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Organoiron chemistry. Annual survey for the year 1992 *

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Contents

1. Introduction

In this Annual Review I attempt to cover the organoiron chemistry reported in journals published during calendar year 1992. 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 review.

The material is organized more-or-less by the Gmelin system, first by increasing number of conjoined iron atoms, then by increasing hapticity of principal organic ligand. The latter is determined by the principle of last position. Thus, (η^3-allyl)(η^5-cyclopentadienyl)(η^2-ethene)iron would be treated with cyclopentadienyliron compounds rather than with allyl- or alkene-iron compounds. However, for purpose of brevity, many reactions of dimers such as dicyclopentadienyltetracarbonyldiiron [Fp_2, $Cp_2Fe_2(CO)_4$], in which

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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. The use of the arrow to denote bonding of alkenes to metals, though common, is inappropriate in view of the major role played by back bonding and the consequent lack of formal charges.

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

2. Reference works and review articles

With the publication of two additional volumes during 1992, the current Gmelin organoiron series has been nearly completed. Newly published are Volume B19 [1], which covers mononuclear organoiron compounds with one η^6 and one η^5 or η^6 ligand, and Volume C6b [2], which covers trinuclear compounds with simple ligands, mostly carbonyls. Volume B19 includes a guide to the entire organoiron series. To complete the series, only an expected volume on highly substituted and bridged ferrocenes, Volume A11, remains.

P. Helquist has contributed a detailed review on "Development of Carbene Complexes of Iron as New Reagents for Synthetic Organic Chemistry" in a recent multi-author volume [3]. M.E. Welker has described "[3 + 2] Cycloaddition Reactions of Allylic and Propargylic Transition Metal Complexes" in a recent *Chemical Reviews* article [4]. In both of these reviews, most of the examples involved derivatives of Fp[$CpFe(CO)_2$] systems or phosphine-substituted analogs.

Oscillator strengths for inner-shell excitation in the gas phase of several types of organoiron compounds, including carbonyls, diene complexes, and ferrocenes, have been derived from electron energy loss spectra. Comparison with spectra of the free ligands and with previous studies provided insights into the effects of iron-ligand bonding on core excitation [5].

3. Reactions of "naked" iron atoms and ions

Theoretical calculations on the geometries and dissociation energies of $FeCH_{1-3}$ and $FeCH_{1-3^+}$ have been explored using various effective core potential models. The Hay and Wadt HW3 model satisfactorily reproduced the trends in Fe–C bond energies of the cations, giving values about 80% of the experimental values [6,7]. The importance of correlation effects was emphasized in calculations on a series of $M{=}CH_2^+$ cations, with M = Sc–Cu [8]. With optimized geometries, the computed binding energies were in good agreement with experimental results [9].

Interaction of iron atoms and ions with methane, leading to oxidative addition, have been investigated by qualitative MO methods. The extent of interaction and occurrence of oxidative addition were greatest for Fe^- and least for Fe^+, suggesting C–H bond activation through metal-to-methane electron transfer [10]. *Ab initio* calculations on interactions of Fe^+ (and other M^+) with ethene have also been reported. The stable species was characterized as an "electrostatic complex" [11]. Coordination of aldehydes and ketones to organometallic fragments was assessed by use of Extended Hückel methods, with the results favoring η^2 coordination to $C_{2v}d^8$ moieties such as $Fe(CO)_2(PR_3)_2$ and η^1 coordination to d^6 $CpML_2$ fragments such as Fp^+, both in agreement with experimental findings [12]. Binding of Fe^+ (and other M^+) with benzene, as indicated by *ab initio* calculations, was largely electrostatic in nature, but calculated binding energies were significantly increased upon inclusion of correlation, which is required to account for back bonding. Calculated binding energies were 214 kJ mol^{-1} for the ^6D state of Fe^+ and 237 kJ mol^{-1} for the ^4F state. Experimental values are 230 ± 20 kJ mol^{-1} [13].

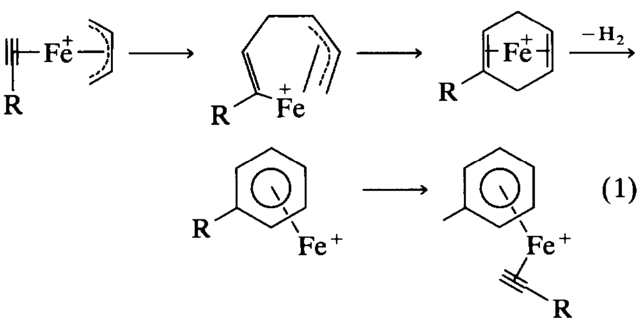
Calculations have also been performed on the insertion of neutral metal atoms, including Fe, into the oxirane C–O bond. The metallacyclic product was energetically favored relative to the starting materials and also relative to [Fe=O + ethene] [14].

Experimental studies of interaction of Fe^+ with organics are becoming ever more informative as they allow discrimination among isomeric species. Thus, the two $FeC_2H_6^+$ species which result respectively from reaction of Fe^+ with ethane $[Fe{-}(C_2H_6)]^+$ and with acetone $[Fe(CH_3)_2]^+$ have been distinguished by threshold collisional activation in a guided ion beam mass spectrometer. Somewhat surprisingly, the former is more stable by about 15 ± 7 kJ mol^{-1} [15]. Likewise, the structures and energies of isomeric $Fe(C_3H_6)^+$ species produced by reaction of Fe^+ with propane, cyclopropane, propene, and cyclobutanone have been defined. $Fe(propene)^+$ (b.d.e. 165 kJ mol^{-1}) was more stable than the ferracycle (b.d.e. 133 kJ mol^{-1} [16]. The results of reaction of Fe^+, formed by electron impact on $Fe(CO)_5$, with propane have been correlated with the electronic state of the ion. The ^6D ground state formed the adduct $Fe(C_3H_8)^+$ despite the presence of the 4s electron, as a result of crossing to the more strongly bound ^4F state. The ^4D second excited state of Fe^+ reacted with substantial dehydrogenation [17].

Reaction of Fe^+ with methyl formate resulted in formation of $HCOOFe^+$ [18]. Reaction of Fe^+ with 2-ethylbutanenitrile, studied by FTICR spectroscopy, was found to occur by three paths: an ion/dipole mechanism which leads to $FeHCN^+$, remote functionalization leading to loss of dihydrogen and ethene from the ends of the chains, and C–CN insertion which eventuates in loss of methane. A comparison of results from sector mass spectrometric studies showed reasonable consistency [19]. Reactions with tertiary isocyanates produced mainly $Fe(HNCO)^+$ by loss of alkene and $Fe(alkene)^+$ by loss of HNCO. An ion/dipole mechanism was invoked [20]. Reaction of Fe^+ or $CpFe^+$ with 1,3,5-trisilacyclohexane resulted in loss of up to three moles of dihydrogen, suggesting formation of a trisilabenzene [21]. $CpFe^+$ formed $CpFeO^+$ and $CpFeO_2^+$ upon reaction with oxirane [22].

Gas phase oxidation of methane by FeO^+ has been studied, and several isomeric intermediates characterized, by collisional activation mass spectrometry. The initial encounter complex, $(CH_4)FeO^+$, underwent isomerization to $CH_3\text{-}Fe\text{-}OH^+$, $(CH_3OH)Fe^+$, and $CH_2{=}Fe(OH_2)^+$, which are converted upon further collisional activation to the final products $FeOH^+$, Fe^+, and $Fe{=}CH_2^+$, respectively. Decarbonylation of glycolaldehyde or acetic acid gave mixtures of $MeFeOH^+$ and $CH_2{=}Fe(OH_2)^+$ [23]. A large isotope effect was observed in reaction of $FeMe^+$ with water, with H_2O giving 94% $FeOH^+$ and D_2O giving 96% $MeFe(OD)_2^+$. Methanol gave $FeOMe^+$. The mechanism involved hydrogen migration from O to Fe in the initial complex, $MeFe(OHR)^+$, followed by reductive elimination of methane [24]. A metathesis reaction between $Fe{=}CH_2^+$ and 1,7-octadiene resulted in formation of $Fe(C_2H_4)^+$ by a mechanistically clean process. Also formed cleanly in a process traceable by isotope labelling was $Fe(C_6H_6)^+$; products $Fe(C_3H_4)^+$ and $Fe(C_4H_6)^+$ resulted from complex sequences of pathways [25].

Reaction of iron carbonyl cations, $Fe(CO)_n^+$ (n = 0–5) with atomic hydrogen or nitrogen led to carbonyl displacement to form $HFe(CO)_{0-3}^+$ or $NFe(CO)_{0,1}^+$ [26]. The $C_6H_6Fe^+$ cation produced by electron impact on FpMe has been found by collisional activation to consist of a mixture of $Fe(benzene)^+$ and $Fe(pentafulvene)^+$ ions. The two independent routes which led to the two isomers differed in the sequence of loss of H_2 and CO [27]. The gas phase complexes of Fe^+ with either norbornadiene or quadricyclane were found to be identical by collisional decomposition, and probably to be identified as $Fe(norbornadiene)^+$. This species reacted further to form $CpFeH(C_2H_2)^+$. Toluene and cycloheptatriene gave similar Fe^+ adducts $[C_7H_7\text{-}FeH^+]$, but these did not intervonvert with those of norbornadiene [28]. $Fe(1,3\text{-butadiene})^+$ reacted very readily with ethyne or propyne as shown in eq. (1).



(1)

Reaction with ethyne-d_2 yielded > 97% elimination of H_2, consistent with the mechanism shown. Ligand coupling did not result with ethene and propene; the adducts $Fe(alkene)(butadiene)^+$ simply redissociated upon collisional activation [29]. $Fe(Butadiene)^+$ reacted with ethanol or propanol in part by interligand two-hydrogen transfer from the alcohol to the butadiene, but competing processes obscured the details [30].

Iron carbonyl anions $Fe(CO)_{1-4}^-$ have been studied in the gas phase, with metal carbonyl bond energies being measured by energy-resolved collision-induced dissociation. Combination of these bond energies with literature electron affinities has allowed estimation of the bond energies of the sequence of neutral iron carbonyls as well. Results have been compared with previous measurements [31]. Reaction of $Fe(CO)_4^-$ with organic electrophiles has been studied by FTICR. Reactivity depended directly upon the electron affinity of the electrophile, and reaction usually resulted in carbonyl displacement [32]. $Fe(CO)_3^-$ underwent addition to propene, butadiene, cyclopentadiene, and benzene, whereas allene and ethyne gave some competitive substitution. $Fe(CO)_2^-$ reacted with propene to form $(OC)_2FeH(\eta^3\text{-}C_3H_5)^-$ and with benzene to form $(OC)_2Fe(\eta^{4?}\text{-}C_6H_6)^-$. Reaction of $Fe(CO)_{2,3}^-$ with cyclopentadiene formed $CpFeH(CO)_{1,2}^-$ [33]. Cyclopropane and $Fe(CO)_2^-$ reacted to form $(OC)_2FeH$-

$(C_3H_5)^-$ along with a greater amount of $(OC)_2Fe(C_3H_4)^-$, the latter thought to contain a π-cyclopropene ligand [34]. Reactions of iron carbonyl anions with silanes and germanes have also been studied [35].

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 sigma bonds (and no carbonyl groups), but also a number of 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 interst 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.

The stabilities of dihydrogen complexes $ML_n(\eta^2\text{-}H_2)$ have been correlated with the electrochemical reduction potentials of the corresponding dinitrogen complexes $ML_n(N_2)$. Those with too high potential are found to lose dihydrogen spontaneously at room temperature; those too low to form dihydrides. For iron, this criterion translates into a need for good electron donor ligands, as indeed are found in the most common iron dihydrogen complexes, $FeH(H_2)L_4^+$. Also consistent with the correlation is the lability of $H_2Fe(H_2)(PEtPh_2)_3$ [36]. Calculations have been carried out on the orientation of the H_2 ligand in the latter complex, which was found to depend upon a balance between back-donation from iron and a "*cis* effect" favoring alignment of Fe–H and Fe–H_2 bonds [37]. *Ab initio* calculations have also been carried out on intramolecular hydrogen exchange in *cis*-$FeH(H_2)(PR_3)_4^+$ complexes; the favored mechanism was an "open direct transfer" involving an open H_3 ligand in the transition state [38]. The barrier to dihydrogen rotation in $FeH(H_2)PP_3^+BPh_4^-$ [$PP_3 = P(CH_2CH_2PPh_2)_3$] has been measured by inelastic neutron scattering to be 7.6 kJ mol^{-1}, greater than in the ruthenium analog [39]. This compound catalyzes hydrogenation of terminal alkynes to alkenes *via* a mechanism involving decoordination of one phosphine arm of the ligand and formation of a σ-alkenyl intermediate [40].

Reaction of $FeH(H_2)L_4^+$ [$L = P(OEt)_2Ph$] with $NO^+PF_6^-$ at low temperature led to formation of $Fe(NO)L_4^+PF_6^-$. Reaction with CO or isocyanates led to displacement of two phosphorus ligands [41]. The crystal structure of $Fe(dppe)(NO)_2$, prepared directly from $Fe(CO)_5$, $NaNO_2$, and dppe, has been reported [42].

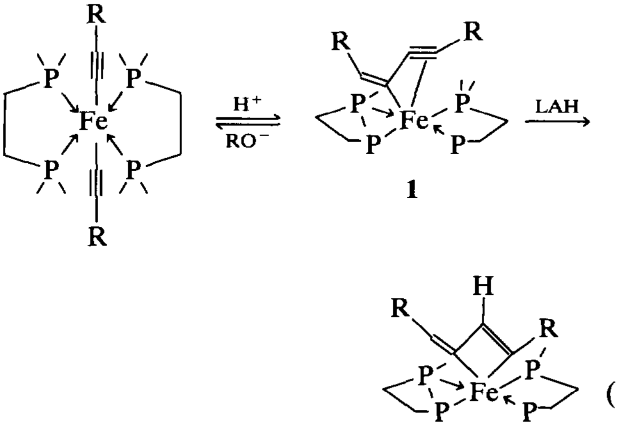
The *ate*-complex $[Li(OEt_2)^+]_4\ FePh_4^{4-}$, from reaction of excess phenyl-lithium with $FeCl_3$, added dihydrogen under one atmosphere pressure at room temperature, forming $[Li(OEt_2)^+]_4\ [\textit{trans}\text{-}H_2FePh_4^{4-}]$. The crystal structure showed normal Fe–C bond lengths of 2.056 Å and Fe–H bond lengths of 1.64 Å. In THF the dihydride underwent loss of biphenyl, forming the binuclear species $[Li(THF)^+]_5[Ph_3Fe(\mu\text{-}H)_3FePh_3]^{5-}$. The latter showed a short Fe–Fe distance of 2.389 Å and reduced dinitrogen [43]. A series of metastable methyl–iron compounds (and some butyl and octyl analogs) has been produced by reaction of methyllithium with $FeCl_3$ in ether [eqn. (2)]. The various

$$FeCl_3 \xrightarrow[\substack{-1/2Me_2 \\ -2\,LiCl}]{2\,MeLi} MeFeCl \xrightarrow[-LiCl]{MeLi} Me_2Fe \xrightarrow{MeLi} Li^+FeMe_3^- \xrightarrow{MeLi} Li_2^+FeMe_4^{2-} \qquad (2)$$

intermediates were said to be stable to −20°C or better, with $LiFeMe_3$ stable to room temperature. The organoiron compounds reacted selectively with β-bromostyrene rather than with ketones [44]. Li_2FeMe_4 was found to be a very effective methylating agent toward vinylic bromides at −78°C, the reaction being unaffected by alcohol or cyano groups as well as ketone groups [45]. $LiFeMe_3$ methylated the *ortho* position of the unsubstituted phenyl ring of PhN=N-*p*-C_6H_4Y ($Y = NMe_2$, NH_2, OMe) [46]. The analogous reagent $NCCH_2FeCl$ has been prepared and used for cyanomethylation of carbonyl compounds, aldehydes being much more reactive than ketones [47]. β-Functionalized ketones were less readily attacked than simple ones, a phenomenon termed "anticheleselectivity" [48].

The catalysis of the Kharasch reaction between ethylmagnesium bromide and various alkyl bromides by *trans*-$Fe(depe)_2Br_2$ has been investigated. The reaction, which forms predominantly alkanes and ethene, involves $[Fe(depe)_2EtBr]^{n+}$ intermediates reacting with free radicals by β-hydrogen abstraction [49]. A catalyst for [4 + 4] cyclization of dienes was prepared by reaction of $(RN{=}CH{-}CH{=}NR)FeCl_2$ [R = (1*R*)-methyl] and $(C_4H_6)Mg \cdot 2THF$. Heterodimerization of 1-pentadiene and 2-methylbutadiene gave 1,7-dimethylcycloocta-1,5-diene in 61% e.e. [50]. Dehydrobromination of 1,2-dibromo-1,1-diphenylethane was effectively catalyzed by iron metal, as well as by iron bromides. Spectroscopic detection of organoiron intermediates in solution was claimed [51].

The bulky chelating diphosphine, 1,2-bis(dibutylphosphino)ethane, $Bu_2PCH_2CH_2PBu_2$, dbpe, has been converted to its $FeCl_2$ derivative and thence to bis(acetylides), *trans*-Fe(dbpe)$_2$(C≡CR)$_2$ [52]. Bis(acetylide) complexes Fe(dmpe)$_2$(C≡CR)$_2$ underwent ligand coupling upon treatment with trifluoroacetic acid to form η^3-butenynyl complexes, **1**, which could in turn be reduced to η^2-butadienediyl complexes [eqn. (3)] [53]. Complex **1** (R = Ph) was also produced by



(3)

reaction of Fe(dmpe)$_2$H$_2$ with diphenylbutadiyne [53]. Analogous butenynyl complexes, Fe[P(OEt$_2$Ph]$_4$(η^3-RCHC$_3$R)$^+$ (R = *p*-tolyl, *tert*-butyl, trimethylsilyl), resulted, along with alkenes RCH=CH$_2$, from reaction of the dihydrogen complex FeL$_4$H(H$_2$)$^+$ with terminal alkynes [54]. The triethyl phosphite complex, in contrast, formed σ-acetylide derivatives, Fe[P(OEt)$_3$]$_5$ (C≡CR)$^+$, and alkenes upon reaction with terminal alkynes [54]. As already noted, the tetraphosphine analog, FeH(H$_2$)(PP$_3$)$^+$ cleanly converted terminal alkynes to alkenes in a process involving σ-vinylic intermediates [40]. Stable vinylic products resulted from reaction of FeH(H$_2$)L$_4^+$ with activated alkynes, HC≡CCO$_2$Me and MeO$_2$CC≡CCO$_2$Me [54]. The synthesis and electrochemistry of the diacetylide-bridged species Cl(dmpe)$_2$Fe(C≡C–C$_6$H$_4$–C≡C)Fe(dmpe)$_2$Cl have been reported. Comparison with mononuclear mono- and diacetylides suggested electronic interaction between the two iron centers [55].

Reaction of H$_2$Fe(H$_2$)L$_3$ (L = PPh$_2$Et, PPh$_2$Bu) with HSnPh$_3$ or HSiMePh$_2$ resulted in loss of dihydrogen and formation of FeH$_3$L$_3$SnPh$_3$ or FeH$_3$L$_3$SiMePh$_2$. The crystal structure of FeH$_3$(PPh$_2$Et)$_3$SnPh$_3$ showed a nearly tetrahedral FeP$_3$Sn core, but low temperature NMR measurements suggested some Fe–H–Sn interaction [56].

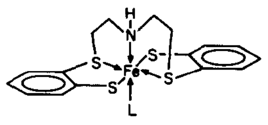
Despite their paramagnetic character and transient nature, alkyliron(III) porphyrins have been characterized by NMR, with the deuterium signal of CD$_3$Fe(tetraphenylporphyrin) being found, for example, at 532 ppm. The methyl group slowly exchanged with the ethyl group of ethyl iodide upon standing in toluene solution [57]. Reaction of HFe(tpp) with alkynes led to formation of vinylic complexes. Reduction and protonation of vinylic complexes, (tpp)Fe(CR=CH$_2$), led to their conversion to alkylidene complexes, (tpp)Fe=C(R)CH$_3$ [58].

Oxidation of organic substrates catalyzed by iron porphyrins continues to draw mechanistic and synthetic interest. Some selectivity has been obtained in (tpp)FeCl-catalyzed monoepoxidation of 1,3-dienes. For example the terminal double bond of 1,3-hexadiene underwent preferential (74%) oxidation [59]. The stereochemistries of the epoxides formed by Cytochrome P450$_{cam}$ from styrene and β-methylstyrene have been compared with those calculated by a molecular mechanics model and found to show good agreement [60]. Halogenated tetraphenylporphyrins favored hydroxylation of aliphatic hydrocarbons rather than ketone formation; a free radical cage process was suggested [61]. Formation of an organoiron intermediate in a cytochrome-induced oxidative step in cephalosporin biosynthesis has been suggested [62].

Use of various iron-based mixtures to functionalize saturated hydrocarbons, forming alcohols or ketones, has received further attention during 1992. Several studies dealt with mechanism and intermediates, based on labelling studies and isotope effects [63–66]. Addition of sulfur reagents to the mixtures has been found to divert some material to sulfur-containing products, such as cyclohexyl disulfide from cyclohexane [67].

4.2. *Iron monocarbonyls, e.g. L$_4$Fe(CO)*

Recombination of carbon monoxide with the unsaturated heme produced by photolysis of the carbonyl complex has been found to be slow on the picosecond time scale, unlike such closely related ligands as isonitriles, whose recombination was diffusion controlled [68]. Increasing the hydrostatic pressure increased the rate of recombination [69]. The nature of the chemical activation required for carbon monoxide but not for other simple ligands has been discussed [69,70]. Formation of a Fe–N and Fe–CO dissociated species in photolysis of carboxyhemoglobin has been studied by photoacoustic calorimetry [71].



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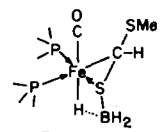

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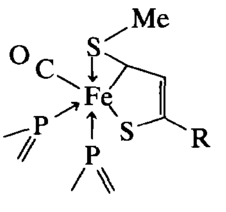
The iron center in **2** has been found to bind effectively to a wide range of donor and acceptor ligands. With strong donors (NH$_3$, N$_2$H$_4$, phosphites, *etc.*), high spin compounds with long Fe–S and Fe–N distances are formed; with CO and other acceptor ligands, low-spin compounds result. The system was assessed as a model for nitrogenases [72]. A group of isonitrile complexes $HFe(dppe)_2(CNR)^+$ has been prepared by displacement of dinitrogen from $HFe(dppe)_2(N_2)^+$ or by treatment of $HFe(dppe)_2Cl$ with a thallium salt in the presence of the isonitrile [73]. Their electrochemical oxidation has been studied [74]. The crystal structure of **3**, formed by $NaBH_4$ reduction of $FeX(CO)(PR_3)_2(\eta^2\text{-}CS_2Me)$, showed a borane molecule coordinated to sulfur and iron. Reaction with pyridine removed the BH_3, forming an unsaturated intermediate which readily added two-electron ligands or reacted with alkynes to form **4** (R = H, Ph) [75].



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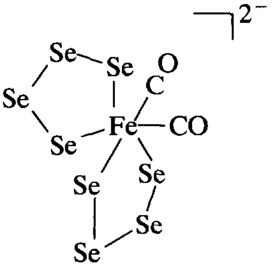

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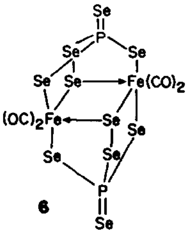
4.3. Iron dicarbonyls, e.g. $L_3Fe(CO)_2$

A one-pot procedure for synthesizing dicarbonyl-*cis*-dihydrido-*trans*-bis(trialkylphosphite)iron(II) complexes, $FeH_2(CO)_2[P(OR)_3]_2$ (R = Me, Et, Ph), using $Fe(CO)_5$, KOH, and the phosphite has been described [76]. The effects of conditions on the outcome of the reaction of $KHFe(CO)_4$ with phosphines have been investigated. Small phosphines in protic media give good yields of $H_2Fe(CO)_2L_2$ under mild conditions, whereas larger phosphines require higher temperatures and afford $Fe(CO)_3L_2$ products. In all cases, $KHFe(CO)_3L$ was found to be the initial product, formed at a rate strongly dependent on phosphine size. Protonation of the intermediate gave $H_2Fe(CO)_3L$, which underwent further substitution at low temperature or, upon heating, lost dihydrogen and formed $Fe(CO)_3L_2$. Similar results were obtained with phosphites; in addition, use of three equivalents of unhindered phosphites allowed synthesis of $Fe(CO)_2L_3$ in very good yields by reaction at 65°C. Reaction of $H_2Fe(CO)_2[P(OEt)_3]_2$ with KH under sonication resulted in generation of the Collman reagent analog, $K_2Fe(CO)_2[P(OEt)_3]_2$ [78]. A crystal structure of Et_4N^+ $HFe(CO)_2[P(OPh)_3]_2^-$ showed a distorted trigonal bipyramidal geometry, with the hydride ligand axial and a Fe–H distance of 1.47 Å. Reaction with diphenyl disulfide afforded $Et_4N^+PhSFe(CO)_2\text{-}[P(OPh)_3]_2^-$ [79].

$FeX_2(CO)_3(CS)$ (X = Br, I) reacted readily with two equivalents of triphenylphosphine at −80°C to form $FeX_2(CO)(CS)(PPh_3)_2$ [80]. Treating $FeBr_2(CO)_4$ with Ph_2PCH_2COPh similarly resulted in formation of $FeBr_2(CO)_2(\eta^1\text{-}P\text{-}PPh_2CH_2COPh)_2$; the latter was converted to the chelated enolate complex $Fe(CO)_2\text{-}(\eta^2\text{-}P,O\text{-}PPh_2CH{=}COPh)_2$ [XRC] by treatment with NaOH [81]. Reaction of $FeBr_2(CO)_4$ with NaSPh resulted in formation of oligomeric $[Fe(CO)_2(SPh)_2]_x$ [82]. $(Ph_2PPy)_2Fe(CO)_2(CS_2)$ showed little catalytic activity for carbonylation of ethanol [83].

The reagent $Me_2SSMe^+BF_4^-$ transferred a methylthiyl group to $Fe(CO)_2L_3$ [L = $P(OMe)_3$] to form $Fe(SMe)(CO)_2L_3^+BF_4^-$; the group was removable by reduction with sodium amalgam [84]. Reaction of *N*-methylimidazole, $Fe(CO)_5$, and elemental selenium resulted in formation of the $Fe(MeN_2C_3H_4)_6^{2+}$ salt of the bis-chelate dianion, **5** [XRC] [85]. Another selenium-rich dianion, **6**, also characterized by means of a crystal structure, resulted from reaction of the $P_2Se_8^{2-}$ dianion with $Fe(CO)_5$ [86]. Reaction of 2-(phenylazo)-pyridines with $Fe_2(CO)_9$ produced, in addition to a simple chelate product, $(\eta^2\text{-}PhN{=}N\text{-}C_5H_4N)Fe(CO)_3$, a more complex product, **7**, having two azo groups which are σ-coordinated to an "inorganic" iron also π-coordinated to an $Fe(CO)_2$ group, as revealed by the crystal structure of the 4-methyl analog. The same product could also be formed from $Fe(PhN{=}NC_5H_4\text{-}N)_3^{2+}$ and $Fe(CO)_4^{2-}$ [87].



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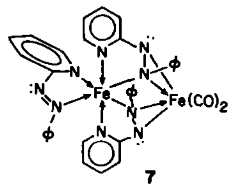

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The acetyl groups were displaced from iron when nucleophiles (Et_2NH, $LiNMe_2$, $EtOH/Et_3N$, NaOMe) reacted with $FeIL_2(CO)_2(COMe)$ or $FeL_2(CO)_3\text{-}(COMe)^+$ (L = PMe_3) [88]. The mechanism of isotopic exchange within $FeIL_2(CO)_2Me$ was found to involve ionization of the iodide ion, rearrangement of the five-coordinate cation, and iodide reentry. "Insertion" to form the acetyl derivative was held to involve a similar mechanism with CO replacing the I$^-$, and migration of methyl to CO upon iodide reentry [89]. The anion-catalyzed equilibration between the alkyl complex, $FeL_2(CO)_2(CNCMe_3)Me^+$, and the iminoacyl, $FeL_2(CO)_2(\eta^2\text{-CMe=NCMe}_3)^+$, was found to involve independent steps of methyl migration and N-coordination [90].

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

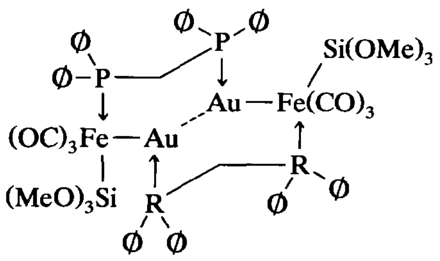
Dissolution of *fac*-(diars)Fe(CO)$_3$Me$^+$ salts [diars = o-$C_6H_4(AsPh_2)_2$] in acetonitrile resulted in a solution containing two equilibrating acyls, (diars)Fe(CO)$_2$(COMe)(NCMe)$^+$, which interconverted by solvent dissociation, forming a pentacoordinate acyl intermediate. The *mer* isomer gave a third, distinct acyl stereoisomer, which only slowly converted to the equilibrating pair [91]. The halide-induced disproportionation of the electrochemically-generated radical cation $Fe(CO)_3(PCy_3)_2^+$ (Cy = cyclohexyl), to give neutral $Fe(CO)_3(PCy_3)_2$ and $FeX_2(CO)_2(PCy_3)_2$, has been studied [92].

The enthalpies of reaction of phosphines with (bda)Fe(CO)$_3$, which cleanly form $L_2Fe(CO)_3$, have been measured calorimetrically. The enthalpies ranged from -150 kJ mol^{-1} for triethylphosphine to -85 kJ mol^{-1} for triphenylphosphine [93]. Free (or solvated?) Fe(CO)$_3$ has been invoked as the active catalyst in isomerization of vinylic alcohols by (bda)Fe(CO)$_3$ [94]. (Bda)Fe(CO)$_3$ has been used to transfer two Fe(CO)$_3$ moieties to the new tetradentate ligand, 1,1,2,2-tetrakis(diphenylphosphinomethyl)ethane. Two six-membered chelate rings were formed [95].

Convenient one-pot syntheses of tricarbonylbis(phosphine)iron compounds using Fe(CO)$_5$, KOH, and the phosphine in ethanol have been reported [96]. Mechanistic studies of these reactions confirm the intermediacy of KHFe(CO)$_4$. Large phosphines react at temperatures above room temperature quantitatively to give the $Fe(CO)_3L_2$ products, whereas smaller phosphines also give some $Fe(CO)_2L_3$. Somewhat different results are obtained in aprotic media as compared to alcohols [77]. Similar results were reported with phosphite nucleophiles. Reaction of KHFe(CO)$_4$ with phosphites in THF resulted in formation of KHFeL(CO)$_3$ in very high yield; protonation with trifluoroacetic acid at -10°C cleanly produced $H_2Fe(CO)_3[P(OR)_3]$ [78].

Quantum yields for photosubstitution of triethylphosphine into pentacarbonyliron have been measured. Both Fe(CO)$_4$L and $Fe(CO)_3L_2$ are primary, single-photon products, and the relative quantum yields are nearly independent of phosphine concentration. The ratio of the two products formed depends on the phosphine used, but not on its concentration. These results parallel older results obtained using $Fe_2(CO)_9$ under thermal conditions. They were rationalized in this instance in terms of formation of a *triplet* Fe(CO)$_4$L intermediate [97]. Reaction of $(C_8H_{14})_2Fe(CO)_3$ with 1,5-bis(diphenylphosphino)pentane at low temperature led to the eight-membered ring chelate complex $[\eta^2\text{-}Ph_2P(CH_2)_5PPh_2]Fe(CO)_3$. In contrast, reaction of the ligand with (maleic acid)Fe(CO)$_4$ in the presence of trimethylamine oxide resulted in formation of a dimer containing a sixteen-membered chelate ring. Both structures were confirmed by X-ray crystallography: in the monomer, the two phosphorus atoms occupied one axial and one equatorial position in the iron trigonal bipyramid; in the dimer, all Fe–P bonds were axial [98]. Unsymmetrical bis(phosphino)ferrocenes, $(C_5H_4PPh_2)Fe(C_5H_4PR_2)$ (R = cyclohexyl, p-tolyl) and their chelate Fe(CO)$_3$ complexes have been prepared [99]. The enthalpies of protonation of $L_2Fe(CO)_3$ complexes at iron, by trifluoromethanesulfonic acid in CH_2Cl_2, have been measured. The most basic compounds were those with small chelate rings [*e.g.* (dmpm)Fe(CO)$_3$, -126 kJ mol^{-1}], with basicity decreasing with increasing chelate ring size. Non-chelate complexes were less basic [*e.g.* $(Me_3P)_2Fe(CO)_3$, -97 kJ mol^{-1}], and phenyl-substituted phosphine ligands conferred less basicity than alkyl-substituted ones [100].

A series of salts, $Na^+Fe(CO)_3(SiR_3)PR'_3)^-$ [R = Me, Ph; R′ = H, Me, Bu, Ph], was prepared by deprotonation of the corresponding hydrides. Reaction with electrophiles led to formation of *mer*-Fe(CO)$_3$(SiR$_3$)(PR′$_3$)El (El = Me, SnMe$_3$, AuPPh, AgPPh$_2$Tol, HgBr). The structures of the gold and silver adducts showed an approximately trigonal bipyramidal coordination around iron, with the metal only modestly perturbing the geometry while bonding to iron in the Fe(CO)$_3$ plane. The mercury compound was more nearly octahedral [101]. A similar mercury compound, Hg[Fe(CO)$_3$Si(OMe)$_3$(η^1-dppm)]$_2$ [XRC], has also been described. Reaction of K$^+$ Fe(CO)$_3$Si(OMe)$_3$(η^1-dppm)$^-$ with AuCl$_2^-$, however, led to recruitment of the bidentate capability of the dppm ligand to stabilize the dimeric species **8** [102]. With CdCl$_2$, the same anion formed [(μ-dppm)Fe(CO)$_3$Si(OMe)$_3$CdCl]$_2$,



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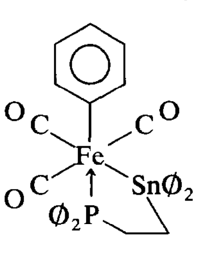
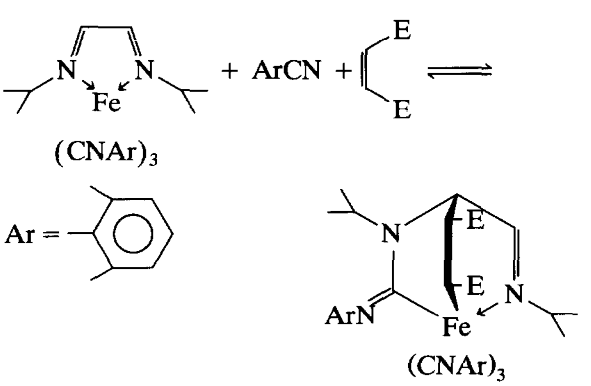
which existed as a dimer by virtue of Cd–Cl–Cd bridges [XRC]. A zinc analog was also prepared. The ketonic ligand Ph$_2$PCH$_2$COPh showed chelating character (using P and O atoms) in related cadmium and mercury complexes [103]. Additional examples of complexes in which both the ketonic ligand and the trimethoxysilyl group showed a tendency toward chelation have also been described [104]. The novel chelate **9** was formed by oxidative addition of a Sn–Ph bond



9

to iron within the intermediate complex, $(OC)_4FePPh_2CH_2CH_2SnPh_3$. The latter was formed from the ligand and $Fe_2(CO)_9$ or $(OC)_4Fe(H)SiMePh_2$ [105].



(4)

In the thermally reversible reaction, eqn. (4), three molecules exhibited temperature-dependent self-assembly and disassembly [106].

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

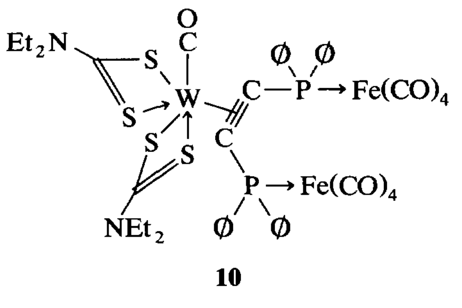
Trans-$Fe(CO)_4Cl_2$ has been identified as a product in an experiment in which $FeCl_2$ was condensed into a CO matrix. EXAFS data were used to obtain bond lengths in the octahedral species [107].

A direct synthesis of $Na_2Fe(CO)_4$ by reduction of anhydrous $FeCl_3$ with sodium naphthalene under a CO atmosphere has been described [108]. Photolysis of $Fe(CO)_4^{2-}$ in a 10 M NaOH glass at 77 K resulted in formation of solvated electrons [109]. Reaction of $Na_2Fe(CO)_4$ with 1.5 equivalent of $AgBF_4$ or $AgNO_3$ occurred with formation, *inter alia*, of a paramagnetic cluster $Ag_{13}[Fe(CO)_4]_8^{4-}$. The crystal structure of the PPN^+ salt showed a centered cuboctahedral Ag_{13} cluster having each triangular face capped by a $Fe(CO)_4$ group [110]. In a modified Collman reaction, disodium tetracarbonylferrate was treated with primary alkyl bromides under a CO atmosphere, followed by reaction with CuCl and oxidation with Ce^{IV}. This resulted in formation of diketones, RCOCOR, in 70–90% yields [111]. Reaction of disodium tetracarbonylferrate with an unsaturated aziridinium ion resulted in an elaborate rearrangement reaction involving formation of a cyclopentanone ring [112].

The zwitterionic compounds $(Me_2N)_3P^+OSiX_2Fe(CO)_4^-$ [X = Me, Cl], prepared by reaction of $SiCl_2X_2$ with $Na_2Fe(CO)_4$ in the presence of hexamethylphosphoramide (HMPA), have been scrutinized by crystallographic study. Both the Fe–Si and Si–O bonds were significantly shorter in the dichloro compound than in the dimethyl compound. The Fe–Si–X angles were slightly larger (110–116°) than tetrahedral. Heating to 120°C resulted in loss of HMPA and formation of the dimeric silylene complex, $[X_2SiFe(CO)_4]_2$. Photolysis in the presence of 2,3-dimethylbutadiene gave the dihydrosilole adduct and the tricarbonyl(diene)iron adduct [113]. Reaction of $PPN^+HFe(CO)_4^-$ with Me_2Se_2 gave $PPN^+MeSeFe(CO)_4^-$. Protonation with HBF_4, even at low temperature, produced $(\mu\text{-}SeMe)_2Fe_2(CO)_6$ [114]. Temperature-dependent Mössbauer spectroscopy of salts of $HFe(CO)_4^-$ have led to a description of the dynamic motions of these salts as due to hydride "tunneling" [115]. The crystalline PPh_4^+ and SPh_3^+ salts of $HFe(CO)_4^-$ show colors due to interionic charge transfer interactions. Irradiation of solutions of the tetraphenylphosphonium salt at long wavelengths corresponding to this charge transfer resulted in formation of $Ph_3PFe(CO)_4$ and benzene. The benzyltriphenylphosphonium salt formed the same $Ph_3PFe(CO)_4$ and toluene, with a quantum yield of 0.015 [116].

An $Fe(CO)_4$ complex of the water-soluble ligand, $P(m\text{-}C_6H_4SO_3Na)_3$, has been prepared [XRC] [117]. Mono- and bis-$Fe(CO)_4$ complexes of the ferrocene ligand, dppf, have also been prepared, and the crystal structure of the mono-adduct reported [118]. The structure of $(\eta^1\text{-dppm})Fe(CO)_4$ has also been reported [119]. In all cases, the phosphine occupied the axial position of the iron trigonal bipyramid. A $Fe(CO)_4$ complex of the more novel phosphine, (*E*)-$Ph_2PC(OSiMe_3)(CF_3)CH{=}C(OSiMe_3)CF_3$ [120], has also been described.

Some mixed-metal complexes of bis(diphenylphosphino)ethyne have been prepared, including **10**, formed by coordination of the free phosphino groups of the tungsten alkyne complex, using $Fe_2(CO)_9$ [121]. The



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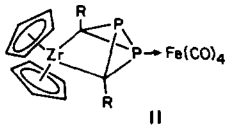
analogous bis-$Fe(CO)_4$ complex of bis(diphenylphosphino)butadiyne [XRC] has also been prepared, and from it complexes having one alkyne moiety coordinated to $Co_2(CO)_6$ or $Pt(PPh_3)_2$ groups [122]. **11** was produced in 63% yield by reaction of the zirconocene bicyclic with $Fe_2(CO)_9$ [123]. One (and only one) phosphorus atom of tetra(*tert*-butyl)tetraphosphacubane was likewise coordinated to a $Fe(CO)_4$ group [XRC] [124]. Coordination of a $Fe(CO)_4$ group to a silylated heptaphosphane was accompanied by loss of the silyl group [eqn. (5)] [125]. Another selective coordination of a polyphosphorus compound occurred when the 1-phosphorus of 3,5,3′,5′-tetra(*tert*-butyl)-1,2,4,1′,2′,4′-hexaphosphaferrocene became coordinated to a $Fe(CO)_4$ group [126].



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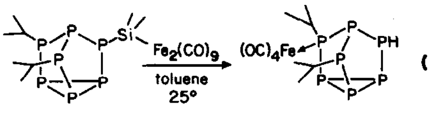

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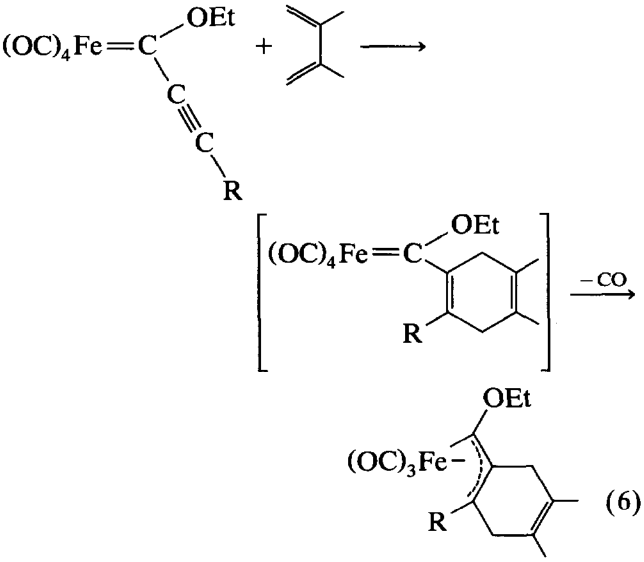
Various stannyl- and stannylene-iron compounds, including *cis*-$(Me_3Sn)_2Fe(CO)_4$, *cis*-$(ClMeSn)_2Fe(CO)_4$, *cyclo*-$[R_2SnFe(CO)_4]_2$ (R = Me, Bu), and related dicyclic compounds, have been studied by ^{119}Sn NMR, including measurement of $^{119}Sn-^{57}Fe$ and $^{119}Sn-^{119}Sn$ coupling constants. High values of the latter in the cyclic compounds suggested some degree of direct tin–tin interactions [127]. On the other hand, the very low $^{29}Si-^{29}Si$ coupling constant in *cyclo*-$(OC)_4FeSiMe_2CH_2CH_2SiMePh$ indicated no direct interaction [128]. *cis*-Bis(carbalkoxy)tetracarbonyliron compounds have been obtained by reaction of oxalyl chloride with $(OC)_4FeCO_2R^-$. Replacement of one carbonyl ligand by triphenylphosphine occurred readily. Neither bis(carbomethoxy)iron compound formed dimethyl oxalate upon thermolysis; instead, methanol and methyl carbonate were formed. Reaction with HBF_4 produced $(OC)_5FeCO_2Me^+BF_4^-$ [129].

4.6. *Carbene complexes, $R_2C = FeL_4$*

Comparatively little was reported on carbene complexes during 1992. Of considerable interest was the formation of alkylidene complexes, (tpp)Fe=CRMe [(tpp) = tetraphenylpoprhyrin dianion; R = Pr, Bu] by reaction of (tpp)FeCl with excess $NaBH_4$ and terminal alkynes RC≡CH, a reaction in which vinylic intermediates presumably played a significant role [58]. A group of alkynylcarbene complexes, $(OC)_4Fe{=}C(OEt)C{\equiv}CR$ (R = Pr, Ph, Cy, ${}^tBu$, $SiMe_3$) were prepared by reaction of alkynyl-lithium reagents with $Fe(CO)_5$, followed by quenching with ethyl fluorosulfonate. Reaction of the trimethylsilyl compound with acyclic 1,3-dienes resulted in formation of η^3-vinylcarbene complexes, as adumbrated in eqn. (6) [130]. The initial Diels–Alder adduct of $(OC)_4Fe{=}C(OEt)C{\equiv}C{-}CMe_3$ and cyclopentadiene was obtained in 92% yield when the reaction was run at 25°C; heating to 50°C resulted in a migration reaction to form **12**. The other alkynylcarbene complexes formed analogs of **12** directly at room temperature [131].



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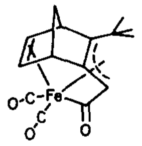

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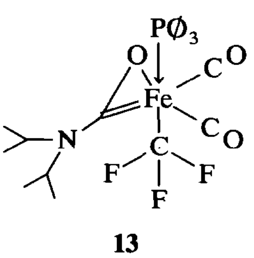
The η^2-carbamoyl compound, **13**, resulted from reaction of the carbamoyltetracarbonylferrate anion, $({}^iPr_2NCO)Fe(CO)_4^-$, with trifluoroacetic anhydride and triphenylphosphine. Its carbenoid structure was clearly shown by its Fe=C bond length of 1.875 Å. The Fe–CF_3 distance was 1.986, and the Fe–O 2.030 Å. Reaction with aqueous HBF_4 resulted in hydrolysis of the CF_3 group, with consequent formation of $Fe(CO)_3(PPh_3)(\eta^2\text{-}{}^iPr_2NCO)^+BF_4^-$ [132].



13

The structures and reactions of so-called "base-stabilized silylene complexes", such as $(Me_2N)_3P^+O$-$SiX_2Fe(CO)_4^-$ were previously discussed; the formation of the cyclodimers $[X_2SiFe(CO)_4]_2$ upon heating the HMPA adduct at 120°C is consistent with intermediacy of some free silylene complex [113].

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

Reactions in which $Fe(CO)_5$ undergoes conversion to more complex organometallic products are described in this survey according to the product structures. Already broached in Section 4.5 was the formation of the $Fe(CO)_5$-electrophile adduct, $MeO_2CFe(CO)_5^+$ [129]. Direct reaction of $Fe(CNR)_5$ (R = *tert*-butyl) with $HgCl_2$ gave the related adducts, $Fe(CNR)_5HgCl^+HgCl_3^-$ and $Fe(CNR)_5(HgCl)_2^{2+}HgCl_4^{2-}$ [133].

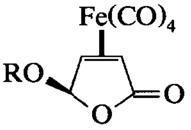
Photolysis of $Fe(CO)_5$ in an oxygen-doped argon matrix at 20 K resulted in formation of several detectible iron-oxygen species, including $(\eta^2\text{-}O_2)Fe(CO)_4$, $Fe(CO)_3(=O)_2$, O_2FeCO, and OFeCO [134]. Reaction of $Fe(CO)_5$ with organic peroxides in hydrocarbon solvents has also been studied [135].

Dissociation of gaseous $Fe(CO)_5$ in contact with a hot rhenium surface has been found to occur by sequential dissociation of CO ligands, followed by ionization of the dissociated species [136].

5. η^2-Alkene and η^3-allyl complexes

Geometric isomers of $Fe(CO)_3(C_2H_4)$, produced by photolysis in matrices at 10 K, have been detected. They have been related to triplet C_{2v} $Fe(CO)_4$, with the more stable isomer having the ethene in the equatorial plane, and the less stable having the ethene axial. The latter slowly rearranges to the more stable form at 10 K in the dark [137]. The crystal structure of $Fe(CO)_2(PEt_3)_2(C_2H_4)$ has been reported; taking the ethene as occupying two coordination sites, the compound shows a distorted octahedral geometry, with *trans* phosphines. The Fe–C and C–C distances were 2.111 and 1.369 Å, respectively. The ethene ligand was readily displaced by diphenylacetylene, giving an example of a mononuclear η^2-alkyne complex, a fairly rare class of compound in organoiron chemistry. Reaction of the ethene complex with thiophene dioxide gave $Fe(CO)_2(PEt_3)_2(SO_2)$ [138]. Another fairly stable ethene complex resulted from photosubstitution of $(dfepe)Fe(CO)_3$ [dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$] with ethene. The product, $(dfepe)Fe(CO)_2(C_2H_4)$, showed *cis* phosphine and CO ligands, and Fe–C and C–C bond lengths of 2.12 (average) and 1.362 Å. Both are similar to those of the bis(triethylphosphine) analog, but the C–C bond length was described as "unusually short". The ethene complex was stable at 25°C, but propene and cyclohexene analogs were labile. Photoreaction of $(dfepe)Fe(CO)_3$ with styrene gave some η^2 complex, along with predominant η^4.

The crystal structure of **14**, the only product formed (62% yield) in reaction of the ligand with $Fe_2(CO)_9$, has also been reported. The C–C bond length here is 1.405 Å and the Fe–C lengths average 2.09 Å, indicating carbonyl-enhanced back bonding, compared to the unsubstituted ethene complexes [140]. An unstable η^2 tetracarbonyliron complex resulted from reaction of $CH_2{=}CHC({=}O)SiMe_3$ with $Fe_2(CO)_9$; with a β-phenyl substituent, however, only the η^4 product resulted [141]. Sulfonyl and sulfinyl alkenes formed fairly stable η^2-$Fe(CO)_4$ complexes with $Fe_2(CO)_9$, $(PhSO_2CH{=}CH_2)Fe(CO)_4$ being formed in 92% yield. Only one diastereomer of the (phenylsulfinyl)ethene complex was formed, albeit in 28% yield. The crystal structure revealed the relative stereochemistry of the two centers. The C–C and average Fe–C distances were 1.407 and 2.06 Å, again consistent with some enhanced back-bonding due to the sulfinyl group [142].



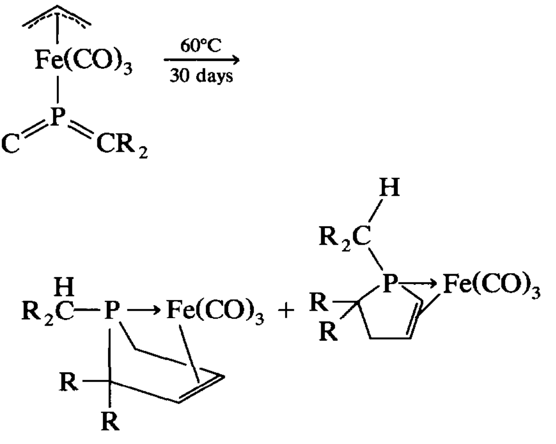
14 (R = (−)menthyl)

Reaction of C_{60}^+ with $Fe(CO)_5$ in the gas phase resulted in initial formation of $C_{60}Fe(CO)_{4,3}^+$, with subsequent reactions forming species with 2–4 iron carbonyl groups per fullerene cluster [143]. Two isomers of FeC_{60}, one prepared by arc vaporization of graphite in a $Fe(CO)_5$ atmosphere and believed to involve endohedral iron, and one prepared in the solid state and believed to involve externally bound iron, have been compared by Mössbauer, mass spectroscopic, EXAFS, and magnetic susceptibility measurements [144].

The boraalkene, (9-fluorenylidene)-(2,2,5,5-tetramethylpiperidino)borane formed η^2-$Fe(CO)_4$ and $Fe(CO)_3L$ [L = PMe_3, PMe_2Ph, $PMePh_2$, PCl_3, and PCl_2Ph] complexes of the C=B bond. The bond lengths in the $Fe(CO)_4$ complex were B–C: 1.518, B–Fe: 2.125, and C–Fe 2.19 Å. The Fe–B and Fe–C distances were shortened by about 0.03 Å in the trimethylphosphine analog. Calculations emphasized the importance of back-bonding into the boron-centered π^*_{BC} bond [145]. η^2-Complexed hetero-double bonds in **3** [75] and **13** [132] were previously described.

Reaction of 7-azabenzonorbornadienes with $Fe_2(CO)_9$ gave, depending on the N-substituent, *exo*-

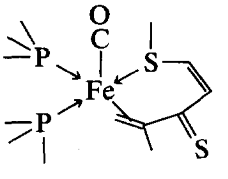
$Fe(CO)_4$ complexes or *exo*-$Fe(CO)_3$ complexes, in which the η^2-alkene-iron bonding was butressed by coordination of the iron also to nitrogen [146]. Even in the $Fe(CO)_4$ complexes, the nitrogen interacted with an axial carbonyl group, as shown by decreasing N–CO distance in the more basic compounds [2.57 Å in the N-SO_2Me compound; 2.26 Å in the N-*p*-tolyl compound] [147]. A chelate η^2 complex, **15**, [eqn. (7);



(7)

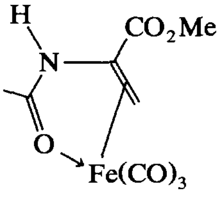
15 **16**

R = $SiMe_3$], analogous to the azanorbornadiene $Fe(CO)_3$ complexes, was the principal product of slow decomposition of the η^3-allylic precursor shown. Formation of **15** was greatly enhanced by treatment of the precursor with tributylphosphine [148]. Cleavage of the Fe–CH bond in **4** [R = CMe=CH_2] led to formation of chelate **17** [75]. Reaction of the stable chelate **18** with



17

methyl-lithium and tertiary alkyl halides, RX, gave amino acid derivatives, AcNHCHRCO_2Me [149].



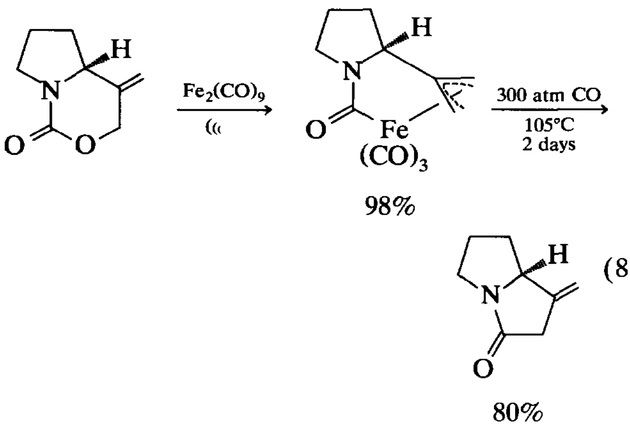
18

The results of photolysis of the propene complex, $Fe(CO)_4(\eta^2\text{-}CH_2{=}CHMe)$, in matrices at 10 K, mirrored those of the previously discussed ethene complex, in that two geometric isomers of the unsaturated $Fe(CO)_3$ product were formed. However, one isomer (with axial alkene?) underwent spontaneous oxidative addition to the allylic C–H bond, forming $HFe(CO)_3(\eta^3\text{-}C_3H_5)$, even at 5 K, whereas the other required warming to 50 K before forming the allylic hydride product. Upon photolysis at 260 nm, the hydride reverted to the reactive (axial?) isomer; some $Fe(CO)_3(\eta^3\text{-}C_3H_5)$ was also formed by hydrogen loss [150].

Reactions of cationic allyl complexes with nucleophiles have drawn attention. Methyl-substituted $Fe(CO)_4(\eta^3\text{-}C_3H_{5-n}Me_n)^+$ [$n = 2$, 3] reacted with functionalized copper–zinc reagents, RCu(CN)ZnI, at the less substituted terminus, giving principally allyl-R adducts. The 1,1,3-trimethylallyl cation gave significant amounts of ketone byproducts, $Me_2C{=}CHCHMeCOR$, however [151,152]. Use of silyl enol ethers and related species as nucleophiles in attack on *E*- and *Z*-$Fe(CO)_4[CH_2CHCH(SiMe_3)]^+$ cations again resulted in attack on the unsubstituted terminus, with a high degree of stereochemical retention in the vinylsilane products [153]. Reaction of the electrophile $ClP{=}C(SiMe_3)_2$ with $K^+Fe(CO)_3(C_3H_5)^-$ at −70°C occurred with formation of a P–Fe bond, the initial product being $Fe(CO)_3(C_3H_5)[P{=}C(SiMe_3)_2]$, which formed a dimer (see Section 9.1) at temperatures above −30° [154]. The lability of this product contrasts with the comparative stability of the bis(methylene)phosphorane shown as reactant in eqn. (7). The byproduct **16** in that equation is an example of a η^3-1-phosphaallyl complex [148].

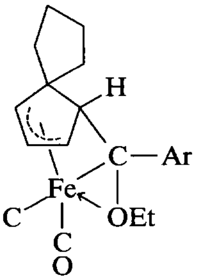
An η^3-propargylic compound, **1**, was illustrated in eqn. (3). **1** (R = Ph) could also be prepared by reaction of diphenylbutadiyne with $(dmpe)_2FeH_2$ in ethanol [53]. Similar η^3-butenynyl derivatives formed when terminal alkynes interacted with $FeH(H_2)[PPh(OEt)_2]_4^+$, but not with $FeH(H_2)[P(OEt)_3]_4^+$, indicating a subtle interplay of factors affecting the outcomes of these ligand coupling reactions [54].

The sequence shown in eqn. (8) represents the key steps in syntheses of pyrrolizidine alkaloids *via* a chelate η^3-allyl intermediate [155].



(8)

The η^3-vinylcarbene product shown in eqn. (6) [130] is but one example of a η^3 or chelated η^3 product formed by conversion of a carbonyl ligand in an organometallic complex to a carbenoid by reaction with an organolithium reagent, followed by an alkylating agent. Further examples are the products **19**, formed by addition of various aryl-lithiums to tricarbonyl(η^4-*spiro*-[4.4]nona-1,3-diene)iron and quenching with cold, aqueous triethyloxonium fluoroborate. Reaction with triphenylphosphine displaced the coordinated ethoxy group in **19**, forming more stable products [156]. **20** [XRC] is a novel chelate bis(η^3-allyl) complex, which resulted from reaction of isoprene with $Fe(CO)_3[\eta^4\text{-}C(CH_2)_3]$ under the influence of trimethylamine oxide. There was no evidence of the alternate regioisomer [157].



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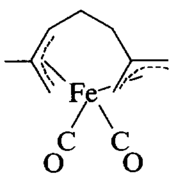


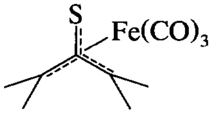
20

6. Compounds with η^4-ligands

6.1. *Trimethylenemethyl complexes*

Ligand coupling of the TMM ligand $[C(CH_2)_3]$ with isoprene to form **20** [157], induced by trimethylamine oxide, was described at the end of the previous section of this survey. Given that the trimethylamine oxide brings about substitution of other ligands, such as phosphines, for CO in $Fe(CO)_3(TMM)$, the reaction would appear to involve initial formation of $Fe(CO)_2(\eta^2\text{-isoprene})(\eta^4\text{-TMM})$, which then undergoes spontaneous ligand coupling. Further work on this interesting reaction will be welcome. Reaction of $Fe(CO)_3(TMM)$ with strongly nucleophilic organolithium reagents in solutions containing HMPA, followed by protonation, gave methallylated products, $CH_2{=}C(Me)CH_2Nu$ [Nu = Ph_2CH, Ph, 2-phenyl-1,3-dithian-2-yl]. Nucleophilic attack on substituted TMM complexes was not very selective, however [158].

A thia-TMM complex, $Fe(CO)_3[SC(CMe_2)_2]$, **21**, resulted from reaction of tetramethylallene episulfide with $Fe_2(CO)_9$. $Fe(CO)_3[SC(CHCMe_3)(CPh_2)$ was prepared similarly; its crystal structure showed a Fe–S distance of 2.308 Å, and Fe–C distances of 2.261 (to CPh_2), 1.937 (to the center C), and 2.180 (to $CHCMe_3$) Å. The thia-TMM ligand was cupped about the iron in the normal manner of TMM complexes. Reactions with triphenylphosphine were also reported [159].

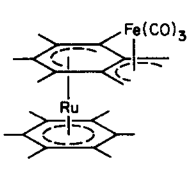


21

6.2. *Complexes of acylic dienes, including heterodienes*

The rotational spectrum of $Fe(CO)_3(\eta^4\text{-butadiene})$ has been measured by microwave spectrometry. The lower limit for the barrier height for internal rotation was found to be 0.48 kJ mol^{-1}. The iron-carbon bond distances were calculated to be 2.22 (C1) and 2.03 (C2) Å, rather different from those in an old and not very precise crystal structure (2.14 and 2.06 Å) [160]. Pulsed high pressure mass spectrometry has been used to measure the thermochemistry of electron capture by the butadiene complex: the enthalpy and entropy for this process were measured as -88 kJ mol^{-1} and $+42$ J K^{-1} mol^{-1}. The large entropy change was consistent with dechelation of one double bond in the anion, as was the comparatively slow rate of electron transfer. Reversible loss of CO was also observed, with a thermal activation energy of 83 kJ mol^{-1} [161].

Amphiphilic compounds containing tricarbonyl(η^4-diene)iron moieties as lipophilic groups, such as $Fe(CO)_3[\eta^4\text{-MeCH=CH-CH=CHCO}_2\text{-}m\text{-}C_6H_4NMe_3^+]$, have been prepared. Reaction with aqueous amines resulted in amide formation [162]. The styrene complex, $Fe(CO)(dfepe)(\eta^4\text{-}CH_2{=}CH\text{-}C_6H_5)$, was the principal product of photoreaction between styrene and $Fe(CO)_3(dfepe)$ [dfepe = $(CF_3CF_2PCH_2\text{-})_2$. The η^2 coproduct underwent slow conversion to the η^4. The η^4-complex served as a source of the Fe(CO)(dfepe) group in reactions with dienes [139]. The novel bimetallic *o*-xylylene complex, **22**, was prepared by treatment of the endocyclically-coordinated ruthenium complex with $Fe(CO)_4(NMe_3)$ [163].



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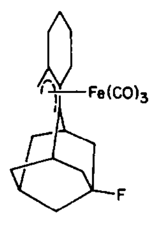
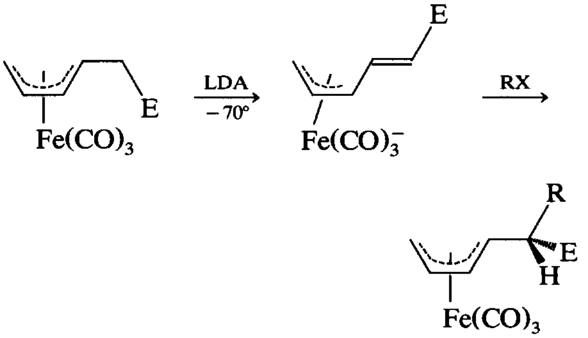
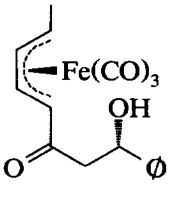


23

A degree of face selection (3 : 2) favored formation of the *syn* product, **23** [XRC], in complexation of the (fluoroadamantylidene)diene using $Fe(CO)_5$ in refluxing dibutyl ether [164]. Bakers' yeast exhibited high chiral discrimination in asymmetric reduction of $Fe(CO)_3$(2,4-hexadiene-1,6-dial), and similarly in selective reduction of one enantiomer of $Fe(CO)_3$(2,4-hexadien-1-al [165]. Alkylation of the carbanion from deprotonation of $Fe(CO)_3(CH_2{=}CH{-}CH{=}CHCH_2{-}CO_2Me)$ produced alkylated products in 87–93% diastereomeric excess. As shown in eqn. (9), the products were those to be expected from generation of an (*E*) double bond and *exo* (or *anti*) attack of electrophile [166]. Reactions of lithioalkynes with the aldehyde group of $Fe(CO)_3(MeO_2CCH{=}CH{-}CH{=}CHCHO$ also occurred predominantly (73–82%) to give *exo* products, which were converted to allenylbutadiene complexes, $Fe(CO)_3(2\text{-}5\text{-}\eta^4\text{-}MeO_2CCH{=}CH{-}CH{=}CH{-}CH{=}C{=}CREt)$ by conversion to carbonates and reaction with complex cuprates [167]. Acid-catalyzed aldol condensations of, for example, $Fe(CO)_3(MeCH{=}CH{-}CH{=}CH{-}C(OSiMe_3){=}CH_2$ with aldehydes gave easily separable diastereomers so that products such as **24** were obtained in pure form. Highly stereoselective reduction of **24** gave 1,3-diols of known absolute configuration [168]. $Fe(CO)_3$-Complexes of octa-5,7-diene-1,4-diols underwent cyclization to tetrahydrofurans via the S_NI mechanism, involving iron-stabilized cations [169].

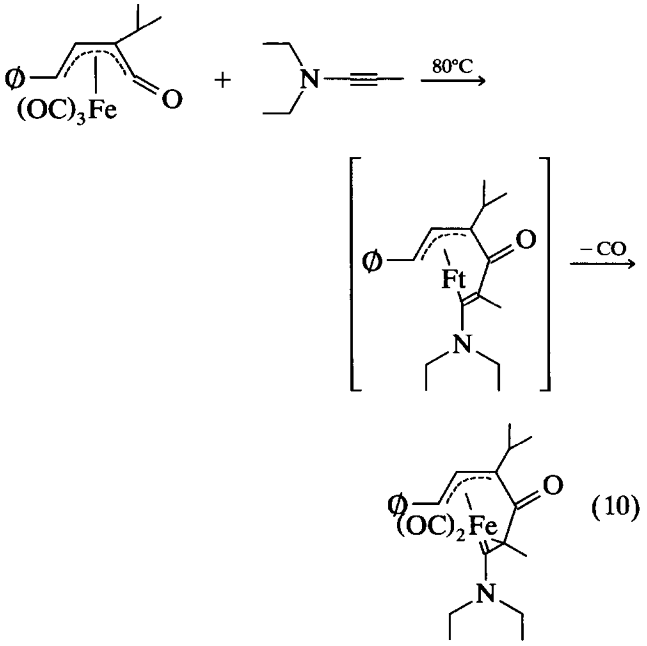


(9)



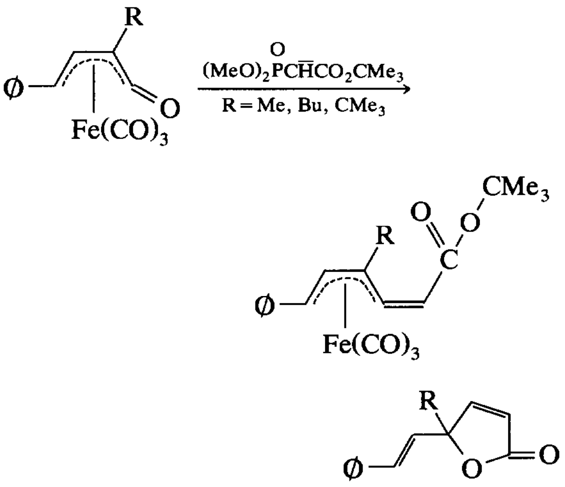
24

Strong carbanion nucleophiles added to the 4-position of tricarbonyl[2-(phenylsulfonyl)butadiene]iron. Workup by protonation with trifluoroacetic acid produced (*E*)-$NuCH_2{=}CHC(SO_2Ph)CH_3$ products in 66–86% yields. Reaction of the 2-(phenylthiyl)butadiene complex with $LiCHPh_2$, in contrast, occurred at the 3-position, and eventuated in formation of 3-benzhydryl-2-methyl-2-(phenylthiyl)cyclobutanone [170]. Treatment of acyclic diene complexes with aluminum halides, usually under 100 atm. CO at 100°C, resulted in cyclocarbonylation to form cyclopentenones. 1,1,3-Trialkylbutadiene complexes reacted, however, under mild conditions [171,172]. Optically active diene complexes reacted stereospecifically [172].



(10)

Thermal addition of alkynes to 1,3-butadien-1-one (vinylketene) complexes occurred by insertion of the alkyne into the Fe–acyl bond. Both electron-deficient and electron-rich alkynes reacted similarly, but the initial diethyl(1-propynyl)amine adduct lost a CO to form a carbenoid product [eqn. (10)]. The crystal structure of the carbenoid product showed a Fe=C bond length of about 1.84 Å [173]. Reaction of the pure enantiomers of $Fe(CO)_3(\eta^4\text{-}PhCH{=}CH{-}CMe{=}C{=}O)$ with (*S*)-α-phenethyl isonitrile gave pure diastereomers of the vinylketenimine complexes, $Fe(CO)_3(PhCH{=}CH{-}CMe{=}C{=}NCHMePh)$. These reacted with alkyl-lithium reagents by *exo* attack at the 2-carbon; workup gave aldehydes or amides with chiral quaternary centers, *e.g.* PhCH=CHCMeRCONHCHMePh, in high optical purity [174]. Reaction of butadienone complexes with phosphonoacetate esters resulted in Wittig–Horner-type condensation to form pentatriene complexes [eqn. (11)]. The new double bond was formed with stereoselectivity as high as 98%. Reaction with ferric chloride resulted in formation of furanones [175]. Reaction of 1,2,4,5-hexatetraenes with CO in the presence of $Fe(CO)_5$ resulted in formation of 2,5-bis(alkylidene)cyclopentanones, a reaction presumed to involve initial formation of (2-5-η^4-hexatetraene) complexes, which underwent metal-to-carbonyl migrations to form the cyclic products [176].

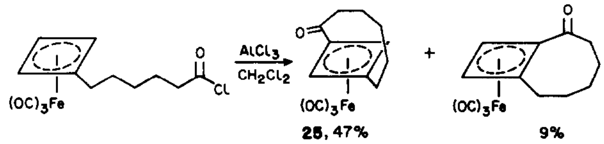


(11)

Stable crystalline η^4 complexes of cinnamylsilanes, PhCH=CH-COSiMe$_2$R [R = Me, CMe$_3$] were prepared using $Fe_2(CO)_9$. Reaction with methyl–lithium led to incorporation of an acetyl group into the ligand, forming PhCH(COMe)CH$_2$COSiMe$_2$R. Under a CO atmosphere, the *tert*-butyl substituted complex was converted by methyl–lithium into the butadienone complex, $Fe(CO)_3(\eta^4\text{-}PhCH{=}CH{-}C(SiMe_2CMe_3){=}C{=}O)$ [141]. A novel approach to enantiomerically enriched complexes used brucine N-oxide to decarbonylate racemic (bda)$Fe(CO)_3$ complexes in the presence of ligands such as trimethyl phosphite. This resulted in formation of enantiomerically enriched compounds of the type (bda)$Fe(CO)_2L$ [XRC: L = $P(OMe)_3$, PBu_3], whose absolute configurations and circular dichroism spectra have been correlated [177]. Reaction of (bda)$Fe(CO)_3$ with sulfinyl-substituted enones, $Me_3CS(O)CH{=}CH{-}COMe$, resulted in transfer of the $Fe(CO)_3$ group, with high facial selectivity directed by the configuration of the sulfinyl group [142]. (Bda)$Fe(CO)_3$ itself has been partially resolved by displacing a carbonyl ligand thermally with a chiral phosphine, chromatographic separation of the resulting diastereomers, and recarbonylation [178]. The ligand properties of 1-azabutadienes have been explored. η^4-Complexes are readily formed; more interestingly, the free azadienes catalyze transfer of $Fe(CO)_3$ groups from $Fe_2(CO)_9$ to dienes at about 60°C, allowing use of *both* irons from the reagent. Attachment of the azabutadiene to a solid support provides a reusable heterogeneous catalyst for conversion of dienes to η^4-$Fe(CO)_3$ complexes [179].

6.3. Complexes of cyclic dienes

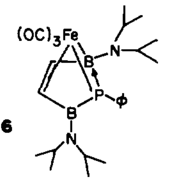
The rotational spectrum of tricarbonyl(cyclobutadiene)iron has been measured by microwave spectrometry; the vibrationally averaged structure showed a square cyclobutadiene ring [180]. Mono- and 1,2-disubstituted cyclobutadiene complexes have been prepared from cyclobutenediones, in 35–83% yields [181]. The iron tricarbonyl complex of dimethyl cyclobutadiene-1,2-dicarboxylate has been used as a source of the free ligand in syntheses of polycyclic molecules by multiple cycloadditions. Cerium(IV) oxidation of the complex in the absence of trapping agents gave a dimer, trimer, and tetramer having fused cyclobutane rings [182]. Use of benzoquinones [183], norbornene, or norbornadiene [184] as trapping agents led to formation of novel polycyclic products. An intramolecular Friedel–Crafts reaction has been used to investigate the preferred stereochemistry of electrophilic attack on the tricarbonyl(cyclobutadiene)iron systems [eqn. (12)]. The preferential formation of **25** is consistent with *exo* attack [185], but anomalies in the spectra reported for **25** need to be resolved before a firm conclusion can be drawn. A 1,3-diphosphacyclobutadiene complex has been prepared by reaction of **11** with hexachloroethane in toluene, which led to loss of zirconocene dichloride [123]. Photoelectron spectra and INDO calculations suggested that the diphosphacyclobutadiene ligand bonded more strongly to iron than cyclobutadiene itself [186].



(12)

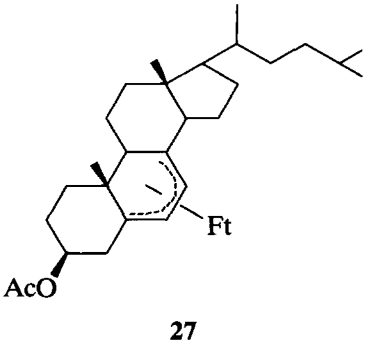
Equation (6) illustrated the conversion of a tricarbonyl(cyclopentadiene)iron complex to a carbenoid, with attendant ligand coupling [156]. Cyclopentadienone complexes have been assembled from trimethylsilyl-substituted alkynes and $Fe(CO)_5$ upon thermal reaction; the 2,5-bis(trimethylsilyl)cyclopentadienones were selectively formed [187]. Application of this reaction to diynes led to cyclopentadienone complexes having 3,4-fused five and six-membered rings. Desilylation of the bis(trimethylsilyl)-substituted tricarbonyliron products was not successful, but replacement of one carbonyl ligand by triphenylphosphine facilitated the desilylation reaction [188]. Carbonylation of the fulvalene complex $(\eta\text{-}C_6H_6)Fe(\mu\text{:}\eta^5,\eta^5\text{-}C_5H_4\text{-}C_5H_4)Fe(\eta\text{-}C_6H_6)$ at −20°C resulted in formation of (μ-fulvalene)bis(tricarbonyliron). Reaction with trimethylphosphine, however, formed the product, (μ-fulvalene)tetrakis(trimethylphosphine)diiron(*Fe–Fe*); in the presence of $NaPF_6$, a redox process led to formation of the dication $[\text{-}C_5H_4Fe(PMe_3)_3^+]_2$, as the PF_6^- salt [189].

The silole complex $(\eta^4\text{-}C_4Ph_4SiMeFp)Fe(CO)_3$ was prepared either by complexation of the silole with $Fe(CO)_5$ or by reaction of $(\eta^4\text{-}C_4Ph_4SiMeCl)Fe(CO)_3$ with NaFp. In either case, the two iron groups were trans; the Fp group occupied a pseudoaxial position in the crystal structure [190]. The crystal structure of the novel heterocyclopentadiene complex **26** has also been reported [191].



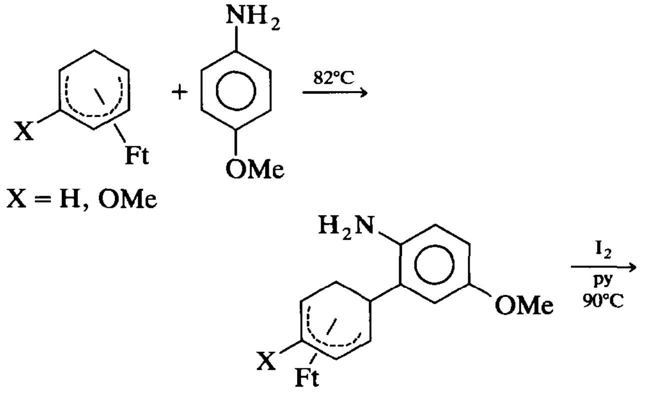
26

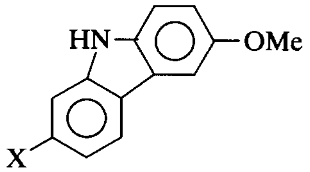
Hydrolysis of **12** produced the $Fe(CO)_3$ complex of 2-(*tert*-butyl)-3-formylnorbornadiene [131]. The effects of temperature on the carbonyl stretching bands of tricarbonyl(norbornadiene)iron have been reinterpreted in terms of a model involving a single potential well, in contrast to earlier analysis in terms of a double well [192]. Six rotational constants derived from the microwave spectrum of tricarbonyl(cyclohexadiene)iron have given rise to structural parameters [Fe–C1 2.125 Å; Fe–C2 1.968 Å] [193] which are rather different from the previous results of a crystal structure of the same compound as a guest in a thiourea matrix [2.102 and 2.032 Å]; they are also quite different from the previously cited microwave results for (butadiene)tricarbonyliron [160]. The structure of tricarbonyl[7-dehydrocholesteryl acetate]iron, **27**, has been studied by both high-field NMR and X-ray crystallography. Removal of the 9-hydride by trityl cation was sterically prevented, but the corresponding cation was prepared by protonation of the 9,11-dehydro analog [194].



27

Interconversion of substituted tricarbonyl(η^4-cyclohexadiene)iron and tricarbonyl(η^5-cyclohexadienyl)iron cations underlies a good deal of important synthetic chemistry. The factors controlling attack of nucleophiles on the cyclohexadienyl cations therefore continue to attract attention, and expansion of the existing catalog of usable nucleophiles also attracts effort. In the category of a novel nucleophile is the conjugate base of the carbenoid $CH_3C(OMe)\text{=}Cr(CO)_5$, which, like other nucleophiles, attacked tricarbonyl(cyclohexadienyl)iron$^+$ at C1, *anti* to the tricarbonyliron group [XRC]. Further deprotonation of the initial product and reaction with a second cyclohexadienyl cation yielded two diastereomers of $(OC)_5Cr\text{=}C(OMe)CH[C_6H_7Fe(CO)_3]_2$ [195]. Cuprate reagents have been used to form carbon–carbon bonds by reaction with cyclohexadienyliron cations: for example, the serine-derived reagent $IZnCu(CN)CH_2CH(NHBoc)CO_2CH_2\text{-}Ph$ was used to form, after treatment with trimethylamine oxide, dihydrophenylalanine derivatives, as diastereomeric mixtures [196]. Diarylcuprates derived from *o*-bromobenzoic acid derivatives have been used similarly, with subsequent lactonization involving the carboxylic acid group, in the synthesis of an antifeedant alkaloid [197]. Vinyl cuprates effectively formed C–C bonds with the tricarbonyl(η^5-2-alkoxy-5-methylcyclohexadienyl)iron cations, in contrast to organozinc or -cadmium reagents, which only effected deprotonation of the 5-methyl group. The position of attack was governed in part by the size of the alkoxy group, methoxy favoring 1-attack and isopropoxy favoring 5-attack [198]. Cyclohexadienyliron cations have been used to arylate 2′-deoxyguanosine at the N2 amino group, the aryl ring resulting from decomplexation and dehydrogenation [199]. Electron-rich anilines reversibly attacked cyclohexadienyliron cations to form C–N bonds at room temperature; on heating to 80°C, C–C bond formation (arylation) occurred. This has been coupled with an oxidative cyclization sequence to form carbazoles [eqn. (13)] [200].

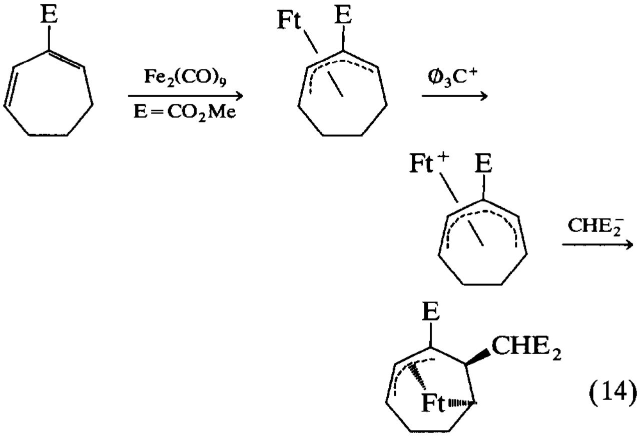




(13)

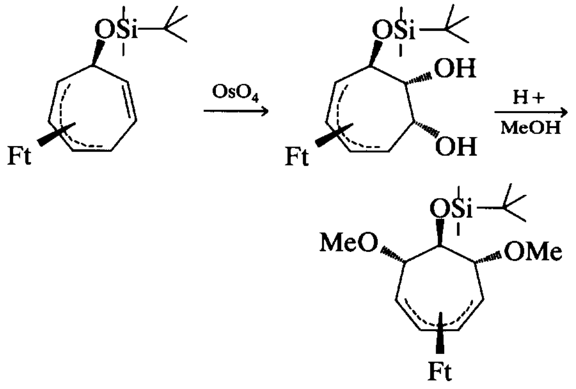
The effects of temperature and pressure on the kinetics of reaction of three 4-substituted pyridines with dienyliron cations have been studied by stopped-flow methods [201–203]. Consistent with earlier reports, the relative reactivities of cyclohexadienyl-, 2-methoxycyclohexadienyl-, and cycloheptadienyl-tricarbonyliron cations were 25 : 4 : 1 at 10°C, using 4-ethylpyridine as nucleophile [201]. The low reactivity of the cycloheptatrienyl cation in both the association and dissociation of the pyridines resulted from both enthalpy and entropy factors.

Isomerization of (7-*exo*-acylcycloheptatriene)tricarbonyliron, the product of acylation of $Fe(CO)_3(C_7H_7)^-$, occurred by deprotonation and reprotonation of the $(C_7H_6COR)Fe(CO)_3^-$ anion. Kinetic reprotonation was found to produce the 5-acylcycloheptatriene complex, and thermodynamic reprotonation the 6-acyl isomer [204]. Mass spectra of some furotropone and furotropilidene complexes have been investigated [205]. Complexation of 2-carbomethoxycyclohepta-1,3-diene with $Fe(CO)_5$ in refluxing dibutyl ether produced predominantly (56%) the more stable 1-carbomethoxycyclohepta-1,3-diene complex. In contrast, complexation with $Fe_2(CO)_9$ in acetone at room temperature produced mostly (55%) the unrearranged complex. Trityl-induced hydride removal from these cycloheptadiene complexes produced the (1- and 3-carbomethoxycycloheptadienyl)tricarbonyliron cations, respectively. Each of these cations underwent attack by dimethyl sodiomalonate at C2, to form $\eta^3:\eta^1$-products, as illustrated in eqn. (14) [206]. Substitution of triphenylphosphine for a carbonyl ligand did not alter this reactivity pattern. This type of attack is not unusual in open pentadienyl- and in cycloheptadienyliron cations, and appears to be favored by the presence of ester substituents [206].



(14)

Adducts of a number of phosphines and diphosphines to tricarbonyl(cycloheptadienyl)iron cations have been prepared, including diphosphine-bridged species such as $[-CH_2PPh_2(\eta^4-C_7H_9)Fe(CO)_3]_2^{2+}(BF_4^-)_2$ [207]. Reactions of nucleophiles with the dicarbonyl-[6-(methoxymethyl)cycloheptadienyl](triphenyl phosphite)iron cation, generated by methoxymethylation of the cycloheptatriene complex, have been studied [208]. Addition of oxygen nucleophiles to the tricarbonyl-(6-*exo*-methylcycloheptadienyl)iron cation occurred cleanly at the 1-position of the cation. Demetallation gave *cis*-6-methylcyclohepta-2,4-dienol derivatives [209]. Stereocontrolled formation of trisubstituted cycloheptadienes was achieved by the route shown in eqn. (15) [210]. Functionalization of cyclooctadiene *via* its dicarbonyl(η^5-cyclooctadienyl)(triphenylphosphine)iron$^+$ cation has been achieved. Reaction of the unsubstituted cation or its 6-*exo*-methoxymethyl derivative with nucleophiles [NaSPh, $NaCH(CO_2Me)_2$] occurred cleanly at the 1-carbon, affording complexed *cis*-5,8-disubstituted cycloocta-1,3-dienes [211].



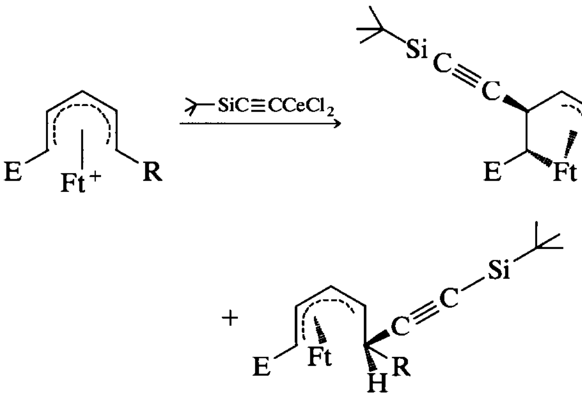
(15)

7. η^5-Dienyl compounds

7.1. *Compounds with open pentadienyl ligands*

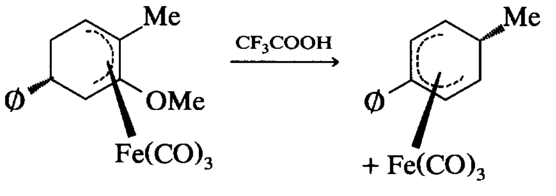
The term, "open", as used here, refers not only to acyclic pentadienyl ligands, but also to cyclohexadienyl and cycloheptadienyl ligands, which do not have a closed cycle of carbon (or other) atoms coordinated to iron. Most of the compounds encountered here are $(\eta^5\text{-dienyl})FeL_3^+$ cations, whose principal chemical property is attack by a nucleophile to give a neutral η^4 product. Accordingly, many of the products have already been described in Section 6. In those cases, this section will concentrate on preparation of the cations and systematics of their reactivity toward nucleophiles.

The tricarbonyl[2-(triethylsilyl)-1,3-hexadienyl]iron$^+$ cation was prepared from tricarbonyl[2-(triethylsilyl)-butadiene]iron by consecutive acetylation, reduction, and acid treatment. A variety of nucleophiles cleanly attacked the C5 terminus of the cation, probably as a result of the steric size of the triethylsilyl group at C2 [212]. The ester-bearing pentadienyl cations [(MeOCO)CHCHCHCHCHR]Fe(CO)$_3^+$ [R = H, Me] underwent attack by the organocerium reagent $Me_3SiC{\equiv}CCeCl_2$ at C3 and C6 (C1 is the ester carbon), as shown in eqn. (16). Formation of the $\eta^3:\eta^1$ product, as in the cycloheptadienyl case [eqn. (14)], is probably fostered by the ester group, which interacts strongly with the Fe–C σ-bond in the product. The diene product formed an allene upon desilylation with tetrabutylammonium fluoride [213]. An alternative route to such allenes [167] was previously described.



(16)

The trifluoroacetic acid-induced conversion of methoxy-substituted tricarbonyl(cyclohexadiene)iron complexes to cyclohexadienyl complexes has been studied. The reaction was found to be dominated by kinetic control, and the products formed generally arose from the best-stabilized intermediates, even when greater degrees of rearrangement were involved. Eqn. (17) illustrates a typical conversion [214]. The trifluoromethyl group in the complex tricarbonyl[3-(trifluoromethyl)cyclohexa-3,5-diene-*cis*-1,2-diol] directed the selective ionization of the 1-hydroxy group on treatment with acid [215]. Many cases of nucleophilic attack on substituted cyclohexadienyl complexes were described in Section 6 [195–200]. In all cases, nucleophiles attacked at terminal positions (C1 or C5) of the cyclohexadienyl complexes, and usually at the less hindered end. Attack at C2 or C4 remains unknown in the (cyclohexadienyl)iron cations, in contrast to open-chain [213] and cycloheptadienyl [206] cases.



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

This section describes results on FpH, Fp$^-$, Fp$^\bullet$, and Fp$^+$ [Fp = (η-C_5H_5)Fe(CO)$_2$], and on compounds (sometimes called "inorganometallics") containing bonds between the Fp group and non-transition metal elements other than carbon. Organic derivatives, FpR and FpCOR, 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.

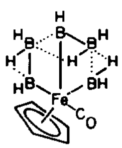
Reaction of $FpPPh_2H^+$ with $NaBH_4$ occurred by phosphine displacement to form FpH and PPh_2H as intermediates; these reacted in turn to form CpFeH(CO)(PPh_2H). Other FpL$^+$ cations [L = various trialkyl phosphites] were said to react with $NaBH_4$ directly by formation of the hypervalent phosphorus species, FpP(OR)$_3$H, which lost CO with simultaneous hydride migration to form CpFeH(CO)[P(OR)$_3$] [216]. CpFe(dppm)H was formed directly by reaction of $FeCl_2$ with dppm, activated magnesium, and cyclopentadiene. A diiron species was also produced. CpFe(dppm)H reacted with CS_2 to form the dithioformate complex, CpFe(η^1-dppm)(η^2-S_2CH) [217]. Crystal structures of CpFe(dppm)H and CpFe(PPh$_3$)$_2$H, obtained by low temperature reaction of the phosphines with CpFe(C_6H_6), have been reported. A large NMR coupling between the Fe–H and one methylene hydrogen of the dppm ligand was explained in terms of the ligand conformation [218]. A crystal structure of the 17-electron radical-cation Cp*Fe(dppe)D$^+$PF$_6^-$ has also been reported. The Fe–P bond distances were fairly normal, averaging 2.21 Å, and the Fe–D distance was about 1.55 Å. The 17-electron cation added trimethylphosphine, but not more crowded phosphines, in solution [219]. It also added CO at −80°C to form the 19-electron species Cp*FeH(η^2-dppe)(CO)$^+$, which gave, upon one-electron reduction with cobaltocene, Fe(CO)(dppe)(η^4-C_5Me_5H) [220]. Protonation of Cp*Fe(dppe)H at −80°C gave a η^2-dihydrogen complex, which at room temperature transformed into Cp*Fe(dppe)H$_2^+$ [219].

Of several metal carbonyl anions tested, Fp$^-$ was the fastest at outer-sphere reduction of Co(o-phenanthroline)$_3^{3+}$. One-electron reductions of iron(III) phenanthroline and pyridinium ions were also investigated [221]. Similar results were obtained for reduction of solvated $CrCl_3$, Fp_2 being the sole iron-containing product in all cases. Reactions of Fp$^-$ with FpX also produced Fp_2, with the rates little affected by the nature of X (Cl, Br, I) [222]. Fp$^-$ reacted with several organotransition metal compounds, $RMn(CO)_5$ [R = Me, CH_2Ph, Ph] and $RMo(CO)_3Cp$ [R = Me, Et, CH_2Ph] by displacement of the manganese or molybdenum group from the organic group, forming RFp. The reactivity sequence observed and the kinetics were consistent with an S_N2 mechanism [223]. Reaction between Fp_2Hg and $(Et_3Ge)_2Hg$ formed $FpHgGeEt_3$ [224].

A complete redox potential diagram relating the oxidation states of Fp monomer and dimer has been derived. The free energy change for homolytic dissociation of Fp_2 in acetonitrile has been estimated as 104 (21) kJ mol^{-1}. Large overvoltages exist in some two-electron changes, such as oxidation of Fp_2 to two $Fp(NCMe)^+$, due to the intermediacy of high-energy intermediates such as Fp_2^+ [225]. What seems to be a complete mechanistic picture of photosubstitution of THF or phosphites into Fp_2 has been obtained by microsecond and nanosecond time-resolved IR spectroscopy. Essentially all reactions can be explained on the basis of three intermediates: $CpFe(\mu\text{-}CO)_3FeCp$, $CpFe(CO)_2^{\bullet}$, and $CpFe(CO)L^{\bullet}$; rate constants for most steps have been estimated [226].

$CpFe(dppe)(\eta^1\text{-}O{=}CMe_2)^+$, derived from photolysis of $CpFe(dppe)(CO)^+$ in the presence of acetone, was a very effective Lewis acid catalyst for the Mukaiyama aldol condensation. Binuclear species derived from $Fp(\mu\text{-}dppe)Fp^{2+}$ were also effective [227].

A ferraborane cluster, **28** [XRC], in which a CpFe(CO) group occupies a vertex in a pentagonal pyramidal cluster, was prepared by photodecarbonylation of FpB_5H_8. 2D-NMR studies of pentaborane derivatives, including FpB_5H_8, $Fp_2B_5H_7$, and $FpB_5H_7PPh_2$, have been interpreted in terms of B–B bond orders and other parameters from MNDO calculations [229]. Photolysis of $FpB_5H_8PPh_2$ resulted in loss of a BH_2 vertex as well as CO, and formation of a Fe–P bond in the product, $CpFe(CO)B_4H_6PPh_2$. Passing a solution of this product through a silica column removed another boron, forming $CpFe(CO)B_3H_7PPh_2$ [XRC] [230]. Fp_3Ga has been prepared from NaFp and $GaCl_3$; the crystal structure showed the expected trigonal planar geometry about the gallium, and an average Fe–Ga bond length of 2.44 Å [231].



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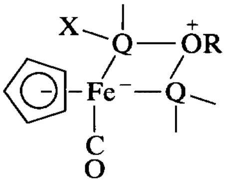
1,3- and 1,4-diFp-substituted decamethylcyclohexasilanes have been prepared from a mixture of the corresponding dichlorides, $Si_6Cl_2Me_{10}$, and separated. The structures were elucidated by 2D NMR methods. After purification, they were reconverted to dihalodecamethylcyclohexasilanes [232]. The silole complex, $FpSi(Me)C_4Ph_4$, and its tricarbonyliron complex [190] were previously mentioned, in Section 6.3. The mass spectra of a series of disilane derivatives, $FpSiMe_2SiMe_2Y$ [Y = Fp, Fc, $(C_5H_4)Fe(CO)_2R$], have been scrutinized. Cleavage of the Si–Si bond was better facilitated by the ferrocenyl group compared to the Fp group [233]. The Si–H bond of $FpSiR_2H$ and $Fp'SiR_2H$ compounds was oxidized by dimethyldioxirane to form silanols, $Fp(')SiR_2OH$, obtained in up to 98% yields [234].

Photolysis of Fp^*SiMe_3 in the presence of $RSiH_3$ [R = CMe_3, CMe_2CHMe_2] resulted in silyl group interchange, forming Fp^*SiH_2R and Me_3SiH. With R = p-tolyl, the bis(silyl) product $Cp^*FeH(CO)(SiMe_3)(SiH_2R)$ formed instead. The cyclopentadienyl analogs formed bimetallic products [235]. Photolysis of $FpCH_2SiMe_2SiMe_2SiMe_3$ resulted in rearrangement to $FpSiMe_2CH_2Si_2Me_5$. In the presence of PPh_3, the Fp' analog was formed. The pentamethylcyclopentadienyl and η^5-indenyl analogs behaved similarly. However, the branched isomers $FpCH_2SiMe(SiMe_3)_2$ reacted differently, forming $FpSiMe_3$ and $FpSiMe_2CH_2SiMe_3$ with loss of silylene units. In refluxing hexane, $FpCH_2SiMe_2SiMe_2SiMe_3$ was stable, the Fp^* analog decomposed to Fp_2^*, and the indenyl analog gave the product with the rearranged chain [236]. The ^{29}Si–^{29}Si coupling in **29** [Q = Si; R = CMe_3; X = $OCMe_3$] (29 Hz) has been found to be much smaller than in $FpSiMe_2SiMe_3$ (128 Hz). Extended Hückel calculations on $Cp(OC)Fe[SiH_2OHSiH_2]$ indicated no Si–Si bonding, the coupling being simply the sum of the two two-bond couplings which result from the cyclic structure [129].



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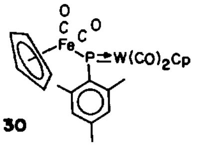
A germanium analog of **29** [Q = Ge; X = R = Me] has been prepared by photolysis of $Fp^*GeMe_2GeMe_2OMe$, in which the methoxy group serves as an internal trap for the initially formed germyl(germylene)iron complex, $Cp^*Fe(CO)({=}GeMe_2)GeMe_2OMe$. The fluxional process of ring opening and dimethylgermylene rotation had a $\Delta G^{\ddagger}$ of 89 kJ mol^{-1} [237]. The mixed silyl–germyl analogs have been similarly prepared; the germylene methyl groups exchange sites in these compounds with a $\Delta G^{\ddagger}$ of 62 kJ mol^{-1}. It was inferred that iron–germylene bonding conferred greater stabilization than iron–silylene bonding [238]. The Ge–H bonds of $FpGeHPh_2$ and $FpGeH_2Ph$ were highly reactive to N-chlorosuccinimide, but not to base. Treatment of the compounds with $LiN(^iPr)_2$ or *tert*-butyl-lithium resulted in deprotonation of the Cp ring rather than the germanium, with migration of the germyl groups to the ring. $FpGeHPh_2$ hydrogermylated phenylethyne in the presence of H_2PtCl_6, but with low regioselection [239]. Treatment of the η^5-indenyl complex $(C_9H_7)Fe(CO)_2SiMe_3$ with $LiN(^iPr)_2$ resulted in deprotonation of the 1-position of the indenyl ligand and migration of the silyl group thereto. Repetition and treatment with Ph_3SnCl led to the 1,3-disubstituted indenyl iron anion, which was quenched with additional Ph_3SnCl. A crystal structure of the resulting product confirmed the substitution pattern [240].

Exclusive isomerization of either FpPHD or $FpPH_2$ has been used to demonstrate laser-stimulated selective reactions and the preparation of pure isotopomers [241]. $Fp^*P(SiMe_3)_2$ and analogs having other heavily substituted Cp rings have been prepared by reaction of Fp^*Br (and analogs) with $LiP(SiMe_3)_2$. The crystal structure of $(\eta\text{-}C_5Me_4Et)Fe(CO)_2P(SiMe_3)_2$ was determined. Reaction of the disilylphosphido complexes with $ArPCl_2$ [Ar = 2,4,6-tri(*tert*-butyl)phenyl] cleanly produced the diphosphenyl complexes $Fp^*P{=}PAr$ [242]. A dimetallophosphonium salt, $FpPH(Mes)W(CO)_3Cp^+BF_4^-$, resulted when $FpCO^+BF_4^-$ was attacked by $MesPHW(CO)_3Cp$ [Mes = 2,4,6-trimethylphenyl]. Deprotonation resulted in formation of **30** [243]. Heating $Fp^*P(R){-}P{=}CR_2$ [R = $SiMe_3$] at 85°C resulted in addition of a C–H bond of the Cp* ligand across the P=C bond [eqn. (18)]; the product was characterized by formation of a $Cr(CO)_5$ adduct, whose crystal structure showed a long Fe–P bond (2.38 Å) [244]. The starting material in the eqn. (18) was prepared by reaction of $Fp^*P(SiMe_3)_2$ with one equivalent of $ClP{=}C(SiMe_3)_2$; with excess of the latter reagent, condensation continued up to the formation of the bicyclic product **31** [XRC, 27% yield] [245]. Reaction of the less hindered KFp with one equivalent of $ClP{=}C(SiMe_3)_2$ at −70°C led to formation of $FpP{=}C(SiMe_3)_2$, but this dimerized spontaneously at 20°C, forming a product assigned the structure **32** [154]. Reaction of Fp^*PH_2 with one equivalent of the reagent $ClP{=}C(SiMe_3)_2$ produced a diphosphirane product, $Fp^*\overline{P{-}C(SiMe_3)_2{-}P}H$, isolated as the $Cr(CO)_5$ adduct. Use of two equivalents of the reagent resulted in formation of a cyclotriphosphine, $Fp_2^*P_3[CH(SiMe_3)_2]$ [246].



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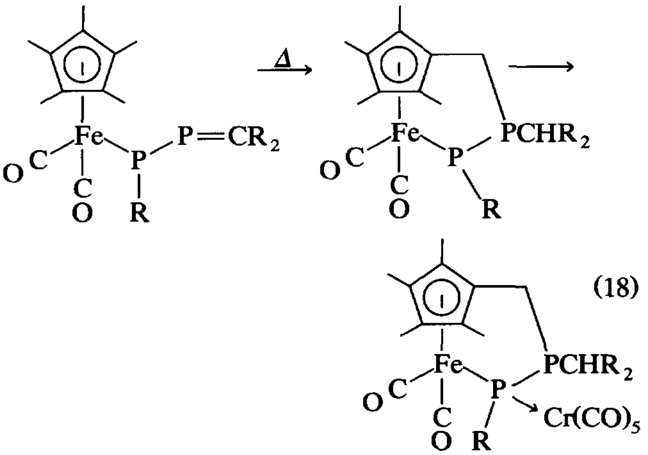

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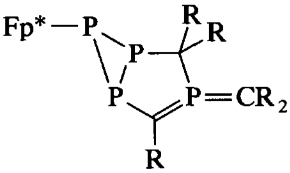

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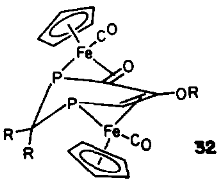
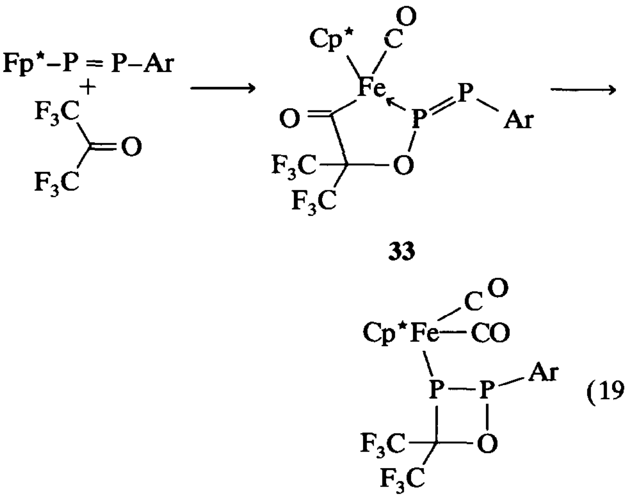


32

Several cycloaddition reactions of diphosphenyl complexes $Fp^*P{=}PAr$ have been reported. Reaction with hexafluoroacetone occurred in a two-stage manner, illustrated in eqn. (19). The crystal structures of both products were obtained; **33** showed rather



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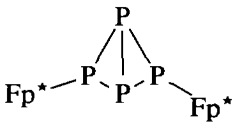
short Fe–P (2.08 Å) and P=P (2.01 Å) bonds, whereas **34** showed longer bonds (Fe–P 2.33 Å, P–P 2.25 Å) [247]. Diethyl azodicarboxylate added to Fp*P=PAr in a cheletropic [1 + 4] cycloaddition to the metallated phosphorus [248]. N-Methylmaleimide gave a [2 + 2] cycloaddition to form a diphosphetane when the two reagents were combined in equal amounts; with excess N-methylmaleimide, a rather bizarre rearranged 1:2 adduct resulted [249]. 1,2,4-Triazolinediones also reacted with the diphosphenyl complex in benzene to form [2 + 2] adducts; however, in ether dimers of the [2 + 2] adducts resulted [250]. Fp*P=PCp*, which was formed by displacement of a Cp^{*-} from Cp*P=PCp* using KFp*, dimerized to a tetraphosphetane, which subsequently lost the elements of Cp$^*_2$ to form the bicyclo[1.1.0]tetraphosphane **35** [251].



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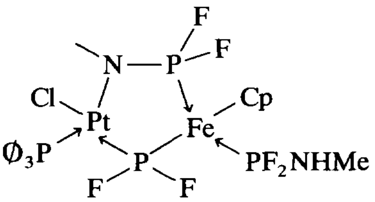
A number of FpPPh$_2$CH$_2$R$^+$BF$_4^-$ salts [R = Ph, CN, SiMe$_3$, CO$_2$Et, PPh$_2$] have been prepared by displacement of water from Fp(OH$_2$)$^+$BF$_4^-$. Conversion of FpPBu$_3^+$ in acetonitrile to CpFe(CO)(NCMe)(PBu$_3$)$^+$ allowed preparation of CpFe(CO)(L)(PBu$_3$)$^+$ [L = Ph$_2$PCH$_2$R] [252]. Reaction of FpI with Me$_2$NN(PPh$_2$)$_2$ led to formation of CpFe(CO)(η^2-PH$_2$PN(NMe$_2$)PPh$_2$)$^+$I$^-$ [XRC] [253]. CpFeCl(η^1-PF$_2$NMePF$_2$)$_2$ reacted with (Ph$_3$P)$_2$Pt(PhCCPh) to form an unexpected bimetallic product, **36** [254]. Sodium methoxide attacked the phosphinite complexes Fp(PPh$_2$OR)$^+$Cl$^-$ [R = Me, Et] at a carbonyl group, to form CpFe(CO)(CO$_2$Me)(PPh$_2$OR). The cationic methylphosphinite compound underwent Arbuzov-type dealkylation in benzene at room temperature, giving Fp–P(=O)Ph$_2$, but the ethylphosphinite did not react under these conditions [255]. Diels–Alder reactions of complexes of 3,4-dimethyl-1-phenylphosphole [DMPP], especially CpFe(CO)(DMPP)I, have been studied. Several chelated products were produced by use of vinylphosphines as dienophiles. An especially interesting example is the formation of **37** on heating CpFe(CO)(DMPP)I in tetrachloroethane [256]. The P–H protons in CpFe(η^2-PPhMe-o-C$_6$H$_4$PPhMe)(PH$_2$Ph)$^+$ were sufficiently acidic to result in formation of the 1-phenylphosphetane complex [XRC] upon reaction with 1,3-dibromopropane and base. The 1-phenyldiarsetane complex [XRC] was prepared by a related route [257].



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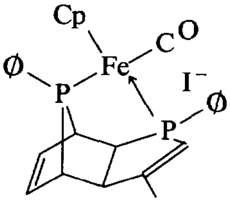

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Rapid exchange of SMe$^+$ groups between FpSMe and Fp(MeSSMe)$^+$ led to averaged Cp and Me signals in the proton NMR spectrum, even at −78°C. Similar SPh$^+$ exchange was also observed [258]. CpFe(CO)(μ-SCMe$_3$)$_2$Fe(CO)Cp reacted photochemically with azobenzene. Both carbonyl groups were displaced, with formation of CpFe(μ-SCMe$_3$)$_2$(μ-PhN=NPh)FeCp [XRC] [259]. Solid state ^{13}C NMR spectra of FpQMe$_2^+$ salts [Q = S, Se, Te] have been used to study the dynamics of Cp ring rotation. The rate increased in the order S < Se < Te [260]. FpSeMe was prepared by reaction of FpI with MeSeCr(CO)$_5^-$ in THF at room temperature [114].

FpCl and FpBr were readily converted to FpCH$_2$X by reaction with diazomethane in the presence of copper powder, but FpI reacted more slowly and incompletely. Fp*CH$_2$X were formed similarly. The iodides, which decomposed at room temperature to Fp$^{(*)}$I and polyethylene, could be prepared from the other halomethyl derivatives using NaI/acetone [261].

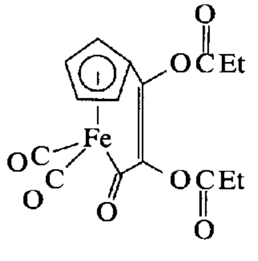
Many derivatives of FpX derive their principal interest from the substituents present on the cyclopentadienyl rings. The ^{13}C and ^{17}O NMR spectra of the full range of ring-methylated derivatives, (η-C$_5$H$_{5-n}$Me$_n$)Fe(CO)$_2$I and (η-C$_5$H$_{5-n}$Me$_n$)Fe(CO)$_3^+$PF$_6^-$, have been obtained, and the effects of methylation on the carbonyl groups assessed [262]. The new ligand, tetramethyl(trifluoromethyl)cyclopentadiene, has been prepared and converted, via the dimer, to (η-C$_5$Me$_4$CF$_3$)Fe(CO)$_2$I. The ligand was described as having the steric properties of pentamethylcyclopentadienyl (Cp*) and the electronic properties of cyclopentadienyl, based on IR and X-ray photoelectron spectroscopic comparisons of various complexes [263]. FpX derivatives containing the very bulky pentaphenylcyclopentadienyl ligand, including (η-C$_5$Ph$_5$)Fe(CO)(PMe$_3$)Br, have been prepared. Steric inhibition of tripodal rotation could be observed at low temperature [264]. Conversion of the racemic binaphthyldimethylenecyclopentadiene to Fp$_2$ analogs by reaction with

$Fe(CO)_5$ gave the C_2 and C_s isomers in a 72:28 ratio. The partially resolved ligand was converted to the enantiomerically enriched FpI analog by formation of the dimer and reaction with I_2 [265]. NOE and 2D-NMR methods have been applied to conformational analysis of a series of $[\eta$-1,3-$C_5H_3(SiMe_3)_2]Fe(CO)LI$ derivatives having L = isonitriles, phosphites, and phosphines. Steric interactions between the trimethylsilyl groups and the phosphites resulted in hindered rotations [266]. Analogous NMR studies [267], as well as studies of absolute integrated IR intensities [268], have also been carried out for several monosubstituted cyclopentadienyl compounds, $(\eta$-$C_5H_4R)Fe(CO)LI$ [R = $CHPh_2$, $CHMe_2$, Ph, CPh_3, $SiMe_3$, CO_2Me, I].

A detailed crystallographic comparison of CpFe(CO)[$P(OMe)_3$]I and CpFe(NO)[$P(OMe)_3$]$I^+BF_4^-$ has been carried out. Very substantial differences were noted in several bond lengths, especially the Fe–I bonds (2.605 *vs.* 2.951 Å), and the Fe–P bonds (2.149 vs. 2.206 Å), attributable to reduced ability of iron to back-bond in the cationic nitrosyl compound [269]. One-step conversion of FpI to CpFe(dppe)I, and ligand substitution reactions of the latter, have been reported [270].

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

Reaction of the carboxylate K^+ CpFe(CO)(PPh_3)-CO_2^- (Fp'CO_2K) with cationic rhenium salts produced μ-carboxylato compounds, Fp'COORe$(CO)_4$L [L = CO, PPh_3, $P(OPh)_3$]. The triphenylphosphine-substituted product, the most stable, was the subject of a crystal structure determination [271]. Reaction of KFp' with Fp'$(C_2H_4)^+$ yielded the bimetallic product, Fp'$COOCH_2CH_2$Fp' as a pair of diastereomers. Alcoholysis to Fp'CO_2R and Fp'CH_2CH_2OR occurred readily [272]. Reaction of NaFp with hexafluoroglutaryl dichloride produced the diacyl, $FpCOCF_2CF_2CF_2COFp$ [XRC]. Its behavior was compared with the previously known hydrocarbon analog [273]. A similar reaction produced the phenylglyoxyl compound, FpCOCOPh, which shows a nearly perpendicular dicarbonyl grouping in the crystal. The compound spontaneously lost CO at 25°C, giving FpCOPh [274]. Reaction of Cp^- with $Fe(CO)_5$, under conditions not clear to this reviewer, followed presumably by quenching with a propanoyl compound, produced **38** [XRC]. This reaction assumes considerable interest, since Fp compounds have rarely resulted from direct reactions of cyclopentadienyl anions with iron carbonyl compounds. An indenyl analog, with coupling to the 1-position of the indenyl ligand, was also prepared [275].



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The crystal structures of Cp'Fe(CO)(COMe)-($PMePh_2$) and CpFe(CO)(COMe)(PMe_2Ph) showed moderately short Fe–P bond lengths of about 2.18 Å, which were attributed to absence of steric repulsions [276]. The crystal structure of Fp'$COCH_2$Ph was also determined, and the structure was successfully reproduced by molecular mechanics calculations [277]. Alkylation and aldol condensations of the enolate from Fp'$COCH_2$Ph have been found to occur with little stereoselection, with the ratio of isomers formed dependent on the base. Formation of tin or aluminum enolates led to improved selectivity in the aldol condensation reactions [278]. Alkylation reactions of the enolate from Fp'$COCH_2$OMe were more selective, showing a tendency to form RR/SS products. Again, stereoselectivity in condensation reactions was improved by formation of tin or aluminum enolates [279]. Pure enantiomers of Fp'COC(=CH_2)OCH_2Ph have been prepared from Fp'$COCH_2OCH_2$Ph by treatment with butyl–lithium to form the enolate, and reaction with (−)-menthyloxymethyl chloride. The diastereomers of Fp'COCH(CH_2OMenth)OCH_2Ph were separated chromatographically, then treated with NaH to generate the optically pure vinyl ethers [280]. A series of organometallic NADH minimics incorporating the Fp' group at the 3-position of the dihydropyridine ring have been used to reduce ethyl phenylglyoxylate stereoselectively to ethyl mandelate, in up to 97% e.e. [281].

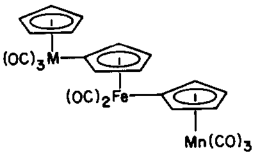
A new molecular modeling program, MMX, has been applied to calculation of conformational energy profiles of the organic groups in FpR, FpCOR, Fp'R, and Fp'COR derivatives. The results were quite consistent with experimental results deriving from variable temperature NMR and IR methods [282]. Similar success was found in matching the calculated rotational conformations of the coordinated triphenylphosphine ligands with crystallographic results [283]. The effects of ligands L on the redox-induced carbonylations of CpFe(CO)LMe [L = any of nineteen different phosphines] have been assessed. Upon oxidation of the starting materials to the 17-electron cations, methyl migration and acetonitrile association occurred rapidly. The rate-limiting step was displacement of acetonitrile in the acetyl cation by CO [284]. Migration of the methyl group to a carbonyl group in resolved (binaphthyldimethylenecyclopentadienyl)(dicarbonyl)-methyliron formed nearly racemic acetyl product, whether the reaction was carried out thermally at 80°C with triphenylphosphine or oxidatively induced at −40°C [265]. The 17-electron complexes $Cp^*FeL_2Me^+$

[L = PMe_3, $P(OMe)_3$, dppe/2] were more easily handled and purified than their air-sensitive neutral precursors, which were obtained directly by reaction of Cp*Fe(acac), the phosphine, and methylmagnesium iodide. Higher homologs could not be obtained as a consequence of free-radical chain side reactions setting in when ethyl or higher Grignard reagents were used [285].

trans-3,4-Bis(dicarbonylcyclopentadienylferriomethyl)tetrahydrofuran has been prepared by displacement of triflate groups by Fp^- [286]. Exclusion chromatography has been used for analysis of FpR and FpCOR compounds [287]. Formation of $CpCH_2X$ compounds by insertion of methylene into Fe–X bonds was previously cited; the halomethyl derivatives were readily converted to alkyoxymethyl or cyanomethyl derivatives by displacement reactions [261]. Silver ion-assisted ionization of $FpCH_2CH_2CH_2Br$ or dissociation of PhSMe from $FpCH_2CH_2CH_2SMePh^+$ cleanly produced cyclopropane. The half-life of the bromopropyl derivative was less than ten minutes, whereas the Γ-bromobutyl compound showed an ionization half-life of 150 minutes and produced no cyclobutane. In the formation of cyclopropane, clean stereochemical inversion was observed at the carbon initially bound to iron. These facts strongly suggest a concerted displacement by the electrons of the Fe–C bond in a W-shaped transition state. The same sort of mechanism is believed to hold in cyclopropanation of alkenes by $Fp{=}CH_2^+$ [288].

Thermolysis of FpCHMePh at 55°C in benzene has been found to produce styrene (45%), ethylbenzene (51%), 2,3-diphenylbutane (8%), and Fp_2 (100%). The effects of free radical traps were also studied. The Fe–C bond dissociation energy for this compound was estimated to be about 117 kJ mol^{-1}. Ionic reactivity was manifested in the insertion of SO_2 into the C–O bond of $FpCH_2CHROMe$ [R = H, Me], to form sulfonate esters, $FpCH_2CHRSO_2OMe$. The reaction occurred with retention at carbon [290].

$FpCH_2Ph$ has seen use as a source of cyclopentadienyl ring-substituted Fp derivatives, since the cyclopentadienyl ring can be deprotonated without migration of the benzyl group, in contrast to a number of other σ-bound groups. Thus, carboxylation of the ring formed $(\eta\text{-}C_5H_4CO_2H)Fe(CO)_2CH_2Ph$, which was converted to $Cp_2M[(O_2CC_5H_4)Fe(CO)_2CH_2Ph]_2$ [M = Ti, Zr]. The titanocene derivative [XRC] showed both carboxylate groups η^1-coordinated, whereas the zirconocene had one coordinated η^2 [291]. Lithiation of $FpCH_2Ph$ and treatment with electrophiles $(IC_5H_4)Fe(CO)_2CH_2Ph$ or $(C_5H_4COCl)Fe(CO)_2CH_2Ph$ resulted in formation of bimetallic products having μ-fulvalene or μ-dicyclopentadienylketone bridging ligands [292]. Similarly, lithiation of $(FpC_5H_4)Mn(CO)_3$ resulted in deprotonation of the iron-bound Cp ring as shown by quenching with $CpM(CO)_3Cl$ [M = Mo, W] to form trimetallics **39** [293].



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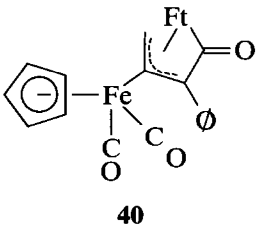
Related to **39** are aryl-Fp derivatives. The electrooxidation of 18 compounds having Fp-groups bound to arene, perfluoroarene, and azine rings has been studied by means of cyclic voltammetry. Both fluoro- and aza-substitution increased the potentials and reversibility of the oxidations. Both *meta-* and *para*-$C_6H_4Fp_2$ were oxidized irreversibly, but the tetrafluoro analogs were better behaved. Presence of a Fp group ortho to a ring nitrogen led to irreversible oxidation. Crystal structures of FpC_6F_5, *para*-FpC_6F_4N, and *para*-$Fp_2C_6F_4$ all showed the mirror plane of the Fp groups perpendicular to the arene rings [294]. A number of Fp-substituted polycyclic arenes have also been prepared via thermal decarbonylation of the corresponding acyls, and converted in three cases to η-$Cr(CO)_3$ derivatives. The tricarbonylchromium group bonded preferentially to the Fp-substituted arene ring [295]. Crystal structures of three (η-aryl-Fp)$Cr(CO)_3$ complexes showed the aryl rings to be non-planar, with the carbon bearing the Fp group bent away from the tricarbonylchromium group, consistent with strong π-electron donation by the Fp groups. The Fe–C distances were 1.99–2.00 Å [296].

Attack of cuprate reagents on some 3-Fp substituted 2-cyclopentenones resulted in replacement of the Fp group by organic groups from the cuprate. Methyllithium, on the other hand, attacked the carbonyl group, leaving the C–Fe bond intact [297]. The butenone complex (*E*)-FpCH=CHCOMe was converted to its enolate by use of $LiN(SiMe_3)_2$ at −70°C; quenching with a wide variety of electrophiles gave chain-extended products in 48–82% yields [298]. Treatment of FpCH=CHPh with *sec*-butyl-lithium, on the other hand, resulted in deprotonation of the Cp ring and migration of the styryl group thereto; quenching with iodine formed $(\eta\text{-}C_5H_4\text{–}CH{=}CHPh)Fe(CO)_2I$ [299].

Reaction of the propargylic compound, $FpCH_2C{\equiv}CPh$, with $Fe_2(CO)_9$ in pentane led to formation of the acyl **40**, isolated in 30% yield [300]. FpI underwent



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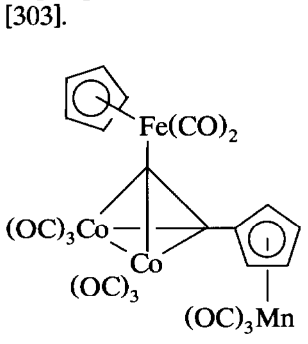
coupling with $Me_3SnC{\equiv}CR$ in the presence of catalytic $(MeCN)_2PdCl_2$ to form alkynyliron compounds, $FpC{\equiv}CR$ [R = H, Pr, Bu, Ph, $C{\equiv}CH$] in good yield. The butadiyne derivative $FpC{\equiv}C{-}C{\equiv}CFp$ was also prepared in this manner [301]. Similarly, $(\eta\text{-}C_5H_4\text{-}CH{=}CHPh)Fe(CO)_2I$ was coupled with $(\eta\text{-}C_5H_4C{\equiv}CSnMe_3)Mn(CO)_3$ to form a bimetallic product. Complexation of the triple bond in that product with dicobalt octacarbonyl finally gave **41** [299]. $FpC{\equiv}CH$ and $Fp^*C{\equiv}CH$ also formed $Co_2(CO)_6$ complexes upon treatment with dicobalt octacarbonyl, but $Fp^*C{\equiv}CFp^*$ formed a $FeCo_2$ cluster [302]. With $Cp_2Ni_2(CO)_2$, the ethynyl complexes formed both normal tetrahedral $Ni_2Cp_2(\mu{:}\eta^2,\eta^2\text{-alkyne})$ adducts and cluster adducts [303].



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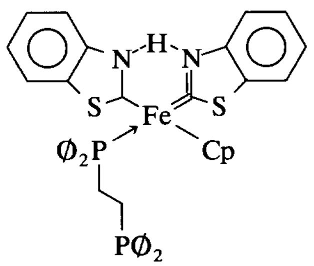
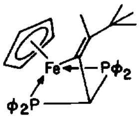


42

Crystal structures of several stable carbenoid derivatives, $CpFeL_2{=}CR_2^+$, have been reported during 1992. Perhaps the most novel is the complex **42**, obtained by reaction of $FeCl_2$ consecutively with dppe, benzothiazolyl-lithium, and cyclopentadiene. The Fe–C distances in the crystal were nonequivalent, 1.94 and 1.89 Å, but the two benzothiazolyl groups were equivalent in the NMR spectrum even at −50°C. The crystal structure of a cationic Fp=thiazolinylidene$^+$ triflate (Fe=C distance 1.95 Å) was also reported [304]. Methylation of $CpFe(dppm)C{\equiv}CPh$ with methyl triflate yielded a vinylidene complex, $CpFe(dppm){=}C{=}CMePh^+OTf^-$, whose crystal structure showed Fe=C and C=C lengths of 1.75 and 1.32 Å. Other electrophilic additions to alkynyl complexes gave an extensive set of vinylidene complexes, including the parent, $CpFe(dppm){=}C{=}CH_2^+$, from protonation and protonolysis of $CpFe(dppm)C{\equiv}CSiMe_3$. Variable temperature NMR studies indicated facile rotation of the vinylidene moieties, with barriers of 30–40 kJ mol^{-1} [305]. Most nucleophiles (Et_3BH^-, MeOH, H_2O) attacked the vinylidene cations at the α-carbon, but alkoxides deprotonated $CpFe(dppm){=}C{=}CH_2^+$, converting it to the neutral ethynyliron compound [306]. Sodium methoxide attacked the dppm ligand of $CpFe(dppm){=}C{=}CMeCMe_3^+$, resulting in formation of **43** [XRC] by



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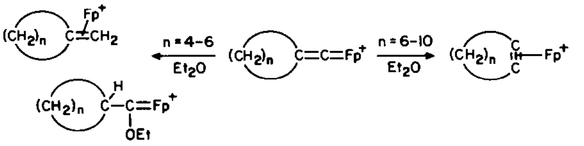
intramolecular nucleophilic attack [307]. Thermolysis of $Fp'COORe(CO)_4L$ produced the carbene-like $\mu_2{:}\eta^3\text{-}CO_2$ complexes, $Fp'{=}CO_2Re(CO)_3L$ [L = CO, PPh_3, $P(OPh)_3$] [271].

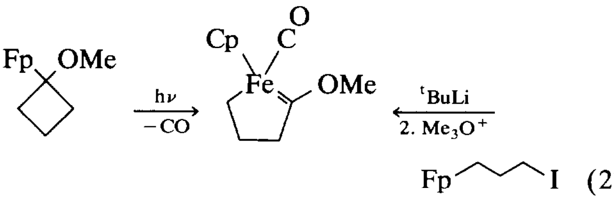
η^2-Alkyne complexes have been found to interconvert with alkenylidenes. Thus, $CpFeL_2(\eta^2\text{-}PhC{\equiv}CH)^+PF_6^-$ [L = $P(OMe)_3$] isomerized on standing in solution at room temperature to $CpFeL_2{=}C{=}CHPh^+PF_6^-$, whose crystal structure showed Fe=C and C=C bond lengths of 1.75 and 1.29 Å [308]. Photoreaction of $CpFe(CO)(dppe)^+$ with 1-alkynes directly formed alkenylidene complexes $CpFe(dppe){=}C{=}CHR^+$. $HC{\equiv}CCPh_2OH$ formed the propadienylidene complex $CpFe(dppe){=}C{=}C{=}CPh_2^+$ [309]. With sufficient ring size, cycloalkylidenecarbene complexes, generated by reaction of $(C_nH_{2n-1})COFp$ with triflic anhydride at −78°C, rearranged upon warming to cycloalkyne complexes, as shown in eqn. (20) [310].



(20)

Carbene precursors suitable for use in cyclopropanation reactions have been prepared by reaction of aldehydes with KFp at −78°C and trapping with chlorotrimethylsilane. The resulting siloxyalkyl complexes, $FpCHR(OSiMe_3)$, gave cyclopropanes on treatment with Me_3SiOTf at −78°C in the presence of alkenes [311]. Related precursors, $FpCR_2OMe$ [R = OMe, H, Ph], were synthesized by reaction of KFp with $R_2COMe^+BF_4^-$, generated *in situ* by reaction of $R_2C(OMe)_2$ and $BF_3{:}OEt_3$ [312]. As previously pointed out, studies on independent generation of $FpCH_2CH_2CH_2^+$ have indicated that it undergoes conversion to cyclopropane with inversion of the iron-bound carbon, foreclosing the intermediacy of ferracyclobutanes in this reaction [288], and probably also in cyclopropanation reactions using $FpCH_2^+$ derivatives. Further improvements in preparation of "Helquist's reagent", $FpCH_2SMe_2^+BF_4^-$, and its use in cyclopropanation of alkenes in 58–96% yield, have been reported [3,313]. Reaction of ethyl diazoacetate with styrene and α-methylstyrene to form cyclopropanes has been found to be catalyzed by $\mathrm{Fp(THF)^+BF_4^-}$, a result which suggests the intermediacy of $\mathrm{Fp{=}CHCO_2Et^+}$ in the cyclopropanation reaction [314].

One-electron reduction of the carbenoids $\mathrm{Fp^*{=}C(OMe)R^+}$ [R = H, Me] gave free radicals, which lost the O-methyl group to form the acyl Fp*COR (which decarbonylated when R = H) or abstracted a hydrogen from solvent to form Fp*CH(OMe)R [315]. Generation of a vacant coordination site on iron in small-ring Fp compounds bearing an α-methoxy group led to alkyl group migration to iron, generating stabilized carbenoid products by ring expansion. The carbenoid product shown in eqn. (21) was also generated by carbonyl attack by a Γ-carbanion, with trimethyloxonium salt quenching, as shown [316]. Application of this methodology to a bicyclo[4.1.0]heptyl derivative resulted in double migration, forming ferracyclopentenes [eqn. (22)], each of which showed Fe=C distances of about 1.84–5 Å in the crystal [317].



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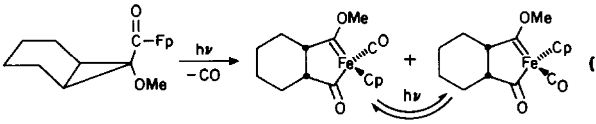

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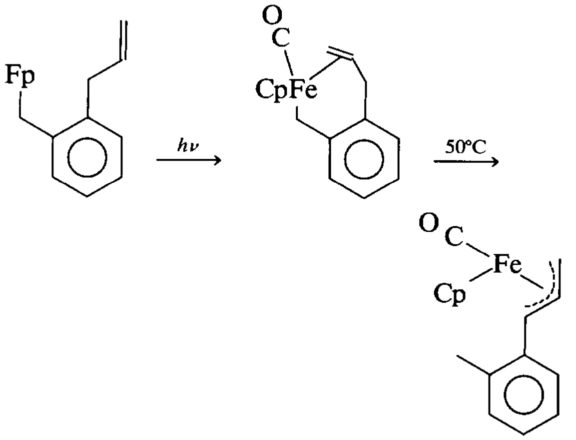
7.4. *Cyclopentadienyliron derivatives of* η^2 *to* η^4 *ligands*

Formation of η^2-alkene and alkyne complexes from alkenylidene complexes [310] was illustrated in eqn. (20). Complexes of dienes having the less highly substituted double bond coordinated to a $\mathrm{Fp^{*+}}$ group have been prepared and treated with the *in situ*-generated methylene complex $\mathrm{Fp^*{=}CH_2^+}$, which cyclopropanated the unprotected double bond. For example, the vinyl group of 4-vinyl-1-cyclohexene became coordinated to the $\mathrm{Fp^{*+}}$ group upon treatment with $\mathrm{Fp^*(OH_2)^+}$, after which cyclopropanation and decomplexation produced the *cis* and *trans* isomers of vinylnorcarane in 60% overall yield [318]. The $\mathrm{Fp^+}$-coordinated double bond is, however, reactive toward nucleophiles, as shown in reaction of $\mathrm{Fp(C_2H_4)^+}$ with nucleoside-substituted phosphite esters to form phosphonate products, $\mathrm{FpCH_2CH_2PO(OMe)(OR)}$ [319].

The crystal structure of the η^2-alkyne complex, $\mathrm{CpFeL_2(MeO_2CC{\equiv}CCO_2Me)^+PF_6^-}$ [L = P(OMe)$_3$], showed Fe–C bond lengths of about 2.02 Å and a C–C bond length of 1.22 Å for the coordinated triple bond [308]. Reactions of numerous nucleophiles with $\mathrm{Fp(PhC{\equiv}CPh)^+BF_4^-}$ in methylene chloride have been studied. In contrast to the Fp′ analogs, which generally give clean attack on the alkyne *anti* to the iron group, the Fp complex gave a mixture of *syn* attack on the alkyne (*tert*-BuS$^-$, *tert*-BuNH$_2$, R$_2$NH), and carbonyl group attack to form *cis*-acyls (OMe$^-$, RNH$_2$, pyrrolidine). Butyl-lithium apparently attacked the cyclopentadienyl ring, from which hydride transfer occurred to produce (η-$\mathrm{C_5H_4Bu}$)Fe(CO)$_2$(*Z*-CPh=CHPh) [320].

As shown in eqn. (23), photolysis of *o*-allylbenzyl-Fp led to carbonyl displacement by the free double bond. At 50°C, the disjoint η^3 product rearranged further to form the η^3-allyl product shown [321]. A bis(hetero-η^3-allyl) complex, **32** [154], was previously illustrated.



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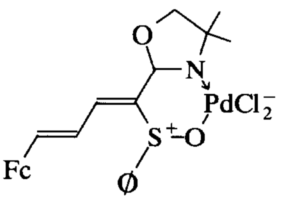
7.5. *Ferrocenes and heteroferrocenes*

No attempt is made in this section at exhaustive coverage of ferrocenes and their chemistry; the very large number of papers in which ferrocenyl groups are present in molecules as bystanders to chemical conversions occurring elsewhere makes complete coverage an impractical task. Instead, I emphasize here some novel uses of ferrocenes, their charge-transfer compounds, bridged ferrocenes, bi- and polymetallic compounds, and heteroferrocenes.

A theoretical study on the formation of ferrocene from atomic iron and cyclopentadiene indicated initiation by insertion of an excited iron atom into the allylic C–H bond of a cyclopentadiene molecule. It was proposed that the resulting high-spin intermediate would bind a second cyclopentadiene and convert to a low-spin complex, which could readily eliminate dihydrogen [322]. Temperature effects on gas-phase electron transfer equilibria of metallocenes have been assessed, and used in thermodynamic cycles to estimate the bond disruption enthalpy [ΔH° $\mathrm{CpFe^+{-}Cp} = 380 \pm 10$ kJ mol^{-1}] and solvation energy of ferricenium ion. A complete thermochemical interpretation of solution electrode potentials was offered [323]. Photodissociation of Cp$^\bullet$ from gas-phase ferricenium ion has been studied directly, with the activation energy estimated to be about 360 ± 30 kJ mol^{-1} [324], in reasonable agreement with the previous study. Ferrocene derivatives having lipophilic side chains have been shown to function as electron carriers through a liquid membrane separating aqueous solutions of ferrocyanide and cerium(IV) [325].

Ferrocene has been found to cocrystallize with buckminsterfullerene, C_{60}, to form a 2:1 solid compound [XRC], which was said to be stabilized by weak charge-transfer interactions without net electron transfer [326]. Reorientation barriers for several metallocenes in the solid state were studied by NMR relaxation methods. Intermolecular interactions dominated the barriers [327]. The molecular dynamics of solid $(C_5D_5)_2Fe^+PF_6^-$ over a temperature range of 185–355 K has been studied by a combination of crystallography, solid state NMR, Mössbauer, and heat capacity studies [328]. Crystallographic data on pentamethylferrocene, CpFeCp*, at 153, 223, and 293 K have been interpreted in terms of thermal librational motion of the rings. Rotational barriers of 7–11 kJ mol^{-1} were estimated [329]. Decamethylferrocene was also studied, in this case by variable temperature spin-lattice relaxation measurements. A ring rotational barrier of 12.5 kJ mol^{-1} was deduced [330].

The presence of bulky substituents in the case of 1,1′,3,3′-tetrakis(trimethylsilyl)ferricenium triflate resulted in slow paramagnetic relaxation at 80 K, revealed by Mössbauer spectroscopy. Below 9 K, magnetic hyperfine splitting could be resolved [331]. Metalation of 1,1′-bis(trimethylsilyl)ferrocene with butyllithium/TMEDA and quenching with chlorodiphenylphosphine produced only one diastereomer of 1,1′-bis(diphenylphosphino)-3,3′-bis(trimethylsilyl)ferrocene, which showed a *cisoid* disposition of the two diphenylphosphino groups in the solid, as shown in the crystal structure [332]. Second-order molecular hyperpolarizabilities of ferrocenyl derivatives have been measured in order to assess the effects of metal complexation. The compound **44** had one of the highest values observed for an organometallic material [333]. Direct introduction of ethynyl groups into ferrocenes was achieved by dilithiation, formation of a cuprate using Me_2SCuI, and reaction with iodoethynes. Desilylation of $(Me_3SiC{\equiv}CC_5H_4)_2Fe$ produced 1,1′-diethynylferrocene, which was very unstable with respect to spontaneous polymerization [334,335].



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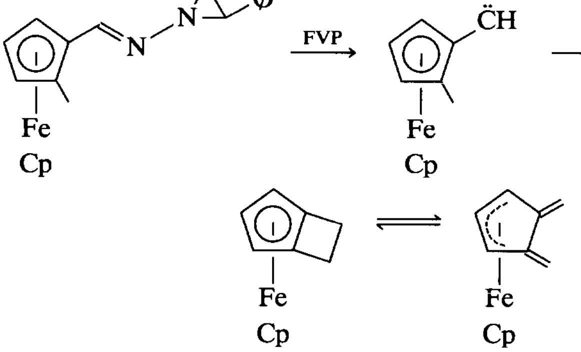
Ferrocenoylacetone was found to exist predominantly (94%) as the enol, FeC(=O)CH=C(OH)Me in chloroform solution; the crystal structure also showed the enol form [336]. This contrasts markedly with [3]-ferrocenophanedione, which showed no detectible enol. Friedel–Crafts acetylation of ferrocenylarylethenes, FcCH=CHAr, occurred either at the double bond (α to the aryl ring) or at the unsubstituted cyclopentadienyl ring [337]. Ferroçocyclobutene has been prepared in 35% yield by a flash vacuum pyrolytic method [eqn. (24)]. Heating the bicyclic product at 200°C in the presence of N-phenylmaleimide gave cycloadducts of maleimide with the *o*-xylylene analog, cyclopentadienyl($\eta^{3?}$-1,2-dimethylene-3-cyclopentenyl)iron, **45** [338].



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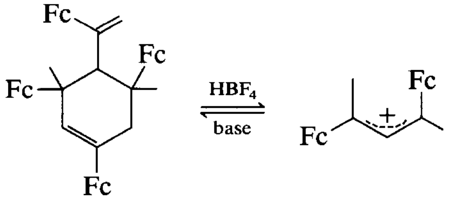
Some enantioselectivity was manifested in reduction of benzoylferrocene and 1,1′-dibenzoylferrocene by $LiAlH_4$-Chirald complex. With benzoylferrocene, the (*R*)-carbinol was predominant, with an optical yield of 53% [339]. Lipase enzymes showed much greater stereoselectivity in catalyzing monoacetylation of 1,2-bis(hydroxymethyl)ferrocene by vinyl acetate. In the best case, lipase from *pseudomonas cepacea* gave an 80% yield of (−)-monoacetate in 100% enantiomeric excess. Many other lipases gave mixtures [340]. Similarly, the enantiomers of [4](1,2)ferrocenophan-1-one were resolved by lipase-catalyzed hydrolysis of the enol acetates [341].

A series of $PdCl_2$ complexes of the type CpFe-[$C_5H_3(CH_2NR_2)(SR')$] and CpFe[$C_5H_3(CHMeNR_2)$-(SR′)] [R = Et, Pr; R′ = Me, Et, ^{i}Pr] were synthesized and used to catalyze hydrogenation of 1,3-cyclooctadiene. The effects of varying the alkyl groups on reactivity and selectivity were assessed [342]. There is a great deal of interest in use of chiral ferrocenes as ligands to induce asymmetric catalysis. In most cases, the compounds employed are derivatives of 1,1′-bis(diphenylphosphino)ferrocene (dppf), having chiral aminomethyl groups adjacent to one diphenylphosphino substituent. Gold complexes of such a compound having a $-CHMeNMeCH_2CH_2NR_2$ side chain have been found to catalyze the asymmetric aldol reaction of isocyanoacetate with aldehydes to form oxazolines.

Enantiomeric excesses of up to 97% were observed [343]. Palladium(dppf) derivatives having crown ether attachments have been found to catalyze asymmetric allylation of β-diketones with e.e. up to 75% [344]. A 2,2″-bis[1-(diphenylphosphino)ethyl]-1,1″-biferrocenyl rhodium complex proved an effective catalyst for asymmetric Michael additions of α-cyanocarboxylates to vinyl ketones or propenal [345]. Numerous papers, not covered here, describe synthesis of ferrocene derivatives having 1,2-disubstitution with groups capable of chelating metals or of ferrocenes substituted with coordinating or chelating groups such as bi- or tripyridyls, crown ethers, *etc.*

The structures and stabilization of metallocenylcarbocations of Group 8 have been discussed, based primarily on NMR and structural data for $FcCPh_2^+$ and congeners. Stabilization and deformation of the diphenylpentafulvene unit from planarity in order to achieve η^6-coordination increase significantly in going from iron to ruthenium to osmium [346]. MNDO and AM1 calculations indicated the possibility of a singlet–triplet transition in the $CpFe(C_5H_4CH_2)^+$ cation, for which a methylene deformation angle of only 5° was calculated. Circular dichroism studies have been carried out on some substituted ferrocenyl phenyl carbinols and on the cations derived from them upon dissolution in trifluoroacetic acid [348]. The 1-ferrocenyl-1-cyclopropyl cation has been observed by low temperature NMR methods; the stabilization provided by the ferrocenyl group clearly inhibited opening to the normally more stable allylic cation [349]. In a cation stabilized by two organometallic moieties, $(\mu\text{-FcCHC}{\equiv}\text{CPr})(\text{MoCp})_2(\text{CO})_4^+\text{BF}_4^-$, the ferrocenyl group was reduced to a role of providing vertical stabilization only, based on the crystal structure, which showed stabilizing structural adjustments in the dimolybdenum cluster, but little perturbation of the ferrocene [350]. Heavily ferrocenyl substituted hydrocarbons can be formed and broken down in reactions controlled by stabilization of intermediate carbocations. An example is shown in eqn. (25). Many related reactions of **46** with other electrophiles have been reported [351–353].



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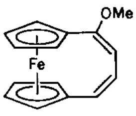
46

[1]Ferrocenophanes (ferrocenes with both rings linked to a single bridging atom) are capable of existence when the bridging atom is large enough. Zirconocene derivatives, (1,1′-ferrocenediyl)bis(*tert*-butylcyclopentadienyl)zirconium, have been prepared and subjected to reaction with protic reagents. There is considerable steric hindrance to attack at zirconium, but the Zr–C bonds could be cleaved by water, alcohols, and carboxylic acids, and also by reaction with free radical reagents such as PhSSPh [354]. Attack of phenyl–lithium on the bridging phosphorus of $Fe[C_5H_4P(Ph)C_5H_4]$ was used to generate $(Ph_2PC_5H_4)Fe(C_5H_4Li)$, useful for synthesizing $(Ph_2PC_5H_4)Fe(C_5H_4PR_2)$ and other chelating 1,1′-bis(phosphino)ferrocenes [355]. Similarly, sila[1]ferrocenophanes have served as monomers for formation of poly(ferrocenylsilanes) upon heating [356].

Molecular mechanics force fields for ferrocenes have been developed mainly from vibrational data; they gave good agreement with the crystal structures of strained ferrocenes including $Fe(C_5H_4SiPh_2C_5H_4)$, tetramethyl[2]ferrocenophane, *etc.* [357]. An independently generated molecular mechanics model has been used to investigate the structures of ferrocenophanes and the dynamics of bridge reversal processes. The calculated energy barrier for [3]ferrocenophanes agreed well with experimental values, but low barriers were calculated for [4]ferrocenophanes, for which rigid bridges have previously been inferred from NMR results. Misinterpretation of the latter was suggested [358]. 1,1′,3,3′,4,4′-[3_3]ferrocenophane has been prepared by a multistep synthesis. Mössbauer data on the ferricenium salt indicated increased metal-ring interaction as a consequence of the bridges' squeezing [359]. Two isomeric [4_2]ferrocenophanes, having C_2 and C_{2v} symmetry, have been synthesized and compared spectroscopically and structurally [360]. Direct construction of a C_4 heteroannular bridge was the unexpected, but useful, outcome of the reaction of 1,1′-bis(trimethylsilylethynyl) ferrocene with KOH/MeOH to form **47** [361]. A configurationally stable chiral dibenzo analog of **47** [XRC] was synthesized by reaction of $Fe(C_5H_4ZnCl)_2$ with 2,2′-diiodobiphenyl in the presence of $Pd(PPh_3)_4$ [362]. Insertion of alkynes into the Si–Si bond of tetramethyldisila[2]ferrocenophane, also using $Pd(PPh_3)_4$ as catalyst, generated disila[4]ferrocenophane derivatives, **48** [R = H, Ph, CO_2Me]. Use of butadiene under the same conditions resulted in two-fold insertion, yielding a 10-atom bridge [363].



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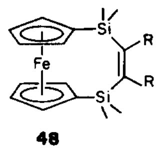

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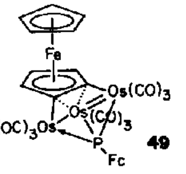
Derivatives of [3]ferrocenophane are among the most readily obtained bridged ferrocenes. Trithia[3]ferrocenophane, for example, is produced by reaction of

1,1′-dilithioferrocene with S_8. Reaction of this compound in turn with tributylphosphine leads to partial desulfurization and formation of the redox-active polymer of dithia[2]ferrocenophane [364]. Triselena[3]ferrocenophane and other selenium-containing ferrocenes have been studied by ^{77}Se NMR [365]. The bridge inversion of Fe[C_5H_4–TeSTe–C_5H_4] has been studied by proton NMR, which indicated an inversion barrier of 56 kJ mol^{-1}. Additional heterobridged [3]ferrocenophanes were prepared from Fe(C_5H_4QSiMe$_3$)$_2$ [Q = S, Se, Te] by reaction with PCl$_3$, AsCl$_3$, SbCl$_3$, and rhodium and iridium dichlorides, LMCl$_2$ [367]. A crystal structure of Fe[C_5H_4–SRh(Cp*)(PMe$_3$)S–C_5H_4] showed eclipsed cyclopentadienyl rings and a long Fe–Rh distance, indicating no direct interaction [368]. Crystal structures of Fe(CO)$_3$ complexes of dppf and related ligands [99] and of Fe[C_5H_4–PPh$_2$Fe(CO)$_3$SPh–C_5H_4 [369] were similar. Chelating dppf complexes of MnCp′(CO) and other metals also showed no direct iron–metal interaction [370]. Several ruthenium and osmium carbonyl complexes prepared by reactions of trithia[3]ferrocenophane with the corresponding metal carbonyl reagents and having two-four metal atoms coordinated to a 1,1′-ferrocenedithiolate ligand showed interaction among the heavy metals but not involvement of iron [371].

Pyrolysis of some (ferrocenylphosphine)-osmium and -ruthenium carbonyls, however, produced cluster products (See Section 11) having direct iron-metal interactions [372–374]. Also produced, in pyrolysis of Os$_3$(CO)$_{11}$(PFc$_2$Ph), was **49**, a coordinated ferrocyne (1,2-dehydroferrocene). Pyrolysis of the bis[Os$_3$(CO)$_{11}$] complex of 1,1′-bis(di-isopropylphosphino)ferrocene gave a related complex of ferroçodiyne (1,2,1′,2′-tetrakisdehydroferrocene), incomprehensibly called "ferrodicyne" by the authors [375]. The iron of ferrocene was shown to act as a donor to silver ion in the crystal structures of some ferrocenediyl cryptand-silver complexes [376]. The hope of securing redox-switchable ligands has led to incorporation of ferrocenyl or ferrocenediyl units into cryptands [377] and other chelating ligands [378]. Enhanced binding of Ni^{II} to an oxidized ferrocenyltetraamine ligand was demonstrated [379].



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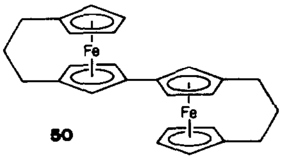
Other organometallic-substituted ferrocenes have been produced by direct or indirect methods. In the former category was reaction of ferrocenyl-lithium or 1,1′-ferrocenyldilithium with CpRu(CO)$_2$Cl or Cp*Ru(CO)$_2$Cl, to give ring-substituted di- and tri-metallic products [380]. An alternative approach to a disubstituted ferrocene was reaction of (η-C_6H_6)Mn(CO)$_3^+$ with NaCp to form the [(6-cyclopentadienyl)-η^5-cyclohexadienyl]Mn(CO)$_3$ product; deprotonation of the Cp ring and reaction with FeCl$_3$ gave the ferrocene, Fe[C_5H_4-η^5-C_6H_6Mn(CO)$_3$]$_2$ [381]. Condensation of ferrocenylsilanes such as 1,1′-bis(dimethylsilyl)ferrocene with HCCo$_3$(CO)$_9$ led to formation of products such as Fe[C_5H_4SiMe$_2$CCo$_3$(CO)$_9$]$_2$ [XRC], whose electrochemical oxidation revealed little interaction between the ferrocene and the methylidynetricobalt clusters [382].

Deprotonation of 1,12-$^{13}C_2$-[1.1]ferrocenophane by butyl-lithium in 2,5-dimethyltetrahydrofuran produced a species with lithium coordinated to the deprotonated carbon, as shown by ^{13}C–^{6}Li coupling in the NMR and by decoupling experiments [383]. Reaction of 1,12-dimethyl[1.1]ferrocenophane with H$^+$BF$_3$OH$^-$ gave dihydrogen and the oxidized dication, which lost a proton on water quenching to form the bridge carbocation. Reduction of the carbocation with NaBH$_4$ restored the starting material with stereochemistry intact, whether the *exo,exo* or the *exo,endo* starting material was used [384]. Reduction of 1,12-[1.1]ferrocenophanedione with Zn/TiCl$_4$ produced the monoketone in 55% yield. Reaction with "Lawesson's reagent" produced monothio and dithioketones, which did not react with tributylphosphine [385]. Crystal structures of [1.1]ferrocenophane and its mono- and diruthenium analogs indicated for all three the syn conformation, somewhat twisted to relieve crowding of inner bridge protons [386]. Synthesis of the [1.1]ferroruthenocene was achieved using 1,1′-bis(6-pentafulvenyl)ferrocene, L-selectride, and RuCl$_2$(SbPh$_3$)$_2$ [387].

Calculation of second-order nonlinear optical responses of many organometallic compounds has been carried out by a modified INDO method. An acentric electron distribution in the organometallic chromophore was found to be desirable for obtention of larger second-order responses [388]. On the synthetic front, ferrocenyl Schiff bases FeCH=NAr and related species have been investigated for nonlinear optical properties. The most promising based on solution studies was FcCH=N–N=CH–$C_6H_4NO_2$-*p*, but a centrosymmetric space group in the crystal foreclosed the possibility of nonlinear optical effects [389]. Several styryl ferrocenes, FcCH=CHAr, however, did show nonlinear efficiencies greater than urea [390]. Of related interest is the ESR study of radical anions of species such as FcC$_6$H$_4$NO$_2$ [391], FeCH=CHC$_6$H$_4$-NO$_2$ [391,392], and FcCH=CHCN [393], which allow experimental characterization of the LUMO's of the neutral species.

In an effort better to understand the mechanism of ferromagnetic coupling in ferricenium tetracyanoethenide charge-transfer salts, several alkyl-substituted ferricenium ions were investigated by NMR. The proton chemical shifts covered a range of 170 ppm, and the ^{13}C 1300 ppm. The results supported the McConnell–Kollmar–Kahn mechanism for coupling within FcR$^+$TCNE$^-$ stacks [394]. Electrical conductivities of FeCp$'_2{}^+$M(dmit)$_2^-$ salts [M = Ni, Pd, Pt; H$_2$dmit = 4,5-dimercapto-1,3-dithiole-2-thione] have been measured and structure-property relationships discussed [395].

The Mössbauer spectrum of the monocation from 1,3-diferrocenylpropan-1-one showed distinct doublets for each iron, indicating, consistent with other spectroscopic data, a trapped valence with intramolecular electron transfer rate less than 10^7 s^{-1}. The effects of crystal packing, especially counterion location in the crystal, on the nature of dihalobiferrocenium salts [(XC$_5$H$_4$)Fe(C$_5$H$_4$–C$_5$H$_4$)Fe(C$_5$H$_4$X)]$^+$PF$_6^-$ or SbF$_6^-$ have been assessed. All salts showed localized structures on the vibrational time scale, but onset of delocalization as seen in Mössbauer spectroscopy varied from 125 K to 350 K, depending on crystal structure [397]. An extensive series of halobenzyl-substituted biferrocenyl triodides mostly manifested "trapped-valence" behavior [398]. A significant effect of substitution pattern in tetraethylbiferrocenium triiodides was found: the 1′,3′,1‴,3‴-tetraethyl compound manifested delocalized behavior in the Mössbauer at 130 K, whereas the 1′,2′,1‴,2‴-isomer did not do so until 200 K. The differences were ascribed in part to variable ring tilting within the ferrocene units [399]. Decamethylbiferrocene has been synthesized in 25% yield by reaction of Cp*Fe(acac) with (–C$_5$H$_4$Tl)$_2$ at −80°C. The crystal structure showed a fully transoid conformation, but the 35-electron PF$_6^-$ salt was localized according to Mössbauer results [400,401]. IR results accorded with this conclusion, and it was concluded that permethylation of the Cp rings decreased the delocalization [402]. The biferrocenium salt having one ferrocene unit linked interannularly by a 1-propanone-1,3-diyl bridge again showed localized behavior [403]. On the other hand, the doubly bridged cation salt **50** showed Mössbauer delocalization at 75 K, indicating an electron-transfer rate above 10^{10} s^{-1}, although it still appeared localized on the vibrational time scale. The analog with pentamethylene bridges was Mössbauer localized even at 300 K [404].



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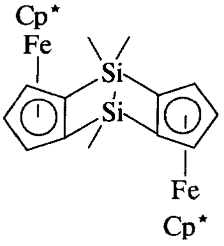
One of the most extensively delocalized mixed-valence systems is the cation of bis(fulvalene)diiron. Functionalized derivatives of this system have been prepared, which allow covalent attachment to electrodes as electroactive films. The effects of these films on redox reactions at the electrodes have been assessed [405]. Several 1,1′-bis(cyclopentadienyl)ferrocenes have been synthesized from ferrocenyldilithium and cyclopentenones. These are potentially suitable for synthesis of substituted bis(fulvalene)diiron complexes by deprotonation and treatment with FeCl$_2$, but in the one reported attempt polymeric products were formed instead. A (dimethylcyclopentadienyl)ferrocene under these conditions did form the expected diferrocenylferrocene in 38% yield [406]. A bis(silylene)bridged dicyclopentadiene ligand has been prepared and converted to ferrocenes such as **51** by deprotonation and reaction with FeCl$_2$ and excess LiCp* [407]. Triferrocenes were also prepared from the same ligand by reaction of the dianion with [C$_5$H$_2$(SiMe$_3$)$_3$]FeCl, or by stepwise construction via the monoanions [408]. Only localized behavior was observed in the electrochemistry of some mixed-metal termetallocenes [409].



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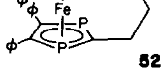
(Azaferrocene)pentacarbonylchromium underwent lithiation by butyl-lithium cleanly at the 3-position of the hetero ring, as indicated by formation of the 3-methyl derivative in 80% yield upon treatment with methyl iodide. The free azaferrocene gave predominantly 2-lithiation, but the reaction was not clean [410]. Azaferrocene reduced an iron(III) porphyrin to the iron(II) product, (por)Fe[(NC$_4$H$_4$)FeCp]$_2$ [XRC], having the azaferrocene units axially coordinated to the iron [411]. Similarly, an axial azaferrocene reduced a cobalt porphyrin upon irradiation [412].

The 3,4-dimethyl-2-(diphenylphosphino)phospholide anion has been prepared and converted to the diphosphaferrocene, a hetero-dppf, in 50% overall yield. The *meso* isomer was predominant. Coordinating ability of this tetraphosphine is being investigated [413]. A number of 1,1′,3,3′-tetraphosphaferrocenes have been prepared by generating the diphospholide anions and allowing them to react with Fe(p-xylene)$_2^{2+}$. A tetraphospha[3]ferrocenophane, **52** [XRC], was similarly



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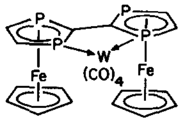
obtained from the tethered bis(diphospholide) dianion [415]. The directly linked phosphorus atoms of 1,1′,2,2′,4,4′-hexaphosphaferrocenes were consistently found to be more basic than the isolated phosphorus atoms, based on preferential coordination to several metal carbonyl groups [126]. Tetraphosphafulvalene dianions were converted to tetraphosphabiferrocenyl analogs by introduction of iron using CpFe(*p*-xylene)$^+PF_6^-$. Coordination as a bidentate ligand to tungsten formed the trimetallic product, **53** [416].



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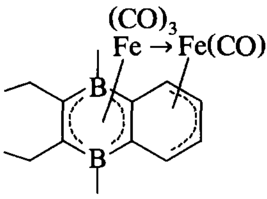
Formation of substituted heteracyclopentadienides of heavier Group 15 elements has also been accomplished, and from them a bismaferrocene [XRC: Fe–Bi bond length 2.64 Å] [417] and 1,1′-distiba- and dibismaferrocenes [418] have been generated. The earliest examples of these were highly substituted, having trimethylsilyl groups at the 2- and 5-positions and methyl groups at the 3- and 4-positions. More recently, a dibismaferrocene having only methyl groups flanking the heteroatoms has been prepared. The Fe–Bi distances averaged 2.68 Å, and the rings were eclipsed in the crystal [419]. Triple-decker complexes having P_5 or As_5 middle decks have been formed by stacking reactions in which a $M(CO)_3$ [M = Group 6 metal] was attached to the heterorings of Cp*Fe(P_5) or Cp*Fe(As_5) [420].

Some carborane-iron derivatives, which may also be considered as boraferrocenes, have been prepared and studied. Among these are Cp*FeH($Et_2C_2B_4H_4$) and its oxidized form Cp*Fe($Et_2C_2B_4H_4$) [421], and some bridged bis(dicarbollide)iron compounds [422,423].

8. Compounds with η^6-arene ligands

Along with the more conventional η^2 and η^4 complexes formed in photochemical reaction of styrene with (dfepe)Fe(CO)$_3$ [dfepe = $(CF_3CF_2)_2PCH_2CH_2P(CF_2CF_3)_2$] was formed a small amount (5%) of an unusual η^6 complex, (η^6-C_6H_5–CH=CH_2)Fe(dfepe) [139]. Bis(η^2-ethene)(η^6-toluene)iron was an effective catalyst for cocyclization of ethyne with nitriles to form 2-alkylpyridines [424]. Reaction of a 1,4-dibora-1,4-dihydronaphthalene with "Grevels' reagent", $Fe(CO)_3(C_8H_{14})_2$, led to formation of a bis-Fe(CO)$_3$ complex having the two metal groups *anti*, and a *syn*-$Fe_2(CO)_5$ complex, **54**. The latter showed a weak Fe–Fe bond of 2.98 Å length.



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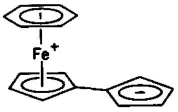
A triple decker complex was formed from the diboranaphthalene and Zn^{2+}[CpFe(η^4-C_8H_{12})$^-$]$_2$ [425].

A summary of the known crystal structures of CpFeAn$^+$ salts was published in connection with a report of the structure of Fe(η^5-C_5H_4COEt)(η-C_6H_6)$^+PF_6^-$. In the published structures, the Fe–C(Cp) distances fall in the range 2.03–2.06 Å and the Fe–C (arene) distances in the range 2.09–2.12 Å [426]. The crystal structure of (cyclopentadienyl)(η^6-octamethylnaphthalene)iron hexafluorophosphate showed an unusual boat-like distortion of the η^6-ring, so that the Fe–C1 and Fe–C4 distances averaged 2.04, with the other Fe–C distances about 2.12 Å. The Fe–Cp distances were a normal 2.03 Å [427]. A low precision crystal structure of [CpFe(C_6Me_6)$^+$]$_2Fe_2Cl_6^{2-}$ has also been reported [428]. Molecular motion in solid CpFe(C_6H_6)$^+AsF_6^-$ has been studied by Mössbauer and differential scanning calorimetric methods over the range 77–315 K. Above 265 K, a monoclinic phase formed, which allowed in-plane rotation of the rings. The activation energy for this rotation in the monoclinic phase was about 29 kJ mol^{-1} [429].

The structure of the charge-transfer salt [CpFe(1,3,5-$C_6H_3Me_3$)$^+$]$_2$ TCNQ^{2-} has been found to incorporate layers of TCNQ moieties separated by the cations [430]. Electrical conductivities of [CpFe(PhMe)$^+$]$_n$M(dmit)$_2$ compounds (structures not reported) have been measured [395].

The presence of NaPF$_6$ affected the outcome of reaction of the electron-rich diradical, (η-C_6H_6)Fe(μ: η^5,η^5-C_5H_4-C_5H_4)Fe(η-C_6H_6) with potential ligands. Thus, CO alone displaced the benzene ligands to form fulvalenebis(tricarbonyliron), but in the presence of NaPF$_6$, the zwitterionic product **56** formed instead [189]. Electroreduction of fulvalenebis(η-hexamethylbenzeneiron)$^{2+}$ gave a mixed-valence monocation, which was shown to be delocalized on the vibrational time scale (rate about 10^{12} s^{-1}). The methylation of the arene rings increased the rate of intramolecular electron exchange [402].



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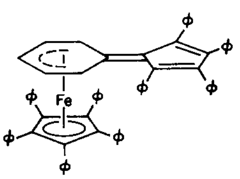
Photolysis of $(C_5Ph_5)Fe(C_6H_6)^+BPh_4^-$ produced a low yield of a rearranged isomer of decaphenylferrocene, **57** [431]. Photolysis of CpFe(η^6-phenothiazine)$^+PF_6^-$ led to release of free phenothiazine. The quantum yields in nucleophilic solvents were nearly 1.0, but were somewhat lower in less nucleophilic solvents. Some ferrocene was formed [432]. Preparation of $CpFe(PhMe)^+PF_6^-$ and study of its photochemical and electrochemical properties have been recommended as a laboratory exercise for undergraduate inorganic chemistry [433]. Electrochemical reduction of several $CpFeAn^+$ complexes having polycyclic and heterocyclic arene ligands has been studied, with emphasis on the effects of varying solvents and temperature. Rates of reaction of the 19-electron neutral complexes with solvents have been measured [434].



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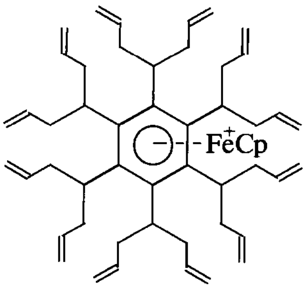
Chain extension reactions of the cation CpFe$(C_6Me_6)^+$ by consecutive methyl deprotonation and alkylation have been used to produce hexabutylbenzene *via* the $CpFe^+$ complex. The hexakis(3-butenyl)benzene complex has been converted to the hexakis(4-iodobutyl) complex by hydroboration and iodination [435]. Treatment of the hexamethylbenzene complex with base and *p*-alkoxybenzyl bromides produced a series of hexakis(2-arylethyl)benzene complexes. A crystal structure of the hexakis(*p*-ethoxyphenylethyl) hexafluorophosphate salt was reported [436]. Prolonged reaction of $CpFe(C_6Me_6)^+$ with allyl bromide and KOH resulted in introduction of twelve allyl groups, resulting in formation of the snowflake cation **58**. Analogous introduction of eight allyl or benzyl groups into the durene cation was secured [437].



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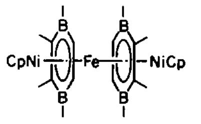
An alternative way to elaborate organic structures using $CpFeAn^+$ complexes is by displacement of halide (usually chloride) from haloarene complexes. Use of the nucleophile $Me_3COCONHOLi$, for example, followed by photochemical decomplexation, led to formation of aryloxycarbamates, $ArONHCO_2CMe_3$ [438]. The nucleophile $Re(CO)_5^-$ was used to displace chloride from chloroarene complexes to form heterobimetallic products in similar fashion [439]. Phenoxide nucleophiles cleanly displaced one chloride from $CpFe(m\text{-}C_6H_4Cl_2)^+$ under mild conditions [440]. Reaction of benzenediols with base and $CpFe(C_6H_6)^+$ led to successful formation of $[CpFe(\eta\text{-}C_6H_5O\text{-}C_6H_4O\text{-}\eta\text{-}C_6H_5)FeCp]^{2+}$. Electrochemical studies indicated electronic isolation of the two organoiron units [441]. Two-fold substitution of imidazolyl or triazolyl groups into $CpFe(o\text{-}C_6H_4Cl_2)^+$ was successfully achieved [442], as was introduction of two anilino or aryloxy groups having long aliphatic chains. The amphiphilic properties of the resulting products were investigated [443]. In one instance, a heteroaryl-substituted carbanion added to the 2-position of CpFe(1,4-$C_6H_4Cl_2)^+$, giving a cyclohexadienyl complex, rather than displacing chloride [444].

Many Japanese patents have been issued describing incorporation of $CpFeAn^+$ salts into optical or holographic recording media, photopolymerized printing plates, and other technical applications [445–452].

A number of examples of CpFe(η^6-tricarbaborane)s (by reaction of FpI with tricarbaborane anions [453] and bis(η^6-tricarbaborane)irons (by reaction of $FeCl_2$ with the anions) [454] have been prepared and studied. Several crystal structures and studies of skeletal rearrangements were reported [455]. Reduction of CpNi$(\eta^6\text{-}C_4H_2B_2Me_4)$ with potassium and treatment with $FeCl_2$ gave the tetradecker **59** in modest yield [456].



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A crystal structure of $Fe(\eta\text{-}C_6H_3Me_3)^{2+}(PF_6^-)_2$ showed bond lengths of 2.11 Å for Fe–CH bonds and 2.14 Å for Fe–CMe bonds [457]. Reaction of this compound and other $Fe(An)_2^{2+}$ salts with triethylaluminum in methylene chloride solution afforded ring-ethylated products, $(\eta\text{-}An)Fe(\eta^5\text{-}AnEt)^+PF_6^-$. Trimethylaluminum, however, reacted in a more complex manner which resulted in formation of chloromethylated products, $(\eta\text{-}An)Fe(\eta^5\text{-}AnCH_2Cl)^+PF_6^-$ [XRC for An = mesitylene] [458]. Loss of the arene ligands upon electroreduction of bis(arene)iron dications in acetonitrile has been studied mechanistically. The monocations were found to be the labile intermediates in the catalytic process, and turnover numbers decreased with increasing methylation of the arene ligand [459,460].

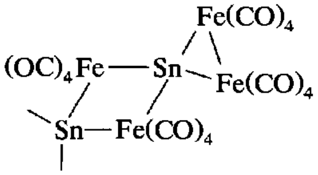
9. Bimetallic compounds

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

The crystal packing in $Fe_2(CO)_9$ has been used as a model in packing potential calculations and analysis by computer graphics of the less compact packing of $Co_2(CO)_8$ [461]. A crystal structure of $Fe_2(CNPh)_9$, prepared by sodium amalgam reduction of $FeI_2(CNPh)_4$, showed a Fe–Fe bond length of 2.46 Å; the bridging isonitrile ligands showed bending, with C=N–C(Ph) angles averaging 132°, whereas the terminal isonitriles approached linearity [462]. $Fe_2(CO)_9$ was used to dechlorinate a 1,2-dichlorocyclobutane derivative to the cyclobutene [463].

Crystal structures of two salts of $Fe_2(CO)_8^{2-}$ have been reported in 1992. The tetraethylammonium salt showed the usual staggered structure of the dianion, but with a Fe–Fe bond length somewhat longer (2.84 Å) than previously found in other salts (about 2.79 Å) [464]. A salt having $Na(NC_5H_5)_4^+$ counterions formed an extended structure through Na $\cdots$ O interactions with the carbonyl oxygens. The dianion remained staggered, and showed a Fe–Fe bond distance of 2.81 Å [465]. The structure of $(OC)_4Fe[\mu\text{-}CuP(CMe_3)_3]_2Fe(CO)_4$ also showed a long Fe–Fe bond (2.85 Å) and Fe–Cu distances in the range 2.51–2.64 Å [466]. $K_2^+Fe_2(CO)_8^{2-}$ was found to be the active species in systems capable of catalyzing reduction of N_2O by CO, and containing iron carbonyl anions and KO^{t}Bu in DMSO [467].

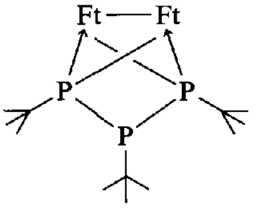
^{119}Sn–^{57}Fe coupling constants have been measured in a number of tin–iron compounds, including μ_4-$Sn[Fe_2(CO)_8]_2$, **60**, and related compounds. Tin–tin couplings in **60** were taken to imply direct tin–tin interactions [127], contrary to the opposite conclusion derived for silicon analogs [129]. Very low chemical shifts were observed for μ_4-Sn atoms [127].



60

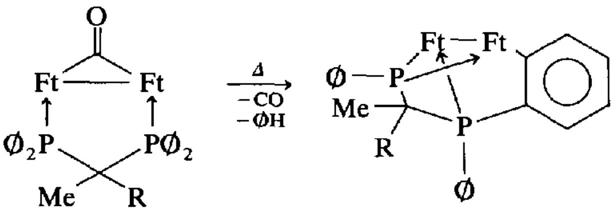
The reactive unsaturated species, $Li^+Fe_2(CO)_6(\mu\text{-}PPh_2)^-$ has been produced in solution at −78°C by reduction of $Fe_2(CO)_6(\mu\text{-}MeCO)(\mu\text{-}PPh_2)$ with $LiBEt_3H$. The unsaturated species was much more reactive than the saturated $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)^-$ anion; it reacted with electrophilic halides ElCl [El = MeC=O, Me_2NC=S, Me_2P=S, and R_2P] to form neutral μ-El products [468].

The substitution product $(dppf)Fe_2(CO)_7$ showed both phosphine groups bonded to the same Fe atom [118]. A more common arrangement has the two phosphine groups of a diphosphine spanning the Fe–Fe bond, as in the uncommon compound **61** [XRC], formed from the cyclotriphosphine $(PCMe_3)_3$ by treatment with iron carbonyls. The center phosphorus atom maintained its reactivity, forming bonds to $Fe(CO)_4$, O, or S upon treatment with appropriate reagents [469].



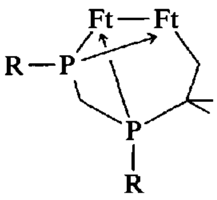
61

Thermal reactions of $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}R_2PCH_2PR_2)$ [R = Me, Et, ^{i}Pr, Ph, OEt] in refluxing toluene have been found to result in carbonyl loss and cleavage of a C–P bond of the diphosphine ligand, to form $Fe_2(CO)_6(\mu\text{-}CH_2PR_2)(\mu\text{-}PR_2)$. Formation of a μ-CH_2PPh_2 ligand over a μ-CH_2PR_2 was preferred in unsymmetrical compounds. Methyl substitution in the dppm ligand surprisingly suppressed cleavage of the C–P bond; eqn. (26) shows the alternate reaction which occurred with the methylated diphosphine [470].



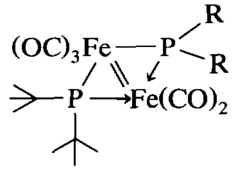
R = H, Me (26)

Ligand cleavage also accompanied thermolysis of the reaction product, **62** [XRC], of R_2PCH_2PRCl [R = *tert*-butyl] and diiron nonacarbonyl. Loss of isobutene upon heating resulted in formation of $Fe_2(CO)_6(\mu\text{-}RPCH_2PR)$, analogous to **61** [471]. The same product type [R = *tert*-butyl, mesityl, diethylamino, etc.] was produced in reaction of dihalodiphosphines, $RPXCH_2PXR$, with diiron nonacarbonyl [472,473], along with triiron clusters to be described in Section 10.1.



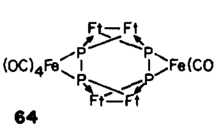
62

The mixed bis(μ-phosphido) cluster, $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}PR_2)$ [R = *tert*-butyl] has been prepared by reaction of $Fe_2(CO)_5(PPh_2H)(\mu\text{-}CO)(\mu\text{-}PPh_2)^-$ with excess R_2PCl. The structure showed the usual butterfly Fe_2P_2 core, with Fe–Fe distance of 2.70 Å and average Fe–P distance of 2.26 Å. Also produced was a small amount of an unsaturated bis(μ-phosphido) cluster, $Fe_2(CO)_5(\mu\text{-}PR_2)_2$, **63**. The latter compound could be produced in higher yield (28%) by reaction of R_2PCl with $Fe_2(CO)_8^{2-}$. It showed a planar Fe_2P_2 core, with a notably shorter Fe–Fe bond (2.49 Å), and unequal Fe–P distances (2.14 Å for P → Fe and 2.37 Å for P–Fe, as shown in the structural drawing) [474]. Unsymmetrical analogs of **63** [R = Ph, cyclohexyl] were prepared independently by a similar method, reaction of $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)^-$ with R_2PCl, or by thermal decarbonylation of the saturated bis(μ-phosphido) cluster. Crystal structures of **63** [R = Ph, *tert*-butyl, cyclohexyl] were very similar to that previously described, confirming the Fe=Fe double bond and unsymmetrical phosphido group bonding [475,476].



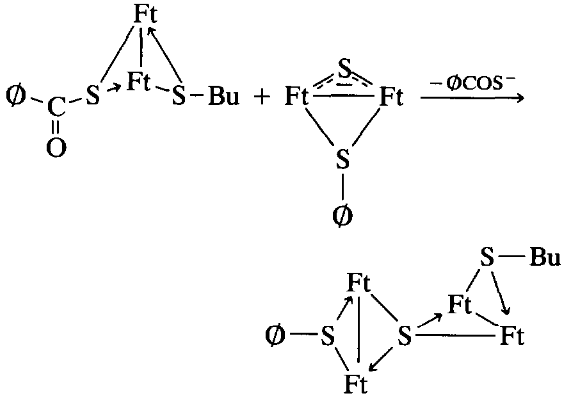
63

A compound containing two P_2 ligands, generated from reaction of white phosphorus with $Fe_2(CO)_9$ in refluxing benzene, has been found to have structure **64**. The two P_2 units and the two $Fe(CO)_4$ units were coplanar, with the $Fe_2(CO)_6$ moieties perpendicular. The bonded phosphorus atoms were separated by 2.13 Å, the non-bonded by 2.60 Å [477].



64

The photochemical reaction of $Fe(C_5H_4SPh)_2$ with $Fe_2(CO)_9$ in acetonitrile resulted in formation, probably *via* $Fe_2(CO)_6[\mu\text{-}S(Ph)(C_5H_4FeC_5H_4SPh)]_2$, of *syn*-$Fe_2(CO)_6(\mu\text{-}SPh)_2$ [XRC] and FcSPh [478]. Addition of allylmagnesium chloride to $Fe_2(CO)_6(\mu\text{-}S_2)$ followed by quenching with FpI formed the product $Fe_2(CO)_6(\mu\text{-}SCH_2CH{=}CH_2)(\mu\text{-}SFp)$, whose crystal structure showed an *endo* Fp group and an *exo* allyl group [479]. Similarly, benzoylation of $Fe_2(CO)_6(\mu\text{-}SBu)(\mu\text{-}S)^-$ MgX^+ formed the μ-SCOPh product, but this reacted in turn with further Grignard adduct as shown in eqn. (27) to form a μ_4-S cluster, **65** [XRC], by displacement of the thiobenzoate group [480]. A number of transition metal derivatives of $Fe_2(CO)_6(\mu\text{-}S_2)$ have been prepared by insertion of unsaturated ML_n fragments generated under photochemical conditions into the S–S bond. Metal groups included $Pd(PPh_3)_2$ and $NbCp(CO)_2$. In other cases new M–Fe bonds formed as well as M–S bonds [481]. Reaction of tetramethylallene episulfide with $Fe_2(CO)_9$ produced, in addition to the previously mentioned (Section 6.1.) thia-TMM complex, **21**, a μ-dithiolate complex, **66** [159].



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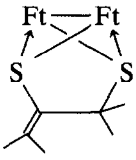
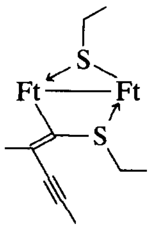


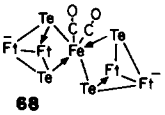


66 **67**

Product **67** [XRC] was one of several products formed in reaction of MeC≡CSEt with iron carbonyls; substantial disruption of the organic ligand clearly has occurred in formation of **67**. Also formed in this reaction were an analog of **65** having μ-SEt groups and an Fe_4 complex [482]. Concentration effects on the UV spectra of organic iron–sulfur complexes have been studied [483]. $Fe_2(NO)_4(\mu\text{-}SMe)_2$, a tumor promoter, has been found among the products of reaction of methionine with Fe^{II} salts and $NaNO_2$ [484].

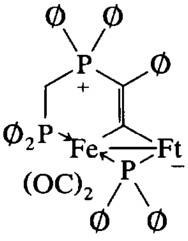
Protonation of $MeSeFe(CO)_4^-$, produced by reaction of $HFe(CO)_4^-$ with $(MeSe)_2$, resulted in generation of $Fe_2(CO)_6(\mu\text{-}SeMe)_2$. No (MeSeH) → $Fe(CO)_4$ could be detected, even at low temperature [114]. The crystal structure of $Fe_2(CO)_6(\mu\text{-}TeFe(CO)_4Te)$, formed by carbonylation of $Fe_3(CO)_9(\mu_3\text{-}Te)_2$, has been determined [485], as has the structure of $(\mu\text{-}MeTe)Fe_2(CO)_6(\mu\text{-}TeCH_2Te)Fe_2(CO)_6(\mu\text{-}TeMe)$, formed by reaction of the same Fe_3 complex with diazomethane [486]. A related, but more elaborate telluride cluster,

68 [XRC], was formed upon reaction of excess $Fe(CO)_5$ with $(PPh_4^+)_2Te_4^{2-}$ in warm DMF [487].



68

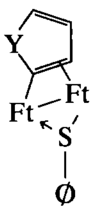
The μ-alkynyl complex, $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu{:}\eta^1,\eta^2\text{-}C{\equiv}CPh)$, **69**, was obtained in a thermal reaction between $[\eta^4\text{-}Cp_2Ti(C{\equiv}CPh)_2]Ni(PPh_2C{\equiv}CPh)$ and $Fe_2(CO)_9$; apparently the nickel complex functioned only as a source of the alkynylphosphine ligand [488]. Reaction of the alkynyl complex **69** with diphosphine ligand has been found to occur by initial attack either at iron or at the β-carbon of the alkynyl ligand. In the case of dppm, this produced **70**, which rearranged to $Fe_2(CO)_4(\mu\text{-}PPh_2)(\mu\text{-}dppm)(\mu\text{-}C{\equiv}CPh)$ only upon prolonged heating. Analogs of **69** with other μ-alkynyl ligands ($-C{\equiv}CCMe_3$, $-C{\equiv}CCHMe_2$) reacted directly by displacement of two CO ligands to afford μ-dppm or μ-dppe products [489].



70

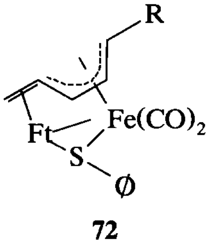
Addition of $Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}PPh_2)$ to alkynes to form μ-alkenyl products has been found to occur predominantly in a *cis* fashion, and with high regiospecificity favoring the formation of α-substituted vinyl groups rather than β. Diynes similarly formed α-alkynylvinyl complexes, such as $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu{:}\eta^1,\eta^2\text{-}C(C{\equiv}CMe){=}CHMe)$ [XRC] [490]. The dppm-bridged hydride $Fe_2(CO)_4(\mu\text{-}H)(\mu\text{-}CO(\mu\text{-}PPh_2)(\mu\text{-}dppm)$ reacted similarly with alkynes, also giving μ-ethenyl products. Both propyne and allene formed the same 2-propenyl bridging ligand. A crystal structure of the isomer with the 2-propenyl ligand *trans* to the dppm was reported; the *cis* isomer was also characterized spectroscopically. The hydride also added to ethyl diazoacetate to form a highly stable product, $Fe_2(CO)_4(\mu\text{-}PPh_2)(\mu\text{-}dppm)(\mu\text{-}HN\text{-}N{=}CHCO_2Et)$ [491]. The cationic μ-hydride, $Fe_2(CO)_6(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}dppm)^+BF_4^-$, like its neutral counterparts, added to alkynes to form μ-alkenyl products such as $Fe_2(CO)_6(\mu\text{-}dppm)(\mu\text{-}PhC{=}CH_2)^+BF_4^-$ [XRC] [492].

The crystal structure of $Fe_2(CO)_6(\mu\text{-}SPh)(\mu\text{-}CH{=}CH_2)$, formed as a byproduct of complexation of $PhSOCH{=}CH_2$, has been determined [142]. Furyl- and thienyl-mercurials reacted with $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SPh)^-$ to form products with $\mu{:}\eta^1,\eta^2$-heteroaromatic ligands, **71** [Y = O, S]. The σ-bond to the furyl ligand was found to be rather short (1.95 Å), and the π-bonding rather unsymmetrical (Fe–C_α 2.15 Å, Fe–C_β 2.33 Å). The more highly aromatic 1-methylpyrrolyl-mercurial gave an acyl complex rather than a π-bound pyrrolyl ligand [493]. Thermal reaction of $Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}CH{=}CH_2)$ compounds with triphenylphosphine or triphenylarsine resulted in replacement of a CO from the π-bound iron by the new ligand [494]. An improved preparation of $Fe_2(CO)_6B_2H_6$ using Me_2SBH_3 and $Fe_2(CO)_9$ has been reported [495].



71

^{13}C NMR data for an extensive series of hydrocarbyl-bridged di- and triiron species have been tabulated, and trends have been identified [496]. Reverse phase HPLC studies of a number of $Fe_2(CO)_6$(hydrocarbon) complexes have also been carried out [497]. Nucleophilic attack of $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SPh)^-$ on 5-bromopenta-1,3-diene led to formation of **72** [XRC], a novel complex of the acyclic pentadienyl group [498]. A diiron complex with overlapping η^2 and η^3 groups, **73**, was obtained by displacement of the chromium group from $PhC{\equiv}CCH_2Cr(NO)_2Cp$, using $Fe_2(CO)_9$ [300]. Photoreaction of allenylketones and amides with $Fe(CO)_5$ gave, depending on substituents, any of three different structural types, illustrated in eqn. (28).



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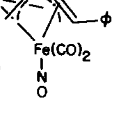

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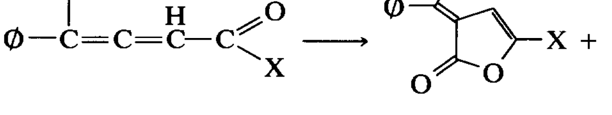
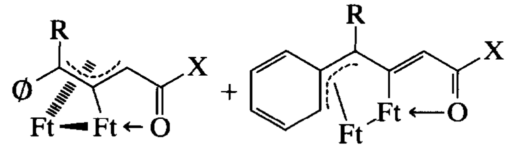
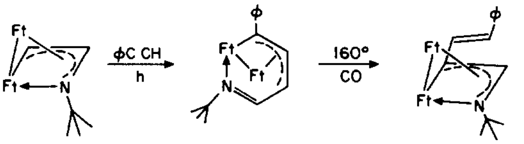




(28)

The crystal structures of two ferra-TMM complexes, having R = Ph, X = NMe$_2$ and R = H, X = Ph, were reported [499].

The mechanism of carbonylation of alkynes to form lactone complexes has been reinvestigated [500]. Photoinsertion of alkynes into ferraazetine complexes, formed by reaction of phosphinimines with Fe$_2$(CO)$_8$(μ-CH$_2$), has been found to occur with a wide variety of alkynes. Terminal alkynes reacted regioselectively as shown in eqn. (29), placing the substituent α to the iron; unsymmetrical internal alkynes gave mixtures. Heating a ferrapyridine complex under 500 psi CO resulted in ring contraction back to a ferraazetine. Heating ferrapyridines in the presence of oxygen resulted in their conversion to pyridones or pyrroles [501]. A study of the photolysis of the azetine complexes in low temperature matrices indicated an intermediate having the N → Fe bond broken; CO insertion into that bond occurred readily. Added alkyne coordinated to the vacant site on iron, and on warming insertion occurred to form the ferrapyridine. The α-styryl ferraazetine complex underwent a novel photoisomerization at low temperature, shown in eqn. (30) [502].



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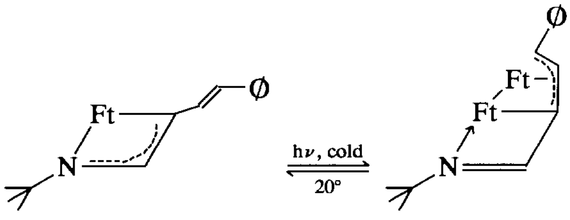

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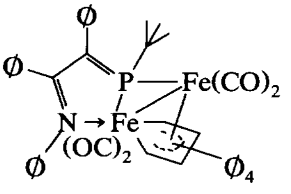
Thermal insertion of diphenylacetylene into Fe$_3$(CO)$_9$(μ-NPh)(μ_3-PCMe$_3$) at 80°C led to formation of the ferrole derivative, **74** [XRC], in 42% yield [503]. Also produced as a result of alkyne insertion, in this case of aminoalkynes RC≡CNEt$_2$ into Fe$_2$(CO)$_7$(μ-PhC≡CNEt$_2$), were ferrole complexes Fe$_2$(CO)$_6$[μ:η^2,η^4-CPhC(NEt$_2$)C(NEt$_2$)CR] [R = Me, CH$_2$Ph, CH$_2$CH=CH$_2$] [504]. Alkynes reacted with Fe$_2$(CO)$_8$(μ-CH–CH=NHR)$^+$ to form ferroles of type **75** or **76**, depending on the alkyne. Crystal structures of **75** (as BF$_3$ adducts) and **76** were reported; the latter showed a strong structural perturbation by the amino substituent, such that the Fe–CNHR bond length was 2.48 Å, as compared to 2.10–2.12 for the remaining three Fe–C distances. The C–N distance was 1.34 Å [505], consistent with substantial double bond character, as in the zwitterionic form illustrated. Electron-donating effects of the amino groups in the previously mentioned 3,4-bis(diethylamino) substituted ferrole complexes are much less pronounced, since the two amino groups are orthogonal to the ferrole ring and not in a position to interact strongly. A cyclobutano-fused ferrole complex was produced in nearly quantitative yield upon reaction of 1,6-diphenyl-1,5-hexadiyne with Fe$_2$(CO)$_9$ [300].



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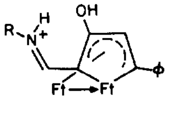

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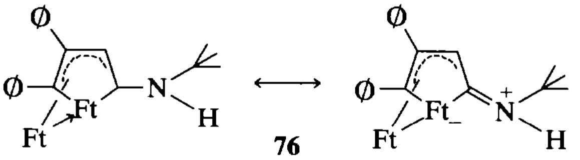
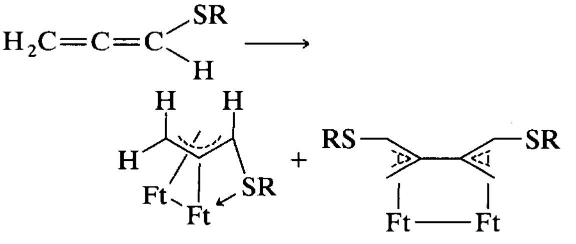


76

Allenyl thioethers, RSCH=C=CH$_2$ [R = Me, Et, Ph], were converted to two types of di-iron complexes upon reaction with Fe$_3$(CO)$_{12}$: a ferra-TMM complex [*cf.* eqn. (28)] and a biallylene derivative, both illustrated in eqn. (31). The ferra-TMM type complex was the only product when α-methoxythioethers RSC(OMe)=C=CH$_2$ were used. The crystal structure of the biallylene complex with R = Ph showed a nearly planar C$_6$H$_6$(SR)$_2$ ligand [506]. A divinylcyclopropane unit functioned as a six-electron donor to an Fe$_2$(CO)$_6$ grouping in the complex **77**, obtained by complexation



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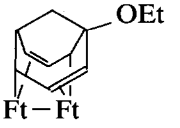

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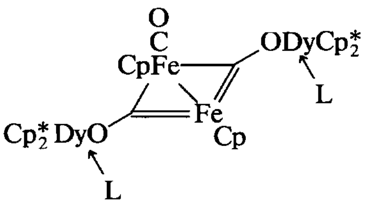
of the ethoxybarbaralane under mild conditions. The compound was described as fluxional, but no details were given [507].

9.2. *Diiron compounds, derivatives of $Cp_2Fe_2(CO)_4$*

Direct measurement of the rate constant for bridge-terminal CO exchange in *cis*-$Cp_2Fe_2(CO)_4$ [*cis*-Fp_2] by EXSY and DANTE methods has revealed a very slow rate at 234 K, contrary to previous estimates [508]. This seems to require some refinement in the classic Adams–Cotton isomerization mechanism. Variable temperature spin-lattice relaxation measurements in the polycrystalline solid have indicated an activation energy of 24.0 kJ mol^{-1} for ring rotation in *trans*-Fp_2^* [330]. The electronic spectra of Fp_2 and FpCl have been interpreted through use of INDO/CI calculations to assign the observed bands [509]. A complete Latimer diagram interrelating the various oxidation states of $Fp_2^{-1,0,+1}$ and $Fp^{-1,0,+1}$ has been constructed. The imputed free energy change for homolytic dissociation of Fp_2 is 105 ± 20 kJ mol^{-1} [225]. Vibrational levels of *cis* and *trans* bridged and unbridged forms of Fp_2 existing in the gas phase have been investigated using FTIR studies of matrix-isolated species [510].

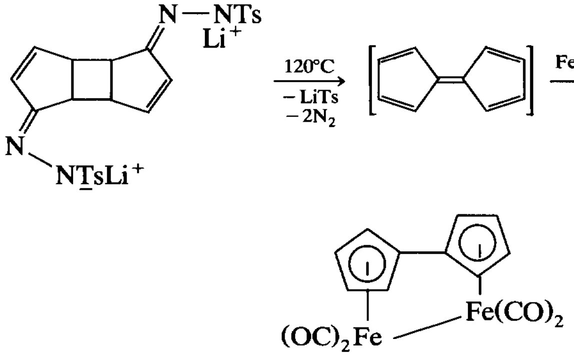
Although one might have thought that everything possible had been said on the subject of photochemistry of Fp_2 and related systems, newer, faster experimental methods continue to shed new light on these reactions. The effect of the solvent cage on recombination of $Fp^•$ radicals produced by photodissociation has been studied by femtosecond IR spectroscopy [511]. A comprehensive paper on photochemical substitution reactions of Fp_2 by the Nottingham group, using microsecond and nanosecond time-resolved IR, elucidated the effect of wavelength on relative amounts of $Fp^•$ and $Cp_2Fe_2(\mu\text{-}CO)_3$ formed in the initial photolysis and their roles in formation of substitution products. It was concluded that all known reactions with phosphites L could be explained in terms of these two intermediates and the rapidly-formed substitution product $CpFe(CO)L^•$ [226]. In contrast, new flash photolysis studies on Fp_2 in hydrocarbon solutions have been interpreted as indicating three new transients, $Cp_2Fe_2(\mu\text{-}CO)_2(\mu{:}\eta^1,\eta^2\text{-}CO)$, $FpFe(CO)_3(\eta^3\text{-}Cp)$, and an isomer of Fp_2 having one η^3-Cp ring and one $\mu{:}\eta^1,\eta^2$-CO group [512]. Photosubstitution with numerous phosphites and phospines generally gave both *cis* and *trans* monosubstitution products, $Cp_2Fe_2(CO)_3L$; trimethyl phosphite also gave some disubstitution. 1-Hexyne gave a transient, believed to be the η^2-alkyne substitution product, as a precursor to the final insertion product, $Cp_2Fe_2(CO)(\mu\text{-}CO)[\mu{:}\eta^1,\eta^3\text{-}CH{=}C(Bu)CO]$ [513]. The primary products of photochemical reaction of Fp_2 with tributyltin hydride were FpH, $FpSnBu_3$, and $CpFeH(CO)(SnBu_3)_2$. Mechanistic results did not favor the intermediacy of $Fp^•$; instead oxidative addition of Bu_3SnH to $Cp_2Fe_2(\mu\text{-}CO)_3$, to form $FpFeH(CO)(SnBu_3)Cp$, was proposed. This intermediate dissociated to FpH and $CpFe(CO)SnBu_3$ with an apparent first order rate constant of 2×10^{-2} s^{-1}. Addition of CO or Bu_3SnH to the unsaturated species completed the reaction [514].

Reaction of $(\eta\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ with a polyether diisocyanate gave a polymer whose backbone contained the Fe–Fe bonds of the Fp_2 unit. Photoreaction with CCl_4, triethyl phosphite, or oxygen, resulted in cleavage of these bonds and degradation of the polymer [515]. A strange oligomer, **78**, of unsaturated units derived from Fp_2 and coordinated at each oxygen to a Cp_2^*Dy moiety has been obtained from NaFp and Cp_2^*DyCl. In structure **78**, the Fe–C and Fe=C bond lengths were about 1.95 and 1.80 Å, respectively, and each ligand L was an oxygen of a CO_2 molecule, which bridged between two dysprosium atoms and thereby bound two of these units together in a macrocycle [516]. A boron analog of Fp_2, *cis*-$(\eta\text{-}C_4H_4BPh)_2Fe_2(CO)_4^{2-}$, was prepared by slow reduction of $(C_4H_4BPh)Fe(CO)_2NMe_3$ with sodium amalgam at −30°C. Protonation gave a μ-hydrido monoanion. An extensive family of borata-Fp analogs was prepared and investigated [517].



78

Tetracarbonyl(μ-fulvalene)diiron, **79**, has been produced in an unexpected manner, illustrated in eqn. (32). The infrared spectrum indicated no bridging carbonyls [518], in contrast to other bridged Fp_2 derivatives, presumably as a consequence of the rigidity



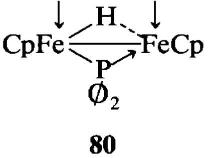
(32)

79

of the fulvalene ligand. The tetrakis(trimethylphosphine) analog of **79**, produced by reaction of (μ-fulvalene)bis(η-benzeneiron) with the phosphine, has also been reported [189]. Carbonylation of $[(\eta\text{-}C_6H_6)(Fe(C_5H_4\text{-})]_2$, however, produced hexacarbonyl (μ:η^4,η^4-fulvalene)diiron rather than **79** [189]. The dimethylsilylene-bridged compound, $(\mu\text{-}C_5H_4\text{–}SiMe_2\text{–}C_5H_4)Fe_2(CO)_4$, showed the normal pair of bridging carbonyl ligands. Studies of its mono- and di-isonitrile analogs in solution showed a preference for carbonyl bridging rather than isonitrile [519].

Photolysis of a mixture of Fp^*SiMe_3 and $ArSiH_3$ led to formation of predominantly *cis* $Cp^*_2Fe_2(CO)_3$(μ-SiHAr) [Ar = *p*-tolyl]. At thermal equilibrium, the *trans* isomer constituted 98% of the mixture. Parameters for thermal isomerization were measured as $\Delta H^{\ddagger} = 71$ kJ mol^{-1} and $\Delta S^{\ddagger} = -90$ J K^{-1} mol^{-1} for the *cis* → *trans* conversion [520]. Isomerization mechanisms involving the three stereoisomers of $[CpFe(CO)]_2(\mu\text{-}CO)[\mu\text{-}SiMe(SiMe_3)]$ have also been studied; the barrier was somewhat higher than in the previous case (about 85 kJ mol^{-1}), and a mechanism involving rotation in the unsaturated intermediate $Fp[\mu\text{-}SiMe(SiMe_3)]Fe(CO)Cp$ was proposed [521].

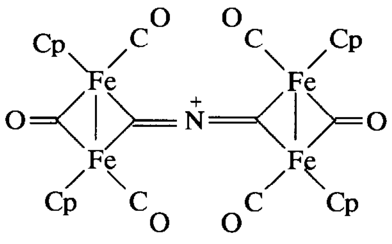
A green derivative of Fp_2, *cis*-$CpFe(PPh_2CH_2Ph)(\mu\text{-}CO)_2Fe(CO)Cp$ [XRC], resulted when $FpPPh_2CH_2Ph^+BF_4^-$ was treated with OH^- [252]. Formation of similar monosubstituted products by photosubstitution has previously been described. The phosphido-bridged product, $[CpFe(CO)]_2(\mu\text{-}H)(\mu\text{-}PMen_2)$ [Men = menthyl] was synthesized by reaction of Fp_2 with dimenthylphosphine in boiling toluene, with $Cp_2Fe_2(CO)_3(PHMen_2)$ a probable intermediate. The *trans* isomer existed as a pair of diastereomers. It served as a moderately enantioselective catalyst for hydrosilylation of acetophenone, with (*S*)-1-phenylethanol being formed in 33% e.e. [522]. The triply-bridged dimer **80**



80

[XRC] was prepared directly by reaction of $FeCl_2$, dppm, activated magnesium, and cyclopentadiene. Reaction with CS_2 led to creation of a monomeric dithioformate [217]. The electronic structures of three isomers of $Cp_2Fe_2S_4$ have been investigated by Extended Hückel calculations [523].

The solution structures and dynamics of Fp_2 derivatives having one or two isonitriles substituted for carbonyl ligands have been reinvestigated by NMR methods. All four isomers of $Cp_2Fe_2(CO)_3(CNMe)$ were detectible in dichloromethane solution, but only two out of six possible isomers of $Cp_2Fe_2(CO)_2(CNMe)_2$ were seen: the *cis* isomer with two bridging isonitriles, and the *trans* with one [524]. Alkylation of these compounds with alkyl triflates invariably leads to products with the $C{=}NR_2^+$ ligand(s) in bridging position(s), and predominantly to products with *cis* cyclopentadienyl rings. Crystal structures of a mono- and a dialkylated product were reported [525]. Bridging isonitrile complexes were also prepared by N-acylation of $Na^+Cp_2Fe_2(CO)_3(\mu\text{-}CN)^-$ with a variety of acylating agents. The crystal structure of $Cp_2Fe_2(CO)_3(\mu\text{-}CNCOC_6F_5)$ showed short Fe-μ-C distances, averaging 1.90 Å, to the acylisonitrile ligand [526]. Protonation of the μ-acylisonitrile complexes occurred at the nitrogen, giving what are formally μ-amidocarbyne ligands. However, the iminoacylisocyanide complex $Cp_2Fe_2(CO)_3(\mu\text{-}C{=}N\text{–}CPh{=}NPh)$ was protonated or ethylated at the imino nitrogen to form more delocalized cations [527]. Reaction of the μ-cyano anion $Cp_2Fe_2(CO)_3(CN)^-$ with phthalyl dichloride produced a displaceable phthalimidyl group, whose loss resulted in formation of the dimeric product **81** in 59% yield. The crystal structure of the tetraphenylborate

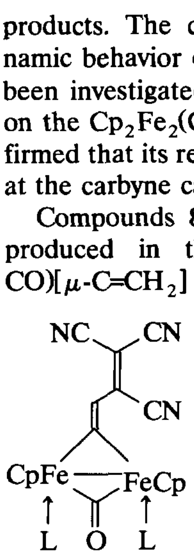


81

showed a nearly linear nitrogen, Fe–C (imino) bonds averaging 1.89 Å in length, and C=N bond lengths of 1.24 Å [528]. Some μ-arylisonitrile complexes have been prepared by reaction of NaFp with $ArN{=}CCl_2$ [529].

The crystal structure of a new polymorph of *cis*-$Cp_2Fe_2(CO)_3(\mu\text{-}CH_2)$ has been determined with high precision [530]. Methylation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CN)SMe]$ with methyl triflate yielded the sulfonium salt. The same sulfonium salt was obtained in an adduct in which two molecules were coordinated to inorganic iron through the nitrile nitrogens [XRC], by methylation of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CN)NMeCOSMe]$ [531]. Dimethyl sulfide was readily displaced from the sulfonium salt by nucleophiles; use of phosphines [Et_2PH, $PhPH_2$, $CyPH_2$] gave phosphonium salts, which were susceptible to deprotonation with triethylamine. The crystal structure of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(CN)PEt_2]$ was reported [532]. Displacement of dimethyl sulfide from the sulfonium salt by H^- and CN^- gave the μ-cyanomethyl and μ-dicyanomethyl products. The crystal structures and solid state dynamic behavior of both compounds (*cis* isomers) have been investigated [533]. Extended Hückel calculations on the $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}CH]^+$ cation have confirmed that its reactions with nucleophiles should occur at the carbyne carbon due to LUMO control [534].

Compounds **82** and **83** [$L = CO$; $L_2 = dppe$] were produced in the reaction between $Cp_2Fe_2L_2(\mu\text{-}CO)[\mu\text{-}C{=}CH_2]$ and TCNE. The crystal structure of **82**



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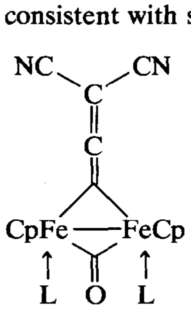
[$L = CO$] showed extensive donation of electron density from the Fe_2C unit into the tricyanovinyl unit. Variable temperature NMR studies showed modest barriers to rotation about the C_α–C_β bond: 67 kJ mol^{-1} for $L = CO$ and 42 kJ mol^{-1} for $L_2 = dppe$, consistent with substantial dipolar character. **83** [XRC,



83

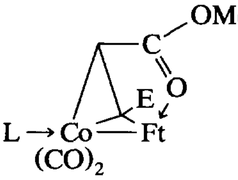
$L_2 = dppe$] underwent reversible protonation at C_β [535]. Diiron alkenylidene complexes have been investigated for non-linear optical properties; the best example, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}CCHCH\text{-}p\text{-}C_6H_4NMe_2]^+$ OTf^- [XRC] was 3.6 times more efficient than urea at frequency doubling, as a powder [536].

9.3. Heterobimetallic compounds

The reaction between $Fe(CO)_4Br_2$, reactive molybdenum carbonyl derivatives [$Mo(CO)_4$(norbornadiene) or $Mo(CO)_3(NCMe)_3$], and $Et_4N^+SPh^-$ resulted in formation of $Et_4N^+(OC)_3Fe(\mu\text{-}SPh)_2Mo(CO)_3SPh^-$ [XRC] [82]. Transfer of a cyclopentadienyliron group from $CpFe(C_6H_6)$ to the cyclooctatetraene ring of $CpCr(\eta^6\text{-}cot)$ occurred during thermal reaction to form $CpFe(\mu{:}\eta^4,\eta^4\text{-}cot)CrCp[Cr\text{–}Fe]$. The product had two unpaired electrons, associated mainly with the chromium atom. The structure revealed a Cr–Fe bond length of 2.73 Å, and a relatively normal iron-diene unit [537]. Electrochemical reduction of $(OC)_3W(\mu{:}\eta,\eta\text{-}C_5H_4\text{-}C_5H_4)Fe(CO)_2[Fe\text{–}W]$ occurred in two one-electron steps, with dissolution of the Fe–W bond. The monoanion dimerized by formation of a Fp_2 derivative, isolated by methylation of the anionic tungsten groups. Oxidation of the dimer dianion restored the μ-fulvalene monomer [538].

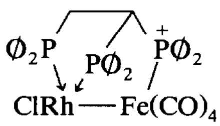
Deprotonation of $Fe(CO)_3(PPh_2H)_2$ with butyllithium, followed by reaction with $RuCl_2(CO)_3(THF)$, formed the iron–ruthenium product, $(OC)_3Fe(\mu\text{-}PPh_2)_2Ru(CO)_3$. This compound was an efficient catalyst for hydroformylation of styrene, with ten times the turnover frequency of the diruthenium analog. The catalyst was recoverable after completion of the reaction [539]. The pyridineimine, $2\text{-}C_5H_4N\text{-}CH{=}NCHMe_2$ (pyca) formed a $FeRu(CO)_6$ complex, hydrogenation of which gave $H_2FeRu(CO)_5$(pyca), having one terminal and one bridging hydride. Reaction with ligands (CO, phosphines) displaced the hydrogen from association with the bimetallic complex. Hydrogenation of the diazabutadiene complex $FeRu(CO)_6(RN{=}CHCH{=}NR)$ [$R = CHMe_2$] at 90°C resulted in reduction of the ligand. The reduced product, $FeRu(CO)_6(RNCH_2\text{-}CH_2NR)$, could also be formed by reaction of $Ru(CO)_3$(dab) with $H_2Fe(CO)_4$ [540].

$CpFeCl(\eta^1\text{-}PNP)_2$ [$PNP = F_2PNMePF_2$] has found use in synthesis of bimetallic complexes via chloride transfer to low-valent metals. With $Co_2(CO)_8$, for example, it forms $CoCl_2$ and $CpFe(\mu\text{-}PNP)_2Co(CO)_2$ [XRC] [254]. Substitution reactions of μ-alkenyl-bridged iron–cobalt compounds, $(OC)_4Fe(\mu{:}\eta^1,\eta^2\text{-}CR{=}CHR)Co(CO)_3$, with phosphines occurred with displacement of a CO from iron. A second phosphine could be introduced in complexes having an α-ester substituent on the alkene, in which case it became coordinated to cobalt. Compound **84** [$L = CO$] under-



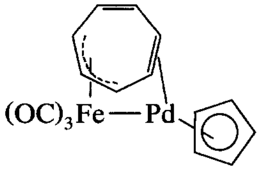
84

went CO displacement by phosphines first at cobalt and then at iron. Crystal structures of mono- and diphosphine derivatives, prepared using dimethylphenylphosphine, were obtained [541]. An iron-rhodium compound of interest as a hydroformylation catalyst, $(OC)_4Fe(\mu\text{-}PR_2)Rh(CO)(PR_2H)$ [R = *tert*-butyl], was prepared by treating $[(R_2PH)_2RhCl]_2$ with $HFe(CO)_4^-$ [542]. The pendant diphenylphosphino group of $(OC)_3Fe[\eta^2\text{-}(Ph_2P)_2CHCH_2PPh_2]$ assisted in formation of an iron-rhodium bond upon reaction with [RhCl(CO)$_2$]$_2$, **85** being the result [543].



85

Reaction of Fp*-C≡C-Fp* with (CpNiCO)$_2$ resulted in formation of Cp*Fe(CO)(μ-CO)$_2$NiCp [XRC]; the fate of the missing C$_2$ unit is unclear [303]. Treating PdCl$_2$(NCPh)$_2$ with NaFp at −78°C, followed by addition of three equivalents of Ph$_2$PH, led to formation of CpFe(CO)(μ-PPh$_2$)Pd(PPh$_2$H)$_2$. Protonation produced a hydrido-bridged cation [544]. A μ-cycloheptatrienyl ligand contributed to stabilization of the bimetallic unit in **86** [XRC], formed from K$^+$ (η^3-C$_7$H$_7$)Fe(CO)$_3^-$ and CpPd(1,5-cod)$^+$BF$_4^-$ at −78°C. Low-temperature limiting spectra of the fluxional product were observable, but details of the "ring-whizzing" were not provided [545]. Treating (MeO)$_3$SiFe(CO)$_3$(μ-dppm)PtH(PPh$_3$) with BF$_3$-OEt$_2$ led to generation of a trifluorosilyl group. The crystal structure of F$_3$SiFe(CO)$_3$(μ-dppm)PtH(PPh$_3$) showed a Fe–Pt bond length of 2.66 Å, and suggested weak intramolecular interactions between the syn hydride and SiF$_3$ ligands [546]. Carbonylation of (MeO)$_3$SiFe(CO)$_3$(μ-PPh$_2$)Pt(PPh$_3$)$_2$ led to facile replacement of the phosphine ligand trans to the diphenylphosphido bridge. The resulting compound rearranged in solution by interchange of silyl and carbonyl ligands, forming (OC)$_4$Fe(μ-PPh$_2$)Pt(PPh$_3$)Si(OMe)$_3$ [XRC] [547].



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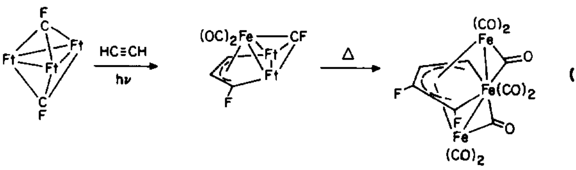
10. Trinuclear cluster compounds

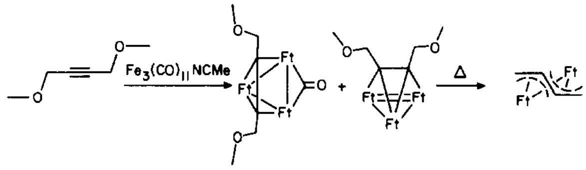
10.1 Tri-iron compounds

The most common 46-electron tri-iron complexes are the double-decker ferrole complexes, [C$_4$R$_4$Fe(CO)$_2$][Fe(CO)$_2$]$_2$(μ-CO)$_2$. Examples have been obtained by further complexation of (ferrole)Fe(CO)$_3$ complexes having 3,4-bis(diethylamino)-2,5-diphenyl substitution [504], and also by ligand coupling and rearrangement of 48-electron complexes, shown in eqn. (33). Both the ferrole isomer shown and the 2,5-difluoro isomer formed in the reaction, along with the corresponding (ferrole)Fe(CO)$_3$ complexes. The crystal structures of both Fe$_3$ complexes were determined [548].



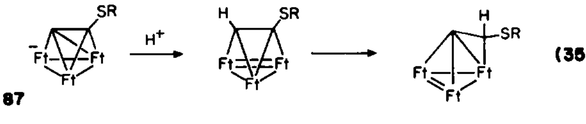
(33)

Complexation of MeOCH$_2$C≡CCH$_2$OMe by reaction with Fe$_3$(CO)$_{11}$(NCMe) led to both 46- and 48-electron complexes, as shown in eqn. (34). Heating the unsaturated complex in hexane led to loss of Fe(OMe)$_2$ and CO to form a butatriene complex. Other alkynyl ethers gave diverse results: MeC≡COEt formed the bis(alkylidyne) cluster Fe$_3$(CO)$_9$(μ-CMe)(μ-COEt), whereas the terminal alkyne reacted with hydrogen rearrangement to form the alkylidene cluster, Fe$_3$(CO)$_9$(μ-CO)(μ_3:η^2-C=CHOEt) [XRC] [549]. Alkynyl thioether complexes were prepared by protonation of **87** [eqn. (35); R = Me, Et, Pr, ^{i}Pr], which had been obtained by sulfonate displacement reactions.



(34)

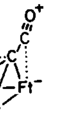
The 46-electron alkynyl thioether complexes rearranged to 46-electron (μ_3:η^2-alkylidene) clusters. **87** also added trimethylphosphine to the carbido carbon; loss of thiolate from the resulting anion gave a 48-electron zwitterionic phosphonium acetylide, Fe$_3$(CO)$_9$(μ_3:η^2,η^2-CCPMe$_3$) [550].



(35)

A metaanalysis of the crystal structures of the Group 8 dodecacarbonyls, M$_3$(CO)$_{12}$, and their simple substitution products has provided additional evidence relative to the mechanism of ligand fluxionality. Existence of an unbridged Fe$_3$(CO)$_{12}$ isomer of D_3 symmetry in solution was supported by some of the structures [551]. Magical angle spinning NMR studies of Fe$_3$(CO)$_{12}$ supported on metal oxide surfaces revealed mobile physisorbed clusters in some cases, with continued fluxionality. On HNa-Y zeolite, Fe$_3$(CO)$_{11}^{2-}$ appeared to be the principal adsorbed species [552]. Reaction of dppf with iron carbonyls gave, *inter alia*, (μ:η^2-dppf)Fe$_3$(CO)$_{10}$ [XRC], having the two phosphorus atoms coordinated across the carbonyl-bridged Fe–Fe bond of $Fe_3(CO)_{12}$ [118].

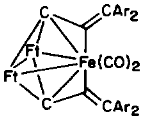
$(PPN^+)_2\{\mu_4\text{-}Cd[Fe_3(CO)_{10}(\mu\text{-}CO)]_2\}^{2-}$ [XRC] was obtained by several metathesis reactions of iron carbonyl anions and cadmium salts. The mercury analog and $PPN^+Fe_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}HgBr)^-$ were also prepared by similar methods [553]. A CuI adduct of the Ft_3CCO^{2-} dianion, **88**, showed a Cu–C distance of 2.01 Å, and a large deshielding of the carbido carbon relative to the free dianion [554].



88

Improved preparations of the 48-electron borane clusters, $Fe_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}BH)(\mu\text{-}CO)$ [from $H_3B\text{-}SMe_2$ and excess $Fe_2(CO)_9$] [495], and $Fe_3(CO)_9(\mu\text{-}H)_4(\mu_3\text{-}BH)$ [from H_3B-THF and $Fe_4(CO)_{13}^{2-}$] [555] have been reported.

A cyanocarbyne complex, $(CpFe)_3(\mu\text{-}CO)_3(\mu_3\text{-}CC{\equiv}N)$ was the product of reaction of Fp_2 with $Ph_3P{=}CHCN$, rather than the expected di-iron cyanocarbene complex. The nitrogen atom readily coordinated to a $W(CO)_5$ group [XRC] [556]. Substitution reactions of nitriles into the bis(alkylidyne)complex $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ were carried out by photolysis in acetonitrile or bonzonitrile solutions. The nitrile ligands were then readily displaced by phosphines under thermal conditions. A crystal structure was reported for $Fe_3(CO)_8(PMe_3)(\mu_3\text{-}CF)_2$. Photoinsertion of alkynes into this product proceeded similarly to the reaction shown in eqn. (33). Thermal reaction of phosphines with the nonacarbonyl led to mixtures of mono-, di- and trisubstitution products [557]. Tetraarylhexapentaene complexes, $(\mu{:}\eta^3,\eta^3\text{-}Ar_2C_6Ar_2)Fe_2(CO)_6$ underwent ligand fission upon reaction with $Fe_3(CO)_{12}$ at 100°C, to form **89** [XRC]. A related allenylidene complex, $Fe_3(CO)_9(\mu\text{-}CO)(\mu_3{:}\eta^2\text{-}C{=}C{=}CPh_2$ [XRC] was obtained from $Ph_2C{=}C{=}CBr_2$ [558].



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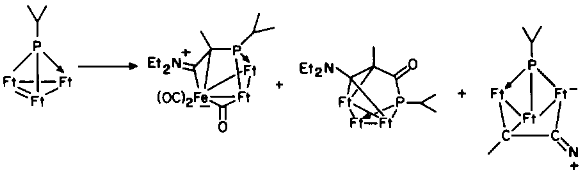
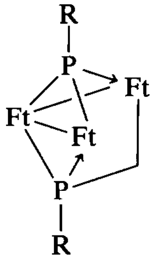
Two-electron reduction of the 48-electron closed cluster, $Fe_3(CO)_9[\mu_3\text{-}P \rightarrow Mn(CO)_2Cp]_2$, gave a 50-electron dianion, which was isolated as the PPN^+ salt and subjected to crystallographic analysis, which revealed two Fe–Fe bonds averaging 2.66 Å in length, and a non-bond Fe–Fe distance of 3.53 Å [559]. Integration of the alkynylamine $MeC{\equiv}CNEt_2$ into the unsaturated phosphido cluster $Fe_3(CO)_9(\mu_3\text{-}PCHMe_2)$ by reaction at room temperature gave both 48- and 50-electron cluster products, illustrated in eqn. (36) [560].



(36)

Similarly, reaction of $RXPCH_2PXR$ [X = Cl, Br; R = Pr, *tert*-Bu, mesityl, NMe_2, NMePh, OAr, *etc.*] with excess $Fe_2(CO)_9$ gave first a transient 48-electron complex, $Fe_3(CO)_9(\mu\text{-}PRCH_2PR)$, which underwent fragmentation to form the 50-electron complex, **90** [472,473].



90

The most common 50-electron Fe_3 complexes are those in which an open Fe_3 triangle is spanned by two four-electron ligands, usually RN, RP, RAs, S, Se, or Te. An example is the bis(nitrene) complex, $Fe_3(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}NC_5H_4N)$, obtained in minor amounts along with major amounts of **7** in reaction of 2-phenylazopyridine with $Fe_2(CO)_9$ in THF [87]. A mixed nitrene–phosphinidene cluster, $Fe_3(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}PCMe_3)$, was synthesized in 85% yield by reaction of $Fe_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)$ with Me_3CPCl_2. Thermal insertion of diphenylacetylene produced **74** [503]. Thermal reaction of $[CpMo(CO)_2]_2(\mu_2{:}\eta^2,\eta^2\text{-}As_2)$ with iron carbonyls resulted in insertion of an entire $Fe_3(CO)_9$ unit into the As–As bond, to form $Fe_3(CO)_9[\mu_3\text{-}AsMo(CO)_3Cp]_2$, which showed the expected square pyramidal structure [561].

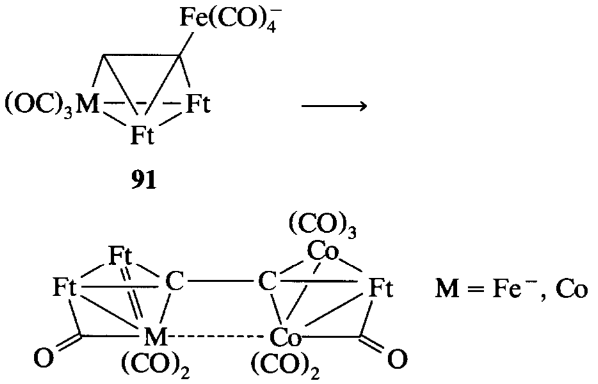
One carbonyl ligand of $Fe_3(CO)_9(\mu_3\text{-}S)_2$ was displaced by a $P(SPh)_3$ ligand in a thermal reaction. The crystal structure of the product was determined [562]. Reaction of $Fe_3(CO)_{12}$ with cyclic thioamides S=C(NHR)(OR) [$R_2 = CH_2$, CH_2CH_2, C_6H_4, *etc.*] resulted in formation of both $Fe_3(CO)_9(\mu_3\text{-}S)_2$ and its carbenoid substitution product, $Fe_3(CO)_8[{=}C(NHR)(OR)](\mu_3\text{-}S)_2$ [563]. The crystal structure of the product derived from benzimidazolethione showed the carbenoid ligand bound to the central iron of the open Fe_3 triangle [564]. Treating $Fe_3(CO)_{10}(\mu_3\text{-}PR)$ [R =

$CHMe_2$, CMe_3, Ph] with YCN^- [Y = S, Se, Te], followed by ethylation with triethyloxonium fluoroborate, gave mixed clusters, $Fe_3(CO)_9(\mu_3\text{-}Y)(\mu_3\text{-}PR)$. Initial substitution by trimethyl phosphite occurred at the center iron, but slow isomerization in solution resulted in a terminal iron-substituted product. Disubstitution products were also prepared and studied in considerable detail [565].

Addition of CO to $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ gave $Fe_2(CO)_6[\mu\text{-}TeFe(CO)_4Te]$ [XRC] [485], which can be considered a 52 electron cluster with one Fe–Fe bond or a di-iron compound with a three-atom bridge. Several related compounds, including **68**, were previously discussed as di-iron compounds in Section 9.1.

10.2. Heterotrimetallic clusters, Fe_2M and FeM_2

Almost all of the trimetallic clusters discussed in this section are 48-electron tetrahedral clusters, composed of three transition metal groups and a non-metal cap. Among the exceptions are a pair of double clusters, **92** [M = Fe^-, Co], shown in eqn. (37), having a 46-electron cluster and a 48-electron cluster joined through an acetylide bridge. The starting material for these clusters, **91** [M = Fe^-], was prepared by displacement of acetate from $Fe_3(CO)_9[\mu_3\text{:}\eta^3,\eta^2\text{-}CCOAc]^-$ by $Fe(CO)_4^{2-}$. Reaction with $Co_2(CO)_8$ resulted first in formation of **91** [M = Co], then construction of the second cluster by metallation of the C–$Fe(CO)_4$ unit by additional $Co_2(CO)_8$. The metal M in the unsaturated cluster could be interconverted between Fe^- and Co using $Fe_2(CO)_8^{2-}$ or $Co_2(CO)_8$. The crystal structure of **92** [M = Co] showed a C–C bond length of 1.36 Å. The individual metals (Fe or Co) were not distinguishable. The two tetrahedra and the carbonyl positions were distorted so as to allow the two $M(CO)_2$ metals to approach to within 2.90 Å, reflecting an attractive interaction which is probably also related to the diamagnetic character of the double clusters [566].

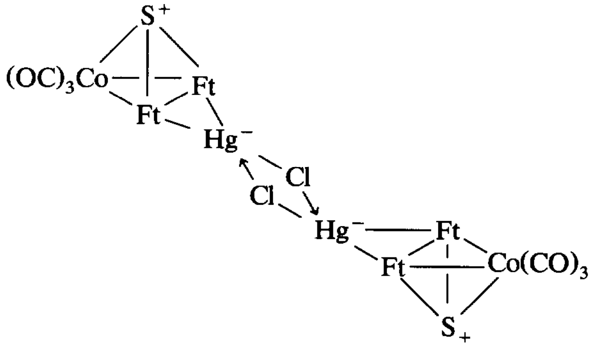


91

92

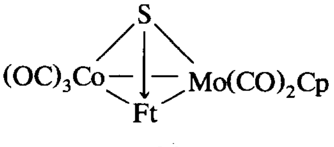
(37)

Reaction of the 46-electron cluster anion $Fe_2Co(CO)_8(\mu_3\text{-}S)^-$ (?) with L_2CuNO_3 or LAuCl [L = PPh_3] resulted in transfer of one or two triphenylphosphine ligands to the cluster to form metallated 48-electron clusters, for example $LCuFe_2Co(CO)_8L(\mu_3\text{-}S)$ [XRC] [567]. Similarly, reaction of $Fe_2Co(CO)_9(\mu_3\text{-}S)^-$ with $HgCl_2$ gave a mercurated cluster unaccountably described as $[(\mu\text{-}S)HgFe_2Co(CO)_9(\mu_3\text{-}Cl)]_2$ [XRC] [568]! It seems indubitable that the sulfur and chlorine in this proposed structure have been interchanged, and that the product is actually **93**. Reaction between diphenylmercury and hydride-containing clusters $(\mu\text{-}H)Fe_2(CO)_6[M(CO)Cp](\mu_3\text{-}COMe)$ [M = Co, Rh] led to loss of benzene and formation of mercury-bridged clusters, $Hg[Fe_2M(CO)_7Cp(\mu_3\text{-}COMe)]_2$. The cobalt-containing cluster had the mercury bridging a Fe–Fe bond, and a terminal carbonyl on the cobalt, whereas the rhodium cluster had the mercury bridging a Fe–Rh bond, and a bridging carbonyl [569].



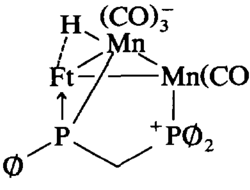
93

$(\mu\text{-}H)Fe_2Co(CO)_9(\mu_3\text{-}PPh)$ was produced in 65% yield by reaction of $Fe_3(CO)_{12}$ with $CpMn(CO)_2(\mu\text{-}PHPh)Co(CO)_3$ in refluxing benzene [570]. Cluster substitution to form **94** [XRC] occurred when $Co_2Fe(CO)_9(\mu_3\text{-}S)$ was treated with $Cp_2Mo_2(CO)_6$ [571]. Reaction of $Fe(CO)_3(NO)^-$ with $Cp'Mo(CO)_3Cl$ occurred with reduction of NO to an NH group in the cluster product, $Cp'Mo(\mu_3\text{-}NH)Fe_2(CO)_6(\mu\text{-}NO)(\mu\text{-}CO)$ [XRC] [572]. Insertion of an $Fe(CO)_4$ unit into two $Mn_2(CO)_6(\mu\text{-}H)_2(\mu\text{-}L\text{-}L)$ compounds using $Fe_2(CO)_9$ led to divergent results when different diphosphorus ligands were used. In the case of tetraethyl diphosphite, two isomers of $FeMn_2(\mu\text{-}H)_2(CO)_{10}[\mu\text{-}(EtO)_2POP(OEt)_2]$, differing in the relative positions of the hydride ligands, were formed. In the case of the



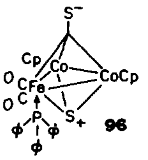
94

dppm ligand, elimination of benzene during reaction led to formation of **95** [XRC] [573].



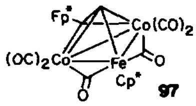
95

Reaction of $CoFe_2(CO)_9(CCO)^-$ with phosphines has been found to occur initially at cobalt, with rupture of a Co–Fe bond. The phosphine eventually migrates to the carbon, forming $CoFe_2(CO)_9(CPR_3)^-$ with restoration of the closed cluster. Fenske–Hall MO calculations were used to rationalize this reactivity pattern [574]. The reactivity of the new methylidyne cluster $HFeRu_2(CO)_{10}(\mu_3\text{-}CNMe_2)$ toward triphenylphosphine has been investigated. Substitution of one or two phosphines occurred exclusively at ruthenium. The mechanism involved rate-determining dissociation of CO, and from the cluster reactivity order $FeRu_2 > Fe_3 > Ru_3$ it was surmised that the dissociation occurred from iron [575]. The CS_2 ligand in $FeL_2(CO)_2(\eta^2\text{-}CS_2)$ underwent fission into S and CS fragments during room temperature reaction with $CpCoL_2$ [$L = PPh_3$], to form **96** [XRC] in 72% yield [576]. A germanium cluster, $Et_4N^+CoFe_2(CO)_9(\mu\text{-}CO)[\mu_4\text{-}GeFe(CO)_4^-]$ [XRC] was obtained from reaction among $\mu_4\text{-}Ge[Co_2(CO)_7]_2$, $Fe_2(CO_8^{2-}$, and $Co_4(CO)_{12}$ [577].



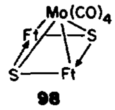
96

Mass spectra of trimetallic cluster complexes of diphenylacetylene, including $(NiCp)_2Fe(CO)_3(PhC\text{-}CPh)$, $CpNiCoFe(CO)_6(PhCCPh)$, and tetrametallic $(CpNi)_2Fe_2(CO)_6(PhCCPh)$, have been studied. Pyrolysis products of these complexes included PhC≡CPh, PhCH=CHPh, C_5H_6, and metallocenes; above 300°C, metallole complexes were observed [578]. Reaction of Fp*–C≡C–Fp* with dicobalt octacarbonyl resulted in formation of the cluster **97**. The two Cp* ligands in **97** interchanged rapidly at room temperature in a fluxional process apparently involving breaking and formation of Fe–Co bonds in the cluster. The exchange was frozen out below −60°C in the NMR [302]. A related ethynediyl complex, $[CpRu(CO)]Fe_2(CO)_6\text{-}[\mu_3{:}\eta^3,\eta^3\text{-}CCRu(CO)_2Cp]$ [XRC] resulted from interaction of $C_2[Ru(CO)_2Cp]_2$ with $Fe_2(CO)_9$ [579].



97

Some 50-electron trimetallic complexes have been formed by insertion of unsaturated metal fragments into the S–S bond of $Fe_2(CO)_6S_2$, with formation of Fe–M bonds as well as S–M bonds. An example is **98**, formed using $Mo(CO)_5(THF)$. The Mo–Fe bonds averaged 2.76 Å in length [580]. A tungsten analog of **98** and a derivative having one sulfur additionally coordinated to a $W(CO)_5$ unit were also produced photochemically [481]. The analogous compounds having selenium and tellurium rather than sulfur resulted from similar reactions; a crystal structure of $Fe_2W(\mu_3\text{-}Te)_2(CO)_{10}$ showed a similar square pyramidal structure, with average Fe–W distances of 2.91 Å [581].

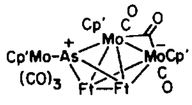


98

11. Tetra- and polynuclear cluster compounds

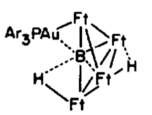
In the gas phase, the highly unsaturated cluster Fe_4^+ has been found to dehydrogenate ethene, forming $Fe_4(C_2H_2)_n^+$, $n = 1\text{–}4$. Collision-induced dissociation using xenon led to formation of carbides when $n = 1$ or 2, but C_6H_6 was ejected as a unit for $n = 3$ or 4. The possibility of a full catalytic cycle was demonstrated [582]. Photolysis of $H_2FeOs_3(CO)_{13}$ in solid matrices at 77 K gave the unsaturated dodecacarbonyl. IR studies located the site of unsaturation at the unbridged osmium atom. Warming to 298 K led to efficient CO recombination [583]. IR comparisons indicated that the same species, perhaps stabilized by interactions with surface hydroxyl groups, was formed on irradiation of $H_2FeOs_3(CO)_{13}$ adsorbed on a silica surface [584].

Absorption of visible light at 532 nm by $(CpFeCO)_4$ results in an excited singlet state, whose lifetime has been measured as 120 ps [585]. The tetrahedral clusters $Et_4N^+MCo_3(CO)_{12}^-$ [M = Fe, Ru] have been studied by solid-state ^{59}Co NMR [586]. Reactions of the same anionic clusters with $HgBr_2$ produced HgBr and $HgCo(CO)_4$ adducts, with the mercury capping the Co_3 face of the cluster. The bromide of the μ_3-HgBr product was readily displaced by $Co(CO)_4^-$, $CpMo(CO)_3^-$, or another $MCo_3(CO)_{12}^-$ cluster. Long mercury-cobalt distances and easy disruption of the mercury bonding, by attack of Cl^-, for instance, suggest weak ionic attractions [587]. $FeCo_3(CO)_{12}^-$ anions were attached to polystyrene beads through phosphine-copper or -gold coordination. The bound clusters were more stable and more selective as catalysts for hydroformylation of 1-hexene than homogeneous analogs. The clusters attached to the polystyrene through gold were more active but less stable than those attached through copper [588]. Trimethylamine substitution into $HFeCo_3(CO)_{12}$, brought about by reaction with trimethylamine oxide, was found to occur at cobalt, based on IR and ^{59}Co NMR studies. The product, $HFeCo_3(CO)_{11}(NMe_3)$ [XRC] was labile in solution, undergoing transformation into $Me_3NH^+FeCo_3(CO)_{12}^-$. The amine ligand was also readily displaced by better ligands, including PPh_3 or SEt_2 [589]. Cophotolysis of $(\mu_3\text{-As})[Cp'Mo(CO)_2]_3$ and $Fe_3(CO)_{12}$ led to a straightforward arsine substitution product, $[Cp'Mo(CO)_2]_3[\mu_4As \rightarrow Fe_3(CO)_{11}]$, and also to the new cluster product, **99** [XRC] [561].



99

Reactions of the 62-electron butterfly cluster $PPN^+HFe_4(CO)_{12}BH^-$ with various LAuCl compounds gave varying results, depending on L. Tri(*o*-tolyl)phosphine or tricyclohexylphosphine gave the expected monooadducts, **100** [XRC, Ar = tri(*o*-tolyl)phosphine], but smaller phosphines gave isomeric products, $L_2Au^+[HFe_4(CO)_{12}BH]_2Au^-$, with two clusters fused together in a face-to-face orientation around the gold atom [590]. Diauration of the anion using $(\mu\text{-dppf})(AuCl)_2$ gave a mixture of two isomers of $Fe_4(CO)_{12}BHAu_2(dppf)$ in solution, with the major isomer having an unsymmetrical attachment of gold atoms to the cluster [591]. A mixed borane cluster, $HFeRu_3(CO)_{12}BH_2$, has been synthesized by photochemical reaction of $Ru_3(CO)_9BH_5$ with $Fe(CO)_5$; the iron atom occupied a wingtip position. Neither the neutral cluster nor the anion resulting from deprotonation showed any fluxionality [592]. Substitution of phosphines into the nitrido clusters $Fe_4(CO)_{12}(\mu_4\text{-N})^-$ or $Fe_4(CO)_{11}(NO)(\mu_4\text{-N})$ resulted in reaction only at the wingtip positions [593].



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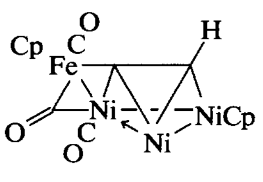
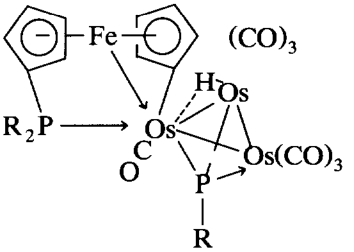


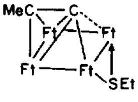
101

The tetranuclear cluster **101** was obtained, along with the more conventional alkyne-Ni_2Cp_2 product type, when FpC≡CH and $(CpNiCO)_2$ were allowed to react. It also resulted from reaction of $(NiCp)_2$-$(\mu:\eta^2,\eta^2\text{-FpCCH})$ with $Ni(CO)_4$ [303]. Consistent with its 64-electron count, it showed a spiked triangular metal skeleton. A substantial family of 64-electron tetrametallic complexes has been synthesized by pyrolysis of various triruthenium or triosmium clusters containing ferrocenylphosphine ligands. The result was oxidative addition of the cluster to a Fc–H bond and formation of a donor-acceptor bond from the ferrocenyl iron to a heavy metal in the cluster. Several examples have been described [372–374], such as **102** [R = ^{i}Pr, XRC], derived from pyrolysis of $[\mu\text{-}Fe(C_5H_4PR_2)_2]Os_3(CO)_{10}$.



102

A 64-electron complex having a square raft geometry rather than the spiked triangle is the product **103** [XRC], one of several products (**67** being another) from reaction of iron carbonyls with MeC≡CSEt [482]. A topologically linear 66-electron complex, **104**, was another among the panoply of products resulting from coordination of Fp*–C≡C–Fp* with metal carbonyls. In this compound the C_2 ligand (with a C≡C distance of 1.24 Å and C–Fe distance of 1.95 Å) functions as a four-electron donor and thus has residual bonding capacity. Consistent with that view, further reaction with ruthenium carbonyl led to an octanuclear cluster, $(\mu_6\text{-}C_2)_2(Cp^*Fe)_2Ru_6(CO)_{14}(\mu\text{-}CO)_3$ [594].



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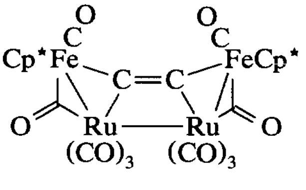
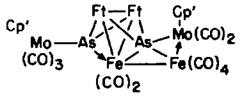


104

$L_nFe_4Z_4$ clusters [Z = S, Te] owe their interest and importance to the variable electron count they are able to sustain without major structural disruption. Additional electrons beyond the minimum result in increasing the size of the cluster as formal iron–iron bonds are lost, but the Fe_4Z_4 superstructure maintains its integrity over a range of oxidation states. One of the most highly unsaturated examples of these clusters is the 56-electron cluster, $(Et_3P)_4Fe_4Te_4$, which has been prepared from $Fe(COT)_2$ and Et_3PTe at room temperature. The Fe–Fe distances in the cluster were all about 2.62 Å, consistent with the unsaturated nature of the cluster [595]. The compounds $(Cp'Fe)_4S_4$ $(PF_6^-)_n$ [n = 0–2] were prepared by reaction of $[Cp'Fe(CO)_2]_2$ with elemental sulfur in refluxing toluene. The crystal structure of the neutral 68-electron complex showed two Fe–Fe bonds of 2.61 Å length, and Fe $\cdots$ Fe nonbonding distances above 3.36 Å. The monocation showed more delocalized bonding, with four Fe–Fe distances of 2.90 Å [596]. Use of excess sulfur in the preparation led to formation of $(Cp'Fe)_4S_5(PF_6^-)_n$ [n = 0–2]. The monocation showed two Fe–Fe distances of 2.66, one intermediate distance of 3.00, and the rest above 3.34 Å, consistent with the 67-electron count and the reduced symmetry imposed by the extra sulfur atom [597]. Mixed-ligand clusters, $Cp_3^*(PhCSCSPh)$-Fe_4S_5 and $Cp_2^*(PhCSCSPh)_2Fe_4S_4$, were formed by refluxing a mixture of Fp_2^*, sulfur, and diphenylacetylene in mesitylene. The crystal structure of the neutral, paramagnetic Fe_4S_5 cluster showed two 2.72 Å Fe–Fe bonds to the iron bearing the dithione ligand, whereas the cation showed three Fe–Fe bonds of length 2.74–2.78 Å [598]. Finally should be mentioned a double cluster, $[Fe_4(CO)_{10}Te_4]_2Te_2^{2-}$, prepared along with **68** by reaction of Te_4^{2-} with $Fe(CO)_5$, in which two Fe_4Te_4 units were joined by a ditellurium unit mutually bonded to two irons of each cluster unit. The individual clusters have a 72-electron count and no Fe–Fe bonds [487].

A pentanuclear cluster, **105** [XRC], was produced by cophotolysis of $Cp'_2Mo_2(CO)_4As_2$ and $Fe_2(CO)_9$. Its unusual spiked-spiked-triangle geometry is supported by the μ_5-As atom [561]. $(PPN^+)_2FeRh_4(CO)_{15}^{2-}$ has been found to be an effective catalyst for reductive carbonylation of nitrobenzene in the presence of methanol to form $PhNHCO_2Me$. Addition of 2,2'-bipyridyl improved both the rate and the selectivity [599]. Several cluster products, including $FeRu_4$, $FeRu_5$, and Fe_3Ru_5 clusters, were produced in the reaction of $Fe_2(CO)_9$ and $Ru_5(\mu\text{-}PPh_2)(\mu_5\text{-}CCPPh_2)(CO)_{13}$; the most complex product [XRC] was **106** [600]. The first two were obtained in smaller amounts, but were shown to be square-planar and octahedral carbido complexes of known types. The structure of the $FeRu_5$ complex was ascertained by crystallography of its dimethylphenylphosphine substitution product, and is represented here as **107** [601]. Structurally related borido clusters, PPN^+ *trans*-$Fe_4Rh_2(CO)_{16}B^-$ and *mer*-$H_2Fe_3Rh_3(CO)_{15}B$, have been described. The latter formed spontaneously on protonation of the former, which arose from cluster expansion of butterfly complex $HFe_4(CO)_{12}BH^-$ using $[Rh(CO)_2Cl]_2$ [602]. A more electron-rich, and hence more open, hexanuclear cluster, **108** [XRC], arose from reaction of $Ru_5(\mu_3\text{-}C{=}CH_2)(\mu_3\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}$ and $Fe_2(CO)_9$ [603].



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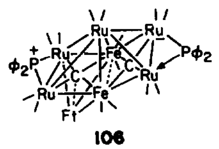

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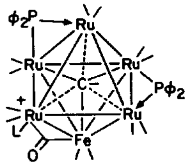

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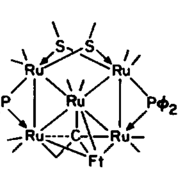

108

Theoretical calculations using a neglect of diatomic overlap (NDO) procedure have been applied to adsorption of CO on a cluster of 12 iron atoms. The results emphasized the importance of σ-electrons in stabilization of the iron–carbon bond [604]. From a thermochemical cycle for ethene on a hydrogen-presaturated Fe(100) surface, the bond energies for Fe–Et and Fe–H bonds have been estimated as 160 and 250 kJ mol^{-1}. Both values are consistent with those of isolable mononuclear compounds [605].

12. List of abbreviations used

An	any arene ring, such as benzene or naphthalene
Ar	an aryl ring, such as *p*-tolyl, MeC_6H_4–
bda	benzylideneacetone, $PhCH{=}CHCOCH_3$
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	bis(dimethylphospino)methane
dppe	1,2-bis(diphenylphospino)ethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphospino)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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