IRON

Annual Survey Covering the Year 1982*

JOHN J. ALEXANDER
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, USA

Contents

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* Iron Annual Survey Covering the Year 1981, see J. J. Alexander, J. Organomet. Chem. 274 (1984) 331.

METAL CARBONYLS

Simple Carbonyls and Carbonylate Anions

Electrochemical reduction of $Fe(CO)_5$ has been studied [1]. No matter what the electrode material, $[Fe_2(CO)_8]^{2-}$ is the reduction product in the absence of water. When water is present, a two-electron reduction to $[HFe(CO)_4]^-$ occurs.

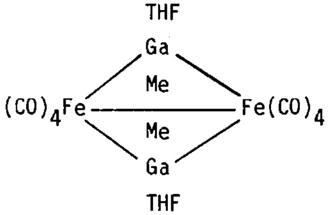
Both $Fe(CO)_5$ and $Fe_3(CO)_{12}$ were found to be weakly adsorbed on silica. In contrast, on alumina, magnesia and ZnO, $[HFe_3(CO)_{11}]^-$ is formed [2]. Irradiation of silica-supported $Fe(CO)_5$ produced only $Fe_3(CO)_{12}$ and not $Fe_2(CO)_9$ [3].

Auger line shape studies on $Fe(CO)_5$, *inter alia*, were reported [4]. A comparison of the He(I) photoelectron spectra of $Fe(CO)_5$ and $Fe(CO)_4(CS)$ was made and discussed in the light of M.O. calculations [5]. A calculation of the ionization potentials of $Fe(CO)_5$ was also reported [6].

The ESR spectrum of $[Fe(CO)_5]^-$ in a single crystal of $Cr(CO)_6$ shows that one CO is bent by electron addition [7].

Complexes with Group III Ligands

The X-ray structure of **1** was determined [8]. $(tppIn)_2Fe(CO)_4$ (tpp = tetraphenylporphinato) was prepared from the reaction between tppInCl and $[Fe(CO)_4]^{2-}$ [9].



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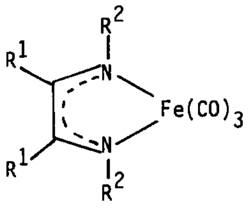


2a R^1 = H, R^2 = *c*-C_6H_{11}
b R^1 = H, R^2 = *t*-Bu
c R^1 = Me, R^2 = *p*-FC_6H_4
d R^1 = Me, R^2 = Ph
e R^1 = Me, R^2 = *p*-$MeOC_6H_4$

Complexes with Group IV Ligands

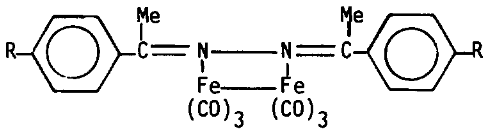
Substitution reactions occur on treating $HFe(CO)_4(SiPh_3)$ with PPh_3 or diphos affording $HFe(CO)_3(PPh_3)(SiPh_3)$ or $HFe(CO)_2(diphos)(SiPh_3)$, respectively. In contrast, PEt_3 deprotonates the hydride giving $(PEt_3H)[Fe(CO)_4(SiPh_3)]$ [10].

Complexes with Group V Ligands

Mössbauer parameters of some forty-six $LFe(CO)_4$ complexes were measured. Many of the complexes have L as a Group V ligand. However, Group IV ligands as well as others were also included [11].

A study of CO displacement in **2** showed that thermal reaction of **2a**, **c**, **d**, **e** with L = phosphines and $P(OMe)_3$ proceeds via a bimolecular rate law in toluene consistent with an associative mechanism (which was also found for the analogous $(Me_4N_4)Fe(CO)_3$ complexes). With **2b** the diazabutadiene ligand is replaced by L. Photochemical substitution proceeds via a dissociative mechanism affording $(R^1_2C_2N_2R^2_2)Fe(CO)_2L$ except for **2a** where diazabutadiene and CO substitution occur at comparable rates [12].

The preparation of **3** was reported [13].



3a R = H; **b** R = Me;
c R = OMe

For some N-bonded azadiene complexes, see the section on Heterodiene Species.

The preparation and characterization of several phthalocyaninato (Pc) complexes of type Fe(Pc)(CO)L (L = N,N-dimethylacetamide, pyridine, piperidine, HMPA and Ph_3PO) were described [14]. The syntheses involved reaction of Fe(Pc) with L and CO in an inert solvent. In the absence of L, $Fe(Pc)(CO)_2$ could be prepared.

A comparative study of CO and O_2 affinities of "capped" iron porphyrins as a function of electronic and steric changes in the equatorial plane was carried out [15]. CO affinities of Fe(II) octaethylporphyrin, octaethylchlorin and octaethylisobacteriochlorin were measured [16]. An Fe(II) porphyrin having a strap carrying a coordinated thiolate residue on one face was prepared. The spectroscopic properties of its CO complex match those of the CO complex of cytochrome P-450 [17].

CO addition to meso-tetrakis(2,4,6-trimethoxyphenyl)porphyrinatoiron(II) and the corresponding ethoxy complex produced diamagnetic species. A 1:2 Fe:CO product was also prepared for the ethoxy compound [18].

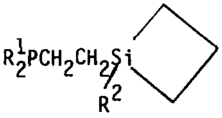
The X-ray structure of (thiocarbonyl)(octaethylporphinato)iron(II), a low-spin five-coordinate complex, displays a linear Fe-C-S group with Fe displaced $0.23\ A^{o}$ from the porphyrin plane [19].

Heme complexes were also among those studied which contain N bonded to Fe. The first directly obtained values for CO affinities and on and off rate constants for CO binding to individual chains within T- and R-state hemoglobin A were measured [20]. Calculations of low-lying triplet states of model carbonyl heme complexes showed that the lowest-lying triplet state is too high in energy to be populated thermally [21]. INDO-SCF-CI calculations on carbonyl hemoproteins were employed to identify the photoactive excited state for CO dissociation as resulting from $d \rightarrow d_{z^2}$ excitation [22].

Preparative procedures for 1,2-ethandiyl(diphenylphosphine) (=diphos) complexes of Fe [23] were described.

The cationic complex $[Fe(CO)_4PCH_2CH_2NMe_3]I$ was prepared and found to exhibit enhanced solubility in polar solvents as well as low catalytic activity for the water gas shift reaction [24].

A series of seventeen complexes $LFe(CO)_4$ was prepared where L = 4 as well as six complexes of the type $L[Fe(CO)_4]_2$ where L = 5 [25].



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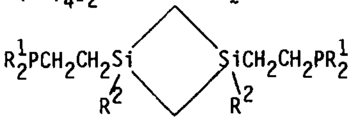


5

Treatment of $Fe(CO)_5$ with R_3PS (R_3 = Ph_3; Bu_3; Ph_2, OEt; Ph_2, SEt; Ph, $-CH_2CH_2-CH_2O-$; Ph_2, $CH_2C(OH)Ph$; Ph_2, $CH_2C(O)Ph$) at 130-150° affords the phosphine complexes $(R_3P)Fe(CO)_4$. These can be oxidized with $CuCl_2$ in MeOH to yield $(R_3P)_2-Fe(CO)_2Cl_2$ from which the free phosphines can be isolated on heating or treatment with N-methylimidazole [26].

$(PPh_3)Fe(CO)_4$ reacts with $(NEt_4)(OH)$ in very concentrated MeOH solution to afford $(Et_4N)[HFe(CO)_3(PPh_3)]$ in 80-90% yield. This is converted to the more soluble K^+ salt on reaction with $K[BH(\underline{sec}\text{-}Bu)_3]$. Refluxing in THF with the borohydride produces $K_2[Fe(CO)_3(PPh_3)]$. The $(PMe_2Ph)Fe(CO)_4$ complex behaves similarly. These dianions deprotonate CH_3CN, react with Ph_3SnCl and undergo facile ligand exchange with ligands which are better π-acceptors than PPh_3 [27].

$Fe(PPh_3)_3(CO)_2$ was found to undergo substitution with $P(OMe)_3$, py, Me_2SO, MeNC as well as oxidative addition with H_2 and Br_2. Ph_2C_2 reacts to give two isomers and CS_2 forms a π-complex [28].

A radical species 6 can be prepared as shown in Scheme 1 and isolated as a solid [29,30].

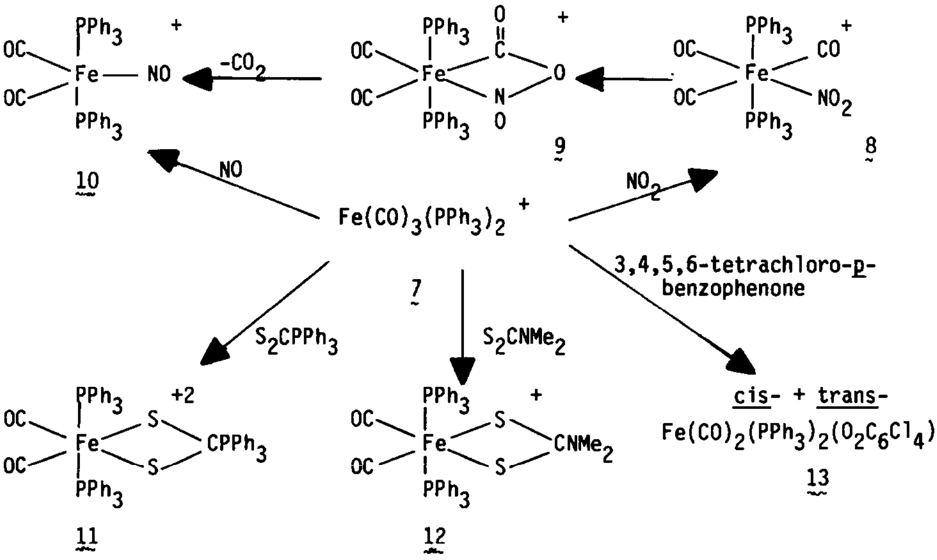
SCHEME 1

$$\{[(Me_3Si)_2CH]_2P\}^{\cdot} + Fe_2(CO)_9 \xrightarrow[\underline{n}\text{-hexane}]{} \{[(Me_3Si)_2CH]_2P\ Fe(CO)_4\}^{\cdot}$$

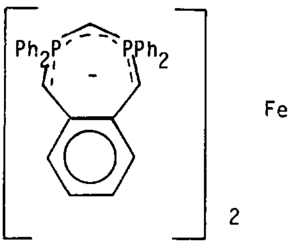
6

Scheme 2 displays chemistry of the radical cation 7 [31].

SCHEME 2



The triple ylid complex 14 was prepared from the reaction of $FeCl_2$ with the Li^+ salt of the ylid in THF at -78°. Magnetic measurements on 14 indicate it to be a high-spin tetrahedral species [32].



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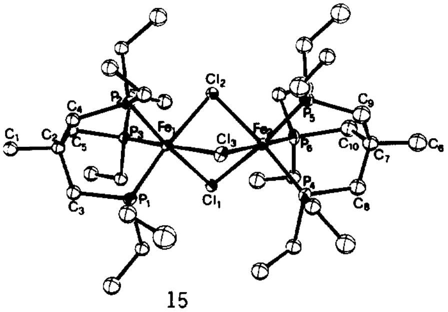
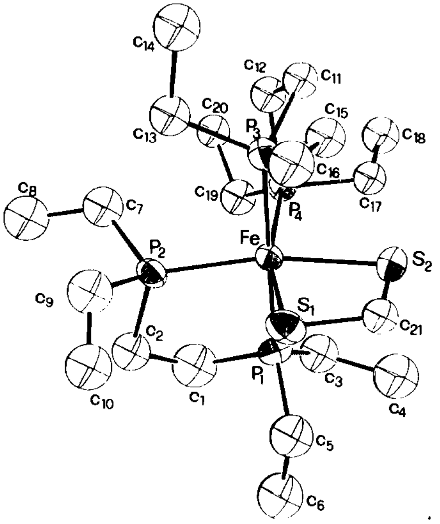


15

The reaction between $Fe(CO)_5$ and several Group V ligands L = PPh_3, $AsPh_3$, $SbPh_3$, $PMePh_2$, PMe_2Ph, $AsMe_2Ph$, $P(C_6H_{11})_3$, $P(\underline{n}\text{-}Bu)_3$, $P(\underline{i}\text{-}Bu)_3$, $P(OMe)_3$, $P(OEt)_3$ and $P(OPh)_3$ in refluxing toluene was found to be catalyzed by $[(\eta^5\text{-}Me_5C_5)Fe(CO)_2]_2$ affording $LFe(CO)_4$ [33].

Fe(II) Phosphine Complexes Containing Hydrido, Halo and Other Ligands

When $FeCl_2$ is allowed to react with $MeC(CH_2PEt_2)_3$ in the presence of $Na(BPh_4)$, the tetraphenylborate salt of 15 is isolated. Its X-ray structure was determined [34]. Et_3PCS_2 and $Fe(BF_4)_2{\cdot}6H_2O$ in the presence of $Na(BPh_4)$ react with $Et_2PCH_2CH_2PEt_2$ (depe) or $Ph_2PCH_2CH_2PPh_2$ (diphos) affording $[(depe)_2Fe(S_2CPEt_3)](BPh_4)_2$ and $[(diphos)Fe(S_2CPEt_3)_2](BPh_4)_2$ ·0.5 acetone, respectively [35]. The depe complex (whose X-ray structure was determined) undergoes nucleophilic attack by hydride ion to afford $[(depe)_2Fe(S_2CH)]^+$, 16, as the tetraphenyl-



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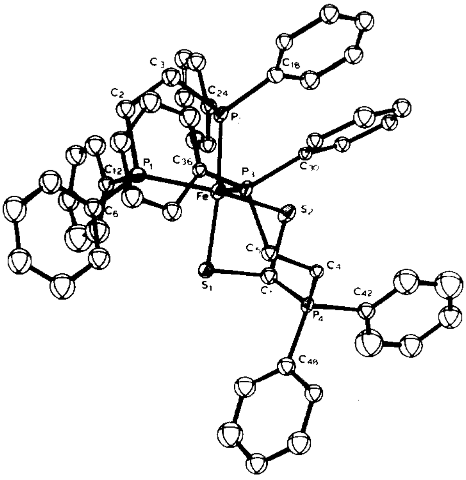


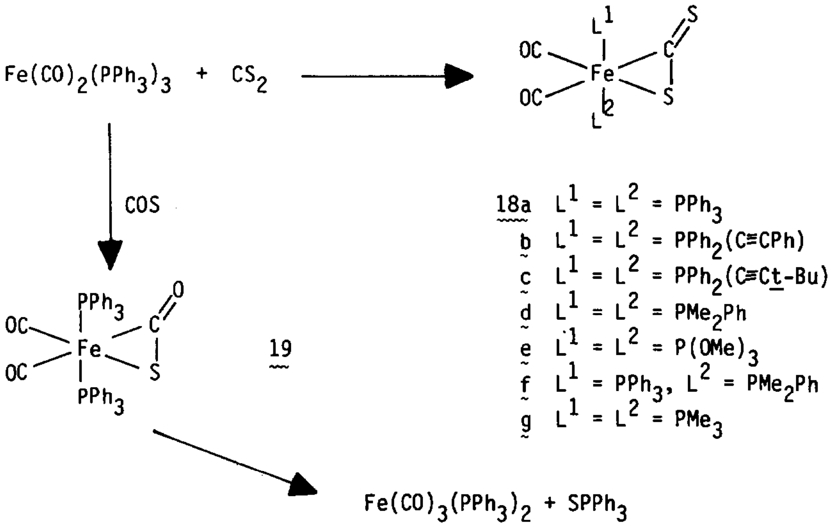
17

borate salt. 16 contains a dithioformato ligand [35]. 17, [(diphos)Fe $S_2C(H)$ - diphos]$^+$, is formally the result of nucleophilic attack by the phosphine on a dithioformato ligand. It can be prepared from the reaction of $Fe(BF_4)_2 \cdot 6H_2O$, diphos, and $K(S_2CH)$ in the presence of $NaBPh_4$. Its X-ray structure was reported [36].

Complexes with Group VI Ligands

$Fe(CO)_2(PPh_3)_3$ is known to react with CS_2 producing 18a. The reaction of the carbonyl phosphine with COS gives products which can be rationalized as proceeding via an analogous intermediate 19 as shown in Scheme 3 [37]. When the reaction is run in COS(l), 19 can be isolated.

SCHEME 3

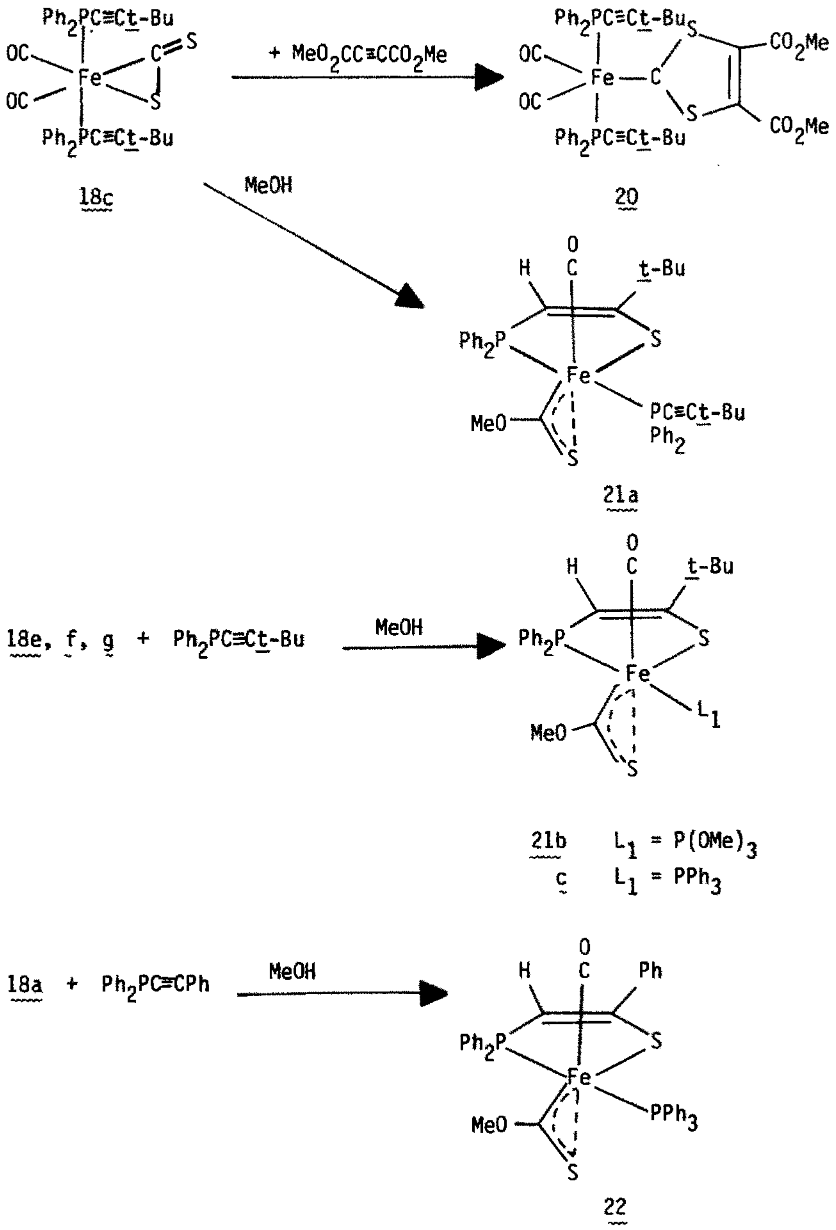


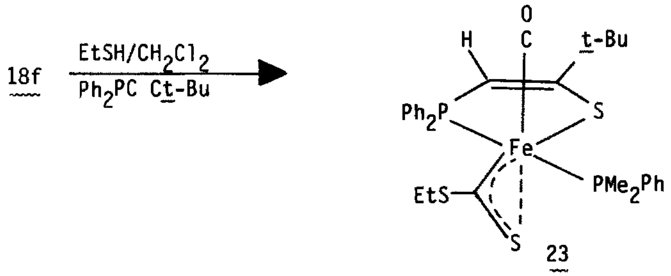
18a $L^1 = L^2 = PPh_3$
b $L^1 = L^2 = PPh_2(C{\equiv}CPh)$
c $L^1 = L^2 = PPh_2(C{\equiv}C\underline{t}\text{-}Bu)$
d $L^1 = L^2 = PMe_2Ph$
e $L^1 = L^2 = P(OMe)_3$
f $L^1 = PPh_3$, $L^2 = PMe_2Ph$
g $L^1 = L^2 = PMe_3$

The uncoordinated S in 18 is a good nucleophile. Coordinated CS_2 also displays 1,3-dipolar character in its reaction with electrophilic alkynes as Scheme 4 shows [38].

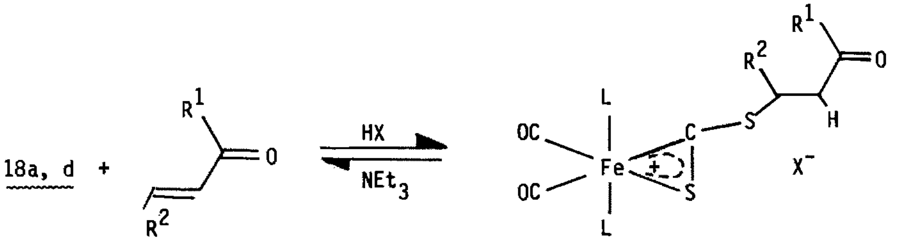
Ethanol reacts similarly. The X-ray structure of 21b was reported [38]. Reactions involving regioselective addition of the non-coordinated S of 18a, d to α,β-unsaturated aldehydes, ketones and esters in the presence of HPF_6 or HBF_4 were investigated as Scheme 5 depicts. When bulky 18a is used, addition to 25 producing 26 is highly stereospecific [39].

SCHEME 4

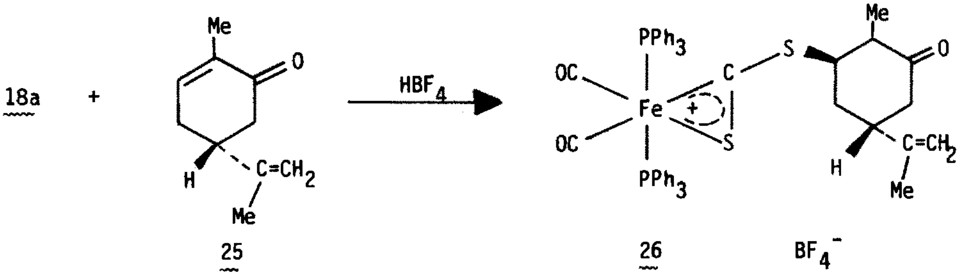

Ph2PC≡Ct-Bu
OC
Fe
C=S
S
18c
+ MeO2CC≡CCO2Me
CO2Me
20
MeOH
H
C
O
t-Bu
Ph2P
MeO
PC≡Ct-Bu
Ph2
21a
18e, f, g + Ph2PC≡Ct-Bu
L1
21b L1 = P(OMe)3
c L1 = PPh3
18a + Ph2PC≡CPh
Ph
PPh3
22



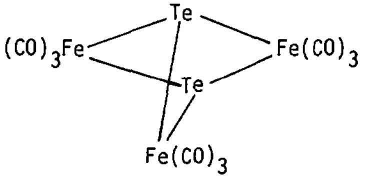
SCHEME 5



24a L = PMe_2Ph; $R^1 = R^2 = H$; X = PF_6
b L = PMe_2Ph; R^1 = Me, R^2 = H; X = PF_6
c L = PMe_2Ph; $R^1 = R^2$ = Ph; X = PF_6
d L = PMe_2Ph; R^1 = OMe, R^2 = H;
X = PF_6
e L = PPh_3; $R^1 = R^2$ = Ph; X = PF_6
f L = PPh_3; $R^1 = R^2$ Ph; X = BF_4



The X-ray structure of 27, which was prepared from the reaction of $Fe(CO)_5$, I_2 and Na_2Te, was determined [40].



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Carbonyl Halide, Hydride and Cyanide Complexes

$H_2Fe(CO)_4$ was found [41] to protonate the N_2 ligands in cis-$W(N_2)_2$-$(PMe_2Ph)_4$ in methanol. Treatment of the reaction mixture with KOH and subsequent distillation afforded ammonia and hydrazine. The yields were improved under an H_2 atmosphere.

Extended Hückel calculations bearing on the roles of $H_2Fe(CO)_4$ and $[HFe(CO)_4]^-$ in the Reppe synthesis were reported [42]. The electrochemical behavior of $[HFe(CO)_4]^-$ is critically dependent on the nature of the solvent [1]. In the absence of water at a Pt electrode one-electron oxidation occurs whereas a three-electron process occurs in the presence of base and water.

The IR spectra of $[HM(CO)_4]^-$ and $[DM(CO)_4]^-$ (M = Fe, Ru, Os) reveal a significant interaction between M-H and CO stretching vibrations [43].

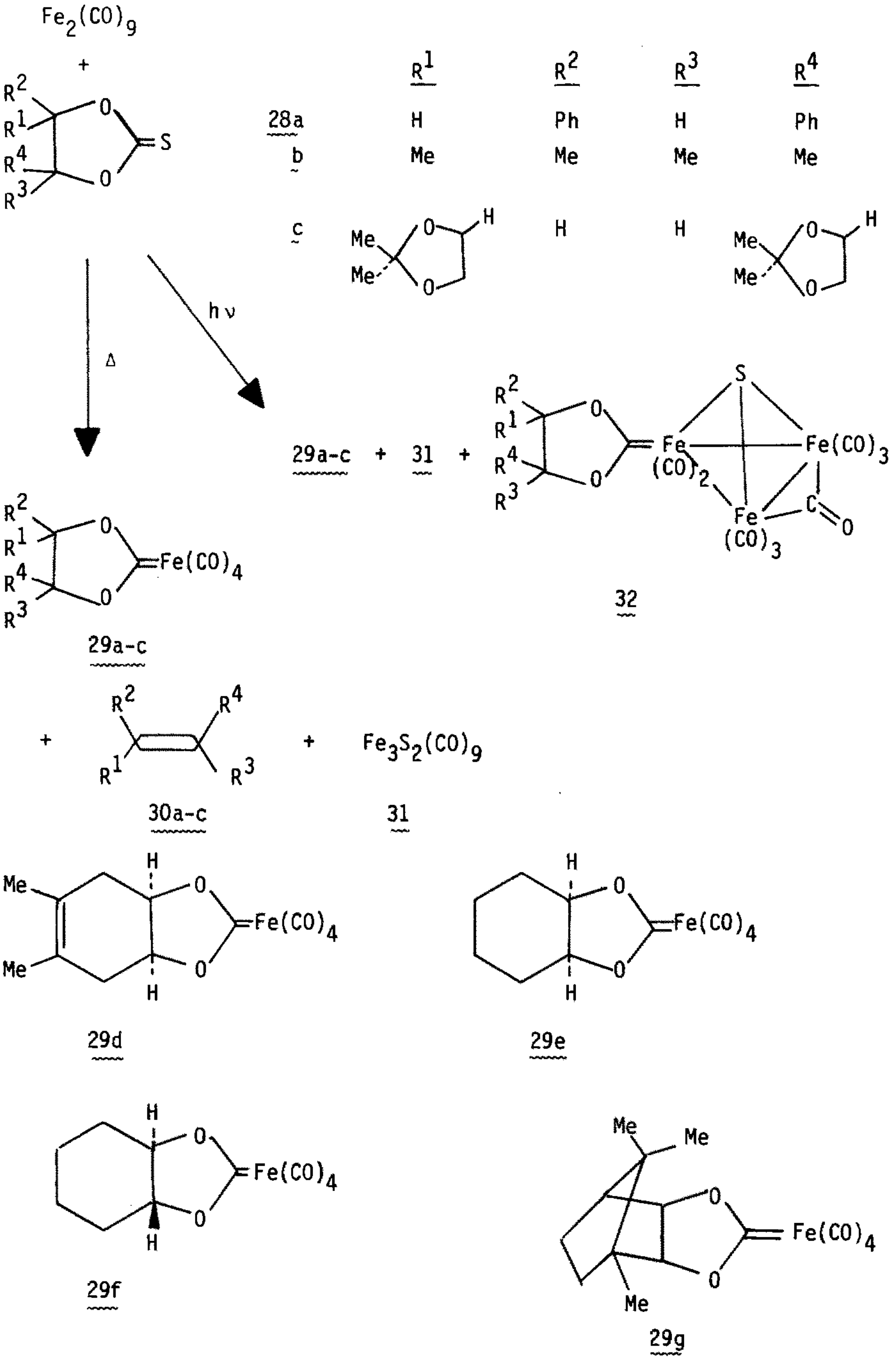
The X-ray structure of $Cp_2Mo(\mu\text{-}H)_2FeBr_2$ prepared from the reaction of $FeBr_2$ with Cp_2MoH_2 was determined [44].

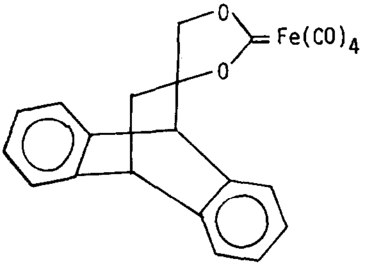
ISOCYANIDE AND CARBENE COMPLEXES

A full paper was published on $CoCl_2 \cdot 6H_2O$-catalyzed substitution reactions of $Fe(CO)_5$ as a preparative route to $Fe(CO)_{5-n}(CNR)_n$ (n = 1-3, R = Me, C_6H_{11}, t-Bu, $PhCH_2$, Ph, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$; n = 4, R = t-Bu; n = 5, R = 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$) [45]. Treatment of $Fe(CO)_4(CNR)$ with RNC and Me_3NO gave $Fe(CO)_3(CNR)_2$.

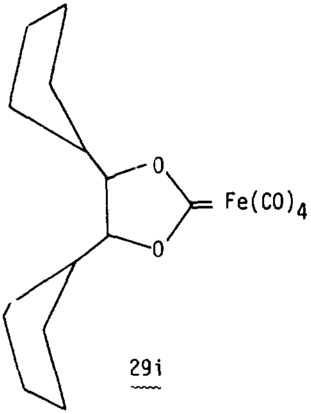
A series of carbene complexes was prepared as shown in Scheme 6 [46]. 29d-j were synthesized in the manner shown starting with the corresponding thiones [46]. 29b was also produced via the photochemical reaction of $Fe(CO)_5$ with 33 [47].

SCHEME 6

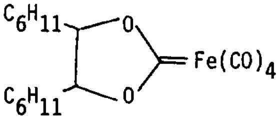

Fe2(CO)9
+
R2
R1
R4
R3
O
O
S
R1
R2
R3
R4
28a
H
Ph
H
Ph
b
Me
Me
Me
Me
c
Me
Me
O
O
H
H
H
Me
Me
O
O
H
Δ
hν
29a-c + 31 +
S
Fe
(CO)2
Fe(CO)3
Fe
(CO)3
C
O
32
Fe(CO)4
29a-c
+
+ Fe3S2(CO)9
30a-c
31
29d
29e
29f
29g
Me
H



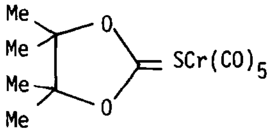
29h



29i



29j



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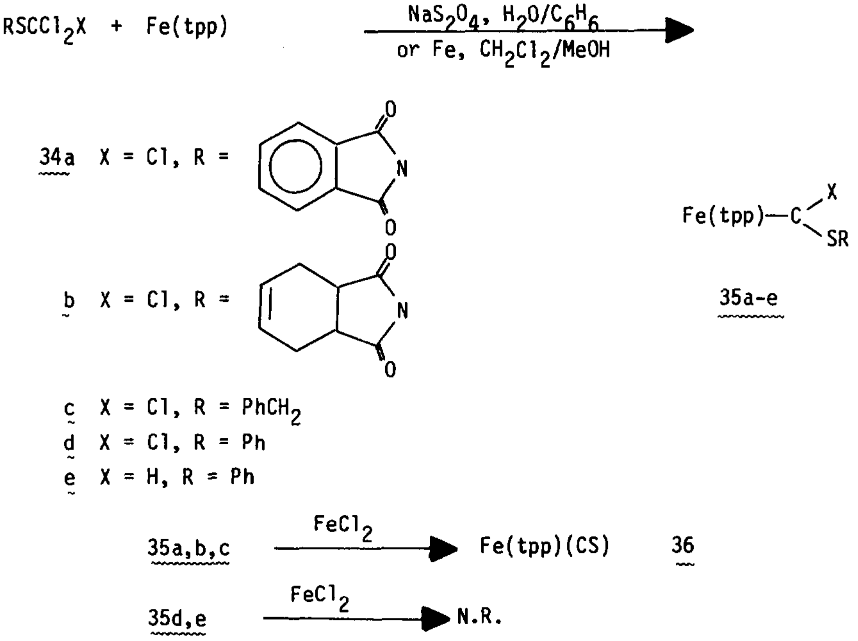
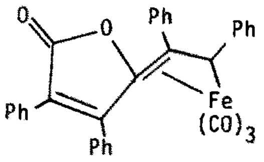
Scheme 7 depicts chemistry involving tetraphenylporphinato (tpp) carbene complexes [48].

SCHEME 7



Analogues of 36 containing other porphinato ligands can be prepared by treating the iron porphinato complex with $PhCH_2SCCl_3$ in the presence of excess Fe powder. Addition of basic ligands L produces Fe(porphinato)(CS)(L) (L = MeOH, EtOH, morphine, *i*-$PrNH_2$, *n*-$BuNH_2$, py, N-methylimidazole and PEt_3). With excess *n*-$BuNH_2$ 36 gives the isocyanide complexes Fe(tpp)(CN*n*-Bu)(NH_2*n*-Bu) [48].

The vinyl carbene complex 37 is one product of the reaction of $Fe_2(CO)_9$ with 38. The other is 39. CO converts 37 to 39; the reaction is reversible. The X-ray structure of 37 was reported [49].



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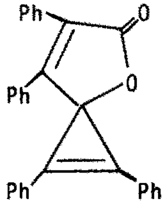

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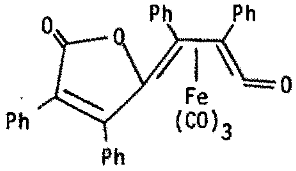

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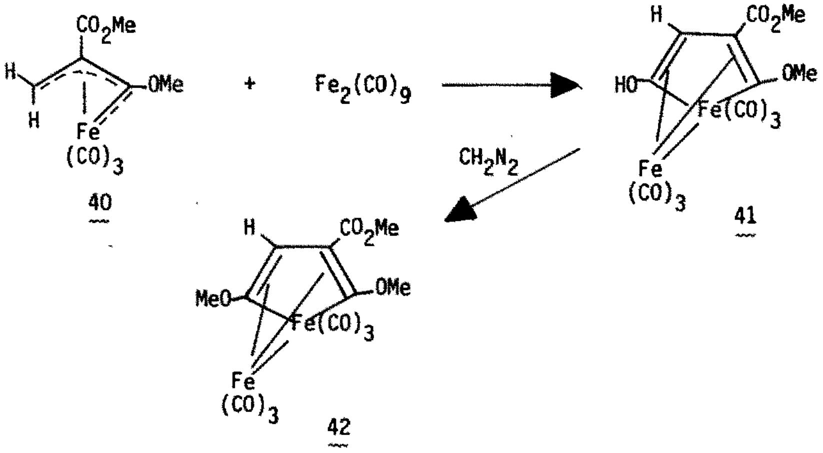
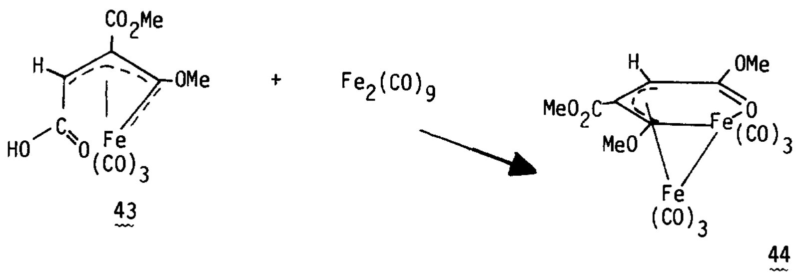
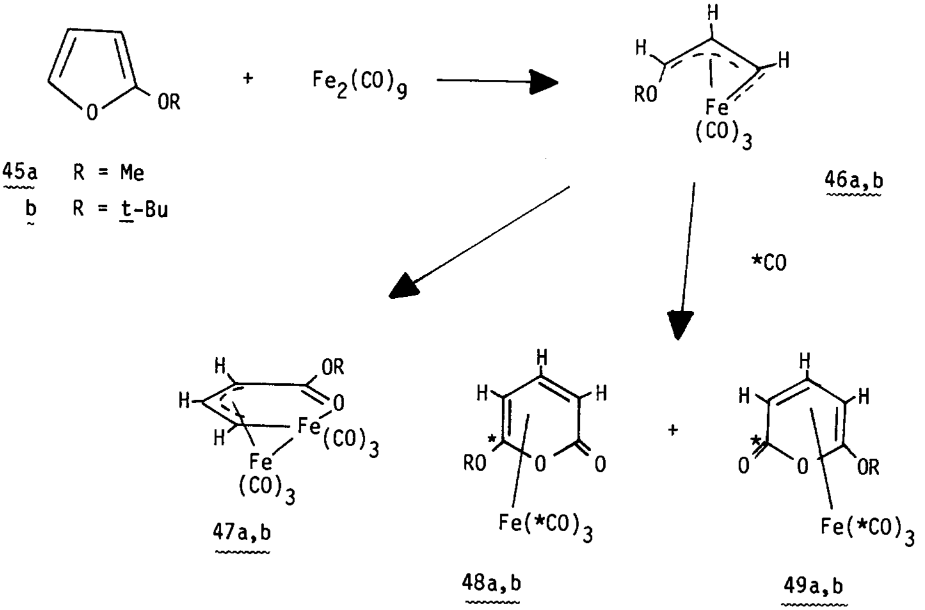
Some chemistry of vinyl carbene complexes is shown in Scheme 8. 40 and 43 react with $Fe_2(CO)_9$ [50] to afford dinuclear products 41 and 44. The X-ray structure of 44 was reported. The identity of the product 47 implicates a vinyl carbene intermediate 46 in the reaction between 45 and $Fe_2(CO)_9$. In the presence of *CO, 46 gives 48a,b and 49a,b [50,51].

SCHEME 8







The vinylidene group in (tpp)Fe[C=C(p-$ClC_6H_4)_2$]Cl is inserted into one of the Fe-N bonds. The Fe(III) atom in this compound has intermediate spin state with μ = 3.9 B.M. between 40 and 300 K. The EPR spectrum shows a rhombic pattern and indicates that the structure is the same both in solid and solution [52]. The "inserted" geometry of the vinylidene group has been confirmed in the X-ray structure of (meso-tetratolylporphinato)Fe[C=C(p-$ClC_6H_4)_2$]Cl·2 CH_2Cl_2 [53].

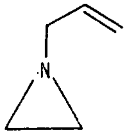
NITROSYL COMPLEXES

A convenient preparation of PPN[$Fe(CO)_3(NO)$] is the reaction of $NaNO_2$ with $Fe(CO)_5$ in the presence of (PPN)Cl [54]. Treatment of $Pb(OAc)_2$ with the sodium salt of $[Fe(CO)_2(NO)\{P(OPh)_3\}]^-$ affords $Pb[Fe(CO)_2(NO)\{P(OPh)_3\}]_4$ which does not dissociate in donor solvents [55].

BINUCLEAR SPECIES (EXCLUDING (η^5-C_5H_5) COMPOUNDS)

In earlier years compounds covered in this section were classified as Cluster Compounds. Since the currently accepted definition of clusters is more restrictive (i.e. compounds involving three or more metals and three or more metal-metal bonds), binuclear complexes are now covered in a separate section. Coverage is in order of the periodic group to which atoms bridging the metal-metal bond belong. Homonuclear complexes precede heteronuclear ones.

When 50 is allowed to react with $Fe_2(CO)_9$, 51 is the product. Its X-ray structure was determined. 51 inserts CS_2 giving 52 [56].



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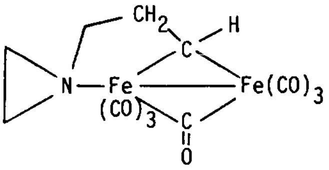

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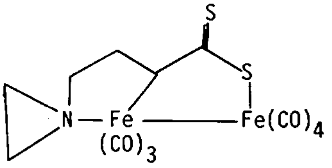
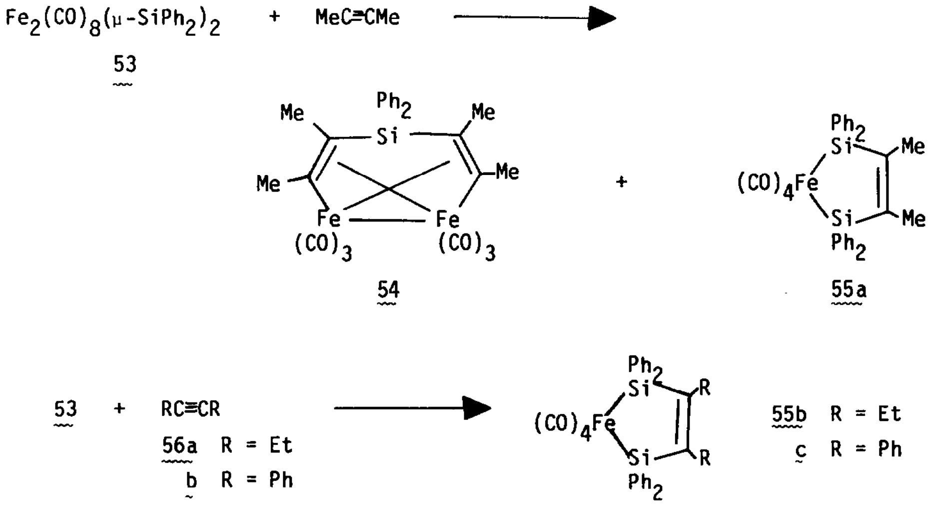


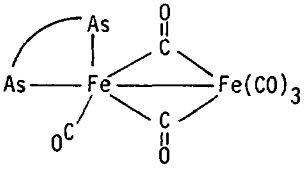
52

Scheme 9 diagrams reactions of the Si-bridged species 53 with alkynes [57]. The X-ray structure of 55b was reported.

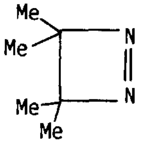
SCHEME 9



The reaction of $Fe_2(CO)_9$ with diars under CO was found to give two products: (diars)$Fe_2(CO)_8$ and 57 (whose X-ray structure was determined) [58]. 57 exhibits fluxional behavior in solution.

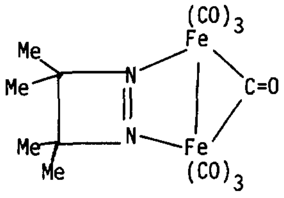


57

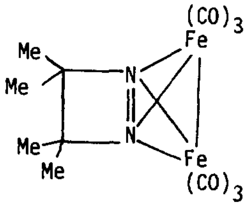


58

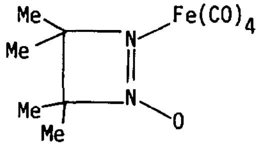
58 was found [59] to react with $Fe_2(CO)_9$ producing 59 and 60. The mono *N*-oxide of 58, on the other hand, gives 59, 60 and 61 in ratios dependent on solvent.



59



60

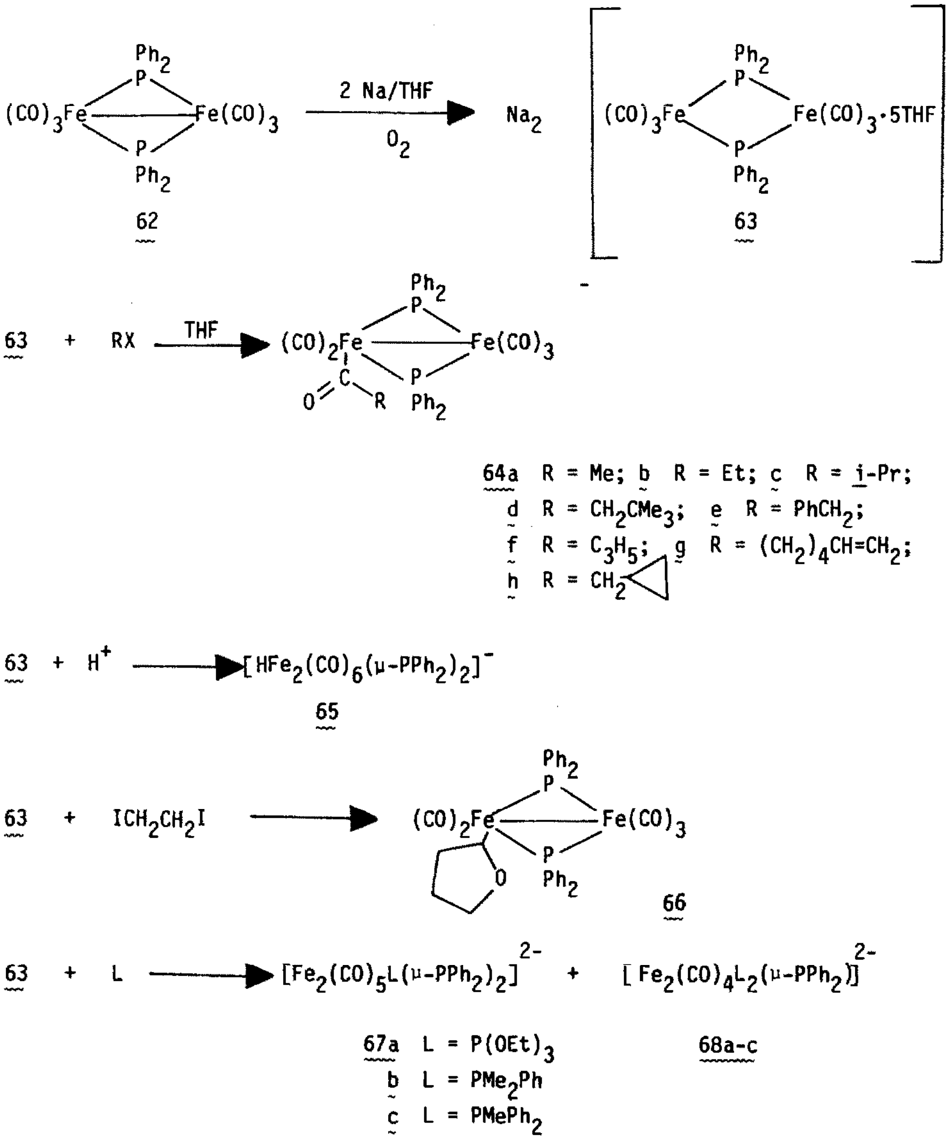


61

p-$RC_6H_4CH{=}NN{=}CHC_6H_4$*p*-R $Fe_2(CO)_6$ (R = H, Me, OMe) were prepared from the reaction of the organic ligand with $Fe_3(CO)_{12}$ in isooctane [60]. DTA curves for the related complexes $(PhCH{=}N)_2Fe_2(CO)_6$, $(C_6H_5C(Me){=}N)_2Fe_2(CO)_6$, (*p*-$BrC_6H_4C(Me){=}N)_2Fe_2(CO)_6$, $(Ph_2C{=}N)_2Fe_2(CO)_6$ and (*o*-$C_6H_4CH_2N{-}N{=}CHPh)Fe_2(CO)_6$ were published [61].

Chemistry of $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$, 62, is summarized in Scheme 10. The dianion 63 contains no Fe-Fe bond. Treatment of the dianion with alkyl halides results in metal-assisted alkyl migration to CO yielding 64 having an Fe-Fe bond. 65, the result of protonation, contains a terminal hydride ligand. X-ray structures of the Na$^+$ and PPN$^+$ salts of 64 show that Na$^+$ coordinates to the acyl O, but PPN$^+$ does not [62].

SCHEME 10



62

63

64a R = Me; b R = Et; c R = i-Pr;
d R = CH_2CMe_3; e R = $PhCH_2$;
f R = C_3H_5; g R = $(CH_2)_4CH{=}CH_2$;
h R = CH_2-cyclopropyl

63 + H^+ $\longrightarrow$ $[HFe_2(CO)_6(\mu\text{-}PPh_2)_2]^-$

65

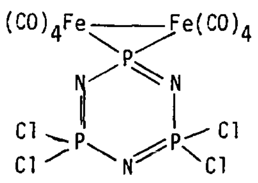
66

63 + L $\longrightarrow$ $[Fe_2(CO)_5L(\mu\text{-}PPh_2)_2]^{2-}$ + $[Fe_2(CO)_4L_2(\mu\text{-}PPh_2)_2]^{2-}$

67a L = $P(OEt)_3$
b L = PMe_2Ph
c L = $PMePh_2$

68a-c

When phosphonitrilic chloride is allowed to react with $Na_2[Fe_2(CO)_8]$ in THF, 69 and 70 are the products [63]. The X-ray structure of 70 was determined.



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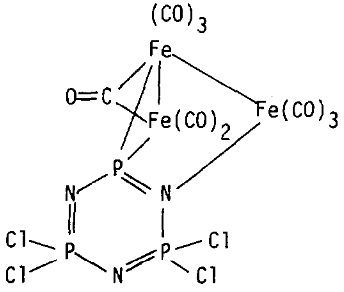
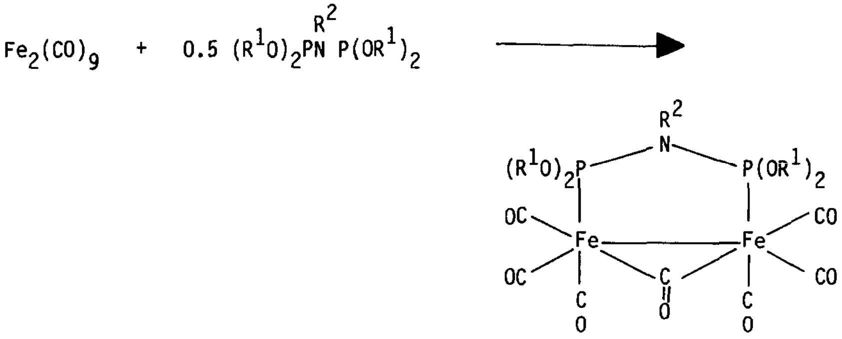


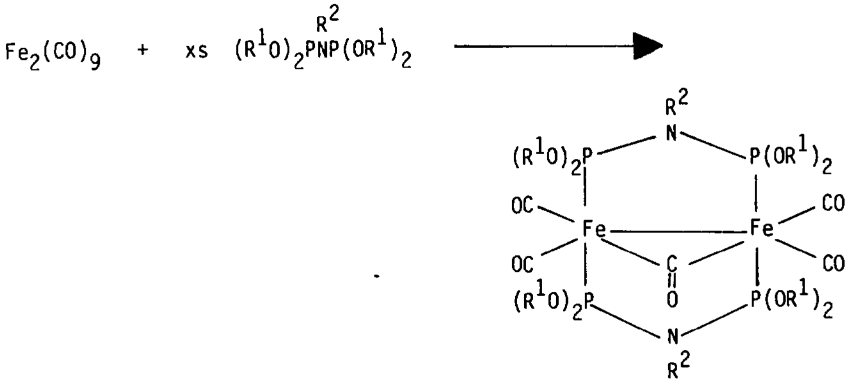
70

Some phosphazene complexes are prepared as shown in Scheme 11. 75a,b,c result from a Michelis-Arbuzov rearrangement. The X-ray structure of 73b was determined [64]. 71e and 72d were synthesized by other workers who also determined the X-ray structure of 72d [65].

SCHEME 11

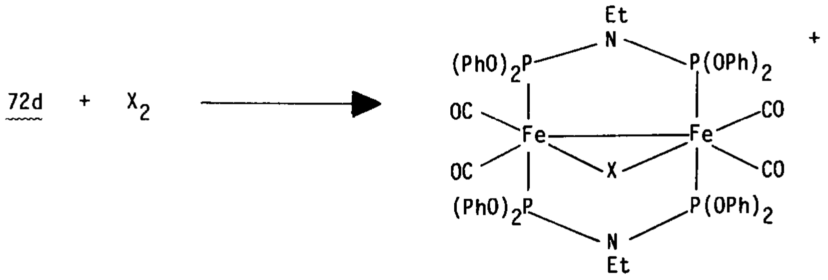


71a R^1 = Me, R^2 = Et
b R^2 = Et, R^2 = Me
c R^1 = *i*-Pr, R^2 = Me
d R^1 = Ph, R^2 = Et
e R^1 = R^2 = Me

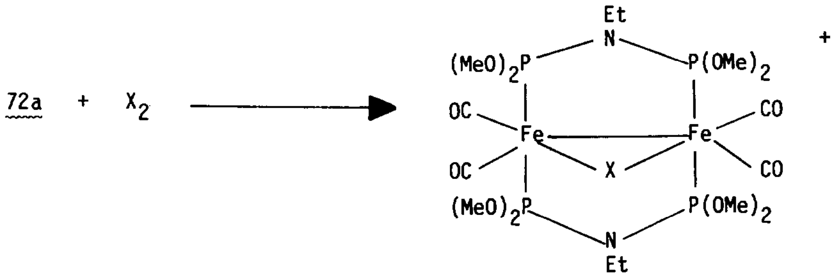


72a R^1 = Me, R^2 = Et
b R^1 = Et, R^2 = Me
c R^1 = i-Pr, R^2 = Me
d R^4 = Ph, R^2 = Et

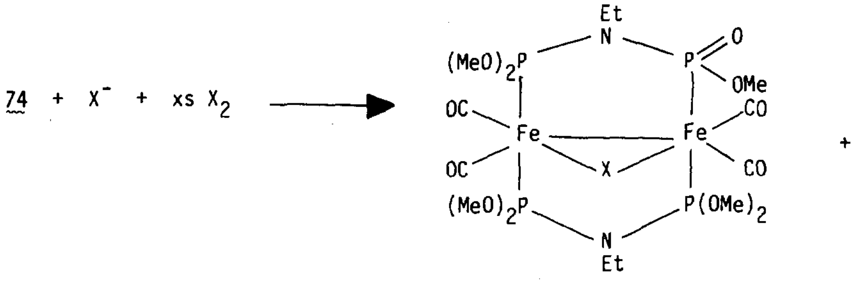
$Fe(CO)_5 + MeN[P(OMe)_2]_2 \longrightarrow$ 72d R^1 = R^2 = Me



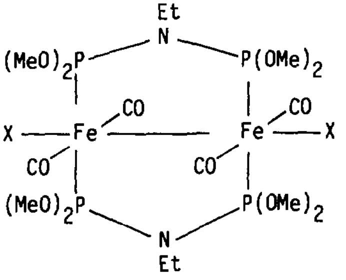
73a X = Cl; b X = Br; c X = I



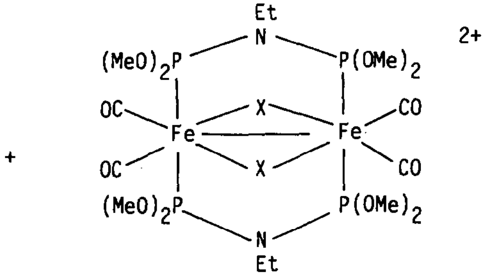
74a X = Cl; b X = Br; c X = I



75a X = Cl; b X = Br; c X = I



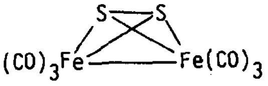
76a X = Cl; b x = Br; c X = I



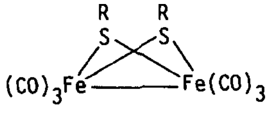
77a X = Cl; b X = Br; c X = I

$Fe_2(PMe_3)_2Cl_2(\mu\text{-P}\underline{t}\text{-Bu})_2$ was prepared from the reaction between $FeCl_2(PMe_3)_2$ and two equivalents of $Li[P(\underline{t}\text{-Bu})_2]$. Its X-ray structure shows that the coordination geometry around each Fe is roughly tetrahedral [66].

The ^{13}C NMR spectra of 78 and 79a,b, which contain bridging S, were reported [67].



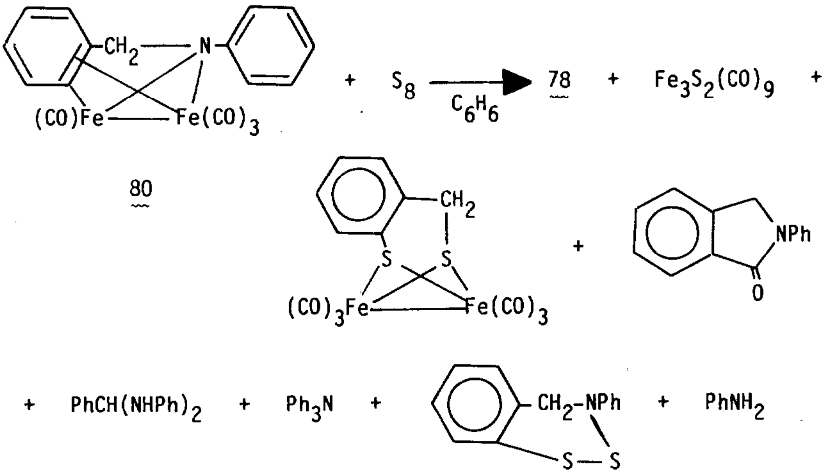
78



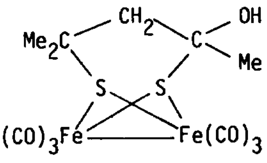
79a R = Me
b R = Ph
c R = H

78, along with $Fe_3S_2(CO)_9$, results from treatment of $H_2Fe(CO)_4$ with $\overline{S_2CH_2C}HMe$ [68]. These products also are produced from the reaction of 80 with S_8 as shown in Scheme 12 [69].

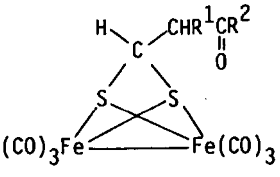
SCHEME 12



79c, which was previously known to react with α,β-unsaturated compounds, was found to react with α,β-unsaturated ketones which are disubstituted at the terminal carbon to add SH across C=C and C=O. For example, the reaction with Me_2C=CHC(O)Me in THF in the presence of piperidine yields 81. EtMeC=CHC(O)Me and $(CH_2)_5C$=C(O)Me react similarly. The alcohol products were converted to $-OSiMe_3$ derivatives for easier purification. Esters did not react. Acetylenic carbonyl compounds with ester or acyl substituents gave 82a,b,c with 79c.

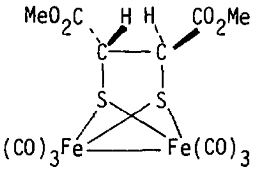


81

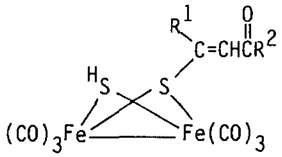


82a R^1 = H, R^2 = Me
b R^1 = H, R^2 = OMe
c R^1 = R^2 = Me

Dimethylacetylene dicarboxylate reacts with 79c affording 83 with an ethylene bridge. The reactions with acetylenic species presumably occur via vinyl intermediates such as 84 which then undergo further addition at either the α- or β-carbon producing products of type 82 or 83, respectively [70].

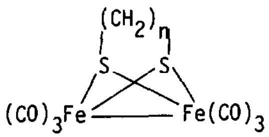


83

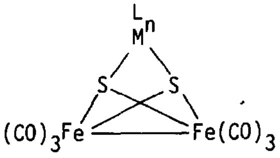


84a $R^1 = H$, $R^2 = Me$
b $R^1 = H$, $R^2 = OMe$
c $R^1 = R^2 = Me$
d $R^1 = CO_2Me$, $R^2 = Me$

A full paper has been published on the preparation of $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ by reduction of 78. The dianion can be alkylated at S with alkyl halides. Reactions with CH_2I_2 and $BrCH_2CH_2Br$ give 85a and 85b, respectively. The anion affords 86a-m on reaction with main group and transition metal halides.

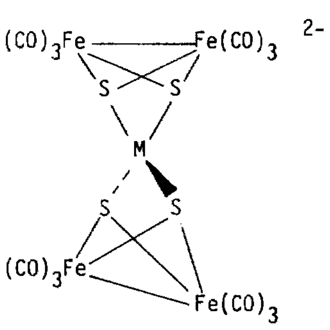


85a n = 1
b n = 2

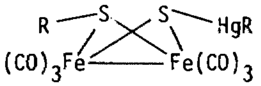


86a $ML_n = SiMe_2$
b $ML_n = SiEt_2$
c $ML_n = SiPr_2$
d $ML_n = SiMePh$
e $ML_n = GeMe_2$
f $ML_n = GePh_2$
g $ML_n = SnMe_2$
h $ML_n = SnEt_2$
i $ML_n = Sn(\underline{t}\text{-}Bu)_2$
j ML_n = Ni(diphos)
k $ML_n = Pd(PPh_3)_2$
l $ML_n = Pt(PPh_3)_2$
m ML_n = CoCp

Dianions 87a-c were also synthesized [71]. 88a,b were also prepared from $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$. Their X-ray structures [72] reveal that neither Fe_2SC nor Fe_2SHg are coplanar, the S-C and S-Hg bonds both being bent in the same direction with respect to the Fe-$(\mu\text{-}S)_2$-Fe skeleton.



87a M = Ni
b M = Pd
c M = Pt



88a R = Me
b R = Et

Despite statements to the contrary in the literature, 79a was found to react with NO yielding the nitrosyl analogue $Fe_2(\mu\text{-SMe})_2(NO)_4$. Only one of the possible isomers is isolated [73]. The nitrosyl anlogues of $[Fe_2(\mu\text{-S})_2(CO)_6]^{2-}$, 90a-c, can be prepared as depicted in Scheme 13. The dianions can be alkylated at E.

SCHEME 13

$$Fe_2(\mu\text{-I})_2(NO)_4 \quad + \quad 2Li_2E \longrightarrow [Fe_2(\mu\text{-E})(NO)_4]^{2-}$$

89

90a E = S
b E = Se
c E = Te

$$\text{90a,b,c} \quad + \quad RX \longrightarrow Fe_2(\mu\text{-ER})_2(NO)_4$$

91a ER = SCH_2Ph
b ER = SCH_2CH_2Br
c ER = SPh
d ER = SePh
e ER = $SeCH_2Ph$
f ER = TePh
g ER = $TeCH_2Ph$

$$Ph_2E_2 \quad + \quad 2Li[HBEt_3] \longrightarrow 2PhELi \quad + \quad H_2 \quad + \quad 2BEt_3$$

79 + 2PhELi

91c E = S
91d E = Se
91e E = Te

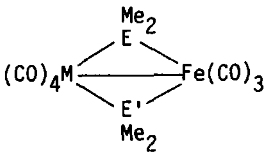
$$89 + Li_2Se \longrightarrow [Fe_2(\mu\text{-}I)(\mu\text{-}Se)(NO)_4]^- \xrightarrow{PhCH_2S^-}$$

$$[Fe_2(\mu\text{-}SCH_2Ph)(\mu\text{-}Se)(NO)_4]^- \xrightarrow{PhCH_2Cl}$$

$$Fe_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SeCH_2Ph)(NO)_4$$

Interestingly (and in contrast to the behavior of the carbonyl dianion), reaction of 90a with $BrCH_2CH_2Br$ leads to 91b instead of the analogue of 85b. Phenyl esters can be conveniently prepared from 89 and PhELi (E = S, Se, Te). 91a-g are mixtures of syn and anti isomers. Mixed derivatives such as 92 are also accessible by stepwise replacement of I in 89. 90a is more stable to O_2 than the carbonyl anion [74].

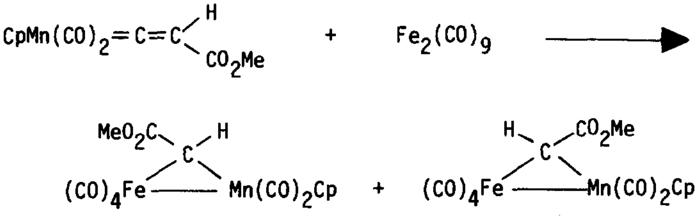
Several heterometallic compounds containing two metals have been prepared. When $K_2[Fe(CO)_4]$ or $Fe(CO)_4I_2$ are allowed to react with $M(CO)_4(EMe_2X)_2$ (M = Cr, Mo, W; E = P, As; X = halide) 92a-g are the main products [75].



	M	E	E'
92a	Cr	P	P
b	Mo	P	P
c	W	P	P
d	Cr	P	As
e	Cr	As	As
f	Mo	As	As
g	W	As	As

Scheme 14 shows the preparative routes to some methylene- and vinylidene-bridged complexes. The X-ray structure of 93a was determined [76].

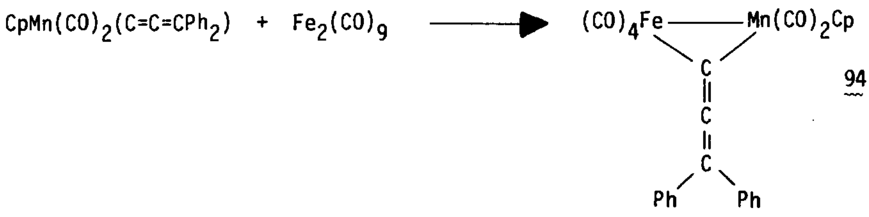
SCHEME 14



93a : 93b

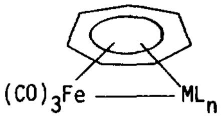
9 : 1

$$CpMn(CO)_2(\eta^2\text{-}HC{\equiv}CCO_2Me) + Fe_2(CO)_9 \longrightarrow \underset{\sim\sim}{93a,b}$$



94

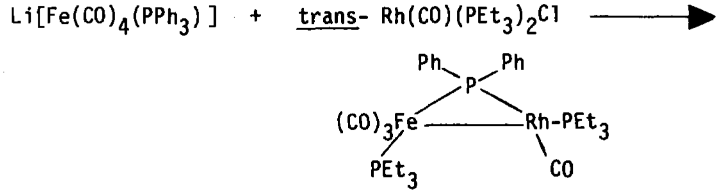
95a-h were prepared from Li[(η^3-C_7H_7)Fe$(CO)_3$] and their temperature-dependent NMR spectra investigated [77],



95a ML_n = Rh(cod)
b ML_n = Rh(C_7H_8)
c ML_n = Rh(C_6H_8)
d ML_n = Ir(cod)
e ML_n = Rh[P(OMe)$_3$]$_2$
f ML_n = Rh[P(OPh)$_3$]$_2$
g ML_n = Pd(η^3-C_3H_5)
h ML_n = Pd(η^3-CH_2C-(Me)CH_2)

Coordinatively unsaturated heterobimetallic complexes containing Ir and Rh have been synthesized. As Scheme 15 shows 97 reversibly adds H_2 and CO [78]. The X-ray structure of 97 was reported.

SCHEME 15



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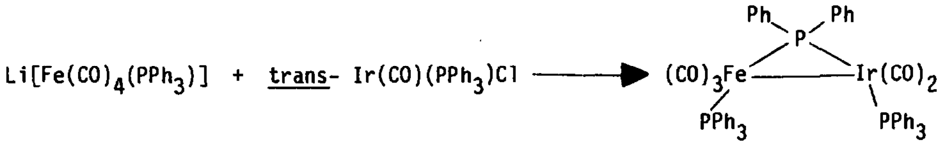
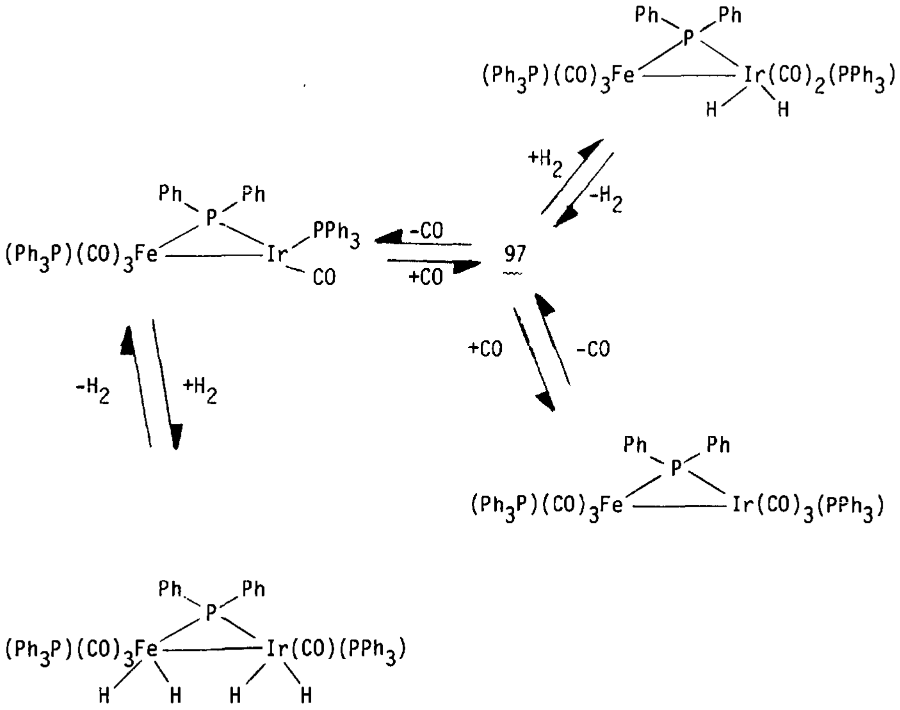
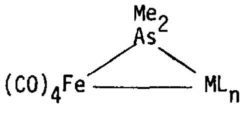


97



Thermal stabilities were found to lie in the order 98c > 98a > 98b. 98a and 98b react with CO at 45°C and 110°, respectively, affording the products of metal-metal bond cleavage, $Fe(CO)_4As(Me)_2Mn(CO)_5$ and $Fe(CO)_4As(Me)_2Co(CO)_4$ [79].



98a $ML_n = Mn(CO)_4$
b $ML_n = Co(CO)_3$
c $ML_n = Mo(CO)_3Cp$

CLUSTER COMPOUNDS

Treated here are compounds which contain more than two metals. Fe_3 complexes are discussed first, followed by complexes of higher nuclearity containing only Fe. Finally, heterometallic complexes of nuclearity three and higher are treated. The only requirement for inclusion in this section is the incorporation of three or more metals in the complexes. Many species have less than the maximum possible number of metal-metal bonds.

Trinuclear Species (All Same Metal)

A study of the electrochemistry of $Fe_3(CO)_{12}$ showed that mono-and dianions are produced in CH_2Cl_2 while only decomposition occurs in THF. Electrochemical behavior does not change in the presence of water [1].

Substitution on $Fe_3(CO)_{12}$ by L yielding $Fe_3(CO)_{11}L$ (L = CN*t*-Bu, PPh_3, P(*o*-tolyl)$_3$) is catalyzed in THF by benzophenone ketyl [80].

The ^{13}C NMR spectra of some L = phosphine and phosphite complexes $Fe_3(CO)_{11}L$ were measured [69].

The observed disorder in solid state structures of the type $M_3(CO)_{12-n}L_n$ (M=Fe, Ru, Os; L = CO, phosphine, isocyanide) was accounted for by a model in which peripheral atoms of L(O, P and N) occupy the same sites while the M_3 triangle has two different orientations related by a 60° rotation about an axis perpendicular to the M_3 plane [81].

The kinetics of reaction of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Ru(CO)_5$ with OMe^- and OH^- were investigated [82]. OH^- was more reactive by far than OMe^- with all these. With OMe^-, $Fe_3(CO)_{12}$ undergoes cluster fragmentation to $[Fe(CO)_4(CO_2Me)]^-$.

The anion $[HFe_3(CO)_{11}]^-$ can be conveniently prepared from $Fe_3(CO)_{12}$ and KF or ($\underline{n}$-Bu_4)NF in THF in the presence of 18-crown-6 [83]. A CNDO calculation of the electronic structure of this anion was reported [84].

When $[HFe_3(CO)_{11}]^-$ is allowed to react with acetylenes, the products are **99a-c** and **100a-c**.

$[Fe_3(CO)_{10}\,C(R^1)=CHR]^{2-}$

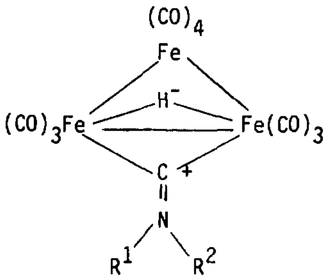
99a $R^1 = R^2 = Me$
b $R^1 = R^2 = Ph$
c $R^1 = Me$, $R^2 = Ph$

$Fe_2(CO)_7(CR^1=CHR^2)$

100a $R^1 = R^2 = Me$
b $R^1 = R^2 = Ph$
c $R^1 = Me$, $R^2 = Ph$

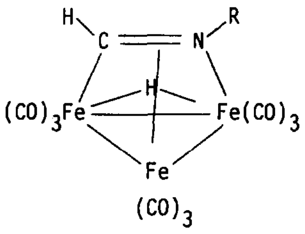
With HC≡CH the product at room temperature is $[Fe_3(CO)_{10}C\,Me]^-$. In refluxing acetone $[HFe_3(CO)_9C=CH_2]^-$ is formed; this can be converted to $[Fe_3(CO)_{10}CMe]^-$ on treatment with CO [85].

Treatment of $[HFe(CO)_{11}]^-$ (as the PPN^+ salt) in THF with four equivalents of isocyanide followed by alkylation with an oxonium salt produces **101**.

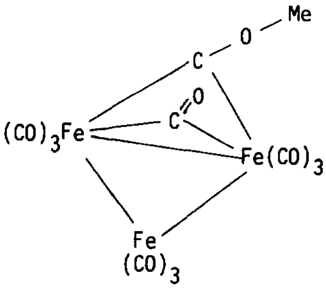


101a $R^1 = R^2 = Et$
b $R^1 = Me, R^2 = Et$
c $R^1 =$ *i*-Pr, $R^2 = Et$
d $R^1 =$ *i*-Pr, $R^2 = Me$

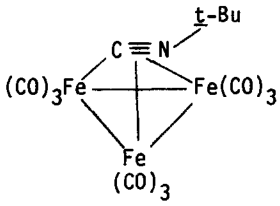
The NMR spectra of **101a-d** indicate the existence of restricted rotation around the C=N bond. Prolonged reaction gives products such as $HFe_3(CO)_9(CNEt_2)$-(CNEt) in which one of the carbonyls of **101** has been replaced by an isocyanide. Protonation of [PPN][$HFe_3(CO)_{10}$(CN*i*-Pr)] was found to give **102a** [86]. Thermolysis of $Fe_3(CO)_{11}$(CN*t*-Bu) produces **103** which is reduced by K[HB*s*-Bu_3] and protonated at the Fe-Fe bond to give **102b** [87].



102a R = *i*-Pr
b R = *t*-Bu

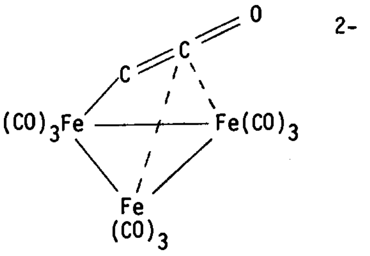


104



103

$[PPN]_2[Fe_3(CO)_{11}]$ was found to give 104 on O-methylation. When 104 is reduced by sodium benzophenone ketyl a ketenyledine cluster, 105, can be identified by ^{13}C NMR. 105 behaves like a carbide cluster on protonation affording 106 whose X-ray structure was determined [88].



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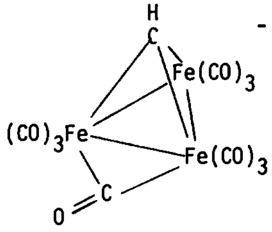
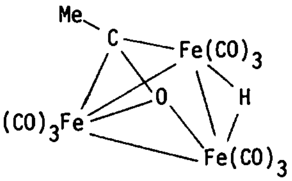
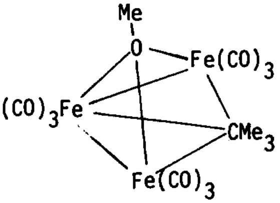


106

The X-ray structures of 107 and 108 indicate the different pathways for reaction of $[Fe_3(CO)_9(\mu_3\text{-}CH_3CO)]^-$ with the electrophiles HBF_4 and $MeOSO_2F$, respectively [89].

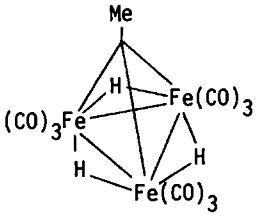


107



108

The C_{3v} symmetry of 109 was revealed by determination of its X-ray structure [90]. The PES and UV-vis spectra of 109 were reported and analyzed with the aid of MO calculations [91]. 110, whose X-ray structure was determined, is one of the



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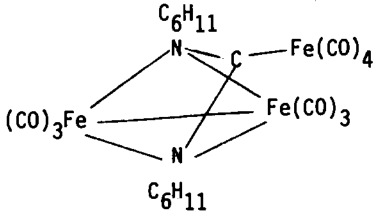
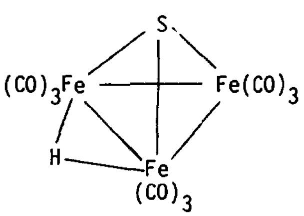


110

products of the reaction between $Fe_3(CO)_{12}$ and $C_6H_{11}N{=}C{=}NC_6H_{11}$. The others are $Fe(CO)_4(CNC_6H_{11})$ and $[Fe_2(CO)_6\{\mu, \mu'-(C_6H_{11}N)_2CHC_6H_{11}\}]$. These latter products also result from the reactions between the carbodiimide and $Fe_2(CO)_9$ or $Fe(CO)_5$ [92].

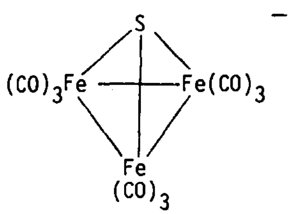
When Ph_2PH is refluxed in toluene with $Fe_3(CO)_{12}$, $Fe_3(CO)_9(\mu_3\text{-}PPh)_2$ results; its X-ray structure was determined [93]. The X-ray structure of **70**, one of the products of the reaction of $Na_2[Fe_2(CO)_8]$ with $(PNCl)_3$ was published [63]. An effort to prepare $(\mu\text{-}RPS)Fe_2(CO)_6$ from the reaction between $RP(S)Cl_2$ and $Fe_3(CO)_{12}$ lead instead to $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}PR)$(R = p-$MeC_6H_4$, t-Bu, Ph) [94].

The X-ray structures of **111a** $Fe_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}S$t-Bu) and its deprotonation product, **111c**, were reported. When **111a** or **111b** is allowed to react with PPh_3, $AsPh_3$ or $SbPh_3$, one, two or three carbonyls may be substituted each on a different Fe atom [95].



111a R = t-Bu

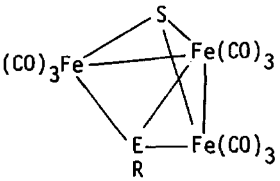
b R = C_6H_{11}



111c R = t-Bu

d R = C_6H_{11}

The anion $[Fe_3(CO)_9(\mu_3\text{-}S$t-Bu$)]^-$, **111c**, eliminates t-BuCl and Cl^- on treatment with XCl_2(X=PR,AsR, S,O). **112a-j** can be isolated. The X-ray structures of **112c** and **112j** have been determined. With SO_2Cl_2, the anion produces **112k** and **112l** [96].

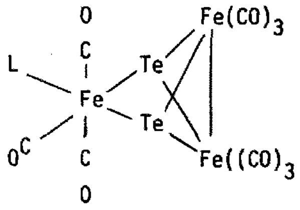


112a ER = Pt-Bu
b ER = Pp-$MeOC_6H_4$
c ER = PPh
d ER = Et_2N
e ER = PMe
f ER = Pc-C_6H_{11}
g ER = p-BrC_6H_4
h ER = Asc-C_6H_{11}
i ER = Ast-Bu
j ER = AsPh
k ER = SO
l ER = Cl

M. O. Calculations on some trimetallic clusters including $Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ were published [97].

$Fe_3(CO)_9(\mu_3\text{-}Te)_2$ was reported to react with Lewis bases L affording products of type **113**. The X-ray structure of **113a** was determined. $Ph_2PCH_2CH_2PPh_2$

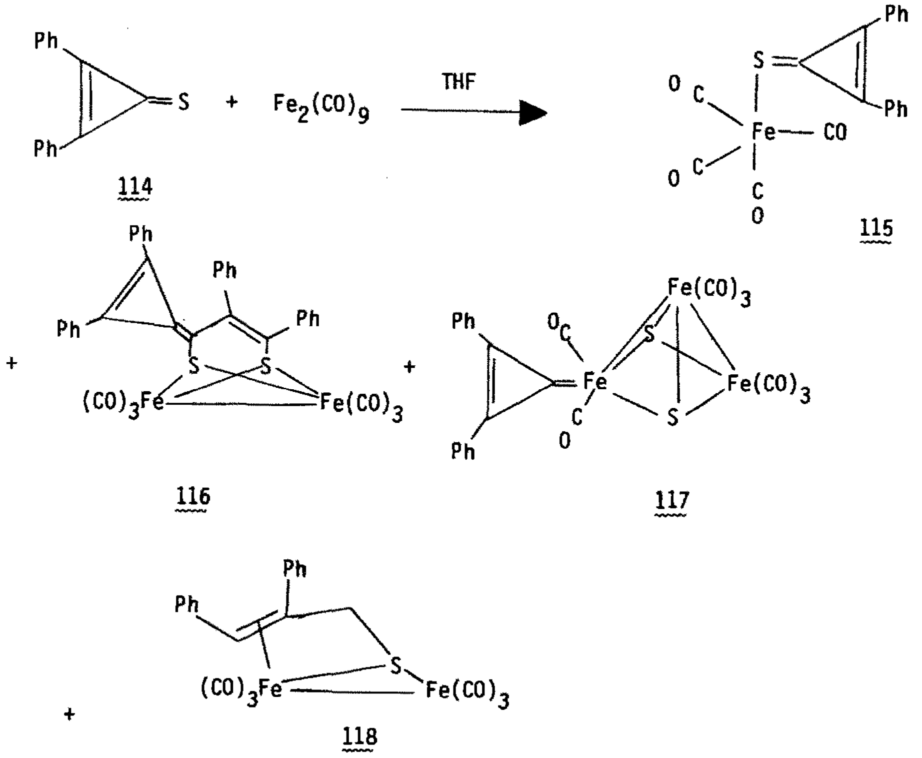
(dppe) gave $[Fe_3(CO)_9(\mu_3\text{-}Te)_2]_2(dppe)$ [98].



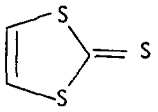
113a $L = PPh_3$
b $L = \underline{t}\text{-BuNC}$
c $L = CO$

Scheme 16 displays the chemistry involved in the reaction between the thione 114 and $Fe_2(CO)_9$. X-ray structures were determined for 116 and 117 [99].

SCHEME 16



A carbene complex 120 which is related structurally to 117 has been synthesized by reaction of 119 with $Fe_2(CO)_9$ [100]. Electrocatalyzed substitution of CO in 120 by $P(OMe)_3$ proceeds stepwise leading to mono-, di- and trisubstituted products [101].



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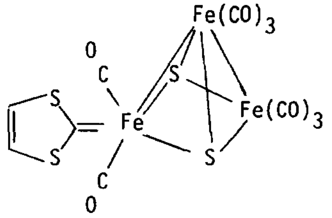
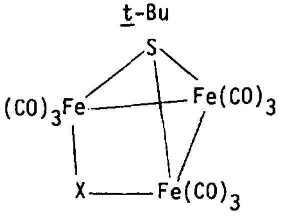


120

[$\underline{t}$-BuNH$_3$][Fe$_3$(CO)$_9$(μ_3-S$\underline{t}$-Bu)], 111a, is attacked by halogens or electrophilic halogenating agents such as $C_6H_{11}NCl_2$, $\underline{i}$-PrNCl$_2$, SOCl$_2$, Cl$_3$CSCl, $\underline{N}$-chlorosuccinimide, POBr$_3$, $\underline{N}$-bromosuccinimide or $\underline{N}$-iodosuccinimide give neutral halogen-bridged species 121 a-c. The X-ray structure of 121a was determined. For 121a, the reaction can be reversed with O$\underline{t}$-Bu$^-$ re-forming the Fe-Fe bond and giving 111a; for 121c, H$^-$ reverses the reaction [102].



121a X = Cl
b X = Br
c X = I

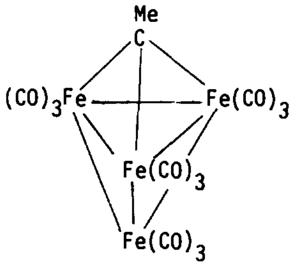
The synthesis of M[Fe$_3$(NO)$_5$S$_2$](M = K,NH$_4$) was reported [103].

Polynuclear Clusters

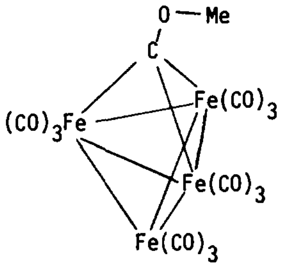
Preparative procedures for [PPN]$_2$[Fe$_4$(CO)$_{13}$] have been published [104].

[Fe$_4$(CO)$_{12}$C]$^{2-}$, which has a butterfly arrangement of Fe(CO)$_3$ groups is a 62-electron cluster. When the anion is allowed to react with MeOSO$_2$CF$_3$, the product is 122 whose X-ray crystal structure was determined as the PPN salt. The reaction involves rearrangement to a μ_3-tetrahedral structure which is the one appropriate for a 60-electron tetrahedral complex. [Fe$_4$(CO)$_{12}$(μ_3-CO)]$^{2-}$ also has a 60-electron tetrahedral structure. When this compound is methylated, the product is 123 with unchanged Fe$_4$C skeleton as shown by X-ray diffraction. 123 has the same electron count as [Fe$_4$(CO)$_{12}$(μ_3-CO)]$^{2-}$. This behavior contrasts with the protonation of [Fe$_4$(CO)$_{12}$(μ_3-CO)]$^{2-}$ which occurs first on an Fe-Fe bond and then on O producing [Fe$_4$(CO)$_{12}$C]$^{2-}$ [105].

ESCA and ^{57}Fe Mössbauer spectra of several clusters were measured; these included [Fe$_4$C(CO)$_{12}$]$^{2-}$, [Fe$_4$C(CO)$_{12}$H]$^-$, Fe$_4$CH(CO)$_{12}$H , [Fe$_4$(CO)$_{12}$(μ-CO)H]$^-$, [Fe$_5$C(CO)$_{14}$]$^{2-}$, Fe$_5$C(CO)$_{15}$ and [Fe$_6$C(CO)$_{16}$]$^{2-}$. The positions of the ESCA C$_{1s}$ peaks indicated a relatively deshielded carbide with increasing nucleophilicity as its coordination number is reduced from six to five to four [106].



122



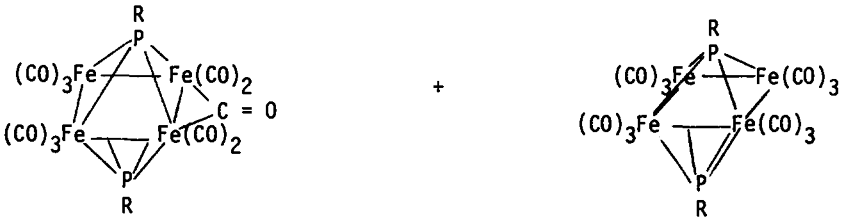
123

A series of clusters was prepared as shown in Scheme 17. **125a,b,c** and **126a,b,c** can be reversibly interconverted. Trimethyl phosphite adds to **125a,b** giving **127a,b**. **127a** can be reversibly converted to **128** or can undergo additional carbonyl substitution producing **129** [107,108].

SCHEME 17

$$Fe_2(CO)_6(\mu\text{-PHR})_2 + Fe_3(CO)_{12} \longrightarrow Fe_3(CO)_9(\mu_3\text{-PR})_2 \quad +$$

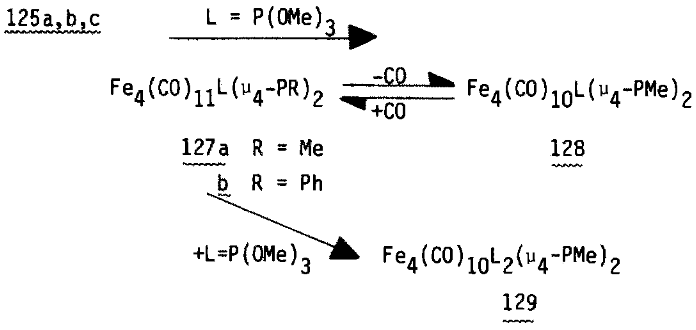
124a R = Me
b R = Ph
c R = *t*-Bu
d R = *p*-tolyl



125a R = Me
b R = Ph
c R = *t*-Bu
d R = *p*-tolyl

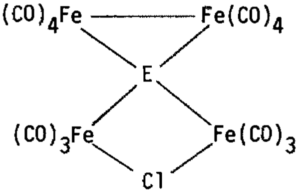
126a R = Me
b R = Ph
c R = *t*-Bu
d R = *p*-tolyl

$$\mathbf{125a,b,c} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} \mathbf{126a,b,c}$$

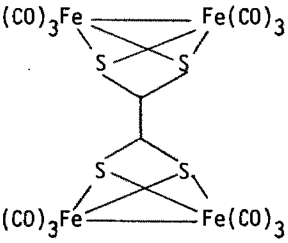


Other tetranuclear complexes, 130a and 130b are products of reactions between $Fe_2(CO)_9$ and PCl_3 or $AsCl_3$, respectively. X-ray structures of both compounds were determined [109].

In hexane at 80°, $Fe_3(CO)_{12}$ and CS_2 produce 131 in which two CS_2 molecules are coupled. 131 was characterized by X-ray diffraction [110].



130



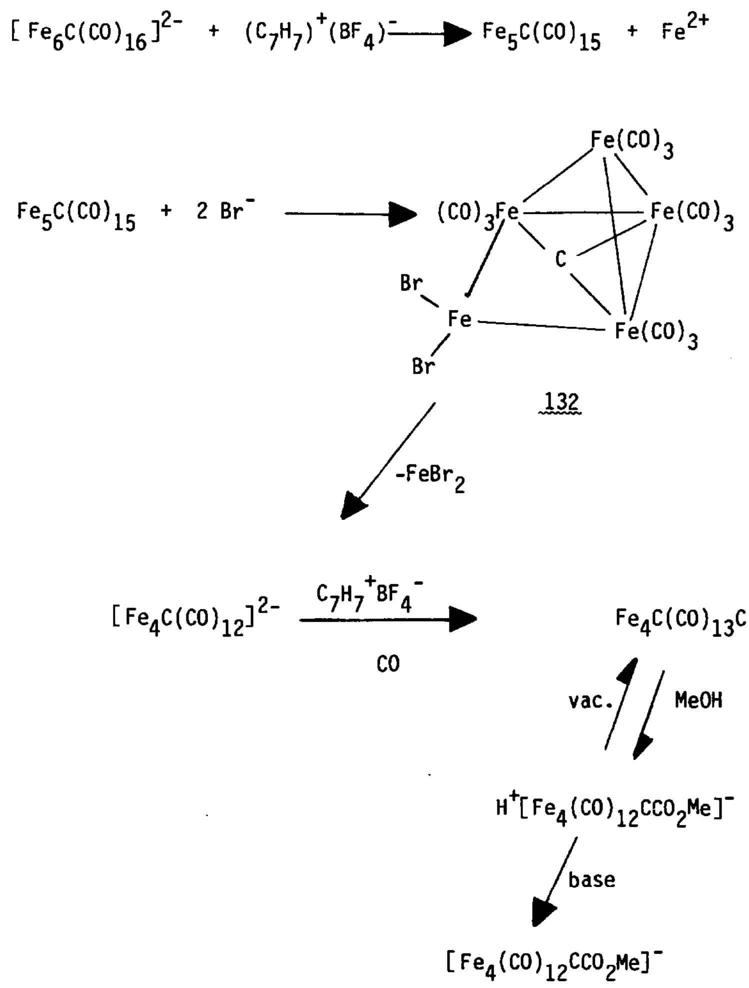
131

$Fe_4(CO)_{12}(\mu_3\text{-}X)_4$ (X = S, Se) were prepared by carbonylation of $Fe_4(NO)_4(\mu_3\text{-}X)_4$ under pressure. Both complexes were characterized by X-ray diffraction [111].

The IR spectra of $M_5C(CO)_{15}$ (M = Fe, Ru, Os) were measured and assigned [112]. When $[Fe_5C(CO)_{14}]^{2-}$ is alkylated using $MeOSO_2F$, methylation occurs at a terminal CO affording $[Fe_5C(CO)_{13}(COCH_3)]^-$ containing a COMe linkage and a μ_2CO. Protonation of the monoanion occurs on an Fe-Fe edge yielding $HFe_5C(CO)_{13}(COMe)$. The general observation that penta- and hexanuclear Fe carbide clusters are unreactive at the carbide C in contrast to the behavior of tetranuclear clusters was rationalized by the results of MO calculations. These calculations showed that a substantial interaction between Fe orbitals and carbide p orbitals leads to a large HOMO-LUMO energy gap in Fe_5 and Fe_6 clusters. The gap between these orbitals (which have significant C character) is smaller for Fe_4 clusters and is calculated to be smaller yet for the presently unknown Fe_3 carbide clusters [113].

The mechanism of the oxidative fragmentation of $[Fe_6C(CO)_{16}]^{2-}$ in presence of Br^- was elucidated and is shown in Scheme 18. The product $[Fe_4(CO)_{12}CCO_2Me]^-$ is the immediate precursor to $Fe_4C(CO)_{13}$. The X-ray structure of 132 showed significant distortion of the square pyramid from C_{4v} symmetry [114].

SCHEME 18

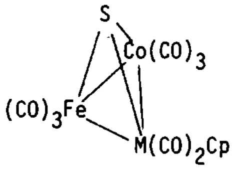


Heterometallic Clusters

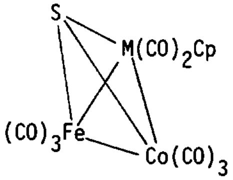
In this section, complexes are treated in order of increasing nuclearity and, for each particular number of metals, in order of the position of the earliest other metals besides Fe in the periodic table.

The trimetallic complex $(Me_3P)_2(CO)_3MnS(\mu\text{-}AsMe_2)Co(CO)_3(\mu\text{-}AsMe_2)Fe(CO)_4$ was prepared [115].

The optical isomers 133a-c and 134a-c were prepared as racemic mixtures [116]. Carbonyl substitution by (-)-*R*-MePrPhP converted these to pairs of diasteriomers which could be separated by fractional crystallization. Each pair was then subjected to CO pressure in the presence of MeI as a phosphine scavenger to isolate the pure optical isomers which are thermally (but not photochemically) stable to racemization. Absolute configurations of the Mo and W compounds were determined by X-ray [117].

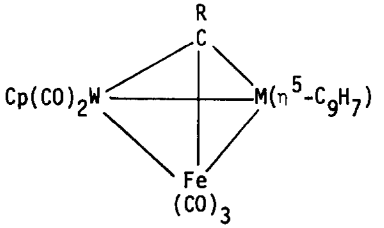


133a M = Cr
b M = Mo
c M = W



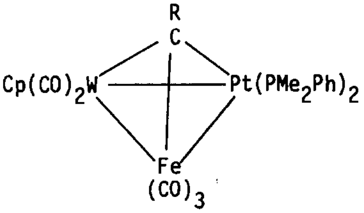
134a M = Cr
b M = Mo
c M = W

When $Fe_2(CO)_9$ reacts with MRh(μ-C*p*-tolyl)Cp(η^5-C_9H_7) (M = Co,Rh), 135a,b are products. The X-ray structure of 134b was reported [118].

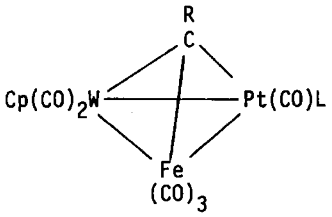


135 R = *p*-tolyl
a M = Co
b M = Rh

Related complexes result from the reaction between $Fe_2(CO)_9$ and WPt(μ-C-*p*-tolyl)(CO)$_2$LCp (L = PMe$_3$,PMe$_2$Ph,PMePh$_2$,PEt$_3$) in THF. The products are 136 (L = PMePh$_2$) and 137a-c (for other L). X-ray structures were determined for 136 and 137a [119].

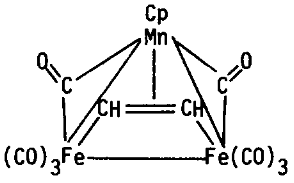


136 R = *p*-tolyl



137 R = *p*-tolyl
a L = PEt$_3$
b L = PMe$_2$Ph
c L = PMe$_3$

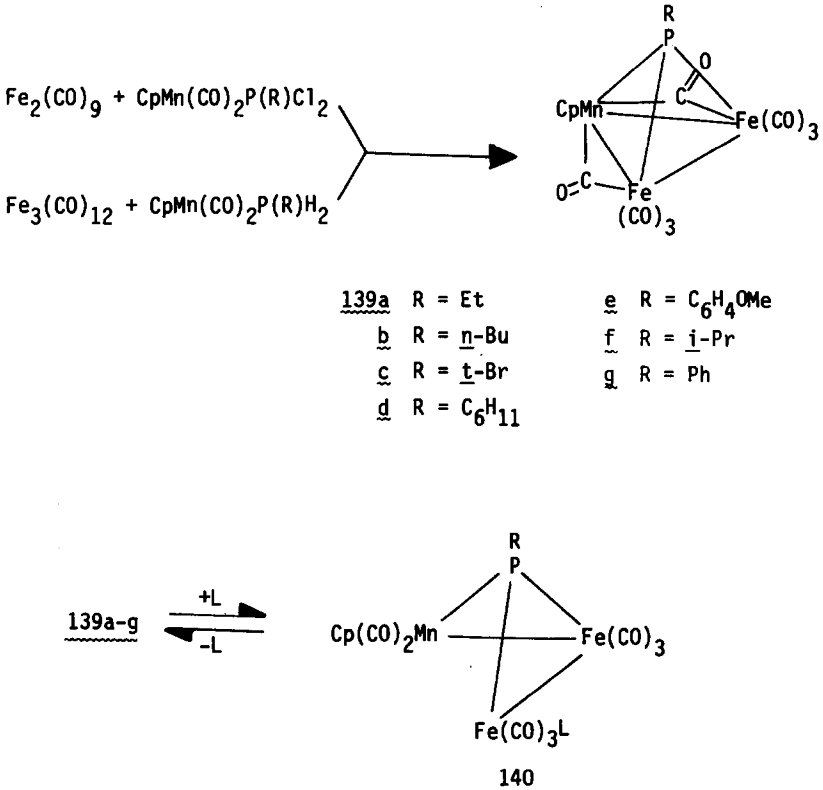
In addition to 93a,b, 138 is a product of the reaction between $Fe_2(CO)_9$ and $CpMn(CO)_2(\eta^2\text{-}HC{\equiv}CCO_2Me)$. The X-ray structure of 138 was determined [120].



138

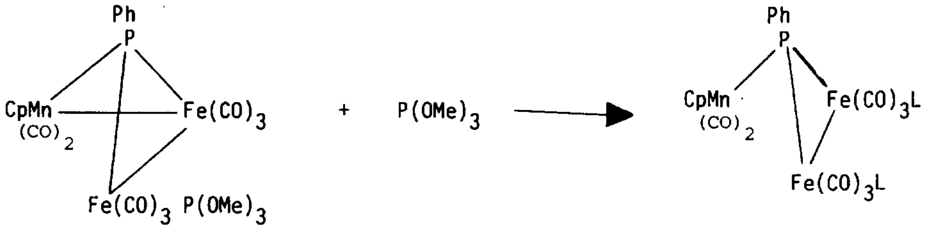
Some phosphido-bridged complexes 139a-g were synthesized as shown in Scheme 19. Reaction with L = CO, phosphines, arsines, stibines opens a Mn-Fe bond leading to complexes of type 140 [121]. When 139g is allowed to react with L = $P(OMe)_3$ a complex of type 140 is obtained which reacts further giving 141 in which both Mn-Fe bonds are broken. Mössbauer spectra of these clusters were measured [122].

SCHEME 19



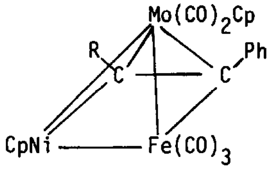
139a R = Et
b R = n-Bu
c R = t-Br
d R = C_6H_{11}
e R = C_6H_4OMe
f R = i-Pr
g R = Ph

140

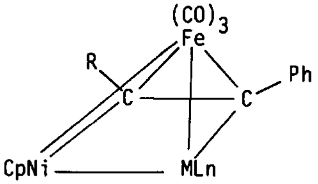


141

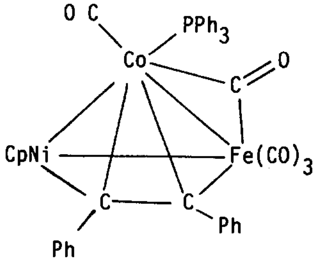
Addition of an $Fe(CO)_3$ fragment by reaction of an alkyne complex with $Fe_2(CO)_9$ resulted in production of 142, 143a,b [123] and 144 [124] all of which were characterized by determination of their X-ray structures.



142 R = CO_2CHMe_2



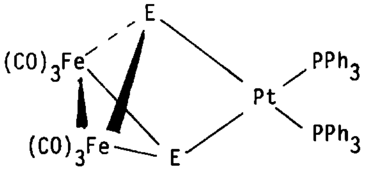
143 R = CO_2CHMe_2
a ML_n = NiCp
b ML_n = $Co(CO)_3$



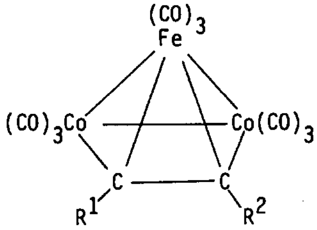
144

$[CpNiFe_2(CO)_6(C_2Ph_2)]^-$, isoelectronic with 144, was prepared and its X-ray structure determined as the $[CpNi(PMe_3)_2]^+$ salt [125].

Treatment of 78 or the S and Se analogues with $Pt(PPh_3)_2(C_2H_4)$ yields 145a-c. The X-ray structure of 145 revealed the Fe-Fe bond to be perpendicular to the PtP_2 plane [126].

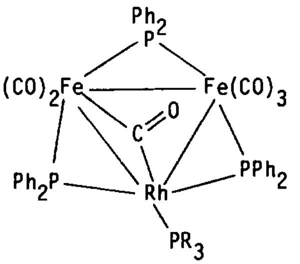


145a E = S
b E = Se
c E = Te



146a R_1 = Me, R_2 = Et
b R_1 = R_2 = Et

146a,b are also isoelectronic with 144 and exhibit fluxional behavior in solution. The X-ray structures of both compounds were reported [127]. $Li[Fe_2(\mu\text{-}PPh_2)_2(CO)_5PPh_2]$, on treatment with trans-$RhCl(CO)(PR_3)$ (R=Et,Ph), affords phosphido-bridged clusters 147a,b, respectively. The X-ray structure of 147b revealed the presence of μ-CO [128].



147a R = Et
b R = Ph

Scheme 20 displays some chemistry of V-containing clusters including the tetranuclear 149. The X-ray structure of 148 was reported [129].

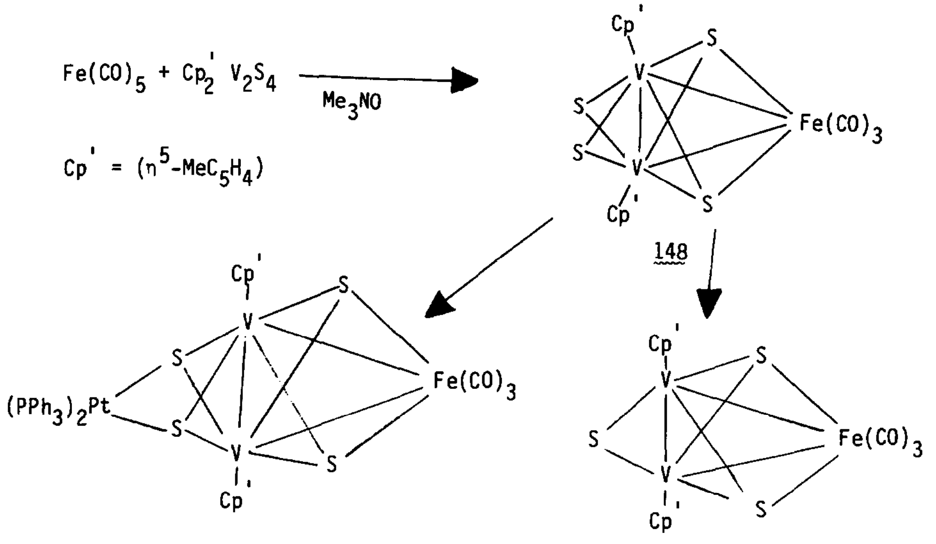
Reaction of 78 with $CpMo(CO)_2{\equiv}Mo(CO)_2Cp$ affords the tetrahedral cluster $Fe_2Mo_2Cp_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6$ (X-ray structure determined) along with $Cp_2Mo_2(CO)_6$ [130].

Synthetic procedures for the clusters $FeRu_3H_2(CO)_{13}$ and $PPN[FeRu_3H(CO)_{13}]$ were described [131]. The synthesis, crystal structure and ^{13}C NMR of $FeOs_3H_2(CO)_{13}$ also were published [132].

The tetrahedral clusters 151a,b were found to add two CO's reversibly producing 152a,b [133].

Treatment of several high nuclearity clusters with HSO_3CF_3 was found to produce significant amounts of methane. Among the clusters tested were $[PPN][FeCo_3(CO)_{12}]$, $[PPN][Fe_3Co(CO)_{13}]$, $[PPN]_2[Fe_4(CO)_{13}]$ and $FeOs_3H_2(CO)_{13}$ [134]. $HFeCo_3(CO)_{12}$ was among the compounds found [41] to protonate N in cis-$[W(N_2)_2(PMe_2Ph)_4]$ in MeOH. Subsequent treatment with base and distillation gave

SCHEME 20



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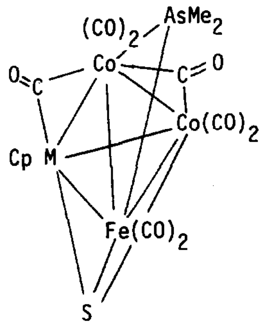
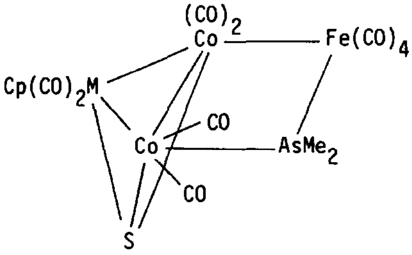
149

150



151a M = Mo
b M = W

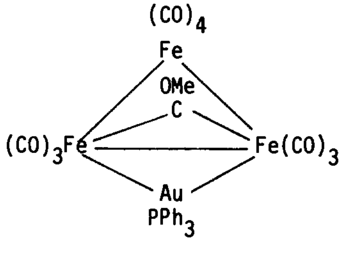


152a M = Mo
b M = W

ammonia and hydrazine. In contrast, protonation of trans-[W(N$_2$)$_2$(dppe)$_2$] in various alcohols ROH afforded trans-[W(OR)(NNH$_2$)(dppe)$_2$]$^+$[FeCo$_3$(CO)$_{12}$]$^-$ (R = Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, C$_6$H$_{11}$, n-C$_6$H$_{13}$, CH$_2$Ph). The X-ray structure of the methoxy compound was reported. Also isolated from the reaction with trans-[Mo(N$_2$)$_2$dppe] were [Mo(OMe)$_2$(dppe)$_2$]$^+$[FeCo$_3$(CO)$_{12}$]$^-$ and [Mo(OMe)(CO)(dppe)$_2$]$^+$-

$[FeCo_3(CO)_{12}]^-$ [42]. $HFeCo_3(CO)_{12}$ was found to react with the tripod ligand $CH(PPh_2)_3$ to substitute one CO on each Co on one triangular face affording $HFe_3Co_3(\mu_2\text{-}CO)_3(CO)_6[CH(PPh_2)_3]$ [135].

153 was produced from the reaction between $Fe_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}$ and Au-$MePPh_3$. Reaction with $Pt(C_2H_4)(PPh_3)_2$ gives 154 whose X-ray structure was determined [136].



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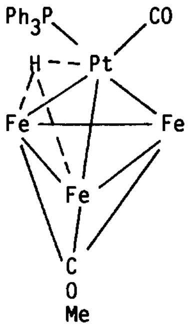
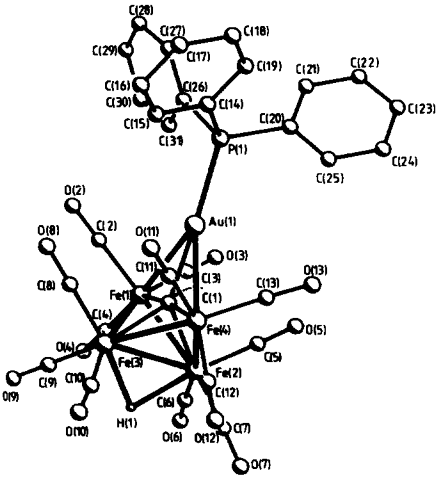
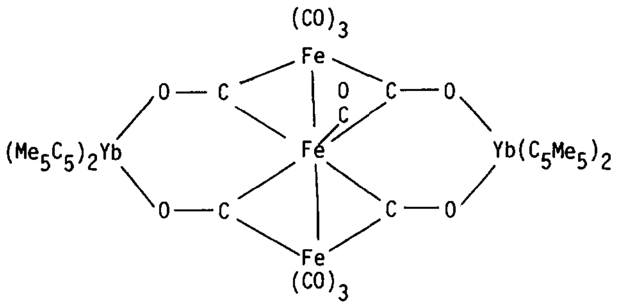


154

$[Fe_4(CO)_{13}]^{2-}$, on treatment with $AuCl(PR_3)$(R=Et,Ph) gives $Fe_4AuC(H)(CO)_{12}(PR_3)$(R=Et,Ph) after protonation. Deprotonation of the hydride and addition of a second mole of $AuCl(PR_3)$ produces $Fe_4Au_2C(CO)_{12}(PR_3)_2$(R=Et,Ph) via attack on the carbide C by $Au(PR_3)$. The structure of the R=Ph compound is shown as 155 [137].

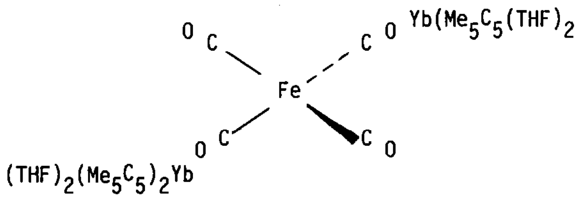
155





156

156 results from the reaction between $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ and $(\eta^5\text{-}Me_5C_5)\text{-}Yb(OEt)_2$ in toluene. Its X-ray structure was determined. Also prepared (starting with $Fe(CO)_5$) was 157 [138]. Sodium amalgam reduction of $[Zn(NH_3)_3][Fe(CO)_4]$



157

in THF gave $[Na(THF)]_2Zn[Fe(CO)_4]_2$ whose X-ray structured showed a coordination geometry around Fe intermediate between a distorted tetrahedron having an Fe-Zn bond at an axial site and a face/edge capping site [139].

Some hexanuclear Fe-Rh clusters are synthesized as shown in Scheme 21. The X-ray structure of 158 and the multinuclear NMR of 159 indicate that both are isostructural with $Rh_6(CO)_{16}$ [140].

When $[Fe_5C(CO)_{14}]^{2-}$ reacts with excess $AuCl(PMe_3)$ in the presence of $Tl(PF_6)$, the product is $Fe_5C(\mu_2\text{-}CO)_3(CO)_{11}(\mu_2\text{-}AuPEt_3)(\mu_4\text{-}AuPEt_3)$ which was characterized by determination of its X-ray crystal structure [141].

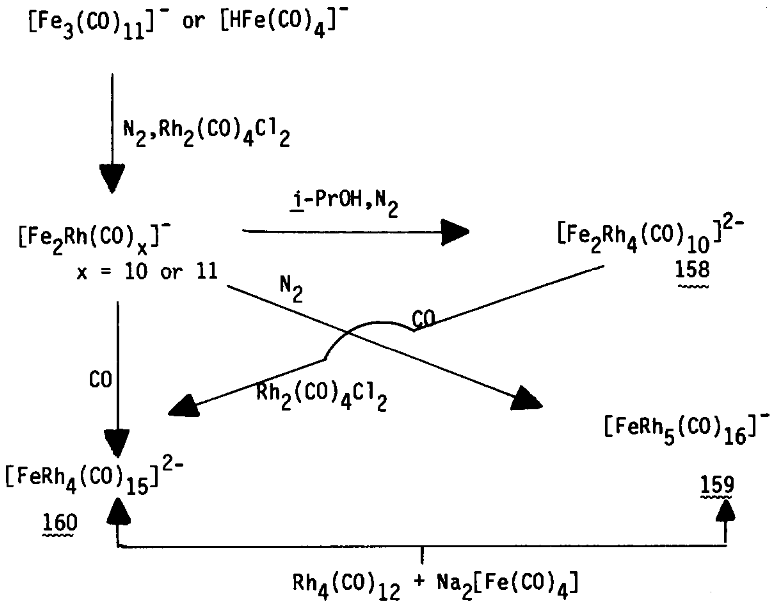
METAL-CARBON σ-BONDED SPECIES

Metal Alkyl Complexes

The gas phase reactions of Fe^+ with alkanes were found to involve insertion into C-C bonds leading to alkane elimination and C-H insertion leading to H_2 elimination [142].

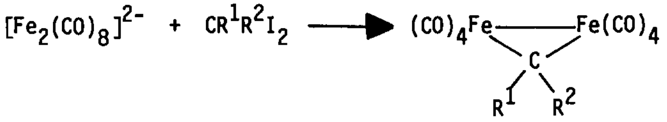
Interest in bimetallic $\mu\text{-}CH_2$ complexes stems from their proposed involvement in CO reduction processes, olefin metathesis, alkyne polymerization and

SCHEME 21



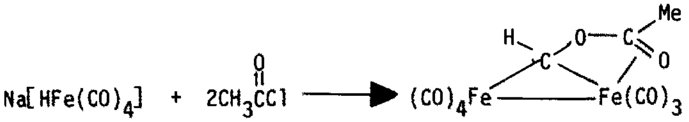
methylene transfer reactions. Scheme 22 depicts some chemistry of complexes containing μ-alkylidene groups. **161a-h** can be prepared from the NEt_4^+ salt, but not the Na^+ salt of the anion. μ-alkylidene complexes **161b-e** having β-H are unstable to CO loss and β-elimination in solution affording olefins and $Fe_3(CO)_{12}$. In contrast **161a, f, h** having no β-H are stable. However, **161g** loses CO

SCHEME 22



161a $R^1 = R^2 = H$
b $R^1 = H, R^2 = Me$
c $R^1 = R^2 = Me$
d $R^1 = H, R^2 = Et$
e $R^1 = H, R^2 =$ i-Pr
f $R^1 = H, R^2 = CO_2Me$
g $R^1 = H, R^2 = C{=}CH_2$

$[Fe_2(CO)_8]^{2-} + CH(OMe)Br_2 \longrightarrow$ **161h** $R^1 = H, R^2 = OMe$



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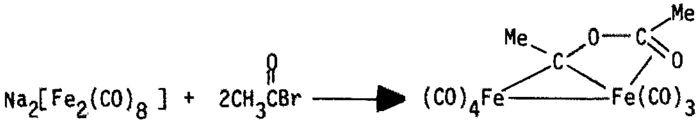

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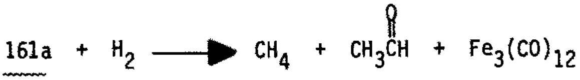
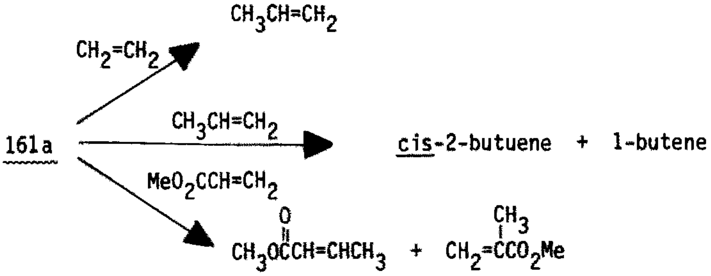
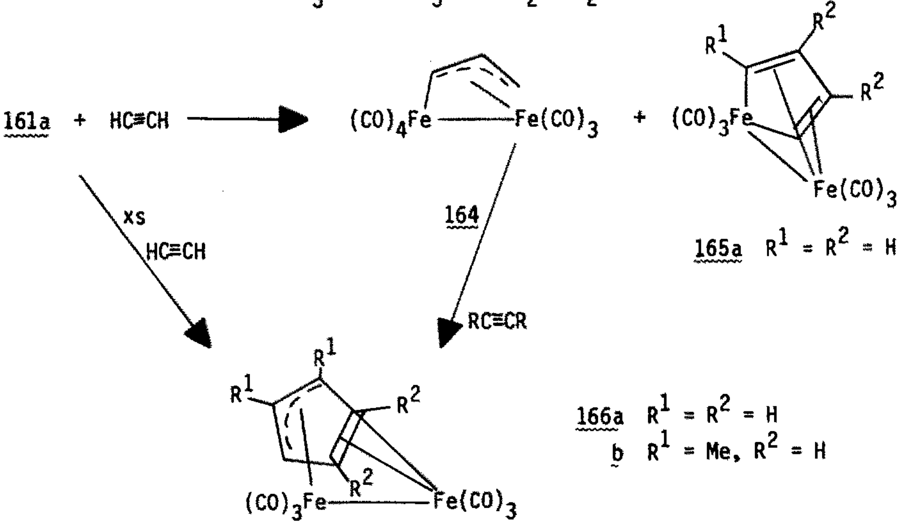


$$\underline{161a} + H_2 \longrightarrow CH_4 + CH_3\overset{O}{\overset{\|}{C}}H + Fe_3(CO)_{12}$$

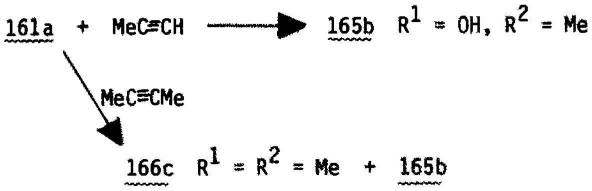




165a $R^1 = R^2 = H$

166a $R^1 = R^2 = H$

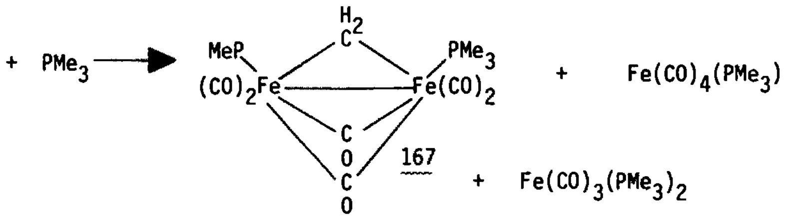
b $R^1 = Me$, $R^2 = H$



$\mathbf{161a} + \text{nucleophiles} \longrightarrow \text{acyls}$

$+ \text{NaI} \longrightarrow CH_3CO_2H$

$+ H_2O \longrightarrow CH_3CO_2H + CH_3CHO + CH_4$



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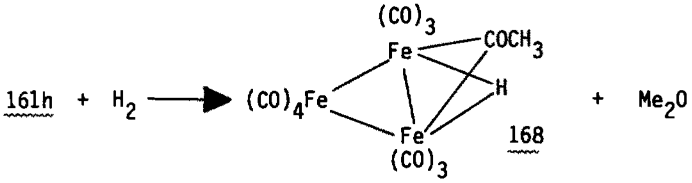
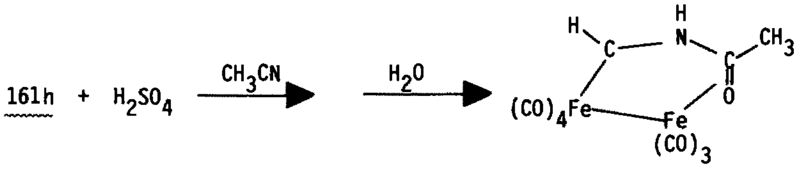


168

$\mathbf{161h} + Fe_2(CO)_9 \longrightarrow \mathbf{168}$



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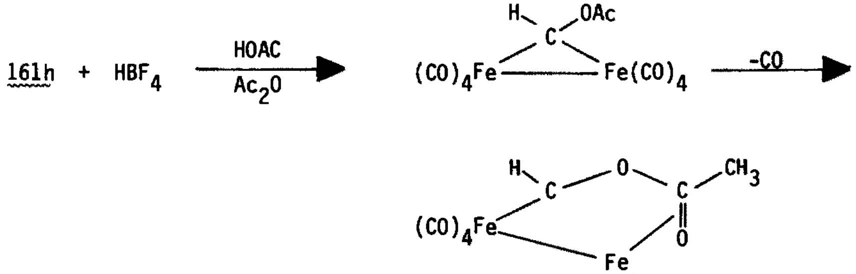

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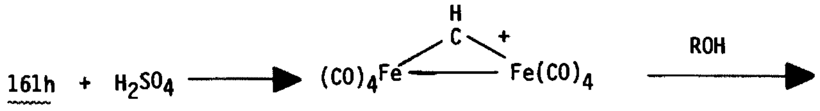

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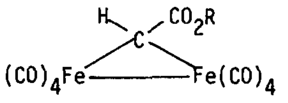
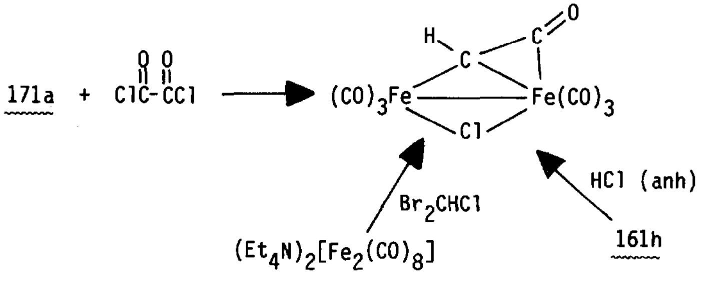


172a R = H
b R = Me

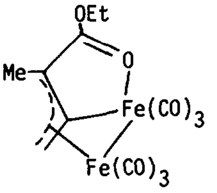


173

producing 164. The reaction of 161a with H_2 may involve oxidative addition of H_2 to one of the irons followed by successive transfer of H to μ-CH_2. CO insertion after the first transfer could account for production of acetaldehyde. Reactions of 161a with olefins could be accounted for by insertion of the olefin into an Fe-C bond affording a bimetallacyclopentane which undergoes β-elimination. Formation of 166a,b from 164 involves alkyne insertion into an Fe-C bond. Complexes with alkoxymethylene ligands such as 161h may be important in Fischer-Tropsch chemistry. The cations 171 generated by hydride abstraction from 161h can be trapped to produce species such as 169, 170, 172 and 173 [143].

The PES of $[Fe(CO)_4]_2CH_2$ (161a), $[Fe(CO)_4]_2C_2H_4$ and $Fe_3(CO)_{12}$ were compared to show that the bridging $(CH_2)_n$ groups are negatively charged. However, the effect is less for C_2H_4 than for CH_2 [144].

When $Fe_2(CO)_9$ and $(EtO_2C)(Me)C{=}C{=}CH_2$ are allowed to react in benzene, 174 is one of the products. Its X-ray structure was determined [145].



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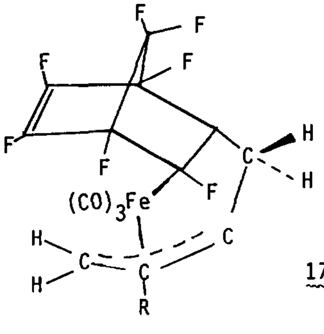
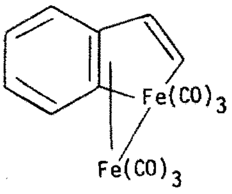


175a R = H
b R = Me

Photolysis of (η^4-$CH_2{=}CHCR{=}CH_2$)$Fe(CO)_3$ with C_7F_8 produces 175a,b [146]. For some structurally similar species, note 204, 205.

Cyclic voltammetry on the ferroles **176** and **177** showed that both are reduced in two reversible one-electron steps. **177** undergoes both reductions at the same potential. However, **176** does not and this permits generation of both the radical anion and the dianion [147].



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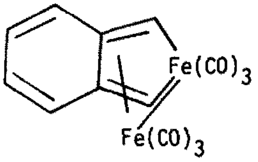

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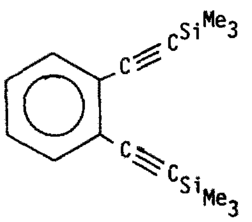
The major product when $Fe_2(CO)_9$ was refluxed in benzene with **178** is **179** [148].



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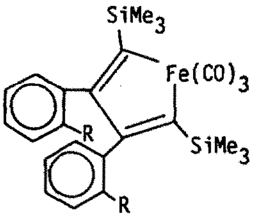


179 R = C≡CSiMe$_3$

A series of complexes *cis*-$R_2Fe(bipy)_2$ (R = Me, Et, *n*-Pr, *n*-Bu; R_2 = $(CH_2)_4$) was synthesized and shown to undergo reversible one-electron oxidation to isolable cations $[$*cis*-$R_2Fe^{III}(bipy)_2]^+$. These were oxidized irreversibly to Fe^{IV} complexes which rapidly decomposed to R_2 and $[Fe(bipy)_2]_x$. The neutral complexes undergo, via a dissociative process, β-elimination and reductive elimination to afford RH and R-H while the Fe^{III} cations decompose via a free-radical path yielding R_2, RH and R-H [149].

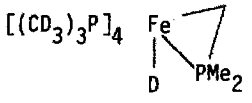
$Na[Fe(Pc)(CH_2CH_2NR_2)]\cdot xTHF$ (Pc = phthalocyaninato; R_2 = Ph_2, x = 4; R_2 = MePh, x = 3; R_2 = $(CH_2)_5$, x = 5) were prepared and found to react with *p*-toluenesulfonic acid, MeOH, $CH_3C(O)Cl$ and MeI to form products of heterolytic fragmentation FePc, C_2H_4 and, depending on the reagent, R_2NH, R_2NH, $MeC(O)NR_2$ and $[Me_2NR_2]I$, respectively [150]. The alkyl-containing anions are oxidized to $[Fe(Pc)(CH_2CH_2NR_2)]\cdot\frac{1}{4}THF$ by Ph_3CCl [151].

Alkyl porphinato complexes also received attention. Reaction of Fe(tpp) (tpp = tetraphenylporphinato) with excess dithionite and either CF_3CCl_3 or CF_3-CHClBr afforded $Fe(tpp)(CCl_2CF_3)$ and $Fe(tpp)CHClCF_3$, respectively [152].

Treatment of Fe^{III}(por)Cl (por = octaethylporphinato, tetraphenylporphinato, tetra-*m*-tolylporphinato, tetra-*p*-tolylporphinato) with MeMgI gave the methyl complexes Fe^{III}(por)(Me)(H_2O) . At -20°, all these insert SO_2 producing Fe^{III}-(por)(SO_2Me) which can be oxidized by O_2 to Fe^{III}(por)(SO_3Me) [153]. Visible spectroscopy was employed to detect the presence of Fe^{III}(tpp)(CH_2-*p*-$C_6H_4NO_2$) as an intermediate in the Fe(tpp)Cl -catalyzed reduction of *p*-$O_2NC_6H_4CH_2Cl$ by ascorbate [154].

It has recently been shown that oxidation of vinylidenecarbene iron porphoryins produces *N*-vinyl- and *cis*-*N*,*N* vinylidene iron porphyrins. It was shown also that $FeCl_3$ oxidation of σ-methyl, vinyl or phenyl Fe^{III}(tpp) complexes leads to Fe^{II} *N*-alkyl(tpp) complexes. Reverse transfer of the R group can be effected by treatment with dithionite [155].

When Fe(D)[P$(CD_3)_3]_4$I was allowed to react with Li(CH_2PMe_2) in Et_2O at -30°, only Fe-D bands due to the presence of **180** were visible initially in the IR spectrum. The subsequent appearance of Fe-H bands demonstrates the intramolecular nature of the cyclometallation [156].



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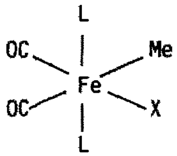
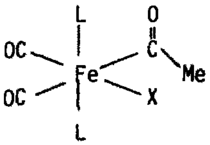


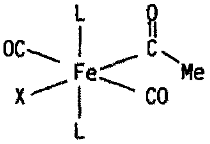
181 L = PMe_3
a X = NCS
b X = CN
c X = CNO
d X = OMe
e X = Cl
f X = Br
g X = I

181a-g were prepared. On carbonylation, **181a-d** gave **182 a-d**; however **181e-g** gave a mixture of **182e-g** and **183a-c** with the proportion of isomer **183** decreasing in the order I > Br > Cl [157].



182 L = PMe_3

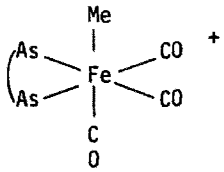
a X = NCS
b X = CN
c X = CNO
d X = OMe
e X = Cl
f X = Br
g X = I



183 L = PMe_3

a X = Cl
b X = Br
c X = I

The CO insertion induced by nucleophiles on **184** ($\overset{\frown}{\text{As As}}$ = diars) was studied. With L = $P(OMe)_3$, $P(OPh)_3$, $PPh(OMe)_2$, $PPh_2(OMe)$ and *CO, **185** is the single kinetic product. For more basic L = $PPhMe_2$ and PMe_3, two kinetic products



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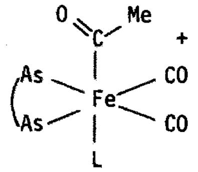

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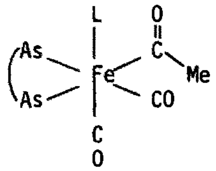

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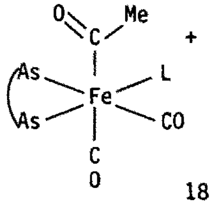
are observed 185 and either 186 or 187. These results suggest nucleophilic attack on a tbp acyl such as 188 stereodirected by the large trans effect of the



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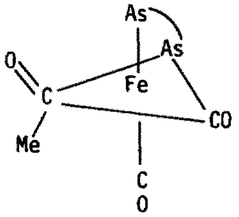


188

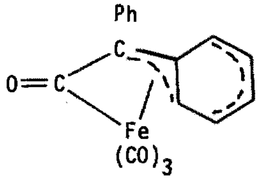
acyl. Consistent with this is the observation that decarbonylation of 185 (L = *CO) removes all the label as would be required by the Principle of Microscopic Reversibility [158].

Formyl, Acetyl and Related Complexes

$Na_2[Fe(CO)_4]$ was found to react with N-formylimidazole in the presence of $B(OMe)_3$ in HMPA producing $Na[Fe(CO)_4(CHO)]$. BF_3 and BEt_3 also act as promoters for this reaction. Some $Na[HFe(CO)_4]$ is also formed, but not from the decomposition of the formyl complex. In the absence of a Lewis acid, $Na_2[Fe(CO)_4]$ simply decarbonylates N-formylimidazole showing that simple hydride transfer is not the route to the formyl [159]. When $[HFe(CO)_4]^-$ is treated with BF_3 under a CO atmosphere in THF, $Fe(CO)_5$ is the product. This suggests the presence of a formyl intermediate since $[Fe(CO)_4(CHO)]^-$ is known to transfer H^- to BF_3 [160].

Treatment of $Na_2[Fe(CO)_4]$ with N-acetylimidazole was found to produce $Na[CH_3C(O)Fe(CO)_4]$ [158].

189 was one of the products resulting from a reaction between $(Ph_2C{=}C{=}O)Fe(CO)_3$ and C_2H_4 [161].



189

Aryl Complexes

$Fe(1,3,5\text{-}Me_3C_6H_2)_2$, $Li[Fe(1,3,5\text{-}Me_3C_6H_2)_3(diox)]$ and $Mg[Fe(1,3,5\text{-}Me_3C_6H_2)_3]_2\cdot THF_{5.75}$ were synthesized from ferrous halides and mesityl Grignard reagent. The neutral mesityl complex reacts with L = phosphines, aminophosphines, phosphites affording $Fe(1,3,5\text{-}Me_3C_6H_2)_2L_n$ (n = 1,2) [162]. A series of Fe(II) tetraaryl carbonyl mercaptide complexes was prepared whose MCD and absorption spectra reproduce well that of cytochrome P-450 [163].

Low-spin PhFe(tpp) (tpp = tetraphenylporphinato) was made from Fe(tpp)Cl and PhMgBr. Treatment with aerobic solutions of acidic MeOH caused Ph-to-N migration known for alkyl, vinyl and vinylidene iron porphyrins [164]. σ-Aryl and σ-vinyl iron porphyrin complexes were generated by electrolysis of a mixture of Fe porphyrin and aryl (or vinyl) halide [165].

$Fe^{III}(oep)(\underline{p}\text{-}XC_6H_5)$ (oep = octaethylporphinato; X = H, OMe, Me) were prepared and found to have $S = \frac{1}{2}$. These aryl porphyrin complexes are photochemically unstable and oxygen sensitive decomposing via homolytic cleavage of the Fe-C bond to give $(\underline{p}\text{-}XC_6H_4)_2$ (X = H, OMe, Me) [166].

Mössbauer measurements on $Fe(C_6Cl_5)_2L_2$ ($L = PEt_3$, PEt_2Ph) were reported [167].

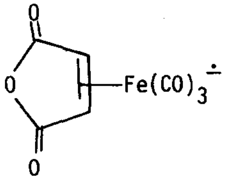
MONOALKENE COMPLEXES

M.O. calculations of the ionization potential of $(\eta^2\text{-}C_2H_4)Fe(CO)_4$ were carried out [6] as well as calculations on $(\eta^2\text{-}Me_2C{=}C{=}CMe_2)Fe(CO)_4$ [168]. When $Fe_2(CO)_9$ is treated with vinyl germanes in hexane at 30-40°, the products $(\eta^2\text{-}CH_2CHGeR^1R^2)Fe(CO)_4$ ($R^1 = R^2 = Et$; $R^1 = R^2 = CH{=}CH_2$; $R^1 = CH{=}CH_2$, $R^2 = Ge(CH{=}CH_2)_3$) can be prepared [169].

X-ray structures of $(\eta^2$-diethyl fumarate$)Fe(CO)_3(PPh_3)$ and $(\eta^2$-diethyl maleate$)Fe(CO)_3(PPh_3)$ show that both complexes are trigonal bipyramids. The phosphine, dimethyl fumarate and a carbonyl ligand are all equatorial while, in the more crowded diethyl maleate complex, the phosphine is axial [170].

A number of styrene complexes $(\eta^2\text{-}CH_2{=}CH\underline{p}\text{-}C_6H_4X)Fe(CO)_4$ (R = H, Me, OMe, Cl, F) were prepared. When they are treated with Br_2 in methanol, $FeBr_3$, CO, HBr and $\underline{p}\text{-}XC_6H_4CH(OMe)CH_2CO_2CH_3$ are formed [171].

Reaction of $Na_2[Fe(CO)_4]$ with olefins in THF affords radical anions whose identities depend on temperature, stoichiometry and time. At -80°, maleic anhydride produces the radical anion of the olefin along with $[Fe_2(CO)_8]^{\dot{-}}$. At room temperature $[Fe_2(CO)_8]^{\dot{-}}$ and 190 are formed. Similar $[(olefin)Fe(CO)_3]^{\dot{-}}$ radicals result with (olefin) = methyl maleic anhydride, dimethyl maleic anhydride, dimethyl maleate, dimethyl fumarate, cinnamonitrile and acrylonitrile. The lability of these seventeen-electron species allows preparation of $P(OMe)_3$-substituted derivatives. The above radicals can all be prepared also by reduc-



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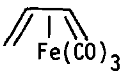

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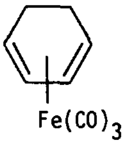

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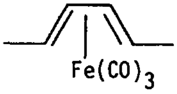

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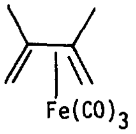

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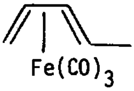


195

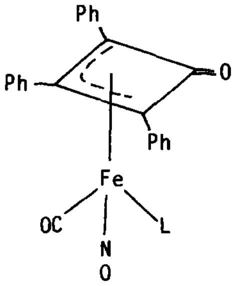
tion of (olefin)$Fe(CO)_4$ with Na/K alloy or sodium naphthalide in THF. This method can be employed to prepare radical anions from the non-activated diene complexes 191-195. One double bond is dissociated in the corresponding radical anions [172].

ALLYL COMPLEXES

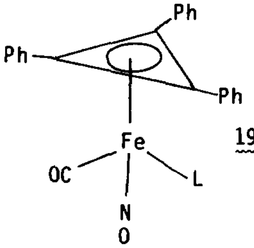
$(\eta^3\text{-}C_3H_5)Fe(CO)_3X$ (X = Cl, Br, I) were found to react with $AgClO_4$ in CH_2Cl_2 yielding $(\eta^3\text{-}C_3H_5)Fe(CO)_3OClO_3$. The perchlorato complex undergoes addition of Lewis bases L = PPh_3, $AsPh_3$ and py to afford $[(\eta^3\text{-}C_3H_5)Fe(CO)_3L]ClO_4$. When L = PPh_3, the cation loses two CO's on reaction with the bidentate anions L' = 8-hydroxyquinolinate, N-phenylsalicylaldimate giving $[(\eta^3\text{-}C_3H_5)Fe(CO)(PPh_3)L']$ [173].

Factors controlling the relative contribution of olefin and allyl structures in Fe complexes containing $=C=C-C^+R$ ligands were discussed in some detail [174].

Cyclopropenium cations were found to react with $[Fe(CO)(NO)L]^-$ (L = CO, PPh_3, PMe_2Ph) to produce oxocyclobutenyl complexes (196a-c) as well as cyclopropenyl complexes 197a-c. 197a reacts with L = PPh_3 or PMe_2Ph to afford mixtures of 196b, 197b and 196c, 197c, respectively [175].



196a L = CO
b L = PPh_3
c L = PMe_2Ph

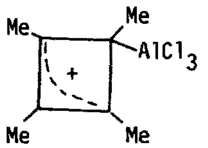


197a L = CO
b L = PPh_3
c L = PMe_2Ph

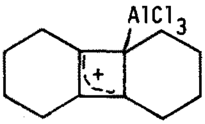
CYCLOBUTADIENE AND TRIMETHYLENEMETHANE COMPLEXES

A valence bond structure/resonance approach was used to calculate bond orders in ten (cyclobutadiene)$Fe(CO)_3$ complexes. Calculated bond orders showed a linear relation to known bond lengths [176]. M.O. calculations were employed to predict sites of addition and nucleophilc attack by both hard and soft reagents for *inter alia*, $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ [177].

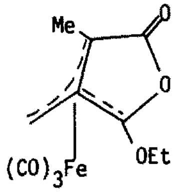
Dihalocyclobutanes were prepared by treating Al halide complexes of cyclobutadienes such as 198a and 198b with $SOCl_2$. Addition of $Fe_2(CO)_9$ to the reaction mixture produces (cyclobutadiene)$Fe(CO)_3$ complexes [178].



198a



198b



199

Tertiary phosphines and phosphites add reversibly to the cyclobutadiene ring of $[(\eta^4\text{-}C_4H_4)Fe(CO)(NO)L]^+$ to give *exo*-phosphonium salts $[(C_4H_4PR_3)\text{-}Fe(CO)(NO)L]^+$. Kinetic studies in nitromethane show that the ring electrophilicity spans a range of ~100 as L is varied in the order L = CO > $P(CH_2CH_2CN)_3$ ~ $P(\text{p-}ClC_6H_4)_3$ > $P(\text{p-}FC_6H_4)_3$ > $AsPh_3$ ≈ PPh_3 > $SbPh_3$ ≈ $P(\text{p-}MeC_6H_4)_3$ > $P(\text{p-}MeOC_6H_4)_3$. Nucleophilicity of the attacking Lewis bases follows the order $P(\text{n-}Bu)_3$ > $P(\text{p-}MeOC_6H_4)_3$ > $P(\text{p-}MeC_6H_4)_3$ > PPh_3 > $P(CH_2CH_2CN)_3$ > $P(O\text{-n-}Bu)_3$ [179].

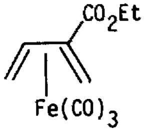
One of the compounds resulting from the reaction between $Fe_2(CO)_9$ and $(Me)(EtO_2C)C{=}C{=}CH_2$ is trimethylenemethane complex 199 [145]. Its X-ray structure was determined.

DIENE AND HIGHER OLEFIN COMPLEXES

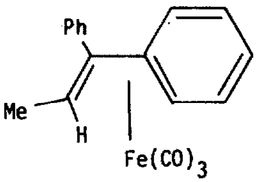
Acyclic Diene Species

^{13}C NMR was employed to determine the activation parameters for intramolecular site exchange of CO groups in fifteen $Fe(CO)_3$ complexes of 1,4- and 2,3-disubstituted 1,3-butadienes, 1,2-dimethylidenecycloalkanes as well as 1,3-cycloalkadienes [180].

The third product (besides 174 and 199) of the $Fe_2(CO)_9/(Me)(EtO_2C)C{=}C{=}CH_2$ reaction is 200 [145]. The second product (besides 189) from $(Ph_2C{=}C{=}O)Fe(CO)_3$ and ethylene is 201 [161].



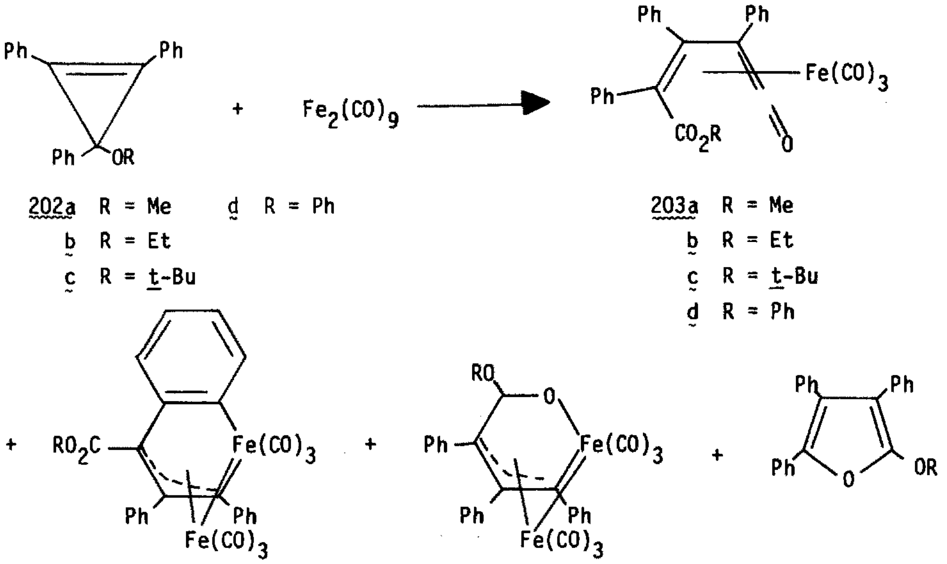
200



201

Scheme 23 delineates the results of allowing the cyclopropenes 202a-d to react with $Fe_2(CO)_9$.

SCHEME 23



202a R = Me d R = Ph
b R = Et
c R = t-Bu

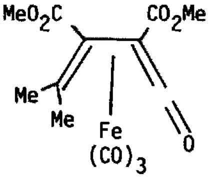
203a R = Me
b R = Et
c R = t-Bu
d R = Ph

204a R = Me
b R = Et
c R = t-Bu
d R = Ph

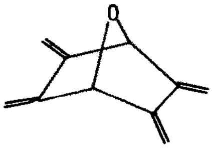
205a R = Me
b R = Et
c R = t-Bu
d R = Ph

206a R = Me
b R = Et
c R = t-Bu
d R = Ph

X-ray structures of 204b and 205a were determined [181] as was that of 207 [182].



207



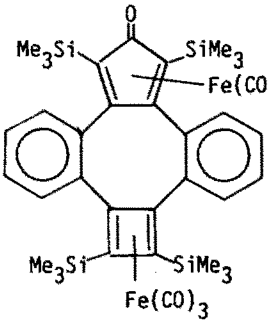
208

The He(I) PES spectra of *endo*, *exo*, *endo-exo* and di-*exo* Fe(CO)$_3$ complexes of **208** were measured and interpreted as indicating a stronger Fe-butadiene bond for *endo* than *exo* geometry. Perturbation of one Fe(CO)$_3$ groups on the uncomplexed diene group was found to be negligible. Additive perturbations occur in the *endo-exo* complex, but an extra effect occurs in the di-*exo* isomer [183].

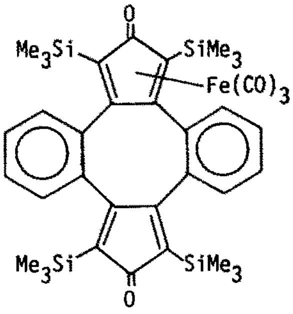
^{13}C NMR, gas phase PES and CNDO calculations allowed no firm conclusions regarding the electronic structure of (butatriene)Fe$_2$(CO)$_6$ [184].

Cyclic Diene and Higher Olefin Species

209, **210** and **211** were products (along with **179**) of the reaction between Fe$_2$(CO)$_9$ and **178** [148].



209



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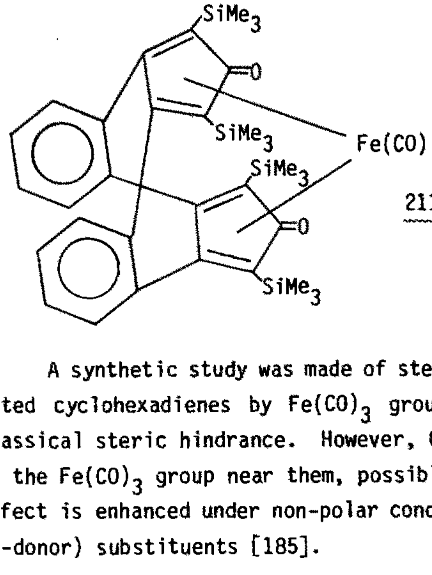
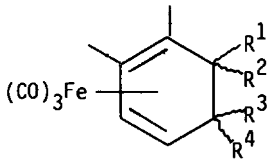


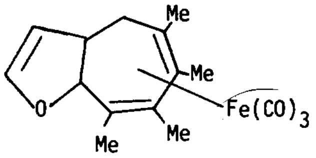
211

A synthetic study was made of stereoselectivity in complexation of substituted cyclohexadienes by Fe(CO)$_3$ groups. Substituting alkyl groups display classical steric hindrance. However, CO$_2$R and related groups favor positioning of the Fe(CO)$_3$ group near them, possibly through prior complex formation. This effect is enhanced under non-polar conditions and reduced by the presence of OMe (π-donor) substituents [185].

^{13}C NMR was employed to assign the stereochemistry of several complexes of type 212 [186].

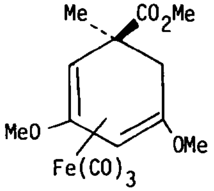


212



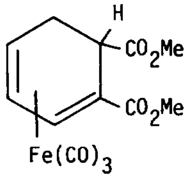
213

213 was prepared via a reaction between the organic ring molecule and Fe$_2$(CO)$_9$ [187]. The X-ray structure was reported for 214 [188].

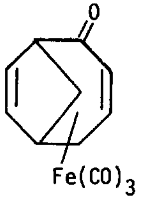


214

The crystal structures of two of the isomers of 215 were published [189]. 216, a complex of a bicyclic ligand, was synthesized [190].

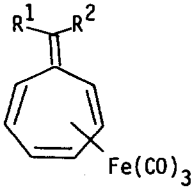


215

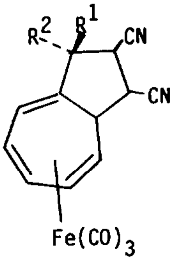


216

Kinetics of the reaction between 217a-e and tcne to give 218a-e were studied. 217e initially forms a 1,3-adduct which rearranges to 218e [191].



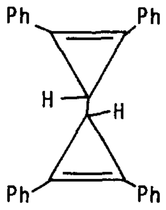
217a R^1 = R^2 = H
b R^1 = R^2 = Ph
c R^1 = OMe,
R^2 = H
d R^1 = p-tolyl,
R^2 = H
e R^1 = Ph, R^2 = H



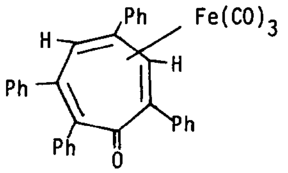
218a R^1 = R^2 = H
b R^1 = R^2 = Ph
c R^1 = OMe,
R^2 = H
d R^1 = p-tolyl,
R^2 = H
e R^1 = Ph, R^2 = H

$\Delta G^{\ddagger}$ for 1,3-Fe shifts in a series of (cycloheptatriene)$Fe(CO)_3$ complexes was measured. Electron-donating groups on the C_7 ring decrease the activation energy for 1,3 shifts relative to C_7H_8 while electron-withdrawing groups increase it. The values of $\Delta G^{\ddagger}$ were not consistent with the symmetry-forbidden closure to a (norcarnadiene)$Fe(CO)_3$-type transition state [192].

$Fe_2(CO)_9$ reacts with 219 producing 220 whose X-ray structure was determined. The tropone ligand can be removed from 220 by oxidation with Ce(IV) [193].



219



220

The site of electrophilic attack by $[CHCl{=}NMe_2]^+$ in the substituted cyclooctatetraene complexes $(\eta^4\text{-}C_8H_7X)Fe(CO)_3$ (X = Me, Ph, Br, CPh_3) was found to be governed largely by steric factors [194].

Heterodiene Species

The heterodiene complexes mentioned here all turn out to be N-bonded to Fe. They are placed here to facilitate their location by workers with an interest in heterodienes as ligands.

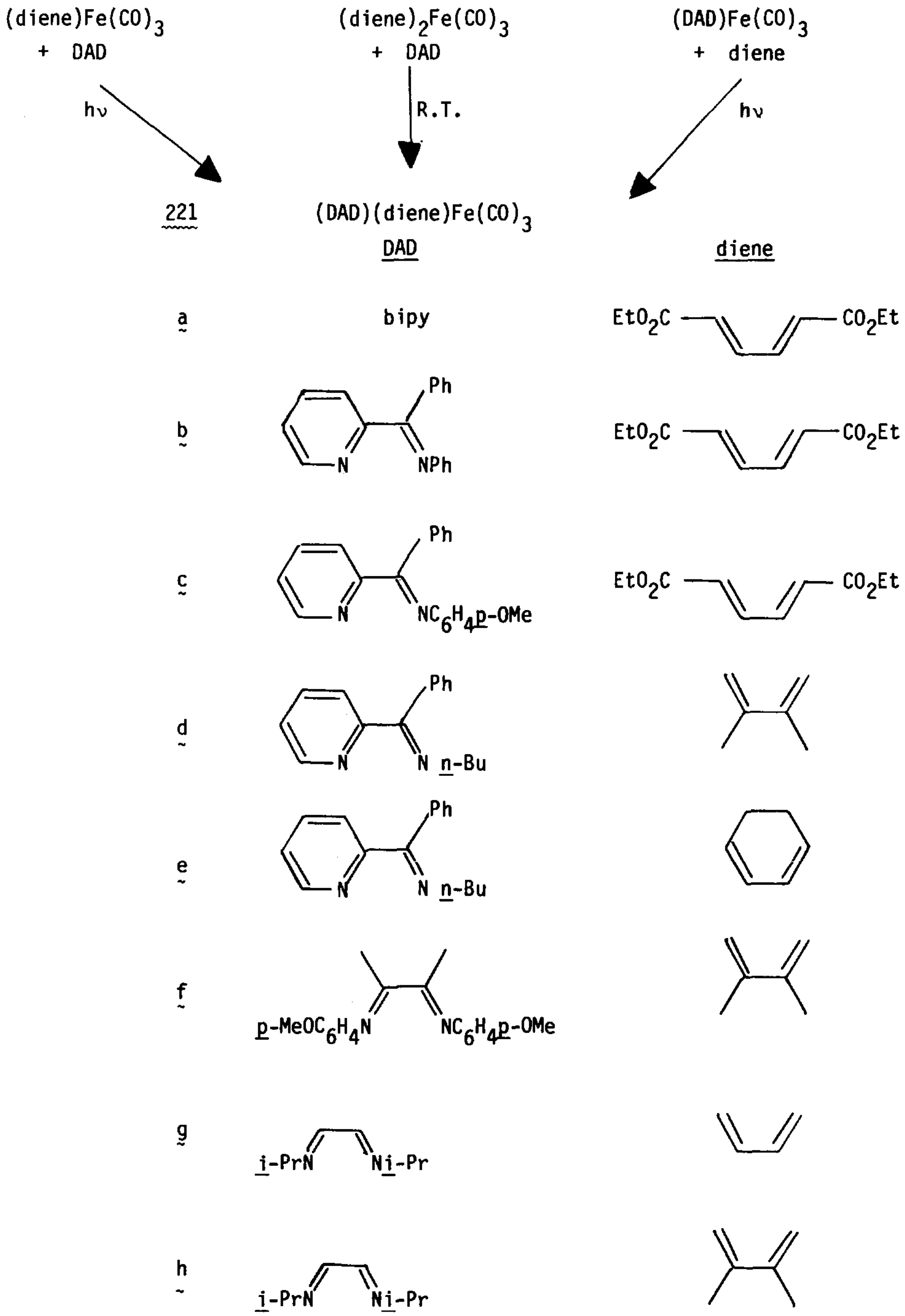
As shown in Scheme 24, mixed complexes containing both diazabutadiene (DAD) and butadiene can be synthesized by several routes. The X-ray structure of 221h indicated that this complex has a square pyramidal structure with both N's in the basal plane. Depending on the identity of the diene ligand, the coordination of the diazabutadiene may be apical-basal in other square pyramidal complexes [195].

NMR was used to investigate fluxionality in the tetraazabutadiene complexes $(Me_4N_4)Fe(CO)_3$, $(Me_4N_4)Fe(CO)L_2$ (L = PMe_3, $P(OMe)_3$, $P(C_6H_{11})_3$, $P(OPh)_3$, $PMePh_2$, PPh_3) and $(Me_4N_4)Fe[P(OMe)_3]_3$. Two isomers can be detected for the disubstituted complexes. As the cone angle of L decreases, the barrier to the intramolecular isomer interconversion also decreases. Both the unsubstituted and trisubstituted complexes exchanged rapidly at low temperatures [196].

DIENYL COMPLEXES

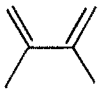
Semempirical calculations of the INDO and charge-iterative extended Huckel types were performed on di(pentadienyl)iron and some methyl derivatives. HeI PE spectra were also reported and compared with that of ferrocene [197].

SCHEME 24

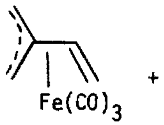

(diene)Fe(CO)3 + DAD
hν
(diene)2Fe(CO)3 + DAD
R.T.
(DAD)Fe(CO)3 + diene
hν
221
(DAD)(diene)Fe(CO)3
DAD
diene
a
bipy
EtO2C
CO2Et
b
Ph
N
NPh
c
NC6H4p-OMe
d
N n-Bu
e
f
p-MeOC6H4N
NC6H4p-OMe
g
i-PrN
Ni-Pr
h

i

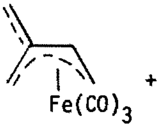
j



[(Cross-conjugated dienyl)Fe(CO)$_3$]$^+$ cations do not possess the unsaturated structure indicated by 222a and predicted by frontier orbital theory. Apparently, they can attain structure 222a at modest energy cost and undergo rotation about the C_2-C_3 bond implicit in this structure. On this basis, the transformation of 223 to 225 depicted in Scheme 25 is intelligible. The ground state of these cations is probably best represented as 222b [198].

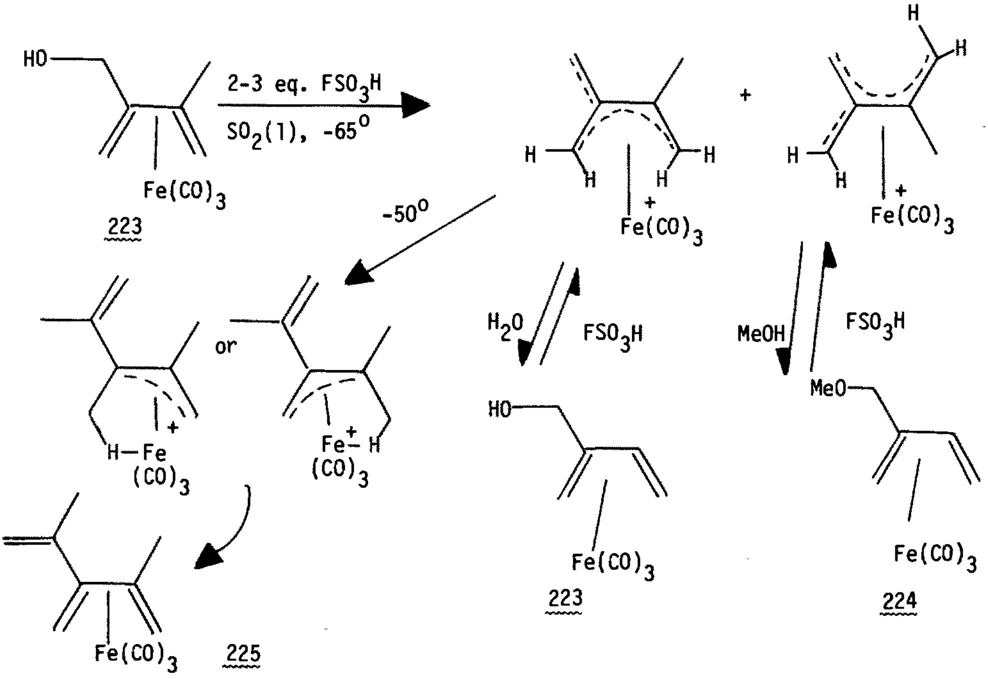


222a



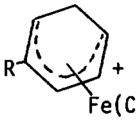
222b

SCHEME 25



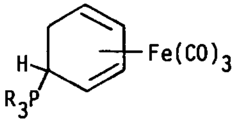
Calculations of ^{13}C shifts for $[(\eta^5-C_6H_7)Fe(CO)_3]^+$ and $[(\eta^5-C_7H_9)Fe(CO)_3]^+$ were made using SCCCMO methods and the Pople-Karplus equation [199]. M.O. calculations were made predicting the sites of addition and nucleophilic attack by both hard and soft reagents on $[(\eta^5-C_6H_7)Fe(CO)_3]^+$ and $[(\eta^5-C_7H_9)Fe(CO)_3]^+$ [177].

The substitution pattern for nucleophilic attack on 226a was established. Amines directly attack the ring affording 5-*exo* products. At low temperatures, alkoxides attack CO yielding COOR derivatives which rearrange at higher temperatures to 5-*exo* alkoxy derivatives. Depending on the particular phosphine and the solvent, either 5-*endo* or 5-*exo* products result [200]. The general pattern of reactivity is in agreement with M.O. calculations [177].



226a R = H

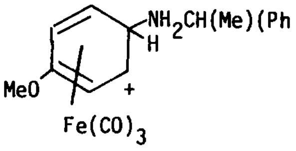
b R = OMe



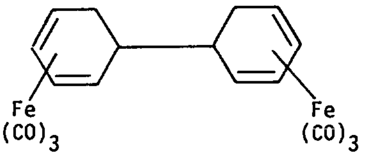
227

A kinetic study of nucleophilic attack on 226a,b by imidazole and py shows that the reactions display a second-order rate law. Imidazole attacks 226a faster than py, but the order is reversed for 226b [201]. The kinetics of addition of phosphines to 226a yielding 227 were studied in acetone. P(*o*-tolyl)$_3$ and $P(CH_2CH_2CN)_3$ added reversibly and $k_{obs} = k_1[PR_3] + k_{-1}$. The remaining phosphines showed second-order kinetics with $k_{obs} = k_1[PR_3]$. A correlation was found between k_1 and Tolman's χ values. A plot of log k_1 vs pK_a showed that phosphine nucleophilicity was generally controlled by bascity except for P(*o*-tolyl)$_3$ and $P(C_6H_{11})_3$ where steric factors predominated [202,203].

Addition of optically active nucleophiles to 226b has furnished interesting results. Kinetic diastereotopic discrimination occurs in the reaction of (R,S)-226b with (R)-(+)$_{589}$-1-phenylethylamine in MeCN. Initial attack occurs at C_5 giving diasteromeric cations 228 which can be deprotonated to neutral diastereomers [204]. When the attacking nucleophile is (S,S)-(-)$_{589}$-*o*-phenylenebis-



228



229

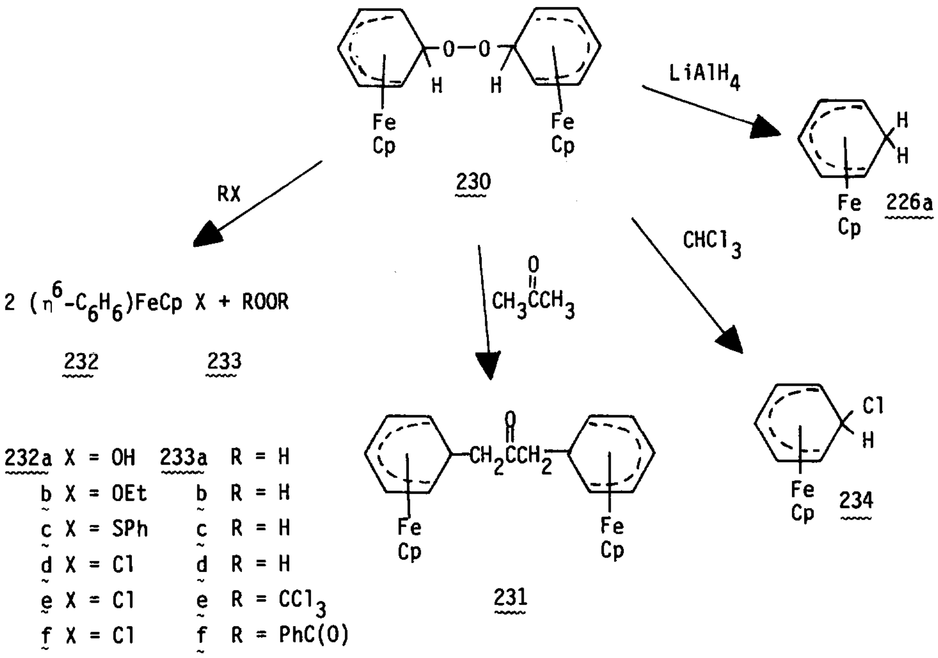
(1,2-methylphenylphosphine), considerable kinetic diastereoselectivity is shown in MeCN and acetone, but less in CH_2Cl_2. Recovery of unreacted 226b gives a route to preparation of the optically active cation. A 50:50 mixture of diastereomers of the addition product equilibrates over 3 days in MeCN to a 60:40 mixture thus demonstrating thermodynamic chiral discrimination [205]. (S,S)-$(-)_{589}$-chiraphos, $(-)_{589}$-neomenthyldiphenylphosphine and $(+)_{589}$-diop all showed kinetic stereoselectivity in addition to 226b [206].

Addition SCN^- to 226a and to $[(\eta^5\text{-}C_6H_7)FeCp]^+$ gave 5-exo NCS isomers which, on exposure to air rearranged to 5-exo SCN complexes [207].

When 226a is reduced with Cr^{2+} in acetone, dimeric 229 is the product [208].

Scheme 26 shows the chemistry of 230 which is the product of reaction of O_2 with (η^6-benzene)FeCp [209].

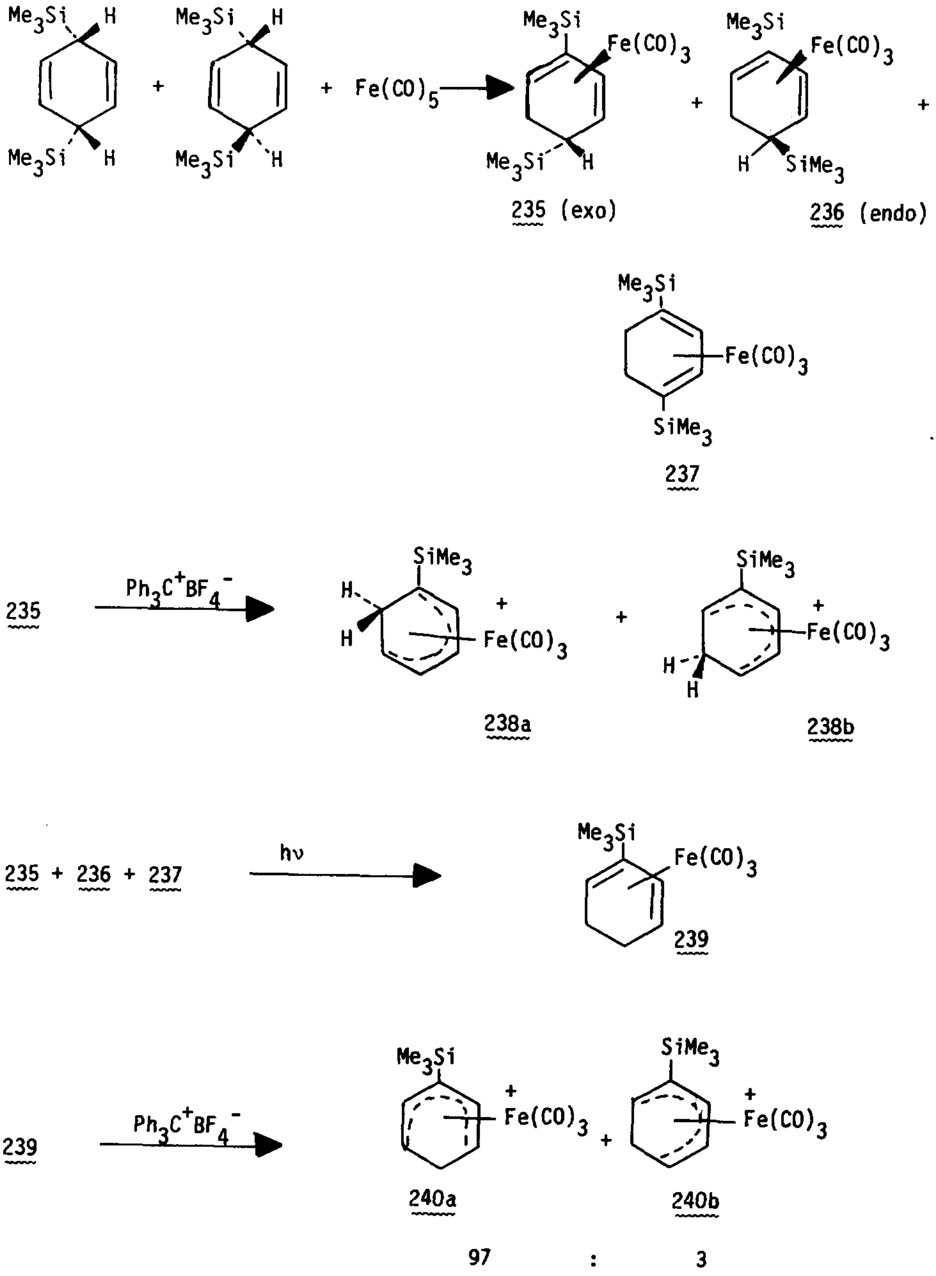
SCHEME 26

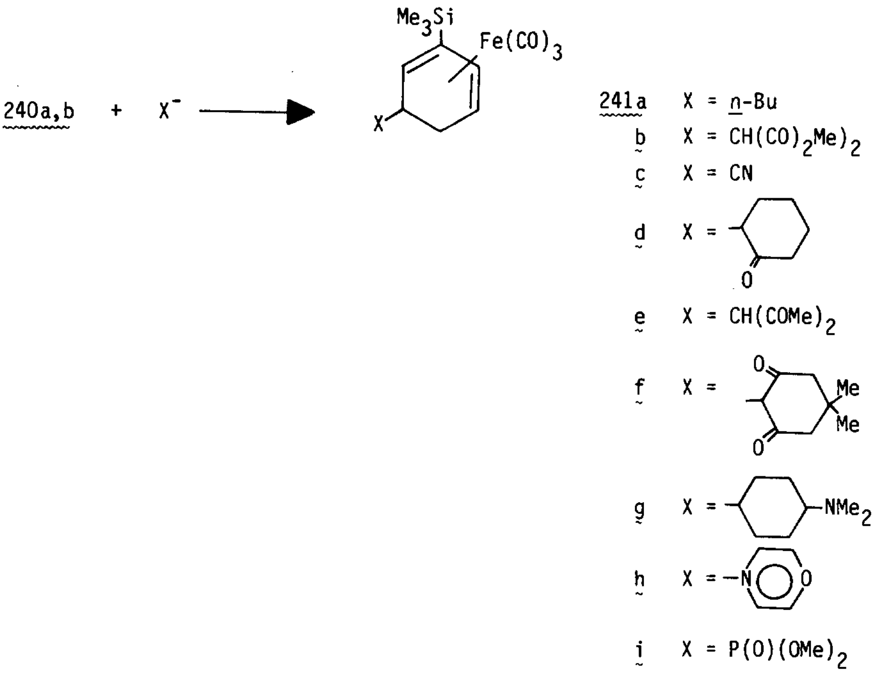


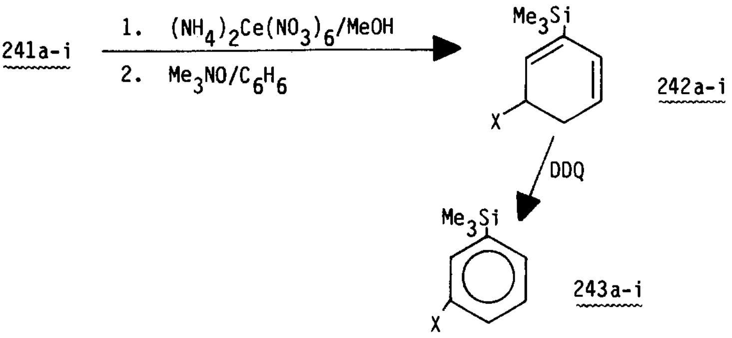
232a X = OH 233a R = H
b X = OEt b R = H
c X = SPh c R = H
d X = Cl d R = H
e X = Cl e R = CCl_3
f X = Cl f R = PhC(O)

Some chemistry involving $[(cyclohexadienyl)Fe(CO)_3]^+$ cations containing $SiMe_3$ substituents appears in Scheme 27 [210, 211]. Substituted benzenes 243 can be synthesized.

SCHEME 27

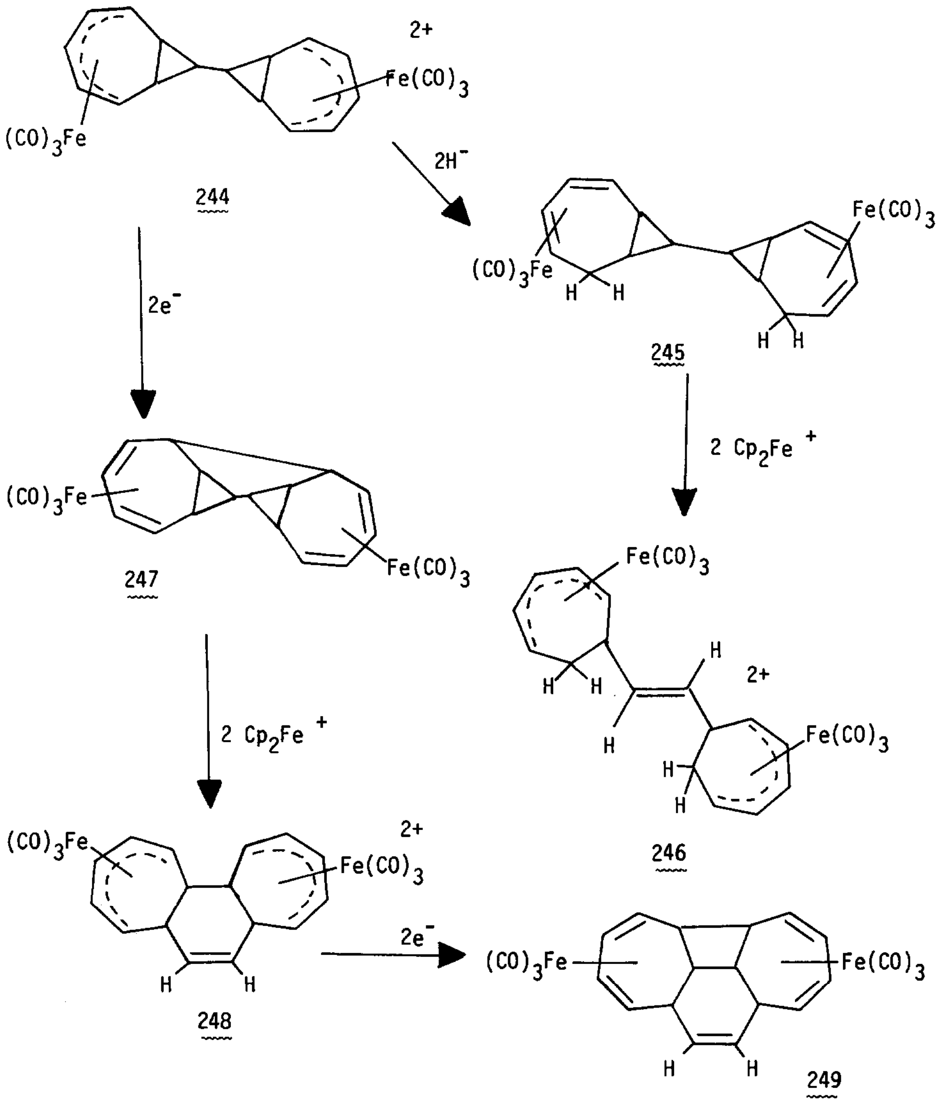

Me3Si
H
+ Fe(CO)5
235 (exo)
236 (endo)
237
SiMe3
Fe(CO)3
235
Ph3C+BF4-
238a
238b
235 + 236 + 237
hν
239
240a
240b
97 : 3





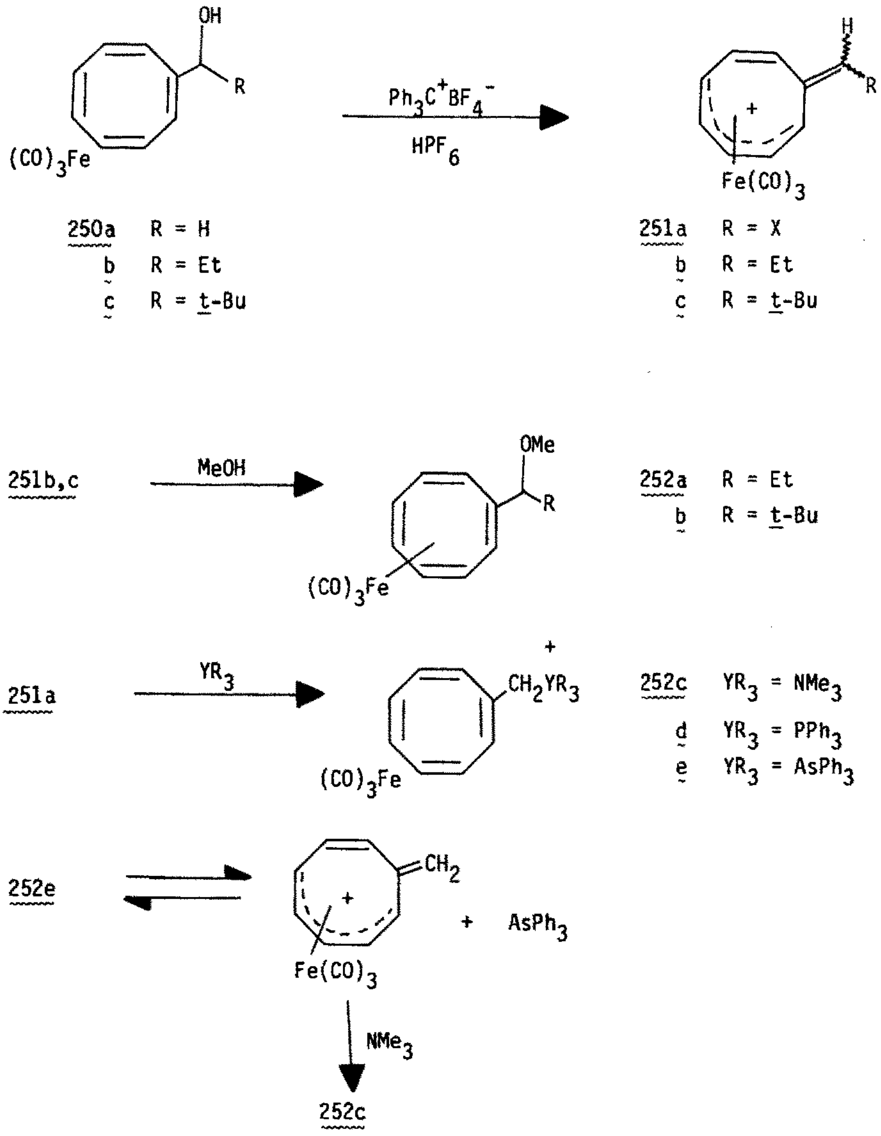
Reductions (both chemical and electrolytic) and oxidations of 244 lead to interesting ring openings and closures as seen in Scheme 28 [212]. The X-ray structures of 245 and 247 were determined.

SCHEME 28



The dienyl cations 251a-b were generated as shown in Scheme 29 and treated with various nucleophlic reagents with results as seen in the Scheme [213].

SCHEME 29



CYCLOPENTADIENYL COMPLEXES

Binuclear Species

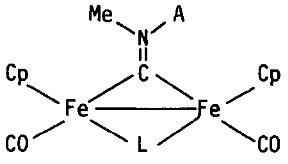
The solid state ^{13}C NMR of *cis*-$Cp_2Fe_2(CO)_4$ shows more resonances than the solution spectrum since the site symmetry is C_1 while the molecular symmetry is C_{2V}. Also reported were the solid state NMR spectra of *trans*-$Cp_2Fe_2(CO)_4$,

$CpFe(CO)_2I$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. The chemical shift values agreed well with those of solution spectra [214].

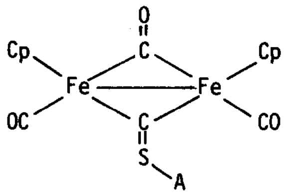
Reflux of $[(\eta^5\text{-}C_5H_4X)Fe(CO)_2]_2$ (X = H, Me, CO_2Me) in toluene in the presence of RNC produces the substituted dimers $[(\eta^5\text{-}C_5H_4X)Fe(CNR)_2]_2$. Exchange reactions between $[(\eta^5\text{-}C_5H_4X)Fe(CNR)_2]_2$ and the unsubstituted dimer afford $[(\eta^5\text{-}C_5H_4X)_2Fe_2(CO)_{4-n}(CNR)_n]$ (n = 1-3). $[(\eta^5\text{-}C_5H_4X)_2Fe_2(CO)_{4-n}(CNR)_n]$ (n = 1, 2) can be prepared from $Na[CpFe(CO)_2]$, RNC and tropylium tetrafluoroborate [214a]. t-BuNC substitution on $Cp_2Fe_2(CO)_4$ was found to be catalyzed by PtO_2, PdO, Pd/C and $Pd/CaCO_3$ [215].

The photoacoustic spectrum of $Cp_2Fe_2(CO)_4$ was reported [216].

Several reactions of the bridging ligands in dimers with Lewis acids were investigated. $Cp_2Fe_2(CO)_2(CNMe)L$ (L = CO, CNMe) react with Lewis acids A = SnX_2, SnX_4, ZnX_2 CdX_2, (X = F, Cl, Br, I), $AsCl_3$, $NiCl_2\cdot 6H_2O$, $AgNO_3$ affording adducts of structure 253 containing an N-A bond. Only adducts having L = CNMe, A = $ZnCl_2$, $ZnI_2\cdot 0.5THF$, $CdCl_2\cdot 0.5THF$, $CdBr_2$, CdI_2 or $SnCl_2$ could be isolated [217].

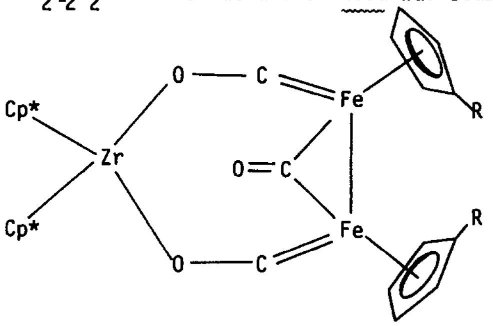


253 L = CO, CNMe



254

$Cp_2Fe_2(CO)_3(CS)$ exists in solution as an equilibrium mixture of cis- and trans-isomers. Lewis acids A = SMe^+, $HgMe^+$, $Fe(CO)_2Cp^+$, $HgCl_2$, $HgBr_2$, $Cr(CO)_5$, $W(CO)_5$ from adducts of structure 254 as shown by IR [218]. 255a,b are formed reversibly from reactions between $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ (R = H, Me) and $[(\eta^5\text{-}Me_5C_5)_2\text{-}ZrN_2]_2N_2$. The structure of 255a was etablished by X-ray [219].

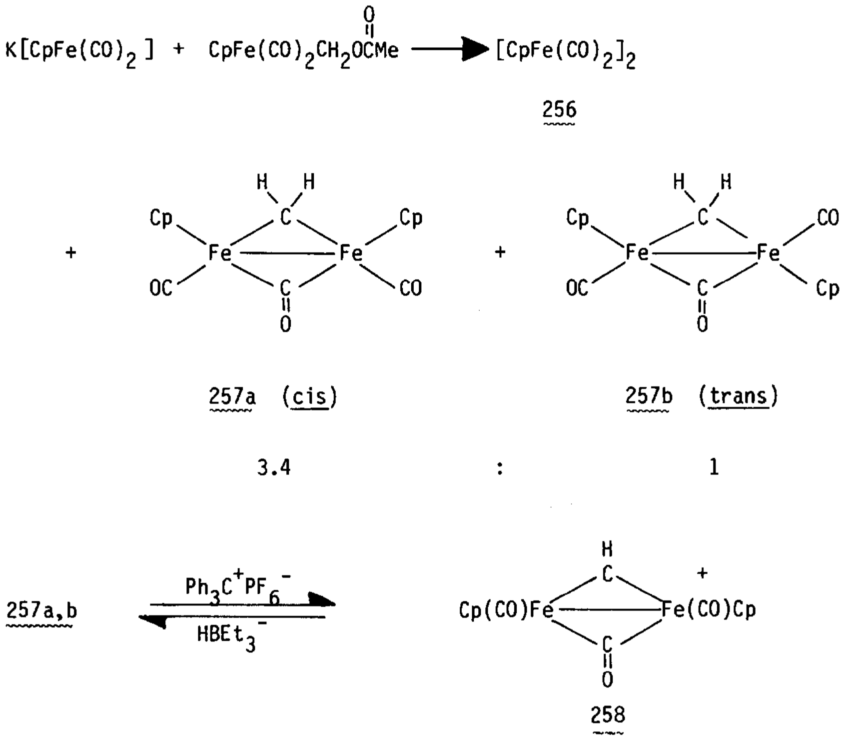


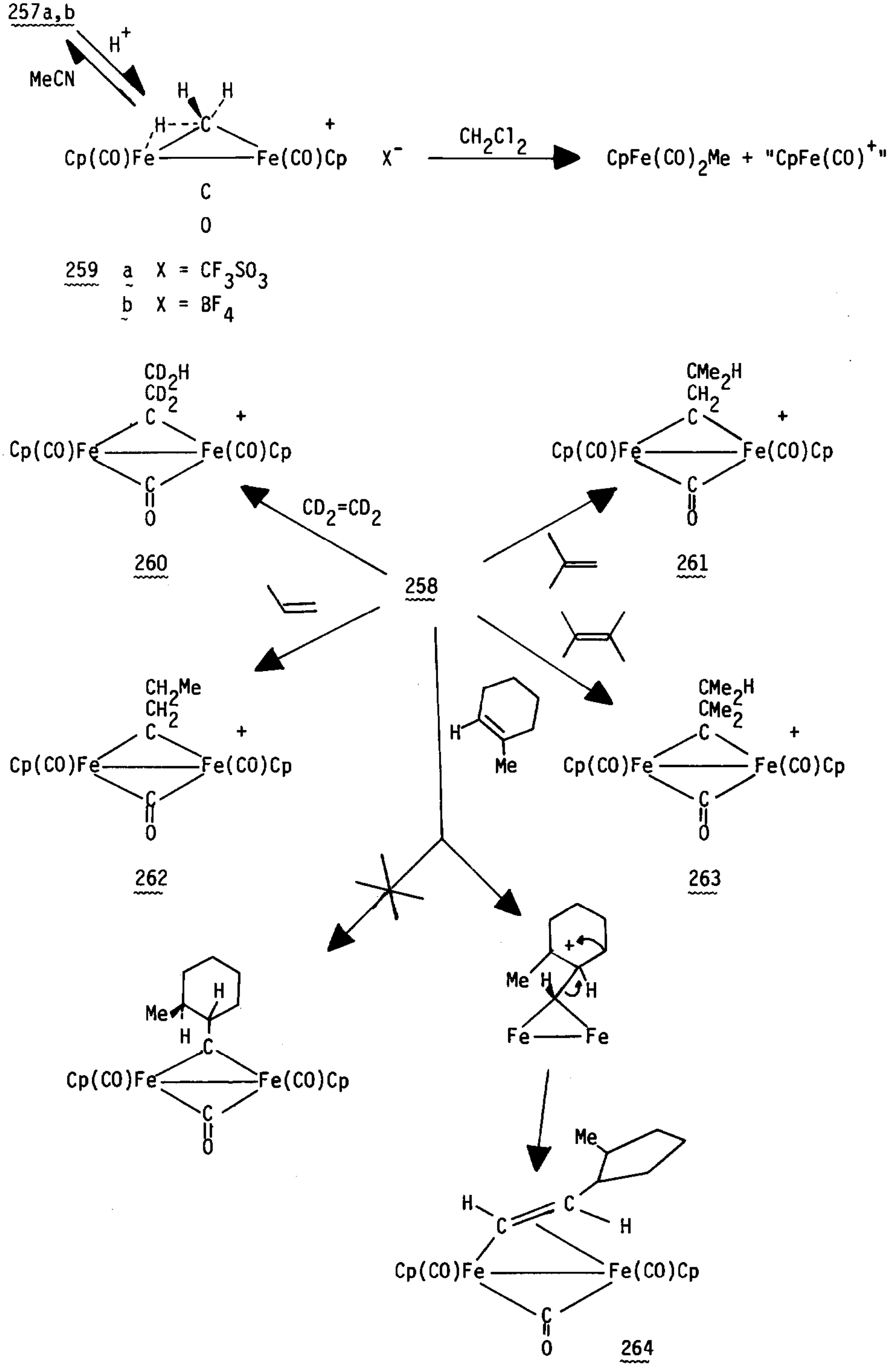
255 Cp* = $\eta^5\text{-}Me_5C_5$
a R = H, b R = Me

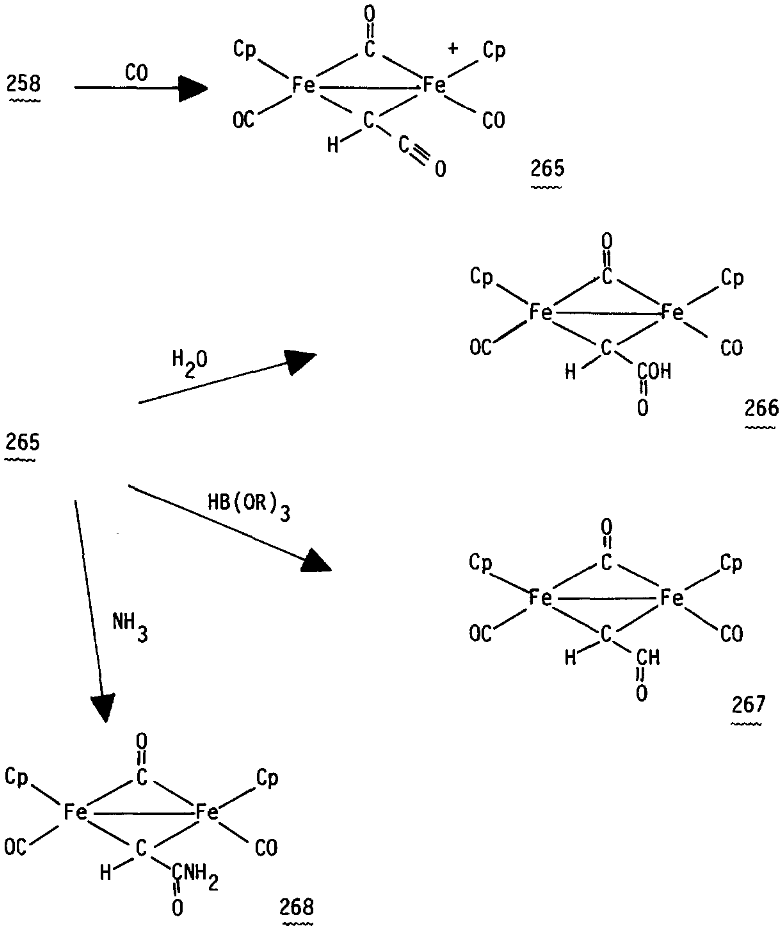
Photolysis of $Cp_2Fe_2(CO)_4$ and $[CpFe(CO)_2]_2Hg$ *in vacuo* with and without the presence of nitrosodurene and also in air gave paramagnetic products which were characterized by ESR [220].

Some complexes containing μ-alkylidene groups have already been discussed in the section on Metal Alkyl Complexes under METAL-CARBON σ-BONDED SPECIES. Scheme 30 presents chemistry involving binuclear μ-alkylidene, -alkylidyne, and -methyl complexes containing Cp ligands. This *cis* ⇄ *trans* isomerization of 257 is faster than that of 256. 258 is the first example of a μ-CH complex containing two transition metals. Only one isomer of 259 was detectable by NMR [221]. 258 behaves like a 2^o carbonium ion and undergoes reactions analogous to hydroboration or hydrozirconation. The additions producing 261-263 are regiospecific [222]. 258 also reacts with CO giving 265, an organometallic analogue of an acylium ion, which reacts with nucleophiles producing 266, 267 and 268 [223]. The X-ray structure of 265 was established [223].

SCHEME 30

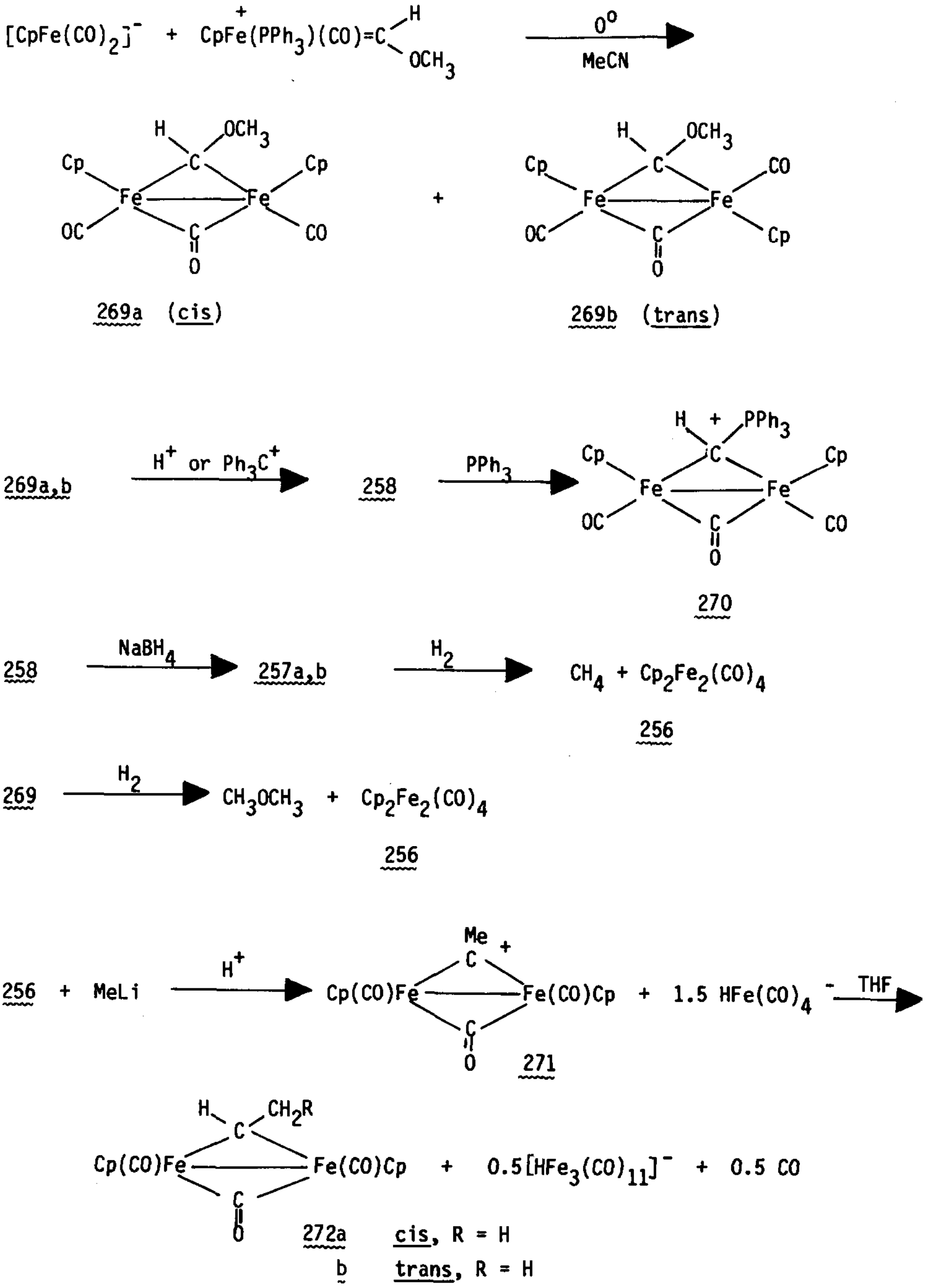


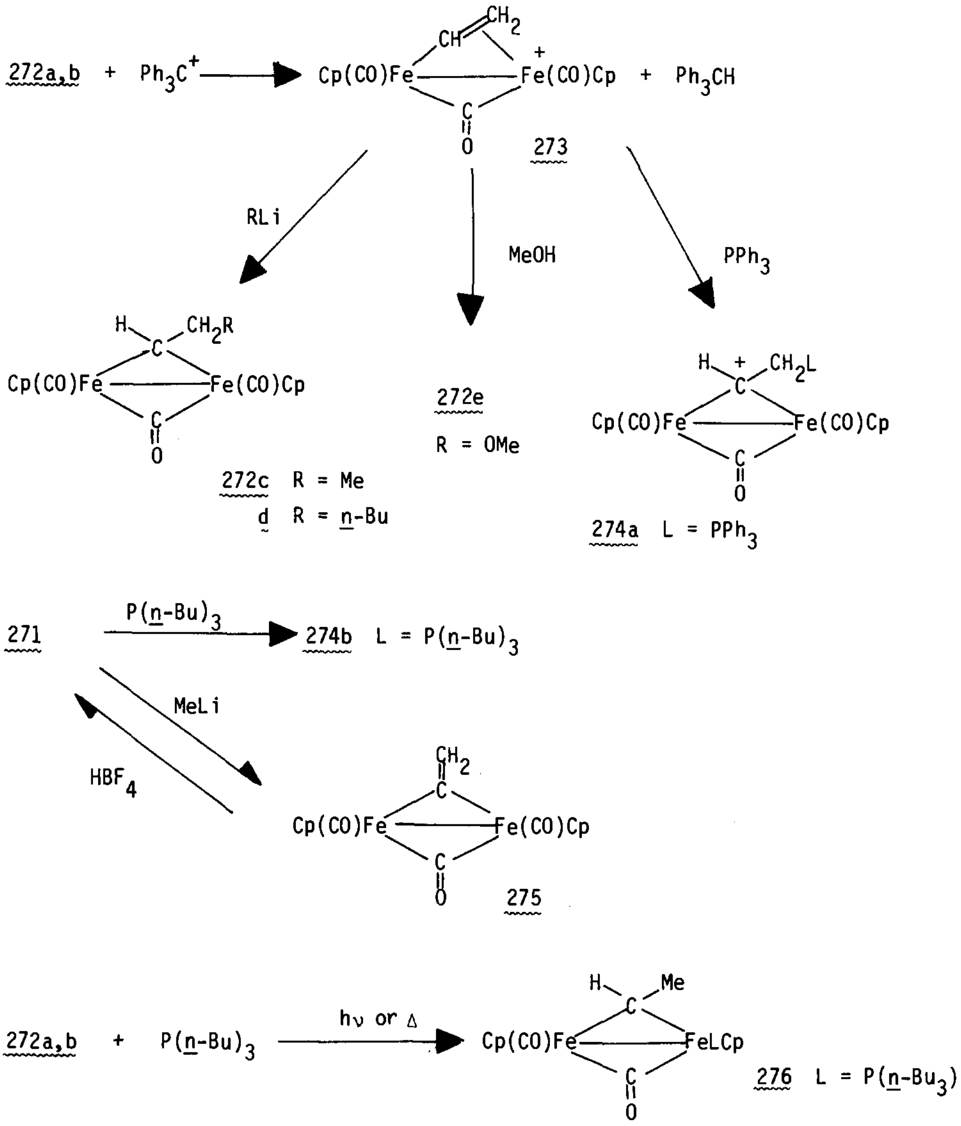

257a,b
H+
MeCN
Cp(CO)Fe
Fe(CO)Cp
X⁻
CH2Cl2
CpFe(CO)2Me + "CpFe(CO)+"
259 a X = CF3SO3
b X = BF4
CD2=CD2
260
258
261
262
263
264
Me
H
Fe
Fe



As Scheme 31 depicts, 258 is also accessible from 269a,b (which exists as an inseparable isomer mixture). In this work 258 was trapped by PPh_3 which converted it to 270. It was also converted to 257a,b by treatment with $NaBH_4$. Reactions of 257 and 269 with H_2 seem to involve addition of H_2 to the bridging alkylidene. Methyl-substituted analogues of 258 and 269 (namely 271 and 272) were also prepared by routes shown. The crystal structure of 272a was reported in 1981. Reaction of 272 with Ph_3C^+ produces 273 which reacts with nucleophiles giving substituted analogues of 272. 271 is deprotonated by MeLi to yield the μ-vinylidene complex 275. The sequence of reactions starting with conversion of 256 to 271 and 272a,b converts μ-CO to μ-alkylidene and -vinylidene ligands [224, 143].

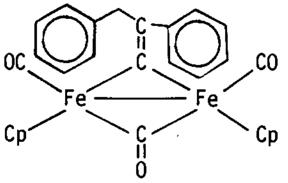
SCHEME 31


[CpFe(CO)2]⁻ + CpFe(PPh3)(CO)=C(H)OCH3
0°
MeCN
269a (cis)
269b (trans)
269a,b
H⁺ or Ph3C⁺
258
PPh3
270
258
NaBH4
257a,b
H2
CH4 + Cp2Fe2(CO)4
256
269
H2
CH3OCH3 + Cp2Fe2(CO)4
256
256 + MeLi
H⁺
Cp(CO)Fe—Fe(CO)Cp
271
+ 1.5 HFe(CO)4⁻
THF
Cp(CO)Fe—Fe(CO)Cp
+ 0.5[HFe3(CO)11]⁻ + 0.5 CO
272a cis, R = H
b trans, R = H

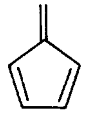


The crystal structure of the μ-vinylidene complex 277 was published [225]. 279 was one of the products of a reaction between 278 and $Fe_2(CO)_9$ in THF [226].

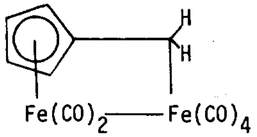
Scheme 32 shows some chemistry of complexes bound together by a Me_2Si bridge, but having no Fe-Fe bonds [227]. 281c (R = CH_2Ph, L = CO) was found to display enhanced photochemical reactivity compared to the corresponding mononuclear species producing biphenyl and Fe-Fe-bonded species via a free-radical process on irradiation [228].



277

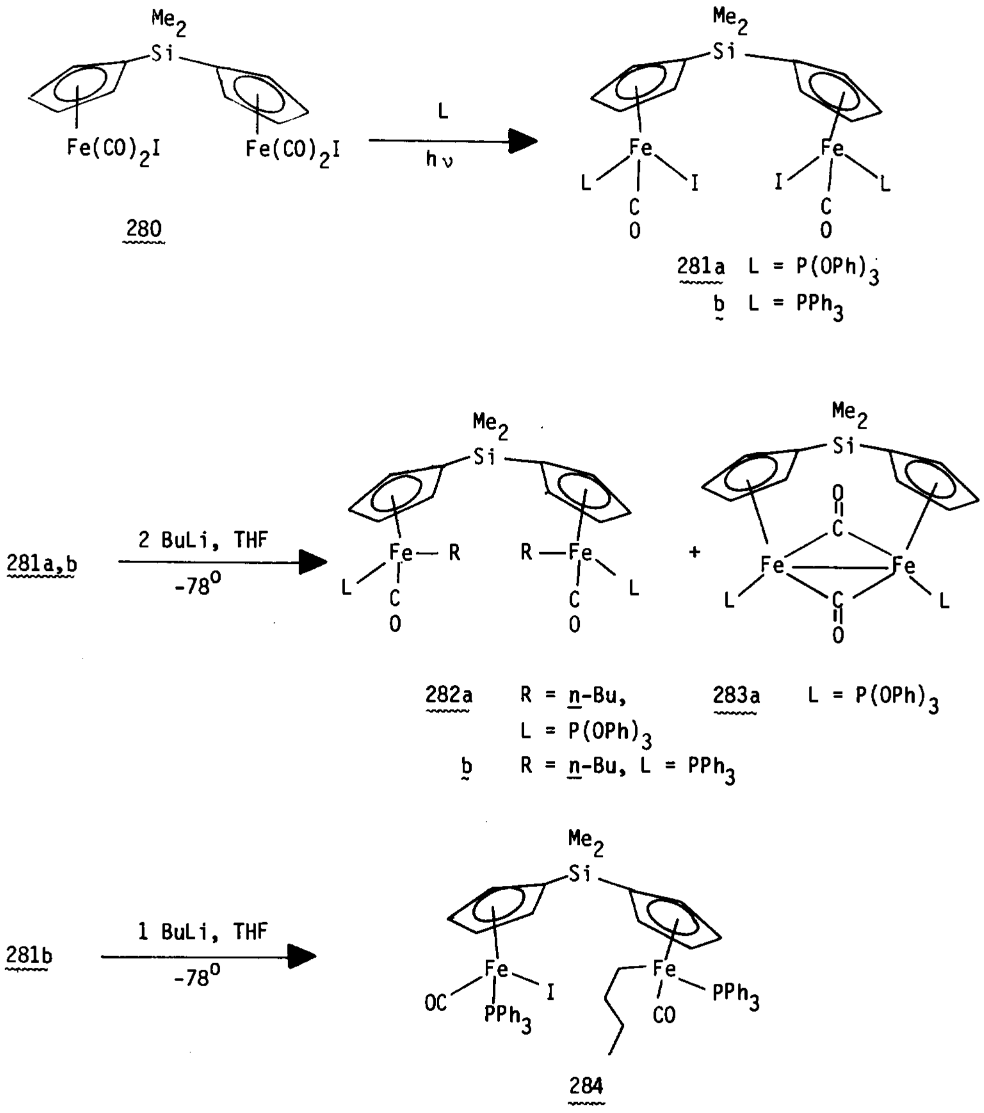


278



279

SCHEME 32



280

281a L = P(OPh)$_3$
b L = PPh$_3$

281a,b

282a R = n-Bu,
L = P(OPh)$_3$
b R = n-Bu, L = PPh$_3$

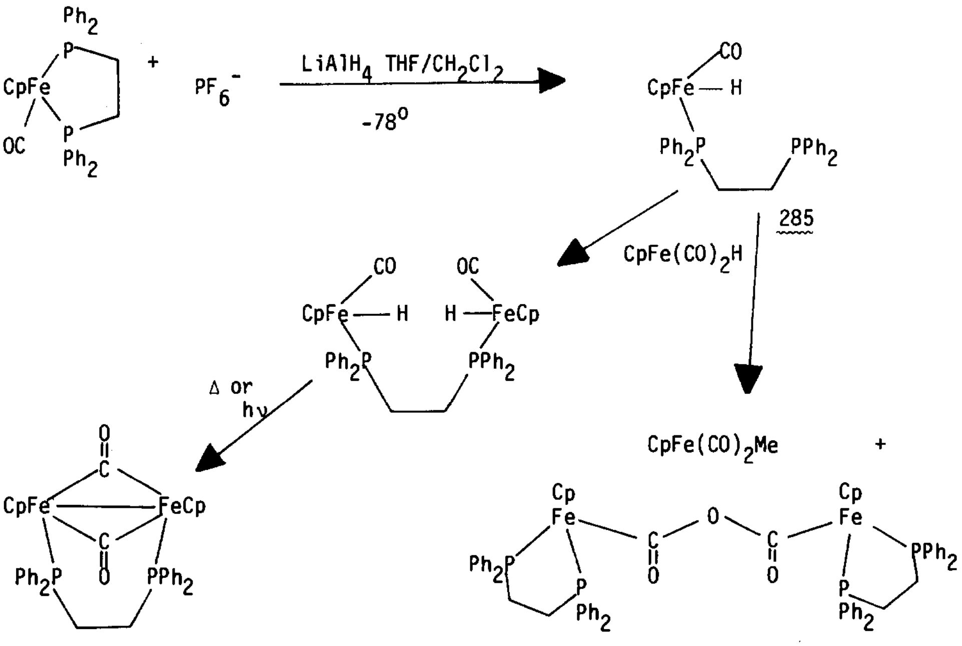
283a L = P(OPh)$_3$

281b

284

A sequence of reactions leading to a dimer containing a μ-diphos, 286, is seen in Scheme 33 [229]. 285 disproportionates to $CpFe(CO)_2Me$ and 287 [230].

SCHEME 33



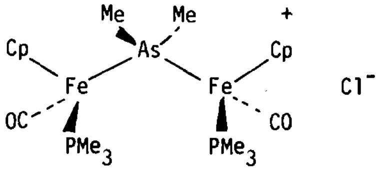
286

287

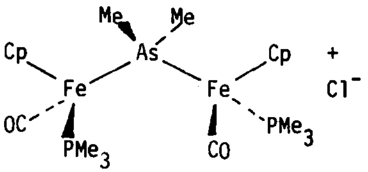
Photochemical reaction of 257 with $Ph_2PCH_2PPh_2$ and subsequent protonation affords $[Cp_2Fe_2(\mu\text{-}CH_3)(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)]PF_6$, the P-substituted analogue of 259. The X-ray structure of this compound was determined and H atoms were located. An Fe-H-C three-center interaction of the type indicated in 259 was found [231].

The complexes $CpFe(CO)(PMe_3)EMe_2$ (E = As, P) can be quaternized at the Group V atom. They were also found to react with 2RPhPCl to oxidize the Group V atom producing $CpFe(CO)(PMe_3)(EMe_2Cl_2)$ (E = As, P). The P compound is stable and was isolated and its X-ray structure determined. The As compound reacts with another mole of starting material affording 288a,b [232].

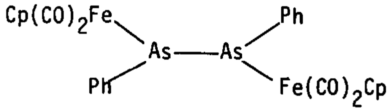
The cyclic arsines c-$(AsPh)_6$ and c-$(AsMe)_5$ react with $Cp_2Fe_2(CO)_4$ yielding 289 and 290, respectively. The X-ray structure of 289 was reported [233].



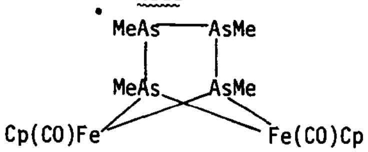
288a



288b



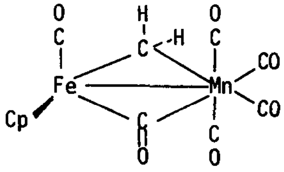
289



290

Several heterobimetallic complexes containing Cp were reported. When $CpFe(CO)_2H$ and $Mn_2(CO)_8(PPh_3)_2$ were allowed to react in room light under argon, the products were $CpFe(CO)_2Mn(CO)_5$, $Cp_2Fe_2(CO)_4$, $HMn(CO)_4(PPh_3)$, $Mn_2(CO)_8(PPh_3)_2$, $Cp_2Fe_2(CO)_3(PPh_3)$ and $Mn_2(CO)_9(PPh_3)$. This mixture suggests the presence of seventeen-electron species which combine unselectively [234].

The structures of two crystalline forms of 291 were both found to exhibit the same geometry for the complex [235]. 292 was prepared from the reaction of $[CpFe(CO)(NCMe){=}C(SMe)_2]^+$ and $[Co(CO)_4]^-$. On oxidation 292 gives 345b, $[CpFe(CO)_2{=}C(SMe)_2]^+$ [236].



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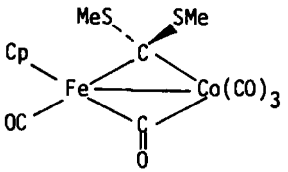
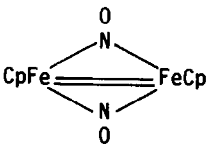
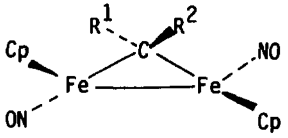


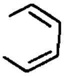
292

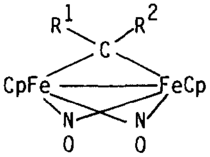
Treatment of the nitrosyl dimer 293 with substituted diazomethanes leads to 294a-c or 295a-d depending on the substituents [237].



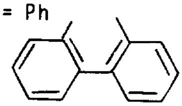
293

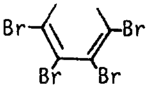


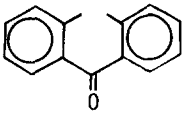
294a $R^1 = R^2 = H$
b $R^1 = H$, $R^2 = Me$
c $R^1, R^2 =$ 



295a $R^1 = R^2 = Ph$

b R^1, R^2 = 

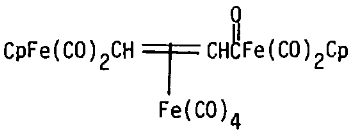
c R^1, R^2 = 

d R^1, R^2 = 

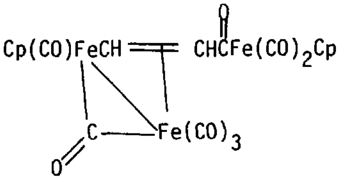
Multinuclear Species

Na[CpFe(CO)$_2$] and ClCH=CHC(O)Cl react to give Cp(CO)$_2$FeCH=CHC(O)Fe(CO)$_2$Cp which, on treatment with Fe$_2$(CO)$_9$ affords 296 and 297 [238].

Photoacoustic spectra of the tetranuclear complexes Cp$_4$Fe$_4$(CO)$_4$ and Cp$_4$Fe$_4$S$_4$ were reported [216].

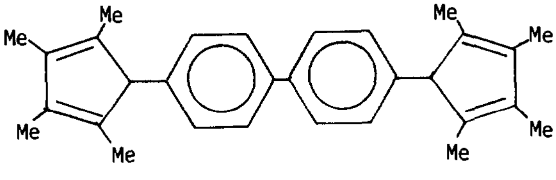


296

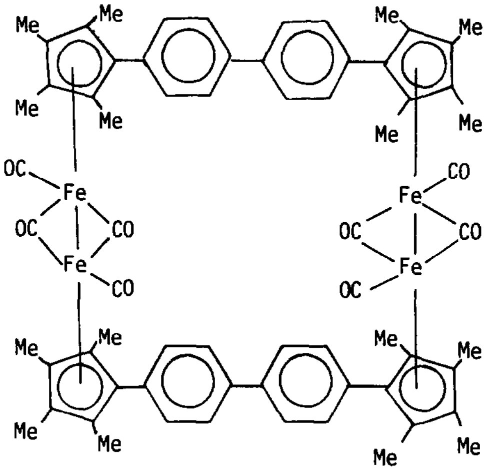


297

Fe(CO)$_5$ and 298 afford 299 [238a].

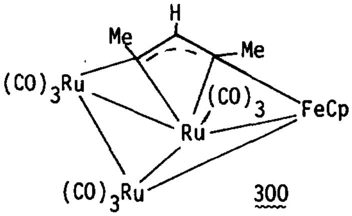


298



299

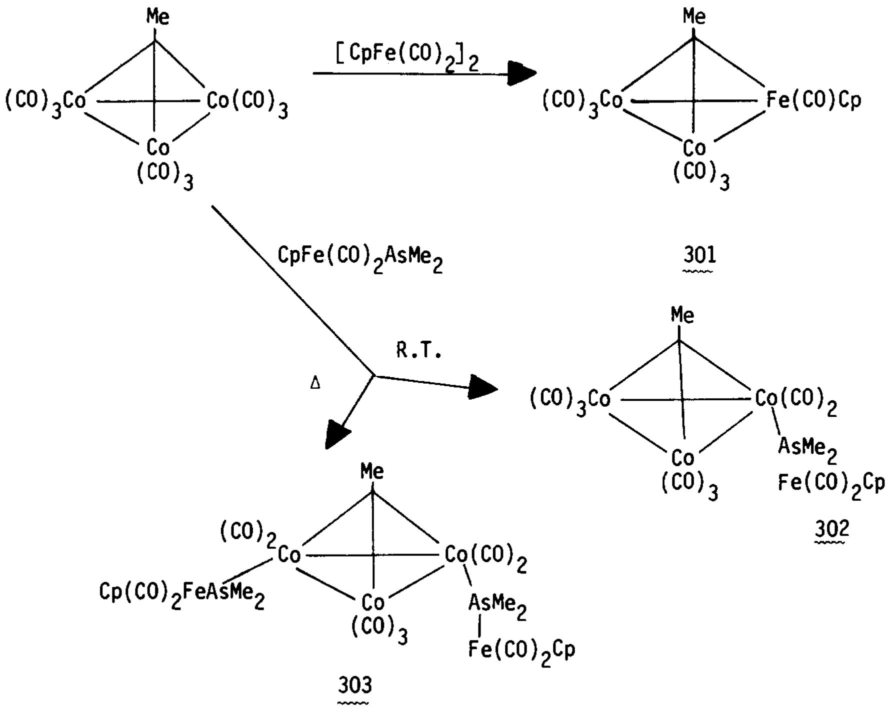
Heteronuclear complexes reported include 300, prepared from $[CpFe(CO)_2]_2$ and $HRu_3(CO)_9C_5H_7$ [239].



300

Scheme 34 shows the preparation of some tetranuclear and pentanuclear complexes containing Co [240, 241].

SCHEME 34



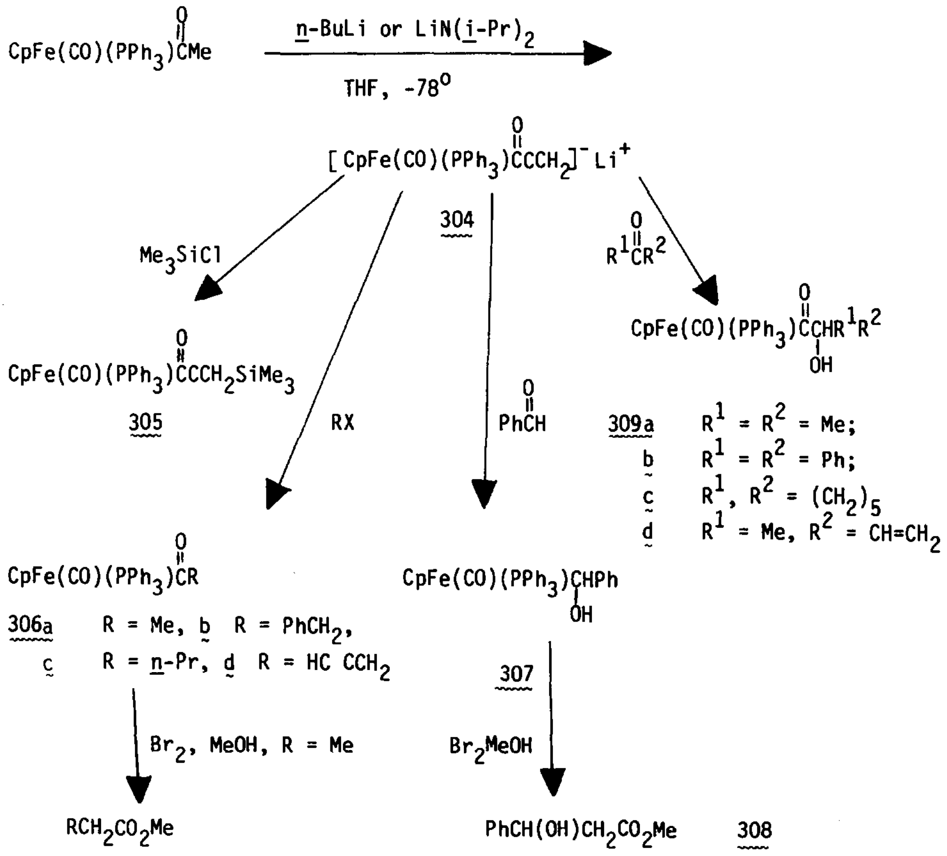
Alcoholysis of $[CpFe(CO)_2]_2Zn$ produced $[ROZn\{Fe(CO)_2Cp\}]_4$ (R = Me, Et) and $CpFe(CO)_2H$. The X-ray structure of the methyl tetramer shows that it involves two interpenetrating tetrahedra, one of O atoms (coordinated to Me and Zn) and one of Zn atoms (coordinated to Fe) [242].

Anionic and Cationic Species

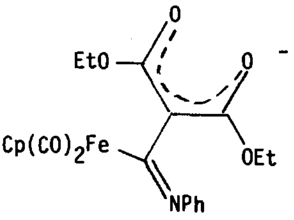
Treatment of $[(\eta^5\text{-}Me_5C_5)Fe(CO)_2]_2$ with Na/Hg gives no reaction. However, a K mirror effects reduction of the dimer to $K[(\eta^5\text{-}Me_5C_5)Fe(CO)_2]$ in THF. The anion can be methylated by MeI affording an 80% yield of $(\eta^5\text{-}Me_5C_5)Fe(CO)_2Me$ [243].

Scheme 35 displays the preparation and chemistry of the anion 304 [244].

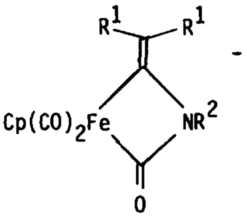
SCHEME 35



Ketenimines form adducts with $[CpFe(CO)_2]^-$ in which they behave as electron-pair acceptors. In the complex 310, ν_{CO} are shifted about 150 cm^{-1} to

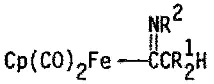


310



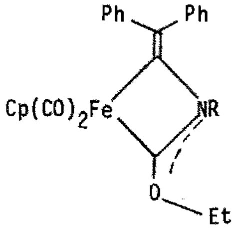
311a R^1 = Ph, R^2 = Me
b R^1 = R^2 = Ph
c R^1 = Me, R^2 = Ph
d R^1 = CO$_2$Et, R^2 = Ph

higher energy than in the parent anions. Less electronegative ketenimines give adducts 311 displaying only one CO stretch; these adducts result from attack of nucleophilic N on coordinated CO. Protonation affords neutral 312 [245]. In contrast alkylation or benzoylation occur on O producing 313 and 314, respectively. The X-ray structure of 313a confirmed the geometry depicted [246].

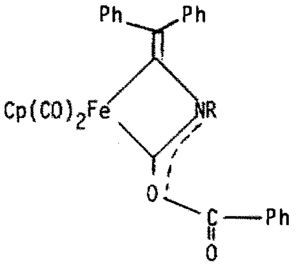


$Cp(CO)_2Fe\text{—}C(=NR^2)CR^1_2H$

312a-d

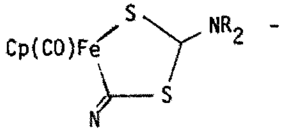


313a R = Me, b R = Ph

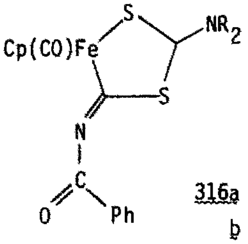


314a R = Me, b R = Ph

CN$^-$ reacted with $CpFe(CO)_2SC(S)NR_2$ producing 315 which can be benzoylated on N yielding 316. The X-ray structure of 316b was determined [247].



315a R = Me
b R = Et



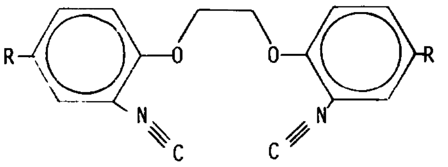
316a R = Me
b R = Et

M.O. calculations were carried out to predict sites of addition and nucleophilic attack by both hard and soft reagents on $[CpFe(CO)_3]^+$ [177]. Calculations of ^{13}C shifts were made, also for $[CpFe(CO)_3]^+$ [199].

Mössbauer parameters were correlated with IR, ^1H NMR and redox data for $[CpFe(CO)_3]PF_6$ as well as $[CpFe(CO)_2(PPh_3)]^+$, $[CpFe(CO)_2(CNMe)]^+$ and $[CpFe(CO)(dppe)]^+$ [248].

Treatment of $(\eta^5\text{-}Me_5C_5)Fe(CO)_2Br$ with $AlCl_3$ and CO gave $[(\eta^5\text{-}Me_5C_5)Fe(CO)_3]^+$ [243].

The X-ray structure of $[CpFe(CO)(CNMe)_2]BF_4$ was reported [217]. Several cationic complexes of the chelating diisocyanides 317a,b containing thirteen-membered chelate rings were synthesized. These were: $[CpFe(CO)(317a)]^+$, $[CpFe(CS)(317a)]^+$ and $[CpFe(CS)(317b)]^+$ [249].



317a R = H
b R = t-Bu

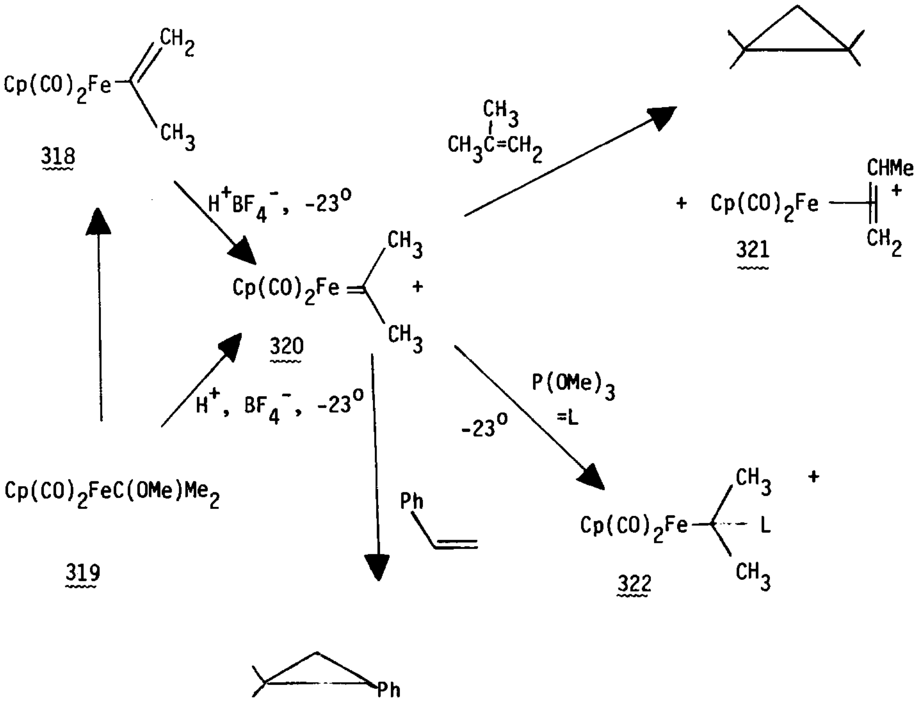
Reduction of $[CpFe(CO)_2L]^+$ (L = CO, PPh_3, $P(OPh)_3$, Me_2CO) with sodium amalgam or Cr^{2+} was found to give $Cp_2Fe_2(CO)_4$ [208].

Methylation of $CpFe(CO)_2CH_2SMe$ (for which a new synthesis was reported) yields $[CpFe(CO)_2CH_2SMe_2][SO_3F]$. The X-ray structure showed that the cation has a very short Fe-C bond length of 206 pm, suggesting the possibility of carbene-like behavior [250].

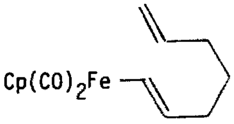
Carbene, Alkylidene and Vinylidine Species

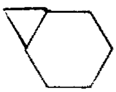
Scheme 36 shows the synthesis and reactivity of the cationic carbene complex 320 [251].

SCHEME 36

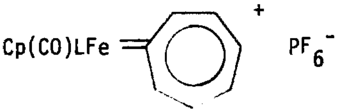


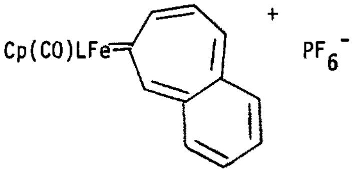
320 and related carbenes $[Cp(CO)_2Fe{=}CMeH]^+$ and $[Cp(CO)_2Fe{=}CMePh]^+$ were generated *in situ* by protonation of the corresponding neutral vinyl species with HBF_4. These carbenes were found to react with 1-decene, isobutylene, styrene and α-methylstyrene to produce cyclopropanes. One case of intramolecular cyclopropanation occurred affording norcarane, 324, from 323 [252].


323


324

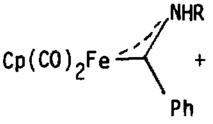
The X-ray structures of 325 and 326a were determined at -35°C. The seven-membered rings were planar and aromatic. The eleven-member ring system of 326a is planar within 1.1°. Short Fe-C distances were found [253].

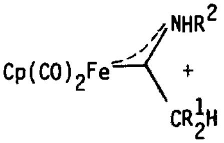

325a L = CO
b L = P(*n*-Bu)$_3$


326a L = CO
b L = P(*n*-Bu)$_3$

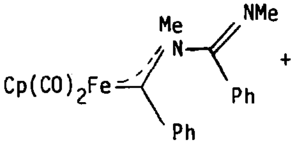
The NMR spectra of 325a,b and 326b were studied down to -105°. No temperature dependence was observed for 325a while 325b and 326b exhibited rotational barriers with that of 326b greater [254].

Reaction of $[CpFe(CO)_2]^-$ with PhC(=NR)Cl and HCl in THF at 0° gave carbene complexes 327a-d isolated as PF_6^- salts [255]. When HCl is omitted and the reaction conducted at reflux, the iminoacyl analogues of 327c,d were isolated.

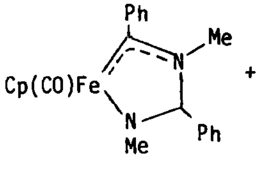

327a R = Me
b R = CH_2Ph
c R = *i*-Pr
d R = Ph


328a R^1 = Ph, R^2 = Me
b R^1 = R^2 = Ph
c R^1 = Me, R^2 = Ph
d R^1 = CO_2Et, R^2 = Ph

328a-d were synthesized by protonation of 312a-d [244]. When PhC(=NMe)Cl is employed, the carbene cations 329 and 330 are products. 330 results from intramolecular CO displacement on 327 by N [256].

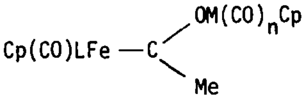


329



330

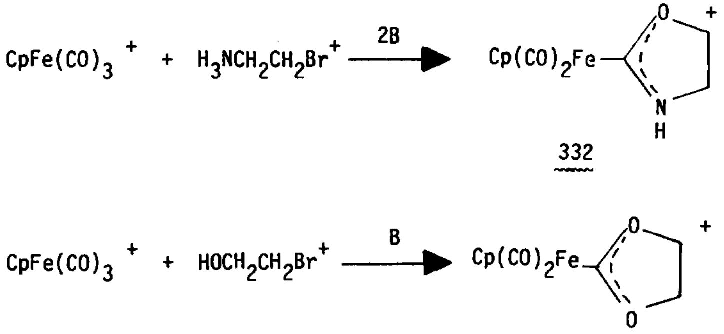
Carbene complexes with O heteroatoms were also reported. Reactions between Cp(CO)LFeC(O)Me (L = CO, PPh_3) and $[CpFe(CO)_2(L')]^+$ or $[CpM(CO)_3(L')]^+$ (M = Mo, W; L' = isobutylene, THF) afford 331a-f. 331c is also produced from the reaction between $CpFe(CO)_2Me$ and $[CpMo(CO)_3(THF)]^+$, a manifestation of CO insertion promoted by electrophiles [257].



331a L = CO, M = Fe, n = 2
b L = PPh_3, M = Fe, n = 2
c L = CO, M = Mo, n = 3
d L = PPh_3, M = Mo, n = 3
e L = CO, M = W, n = 3
f L = PPh_3, M = W, n = 3

Carbene complexes having two heteroatoms were synthesized as shown in Scheme 37. Products with six-membered rings could not be made [258].

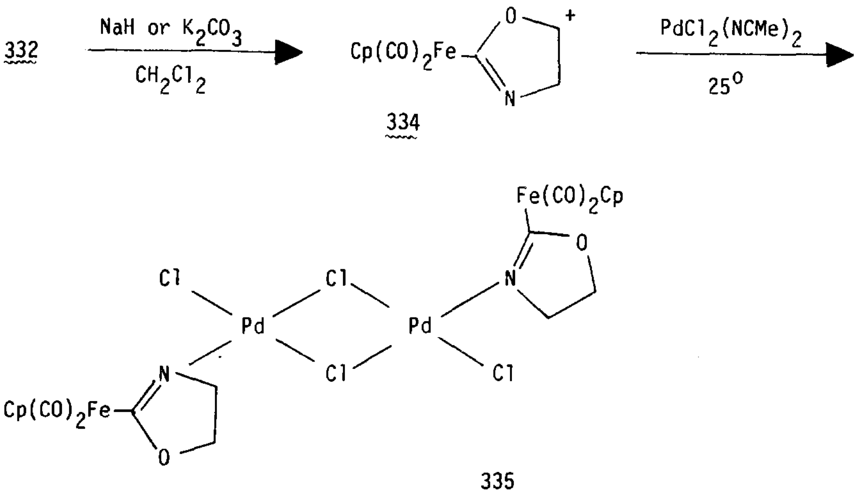
SCHEME 37



332

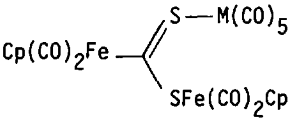
333

B = NaH, K_2CO_3, NEt_3

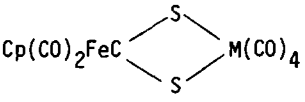


335

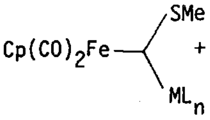
Sulfur-containing complexes which contain other metals were also synthesized. When $M(CO)_5(THF)$ (M = Mo, W) react with $CpFe(CO)_2C(S)SFe(CO)_2Cp$, 336a,b are the products [259]. A reaction of $[CpFe(CO)_2(CS_2)]^-$ with $M(CO)_5Br$ (M = Mn, Re) produces 337a,b. These react with PPh_3 to substitute one of the Mn or Re carbonyl ligands. The same reactants at -78° afford $Cp(CO)_2FeC(S)SRe(CO)_5$ which was methylated to the cationic complex 338a [260,261]. 338b is prepared by methylation of $[CpFe(CO)_2]_2CS_2$ [260].



336a M = Mo, b M = W



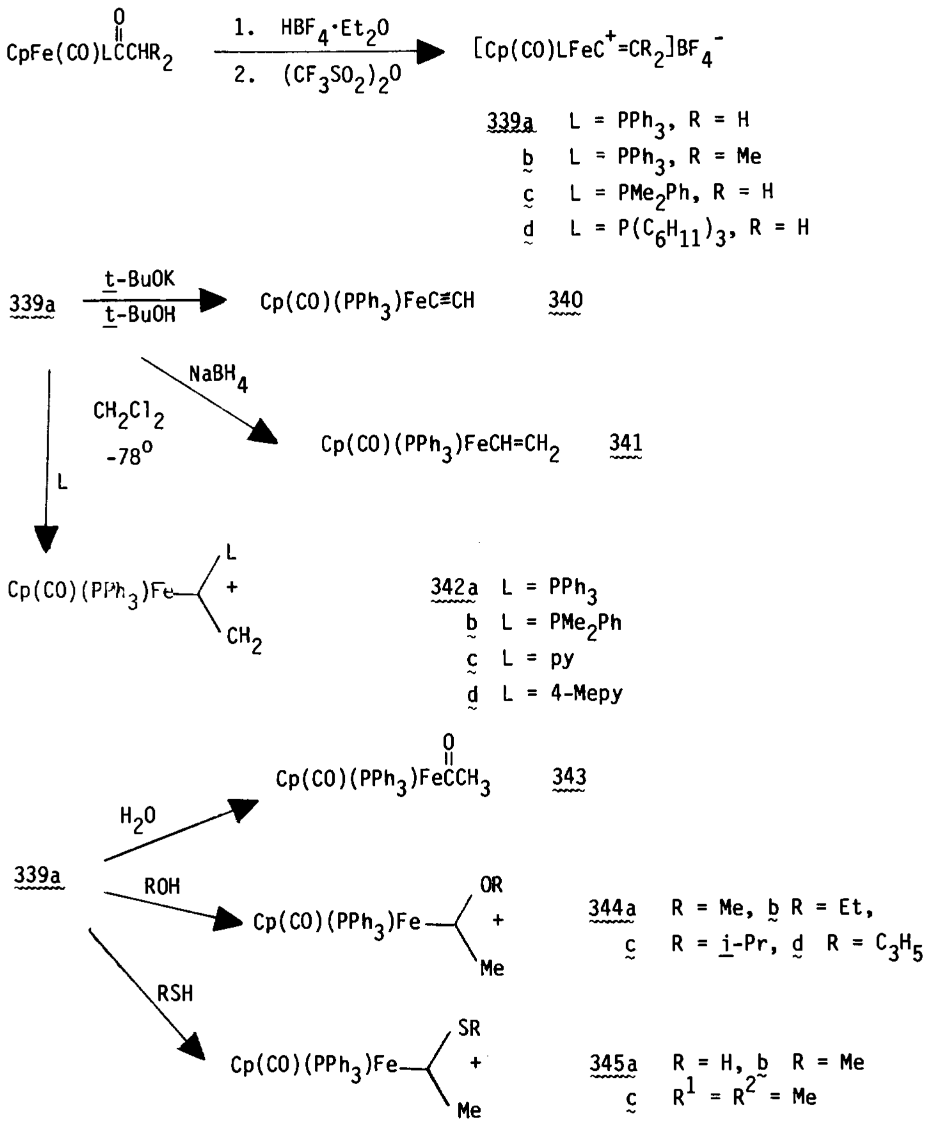
337a M = Mn, b M = Re

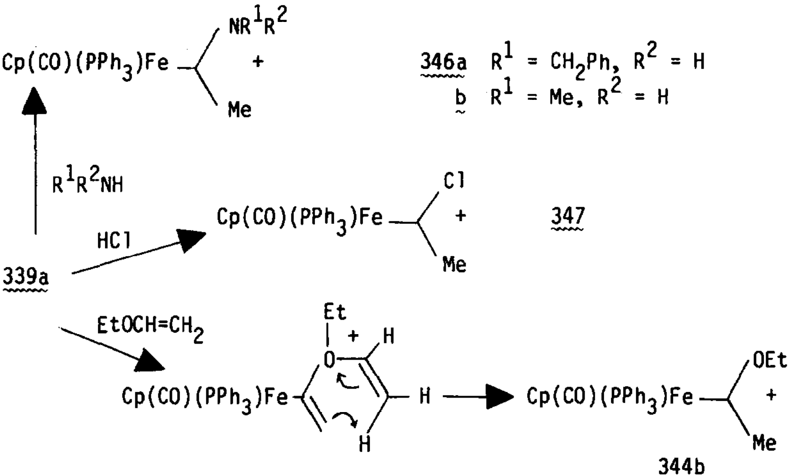


338a $ML_n = Re(CO)_5$
b $ML_n = Fe(CO)_2Cp$

Scheme 38 depicts the synthetic route to some vinylidene complexes 339a-d. 339a (whose X-ray structure was reported) undergoes a number of interesting reactions including deprotonation to give 340 and hydride addition to give 341 as well as adduct formation to give 342a-d [262]. A variety of species containing OH, NH, SH and C=C adds across the vinylidene double bond [263].

SCHEME 38



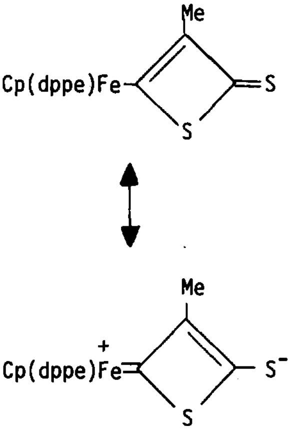


346a $R^1 = CH_2Ph$, $R^2 = H$
b $R^1 = Me$, $R^2 = H$

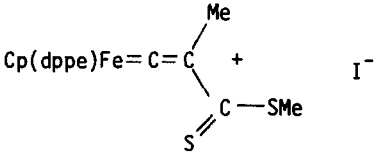
347

344b

Electrophilic CS_2 attacks the electron-rich triple bond of Cp(dppe)Fe-(C≡CMe) (dppe = bis(diphenylphosphino)ethane) affording 348 which was methylated to produce 349 which was characterized by its X-ray structure [264].



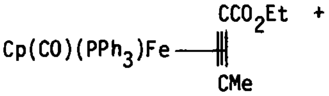
348



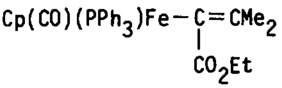
349

Alkene and Alkyne Derivatives

Regioselective nucleophilic addition to 350 occurs on reaction with Li-(Me_2Cu) producing 351 [265], whose X-ray structure was determined.



350



351

Compounds Containing M-C Bonds

Irradiation of CpFe(CO)$_2$Me in the presence of L = PPh$_3$, P(O-o-tolyl)$_3$, P(OCH$_2$)$_3$CEt, ^{13}CO in isooctane gave CpFe(CO)LMe with $\Phi \sim 0.7$ independent of the nature or concentration of L. This result suggests the presence of CpFe(CO)Me and not (η^3-C$_5$H$_5$)Fe(CO)$_2$Me produced by ring slippage. The value of Φ rules out homolytic methyl cleavage or methyl migration as primary photoreactions. However, no CpFe(CO)Me could be detected by photolysis in inert paraffin matrices at 44-77 K.

When CpFe(CO)$_2$Me is irradiated in isooctane in the presence of 1M 1-pentene, CO is lost and CpFe(CO)(1-pentene)Me is formed at temperatures as low as -90^{o}C. On warming to -20^o, almost complete regeneration of CpFe(CO)$_2$Me occurs. Evidently the dicarbonyl complex is very photolabile at -90^{o}C while the olefin complex is very thermally labile.

Irradiation of CpFe(CO)$_2$Et (which contains a β-H) yields CpFe(CO)$_2$H and C$_2$H$_4$, the products of β-elimination. In the presence of large quantities PPh$_3$, only CpFe(CO)$_2$(PPh$_3$)Et is formed on irradiation. With small amounts of PPh$_3$ present, irradiation of other alkyl complexes produces CpFe(CO)(PPh$_3$)(alkyl) and CpFe(CO)(PPh$_3$)H. This behavior is consistent with capture by PPh$_3$ of the primary photoproduct and the product from alkene loss after β-elimination, respectively. A sufficiently large [PPh$_3$] captures all of the CpFe(CO)(alkyl) intermediate and supresses β-elimination.

The β-elimination is reversible as shown by the presence of some 2-pentene in the photolysis products of CpFe(CO)$_2$(n-C$_5$H$_{11}$). This reversibility can account for the already known production of isomeric alkene mixtures on thermolysis of CpFe(CO)(PPh$_3$)(alkyl) complexes.

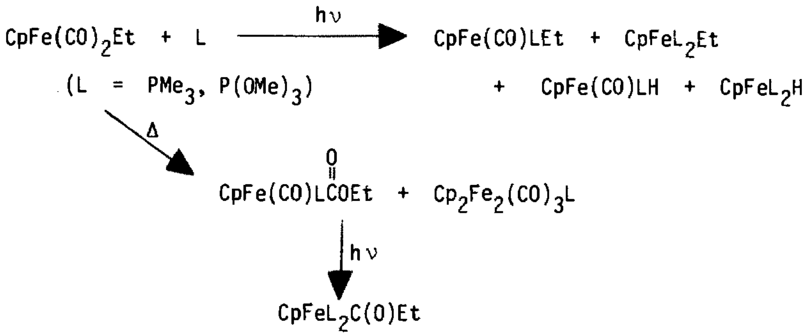
Irradiation of CpFe(CO)$_2$Et in inert matrices at 77 K resulted in the detection of only CpFe(CO)$_2$H, but not CpFe(CO)(C$_2$H$_4$)H. However, irradiation of CpFe(CO)$_2$(n-C$_5$H$_{11}$) in neat 1-pentene at -140^{o}C gave CpFe(CO)(1-pentene)(n-C$_5$H$_{11}$) which, on warming to -40^o produced CpFe(CO)$_2$H. In the presence of PPh$_3$, CpFe(CO)(PPh$_3$)(n-C$_5$H$_{11}$) was detected at -78^{o}C.

The activation energy for β-H transfer to Fe was estimated to be ~6 kcal mol^{-1}, lower than the ~10 kcal mol^{-1} seen for Mo and W alkyls [266].

Electrocatalysis of insertion of CpFe(CO)$_2$Me induced by PPh$_3$ giving CpFe(CO)(PPh$_3$)C(O)Me was observed [267].

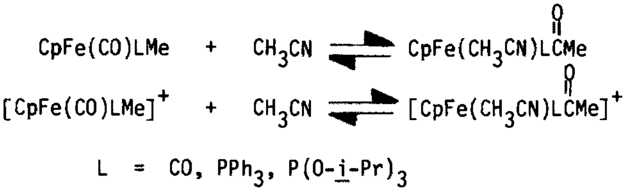
Scheme 39 shows some substitution and insertion reactions consistent with the photochemical results discussed above [268]. Although the X-ray structure of CpFe(PMe$_3$)$_2$C(O)Et shows the propionyl group to be η^1-coordinated, NMR and IR data were said to be more typical of η^2-coordination [268].

SCHEME 39



Cyclic voltammetric methods were employed to show that the equilibrium constant for the second reaction of Scheme 40 is $\geq 10^{12}$ larger than that for the first reaction. The difference is primarily attributable to the increase in the forward rate constant for insertion in the seventeen-electron cation [269].

SCHEME 40



$$CpFe(CO)LMe + CH_3CN \rightleftharpoons CpFe(CH_3CN)L\overset{O}{\overset{\|}{C}}Me$$

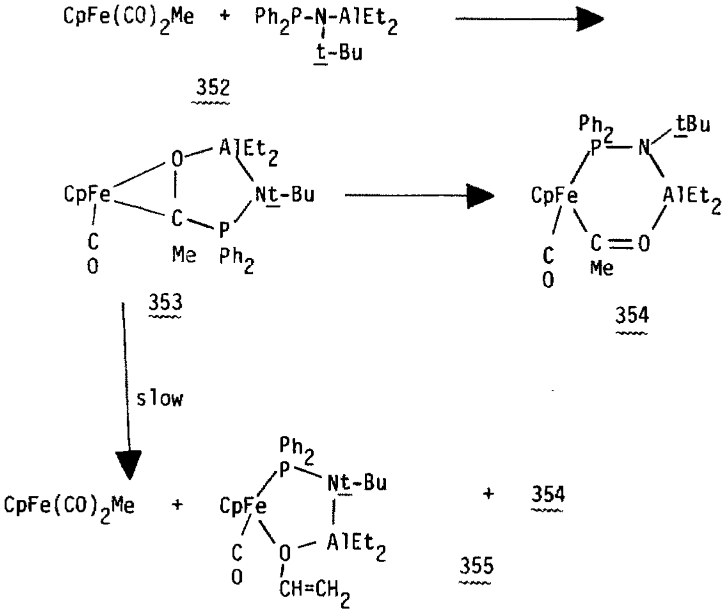
$$[CpFe(CO)LMe]^+ + CH_3CN \rightleftharpoons [CpFe(CH_3CN)L\overset{O}{\overset{\|}{C}}Me]^+$$

$$L = CO,\ PPh_3,\ P(O\text{-}\underline{i}\text{-}Pr)_3$$

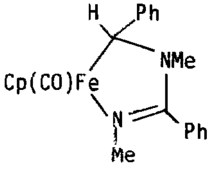
CO insertions are known to be enhanced in the presence of Lewis acids. Treatment of $CpFe(CO)_2Me$ with BF_3 followed by diborane reduction of the products yields CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 with most of the products being C_2. In the absence of BF_3, no chain growth was observed in the products [270].

An amphoteric ligand **352** containing a Lewis acid group and a Lewis base capable of bonding to Fe was employed to achieve the results set out in Scheme 41. The X-ray structure of **353** was reported. The mixture of **354** and **355** from the slow decomposition of **353** cannot be separated [271].

SCHEME 41

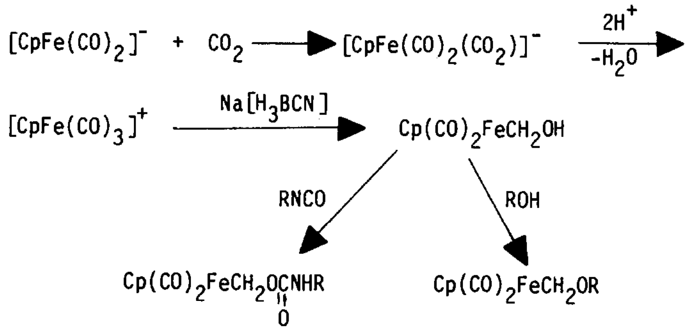


356, along with 329 and 330, results from the reaction between $[CpFe(CO)_2]^-$ and PhC(=NMe)Cl [256].


356

The reactions diagrammed in Scheme 42 lead to the alkyl complexes 357 and 358 and represent an overall conversion of CO_2 to C_2 or higher coordinated ligands [272].

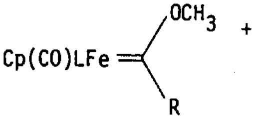
SCHEME 42



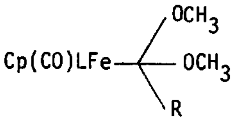
357a R = Me
b R = Ph

358a R = Me
b R = Et

Ketal complexes, 360a-c, were prepared by treating the carbene complexes 359a-c with methoxide. 360a,b can be converted back to carbene complexes by protonation or reaction with Ph_3C^+ [273].

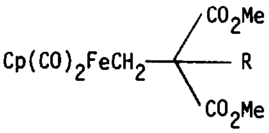


359a L = CO, R = H
b L = PPh_3, R = H
c L = CO, R = Ph



360a L = CO, R = H
b L = PPh_3, R = H
c L = CO, R = Ph

361b was synthesized from $[CpFe(CO)_2]^-$ and $XCH_2C(CO_2Me)_2$. It is stable in contrast to 361a which contains a β-H. Fe-C bond cleavage in 361b by H^+, Br_2, Ce(IV) and Hg(II) occurs without major amounts of ester group migration [274].

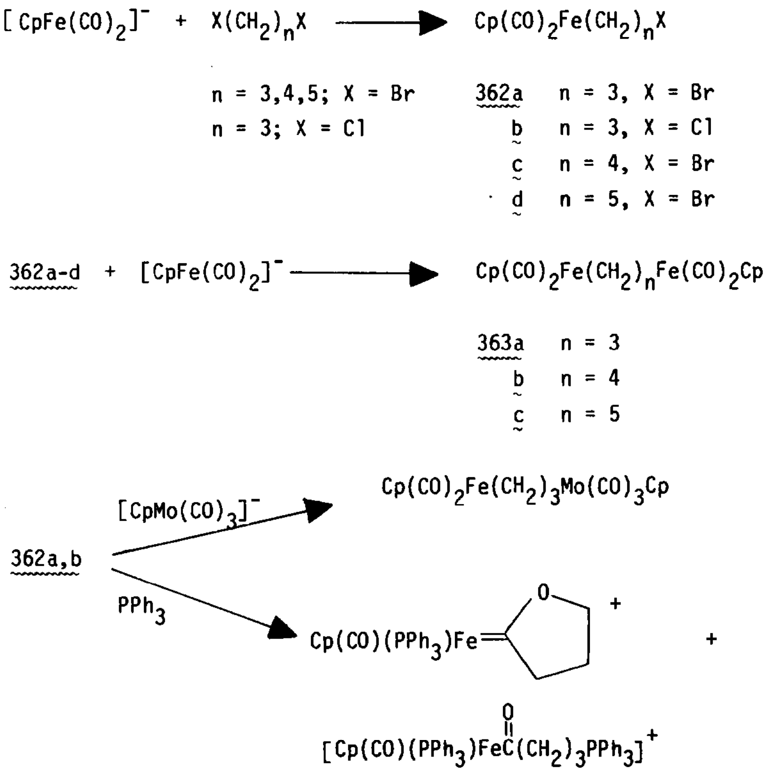


361a R = H
b R = Me

Contrary to earlier reports, cyclopropyl complexes can be prepared by photochemical decarbonylation of the appropriate acyls. Three such complexes were prepared by photolysis in acetone-d_6 rather than petroleum ether [275].

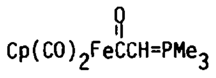
Some complexes were prepared from α,ω-halo-alkanes as shown in Scheme 43 [276].

SCHEME 43

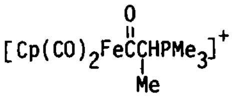


NMR evidence was presented for the presence of a formyl complex CpFe(diphos)C(O)H in the reduction of $[CpFe(diphos)CO]^+$ by $Li(AlH_4)$ or $Li(BHEt_3)$ between -70° and -50°C [277].

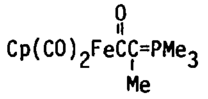
Methylation of 364 occurs at C to give 365 which reacts with $Me_3P{=}CH_2$ to produce 366 which in the presence of a trace of ylid, rearranges to 367 [278].


$\mathrm{Cp(CO)_2Fe\overset{O}{\overset{\|}{C}}CH{=}PMe_3}$

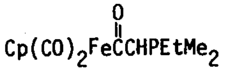
364


$[\mathrm{Cp(CO)_2Fe\overset{O}{\overset{\|}{C}}\underset{Me}{\underset{|}{C}}HPMe_3}]^+$

365

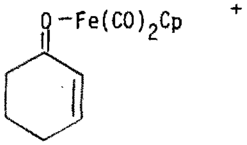

$\mathrm{Cp(CO)_2Fe\overset{O}{\overset{\|}{C}}\underset{Me}{\underset{|}{C}}{=}PMe_3}$

366

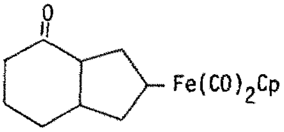

$\mathrm{Cp(CO)_2Fe\overset{O}{\overset{\|}{C}}CHPEtMe_2}$

367

The allyl group $CpFe(CO)_2(CH_2CH=CH_2)$ behaves as a 1,3-dipole in its reaction with 368 to afford 369 [279].

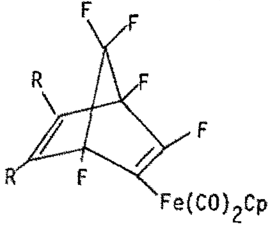


368



369

The fluoroalkyl complexes 370a,b result from treatment of the hexafluorodiene with $[CpFe(CO)_2]^-$ [280].



370a R = H

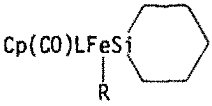
b R = Me

M.O. calculations on $CpFe(CO)_2C{\equiv}CH$, $CpFe(PH_3)_2C{\equiv}CH$, $CpFe(PH_3)_2CH{=}CH_2$ as well as the methylene complex $[CpFe(PH_3)_2CH_2]^+$ and the vinylidene complexes $CpFe(CO)_2{=}C{=}CH_2$ and $CpFe(PH_3)_2{=}C{=}CH_2$ (inter alia) were carried out. The methylene and vinylidene complexes were calculated to form strong Fe-C bonds whereas weak Fe-C bonds were calculated for vinyl and acetylide complexes [281].

Complexes Containing Group IV Ligands Other Than C

The ^{29}Si NMR spectra of $CpFeL_2R$ complexes (L = CO, phosphines; R = SiH_3, CH_2SiH_3, polysilyl) were measured [282].

Reaction of $[CpFe(CO)_2]^-$ with silacyclohexanes gave 371a-c which gave 371d-f on photolysis with PPh_3. The X-ray structure of 371f was reported [283].



371a L = CO, R = H

b L = CO, R = Me

c L = CO, R = Ph

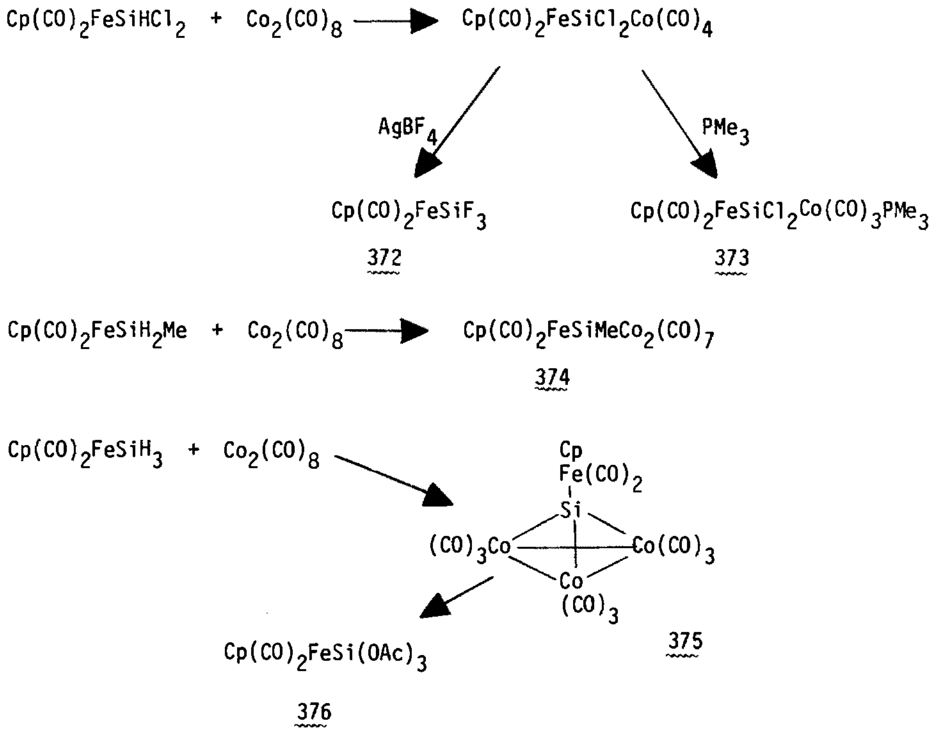
d L = PPh_3, R = H

e L = PPh_3, R = Me

f L = PPh_3, R = Ph

The synthesis and reactivity of some Fe-Si complexes containing Co is shown in Scheme 44 [284].

SCHEME 44



Reaction of $[CpFe(CO)_2][CpMo(CO)_3]SnCl_2$ with either $Co_2(CO)_8$ or $Tl[Co(CO)_4]$ affords $[CpFe(CO)_2][CpMo(CO)_3][Co(CO)_4]SnCl$ whose X-ray structure demonstrates tetrahedral coordination about Sn. Also prepared was $[CpFe(CO)_2][CpNi(CO)]$-$[Co(CO)_4]SnCl$ [285].

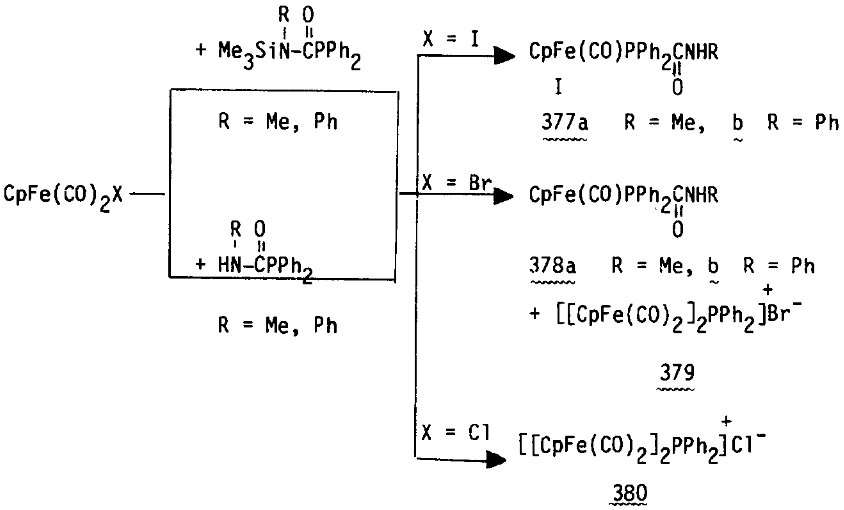
Photolysis of $CpFe(CO)_2SnPh_3$, $CpFe(CO)(PPh_3)SnPh_3$ and $CpFe(CO)_2PbPh_3$ were carried out in vacuo with and without the presence of nitrosodurene and also in the presence of air. ESR was employed to characterize the paramagnetic products [220].

Complexes Containing Group V Ligands

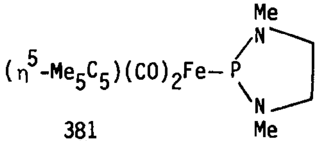
A kinetic study was made on the reaction of $CpFe(CO)(dmso)C(O)CH_2C_6H_{11}$ with phosphines. The rate of dmso displacement was found to drop as the cone angle of the phosphine increased [286]. The aminophosphines $Ph_2PN(R)\overset{*}{C}H(Me)Ph$ were found to be good resolving agents for CpFe(CO)LX. For example, $CpFe(CO)[Ph_2PN(Me)$-(S)-$\overset{*}{C}H(Me)Ph]I$ could be separated into a diastereomeric pair and the P-N bond cleaved giving the enantiomers of $Cp\overset{*}{F}e(CO)(PPh_2F)I$ [287].

Some phosphine complexes were synthesized as shown in Scheme 45 [288].

SCHEME 45



A phosphenium ion complex, 381, was prepared. The X-ray structure showed pyramidal rather than planar geometry around P [289].

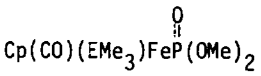


381

$Cp(CO)(PR_3)FeEMe_2$

382a E = P, R = Me
b E = P, R = Et
c E = P, R = OMe
d E = P, R_3 = Me_2Ph
e E = As, R = Me
f E = As, R = Et
g E = As, R = OMe
h E = As, R_3 = Me_2Ph
i E = Sb, R = Me
j E = Sb, R = Et
k E = Sb, R = OMe
l E = Sb, R_3 = Me_2Ph

Complexes 382a-l were made by phosphine substitution on $CpFe(CO)_2EMe_2$ (E = P, As, Sb). 382c,g,k rearrange to 383a,b,c. $P(OMe)_3$ displaces the EMe_3 ligands in 383a-c. 382a-l are nucleophlic organometallic Lewis Bases. For example 382i can be alkylated at Sb by MeI. 382i reacts with $CpFe(CO)_2Cl$ and $CpFe(CO)(PMe_3)Br$ to afford 384a and 384b, respectively [289a].



$Cp(CO)(EMe_3)Fe\overset{O}{\overset{\|}{P}}(OMe)_2$

383a E = P, b R = As,
c R = Sb

$[Cp(CO)(PMe_3)FeSbMe_2Fe(CO)LCp]^+X^-$

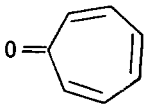
384a L = CO, X = Cl
b L = PMe_3, X = Br

Complexes with Group VI Ligands

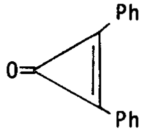
New ketone complexes 385a-c having O coordinated to Fe were prepared, and the X-ray structure of 385a reported [290].

$[Cp(CO)_2FeL]^+BF_4^-$

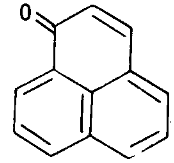
385a L =



b L =



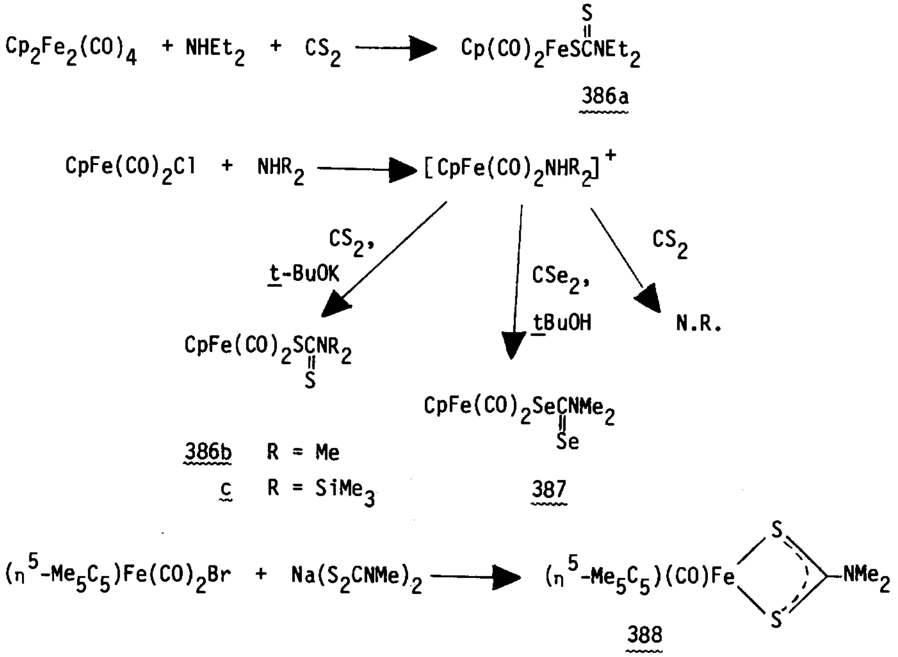
c L =



Treating $CpFe(CO)_2I$ with $AgAsF_6$ in $SO_2(\ell)$ has allowed isolation of $[CpFe(CO)_2(SO)_2]AsF_6$ whose X-ray structure was reported [291].

Dithio- and diselenocarbamato complexes were made in the fashion depicted in Scheme 46 [292].

SCHEME 46



Halide Complexes

The ^{57}Fe NMR spectra of $CpFe(CO)_2X$ showed that Fe nuclear screening increases in the order $Cl<Br<<I$ [293].

ARENE AND RELATED COMPLEXES

Variable temperature solution EPR spectra were reported for nineteen-electron complexes $Cp(\eta^6-C_6H_6)Fe$ and related ring-alkylated compounds as well as compounds doped into diamagnetic hosts and in frozen solutions. The results were consistent with a d^7 configuration with the unpaired electron mainly localized on Fe [294].

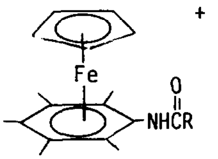
Salt effects were observed on the reactivity of $O_2^{\dot{-}}$ generated from the electron reservoirs $Cp(\eta^6$-arene)Fe. In the presence of $NaPF_6$, the reaction products are only $[Cp(\eta^6$-arene)$Fe]^+PF_6^-$ (which precipitates) and NaO_2. Without PF_6^-, deprotonation of the cation occurs if benzylic H is present to afford neutral complexes of the type $Cp(\eta^5-C_6H_5{=}CH_2)Fe$; alternatively a neutral peroxide such as $[CpFe(\eta^5-C_6H_6O)]_2$ forms in the absence of benzylic H [295].

Some cations peralkylated on the Cp and arene rings were synthesized as precursors to sterically protected electron reservoirs of the type $CpFe(\eta^6$-arene). Steric protection was desired so that the radical anion of the reacting substrate generated by electron transfer from the nineteen-electron species would not react further with the Fe-containing cation. Treating cations such as $[Cp(\eta^6-C_6Me_6)Fe]^+$ with excess *t*-BuOK and RX (RX = MeI, $PhCH_2Br$) in THF gave products such as $[Cp(\eta^6-C_6Et_6)Fe]^+$. Also, $[Cp(\eta^6-C_6Et_6)Fe]^+$ gave $[Cp(\eta^6-C_6Et_5($*i*-Pr$))Fe]^+$ via $CpFe(\eta^5-C_6Et_5CHMe)$. The X-ray structure of $[Cp(\eta^6-C_6Et_6)Fe]PF_6$ showed that three arene carbons are eclipsed or nearly eclipsed by Cp C's due to the bulk of the ethyl groups and mismatch of C_5 and C_6 rings. Et groups on these eclipsed C's point away from Fe [296].

When $[Cp(\eta^6-C_6R_6)Fe]^+$ (R = H, D, Me) are reduced by $NaBH_4$ or $LiAlH_4$, the final products are $Cp(\eta^5-C_6R_6H)Fe$. Intermediates $Cp(\eta^6-C_6R_6H)Fe$ were detected by ESR in THF and DME but not in ether at low temperature [297].

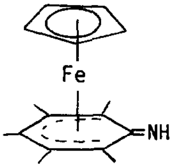
Azaferrocene was found to react with π-acid ligands L = CO, CNR, R_2NPF_2 giving $CpFeL_2(\eta^1$-*N*-pyrrolyl) complexes. These species in arene solvents in the presence of $AlCl_3$ afforded $[Cp(\eta^6$-arene)$Fe]^+$ cations (arene = benzene, toluene, *m*-xylene, *p*-xylene, mesitylene) [298]. Conversely, the arene ligands in $[Cp(\eta^6$-arene)$Fe]^+$ (arene = $C_6H_5NO_2$, *o*-, *m*-, *p*-nitrotoluene, $C_6H_5NH_2$ and *o*-, *m*- and *p*-$Me(NH_2)C_6H_4$) were displaced on heating with L = $P(OEt)_3$ giving $[CpFeL_3]^+$ [299].

Some twenty $[Cp(\eta^6$-aminoarene)$Fe]^+$ complexes were synthesized by reactions of amines with $[Cp(\eta^6-C_6H_5Cl)Fe]^+$ [299]. $[Cp(\eta^6-C_5Me_5NH_2)Fe]^+$ was prepared from ferrocene and pentamethylaniline. When the cation was deprotonated with *t*-BuOK and then treated with RC(O)Cl, the products were **389a-d**. **389a-d** also result from the reaction of the cation with acid chlorides in acetone [300].

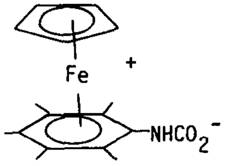


389a R = Me c R = p-$MeC_6H_4SO_2$
b R = Ph d R = camphorsulfonyl-d_{10}

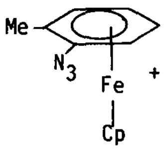
When the neutral complex Cp(η^6-$C_6Me_5NH_2$) Fe is allowed to react with O_2 at -10°C in toluene 390 is produced. On treatment with 1 atm CO_2 at 20°C, 390 gives 391, related to 389 [301].



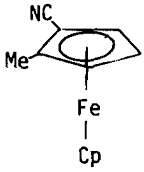
390



391



392

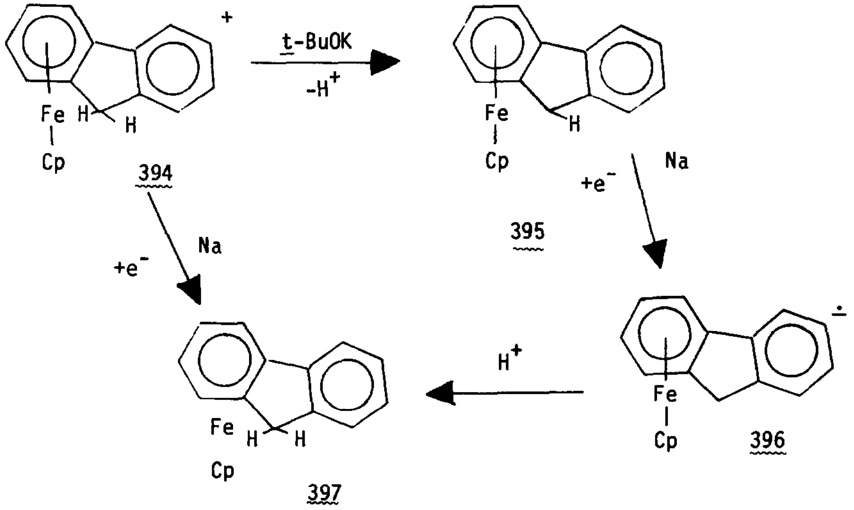


393

Photolysis of 392 produces the product of ring contraction 393. 393 is also the product from the p-substituted arene complex. However, the m-complex yields 1,2- and 1,3-substituted ferrocenes [302].

Radical anion species, 396, was prepared as depicted in Scheme 47 [303].

SCHEME 47



Multilayered $[Cp(\eta^6\text{-cyclophane})Fe]^+$ complexes were synthesized where cyclophane=*anti*-[2.2]metacyclophane, *anti*-4,12-dimethyl-[2.2]metacyclophane, *anti*-4,12-dimethyl-7,15-dimethoxy-[2.2]metacyclophane and [2.2]-(2,5)thiophenophane. Triple-layered complexes $[(\eta^6,\eta^6\text{-}$*anti*$\text{-[2.2]metacyclophane})\{CpFe(CO)_2\}_2]^{2+}$ and $[(\eta^6,\eta^6\text{-}$*anti*$\text{-4,12-dimethyl-[2.2]metacyclophane})\{CpFe(CO)_2\}_2]^{2+}$ were also prepared. The procedure involved photolytic displacement of C_6Me_6 from $[Cp(\eta^6\text{-}C_6Me_6)Fe]^+$ or treatment of ferrocene with Al and $AlCl_3$ in the presence of the cyclophane. NMR spectra of the complexes were reported [304].

Improved syntheses of $[(\eta^6\text{-}C_6Me_6)_2Fe]^{n+}$ (n = 1, 0) by Na/Hg reduction of the n = 2 cation were published [305].

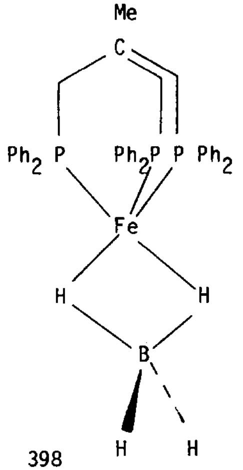
Co-condensation of Fe, arene and dienes led to the production of significant quantities of $(\eta^6\text{-arene})(\eta^4\text{-diene})Fe$ complexes [306]. Also produced similarly were $(\eta^6\text{-toluene})Fe(bipy)$ [307] and $(\eta^6\text{-arene})FeL_2$ (L = phosphine, phosphite) [306]. The X-ray structure of $(\eta^6\text{-toluene})Fe(bipy)$ indicated an alternating pattern of C-C bond lengths in the bipy ligand suggesting the destruction of delocalization [307].

BORANE AND CARBORANE COMPLEXES

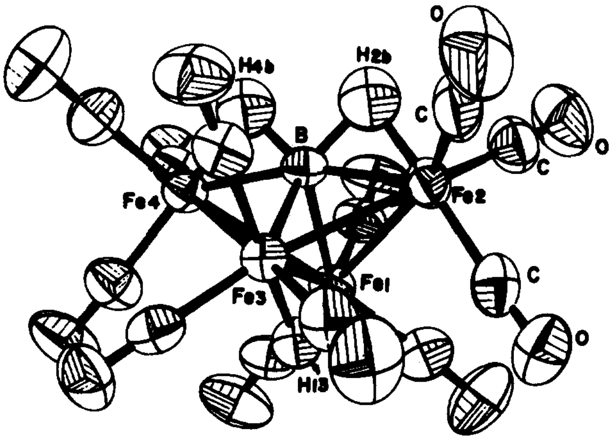
Reduction of $Fe(BF_4)_2$ with $NaBH_4$ in the presence of $(Ph_2PCH_2)_3CMe$ gave **398**, whose X-rav structure was determined [308].

M.O. calculations on B_5H_9 and the isoelectronic $1\text{-}[Fe(CO)_3]B_4H_8$, $2\text{-}[Fe(CO)_3]B_4H_8$ and $1,2\text{-}[Fe(CO)_3]_2B_3H_7$ demonstrated the validity of the isolobal analogy as applied to these clusters [309]. $2\text{-}[CpFe(CO)_2]B_5H_8$ was prepared via the reaction between LiB_5H_8 and $CpFe(CO)_2I$ [310].

The preparation and X-ray structure of **399** were reported. **399** obeys Wade's rule if B is assumed to be interstitial. The complex is isoelectronic with $HFe_4(CH)(CO)_{12}$ [311].



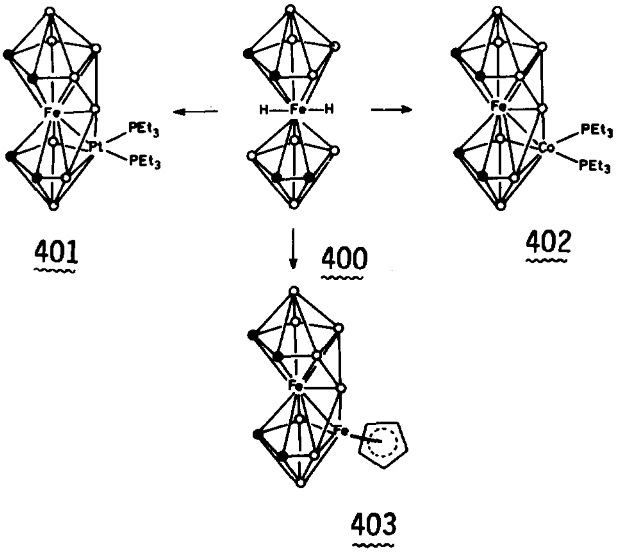
398



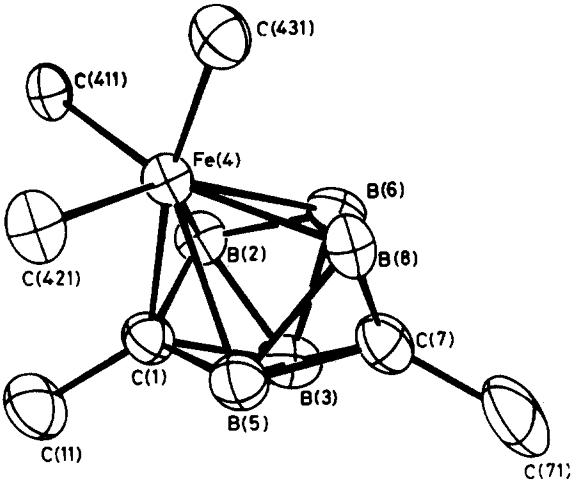
399

Scheme 48 depicts reaction products of 400, $FeH_2(2,3-Me_2-2,3-C_2B_4H_4)_2$. The products 401, 402 and 403 are all electron-hyperdeficient clusters. The X-ray structure of 397 was reported [312].

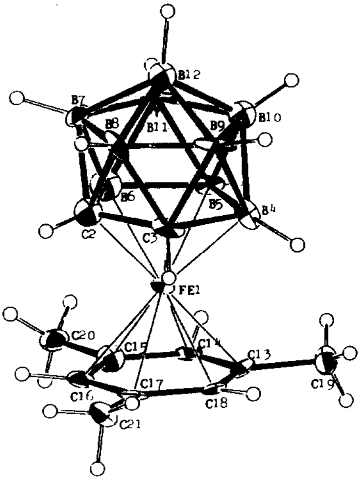
SCHEME 48



When Fe(CN*t*-Bu)$_5$ is allowed to react with *closo*-2,4-Me_2-2,4-$C_2B_5H_5$, 404 is the product. Its X-ray structure showed that Fe occupies a five-connectivity vertex [313].

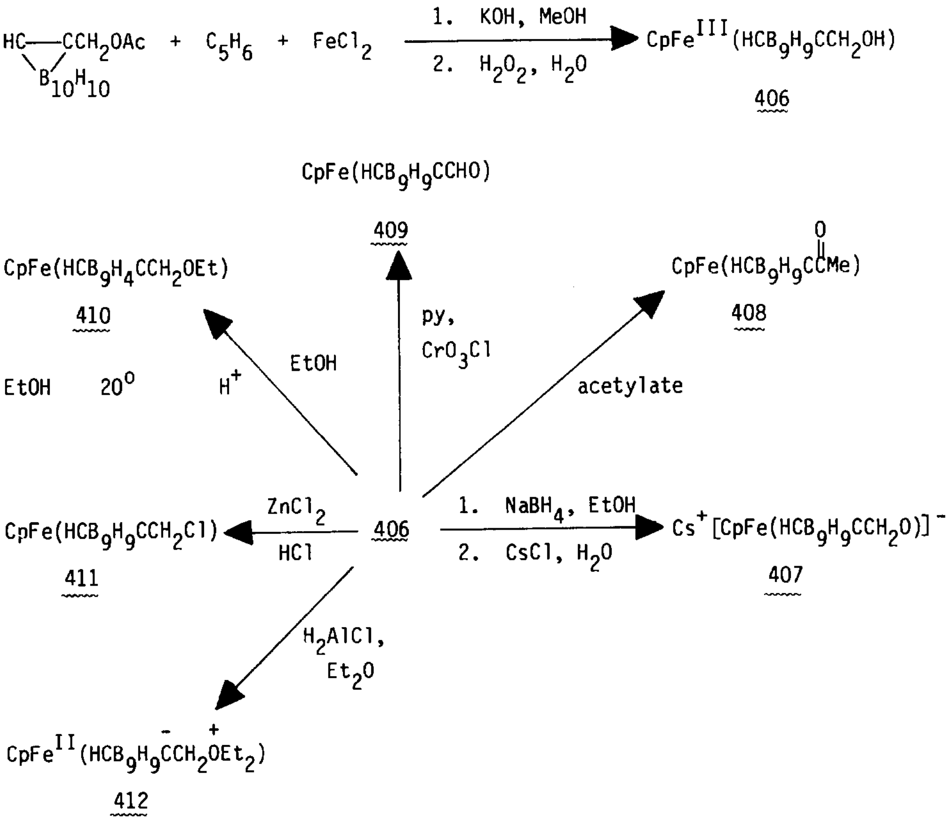


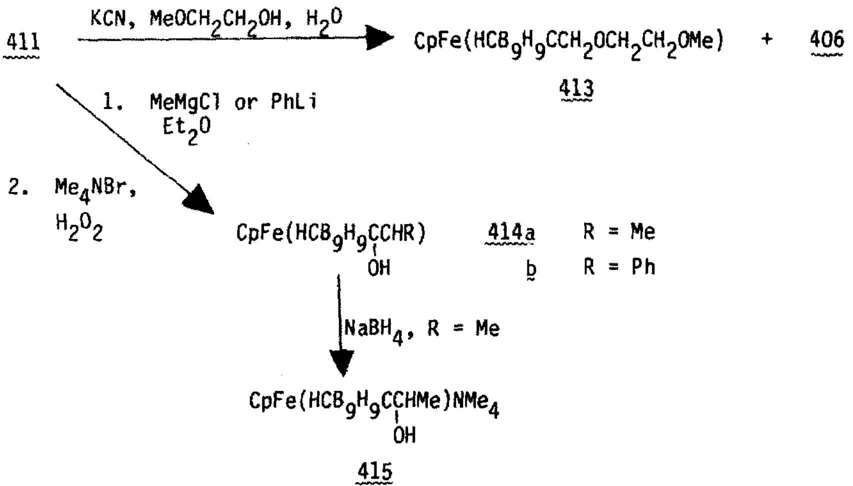
404



405

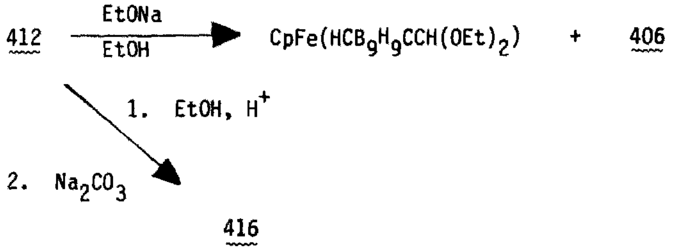
SCHEME 49

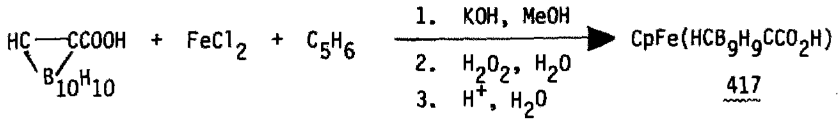




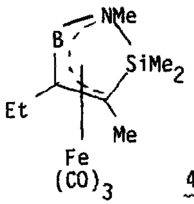
An arene ligand in $[(\eta^6\text{-arene})_2Fe]^{2+}$ (arene = mesitylene, hexamethyl-benzene) can be displaced by reaction of the PF_6^- salts with $Tl[1,3,5\text{-}Tl(C_2B_9H_{11})]$. The products $[(\eta^6\text{-arene})(C_2B_9H_{11})Fe]$ are isoelectronic with $[Cp(\eta^6\text{-arene})Fe]^+$ and ferrocene. 405 shows the X-ray structure of the mesitylene complex [314].

Scheme 49 displays chemistry of Fe^{III} complexes containing the $[C_2B_9H_{11}]^{2-}$ ligands. The substitution is on the C numbered C_2 in 405 [315].





418 having a ligand containing B, C, Si and N acting as a four-electron donor was prepared and its X-ray structure determined [316].



418

Work reported in this section is organized insofar as feasible on the basis of the nature of the organic product. After some research on catalysis of the Water Gas Shift, alkanes, olefins, dienes, alcohols, aldehydes, ketones, carboxylic acids and heterocycles are treated.

The mechanism of Water Gas Shift catalysis by $Fe(CO)_5$ was shown to be as follows:

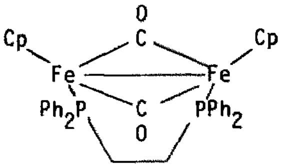
$$Fe(CO)_5 + OH^- \longrightarrow [HFe(CO)_4]^- + CO_2$$
$$[HFe(CO)_4]^- + H_2O \longrightarrow H_2Fe(CO)_4 + OH^-$$
$$H_2Fe(CO)_4 \longrightarrow H_2 + Fe(CO)_4$$
$$Fe(CO)_4 + CO \longrightarrow Fe(CO)_5$$

In more basic media, the first step would be:

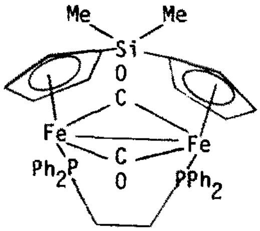
$$Fe(CO)_5 + 3OH^- \longrightarrow [HFe(CO)_4]^- + CO_3^{2-} + H_2O$$

Since H_2 elimination occurs from the protonated species $H_2Fe(CO)_4$, the solution must be sufficiently acidic to maintain a significant concentration of this molecule. However, the solution must also have high enough $[OH^-]$ to allow OH^- attack in the CO_2-producing step. These conflicting pH requirements make $Fe(CO)_5$ a poor WGS catalyst [317].

Hydridic reduction of $Cp_2Fe_2(CO)_4$ was recently shown to produce hydrocarbons up to C_4. That terminal CO's are required for this reaction was demonstrated by the fact that no hydrocarbons were produced by reduction of 419 or 420 [318].

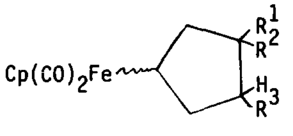


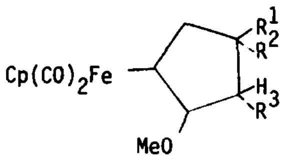
419



420

$CpFe(CO)_2CH_2CH=CH_2$ reacts with substituted olefins $R^1R^2C=CR^3H$ producing complexes 421a-g having cyclopentane ligands [319]. The substituted allyl complex $CpFe(CO)_2CH_2CH=CH(OMe)$ also reacted with olefins $R^1R^2C=CR^3H$ producing

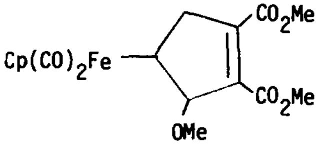




	R^1	R^2	R^3
421a	CO_2Et	CN	CO_2Et
b	CO_2Et	CO_2Et	H
c	CO_2Me	CO_2Me	CO_2Me
d	CN	CN	CO_2Et
e	CO_2Et	CN	CN
f	CN	CO_2Et	CN
g	CO_2Me	CO_2Me	H

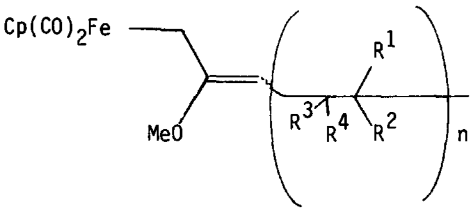
422a-f

421a-f and 422a-f. Dimethylacetylenedicarboxylate gave 423 [320]. 421, 422 and 423 can all be demetallated via oxidative carboxylation or acid cleavage or β-H abstraction.

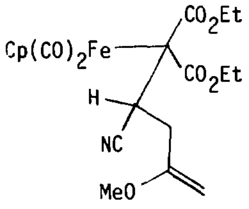


423

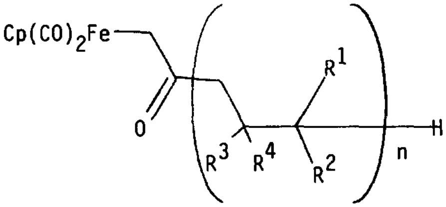
$CpFe(CO)_2CH(OMe)CH=CH_2$, on treatment with $R^1R^2C=CR^3R^4$ produces a mixture of products 424, 425 and 426a,c,d,e the exact composition of which is very solvent dependent. On the chromatography column, 424a-j were hydrolyzed to 426a-j and 425 to 427.



425



	R_1	R_2	R_3	R_4	n
424a	CO_2Me	CO_2Me	H	CO_2Me	1
b	CN	CO_2Et	H	CO_2Et	1
c	CO_2Et	CO_2Et	CO_2Et	CO_2Et	1
d	CO_2Me	CO_2Me	CO_2Me	CO_2Me	1
e	CO_2Et	CO_2Et	H	H	1
f	CO_2Et	CO_2Et	H	H	2
g	CO_2Et	CO_2Et	H	H	3
h	CO_2Me	CO_2Me	H	H	1
i	CO_2Me	CO_2Me	H	H	2
j	CO_2Me	CO_2Me	H	H	3



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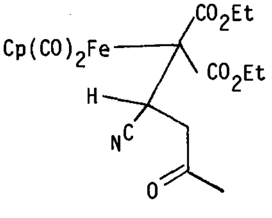
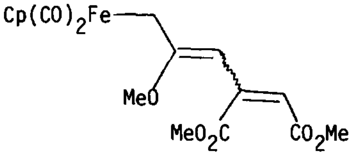
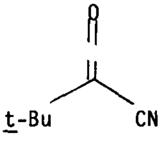


427

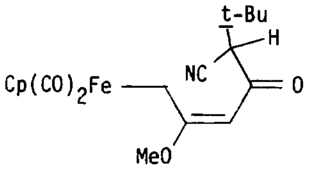
Dimethylacetylenedicarboxylate gave 428 while 429 gave 430a,b [321].



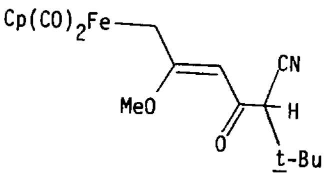
428



429



430a

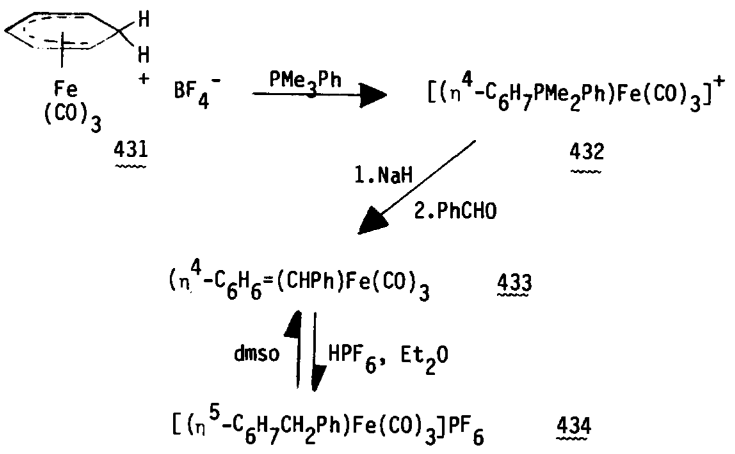


430b

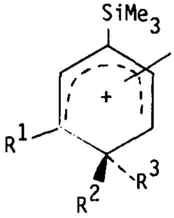
Photoisomerization of 1-pentene was catalyzed by $Fe(CO)_4L$ (L = CO,PPh_3, $P(OMe)_3$, $P(\underline{o}\text{-tolyl})_3$)[322]. $[CpFe(CO)_2(THF)]BF_4$ and $[CpFe(CO)_2\,(\text{isobutylene})]BF_4$ were found to catalyze condensation of methyl propiolate or tetrolate with olefins to produce 1,3-dienes, cyclobutenes and 5,6-dihydro-2-pyrones [323].

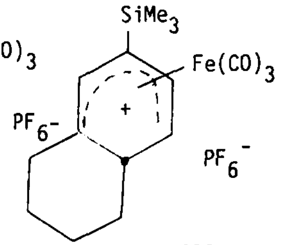
Olefin bonds are made via the routes indicated in Scheme 50 for a six-membered ring involving the production of phosphonodiene cations and their subsequent reaction with aldehydes or ketones [324]. Five, seven and eight-membered dienyl and diene complexes reacted similarly.

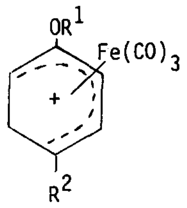
SCHEME 50



Cyclohexadienylium iron tricarbonylcations, substituted analogues of 431, have received a good deal of attention since addition of nucleophiles to these cations produces dienes. The directive role of the $SiMe_3$ ring substituent was exploited in the production of 435a-d and 436 by hydride abstraction from diene complexes [325].







436

437

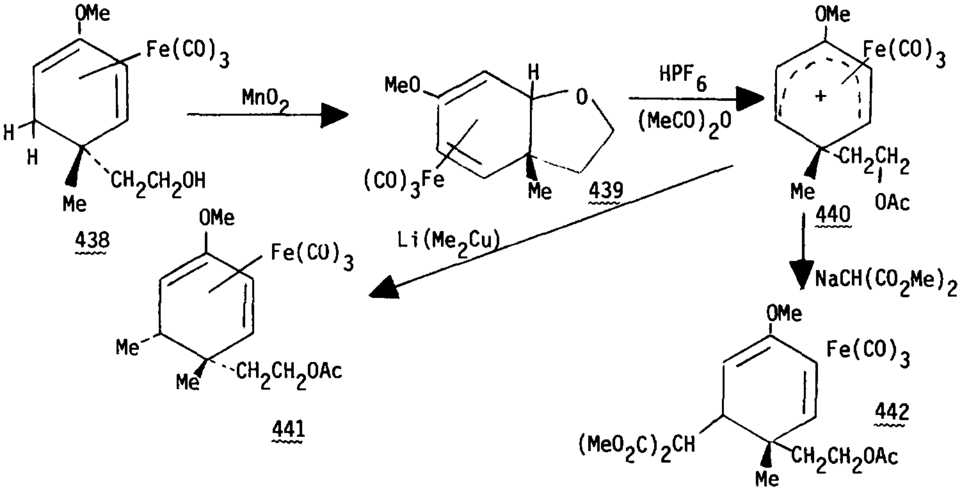
435a $R_1 = R_2 = R_3 = H$
b $R_1 = R_2 = H, R_3 = Me$
c $R_1 = Me, R_2 = R_3 = H$
d $R_1 = H, R^2 = R_3 = Me$

The regioselectivity of enolate addition to complexes of the type 437 was investigated. Better selectivity for addition to the R^2-substituted C as opposed to the unsubstituted C's adjacent to OR^1 was observed for R^2=i-Pr than for R^2=Me [326]. The position of attack was also controlled by the nature of the enolate [326] and its countercation [327].

O-silylated enolates and (allyl)trialkylsilanes were found to react with cyclohexadienylium iron tricarbonyl salts with C-C bond formation yielding (η^4-cyclohexadiene)$Fe(CO)_3$ complexes in good to excellent yields. Conversion of these complexes to synthetically useful products was achieved [328].

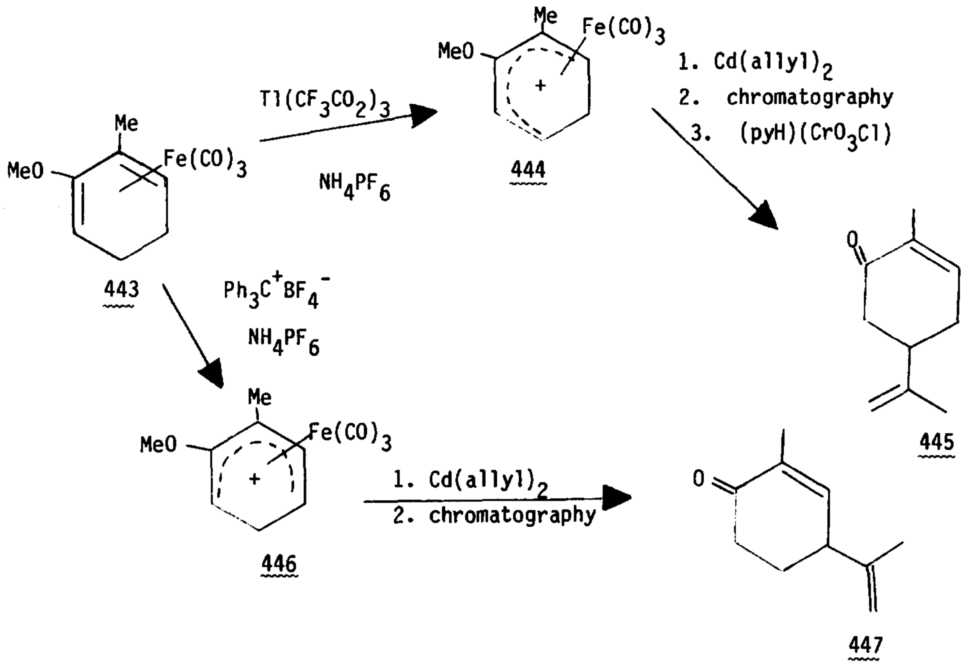
Scheme 51 demonstrates the stereochemical control achieved in diene syntheses by using cyclohexadienylium iron tricarbonyl cation [329].

Scheme 51

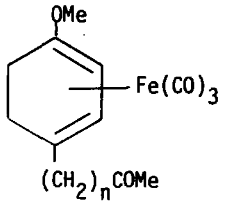


Another such example is provided in Scheme 52 [330].

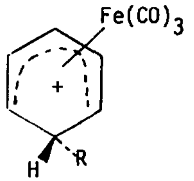
SCHEME 52



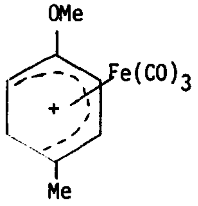
Spirocycles were synthesized by reactions of appropriate nucleophiles with cations derived from **448** [331]. 6-*exo* substituted cyclohexadienylium iron tricarbonyl salts of type **449** were prepared [332]. Also, reactions of cyclohexadienylium salts with amine nucleophiles were investigated [333]. **450** was used as a synthon for *D*-homoaromatic steroids [334].



448a n=2, b n = 3

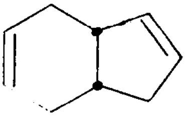


449

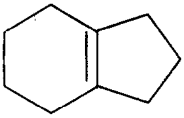


450

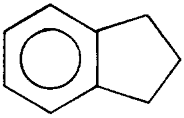
Fe(CO)$_5$ and Cp$_2$Fe$_2$(CO)$_4$ was found to catalyze the disproportionation of **451** to **452** and **453** [335].



451



452



453

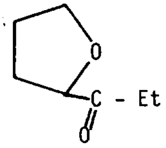
The direct homologation of methanol to ethanol by synthesis gas is catalyzed by $Fe(CO)_5$ [336]. $Fe_3(CO)_{12}$ acts as a catalyst precursor for hydrogenation and hydroformylation of styrene [337].

$[HFe(CO)_4]^-$ and $[EtFe(CO)_4]^-$ react in THF at 0^0 to produce CH_3CH_2CHO suggesting a bimolecular step to account for aldehyde production in the Reppe synthesis. Consistent with the hypothesis was the observation of much slower aldehyde production from $[EtFe(CO)_4]^- + H_2$ [338].

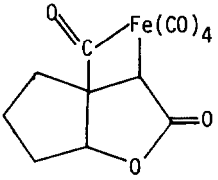
Stereo- and enantioselective syntheses of cis- and trans- hemicaronic aldehydes starting with $(\eta^4\text{-MeCH=CHCH=CHCHO})Fe(CO)_3$ were devised [339].

Ethyl phenyl ketone was the product of a reaction between $[Fe(CO)_4C(O)Ph]^-$ and ethylene [340]. $[Fe(CO)_4C(O)R]^-$ (R=Me, n-Bu, n-pentyl, n-hexyl) acylated allyl ligands on Pd complexes give α-β and β-γ unsaturated ketone ligands as products [341].

The ketone 454 was synthesized via a free radical reaction in THF of CO, Et_2Mg and EtMgBr in the presence of $Fe_2(CO)_9$ [342].



454



455

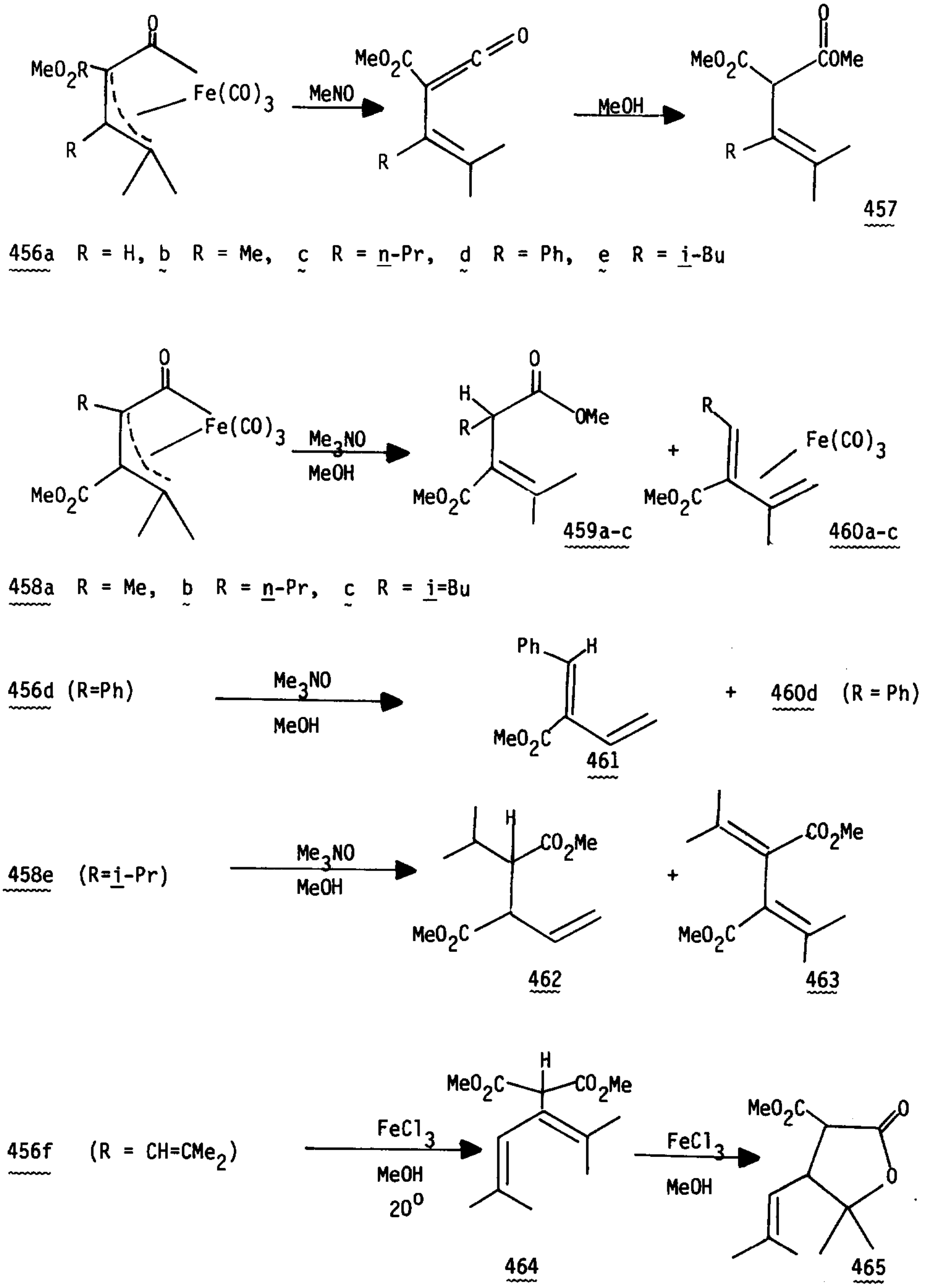
Twelve different lactone complexes of $Fe(CO)_3$ were thermally decomposed in deoxygenated solvents giving products arising from decarbonylation, decarboxylation and rearrangement. The X-ray structure of one product, 455, was reported [343].

β-ketosulfides, thioesters and disulfides were obtained from $Fe(CO)_5$- promoted reactions between α- thiocarbanions and MeI or acyl halides [344].

$Fe(CO)_3$ was used as a control group for selective alkaline hydrolysis of η^4-cyclohexa-1,3-dienecarboxylic ester complexes. Half-hydrolysis of diester complexes was achieved [345].

η^1, η^3-allyl complexes 456, 458 are formed from cyclopropenes and $Fe_2(CO)_9$. These complexes are vinyl ketone precursors and can be oxidized with $FeCl_3$ or Me_3NO yielding esters, dienes and lactones as shown in Scheme 53 [346].

SCHEME 53



457

456a R = H, b R = Me, c R = n-Pr, d R = Ph, e R = i-Bu

459a-c

460a-c

458a R = Me, b R = n-Pr, c R = i=Bu

456d (R=Ph)

461

460d (R = Ph)

458e (R=i-Pr)

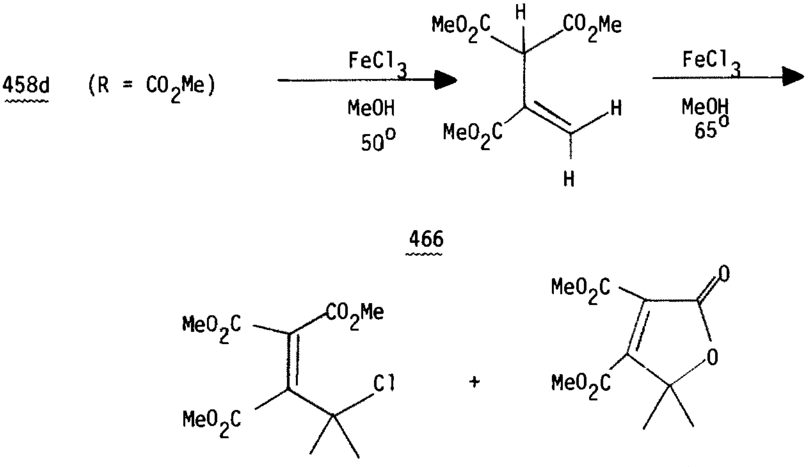
462

463

456f (R = CH=CMe$_2$)

464

465



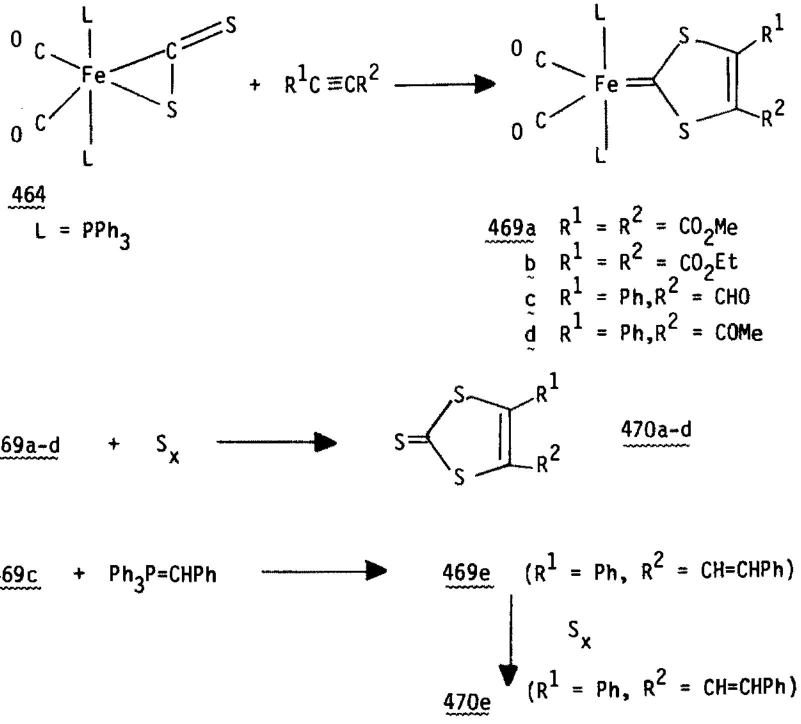
466

467

468

Sulfur-containing heterocycles were prepared by methods shown in Scheme 54 [347].

SCHEME 54



464

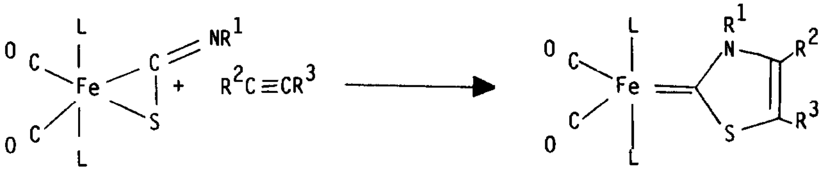
L = PPh$_3$

469a $R^1 = R^2 = CO_2Me$

b $R^1 = R^2 = CO_2Et$

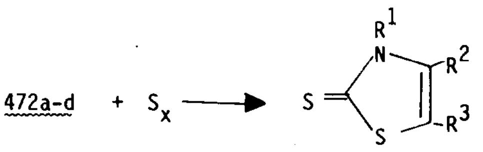
c R^1 = Ph, R^2 = CHO

d R^1 = Ph, R^2 = COMe



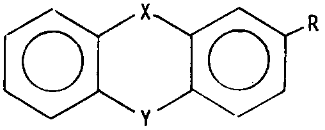
471 L = PPh_3
a R^1 = Me
b R = Ph

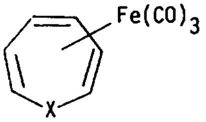
472a R^1 = Me, R^2 = R^3 = CO_2Me
b R^1 = Ph, R^2 = R^3 = CO_2Me
c R^1 = Ph, R^2 = R^3 = CO_2Et
d R^1 = R^2 = Ph, R^3 = CHO



473a-d

The heterocycles 474a-e were synthesized by thermolysis of [Cp(η^6-heterocycle)Fe]$^+$ complexes prepared from the reaction between [Cp(η^6-1,2-$Cl_2C_6H_4$)Fe]$^+$ and 1-R, 3-XH, 4-YH-C_6H_3 in the presence of K_2CO_3[348].

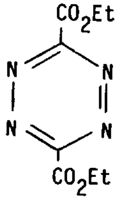




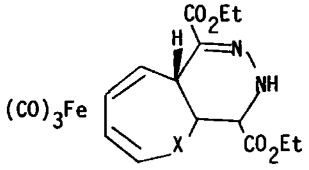
474a X = Y = O, R = H
b X = S, Y = O , R = H
c X = Y = S, R = Me
d X = NH, Y = O, R = H
e X = NH, Y = S, R = H

475a X = NCO_2Et
b X = CH_2
c X = C = O
d X = Np-tolyl

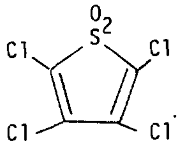
The diene complexes 475a-d react with 476 giving 477a-d. 475 a-c produce adducts 479a-c on reaction with 478. Finally, 475b adds 480 giving 481 [349].



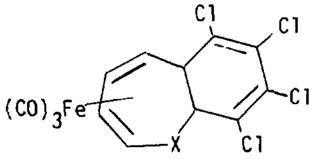
476



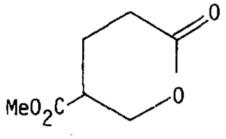
477a X = NCO_2Et
b X = CH_2
c X = C = O
d X = Np-tolyl



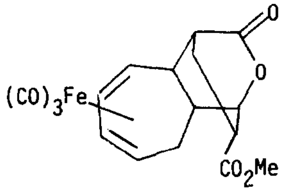
478



479a X = NCO_2Et
b X = CH_2
c X = C = O
d X = Np-tolyl



480



481

REVIEWS AND DISSERTATIONS

Reviews

Several review articles, listed alphabetically by author, are of interest.

"Phosphido-bridged Iron Group Clusters" by A. J. Carty [350].

"Structural Chemistry and Reactivity of Cluster-bound Acetylides: Close Relatives of the Carbides?" by A. J. Carty [351].

"Preparation and Properties of Metallacyclic Compounds of the Transition Elements" by S. D. Choppell and D. J. Cole-Hamilton [352].

"Aromatic Compounds of the Transition Elements" in Rodd's Chemistry of Carbon Compounds, S. Coffey and M. F. Ansell, eds. [353].

"Metallacarboranes and Metallaboranes in Organometallic Synthesis" by R. N. Grimes [354].

"Synthesis Using 1,3-Dienetricarbonyliron Complexes" by D. Hoppe [355].

"Hydrocarbon-Metal π - Complexes" by J. A. S. Howell [356].

"Transformation of Organic Substrates on Metal Cluster Complexes" by H. D. Kaesz, C. B. Knobler, M. A. Andrews, G. van Buskirk, R. Szastak, C. E. Strouse, Y. C. Lin and A. Mayr [357].

"Arene-Metal Complexes" by E. L. Muetterties, J. R. Blacke, E. J. Wucherer and T. A. Albright [358].

"Complexes Containing Metal-Carbon σ-Bonds of the Groups Iron, Cobalt and Nickel" by S. D. Robinson [359].

"On the α-Carbenium Center Stabilization in (Olefin) Iron Carbonyl Complexes. Realization of Olefin and Allyl Structures" by M. I. Rybinskaya [360].

"Investigation of Paramagnetic Metallocenes and Diarene Complexes of the Transition Metals by Magnetic Resonance Methods" by S. P. Solodovnikov [361].

"π-Cyclopentadienyl, π-Arene and Related Complexes" by W. E. Watts [362].

"Photogeneration of Reactive Organometallic Species" by M. S. Wrighton, J. L. Graff, R. J. Kazlauskas, J. C. Mitchener and C. L. Reichel [363].

Dissertations

Dissertations are listed in order of their appearance in Dissertation Abstracts.

"Part I. Synthesis and Characterization of Bis(iron dicarbonyl cyclopentadienyl)sulfanes" by M. A. El-Hannawi [364].

"Electron-Rich Complexes of Iron and Ruthenium with Phosphorus Ligands" by D. M. Komar [365].

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"Synthesis and Structural Characterization of Multinuclear Transition Metal Phosphino and Hydrido Complexes" by D. M. Ho [368].

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