

Hydroxylation of aromatic compounds in modest yields has also been achieved using a Fe–acetic acid–oxygen system; an electrophilic oxo species, $(AcO)_2$-Fe=O, was proposed as the reactive intermediate [58]. Iron complexes of macrocyclic ligands such as cyclam (1,4,8,11-tetraazacyclotetradecane) have been found to catalyze alkene epoxidation by 30% aq. hydrogen peroxide in methanol or acetonitrile solutions. The epoxidations were stereospecific, and little allylic oxidation took place, both results suggesting little involvement of free radicals. Direct reaction of an L_4FeOOH intermediate with alkene, prior to peroxy bond cleavage, was suggested [59]. In contrast, using tetraarylporphyrins and tert-butyl hydroperoxide to epoxidize alkenes, tert-butylperoxy radical was implicated as the oxidizing species rather than (por)Fe=O or (por)FeOOR [38].

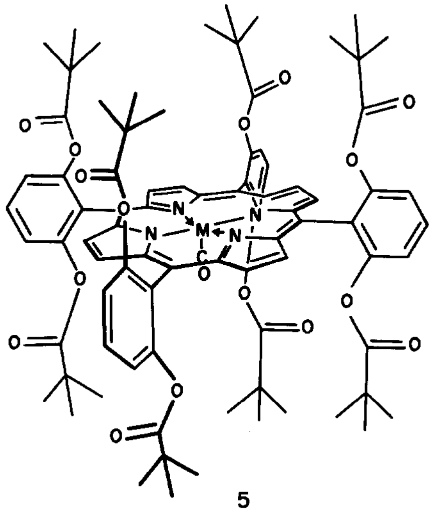
4.2. *Iron monocarbonyls and carboxylates, e.g., $L_4Fe(CO)$ and $L_4Fe(CO_2)$*

The compounds $(Et_3P)_2Fe(CO)(NO)OC(=O)Ar$ (Ar = Ph and methoxy-substituted phenyl groups) have been prepared by reaction of $(Et_3P)_2Fe(CO)_2(H)OCOAr$ with N-methyl-N-nitroso-*p*-tolylsulfonamide. Lithium aluminum hydride reduced the carboxylate ligand off, forming the hydride $(Et_3P)_2Fe(CO)(NO)H$. The same hydride and several analogs could be prepared by reaction of $(R_3P)_2Fe(CO)_2Cl_2$ (R = Me, Et, Me_2CHO) with Me_3CLi and $NOBF_4$ to form $(R_3P)_2Fe(CO)(NO)Cl$ [XRC], followed by reduction with $NaBH_4$. The crystal structure of $(Me_3P)_2Fe(CO)(NO)H$ was determined [60].

The partial quadrupole splittings of the ligands in a group of (diphosphine)FeXY compounds have been determined. Included were data for $(depe)_2Fe(CO)H^+$ and $(depe)_2Fe(N_2)H^+$. Based on correlation between p.q.s. values, phosphine cone angles, and stability, several unknown complexes were suggested as likely to be characterizable; these included *trans*-$(depe)_2FeCl(CO)^+$, $-Cl(N_2)^+$, $-(CO)_2^{2+}$, and $-(N_2)^{2+}$ complexes [61]. Electrochemical oxidation of $(depe)_2Fe(CNMe)H^+$ has been studied by cyclic voltammetry, using a computer simulation method which allowed evaluation of the rate constants for the multistep mechanism [62].

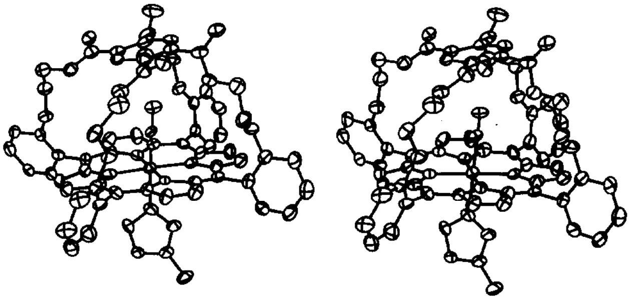
The infrared spectrum of $(Me_3P)_4Fe(CO_2)$ has been assigned completely, based on normal coordinate analysis. The bonding of the carbon dioxide ligand has been found to be intermediate between η^1 and η^2 [63]. In the full paper, two CO vibrational modes were described as particularly sensitive to the mode of CO_2 bonding, a stretching mode at 1150 cm^{-1} and an out-of-plane bending at 550 cm^{-1} [64]. Iron ("0") porphyrins, $(Por)Fe^{2-}$, have been found to catalyze the electrochemical reduction of CO_2, to give principally CO. The presence of Mg^{2+} improved the rate of reaction, and the stability of the catalyst, which otherwise underwent carboxylation and/or hydrogenation after a few catalytic cycles. The proposed mechanism involved formation of $(Por)Fe{=}CO_2^{2-}$, association of a second CO_2 molecule to form $(Por)Fe{=}C(-O^-)OCO_2^-$, and magnesium-assisted decomposition of the latter to form (Por)Fe(CO) and $MgCO_3$ [65].

Association of CO with iron in a series of difluorodioximatoborate complexes **4** ($R_2 = Me_2$, *o*-phenylene, 1,2-naphthylene; L = THF, DMF, DMSO, *etc.*), by displacement of a weakly-bound solvent ligand, has been studied by flash photolysis. Rate and equilibrium constants ranged over six orders of magnitude [66].



5

The kinetics of binding of O_2 and CO to "double-sided" porphyrinatoiron(II) complexes **5** has been studied. The steric size of the substituents resulted in weaker binding of CO, an effect attributed to steric repulsions with the axial imidazole ligand [67]. Relaxation of steric strain by incorporation of neopentyl groups rather than the tert-butyl groups of **5** resulted in lowering of the bound CO stretching frequency, suggesting that CO and O_2 binding could be modulated by changes in the iron-imidazole binding in the rear pocket of the macrocycle [68]. The crystal structure of a "capped" porphyrinato iron carbonyl, **6**, has been reported. The CO was bound to the capped face of the porphyrin, and a methylimidazole to the open face. The rakishly tipped cap caused bending and tilting of the CO relative to the axis normal to the porphyrin plane. The cap was displaced by 1.6 Å away from its position relative to the porphyrin ring in $PorH_2$ so as to accommodate the iron with its CO ligand [69].



6

Picosecond- to millisecond-scale absorption difference spectroscopy has been employed to study photolysis of the histidine–heme–CO complex. Both axial ligands were expelled simultaneously upon excitation. The vacant coordination sites were then filled by (1) water, (2) CO, then (3) the water was displaced by histidine [70]. A volume profile analysis of the formation and dissociation of carbonylmyoglobin has been carried out, using stopped-flow techniques. The volume of activation for decarbonylation was found to be -3.8 ± 1.6 cm^3 mol^{-1}. Direct measurement from the pressure dependence of the equilibrium gave a reaction volume of -3.0 ± 0.6 cm^3 mol^{-1}. Comparison with values for O_2 suggested different mechanisms, with bond-formation rate determining for CO [71].

4.3. *Iron dicarbonyls, e.g., $L_3Fe(CO)_2$*

The η^1-carboxylato compounds, $(Et_3P)_2Fe(CO)_2(H)OC(=O)Ar$, described in the last section as precursors to iron nitrosyl hydride complexes, were prepared by reaction of the μ-dinitrogen complex $[(Et_3P)_2Fe(CO)_2]_2N_2$ with benzoic and substituted benzoic acids [60]. Attempted reaction of cobalt atoms with $Fe(CO)_2(NO)_2$ and mesitylene in an attempt to produce cluster products gave no apparent reaction [72].

Isocyanic acid ligands in the iron complexes $(bpy)Fe(CN)_2(CNH)_2 \cdot 2H_2O$ and $Fe(CN)_2(CNH)_4$ could be converted to organic isocyanide ligands (CNR, R = Me, Et) directly by reaction with $ROH/PPh_3/EtO_2CN{=}NCO_2Et$ (Mitsunobo conditions) [73].

4.4. *Iron tricarbonyls, e.g., $L_2Fe(CO)_3$*

A high-yield, single-step synthesis of *trans*-tricarbonylbis(phosphine)iron compounds has been achieved by refluxing the phosphine with pentacarbonyliron and sodium hydroxide in n-butanol. Phosphines successfully used were PPh_3, PPh_2H, PBu_3, $PPh_2CH{=}CH_2$, and PPh_2Me [74]. IR, Mössbauer, and ^{31}P NMR spectra of twenty $L_2Fe(CO)_3$ complexes having phosphine or phosphite ligands have been measured and correlated. Linear relationships between isomer shift and quadrupole splittings in the Mössbauer spectra and between coordination shifts and isomer shifts were interpreted in terms of counterbalancing P-to-Fe σ-donation and Fe-to-P back-donation [75]. Heats of protonation of some $(R_3P)_2Fe(CO)_3$ complexes with triflic acid in 1,2-dichloroethane have been measured by titration calorimetry. The protonation enthalpies ranged from -59 (PPh_3) to -97 (PMe_3) kJ mol^{-1}, and were related linearly to phosphine basicity and to carbonyl stretching frequency [76].

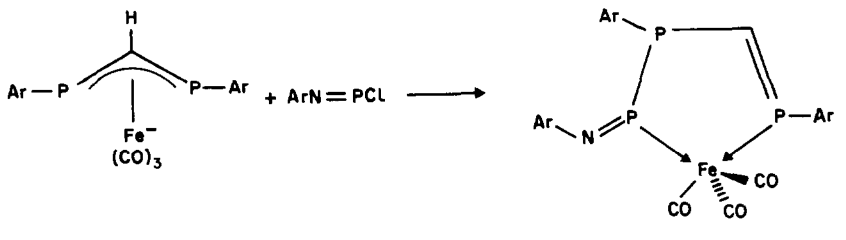
A 17-electron species, $(Ph_3P)_2Fe(CO)_3^+\ PF_6^-$, has been examined by X-ray crystallography and by EPR study in a $(Ph_3P)_2Co(CO)_3^+\ PF_6^-$ crystal matrix. The preferred geometry of the radical-cation has been found to be a C_{2v} square pyramid with *trans* phosphines, in contrast to the trigonal bipyramidal geometry of the closed shell neutral species [77]. The analogous $(dppe)Fe(CO)_3^+$ radical-cation has been prepared electrochemically. Its CO stretching frequencies were about 90 cm^{-1} higher than in the neutral compound. The chelating ligand led to easier oxidation than was the case for bis(phosphine)$Fe(CO)_3$ complexes, but the resulting cations were more chemically reactive [78].

Diphosphazene $(CF_3)_2P{-}N{=}PPh_3$, prepared from $(CF_3)_2P{-}N_3$ and PPh_3, formed $LFe(CO)_4$ and *trans*-$L_2Fe(CO)_3$ complexes upon reaction with $Fe_2(CO)_9$ in hexane. The two P–N bond lengths, which were somewhat unequal (1.612 and 1.576 Å) in the free ligand, were nearly equal (1.576 and 1.565 Å) in the $L_2Fe(CO)_3$ complex; the P–N–P angle also opened from 131° to 150°. These changes suggested coordination as a phosphodiimide: $[Ph_3P{=}N{=}P(CF_3)_2]_2Fe(CO)_3$ [79].

Reaction of 1,2,4,5-tetrakis(diphenylphosphino)benzene with an excess of nonacarbonyldiiron afforded the bis$[Fe(CO)_3]$ complex [XRC] [80]. Heating (η^1-dppf)$Fe(CO)_4$ in solution or in the solid state afforded the chelate complex (dppf)$Fe(CO)_3$. Kinetic study by IR and NMR methods in solution and by thermogravimetry and differential scanning calorimetry in the solid indicated a first-order dissociative mechanism [81]. Reaction of 1,1′-dilithioferrocene with chlorophenylisopropylphosphine produced the dppf analog, 1,1′-bis(phenylisopropylphosphino)ferrocene as a separable mixture of *meso* and racemic stereoisomers [XRC]. Each reacted with tricarbonylbis(*cis*-cyclooctene)iron to form stereoisomeric chelate $Fe(CO)_3$ complexes [82].

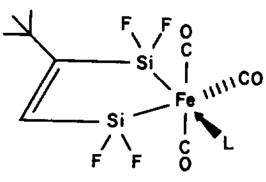
Equation (3) shows the reaction of a diphosphaallyl ferrate complex with a chloroiminophosphine [in both reagents, Ar = 2,4,6-tri(tert-butyl)phenyl] to form a novel chelate complex [XRC] in 76% yield [83].

Variable temperature NMR studies of 7 (L = PMe_3, PEt_3, PPh_3, and PPh_2Me), including ^{13}C, ^{19}F, and ^{31}P nuclei, have revealed polytopal rearrangements. The free energy of activation was highest for L = PMe_3 (70 kJ mol^{-1}) and least for L = PPh_3 (52 kJ mol^{-1}). A "trigonal twist" mechanism for the ligand permutations was preferred [84]. *mer*-$FeH[Si(OR)_3](CO)_3L$ (R



(3)

= Me, Et; L = η^1-dppm, Ph_2PCH_2COPh, Ph_2PH) were prepared by carbonyl displacement from the tetracarbonyl precursors. Deprotonation with KH, followed by reaction with Group 11 metal compounds gave metallated derivatives. The $Ph_3AsAgFe[Si(OMe)_3](CO)_3$(dppm) product lost triphenylarsine in solution to form the cyclized product, **8**, also preparable directly from the anion and $Ag(NCMe)_2^+$. The X-ray structure of $Ph_3PCu(\mu$-dppm)$Fe[Si(OMe)_3](CO)_3$ was reported [85].



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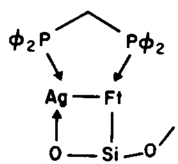


8

The cation $(Me_3P)_2FeMe(CO)_2(CNR)^+$ isomerized by methyl migration to the isonitrile ligand, to form $(Me_3P)_2Fe(CO)_2(\eta^2$-CMe=NR$)^+$. This migration was catalyzed by halide, nitrate, and perchlorate anions, but not by hexafluorophosphate or tetraphenylborate [86].

4.5. *Iron tetracarbonyls, e.g., $LFe(CO)_4$ and $R_2Fe(CO)_4$*

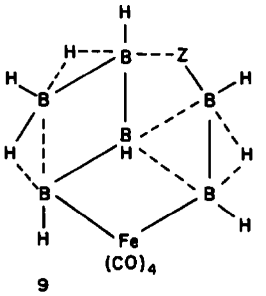
The butterfly isomerization of $Fe(CO)_4$, based on a Jahn–Teller mechanism, has been characterized by means of a specific permutational isomerism [87].

The gas phase acidity of $H_2Fe(CO)_4$ has been determined by ICR studies involving deprotonation by reference bases. The ΔH_{acid} value was about 1330 kJ mol^{-1}, ranking $H_2Fe(CO)_4$ as a very strong acid. From this value, the electron affinity of $HFe(CO)_4$ was calculated to be 2.8 eV. Reaction of $H_2Fe(CO)_4$ with thermal electrons occurred dissociatively, forming $H_2Fe(CO)_3^-$ and $Fe(CO)_4^-$ [88]. Loss of H_2 upon photolysis of $H_2Fe(CO)_4$ has been studied through contracted multireference configuration interaction calculations. The reverse process, oxidative addition of H_2 to $Fe(CO)_4$, was predicted to have a modest thermal barrier, less than 42 kJ mol^{-1} [89].

Reaction of an excess of $H_2Fe(CO)_4$ with $Cp_2Mo(\eta^2$-$CO_2)$ at −10° caused reduction of the coordinated carbon dioxide, forming $Cp_2Mo(H)CO^+$ $HFe_3(CO)_{11}^-$ and water [90]. $KHFe(CO)_4^-$ in methanol reduced aryl halides to arenes. Under 1 atm CO and in the presence of an excess of KOMe, the reaction was catalytic. It involved electron transfer to the aryl halide, loss of halide to form the aryl radical, which either extracted a hydrogen atom from KOMe or formed $ArFe(H)(CO)_4$. The latter gave ArH by reductive elimination. Use of a mixed metal system including $HFe(CO)_4^-$ and $Co(CO)_4^-$ resulted in carbonylation of iodobenzene to form benzoate, as a result of the phenyl radical reacting with $Co(CO)_4^-$. Bromobenzene itself was unreactive, but could be entrained in the chain reaction initiated by iodobenzene [91]. The use of $HFe(CO)_4^-$ to prepare stabilized compounds containing multiple bonds to phosphorus has been reviewed [5].

Reactions of $Fe(CO)_4^{2-}$ with various metal carbonyl species have been found to occur by different mechanisms. With metal carbonyl cations, formal CO^{2+} transfer resulted, *via* a μ-CO intermediate. With $Mn_2(CO)_{10}$ and $BrMn(CO)_5$, single electron transfer predominated [92]. Ytterbium salts of $Fe(CO)_4^{2-}$ have been prepared by reaction of the metal with $Fe_3(CO)_{12}$ in liquid ammonia and replacement of coordinated ammonia by acetonitrile to form $(CH_3CN)_3Yb^{2+}$ $Fe(CO)_4^{2-}$ as an acetonitrile solvate. The crystal structure showed an elaborate arrangement of units forming a ladder-polymer structure *via* coordination of Yb to oxygens of two $Fe(CO)_4$ units and iron of another [93].

Treatment of $Na_2Fe(CO)_4$ with R_2BI (R = octyl, decyl) under CO, followed by oxidation with HO_2^-, resulted in formation [*via* $R_2BFe(CO)_4^-$?] of ketones, R_2CO, in about 30% yield. The principal products were alcohols ROH [94]. NMR and IR spectral data have been reported for $B_6H_{10}Fe(CO)_4$ (**9**, Z = H) and for a cuprated analog, $(Ph_3P)_2CuB_6H_9$ [**9**, Z = $Cu(PPh_3)_2$], prepared by reaction of the potassium salt of the ferraborane with $(Ph_3P)_2CuBr$ [95]. The $In[Fe(CO)_4]_3^{3-}$ trianion has been produced in a methathetical reaction between $Na_2Fe(CO)_4$ and $InBr_3$. The crystal structure of the benzyltrimethylammonium salt showed a trigonal indium bound to three $Fe(CO)_4^-$ groups, with an average In–Fe distance of 2.63 Å. Reaction with $InBr_3$ gave comproportionated species $InBr[Fe(CO)_4]_2^{2-}$ and $InBr_2[Fe(CO)_4]^-$; the latter existed in the crystal (Et_4N^+ salt) as a cyclodimer with In–Fe distances averaging 2.67 Å. Presumably related cyclic species, $In_2[Fe(CO)_4]_6^{n-}$ (*n* = 2, 4) resulted from oxidation of the trianion by appropriate quantities of Ag^+ [96].



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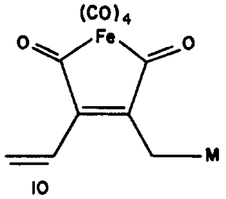
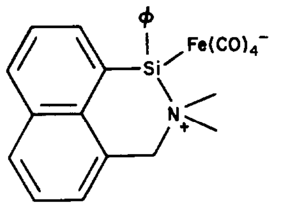


10

Maleoyl complexes **10** were formed in high yield by reaction of the unsaturated organometallics CH_2=CH–C≡C–CH_2M [M = $CpW(CO)_3$, $Mn(CO)_5$] with $Fe_2(CO)_9$ under flowing CO. Under static conditions, bi- and tri-metallic species, *vide infra*, were the principal products [97].

Reaction of [8-(dimethylaminomethyl)-1-naphthyl]-phenylsilane with $Fe(CO)_5$ led to dehydrogenation and formation of the zwitterionic adduct **11**, in 82% yield [98]. The outcome of the reaction of various bis(silyl)$Fe(CO)_4$ compounds with phosphines was dependent on the silyl and phosphine substituents: with $(Cl_3Si)_2Fe(CO)_4$ and triphenylphosphine, for example, CO displacement was the only result, whereas with more basic phosphines, dimeric products $Fe_2(CO)_6(PR_3)_2(\mu\text{-}SiCl_2)_2$ formed instead. The dimeric products did not form in reaction of $(R_3Si)_2Fe(CO)_4$ with phosphines [99].



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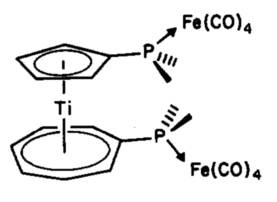


XI

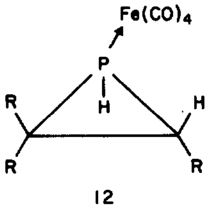
Stoichiometrically analogous but structurally different products resulted when m(μ-OR)$_3$Pb(μ-OR)$_3$m (m = Ge, Sn; R = tert-butyl) reacted with $Fe_2(CO)_9$. Both products had composition $m_2Pb(OR)_6[Fe(CO)_4]_2$, but the crystal structure of the germanium compound showed a spirocyclic structure with four-coordinate lead joining two Pb–$Fe(CO)_4$–$Ge(OR)_2O(R)$ rings, whereas the tin compound showed six-coordinate lead, resulting from all six tert-butoxy groups bridging lead and tin, and terminal $Fe(CO)_4$ groups bound to tin [100].

Stepwise reaction of the diazaferrocene-pyrrole adduct $[\eta^5\text{-}C_4Me_4N(HNC_4H_4)]_2Fe$ with iron carbonyl reagents resulted in replacement of the pyrroles consecutively by terminal $Fe(CO)_4$ groups, giving finally $[C_4Me_4N \rightarrow Fe(CO)_4]_2Fe$ [101]. Phosphorus-coordination resulted when a zirconaazaphosphirane was treated with $Fe_2(CO)_9$ to break the P → Zr bond of the three-membered ring and form $RN(SiMe_3)PH[\rightarrow Fe(CO)_4]\text{-}NRZrCp_2Cl$ [R = tert-butyl]. The N–Zr bond was readily hydrolyzed, resulting in formation of $RN(SiMe_3)PH \rightarrow [Fe(CO)_4]NHR$ [102].

Microwave dielectric relaxation has been used to probe the fluxionality of $(F_3P)Fe(CO)_4$ and other $(F_3P)_nFe(CO)_{5-n}$ species [103]. The conformations of the aryl rings in (o-tolyl)$_3PFe(CO)_4$ have been investigated by variable temperature NMR methods. At −75°C, the ^{13}C NMR spectra showed individual CO's in a 3:1 ratio for the isomer with all three methyl groups *exo* and a broadened resonance for the *exo*$_2$–*endo* isomer, whose Berry-type rotational barrier was about 13 kJ lower [104]. Kinetic study of the thermal decarbonylation of (η^1-dppf)$Fe(CO)_4$ suggested that the reaction followed a first-order dissociative mechanism, with chelation following the carbonyl loss [81].

Interest in the use of diphosphines to join two metal atoms continues, and has resulted in the preparation of several new complexes. For example, the mono- and di-[$Fe(CO)_4$] complexes of $RXPCH_2PRX$ (R = isopropyl, tert-butyl, and bulky trisubstituted aryl groups; X = Cl, Br) were prepared by straightforward complexation of the diphosphines using $Fe_2(CO)_9$. In the case where X = Cl and R = tert-butyl, the diastereomeric products were separated, and a crystal structure carried out on the *meso* isomer, which showed the phosphines in equatorial positions of the iron trigonal bipyramids [105]. X-Ray photoelectron spectra of dppf, (η^1-dppf)$Fe(CO)_4$, and $(OC)_5Mo(\mu\text{-dppf})Fe(CO)_4$ showed that free and coordinated phosphorus could be distinguished, as could even phosphorus atoms coordinated to different metals. Measurement of the binding energies of the two nonequivalent phosphorus sites in the same sample reduced calibration and sample charging complications [106]. Coordination of the substituted dppf analog, $(\eta^5\text{-}Ph_2PC_5H_4)Fe[1,2\text{-}C_5H_3(PPh_2)(CHMeNMe_2)$ by reaction with iron carbonyls produced a monodentate $Fe(CO)_4$ complex, with coordination to the less hindered diphenylphosphino group, and a bidentate bis[$Fe(CO)_4$] complex. $CpFe[1,2\text{-}C_5H_3(CHNMe_2)(PPh_2)]$ similarly formed the P → $Fe(CO)_4$ complex on reaction with any of the iron carbonyls. In neither case was there evidence of amino group coordination [107]. The μ-dppe complex, $CpFe[P(OMe)_3]_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)Fe(CO)_4^+$ resulted from reaction of the $CpFe[P(OMe)_3]_2(\eta^1\text{-dppe})^+$ precursor with $Fe_2(CO)_9$ [108]. A novel organometallic μ-diphosphine coordinated two $Fe(CO)_4$ groups in **XI** [109].

Several $Fe(CO)_4$ complexes of novel cyclic or unsaturated phosphines have been reported. Thus, reaction of the chlorophosphirane precursor with $HFe(CO)_4^-$ led directly to the phosphirane complex **12** (R = $SiMe_3$) [110]. The exotic **13** resulted, along with a mononuclear complex, from direct reaction of the diboradiphos-



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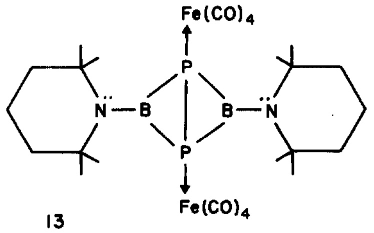


13

phetane with $Fe_2(CO)_9$ [111]. A similar reaction was used to prepare a phosphaalkene complex, $Fp^*CH=P[\rightarrow Fe(CO)_4]CH(SiMe_3)_2$ [112].

$Me_3SbFe(CO)_4$ has been prepared. An anionic arsenic compound, $Me_2Sb[Fe(CO)_4]_2^-$ [XRC], resulted from reaction of Me_2AsCl with anionic ferrates, $Fe_3(CO)_{11}^{2-}$ or $Fe_4(CO)_{13}$ [113]. Stepwise reaction of $Na_2Fe(CO)_4^{2-}$ with Ph_2BiCl produced first $Ph_2BiFe(CO)_4^-$, then $(Ph_2Bi)_2Fe(CO)_4$. The latter product decomposed in solution to form cyclic $[PhBiFe(CO)_4]_2$, also obtainable in low yield from $PhBiBr_2$. All three iron-bismuth compounds were characterized by crystal structures, the anion as a PPN^+ salt. In the anion, the pyramidal diphenylbismuth group was axial, and the Bi–Fe distance was 2.68 Å. In the octahedral $(Ph_2Bi)_2Fe(CO)_4$, the Bi–Fe bonds averaged a long 2.83 Å. The cyclodimer formed a planar parallelogram, with *trans* phenyl substituents, and Bi–Fe bonds averaging 2.78 Å [114].

Tetramethylthiophene served as a bridging ligand in $Cp^*Rh(\mu,\eta^1,\eta^4\text{-}SC_4Me_4)Fe(CO)_4$, **14**, [XRC] in which a Cp* Rh group was attached to the diene unit and the iron tetracarbonyl group to the sulfur. The compound resulted from reaction of $Cp^*Rh(\eta^4\text{-}C_4Me_4S)$ with $Fe(CO)_5/Me_3NO$. Heating resulted *inter alia* in desulfurization, with insertion of an $Fe(CO)_3$ unit into the ring. The ferrole product also resulted directly from reaction of the precursor with $Fe_3(CO)_{12}$ at 110°C [115]. An iridium analog of **14**, $Cp^*Ir(\mu,\eta^1,\eta^4\text{-}SC_4H_2\text{-}2,5\text{-}Me_2)Fe(CO)_4$, was one of eight products formed when the iridium thiophene complex was treated with iron carbonyls. Again, heating with $Fe_3(CO)_{12}$ resulted in partial or complete desulfurization, the mechanism of which was discussed [116]. The η^2-selenophene complex $Cp^*Re(CO)_2(\eta^2\text{-}C_4H_4Se)$ was also converted to the $Se \rightarrow Fe(CO)_4$ derivative, in 25% yield, upon reaction with $Fe_2(CO)_9$ [117].

4.6. Carbene complexes, e.g., $R_2C=FeL_4$

Several ethoxyalkynylidene complexes, **15**, $RC{\equiv}C\text{-}C(OEt){=}Fe(CO)_4$ (R = propyl, cyclohexyl, tert-butyl, phenyl, and trimethylsilyl) were formed by reaction of ethynyl-lithium reagents with pentacarbonyliron, followed by O-ethylation using ethyl fluorosulfonate. However, use of ethoxyethynyl-lithium resulted in formation of (2,3-diethoxycyclopropen-1-ylidene)tetracarbonyliron, by migration of an ethoxy group. **15** (R = $SiMe_3$) served as a dienophile toward 2,3-dimethyl-1,3-butadiene and cyclopentadiene [118]. Cyclopropylidene complexes were said to be produced in 52–60% yield upon treatment of 1-alkyl-2,2-dichlorocyclopropanes with $Na_2Fe(CO)_4$ [119].

Methyl propynoate displaced dinitrogen from $(OC)_2L_2Fe\text{-}N{\equiv}N\text{-}Fe(CO)_2L_2$ [L = PEt_3, $P(OMe)_3$, $P(OCHMe_2)_3$], giving the η^2-alkyne complex and its vinylidene isomer, $(OC)_2L_2Fe{=}C{=}CHCO_2Me$, in solution. These were characterized by the products of further reaction with methyl propynolate [120], which will be described with other η^3 compounds in Section 5 of this Review. Also described later are the products of reaction of $PhC(OEt){=}Fe(CO)_4$ with ketenimines [121], and the reactions of the carbenoid products with alkynes [122].

The base-free silylene complex, $(Me_3CS)_2Si{=}Fe(CO)_4$, from reaction of the dichlorosilane with $Na_2Fe(CO)_4$, could be observed directly by NMR spectroscopy and isolated as the HMPA adduct. The latter showed a Si–Fe bond length of 2.278 Å and a Si–O (HMPA) bond length of 1.734 Å. Photolysis of the HMPA adduct produced polysilanes or, in the presence of dimethylbutadiene, the 1,4-adduct of the silylene to the butadiene [123]. Related to this silylene complex is the intramolecular adduct **11** [98] previously discussed.

4.7. Some reactions and properties of $Fe(CO)_5$

Reactions in which $Fe(CO)_5$ undergoes conversion to more complex organometallic products are treated according to the product structures. In this section I discuss some simple reactions which leave the five carbonyl ligands attached or result in formation of isonitrile derivatives.

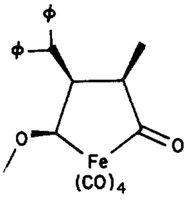
Protonation of $Fe(CO)_5$ has been analyzed theoretically, in terms of electrostatic, charge-transfer, and exchange-repulsion interactions based on Extended Hückel wavefunctions. Omission of the charge-transfer term leads to a prediction of O-protonation; with that term included, Fe-protonation is predicted. The results were presented as reactivity surfaces [124,125]. Experimental studies of $Fe(CO)_5$ protonation by pulsed-ionization high-pressure MS studies led to the conclusion, based on slow kinetics and negative temperature dependence of the rate, that protonation occurred on iron and led to loss of fluxional motion. The proton affinity was found to be 837 kJ mol^{-1} [126].

Coordination of $Fe(CNR)_5$ (R = phenyl, *p*-tolyl, tert-butyl) with mercury in $(RNC)_5Fe \rightarrow HgI_2$ also involved attachment of the Lewis acid to iron, as shown by the crystal structure of the *p*-tolylisonitrile compound. The Fe–Hg bond length was 2.551 Å [127]. The tri(isonitrile) ligand, $MeC(CH_2NC)_3$, reacted with $Fe(CO)_5$ to form air- and light-sensitive $MeC[CH_2NCFe(CO)_4]_3$ [128].

Reactivity of $Fe(CO)_5$ toward some Group 15 and 16 oxides, LO, as potential oxygen atom transfer reagents, has been assessed. The reactivity order found, for reaction to form $LFe(CO)_4$ and CO_2, was $Ar_2TeO > Ar_2SeO > Ph_3SbO > Ph_3AsO \gg Ph_3PO$, Ph_2SO (Ar = *p*-methoxyphenyl) [129].

5. η^2-Alkene and η^3-allyl complexes

Compound **10**, previously described, has an organic ligand η^2-bound to a tetracarbonyliron group, although it is not an alkene complex. A similar η^2 product, **16**, [XRC] was formed upon reaction of benzhydryl-lithium with (η^4-*cis*-1-methoxy-1,3-butadiene)tricarbonyliron, followed by acid quenching [130].



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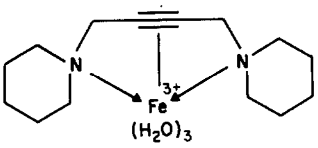

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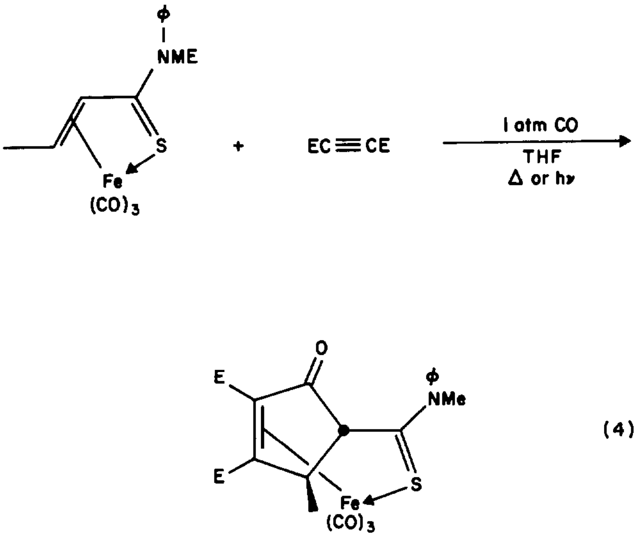
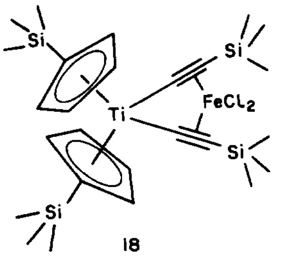
Complexation of CH_2=CH–BXNMe$_2$ (X = Br, Me) with $Fe_2(CO)_9$ in the dark led to the η^2-vinyl–Fe(CO)$_4$ products [XRC, X = Me] [131]. Two examples of η^2-complexes of "inorganic" iron with alkynes, **17** [132] and **18** [133], have been reported. **17** was prepared directly from 1,4-piperidino-2-butyne and ferric nitrate in acetone/dioxane [132]. **18** was similarly prepared by direct addition, and its identity was confirmed by a crystal structure. The iron was coordinated in a distorted tetrahedron, with Fe–C distances of 2.23 and 2.20 Å. Magnetic measurements revealed a high-spin d^6 configuration [133].





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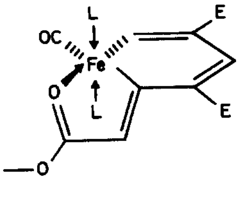

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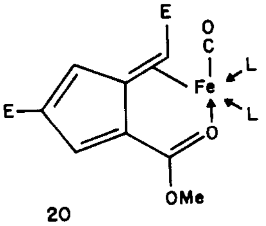
The initial products from reaction of $L_2(OC)_2Fe$–N≡N–Fe(CO)$_2L_2$ with methyl propynoate, thought to be (η^2-HC≡CE)Fe(CO)$_2L_2$ and ECH=C=Fe(CO)$_2L_2$, reacted by further addition of two moles of methyl propynoate, eventuating in formation of products **19** and **20** [XRC]. The iron in the latter product was unsymmetrically bound to the exocyclic double bond of the pentafulvene unit, with distances of 2.02 Å to the exocyclic carbon bearing the ester group and 2.17 Å to the endocyclic carbon [120].



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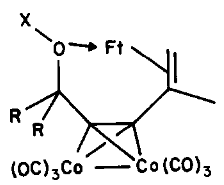

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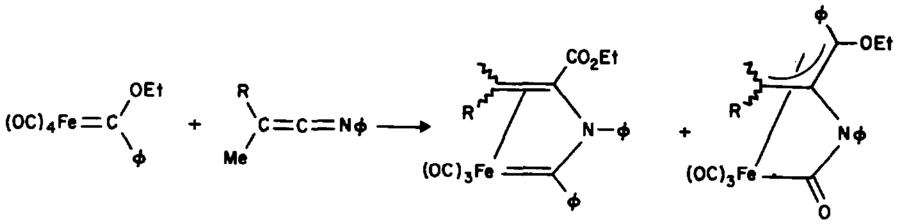
Equation (4) shows further examples of η^2 alkene complexes supported by additional bonding to otherwise-unshared electron pairs in the organic ligand. The starting material in eqn. (4) was prepared by direct reaction of the thiocrotonamide with iron carbonyls; many other unsaturated thioamides and thioesters gave analogous products. A crystal structure of the N,N-diethylthiocinnamamide analog confirmed the η^3 bonding shown, and revealed a short (1.33 Å) C–N bond and a long (1.73 Å) C–S bond [134]. Compounds **21** (X = PhCO, MeCO, Me, Me$_3$CSiMe$_2$; R = H, Me, Ph) were prepared by complexation of the cobalt-containing ligand using bis(cyclooctene)tricarbonyliron [135].

Two distinct types of 1:1 adducts formed in the reaction of $(OC)_4Fe$=C(OEt)Ph with ketenimines RCMe=C=NPh (R = Me, Et, Me$_2$CH) [eqn. (5)]. Alkylation of the allyl-type adduct with Et_3O^+ occurred at the acyl oxygen. Protonation of the other adducts resulted in ring contraction with formation of four-membered metallacycles [121]. Light-induced addition of alkynes [eqn. (6)] gave homopyrroles, free and complexed dihydropyridines, and a zwitterionic pyrrolium carbonylferrate [XRC]. The reactions were rationalized in terms of initial alkyne insertion into the Fe=C bond to form a chelated 5-aza-1-ferra-1,3,6-triene, which rearranged to the products shown [122].

Diels–Alder addition of 2,3-dimethylbutadiene to the triple bond of $(OC)_4Fe$=C(OEt)C≡C–SiMe$_3$, **15**, was followed by intramolecular displacement of a CO by the nascent double bond, giving the η^3 carbenoid **22** [118]. The product of reaction of phenylacetylene with $(dmpe)_2FeH(H_2)^+$ was found by crystal structure de-



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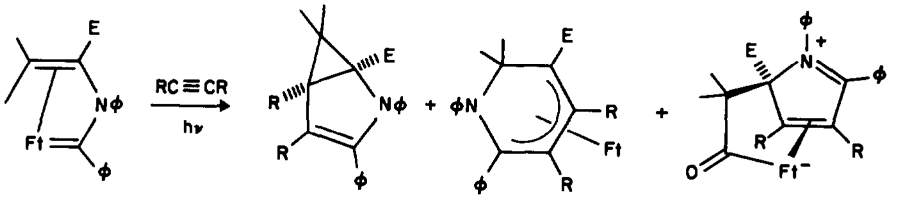

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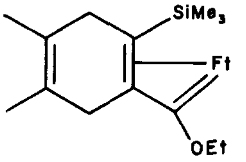
termination to have structure **23**, requiring ligand coupling and hydrogen migration [48].



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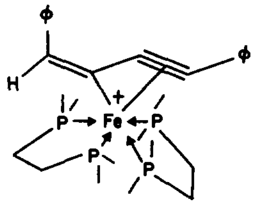
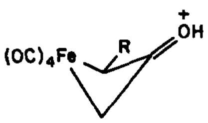


23

More conventional η^3-allyl complexes, 1- and 2-(trimethylsiloxyallyl)Fe(CO)$_2$NO, have been prepared by reaction of the siloxyallyl halides with Fe(CO)$_3$NO$^-$. Reactions with both carbon nucleophiles and carbon electrophiles occurred at the less hindered end of the 1-trimethylsiloxyallyl complex [136]. The electrochemical reduction of (η^3-C$_3$H$_5$)Fe(CO)$_3$X at mercury and platinum electrodes has been studied by cyclic voltammetry, abetted by theoretical calculations. Formation of heterometallic intermediates on the mercury surface was inferred [137]. The reaction of "Fe(C$_3$H$_5$)$_2$" with norbornadiene has been studied. Four C$_{10}$H$_{12}$ isomers were characterized as products, with the major product (55%) being formally an *exo*-[2 + 2] adduct of allene and norbornadiene; the *endo*-[2 + 2 + 2] adduct (31%) was next in quantity [138].

Dehydrohalogenation of (η^3-RCH–C(OH)–CH$_2$)-Fe(CO)$_3$X (R = H, Me; X = Br, Cl) with AgBF$_4$/pyridine gave the tricarbonyl(oxyallyl)iron dimers; in the presence of CO, however, the salts (η^3-RCHC(OH)CH$_2$)Fe(CO)$_4^+$ BF$_4^-$ were formed. These showed exceptionally large *geminal* coupling constants of about 6 Hz, suggesting significant contribution of an η^2 structure, **24**. Treatment with furan did not result in cycloaddition [139]. Coupling of substituted allyl-Fe(CO)$_4^+$ cations with η^1-allyl metal compounds has been explored. For example, reaction of (η^3-1-phenylallyl)Fe(CO)$_4^+$ with CH$_2$=CH–CH$_2$ML$_n$ gave preferential coupling at the 3-carbon with ML$_n$ = SiMe$_3$, but at the 1-carbon with ML$_n$ = SnBu$_3$ or Fp. Reactions of (η^3-1,1-dimethylallyl)Fe(CO)$_4^+$, a potential isoprenylating reagent, were beset by the occurrence of deprotonation at the expense of the desired coupling [140].



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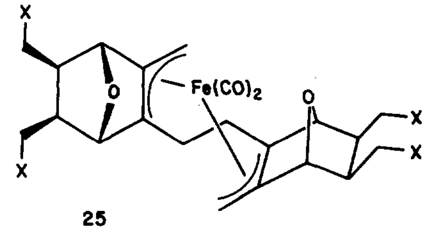

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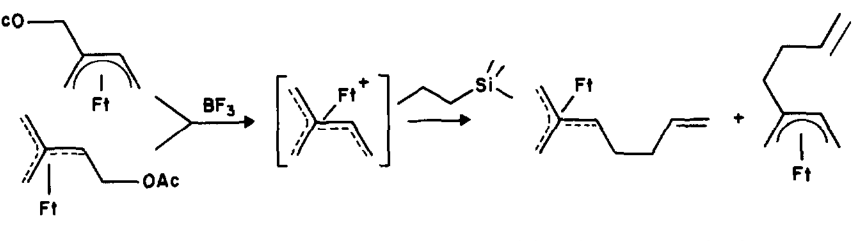
The bis(allyl) complex, (depe)Fe(η^3-pentadienyl)$_2$ [XRC] was prepared by attack of two moles of K$^+$C$_5$H$_7^-$ on (depe)$_2$FeCl$_2$. Both allyl groups were *syn* and "W-shaped" in the crystal, although NMR spectroscopy indicated some *syn–anti* isomer to be present in solution. The bis(pentadienyl) complex reacted with protonated depe with loss of 1,3-pentadiene and formation of (depe)$_2$Fe(η^3-C$_5$H$_7$)$^+$ [XRC], the Fe–P and Fe–C distances in which were 0.03–0.05 Å longer than in the neutral compound. The cation decomposed at temperatures above −20°C [141]. The bis(allyl) products **25** (X = Cl, OSO$_2$Me) were obtained as ligand-coupling byproducts (*ca.* 5% yields) from the reaction of 2-*exo*-3-*exo*-bis(chloromethyl)-5,6-bis(methylidene)-7-oxabicyclo[2.2.1]heptane and its mesyloxy analog with Fe$_2$(CO)$_9$ at room temperature [142].

Addition of LiR (R = CHPh$_2$, CMe$_2$CN) to (η^4-1,3-cyclohexadiene)Fe(CO)$_3$ at room temperature formed the (η^3-cyclohexenyl)Fe(CO)$_3^-$ anion; quenching with bromine resulted in formation of (5-*exo*-*R*-1,3-cyclohexadiene)Fe(CO)$_3$ products [143]. Attack of Ph$_2$CHLi on (η^4-*cis*-1-methoxy-1,3-butadiene) gave predominantly (71%) attack at the 2-position, which led to the formation of **16** upon acid quenching; some



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attack at the 1-position also took place, resulting in a substitution reaction, forming tricarbonyl(η^4-5,5-diphenyl-1,3-pentadiene)iron (27%) [130]. Attack of benzyhydryl-lithium on the 3-position of tricarbonyl(2-methoxybutadiene)iron at −78°C gave a butenyliron anion, which could be intercepted by various electrophiles to give synthetically useful results. Reaction with RX gave unsaturated ketones, CH_2=C(OMe)CH-($CHPh_2$)CH_2C(=O)R (R = Me, CH_2Ph). Benzoyl chloride converted the butenyliron anion to the diketone MeC(=O)CH(CPh_2)CH_2C(=O)Ph. Bromination in the presence of CO, with an aqueous workup, formed a lactone product [144].

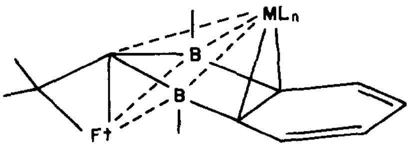
6. Compounds with η^4 ligands

6.1. Trimethylenemethyl complexes

A carbonyl ligand in [η^4-C(CH_2)$_3$]Fe(CO)$_3$ has been replaced by several phosphines and by tert-butyl isonitrile, using trimethylamine oxide to induce the replacement reaction. TMM ligand rotation was observable by variable temperature NMR spectroscopy in some cases. A crystal structure of (TMM)Fe(CO)$_2$-[PPh(*cyclo*-C_6H_{11})$_2$] showed a structure similar to that of other TMM compounds [145].

Reaction of [2-(acetoxymethyl)-1,3-butadiene]tricarbonyliron or of [(acetoxymethyl)trimethylenemethyl]tricarbonyliron with allyltrimethylsilane/$BF_3 \cdot OEt_2$ at −78°C gave essentially the same mixture of products, [eqn. (7)], in which the TMM isomer predominated by a factor of about 7:1. Since the TMM products are likely to be thermodynamically less stable than the diene products, kinetic factors must be responsible for their predominant formation. It appears that, in the putative common intermediate, [CH_2CHC(CH_2)$_2$]Fe-(CO)$_3^+$, C-4 may be comparatively weakly bonded to iron, and thus most susceptible to attack by nucleophiles. Analogous results were obtained using other nucleophiles, including Et_3SiD and Me_3Al [146]. Another group has independently studied these and similar reactions, with consistent results. They have particularly emphasized the stereospecificity of the reaction; thus the two diastereomers of [(CH_2)$_2$CCHCHMeOH]-Fe(CO)$_3$ each cleanly gave a different diastereomer of the allylated TMM product, presumably with retention of configuration. Similarly, diastereomeric secondary alcohol diene complexes [η^4-CH_2C(CHROH)CH-CH_2]Fe(CO)$_3$ formed diastereomeric TMM complexes [147].

A sila-TMM complex has been prepared, in 59% yield, by reaction of 1,1-dimesityl-2-neopentylidenesilirane with nonacarbonyldiiron. The crystal structure showed a Si–C distance of 1.84 Å and Fe–Si distance of 2.42 Å. Iron–carbon distances in the hetero-TMM unit were normal [148]. A dibora-TMM structural moiety was incorporated into a slipped triple decker structure in compounds **26**. The bis[Fe(CO)$_3$] compound [**26**, ML_n = Fe(CO)$_3$] was prepared by reaction of the diboraisobenzofulvene with an excess of (C_8H_{14})$_2$Fe-(CO)$_3$. Its crystal structure showed Fe–B distances of 2.37 and 2.40 Å in the dibora-TMM unit, and normal Fe–C distances of 2.10 and 1.92 Å. The η^5-Fe(CO)$_3$ group was most tightly bound to C(2) (2.02 Å) and 2.23–2.26 Å from the other atoms in the five-membered ring. Formation of the bis[Fe(CO)$_3$] compound was thought to involve the slippage of the Fe(CO)$_3$ group in the known [η^5-C_6H_4(BMe)$_2$C=CMe$_2$]Fe(CO)$_3$ to η^4, followed by attachment of the new η^5 group [149]. Consecutive treatment of the diboraisobenzofulvene with (C_8H_{14})$_2$Fe(CO)$_3$ then CpCo(C2H$_4$)$_2$ gave **26** (ML_n = CoCp). The crystal structure showed a dibora-TMM unit very similar to the bis-[Fe(CO)$_3$] compound [150].



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6.2. Complexes of acyclic dienes, including heterodienes

An investigation of the reaction of 1,2-bis(halomethyl)benzenes with iron carbonyl reagents has suggested that formation of the product, tricarbonyl(η^4-*o*-xylylene)iron, involves reduction of the dihalide to free *o*-xylylene, some of which gets trapped by iron reagent, but much of which escapes to form poly(*o*-xylylene) or other byproducts. The yield of complex was optimum (but still only 30–40%) when $Na_2Fe_2(CO)_8$ in solution or $Na_2Fe(CO)_4$ under heterogeneous conditions was used. Formation of free benzocyclobutadiene en route to complexation was also indicated in the reaction of 1,2-dibromobenzocyclobutene with iron carbonyls, and the authors suggested that the mechanism may be a general one [151].

The *exo*-$Fe(CO)_3$ diene complex was formed in 75% yield upon reaction of nonacarbonyldiiron and 2-*exo*-3-*exo*-bis(chloromethyl)-5,6-bis(methylidene)-7-oxabicyclo[2.2.1]heptane, along with 5% of the unexpected product **25** [142]. The methyl-substituted oxyallyl dimer $[(\mu\text{-}CH_2C(O)CHMe)Fe(CO)_3]_2$ readily underwent a hydrogen migration and dissociation to form (η^4-1,3-butadien-2-ol)$Fe(CO)_3$ [139]. Selective oxidative degradation of dienyne complexes in which the triple bond was coordinated to a $Co_2(CO)_6$ group and the diene to a $Fe(CO)_3$ group selectively removed the cobalt carbonyls, giving the first examples of (diene)$Fe(CO)_3$ complexes having free triple bonds [152].

A novel route to an η^4-styrene complex [XRC] was the reaction of an isomerized carbene complex with triphenyl phosphite [eqn. (8)]. In complexes derived from butadiene, which lacked the extra methyl group, phosphines and phosphites simply displaced the oxygen from coordination to the iron [153].

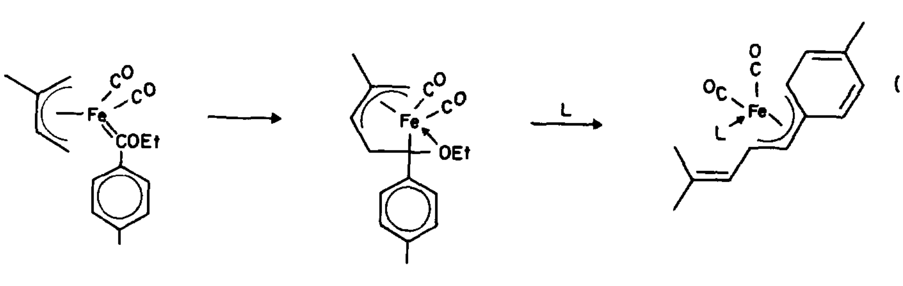
The IR spectrum of (butadiene)tricarbonyliron in supercritical xenon solution showed a temperature-independent IR spectrum, showing it to be rotationally static on the IR time-scale. This is consistent with previous NMR studies, which showed a rotational barrier of about 37 kJ mol^{-1} [154]. Variable temperature ^{13}C and ^{31}P NMR studies of (diene)$Fe(CO)_2L$ complexes, having L = phosphines, phosphites, or isonitriles, abetted by molecular modelling and crystal structures of (η^4-2,3-dimethyl-1,3-butadiene)$Fe(CO)_2$-PPh_3 and (η^4-*trans*,*trans*-2,4-hexadiene)$Fe(CO)_2PPh_3$, have been used to define solution structures and conformer populations [155].

Electron momentum distributions for the valence region of (butadiene)tricarbonyliron have been studied by (e, 2e) spectroscopy and compared with results of SCF-MO calculations. For binding energies of 8–11 eV, the experimental momentum distributions reflected predominantly the butadiene HOMO, the experiment being relatively insensitive to iron contributions. At higher energies, butadiene σ-orbitals and then CO σ-orbitals were dominant [156]. Extended Hückel calculations on reactions of (butadiene)tricarbonyl with nucleophiles have suggested that soft nucleophiles should attack (if at all) at C1, and hard nucleophiles at C2; the latter is generally borne out by experiment. The results were presented as graphic reactivity surfaces [124,125].

The iron tricarbonyl complex of fumaraldehyde, (η^4-*E*-HCO–CH=CH–CHO)$Fe(CO)_3$, was synthesized from the acetal $(MeO)_2CH$–CH=CH–CHO by complexation and deprotection with acidified silica. Reaction with alkylcerium and Grignard reagents gave diastereomeric alcohols by attack at the free aldehyde group [157]. Reaction of the chromium-coordinated benzylideneacetophenone derivative, $(OC)_3Cr(o\text{-}Me\text{-}C_6H_4)CH{=}CH\text{–}C({=}O)\text{–}Ph$, with $Fe_2(CO)_9$ gave only one diastereomeric $Fe(CO)_3$ product, which was shown by X-ray crystallography to be the (*RS,SR*) isomer [158]. Likewise, the sulfinyl group in RS(O)–CH=CH–C(=O)Me (R = Ph, ^tBu) directed the incoming iron carbonyl group so that only a single diastereomeric $Fe(CO)_3$ complex, isolated in 64–67% yield, formed. Sulfonyl complexes were also prepared, in 87–89% yield [159]. Electrochemical oxidation of (η^4-PhCH=CH–C(=O)–CH_3)$Fe(CO)_2L$ (L = phosphines or phosphites) in DMF led to decomposition to free benzylideneacetone and L *via* a mechanistically complex process. The oxidation voltage was correlated with the electron-donating power and polarizability of L [160].

A coordinated 1-phosphadiene complex, {η^4-PhP[→$W(CO)_5$]=CH–CH=CH–CHO}$Fe(CO)_3$, was synthesized by reaction of [η^2-$(MeO)_2CH$–CH=CH–CHO]-$Fe(CO)_4$ with PhPH[→$W(CO)_5$]P(O)$(OEt)_2$, followed by deprotection. The aldehyde group reacted normally with nucleophiles, the complexed phosphadiene unit remaining undisturbed. A 2-phosphadiene complex, {η^4-PhCH=CH–P[→ $W(CO)_5$]=CH–$CHMe_2$}$Fe(CO)_3$ [XRC], was also prepared, by complexation of the comparatively stable 2-phosphabutadiene ligand with $Fe_2(CO)_9$ [161].

Very unstable heterodiene complexes, (η^4-CH_2=CH–BR–NMe_2)$Fe(CO)_3$, (X = Br, ^tBu, Me) were formed by the action of light on the (η^2-alkene)$Fe(CO)_4$ precursors. They were investigated in solution by means



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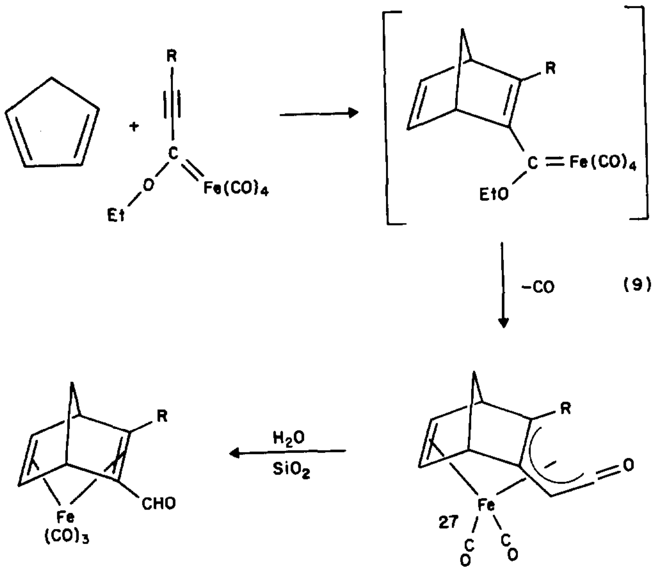
of IR and NMR spectroscopy, but were not isolable [131].

Cycloaddition of cyclopentadiene with the carbene complex $Me_3Si-C{\equiv}C-C(OEt){=}Fe(CO)_4$ was followed by CO insertion to form the vinylketene complex **27** (R = $SiMe_3$) [eqn. (9)] (*cf.* **22**) **27** rearranged on silica to the norbornadiene complex shown [118].



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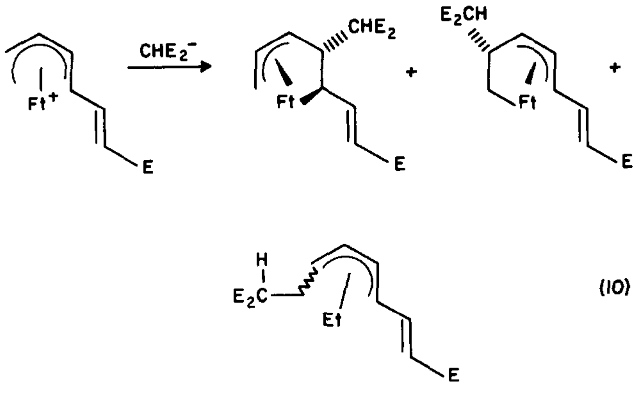
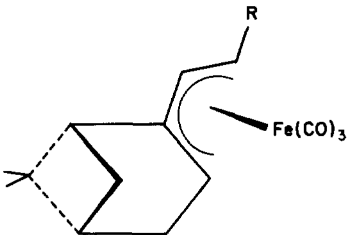
Several complexes of α,β-unsaturated ketones, [η^4-$PhCH{=}CH-C(R){=}O]Fe(CO)_3$, were converted to vinylketene complexes [η^4-$PhCH{=}CH-C(R){=}C{=}O]Fe(CO)_3$ (R = Me, Bu, ^{t}Bu, Ph) by treatment with methyl-lithium under CO at −78°C, followed by quenching with tert-butyl bromide [XRC, R = Me]. Analogous treatment of the aldehyde complex [η^4-$PhCH{=}CH-CH{=}O]Fe(CO)_3$ gave, however, free aldehyde (55%), a coupled product, $(PhCH{=}CH-CH{=})_2$ (5%), and the $Fe(CO)_3$ complex of the latter (5%). Heating the vinylketene complexes with isonitriles R′NC at 80°C transformed them into vinylketenimine complexes, [η^4-$PhCH{=}CH-C(R){=}C{=}NR']Fe(CO)_3$ [162]. Vinylketene complexes underwent conversion to vinylallene complexes [η^4-$PhCH{=}CH{=}CR{=}C{=}CHE]Fe(CO)_3$ upon reaction with phosphonoacetate anions, $(EtO)_2P(O)CHE^-$. Stereoselectivity as high as 98%, in favor of the isomer with the ester group *anti* to the tricarbonyliron group, was observed in the case of the tert-butyl ester [163].

The bimetallic diene complex [η^4-$CH_2{=}CH-CH{=}CH-CH_2Mo(CO)_3Cp]Fe(CO)_3$ [XRC] resulted from reaction of (pentadienyl)$Fe(CO)_3^+$ with the molybdenum nucleophile, $CpMo(CO)_3^-$. The adduct underwent spontaneous homolysis of the C–Mo bond in solution, with $\Delta H^\ddagger$ about 120 kJ mol^{-1} [164]. Attack of malonate anion on an extended pentadienyliron cation [eqn. (10)] occurred indiscriminately at each of three different positions. The cation was prepared from (η^4-$HOCH_2CH{=}CH-CH{=}CH-CHO)Fe(CO)_3$ by Wittig–Horner chain extension, using $(EtO)_2P(O)CH_2$-CO_2Et, followed by treatment with acid [165]. Intramolecular trapping of (pentadienyl)$Fe(CO)_3^+$ cations by pendant OH groups has provided a route to optically-active tetrahydropyrans and tetrahydrofurans [166]. Piperidines were produced similarly by intramolecular nucleophilic attack of protected amino groups on such cations [167].



(10)

Friedel–Crafts-type acylation of (butadiene)tricarbonyliron with chloroacetyl chloride gave the *Z*-acyl complex. Stereoselective reduction with lithium aluminum hydride, decomplexation with Ce^{IV}, and cyclization gave the terminal epoxide of *cis*-hexatriene. Other triene mono-epoxides, either free or $Fe(CO)_3$-complexed, were prepared similarly [168].



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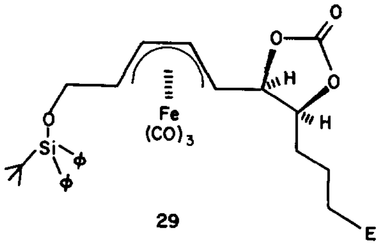
Complexation of (+)-nopadiene and derivatives with $Fe(CO)_3$ groups proceeded diastereoselectively, to form **28** (R = H, CHO, COMe, CO_2H). Several chemical transformations were studied, with emphasis on stereochemistry. For example, attack of EtMgBr or $NaBH_4$ on the ketone gave single diastereomeric products. Friedel–Crafts-type acylation with $MeCO^+$ $AlCl_4^-$ failed [169]. The crystal structures of the *erythro*- (**29**) and *threo*-carbonates, which were key intermediates in syntheses of lipoxin A4 and related natural products, have been determined [170].



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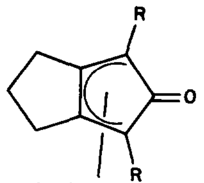

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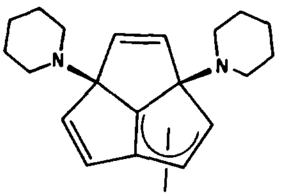
6.3. Complexes of cyclic dienes

The highly substituted 2-diethylamino-3,4-dimethyl-1-phenylsulfonylcyclobutadiene, formed by [2 + 2]-cycloaddition of diethyl(1-propynyl)amine and phenyl 1-propynyl sulfone, was intercepted by reaction with $Fe(CO)_5$ to form the $Fe(CO)_3$ complex [171].

Reaction of 2,7-nonadiyne or 1,7-bis(trimethylsilyl)-1,6-heptadiyne with $Fe(CO)_5$ in toluene at 135°C produced the bicyclic cyclopentadienone complexes **30** (R = Me, $SiMe_3$) in high yield. Hept-1-en-6-yne derivatives underwent similar Pauson–Khand cyclization to form (uncomplexed) fused cyclopentenones [172]. The X-ray crystal structure of the dihydroacepentalene complex **31** showed the tricarbonyliron group bound to the convex face of the tricyclic ligand. In contrast to the cyclopentadienylcobalt analog, **31** showed no haptotropy in NMR studies [173].



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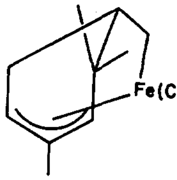

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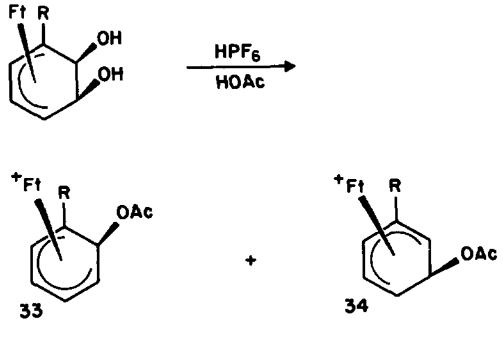
Coordination of the free diene unit of (η^1-thiophene)$Re(CO)_2Cp^*$ was achieved by reaction with $Fe_2(CO)_9$ [XRC], indicating heightened reactivity resulting from coordination of sulfur to rhenium. Analogs containing 2- and 3-methylthiophene and a $CpRe(CO)_2$ were similarly prepared [174]. A selenophene analog also resulted *inter alia* from complexation of (η^2-C_4H_4Se)$Re(CO)_2Cp^*$ with $Fe_2(CO)_9$, in which case the rhenium group shifted to coordination to the selenium upon iron coordination to the diene moiety [117].

Equation (6) [122] showed an example of formation of an iron tricarbonyl-coordinated six-membered ring, in that case a dihydropyridine ring, by a rearrangement reaction. Another example arose during prolonged refluxing of (−)-α-pinene with $Fe(CO)_5$ in dioxane, which resulted in formation of **32**, whose structure was based upon spectroscopic data, confirmed by a crystal structure of its triphenylphosphine substitution product. Heating at 140°C resulted in further rearrangement, to form (−)-tricarbonyl(η^4-2,5,6,6-tetramethyl-1,3-cyclohexadiene)iron. Treating **32** with Al_2Cl_6/CO at 0°C gave a pair of isomeric trimethylbicyclo[3.2.1]octenones. Oxidation with sodium nitrite in the presence of benzaldehyde gave benzylidene derivatives of the same bicyclic ketones [175]. Addition of RLi (R = Ph_2CH, Me_2CCN) to tricarbonyl(cyclohexadiene)iron occurred at the 1-position; oxidation of the resulting allylic complexes with bromine generated tricarbonyl[5-*exo*-*R*-cyclohexadiene]iron products [143].

The crystal structure of dicarbonyl(η^4-cyclohexadiene)(tri-*o*-tolylphosphine)iron showed a square pyramidal structure about the iron, and an exo_2 conformation of the *o*-tolyl rings of the phosphine. In solution, tolyl ring rotation and basal site exchange of the phosphine occurred at equal rates [176]. The circular dichroism spectra and absolute configurations of a series of 1-substituted derivatives of tricarbonyl(cyclohexadiene)iron compounds have been correlated. The electronic character of the substituent strongly influenced the character of the longest wavelength band [177].

In contrast to acyclic (dienyl)$Fe(CO)_3^+$ cations, which reacted with $CpMo(CO)_3^-$ anions by adduct formation, (η^5-cyclohexadienyl)$Fe(CO)_3^+$ reacted by single electron transfer; the resulting radicals then combined to form homodimers, $Cp_2Mo_2(CO)_6$ and 5,5′-bi(cyclohexadienyl)$Fe_2(CO)_6$. Heteroadducts were formed only at −78°C [164]. Addition of the organometallic nucleophiles $M(CO)_4^{2-}$ (M = Os, Ru) to the cyclohexadienyl cation, in contrast, formed novel hydrocarbon-bridged heterotrimetallic complexes $(OC)_3Fe[(\eta^4:\eta^1\text{-}C_6H_7)\text{-}M(CO)_4\text{-}(\eta^1:\eta^4\text{-}C_6H_7)]Fe(CO)_3$ [178]. Complex cuprates RCu(CN)ZnI attacked the cyclohexadienyl cation to form 5-*exo*-*R*-cyclohexadiene complexes; the alkylated product with R = $CH_2CH_2CH_2CO_2Et$ was obtained in 83% yield [179].

A trifluoromethyl group has been found to impose a strong degree of regiocontrol in formation of cyclohexadienyl complexes from cyclohexadienediol complexes [eqn. (11)]. For R = Me, the products **33** and **34**

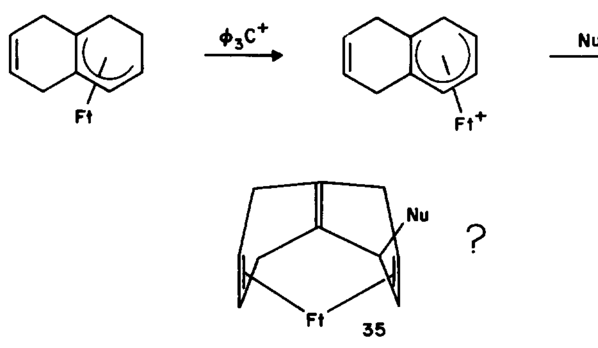


(11)

were obtained in equal amounts; for R = OMe, Cl, and CF_3, the **33**/**34** ratio changed to 2 : 1, 7 : 2, and > 99 : 1, respectively. **33** (R = CF_3) was isolated in 86% yield. The substituent in (2-trifluoromethylcyclohexadienyl)-$Fe(CO)_3^+$ directed nucleophilic attack to the 5-position [180]. 1-Alkoxy and acetoxy substituents in cyclohexadienyl cations proved to have complementary effects. For example, methyl-lithium at −78°C attacked the 1-ethoxy cation predominantly at the 1-position (83%) and the 1-acetoxy cation at the 5-position (62%) [181].

Nucleophilic attack on cyclohexadienyl complexes has been used as part of a route to isoquinuclidines. Thus, cyanide attacked tricarbonyl(η^5-2-methoxy-5-methylcyclohexadienyl)iron$^+$ at the 5-position. The cyano group in the resulting diene complex was reduced by H_2/Ni, and the iron group then removed oxidatively, followed by straightforward synthetic manipulations. Unfortunately, the scheme was successful only when a 5-substituent prevented aromatization of the diene intermediate [182].

The product of complexation of 1,4,5,8-tetrahydronaphthalene with $Fe(CO)_5$ under photochemical conditions, assumed to be an $Fe(CO)_3$ complex of the unconjugated starting material [183], is probably tricarbonyl(1,2,4a,8a-η^4-3,4,5,8-tetrahydronaphthalene)iron, as shown in eqn. (12). Hydride removal gave a bicyclic cyclohexadienyl cation, whose reactions with nucleophiles were investigated. The structure **35** proposed for the products [Nu = CHE_2, CN, $ClCH_2CO_2$, $CH(COMe)_2$] [183] clearly deserves further investigation.



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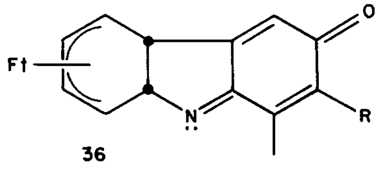

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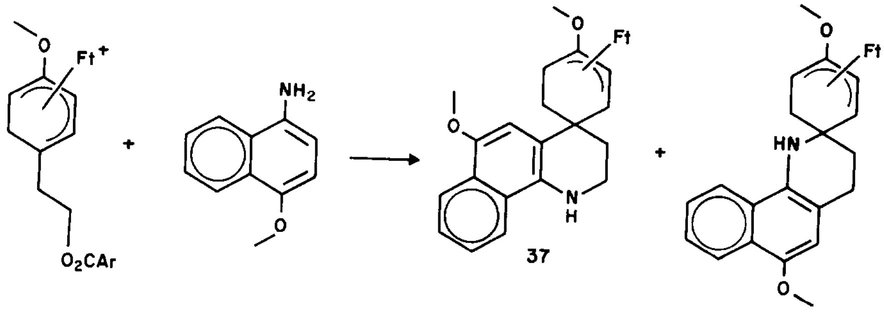
Syntheses of carbazole derivatives using cyclohexadiene and cyclohexadienyl complexes have been further exploited. Thus, **36** (R = H, Me) has been prepared by attack of substituted 4-methoxyaniline derivatives on $(C_6H_7)Fe(CO)_3^+$, followed by oxidative closure of the five-membered ring. The iron tricarbonyl group allowed highly selective allylation of C4a of **36** [184]. Analogous chemistry was used to synthesize "carbazomycin E" [185]. Spiroannulation reactions ensued when substituted anilines reacted with the substituted cyclohexadienyliron cations shown in eqn. (13). The structure of the main product **37** (9 : 1 ratio) was confirmed by X-ray crystallography. *p*-Methoxyaniline gave only the analog of **37** [186]. Use of a 6-aminoindoline derivative provided entree to a tetracyclic structure analogous to **37**, and similar to one found in some alkaloids [187].

An unnatural tricyclic species, 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene, underwent complexation with $(cyclooctene)_2Fe(CO)_3$ to afford three products: an η^6-$Fe(CO)_3$ complex (29%), an $\eta^4 : \eta^6$-bis[$Fe(CO)_3$] complex (21%), and a $\eta^4 : \eta^4 : 6$-tris[$Fe(CO)_3$] (43%). All were characterized by X-ray crystallography [188]. Complexation of a hindered, and therefore fairly stable, *o*-xylylene, occurred with modest regioselectivity and face selectivity to produce principally **38**. Products having η^4-$Fe(CO)_3$ complexation of both faces of the A-ring were also obtained [189]. *Trans*-15,16-dihydro-15,16-dimethylpyrene did not form iron complexes with $Fe_2(CO)_9$ or with sources of "$CpFe^+$." However, its benzo derivative did form complex **39** (40%), and in the process the diatropic ring current of the hydrocarbon was converted into a paratropic one [190].

(η^4-Cycloheptadiene)$Fe(CO)_2$[(+)-Ph_2PR] (R = neomenthyl) crystallized as a single square pyramidal diastereomer, which was structurally characterized. In



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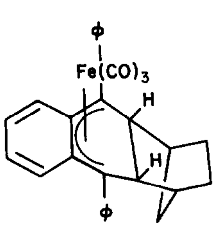

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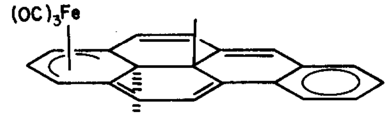

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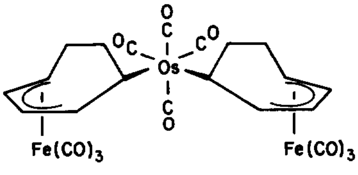

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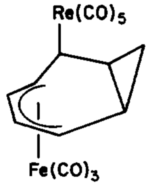

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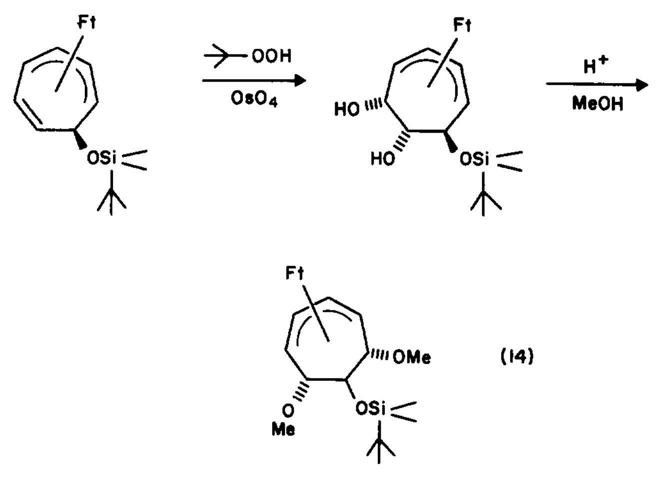
solution, both diastereomers were detectible, in unequal amount [176].

Iron tricarbonyl complexes of two stabilized heptafulvenes, $[(1-4)\eta^4\text{-}C_7H_6\text{=}CXE]Fe(CO)_3$ (X = CN, E; E = CO_2Et) were obtained by photoreaction with $Fe(CO)_5$. Enantiomerization by metallotropy occurred rapidly in the diester and more slowly in the cyanoester [191]. A stable η^4-iron tricarbonyl complex of the labile compound thiepin has been obtained from the thiepin sulfone complex by forming an O-arylated cation using *p*-tolyldiazonium ion, then reducing with SmI_2 [192].

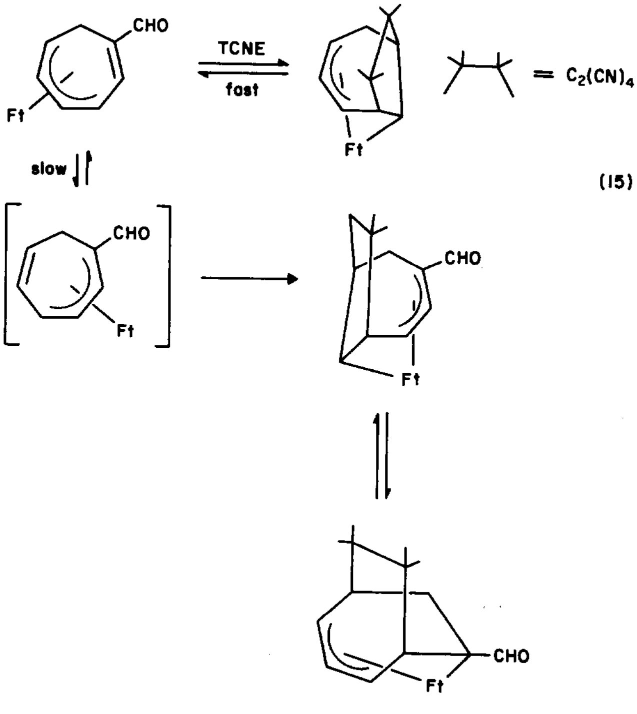
Reactions of the uncoordinated double bond of tricarbonyl(η^4-cycloheptatriene)iron or its triphenyl phosphite substitution product occurred with high stereocontrol. Thus, hydroboration cleanly introduced a 6-*anti*-OH group [193]. This result was not altered by 7-*anti*-methyl or 7-*syn*-siloxy substituents in the starting material. Oxidation of the free double bond with Me_3COOH/OsO_4 resulted in introduction of two *anti* OH groups, and acid-induced rearrangement allowed generation of alternate stereochemistry of the oxygen substituents [eqn. (14)] [194]. Dicarbonyl(η^4-cyclohepta-3,5-dienone)(triphenyl phosphite)iron was generated by Swern oxidation of the alcohol. The ketone was methylated by treatment with lithium diisopropylamide at −100°C, followed by methyl iodide. Either one or two methyl groups could be introduced, both *anti* to the iron tricarbonyl group [193].



(14)

Addition of $Os(CO)_4^{2-}$ to (η^5-cycloheptadienyl)$Fe(CO)_3^+$ led to formation of the adduct **40** [XRC] [178]. The *cis* relationship of the two metal groups about each cycloheptadienyl ring is unexpected, and may suggest a mechanism other than simple nucleophilic attack. $Re(CO)_5^-$ gave the expected *anti* adducts with acyclic and cyclic hexadienyliron cations, including (η^5-cycloheptadienyl)$Fe(CO)_3^+$; however, reaction of the same cation with $Mn(CO)_5^-$ led to single electron transfer, forming the homodimers $[(C_7H_9)Fe(CO)_3]_2$ [XRC] and $Mn_2(CO)_{10}$. The rhenium anion gave the normal adduct **41** with (bicyclo[5.1.0]heptadienyl)$Fe(CO)_3^+$ [195].

The reaction of tricarbonyl[(3–6)η^4-1-formyl-1,3,5-cyclohe ptatriene]iron with TCNE has been studied. A fast and reversible [3 + 2] cycloaddition involving the free double bond was followed by a slow and irreversible addition, probably to the not directly detectible haptomer [eqn. (15)]. The latter [3 + 2] adduct underwent slow interconversion with an isomeric [5 + 2] adduct. The ethylene ketal gave only the expected



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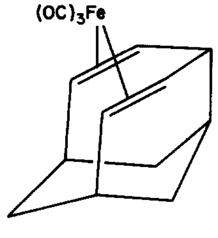

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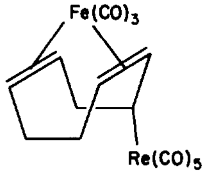

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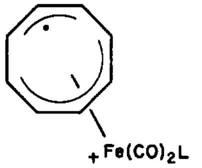

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[3 + 2] adduct, which underwent conversion to a [6 + 2] adduct [196]. The initial [3 + 2] adduct of mesityl cyanate with the C=N bond of (N-*p*-tolyl troponimine)Fe(CO)$_3$, stable in methanol at room temperature, underwent facile zwitterionic rearrangement in hexafluoroisopropanol under similar conditions. The principal product resulted from inversion at C-7 [197].

Complex **42** [XRC] was prepared by direct complexation of the hydrocarbon, considered a "strongly homoconjugated" one. The Fe(CO)$_3$ group was approximately square pyramidal, and the iron was nearly equidistant from all four coordinated carbons [198]. Pentacarbonylrhenium anion attacked the unconjugated tricarbonyl[(1–3;5,6)η^5-cyclooctadienyl]iron to form the adduct **43** [195]. Gamma irradiation of (η^4-C_8H_8)Fe(CO)$_2$L [L = CO, P(OPh)$_3$] in CFCl$_3$ at 77 K produced the radical cation, whose ESR spectrum was interpreted in terms of a metal-based radical with considerable spin density on the ring, perhaps representable as **44**. Irradiation in methyltetrahydrofuran or methanol produced radical anions. The initially formed anion had the odd electron localized largely in the free diene LUMO; on annealing this underwent conversion to the 17-electron isomer, (η^2-COT)Fe(CO)$_3^-$ [199].

7. η^5-Dienyl complexes

7.1. *Compounds with open pentadienyl ligands*

The term "open," as used in this Section, refers not only to acyclic pentadienyl ligands, but also to cyclohexadienyl and cycloheptadienyl ligands, which do not have a closed cycle of carbon (or hetero) atoms coordinated to iron. Most of the compounds encountered here are (η^5-dienyl)Fe(CO)$_3^+$ cations, whose principal chemical property is attack by a nucleophile to give a neutral η^4 product. Accordingly, many of the products have been described in Section 6. In those cases, this section will concentrate on preparation of the cations and a brief summary of their reactivity.

Attack of the organometallic nucleophile CpMo(CO)$_3^-$ on the acyclic (η^5-pentadienyl)- and (η^5-hexadienyl)Fe(CO)$_3^+$ cations occurred at the 1-position in each case. In contrast the cyclic (cyclohexadienyl)- and (cycloheptadienyl)Fe(CO)$_3^+$ cations reacted by single electron transfer. The different behavior of the cyclic and acyclic systems was discussed in terms of the greater reorganization energy required for outer-sphere electron transfer in the acyclic cases [164].

Unselective attack of a malonate nucleophile on a η^5-heptadienyl cation was illustrated in eqn. (10) [165]. It may be contrasted with clean intramolecular attack by alcohol and amine nucleophiles on (η^5-1-carbomethoxypentadienyl)Fe(CO)$_3^+$ cations having functionalized side chains at C(5) [166,167] and by clean attack of the cuprate RCu(CN)ZnI (R = $CH_2CH_2CH_2CO_2Et$) at C(1) of the unsubstituted (pentadienyl)iron cation [179].

Attack of RCu(CN)ZnI (same R) at C(1) of tricarbonyl(cyclohexadienyl)iron cation has also been demonstrated [179]. Several diarylzinc and diarylcuprate reagents reacted analogously, leading, after decomplexation and aromatization, to substituted biaryls, including the alkaloid lycorine [200]. Use of electron-rich anilines as carbon nucleophiles toward (C_6H_7)Fe(CO)$_3^+$ played an important role in synthesis of further carbazole alkaloids [184,185].

Equation (11) illustrates the effect of substituents in governing the generation of isomeric (cyclohexadienyl)iron cations. The cation **33** (R = CF$_3$) reacted with nucleophiles selectively at C(5), the less hindered terminus. Attack by hydride, followed by treatment with HPF$_6$ to remove acetic acid allowed formation of the tricarbonyl(2-trifluoromethylcyclohexadienyl)iron$^+$ cation, which also underwent selective attack at C(5) by malonate anion [180]. Attack of methyllithium at −78°C on (1-ethoxycyclohexadienyl)-Fe(CO)$_3^+$ occurred predominantly (83%) at the 1-carbon; treating the product with acid generated the (1-methylcyclohexadienyl)iron cation cleanly. In contrast, methyllithium reacted at the 5-position of (1-acetoxycyclohexadienyl)Fe(CO)$_3^+$, and acid treatment of the product led to formation of the (3-methylcyclohexadienyl)iron cation [181]. Steric effects have been assessed in the addition of hydride (from NaBH$_4$) to (2-alkoxy-5-alkylcyclohexadienyl)iron cations. Addition of hydride at C(5) was on the *endo* face [201], suggesting an iron hydride intermediate rather than direct addition at C(5). Addition of cyanide to (2-methoxy-5-methylcyclohexadienyl)Fe(CO)$_3^+$ occurred normally at the 5-*exo*-position [182]. Equation (13) illustrates analogous reactions of an arylamine, followed by intramolecular reaction to form spiroannulated products [186].

Tricarbonyl(η^5-cycloheptadienyl)iron cations underwent one-electron transfer with CpMo(CO)$_3^-$ [164], but formed the adduct **40** with Os(CO)$_4^{2-}$ [178]. The ESR spectrum of the radical cations from (η^4-cyclooctatetraene)Fe(CO)$_2$L may be taken to suggest the η^5 structure shown as **44** [199].

7.2. *Cyclopentadienyldicarbonyliron hydride (FpH) and related compounds*

This section describes results on FpH, Fp, Fp$^+$, and Fp$^-$ [Fp = (η^5-C$_5$H$_5$)Fe(CO)$_2$], and on compounds containing bonds between the Fp group and non-transition elements other than carbon. Organic derivatives, Fp-R and Fp-C(=O)R, are treated in Section 7.3. Derivatives with one or more CO groups replaced by other two-electron ligands or with substituted cyclopentadienyl groups are treated alongside the analogous Fp compounds. Fp-M compounds (M = Group 3–10 transition metal) are treated as bimetallic compounds, in Section 9.3.

Fp$^+$ in the gas phase has been found to form an adduct with methane, a reaction which does not occur in sulfuric acid solution. With ethane in the gas phase, Fp(C$_2$H$_4$)$^+$ was formed [19]. Thermal and photochemical reactions of Fp$_2^*$ with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) have been found to occur *via* Fp$^{*\cdot}$ radicals, based on ESR and spin trapping experiments. The radicals transferred an electron to the DDQ, forming (Fp^{*+})$_2$ (DDQ)$_2^{2-}$ as the only iron-containing product [202].

In a study of metal carbonyl anions and dimers, Fp$^-$ was found to be the strongest reducing agent of those studied, with the reduction potential for Fp$^\cdot$ estimated to be −1.186 V *vs.* SHE. Fp$^-$ quantitatively reduced all other homonuclear metal carbonyl dimers (ML$_n$)$_2$ to ML$_n^-$ [203]. It also reduced Fe$_3$(CO)$_{12}$ to Fe$_3$(CO)$_{11}^{2-}$. The two-electron reduction potential of Fp$_2$ was estimated as −1.7 V based on activity series studies [204].

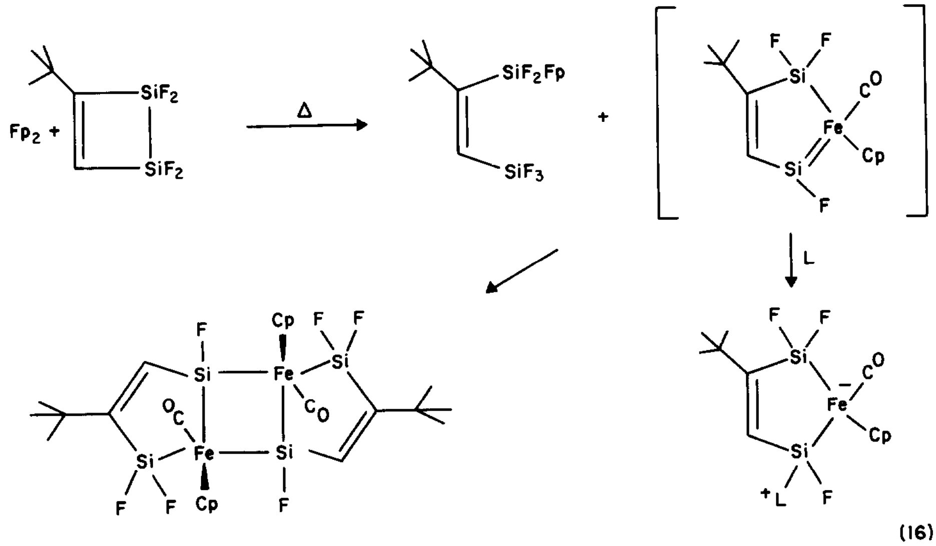
The hydride Cp*Fe(dppe)H has been prepared directly from Cp*H and (dppe)FeCl$_2$ by reduction with a sonochemically activated colloidal potassium dispersion (50% yield), or by LiAlH$_4$ reduction of Cp*Fe(dppe)Cl. A reversible one-electron oxidation wave was found in the cyclic voltammogram [205]. Rates of hydrogen transfer reactions from metal hydrides to the persistent radical Ar$_3$C$^\cdot$ (Ar = *p*-tert-butylphenyl) have been measured. FpH was the most reactive of those studied, with $k_2 = 12000$ M^{-1} sec^{-1}, $\Delta H^\ddagger$ 24 kJ mol^{-1}, and $\Delta S^\ddagger$ −87 J deg^{-1} mol^{-1}. Fp*H reacted much more slowly, k_2 being 300 M^{-1} sec^{-1}, due mostly to a higher $\Delta H^\ddagger$ (31 kJ mol^{-1}). Reduction of (η^5-Ind)Fe(CO)$_3^+$ (Ind = indenyl, C$_9$H$_7$) with NaBH$_3$CN at low temperature initially formed (η^3-Ind)Fe(CO)$_3$H, which decarbonylated on warming to give the normal hydride product, (η^5-Ind)Fe(CO)$_2$H [207].

The crystal structure of K$^+$Fp$^-$, prepared by reaction of "KSi" with Fp$_2$, has been determined. The anion showed an OC–Fe–CO angle of 92°, with the ring centroid and the two CO's approximately coplanar about the iron. Strong K–O interactions led to formation of polymeric chains in the crystal [208]. The crystal structure of FpHg[Ru$_3$(CO)$_9$(C≡C–CMe$_3$)], prepared by Fp$^-$ displacing I$^-$ from IHg[Ru$_3$(CO)$_9$(C≡C–CMe$_3$)], has also been reported. It showed a planar, three-coordinate mercury, bonded to iron (2.51 Å) and two Ru atoms of the cluster. The geometry about iron appeared to be pyramidal [209].

Fp$_2$InCl has been prepared by reaction of NaFp and InCl$_3$ or by oxidative addition of Fp$_2$ to InCl. The crystal structure showed a dimer, with the monomer units joined by chlorine bridges. The Fe–In–Fe angles were 131°, and the Cl–In–Cl angles 80°. Lewis bases coordinated to indium, giving tetrahedral Fp$_2$In(L)Cl monomers. The crystal structure of the dimethylphenylphosphine adduct was determined, showing that coordination of the phosphine increased the In–Fe distances slightly [210].

The valence photoelectron spectra of FpSiCl$_3$ and FpSiMe$_3$ have been compared. The splitting pattern of the t$_{2g}$-based metal orbitals in the latter was very similar to those of FpH and FpMe, giving no evidence of back-bonding to the silane. There was reduced splitting in the trichloride, however, leading to the suggestion that SiCl$_3$ is a better π-acceptor than CN, and about half as effective as CO. The acceptor orbital of the silicon had significant Si–Cl σ^* character [211]. The crystal structure of FpSiPh(SiMe$_3$)$_2$ showed two distinct conformers in the crystal, with slightly different Fe–Si bond lengths and Si–Si–Si angles [212]. NMR studies of 1-[Co(CO)$_3$PPh$_3$]-*cyclo* > -Si$_6$Me$_{10}$-4-Fp indicated strong interactions between the Si–Fe bond and the Si–Si bonds within the cyclohexasilane ring; the Si–Co group did not show an analogous effect [213].

The photochemical reactions of FpSiMe$_3$ and FpSi$_2$Me$_5$ have been compared in low-temperature matrices and, using fast time-resolved infrared spectroscopy, at room temperature. Carbonyl loss was the dominant initial process in both cases, but differences arose in subsequent steps. CpFe(CO)SiMe$_3$ reacted readily with CO or phosphines to generate stable products; CpFe(CO)Si$_2$Me$_5$, however, was unreactive toward CO or phosphines, and underwent an intramolecular rearrangement to CpFe(CO)(=SiMe$_2$)SiMe$_3$. This intermediate ejected Me$_2$Si in a subsequent photochemical step, leading to CpFe(CO)(L)SiMe$_3$ products



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[214]. Photolysis of $FpSiMe_2SiMe_2Fp$ produced primarily $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}SiMeSiMe_3)FeCp(CO)$, **45**, along with some $FpSiMe_3$ [215]. More prolonged photolysis of **45** resulted in formation of $CpFe(CO)(\mu\text{-}SiMe_2)_2FeCp(CO)$ [216]. Photolysis of $FpSiMe_2SiMe_2\text{-}Fc$ resulted in formation of $FpSiMe_2Fc$ and $FpSiMe_3$ in a 3:1 ratio, whereas $FpSiMe_2SiMe_2Cl$ gave $FpSiMe_2Cl$ and $FpSiMe_3$ in a 4:1 ratio; thus, ejection of $SiMe_2$ was favored over other silylenes [215]. Photochemical rearrangement of $Fp^*CH_2SiMe_2SiMe_3$ produced $Fp^*SiMe_2CH_2SiMe_3$, in a process thought to involve a cyclic ferrasilirane intermediate. The indenyl analog behaved similarly [217]. Reaction of Fp_2 with a disilacyclobutene [eqn. (16)] also generated a coordinated silylene intermediate, which could be intercepted by nucleophilic solvents, or in their absence, formed the dimer shown [XRC] [218].

The catalytically active species in FpMe-catalyzed hydrosilylation of acetophenone by diphenylsilane has been isolated by reaction of FpMe and an excess of Ph_2SiH_2. Obtained in 8% yield, it was identified as $CpFe(CO)(SiPh_2H)_2H$. The two Si-H protons were equivalent by NMR spectroscopy at −80°C, indicating classical bonding [219]. A tin analog of this intermediate, $CpFe(CO)(SnPh_3)_2H$ [XRC], was also prepared by a different group, from $FpCH_2CH_2Ph$ and Ph_3SnH [220].

Photochemical reactions of digermyl, silylgermyl, and germylsilyl species have been compared. Photolysis of $FpGeMe_2GePh_3$ produced mostly $FpGeMePh_2$ (82%), along with small amounts of $FpGeMe_2Ph$ (10%) and $FpGePh_3$ (8%). $FpSiMe_2GeMe_3$ produced $FpSiMe_3$ almost quantitatively, but $FpSiMe_2GePh_3$ yielded a mixture of $FpSiMePh_2$ (66%), $FpSiMe_2Ph$ (20%), and $FpSiPh_3$ (14%). The results showed that formation of germylene complexes as intermediates was favored over formation of silylene complexes [221].

Displacement of bromide from 1,1-dibromo-3,4-dimethylgermacyclopent-3-ene led to the formation of Fp derivatives, $FpGe(Y)[C_4H_4Me_2]$ [Y = H, Br, $Co(CO)_4$, Fp] [222].

Reduction of Fp_2SnCl_2 with lithium produced $(Fp_2SnCl)_2$ as an intermediate, characterized by ^{119}Sn NMR spectroscopy. Further reduction produced the stable stannylene Fp_2Sn, which was monomeric in benzene solution [223]. A study of iodination of tin–metal bonds showed the tin–iron bond to be among the more reactive: for example, one equivalent of iodine converted $FpSnMe_2Mn(CO)_5$ to FpI and $ISnMe_2Mn(CO)_5$ [224].

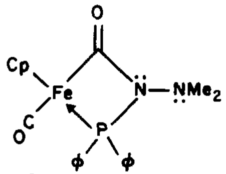
Several Fp-Group 15 cationic compounds have been prepared by oxidation of Fp_2 with ferrocenium ion in the presence of an excess of ligand. The ligands included many pyridines and nitriles. The crystal structure of $Fp\text{-}NC_5H_5^+\ SbF_6^-$ showed a Fe–N bond length of 1.98 Å, as compared to 2.05 in $C_5H_5N \rightarrow Fe(CO)_4$. Effects of pyridine and nitrile substituents on the properties of the compounds were assessed. The nitrile ligands were readily displaced by nucleophiles, including I^-, CN^-, phosphines, phosphites, Ph_3As, and Ph_3Sb [225]. Halophosphines, -arsines, and -stibines displaced acetonitrile readily from $CpFe(dppe)(N{\equiv}CMe)^+$ or $CpFe[P(OMe)_3]_2(NCMe)^+$. One product of such a reaction, $CpFe[P(OMe)_3]_2(PCl_2CMe_3)^+\ PF_6^-$, was characterized by a crystal structure determination. The chlorides in the complexes could be displaced by F^- using (crown)$K^+\ F^-$ in acetonitrile, or by H^- using $LiAlH_4$, giving rise to many additional compounds, including PH_3 complexes [226]. The crystal structures of three complexes, $CpFe[P(OMe)_3]_2L^+PF_6^-$ [L = NCMe, $P(OMe)_3$, $SbPh_3$], prepared by reaction of $CpFe(xylene)^+$ with the ligands under irradiation or by acetonitrile displacement as above, were determined [108]. Neutral ferracarborane analogs of these compounds, (fcb)Fe-(CO)$_2$L [fcb = 3,1,2-FeC$_2$B$_9$H$_{11}$, L = PPh$_3$, CO, NCMe, P(OMe)$_3$] have also been reported, the result of oxidation of (fcb)$_2$Fe$_2$(CO)$_4^{2-}$ with CuCl in the presence of the desired ligand [227].

Bimetallic complexes of phenylacetonitrile having the nitrile coordinated to a Fp$^+$ group and the ring coordinated to Cr(CO)$_3$ or Co$_4$(CO)$_9$ have been prepared [228]. Cyanide-bridged bimetallics CpFe(dppe)–C≡N–ML$_n^+$ [ML$_n$ = FeCp(dppe), Mn(CO)$_2$L$_2$, *etc.*] have been prepared and studied electrochemically. In the diiron compound, it was inferred that the N-bound iron oxidized more readily than the C-bound iron [229].

Pyramidal inversion about phosphorus in FpPH$_2$ has been studied by application of picosecond IR laser pulses aided by potential energy surfaces derived from theory [230].

Displacement of iodide from FpI by the phosphorus atom of Me$_2$NNPPh$_2$Li was followed by attack of the basic nitrogen on a carbonyl, forming **46** [XRC]. The ring was reversibly opened on N-protonation using HCl [231]. Reaction of FpP(=O)(NEt$_2$)OMe with one equivalent of BCl$_3$ gave an acid-base adduct, with coordination of the boron to the phosphoryl oxygen. Addition of further BCl$_3$ resulted in replacement of the methoxy group by chlorine. The Fe–P bond length in the latter product was 2.193 Å [232]. Displacement of chloride from Fp*PCl$_2$ by Ph$_2$C=NSiMe$_3$ yielded Ph$_2$C=N–P(Fp*)–N=CPh$_2$ [XRC] [233]. FpP[=C(SiMe$_3$)$_2$]$_2$, prepared by reaction of KFp with ClP[=C(SiMe$_3$)$_2$]$_2$, rearranged at 75°C to a phosphaferrocene by incorporating both carbonyl groups, which underwent O-trimethylsilylation, into the phospholyl ring [234]. Similarly, a 1,2-diphosphaferrocene resulted from reaction of FpBr with (Me$_3$Si)$_2$P–P=C(SiMe$_3$)$_2$; the mechanism shown in eqn. (17) (R = SiMe$_3$) was suggested [235].

The crystal structure of the phosphirane complex, Fp–$\overline{\text{P–CHR–C}}R_2$ (R = SiMe$_3$), prepared by displacement of chloride from the chlorophosphirane, showed an unusually long Fe–P bond (2.33 Å) [110]. Reaction of Fp*P=NAr (Ar = 2,4,6-tri-tert-butylphenyl) with Me$_3$SiCl resulted in addition to the P=N double bond, forming Fp*PCl–N(Ar)SiMe$_3$. Alkylation of the iminophosphine complex by trialkyloxonium salts occurred at nitrogen; the resulting cation Fp*P=N(Ar)R$^+$ (R = Me, Et) displayed phosphenium ion character such that insertion into a C–H bond resulted in formation of **47** [236].



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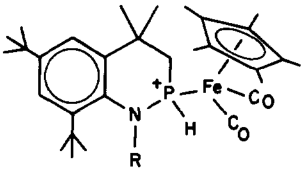

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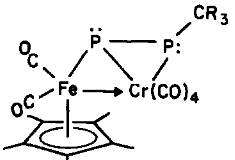

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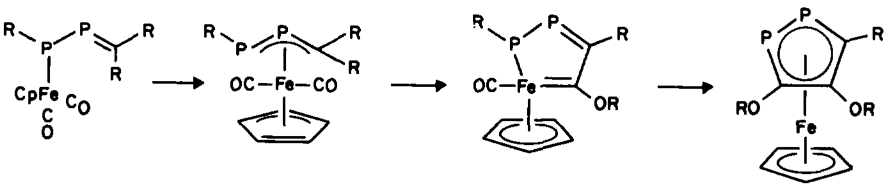
Introduction of a chromium carbonyl group into Fp*PR–P=CR$_2$ (R = SiMe$_3$) by reaction with (*Z*-cyclooctene)Cr(CO)$_5$ resulted in rearrangement, with formation of the ferradiphosphaallyl complex **48** and the Cr(CO)$_5$ complex of a diphosphaferrocene [*cf.* eqn. (17)] [both XRC]. **48** showed several long bonds, including Fe–P (2.313 Å) and Fe–Cr (2.945 Å) [237]. Fp*P=PAr (Ar = 2,4,6-tri-tert-butylphenyl) and N-methylmaleimide reacted by [2 + 2] cycloaddition to form a diphosphetane ring, as a mixture of stereoisomers [238]. With diethyl azodicarboxylate, Fp*P=PAr reacted by [1 + 4] cycloaddition, forming **49**. The Fe–P bond length in **49** was 2.24 Å, and the P–P 2.07 Å [239]. The cyclic azo compound, 4-phenyl-1,2,4-triazoline-3,5-dione, reacted in benzene solution by [2 + 2] cycloaddition, giving a fused diazadiphosphetidine product [XRC]. In ether, however, the reaction produced a dimeric macrocycle, **50** [XRC], strongly suggesting a dipolar addition mechanism [240].

A cyclotetraphosphine, 1,3-diFp*-2,4-di-tert-butyltetraphosphetane, a dimer of Fp*P=PCMe$_3$, was the principal product of reaction of Fp*P(SiMe$_3$)$_2$ with ^{t}BuPCl$_2$. Also detected by ^{31}P NMR spectroscopy were the triphosphirane P$_3$(Fp*)(CMe$_3$)$_2$ and Fp*P(SiMe$_3$)-P(Cl)CMe$_3$ [241]. Fp*P(SiMe$_3$)$_2$ was converted to Fp*PCl$_2$ by reaction with two equivalents of hexachloroethane; interaction of the two phosphines was then used to generate the triphosphirane (Fp*P)$_3$ and



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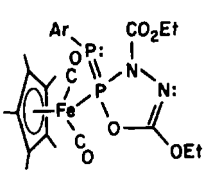

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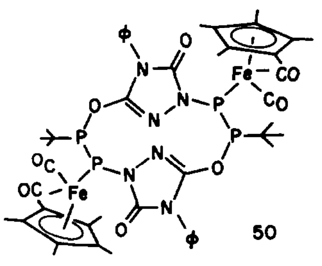

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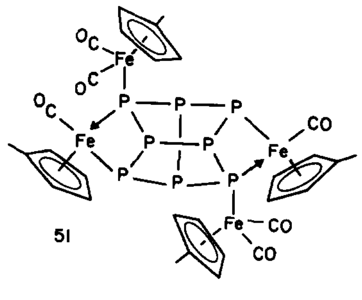
a bicyclo[1.1.0]tetraphosphine, $Fp_2^*P_4$, formally the product of adding Fp_2^* to one P–P bond of P_4 [242]. The triphosphirane was converted to a $Cr(CO)_4$ derivative by reaction with (norbornadiene)$Cr(CO)_4$. The crystal structure of the chromium complex showed the P_3 triangle bonded to three Fp* groups in a *cis,trans* arrangement, with the *cis*-configured phosphorus atoms also bonded to the $Cr(CO)_4$ moiety [243]. Cophotolysis of Fp'_2 and P_4 did not result in formation of Fp'_2P_4, as might have been expected, but instead to a more complex product, **51**, containing an α-P_8 core. The $P \rightarrow Fe$ bonds in **51** were significantly shorter (2.25 Å average) than the P–Fe bonds (2.32 Å). Stabilization of the P_8 fragment by electron donation into iron orbitals was inferred from the shortening of the P–P bonds compared with those in similar units in elemental phosphorus [244].

A range of compounds $FpQR_3^+$, with Q including all the elements in Group 15, has been made by displacement of THF from $Fp(THF)^+$ salts or, in some cases, by oxidation of Fp_2 in the presence of the ligand. Consideration of NMR data, displacement reactions, and structural results led to the conclusion that the Fe–Q bond strength decreases in the order $P > As > Sb > N > Bi$. $FpBPh_3^+$ BF_4^- showed a Fe–Bi bond length of 2.57 Å in the crystal [245]. The crystal structure of PPN^+ $Fp_2BiCl_2^-$ has also been reported; with a Fe–Bi bond length of 2.68 Å, the geometry around bismuth was almost SF_4-like: Fe–Bi–Fe angle 111°, Cl–Bi–Cl angle 156°, Cl–Bi–Fe angles 94–99° [246]. Photolysis of FpSC(= O)R in the presence of Group 15 ligands QPh_3 gave rise cleanly to CpFe(CO)(QPh_3)SC(= O)R. The relative rates of photosubstitution fell in the order $P > As > Sb$. Not surprisingly, tert-butyl substitution on the Cp ring slowed the reaction. The group R also affected the rate, with 3,5-dinitrophenyl > *p*-nitrophenyl > methyl > tert-butyl > phenyl [247].



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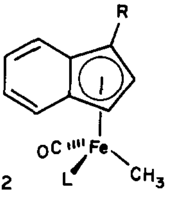

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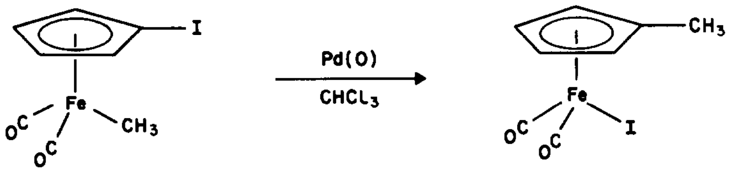
X-Ray structural studies on $FpYMe_2^+$ BF_4^- (Y = S, Se, Te) and Extended Hückel calculations on Fp-Group 16 cations $Fp\text{-}YMe_2^+$ indicated that inertness and stability decrease in the order $Te \gg Se > S > O$, an order different from that found in the Group 15 cations. π-Bonding effects were unimportant in the Group 16 cations, and the Fe–Y bond lengths increased from 2.264 to 2.381 to 2.533 Å on going from S to Se to Te [248]. $CpFeL_2YMe_2^+$ salts were synthesized by displacement of nitriles from $CpL_2(NCR)^+$ (L = trimethyl- or triphenylphosphite, dppe/2). The Fe–S bond length in $CpFe[P(OMe)_3]_2SMe_2^+PF_6^-$ was shorter (2.238 Å) than in the Fp analog [249]. The crystal structure of $CpFe[P(OPh)_3]_2TeMe_2^+BF_4^-$ has also been reported; at 2.539 Å, the Fe–Te bond length is nearly identical to that in the Fp analog [250].

A benzenethiol complex, $CpFe[P(OMe)_3]_2SHPh^+$-PF_6^-, was prepared by treating $CpFeL_2Cl$ with silver ion, followed by benzenethiol. Air oxidation produced a radical-cation, $CpFeL_2SPh^+PF_6^-$ [251]. Displacement of iodide by 2-propene-1-thiolate salts similarly gave $FpSCH_2CH{=}CH_2$ and $Fp'SCH_2CH{=}CH_2$ [252]. Reaction, at 100°C, of FpMe with 4,5-diphenyl-3,6-dihydro-1,2-dithiin-1-oxide, intended to serve as a source of S_2O, unexpectedly gave the thiocarboxylate complex FpSC(=O)Me in 55% yield. Similar results were obtained using Fp*Me and Fp*Et [253]. Thermal decomposition of $[CpFe(CO)SPh]_2$, alone or on a silica surface, was studied by Mössbauer spectroscopy. At 130°C, some ferrocene apparently formed, but at higher temperatures only amorphous iron oxides resulted [254]. Reaction of 1-selenoglucose [RSeH] with Fp_2 was used to prepare FpSeR [255].

A novel methyl-iodine exchange reaction [eqn. (18)] was catalyzed by a Pd^0 catalyst, generated by reaction of $(MeCN)_2PdCl_2$ with R_4Sn [256]. Halide exchange in FpI and Fp'I was induced by visible light. Tetrabutylammonium bromide served as the source of bromide. In the presence of both triphenylphosphine and Bu_4N^+ Br^-, tandem substitution converted $CpFe(CO)_2I$ to CpFe(CO)(PPh_3)Br (Fp'Br) in high yield. The actual halide exchange process presumably occurred in the 16-electron intermediate, CpFe(CO)X [257]. The enantiomers of Fp'I were separable on a commercially available chiral HPLC column, but not Fp'Me [258].

Infrared spectra of solid FpI were measured by photoacoustic, attenuated total reflectance, and transmission techniques [259]. ^{127}I NQR spectra of FpI and derivatives with 1–5 methyl groups on the cyclopenta-



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dienyl ring were recorded. The quadrupole coupling constant decreased with increasing ring methylation [260]. FpI was reduced by $HSi(OR)_4^-$ [261] or $H_2Si(OR)_3^-$ [262] to Fp·; Fp_2 was obtained in high yield.

7.3. Fp-Acyl, -alkyl, and -carbene complexes

A strong hydrogen bond was indicated in the crystal structure of the adduct CpFe(dppe)C≡N···H–N≡C–$Cr(CO)_5$. The Fe–CN bond length was 1.86, and the C≡N 1.16 Å [263].

IR spectra of $Fp^*CO^+BF_4^-$ [XRC] in methylene chloride solution showed distinct peaks due to paired and unpaired ions [264]. Reaction of $Fp'CO^+$ with KOH in aq. acetone gave the hydrated salt $FpCO_2^-K^+ \cdot 3H_2O$. Reaction of the hydrated and anhydrous salts and their Cp* analogs with acids and methylating agents showed competitive cleavage of C–O and O–M bonds. C–O Cleavage was favored by the lithium counterion and by the Cp* ligand. The potassium salts transferred oxygen to $Mn(CO)_5PPh_3^+$, but formed $Fp'C(=O)OSnPh_3$ upon reaction with Ph_3SnCl [265]. Reaction of Na^+ $FpCO_2^-$ with Cp_2MCl_2 (M = Ti, Zr) at low temperatures formed $FpCO_2MCp_2Cl$, in which both metallocarboxylate oxygens were coordinated to the Group 4 metal. The zirconium compound was more stable, but both decomposed in benzene solution to form Fp_2 and $(Cp_2MCl)_2O$. Protonation of $FpCO_2ZrCp_2Cl$ with HBF_4 afforded $FpCO^+$ [266]. $FpCO^+$ catalyzed CO exchange in $Co(CO)_4^-$, through the agency of Fp-C(=O)-$Co(CO)_4$ [267].

Molecular mechanics calculations satisfactorily reproduced the conformation found in the crystal for $CpFe(CO)(PPh_3)COCH_2OMe$ ($Fp'COCH_2OMe$) [268]. Dynamic processes involving the triphenylphosphine ligand in Fp'COMe have been investigated through low temperature NMR studies of the parent compound and derivatives having fluorinated rings. Rotation about the P–C bonds remained facile even at −90°C, in agreement with a $\Delta G^\ddagger$ of 21 kJ mol^{-1}. Rotation about the Fe–P bond required more energy (calculated $\Delta G^\ddagger$ 50, experimental 43 kJ mol^{-1}) and involved correlated motion of the phenyl rings to minimize steric interactions [269]. Crystal structure and conformational analysis of $(Ind)Fe(CO)(PPh_3)COMe$ have also been reported [270].

Deprotonation and alkylation of the indenyl complex were used to convert it to propanoyl and butanoyl homologs. Conversion of these in turn to the 2-methylbutanoyl complex by deprotonation and alkylation proceeded in each case with high diastereoselectivity. The aldol reaction of the diethylaluminum enolate with acetaldehyde also occurred with high (95:5) diastereoselectivity [270]. This reaction sequence was used to synthesize optically-active β-lactones, *trans*-3*R*-methyl-4-R-oxetan-2-ones (R = Me, Et, CMe_3) by treating Fp'COEt sequentially with BuLi, Et_2AlCl, RCHO, and Br_2 at −78°C. Yields were 67–90% [271]. Reaction of the aluminum and tin enolates of Fp'COMe with 2,3-O-isopropylidene-D-glyceraldehyde occurred with complementary diastereoselectivities, rationalizable in terms of existing models for double asymmetric induction [272]. Synthesis of the β-lactone (−)-tetrahydrolipstatin was achieved through application of the same methodology to (*S*)-$Fp'COC_7H_{15}$ and (*S*)-3-benzyloxytetradecanal [273].

Michael addition of the racemic $Fp'COCH_2^-$ enolate to racemic $Fp'COCH=CH_2$ at low temperatures occurred with complete self-recognition, the *meso*-$Fp'COCH_2CH_2CH_2COFp'$ product being formed exclusively and isolated in 95% yield [274]. The enolate $Fp'COCH_2^-$ attacked $(\eta^7\text{-}C_7H_7)M(CO)_3^+$ (M = Cr, Mo) at a ring carbon to generate the *exo* coupling product [XRC, M = Mo] [275].

Time-resolved infrared techniques have been used to study the flash photolysis of FpMe. Initially formed in the photolysis was CpFe(CO)COMe, as a solvent-coordinated species. Recombination with CO at 1 atm did not effectively compete with rearrangement ($k_1 = 5\text{–}7 \times 10^4$ sec^{-1} in cyclohexane) to $CpFe(CO)_2Me$. Triphenylphosphine was, however, an effective trapping agent ($k_2 = 2.4 \times 10^6$ M^{-1} sec^{-1}) at concentrations as low as 0.005 M. The quantum yield for conversion of FpCOMe to FpMe was solvent-independent, $\Phi_{313} \approx 0.63276$. Irradiation of $FpCH_2Ph$ led to formation of benzyl and Fp radicals, which gave radical addition products with activated alkenes. Either alkyl or acyl complexes, FpR or FpCOR, (R = CH_2Ph, decyl, neopentyl) gave the same products with acrylonitrile, indicating that interconversion was fast compared to the addition processes under photolytic conditions [277].

The mechanism of oxidatively-induced carbonylation of CpFe(CO)LMe (L = numerous phosphines) in methylene chloride has been studied. Carbonylation of (+)-Fp'Me was found to produce racemic Fp'COMe, due to configurational instability of the cation $Fp'Me^+$. $CpFe(^{13}CO)(PPh_3)COMe$ resulted when carbonylation was conducted under one atmosphere of ^{13}CO [278]. Oxidation of acyl compounds FpCOR by Ce^{IV} in dry acetonitrile formed free radicals, as shown, for example, by formation of 4-chloro-1-butene from cyclopropylacetyl-Fp in the presence of CCl_4. In the absence of CCl_4, the products of oxidation were predominantly RCO_2R and $FpCO^+$ [279].

Theory has been applied to study of methyl migration reactions including FpMe → CpFe(CO)COMe; geometries along the reaction coordinate were determined using PRDDO, then energies calculated using larger basis sets. Low energy barriers were found [280]. Contrary to an earlier report, reaction of $FpCH_2CH_2CH_2Fp$ with triphenylphosphine produced nearly equal amounts of racemic and *meso* $Fp'COCH_2CH_2CH_2COFp'$; this is in contrast to formation of this product by Michael addition, which cleanly produced *meso* product [274]. The μ-terephthalyl compound 1,4-$C_6H_4(COFp)_2$ has been prepared. Photosubstitution with triphenylphosphine in toluene gave 1,4-$C_6H_4(COFp')_2$ and 6% of 1,4-$C_6H_4(Fp')_2$. Reaction of the μ-phenylene compound with synthesis gas at 70°C gave some $C_6H_4(CH_2OH)_2$ [281]. Fp-Alkyls included in cavities in cyclodextrins underwent insertion reactions with CO (100°C, 100 atm) and SO_2 (25°C) at rates which depended on the cavity size [282].

A ferracarborane analog of the Fp^- anion, $[closo\text{-}3,1,2\text{-}FeC_2B_9H_{11}](CO)_2^{2-}$ was converted to alkyl and acyl derivatives by reaction with appropriate electrophiles. In analogy to the Fp compounds as described above, $(3,1,2\text{-}FeC_2B_9H_{11})(CO)_2Me^-$ reacted thermally with trimethylphosphine to form the acyl complex, $(3,1,2\text{-}FeC_2B_9H_{11})(CO)(PMe_3)COMe^-$ [XRC, PPN salt] [283].

Hydrosilylation of Fp-acyls has been carried out, using manganese acyls as catalysts, and forming $FpCHR(OSiR'_3)$ products using many different hydrosilanes [284]. Use of $(Ph_3P)_3RhCl$ as catalyst with diphenylsilane allowed over-reduction, converting the initially formed $FpCHR(OSiPh_2H)$ to $FpCH_2R$. The combination of over-reduction and carbonylation could be used to cause homologation, allowing conversion of Fp'COMe to $Fp'COCH_2CH_2CH_2Me$. The electron-donating effect of the triphenylphosphine ligand favored over-reduction; thus, FpCOMe gave 95% $FpCHMeOSiPh_2H$ in two hours, whereas Fp'COMe gave 74% $Fp'CH_2Me$ in six hours. $Fp'CH_2OMe$ was reduced to $Fp'CH_3$ (87%), whereas $FpCH_2OMe$ was inert. These effects were attributed to stabilization of a cationic alkylidene intermediate, $Fp(')\text{=}CHR^+$, in the reduction reaction [285].

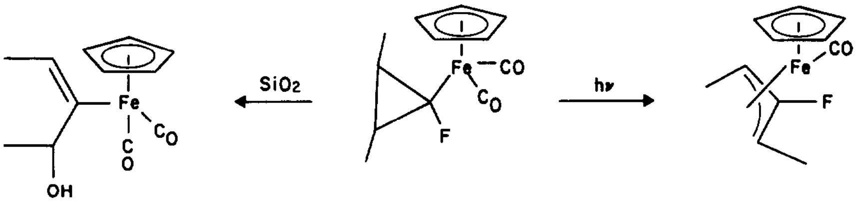
Cp*Fe(dppe)Me was prepared either from FpMe by photosubstitution or from Cp*Fe(dppe)Cl by reaction with MeLi. One-electron oxidation gave persistent 17-electron $Cp^*(dppe)Me^+$, which was studied by ESR, Mössbauer, and NMR methods, supported by Extended Hückel calculations [205]. A systematic study of the synthesis of FpR compounds from FpX (X = I, THF^+) and organolithium or Grignard reagents has been carried out. The use of $Fp(THF)^+$ resulted in better yields and less Fp_2 formation [286]. A series of long chain FpR compounds (R = hexyl through dodecyl) has been prepared using NaFp and RX. The series showed melting point alternation [287]. $FpCH_2C_6H_4CH\text{=}CH_2$ has been prepared and copolymerized with styrene and other monomers [288].

Molecular mechanics calculations have been applied to FpR compounds, and used to interpret low-temperature infrared spectra. For $R = CH_2Ph$, the C_s rotamer (phenyl *anti* to Cp) was found most stable; for $R = CH_2CH_3$, the C_s and C_1 (methyl staggered with respect to Cp) were of comparable stability, although the MMX calculations suggested a preference for the C_1 [289]. Chiral indenyl complexes **52** (R = Me, ^tBu; L = various phosphines) have been prepared as mixtures of four stereoisomers. Introduction of the chiral phosphine L = (*S*)-(+)-$Ph_2PN(Me)CHMePh$ allowed NMR differentiation of the four diastereomers of each series. Some were isolable by liquid chromatography. The iron center epimerized on heating, but complete configurational stability of the planar chirality arising from the substituted indenyl ligand was observed, even under drastic conditions [290].

FpMe was an efficient precatalyst for hydrosilylation of acetophenone by Ph_2SiH_2, the catalyst being formed by conversion of FpMe to $CpFe(CO)(SiPh_2H)_2H$ in the reaction mixture [219]. Similarly, reaction of FpR or FpCOR with $HQMe_3$ ($R = CH_2CH_2Ph$; Q = Si, Sn) produced $CpFe(CO)(QMe_3)_2H$. The principal organic products were RCH_2OSiMe_3 or RCH_2OH, respectively. The reaction involved formation of RCHO (obtained in good yield when $HSnMe_3$ was the limiting reagent), which underwent Fp-catalyzed reduction to the final products. Irradiation of FpR, Fp'R, or Fp'COR in the presence of $HQMe_3$ produced RH [220].

$FpCH_2CH\text{=}CH_2$ reacted with aldehydes RCHO in the presence of boron trifluoride or other Lewis acids to form zwitterionic adducts, $Fp^+(\eta^2\text{-}CH_2\text{=}CHCH_2CHROBF_3^-)$. Workup by reaction with NaI in wet acetone formed homoallylic alcohols $CH_2\text{=}CHCH_2CHROH$ [291]. The same sequence has been successfully applied to a number of ketones [292].

Two α-fluorocyclopropyl-Fp complexes have been prepared by displacement of Br from *geminal* bro-



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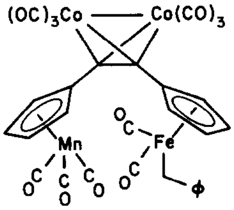
mofluorocyclopropanes. They were thermally and photochemically reactive [eqn. (19)] [293]. Photolysis of $FpCH_2PEt_2$ (from $FpCH_2Cl + PHEt_2$, followed by deprotonation) resulted in formation of a cyclic ferraphosphirane species, $CpFe(CO)(\eta^2\text{-}CH_2PEt_2)$. Treatment with acid formed $CpFe(CO)_2PEt_2Me^+$ [294]. Photolysis of the protonated species, $FpCH_2PHEt_2^+$ formed the iron-protonated ferraphosphirane; CO treatment caused further migration of the proton to carbon, again forming $FpPEt_2Me^+$ [295].

A series of heterodinuclear compounds, $Fp(CH_2)_nRu(CO)_2Cp$ ($n = 3\text{–}6$), has been prepared by displacement reactions from the iodoalkyl-Fp precursors. Their thermal behavior was examined by differential scanning calorimetry [296]. Several reactions of dinuclear compounds $Fp(CH_2)_nFp$ with nucleophiles and electrophiles were studied; the behavior observed was unexceptional [297]. Consecutive palladium-catalyzed coupling reactions were used to convert $(\eta^5\text{-}C_5H_4I)Mn(CO)_3$ and $(\eta^5\text{-}C_5H_4I)Fe(CO)_2CH_2Ph$ to $(OC)_3Mn(\eta^5\text{-}C_5H_4\text{-}C{\equiv}C\text{-}\eta^5\text{-}C_5H_4)Fe(CO)_2\text{-}CH_2Ph$; reaction with $Co_2(CO)_9$ gave the heterotrimetallic product **53** [XRC] [298].

Reaction of $FpCH_2C{\equiv}CR$ (R = Me, Ph, $CMe{\equiv}CH_2$) with 4,5-diphenyl-3,6-dihydro-1,2-dithiin-1-oxide, a source of S_2O, occurred *via* [2 + 3]-cycloaddition to form five-membered ring thiosulfinate esters. Direct attack on the dithiin oxide was implicated [299]. Alkynyl-Fp compounds have been generated by reaction of $LiC{\equiv}CR$ (R = H, $SiMe_3$, CMe_3, CO_2Me, Ph) with FpBr. In the case of $LiC{\equiv}CCO_2Me$, copper catalysis proved helpful. Photochemical substitution at −20°C converted $FpC{\equiv}CR$ into $CpFe(dppm)C{\equiv}CR$ [XRC, R = Ph] [300]. Treating $Fp'C{\equiv}CPh$ with N-chloro- or N-bromosuccinimide resulted in *anti*-addition to the triple bond, forming $Fp'C(NC_4H_4O_2) = CPhX$ [XRC, X = Cl] [301].



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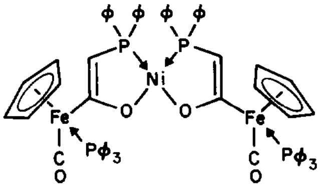

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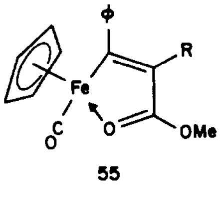
Fp'COMe was converted to $Fp'COCH_2PPh_2$ [XRC]. Deprotonation of the latter and treatment with $NiCl_2$ yielded the enolate complex **54** as a 70:30 mixture of *meso* and racemic forms. Recrystallizations yielded 95% *meso* [XRC] [302].

Whereas reaction of $(\eta^2\text{-}Fp^*C{\equiv}CH)Fp^{*+}$ with sodium methoxide resulted in deprotonation and formation of $Fp^*C{\equiv}CFp$, $(\eta^2\text{-}FpC{\equiv}CPh)Fp^+$ underwent attack at a carbonyl group of the η^2-Fp moiety, followed by cyclization to metallacycles **55** (R = H, Fp); [XRC]. The reaction of $(\eta^2\text{-}PhC{\equiv}CPh)Fp^+$ with sodium methoxide also produced **55** (R = Ph). $(\eta^2\text{-}Fp^*C{\equiv}CPh)Fp^*$ gave a complex mixture including not only analogs of **55** (R = H), but also a dinuclear μ-vinylidene complex [303]. $FpC{\equiv}Mo(CO)_2Tp$ [XRC, Tp = tris(3,5-dimethylpyrazolyl)borate] was synthesized by reaction of KFp and $Tp(OC)_2Mo{\equiv}CCl$. The C≡Mo bond length was 1.82 Å, and the C–Fe an also-short 1.91 Å. Reaction with CS_2 under photolysis resulted in insertion into the C–Fe bond, forming $TpMo(CO)_2{\equiv}C\text{–}CS_2Fe(CO)Cp$. Protonation occurred at the methyne carbon, but NMR studies of the product, $[TpMo(CO)_2{=}CHFp]^+$, including the vinyl CH at δ 1.94 and J_{CH} of 72 Hz, showed delocalization of the C-H electrons (so-called "agostic" hydrogen) [304].

Lithiation of the trimetallic compound $(Fp\text{-}C_5H_4)Fe(CO)_2(C_5H_4)Mn(CO)_3$ with BuLi at −78°C, followed by treatment with FpI, in an effort to extend the chain by another Fp unit, was foiled by unselective reactivity. It did prove possible to extend $(Fp\text{-}C_5H_4)Fe(CO)_2CH_2Ph$ by another unit, forming the tri-iron chain, by action of FpCl on the unsubstituted ring [305].

Several aryl-Fp compounds having Fp groups bound to pyridine, pyrazine, pyridazine, and pyrimidine rings have been prepared by Fp^- displacement of chloro or fluoro substituents from the azine rings. A crystal



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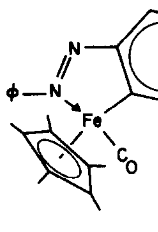

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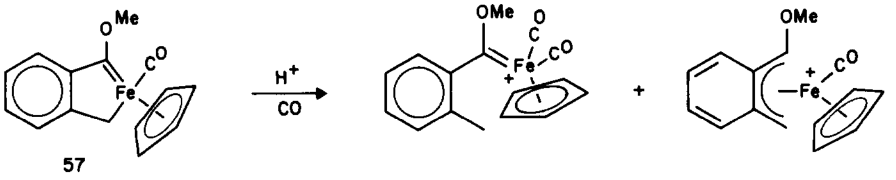

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structure of 4,6-diFp-2-(methylthio)pyrimidine was reported [306]. Fp*Me and azobenzene reacted with heating or irradiation. Methane and CO were evolved, and the metallacycle **56** resulted [307]. An NADH mimic, Fp′COC$_6$H$_8$N, where C$_6$H$_8$N is a 3-(1-methyl-1,4-dihydropyridine) ring, has been prepared from nicotinyl chloride and subjected to X-ray crystallographic structure determination, which showed one face of the dihydropyridine ring blocked by the bulky triphenylphosphine ligand. The homochiral analog having a Ph$_2$PO-(−)-menthyl ligand reduced ethyl benzoylformate to ethyl mandelate in 52% enantiomeric excess [308]. Use of these compounds as asymmetric reducing agents has been patented [309].

MO Calculations on addition reactions of vinylidene compounds such as $Fp = C = CR_2^+$ have been carried out. The reactions were HOMO-controlled, with nucleophiles predicted to react at the α-carbon and electrophiles at the β [310]. $Fp'{=}C{=}CH_2^+$ reacted with 1-phenylpropyne by [2 + 2]-cycloaddition, giving a stable cyclobutenylidene complex [XRC]. Reaction with phenyl-lithium at −60°C formed 1-Fp′-2-methyl-3,3-diphenylcyclobutene [311].

The methoxycarbene complex Cp*Fe(CO)(PMePh$_2$)=CHOMe$^+$ OTf$^-$ has been prepared by methylation of the formyliron precursor. Reaction of Cp*Fe(CO)(PMePh$_2$)CH$_2$OMe with trityl salts, in contrast, produced the unstable methylene complex [312]. The cyclic carbene complex **57** rearranged on protonation under an atmosphere of CO as shown in eqn. (20). The *o*-xylylene complex was the principal product in the absence of CO. With trimethylsilyl triflate at −85°C, **57** underwent ring contraction to form benzocyclobutenylidene=Fp$^+$ OTf$^-$ [313].

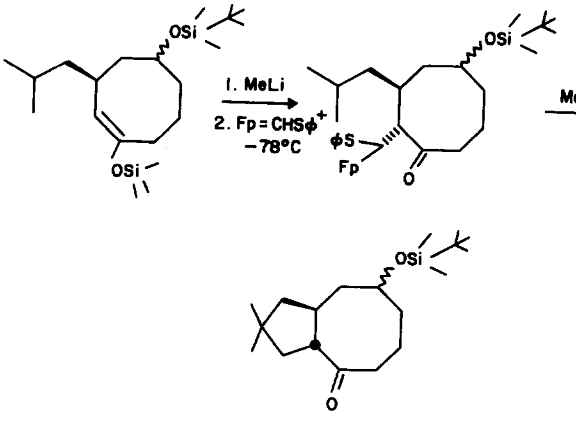
Enantiomerically pure or enriched ethylidene complexes CpFe(CO)L=CHMe$^+$ [L = PMe$_3$, PEt$_3$, (*S*)-PPh$_2$CHMeEt] have been obtained by three different methods, and used to study the mechanism of carbene transfer to alkenes. At temperatures around −100°C in methylene chloride, the ethylidene complexes were shown by NMR spectroscopy to exist in anticlinal (major) and synclinal (minor) forms. Reaction with prochiral alkenes (styrene, vinyl acetate, isopropenyl acetate) gave methylcyclopropanes with high enantioselectivity. The reaction involved attack of the less stable, synclinal isomer on the alkene, followed by backside attack of the electrophilic γ-carbon on the Fe–C$_\alpha$ bond [314]. The transition state for the latter step was modelled by reaction of FpCH$_2$CH$_2$CH(OMe)Ph with trimethylsilyl triflate; ionization of the methoxy group under these conditions was accompanied by attack of the nascent electrophilic center on C$_\alpha$, resulting in inversion at C$_\alpha$, as shown by specific deuterium labelling [315].

Reduction of $Fp{=}\overline{C(SCH_2CH_2S})^+$ with Li$^+$ Et$_3$BH$^-$ was accompanied by loss of CO and formation of CpFe(CO)(η^2-SCHSCH$_2$CH$_2$), which in solution was in equilibrium with a dimer. Reaction with triphenylphosphine formed the 2-Fp′-1,3-dithiolan [316]. Synthetic application of a sulfur-stabilized carbene complex is illustrated in eqn. (21), which shows part of a total synthesis of pentalenene [317].

7.4. Cyclopentadienyliron derivatives of η^2 to η^4 ligands

An unusual alkyne complex, CpFe(CO)(COMe)(η^2-HC≡CF) was produced, along with CH$_3$CF$_3$, upon reaction of FpMe with 1,1-difluoroethene in refluxing toluene [318]. Zwitterionic adducts Fp$^+$(η^2-CH$_2$=CHCH$_2$CR$_2$OBF$_3^-$) were the initial products of the BF$_3$-induced reaction of aldehydes and ketones with FpCH$_2$CH=CH$_2$ [291,292]. Hydride transfer to Ph$_3$C$^+$ occurred normally in Fp(CH$_2$)$_5$Fp, giving the expected (μ : η^1,η^2-1-pentenyl) Fp$_2^+$; similar reactions were also reported for Cp′ analogs having four or six methylene groups and for Cp* analogs having four [297].

The solid-state infrared spectra of Fp(η^2-CH$_2$=CR$_2$)$^+$ BF$_4^-$ (R = H, Me) were investigated, using photoacoustic, attenuated total reflectance, and transmis-



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sion methods. Vibrational assignments were proposed [259]. Addition of glycine ethyl ester to coordinated double bonds of Fp-alkene cations led to preparation of compounds $FpCH_2CHRNH_2^+CH_2CO_2EtBF_4^-$ [319].

The formation of η^2-phosphaalkene species by photolysis of $FpCH_2PEt_2$ [294] or $FpCH_2PEt_2H^+$ [295] was previously cited. The phosphaallyl complex $Cp^*Fe(CO)[\eta^3\text{-RP-CH-C(=O)}]$ [R = $CH(SiMe_3)_2$] reacted with selenium to form **58** [XRC], without interruption of the η^3 bonding; sulfur reacted similarly [112].

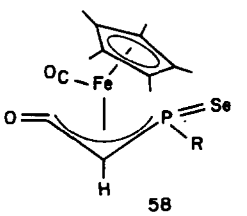
Equation (19) illustrated the formation of a η^3-allyl product by opening the ring of an α-fluorocyclopropyl-Fp compound upon photolysis. The ring opening was stereospecific, occurring disrotatorily away from the iron. Accordingly, the analogous 7-(7-fluoro-bicyclo-[4.1.0]heptyl)iron compound, which could not react similarly due to excessive strain in the allyl product, was more photostable [293]. η^3-Allyl derivatives were formed [XRC, PPN^+ salt] when $(3,1,2\text{-}FeC_2B_9H_{11})(CO)_2^{2-}$ was allowed to react with allyl or methallyl chloride, followed by UV irradiation [283].

The cationic *o*-xylylene complex shown as a product in eqn. (20), the main product of protonation of **57** in the absence of CO [313], is the only example of an η^5,η^4 complex to be described during 1991.

7.5. Ferrocenes and heteroferrocenes

No attempt is being made in this section at exhaustive coverage of ferrocenes and their chemistry; rather, I emphasize some novel uses of ferrocenes, their charge-transfer compounds, bridged ferrocenes, bi- and polymetallic compounds, and heteroferrocenes.

Electro-oxidation of ferrocenylmethyl cholestanyl ether in methylene chloride solution resulted in aggregation to form vesicles, which could be isolated and transferred to water solution. Reduction to the neutral ferrocene collapsed the aggregates [320]. Ferrocene-based molecular receptors have been synthesized from ferrocene-1,1′-dicarboxylic acid. Two such units were joined through various diamine spacers to form $HO_2CC_5H_4CO\text{-}Y\text{-}COC_5H_4CO_2H$, and found to bind several amines selectively. Rotation of the ferrocene rings was considered helpful in generating an optimum induced fit [321]. This work has been highlighted in a review entitled, "Sandwiches Bring a New Element in Molecular Recognition" [322]. Several examples of ferrocenes and ferrocenium ions encapsulated in cyclodextrin channels have been prepared and subjected to X-ray crystal structure determination [323].



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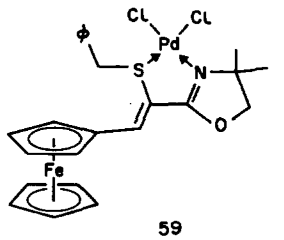

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Variable temperature NMR studies of $(\eta^5\text{-}1,3\text{-}C_5H_3R_2)_2Fe$ (R = CMe_3, CMe_2Et) have provided barrier energies of 50–57 kJ mol^{-1} for ring rotation, primarily between a pair of conformational enantiomers having the rings eclipsed and the substituents staggered. 1,1′,3,3′-Tetraphenylferrocene showed no rotational restriction even at 173 K [324]. ^{13}C Spin–lattice relaxation times for substituted ferrocenes have been used to gauge the relative importance of molecular tumbling and internal rotations. Triphenylmethylferrocenes showed only rigid molecular tumbling, ring rotations appearing locked [325]. ^{13}C and ^{57}Fe NMR data for ferrocenes and ferrocenylcarbenium ions have been correlated with 57-iron Mössbauer data. For neutral ferrocenes, a linear correlation was found between the Mössbauer quadrupole splitting and the 57-iron chemical shift. The spectra of the ferrocenylcarbenium ions were interpreted in terms of a change in structure toward $(\eta^6\text{-}C_5H_4{=}CH_2)FeCp^+$. Ring tilting effects in ferrocenophanes were also discussed [326].

Electrochemical studies of oxidation of 34 ferrocene derivatives FcCHRZ (R = H, alkyl, aryl, or ferrocenyl; Z = group containing N, O, P, or S) have been reported. The oxidation potential was correlated with the Hammett σ_P and Taft polar σ^* parameters of the substituents, or used to deduce new values in some cases [327]. Electrochemical oxidation of $(Ph_2PC_5H_4)_2Fe$ (dppf) involved oxidation of the iron, after which intramolecular electron transfer produced a phosphinium radical cation. This ultimately formed protonated or oxygenated phosphine groups by reaction with adventitious water [328].

One-electron reversible reduction of dibenzo[*a*,*c*]ferrocene or its isomer, $CpFe(\eta^6\text{-}C_{13}H_9)$, induced rapid haptotropic interconversion. In the radical anions, the equilibrium favored the η^6 form. Reversible oxidation of dibenzoferrocene was also observed at temperatures below −70°C [329]. At higher temperatures, the cation underwent rapid solvolytic decomposition [330].

Decaethylferrocene and several electron-transfer salts have been prepared. The structure of the 1:1 TCNQ salt showed an alternating donor-acceptor stack, and manifested ferromagnetic coupling [331]. The salt with 2,3,5,6-tetrafluoro-7,7′,8,8′-tetracyano-*p*-quinodimethane (TCNQ-F_4), however, had the stoicheometry $C_{10}Et_{10}Fe^+$ $(TCNQ\text{-}F_4)_2^-$, due to formation of a dimeric anion. There was no long-range magnetic ordering [332]. An attempt to synthesize decaisopropylferrocene by reaction of $C_5(CHMe_2)_5^-$ with $FeCl_2$

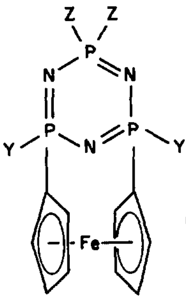
yielded stable $C_5(CHMe_2)_5$ radicals [XRC] instead of the expected ferrocene [333]. Octaethylferrocene and TCNQ, like decaethylferrocene, yielded a 1:1 electron-transfer salt with one-dimensional donor-acceptor stacks [XRC]; again TCNQ-F_4 gave a 1:2 salt [XRC] [334]. Bis(heptamethylindenyl)iron formed a 1:1 electron-transfer salt with TCNE, which showed paramagnetic behavior [335].

A series of ferrocenyl pyridinium salts, (*E*)-FcCH=CH(4-C_5H_4N-1-Me)$^+X^-$, has been prepared. With the optimum counterion, frequency doubling behavior 220 times as effective as urea was observed. The crystal structure of the nitrate salt was determined [336]. Coordination to palladium in **59** resulted in enhancement of the molecular hyperpolarizability compared to the free sulfide or sulfoxide [337].

Treatment of acetals $FcCH(OR)_2$ with trifluoroacetic acid or trityl fluoroborate generated stable $FcCHOMe^+$ cations, isolable as BF_4^- salts [338]. Arylation of ferrocene with *o*-nitro or *o*-cyanobenzenediazonium salts, followed by reduction to amino groups, acylation, and cyclization, was used for synthesis of tricyclic amines [339].

Many transformations of substituted ferrocenes by enzymatic reactions, especially oxidations and reductions of functional groups, have been described in a review entitled "The Biochemical Reactions of Organometallics with Enzymes and Proteins" [340]. Ferrocenes solubilized by means of charged side chains and ferrocenium ions have been tested *in vitro* against tumor cells. Some ferrocenium ions, particularly Cp_2Fe^+ $FeCl_4^-$, showed anti-tumor activity [341].

X-ray crystal structures of trimethylene- and pentamethylene-bridged ferrocenium cations, as the iodide and triiodide, respectively, have been reported. The electronic ground state of the bridged cations was judged to be $^2E_{2g}$, from EPR and Mössbauer measurements, and the effects of ring tilting on these results and on NMR chemical shifts were assessed [342]. A number of differently substituted cyclophosphazene-bridged ferrocenes, **60** (Y = Z = OCH_2CF_3; Y = Z = OPh; Y = F, Z = Ph; and others) have been synthesized from **60** (Y = Z = F). The crystal structures showed strained, non-planar cyclophosphazene rings [343]. Reaction of the tetrafluoride with three equivalents of $LiBEt_3H$ produced the hydridophosphazene anion, **60** (Y = F, Z = H, BEt_3^-); [XRC] [344].



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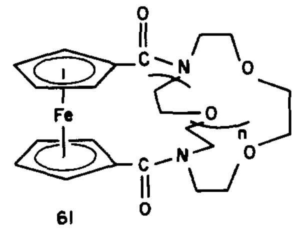

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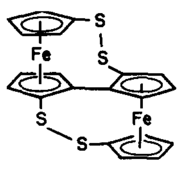
Several studies of crown ether- or cryptand-bridged ferrocenes have been reported. Crystal structures of 1,1′-bis(N-methylcarbamyl)ferrocene and 1,10-(ferrocene-1,1′-dioyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane, **61** (*n* = 2) have been reported. The latter showed a highly distorted structure, with only the four ether oxygens available for metal bonding. Some binding of Li^+ was detectable [345]. The smaller 1,7-(ferrocene-1,1′-dioyl)-1,7-diaza-4,10,13-trioxacyclopentadecane, **61** (n = 1), formed 1:1 complexes with divalent cations; in the complexes the amide carbonyls adopted a *cis* conformation unlike that of the free host [346]. A sulfur analog of these hosts, $Fe[C_5H_4(SCH_2CH_2)_3SC_5H_4]$, 1,4,7,10-tetrathia[10]ferrocenophane, and homologs with additional methylene groups, formed complexes with Pt^{2+}, in which ^{195}Pt NMR data suggested some interaction between platinum and iron [347].

Reaction of biferrocenyl, $[CpFeC_5H_4^-]_2$, with an excess of butyl-lithium–TMEDA led to tetralithiation. Reaction of the product with S_8 led to formation of two products; the principal one, **62**, had S_2 bridges interconnecting the two ferrocenyl units. The minor product had S_3 bridges joining the rings within each ferrocene unit. A selenium analog of **62** was also prepared [348]. Compounds with three or more ferrocenyl units joined by Group 16 bridges have been prepared by several methods, for example, $(FcSC_5H_4)_2Fe$ by reaction of dilithioferrocene with diferrocenyldisulfide, and selenium and tellurium homologs by analogous reactions. Use of trithia[3]ferrocenophane, followed by air oxidation of the thiolate, led to the tetranuclear product, $[(FcSC_5H_4)Fe(C_5H_4\text{-}S\text{–})]_2$. Oligomers were formed by oxidation of mixtures of ferrocenethiol and -dithiol [349]. 1,2,1′,2′-Bis(tetramethyldisilanediyl)ferrocene [XRC] was synthesized by reaction of the doubly-bridged organosilyl dianion with $FeCl_2$ [350].

Attack of nucleophiles ($LiAlH_4$, MeMgI, PhMgBr) on the ketone $(FcCOC_5H_4)Cr(CO)_2(NO)$ resulted in loss of the chromium moiety and formation of the 6-ferrocenylpentafulvene, C_5H_4=CRFc (R = H, Me, Ph), also preparable from FcCOR and cyclopentadiene



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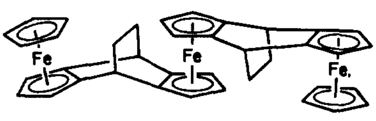


63

under basic conditions [351]. Examples of more stable ferrocenylcarbinols FcCHROH [R = η^6-$C_6H_5Cr(CO)_3$, η^6-$C_6H_5Co_4(CO)_9$] have been described, however [352]. The monoenolate of 1,1'-diacetylferrocene attacked a ring carbon of $(\eta^7\text{-}C_7H_7)M(CO)_3^+$ (M = Cr, Mo) to form a bimetallic product [XRC, M = Mo] [353]. Another such product, $FcCORe(CO)_5$ [XRC], was prepared from ferrocenoyl chloride and the pentacarbonylrhenium anion [353].

Complexes of 1,1'-bis(methylthio)ferrocene and its selenium analog with $PtCl_2$ have been prepared and studied by NMR spectroscopy. At −10°C the sulfur compound existed primarily as the racemic form, but upon heating pyramidal inversion of the sulfur atoms became rapid; $\Delta G^\ddagger$ was 64 kJ mol^{-1}. For the selenium compound, an equal mixture of *meso* and racemic forms was seen at room temperature; inversion occurred with $\Delta G^\ddagger$ of 79 kJ mol^{-1} [354]. Reaction of $CpFe(\eta^5\text{-}C_5H_4CSNMe_2)$ with lithium tetrachloropalladate resulted in *ortho*-cyclopalladation, with formation of a C_3PdS ring [355].

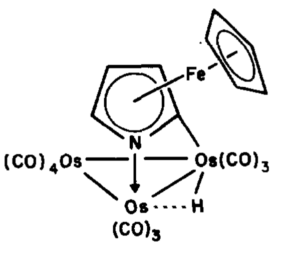
Biferrocenium cations, $[(RC_5H_4^-)Fe(C_5H_4^-)]_2$ (R = H, Et, Pr, Bu, benzyl, and halobenzyl groups) have been prepared and studied as triiodide salts. The substituents dramatically affected the rates of intramolecular electron transfer through their effects on crystal packing. The bis *o*-halobenzyl salts showed average valence behavior even at 77 K [356]. The crystal structure of 1,1'-bis[(8-ferrocenyl)-1-naphthyl]ferrocene, a segment of a hypothetical polymer made up of alternating naphthalene-1,8-diyl and ferrocene-1,1'-diyl units, has been determined. The two naphthalene nuclei were *cis* with respect to the central ferrocene [357].

A crystallographic comparison of bis(fulvalene)diiron$^+$ and bis(fulvalene)ironcobalt$^+$, each as a PF_6^- salt, has revealed strong similarities, consistent with valence-averaged electronic structures [358]. Electrochemical reduction of the iron-cobalt cation yielded a stable anion; cyclic voltammetry even showed formation of a dianion [359]. Treatment of the 4,8-ethano-2,4,6,8-tetrahydro-*s*-indacenediyl dianion consecutively with $FeCl_2$ and then LiCp produced *syn,syn* and *syn,anti* bis-FeCp derivatives [XRC] and **63**. Voltammetric oxidation of **63** showed three independent potentials [360]. A similar reaction of 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacenediyl dianion with $FeCl_2$ and LiCp produced *anti* and *syn* diferrocenes, *anti,anti*- and *anti,syn*-triferrocenes, and two tetraferrocenes. Reaction of *syn*-$CpFe(C_5H_3)(SiMe_2)_2(C_5H_3)FeCp$ with HBF_4 resulted in cleavage of C–Si bonds, with formation of $(FSiMe_2C_5H_4)_2Fe$. Oxidation with Ag^+ gave a monocation, whose NMR spectra revealed intramolecular electron exchange. Electrochemical oxidation of the various compounds was extensively studied [361].

Photoinduced electron transfer processes have been found important in the synthesis of azaferrocene from FpI, pyrrole, and diisopropylamine, and also in the photochemistry of azaferrocene-cobalt complexes [362]. Resonance electron capture mass spectrometry has been used to study azaferrocene and its chromium pentacarbonyl complex, $CpFe[\eta^5\text{-}C_4H_4N \rightarrow Cr(CO)_5]$. The radical-anion produced by capture of a thermal electron by azaferrocene had a lifetime of 34 μs, decomposing by spontaneous electron detachment. The chromium complex decomposed by loss of the elements of a Fp group, probably forming $(\eta^5\text{-}C_4H_4N)Cr(CO)_3^-$ [363]. Azaferrocene reacted with $Os_3(CO)_{10}(NCMe)_2$ to form an *ortho*-metallated product, **64** [XRC]. **64** underwent reversible one-electron oxidation; the resulting cation showed only modest changes in carbonyl frequencies, indicating electron removal predominantly from the azaferrocenyl moiety [364].

The formation of phosphaferrocenes [234] and 1,2-diphosphaferrocenes [235] by rearrangement of $FpP(=CR_2)_2$ and $FpP(PR_2)=CR_2$ ($R = SiMe_3$), respectively, has already been cited, and one example was illustrated in eqn. (17). In a presumably closely related process, $Fp^*PRP=CR_2$ formed, besides **48**, a 1,2-diphosphaferrocene, **65** [XRC], upon reaction with (*Z*-cyclooctene)$Cr(CO)_5$ [237].

Reaction of lithium 2,5-di-tert-butylpyrrolide with $FeCl_2$ proceeded straightforwardly, to form the 1,1'-diazaferrocene [XRC], in 56% yield [365]. The hydrogen-bonded tetramethylpyrrole molecules were displaced stepwise from $(\eta^5\text{-}C_4Me_4N)_2Fe \cdot 2C_4Me_4NH$ by reaction with several acids, including H^+, Me^+, $MeCO^+$, BH_3, BF_3, and $Fe(CO)_4$. $(\eta^5\text{-}C_4Me_4NH)_2Fe_2^+$ could be deprotonated once with BuLi without rearrangement, but removal of the second proton caused loss of the η^5 structure, with formation of the amide $Fe_2(NC_4Me_4)_4$ [101]. Reduction of a mixture of $Me_3CC\equiv P$ and $Me_2CHC\equiv P$ with sodium gave a mixture of nine di- and tri-phospholide anions. Treatment of the mixture with $FeCl_2$ resulted in formation of tetra-, penta-, and hexaphospha-ferrocenes [366]. A stibolide anion was formed by reaction of 2,5-dimethyl-1-phenylstibole with



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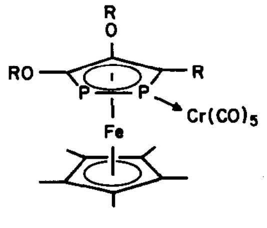

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lithium to cleave the phenyl–Sb bond, then converted to the 1,1′-distibaferrocene [XRC] by reaction with $FeCl_2$. A close inter-ring Sb · · · Sb distance of 3.68 Å was noted [367].

A triborataferrocene derivative, (η^5-indenyl)Fe($Et_2C_2B_4H_4$)$^-$ resulted from haptotropic rearrangement of the η^6-indenyl precursor at temperatures above 0°C. The anion underwent reversible protonation on iron and air oxidation to a neutral Fe^{III} species [368]. ($Et_2C_2B_4H_4$)Fe(η^5-C_4Me_4S) was prepared by displacement of cyclooctatriene from ($Et_2C_2B_4H_4$)Fe(C_8H_{10}) by tetramethylthiophene. Oxidation occurred reversibly at +0.05 V relative to ferrocene. Decapitation by reaction with TMEDA at 80°C resulted in formation of ($Et_2C_2B_3H_5$)Fe(η^5-C_4Me_4S) [369].

Several new bis(dicarbollyl)iron species, including uncharged analogs of ferrocenes, have been synthesized and characterized. Crystal structures were reported for two of them [370]. Bis(dicarbollyl)iron^{2-} showed one reversible electrochemical reduction step in organic solvents [371].

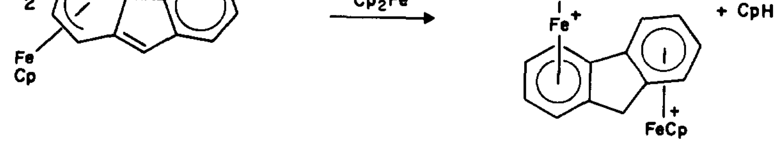
The previously described anion, (η^5-indenyl)Fe($Et_2C_2B_4H_4$)$^-$ underwent cluster expansion on treatment with LiCp*/$NiBr_2$ to form an eight-vertex $FeNiC_2B_4$ cluster [XRC]. Another such cluster was generated similarly from Cp*Fe($Et_2C_2B_4H_4$)$^-$. Trimetallic clusters such as Cp*Fe($Et_2C_2B_4H_4$)Ni($Et_2HC_3B_2Me_2$)CoCp were also generated [368]. Borataferrocenes CpFe(η^5-C_4H_4BR)$^-$ readily underwent stacking reactions to form triple-decker complexes, such as CpFe(μ-C_4H_4BR)M$(CO)_3^-$ (M = Cr, Mo, W) upon treatment with Group 6 metal carbonyls. The chromium compound underwent reversible, and the other irreversible, electrochemical oxidation. Protonation and benzylation occurred at the chromium atom. Reaction of the borataferrocene with $Mn(CO)_3(NCMe)_3$ produced the symmetrical species (μ-C_4H_4BR)$[Mn(CO)_3]_2$ and (μ-C_4H_4BR)$(FeCp)_2$ rather than the expected Fe-Mn compound [372].

8. Compounds with η^6-arene ligands

Theoretical calculations (Extended Hückel and SCF-MSO Xα) have been applied to molecular fragments thought to be capable of existing in interstellar regions of space. These included (benzene)Fe, (coronene)Fe, and their cations [373]. Meanwhile, back on Earth, the reaction of "Grevels' reagent," $(cyclooctene)_2Fe(CO)_3$, with 9,10-dihydro-9,10-dimethyl-9,10-diboraanthracene produced three products, all having η^6-coordination of the center B_2C_4 ring to a $Fe(CO)_3$ group. In addition, one or both of the benzo rings was η^4 coordinated to additional $Fe(CO)_3$ groups. All three structures were confirmed by X-ray crystallography [188]. When the reactive species $(PhMe)_2Fe$ was allowed to interact with diphenylacetylene at −60 to +20°C, coupling of the acetylenes generated (η^4-C_4Ph_4)Fe (η^6-PhMe) [XRC] and the 1,2,3,4-tetraphenylbutadiene complex, (η^4-$C_4Ph_4H_2$)Fe(η^6-PhMe) [374].

Rapid haptotropic interconversion of (η^6-fluorenyl)FeCp and its η^5 isomer followed upon electrochemical reduction at low temperatures. The η^6 isomer was favored in the anion [329]. (η^6-Indene)Fe($Et_2C_2B_4H_4$) [XRC] was synthesized by displacement of cyclooctatriene from (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) at 180°C. Reversible deprotonation at −78°C gave the η^6-indenyl anion. At or above 0°C, the anion rearranged to (η^5-indenyl)Fe($Et_2C_2B_4H_4$)$^-$ [368]. (η^6-2,3-dimethylindole)Fe($Et_2C_2B_4H_4$), prepared in the same manner as the indene complex, was readily deprotonated by BuLi of KH at 0°C, but did not show $\eta^6 \rightarrow \eta^5$ rearrangement. Methylation gave (η^6-1,2,3-trimethylindole)Fe($Et_2C_2B_4H_4$) [369]. Oxidation of several fluorene and fluorenyl complexes has been studied, using cyclic voltammetry, controlled potential electrolysis, and chemical oxidation. Equation (22) shows one novel result, involving chemical oxidation of (η^6-fluorenyl)FeCp [330].

A US patent has been granted for methods of preparing $CpFeAn^+$ from ferrocene, arene, and Lewis acid, or using cyclopentadienyl anion-Lewis acid complexes [375]. Synthesis of a series of (η^5-C_5Ph_5)$FeAn^+$ salts (An = benzene, toluene [XRC], xylenes, mesitylene, 1,2,4,5-tetramethylbenzene, hexamethylbenzene) has been achieved by reaction of $(C_5Ph_5)Fe(CO)_2Br$ and the arene in the presence of aluminum chloride. Two reversible electrochemical reductions were observable in each case [376]. Some ^{13}C NMR data have been reported for $CpFe(PhX)^+$ [326]. Mössbauer spectra of several salts of $CpFe(PhF)^+$ have been studied over a broad temperature range. The results on the



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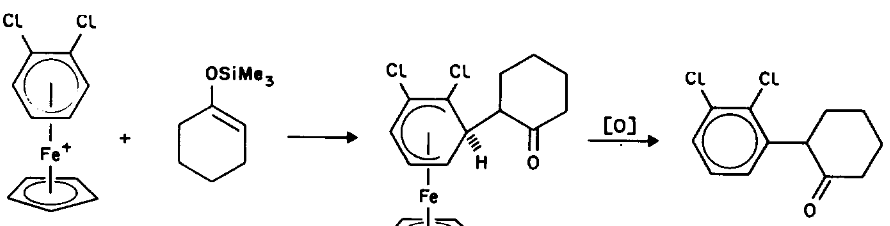

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hexafluorophosphate indicated facile isotropic reorientation of the cation, with an activation energy of 19.6 kJ mol^{-1}. The crystal structure at 300 K showed a primitive cubic cell, with totally disordered cations. Its AsF_6^- and SbF_6^- salts showed similar Mössbauer behavior, but the BF_4^- salt showed temperature independent behavior [377]. Carbon-13 spin–lattice relaxation times for a series of CpFeAn$^+$ salts have been reported [325].

The conformation of the arene substituents in CpFe[η^6-$C_6(CH_2CH_2Ph)_6$]$^+$ PF_6^- was investigated by means of a crystal structure. All of the phenethyl groups were distal relative to the FeCp group. Variable temperature NMR studies suggested that this conformation was maintained in solution [378].

TCNQ$^-$ salts of several CpFeAn$^+$ cations [An = benzene, toluene, chlorobenzene, mesitylene, tri(tert-butyl)benzene, hexamethylbenzene, hexaethylbenzene] were prepared, and their conductivity and magnetic behavior were examined. The magnetic behavior was as expected for linear chains of $S = 1/2$ anions. The antiferromagnetic exchange coupling decreased as substituent size on the arene ring increased [379]. Crystal structures of several solids incorporating CpFe(C_6H_6)$^+$, CpFe(C_7H_8)$^+$, CpFe(C_8H_8)$^+$, and related cations, all as PF_6^- salts, in α-cyclodextrins have been obtained [323].

Two-electron reduction of the biphenyl complex, [CpFe(C_6H_5–)]$_2^{2+}$, occurred in a single, fast, two-electron wave in cyclic voltammetry experiments, whereas the Cp* analog showed two close one-electron waves. The neutral product was structurally characterized as a bicyclohexadienylidene complex, [CpFe(η^5-C_6H_5=)]$_2$. The averaged-valence 37-electron monocation has been structurally characterized; it showed a nearly flat biphenyl ligand and η^6 coordination of each iron [380]. ($\mu:\eta^6;\eta^6$-9,9′-Bifluorenylidene)bis(FeCp)$_2^+$ was formed by reaction of CpFe(η^6-9-fluorenol)$^+$ with acetyl chloride. Electrochemical reduction showed addition of four consecutive electrons, finally to yield CpFe(η^6-$C_{13}H_9$) [381].

Several Japanese patents claiming practical applications of CpFeAn$^+$ derivatives have been issued. Uses described include holographic materials [382], photopolymerizable materials for image formation [383], photosolubilization media for image formation [384], photopolymerizable material sensitive to various light wavelengths [385,386], and optical recording paper [387].

Replacement of the arene in CpFeAn$^+$ by conventional two-electron ligands is catalyzed by one-electron reduction. Thermochemical and kinetic studies of this process have been carried out. Replacement of benzene or anisole by three trimethyl phosphite ligands was found to have an enthalpy of -201 kJ mol^{-1}; replacement of methyl benzoate or p-xylene: -189 kJ mol^{-1}. The rates of displacement by acetonitrile in the neutral 19-electron complexes followed the sequence anisole > benzene > p-xylene > ethyl benzoate [388].

Rates of methoxydechlorination of CpFe(RC_6H_4Cl)$^+$ gave a linear correlation with Hammett σ_P values [389]. Reaction of sodium phenoxide with CpFe(p-$C_6H_4Cl_2$)$^+$ gave the 1,4-diphenoxybenzene complex [390]. Substituted dibenzo[b,e]-1,4-dioxin derivatives were prepared from CpFe(p-dichlorobenzene)$^+$ by treatment with substituted catechols and base, followed by decomplexation using UV irradiation [391]. Displacement of chloride from CpFe(p- or m-chlorotoluene)$^+$ by α-methylbenzylamine gave diastereomeric mixtures, with no evident stereoselectivity. In contrast, the o-dichlorobenzene complex gave one diastereomer preferentially. ^{13}C NMR spectroscopy was used to identify and quantify the regioisomeric and stereoisomeric products formed from CpFe(3,4-dichlorotoluene)$^+$ [392].

The chlorobenzene complex underwent oxidative addition upon treatment with Pd(PPh_3)$_4$. The crystal structure of the product, CpFe(η^6-$C_6H_5Pd(PPh_3)_2Cl$), showed a Pd–C σ-bond of 2.03 Å length, and increased distance (2.16 Å) of iron from the carbon bearing the palladium group, as compared with the other Fe–C$_{\text{phenyl}}$ distances (2.05 ± 0.05 Å). The C–Pd bond was reactive toward CO and alkenes [393].

The stabilization of α-carbanions by organometallic groups has been exploited in the synthesis of highly deuterated ligands using NaOD/D_2O at 100°C. These exchange reactions were used to prepare CpFe[$C_6(CD_3)_6$]$^+$, CpFe[$C_6(CD_2CH_3)_6$]$^+$, [$C_5(CD_3)_5$]Fe(C_6-

$H_6)^+$, and $CpFe(C_6Me_6)$-d_{23}^+. The latter was converted to perdeuterated Fp_2^* by heating to 150°C under 40 atm CO [394].

Silyl enol ethers have been used to introduce ketoalkyl groups onto aromatic rings as shown, for example, in eqn. (23). Ethyl trimethylsilylacetate similarly was used to introduce an acetate ester side chain [395]. Attack of various stabilized carbanions on $CpFe(C_6H_5$-$NO_2)^+$ or analogs containing other electron-withdrawing groups on the arene ring occurred preferentially *ortho* to the electron-withdrawing nitro group. Alkyl, dichloromethyl, or trichloromethyl anions, however, added non-selectively. If extended reaction times were used, *meta*-trichloromethylated products predominated due to the size of the group [396].

Time resolved spectroscopy was used to probe the course of photolysis of $CpFeAn^+$ X^- in the presence of epoxides. The key intermediate identified resulted from addition of the anion to the iron, forming $CpFe(\eta^4$-$An)X$. This was attacked by solvent or by epoxide, to displace the arene. The coordinated epoxide reacted with further epoxide molecules to form oligomers (crown ethers) or polymers [397]. $CpFeAn^+$ BF_4^- have been found to catalyze oxidation of hydrocarbons in acetonitrile solution under irradiation. The mechanism proposed involved a peroxy intermediate $[CpFe(\eta^4$-$An)O_2?]$ [398].

The electrochemistry of $(\eta^5$-$C_2Et_2B_4H_4)FeAn$ complexes has been explored. Reversible one-electron oxidation produced species analogous to ferrocenium ions. One-electron reduction gave persistent anionic species similar to the 19-electron CpFeAn. Methyl substitution in the arene ring produced a consistent negative shift in the E^0 values, with the difference in the two waves a constant 3.1 V [399]. The phenyl group in $(\eta^5$-$C_2Et_2B_4H_4)Co(\eta^5$-$C_5Me_4CH_2Ph)$ displaced cyclooctatriene from $(\eta^5$-$C_2Et_2B_4H_4)Co(C_8H_{10})$ under rigorous conditions, to form a bis(carborane) complex. Several additional examples involving pendant benzyl groups were also described [400].

The bis(arene) complex, $(C_6Me_6)_2Fe^{2+}$ $CoCl_4^{2-}$, was found to be especially active in a screening of iron sandwich-type compounds for anti-tumor activity [341]. Bis(arene)iron dications form charge-transfer compounds with ferrocene and with electron-rich arenes. Crystals of 1:1 compounds showed alternate donor-acceptor stacking. Irradiation of the charge transfer bands in solution led to efficient photosubstitution of the arene ligands, because of spontaneous arene loss from 19-electron An_2Fe^+ [401].

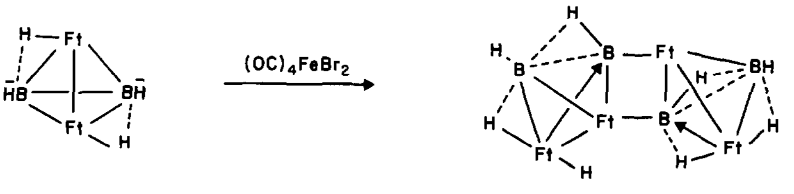
9. Bimetallic compounds

9.1. Diiron compounds, derivatives of $Fe_2(CO)_9$

The bonding in $Fe_2(CO)_9$ has been reconsidered from the points of view of theory and the isolobal analogy. It was concluded that Pauli repulsion effects involving valence electrons on one fragment and outer core electrons on the other were generally important for organometallic fragments, especially those including first-row transition elements, and that these effects generally resulted in longer, weaker bonds compared to those in organic isolobal analogs [402].

Solid-state ^{13}C NMR spectroscopy has been applied to measuring the degree of asymmetry of semibridging carbonyl groups. The lowest frequency tensor component and the chemical shift anisotropy were found to correlate with the degree of asymmetry, unlike the isotropic chemical shift. Compounds studied included $Fe_2(CO)_9$, $(PhCCPh)Fe_2(CO)_6$, *cis*- and *trans*-Fp_2, and some tri-iron compounds [403]. $Fe_2(CO)_9$ was found to yield only traces of doubly charged ions in the mass spectrum, in contrast to bimetallic species with halogen bridges or unsaturated ligands [404].

Copper-bridged $Fe_2(CO)_8$ compounds were prepared straightforwardly by reaction of $Fe_2(CO)_8^{2-}$ with $Cu(NCMe)_4^+PF_6^-$ and R_3P or $R_2PCH_2CH_2PR_2$ (R = cyclohexyl). The crystal structure of $(R_3PCu)_2Fe_2(CO)_8$ showed a long Fe–Fe bond (2.86 Å, *cf.* 2.79 in the dianion), unsymmetrically bridged by the two R_3PCu groups, with short and long Fe–Cu distances of 2.48 and 2.59 Å. The monocuprated anion, as the Ph_4P^+ salt, showed a symmetrically placed copper spanning a 2.90 Å Fe–Fe bond. Some silver analogs were also prepared [405]. In contrast to the evident stability of Ph_4P^+ $Fe_2(CO)_8(\mu$-$CuPR_3)^-$ was the reported air- and thermal-instability of $Et_4N^+Fe_2(CO)_8(\mu$-Cu-$PPh_3)^-$ [406]. Some diphosphine-bridged digold derivatives, $Au_2Fe_2(CO)_8(\mu$-LL), (LL = dppm, dppe, dppp) have been prepared by similar means. The dppm compound showed a nearly square Au_2Fe_2 array, with Au···Au 2.91, Au–Fe 2.53, and Fe–Fe 2.90 Å dis-



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tances; the two gold atoms were bridged by the diphosphine. Reaction of the dppe compound with an excess of $Fe_2(CO)_8^{2-}$ gave a product in which the diphosphine coordinated to the gold atoms of separate $AuFe_2(CO)_6(\mu\text{-}CO)_2^-$ units. Results of Extended Hückel calculations were consistent with the formation of two Fe–Au bonds by the unbridged $Fe_2(CO)_8$ fragment, and formation of the triangular $AuFe_2$ unit by the doubly-bridged fragment [407]. Unexplained by these calculations is the unbridged nature of $(\mu\text{-}R_3PCu)Fe_2(CO)_8^-$, as described above.

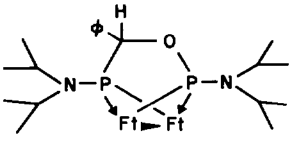
Deprotonation of $B_2H_6Fe_2(CO)_6$ by butyl-lithium gave the dianion, which underwent oxidative coupling upon treatment with $Fe(CO)_4Br_2$ [eqn. (24)] [408]. The product of reaction of 1,1-dihydro-1-silaphenalene with $Fe_2(CO)_9$ was formed by replacing two bridging carbonyl ligands of $Fe_2(CO)_9$ with bridging silylene units [XRC] [409]. Relatively basic phosphines, such as PMe_3, converted *cis*-$Fe(CO)_4(SiCl_3)_2$ into the diiron compounds, $Fe_2(CO)_{7-n}(PMe_3)_n(\mu\text{-}SiCl_2)_2$ ($n = 1, 2$) [99].

Reaction of $Fe_2(CO)_8^{2-}$ with $Ni(CO)_{4-n}(PR_2Cl)_n$ ($n = 1, 2$; R = tert-butyl, cyclohexyl, phenyl) unexpectedly resulted only in phosphido group transfer, forming $Fe_2(CO)_6(\mu\text{-}PR_2)_2$ or $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PR_2)^-$. The latter anions could also be prepared by reaction of $R_2PFe(CO)_4^-$; with $Fe(CO)_5$ or $Fe_2(CO)_9$, *via* the intermediate $(OC)_4FePR_2Fe(CO)_4^-$. Their electronic structure was studied by Extended Hückel calculations, which suggested significant nucleophilic reactivity of both O and Fe. Reaction with acids and with Ph_3PM^+ (M = Cu, Ag, Au) occurred at the irons. The crystal structure of $(OC)_6Fe_2(\mu\text{-}CO)[\mu\text{-}P\text{-}(CMe_3)_2](\mu\text{-}AgPPh_3)$ was determined [410]. The compounds $(OC)_6Fe_2(\mu\text{-}CO)(\mu\text{-}PPh_2)(\mu\text{-}MPPh_3)$ were also independently obtained by another group, who reported the structure of the copper representative [406].

Diazenes, $p\text{-}RC_6H_5N{=}N\text{-}CMe_3$ (R = H, Me, OMe), reacted with $Fe(CO)_5$ under irradiation to form first an *ortho*-metallated intermediate, which rearranged thermally to form *o*-semidine complexes **66** [XRC, R = H] [eqn. (25)] [411].

The reaction mixture from $Fp^*P(SiMe_3)_2$ and $RPCl_2$ (R = tert-butyl) contained a tetraphosphetane, a triphosphirane, and a diphosphine. Reaction with an excess of $Fe_2(CO)_9$ resulted in formation of the tetrahedrane derivative $(OC)_3Fe[\mu:\eta^2,\eta^2\text{-}Fp^*P\text{–}PR]Fe(CO)_3$ and a product with a carbonyl inserted into the P–P bond, $(OC)_3Fe[\mu:\eta^2,\eta^2\text{-}Fp^*P\text{–}C(=O)\text{–}PR]Fe(CO)_3$ [241]. Reduced analogs of the latter, $(OC)_3Fe(\mu:\eta^2,\eta^2\text{-}RPCH_2PR)Fe(CO)_3$ [R = Me, $CHMe_2$, CMe_3, $N(SiMe_3)_2$, 2,4,6-$(^iPr)_3C_6H_2$, *etc.*] were obtained upon treatment of $CH_2(PRCl)_2$ with $Fe_2(CO)_9$. The crystal structure of the tri-isopropylphenyl compound showed a P–C–P angle of 84°. A plausible intermediate in the formation of these products, $(OC)_3Fe(\mu\text{-}Cl)[\mu\text{-}RPCH_2PRClFe(CO)_4]Fe(CO)_3$, was isolated in some cases, along with diphosphiranes and their $Fe(CO)_4$ complexes [105].

Reaction of $(OC)_3Fe(\mu:\eta^2,\eta^2\text{-}R_2NPC(=O)PNR_2)Fe(CO)_3$ (R = isopropyl) with benzaldehyde in refluxing toluene resulted in replacement of the bridging carbonyl group by the aldehyde, forming **67**. Formaldehyde, acetophenone, and cyclohexanone reacted similarly [412]. Phosphonium methylides such as $(p\text{-}MeC_6H_4)_3P{=}CH_2$, reacted to form **68** [XRC] rather than Wittig-type products [413].



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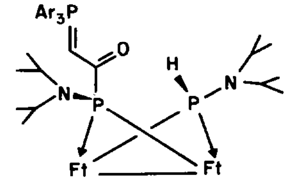
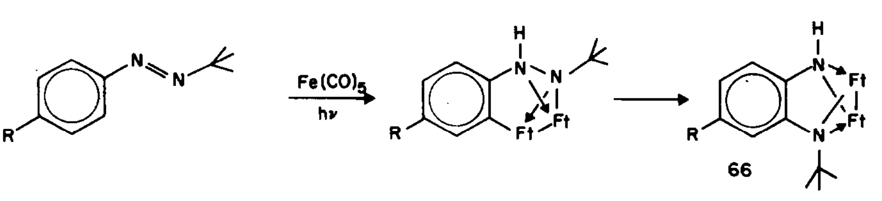


68

$(OC)_2Fe(\mu:\eta^1,\eta^2\text{-}Ph_2PCH{=}CH_2)(\mu\text{-}dppm)Fe(CO)_3$ was formed upon reaction of diphenylvinylphosphine with $(\mu\text{-}dppm)Fe_2(CO)_7$ under UV irradiation. Heating resulted in decarbonylation and cleavage of the P–C bond, to form $(OC)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}dppm)(\mu\text{-}CH{=}CH_2)Fe(CO)_2$. At higher temperatures, "windshield wiper" fluxionality of the vinyl ligand was observed [414].

The mechanistic details of electrochemical oxidation of $(\mu\text{-}dppm)_2Fe_2(CO)_5$ and related species were found to depend upon the nature of the bridging ligand, particularly its size, and the coordinating ability of the solvent. The end products in all cases were dications incorporating a solvent ligand [415].

Preparation of $(OC)_3Fe(\mu\text{-}AsMe_2)_2Fe(CO)_3$ has been reported [113]. The mixed double-cluster compound **69** [XRC] has been prepared through interaction of $MeAsI_2$ and $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SCMe_3)^-$ [416]. Reaction of either $Cp^*(OC)Fe[\eta^3\text{-}RP\text{–}CH\text{–}C(=O)]$ or $Fp^*CH{=}P(R)Fe(CO)_4$ [R = $CH(SiMe_3)_2$]



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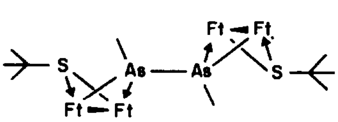
with an excess of $Fe_2(CO)_9$ led to formation of the cluster compound **70** [XRC] [112]. The crystal structure of the mixed cluster compound $(OC)_3Fe(\mu\text{-}PMe_2)(\mu\text{-}SCMe_3)Fe(CO)_3$ showed, not surprisingly, an equatorial tert-butyl group on the sulfur [417].



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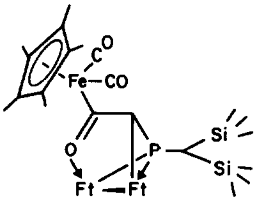
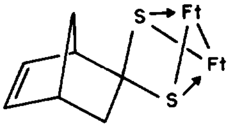


70

Hexacarbonylbis(μ,η^2-decanoyl)diiron has been synthesized by reaction of decanoyl chloride (or 1-chlorodecane) with $Na_2Fe(CO)_4$, followed by CuOTf. The acyl carbon resonance at δ 295 bespoke substantial carbenoid character. Thermal decomposition in cyclohexane showed clean first-order kinetics and a very negative entropy of activation. Products were R_2, R_2CO, RCOCOR ($R = C_9H_{19}$) and $Fe(CO)_5$. Reaction with MeI produced RCOR (75%), along with RMe, RI, and RCOMe. Reaction with triphenylphosphine cleanly produced ketone RCOR (98%); the iron-containing products were $Ph_3PFe(CO)_4$, $(Ph_3P)_2Fe(CO)_3$, and $Fe_3(CO)_{12}$ [418].

Reaction of the thio-bridged anion, $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}SEt)Fe(CO)_3^-$, with *trans*-PhCH=CHCOCl or *trans*-PhCH=CHBr resulted in carbonyl substitution, forming $(OC)_3Fe(\mu\text{-}CH = CHPh)(\mu\text{-}SEt)Fe(CO)_3$ [XRC] [419]. Treatment of the thio-bridged anion with alkyl- or arylmercuric halides, however, resulted in attack at the bridging carbonyl to form bridging acyl groups in the products, $Fe_2(CO)_6(\mu\text{-}COR)(\mu\text{-}SEt)$. When vinylmercuric halides were used, the acyl complexes were less stable and decomposed in several cases to vinyl complexes, $Fe_2(CO)_6(\mu\text{-}CH{=}CHR)(\mu\text{-}SEt)$ (R = H, Ph, Cl). $MeOCH_2CH_2HgCl$ surprisingly gave the bridging carboxylato complex, $Fe_2(CO)_6(\mu\text{-}O_2CMe)(\mu\text{-}SEt)$, more readily prepared using $Hg(O_2CMe)_2$. The crystal structure of $Fe_2(CO)_6(\mu\text{-}O_2CMe)(\mu\text{-}SCMe_3)$ was determined [420].

Reaction of a mixture of an excess of styrene, sulfur, and $Fe_3(CO)_{12}$ at 60°C resulted in formation of $S_2Fe_2(CO)_6$, $Fe_2(CO)_6(\mu\text{-}SC({=}O)S)$, $Fe_2(CO)_6(\mu\text{-}SCH_2CHPhS)$, $Fe_2(CO)_6(\mu\text{-}SSCH_2S)$ [XRC], and $PhCHCH_2S_4$. An additional product from the similar reaction of norbornadiene, beyond the three previously characterized, proved to be **71** [XRC]. All four products were thus found to have the composition $(C_7H_8S_2)Ft_2$, with the organic moieties resulting from norbomadiene being attached in various ways to the S_2Ft_2 unit [422]. Reaction of 1,3-cyclohexadiene with sulfur and $Fe_3(CO)_{12}$ produced an adduct with the two sulfur atoms of S_2Ft_2 added to one double bond [423]. The crystal structure of $(OC)_3Fe(\mu\text{-}SCH_2OMe)(\mu\text{-}SPh)Fe(CO)_3$ showed an axially disposed phenyl and an equatorial methoxymethyl group [424]. Reactions between $(OC)_3Fe(\mu\text{-}S)(\mu\text{-}SR)Fe(CO)_3^-$ MgX^+ (R = Ph, CH_2Ph) and $(OC)_3Fe(\mu\text{-}SR')(\mu\text{-}SCOPh)Fe(CO)_3$ (R' = Me, Et, Ph, $CH_2CH{=}CH_2$) resulted in displacement of thiobenzoate to form "asymmetrical twin clusters," **72** [XRC, R = Ph, R' = Et], as well as the symmetrical diphenyl compound [425].



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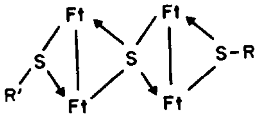
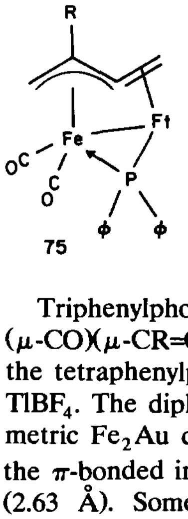


72

$Fe_2(CO)_4(\mu\text{-}SEt)_2\ (PPh_3)_2$ has been used to promote the reaction of N-methylpyrrolidine with $Ru_3(CO)_{12}$ [426]. Reaction of $[Fe(CO)_2L]_2(\mu\text{-}SMe)_2$ (L = PPh_3, PMe_2Ph, PEt_2Ph) with $Me_2SSMe^+\ BF_4^-$ led to insertion of a thiomethyl cation into the Fe–Fe bond, forming $[Fe(CO)_2L]_2(\mu\text{-}SMe)_3^+BF_4^-$ as a single isomer. Variable temperature NMR studies on the dimethylphenylphosphine compound showed hindered Fe–P rotation at low temperatures and sulfur inversion at higher temperatures [427]. The reaction was generalized to form $Fe_2(CO)_4L_2(\mu\text{-}Y)(\mu\text{-}Z)^+$ products (L = same, PMe_3, CO; Y, Z = SMe, SPh, S-*p*-tolyl, PMe_2). The SR^+ group inserted stereospecifically, *trans* to the phosphine ligands in the starting material. This allowed synthesis of isomers of $[(Me_3P)Fe(CO)_2]_2(\mu\text{-}SMe)_2(\mu\text{-}SPh)^+$. Insertion of MeS^+ into either isolable stereoisomer (eq,eq or eq,ax) of $Fe_2(CO)_6(\mu\text{-}SMe)_2$ resulted in the formation of the same product, with C_3 symmetry. An intermediate thought to be $(MeS)(OC)_3Fe(\mu\text{-}SMe)_2Fe(NCMe)(CO)_3^+$ was detected by NMR spectroscopy. The crystal structure of $Fe_2(CO)_4(\mu\text{-}SMe)_3\ (PMe_2Ph)_2^+\ BF_4^-$ was reported [428].

The coordinated selenophene, $Cp^*Re(CO)_2(\eta^2\text{-}C_4H_4Se)$, upon reaction with $Fe_2(CO)_9$, underwent partial cleavage of a C–Se bond to form **73**, besides previously described η^1(*Se*)-$Fe(CO)_4$ and η^4-$Fe(CO)_3$ products [117]. Free selenophene reacted very similarly with $Fe_3(CO)_{12}$, giving the same structure as **73**, but lacking, of course, the rhenium group [429]. $Fe_2(CO)_6(\mu\text{-}SeTe)$, for which an improved synthetic method has been developed, cleanly added a $Pt(PPh_3)_2$ unit to the Se–Te bond upon treatment with $(C_2H_4)Pt(PPh_3)_2$ [430]. The palladium adduct was formed similarly [431]. $Fe_2(CO)_6(\mu\text{-}TeCH_2Te)$ [XRC] and $Fe_2(CO)_6(\mu\text{-}TeCH_2CH_2Te)$ were both produced in the reaction of $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ with diazomethane at room temperature [432]. With an excess of diazomethane, the double cluster **74** [XRC] arose [433].

The reaction between silica-supported $Fe_2(CO)_8(\mu\text{-}CH_2)$ and mixtures of CD_3OD, H_2, and CO has been used to investigate the mechanism of formation of ethanol from syngas. The amount of deuterium in the acetyl group of CH_3COOCD_3 decreased with decreasing CD_3OD/H_2 ratio. This result was taken as support for a sequence involving metalloxycarbene, carbene, ketene, and acetyl complexes [434]. Two methylene groups were transferred to the acetylide ligand of $(OC)_3Fe(\mu\text{-}PPh_2)(\mu:\eta^1,\eta^2\text{-}C{\equiv}CCMe_3)Fe(CO)_3$ upon reaction with an excess of diazomethane, forming a novel $\mu:\eta^2,\eta^3$-2-butadienyl ligand in **75** (R = CMe_3). An analogous compound, **75** (R = Me) resulted from hydrometallation of $CH_2{\equiv}C(Me)\text{-}C{\equiv}CH$ by $HFe_2(CO)_7(\mu\text{-}PPh_2)$. The Fe-P bond lengths in **75** (R = Me) provided a vivid illustration of Fe–P bond length differences, the P → Fe bond being 2.16 Å long, and the P-Fe bond 2.27 Å [435].



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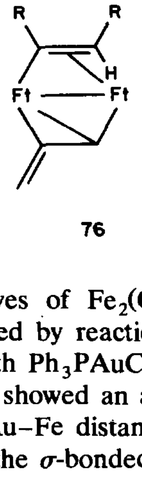
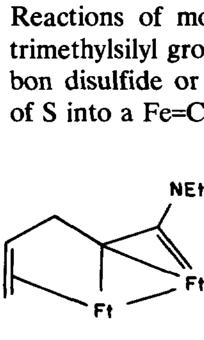


76

Triphenylphosphine-gold derivatives of $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CHR)^-$ were produced by reaction of the tetraphenylphosphonium salt with Ph_3PAuCl and $TlBF_4$. The diphenylethenyl product showed an asymmetric Fe_2Au core, with a longer Au–Fe distance to the π-bonded iron (2.76 Å) than to the σ-bonded one (2.63 Å). Some linked clusters joined by bridging diphosphines were prepared using dppm, dppe, *etc.* [436].

New routes to μ-alkenyl anions have been explored. Reaction of $HFe_2(CO)_8^-$ with diphenylacetylene produced $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CPh{=}CHPh)^-$ in 80% yield. The same product was obtained using $NaBH_4/Fe_2(CO)_9$ (45%) or $HCOFe(CO)_4^-/Fe_2(CO)_9$ (80%). Use of $HFe_2(CO)_8^-$ with phenylacetylene gave a mixture of regioisomers, one of which, $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CH{=}CHPh)^-$, could be obtained in pure form (50% yield) from cinnamyl chloride and $Fe_2(CO)_8^{2-}$. Reaction of propargyl chloride with the (μ-CR = CHR) alkenyl anions (R = H, Ph) led to formation of **76** [437]. **77**, in which a 1-diethylamino-4,1-pentenyne ligand functions as a six-electron donor, formed at room temperature from spontaneous decarbonylation of $(OC)_4Fe\{\mu:\eta^1,\eta^2\text{-}[C(CH_2CH{=}CH_2)\ CNEt_2]\}Fe(CO)_3$. Reactions of more stable analogs, having methyl or trimethylsilyl groups rather than allyl groups, with carbon disulfide or ethylene sulfide resulted in insertion of S into a Fe=C aminocarbene bond [438].



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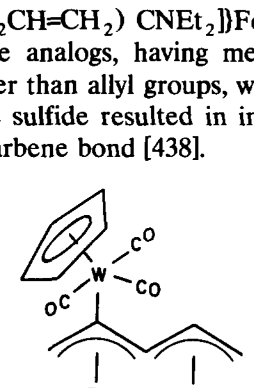
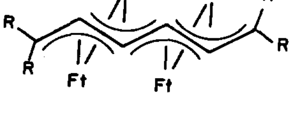


78

Treating $CpW(CO)_3CH_2C{\equiv}CCH{=}CH_2$ with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ led to formation of **78** [XRC], along with previously described **10** and a WFe_2 trimetallic cluster [97]. Reduction of $ClCR_2C{\equiv}C\text{-}C{\equiv}CCR_2Cl$ (R = H, Me) with zinc in the presence of $Fe_3(CO)_{12}$ gave modest yields of (hexapentaene)bis-$[Fe_2(CO)_6]$ complexes, **79**. Both *cis* (shown) and *trans* isomers were obtained, and heating or photolysis of **79** (R = H) resulted in conversion to the *trans* isomer [XRC] [439].

Reaction of $CH_2{=}C{=}C(OMe)Li$ with $Fe_3(CO)_{12}$, followed by acylation with benzoyl chloride, produced an example of the well-known class of ferrole complexes, **80** [XRC]. Alkynyl-lithium reagents gave μ-alkynyl products, $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}C{\equiv}CR)^-$. Treatment of the latter with sulfenyl chlorides gave $Fe_2(CO)_6(\mu\text{-}SR')(\mu\text{-}C{\equiv}CR)$ in moderate yields [440].

The unsubstituted ferrole complex $(\mu:\eta^2,\eta^4\text{-}C_4H_4)Fe_2(CO)_6$, was among the products of reaction of $Fe_3(CO)_{12}$ with selenophene (34%) or tellurophene (25%). In the former case, $(\mu:\eta^2,\eta^3\text{-}C_4H_4Se)Fe_2(CO)_6$ (**73**, but lacking the rhenium group) was also isolated, in 29% yield [429]. The molecular structure of the tetraethylferrole complex $(C_4Et_4)Fe_2(CO)_6$ has been reported and discussed [441]. A substituted ferrole, in which the ferrole iron is coordinated (N,N′) to a 1,4-diazabutadiene ligand, replacing two CO's in the equatorial plane, has been discussed from the standpoint of discrete variational Xα calculations and UV photo-



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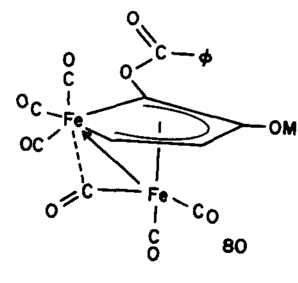

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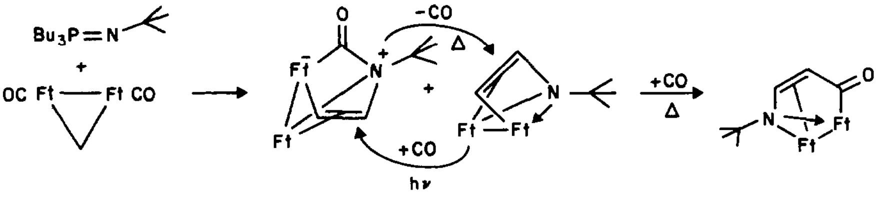


(26)

electron spectral results [442]. A ferrole complex, $[\mu : \eta^2,\eta^4\text{-}C_4(CO_2Me)_4]Fe_2(\eta^6\text{-}PhMe)_2$ [XRC], in which the three carbonyl groups commonly found on each iron were replaced by η^6-toluene ligands, was formed upon reaction of $(PhMe)_2Fe$ with dimethyl acetylenedicarboxylate [374].

Reaction of $(C_4Et_4)Fe_2(CO)_6$ with dppm in the presence of trimethylamine oxide produced the flyover-bridge complex $(\mu : \eta^3,\eta^3\text{-}C_2Et_2COC_2Et_2)\text{-}Fe_2(CO)_5(\eta^1\text{-dppm})$ [XRC], the result of CO insertion into the central C–C bond of the ferrole ring [443]. Equation (26) summarizes some conversions ensuing when $(\mu\text{-}CH_2)Fe_2(CO)_8$ reacted with phosphine imides, here $Bu_3P{=}NCMe_3$. The final 2-ferra-4-pyrrolin-3-one complex underwent alkylation or protonation at oxygen, giving cationic azaferrole complexes [444].

The well-known symmetrical acenaphthylene complex, $(\mu : \eta^3,\eta^5\text{-}C_{12}H_8)Fe_2(CO)_5$, isomerized upon irradiation with visible light, forming an unsymmetrical isomer by allylic shift of the η^3-$Fe(CO)_3$ group. The unsymmetrical isomer, which was 9.7 kJ mol^{-1} less stable than the symmetrical one, based upon equilibration, could be obtained almost quantitatively with sufficient irradiation. It was stable in the solid, but reverted in solution to the more stable isomer.The crystal structure showed a slightly elongated (2.80 *vs.* 2.77 Å) Fe–Fe bond in the less stable, unsymmetrical isomer [445].

9.2. Derivatives of $Cp_2Fe_2(CO)_4$

The photochemistry of Fp_2 in cyclohexane solution was investigated by femtosecond-range infrared spectrometry. 580-Nanometer photolysis produced an excited intermediate with a 1 ps lifetime, which dissociated by more than one channel to form singly bridged or unbridged dimers, and/or homolytically cleaved species, $Fp^{\cdot}$. Solvation of these species occurred over a time-span of about 10 ps. About half the photodissociated species recombined within about 20 ps, probably through a singly-bridged intermediate. It was considered improbable that singly-bridged intermediates would participate in bimolecular reactions with other solutes. Visible light was of insufficient energy to produce $CpFe(\mu\text{-}CO)_3FeCp$ [446]. Photolysis of Fp_2 in the presence of RX produced carbon-centered radicals, by agency of Fp abstracting halogen atoms from RX, forming FpX. Adducts to vinylic substrates were obtained; for example photolysis of a MeOD solution of Fp_2, cyclohexyl iodide, and acrylonitrile produced $C_6H_{11}CH_2CHDCN$ in 90% yield, with FpI and ferrocene as iron-containing byproducts [447].

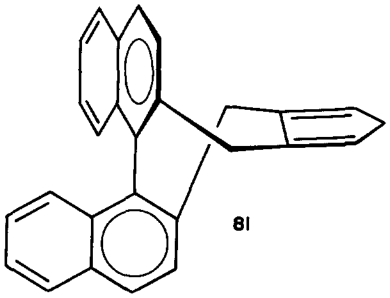
Photochemically reactive polymers incorporating Fp_2 units have been synthesized. For example, the diol $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ and hexamethylene diisocyanate reacted to form an oligourethane, which upon photolysis underwent Fe–Fe bond homolysis reactions like those of Fp_2, which ruptured the oligomer backbone [448]. For example, photolysis in the presence of carbon tetrachloride produced $\{Cl(OC)_2Fe[\eta^5\text{-}C_5H_4CH_2CH_2OCONH(CH_2)_3\text{-}]\}_2$. Photochemical decomposition occurred also in the solid state over a period of several weeks, in the presence of oxygen [449].

Fp_2 has been found to be relatively difficult to reduce, compared to other compounds with metal–metal bonds. The two-electron reduction potential has been estimated as −1.7 V. Reaction of Fp^- with $M_3(CO)_{12}$ led to formation of Fp_2 and $M_3(CO)_{11}^{2-}$ (M = Fe, Ru, Os) [204]. One-electron electrochemical reduction of Fp_2 (and Fp_2^*) at low temperature gave stable radical-anions; at room temperature, two-electron reduction to Fp^- was observed. At intervening temperatures, dissociation of radical-anion to Fp^- and $Fp^{\cdot}$, followed by reduction of the latter in solution by radical-anion was observed. The rate of cleavage for Fp_2^- at 0°C was 100-fold faster than for Fp_2^{*-} [450]. The radical cations of Fp_2 and Fp_2^*, generated electrochemically in methylene chloride solution, have been investigated by IR and ESR spectroscopy. Both *cis* and *trans* forms were observable for Fp_2^+, but only *trans* was observable for Fp_2^{*+}. Formation of acetonitrile adducts was observed, and their fast decomposition to $FpNCMe^+$ and $Fp^{\cdot}$ [451].

Fp_2 has been used to catalyze the ternary addition reaction of a perfluoroalkyl iodide, R_FI, an enol ether, $CH_2{=}CHOR$, and an alcohol to form acetal adducts, $R_FCH_2CH(OR)_2$, in yields of 63–95% [452].

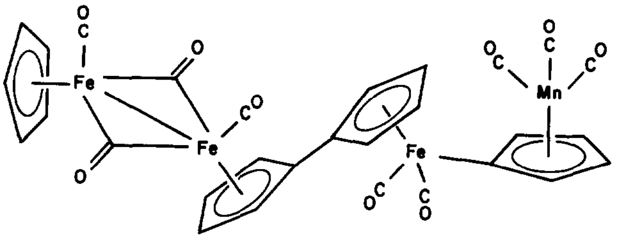
Cothermolysis of $Fe(CO)_5$ and tert-butylcyclopentadiene or 1,3-di-tert-butylcyclopentadiene at or below 130°C gave ring-substituted Fp_2 derivatives in satisfactory yields [453]. $[(\eta^5\text{-}C_5H_4SiMe_2SiMe_3)Fe(CO)_2]_2$ [XRC] was produced similarly from the pentamethyldisilylcyclopentadiene. Several standard reactions (*e.g.*, with I_2 and sodium amalgam) were reported [454].

Reaction of the optically-active (R)-(+)-binaphthylcyclopentadiene **81** with Fe(CO)$_5$, in refluxing toluene containing norbornene as a hydrogen acceptor, produced the (R,R)-(+)-Fp$_2$ derivative in 45% yield. Use of racemic **81** gave racemic and *meso* dimers in a 72:28 ratio [455].



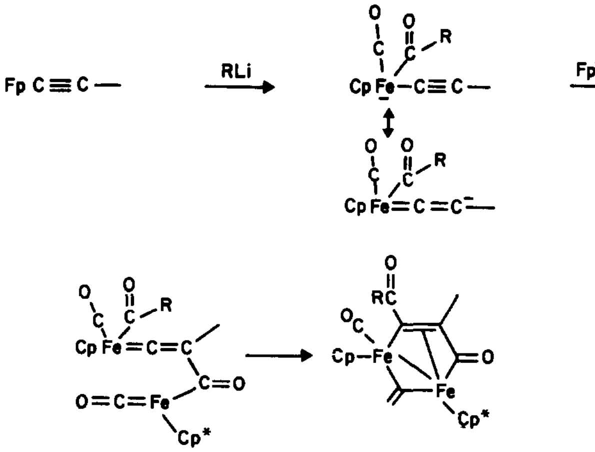
81

Tetrametallic cluster **82** [XRC] was obtained from the trimetallic precursor [(FpC$_5$H$_4$)Fe(CO)$_2$–C$_5$H$_4$]Mn(CO)$_3$ upon reaction with butyl-lithium, followed by FpI. The reaction, intended to generate an additional Fe–C bond, instead formed a Fe–Fe bond [305]. The bridged dimer, (μ; η^5,η^5-1,1′,3,3′-tetra-tert-butyl-5,5′-fulvalene)tetracarbonyldiiron reacted with halogens by cleavage of the Fe–Fe bond and formation of Fe–X bonds. Alkylated derivatives were also prepared by standard methods. Because of the highly hindered nature of the substituted fulvalene ligand, it was assumed that the irons remained *cisoid* in all derivatives [456]. One-electron reduction of (μ; η^5,η^5-fulvalene)FeW(CO)$_5$ gave the dimeric dianion, {[(OC)$_3$W(C$_5$H$_4$)-C$_5$H$_4$]Fe(CO)$_2$}$_2^{2-}$, which readily underwent methylation at tungsten [457].



82

Reaction of Fp$_2$ and CN$^-$ produced (CpFe)$_2$(μ-CO)$_2$(CO)(CN)$^-$. The crystal structure of the PPN$^+$ salt showed the cyano and carbonyl ligands disordered between the two terminal positions of the *cis*-dimer. In solution, both *cis* and *trans* isomers were observed by NMR spectroscopy, as was a cyanide migration, more rapid in the *trans* isomer, which rendered the cyclopentadienyl resonances equivalent in each isomer [458]. Isonitrile derivatives (CpFe)$_2$(CO)$_{4-n}$(CNAr)$_n$ (Ar = various methylphenyl groups; n = 1, 2) have been prepared by two methods: photosubstitution of ArNC into Fp$_2$ and direct reaction of Fe(CO)$_5$, dicyclopentadiene, and ArNC at 145°C [459].



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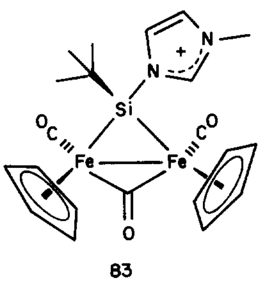
Methylation of the thiomethyl group of (CpFeCO)$_2$(μ-CO)[μ-C(CN)SMe] generated a dimethyl sulfide leaving group. Reactions with nucleophiles (NaBH$_4$, PhNH$_2$, alcohols, W(CO)$_5$CN$^-$) led to displacement of this leaving group. The methylamine adduct reacted further, losing HCN to form the isonitrile complex (CpFeCO)$_2$(μ-CO)(μ-C=NMe) [460]. Formation of several (CpFeCO)$_2$(μ-CO)[μ-C(CN)OR] products by alcohol displacement was reported. Photolysis of the R = CH$_2$–CH=CH$_2$ product resulted in displacement of a CO by the double bond [XRC] [461].

Solid-state ^{13}C NMR studies of *cis*-(CpFeCO)$_2$(μ-CO)(μ-CH$_2$) have been carried out. A very large paramagnetic chemical shielding tensor element, which arises as a result of the weak carbon–iron bonds, was identified [462]. Irradiation of (CpFeCO)$_2$(μ-CO)(μ-CHMe) led exclusively to the formation of (CpFe)$_2$(μ-CO)$_2$(μ-CHMe)(*Fe*=*Fe*). Reactions of this intermediate were studied by laser flash photolysis experiments. Two-electron ligands gave the expected CpFeCO(μ-CO)(μ-CHMe)FeLCp (L = CO, MeCN, R$_3$P), by an associative bimolecular process. CCl$_4$ reacted to form FpCl [463].

Whereas reaction of (η^2-FpC≡CPh)Fp$^+$ with sodium methoxide yielded the metallacycle **55** (R = Fp), the pentamethylcyclopentadienyl analog gave a more complex mixture containing the analog of **55** and a vinylidene complex, (Cp*FeCO)$_2$(μ-CO)[μ-C=C(Ph)CO$_2$Me]. A proposed mechanism involved attack of methoxide at a carbonyl of the cationic Fp* group and migration of the ester group to the alkyne β-carbon [303]. Similarly, reaction of the cation (η^2-Fp*C≡CH)Fp*$^+$ with RLi (R = butyl, tert-butyl) yielded acylvinylidene complexes, (Cp*FeCO)$_2$(μ-CO)(μ-C=CHCOR) [XRC, R = tert-butyl]. Reaction with LiHBEt$_3$ afforded the unsubstituted vinylidene complex, $(Cp^*FeCO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ [464]. Attack of RLi (R = Me, Bu, Ph) on $FpC{\equiv}CMe$ at low temperature, followed by quenching with Fp^*Cl, proceeded as shown in eqn. (27). Carbonyl attack as shown was verified by use of ^{13}C carbonyl-labelled starting material [465].

$(CpFeCO)_2(\mu\text{-}CO)(\mu\text{-}SiMeSiMe_3)$ has been produced by photolysis of $FpSiMe_2SiMe_2Fp$ [215]. The product existed in solution as a mixture of three geometric isomers. A crystal structure of one isomer showed the cyclopentadienyl rings and the trimethylsilyl group all-*cis* with respect to the Fe_2CSi ring. Continued photolysis led to formation of $(CpFeCO)_2(\mu\text{-}SiMe_2)_2$ [216]. The crystal structure of **83**, prepared by displacement of iodide from the iodosilane by N-methylimidazole, showed some unexpected features: the Fe–Si bonds were shorter (2.26 Å) than those in the $\mu\text{-}SiMeCMe_3$ analog (2.30 Å), and the Si–N bond (1.88 Å) was long compared to typical values of 1.75 Å [466]. Substantial ionic character in the $SiFe_2$ ring may be suggested.



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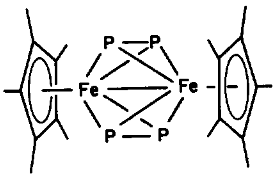
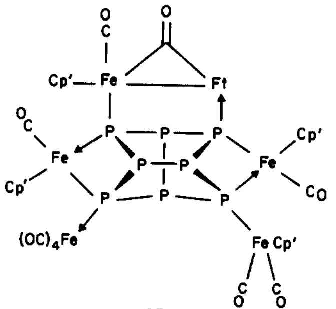


84

Reaction of $PhN[P(OPh)_2]_2$ with Fp_2 at 80°C led primarily to displacement of the two terminal carbonyls to form $(CpFe)_2(\mu\text{-}CO)_2[\mu\text{-}(PhO)_2PN(Ph)P(OPh)_2]$. A small amount (5%) of an isomeric product from cleavage of the diphosphazane, $(CpFeCO)_2[\mu\text{-}P(OPh)_2][\mu\text{-}(PhO)_2P{=}NPh]$ also formed [467]. The crystal structure of a 2:3 charge-transfer salt of $(CpFe)_2(\mu\text{-}CO)_2[\mu\text{-}Ph_2PN(Et)PPh_2]^+$ with $(TCNQ)_3^{2-}$ was determined; the cations and anions formed segregated stacks. The radical-cation showed a Fe–Fe distance of 2.495 Å, slightly shorter than in the neutral compound [468].

Cophotolysis of Fp_2^* and P_4 led to the formation of $(Cp^*Fe)_2(\mu_2:\eta^2\text{-}P_2)_2$, **84** [XRC]. Reversible oxidation was observed in the cyclic voltammogram. The bridging diphosphide ligands were unreactive compared to bridging disulfide ligands [469]. **84** may be compared to **51**, produced by a similar reaction of the (methylcyclopentadienyl)iron dicarbonyl dimer. Thermal reaction of **51** with iron carbonyls led to formation of **85** [XRC]. The P_8 cage was compared to units in the complex structure of violet phosphorus [244].



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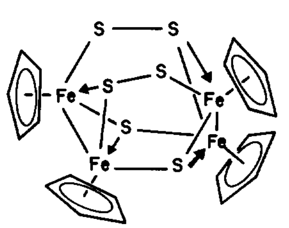
The crystal structure of $(CpFeCO)_2(\mu\text{-}SEt)_2$ has been determined. The Fe–S distances averaged 2.27 Å, and the distance between non-bonded iron atoms was 3.43 Å [470]. Two-electron oxidation of $(Cp^*Fe)(\mu:\eta^1,\eta^1\text{-}S_2)(\mu:\eta^2,\eta^2\text{-}S_2)$ produced a dication similar to **84** in structure, but lacking the Fe–Fe bond, due to the presence of two additional electrons. Electrochemical and spectroscopic studies of the isomerization process revealed that the isomerization occurred at the radical-cation stage [471]. The crystal structure of $(CpFe)_4S_6$, **86**, has been redetermined [472]. The Fe-Fe bond lengths were 2.64 Å [472]. Charge-transfer salts of the heterocubane $(CpFe)_4(\mu_3\text{-}S)_4$ and its Cp′ derivative with $(FeNO)_4(\mu_3\text{-}S)_4$ and TCNQ have been prepared. Crystal structures, electrical conductivity, and magnetic properties have been studied [473].



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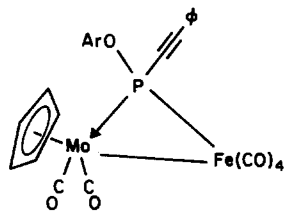

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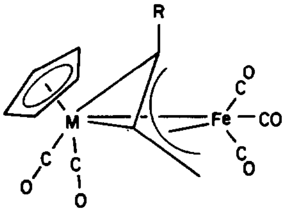
9.3. Heterobimetallic compounds

A compound with an unsupported Fe–Mo bond, $Fp\text{-}Mo(CO)_2(C_7H_7)$, was prepared by reaction of NaFp with $(C_7H_7)Mo(CO)_2Br$. The compound was "thermally and photochemically quite sensitive," decomposing to homodimers in the presence of light. The Fp* analog was too unstable to isolate [474]. Reaction of $PhC{\equiv}CP(OAr){=}Mo(CO)_2Cp$ (Ar = 2,4,6-tri-tert-butyl) with $Fe_2(CO)_9$ led to a product, **87**, having the P=Mo double bond of the starting material coordinated to a $Fe(CO)_4$ group [475]. Products very similar to **87**, but having more conventional μ-diphenylphosphido bridges, were formed upon reaction of $Br_2Fe(CO)_4$ and $CpM(CO)_2PPh_2^{2-}$ (M = Cr, Mo, W) [476].

Reactions of propargyl complexes $Cp(OC)_3MCH_2\text{-}C{\equiv}CR$ (M = Mo, W; R = Me, Ph, *p*-tolyl) with iron carbonyls led to formation of bimetallic μ-allenyl products, **88** [XRC, M = W, R = *p*-tolyl] and trimetallic products. **88** reacted with iodine to form RCI=C=CH$_2$. Reaction with triphenylphosphine in the presence of trimethylamine oxide resulted in substitution at iron [477]. The redox chemistry of the fulvalene complex $(OC)_3W(\mu:\eta^5,\eta^5\text{-}C_5H_4C_5H_4)Fe(CO)_2$ showed distinguishable behavior of the two metal centers. One-electron reduction with CpFeAn broke the Fe–W bond, forming a tungsten anion. The 17-electron iron radicals then dimerized to form the Fp$_2$ derivative. Further reduction to the dianion was also possible [457]. Heating a mixture of $[CpMo(CO)_3]_2$, $[CpW(CO)_3]_2$, and $Te_2Fe_3(CO)_9$ in toluene led to formation of the mixed compound $Cp_2M_2(\mu\text{-}Te)_2Fe(CO)_3$ [M = 1.2 W: 0.8 Mo]. The crystal structure showed one CpM(CO)$_2$ unit (predominantly Mo) inserted into the Te–Te bond of a FeMTe$_2$ tetrahedron (M predominantly W), but having no metal–metal bonds [478]. The pure molybdenum analog had been reported in 1985.



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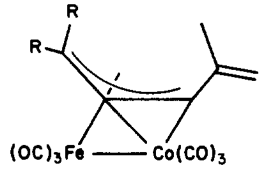
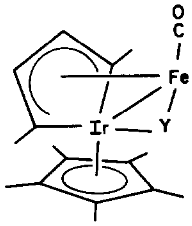


89

$Re(CO)_5^-$ displaced $Mn(CO)_5^-$ from attachment to FpMn(CO)$_5$, perhaps through a trimetallic intermediate with η^3 coordination of the Cp ring on the iron [203]. FpRe(CO)$_3$L complexes (L = 4,4′-dimethyl-2,2′-bipyridyl; 2-formylpyridine N-isopropylimine) showed strong metal-to-ligand charge transfer absorptions in the visible spectrum, and manifested wavelength-dependent photochemistry. Photolysis of the complexes in the visible region caused homolysis of the Fe–Re bond, whereas UV light caused decarbonylation accompanied by CO-bridging [479]. Interaction of $RCOFe(CO)_4^-$ (R = Me, Ph) and $[(OC)_4ReBr]_2$ at 0°C gave an acyl-bridged product, $(OC)_4Fe(\mu\text{-}RCO)Re(CO)_4$ [XRC]. The manganese analogs were thermally unstable [480].

The bonding in $(OC)_3Fe[\mu\text{-}(Me_2CH)NCH_2CH_2N(CHMe_2)]Ru(CO)_3$ has been examined by analysis of UV photoelectron spectra and use of discrete variational Xα calculations. It was concluded that most of the metal-nitrogen bonding was π in character, with only weak σ contributions [442].

Heating the mixed-metal chelate compounds **21** in inert solvents resulted in conversion to bimetallic compounds **89**. A crystal structure of **89** (CR$_2$ = CHPh) was reported [135]. The bimetallic cobaltaferrocene, $CpFe[\mu:\eta^5\text{-}C_4E_4Co(CO)_3]$ (E = CO$_2$Me) was among the many products of reaction of Fp$_2$ and $(C_2E_2)Co_2(CO)_6$ [481], but most of the products were tetrametallic, and will be discussed in Section 11. The tetramethylferrole complex $Cp^*Rh[\eta^5\text{-}C_4Me_4Fe(CO)_3]$ [XRC] was formed upon desulfurization of the tetramethylthiophene complex, $Cp^*Rh(\eta^4\text{-}C_4Me_4S)$ by $Fe_3(CO)_{12}$ or in thermolysis of **14** [115]. In reaction of $Cp^*\ Ir(\eta^4\text{-}C_4H_2Me_2S)$ with $Fe_3(CO)_{12}$, however, the iridacycle **90** [Y = S → Fe(CO)$_4$] formed rather than the ferrole. Carbonylation of this product under one atmosphere of CO formed **90** (Y = CO). Implications of these conversions on the mechanism of hydrodesulfurization were discussed [116].



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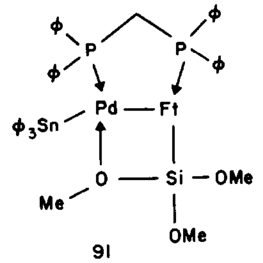

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The loose ends of $CpFeCl(F_2PNMePF_2)_2$ were used to form bimetallic compounds by reaction with $[Rh(CO)_2Cl]_2$ and $(PhMe_2P)_2Ir(CO)Cl$. The crystal structure of $CpFe(\mu\text{-}F_2PNMePF_2)_2IrCl_2(PMe_2Ph)$ showed a somewhat long (2.83 Å) Fe–Ir bond [482]. Similarly, $HFe[Si(OMe)_3](CO)_3(\eta^1\text{-dppm})$ or its conjugate base reacted to form products, $LRh(\mu\text{-dppm})[\mu_2:\eta^2\text{-}MeOSi(OMe)_2]Fe(CO)_3$ [L = CO, PPh$_3$, P(OPh)$_3$], in which the iron–rhodium bond was supported by a bridging methoxysilyl group in addition to the dppm. The methoxysilyl bridge could be opened by carbonylation of the rhodium carbonyl compound [483]. Reaction of $Fe[Si(OMe)_3](CO)_3(\eta^1\text{-dppm})^-$ with $[(\eta^3\text{-}C_3H_5)MCl]_2$ (M = Pd, Pt) gave $(\eta^3\text{-}C_3H_5)M(\mu\text{-dppm})Fe(CO)_3[Si(OMe)_3]$. Reaction of the latter with HSnPh$_3$ produced **91**, in which the allyl ligand was replaced by a triphenylstannyl group and the methoxysilyl bridge [484]. Dynamic exchange of methoxy groups between bridging and terminal positions was studied in the rhodium [483] and palladium [484] compounds.

10. Trinuclear cluster compounds

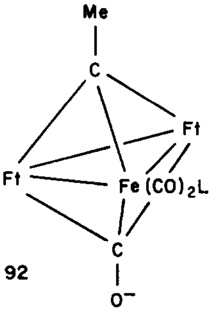
10.1. *Fe$_3$ clusters*

The bonding in $Fe_3(CO)_{12}$ has been analyzed, considering the compound as an Fe(CO)$_4$ complex of $(OC)_3Fe(\mu\text{-}CO)_2Fe(CO)_3$. Similarities and differences in isolobal organic and inorganic fragments were discussed [402]. The packing of $Fe_3(CO)_{12}$ molecules in crystals and the disorder therein have been discussed from the perspective of molecular recognition phenomena [485]. $Fe_3(CO)_{10}L(C{\equiv}NCF_3)$ compounds [L = PMe_3, PEt_3, $P(OMe)_3$, $P(OEt)_3$, $CNCMe_3$] have been prepared by Me_3NO-induced substitution reactions. The complexes bearing the phosphine ligands existed as only one isomer in solution; the crystal structure of the trimethylphosphine complex showed the isonitrile in a bridging position, with the phosphine adjacent. The other compounds showed two or three isomers in solution; a crystal structure of the trimethyl phosphite compound again showed a bridging isonitrile, with the phosphite on the unbridged iron [486].

It has been proposed that fast substitution of triphenylphosphine into $Fe_3(CO)_{12}$ at room temperature is in fact catalyzed by triphenylphosphine oxide, as an unavoidahle contaminant in the phosphine. EPR studies showed that the radical-anion of $Fe_3(CO)_{12}$ is a steady-state species during the reaction, with formation of $Fe_3(CO)_{11}^-$ the rate-limiting step [487]. Substitution of phosphines into $Fe_3(CO)_{12}$ has also been catalyzed by (α-diimine)$Mn(CO)_3L^{\cdot}$ radicals, formed by *in situ* photolysis of $(OC)_5Mn{-}Mn$(α-diimine)$(CO)_3$ in the presence of L. The mechanism was again thought to involve electron transfer [488]. $Fe_3(CO)_{12}$ underwent two-electron reduction by $M_3(CO)_{11}^{2-}$ (M = Ru, Os), by an outer sphere mechanism [489].

The carbon dioxide complex $Cp_2Mo(\eta^2\text{-}OCO)$ formed $Cp_2Mo(CO)H^+$ $HFe_3(CO)_{11}^-$ upon treatment with $H_2Fe(CO)_4$ at −10°C [490]. A crystal structure of dicyclohexylammonium hydridoundecacarbonyltriferrate, obtained unexpectedly from reaction of $(C_6H_{11})_2NBBr_2$ with $Na_2Fe_2(CO)_8$, was reported [491], as was also that of PPN^+ $HFe_3(CO)_{11}^-$ [492]. Et_3NH^+ $HFe_3(CO)_{11}^-$ was found to be an effective catalyst for hydrohydroxymethylation (*i.e.* hydroformylation and reduction) of propene, due to the presence in solution of both mono- and trinuclear anions, which play complementary roles in the reaction [493].

Solid-state ^{13}C NMR spectroscopy has been applied to the study of semibridging carbonyl groups. Among the substances studied were the trinuclear complexes $Fe_3(CO)_9(PhC{\equiv}CPh)_2$, $Fe_3(CO)_{12}$, and $Ph_3PFe_3(CO)_{11}$ [403]. Reaction of triphenylphosphine with $HFe_3(CO)_9(\mu_3:\eta^2\text{-}C{=}CH_2)^-$ resulted in conversion of the vinylidene ligand into an ethylidene by hydrogen transfer, to form $Fe_3(CO)_8(PPh_3)(\mu_3\text{-}CO)(\mu_3\text{-}CMe)$, **92**.



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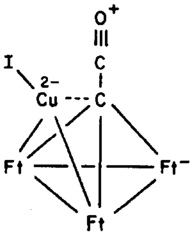

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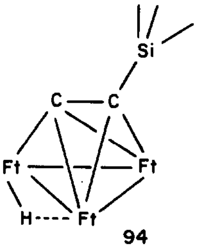
Diphenylphosphinoalkynes reacted similarly, with no involvement of the triple bonds [494]. Treating the ketenylidene cluster $Fe_3(CO)_9CCO^{2-}$ with $Cu(NCMe)_4^{2+}$ then PPN^+ I^- led to formation of **93** [XRC], having the copper bonded to a CFe_2 face. The qualitative analogy between protonation and addition of Group 11 cations to anionic clusters breaks down in this case, since protonation of the ketenylidene cluster results in formation of a μ_3-CH ligand and carbonyl migration [495]. The silica-supported ketenylidene cluster was used in a study of the formation of ethanol from syngas [434].

Extended Hückel calculations have been applied to a study of the variation from μ_2 to μ_3 of the carbyne moiety in $HFe_3(CO)_{10}(\mu\text{-}CR)$ [R = H, OMe, NH_2]. Antibonding interactions favored the μ_2 arrangement in all cases [496]. The crystal structure of $HFe_3(CO)_9(CCSiMe_3)$, **94**, an unexpected product from condensation of nickel atoms into a methylcyclohexane solution of bis(trimethylsilyl)acetylene and $Fe(CO)_5$ at −120°C, has been determined [497]. Heating $Fe_3(CO)_{10}L(\mu\text{-}CNCF_3)$ (L = trimethyl- and triethyl- phosphine or



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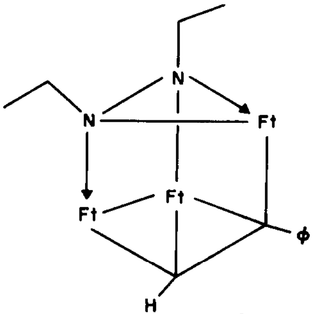

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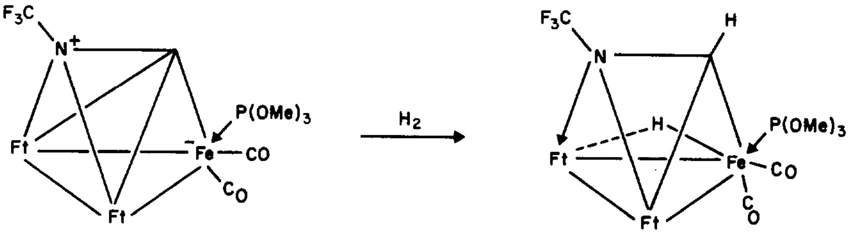

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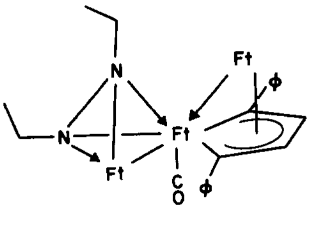
phosphite) at 95°C led to loss of two CO's and formation of the cluster $Fe_3(CO)_9L(\mu_3:\eta^2\text{-CNCF}_3)$ [XRC], structurally similar to **94**. Hydrogenation of this cluster [eqn. (28)] formed $Fe_3(CO)_8L(\mu_3$: $\eta^2\text{-CH=NCF}_3)(\mu\text{-H})$, which existed as a mixture of three isomers having different positions of the ligand L. Hydrogenation could also be achieved stepwise using $NaBH_4$ followed by protonation [498].

Reaction of 1,4-dimethoxy-2-butyne with $Fe_3(CO)_{11}$-(NCMe) gave both the 48-electron cluster $Fe_3(CO)_9$-$(\mu\text{-CO})(\mu_3:\eta^2\text{-MeOCH}_2\text{CCCH}_2\text{OMe})$ [XRC], having the alkyne ligand parallel to an Fe–Fe edge, and the unsaturated 46-electron perpendicular cluster, $Fe_3(CO)_9(\mu_3:\eta^2\text{-MeOCH}_2\text{CCCH}_2\text{OMe})$ [499].

$(CpFe)_3(\mu\text{-CO})_3(\mu_3\text{-NO})$ has been prepared by reaction of Fp_2 and NO in refluxing xylene [500]. Syntheses of $Fe_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-PR})$ have appeared from three different countries. In one case, the clusters (R = Me, *p*-tolyl) were prepared by refluxing $Fe(CO)_4$-(PH_2R) in toluene [501]. Several examples (R = Ph, cyclohexyl, *p*-anisyl, tert-butyl, *β*-cyanoethyl) were prepared, in high yield, by direct reaction of RPH_2 with $Fe_3(CO)_{12}$ [502]. Clusters with $R = Fe(CO)_4^-$ resulted from reaction of PCl_3 with either $Fe_3(CO)_{11}^{2-}$ or $Fe_4(CO)_{13}^{2-}$. The crystal structure of $Fe_3(CO)_9(\mu\text{-H})[\mu_3\text{-P–Fe(CO)}_4^-]^-$ dianion, as its tetraphenylphosphonium salt, was determined [503]. Treating the same Fe_3 and Fe_4 dianions with halo derivatives of antimony and bismuth led to formation of $Fe_3(CO)_{10}(\mu_3\text{-Q})^-$ (Q = Sb, Bi) and $HFe_3(CO)_9(\mu_3\text{-SbCMe}_3)$ [113].

The tri-iron complexes $Fe_3(CO)_9(\mu\text{-CO})(\mu_3\text{-PR})$, $Fe_3(CO)_9(\mu\text{-H})_2(\mu_3\text{-PAr})$, and $Fe_3(CO)_9(\mu_3\text{-PR})_2$ showed moderate activity in hydrogenation of diphenylacetylene and isomerization of stilbene [504]. The azoethane-bridged cluster $Fe_3(CO)_9(\mu_3:\eta^2\text{-EtN=NEt})$ was converted to a carbenoid derivative by addition of phenyl-lithium to a carbonyl group, followed by ethylation. Oxidative or thermal degradation of the carbenoid gave 3-ethoxy-1,2-diethyl-3-phenyldiaziridine and EtN=C(Ph)OEt. Reactions of the parent azoethane cluster with alkynes led to formation of expanded clusters **95** and **96** [both XRC]. **96** existed in solution as two separable isomers; the one not shown had the terminal Fe incorporated in the ferrole ring and a semibridging carbonyl group. Clusters like **96**, but derived from 2-butyne, could be prepared from the ferrole complex $[C_4Me_4Fe(CO)_3]Fe(CO)_3$ by reaction with $Fe_2(CO)_9$ and azoethane [505].



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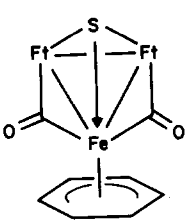
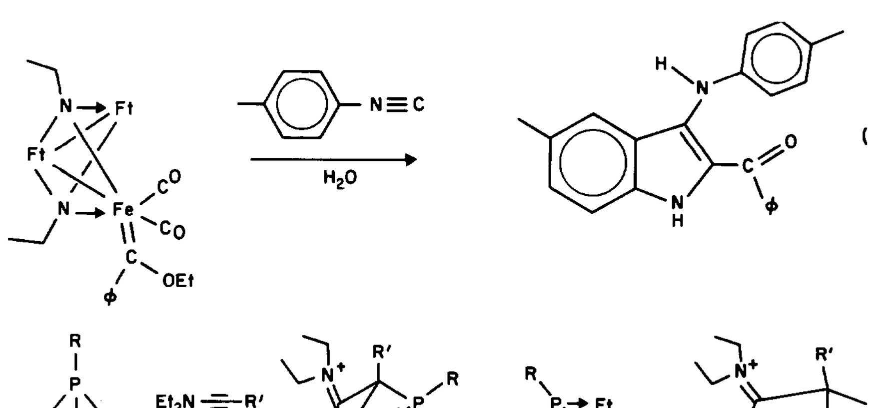


97

μ_3-Thio-bridged cluster **97** [XRC] was formed, along with S_2Fe_2 clusters, in the reaction of cyclohexadiene, sulfur, and $Fe_3(CO)_{12}$ [423].

96 is a 50-electron cluster with the expected open Fe_3 geometry. The closed 48-electron cluster Fe_3-$(CO)_9(EtN=NEt)$ from which **96** was derived formed another 50-electron cluster, $Fe_3(CO)_9(\mu\text{-NEt})_2$, upon heating. Treatment of the latter with phenyl-lithium, followed by a triethyloxonium salt, converted a carbonyl ligand on a terminal iron into an ethoxyphenylcarbene ligand. Reaction of the carbene cluster with moist *p*-tolyl isocyanate led to coupling of two isocyanides and incorporation of a benzoyl unit from the carbene to produce an indole derivative [eqn. (29)]



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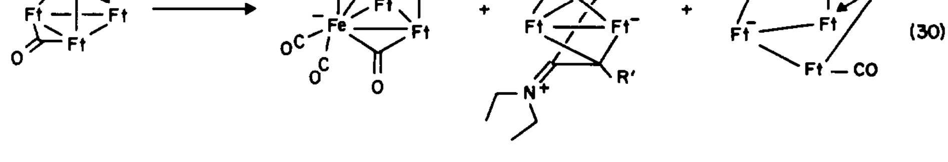

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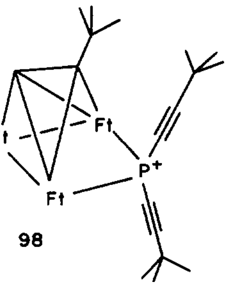
[505]. Closely related carbene clusters, $Fe_3(CO)_8[CX_2](\mu_3\text{-}PR)(\mu_3\text{-}S)$ ($X = NH_2$, NHMe, Me; R = $CHMe_2$, CMe_3, Ph, *p*-anisyl) were prepared by reaction of $Fe_3(CO)_{10}(\mu_3\text{-}PR)$ with thioureas or thioacetamide. The crystal structure of the product from thioacetamide (X_2 = Me, NH_2) showed a Fe–carbenoid carbon bond length of 1.97 Å and a C–N bond length of 1.28 Å [506]. The same μ_3-phosphinidene starting materials underwent cluster expansion upon reaction with aminoalkynes $Et_2N\text{-}C{\equiv}C\text{-}R'$(R' = H, Ph, $SiMe_3$) [eqn. (30)] [507].

Heating $Fe_3(CO)_{11}$ [P(–C≡C–CMe_3)$_3$], formed *in situ* from the tris(alkynyl)phosphine and $Fe_3(CO)_{12}$, at 50°C in hexane formed the 50-electron alkynyl cluster **98** [XRC] in 94% yield [508]. Reaction with an excess of FpCl converted $Fe_3(CO)_9(\mu\text{-}H)(\mu_2\text{-}PHSiMe_3)(\mu_3\text{-}PSiMe_3)$ into $Fe_3(CO)_9(\mu_3\text{-}PFp)_2$. Although FpI and Fp*Cl did not react under the same conditions, in the presence of water they yielded monosubstituted clusters $Fe_3(CO)_9[\mu_3\text{-}PFp(*)](\mu_3\text{-}PH)$. These could then be converted to mixed-ligand examples by further reaction with FpCl or derivatives [509]. The fluxional behavior of $Fe_3(CO)_9(\mu_3{:}\eta^2\text{-}RCCR)(\mu_3\text{-}PR)$ has been analyzed, and a simple MO model for the redox behavior of structurally related *nido* and *closo* clusters was offerred [510].



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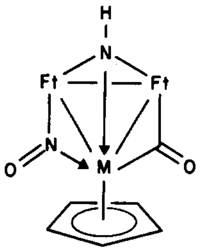


99

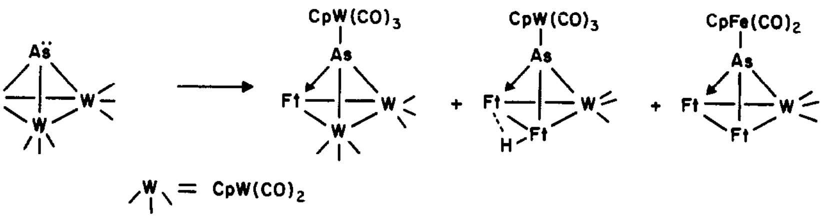
The reaction products obtained from interaction of norbornadiene, sulfur, and $Fe_3(CO)_{12}$ included, in addition to organosulfur complexes, $Fe_3(CO)_9(\mu_3\text{-}S)_2$ and $Fe_3(CO)_9(\mu_2\text{-}CO)(\mu_3\text{-}S)$ [422]. The same disulfide was produced while irradiating $Fe(CO)_5$ in the presence of phenylisothiocyanate, PhNCS. Of greater interest was the formation of two isomers of $Fe_3(CO)_8(CNPh)(\mu_2\text{-}S)_2$, one [XRC] having the phenyl isonitrile ligand on the central iron of the open triangle, and the other on a terminal iron [511].

An improved method has been developed for isolation of $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ In pure form. Treatment with $Pt(PPh_3)_4$ resulted in introduction of two triphenylphosphine ligands, replacing two CO ligands; some cluster degradation to $Fe_2(CO)_6[\mu\text{-}SePt(PPh_3)_2Te]$ also took place. Likwise, free triphenylphosphine added to form the opened 52-electron cluster, $Fe_2(CO)_6[\mu\text{-}SeFe(CO)_3(PPh_3)Te]$ [430]. In similar fashion, $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ was used as a progenitor for clusters containing the Ft_2Te_2 moiety as a ligand to other metals. The reactions were thought to involve a 52-electron adduct, in which the $Fe(CO)_3L$ group underwent replacement by other metal groups [512].

10.2. Heterotrimetallic clusters, Fe_2M and FeM_2

Reactions of iron carbonyl anions with $PtCl_2(CO)L$ or $PtCl_2L_2$ led to formation of tri-, tetra-, and pentametallic clusters, sometimes with ligand redistributions between metal atoms. One of the products, $[(OC)_4Fe]_2Pt(PEt_3)_2$, was characterized by a crystal structure, which showed a closed triangle of metal atoms with Fe–Pt bond length of 2.64 Å and Fe–Fe of 2.69 Å. The apparent electron-deficiency of this 46-electron cluster was due to the well-known tendency of platinum to forego use of its highest-energy d-orbital [513]. Another 46-electron cluster was the double-decker $(OC)_3Re[\mu_3{:}\eta^4,\eta^4\text{-}CH{=}CH\text{-}C_6H_4Fe(CO)_3]\text{-}Re(CO)_3$, formed in the reaction of $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)$ with $Fe_3(CO)_{12}$ in refluxing toluene. The crystal structure showed a benzo[b]ferrole ring coordinated on each face by a tricarbonylrhenium group, with Re–Fe bond lengths of 2.67 Å [514].

The more heavily populated realm of 48-electron clusters included $(Cp^*Rh)_2(\mu\text{-}CO)(\mu_3\text{-}S)Fe(CO)_3$ [XRC], which was among the products of pyrolysis of **14** [114]. μ_3-Imido ligands, generated by reduction of nitrosyl ligands, have been incorporated in several 48-electron clusters. For example, reaction of Na^+ $Fe(CO)_3NO^-$ with $CpM(CO)_3Cl$ (M = Mo, W) in methanol/THF at room temperature generated $CpMFe_2(\mu_3\text{-}NH)(\mu_2\text{-}NO)(\mu_2\text{-}CO)(CO)_6$, **99**. The Cp′ analogs were similarly prepared [515]. The crystal structures of both the molybdenum [516] and tungsten [517] compounds were reported. $[Cp'Fe(NO)]_2$ and an

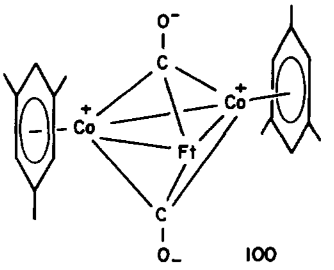


(3)

excess of $\mathrm{Cp'Co(C_2H_4)_2}$ interacted under photochemical or mild thermal conditions to produce two similar trimetallic cluster products, $\mathrm{Cp'_3CoFe_2(\mu_3\text{-}NH)_2}$ and $\mathrm{Cp'_3Co_2Fe(\mu_3\text{-}NH)(\mu_3\text{-}NO)}$, along with a tetranuclear compound. The very labile $\mathrm{Cp'_3Co_2Fe(\mu_3\text{-}NH)_2}$, a 49-electron compound, was also produced during the reaction [518]. $(\mu_3:\eta^2\text{-EtN{\equiv}NEt})\mathrm{Fe_2Ru(CO)_9}$ has been formed in cluster buildup reactions from $(\mu_2:\eta^2\text{-EtN{\equiv}NEt})\mathrm{Fe_2(CO)_6}$ [519].

Temperature-dependent ^{13}C NMR spin–lattice relaxation times and nuclear Overhauser enhancements in $(\mu_3\text{-PPh})\mathrm{Co_2Fe(CO)_9}$ have led to values of the spinning diffusion coefficient for the molecule, which were about 30% lower than for $(\mu_3\text{-CPh})\mathrm{Co_3(CO)_9}$ or free benzene. It was concluded that phenyl ring rotation in the phosphinidene complex encountered a barrier resulting from the non-degenerate 2e molecular orbitals arising from the presence of the tricarbonyliron unit [520]. Attack of $\mathrm{R_3BH^-}$ (R = Et, sec-butyl) on the cluster at −78°C resulted in attack at the phosphorus, with heterolytic cleavage of a P–Co bond, forming $\mathrm{Co_2Fe(CO)_9(\mu_2\text{-}PHPh)^-}$. Grignard reagents transferred an electron to $(\mu_3\text{-PPh})\mathrm{Co_2Fe(CO)_9}$, but methyl-lithium, methoxide and hydroxide ions at −78°C attacked a cobalt-bound carbonyl group. On warming to room temperature, the methoxy group in $(\mu_3\text{-PPh})\mathrm{Co_2Fe(CO)_9(CO_2Me)^-}$ rearranged to phosphorus, forming $\mathrm{Co_2Fe(CO)_9(\mu_2\text{-}PPhOMe)^-}$ [521].

Replacement of tungsten groups from the trimetallic cluster $\mathrm{[CpW(CO)_2]_3(\mu_3\text{-}As)}$ by tricarbonyliron groups occurred [eqn. (31)] upon treatment with iron carbonyls under various conditions. Photoreaction with $\mathrm{Fe(CO)_5}$ gave the $\mathrm{FeW_2}$ cluster, whereas thermal reaction gave the $\mathrm{Fe_2W}$ product. Thermal reaction with $\mathrm{Fe_2(CO)_9}$ formed the Fp-substituted cluster besides the others. All three were characterized by crystal structures [522].



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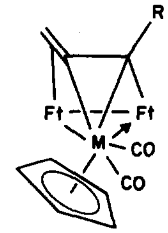
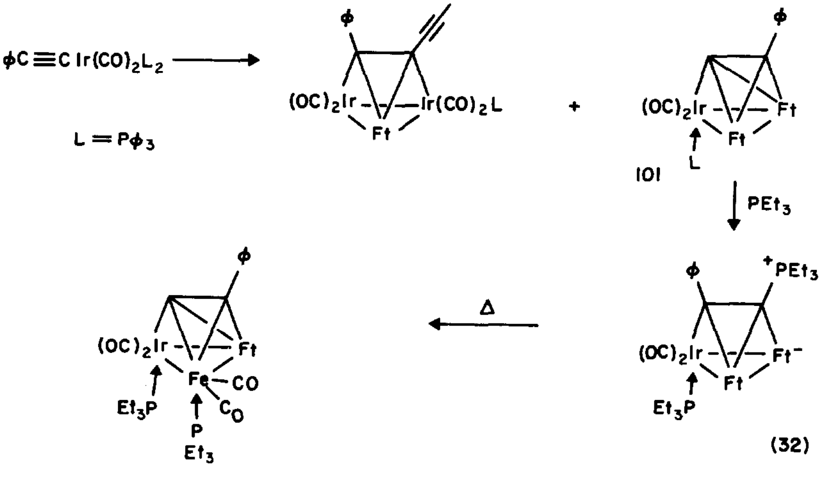


102

Anionic trinuclear clusters $\mathrm{Fe_2Mn(CO)_{12}^-}$, $\mathrm{Fe_2Re(CO)_{12}^-}$, and $\mathrm{CpNiFe_2(CO)_8^-}$ were synthesized by reaction of $\mathrm{Fe_3(CO)_{11}^{2-}}$ or $\mathrm{Fe_4(CO)_{13}^{2-}}$ with $\mathrm{(OC)_5MBr}$ (M = Mn, Re) or $\mathrm{CpNi(PPh_3)Cl}$. The anion in $\mathrm{PPN^+Fe_2Mn(CO)_{12}^-}$ showed disorder in the crystal, like that in $\mathrm{Fe_3(CO)_{12}}$. The crystal structure of the $\mathrm{Fe_2Ni}$ anion showed carbonyl groups bridging the two Fe–Ni bonds [492]. A μ_3-arrangement of the carbyne ligand in $\mathrm{CpRhFe_2H(CO)_7(\mu_3\text{-}CR)}$, in contrast to the prevailing μ_2 bonding mode in $\mathrm{Fe_3H(CO)_{10}(\mu_2\text{-}CR)}$, has been attributed to the directionality of the orbitals of the Rh(CO)Cp unit, based upon Extended Hückel calculations [496]. Cocondensation of cobalt atoms, mesitylene, and $\mathrm{Fe(CO)_5}$ at −196°C or condensation of cobalt atoms into a solution of mesitylene and $\mathrm{Fe(CO)_5}$ in methylcyclohexane at −120°C led to formation of cluster **100** [XRC]. Use of nickel atoms, pentamethylcyclopentadiene, and $\mathrm{Fe(CO)_5}$ led to the isoelectronic product $\mathrm{(Cp^*Ni)_2Fe(CO)_3(\mu_3\text{-}CO)_2}$. Several $\mathrm{Ni_1}$ and $\mathrm{Ni_2}$ byproducts also formed [72].

Reactions of the electrophilic methylene group of $\mathrm{Co_2Fe(CO)_9(\mu_3\text{-}C{=}CH_2)}$ with soft nucleophiles [$\mathrm{PR_3}$, $\mathrm{Me_2SO}$, $\mathrm{CN^-}$, $\mathrm{SCN^-}$, $\mathrm{CHXE^-}$ (X = Br, CN, E), and $\mathrm{ECH{=}PPh_3}$] led to formation of zwitterionic or anionic $\mathrm{Co_2Fe(CO)_9(\mu_3\text{-}CCH_2Nu)}$ adducts [XRC, Nu = $\mathrm{PMe_3}$]. The phosphine adducts rearranged, with car-



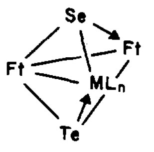
(32)

bonyl loss, to $Co_2Fe(CO)_9(PR_3)(\mu_3\text{-}C{=}CH_2)$ upon heating. The malonate addition product could be protonated at iron; warming the product resulted in hydrogen evolution, forming a substituted vinylidene product, $Co_2Fe(CO)_9(\mu_3\text{-}C{=}CHCHE_2)$ [523].

Iron-iridium clusters were formed in the reaction of $PhC{\equiv}C\text{-}Ir(CO)_2(PPh_3)_2$ with iron carbonyls [eqn. (32)]. Substitution reactions of phosphines showed substantial mobility of the alkynyl ligand relative to the Fe_2Ir unit [524]. Like the phosphine, hydride from R_3BH^- attacked **101** at the β-carbon of the phenylethynyl moiety; protonation of the resulting anion gave a Fe–Fe bridging hydride. Direct hydrogenation of **101** gave the same product, accompanied by its alkylidene isomer, $Ph_3PIrFe_2(CO)_8(\mu\text{-}H)(\mu_3:\eta^2\text{-}C=CHPh)$ [XRC]. The latter was also formed thermally from $Fe_2Ir(CO)_8(\mu\text{-}H)(\mu_3\text{: }\eta^2\text{-}HCCPh)$. Mono-, di-, and tri-gold derivatives of these Fe_2Ir clusters were also prepared [525].

As part of a comparison of structures and properties of *closo* acetylene and acetylide clusters, $CpNiFe_2(CO)_6(\mu_3\text{: }\eta^2\text{-}C{\equiv}CCHMe_2)$ has been prepared from $CpNi(CO)_2$, $Ph_2PC{\equiv}CCHMe_2$, and $Fe_2(CO)_9$. Its structure and that of $CpNiFe_2(CO)_5(PPh_3)$ $(\mu_3:\eta^2\text{-}C{\equiv}CCMe_3)$ were determined. The acetylide complexes showed shorter metal–C_α distances and larger M–C_α–C_β angles than acetylene complexes such as $Fe_3(CO)_9(RCCR)$ [526]. The allenyl complex **102** [XRC, M = W, R = Ph] was formed from **88** in reaction with $Fe(CO)_5$ [477]. Another example (M = W, R = vinyl) resulted, along with **10** and **78**, from direct reaction of $CpW(CO)_3\text{-}CH_2\text{-}C{\equiv}C\text{-}CH{=}CH_2$ with $Fe_2(CO)_9$ in hexane at room temperature [97]. A closely related carborane analog was formed through the interaction of $Fe_2(CO)_9$ with $(\eta^5\text{-}Me_2C_2B_9H_9)W(CO)_2{\equiv}C\text{-}C{\equiv}C\text{-}CMe_3$. In this product [XRC], the $(\mu_3\text{: }\eta^1,\eta^2,\ \eta^2$-allenyl) fragment was also linked to the carborane through a ketone group [527].

50-Electron complexes **103** [ML_n = $Ru(CO)_3$, CpCo] have been synthesized from $Fe_2(CO)_6(\mu\text{-}SeTe)$ by reaction with $Ru(CO)_4(C_2H_4)$ or $CpCo(CO)_2$. The CpCo group was replaced from the Fe_2Co cluster by a $Pt(PPh_3)_2$ group, upon reaction with $Pt(PPh_3)_4$ [528].



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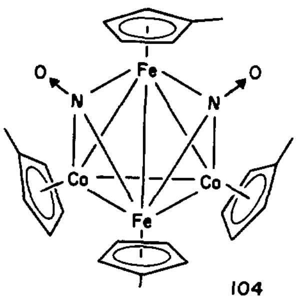
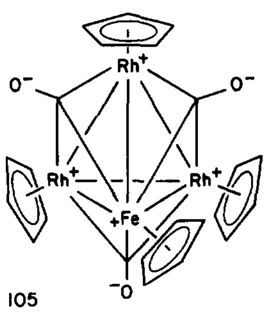


104

11. Tetra- and polynuclear cluster compounds

Proton spin–lattice relaxation studies of $H_2FeM_3(CO)_{13}$ (M = Ru, Os) have been carried out. Since the relaxation rates are dominated by the intramolecular dipolar interaction with other protons, the different rates of the H,H and H,D isotopomers could be related to structure [529]. Preparation of $HFe_3Ir(CO)_{12}^{2-}$ by reaction of $HFe(CO)_4^-$ and $Ir(CO)_3Br$ in a 3:1 ratio, and its protonation to form $H_2Fe_3Ir(CO)_{12}^-$ have been described [530].

Reaction of $[Cp'Fe(NO)]_2$ and an excess of $Cp'Co(C_2H_4)_2$ resulted in formation of $Cp'_4Co_2Fe_2(\mu_3\text{-}NO)_2$, **104** [XRC], along with previously described trimetallic clusters. **104** showed the tetrahedral array of metal atoms expected for a 60-electron cluster, supported by two Fe_2Co face-bridging nitrosyls [518]. The two nitrosyls could be replaced by three carbonyls, as found in the cationic cluster $Cp_4FeRh_3(\mu_3\text{-}CO)_3^+PF_6^-$, **105**. This compound was synthesized by reaction of $CpFeAn^+$ with $[CpRh(\mu\text{-}CO)]_3$; the yield was best (65%) when the displaced arene was nitrobenzene. The xylene complex gave a 24% yield, and the benzene complex only 6%. Photolysis of the cluster in acetone gave back $[CpRh(CO)]_3$, presumably along with $CpFe(OCMe_2)_3^+$ [531].



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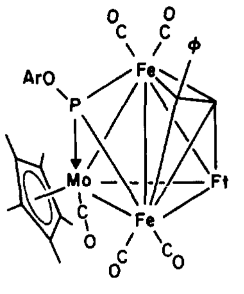

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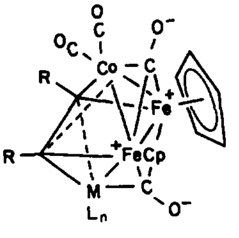
Displacement reactions of ligands with $HFeCo_3(CO)_{12}$ have been studied with the aid of ^{59}Co NMR spectroscopy. Monosubstitution led to derivatives $HFeCo_3(CO)_{11}L$ [L = PPh_2H, $P(C_6H_{11})_2H$, PPh_3, NMe_3, SMe_2] with the ligand L axially bound to cobalt. The crystal structure of the diphenylphosphine compound was determined. Further substitution with trimethylamine (introduced using trimethylamine oxide) gave the disubstituted product in which all three cobalt atoms were distinguishable in the NMR spectra [532]. The 60-electron cluster **106** resulted from reaction of **87** with an excess of $Fe_2(CO)_9$ at 85°C. In formation of **106**, the alkynyl carbon–phosphorus bond was cleaved to form phosphinidene and alkynyl ligands [475]. A sulfur-supported tetrahedral cluster, $(CpCr)_3(\mu_3\text{-}S)_3FeSPh$ [XRC], was prepared in 52% yield through



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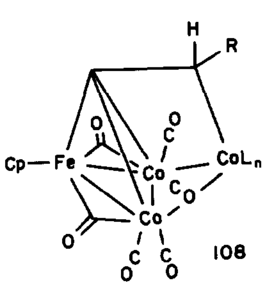
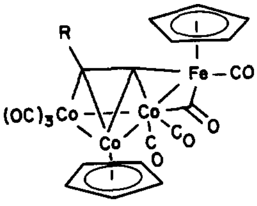


108

interaction of $Fe_2(CO)_6(\mu\text{-SPh})_2$, $(CpCr)_2(\mu\text{-S})(\mu\text{-SCMe}_3)_2$, and trimethylamine oxide [533].

Refluxing Fp_2 with $Co_2(CO)_6(\mu\text{: }\eta^2,\ \eta^2\text{-RCCR})$ (R = CF_3, CO_2Me) in octane afforded the isoelectronic clusters $(CpFe)_2Co_2(CO)_4(\mu_3\text{-CO})_2(\mu_4\text{-RCCR})$ and $(CpFe)_3Co(CO)_2(\mu_3\text{-CO})_2(\mu_4\text{-RCCR})$, assigned structures **107** [ML_n = CpFe or $Co(CO)_2$, respectively]. Although they are 60-electron clusters, the proposed structures contain a butterfly arrangment of metals, and therefore are electron-deficient. Thermolysis of **107** [$ML_n = Co(CO)_2$] in toluene in the presence of Me_3NO resulted in formation of electron-precise bis(alkylidyne) clusters $(CpFe)_2Co_2(CO)_5(\mu_3\text{-CR})_2$. Also formed in the reaction were cobaltole and Co_4 clusters. Terminal acetylene complexes $Co_2(CO)_6(\mu\text{: }\eta^2,\ \eta^2\text{-RCCH})$ gave, besides analogs of **107**, 62-electron vinylidene complexes **108** [$L_n = (CO)_3$] and 64-electron alkynyl clusters **109**. Heating **108** [$L_n = (CO)_3$] in toluene resulted in displacement of the carbonyl ligands from the wingtip cobalt by toluene, forming **108** ($L_n = \eta^6$-PhMe, R = CF_3); [XRC]. Both **108** and **109** showed structures consistent with their electron count [481].



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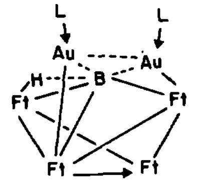

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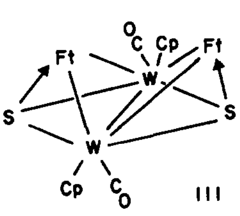
The butterfly compound $HFe_4(CO)_{12}C\text{-}BH_2$ was prepared by reaction of $Fe_4(CO)_{13}^{2-}$ with $H_3B \leftarrow SMe_2$ followed by protonation. Boron-substituted derivatives $HFe_4(CO)_{12}C\text{-}BHX$ (X = H, Cl, Br, OH) and $HFe_4(CO)_{12}C\text{-}BX_2$ (X = Cl, Br) were prepared by reaction with AlX_3. The iron-carbide cluster served to shield the borane sterically and to donate electrons from the $C\text{-}Fe_{\text{wingtip}}$ bonds to the boron 2p orbital. Triethylamine did not form an adduct with the boron, but instead deprotonated the cluster [534]. The crystal structure of $Fe_4(CO)_{12}BH[AuAsPh_3]_2$, **110**, showing the gold groups bridging $Fe_{\text{wingtip}}\text{-}B$ and $Fe_{\text{hinge}}\text{-}B$ edges, has been determined [535]. The NMR properties of the pseudo-interstitital atoms in Fe_4A and Fe_3MA (A = B, C, N) clusters have been related to the degree of steric compression experienced by A upon incorporation into the cluster. The deshielding observed for carbon and, especially, boron reflects substantial compression. Nitrogen, in contrast, experiences little or no compression and exhibits normal chemical shifts [536].

The 62-electron butterfly cluster $Fe_2Pt_2(CO)_7(\mu\text{-CO})_2L_4$ (L = PEt_3) was one of several products which resulted from reaction of *cis*-PtL_2Cl_2 and $Fe(CO)_4^{2-}$. The two platinum atoms formed the body of the butterfly, and the two irons the wingtips. Each bore one triethylphosphine ligand, and one iron shared bridging carbonyls with the two platinum atoms [513]. The crystal structure of a sulfur-supported butterfly cluster, $(CpWCO)_2Fe_2(CO)_6S_2$, **111**, has been reported [537]. In contrast, the isoelectronic 62-electron clusters $Fe_2Ru_2(CO)_{11}SeTe$ and $Fe_3Ru(CO)_{11}SeTe$ adopted an overall octahedral structure, **112**, having a planar array of metal atoms and four-coordinate Group 16 atoms. The compounds were prepared by reaction of $Ru(CO)_4(C_2H_4)$ with $Fe_2M(CO)_9(\mu_3\text{-Se})(\mu_3\text{-Te})$ (M = Fe, Ru) [538]. The apparent electron-deficiency in **112** might be relieved by selenium or tellurium acting as a six-electron donor rather than four as shown. However, this is not possible in the structurally analogous nitrene-bridged clusters $FeM_3(CO)_{11}(\mu_4\text{-NEt})_2$ (M = Fe, Ru), prepared from $FeM_3(CO)_{12}(EtNNEt)$ or $M_3(CO)_9(\mu_3\text{: }\eta^1,\ \eta^1,\ \eta^3\text{-EtNNEt})$. In the Fe_4 compound, the Fe–Fe bonds reflected the unsaturation of the cluster in their shortness (2.40 ± 0.01 Å) [519]. Calculations on the hypothetical clusters $Fe_4(CO)_{12}(\mu_4\text{-N})_2^{2+}$ and $Fe_4(CO)_{11}(\mu_4\text{-N})_2$ have suggested that they may be capable of existence, possibly with an N–N bond penetrating the Fe_4 plane [539].



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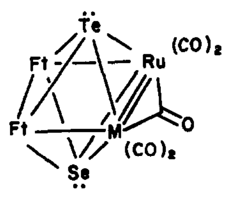
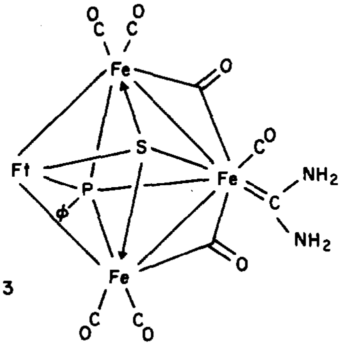


112

The cluster $Fe_4(CO)_{11}(\mu_4\text{-PCMe}_3)_2$ was reduced by phenyl-lithium to the 63-electron radical anion. Ethylation occurred at the oxygen of the bridging carbonyl group, giving a persistent radical species. The crystal structure was little changed from that of the 62-electron parent [540].

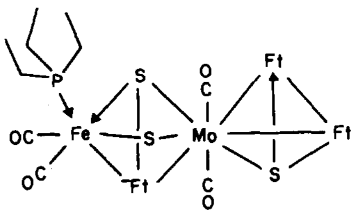
Reaction of $Fe_3(CO)_9(\mu_3\text{-PCHMe}_2)(\mu_3\text{-Te})$ with $Fe_2(CO)_9$ in toluene led to formation of $Fe_4(CO)_{11}$

(μ_4-PCHMe$_2$)(μ_4-Te), whose crystal structure showed an octahedral arrangement of atoms, consistent with a 64-electron cluster resulting from Te acting as a six-electron donor [510]. The sulfur analog of this cluster has been prepared, as has a derivative bearing a diaminocarbene ligand, **113**, both obtained from the reaction of $Fe_3(CO)_8[C(NH_2)_2](\mu_3\text{-PPh})(\mu_3\text{-S})$ with $Fe_2(CO)_9$. The carbene ligand in the latter was found to render the synthesis "considerably easier" [541].



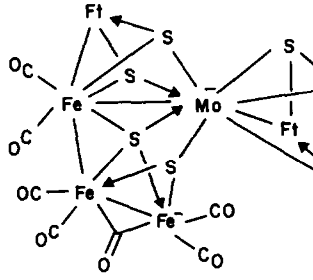
113

Crystals of $(CpFe)_4S_4^+PF_6^-$ showed polymorphism, but similar molecular structures resulted from both crystal forms investigated [542]. $(CpFe)_4S_4$ was used as an "electron mediator" in catalyzing the incorporation of CO_2 into ethanolamines, to form 2-oxazolidines [543].



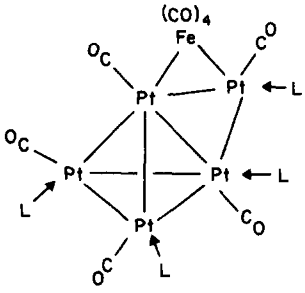
114

Sulfur bridges supported the molecular structures of several Fe-Mo clusters of higher nuclearity, formed in the reaction between $Fe_2(CO)_6S_2^{2-}$ and $Mo(CO)_4I_3^-$. Structures were reported of salts of $Mo_2Fe_2S_2(CO)_{12}^{2-}$, which showed two $FeMo(CO)_6S$ units conjoined through additional Fe–S bonds, $MoFe_4S_3(CO)_{13}(PEt_3)^{2-}$, **114**, and $MoFe_6S_6(CO)_{16}^{2-}$, **115**. Schemes including partial oxidation of the $Ft_2S_2^{2-}$ starting material before condensation were proposed, and the relevance of these products to the FeMo-cofactor of nitrogenase was discussed [544]. Oxidation of $(\mu\text{-SCMe}_3)(CpCr)_2(\mu_3\text{-S})_2Fe(CO)_3$ with iodine led to loss of the carbonyl groups from iron and formation of $[(\mu\text{-SCMe}_3)(CrCp)_2(\mu_3\text{-S})_2]_2Fe^+FeI_4^-$ [XRC]. Prolonged treatment with selenium powder led to formation of $Fe_2(\mu\text{-Se}_2)[(\mu_3\text{-S})_2(CrCp)_2(\mu\text{-SCMe}_3)]_2$ [XRC] [545]. A nonanuclear cluster, $Fe_3(CrCp)_6(CO)_3S_9$ [XRC], was formed in a similar way, by oxidative decarbonylation of $Fe_2(CO)_6(SPh)_2$ in the presence of $(CpCr)_2(SCMe_3)_2S$. This product showed quasi-cubic Cr_3FeS_4 units joined through the iron vertices by a $[SFe(CO)_3]$ bridge [533].

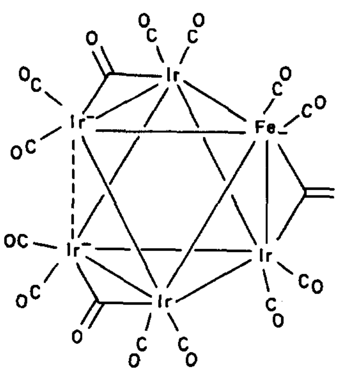


115

Column chromatography of the reaction mixtures from $PtCl_2(CO)L$ or $PtCl_{12}L_2$ and iron carbonyl anions, which initially contained $FePt_2$, Fe_2Pt, and Fe_2Pt_2 clusters, led to cluster condensation, forming the hexanuclear cluster **116** (L = PEt_3) [513]. The trianion $FeIr_5(CO)_{15}^{3-}$, **117**, [XRC] was prepared by incorporating an additional iridium into $FeIr_4(CO)_{15}^{2-}$ using $Ir(CO)_4^-$. It was monoprotonated using one equivalent of acid, but an excess of acid led to an unstable dihydride, which transformed at room temperature into $FeIr_5(CO)_{16}^-$ [XRC]. The electrochemistry of these clusters was studied in order better to understand their interconversions [530]. Salts of $Fe_2Rh_4(CO)_{16}^{2-}$, sup-



116



117

ported on metal oxide surfaces and mildly oxidized, served as catalysts for formation of 4,6-dimethyl-2-pyrone by cycloaddition of propyne and carbon dioxide [546].

Adsorption of ethene onto a hydrogen-saturated Fe(100) surface resulted in formation of ethyl groups, but no ethane. Coadsorption of ethene and CO, however, resulted in formation of ethane at 170 K, a result consistent with weakening of Fe–H bonds by adsorbed CO. Effects of competition between ethene and CO for surface sites were studied [547]. At 110 K, ethene adsorbed reversibly on a hydrogen-saturated Fe(100) surface. Warming to 160 K resulted in desorption in competition with ethyl group formation. Decomposition of surface-bound ethyl groups by "β-hydride elimination" occurred with an activation barrier of 51 kJ mol^{-1} and a primary isotope effect at 219 K of 4.9 ± 0.5 [549]. Hydrogen exchange reactions of higher alkenes on deuterium-saturated Fe(100) were also studied. Below 200 K, propene and 1-butene desorbed without incorporation of deuterium. Above 200 K, deuterium was incorporated into alkenes, and deuterated alkanes were also formed. The deuteration sites suggested formation of primary alkyl groups on the iron surface [549].

12. Postscript

At 549 references, this review includes somewhat more references than 1990's [504]. Some of the difference is due to the inclusion this year of some material on ferrocenes. Allowing for that, there is a fairly constant amount of work on organoiron chemistry being published annually, which has averaged 536 papers during the last six years.

13. List of abbreviations used

An	any arene ring, such as benzene or naphthalene
Ar	an aryl ring, such as *p*-tolyl, MeC_6H_4-
Bu	butyl, C_4H_9
Cp	cyclopentadienyl, C_5H_5
Cp′	methylcyclopentadienyl, C_5H_4Me
Cp*	pentamethylcyclopentadienyl, C_5Me_5
DMF	N,N-dimethylformamide
depe	1,2-bis(diethylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	1,2-bis(dimethylphosphino)methane
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
E	an ester group, usually carbethoxy or carbomethoxy
Et	ethyl, C_2H_5
Fp	cyclopentadienyldicarbonyliron, $CpFe(CO)_2$
Fp′	cyclopentadienyl(carbonyl)(triphenylphosphine)iron
Fp*	(pentamethylcyclopentadienyl)dicarbonyliron, $Cp^*Fe(CO)_2$
Ft	a tricarbonyliron group, $Fe(CO)_3$
L	a two-electron donor ligand, such as a phosphine
M	any transition metal
Me	methyl, CH_3
Nu^-	a nucleophile
Ph	phenyl, C_6H_5, also shown as φ in structures
Por	any porphyrin ligand, coordinated as a dianion
PPN^+	$Ph_3P=N=PPh_3^+$
Pr	propyl, $CH_2CH_2CH_3$
R	any unicovalent organic group such as methyl
TCNE	tetracyanoethylene
THF	tetrahydrofuran
Tf	trifluoromethanesulfonyl group, F_3CSO_2
X	any halogen
[XRC]	X-ray crystal structure reported for this compound

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